Contaminant variability in a sedimentation area of the river Rhine

Herman Winkels

Contaminant variability
in a sedimentation area
of the river Rhine

Variabiliteit van verontreinigingen in een sedimentatiegebied van de Rijn

BIBLIOTHEEK
LANDBOUWUNIVERSITEIT
WAGENINGEN

Stellingen

1. Bij het kiezen voor een bemonsteringsstrategie van waterbodems dient alle ruimtelijke informatie over het ontstaan en de verontreiniging van de sedimenten te worden gebruikt.

   (dit proefschrift)

2. Een bemonsteringsprogramma voor waterbodems wordt vaak gebaseerd op een equi-distant rooster of er wordt gebruik gemaakt van geneste bemonstering. Waterbodems moeten echter bemonsterd worden in een fijnmazig grid in combinatie met enkele ruimtelijk verspreide waarnemingen.

   (Warrick and Myers, 1987; Webster and Oliver, 1992)

3. De diepte tot welke verontreinigd slib dient te worden verwijderd in het Ketelmeer verschilt per te saneren deelgebied. De nauwkeurigheid waarmee de sanering per deel-gebied uitgevoerd kan worden is afhankelijk van de extra diepte die als veiligheidsmarge voor de sanering van elk deelgebied wordt aangehouden. Daar waar de verontreinigde laag dikker is, zoals te Ketelhaven, zullen de kosten per m^2 hoger zijn om dezelfde nauwkeurigheid te halen als elders in het Ketelmeer.

   (dit proefschrift)

4. De stuwmeren in het stroomgebied van de Volga vormen een chemische tijdbom.

   (dit proefschrift)

5. Oude lodingskaarten geven niet meer dan een indicatie van de waterdiepten en zijn onderling niet vergelijkbaar, daar ze met onnauwkeurige en verschillende methoden zijn bepaald.

   (dit proefschrift)

6. De Noordzee en de Waddenzee zijn in hoge mate afgeschermd van verontreiniging door het afdammen van de riviermondingen van de Rijn door de aanleg van grote waterstaatskundige werken. Naties die de verantwoordelijkheid op zich hebben genomen voor deze zeeën, moeten daarom meebetalen aan de sanering van de hierdoor verontreinigde waterbodems in Nederland.

7. Hydrologische modellen moeten altijd getoetst worden aan de uitkomst van veldonderzoek.

8. Goedheid is veel belangrijker dan verstand.

   (Edith Stein)

9. Het is ongerijmd dat verkeersdrempels, rotondes en stoplichten worden aangelegd op nagenoeg elke kruising in Nederland om de verkeersveiligheid te vergroten, terwijl tegelijk verkeerslessen uit het basisonderwijs verdwijnen.

10. Natuurontwikkeling in Nederland is vergelijkbaar met het werk van een filatelist; de verzameling begint pas ergens op te lijken als deze nagenoeg compleet is.

11. Succes hebben wil niet altijd zeggen dat het goed gaat.

12. Blijf daar wonen waar uw geluk is, want geluk is uiterst gevoelig voor verhuizing.

    (Carpool Wageningen-Lelystad)

Stellingen behorend bij het proefschrift van H.J. Winkels:
Contaminant variability in a sedimentation area of the river Rhine

Wageningen, 8 december 1997.

one small step for science sake, I did it ..

For Mara

CONTENTS

Summary

Aquatic sediments in sedimentation zones of major rivers are in general sinks for pollutants. The sedimentation zone Ketelmeer/IJsselmeer is an important sink for contaminants of the river Rhine (i.e. river IJssel). Recent and historical pollution interact here. Redistribution of suspended solids and erosion of deposited sediment in the shallow Dutch lakes (due to wave action) are likely to change contamination levels of sediments in these lakes, which is the subject of this thesis. The aim of this research was to study and explain the variability of contaminants in the sedimentation area Ketelmeer/IJsselmeer in order to predict the fate of the contaminants in the future. For this purpose a number of methodologies and models were developed and/or adapted.

Chapter 2 describes the collection and analysis of sediment cores, top-layer sediments and geologically different layers in Lake Ketelmeer. Sediment cores were sectioned into thin slices and the year of deposition of each layer was determined using radio-chemical analyses. The contaminant concentrations were plotted versus the year of deposition of each sediment layer to (re-)construct the history of contamination. Similar vertical changes in contaminant concentrations were found as in a number of sediment cores sampled in sandpits in Lake Ketelmeer. Further, differences in concentration between the top-layer sediments and the degree of contamination in the entire recent IJsselmeer deposits (IJm-deposits) of Lake Ketelmeer were found. The older Zuiderzee deposits (Zu-deposits) underlying the IJm-deposits have low background values for heavy metals, PAHs and PCBs. This indicates that downward transport of these contaminants with infiltrating water is negligible in this lake. The concentrations of metals and PAHs in the sediment cores reflect, without any serious alterations, the historical input of the past five decades. The pollution history is characterized by, in the early 1940s, low concentrations of metals and already elevated levels of PAHs; a possible reduction of these contaminants during the Second World War and attaining, their highest levels between 1955 and 1970. Rather low levels occur in recently deposited sediments, some of which are the lowest ever observed over the last five decades (Pb, As, and all studied PAHs). Almost all chlorinated compounds showed a certain decline in concentration in anaerobic sediments as compared to samples of the top-layer collected in 1972 and stored in the laboratory, which still reflect the original pollution input. For several PCBs this decline proved to be significant; it may have been caused by microbial dechlorination reactions in the anaerobic sediment. Consequently, the concentration profiles of the chlorinated compounds do not reflect the original pollution history directly. Despite the attenuation of concentration, peaks in PCB concentration profiles were still observed. The following trends in concentrations of PCBs can be currently observed in Lake Ketelmeer sediment:
- Almost all PCBs studied had rather low concentrations in the early 1940s.
- The highest levels of PCBs occurred between 1960 and 1975.
- Recently deposited sediments also have elevated levels of PCBs as compared to the levels in layers from the early 1940s.

Overall, recently deposited material is far less-polluted than sediment deposited in the 1960s and 1970s. These findings prove that in this lake older, highly polluted sediments are buried under a younger, less-polluted layer. However, at some locations, such as in dredged parts or erosive zones, the

highly polluted layers may remain uncovered, so aquatic organisms may still be exposed to highly polluted sediments from the 1960s and 1970s through the benthic food chain.

In *Chapter 3* attention is focused on the distribution and geochronology of the sediments of Lakes Ketelmeer and IJsselmeer. The concentrations of metals, PCBs, PAHs and various sediment characteristics were determined in 77 samples of the surface sediments and one 3 m core of both lakes. Absolute concentrations of these pollutants were normalized for sediment composition (e.g. clay fraction and organic matter contents). In Lake IJsselmeer the youngest geological layer (IJm-deposit) is mainly found in deep sedimentation areas (25%). This deposit is severely polluted in Lake Ketelmeer (Chapter 2). Concentrations of all polluting compounds in the IJm-deposit of Lake Ketelmeer proved to be 1.6 - 9 times higher than in Lake IJsselmeer. Concentrations in the same deposit in Lake IJsselmeer were 2 - 4 times higher than those in the older sandy sediments of the lake. Concentrations of heavy metals, As and PCBs initially increase with depth, but then decrease to lower or even background levels. This corresponds with the inputs of the river IJssel during the past five decades. As the distance from the river mouth (i.e. Lake Ketelmeer) to Lake IJsselmeer increases, there is a decrease in the degree of pollution in this IJm-deposit. The hypothesis is developed that primary production (with related calcite formation) and mixing with eroded sediment from elswhere in Lake IJsselmeer are together responsible for this dilution.

Chapter 4 describes the core sampling and analysis for two similar sedimentation zones of two major river deltas. Uniformly soft anoxic sediments in the Volga and Danube deltas were collected, using satellite images, which reflect the concentration of suspended solids. Cesium-isotope dating and measurement of the concentration profiles of heavy metals and PAHs, which reflect (without serious alterations) the historic pollution input into these rivers, were used in the comparison. The contents of the 7 PCBs investigated and of cadmium were below the detection limits for all sediment samples in the Volga and Danube deltas. Low, more or less constant concentrations of arsenic, copper, zinc and all studied PAHs were observed in sediments of the last five decades in the Volga river. Nickel concentrations in Volga delta sediments were rather high, and recently deposited sediments seemed to show slightly increasing levels for zinc, chromium and arsenic. The pollution history of the Danube is characterized by low concentrations of metals but elevated PAH levels in the early 1940s; increasing levels of metals and PAHs between 1950 and 1987; and decreasing levels in more recently deposited sediments. When comparing the concentrations of heavy metals, PAHs and PCBs in the aquatic sediments of the rivers Rhine, Danube and Volga deltas for the past five decades it is evident that the Volga delta was, and still is, the cleanest of the three. A combination of natural (background) inputs, industrial inputs and man made technical changes in the river systems (like the building of storage lakes) can explain most differences in the historical contaminant profiles of the three deltas. Nowadays the concentrations of heavy metals (except copper and nickel), PAHs and PCBs in sediments of the river Rhine are still higher than in the other two rivers, but the sediment loading rate for heavy metals (except cadmium and zinc) of the Danube is higher than for the other two rivers.

In *Chapter 5* the geostatistical sampling approach chosen for Lake Ketelmeer is explained. When monitoring contaminants and related sediment characteristics in an aquatic environment, their spatial variability needs to be taken into account. The sampling strategy covered short-distance variability (65 m) and long-distance variability (500 m) of the investigated variables. In Lake Ketelmeer we chose three sub-areas. The distances between sampling points takes into account the size of each sub-area. With this approach the number of sampling points needed to monitor trends of contaminants in sediments can be minimized, taking into account the necessary accuracy. The choice of sampling strategy for monitoring sub-areas, characterised by either water depth, sedimentation/erosion behaviour or sediment type, will result in different sampling spacings. For example, in Lake Ketelmeer the optimal sampling distance for monitoring Benzo(A)pyrene (BAP) in the central part of the lake was larger than

near the harbour and shore, where gradiënts in water depth are steeper. Thus, when designing a dredging programme to remove seriously contaminated sediments, the identification of sub-areas is essential to ensure the adequate dredging of the sediments. If spatial variability is not taken into account for dredging contaminated layers, seriously contaminated spots may be overlooked or rather clean sediments may be dredged needless. Thorough (although expensive) spatial investigations of the contaminated layer before dredging starts, identifying critical sub-areas, is therefore recommended. Practical, cost-effective, geostatistical methods allow an efficient use of limited financial resources for monitoring aquatic sediments.

Another important process affecting sediment concentration profiles is consolidation. *Chapter 6* deals with this physical process of settling of suspended solids and the loss of water after deposition. Consolidation in principle can be described by mathematical models, but because of local circumstances in the Lake IJsselmeer area an empirical approach seemed more reliable. Five representative cores of the IJm-deposit were taken from deep zones of the lakes. Periodic water depth surveys at these locations over the last sixty years provided information on the net sedimentation rate and total thickness of the IJm-deposit at known time intervals. To calculate a time-equivalent of the depth scale, correction factors for sediment consolidation were needed. These factors were based on a simplification of the various stages of compression (i.e. 0%, 30% and 45%). A factor n, which represents changes of water content of the sediment as a dependent variable of clay content, was derived for each layer, making it possible to determine the initial, uncompressed thickness of each layer by an inverse calculation procedure. Hence, a fairly reliable time-scale for depth could be reconstructed. This time-scale was compared with radio-isotope-dated layers and the results showed close consistency.

Annual variability of contaminants in the IJsselmeer area is described in *Chapter 7*. Measurements of the concentrations of six heavy metals in suspended solids, discharged by the river IJssel, and settling solids at two locations in Lake IJsselmeer showed a typical spatial gradient. The heavy metals concentrations decreased with increasing distance from the river IJssel inlet. This spatial gradient corresponds with gradients observed in the bottom sediment (Chapter 3). Measurements in sediment cores from Lake Ketelmeer, i.e. the river mouth, and the central part of Lake IJsselmeer showed that the heavy metals concentration in sediments, deposited during the same periods, is 2 to 3 times higher in Lake Ketelmeer than in Lake IJsselmeer. The concentration gradient in the settling solids is still significant when changes in the clay and organic matter content are accounted for by using normalized metal concentrations. A rough sediment mass balance for heavy metals, based on river input data and observed sedimentation fluxes, indicates that the total internal sedimentation fluxes of heavy metals in Lake IJsselmeer far exceed the external aereal loading by the river. Due to the complexity of the relationships between the measured variables, the heavy metal concentrations and variables related to primary production and erosion, single correlation analysis did not reveal clear relations and processes that could explain this dilution. Principal component analysis and stepwise multiple regression however showed that the variation in the heavy metals concentration in settling solids is related to wind velocity and clay content, both of which are related to resuspension/erosion of sediments; or alternatively, to pH, chlorophyll and $CaCO_3$, which are in turn related to algal growth in the lake. Resuspension/erosion-related variables are the dominant factors explaining the variation in heavy metals concentration in the southern part of Lake IJsselmeer, whereas algal-growth-related variables explain most of the variation in the metal concentrations in settling solids in the central part of the lake. In this central part, where algal concentrations are high, the negative relation between the concentration of most of the heavy metals in settling solids and the chlorophyll and organic matter concentration in the water compartment justifies the conclusion that dilution of contaminated suspended solids by primary production is active there. In the southern part of the lake, the heavy metals concentration is positively related to wind velocity and clay content. This indicates that resuspension of recent deposits con-

General introduction

Introduction

In the aquatic environment chemical substances, including heavy metals, arsenic, polychlorinated biphenyls (PCBs) and polychlorinated aromatic hydrocarbons (PAHs), originating from natural and cultural (industrial) point sources and from diffuse sources, have been detected during the last decades (Anonymous, 1992; Beurskens, 1995). These contaminants tend to concentrate on solids, either suspended or settling and in sediments. The fate of these contaminants in lakes or rivers depends on physical transport, physico-chemical distribution, and transformation processes (Koelmans, 1994). Characteristics of the aquatic system as well as the properties of the contaminant in question determine the rate and extent of processes like transport by water flow, sedimentation, resuspension, erosion and (photo)-(bio-)chemical degradation (Baughman and Burns, 1980; Burns and Baughman, 1987).

In sedimentation zones, where stream velocities decrease, the suspended solids settle with the associated contaminants. The main sedimentation zones of major rivers are their deltas. Here accumulation of contaminated suspended solids is likely to occur. The flow of water and the deposition of particles in deltas is different for each river. It depends e.g. on the origin and discharge of the river, the size of the catchment area, the slope of the riverbed between catchment area and delta, stream velocities in branches, marine processes such as surf and tide (tidal interactions) and the anthropogenic influences, like canalization and riverbed control (Summerfield, 1991; Reading, 1996). The anthropogenic influences responsible for contamination in the entire catchment area will therefore result in spatial and temporal contaminant variability in the deltas.

The river Rhine enters the North Sea in the Netherlands; it drains a highly industrialized part of northwestern Europe. The river has a controlled (endiked) riverbed, is partly canalized and has its main sedimentation zones in front of the Dutch coastline, due to coastal protection works. Sedimentation occurs further in major lakes in central (Lake Ketelmeer/Lake IJsselmeer) and western parts (Hollandsdiep/Haringvliet) of the Netherlands. During the last decades water quality monitoring programs have provided information on the pollution history of this river. Also sampling of sediments in the sedimentation zones of this river started during the last decade, as a preparation for future dredging of contaminated sediments in these lakes.

Aquatic sediments in sedimentation zones of major rivers are in general sinks of pollutants (Salomons and Förstner, 1984; Van der Weijden and Middelburg, 1989). The sedimentation zone Ketelmeer/IJsselmeer is an important sink of contaminants of the river Rhine (i.e. river IJssel). Recent and historical pollution interact here. Redistribution of suspended solids and erosion of deposited sediment in the shallow Dutch lakes (due to wave action) is likely to change contamination levels of sediments in these lakes, which is the subject of this thesis.

The aim of this research is to study and explain the variability of contaminants in the sedimentation area Ketelmeer/IJsselmeer in order to predict the fate of the contaminants in the future. Therefore methodologies and models are developed and/or adapted in this study. Below general information is presented on the studied IJsselmeer area and its contaminant levels in the central part of the Netherlands. The outline of this thesis is presented in the last section.
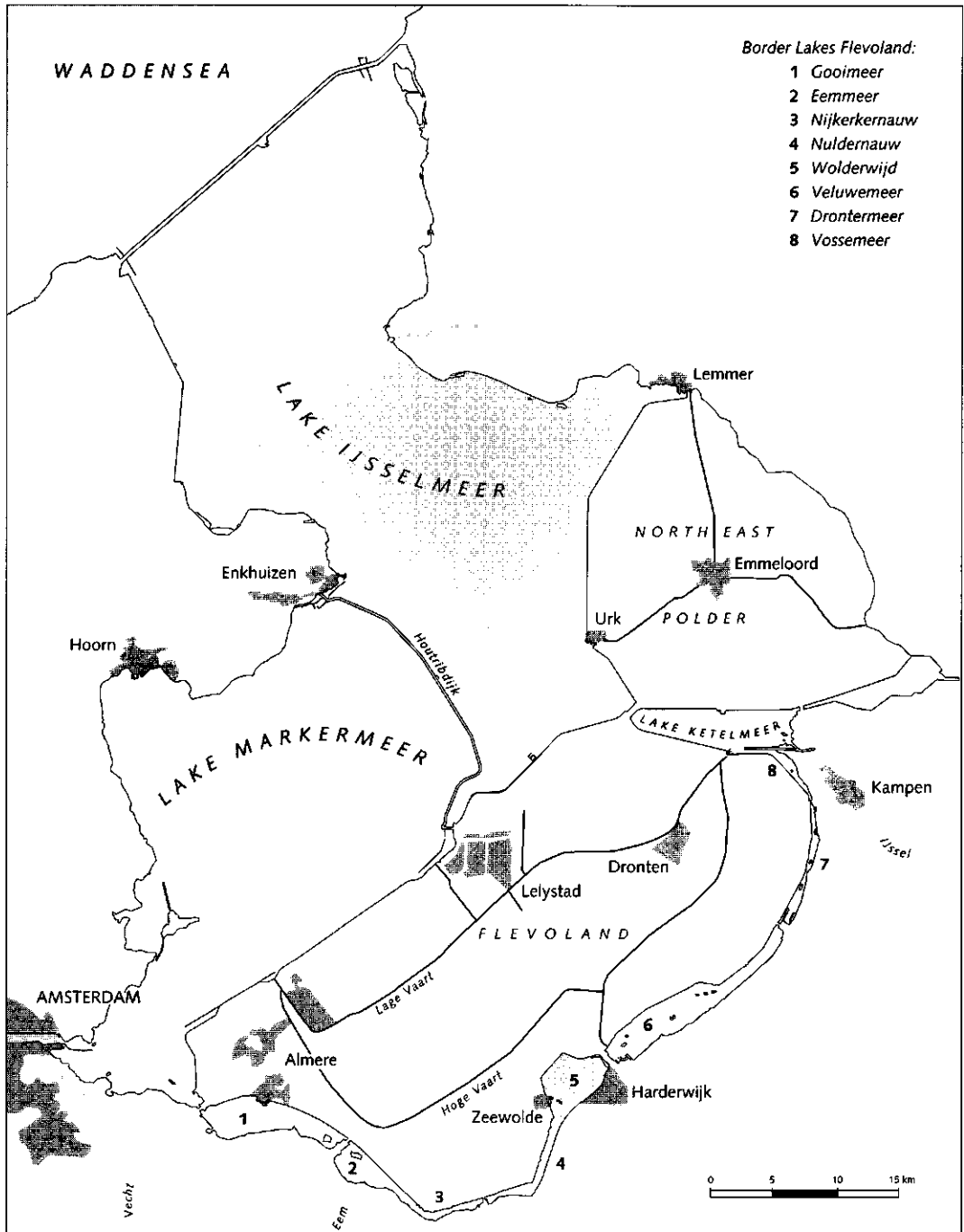
Fig. 1.1. The IJsselmeer area.

IJsselmeer area

Before 1932 the Zuiderzee in the centre of the Netherlands had an open connection with the Wadden Sea (Fig. 1.1), which is connected to the North Sea. Hence the water was saline. In this environment during the period 1600-1932, the Zuiderzee sediments (Zu-deposits; Fig. 1.2), were deposited in this area. These sand or clay deposits can be visually identified by the presence of shell fragments (*Mya arenaria*).

The Zuiderzee Project involved the damming of the Zuiderzee, the creation of a large freshwater lake, named the IJsselmeer, and the creation of over 2000 km^2 of new land (Van Duin and De Kaste, 1985; Van Duin, 1992). With the reclamation of the polders of Flevoland also border lakes were developed between these polders and the main land on the East and South sides (Fig. 1.1; numbers 1-8).

When the influence of tidal waves with their strong erosive potential was excluded from this area, the original water depths readjusted to the new conditions. In these shallow freshwater lakes the importance of water movement, horizontal transport of solids by advection and dispersion, resuspension of bottom sediment due to wind-induced wave action, sedimentation and erosion became dominant (Van Duin, 1992). Ente (1981) showed that deeper zones in Lake IJsselmeer and Markermeer became more shallow due to deposition of freshwater sediment. He defined these freshwater mostly loamy sediments deposited during the period 1932 till nowadays as the IJsselmeer-deposit (IJm-deposits). IJm-deposits are thought to be partly eroded Zu-deposits mixed with settling sediment entering the area through the river IJssel.

Table 1.1. Comparison of sizes, water depths and range of contamination in the top layer sediments of all interlinked lakes in the IJsselmeer area.

	Lake Ketelmeer (n = 36)			Lake IJsselmeer (n = 54)			Lake Markermeer (n = 35)			Border Lakes Flevoland[1] (n = 86)		
Size (km^2)	38			1136			680			107		
Aver. waterdepth (m)	3.5			4.7			3.9			2.0		
Range of contamin. (mg/kg) Aver. (stand. dev.)												
As	20 -	31	**24** (3)	2 -	29	**11** (7)	4 -	25	**15** (5)	2 -	40	**8** (5)
Cd	4 -	27	**10** (6)	0.5 -	7	**2** (2)	0.5 -	2	**0.7** (0.3)	0.4 -	6	**0.9** (0.7)
Cr	67 -	315	**174** (62)	2 -	133	**38** (29)	17 -	75	**55** (15)	3 -	144	**27** (21)
Cu	84 -	192	**117** (26)	0.5 -	81	**22** (18)	5 -	33	**18** (7)	1 -	92	**14** (14)
Hg	1.1 -	2.9	**2.1** (0.5)	0.1 -	2.6	**0.4** (0.4)	0.1 -	0.6	**0.2** (0.1)	0 -	1.6	**0.1** (0.2)
Pb	91 -	272	**156** (43)	0.5 -	138	**36** (33)	4 -	57	**28** (16)	1 -	195	**19** (24)
Ni	44 -	60	**49** (4)	0.5 -	61	**17** (13)	7 -	28	**20** (5)	2 -	58	**17** (11)
Zn	918 - 2366		**1286** (342)	15 - 1046		**30** (233)	31 - 275		**126** (78)	8 - 803		**136** (138)
Σ7PCBs[2]	0.05 - 1.13		**0.24** (0.16)	0.01 - 0.15		**0.03** (0.03)	0.01 - 0.04		**0.03** (0.01)	0.01 - 0.41		**0.05** (0.06)
Σ10PAHs[3]	5.4 - 17.5		**12.1** (2.9)	0.02 - 6.9		**2.0** (1.7)	0.5 - 4.3		**1.7** (0.8)	0.11 - 59		**4.6** (10.8)

[1] Border Lakes Flevoland: Lake Gooimeer, Lake Eemmeer, Lake Nijkerkernauw, Lake Nuldernauw, Lake Wolderwijd, Lake Veluwemeer, Lake Drontermeer and Lake Vossemeer (numbers 1-8 in Fig. 1.1)

[2] PCB-congeners (IUPAC no.): 28, 52, 101, 118, 138, 153 and 180

[3] PAHs: fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, fluorene, benzo[b]fluoranthene, anthracene, phenanthrene, benzo[ghi]perylene, indenopyrene and chrysene

Fig. 1.2. The sediments of the Zuiderzee before the enclosure of the barrier dam in 1932.

Legend
- Sand
- Loamy sand
- Loam
- Clay
- Peat
- Boulder clay

0   4   8   12 km

During the period 1988-1995 all interlinked lakes in this area were investigated for their geological structure, toplayer composition and the degree of contamination of this toplayer at 211 locations. Present sediment types for all interlinked lakes are given in Figure 1.3. Present lake sizes, average water depths and range of contamination for heavy metals and the groups of 7 polychlorinated biphenyls (PCBs) and 10 polycyclic aromatic hydrocarbons (PAHs) are presented in Table 1.1.

To study these spatial variations of contaminant contents in toplayer sediment, differences in sorption affinity of the particles should be accounted for. This can be done by standardization with respect to the contents of the different absorbing components in sediments. In this chapter normalized contaminant contents (corrected amounts) are calculated using clay and organic matter contents at each location (Dutch standards, see for calculation methodology Chapter 3). In most chapters of this thesis, except Chapter 2, 5 and 8, normalized contaminant contents are presented.

Lake Ketelmeer (38 km^2) was created as a wide river mouth between two constructed polders. The dike at its present northern boundary was constructed in 1938 and the southern one in 1953. It is the first sedimentation basin of the river IJssel, a northern branch of the Rhine. Enrichment with nutrients and contamination with heavy metals and organic pollutants, is mainly caused by this river. It has slightly contaminated sandy sediments in the eastern part and severely contaminated loamy sediments in the central and western part (Winkels and Van Diem, 1990). Dredging of this contaminated material is foreseen for the loamy sediments (IJm-deposits) in the near future.

Lake Ketelmeer has an open connection with Lake IJsselmeer, a large (1136 km^2), shallow eutrophic lake, with mainly sandy sediments and with high net sedimentation rates of fine settling solids in its deeper parts (Vink and Winkels, 1991). The IJm-deposits cover the deepest part, which is 25% of the IJsselmeer lake bed. Only these IJm-deposits in this lake are slightly contaminated with mainly heavy metals. During the summer in Lake IJsselmeer an internal production process is clearly reflected in an enhanced concentration of organic matter and in the occurrence of algal blooms (Hoogeveen, 1995). Nutrient concentrations in the area are usually exceeding 0.1 g P $\cdot$ m^{-3} and 2.2 g N $\cdot$ m^{-3}. These are typical Dutch standards which should be met, to have acceptable nutrient concentrations in this lake (de Rijk, 1990). In general green algae make up more than half of the biomass in Lake IJsselmeer (>100 mg $\cdot$ m^{-3} chlorophyll-a), mainly *Scenedesmus* species. Most often blooms of *Microcystis aeruginosa* occur (Berger and Sweers, 1988).

The Houtribdijk, separating Lake Markermeer from Lake IJsselmeer, was constructed in 1975. Nowadays Lake Markermeer (680 km^2) is a shallow eutrophic lake with mainly loamy and clayey deposits at the bottom. The IJm-deposits are found in the deeper eastern part of this lake. The sediments are in general not contaminated with heavy metals, PCBs or PAHs (Winkels, 1994). The water quality of the lake, with respect to contamination, phytoplankton blooms and eutrophication, is good, compared to other lakes in the area (Van Duin, 1992). Processes in the lake are dominated by the intensive resuspension and subsequent settling of sediment. This results in a highly fluctuating suspended solids content in the water, which is held responsible for the absence of blooms such as those of *Oscillatoria agardhii* in this lake (Berger et al., 1986).

The so called border lakes of Flevoland (nrs. 1 to 8 in Figure 1.1) are rather shallow and vary in their physical characteristics from one lake to the other. All kinds of sediments are found here and annual nutrient input fluxes are mostly high, up to 30 g P $\cdot$ m^{-2} and 90 g N $\cdot$ m^{-2} in Lake Eemmeer and Lake Gooimeer (Berger, 1987). The sediments in these lakes are in general not contaminated with heavy metals, PCBs or PAHs (Vink and Winkels, 1996). Higher PAH-levels in the sediments are mainly found in harbors.

Figures 1.4 and 1.5 give an impression of spatial variability of contaminants in this area. The figures are based upon the analysis of the toplayer (211 locations) in this area. Iso-lines of normalized sediment concentrations have been drawn in these figures, taking into account the location of different

Legend

■ Sand

□ Loamy sand

▦ Loam

■ Clay

■ Peat

■ Boulder clay

▨ Sandpit or dredged parts shipping route

0   4   8   12 km
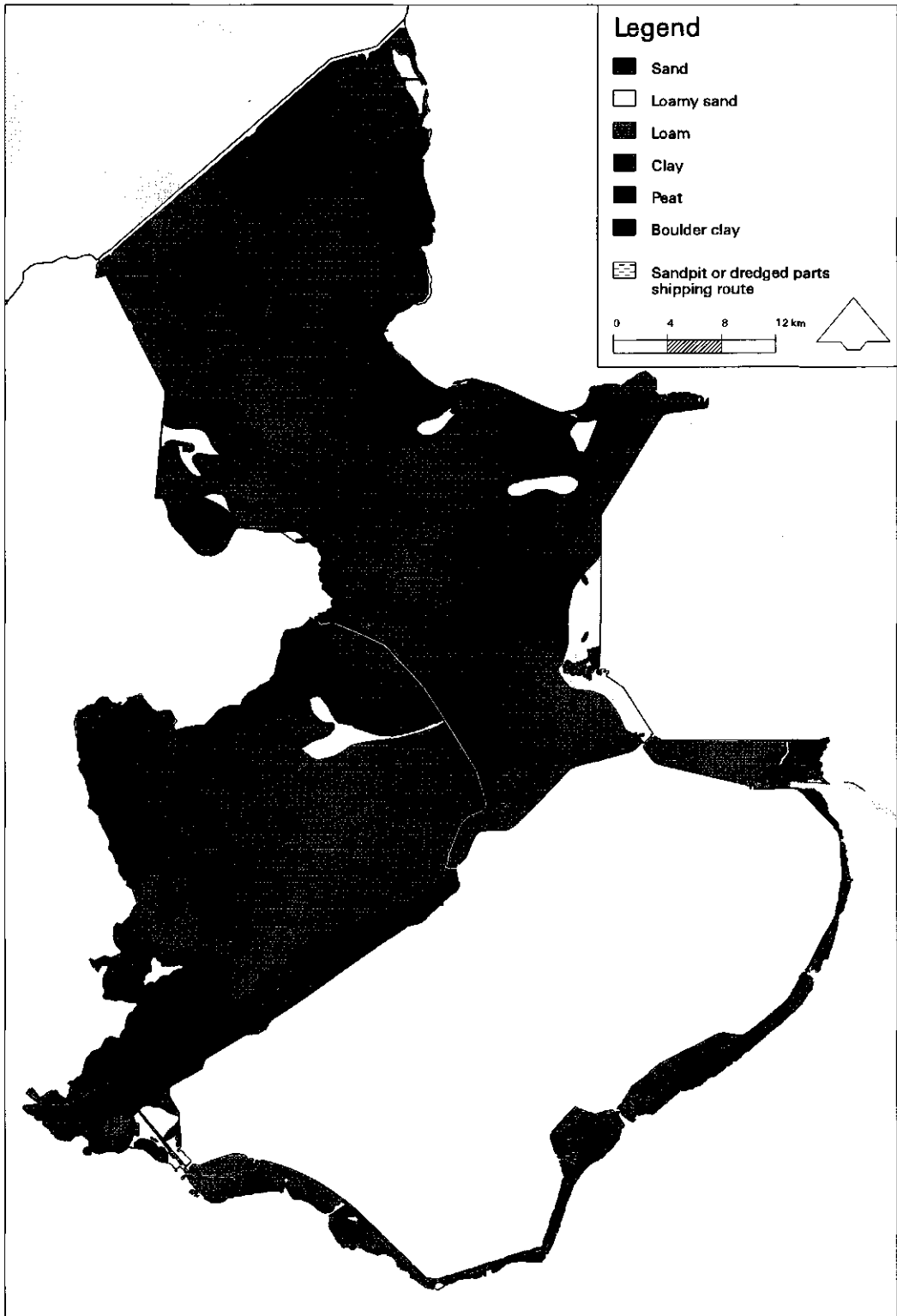
Fig. 1.3. The present-day toplayer sediments (0-0.05 m) in the lakes of the IJsselmeer area.

Legend

Corrected amount in mg/kg dm

- < 2.0
- 2.0 - 7.5
- 7.5 - 12.0
- > 12.0

Sandpit or dredged parts
shipping route

0   4   8   12 km
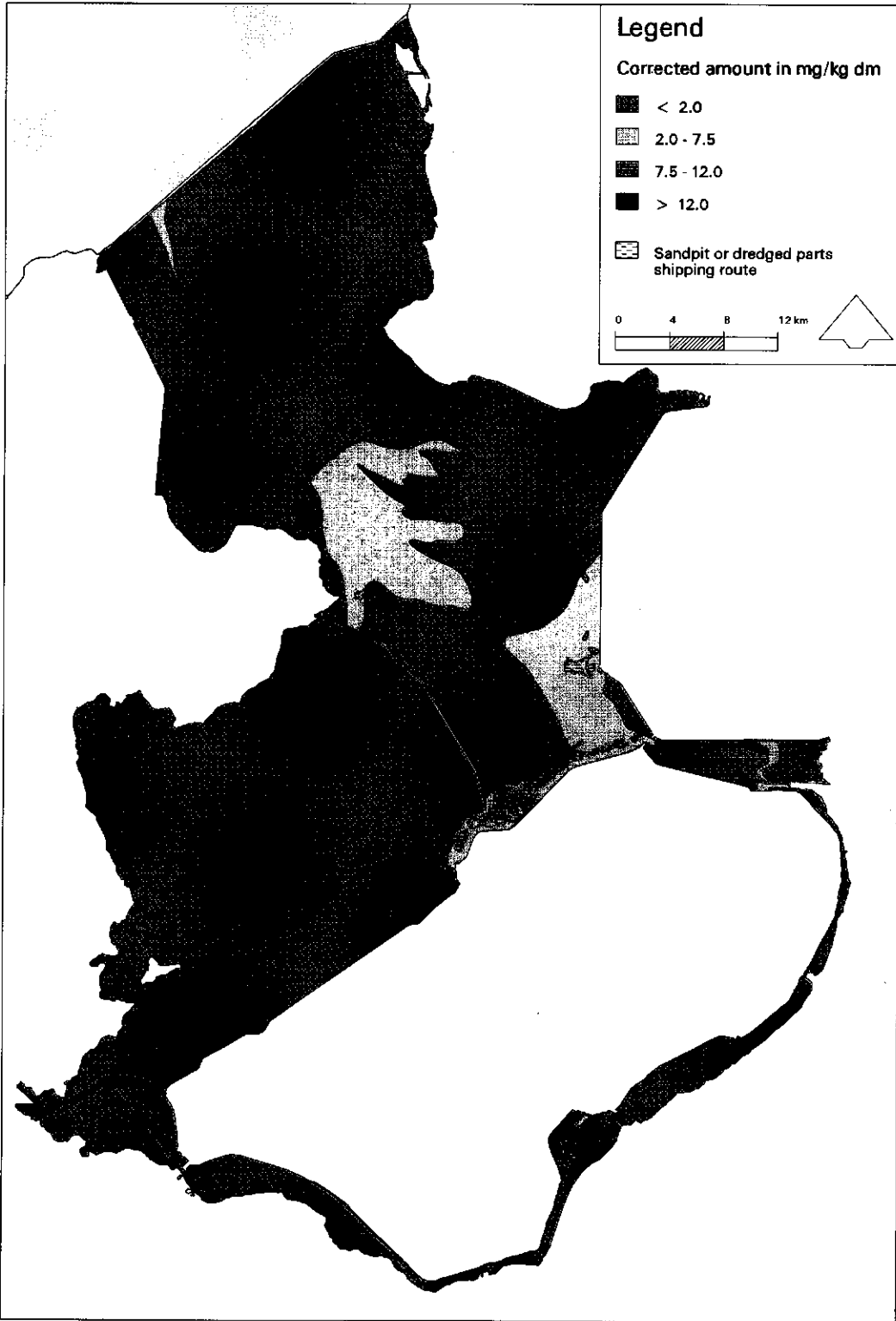
Fig. 1.4. The variability of cadmium concentrations in the toplayer sediments of the lakes in the IJsselmeer area.

Legend

Corrected amount in mg/kg dm

- < 1.0
- 1.0 - 10.0
- 10.0 - 40.0
- > 40.0

Sandpit or dredged parts shipping route

0   4   8   12 km

Fig. 1.5. The variability in concentrations of the sum of ten individual PAHs in the toplayer sediments of the lakes in the IJs-selmeer area.

sediment types in the area (Fig. 1.3). Figure 1.4 indicates that the river IJssel is the direct source of heavy metal contamination for this area, as can be seen in the present spatial variability of cadmium contamination. Figure 1.5 shows that besides the river IJssel also other sources (like atmospheric deposition and point sources) are responsible for the contaminant variability of $\Sigma 10$PAHs in this area. In Appendix 1 a geochemical characterization of the IJm-deposits in Lake Ketelmeer, Lake IJsselmeer and Lake Markermeer is presented. It shows that within this deposit the spatial chemical and contaminant variability in the area is high.

Outline of this thesis

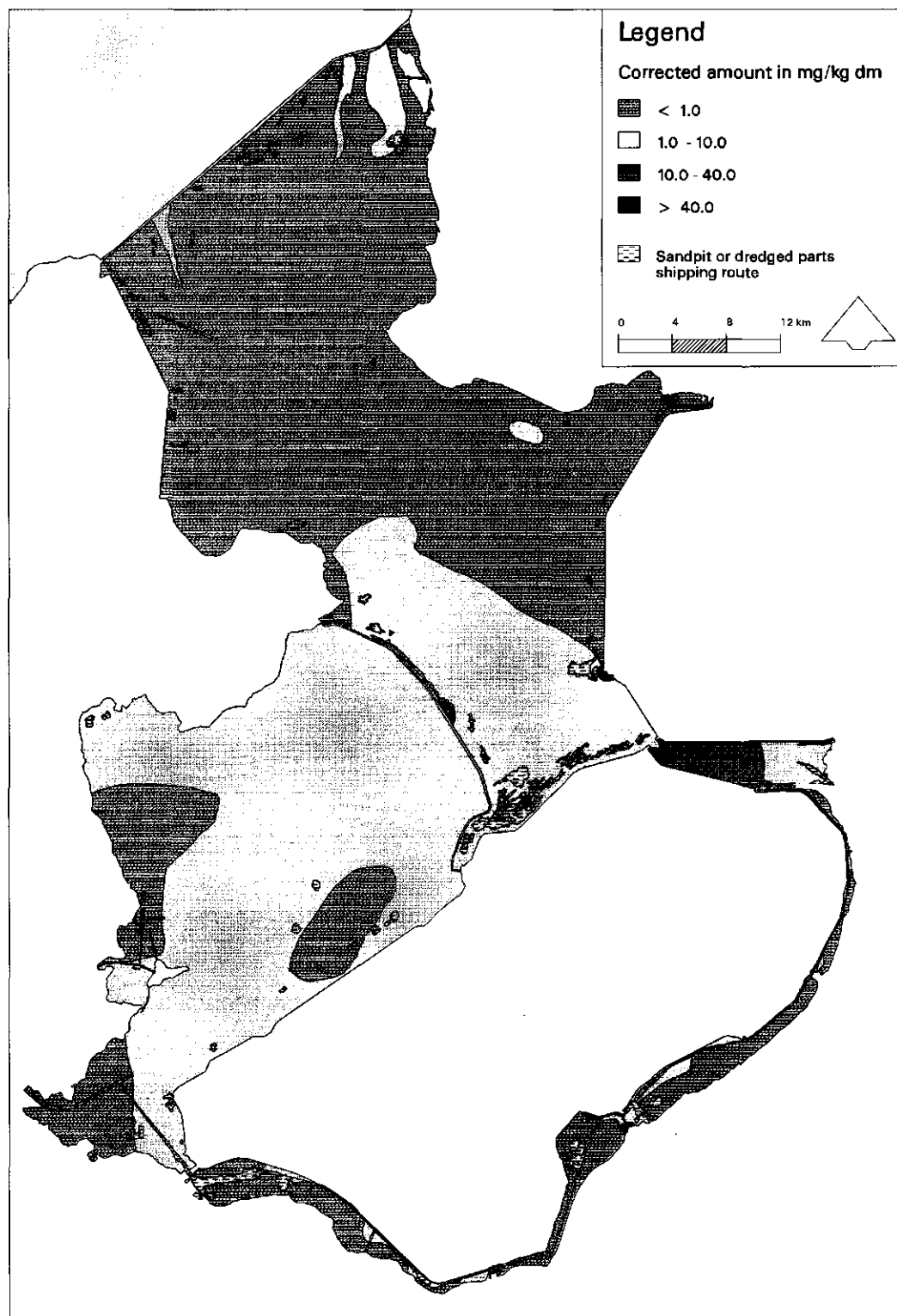*Chapter 2* describes the results of sampling and analysis of aquatic sediments in Lake Ketelmeer, and the reconstruction of the historical input of contaminants by the river Rhine. The levels of priority pollutants (heavy metals, arsenic, PCBs and PAHs) in dated sediment cores from this lake are used in this analysis. Area-specific geological time markers and radionuclide time tracers are used to establish present-day and historical levels of pollution since the late 1930s. Postdepositional redistribution of pollutants and possible transformations are evaluated as well.

In *Chapter 3* the distribution and geochronology of the priority pollutants is described for a larger sedimentation zone, Lake Ketelmeer and Lake IJsselmeer. The contents of these contaminants in the top layer differ substantially due to differences in type of sediment between both lakes. Therefore absolute contents are corrected here according to a Dutch normalization procedure. Furthermore dilution of the polluted suspended solids with local sediments in Lake IJsselmeer is demonstrated. For this previous (former) sampling results and a study of deeper cores in both lakes is used.

The information on the present contents of priority pollutants of deposits in the Rhine delta has increased during the last decades, but a comparison with other major European rivers has not been made so far. *Chapter 4* presents such a comparison. The same geochronological approach of sampling, analysis and dating core samples is applied (Chapter 2) here to reconstruct historic input profiles of priority pollutants in the deltas of the Danube and Volga river. Also differences in contaminant levels during the last five decades between the Rhine, the Danube and the Volga delta are discussed.

In *Chapter 5* spatial statistics is used to study the variability within contaminated sediments of three zones in Lake Ketelmeer. Application of this geostatistical approach in an aquatic environment is relatively new. These three zones are selected for sampling, using prior knowledge of sediment type, sedimentation/erosion zones, water depth and shipping routes. Optimal sampling distances for assessment of the contamination levels and of the thickness of the contaminated layer in the sediments are estimated taking spatial variability in these zones into account. A new optimal, cost-effective method for accurate aquatic monitoring is investigated as a preparatous step to the decision making on the removal of contaminants in the future.

Another approach for reconstruction of pollution history is shown in *Chapter 6*. Here also the in-situ consolidation of aquatic lake deposits during several decades in Lake IJsselmeer area is described. The subsequent loss of water volume in these aquatic sediments due to consolidation is investigated to quantify this process.

Measurements in sediment cores showed that the heavy metal concentrations in deposits from the river IJssel are 2 to 3 times lower in Lake IJsselmeer than near the river mouth. *Chapter 7* evaluates the effects of sediment erosion and primary production on the temperal and spatial variability of the heavy metals concentration in settling solids in Lake IJsselmeer. It focusses on the annual differences between historic input of the river IJssel in the region and the annual amount of metals on settling solids at two locations in Lake IJsselmeer. Furthermore wind speed and direction and the suspended solids, organic

Geochronology of priority pollutants in Lake Ketelmeer, a sedimentation area of the river Rhine

Abstract - Toplayer samples and subsequently three and eight sediment cores were taken from Lake Ketelmeer, a sedimentation area of the Rhine River, located in the central part of the Netherlands. Priority pollutants (8 metals, 6 planar and mono-ortho polychlorinated biphenyls and 8 polycyclic aromatic hydrocarbons) were determined in all or in a selected number of samples and cores. Present-day and historical levels of pollutants since the late 1930s were established through the use of radionuclide time tracers (^{137}Cs, ^{134}Cs) and area-specific geological time markers. Postdepositional redistribution of pollutants and possible transformations were evaluated by analyzing sediment toplayer samples that were taken in 1972. Disappearance in the anaerobic sediment was observed for several chlorinated biphenyls. For the metals and polycyclic aromatic hydrocarbons trends in the concentration profiles during the last five decades are described. Rather low concentrations of almost all studied chlorinated compounds were observed in the early 1940s. These low levels were in contrast to the metal and PAH concentrations, which were already high in the late 1930s but decreased during the second world war. For all studied compounds, maximum concentrations were found between 1955 and 1975. Cadmium and nickel levels remained high until 1980. Recently deposited sediments showed lower pollutant levels. The levels of lead, arsenic, and all studied PAHs were the lowest observed in the past five decades.

Introduction

A wide range of chemical substances, including heavy metals, radionuclides, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) can be detected in natural aquatic environments. These pollutants originate from a variety of direct and indirect sources. The high affinity of these pollutants for particles within the water column results in relatively high pollution levels of the suspended solids. Where stream velocities decrease, for example in the lower stretches of rivers, the suspended solids settle with the associated pollutants. Once delivered to the bottom sediments, particle and pollutant burial will be affected by resuspension and bioturbation. Sediment mixing by zoobenthos at the sediment-water interface may lower pollutant concentration peaks and distribute pollutants vertically, as can be observed in sediment cores from areas with high biological activity and relatively low sedimentation rates (Robbins, 1982). Other processes such as molecular diffusion, transport with infiltrating water, and biotransformation of the organic pollutants, may also alter the pollutant profile recorded in the sediment.

Dated sediment cores have the potential for providing detailed chronologies of pollutant input as long as bioturbation, molecular diffusion, transport with water and biotransformation are (or may be considered to be) negligible. Based on dated sediment cores, the depositional history of metals, PCBs, PCDDs, PCDFs, and PAHs has been documented for the North American Great Lakes (Förstner and

(IJm) deposit, is defined as the silty sediment deposited since 1932. The underlying Zuiderzee (Zu) deposit, a saltwater clay deposit, can be identified by the presence of shellfragments (*Mya arenaria*). The average thickness of the IJm-deposit is 0.45 m. The net sedimentation rate (presently approximately 0.01 m per year) has doubled since 1953 and accelerated deposition occurs in deeper zones (Winkels *et al.*, 1990). Toplayer samples, samples of the total IJm-deposit and samples of the Zu-deposit were taken evenly spread over the central and western part of the lake. The sediment cores were taken at locations known for their thick IJm-deposits. The majority of Lake Ketelmeer sediment is anaerobic; only the toplayer (1-3 cm) at the interface with the water is aerobic. Chemical characterization of the IJm-deposit indicates that illite is the dominant clay mineral (60% w/w), with smaller contributions of montmorillonite (20% w/w) and kaolinite (20% w/w) (Rijniersce, 1983).

Sample collection and treatment
In 1987 at twenty different locations toplayer (0.15 m in diameter and average length 0.1 m) and total samples (0.15 m in diameter and average length 0.45 m) of the IJm-deposit were taken with an open auger (Fig. 2.1). At five of these locations also the underlying Zu-deposit was sampled (0.15 m in diameter and length 0.05 m). In certain areas of Lake Ketelmeer the geological, chronological sedimentation sequence is disturbed by sandpits, which were dug to gain sand for road and dike construction in the polders. Here accelerated deposition of the IJm-deposit occurs, since the moment these pits were created. In three of these sandpits, created in 1960, 1966 and 1986 (Fig. 2.1), respectively, cores were taken with an open auger. These cores, containing IJm-deposits only, were sectioned into four, five and two depth intervals, respectively.

Subsequently, in 1988 and 1990 eight undisturbed sediment cores (0.15 m in diameter and average length of approximately 1 m) were taken with an open auger (Fig. 2.1). These cores, also containing mainly the IJm-deposit, were sectioned into 0.05 to 0.10 m intervals. One of these cores, taken from a former sandpit (created in 1938), was sectioned into 0.25 m intervals. At this location the thickness of the IJm-deposit was about 4.2 m.

All samples were put in glass jars with screw caps, refrigerated at 4 °C and transported. Before subsamples were taken for the different chemical analyses, samples were freeze dried and homogenized.

Finally sediment toplayer samples (0.05 m) from 1972 were collected by the Institute for Soil Fertility Research, Haren, the Netherlands. The 10 samples taken in 1972 originate from the same areas as the eight sediment cores taken for this study. After collection in 1972, the toplayer samples were dried overnight at 40 °C and stored in jars with screw caps at room temperature in the dark. Losses of organic pollutants during the drying procedure were negligible (Japenga *et al.*, 1990). In these toplayer samples only some heavy metals were determined soon after collection. Together with all other samples the organic pollutants were measured in these toplayer samples from 1972.

Sediment dating
The age of the twenty toplayer samples and of the twenty samples from the total IJm-deposit are not known a priori, but toplayer samples are thought to represent recent deposition of contamination.

The age of the different layers in the sediment cores was estimated by several methods. First, the well known geological history of this area offers some valuable recognition points in the cores. The interface between Zu-deposit and IJm-deposit is visually recognizable and indicates the early 1930s. Until 1953, when the southern dike of Lake Ketelmeer was completed, sedimentation occurred over a much larger area. As a result, only a thin sediment layer represents the period of 1930 to 1955. The core samples from the former sandpits, represent sediment deposited after the moment they were created. These sandpits act as sediment traps with high sedimentation rates (approximately 0.15 m per year). Second, ^{137}Cs and ^{134}Cs gamma activities were determined on 25 to 250 cm^3 of freeze dried core

sediment by counting up to 1000 min with a coaxial G detector (P-type) coupled to a multichannel analyzer. The Canberra S 340 DOS/SPECTRAN-AT application software package was used for operation of the system and analysis of the recorded gamma spectra. Third, heavy metal concentrations in sediment layers were related to the well known metal pollution history of the Rhine River. The use of the ^{210}Pb-dating technique (Robbins and Edgington, 1975) proved to be problematic in these cores, probably due to high and variable discharges of ^{210}Pb or mother nuclides (^{226}Ra) in the Rhine River.

Analysis of organic carbon and heavy metals
The organic carbon content of the sediment samples was measured by an element analyser (Carlo Elba NA 1500, Milan, Italy) after removal of carbonates with phosphoric acid.

Heavy metal contents of the freeze-dried sediment core samples were determined after sample treatment with strong acids: hydrochloric acid for Cd and Pb, a mixture of sulfuric acid, nitric acid and hydrogen peroxide for As, Cr, Cu, Ni, and Zn; and a mixture of sulfuric acid, nitric acid, and potassium persulfate for Hg. Cadmium, Cr, Cu, Ni and Pb were analyzed by graphite furnace atomic absorption spectrometry (Perkin Elmer 5000, Norwalk, CT). Zinc was analyzed by flame atomic absorption spectrometry (Perkin Elmer 5000). Arsenic was analyzed using the hydride technique (Perkin Elmer 5000 + MHS1) and Hg by a mercury monitor (Milton Roy, HGM 2300, Rochester, NY). Toplayer samples and samples of the total IJm-deposit were analyzed for heavy metals using a similar approach as described by Hofstee (1983). Zinc, Cu, Cd, Pb and Cr contents in the toplayer samples from 1972 were determined at the Institute for Soil Fertility Research by similar analytical methods (Japenga *et al.*, 1990).

Analysis of PCBs
Seven PCBs, i.e. PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180 were determined in all toplayer and total IJm-deposit samples and in the three sandpit cores (all sampled 1987). These PCBs were analysed according the methodology described by Van Zoest en Van Eck (1990). Six mono and planar PCBs (sampled in 1998-1990), i.e. PCB 77, PCB 105, PCB 118, PCB 126, PCB 156, and PCB 169 were analysed in all layers of three selected cores and in five toplayer samples from 1972. Latter analyses were performed in combination with analyses of PCDDs and PCDFs. Sediment sample clean-up and analytical procedures were adopted from the literature (Smith *et al.*, 1984; Rappe, 1984), however, some minor modifications were applied as described by Beurskens *et al.* (1993). The extracts were analyzed by GC/MS (Hewlett Packard 5890-5971, Avondale, PA) operating in the selective ion monitoring (SIM) mode. The planar and mono-ortho PCBs were analyzed with a 60 m capillary column (SE 30, 0.25 mm i.d., film thickness 0.25 μm).

Analysis of PAHs
The PAH compounds evaluated in this study included fluoranthene (Flu), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), fluorene (Fle), benzo[b]fluoranthene (BbF), anthracene (Ant), phenanthrene (Phen), benzo[ghi]perylene (Bghi) and indenopyrene (Ind). Sediment samples were extracted twice with acetone for 15 min. Acetone was removed by mixing the extracts with petroleum ether and washing them with water. After separation, the aqueous phase was extracted with a second portion of petroleum ether. The combined petroleum ether extract was dried with Na_2SO_4 and concentrated with a Kuderna-Danish condensor (Technoglas, Voorhout, the Netherlands) to a volume of 5 ml. The extract volume was further reduced with a gentle stream of clean nitrogen to 1 ml. Extract cleanup consisted of passing the extract through a column of 2 g 11% (w/w) deactivated alumina (alumina W200, Super I Woelm, ICN, Enschwede, Germany) and through a column of 2 g 6% (w/w) deactivated silica (Merck 7754, Darmstadt, Germany). After sample cleanup a solvent exchange to acetonitrile was carried out.

The sample extracts were injected into an HPLC (Perkin Elmer pump 250 and Spark Marathon autosampler, Emmen, the Netherlands) fitted with a 25 cm Vydac 201 TP-5 column (4.6 mm i.d.). The extracts were eluted isocratically for 5 min with 50% (v/v) acetonitrile in water and subsequently with a linear gradient to 100% acetonitrile in 15 min. The mobile-phase flow was 1.5 ml/min. The column effluent was monitored with a fluorescence detector (Perkin Elmer LS40) and a UV-detector (Kratos 783, Kratos Analytical, the Netherlands).

All concentrations of radionuclides and pollutants are reported on a per-dry-weight-of-sediment basis. Concentrations of pollutants have not been corrected according to a Dutch normalization procedure as described in Chapter 3 of this thesis. Normalized results would give similar results to the raw data presented here, because IJm-deposits in Lake Ketelmeer have a rather constant clay and organic matter content. For this reason and to compare the results of this chapter with Chapter 4, we choose to present only absolute contents of contaminants in these two chapters. For purposes of numerical calculation and graphical display, all concentrations below detection levels were assumed to be one-half the detection level.

Results and discussion

A. Sampling in 1987
Contamination IJm- and Zu-deposits
Table 2.1 gives average values, ranges and standard deviations for heavy metals, PCBs and PAHs in the IJm- and Zu-deposits. Zu-deposits contain significantly less heavy metals and PCBs and PAHs than the IJm-deposit in this lake (t-test $P < 0.05$). In the Zu-deposits the metal concentrations were in the same range as natural background levels (Salomons, 1989). This indicates that during the deposition of the IJm-deposit (last 60 years) downward transport of heavy metals, PCBs and PAHs with infiltrating water is insignificant.

Table 2.1. Concentration levels of priority pollutants in toplayer and total IJsselmeer-deposit (IJm$_{top}$, IJm$_{tot}$) and in the underlying Zuiderzee-deposit (Zu).

	IJm$_{top}$			IJm$_{tot}$			Zu	Natural[1]
	Range	Av.	Sd	Range	Av.	Sd	Range	
Arsenic (mg/kg)	15 - 24	21	3	21 - 133	65	26	9 - 19	15
Cadmium (mg/kg)	5 - 21	9.4	4.7	11 - 28	17	4	0.1 - 0.4	0.25
Chromium (mg/kg)	87 - 240	163	44	140 - 525	344	97	52 - 85	72
Copper (mg/kg)	59 - 190	101	29	110 - 243	183	39	8 - 21	13
Mercury (mg/kg)	1.0 - 2.5	1.7	0.5	3 - 10	6	2	< 0.1	0.1
Lead (mg/kg)	72 - 270	138	46	125 - 400	264	67	11 - 40	21
Nickel (mg/kg)	28 - 61	40	8	37 - 75	55	9	19 - 30	29
Zinc (mg/kg)	634 - 1760	1034	338	1100 - 2235	1819	351	43 - 123	68
Σ7PCBs[2] (μg/kg)	45 - 300	166	69	300 - 1180	751	228	< 50	
Σ6PAHs[3] (mg/kg)	2.9 - 6.4	4.7	1.2	3 - 12	7	3	< 0.2	

[1] Natural background levels; Source Salomons (1989)

[2] PCB-congeners (IUPAC no.): 28, 52, 101, 118, 138, 153 and 180

[3] PAHs: fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene and Indenopyrene

Table 2.2. Concentrations of heavy metals, PCBs and PAHs in the IJsselmeer-deposit of three sandpits at different depths.

	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn	PCB28	PCB118	PCB180	Flu	BaP	Bghi
Sandpit 1986														
0 - 0.15 m	23	4.9	158	94	1.6	119	47	702	45	15	20	1.1	0.5	0.6
0.15 - 0.30 m	21	4.7	150	88	1.4	109	49	720	55	20	25	1.0	0.6	0.6
Sandpit 1966														
0 - 0.35 m	20	6	177	98	2	128	39	784	50	15	15	0.6	0.6	0.5
0.35 - 0.70 m	22	13	202	127	2	170	49	1078	85	30	25	1.4	0.7	0.6
0.70 - 1.05 m	24	21	314	160	3	233	55	1358	150	40	30	1.6	0.7	0.5
1.05 - 1.40 m	33	37	513	250	5	334	66	2048	200	75	60	1.5	0.9	0.9
1.40 - 2.70 m	55	25	490	252	9	335	73	2074	350	80	80	2.0	1.0	0.9
Sandpit 1960														
0 - 0.35 m	24	9	221	118	2	152	48	1063	65	25	25	1.7	0.8	0.7
0.35 - 0.80 m	36	9	237	108	3	161	42	979	85	25	40	2.4	0.9	0.8
0.80 - 1.50 m	34	31	438	226	5	311	69	2002	200	60	40	2.2	0.9	1.1
1.50 - 3.00 m	97	23	510	292	11	400	68	2519	450	100	100	2.7	1.5	1.6
3.00 - 4.80 m	170	16	535	304	12	517	64	3653	100	70	95	3.6	2.3	2.2

The toplayer of the IJm-deposit (IJm_{top}) contains significantly less heavy metals, PCBs, and PAHs than the total IJm-deposit (IJm_{tot}) at the same location in Lake Ketelmeer (*t*-test $P < 0.05$). The observed priority pollutant contents in IJm_{top} are in agreement with concentrations found in flood plain toplayer samples (Japenga *et al.*, 1990) and recent monitoring results (Heymen, 1990). Concentrations in IJm_{tot} indicate that concentrations for these priority pollutants were considerably higher before than they are nowadays.

Contamination changes in three sandpits
In Table 2.2 concentrations of heavy metals, three PCBs and three PAHs in the IJm-deposits are given at different depths in the sandpits created in Lake Ketelmeer in 1986, 1966 and 1960, respectively.

The youngest sandpit contains the lowest concentrations of all contaminants. Contamination levels of all priority pollutants increase with depth in sandpit 1966. In the deeper parts of the sandpit created in 1960 concentrations stablize or decrease for cadmium, chromium, copper, mercury, lead and investigated PCBs. For every contaminant the concentration in all sandpits can be combined and drawn into one graph; this corresponds with a concentration profile for this contaminant during the last 30 years. Figure 2.2 shows one of these concentration profiles for PCB 118. The degree of contamination in the IJm-deposit is clearly decreasing during the last decade and was substantially higher in the sixties and seventies, which is in agreement with recent monitoring results (Heymen, 1990) and with concentrations found in river flood plain samples over the last three decades (Japenga *et al.*, 1990). Hence, high vertical contaminant variability occurs in the IJm-deposits of Lake Ketelmeer.

B. Core sampling in 1988-1990
Radiocesium activities
In all cores, activity of ^{137}Cs ($t_{1/2} = 30.17$ years) showed two maxima. One ^{137}Cs maximum, in the sam-
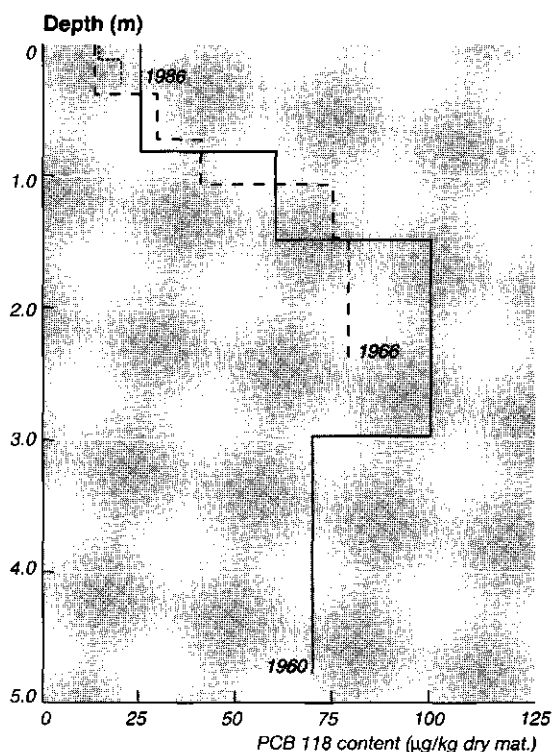
Depth (m)

Figure 2.2. Polychlorine biphenyl (nr. 118) concentration at various depths in the IJm-deposit of three sandpits (different ages) in Lake Ketelmeer.

ples from near the surface, always correlated with elevated activities of ^{134}Cs ($t_{1/2}$ = 2.06 y), indicating the fallout from the nuclear power plant accident in Chernobyl in April 1986. The second ^{137}Cs maximum, found in the deeper layers, was related to the fallout from nuclear weapon testing in the early 1960s. Besides the radiocesium activities, several other markers were used to estimate the age of the different layers. The visually recognizable interface between the IJm- and Zu-deposits indicated the year 1932. In the core taken from the former sandpit, this interface represented the year 1938. Heavy metal concentrations in sediment layers were compared to pollution levels in dated sediment samples from other locations in the Rhine (Salomons and de Groot, 1977). Based on this information, the sediment core layers were dated into periods that varied between two and ten years. The depth of the IJm-deposit in the various sediment cores varied between 25 and 420 cm, indicating highly variable sedimentation rates.

If sedimentation rates are not identical, graphic presentation of radionuclide activities or pollutant concentrations plotted against depth is possible only for the individual cores. However, after age estimation of the different layers, data from all cores can be combined into one graph plotted to the estimated year of deposition instead of depth. This method of data handling can introduce some inaccuracy. Bioturbation or transport with infiltrating water will have less effect on sediment core pollutant profiles at a location with high sedimentation rates than at locations with low sedimentation rates (Eisenreich *et al.*, 1989).
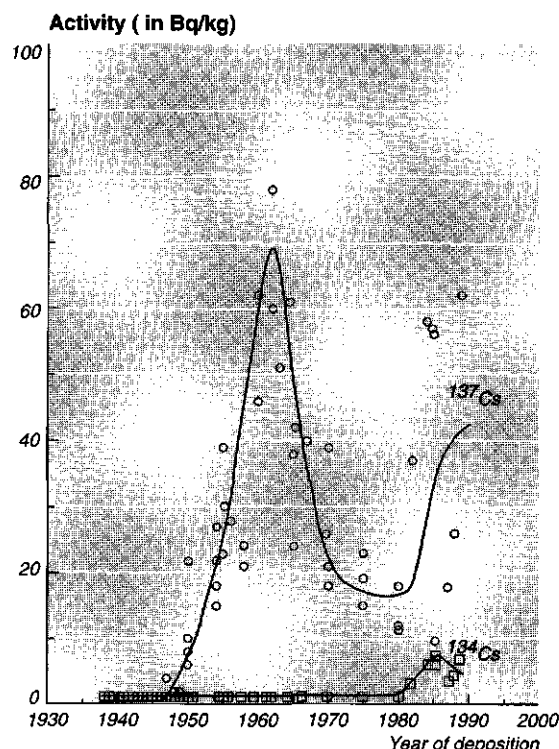
Activity (in Bq/kg)

Figure 2.3. Cesium activities in sediment layers from 8 cores vs. the estimated years of deposition. Average activities are indicated by visually fitted curves.

In Figure 2.3, Cs activities are plotted against estimated year of deposition. A certain amount of variation in activities can be observed, especially in the ^{137}Cs activity of the near surface samples. Nevertheless, a clear pattern in Cs activities during the last five decades can be distinguished and is indicated by the visually fitted curves.

Organic carbon
The organic carbon (OC) content of suspended solids and sediment plays an essential role in the behavior and fate of pollutants in the aquatic environment (Capel and Eisenreich, 1990). Mineralization processes affect the organic matter in sediments. If a constant input of OC has occurred in the past, a decreasing OC content may be expected at increasing depth in the sediment. In Lake Ketelmeer the OC content in the layers of the sediment cores varied widely (Fig. 2.4A). Surprisingly, the recently deposited layers have the lowest OC content. The highest levels are found in layers that were deposited between 1950 and 1970. The OC content of the toplayer samples taken in 1972 is also shown in Figure 2.4A. Because these 5 cm toplayer samples probably reflect an average sediment composition for a four to six year period, they are put in the graph at 1969. The average OC content of these samples is somewhat higher than the OC content in the core layers dated around 1970. This difference indicates a small decrease in the carbon content of the sediment, which is probably the result of mineralization. Benthic processes in the sediment samples from 1972 have been interupted (by drying the samples). However, the influence of other processes like resuspension, internal production and bioturbation can-
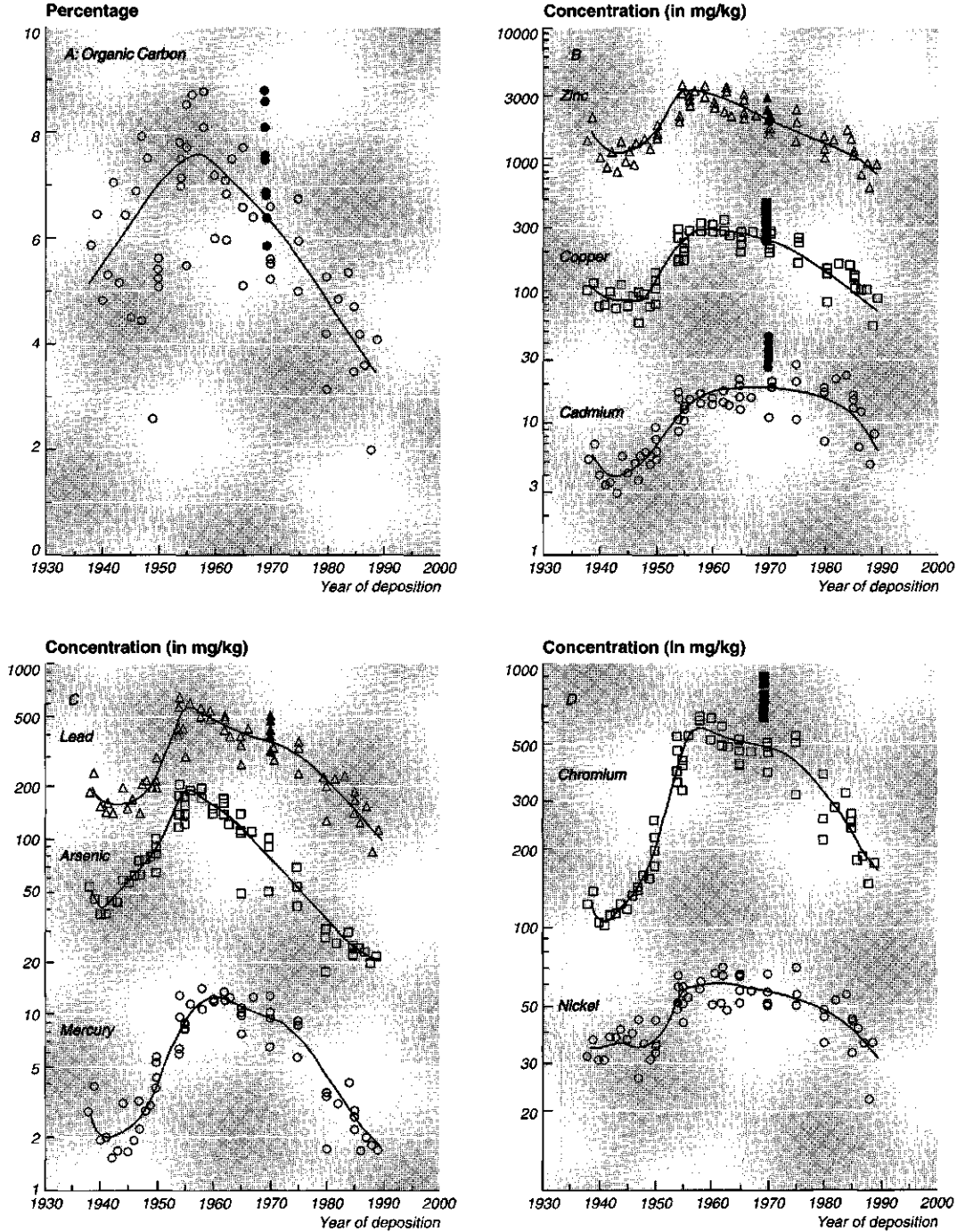
Figure 2.4. Organic carbon content (A) and metal concentrations (B,C,D) in sediment core samples (O, □, △) and in toplayer samples from 1972 (●, ■, ▲) vs. the estimated years of deposition. The average concentrations in sediment core samples are indicated by visually fitted curves.

not be excluded. The internal OC production in Lake Ketelmeer (approx. 1 $gC/m^2 \cdot$ jaar) is about 0.25% of the OC load of the river (*Pers. Comm. Rijkswaterstaat*). The steady decrease in the OC content since 1960 is directly related to a decrease of the total OC load in the Rhine and IJssel rivers (International Commission on Protection of Pollution of the River Rhine, 1989). This decline probably results from the construction of wastewater treatment plants in the drainage basin of the Rhine since the 1960s.

Heavy metals

The concentration profiles of eight heavy metals are also shown in Figure 2.4. Under the anoxic conditions prevailing in Lake Ketelmeer sediments, heavy metals are relatively immobile and, therefore, heavy metal profiles are likely to reflect the historic inputs. The 1972 toplayer samples offered an opportunity to test this assumption. The concentrations of some metals in these old toplayer samples are shown in Figure 2.4. The levels in the toplayer samples from 1972 were somewhat higher, especially for Cd and Cr, than the levels found in the core layers dated around 1970. This difference may have been caused by deviations in the analytical methods, as heavy metal concentrations in sediment cores and in toplayer samples from 1972 were not determined by the same laboratory. In addition, the decrease in metal concentrations in the sediment cores may have been caused by resuspension and bioturbation. The 1972 toplayer samples reflected levels that may have been lowered afterwards by these processes. Based on the limited changes observed between heavy metal contents in the core samples and toplayer samples from 1972 the impact of these processes seems low, and, therefore, the profiles reflect the historic inputs without serious alterations.

All heavy metal levels were very low between 1940 and 1950. The concentrations at the end of the 1930s appeared to be higher than the concentrations in the early 1940s (Second World War). From 1950 to 1965 all the studied heavy metals showed a steady increase in concentration. For all metals except Cd and Ni, a clear decrease from about 1965 was observed. Cadmium and Ni levels started to decrease since the early 1980s. In the recently deposited sediment heavy metal levels were either similar (Zn, Cu, Hg, and Ni) or below (Pb and As) the levels observed in the 1940 to 1950 period. Presently, Cd and Cr levels are still somewhat higher than the levels in the 1940 to 1950 period. The observed patterns in metal concentrations are in agreement with concentrations found in Rhine River flood plain samples over the last three decades (Japenga *et al.*, 1990).

The data from the nondegradable, relatively immobile metals indicate that resuspension and bioturbation have had only limited effects on the pollutant profiles. Consequently, combination of data from all dated cores into one graph appeared to be a feasible and elegant method to interpret the results. However, other processes, such as diffusion and transport with infiltrating water, may have affected the concentration profiles of some mobile organic pollutants, like di- and tri-chlorobenzenes (Zwolsman, 1992). However, the concentrations of the selected PCBs (Table 2.2) were all below the detection limit (10 ng/kg) in the Zu-deposit, indicating that no downward transport had occurred.

Polychlorinated biphenyls

The concentrations of four PCBs are shown in Figure 2.5. The concentration profile for PCB 118 (Fig. 2.5 C) is similar to Figure 2.2 for the period 1960-1988. The average PCB 77 and PCB 118 levels in the samples from 1972 are somewhat higher than the levels found in the sediment cores. This difference between the stored 1972 samples and sediment cores is even more pronounced for PCB 105 and PCB 156. The difference in concentrations between toplayer samples from 1972 and core layers that had been deposited around 1970 were tested for the six studied PCB congeners (Table 2.3).

The differences proved to be significant at a 0.05 level for all tested congeners, except for PCB 77 and PCB 118. Significant reductions varied between 70 and 88%. These reductions indicated that
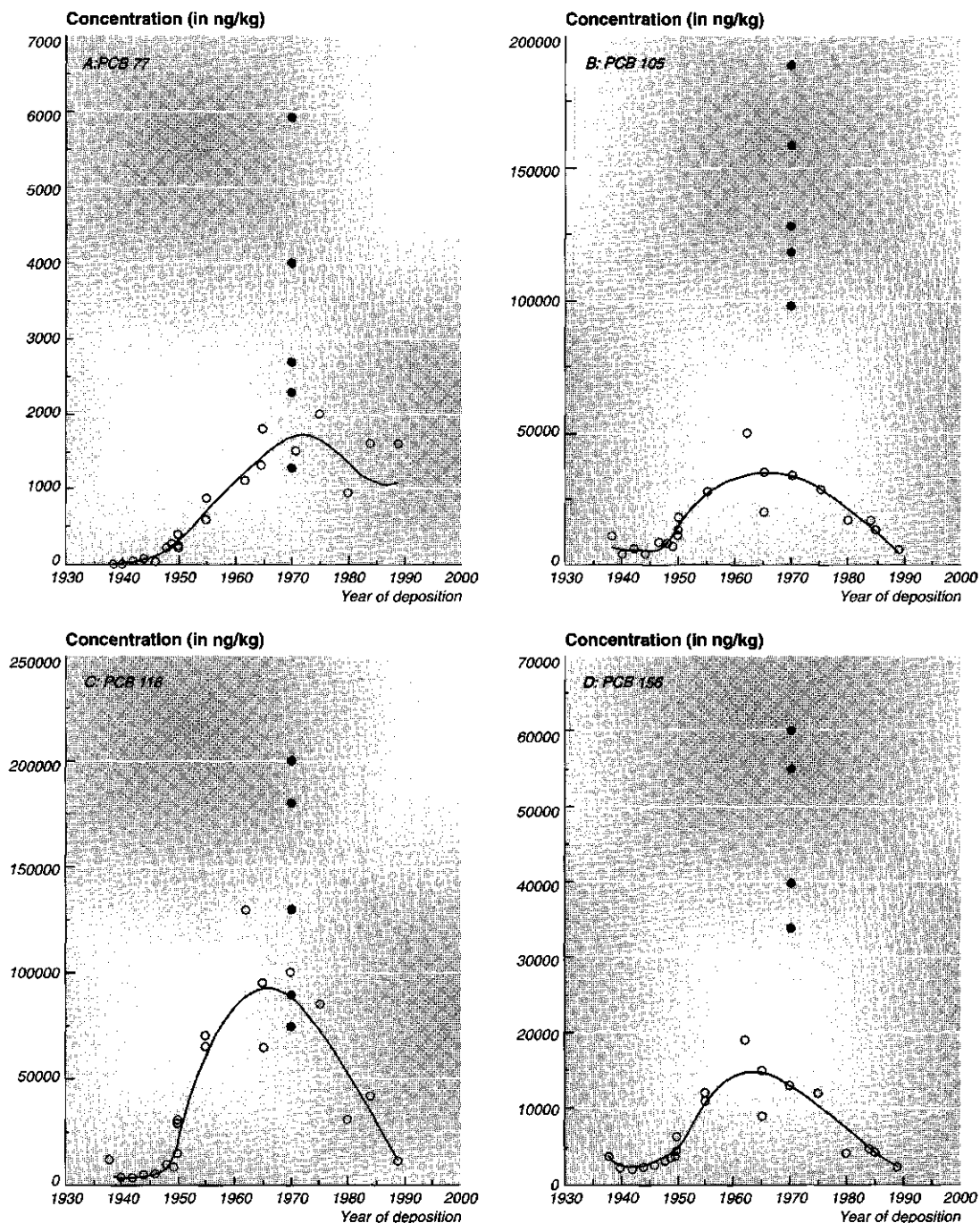
Figure 2.5. Concentrations of 3,3',4,4'-tetrachlorobiphenyl (A), 2,3,3',4,4'-pentachlorobiphenyl (B), 2,3',4,4',5-pentachloro-biphenyl (C) and 2,3,3',4,4',5-hexachlorobiphenyl (D) in sediment core samples (O) and in toplayer samples from 1972 (●) vs. the estimated years of deposition. The average concentrations in sediment core samples are indicated by visually fitted curves.

Table 2.3. Comparison of mean PCB concentrations in toplayer samples (n = 5) collected in 1972 and mean concentrations in recently sampled core layers (n = 5) deposited around 1970.

| PCB (IUPAC no.) | Concentration (ng/kg) | | Reduction (%) [1] |
	Toplayers collected in 1972	Sediment core layers from ±1970	
77	3,240	1,540	
105	140,000	33,600	76
118	135,000	95,000	
126	157	19	88
156	46,000	13,600	70
169	83	10	88

[1] Numerical values are given for decreases that are significant by the t-test at the 0.05 confidence level.

PCBs have disappeared from the anaerobic lake sediment, which may be the result of microbial dechlorination processes in the anoxic sediment. It has been established that disappearance of higher chlorinated biphenyls in the Hudson sediment (Brown *et al.*, 1987a and 1987b) is a result of microbially mediated reductive dechlorination reactions (Quensen *et al.*, 1988 and 1990). Unlike the studies in the Hudson, we were unable to demonstrate an accumulation of reaction products like lower chlorinated biphenyls in Lake Ketelmeer sediment, due to the limited number of congeners analyzed.

If the findings in Lake Ketelmeer can be attributed to microbial processes, this type of dechlorination seems to alter the concentrations of the individual congeners at different rates; PCB 77 and PCB 118 seem to be the most recalcitrant congeners. The other four PCBs show an average reduction of 80% during 20 years of "environmental incubation". Assuming first-order kinetics for the microbial processes, a half-life of nine years can be estimated for these PCBs in the anaerobic Lake Ketelmeer sediment.

Although the origin of the observed reduction remains uncertain, it has been demonstrated clearly that the constructed concentration profiles of the planar and mono-ortho PCBs in Lake Ketelmeer sediment underestimated the historic inputs. Despite the substantial reductions, peaks in PCB profiles could still be recognized. The present pollution levels in the sediment layers are characterized as follows (shown partly in Fig. 2.5). The concentrations of the planar PCBs (77, 126, and 169) were below or just above the detection limit (10 ng/kg) in sediment layers from the early 1940s. On the other hand, the mono-ortho PCBs (105, 118, and 156) had elevated levels in these layers. In general, PCB concentrations showed a rapid increase from sediment layers dated around 1950 and reached maximum concentrations in layers from the 1960s and 1970s. A similar pattern has been reported for PCBs in stored Rhine River floodplain samples, with highest concentrations in the early 1970s (Japenga *et al.*, 1990). In recently deposited sediments, concentrations of PCB 126 and PCB 169 were again below the detection limit. Recent pollution levels of PCB 77 were still elevated, as compared to the pollution levels in layers from the 1940s. The recent concentrations of the mono-ortho PCBs (105, 118, and 156) were relatively low and similar to the concentrations in layers from the early 1940s. Concentrations started to decrease after about 1970. This decrease started before an official PCB ban was introduced in European countries. The production of PCBs in the Rhine area stopped in 1983, and usage in German coal mines has been prohibited since 1985 (Friege *et al.*, 1989).

alterations, the historic inputs during the past five decades. The pollution history is characterized as follows:
- Low concentrations of metals were observed in the early 1940s, PAHs levels were already elevated. For both metals and PAHs, sediment cores presumably reflect a reduction in emissions during the Second World War.
- Highest levels of metals and PAHs were found between 1955 and 1970. Cadmium and nickel levels remained high until 1980.
- Recently deposited sediments had rather low levels, some of which were the lowest ever observed during the last five decades (Pb, As, all studied PAHs).

Almost all chlorinated compounds showed some disappearance in the anaerobic sediment, as compared to the levels in stored 1972 toplayer samples that reflected the original pollution input. For several PCBs this disappearance proved to be significant and may have been caused by microbial dechlorination reactions in the anaerobic sediment. Consequently the concentration profiles of the chlorinated compounds do not reflect the original pollution history. Despite these disappearances, peaks in PCB concentration profiles are still observed. Presently, the following trends in concentrations of PCBs can be observed in Lake Ketelmeer sediment:
- Almost all studied PCBs had rather low concentrations in the early 1940s.
- Highest levels of PCBs were found between 1960 and 1975.
- Recently deposited sediment has elevated levels of PCBs, as compared to the levels in the layers from the early 1940s.

The overall picture indicates that the recently deposited material is far less polluted than the sediment deposited in the 1960s and 1970s. These findings suggest that highly polluted sediments from the past are buried under a less polluted layer. However, the locations selected in this study have high sedimentation rates and may differ from other locations. Altered sedimentation rates occur near shipping routes where resuspension is high, or in harbors, where frequent dredging activities remove recently deposited material. At these locations the highly polluted sediment layers may remain uncovered and the aquatic organisms may still be exposed to the highly polluted sediment from the 1960s and 1970s.

Acknowledgements

Chapter 3

Distribution and geochronology of priority pollutants in a large sedimentation area, river Rhine, the Netherlands

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based on:
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Normalizing the metal contents according to this method seems adequate. The absorption (capacity) due to content of clay minerals, organic matter and Fe-Mn-(oxy)-hydroxides is taken into account. Iron- and Mn-(oxy)-hydroxides are thought to be associated with the clay fraction (Koelmans and Lijklema, 1992). If the organic matter content of a sample is > 30% or < 2%, these two percentages have to be used in the correction procedure.

Organic pollutants were corrected according to:

$$Y = X \cdot \frac{10}{O} \qquad (2)$$

With:

Y = Corrected organic pollutant content (mg/kg dry matter)
X = Absolute organic pollutant content (mg/kg dry matter)
O = Organic matter content (%)

Normalizing absolute contents in the IJm-deposit generally result in 15% higher values, as a consequence of a low average clay content in both lakes. For the mainly sandy sediments of Lake IJsselmeer the corrected values are in general 60% higher due to low organic matter and clay contents. Values lower than the detection limits can not be normalized with this method.

Results and discussion

Recent surficial sediments
The thickness of the IJm-deposit was determined at every sample site using an open auger (so called Vrij-Wit-auger). In Lake IJsselmeer, thick layers (> 3 m) of this deposit were found in the deeper central zone. In Lake Ketelmeer this deposit is absent in the east, where a non-contaminated sandy delta occurs. At the mouth of the river IJssel, thick layers of this deposit (> 1 m) are found. In the entire central and western part of the lake smaller amounts of the IJm-deposit are present. The surface samples of the IJm-deposit, including worm burrows and mounds, appear to remain undisturbed with the Jenkins mudsampler. In Fig. 3.2 the IJm-deposit is indicated by a grey tone.

Table 3.2 gives the normalized mean concentrations (including standard deviation) for all priority pollutants and other compounds in the recent (previous 5-10 a) IJm-deposit in both lakes and the older sandy surficial layer in Lake IJsselmeer. These mean values and standard deviations are based on data of approximately 25 to 30 different sample sites, except for the PAHs where only 15 sample sites were used.

Clay and organic matter contents in the IJm-deposit are similar in both lakes. The organic matter content of the IJm-deposit is highly variable in Lake IJsselmeer, which might be related to the high carbonate contents in the sediment of this lake. In general, high carbonate contents are considered to be the result of increased production due to algae blooms in this eutrophic lake in the summer (Salomons and De Groot, 1978). Algae consumption of CO_2 enhances the pH of the water and results in precipitation of calcite (Del Castilho and Salomons, 1986). Algae blooms are common in Lake IJsselmeer but have never been encountered in Lake Ketelmeer.

The distribution pattern of normalized Pb in surficial sediment of both lakes is shown in Fig. 3.2. Results indicate that Pb is distributed fairly uniformly over Lake Ketelmeer. In Lake IJsselmeer Pb contents of the surficial sediments are 2.7-10 times lower. Here the amount of Pb follows the pattern of the IJm-deposit in this lake. These patterns are indicative for all studied pollutants.

Heavy metal and As contents of the IJm-deposit are in Lake Ketelmeer 1.6-5.4 times higher than in Lake IJsselmeer. There is also a significant difference (factor 2-4) between the contents in the older
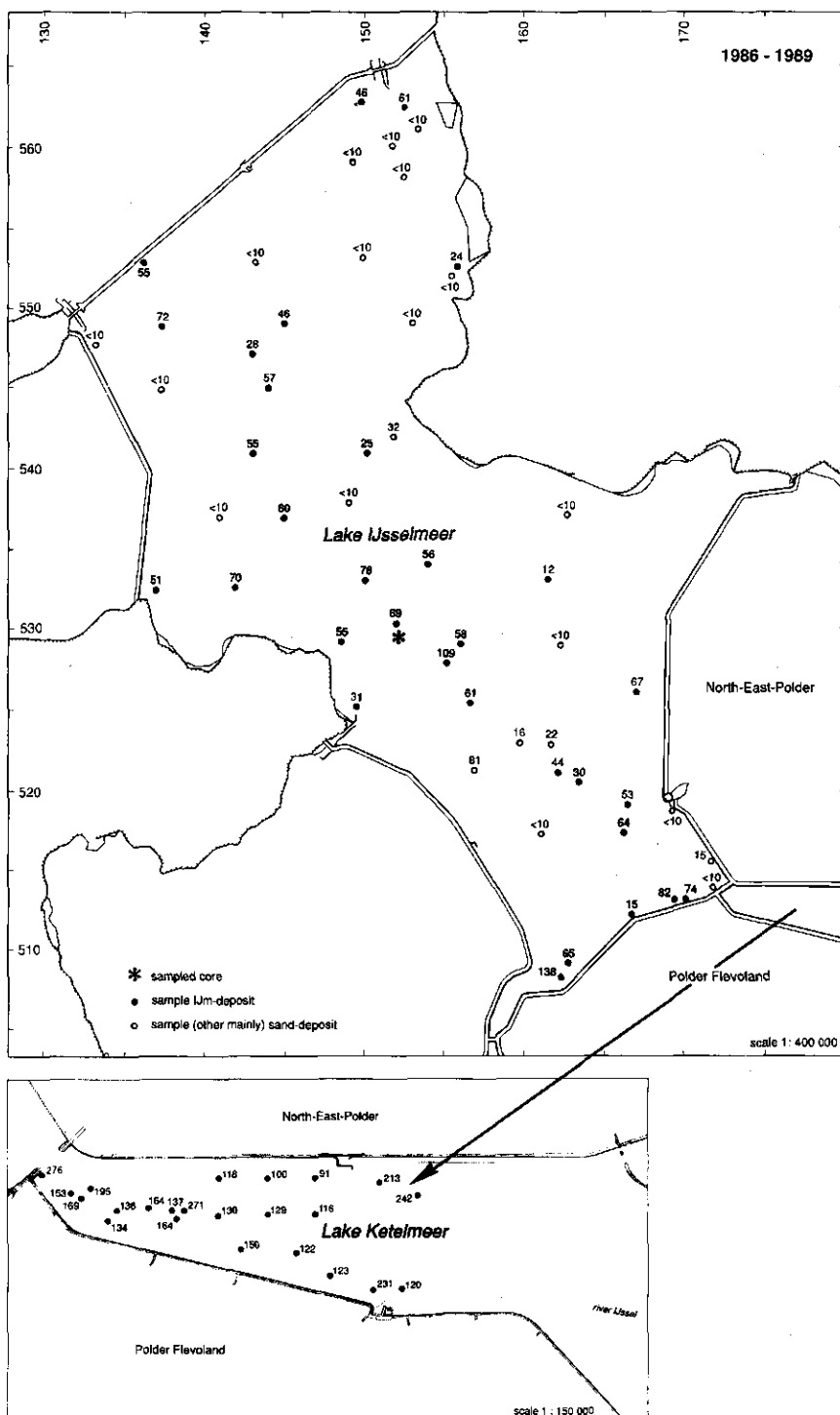
Fig. 3.2. Normalized Pb contents (mg/kg dry matter) in surficial sediments of Lake Ketelmeer and Lake IJsselmeer in the period 1986-1989.

Table 3.2. Mean normalized content($\bar{x}$) and standard deviations (σ) for several priority pollutants and other compounds in the recent (1986-1989) surficial sediments (IJm-deposit and older sandy sediments) in Lake IJsselmeer and Lake Ketelmeer.

| | Lake IJsselmeer | | | | Lake Ketelmeer | |
| | IJm-deposit | | Sand | | IJm-deposit | |
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
Clay frac. content (%)	17.0 ±	5.5	2.1 ±	1.6	17.9 ±	4.1
Org. matter content (%)	7.9 ±	4.4	0.9 ±	1.2	6.9 ±	1.5
CaCO$_3$ content (%)	35.4 ±	11.5	9.5 ±	10.4	9.5 ±	1.7
Metals						
(mg/kg dry matter)						
As	14.9 ±	6.6	6.2 ±	5.3	24 ±	3
Cd	2.4 ±	1.7	1.1 ±	1.1	13 ±	7
Cr	59.4 ±	21.9	16.6 ±	16.1	191 ±	58
Cu	34.4 ±	13.3	8.5 ±	10.9	124 ±	34
Hg	0.7 ±	0.4	0.2 ±	0.3	2 ±	0.5
Pb	59.5 ±	25.3	15.9 ±	18.6	160 ±	52
Ni	24.8 ±	6.3	9.1 ±	12.9	49 ±	5
Zn	463.9 ±	138.5	146.1 ±	154.8	1290 ±	406
Polychlorinated biphenyls						
(μg/kg dry matter)						
PCB 28	6.1 ±	6.7	2.8 * ±	2.2	52 ±	24
PCB 52	5.9 ±	8.6	2.8 * ±	2.2	44 ±	20
PCB 101	4.3 ±	3.8	2.8 * ±	2.2	39 ±	15
PCB 118	4.1 ±	2.9	2.8 * ±	2.2	20 ±	4
PCB 138	7.2 ±	6.3	2.8 * ±	2.2	34 ±	16
PCB 153	6.3 ±	4.7	2.8 * ±	2.2	34 ±	12
PCB 180	3.8 ±	2.5	2.8 * ±	2.2	21 ±	6
Sum 7 PCBs	40.9 ±	35.8	19.3 ±	15.8	218.8 ±	63.7
Polynuclear aromatic hydrocarbons						
(mg/kg dry matter)						
Fluoranthene	0.7 ±	0.5	0.30 ±	0.30	1.7 ±	0.9
Benzo(k)fluoranthene	0.1 ±	0.1	0.05 ±	0.08	0.5 ±	0.3
Benzo(b)fluoranthene	0.4 ±	0.2	0.10 ±	0.10	1.0 ±	0.4
Benzo(a)pyrene	0.2 ±	0.1	0.08 ±	0.10	0.9 ±	0.4
Benzo(ghi)perylene	0.2 ±	0.1	0.06 ±	0.08	0.7 ±	0.3
Indeno(1,2,3-cd)pyrene	0.2 ±	0.1	0.06 ±	0.07	1.8 ±	1.5
Sum 6 PAHs	1.9 ±	1.1	0.60 ±	0.80	4.7 ±	1.5

* based on values below the detection limits

sandy sediments and the IJm-deposit in Lake IJsselmeer. The contents of the lower chlorinated PCBs in the IJm-deposit are eight times higher and the other PCBs are just five times higher in Lake Ketelmeer compared to Lake IJsselmeer, whereas PAHs are 2-9 times as high. The contents of organic pollutants differ significantly (factor 1.5-3) between the IJm-deposit and the older sandy deposits of Lake IJsselmeer. The degree of pollution decreases in the IJm-sediment deposited further from the river mouth.
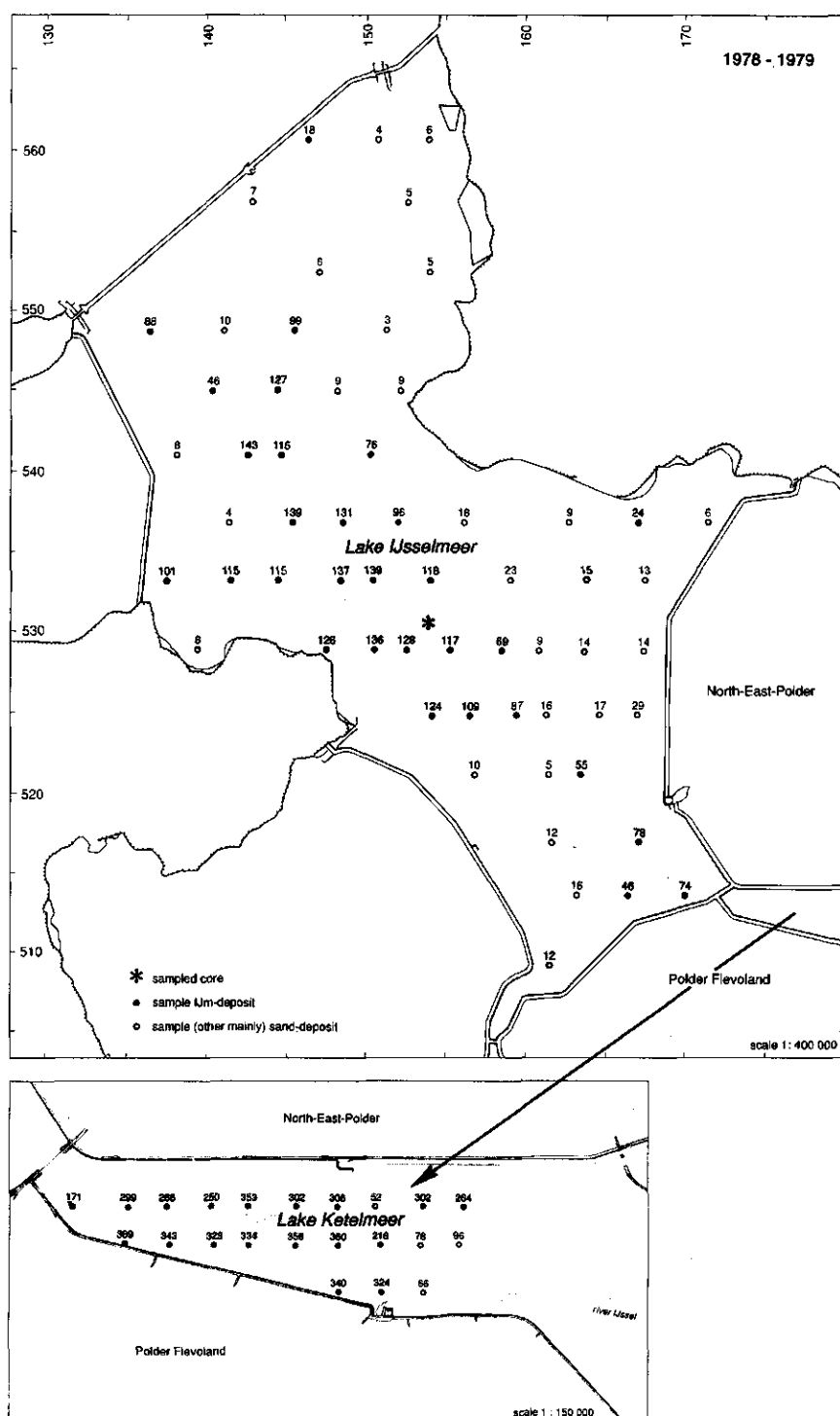
Fig. 3.3. Normalized Pb contents (mg/kg dry matter) in surficial sediments of Lake Ketelmeer and Lake IJsselmeer in the period 1978-1979.

Older surficial sediments
In 1978-1979 Ente (1984) sampled surficial sediments in both lakes for a few heavy metals and other compounds. The normalized mean concentrations (including standard deviations) for the heavy metals Cd, Hg and Pb in the IJm-deposit of Lake IJsselmeer are 5.2 (3.0), 1.5 (0.8) and 99 (35). For Lake Ketelmeer these concentrations and standard deviations are 25.6 (12.5), 5.6 (2.8) and 305 (53). These values are based on ≈ 30 sample sites in Lake IJsselmeer and 18 in Lake Ketelmeer.

The distribution pattern of normalized Pb in surficial sediment of both lakes in 1978-1979 is shown in Fig. 3.3. Absolute lead contents of Ente (1984) have been normalized and drawn in this figure, which can now be compared with Fig. 3.2. Results indicate that Pb was distributed fairly uniformly over Lake Ketelmeer and the contents in the surficial sediments were 1.9 times higher 10 years before. In Lake IJsselmeer Pb contents of the surficial sediments were 1.7 times higher in 1978. Here the amount of Pb also followed the pattern of the IJm-deposit in the lake.

In Lake Ketelmeer the clay fraction, organic matter and carbonate contents have not changed much over the last 10 a. Comparing data of Ente (1984) to those in Table 3.2, a slight decrease of the clay fraction content and an increase of the carbonate content in time can be noticed in Lake IJsselmeer. In the sandy part of Lake IJsselmeer, neither the heavy metal contents nor the contents of the other compounds have changed over the last 10 a. The heavy metal contents in the IJm-deposit of both lakes were two times as high as they are today. This phenomena corresponds to the decreasing pollution of the river Rhine, e.g. IJssel, during the last 10 a (Van Gogh, 1988; Salomons and Eysink, 1981).

The deposition of the IJm-sediment in Lake IJsselmeer is still occuring in the deeper parts of this lake. The physical conditions of both lakes do not seem to have changed much during the last 10 a; both are well-mixed freshwater lakes where wind-induced resuspension and sedimentation (Ten Hulscher *et al.*, 1992; Lijklema *et al.*, 1994) is found in a clockwise flow pattern in Lake Ketelmeer (Toet and Blom, 1989) and reverse in Lake IJsselmeer (Verhagen, 1988). Due to high loads of N and P over the last 10 a in Lake IJsselmeer, algae blooms have become common phenomena in the summer (Berger, 1987).

Deeper cores
Vink and Winkels (1991) give the results from the core sampled in eleven intervals at a deep location (see * in Fig. 3.2) in Lake IJsselmeer. This area was an erosive tidal sandy gully before the enclosure

Table 3.3. Water depths, changes in thickness of the IJm-deposit and calculated actual core depths and net sedimentation rates during the last 60 a in a deeper zone of Lake IJsselmeer.

Year	Water depth (m*)	Increase IJm-deposit** (m)	Net sedimentation rate** (cm/a)	Actual depth core (m) a	b
1989	6.3	0.3	2.1	0	0
1975	6.6	0.6	3.3	0.3	0.3
1957	7.2	0.2	2.9	0.9	0.7
1950	7.4	0.5	5.0	1.1	0.8
1940	7.9	1.6	40.0	1.6	1.3
1936	9.5			3.2	2.6

* m: meters below mean sea level
** *These columns give the result of comparing the actual water depth, e.g. increase IJm-deposit of the next row with this row*
a Actual depth core without consolidation
b Indication actual depth core with rough assumption of consolidation factor (see also Chapter 6)

of the barrier dam in 1932. Afterward, rapid sedimentation of the IJm-deposit occurred in this deep zone (Ente, 1981). All priority pollutants have been normalized and contents seem to change radically during the last 60 a. This phenomenon is also evident for the other analysed compounds. In the core, concentrations of heavy metals, As and PCBs increase in depth to a maximum and then decrease to lower levels or background.

Water depths at this gully during the period 1936-1989 give a good impression of the net sedimentation rate and give a rough indication of a time scale (Table 3.3). Changes in dry matter content with depth indicate consolidation of the IJm-deposit. The actual thickness of the IJm-deposit was 3.2 m. This total layer has been devided over the years (1932-1989) based on former water depths, dry matter contents, net sedimentation rate and consolidation. Combining this method with ^{137}Cs- (Comans et al., 1989) and/or ^{210}Pb-dating (Eakins and Morrison, 1978) could improve the accuracy of the results.

Beurskens et al. (1993) presented the geochronology of priority pollutants, based on eight cores in Lake Ketelmeer and were able to derive consistent concentration profiles (based on sediment dating in the IJm-deposit of this lake). One of these cores is presented with a corresponding time axis (on the right) in Fig. 3.4 for the Pb contents during the last 50 a. The left axis of the figure shows the depth intervals and the derived time scale for the core of the IJm-deposit in Lake IJsselmeer. The two normalized Pb concentration profiles have a similar shape. Furthermore, if the left axis is used to interpret recent Pb contents and contents at 1978 in the IJm-deposit of Lake IJsselmeer, these values correspond with the average Pb contents as presented before. Also, the mean Pb content of the surficial sediment in Lake Ketelmeer at 1978 corresponds with the Pb concentration profile of Lake Ketelmeer (Fig. 3.4).
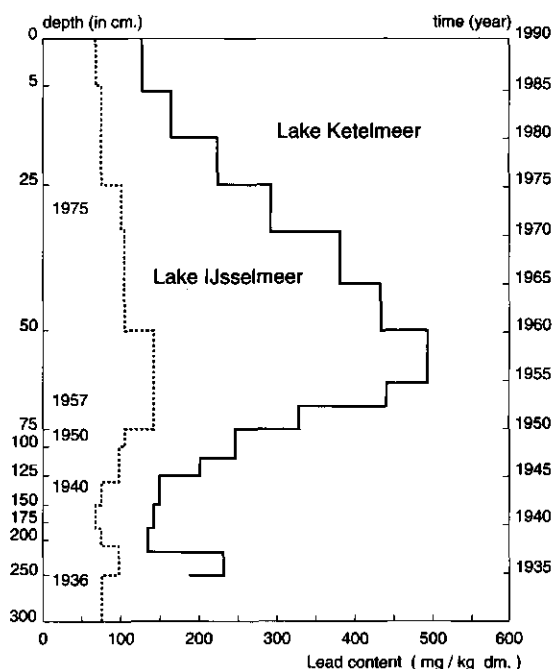
Fig. 3.4. Normalized Pb contents in deeper zones (based on two cores) of the IJsselmeer-deposit in Lake IJsselmeer and Lake Ketelmeer from 1932 to 1989.

Using the normalized values from Vink and Winkels (1991) for all other priority pollutants, similar concentration profiles can be derived.

The decrease of contents of priority pollutants in the IJm-deposit, going from Lake Ketelmeer to the deeper zones in Lake IJsselmeer, can be characterized as a diluting factor. Both the recent increase of carbonates in Lake IJsselmeer and a change of clay fraction content in time seem to be responsible. Winnowing, erosion, resuspension and transport of other fine sediment (clay fraction) in the entire Lake IJsselmeer, prior to the reclamation works (before 1975), seem responsible for the fine, older IJm-deposit in the deeper zones of the present Lake IJsselmeer. This fine sediment and other eroded sediment is thought to be mixed and transported together with the fine particulate load of the river IJssel and deposited in the deeper zones of Lake IJsselmeer. Apart from authigenic carbonate precipitation, chemical processes are assumed to be less important for the dilution of pollution than the physical processes mentioned previously. It is remarkable that for each contaminant a different diluting factor is found.

Chapter 4

Geochronology of priority pollutants in sedimentation zones of the Volga and Danube delta in comparison with the Rhine delta

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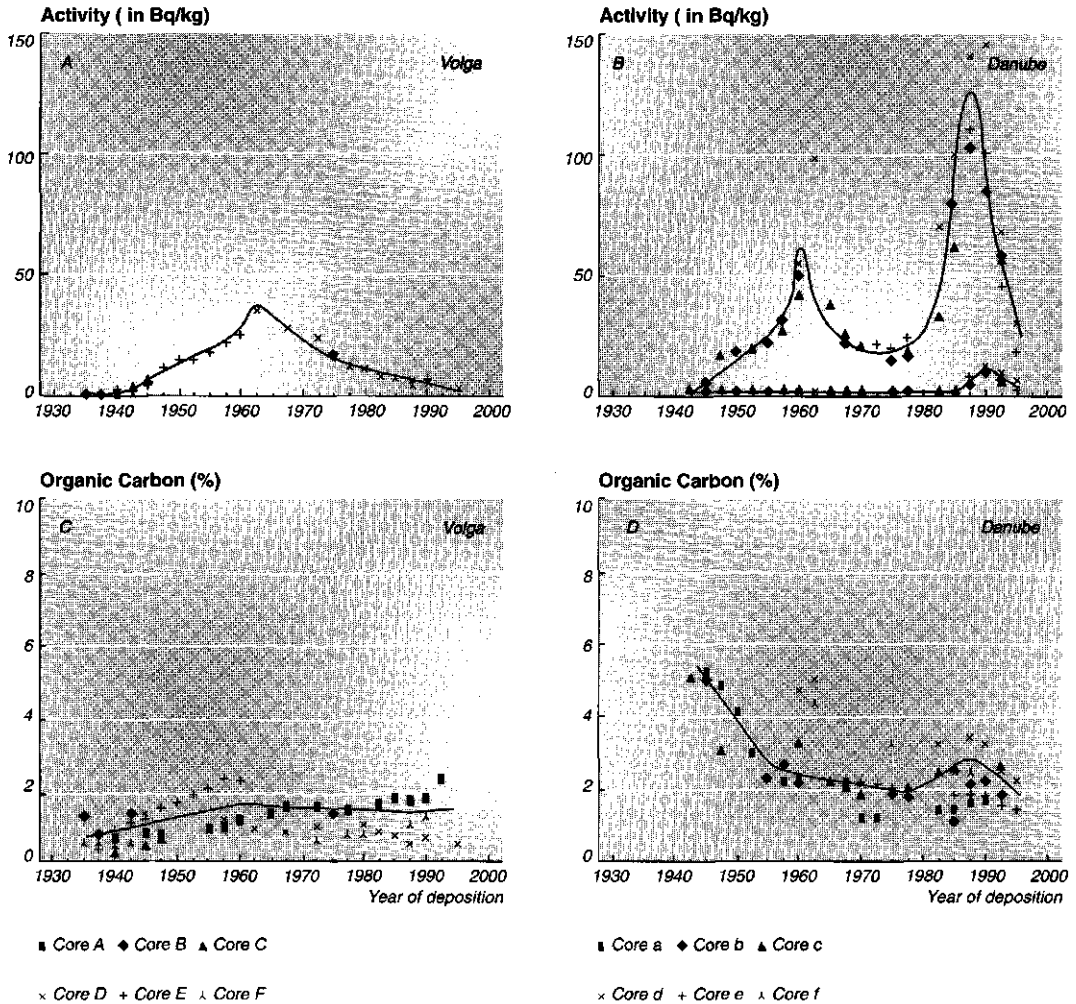
Fig. 4.2. Cesium activities (A, B) and organic carbon contents (C, D) in sediment core samples from the Volga (cores A, B, C, D, E and F) and Danube delta (cores a, b, c, d, e and f) vs. the estimated years of deposition. Average activities and contents in sediment core samples are indicated by visually fitted curves.

high sedimentation rates than locations with low sedimentation rates (Eisenreich *et al.*, 1989).

In Figure 4.2A and 4.2B, Cs activities are plotted against estimated year of deposition for both deltas. A certain amount of variation in activities can be observed, especially in the ^{137}Cs activity of the near surface samples in the Danube delta. Nevertheless, a clear pattern in Cs activities during the last five decades can be distinguished and is indicated by visually fitted curves.

Organic Carbon
The organic carbon (OC) content of suspended solids and sediment plays an essential role in the behavior and fate of pollutants in the aquatic environment (Capel and Eisenreich, 1990). Mineraliza-

tion processes affect the organic matter in sediments. Based on the climatic differences between both deltas, the impact of mineralization (related to higher temperatures and higher biological activity) in the Volga delta is thought to be higher than in the Danube delta. If a constant input of OC has occurred in the past, a decreasing OC content may be expected at increasing depth in the sediment. In the Volga delta (Fig. 4.2.C) a constant low organic input by the river can be observed and these mineralization processes probably occured here. However, in the Danube delta the OC content in the layers of the sediment cores were higher and varied widely (Fig. 4.2.D). Surprisingly, the recently deposited layers have the lowest OC content. The highest levels are found in the deepest layers in the Danube delta. This can be explained by the fact that these young clayey deposits are found on top of detritus and peat. Local organic material in these lakes is probably mixed with the clayey material during deposition in the past. The steady decrease in the OC content in the Danube delta is also partly related to a decrease of the total OC load in the Danube river upstream (Gherghisan and Oosterberg, 1995). This decline probably results from the construction of wastewater treatment plants in the drainage basin of the Danube since the 1960s.

Heavy metals

The concentration profiles of three heavy metals (absolute values) of all cores are shown for both deltas in Figure 4.3. Although only three metals are shown in Figure 4.3, similar concentration profiles have been made for all other metals (Winkels *et al.*, 1995; 1996). Nevertheless, all metal results are discussed below for both deltas.

Under the anoxic conditions prevailing in the sediments of deltas, heavy metals are relatively immobile and therefore, heavy metal profiles are likely to reflect the historic inputs without serious alterations (Beurskens *et al.*, 1993).

Surprisingly low, constant concentrations of arsenic, chromium, copper and zinc are found during the last five decades in the sediments of the Volga delta. The lowest concentrations of the heavy metals Ni, Zn, Cu and Cr were observed in the early 1940 in this delta. Recently deposited sediments in the Volga delta seem to show slightly increasing levels for the metals zinc and arsenic. These low metal concentrations in the sediment cores in the Volga delta are in agreement with concentrations found in the sediments sampled evenly spread over the entire delta (Lychagin *et al.*, 1995). The heavy metals in the sediments of the Volga delta seem to have natural background values.

The heavy metal profiles in the Danube delta all have a typical pattern. The recent decrease of all heavy metal inputs into the river Danube since 1987 indicate the recent failure of industrial production due to political changes in eastern Europe. The heavy metals zinc, mercury and copper have increasing contents till 1987, probably corresponding with increasing industrialization in central and eastern Europe in the period before 1987. The highest nickel content is found in the period around 1953. After this period the nickel contents are slowly decreasing. The recently deposited sediments in the Danube delta have the lowest arsenic, nickel, lead and chromium contents ever observed during the last five decades.

The heavy metal contents, except cadmium and chromium, are in general higher in the Danube delta than in the Volga delta during the last five decades.

The data from the nondegradable, relatively immobile metals indicate that resuspension and bioturbation have had only limited effects on the pollutant profiles. Consequently, combination of data from all dated cores into one graph appeared to be a feasible and elegant method to interpret the results. However, other processes, such as diffusion and transport with infiltrating water, may have affected the concentration profiles of some organic pollutants (Beurskens *et al.*, 1993).

To illustrate that visually fitted curves do not change due to changing clay fraction and organic matter contents, Figure 4.4 has been drawn. In this figure normalized chromium contents have been drawn

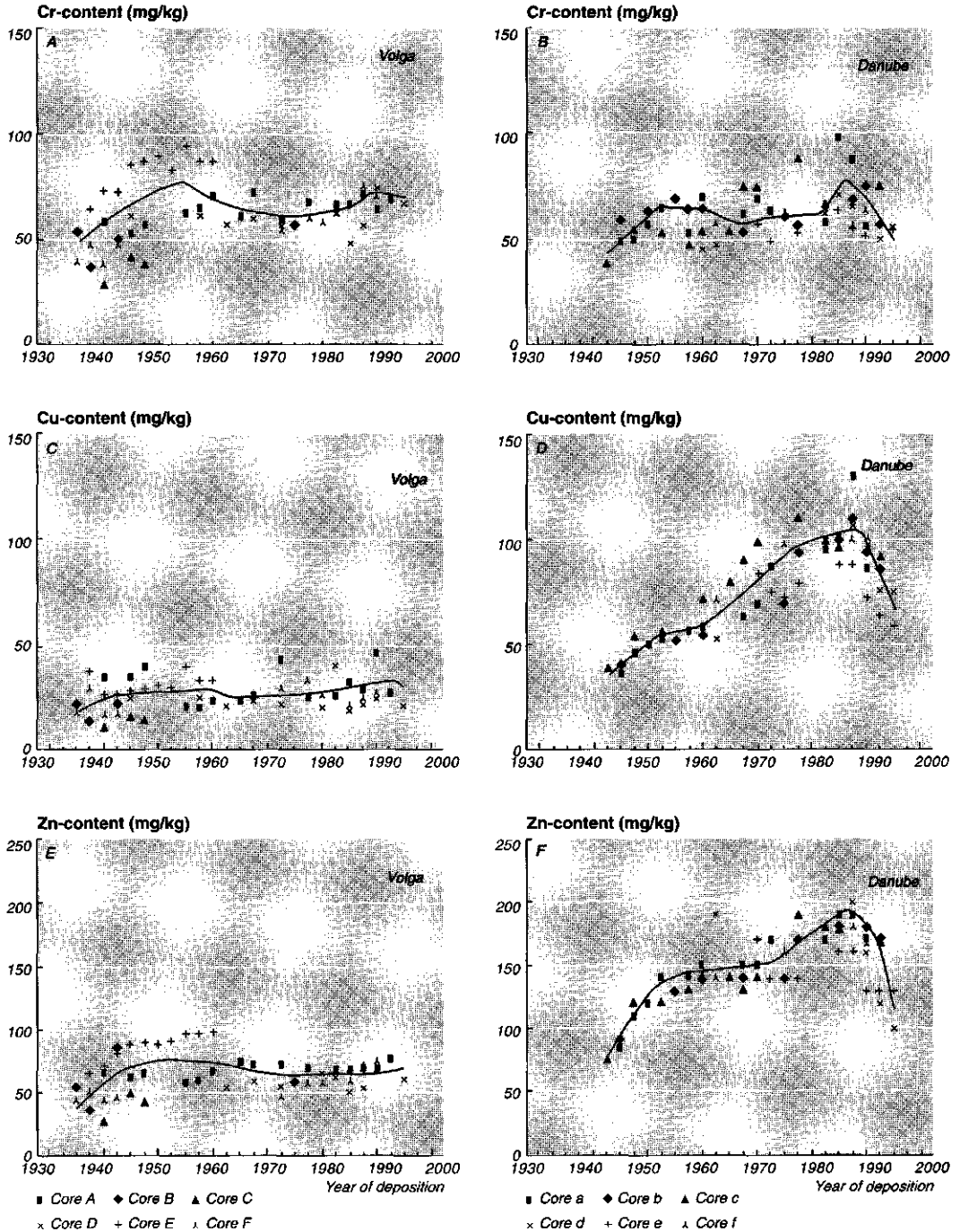**Fig. 4.3.** Concentrations of chromium (A, B), copper (C, D) and zinc (E, F) in sediment core samples from the Volga (cores A, B, C, D, E and F) and Danube delta (cores a, b, c, d, e and f) vs. the estimated years of deposition. Average contents in sediment core samples are indicated by visually fitted curves.
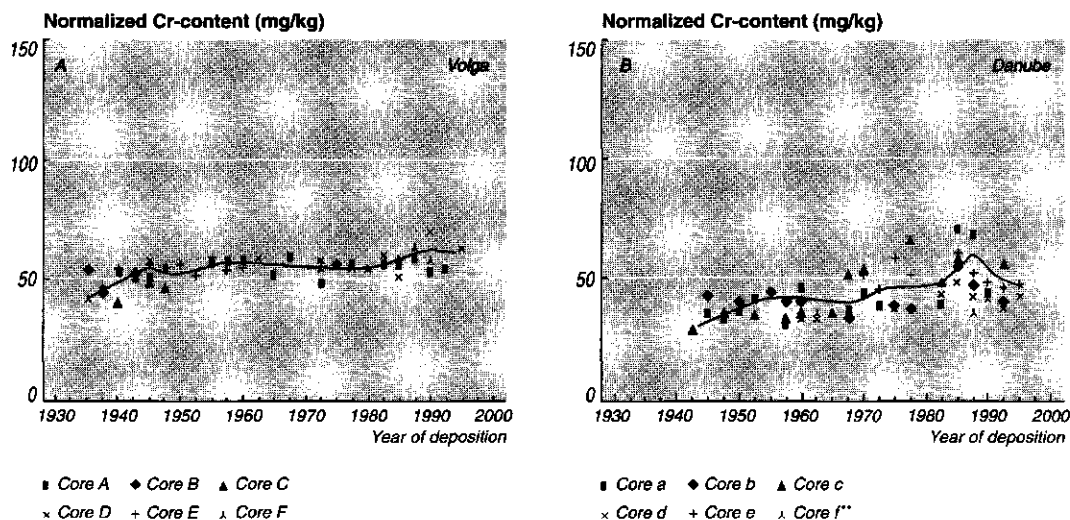
Fig. 4.4. Normalized concentrations of chromium (A, B) in sediment samples from the Volga (Cores A, B, C, D, E and F) and Danube delta (cores a, b, c, d, e and f) vs. the estimated years of deposition. Average contents in sediment core samples is indicated by a visually fitted curve.

for all cores in both deltas. The normalized chromium contents have the same historic pollution pattern by the Volga and Danube river as that in Figure 4.3A and B. Because the differences in physical characteristics between the cores in the sediments of the Volga delta are higher than in the Danube delta, the differences between absolute and normalized contents are also higher here. Nevertheless, the normalized results do not differ in a way that the results of this study are substantially affected.

PCBs and PAHs
The concentrations of seven investigated PCB-congeners in the sediments of the Volga and Danube delta were for all samples in every core below detection limit (< 0.005 mg/kg). The absence of or low production rates of PCBs in middle and eastern European countries, might be responsible. Furthermore microbial dechloration processes in the anoxic sediment in these deltas might have had influence, as has been shown in other anoxic sediments in the field and in the laboratory (Brown *et al.*, 1987a,b; Quensen *et al.*, 1988, 1990; Beurskens *et al.*, 1993).

Ten different PAHs were determined in all layers of the twelve cores from both deltas. Recently, McFarland and Sims (1991) presented a thermodynamic evaluation of the biodegradability of PAHs under anaerobic conditions. They indicated that microbially mediated transformation of PAHs in anaerobic environments may occur under denitrification conditions, but is unlikely to occur under sulfate-reducing and methanogenic conditions. In laboratory experiments, microbial transformation of the bicyclic naphthalene and acenaphthene has been shown under denitrification conditions (Mihelcic and Luthy, 1988). Because methanogenic conditions prevail in sediment from both deltas, postdepositional biodegradation of PAHs can be excluded. Consequently the concentration profiles of PAHs in both deltas will presumably reflect the unchanged historic inputs.

The sediments of the Volga delta are not contaminated with PAHs and have low natural background values. In Figure 4.5 the concentration profile is shown for the sum of ten individual PAHs in the
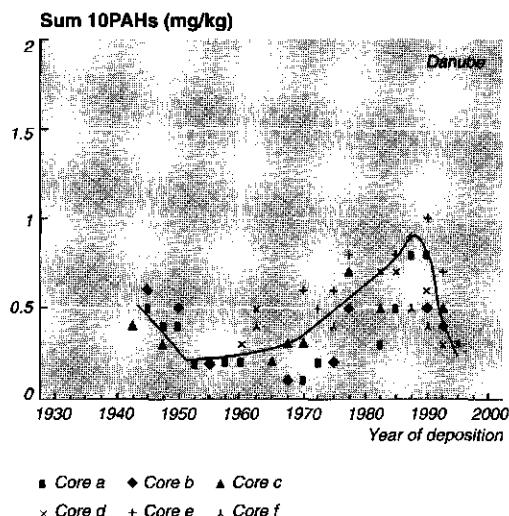
Sum 10PAHs (mg/kg)

Fig. 4.5. Concentrations of sum 10 PAHs in sediment core samples from the Danube delta (cores a, b, c, d, e and f) vs. the estimated years of deposition. The average content in sediment core samples is indicated by a visually fitted curve.

Danube delta. In this figure there is a slow increase in the PAH contents during the period 1970-1987. The recent decrease of all PAH contents in the sediment of the Danube delta corresponds with the decrease of PAH inputs into the river since 1987, presumably reflecting the recent failure of industrial production due to political changes in eastern Europe. The higher PAH levels in the deepest layers in the Danube delta might be due to higher natural background levels in the underlying peaty layers. Local organic material with higher natural PAH levels in these lakes is probably mixed with the clayey material during deposition in the past.

B. Comparison with the Rhine delta
Radiocesium activities and organic carbon
If one compares the radiocesium curves with those from the Rhine delta (Chapter 2), the ^{137}Cs maximum of the early 1960s has similar activities in all deltas. The fallout from the nuclear power plant accident in Chernobyl is responsible for no measurable activities in the Volga delta and twice higher activities in the Danube delta than in the Rhine delta. This can be explained based on their geographical location and the mainly south-western winds during and after the accident.

The organic matter contents in the aquatic sediments of the Volga and Danube delta are respectively three times and twice as low as those in the Rhine delta (Chapter 2). The impact of mineralization processes, due to climatic differences, and the carbon input into the rivers during the years can explain most differences in organic carbon in the historic carbon profiles of the three deltas.

Priority pollutants
As an example, in Figure 4.6 the absolute contents of arsenic, nickel and sum 6 PAHs are presented for all three river deltas during the last five decades. The visually fitted curves for each contaminant are given, based on the concentration profiles derived in this paper, by Winkels *et al.*, 1995 and 1996 and in Chapter 2. The highest arsenic contents have been found in the delta of the river Rhine. The lowest contents are found in the delta of the river Volga. The Danube delta has arsenic contents in between the

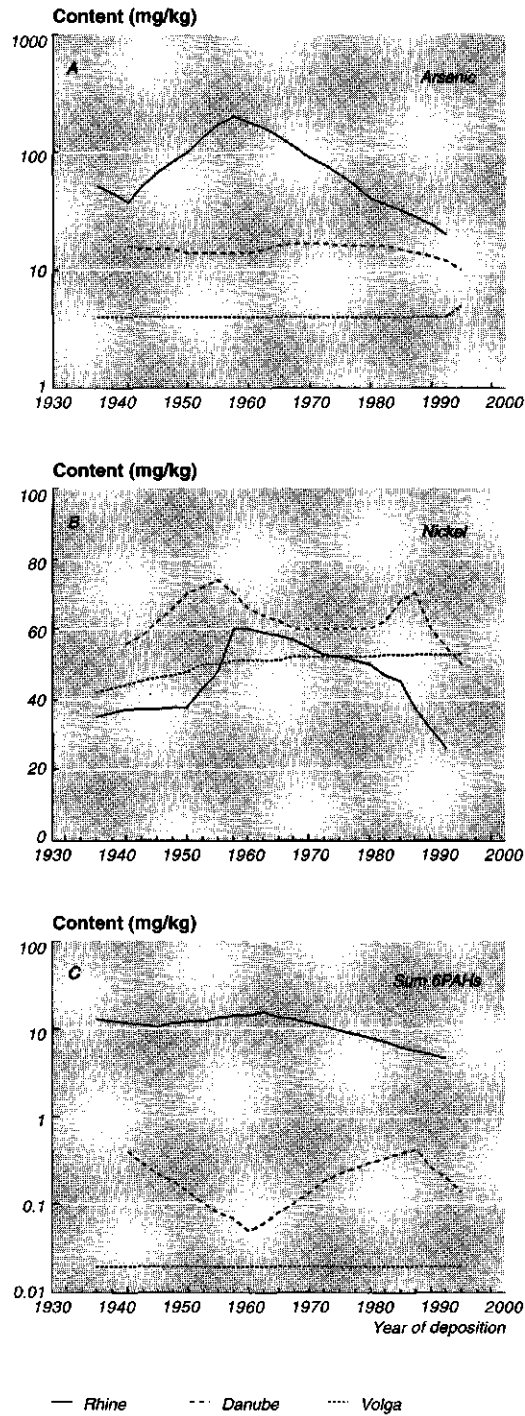**Fig. 4.6.** Average contents of arsenic (A), nickel (B) and sum 6 PAHs (C) in sediments from the deltas of the rivers Rhine, Danube and Volga vs the estimated years of deposition.

Table 4.3. Average contents of heavy metals, PAHs and PCBs in the sediments in the deltas of three major European rivers during three time periods (in mg/kg).

	Rhine delta			Danube delta			Volga delta		
	1940	*1970*	*1990*	*1940*	*1970*	*1990*	*1940*	*1970*	*1990*
Arsenic	38	90	24	16	17	13	4	4	4
Cadmium	5	16	6	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Chromium	100	440	160	50	60	60	56	65	70
Copper	90	260	80	38	78	64	21	28	28
Mercury	2	10	2	0.1	0.7	1	< 0.1	< 0.1	< 0.1
Lead	190	390	100	36	56	50	12	12	12
Nickel	37	55	32	56	60	60	44	52	53
Zinc	1400	2000	800	90	150	140	52	64	68
Σ7PCBs [1]	< 0.04	1.2	0.2	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
Σ6PAHs [2]	11.8	11.6	5.2	0.4	0.1	0.3	0.02	0.02	0.02

[1] PCB-congeners (IUPAC no.): 28, 52, 101, 118, 138, 153 and 180

[2] PAHs: fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene and Indenopyrene

other deltas during the last five decades. For the sum of six individual PAHs similar differences have been found between the three deltas. Contents of nickel are similar in all deltas during the last five decades. Similar figures can be derived for all other heavy metals, individual PAHs and PCBs. In Table 4.3 the results have been summarized for three specific years during the last five decades.

The Rhine delta is the most contaminated delta, it has the highest levels of heavy metals (except nickel), PCBs and PAHs during the last five decades. The delta of the river Danube has elevated contents of heavy metals and PAHs, but is less contaminated than the Rhine delta.

The Volga delta is not contaminated, it has mainly background levels of heavy metals, PAHs and PCBs. If the actual (1990) heavy metal contents on the suspended solids in all rivers are compared the contents in the river Rhine are the highest (except for nickel) and lower levels are found in the rivers Volga and Danube.

The natural (background) input, due to geologic differences in each catchment area, and pollution input by industrial activity into the rivers during the years can explain most differences in the historic contaminant profiles of the Danube and Rhine delta. For the Volga delta only the first reason (natural background input) can explain the low and constant historical contamination. The sediments in the Volga delta reflect an almost natural unpolluted river system. Nevertheless industrialization in the Russian Federation has undoubtfully resulted in contamination of the Volga river. Presumably the sediments of the Volga delta are not contaminated, because contamination is trapped by the sediments in artificial storage lakes upstream of Volgograd (Batoyan and Zajtsev, 1985). Possibly, the recently increasing levels of zinc and arsenic in this delta are a first result of the not permanent trapping of the contamination in these storage lakes. If so, the storage of these contaminated sediments could be considered a chemical time bomb for the delta in the near future (Gerasimova and Hekstra, 1994). Furthermore the natural meandering of the river Volga in its large floodplain and high biological activity due to higher temperatures in this region might have had a purifying effect on the concentrations of contaminants here.

Based on the average discharge in each river and their average contents of suspended solids, also the load of pollutants can be calculated for each delta. The results of these calculations are presented in Table 4.4.

Table 4.4. Estimated heavy metal-, PAH- and PCB-loads deposited in the deltas of three major European rivers during three periods (in tons a year).

	Rhine delta			Danube delta			Volga delta		
	1940	*1970*	*1990*	*1940*	*1970*	*1990*	*1940*	*1970*	*1990*
Arsenic	105	250	67	192	204	156	21	21	21
Cadmium	14	44	17	-	-	-	-	-	-
Chromium	277	1221	444	601	721	721	293	340	366
Copper	250	722	222	457	937	769	110	146	146
Mercury	6	28	6	1	8	12	-	-	-
Lead	527	1082	277	432	673	601	63	63	63
Nickel	103	153	89	673	721	721	230	272	277
Zinc	3885	5550	2220	1081	1802	1682	272	334	355
Σ7PCBs [1]	-	3.2	0.5	-	-	-	-	-	-
Σ6PAHs [2]	33	32	14	5	1	4	0.1	0.1	0.1

[1] PCB-congeners (IUPAC no.): 28, 52, 101, 118, 138, 153 and 180

[2] PAHs: fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene and Indenopyrene

Around 1940 and 1990 the load of most pollutants (except Hg, Cd and PCBs) is the highest in the river Danube. Around 1970 the load of all pollutants is the highest for the river Rhine. The Volga river has the lowest loads during the last five decades.

Conclusions

- Sampling uniformly soft anoxic aquatic sediments in the Volga and Danube delta, using Cs-isotope-dating and satellite images (with intensity of suspended solids) resulted into concentration profiles of heavy metals and PAHs that reflect, without serious alterations, the historic pollution input into these rivers.
- The contents of 7 investigated PCBs (<0.005 mg/kg) and cadmium (<0.5 mg/kg) were below detection limit for all sediment samples in the Volga and Danube delta.
- Low and hardly changing concentrations of arsenic, copper, zinc and all studied PAHs were observed during the last five decades in the aquatic sediments of the Volga river. Nickel concentrations in the aquatic sediments in the Volga delta are rather high. Recently deposited sediments seemed to show slightly increasing levels for the heavy metals zinc, chromium and arsenic.
- The pollution history of the Danube is characterized as follows:
  * Low concentrations of metals were observed in the early 1940s. PAHs levels were already elevated.
  * Increasing levels of metals and PAHs were found between 1950 and 1987. Around 1987 the highest levels ever observed in this delta were found for both metals and PAHs.
  * Recently deposited sediments had rather low concentrations of metals and PAHs.
- If the contents of heavy metals, PAHs and PCBs in the aquatic sediments in the deltas of the rivers Rhine, Danube and Volga are compared, it is clear that the Volga delta is and was the cleanest delta during the last five decades.
  Nowadays the contents of heavy metals (except copper and nickel), PAHs and PCBs in the aquatic sediments of the river Rhine are still highest compared to the other two rivers.

defined as half the co-variance between pair differences of the two variables $Z(x)$ and $Y(x)$. The cross-variogram $\hat{\gamma}_{zy}(h)$ is estimated as half of the average product of h-increments relative to two different attributes Z and Y (Deutsch and Journel, 1992):

$$\hat{\gamma}_{zy}(h) = \frac{1}{2N_{zy}(h)} \sum_{i=1}^{N_{zy}(h)} \{z(x_i) - z(x_{i+h})\}\{y(x_i) - y(x_{i+h})\} \tag{2}$$

where $\{z(x_i), z(x_{i+h})\}$ and $\{y(x_i), y(x_{i+h})\}$ denote the ith pair of observations on $Z(x)$ and $Y(x)$, respectively, separated by distance h; and $N_{zy}(h)$ is the total numbers of such pairs.

The variograms between current and future observation points can be used to calculate the optimal grid spacing for sampling (OGS, necessary to monitor each variable in a regular grid) to acheive a pre-determined level of accuracy (PA). The PA, in the same units as the variables, is defined as the highest uncertainty that exists on an interpolated map. It is equal to the kriging standard deviation in the most isolated location of prediction, i.e. the centre point of a square grid cell with observations in each of the corners of this cell. The kriging standard deviation is

$$St.dev. = \sqrt{g_0'\, G^{-1}\, g_0 - x_a\, Vx_a} \tag{3}$$

where g_0 is the vector with variogram values between observation location and the prediction location, G is the $n \times n$ matrix with variogram values among the observation location, I_n is the vector of n elements all equal to 1, $x_a = 1 - g_0'\, G^{-1}\, I_n$ and $V = (I_n'\, G^{-1}\, I_n)^{-1}$. One may notice that equation (3) does not depend upon the vector of observations. Because it does depend upon the variogram and upon the configuration of the data points, it may be used to optimize the configuration of the sampling scheme as follows. Given the variogram, the maximum occurring uncertainty for e.g. a square grid with mesh b is determined. If this uncertainty is below the specific level b_0, b is doubled, otherwise b is halved until the value b_0 is reached.

In this study, the iterative computer program OPTIM was used to calculate the optimal grid spacing (OGS), based on predetermined accuracies (PA) of each variable in a triangular and square grid. Starting with the largest spacing, grid spacing is reduced until PA is reached. Minimizing prediction errors is only useful if the original data set is not severely clustered (Isaaks and Srivastava, 1989). In this study, the optimal spacing for a square grid was calculated for the selected variables (CF, OM, Cu, BAP and TC) using their specific variograms with fitted models. OPTIM was not used for the variables which have declustered means that differ more than 15% from their ordinary mean values.

Predetermined accuracy can be based on governmental regulations, but other practical values can be chosen as well. We optimized grid spacing with the (individual) standard deviation of the variable in each group as PA_1, yielding OGS_1. Variograms with a nugget value have a minimum predetermined accuracy (MPA). A PA lower than the square root of the nugget value for these variables cannot be achieved. For monitoring purposes, it is interesting to compare optimal grid sizes of the same variable between the sample domains. For example, we chose a PA_2 just above the highest MPA of each variable and calculated OGS_2.

Results and discussion

Summary statistics and correlations
Summary statistics for 10 parameters of all samples ($n = 138$), and separately for sub-areas G_1 ($n = 55$), G_2 ($n = 53$) and G_3 ($n = 40$) are given in Table 5.1. Standard deviations are rather high for all samples,

Table 5.1 Summary statistics for variables in the top layer of sediments in Lake Ketelmeer for all samples, stratified according to G_1, G_2 and G_3.

Variable[1]	All samples n = 138				G_1: Central zone n = 55							G_2: Eastern sandy part n = 53							G_3: Southern anoxic delta/shipping route n = 40						
	M[2]	SD[2]	Min[2]	Max[2]	M	SD	Min	Max	Md[2]	Mc[2]	Sk[2]	M	SD	Min	Max	Md	Mc	Sk	M	SD	Min	Max	Md	Mc	Sk
TC (cm)					28	13	2	55	29	25	-0.24	3.2	1.9	0.5	7.6	3.2	2.3	0.63	57	26	2	105	61	49	-0.12
CF (%)	10.7	6.4	0.5	21.5	16.2	2.7	5.6	21.5	16.5	15.2	-1.37	1.4	0.9	0.4	5.4	1.1	1.3	2.29	14.2	2.6	5.6	20.0	14.1	13.5	-0.52
OM (%)	4.5	2.6	0.4	8.4	6.5	1.2	2.4	8.4	6.7	6.1	-1.58								6.3	1.1	2.4	8.4	6.3	6.0	-1.02
BBF (mg/kg)	0.46	0.37	0.01	1.08	0.61	0.20	0.02	1.00				0.07	0.17	0.01	0.90				0.83	0.17	0.29	1.08			
BKF (mg/kg)	0.19	0.15	0.01	0.49	0.24	0.09	0.07	0.49				0.03	0.06	0.01	0.35				0.34	0.09	0.11	0.48			
BGP (mg/kg)	0.35	0.29	0.01	1.11	0.52	0.23	0.02	1.11				0.05	0.09	0.01	0.50				0.60	0.20	0.02	1.11			
IND (mg/kg)	0.29	0.23	0.01	0.75	0.37	0.14	0.08	0.64				0.04	0.09	0.01	0.50				0.52	0.12	0.09	0.75			
FLU (mg/kg)	0.73	0.60	0.01	1.85	0.92	0.33	0.05	1.82				0.11	0.31	0.01	1.80				1.34	0.30	0.46	1.85			
BAP (mg/kg)	0.50	0.43	0.01	1.73	0.74	0.38	0.02	1.73	0.61	0.74	0.66	0.06	0.14	0.01	0.70	0.01	0.05	3.84	0.86	0.25	0.26	1.73	0.84	0.83	0.87
Cu (mg/kg)	60	35	3	130	84	19	19	120	89	77	-1.41	22	16	3	63	22	13	0.56	85	15	32	130	84	81	-0.09
Cd (mg/kg)	5.6	3.0	0.9	18.0	7.5	2.2	0.9	14.0				2.8	1.6	0.9	6.5				7.1	2.3	3.6	18.0			

[1] TC, CF, OM, BBF, BKF, BGP, IND, FLU, BAP, Cu, Cd are thickness of contaminated layer, clay fraction, organic matter, benzo(B)fluoranthene, benzo(K)fluoranthene, benzo(Ghi)perylene, idenopyrene, fluoranthene, benzo(A)pyrene, copper and cadmium contents, respectively.

[2] M, SD, Min, Max, Md, Mc and Sk are mean, standard deviation, minimum, maximum, median, declustered mean and skewness of the sample groups, respectively.

due to large differences in degree of contamination between G_2 and the other sub-areas. G_2 contains all the sandy samples, in the eastern part of Lake Ketelmeer, with less clay and organic matter, and lower contaminant levels. Low levels (close to detection limits) of polycyclic aromatic hydrocarbons and organic matter within G_2 are mainly responsible for the rather high standard deviations for those variables. Positively skewed distributions are found for the same parameters at G_2, again with high standard deviations.

Except for TC, samples of G_1 and G_3 have comparable variables according to their average values, distributions and standard deviations. Average contents give a good indication of the degree of contamination in the top layer of Lake Ketelmeer. These values correspond to and underline the recent improvement of water and sediment quality reported in other studies (Winkels *et al.*, 1990; Beurskens *et al.*, 1993; Beurskens *et al.*, 1994).

A *t*-test shows that all values of parameters and contaminants are significantly lower in G_2 than in G_1 or G_3. Based on the summary statistics, all predefined groups chosen with this sampling strategy are significantly different from each other for at least one variable.

Declustering weights are less than 1 for the sample points in the crosses, leading to low declustered means for the selected variables in all groups (Table 5.1). The chosen sampling scheme with crosses is therefore responsible for declustered means 11.5% lower than calculated means for each variable. The declustered means of especially the clay fraction content and the copper content in sub-area G_2 are very low, probably because the cross is incidentically located in a region of low clay content.

Correlations between parameters (Table 5.2) are in general high (one tailed significance = 0.001) for all variables and contaminants, excepting Cd, which only relates to OM and Cu. All other compounds correlate significantly with each other and with organic matter. Significant correlations have been found between organic matter and metals in this lake (Ente, 1981). Winkels *et al.* (1990) proved that polychlorinated biphenyls are also related to the organic matter content in sediments. In the present study, correlations are also significant between the PAHs and organic matter and between each of the PAH variables. These relations indicate that the investigated PAHs originate mainly from atmospheric depositon, related to the combustion of fossil fuels (Beurskens *et al.*, 1993). These correlations also support the choice of BAP as a selected variable.

Table 5.2. Correlation coefficients of sediment characteristics and contaminants in Lake Ketelmeer (all 138 samples). One tailed significance: * = 0.001.

	CF[1]	OM[1]	BBF[1]	BKF[1]	BGP[1]	IND[1]	FLU[1]	BAP[1]	Cu[1]	Cd[1]
CF	1.00	0.88*	0.58	0.53	0.56	0.54	0.51	0.54	0.82*	0.56
OM		1.00	0.72*	0.70*	0.69*	0.68*	0.67*	0.69*	0.93*	0.67*
BBF			1.00	0.92*	0.84*	0.96*	0.98*	0.82*	0.70*	0.45
BKF				1.00	0.82*	0.90*	0.93*	0.81*	0.67*	0.42
BGP					1.00	0.81*	0.79*	0.87*	0.63*	0.39
IND						1.00	0.95*	0.78*	0.65*	0.40
FLU							1.00	0.78*	0.66*	0.42
BAP								1.00	0.63*	0.43
Cu									1.00	0.82*
Cd										1.00

[1] CF, OM, BBF, BKF, BGP, IND, FLU, BAP, Cu, Cd are clay fraction, organic matter, benzo(B)fluoranthene, benzo(K)fluoranthene, benzo(Ghi)perylene, idenopyrene, fluoranthene, benzo(A)pyrene, copper and cadmium contents, respectively.

Table 5.3. Estimated parameters of spherical or linear variogram models for selected variables in top layer sediments of three groups in Lake Ketelmeer.

Group	Variables[1]	model type[2]	nugget	sill	range (m)	rss[3]	R[2][3]
G_1	TC (cm)	S	40	162	756	246	
	CF (%)	S	0	5.9	1034	6.2	
	OM (%)	L	0.1	-	-		0.92
	BAP (mg/kg)	S	0.037	0.18	1828	0.008	
	Cu (mg/kg)	S	0	944	4398	233495	
G_2	CF	S	0.89	5.2	1877	1.9	
	OM	S	0.21	1.01	1035	0.47	
	BAP	S	0.0001	0.07	1132	0.0014	
	Cu	S	0	363	1516	10700	
G_3	TC	S	117	1022	1968	543814	
	CF	L	3.6	-	-		0.53
	OM	L	0.36	-	-		0.72
	BAP	S	0	0.08	1225	0.0015	
	Cu	S	152	279	2098	43314	

[1] TC, CF, OM, BAP, Cu are thickness of contaminated layer, clay fraction, organic matter, benzo(A)pyrene and copper contents, respectively.

[2] Spherical model (S) defined as:

$$\gamma(h) = N_o + c\,(\,3h/2a - 1/2(h/a)^3\,) \qquad for\ h < a$$
$$\gamma(h) = c \qquad for\ h \geq a$$

Linear model (L) defined as:

$$\gamma(h) = N_o + bh \qquad for\ h \geq 0$$

where N_o, a and c represent the nugget, the range and the sill value, respectively.

[3] rss = the residual sum of squares for spherical models; R^2 = squared correlation coefficient for linear models.

Spatial variability

Estimated variogram parameters are given in Table 5.3. Variograms were calculated using 8, 10 or 15 lags, with lag length varying from 185 m to 350 m. Variograms of CF and OM are shown in Fig. 5.3; variograms of Cu and BAP in Fig. 5.4; and variograms of TC in Fig. 5.5. Some distance classes contain less than 30 pairs of points, but they are given as well. Those variogram values are likely to be overestimated, so they were given less attention when fitting the models. In general, the spatial variability of the investigated variables in the sediments of this lake can be succesfully described by variograms. Three out of six variograms of the sediment characteristics do not reach a sill value, yielding a linear model. The sill value for CF is reached at a shorter range in G_1 than in G_2, whereas the range almost doubles in G_2 compared to G_1. For both contaminants, spherical models were fitted, the goodness-of-fit expressed in Table 5.3 by the residual sum of squares (rss). A low rss value indicates an adequate fit of the spherical models. For the linear models, the goodness-of-fit is indicated by the squared correlation coefficient (R^2). The measurement errors expressed as nugget values for Cu and BAP are close to zero. The sill value for these contaminants is reached in G_1 at a larger range than in the other sub-areas, whereas the rss value indicates a less adequate fit. The nugget values for TC are rather high in both sub-
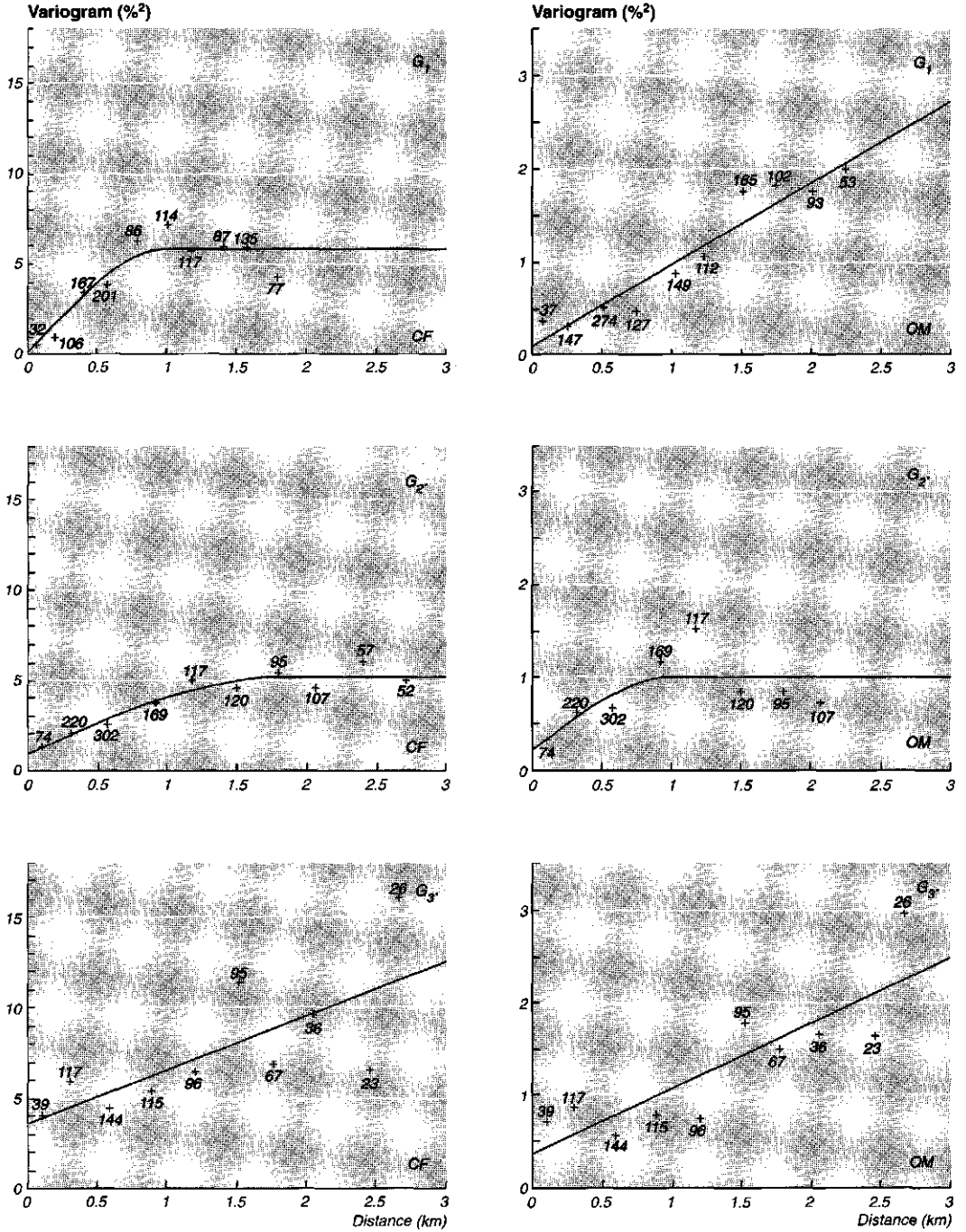
Fig. 5.3. Variograms of clay fraction (CF) and organic matter (OM) for sub-areas G_1, G_2 and G_3.
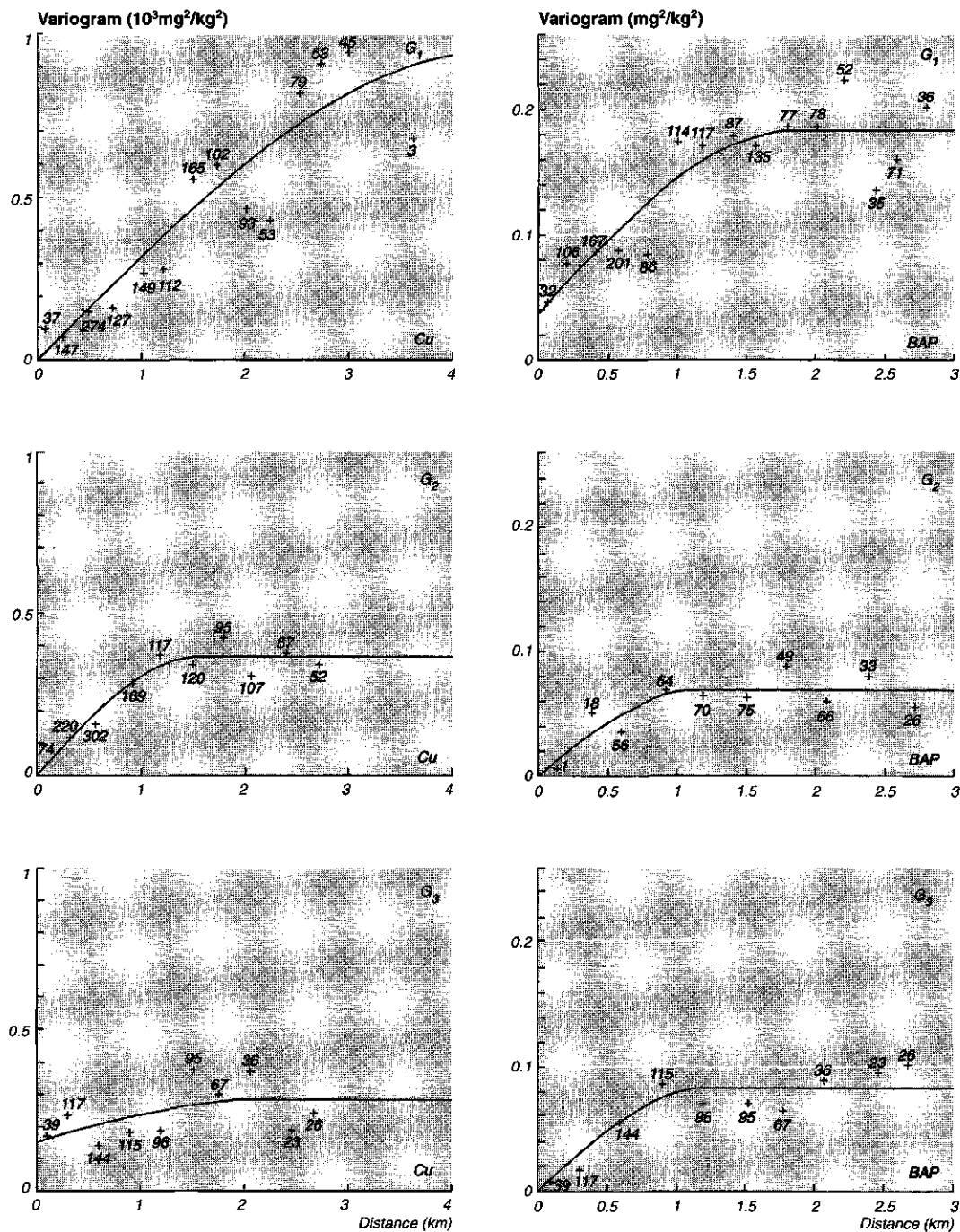
Fig. 5.4. Variograms of copper (Cu) and benzo(A)pyrene (BAP) for sub-areas G_1, G_2 and G_3.

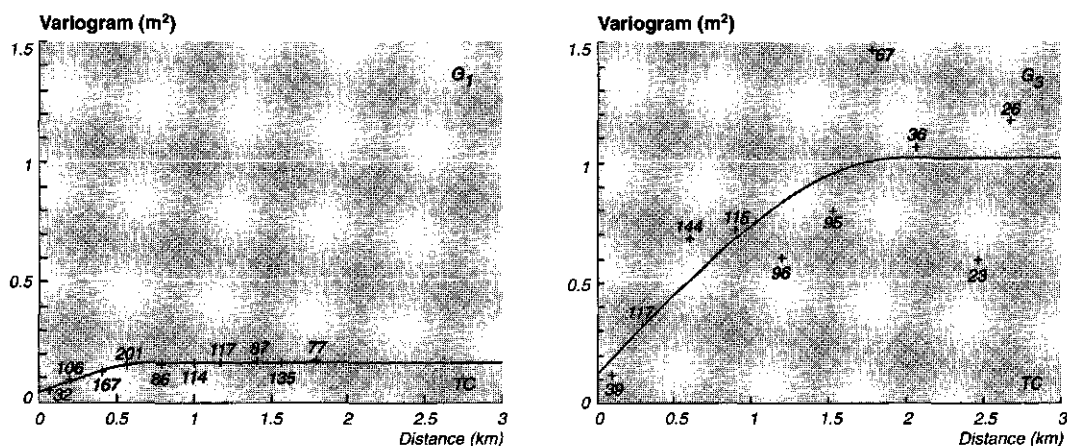Variogram (m²)   Variogram (m²)

Fig. 5.5. Variograms of thickness contaminated layer (TC) for sub-areas G_1 and G_3.

areas. Sill values for TC are reached at different ranges in both sub-areas, showing a high short-distance variability in G_1.

Correlations exist between contaminants and organic matter, and between the copper and clay fraction contents. To investigate the spatial dependence between these variables, cross-variograms were constructed (Figs. 5.6, 5.7, 5.8). If spatial co-dependency was found, correlation coefficients (r^2) are given in the upper-left corner of the figures. CF-Cu and CF-BAP are spatially co-dependent parameters in G_3, whereas OM-Cu and OM-BAP are spatially co-dependent in G_1 and G_3. Spatial variation in contaminants therefore probably relates to spatial variation in organic matter content. Further, TC is spatially co-dependent with OM and CF in G_1. In G_2, spatial variation of contamination does not relate to sediment characteristics.

Sampling strategy for monitoring and dredging
Analysis of spatial variability through the design of an adequate sampling grid could be helpful when monitoring similar ecosystems in the future. For the dredging of 20 km² in Lake Ketelmeer (to be executed before 2000), a grid pattern for adequate measurement of the thickness of the contaminated layer has to be chosen. We used OPTIM to determine the grid spacing necessary to achieve a predetermined level of accuracy. OPTIM was only used on variables in groups with declustered mean values similar (less than 15% difference) to ordinary mean values. In Fig. 5.9, the required grid spacing for three variables is given as a function of precision obtained in Lake Ketelmeer. In the central part of the lake (G_1), we notice that a grid spacing of 607 m yields interpolated TC maps with a maximum uncertainty of 12 cm. For G_3 the same accuracy was reached with a grid spacing of 33 m. This means that in harbors and near the shores of the lake or shipping routes, the thickness of the contaminated layer has to be surveyed with a grid spacing that is 18 times as dense. The minimum predetermined accuracy possible for TC is a very important factor for dredging. If the thickness of the layer in G_3 cannot be estimated with an accuracy greater than 12 cm, then it is not necessary to dredge it more accurately either. This does not mean, however, that dredging equipment does not need to be very accurate. Accuracy of both equipment and monitoring needs to be taken into account when removing contaminants. Therefore, when removing contaminated layers dredging should be done to an overdepth of at least
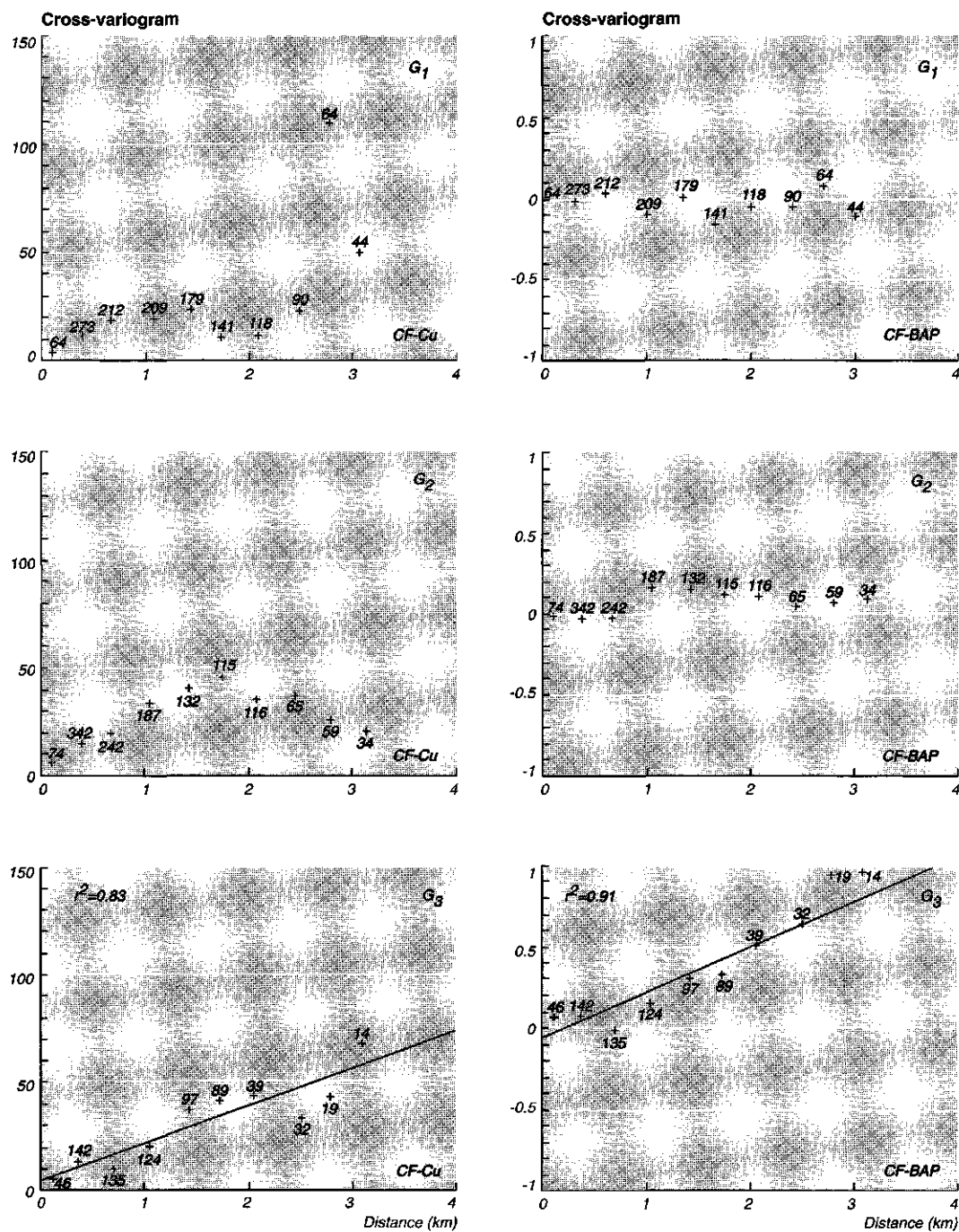
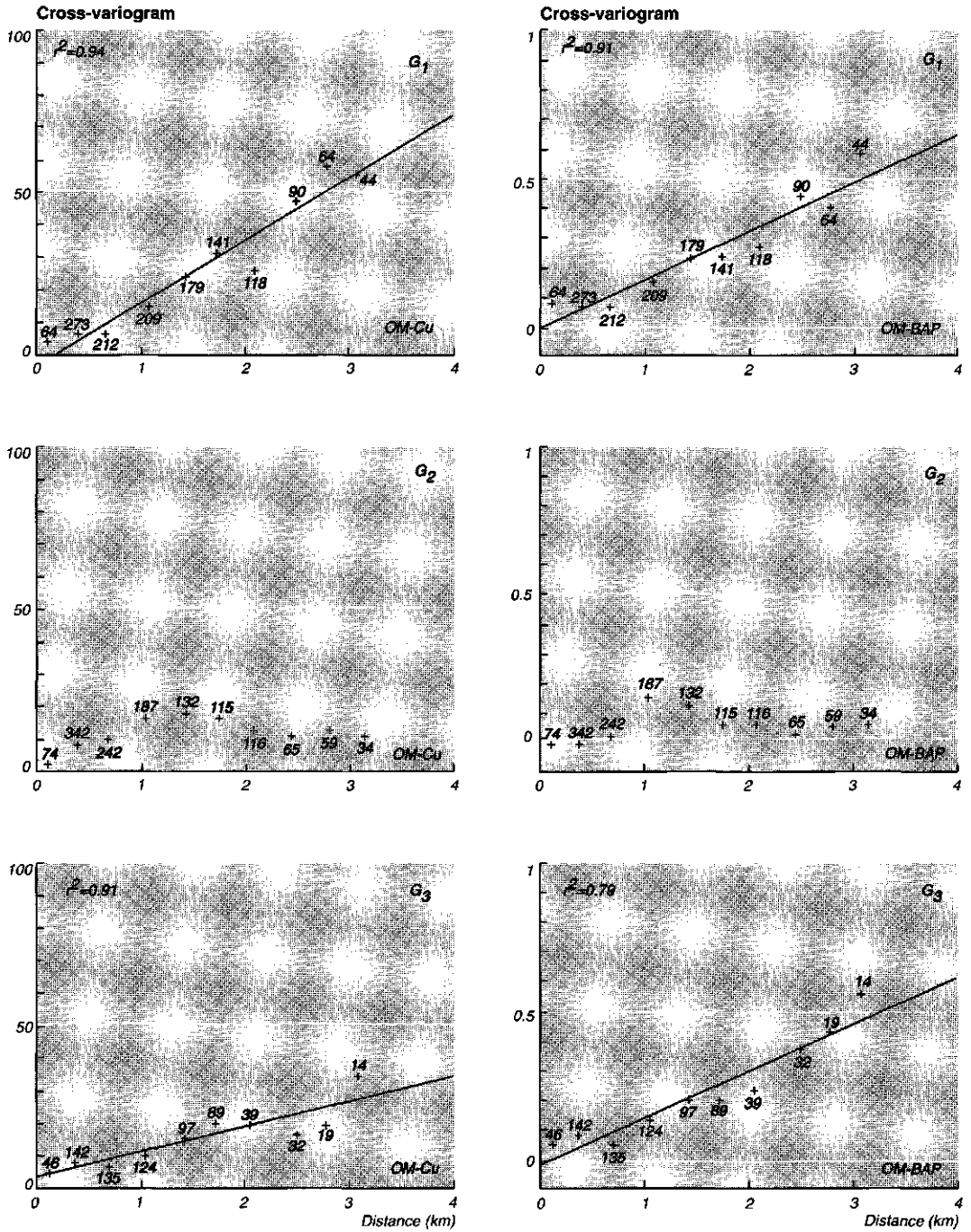**Fig. 5.6.** Cross-variograms of clay fraction (CF) with copper (Cu) and with benzo(A)pyrene (BAP) for sub-areas G_1, G_2 and G_3.

Fig. 5.7. Cross-variograms of organic matter (OM) with copper (Cu) and with benzo(A)pyrene (BAP) for sub-areas G_1, G_2 and G_3.
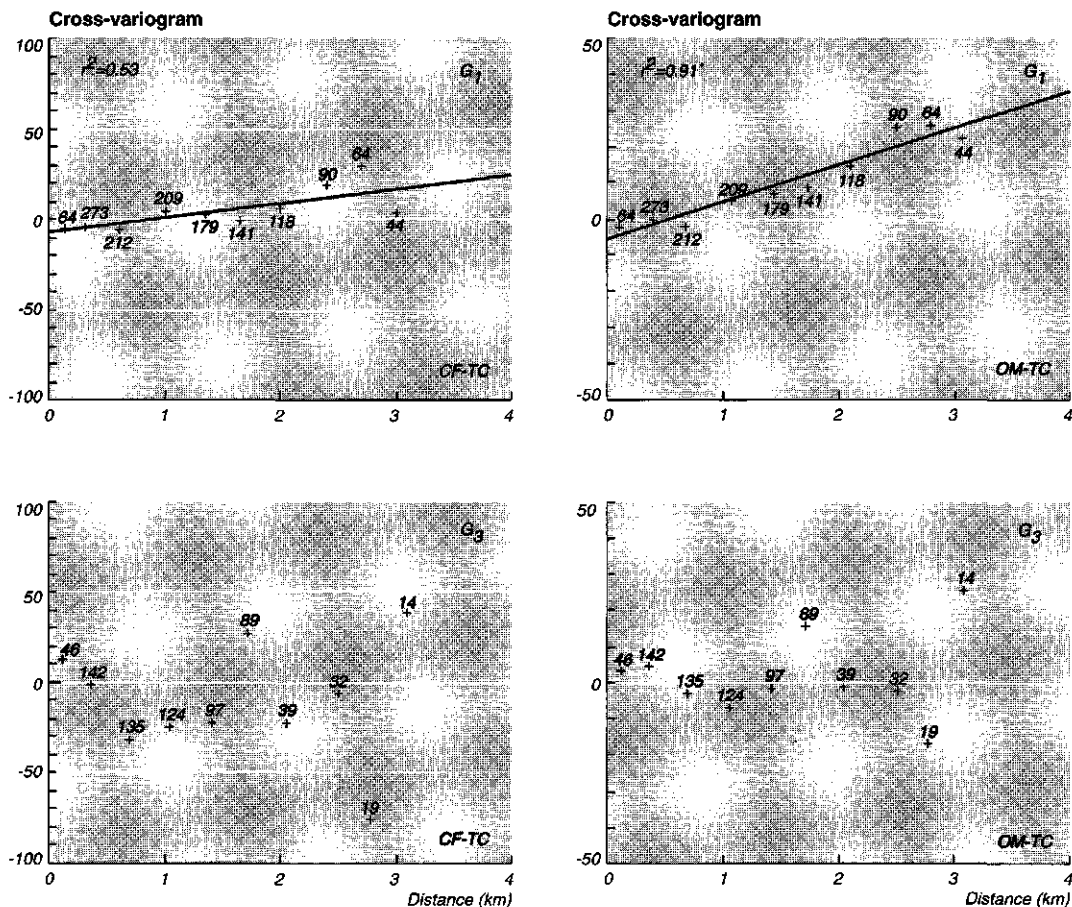
Fig. 5.8. Cross-variograms of clay fraction (CF) and organic matter (OM) with thickness contaminated layer (TC) for sub-areas G_1 and G_3.

7 cm in G_1, and preferably 12 cm in sub-area G_3, to make sure all contamination is removed. Removal cost will of course be higher.

Table 5.4 gives two predefined accuracies (PA$_1$, PA$_2$) with corresponding optimal grid spacings (OGS$_1$, OGS$_2$) for the variables in each group. PA$_1$ is the standard deviation of each variable in Table 5.1. For monitoring purposes, we chose as an example a PA$_2$ just above the highest MPA of each variable, yielding OGS$_2$. In Table 5.4 the minimum predetermined accuracy (MPA) is given between brackets for each variable in each group. Table 5.4 is depicted by Fig. 5.9, which shows the optimal grid mesh for Cu, BAP and TC for two or three sub-areas. To obtain interpolated Cu maps with a maximum uncertainty of 14 mg/kg, sample spacing should be 1150 m in G_1 and 450 m in G_3. To obtain Cu maps with a maximum uncertainty equal to the standard deviation of the variable within the group, spacing should be 2000 m in G_1 and 818 m in G_3. For BAP, sample spacing must be 270 m in G_1, 1023 m in G_2 and 968 m in G_3, to reach a predefined accuracy of 0.25 mg/kg. This proves the necessity to divide the aquatic ecosystem into sub-areas to reliably sample its sediment.

For sensitivity analysis, the OPTIM program was tested for the BAP contents in G_1, where for the

Table 5.4. Required sample spacing for monitoring of variables, based on predefined accuracies, in groups of top layers of sediments in Lake Ketelmeer.

Group	Variables[1]	Mean	PA_1[2]	OGS_1[2]	PA_2[2]	OGS_2[3]	[MPA[4]]
G_1	TC	28	13	883	12	607	[6.5]
	CF	16.2	2.7	4000	2	731	[-]
	OM	6.5	1.2	2707	0.65	607	[-]
	BAP	0.74	0.38	1306	0.25	270	[0.20]
	Cu	84	19	1985	14	1148	[-]
G_2	OM	1.4	0.9	738	0.65	248	[0.47]
	BAP	0.06	0.14	375	0.25	1023	[0.01]
G_3	TC	57	26	1243	12	33	[11.1]
	CF	14.2	2.6	1404	2	60	[1.95]
	OM	6.3	1.1	1919	0.65	59	[0.61]
	BAP	0.86	0.25	968	0.25	968	[-]
	Cu	85	15	818	14	458	[12.7]

[1]   TC, CF, OM, BAP, Cu are thickness of contaminated layer, clay fraction, organic matter, benzo(A)pyrene and copper contents, respectively.

[2]   Predetermined Accuracy (in cm, % or mg/kg) with PA_1 as the standard deviation of the parameter within its group and with PA_2 as an example to compare the sub-areas for each variable.

[3]   Optimal regular Grid Spacing for monitoring (in m) with OGS_1 based on PA_1 and OGS_2 based on PA_2.

[4]   Minimum Predetermined Accuracy (in cm, % or mg/kg).

Table 5.5. Sensitivity of OPTIM for three different nugget effects (N_0) on the sample spacing of benzo(A)pyrene (BAP) in G_1 with the fitted spherical variogram (Table 5.3), based on a predefined accuracy of 0.001.

OGS^1 (m)	Precision obtained (mg/kg)		
	$N_0 = 0.037$	$N_0 = 0.18$	$N_0 = 0$
2000	0.429	0.437	0.427
1000	0.342	0.437	0.291
500	0.282	0.437	0.203
250	0.247	0.437	0.143
125	0.226	0.437	0.101
62.5	0.214	0.437	0.071
31.2	0.207	0.437	0.050
15.6	0.203	0.437	0.036
7.8	0.201	0.437	0.025
3.9	0.199	0.437	0.018
2.0	0.199	0.437	0.013

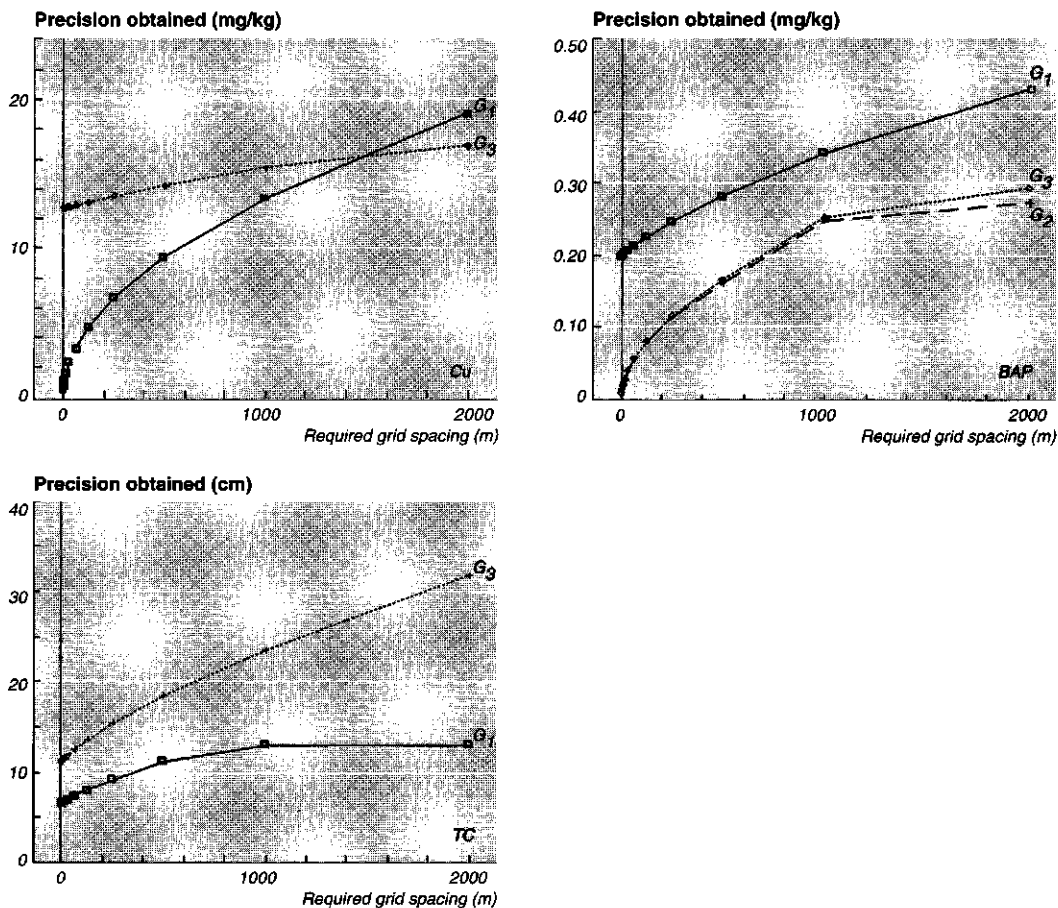[1]   Optimal regular Grid Spacing (OGS) in meters

Fig. 5.9. Sample spacing required to measure thickness of contaminated layer (TC), copper (Cu) and benzo(A)pyrene content (BAP) in sub-areas G_1, G_2 (only BAP) and G_3, as a function of the required accuracy.

spherical variogram model N_0 is set to equal the fitted value (0.037), the sill (0.18) and 0, respectively (Table 5.5). OPTIM is not sensitive, i.e. the uncertainty is high and does not change if the spherical model changes into a pure nugget effect. If $N_0 = 0$, however, precision is reduced by factors 0.3 and 0.55 for the sample spacings of 500 m and 125 m, respectively; OPTIM is therefore sensitive to the presence of a nugget effect.

To *monitor one contaminant in the entire lake* the results for each sub-area given above are used to select an optimal sampling pattern for the future. As an example, the BAP results in this lake have been used. To identify the optimal sampling pattern for future BAP monitoring in the entire lake, the first and most logical solution is to choose the densest network, giving the highest accuracies for all sub-areas. This would result in too many sampling points in at least two sub-areas, so it would be unnecessarily expensive. Further, it is doubtful whether the predefined sub-areas are representative of the non-visited areas. The second option is to sample each sub-area based on the calculated accuracies for BAP, which is statistically a good choice but causes a problem when deciding upon a pattern outside these areas and for G_{1+3}, the overlapping area of G_1 and G_3. For those areas, one could choose a sampling distance that

is the average distance of the predefined sub-areas. Another possibility is to recalculate the entire area by enlarging sub-areas with the zones which are located closest. This would result into a denser pattern (with higher costs) for the enlarged sub-areas to achieve the same predefined accuracy. The third option is to sample non-visited areas also and to calculate the minimum necessary grid spacing for BAP in these regions.

From the data in Table 5.4, it is difficult to choose the *optimal sampling grid for future contaminant monitoring* in this lake. For example, one could select the calculated grid spacing of Cu or BAP in G_1, but then the choice of the predefined accuracy for each contaminant would be different. We suggest a choice using the following practical cost-effective methodology:

1. If the budget is sufficient, then the densest grid spacing should apply to all variables; non-visited areas should be sampled with a similar dense pattern. If the budget is limited, use Rules 2 and 3.
2. If high correlations between variables are found ($R^2 > 0.8$), and they are spatially co-dependent ($r^2 > 0.8$), then the largest sample spacing of the two variables based on similar PA values can be used. Because contaminants are more expensive to analyse than sediment characteristics, it is also possible to substitute a contaminant with a cheaper variable (to analyse). Optimum cost-effectiveness can be obtained by substituting the largest sample spacing for the densest one, and to replace the contaminant with the sediment characteristic cheapest to analyse. If no good correlations and co-dependencies are found, then the densest, and more expensive, sample spacing must be chosen.
3. If threshold values of contaminants on which monitoring needs to be based are, according to governmental regulations, exceeded in a sub-area, then the sample spacing of this contaminant is used to monitor this sub-area, or use its substitute based on Rule 1. If not, use the densest grid size.

We used this methodology for G_1, where high correlations and co-dependence exist between OM and Cu. Assuming the highest PA of BAP (a 33% difference from the mean) and non-excedance of threshold values (based on Dutch governmental regulations) for each contaminant in Lake Ketelmeer, the grid size for monitoring contaminants would be 270 m. For this grid size, BAP needs to be analysed at every sampling point and OM has to be sampled in a grid size of approximately 2700 m. For practical reasons related to the total size of the area, OM can be measured at every hundredth BAP sample point. Based on the relation between OM and Cu, copper contents can also derived for this sub-area from measurements of OM.

If this geostatistical approach had not been used for contaminant monitoring and to calculate the thickness of the contaminated layer in Lake Ketelmeer, accuracies would have been lower and survey costs would have been higher. In general, in the Netherlands and other countries, grid patterns are based upon the limited financial budgets available for aquatic monitoring. Previously, budgets for the removal of contaminated sediments in other Dutch harbours have been exceeded because monitoring failed to produce accurate maps for dredging (Rijkswaterstaat, *Pers. comm*). Denser sampling patterns should therefore help to reduce dredging costs. Efficient use of limited financial resources for aquatic monitoring is possible using this geostatistical approach, that is, by choosing predefined sub-areas based on the best available knowledge of the area to sample.

Conclusions

This study leads to the following conclusions.
- When monitoring contaminants and related sediment characteristics in an aquatic environment their spatial variability must be taken into account.

- The number of sampling points for monitoring contaminants in sediments can be minimized, taking into account the necessary accuracy, using a geostatistical approach with predefined sub-areas.
- The choice for a sampling strategy for monitoring predefined sub-areas based on water depth, sedimentation/erosion behavior and type of sediment results in different sample spacings. For example, in Lake Ketelmeer a larger sample spacing for BAP monitoring applies to the central part of the lake than near the harbor and shore, areas with varying water depths. A procedure is defined in this chapter to arrive at a single sampling strategy.
- For removal of contaminants, the choice of predefined areas is essential to adequately dredge contaminated sediments. If spatial variability is not taken into account while dredging contaminated layers, decontamination of sediments will probably fail. We therefore recommend thorough (although expensive) spatial investigations of the contaminated layer before dredging.
- Efficient use of limited financial resources for aquatic monitoring is possible using practical, cost-effective, geostatistical methods.

Acknowledgements

Chapter 6

In-situ consolidation of lake deposits; an empirical model to reconstruct pollution history

J.P.M. Vink and H.J. Winkels

In-situ consolidation of lake deposits; an empirical model to reconstruct pollution history

Abstract - In the past, much effort is put in the development of sophisticated mathematical models, describing settlement and consolidation of water deposited sediments. Such models often aim at completeness and accuracy in modeling the physical processes involved. However, as a result of the generality of the descriptions, the models often fail to compute local circumstances satisfactorily. In specific cases, the empirical approach may prove to be highly competative and reliable.

In large water bodies in the central part of the Netherlands, the alluvial "IJsselmeer-deposit" is a common type of fresh water sediment. Its deposition and settlement started in 1932, when anthropogenic activities changed the physical and chemical conditions of the lakes drastically. Five representative cores of this sediment were taken in deep zones of the lakes. Periodic water depth surveys over the last sixty years at these locations provided information on the net sedimentation rate and the total thickness of this IJsselmeer-deposit at known time intervals. In order to calculate a time-equivalent of the depth scale, correction factors for soil consolidation are introduced. A decrease in the total thickness of individual sediment layers is proportional to the decrease of its volume, which is derived from in-situ characteristics. Correction factors are based on a simplification of various stages of compression (i.e. 0%, 30% and 45%). A factor n, which represents changes of water content of the sediment as a dependence of clay content, is derived for each layer, allowing an inverse calculation procedure to determine the initial, uncompressed thickness of each layer. Hence, a fairly reliable time scale in depth can be reconstructed. Furthermore, the radionuclide activity was measured in some cores and the degree of organic and inorganic pollution was determined in numerous layers of all cores. Cs-isotopic tracers (^{137}Cs, ^{134}Cs) give a good reconstruction of the last six decades of physical changes of the sediment and the degree of pollution, assuming post depositional redistribution and transformation of pollutants to be negligible. The results showed close coherence to calculated time-scales.

Introduction

Two large water bodies in the Netherlands, Lake IJsselmeer and Lake Markermeer (Fig. 6.1a,b), accumulate substantial amounts of suspended solids supplied by river IJssel, a northern branch of the Rhine. In undisturbed areas, the sedimentation pattern will follow the natural chronological (undisturbed) sequence. These areas may provide useful information on physical and chemical changes of the sediment that have occurred over time (Vink and Winkels, 1991; Beurskens et al., 1993). The sedimentation rate is especially high in deep parts and sandpits and therefore provides a reliable image of transitions of the sediment in depth and time.

If regular depth soundings are available in time (yr), changes in water depth (m) may be translated
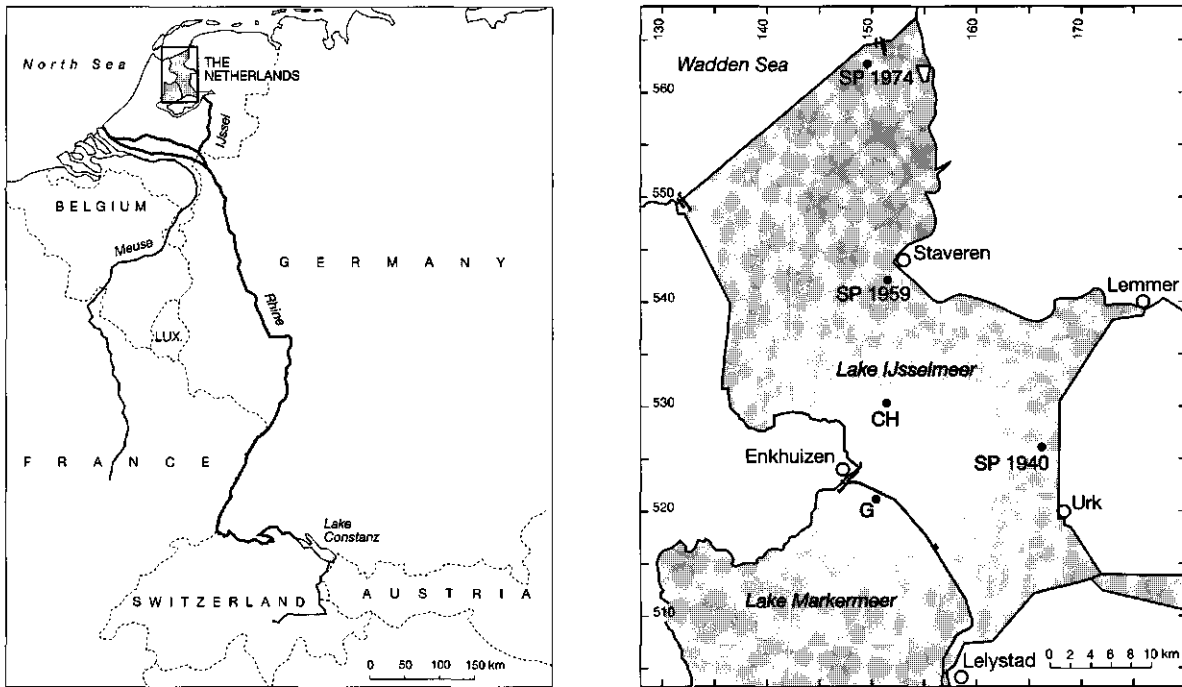
Fig. 6.1. Map and sampling locations of the lakes IJsselmeer and Markermeer.

to sedimentation rates (m · yr^{-1}). However, depth-time correspondence may not unconditionally be derived from soundings. Because of an increasing sediment load over time, underlying deposits will be compressed, which is accompanied by loss of pore water. This process is known as consolidation. Since the degree of consolidation submitted to a specific sediment layer at a certain depth is not known, the time boundaries will change in time. A reliable indication of the specific time of deposition therefore cannot be given.

Complex physically-based models of sediment compaction based on the physics of soil consolidation were, among others, presented by Gibson (1958) and Perrier and Quiblier (1974). Although physical descriptions are sound, it is difficult to obtain reliable soil parameters. Moreover, variations of experimental errors may superimpose and decrease the reliability of such models, and one may rightly question the general accessibility. In this study, an attempt is made to recognize and distinguish the major degrees of consolidation that occur in thick (> 2 m) sediment layers on the basis of empirical rather than physical laws. A characteristic "water-factor" for recently deposited sediments has to be derived.

It is not the purpose of this chapter to discuss historical inputs of pollutants, since this was done by several authors (Vink and Winkels, 1991; Beurskens *et al.*, 1993; Winkels *et al.*, 1992). Here, we tried to reconstruct the effects of anthropogenic activity on the geochemical history of recent lake deposits, and to introduce a reliable time saving, cost saving (as opposed to isotopic dating) calculation procedure for the dating of sediment layers in aquatic sediments, based on consolidation due to sediment loads.

Methods

Borings and sampling

The sediments of the freshwater Lake IJsselmeer are mainly of holocene origin. Half of the total lake bottom area is covered with marine sands. After the enclosure of this lake from the sea in 1932, salt concentrations gradually decreased and a loamy sediment, the IJsselmeer deposit, was deposited in freshwater conditions. Sediments were partly provided by the river IJssel, an offspring of the Rhine, and partly by internal redistribution (see chapter 3). Today, nearly 25% of the lake bed is covered with this type of sediment. The total volume of this sediment is estimated to be $280 \times 10^6 \, m^3$ (approximately 160 billion kg dry matter), which was deposited at a mean net rate of 0.017 m/yr (Vink and Winkels, 1991).

Sand pits, which originate from large scale sand extractions for public works, like the construction of dikes, have been filled naturally with this clayey, freshwater deposit. Figure 6.2 shows over an 18 km section how the deep parts of Lake IJsselmeer have been filled since 1936, when the first depth soundings of this area were made. Note the variation in sedimentation rates in successive time intervals. For sediments found in a former erosion gully in the central part (in the following text referred to as "channel"; in Fig. 6.2 indicated with the arrow), a simple and reliable sedimentation rate model could be fitted from the data: $D = t^{0.3}$ (correlation $r = 0.994$) in which D is the layer thickness (m) and t is the time in years.
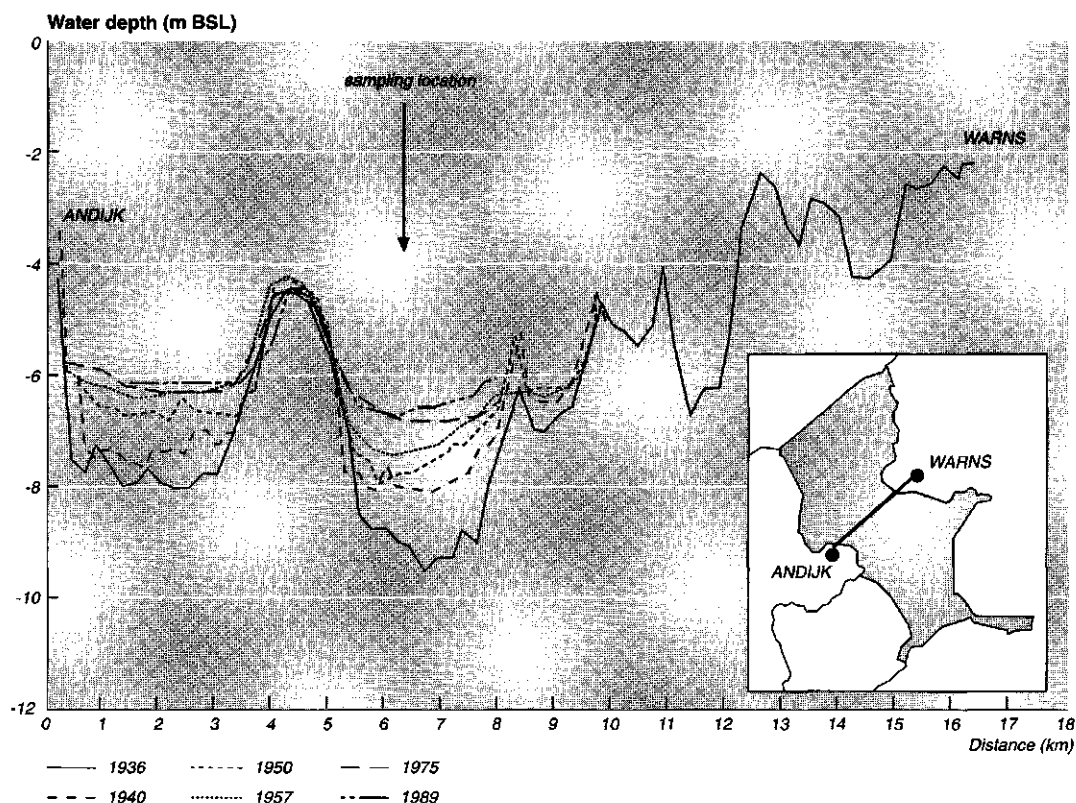

Fig. 6.2. Sedimentation profile over an 18 km row in Lake IJsselmeer. The sampling location in the channel is indicated by the arrow.

Four locations in Lake IJsselmeer (Fig. 6.1b; three sandpits, "SP" and a deep part of the channel, "CH") were selected for sampling. An additional sampling site was chosen in Lake Markermeer, "G", where individual layers of sediment in a former erosion gully were sampled and ^{134}Cs and ^{137}Cs dated. The sandpits in Lake IJsselmeer originate from different time periods: 1940, 1959 and 1974. All locations were at a fair distance from each other (5 km or more) and contain a thick (> 2 m) sediment layer.

Sediments of these locations were sampled in October 1989 from a ship with an auger in combination with a hoisting crane. Water depth varied from 4-6 m. Layers were sampled in 0.25 m increments, except for the top (0-0.05 m) and deep layers (0.50 m stepwise). Samples were stored in glass jars and sealed and analyzed for clay, organic matter and lime content and several organic and inorganic pollutants (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, mineral oil, extractable organic chlorides, and PCB 28, 52, 101, 118, 138, 153, 180). Concentrations were corrected according to Dutch standards, which implies the standardization to 25% clay and 10% organic matter (Vink & Winkels, 1991; Winkels *et al.*, 1992). Consequently, concentrations from soil layers with different physical characteristics may directly be compared. From all locations, historical sounding data were collected.

Calculations and system conditions

Consolidation of sediment layers is the physical result of a decreasing specific volume (cm^3/g) due to loss of pore water. Smits *et al.* (1962) were the first to describe by a great number of observations a relationship between the specific volume and the clay and organic matter content in the subaqueous deposits from the IJsselmeer which were water saturated. The relationship with the water content can be expressed in its most general form by:

$$A = c + n(L + bH) \qquad (1)$$

With:

A = Water content (g/100g dw);
c = Constant, which represents the water content of a pure sandy soil without clay or organic matter;
n = Water factor, which represents the influence of clay content on the water content A;
L = Clay content in weight %;
b = Weight factor for the influence of organic matter compared to that of the clay content;
H = Organic matter content in weight %.

The values of the constants c (20) and b (3) were empirically determined using a large data set. For the constant b, Zonneveld (1960) calculated a value of 4 for inundated sediments in the Biesbosch delta, the Netherlands, and attributed this value to a lower level of decay of the organic matter in this soil. The degree of decay does play a significant role in the water retaining capacity of organic matter, as is confirmed by many authors (Suffet and MacCarthy, 1989; Schwartzenbach *et al.*, 1993). In 1973, De Glopper stated that for the types of sediments found in the IJsselmeer area a value for b of 3 is plausible, provided there are no additional peat or plants remnants found. If the organic matter content is greater than 12%, a value of 4 seems more reliable.

Specific volume SV and water content A are inversely related, and are a function of the specific weight SW (g · cm^{-3}) of the in situ sediment. SW is calculated the conventional way as split fractions for organic ($SW \approx 1.50$ g · cm^{-3}) and inorganic ($SW \approx 2.65$ g · cm^{-3}) contents for each layer increment. Within the clay and organic ranges of the IJsselmeer deposits, a linear correlation between SW and SV is assumed. Consequently, one may transpose variations of initial (recently deposited) and ultimate (consolidated) specific volumes to variations in layer thickness. Hence:

$$d_i : d_u = SV_i : SV_u \qquad (2)$$

With:

d_i =   Intial layer thickness (m);
d_u =   Ultimate layer thickness (m);
SV_i =   Initial specific volume ($cm^3 \cdot g^{-1}$);
SV_u =   Ultimate specific volume ($cm^3 \cdot g^{-1}$);

For each layer, the relative loss $((d_i-d_u)/d_i) \cdot 100\%$ may be calculated. To do this, each sediment layer has to be treated as a young, recently deposited sediment with its own specific n-factor, δA (water content)/δL (clay content). However, a representative or best estimate value for this n-factor is not known for young or recently deposited aquatic sediments, since the suspended solid/sediment boundary is a diffuse one. In turbulent systems, this boundary may be as thick as 0.05 m (Vink and Winkels, 1991). Therefore, the 0.05 m top layer is not included in this consolidation calculation procedure. It is assumed, that the n-factor in the second layer, 0.05-0.25 m, will provide a fair estimate for a first approach. Calculations were carried out for each of the three IJsselmeer sandpits, the channel and the former erosion gully of Lake Markermeer. Results are presented in Figure 6.3. For stable sediment, which is not consolidated and not subjected to resuspension, the n-factor has a value of approximately 4.7. It should be noted that this value applies solely to these types of clayey aquatic sediments. A thin, sandy layer (3.2% clay, 0.8% organic matter) in sandpit 1974 does not seem to follow the suggested empirical laws. This data point is not processed in the rectilinear optimization.
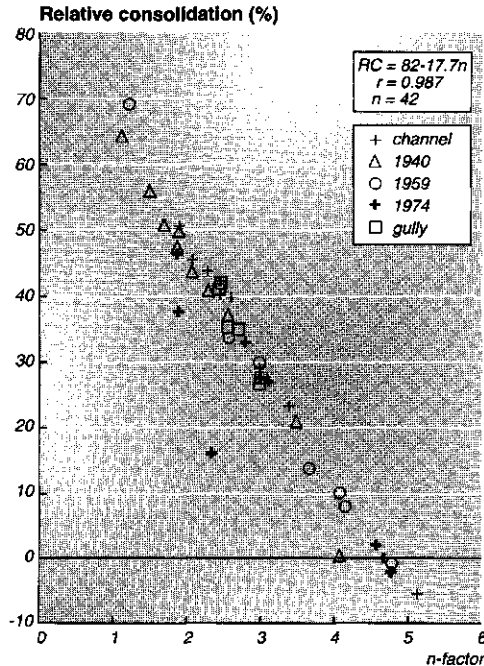

Fig. 6.3. Relative consolidation per layer in three sandpits, a channel (IJsselmeer) and an erosion gully (Markermeer) as a function of the n-factor.

The calculation procedures described above were carried out for the data that were obtained from the sediment of the former erosion gully of Lake Markermeer in 1989. Ten years earlier, in 1979, the very same location was sampled by and described by Ente (1981). Identical sedimentation rates in corresponding time intervals of the two locations were assumed. This assumption seems justified, since the total thickness of sediment in this gully has increased with 0.1 m in 10 years, which is of the same magnitude as the mean sedimentation rate stated before. Tables 6.1 and 6.2 are examples of this calculation procedure, carried out for the sampled locations.

Next to sediment parameters, the successive model parameters are calculated (eq. 1), resulting in a loss of thickness of each layer. A value of 4.7 was assigned to the initial n-factor.

Table 6.1. Physical characteristics and calculated parameters from the erosion gully Lake Markermeer, sampled in **1979**.

Depth (m)	Thickness (m)	< 2 μm	Org. matter	% dry matter	A-fig	n factor	Spec. volume	A-fig initial	Spec. volume end	Initial thickness (m)	Range (m)	Loss (%)
0 -0.15	0.15	17.1	5.6	39.7	152.1	3.9	1.91	179.3	2.19	0.15	0.15	-
0.15-0.30	0.15	21.5	5.7	39.6	152.8	3.4	1.92	201.4	2.41	0.188	0.338	20.2
0.30-0.50	0.20	18.1	4.6	46.6	114.8	3.0	1.54	169.9	2.09	0.272	0.610	26.4
0.50-0.70	0.20	22.3	4.8	44.4	125.4	2.9	1.65	192.5	2.32	0.282	0.891	29.0
0.70-0.90	0.20	27.8	5.4	41.1	143.6	2.8	1.83	226.8	2.66	0.291	1.182	31.3
0.90-1.10	0.20	35.6	5.7	38.0	163.5	2.7	2.03	267.7	3.07	0.303	1.485	33.9
1.10-1.30	0.20	44.4	5.9	34.7	187.8	2.7	2.27	311.9	3.51	0.309	1.794	35.3
1.30-1.60	0.30	46.3	6.0	35.0	186.0	2.6	2.25	322.2	3.62	0.481	2.275	37.7
1.60-1.90	0.30	47.9	5.1	36.7	172.6	2.4	2.12	317.0	3.56	0.505	2.780	40.5
	1.90						Total thickness :			2.78 m		
							Relative loss :			**31.7 %**		

Table 6.2. Physical characteristics and calculated parameters from the erosion gully Lake Markermeer, sampled in **1989**.

Depth (m)	Thickness (m)	< 2 μm	Org. matter	% dry matter	A-fig	n factor	Spec. volume	A-fig initial	Spec. volume end	Initial thickness (m)	Range (m)	Loss (%)
0 -0.05	0.05	10.2	3.3	43.0	132.6	5.6	1.71	114.5	1.53	0.05	0.05	-
0.05-0.25	0.20	16.6	5.9	44.8	123.2	3.0	1.63	181.2	2.21	0.271	0.321	26.3
0.25-0.50	0.25	24.8	5.5	40.9	144.5	3.0	1.84	214.1	2.53	0.345	0.666	27.5
0.50-0.75	0.25	28.3	5.9	41.9	138.7	2.6	1.78	236.2	2.76	0.387	1.053	35.4
0.75-1.00	0.25	24.2	5.1	45.9	117.9	2.5	1.57	205.7	2.45	0.390	1.443	35.9
1.00-1.50	0.50	43.8	6.2	37.2	168.8	2.4	2.08	313.3	3.53	0.847	2.289	40.9
1.50-2.00	0.50	46.3	5.1	37.7	165.3	2.4	2.04	309.5	3.49	0.853	3.142	41.4
	2.00						Total thickness :			3.14 m		
							Relative loss :			**36.3 %**		

The introduction of a time scale: inverse consolidation

The relative loss of thickness of a specific soil layer is expressed in equation 2 (last two columns of Tables 6.1 and 6.2). Likewise, one can transpose a compressed layer to its original thickness prior to compression, such as $((d_u/(d_u-d_i)) \cdot 100\%$. After processing all consolidation/depth calculations (51 observations), three major degrees of consolidation were distinguished as depth dependant variables:

1) 0% Compression is submitted to the upper 0.05-0.25 m layer. The top 0.05 m is not taken into account for reasons described before;
2) A 30% compression for 0.25-0.75 m layer depth;
3) A mean 45% compression for layers deeper than 0.75 m;

The initial layer thickness D_i is now expressed as:

$$D_i = \sum \delta d_n \cdot j_n \tag{3}$$

in which δd_n is the thickness of the consolidated layer increment and j_n is the reciprocated degree of consolidation. The value of j_n may vary between 1 and, theoretically, 100 but will rarely exceed 3 in natural situations.

For simplicity (n is finite) this series is reduced to $\delta d_1 \cdot j_1 + \delta d_2 \cdot j_2 + \delta d_3 \cdot j_3$, using the values 1 (100/(100-0)), 1.43 (100/(100-30)) and 1.82 ((100/100-45) for j_1, j_2 and j_3, respectively. For the Markermeer location $j_3 = 1.67$, since maximum consolidation is not yet reached because of insufficient layer thickness (sediment load). For each time interval, the compressed soil layers are "expanded" to their original thicknesses. This approach enables the reconstruction of sedimentation rates in unknown time intervals, such as 1932-1936 in the channel. Calculations proved an initial deposit thickness of 1.07 m (uncompressed), which was consolidated to 0.77 m in 1936, and has reached a thickness of 0.6 m in 1989. Therefore, the 1936 boundary line is submitted to 0.6 m above the underlying pleistocene sand layer. This "backstripping technique" is used to account for compaction due to progressive burial of sediments. The procedure resulted in a depth-dependent time scale, of which some examples will be discussed.

Radionuclide time tracing

To test the use of the model to date pollution depositions, a comparisson with other means of historical dating was carried out. Several authors (Robbins and Edgington, 1975; Beurskens *et al.*, 1993) reported on sediment time dating with the use of radionuclides. Therefore, the activity of various radionuclides (^{134}Cs, ^{137}Cs, ^{226}Ra, ^{210}Pb/^{210}Po) were measured in 7 subsequent layers of the sediment from the former erosion gully in Lake Markermeer. Up to 17 hours counting (analytical detection limit = 1 Bq $\cdot$ kg^{-1}) of gamma-activity in 7 subsequent sediment layers (0-0.05, 0.05-0.25, 0.25-0.50, 0.50-0.75, 0.75-1.00, 1.00-1.50 and 1.50-2.00 m below lake bed) were measured with a coaxial germanium detector in combination with a multichannel analyzer. Relevant time marks for ^{137}Cs are 1953 (first largescale appearance), 1959 (first fallout maximum caused by nuclear testings), 1963 (second fallout maximum) and 1986 (Chernobyl power plant accident and first elevated ^{134}Cs activity). If compared with τ-spectra (activity amplitude) a fair indication of the time of deposition can be given (Fig. 6.4). It appeares that ^{226}Ra can not be used as a tracer. Activities of this radionuclide remain constant over time, which is attributed to a probable absence of (industial) ^{226}Ra deposition from the river Rhine into Lake Markermeer.

Results and discussion

In Figure 6.5 it is shown how the degree of consolidation is proportionally related to depth (overlying layer thickness). Within the decade 1979-1989, an additional net sedimentation of 10.0 cm could be observed. Due to increasing consolidation, the graph has moved along the x-axis. Settlement of sediments appears to be active in the upper layers, whereas in the deep parts maximum compression for this sediment layer thickness is approached.

A historical reconstruction by means of inverse consolidation calculations and radionuclide (^{137}Cs) dating show remarkable coherence (Fig. 6.6). In essence, these methods have a different approach; in the inverse calculation procedure, the sediment layer depth at a given time is the unknown parameter, whereas in the radionuclide dating the time is a variable, and has to be interpolated between known fall-out maxima.
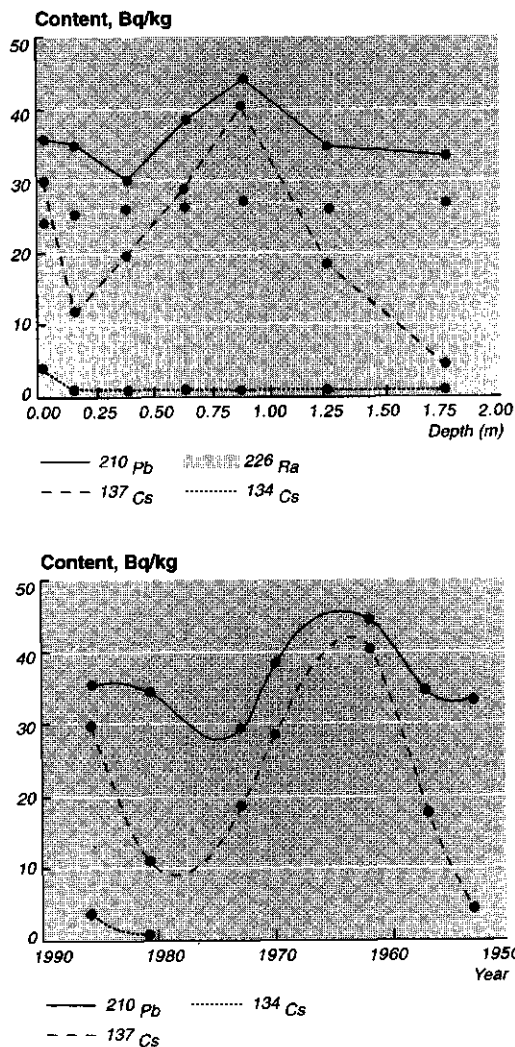

Fig. 6.4. Radionuclide measurements in sediment layers (top) and subsequent time dating (below).
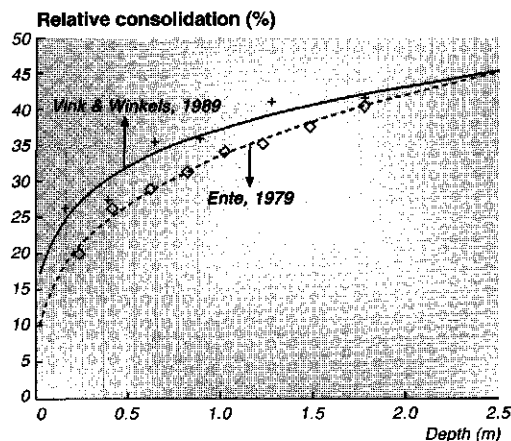
Fig. 6.5. Relative consolidation as a function of depth in a former erosion gully in Lake Markermeer. Data from 1979 (Ente, 1981) and 1989 (Vink and Winkels, 1991) were processed according to the three-step consolidation model and show close correspondence to first rate regression (correlation coefficient = 0.99 and 0.95, respectively).
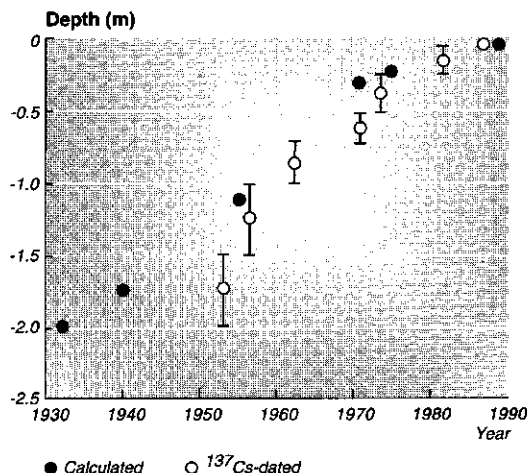

Fig. 6.6. Sediment dating according to the inverse consolidation procedure (●) and according to the radionuclide ^{137}Cs (○). Note the variance (bars) of the datapoints obtained with the last method which is an inevitable result of sediment layer thickness. Dating is based on interpolation between known fallout optima.

This technique of using radionuclides was applied by Robbins and Edgington (1975) to date sediment layers in Lake Michigan, U.S.A. with ^{210}Pb and ^{137}Cs, whereas Beurskens *et al.* (1993) used ^{134}Cs and ^{137}Cs to establish the 1986 and early 1960's time markers in sediments of Lake Ketelmeer, the Netherlands.

A reconstruction of physical transitions of the sediment in time is shown in Figure 6.7A. Note the significant decrease of clay content in time, represented by the area left of the < 2 μm line. Vink and
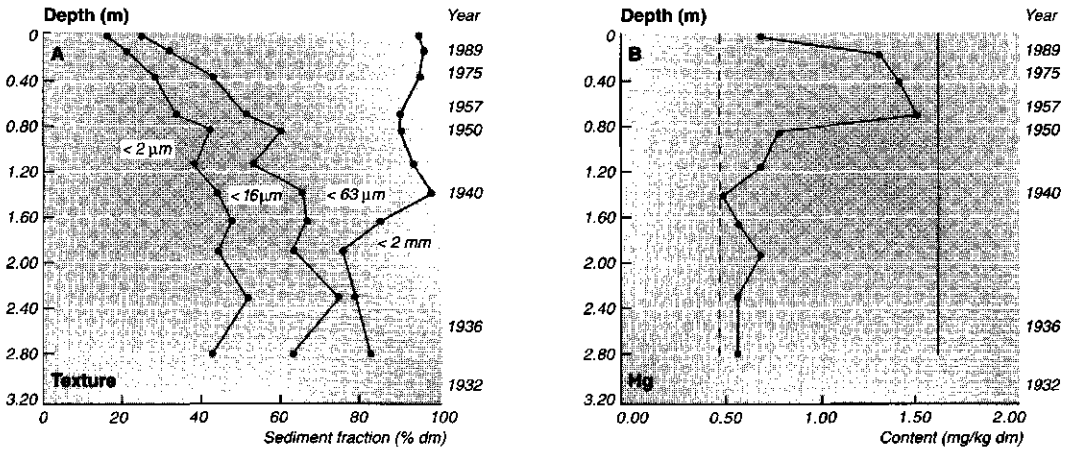
Fig. 6.7. A historical reconstruction of (a) physical transitions of the sediment and (b) degree of pollution.

Winkels (1991) and Winkels *et al.* (1992) ascribed this phenomenon to altered hydrological conditions due to human interference during the last six decades.

Figure 6.7b gives an arbitrary example of the pollution history of Lake IJsselmeer (here represented by mercury). The vertical lines represent Dutch environmental quality standards. Concentration profiles and trends agree with findings of Beurskens *et al.* (1993) and Winkels *et al.* (1992) from sediment of Lake Ketelmeer, which has an open connection to Lake IJsselmeer.

When data of sedimentation history are available, the inverse consolidation procedure may prove to be a reliable, time saving and financially beneficial method for time-dating water deposited sediments. For water deposited sediments, a characteristic *n*-factor may be derived as a representative value for recently deposited material. As far as reliability is concerned, the empirical approach may in many cases prove to match any complex physically-based model.

Chapter 7

Dilution of riverine heavy metal input by resuspension and algal growth in Lake IJsselmeer, the Netherlands

H.J. Winkels, G. Blom, S.B. Kroonenberg and L. Lijklema

Dilution of riverine heavy metal input by resuspension and algal growth in Lake IJsselmeer, the Netherlands

Abstract - This study evaluates the effects of sediment erosion and primary production on the temporal and spatial variability of heavy metals concentration in settling solids in lakes IJsselmeer and Ketelmeer. Measurements in sediment cores showed that heavy metals concentrations in deposits from the river IJssel, a branch of the river Rhine, are 2 - 3 times lower in Lake IJsselmeer than they are close to the river mouth, in Lake Ketelmeer.

Settling solids were sampled fortnightly using sediment traps at two sites in Lake IJsselmeer and contents of clay, organic matter, calcium carbonate, six heavy metals and $\delta^{13}C$ and $\delta^{18}O$ values were measured. Wind speed and direction, suspended solids, organic matter, chlorophyll, phaeophytin and oxygen concentrations were measured in the water compartment, as was pH, temperature and Secchi depth. Regression and multivariate analyses were used to evaluate the relationships within the data set. Principal components analysis and stepwise multiple regression show that the variation in the heavy metals concentration in settling solids is related to the windspeed and clay content, both variables that are related to erosion of sediments; and to pH, chlorophyll and $CaCO_3$, which are related to algal growth in the lake. This supports the hypothesis that the spatial gradient in the heavy metals concentrations in deposited solids in Lake IJsselmeer is the result of dilution of contaminated sediments due to erosion of older, less contaminated sediments and primary production related to algal growth.

Introduction

In aquatic ecosystems, cycling of nutrients, organic pollutants and heavy metals is often dominated by the processes resuspension, sedimentation and horizontal transport of sediments (Håkanson and Jansson, 1983; Lijklema *et al.*, 1994). The close relationship between the fate of pollutants and sediment transport is due to the affinity of contaminants for particulate materials. In many river basins with upstream inputs of contaminants, sedimentation of contaminated suspended solids has resulted in high contaminant concentrations in bottom sediments in areas with low flow velocities and turbulence. This is clearly so in the delta of the river Rhine (Winkels *et al.*, 1992).

The river IJssel, a branch of the river Rhine with an average discharge of 300 m³/s (Blom and Toet, 1993), flows via Lake Ketelmeer (38 km², average depth 3.5 m) into Lake IJsselmeer (1 136 km², average depth 4.7 m). In the period 1960 - 1980 the river Rhine was heavily loaded with heavy metals and organic micro-pollutants. Settling of contaminated solids has created a layer of heavily polluted sediments in Lake Ketelmeer with an average thickness of 0.55 m (approximately 15 million m³) (Winkels *et al.*, 1990; Beurskens *et al.*, 1993 and 1994). Contamination of deposits in Lake IJsselmeer, which is a reservoir for drinking-water production and an internationally recognized breeding ground for waterfowl, has been shown by several authors (Van Eerden and Zijlstra, 1986; Berger and Sweers, 1988; Vink and Winkels, 1991). However the concentrations of contaminants in these deposits are much

lower than those in Lake Ketelmeer. This raised the question of whether mixing of contaminated solids discharged by the river IJssel with sediments from other sources could account for the observed decrease in the contaminant concentration in the downstream direction.

A sediment and contaminant mass balance for Lake Ketelmeer (Ten Hulscher *et al.*, 1992) showed the importance of erosion of sediments deposited in previous decades for the water quality of this lake. Nowadays the concentrations of contaminants in the solids transported by the river IJssel to Lake Ketelmeer are lower than those of the lake's bottom sediment. Blom and Toet (1993) developed a sediment transport model for Lake Ketelmeer to simulate sedimentation, resuspension and horizontal transport of solids by flow. Using as input data the contaminant concentration in the solids discharged by the river IJssel, they were able to reproduce changes in the contaminant concentrations in the water compartment and bottom sediment quite well in addition to modelling the physical transport fluxes. Although Lake Ketelmeer is much smaller and shallower than Lake IJsselmeer, sediment erosion in Lake IJsselmeer might still influence the observed spatial gradient in contaminant concentrations.

Koelmans and Lijklema (1992) concluded that primary production in the eutrophic Lake Volkerak-Zoom decreases by dilution the cadmium concentration in the (total) suspended solids. In summer, primary production in the central part of Lake IJsselmeer is high, which increases the organic matter concentration in the water and also the production of carbonates (Del Castillo and Salomons, 1986; Winkels *et al.*, 1992; Hoogeveen, 1995). So primary production may be a factor contributing to the decrease of contaminant concentrations in the suspended solids in Lake IJsselmeer.

Temporal and spatial changes in the suspended-particulate contaminant concentrations are usually monitored by centrifuging out suspended solids in water samples. Settling solids are sampled by collecting material in sediment traps (Ten Hulscher *et al.*, 1992, Salomons and De Groot, 1978; Van der Weijden and Middelburg, 1989; Heymen, 1990; Hoogeveen, 1995). Blom *et al.* (1992) pointed out that contaminant concentrations in settling solids, collected with sediment traps, may differ from concentrations in suspended solids, obtained by centrifuging. These differences are related to differences in fall-velocity distribution, which are in turn related to differences in particle size distribution and in organic matter content between suspended and settled solids. Hence affinities and adsorption capacities on a unit weight basis will also differ for suspended and settled material.

Our objective was to evaluate the effects of sediment erosion and primary production on the temporal and spatial variability of heavy metals concentration in settling solids in Lake IJsselmeer.

Research area and methods

Research area
Dutch reclamation activities during the last century resulted in several freshwater lakes being created in the central part of the Netherlands. Lake Ketelmeer became a wide river mouth of the river IJssel as a result of the construction of two polders: the northern boundary is a polder dike constructed in 1938; the southern boundary a polder dike that was completed in 1953. Lake Ketelmeer has an open connection with Lake IJsselmeer. Lake IJsselmeer (Figs. 7.1A and 7.1B), created in 1932 by damming the former marine/brackish Zuiderzee, is one of Europe's largest inland freshwater bodies. It is a shallow lake with a bottom of mainly sandy sediments that has high net rates of sedimentation of fine settling solids in its deeper parts (Vink and Winkels, 1991 and 1994). Zuiderzee (Zu) deposits are defined as marine/brackish sediments (in this lake mostly sandy) that were deposited in the period 1600- 1932. This Zu-deposit can be identified by the presence of shell fragments (*Mya arenaria*). IJsselmeer deposits (IJm), defined as the freshwater sediments deposited since 1932, have been partly provided by
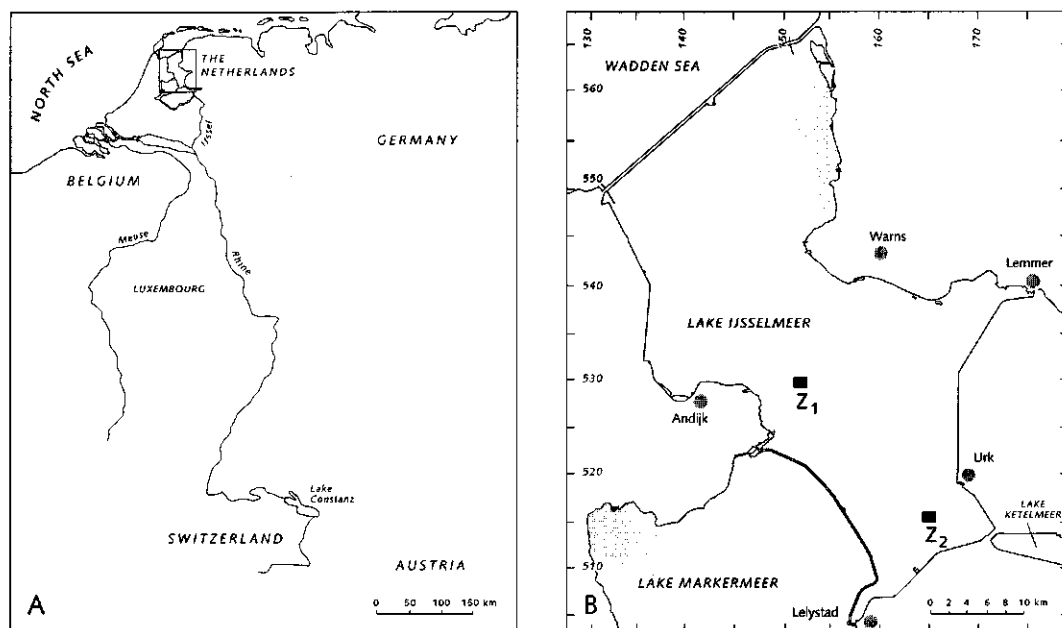
Fig. 7.1. Map and sampling locations in Lake IJsselmeer.

the river IJssel, but internal redistribution has also affected the sediment composition (Ente, 1981). The IJm-deposit covers the deepest part, which is 25% of Lake IJsselmeer, while the sandy Zu-deposit covers the remaining-shallower-75% of the lake bed.

During the summer primary production in Lake IJsselmeer is reflected by an increase of organic matter content and the occurrence of algal blooms (Hoogeveen, 1995), leading to a high carbonate content of sediments (Winkels *et al.*, 1992).

Sampling and chemical analyses
From 1 April to 7 December 1992, samples were taken from two observation platforms in Lake IJsselmeer located at different distances (Z_1 and Z_2; Fig. 7.1B) from the IJssel mouth. Z_1 (water depth 6.4 m) was located in the central part of the lake and Z_2 (water depth 5.2 m) in the south, near Lake Ketelmeer. Water samples were collected automatically every week and settling solids, collected in sediment traps, were retrieved and analysed fortnightly. Settling solids were also retrieved and analysed monthly from the river Rhine at Lobith (approximately 150 km upstream of the Rhine's mouth), on the Dutch-German border. Settling solids were sampled at Lobith throughout the whole of 1992. Heymen (1990) proved that heavy metal contamination in the river Rhine is also representative of the contamination of the river IJssel.

Sediment material was collected for analysis with six 60-cm-long cylindrical traps of 6 cm diameter located at mid-water depth. The traps were emptied every two weeks. After the traps were emptied and their contents transported to the laboratory, resuspended material was allowed to settle for 24 hours at 4 °C before the supernatant was siphoned off. The samples from the sediment trap were then immediately frozen, freeze-dried and stored.

Usual procedures (Hofstee, 1983) were used to analyse sample material, which had been homoge-

nized, for clay fraction content (Clay), organic matter content (OM), carbonate content ($CaCO_3$), suspended-solids content in sediment trap (SSsed), organic matter in sediment trap (OMsed), and contents of cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). Carbon (^{12}C and ^{13}C) and oxygen (^{16}O and ^{18}O) content were analysed by treating the samples with 95% (v/v) phosphoric acid solution and measuring the liberated carbon dioxide by mass spectrometer according to standard procedures (Mook and Grootes, 1973).

The water samples were analysed by usual procedures (Hofstee, 1983) to determine suspended solids (SSw), organic matter (OMw) and pH. Chlorophyll-a (CHL) and phaeophytins (PHA) were extracted with acetone and measured by a Beckman (Fullerton, CA) DU-64 spectrophotometer according to Golterman *et al.* (1978). In the field dissolved oxygen (O_2) and temperatue (T) were measured at mid water depth with an amperometric oxygen electrode (54-ARC, Yellow Springs, USA), and Secchi-disk depth (Sd) was measured with a white disk with three large circular holes in it. Wind speed (Wind) and direction were obtained from a nearby meteorological station.

Calculation of $\delta^{13}C$ and $\delta^{18}O$

During photosynthesis, algae preferentially use the lighter isotope of carbon ($^{12}CO_2$) in aquatic ecosystems, causing an enhanced relative contribution of $\delta^{13}C$ ($\delta^{13}C$) to $CaCO_3$ precipitates (Lynch-Stieglitz *et al.*, 1995), which are a result of the increase of the pH induced by algal growth (Mook, 1970; del Castillo and Salomons, 1986). Mineralization of dead algae will, on the other hand, result in a decrease of $\delta^{13}C$ value in the IJm-deposits. Higher $\delta^{13}C$ values also indicate an aquatic system with a higher salt content (Salomons *et al.*, 1975).

The ratio of ^{18}O to ^{16}O is related to precipitation and evaporation and should therefore show seasonality. Precipitation leads to an increase, and evaporation to a decrease, of this ratio (Salomons *et al.*, 1975). The ratios of carbon and oxygen isotopes are usually evaluated by calculating the relative deviation from that of a standard (PDB) reference value for carbon and oxygen:

$$\delta X(‰) = \frac{Rs - Rst}{Rst} \cdot 10^3 \qquad (1)$$

With:

X = ^{13}C or ^{18}O, respectively

Rs = ^{13}C to ^{12}C ratio or ^{18}O to ^{16}O ratio, respectively, for the sample

Rst = a standard ratio for carbon (PDB sea water: -1.06‰) or oxygen (PDB sea water: -4.14‰), respectively.

Normalization of concentrations

To study variations in time and space of contaminant concentrations, differences in adsorption affinity of the contaminant particles should be accounted for. This can be done by standardization with respect to the contents of the different adsorbing components in the suspended solids. Geochemical phases such as clay minerals, iron oxides and hydroxides, manganese oxides and hydroxides, and organic matter are the principal adsorbents of heavy metals (Singh and Subramanian, 1987; Koelmans and Lijklema, 1992). However, all oxides and hydroxides were not analysed. Thus the heavy metal contents were normalized per unit weight of clay (indicated by cC, similar to cCd) and organic matter (indicated by oC, similar to oCd). Both the original and normalized data were used for the study of heavy metal concentrations in relation to other characteristics measured.

Based on the content of each heavy metal and its average value during 1992 at each location, a sum of heavy metals (ΣHM) can be calculated for all six heavy metals studied. Similarly, ΣoHM and

Σ_cHM represent the sum of normalized heavy metals contents for organic matter and clay content, respectively.

Input flux calculation

To evaluate the impact on Lake IJsselmeer of the heavy metal load of the river IJssel, the load per unit surface area (areic loading) was calculated. This average areic loading flux, Afl_{ij}, is calculated from the monthly values of C_{RI}, SS_{RI} and I_{ij}:

$$Afl_{ij} = \frac{\sum_{1}^{12} (C_{RI} \cdot SS_{RI} \cdot I_{ij})_{Jan.}}{12 \cdot S}$$
(2)

With:

Afl_{ij} = average areic heavy-metal input flux (mg C $\cdot$ m^{-2} $\cdot$ d^{-1})
C_{RI} = heavy metal content suspended solids river (mg C $\cdot$ kg^{-1})
SS_{RI} = suspended solids content river input (kg $\cdot$ m^{-3})
I_{ij} = average discharge river (m^3 $\cdot$ d^{-1})
S = area of lakes IJsselmeer and Ketelmeer (m^2)
1-12 = number of month

Statistics

Correlation analysis on the data was performed with the statistical software package SPSS (SPSS, 1996), using a one-tailed t-test with $P < 0.05$. Principal component analysis and stepwise multiple regression were also performed with the package. These statistical analyses were performed to identify and describe relationships among the measured variables. Typically, this yields a large amount of data. Representative data are given in this chapter.

Results and discussion

Spatial variation

Table 7.1 summarizes the means and standard deviations of the variables sampled in settling solids at Z_1 and Z_2 in 1992. The values at both locations are compared with river Rhine input (RI) near Lobith and with the entire top layer sediment (IJm-deposits and Zu-deposits) of Lake IJsselmeer. These IJm- and Zu-deposits had been sampled 4 years earlier (Vink and Winkels, 1991). Winkels and Stein (1997) recently reported the contents of clay, organic matter and heavy metals in the IJm-deposit of Lake Ketelmeer. These contents are similar to the river-input concentrations (RI) given in Table 7.1. Clay fraction and organic matter contents were higher in the sediment traps than in the deposited sediments in Lake IJsselmeer. Organic matter contents of river-input at Lobith and at Z_2 are similar. Carbonate contents and δ^{13}C values were lower in river-input, while heavy metal contents were higher (except Cd) than in Lake IJsselmeer. Heavy metal contents at Z_1 and Z_2 are generally similar to contents in the IJm-deposits but higher than contents in the sandy Zu-deposits. Furthermore, heavy metal contents in the Zu-deposits were lower than in IJm-deposits in Lake IJsselmeer. Table 7.2 summarizes the values of the variables measured in the water. Most values were higher at Z_1 than at Z_2.

A t-test (two-tailed 95%; $P < 0.01$) was performed on all data measured at both locations in Lake IJsselmeer. The comparison of contents of heavy metals in sediment traps at Z_1 and Z_2 makes it clear that the heavy metals concentration is significantly higher at Z_2. Most heavy metal contents normalized
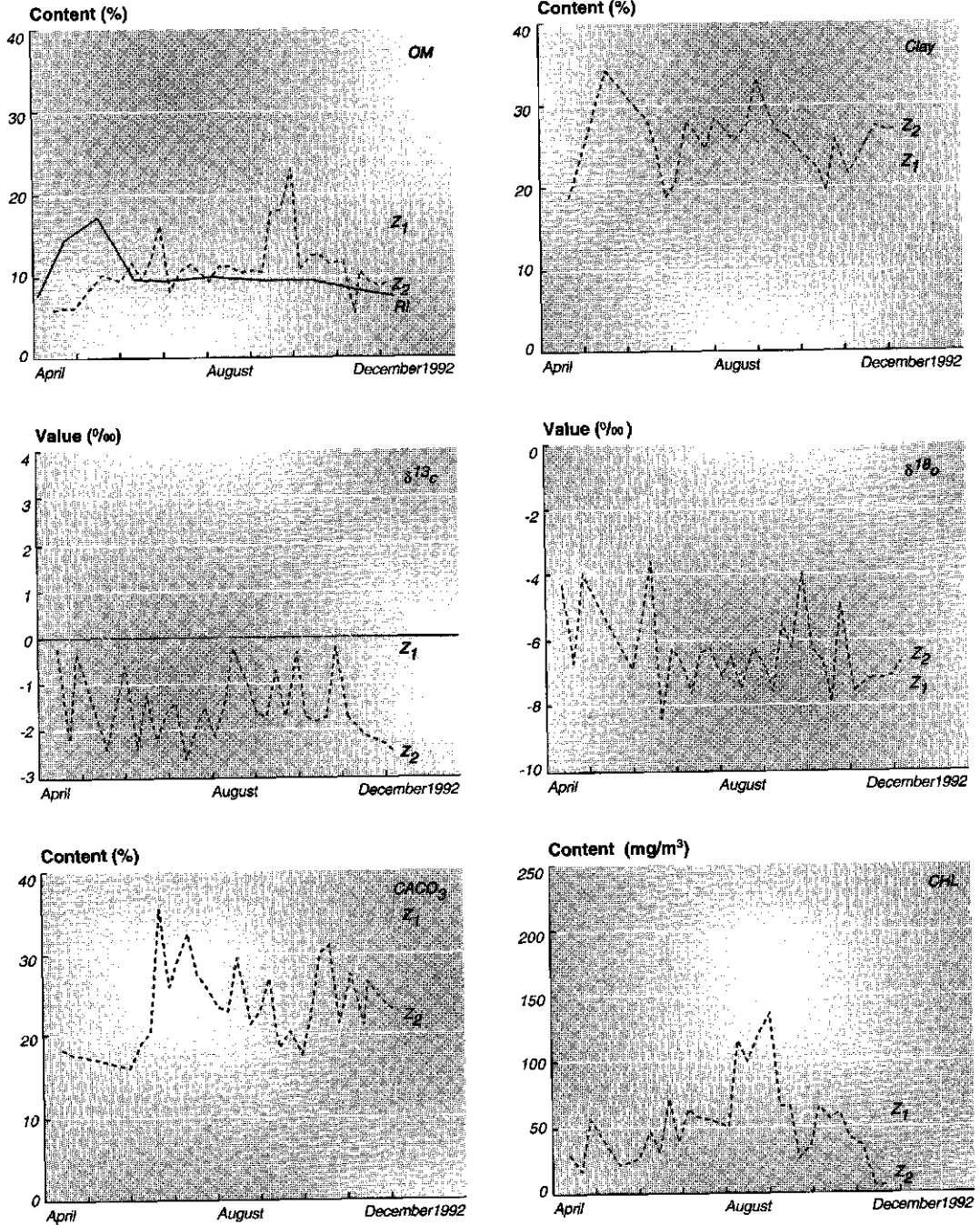
Fig. 7.3. Fortnightly and monthly changes of organic matter (OM), clay (Clay), carbonates (CaCO$_3$), chlorophyll (CHL) contents and δ^{13}C- and δ^{18}O-values in settling solids at Z$_1$ and Z$_2$ and in river input (RI) in 1992 in Lake IJsselmeer.

Table 7.5. Correlation coefficients of sediment characteristics and contaminants in settling solids and water at Z_1 in Lake IJsselmeer (n = 31). One tailed significance bold and underlined: $P < 0.01$.

	Clay	OM	CaCO$_3$	SSsed	OMsed	SSw	Omw	pH	S$_d$	T	O$_2$	CHL	PHA	Wind	δ¹³C	δ¹⁸O	Cd	Cr	Cu	Ni	Pb	Zn
Clay	1.00	0.43	**-0.63**	-0.11	-0.04	0.16	0.26	0.11	0.21	0.04	-0.05	**0.47**	0.30	-0.17	**0.55**	**0.57**	-0.02	-0.31	-0.06	0.02	0.09	-0.22
OM		1.00	**-0.85**	-0.16	-0.05	**0.46**	**0.72**	-0.11	-0.26	-0.34	0.02	**0.77**	**0.56**	-0.06	**0.55**	0.34	-0.08	**-0.50**	-0.40	-0.24	-0.24	**-0.49**
CaCO$_3$			1.00	0.35	0.25	-0.34	**-0.53**	-0.05	0.00	0.16	0.00	**-0.67**	**-0.50**	0.36	**-0.64**	**-0.56**	0.17	**0.63**	0.41	0.27	0.35	**0.62**
SSsed				1.00	**0.98**	0.07	-0.01	-0.42	-0.21	-0.44	0.08	-0.30	0.01	**0.64**	-0.18	-0.03	0.39	**0.50**	0.15	0.26	0.40	0.41
OMsed					1.00	0.15	0.08	-0.39	-0.25	-0.46	0.09	-0.17	0.07	**0.62**	-0.09	0.02	0.30	0.39	0.07	0.19	0.32	0.30
SSw						1.00	**0.88**	-0.30	-0.23	-0.49	0.27	**0.64**	**0.59**	0.25	0.20	0.08	-0.09	-0.12	-0.41	0.12	-0.22	-0.30
OMw							1.00	-0.25	-0.31	-0.41	0.14	**0.83**	**0.54**	0.16	0.40	0.13	-0.13	-0.29	**-0.53**	-0.01	-0.22	-0.40
pH								1.00	0.40	**0.74**	0.11	0.16	-0.11	-0.50	0.22	0.11	**-0.59**	**-0.51**	0.13	-0.38	-0.42	-0.43
S$_d$									1.00	0.37	**0.46**	-0.22	-0.16	-0.40	-0.14	0.05	0.03	0.03	0.13	0.37	0.06	-0.02
T										1.00	0.23	-0.07	-0.43	**-0.62**	0.15	0.07	-0.43	-0.34	0.16	-0.24	-0.26	-0.20
O$_2$											1.00	0.03	0.28	0.06	-0.15	-0.16	0.04	0.17	0.20	0.31	0.07	0.01
CHL												1.00	**0.53**	-0.14	**0.60**	0.25	**-0.50**	**-0.64**	-0.39	-0.32	0.42	**-0.63**
PHA													1.00	0.03	0.23	0.26	0.04	-0.18	0.03	0.05	-0.10	-0.23
Wind														1.00	-0.24	-0.19	-0.09	-0.31	-0.01	0.31	**0.45**	**0.46**
δ¹³C															1.00	**0.80**	0.37	**0.51**	-0.01	-0.33	0.30	**-0.53**
δ¹⁸O																1.00	-0.35	**-0.55**	-0.21	-0.07	-0.10	-0.28
Cd																	1.00	**0.74**	0.23	**0.58**	**0.72**	**0.70**
Cr																		1.00	**0.50**	**0.71**	**0.81**	**0.92**
Cu																			1.00	0.23	**0.52**	**0.59**
Ni																				1.00	**0.58**	**0.60**
Pb																					1.00	**0.90**
Zn																						1.00

Table 7.7. Results principal component analyses at two locations in Lake IJsselmeer

Z_1											
Factor 1		Factor 2		Factor 3		Factor 4		Factor 5		Factor 6	
Var.	Score	Var.	Score	Var.	Score	Var.	Score	Var.	Score	Var.	Score
Cd	0.89	OMw	0.87	$\delta^{18}O$	0.89	OMsed	0.95	S_d	0.84	Cu	0.88
Pb	0.82	SSw	0.84	Clay	0.81	SSsed	0.93	O_2	0.79		
Cr	0.80	PHA	0.79	$\delta^{13}C$	0.80	Wind	0.68				
Zn	0.79	CHL	0.74	$CaCO_3$	-0.65						
Ni	0.74	OM	0.74								
pH	-0.69	T	-0.60								

Accounts for **84.9%** of variance in data set

Z_2													
Factor 1		Factor 2		Factor 3		Factor 4		Factor 5		Factor 6		Factor 7	
Var.	Score	Var.	Score	Var.	Score	Var.	Score	Var.	Score	Var.	Score	Var.	Score
Pb	0.97	SSsed	0.96	PHA	0.93	CHL	0.88	$\delta^{18}O$	0.90	O_2	0.86	S_d	-0.70
Zn	0.95	OMsed	0.95	SSw	0.90	OMw	0.61	$CaCO_3$	-0.90	pH	0.73	$\delta^{13}C$	0.59
Ni	0.93	Wind	0.61	OMw	0.71					Cu	-0.59		
Cr	0.85	T	-0.53										
Clay	0.71												
Cd	0.55												

Accounts for **87.5%** of variance in data set

The affinity of the heavy metals for organic carbon differs significantly at Z_2 from Z_1 in Lake IJsselmeer. The increase of carbon at location Z_1 has no influence on the adsorption of heavy metals, but it is responsible for dilution there. The influence of mainly CHL, $CaCO_3$ and Clay explains the behaviour of each and the sum of all heavy metal contents at Z_1 during 1992. The influence of Wind, pH, Clay and partly OMw explains the behaviour of each and the sum of all heavy metal concentrations at Z_2 during 1992. This suggests that besides the effect of river input, sedimentation, erosion - and hence dilution - and, to a lesser extent, also algal growth determine the heavy metal concentrations in the suspended solids.

Conclusions

Measurements of the concentrations of six heavy metals in suspended solids, discharged by the river IJssel, and of settling solids at two locations in Lake IJsselmeer show a typical spatial gradient. The heavy metal concentrations decrease with increasing distance from the river's mouth. This spatial gradient is also found when heavy metal concentrations are normalized for clay and organic matter content. Measurements in sediment cores from Lake Ketelmeer and the central part of Lake IJsselmeer show that the heavy metal concentrations in sediments, deposited in the same periods are 2 - 3 times higher in Lake Ketelmeer. Therefore, this spatial gradient is reflected in the bottom sediment.

Table 7.8. Results stepwise multiple regression for heavy metals and normalized heavy metals at two locations in Lake IJsselmeer

Relation		Z_1	R^{2*}
oCd	=	-0.012 CHL + 0.003 OMw + 0.183	0.71
cCd	=	-0.001 CHL + 0.001 PHA + 0.007 OMw - 0.001 SSw + 0.108	0.82
oCr	=	-0.007 CHL + 0.050 CaCO$_3$ + 0.872	0.69
cCr	=	0.037 CaCO$_3$ - 0.002 CHL - 0.030 T + 0.681	0.71
oCu	=	-0.152 OMw + 0.031 SSw + 3.963	0.62
oNi	=	-0.007 CHL + 0.011 S$_d$ + 1.820	0.54
oPb	=	-0.018 CHL + 5.455	0.54
oZn	=	-0.068 CHL + 0.633 CaCO$_3$ + δ^{18}O + 15.108	0.71
ΣoHM	=	-0.022 CHL + 0.257 CaCO$_3$ + 0.268 Clay - 6.442	0.85

Relation		Z_2	R^2
Cd	=	-0.975 pH + 0.248 Wind + 9.386	0.63
Cr	=	5.417 Wind - 7.185 pH + 0.971 Clay - 0.101 CHL + 52.579	0.69
Cu	=	-22.912 pH + 244.682	0.26
Ni	=	0.800 Clay - 0.358 T - 0.039 CHL + 17.015	0.67
Pb	=	1.998 Clay + 6.543 Wind - 8.329 δ^{13}C - 12.484	0.69
Zn	=	40.799 Wind + 12.505 Clay - 0.704 CHL - 69.795	0.70
ΣHM	=	0.552 Wind - 1.362 pH + 1.034 Clay - 0.061 OMw + 12.672	0.72

* Correlation coefficients or adjusted correlation coefficients with a significance level of $P < 0.05$.

A simple sediment mass balance, based on data on river IJssel input and observed sedimentation fluxes, indicates that the total internal sedimentation fluxes of heavy metals in Lake IJsselmeer are far greater than the areic input load of the river into the lake.

Due to the complexity of the relations between measured variables, heavy metals concentrations and variables related to primary production and erosion, single correlation analysis do not reveal clear relations and processes that explain this dilution. Principal components analysis and stepwise multiple regression show that variation in heavy metals concentration in settling solids is related to wind velocity and clay content, both of which are related to resuspension/erosion of sediments; or, alternatively, pH, chlorophyll and CaCO$_3$, which are related to algal growth in the lake. Resuspension/erosion-related variables are the dominant factors explaining the variation in the heavy metals concentration of the southern part of the lake, whereas algal growth-related variables explain most of the variation in the heavy metals concentration in settling solids of the central part of Lake IJsselmeer. There, where algal concentrations are high, the negative relation between the concentration of most heavy metals in settling solids and the concentration of chlorophyll and organic matter in the water compartment justifies the conclusion that dilution of contaminated suspended solids caused by primary production is relevant. In the southern part of the lake, the heavy metals concentration is positively related to wind velocity and clay content. This indicates that resuspension of recent deposits contributes to the heavy metals concentration in the water compartment. The gradual increase in the

production related to algal growth, and resuspension/erosion of older deposits in Lake IJsselmeer.

In shallow lakes the internal cycling and horizontal distribution of contaminated sediments is often dominated by wind induced resuspension and horizontal transport of sediments (Håkanson and Jansson, 1983; Lijklema *et al*, 1994). In two lakes in the area, Lake Markermeer (Van Duin, 1992; Van Duin *et al.*, 1992) and Lake Ketelmeer (Blom and Toet, 1993) the model STRESS-2d (Sediment Transport, Resuspension and Sedimentation in Shallow lakes) was successfully applied to simulate suspended solids concentrations and sedimentation patterns. This model includes a description of bottom sediment resuspension/erosion due to wind induced waves, sedimentation and advective and dispersive horizontal transport. The model also includes a description of the effects of resuspension and sedimentation on the bottom sediment composition (Blom *et al.*, 1992). The bottom model is based on a 2-layer concept. On top of a more or less consolidated sediment layer is a thin top layer, with a high water content. This top layer can be depleted by resuspension in periods and areas where resuspension exceeds sedimentation. When the top layer is depleted erosion of the underlying layer starts. Erosion was however simulated in a rather simple way: with a constant velocity. In a situation like in Lake IJsselmeer, where a focus on the erosion processes is needed, a model in which erosion of consolidated sediments is related to the hydrodynamic forces induced by wind is more appropriate.

Because of the time scales of resuspension and erosion and the effects of depth gradients on these processes, a sediment transport model necessarily has a high resolution in time and space. Using such a model for a period of several decades would result in extravagant computing times. While the characteristic time scales for resuspension and erosion and the resulting dynamics of the thickness and composition of the sediment top layer and the concentration in the water compartment are in the order of less than an hour up to a day, the changes in the composition of the more or less consolidated sediment layers are expected to have a much larger characteristic time scale (weeks up to years). This raised the question whether it is possible to develop a model which, based on an integration of simulated transport fluxes in time and space, simulates the morphology and composition of sediments on the long term. This study aims to develop this model.

A first objective of this study is to reconstruct the sediment (re-)distribution processes in the past in order to evaluate to what extent redistribution of old deposits has contributed to the sedimentation and so to dilution of the contaminated sediments supplied by the river IJssel in sedimentation areas in Lake IJsselmeer. This reconstruction then should result in an instrument for simulation of the changes in sediment composition and contamination in the future, given the changes to be expected in the contaminant loads of the river IJssel. The instrument thus should describe the sediment fluxes in the area.

In this chapter an integrated modelling approach is discussed. Two models are adapted and combined. The model STRESS-2d is modified. A better description of erosion is included. A new model, DIASPORA (Diagenesis of Aquatic Sediments and Dispersion of Pollutants due to Resuspension and Sedimentation in Aquatic Ecosystems) is developed. This model simulates the changes in morphology by integrating STRESS-2d results but also simulates the changes in contaminant concentrations due to sediment transport in the system. The model is calibrated by using an extensive data set including suspended solids measurements and observed sedimentation fluxes and validated by comparing the DIASPORA results with historical records on sedimentation fluxes and contaminant concentrations in the area. This approach and simulation results of the coming decades are discussed below.

Research area and methods

Research area
Lake IJsselmeer (Fig. 8.1) was created in 1932, by damming the former marine/estuarine Zuiderzee.

- Z_1/Z_2 Monitoring sites for
  SS, fluxes, etc.

- Y_1 Sediments core in the
  deep channel

- Y_2/Y_3 Dredging pits,
  created in 1959/1974

- K Dredging pit,
  created in 1938

- Houtrib One of the monitoring sites
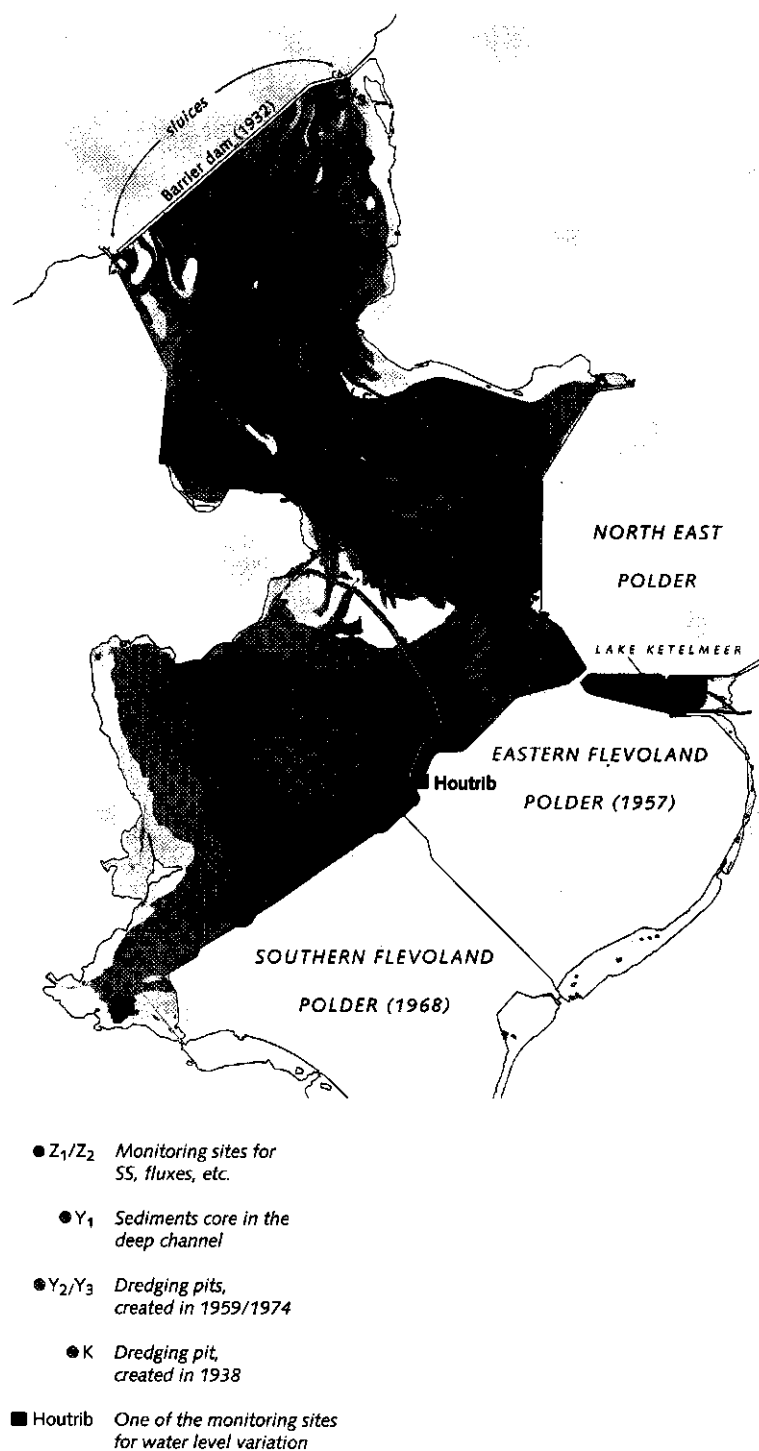 for water level variation

Fig. 8.1. Bathometry of Lake IJsselmeer area, the names and ages of the most relevant dikes and polders and monitoring sites used in this study.

Later large polders were constructed in the southern part of the area. In figure 8.1 the relevant histori-cal information is summarized.

The depth gradients in Lake IJsselmeer (Fig. 8.1) still reflect the hydrodynamic forces in the former marine situation. In the centre of the lake, where the width was relatively small, deep tidal channels are still present. Nowadays these are areas with high sedimentation fluxes and predominantly fine sediments (clay, silt), while the surrounding area is sandy (Chapter 1; Figs. 1.2 and 1.3). Also the deep pits, created by dredging of sand for the construction of dikes, are areas with high sedimentation. In the southern part of the lake, the area near which the polders were constructed and in the present Lake Markermeer, brackish clay still can be found.

The major changes in the hydrodynamics of the lake in 1932 resulted in a redistribution of fine sediments in the area. Erosion of clay and silt, which was deposited in the southern part of the lake, and internal transport due to wind induced currents, are supposed to have contributed to deposition of fine sediments in the deep areas in the lake. Due to the construction of polders the areas with old clay and silt deposits were step by step isolated from the remaining Lake IJsselmeer (see Fig. 8.1). So, since 1975 the river IJssel, which always has been a major sediment source, remained as the sole sediment source.

The hydrology of the area is dominated by the inflow of the river IJssel with an average discharge of 300 m^3/s (Blom and Toet, 1993). The river water flows via Lake Ketelmeer (38 km^2, average depth 3.5 m) into Lake IJsselmeer. Through sluices (Fig. 8.1) water is let out into the Wadden Sea at ebb tide. Due to its size and relatively shallowness (1136 km^2, average depth 4.7 m) wind induced currents dominate the flow pattern in the lake.

The model STRESS-2d
STRESS-2d was originally developed by Van Duin and Blom (Blom *et al.*, 1992; Van Duin, 1992; Van Duin *et al.*, 1992). In the model the 2-dimensional transport equation, including resuspension, erosion and sedimentation as source and sink terms is solved numerically, using an alternating direction implicit solution technique (Stelling, 1984). The simulated processes are schematically shown in Figure 8.2.

Water movement and horizontal transport of solids are computed with the 2-dimensional hydrody-namical model WAQUA (Stelling, 1984). This model simulates flow velocities and water levels, with in- and outflow and wind stress as boundary conditions and driving forces. In Lake IJsselmeer area the main inflow is the river IJssel and outflow is to the Wadden Sea, resulting in an overall advective south-east to north-west flow on which wind induced circulation flows are superimposed.

The description of sedimentation is based on well known concepts (Sheng and Lick, 1979; Som-lyòdy, 1980; Lick, 1982; Aalderink *et al.*, 1984):

$$\Phi_s = w_s \cdot SS \tag{1}$$

in which Φ_s is the sedimentation flux (g m^{-2} s^{-1}), w_s the fall velocity (m s^{-1}) and SS the suspended solids concentration (g m^{-3}). For resuspension and erosion a modification of the description by Lam & Jaquet (1976) is used:

$$\Phi_r = K_r \cdot (U_b - U_{b,cr,r}) \quad if \ (U_b > U_{b,cr,r}) \tag{2}$$

$$\Phi_e = K_e \cdot (U_b - U_{b,cr,e}) \quad if \ (U_b > U_{b,cr,e}) \tag{3}$$

with $\Phi_{r/e}$ the resuspension resp. erosion flux (g m^{-2} s^{-1}), $K_{r/e}$ the resuspension resp. erosion constant
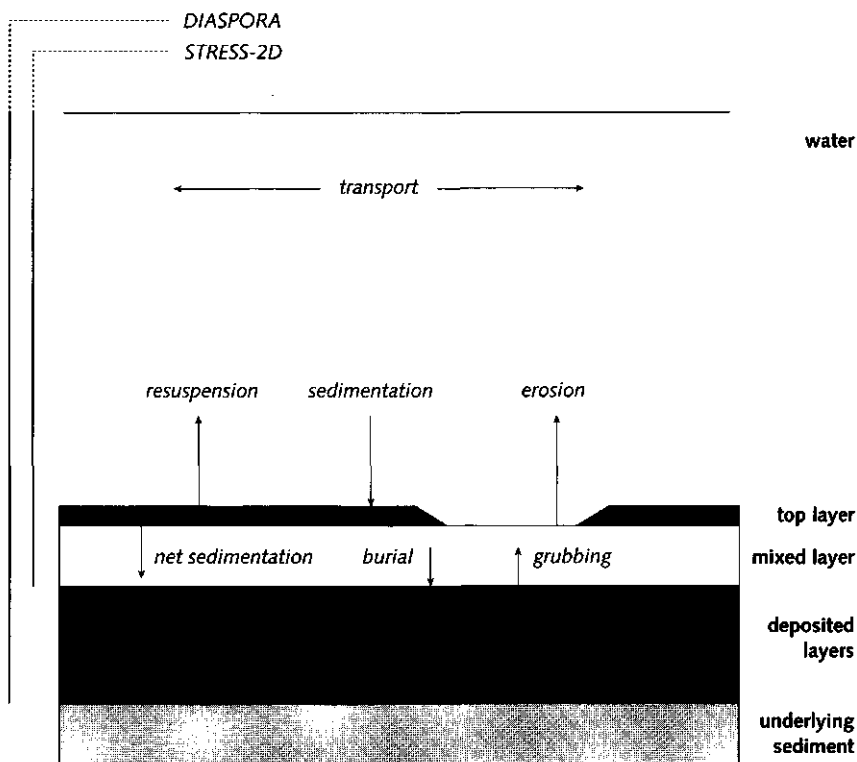
Fig. 8.2. Schematic presentation of the processes and compartment included in the models STRESS-2d and DIASPORA.

(g m^{-3}), U$_b$ the orbital velocity (m s^{-1}) and U$_{b,cr,r/e}$ the critical orbital velocity for resuspension resp. erosion (m s^{-1}). Because the minimal force needed to erode particles from the consolidated bottom sediment layer is higher than the force required to resuspend particles from the non-consolidated top layer the critical orbital velocity for erosion will be much higher than the one for resuspension. Both resuspension and erosion can be limited by depletion of the top layer resp. underlying sediment layer.

The orbital velocity is a function of the wave height, length and period, which in their term are a function of wind speed, fetch length and local depth. To simulate the wave characteristics the CERC (1977) model is used, with an adapted wind speed according to Bouws (1986). The orbital velocity is calculated with (Phillips, 1966);

$$U_b = \frac{\pi H_s}{T_s \cdot \sinh(2 \pi d/L)} \tag{4}$$

in which H$_s$ is the significant wave height (m), T$_s$ the significant wave period (s), L the wave length (m) and d the local water depth (m).

To account for the variability in sedimentation and resuspension characteristics (Blom *et al.*, 1992; Lijklema *et al.*, 1994) 5 sediment fractions are distinguished. These fractions are based on fall velocity distribution measurements (Van Duin, 1992; Van Duin *et al.*, 1992). All fractions have a characteristic

Table 8.1. Fall velocity ranges of the sediment fractions.

fraction 1			w_s	>	$311 \ 10^{-6}$	m s^{-1}
fraction 2	$160 \ 10^{-6}$	<	w_s	>	$311 \ 10^{-6}$	m s^{-1}
fraction 3	$40 \ 10^{-6}$	<	w_s	>	$160 \ 10^{-6}$	m s^{-1}
fraction 4	$11 \ 10^{-6}$	<	w_s	>	$40 \ 10^{-6}$	m s^{-1}
fraction 5			w_s	>	$11 \ 10^{-6}$	m s^{-1}

combination of resuspension and erosion parameters (K_r, K_e, $U_{b,cr,r}$, $U_{b,cr,e}$) and fall velocities (w_s); the latter of course within the defined fall velocity ranges for each fraction (Table 8.1).

The mass of all fractions in both sediment layers is calculated dynamically as a function of resuspension, erosion, sedimentation, burial and mixing between the sediment layers. Burial of sediment from the top layer is triggered by a maximal thickness of this layer (Klaver and Van de Ven, 1995).

Depth gradients in Lake IJsselmeer are locally rather steep. Thus a high spatial resolution is needed. A grid size of 250 × 250 has been selected. To avoid instability the maximal time step is 10 minutes. For simulation of sediment transport in retrospect for the period before the dikes and polders were created, a more coarse model with a grid size of 1 × 1 km was used. In the areas outside the present Lake IJsselmeer depth changes are more gradually, which justifies the use of a coarse grid. The Lake IJsselmeer model is nested into the coarse model. Observed wind speeds and directions and estimated inflows and outflows derived from a water balance based on measurements in the major inflows and outflows and data on the water level variation in the lake, are used as hydrodynamical boundary conditions. The suspended solids concentrations in the inflows are taken from literature. The initial concentrations of the sediment fractions in de sediment were measured at some sites and then extrapolated based on information on the spatial distribution of different sediment types in the lake.

The model DIASPORA

The model DIASPORA simulates the changes in morphology and composition of the sediments in the lake over a long period; years up to decades. The model is based on the assumption that the sediment concentration and composition in the water compartment and in the top layer are very dynamic, but the effects of this rapid sediment-water interaction on the thickness and composition of the underlying sediment layer are minimal on a small time scale. Thus for this layer the integrated net effects over a longer period are relevant.

To simulate the changes in contaminant concentrations due to sediment transport, sediment classes are used. These can characterize sediments present in the initial situation in different areas within the lake as well as sediments supplied by incoming rivers in various periods. This makes it possible to trace the redistribution of old deposits with low contaminant concentrations and to evaluate the distribution pattern of incoming solids, with contaminant concentrations varying in time. These sediment classes thus represent sediments with various quality. Superimposed on this subdivision with respect to quality is a physical subdivision in 5 fractions, which is used in STRESS-2d. This physical characterization distinguishes settling rates, resuspension and erosion constants and critical orbital velocities. In DIASPORA the combination of these two classifications is used, leading to a matrix which combines contamination- and transport-characteristics (quality classes superimposed upon "size"-fractions).

Like in the model STRESS-2d several sediment layers are distinguished (Fig. 8.2). Due to the intensive transport between the water compartment and the sediment top layer the concentrations of sediment classes in both these compartments are closely interacting. It can be shown that in a stationary situation in a well mixed compartment the relative concentration of each of the sediment classes is the

weighted average of their relative contribution to the incoming fluxes. For the water compartment this is:

$$C_{w,i,j} = \sum_m C_{w,i,j} \cdot \frac{T_{i,j} + A\,\Phi_{r,i,j} + A\,\Phi_{e,i,j}}{\sum_m (T_{i,j} + A\,\Phi_{r,i,j} + A\,\Phi_{e,i,j})} \tag{5}$$

with $C_{w,i,j}$ the concentration in the water of quality class j of "size" fraction i (g m^{-3}), $T_{i,j}$ the load by horizontal transport (g s^{-1}), A the surface area of the compartment (m^2), $\Phi_{r,i,j}$ the resuspension flux of class j of fraction i (g m^{-2} s^{-1}) and $\Phi_{e,i,j}$ the erosion flux (g m^{-2} s^{-1}). $\sum_m$ is the sum for m classes of fraction i. Equation 5 is solved for all fractions of all sediment classes.

In the model the only incoming flux in the top layer is the sedimentation flux. Thus the relative concentration of each class in a specific sediment fraction is equal to the relative concentration in the water compartment.

Under the top layer a second layer is defined. It is assumed to be well mixed due to biological activity. The thickness of this layer is estimated on the basis of observed ^{134}Cs/^{137}Cs-ratios in profiles in Lake Ketelmeer about one month after the Chernobyl-accident (Hettling, 1987). These observations showed no ratio gradient in the upper 10 to 20 cm of the sediment profile. Similar results were found in the Netherlands in Hollandsch Diep/Haringvliet and in the Oostvaardersplassen (Hettling, 1987).

The mass of each sediment fraction and class in this layer is affected by net sedimentation and erosion, both fluxes at the upper boundary of this layer, and by burial of sediments in situations with net sedimentation for a long period at the lower boundary. In areas where erosion dominates the underlying layers can be grubbed up. The mass balance equation for each sediment class of a sediment fraction is:

$$\frac{\delta M_{m,i,j}}{\delta t} = \Phi_{n,i,j} - \Phi_{e,i,j} - \Phi_{b,i,j} + \Phi_{g,i,j} \tag{6}$$

in which $M_{m,i,j}$ is the mass per unit of area of sediment class j of fraction i in the mixed layer (g m^{-2}), $\Phi_{n,i,j}$ is the net sedimentation flux (g m^{-2} s^{-1}), $\Phi_{e,i,j}$ is the erosion flux (g m^{-2} s^{-1}), $\Phi_{b,i,j}$ the burial flux (g m^{-2} s^{-1}) and $\Phi_{g,i,j}$ is the flux due to grubbing (g m^{-2} s^{-1}). The net sedimentation flux is the difference between the sedimentation and resuspension flux.

The flux of each class of a sediment fraction is a function of the total mass of this fraction transported over a boundary layer and the relative concentration of this sediment class in the compartment from which the fluxes originate. For instance for the burial flux:

$$\Phi_{b,i,j} = \sum_m \Phi_{b,i,j} \cdot \frac{M_{m,i,j}}{\sum(M_{m,i,j})} \tag{7}$$

with $\Phi_{b,i,j}$ the burial flux of class j of fraction i (g m^{-2} s^{-1}), m the total number of classes and $M_{m,i,j}$ the mass of sediment class j of fraction i in the mixed layer (g m^{-2}). $\sum(M_{m,i,j})$ is the total mass of fraction i in the mixed layer (g m^{-2}).

At user defined intervals a new layer in between the layer deposited in a previous period and the mixed layer is created. In periods with net sedimentation the mass within this layer increases due to burial. In periods with erosion the mass decreases due to grubbing. In areas where erosion dominates deposited layers will be absent. Then sediments from the lowest layer, which is infinite, can be grubbed up.

To evaluate the effects of sediment transport on morphology and contaminant concentration the model also has to account for consolidation of sediments and the deposition of internally produced $CaCO_3$. Based on field observations (Vink and Winkels, 1991) the density of the dry sediment is estimated 2552 kg m^{-3}. A relationship between the porosity of sediment layers and the depth in the sediment column was derived:

$$Porosity = 0.90 - 9.27 \; 10^{-2} \cdot Z \qquad (8)$$

with Z is the distance of the sediment layer to the sediment-water interface (m).

Since about 1950 the deposition of solids in Lake IJsselmeer has increased due to $CaCO_3$ precipitation. This is reflected in an increasing $CaCO_3$ content in deposited sediment layers. The $CaCO_3$ content increased from 14% in 1950 to 37% in sediment deposited in ± 1990 (Vink and Winkels, 1991). It was assumed that the $CaCO_3$ production before 1950 was minimal and that the $CaCO_3$ content in deposits from that period reflects the content in the incoming sediment loads. The $CaCO_3$ production is accounted for by introducing a new empirical constant f_{CaCO3}, with a value 1 till 1955 and increasing gradually to 1.3 in 1990. The total mass within a sediment layer is calculated as:

$$M_{x,total} = M_{x,sed} \cdot f_{CaCO3} \qquad (9)$$

in which $M_{x,total}$ is the sediment mass per unit of area (g m^{-2}) in layer x. The layers to which this applies are the mixed layer and the underlying deposited layers. $M_{x,sed}$ is the areal mass of the sediments (g m^{-2}) (excluding internally produced $CaCO_3$). It should be noted that the calculation of thickness and total mass in a layer is done in the post-processing stage. Both are not affecting the simulation of the sediment transport fluxes, but become important when the effects of sediment transport on morphology and contaminant concentrations are evaluated.

Simulations with the model DIASPORA are based on the simulation results of the STRESS-2d model, discussed in a previous section. The variables used at the model interfaces are summarized in Table 8.2. To solve the mass balances of the second and underlying sediment layer, concentrations of all sediment fractions and classes in the water compartment and sediment top layer are needed. The weekly averaged concentrations of sediment fractions are computed from STRESS-2d results. The concentrations of sediment classes are calculated using Eq. 5. Solving this equation for all grid cells results in a matrix-equation, which is solved numerically by iteration.

In the model DIASPORA two different time constants are used to solve the sediment layer mass balances. The sediment mass balance of the mixed layer is solved with a time step of 1 week. Given the sedimentation fluxes within the lake (discussed later) and a characteristic thickness of the well mixed layer of 0.15 m it can be shown that the changes in the composition within a period of one week are very small. For the processes at the lower boundary of the mixed layer (the deposition of sediments or the grubbing of formerly deposited layers) a time step of 1 year is used.

Table 8.2. SRESS-2d results used in DIASPORA.

$C_{w,i}$	the weekly and spatially averaged concentration of a fraction i in the water	(g m^{-3})
$\Phi_{s,i}$	the weekly (and usually spatially averaged) sedimentation flux of a fraction i	(g m^{-2} s^{-1})
$\Phi_{r,i}$	the weekly (and usually spatially averaged) resuspension flux of a fraction i	(g m^{-2} s^{-1})
$\Phi_{e,i}$	the weekly (and usually spatially averaged) erosion flux of a fraction i	(g m^{-2} s^{-1})
$T_{a \rightarrow b, i}$	the weekly and spatially averaged load from compartment a to compartment b, due to horizontal transport by advection and dispersion, for fraction i	(g s^{-1})

Because of computing time a coarse grid is preferable. The size used is 1 × 1 km. However in areas with steep depth gradients and thus a high spatial variation in resuspension and erosion fluxes, the effects of sediment transport on the mass and composition of the sediment are evaluated on a scale of 250 × 250 m. This is done by assuming that the water compartment (1 × 1 km) is well mixed, but for each of the sixteen 250 × 250 m cells within this compartment individual sediment mass balances for the bottom layers are solved. These are based on the local resuspension, erosion and sedimentation fluxes in these sections, as simulated with STRESS-2d.

Field observations and experiments
In this study suspended solids concentrations were measured continuously for several months at two locations (Z_1 and Z_2) in Lake IJsselmeer (Fig. 8.1). At both locations the concentrations of the sediment fractions in water were measured regularly. The method described by Van Duin (1992; Van Duin *et al.*, 1992) was used. At 9 locations throughout the lake sedimentation fluxes were measured at two-weekly intervals, using cylindrical sediment traps with an internal diameter of 6 cm and a length of 60 cm. In the material collected with the traps the concentration of sediment fractions was also measured. At a number of stations around the lake the water level was observed twice a day.

To measure the concentration of sediment fractions in the bottom sediment box-core samples were taken. Sub-samples were taken using cylinders with an internal diameter of 12.4 cm and a height of 40 cm. These were used in resuspension/erosion experiments, using a simple experimental setup described by Tsai and Lick (1986).

Results

Model calibration
Using a wind drag coefficient of 0.0021 (dimensionless) and a Manning coefficient of 0.026 ($m^{1/3}$ s^{-1}) a reasonable reconstruction of the water level variation is obtained. Some results are shown in Figure 8.3.
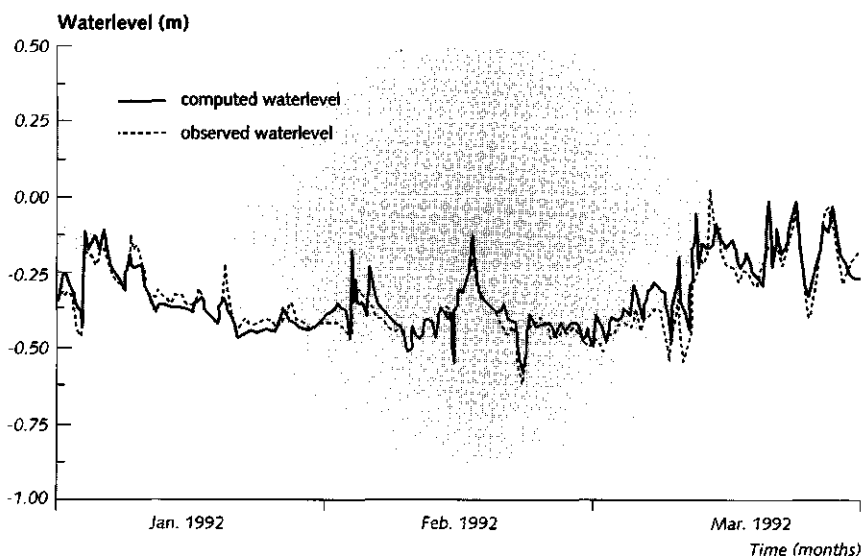

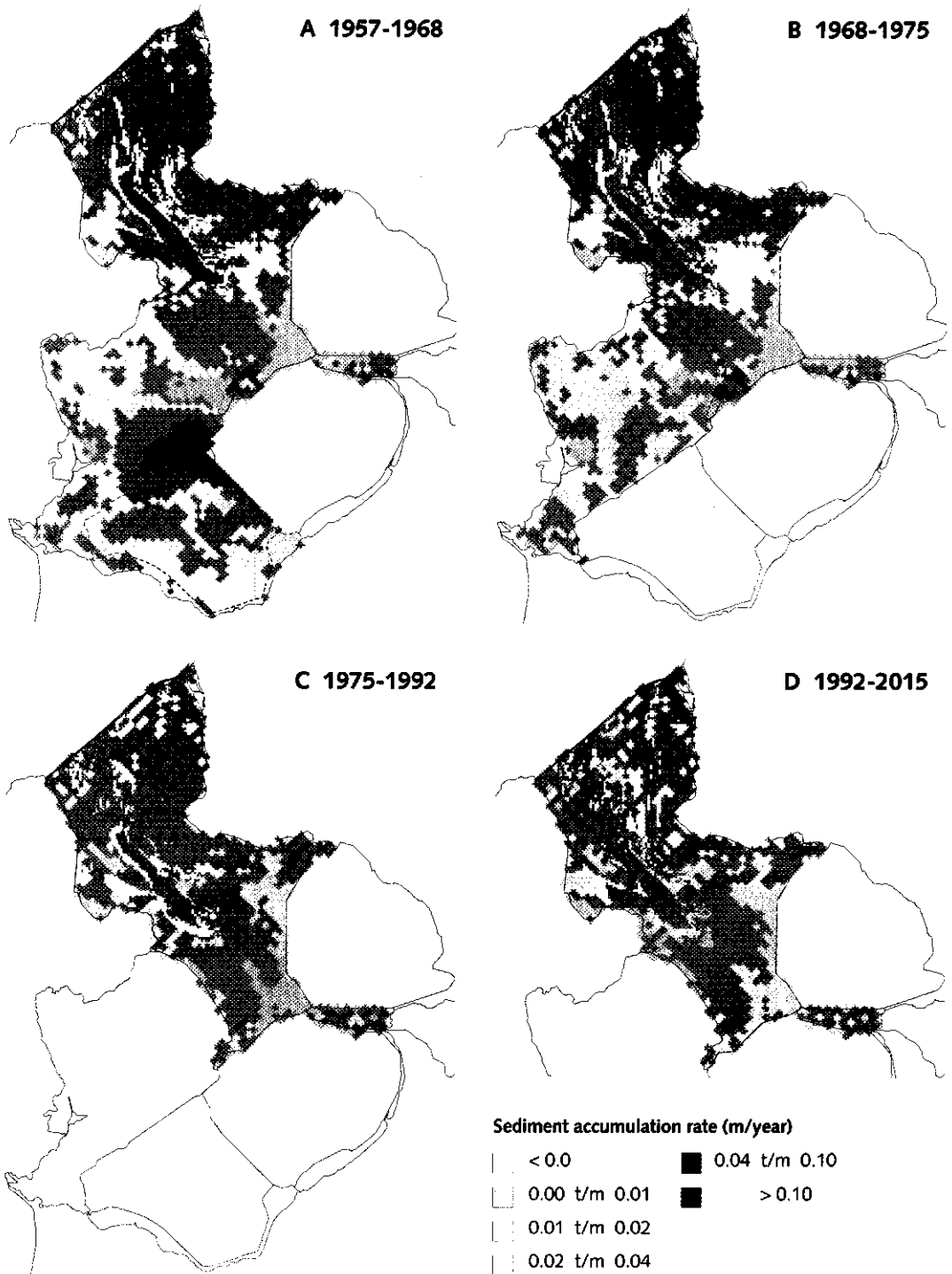**Fig. 8.3.** Observed and simulated water level variation at location Houtrib sluice.

Fig. 8.6. Simulation growth of the sediment layer (m year^{-1}) in 4 periods.

Table 8.4. Observed and **simulated** net sedimentation (cm year⁻¹) in deep pits and channels in Lake IJsselmeer and in general in Lake Ketelmeer.

	1957-1968		1968-1975		1975-1992		1992-2015
Lake Ketelmeer	0.5	**0.4**	1	**0.7**	1	**1.1**	**1.1**
Y_1	3	**3.5**	3	**3.8**	2	**2.8**	**3.6**
Y_2					5	**3.6**	**2.1**
Y_3	4	**4.1**	4	**3.6**	2	**1.8**	**1.7**

Tabel 8.5. Lead content of the solids supplied by the river IJssel (partly prognostic).

Period	Pb-content (mg kg⁻¹)
1957-1962	502
1962-1967	440
1967-1972	420
1972-1975	250
1975-1980	200
1980-1985	160
1985-1992	150
1992-1997	141
1997-2002	92
2002-2007	66
2007-2012	57
2012-2015	47

Based on the sediment transport simulation results the spatial distribution and temporal variation of the lead concentration in Lake IJsselmeer was simulated. In Table 8.5 the Pb content of the solids supplied by the river IJssel, used as an input variable, is presented. Figure 8.7 shows the simulated Pb content at seven characteristic dates for the upper 5 cm of the sediments. In this discussion we focus on results of the simulation for the deep channel in the centre of the present Lake IJsselmeer; a major sedimentation area. These results show a gradual decrease in the Pb-content in the period from 1957 till 1970. The simulated contaminant concentration in the former tidal channel in 1979 (Fig. 8.7a D) is higher than in 1970, despite the fact that the Pb loads by the river IJssel are decreasing and the dilution by internally produced $CaCO_3$ is increasing. Due to the construction of the polder Southern Flevoland and later the dike separating Lake Markermeer from Lake IJsselmeer the internal redistribution of sediments, with a lower Pb content than the solids supplied by the river IJssel, was blocked. However, after this period the Pb-content is decreasing again (results are shown for 1987, 1997 and 2005 in Fig. 8.7b), due to the decreasing contaminant loads by the river IJssel.

Simulation results are compared with observed changes in the Pb-content in sediment cores in Lake Ketelmeer and Lake IJsselmeer in Table 8.6. At all sites the observed concentrations and temporal variation is reconstructed quite well.

In order to simulate the effects of dredging the contaminated sediment layer in Lake Ketelmeer a simulation was done for a situation in which the contaminant content in Lake Ketelmeer was reduced to only 10 (mg kg⁻¹) in 1992. Results (Fig. 8.7b H) show that the decrease of Pb concentrations in Lake

Table 8.6. Observed and **simulated** Pb-contents of deposited sediments (mg kg^{-1}) at 4 sites in deep pits or channels in Lake IJsselmeer area in various years (observed data based on Winkels and Vink (1991) and Beurskens et al. (1993)).

	K*		Y$_1$*		Y$_2$*		Y$_3$*	
2005		47		44		30		27
1997		83		63		42		14
1987	120	130	60	66	45	41	36	42
1979	220	184	70	72			25	21
1970	350	295	94	74			56	53
1960	480	419	110	128			37	31

* Sites K, Y$_1$, Y$_2$ and Y$_3$ can be found in Fig. 8.1.

IJsselmeer is faster than in simulations with the original contaminant concentrations in Lake Ketelmeer (Fig. 8.7b G).

Discussions and conclusions

The modelling approach used in this study seems to produce satisfactory results. The model STRESS-2d gives a reasonable reconstruction of resuspension, erosion, sedimentation and horizontal sediment transport processes, resulting in good simulation results for the total suspended solids concentration and reasonable results for the variation in the sedimentation fluxes. The latter were somewhat under-estimated at site Z$_1$. This is partly due to the fact that STRESS-2d does not account for the internal production of CaCO$_3$ and organic matter.

Long term sedimentation patterns were obtained by simulating the sediment transport dynamics for the period of one year followed by integration of these results in time and space and extrapolation of the results for a period of a decade or more. These results are used in the model DIASPORA to simulate the changes in morphology and Pb-content. In DIASPORA the effects of internal CaCO$_3$ production and consolidation of sediment layers is accounted for. DIASPORA reconstructs the spatial and temporal variation in the net sedimentation fluxes and the growth of the sediment layer in sedimentation areas quite well. Using DIASPORA and information on the changes in the contaminant content in the solids supplied by the river IJssel resulted in a good reconstruction of the Pb content in sediment cores in Lake IJsselmeer. The simulated spatial variation in the Pb-concentrations fits well on the observed concentrations in 1978 and 1986, discussed in Chapter 3 (Figs. 3.3 and 3.2).

Simulation results show a decreasing Pb-concentration in sedimentation areas in Lake IJsselmeer in the period from 1957 till 1970. The results reflect the decline in the Pb-content of the solids supplied by the river IJssel in this period and also the increasing CaCO$_3$ production. In 1967 10% of the simulated sediment accumulation is attributed to internal CaCO$_3$ production. The decrease in the Pb content in the sedimentation areas in Lake IJsselmeer is however dominated by the effects of internal redistribution of sediments in the area. Especially in the southern part of the lake much sediment is eroded, which leads to dilution of contaminated solids. This becomes clear when the simulation results for 1979, some years after construction of the polder Southern Flevoland, are analyzed. The construction of the polder and later the dam separating Lake Markermeer from Lake IJsselmeer disconnected Lake IJsselmeer from the (former) erosion areas in the south. The decreased dilution resulted in a temporary increase of the Pb concentration in the large sedimentation areas in Lake IJsselmeer. This despite the decreasing Pb-content in the solids supplied by the river IJssel and the increasing dilution by CaCO$_3$
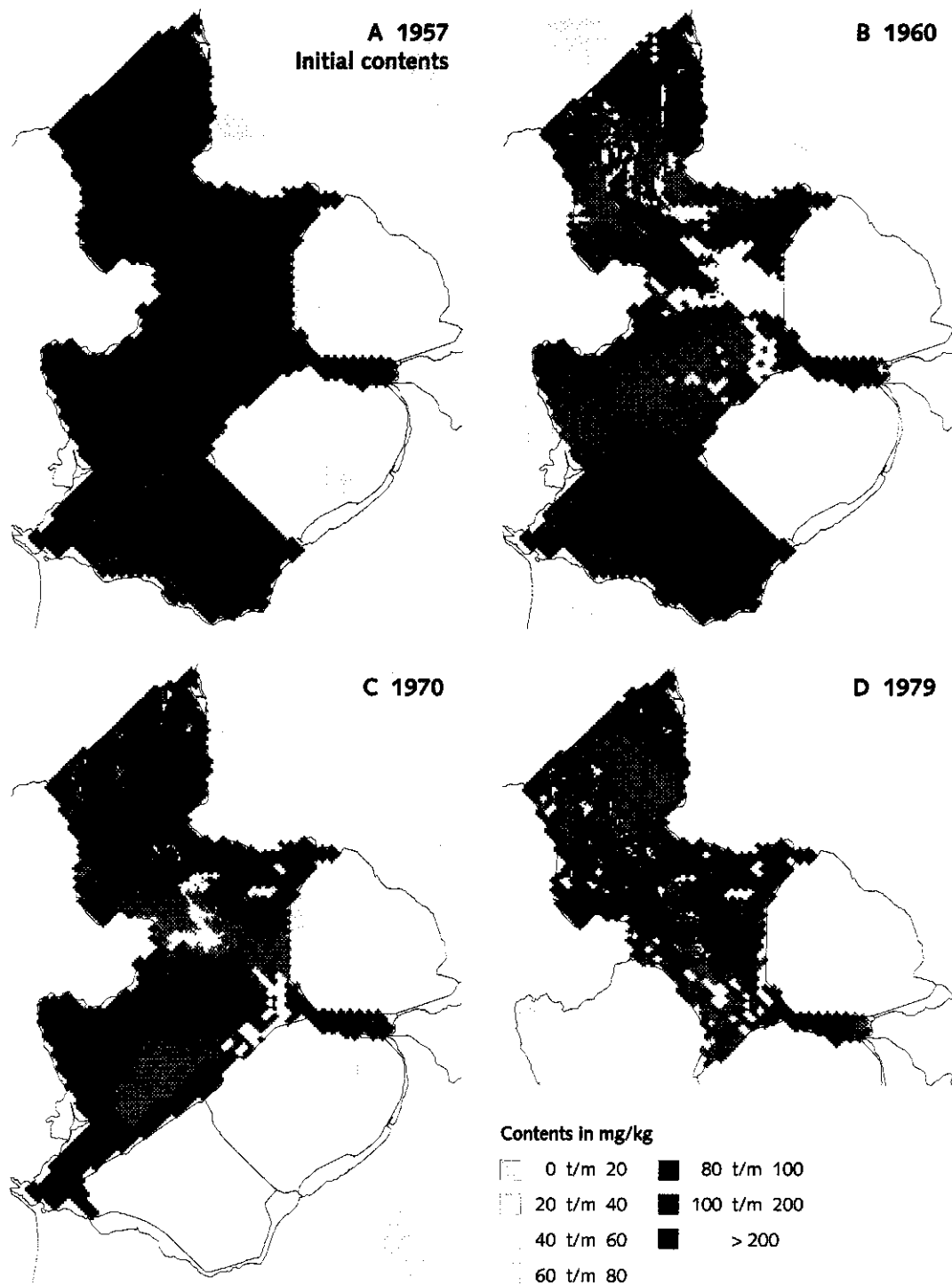
A 1957
Initial contents

B 1960

C 1970

D 1979

Contents in mg/kg

	0 t/m 20	■	80 t/m 100
	20 t/m 40	■	100 t/m 200
	40 t/m 60	■	> 200
	60 t/m 80		

Fig. 8.7a. Simulation Pb-concentration in the upper 5 cm at various moments (A-D).
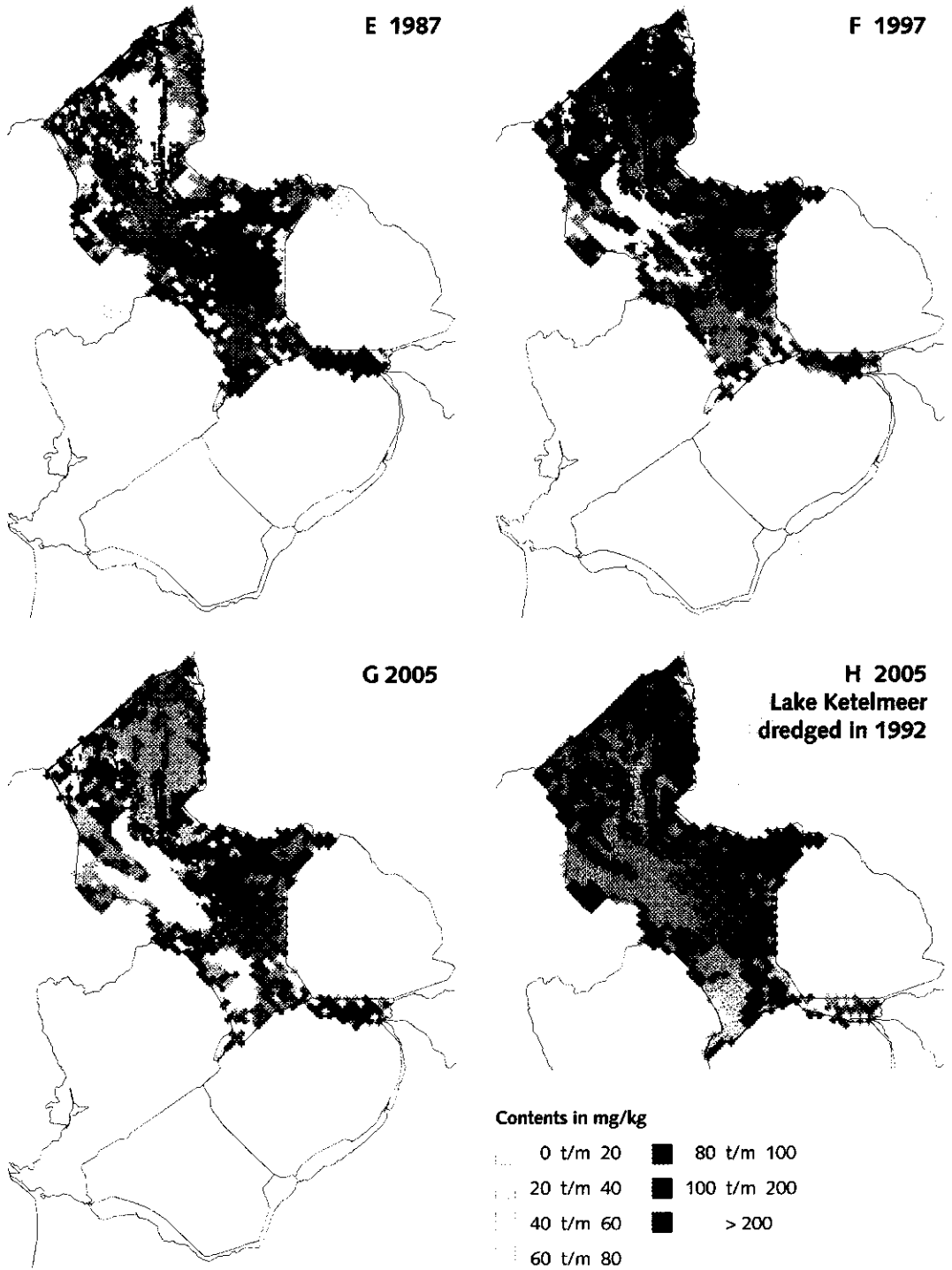
Fig. 8.7b. Simulation Pb-concentration in the upper 5 cm at various moments (E-G). Simulation results for a scenario in which Lake Ketelmeer is dredged in 1992 are included (H).

production. After 1980 however the Pb concentrations decreased, due to the continued decline in the loads by the river IJssel.

These simulation results support the conclusion of Winkels *et al.,* (1997; in prep.; Chapter 7) that the temporal and spatial variability in the contaminant concentrations in the Lake IJsselmeer area is primarily related to internal redistribution of old deposits in the IJsselmeer area and dilution by internally produced $CaCO_3$.

The models STRESS-2d and DIASPORA provide a usefull instrument to simulate the effects of a reduction of the contaminant loads or dredging of lake areas on the contaminant distribution within Lake IJsselmeer. The model can be adapted for other contaminants than Pb, which was used as a prototype in this study. To improve the desciption of the effects of algal growth and to simulate the distribution of nutrients DIASPORA should be integrated with a eutrophication model.

Acknowledgements

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Samenvatting

De waterbodems in sedimentatiegebieden van grote rivieren kunnen beschouwd worden als verontreinigde opslagplekken. Het sedimentatiegebied Ketelmeer/IJsselmeer is een dergelijke belangrijke opslagplaats van verontreinigingen van de rivier de Rijn (ofwel de IJssel). Recente en historische verontreinigingen doen hun invloed hier gelden. De herverdeling van gesuspendeerde stoffen en van reeds afgezet sediment als gevolg van erosie (via door wind geïnduceerde golfwerking) in de ondiepe Nederlandse meren, zal de verontreinigingsniveau's van deze sedimenten in die meren beïnvloeden. Het doel van dit onderzoek was de variabiliteit van de verontreiniging in de waterbodems van het Ketelmeer en IJsselmeer te bestuderen en te verklaren met als doel het gedrag en het lot van deze verontreinigingen voor de toekomst te voorspellen. Hiervoor zijn diverse methoden en modellen ontwikkeld of aangepast.

Hoofdstuk 2 beschrijft het bemonsteren, de analyse en de interpretatie van de verkregen resultaten voor boorkernen, toplaag monsters en geologisch verschillende sedimentlagen uit de waterbodem van het Ketelmeer. De boorkernen uit het Ketelmeer zijn in laagjes verdeeld en elk laagje is gedateerd met behulp van radiochemische technieken (cesium-isotopen), zodat het afzettingstijdstip uit het verleden van elk laagje achterhaald werd. Elk laagje werd tevens geanalyseerd op het voorkomen van metalen en organische verontreinigingen. Door de concentraties van deze verontreinigingen per laagje uit te zetten tegen het afzettingstijdstip is het mogelijk de verontreinigingsgeschiedenis door de rivier de IJssel te achterhalen. De aangetroffen concentratie veranderingen met de diepte en dus in de tijd werden ook waargenomen in de kernen die waren gestoken in zandwinputten (plekken met dikke pakketten jong sediment, waar zand was gewonnen bij de aanleg van de polderdijken) in het Ketelmeer. Opmerkelijk waren ook de verschillen in verontreinigingsniveau tussen de toplaag van sediment uit de recente IJsselmeer Afzettingen (IJm-afzetting) en die van de gehele laag van deze afzettingen in het Ketelmeer. De hieronder aangetroffen, oudere Zuiderzee Afzettingen (Zu-afzetting) hebben natuurlijke, lage gehaltes aan metalen, polycyclische aromatische koolwaterstoffen (PAK's) en polychloorbiphenylen (PCBs). Hieruit valt af te leiden, dat het verticale transport van deze verontreinigingen met infiltrerend water verwaarloosbaar is in dit meer. De metaal- en PAK's-concentraties in de IJm-afzetting uit de boorkernen geven een goed beeld van de historische belasting door de rivier de IJssel gedurende de laatste vijftig jaar. Deze historische belasting ziet er als volgt uit: lage concentraties aan metalen en iets verhoogde concentraties aan PAK's in het begin van de jaren veertig; een mogelijke verlaging van deze gehalten gedurende de Tweede Wereldoorlog en de hoogste concentraties van deze stoffen gedurende de periode 1955-1970. Recent afgezette sedimenten hebben (opnieuw) relatief lage gehalten, waarbij voor sommige stoffen (lood, arseen en alle PAK's) geldt, dat de gehalten hiervan zelfs de laagste zijn die ooit werden aangetroffen gedurende de laatste vijf decades. Bijna alle gechloreerde componenten vertonen een afname in concentratie rond het begin van de jaren zeventig in de anaerobe sedimenten van het Ketelmeer, als ze worden vergeleken met oude toplaagmonsters uit 1972, die waren bewaard en alsnog zijn geanalyseerd. Voor diverse PCB's is een significante afname in de concentratie vastgesteld, welke het gevolg kan zijn van een anaerobe microbiële dechlorering in het sediment. Hierdoor zijn de concentratieprofielen van deze gechloreerde componenten geen directe

afspiegeling van de orginele historische belasting door de rivier. Ondanks de afname van de concentratie van PCB's zijn toch de navolgende trends herkenbaar in de concentratieprofielen uit het Ketelmeersediment:

- De boorkernen hebben lage concentraties voor alle bestudeerde PCB's in het begin van de jaren veertig.
- De hoogste gehalten worden aangetroffen in de periode 1960-1975.
- De recente sedimenten bevatten nog steeds verhoogde gehalten in vergelijking met het begin van de jaren veertig.

Algemeen kan geconcludeerd worden, dat recent afgezet sediment in het Ketelmeer duidelijk lagere gehaltes aan verontreinigingen bevat dan sediment dat is afgezet in de periode 1960-1970. Hiermee is duidelijk dat in dit meer zwaar verontreinigde sedimenten momenteel worden afgedekt met een laagje minder verontreinigd sediment. Desalniettemin zullen er plekken in het Ketelmeer zijn, zoals erosieve deelgebieden en gebieden waar vaargeul onderhoud werd uitgevoerd, waar deze sterk verontreinigde sedimenten uit de jaren zestig en zeventig aan het wateroppervlak liggen en daar de aquatische bodemfauna negatief beïnvloeden via het benthische voedselweb.

In *Hoofdstuk 3* is aandacht besteed aan de verspreiding van de verontreinigingen (in het horizontale vlak, het vertikale vlak en in de tijd) in de waterbodems van het Ketelmeer en het IJsselmeer. Hiervoor werden de concentraties aan metalen, PAK's, PCB's en diverse sedimentkarakteristieken bepaald in 77 toplaag sedimentmonsters en twee (3 meter lange) boorkernen uit beide meren. Om de ernst van de verontreiniging te kunnen schatten werden de geanalyseerde, absolute verontreinigingsgehalten op het lutum- en organische stof-gehalte van elk individueel sedimentmonster genormaliseerd. Hiermee wordt vergelijking van de mate van verontreiniging voor zandige en slibrijke sedimentmonsters (die in deze meren voorkomen) mogelijk. In 25% van het IJsselmeer wordt de jongste geologische laag (de IJm-afzetting) aangetroffen; dit betreft de diepe delen (de netto sedimentatiegebieden) van dit meer. Deze IJm-afzetting is in het Ketelmeer ernstig verontreinigd (zie ook Hoofdstuk 2). De gehaltes aan bovengenoemde verontreinigende stoffen zijn echter in de IJm-afzetting in het IJsselmeer een factor 1,6 tot 9 lager dan in dezelfde afzetting in het Ketelmeer. In de overige 75% van het IJsselmeer liggen voornamelijk oudere, zandige afzettingen aan het oppervlak, die een factor 2 tot 4 lagere gehalten aan verontreinigende stoffen hebben dan de IJm-afzetting uit dit meer. Uit beide boorkernen valt af te leiden, dat de gehalten aan metalen, arseen en PCB's in de IJm-afzetting eerst toenemen met de diepte en later weer afnemen (soms tot onder de detectie grens). Deze trend komt overeen met de geschiedenis van de belasting met verontreinigingen door de rivier de IJssel gedurende de laatste 5 decades. Als de boorkernen uit de IJm-afzetting in beide meren worden vergeleken blijkt de verontreinigingsgraad af te nemen met een toenemende afstand tot de IJsselmonding. De hypothese is ontwikkeld dat verdunning in het IJsselmeer tot stand komt door zowel bijmenging met geërodeerd sediment uit dit meer als door kalkprecipitatie ten gevolg van primaire productie.

In *Hoofdstuk 4* wordt de verwerking en de interpretatie van boorkernen uit vergelijkbare sedimentatiegebieden van twee grote rivierdelta's beschreven. Op uniforme wijze zijn hiervoor in de Wolga en Donau delta's anaerobe slibrijke sedimenten bemonsterd, waarbij gebruik is gemaakt van satelietbeelden, welke de zwevende stofgehaltes in het water weergeven. Via de datering van bemonsterde laagjes (met behulp van cesium-isotopen) en door het meten van de concentraties van metalen, PAK's en PCB's hierin, zijn concentratieprofielen afgeleid welke voor metalen en PAK's de historische belasting op deze rivieren weergeven. De gehaltes van de bestudeerde 7 PCB's en van cadmium waren in alle sedimentmonsters uit beide delta's zodanig laag, dat de detectie grens niet werd overschreden. Lage en nagenoeg niet veranderende concentraties aan arseen, koper, zink en alle bestudeerde PAK's werden waargenomen in sedimenten uit de Wolga delta, die waren afgezet gedurende de laatste vijftig jaar. Verder waren de concentraties aan nikkel iets verhoogd en bevatten de meest recente sedimenten

uit deze delta enigszins stijgende gehalten aan zink, chroom en arseen. De historische belasting voor de Donau delta ziet er voor metalen en PAK's als volgt uit: lage concentraties metalen en verhoogde concentraties aan PAK's in het begin van de jaren veertig; toenemende gehaltes voor deze stofgroepen in de periode 1950-1987 en afnemende gehaltes na laatstgenoemde periode in de recente sedimenten. Bij vergelijking van de verontreinigingsgraad (metalen, PAK's en PCB's) van de sedimenten uit de delta's van Wolga, Donau en Rijn, blijkt de Wolga delta nu en in het recente verleden de schoonste van de drie te zijn. De aangetroffen verschillen in verontreinigingsgraad gedurende de laatste vijftig jaar in deze drie delta's kunnen verklaard worden door (i) een verschil in natuurlijke achtergrondgehalten voor de rivieren; (ii) een verschillende intensiteit van industriële activiteiten en daarmee gepaard gaande belasting van de rivieren en (iii) een verschillend beheer in de stroomgebieden van de rivieren (bijvoorbeeld door aanleg stuwmeren). De thans afgezette sedimenten in de Rijn delta bevatten nog steeds de hoogste gehalten aan metalen (behalve koper en nikkel), PAK's en PCB's in vergelijking met beide andere delta's, maar het belastingsniveau door de industrie op deze rivieren is voor de Donau inmiddels het hoogst voor de meeste zware metalen.

In *Hoofdstuk 5* wordt een voor het Ketelmeer gekozen geostatistische bemonsteringsaanpak voor sedimenten uitgelegd. Als verontreinigingsgehalten en daaraan gerelateerde sediment karakteristieken worden gevolgd in de tijd in een aquatisch milieu, dient rekening te worden gehouden met de ruimtelijke variabiliteit van deze grootheden. De hier gekozen bemonsteringsstrategie voor sedimenten dient dan ook de variabiliteit van deze variabelen op zowel korte (65 m) als langere afstand (500 m) te verdisconteren. In het Ketelmeer werden drie deelgebieden voor onderzoek gekozen, waarbij de grootte van deze gebieden mede bepalend was voor bovengenoemde afstanden tussen de verschillende bemonsteringspunten. De drie deelgebieden zijn vooraf gekozen op basis van verschillen in waterdiepte, verschillen in sedimentatie/ersosie gedrag en op basis van verschillen in sediment type (klei of zand). Voor het monitoren van verontreinigingstrends in sedimenten kan via deze bemonsteringsstrategie het aantal monsterpunten worden geminimaliseerd, afhankelijk van de nauwkeurigheid waarmee de verontreinigingsgraad dient te worden vastgesteld. De keuze voor een dergelijke bemonsteringsstrategie om verontreinigingstrends in sedimenten te monitoren zal voor elk deelgebied kunnen leiden tot een andere afstand tussen de monsterpunten. In het centrale deel van het Ketelmeer wordt bijvoorbeeld een optimale bemonsteringsafstand voor het monitoren van de gehalten aan Benzo(A)pyrene (BAP) gevonden, die groter is (minder punten per vierkante kilometer) dan in het zuidelijke deel nabij Ketelhaven, waar de gradiënten in waterdiepte groter zijn. Op vergelijkbare wijze werd ook gevonden, dat voor het saneren (afgraven) van de verontreinigde laag in het Ketelmeer een op bovenstaande gebaseerde keuze van deze deelgebieden in een saneringsbestek noodzakelijk is, om het nauwkeurig verwijderen van deze laag te kunnen garanderen. Als geen rekening wordt gehouden met de ruimtelijke variabiliteit van de dikte van de verontreinigde laag is de kans groot dat sterk verontreinigde putgebieden onvolledig of niet en gedeeltelijk schone sedimenten wel worden afgegraven. Daarom wordt aanbevolen voorafgaand aan de sanering nauwkeurig (hoewel kostbaar) ruimtelijk onderzoek naar de dikte van de verontreinigde laag per vooraf geïdentificeerd deelgebied uit te voeren. Voor het monitoren van verontreinigingstrends zijn pragmatische, geostatistische methoden beschikbaar die, afhankelijk van de gewenste nauwkeurigheid, de bemonsteringskosten kunnen beperken.

Een ander belangrijk proces, dat de concentratie profielen in sedimenten beïnvloedt, is consolidatie. *Hoofdstuk 6* behandeld dit fysische proces waarbij zwevende stof sedimenteert en na afzetting water verliest. In principe is het mogelijk (en vaak gedaan) om dit consolidatieproces met mathematische modellen te beschrijven, maar vanwege de specifieke omstandigheden in het IJsselmeergebied leek een empirische aanpak beter. Vijf representatieve kernen van de IJm-afzetting in diepe sedimentatiegebieden werden, verspreid over het IJsselmeergebied gestoken. Daarnaast waren periodieke dieptelodingen beschikbaar op deze vijf plekken gedurende de laatste zestig jaar. Dit verschafte informatie

met betrekking tot de totale dikte van deze IJm-afzetting en de netto sedimentatiesnelheid gedurende bepaalde periodes. Om een equivalent van de diepte voor de tijdsas te kunnen achterhalen zijn correctiefactoren noodzakelijk voor de mate van consolidatie in het sediment. Deze correctiefactoren zijn gebaseerd op de verschillende stadia van compressie van het sediment (0%, 30% en 45%). Hiervoor werd een factor n voor elk bemonsterd laagje afgeleid, die de verschillende watergehaltes weergeeft als afhankelijke van het aanwezige lutumgehalte. Via deze n-factor was het mogelijk de initiële, ongeconsolideerde dikte van elk laagje via een omrekening terug te rekenen. Door deze procedure werd het mogelijk een redelijke betrouwbare tijdsas m.b.t. de diepte te reconstrueren. Vergelijking met datering door cesium-isotopen voor een aantal kernen toonde goede overeenstemming.

De jaarlijkse variabiliteit aan verontreinigende stoffen in het IJsselmeergebied wordt beschreven in *Hoofdstuk 7*. Frequente metingen van gehaltes van zes zware metalen in de zwevende stof in de IJssel en in het bezinkend slib op twee plekken in het IJsselmeer gaven een kenmerkende ruimtelijke gradiënt te zien. De gehaltes aan zware metalen namen gedurende het hele jaar af met een toenemende afstand vanaf de IJsselmonding. Deze ruimtelijke gradiënt komt overeen met de gradiënt die ook werd aangetroffen in de afgezette sedimenten in dit gebied (Hoofdstuk 3). Metingen in boorkernen uit het Ketelmeer (nabij de IJsselmonding) en uit het centrale, diepere deel van het IJsselmeer laten zien, dat de gehaltes aan zware metalen in de gelijktijdig afgezette sedimenten van het Ketelmeer 2 tot 3 keer hoger zijn dan in het IJsselmeer. Bovengenoemde concentratiegradiënt in het bezinkend slib blijft ook significant als de gehalten aan zware metalen worden genormaliseerd m.b.t. het lutum- en organische stof-gehalte van elk individueel bezinkend slibmonster. Op basis van een ruwe sedimentbalans voor deze zware metalen, gebaseerd op aanvoergegevens van de rivier en op de gemeten sedimentatie fluxen, wordt duidelijk dat de totale interne fluxen van zware metalen in het IJsselmeer veel groter zijn dan de externe aanvoer door de rivier de IJssel. Naast zware metalen zijn ook diverse sedimentkarakteristieken en een aantal variabelen die verband houden met primaire produktie gedurende een jaar gemeten in het bezinkend slib en in het water op twee lokaties in het IJsselmeer. Via enkelvoudige correlaties is getracht het gedrag van de zware metalen in de tijd en de gevonden ruimtelijke gradiënt te verklaren, maar de complexiteit van de relaties tussen de zware metalen en de variabelen die een indruk geven van primaire produktie en/of erosie stond dit niet toe. Door toepassing van statistische technieken zoals factor analyse (PCA) en stapsgewijs, meervoudig correlatieonderzoek (SMR) werd echter duidelijk dat de variatie van de concentratie van zware metalen in bezinkend slib in het zuidelijk deel van het IJsselmeer een verband toont met de windsnelheid ter plekke en met het lutumgehalte (beide variabelen worden beïnvloed door resuspensie van sediment), terwijl ze in het centrale deel van het IJsselmeer gerelateerd zijn aan de pH, het chlorophyll- en het kalkgehalte (deze variabelen worden beïnvloed door de jaarlijks optredende algenbloeien). De negatieve correlatie tussen de meeste zware metalen in het bezinkend slib en het chlorophyll gehalte en het organische stofgehalte in het water rechtvaardigt de conclusie, dat in het centrale deel van het IJsselmeer, waar de algen concentraties in de zomer hoog zijn, een verdunning optreedt van de verontreinigde zwevende stofdeeltjes als gevolg van primaire produktie. In het zuidelijk deel van het IJsselmeer duidt de positieve correlatie van de meeste zware metalen in het bezinkend slib en van het lutumgehalte met de windsnelheid ter plekke op resuspensie van recent afgezette sedimenten als verklaring voor de variatie in de gehalten zware metalen in de zwevende stof in het water. De geleidelijke toename van de $\delta^{13}C$-waarde vanaf de IJsselmond via het zuidelijke deel van het IJsselmeer tot het centrale deel van het IJsselmeer duidt er op dat zoet water sedimenten in dit gebied worden gemengd met geërodeerde Zu-afzettingen, die van oorsprong marien (zout) zijn. Op basis van dit onderzoek kan derhalve geconcludeerd worden, dat de afname van de gehaltes aan zware metalen in de zwevende stof en in de waterbodem van het IJsselmeer ontstaat door een verdunning van deze verontreiniging door erosie van oudere sedimenten en door primaire produktie gerelateerd aan algenbloei.

In *Hoofdstuk 8* wordt de opgedane kennis betreffende de verontreinigde sedimenten, de verdunning, het transport en processen zoals consolidatie en primaire produktie, welke optreden in dit onderzoeksgebied, samengebracht in een model kader. Daarbij werd een reconstruktie van de sediment transportprocessen en de daaraan gerelateerde verdunning van de verontreiniging in het IJsselmeergebied gemaakt voor enkele decades. Deze excercitie vormde de basis voor een schatting van de toekomstige sedimentsamenstelling en verontreinigingsgraad, welke afhankelijk van de verwachte belasting door de rivier de IJssel werd gemodelleerd. Het aangepaste model STRESS-2d reconstrueert de resuspensie, de erosie, de sedimentatie en de horizontale sediment transportprocessen gedurende een jaar. De gesimuleerde resultaten hiervan kwamen goed overeen met de gemeten totale zwevende stof concentraties en de sedimentatie fluxen in het IJsselmeer. Het model is vervolgens genest in het nieuw ontwikkelde model DIASPORA, dat de morfologische veranderingen t.g.v. netto sedimentatie fluxen op de langere termijn goed simuleert. DIASPORA houdt hierbij rekening met de effecten van biogene kalkprecipitatie en de consolidatie van het sediment na afzetting. De afname van de loodconcentratie in de sedimentatiegebieden in het IJsselmeer komt overeen met de gereduceerde input van lood in de door de IJssel aangevoerde zwevende stof, maar wordt gedomineerd door de effecten die interne transport processen van sedimenten in het gebied hierop hebben. De modelresultaten bevestigen dan ook bovengenoemde slotconclusie uit hoofdstuk 7. Simulatie van de sedimentatiefluxen en voorspellingen voor de gehaltes aan lood in de waterbodem werden uitgevoerd voor een constante sedimentaanvoer en voor een 50% reductie van de loodaanvoer door de IJssel. De resultaten laten een voortgaande daling van de loodgehaltes in de sedimentatiegebieden van het IJsselmeer zien en een extra zuiveringseffect als gevolg van de sanering (afgraving) van verontreinigde sedimenten in het Ketelmeer.

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CURRICULUM VITAE

Herman (Hermannus Johannes) Winkels is op 17 december 1960 geboren te Wierden. In 1979 behaalde hij het Atheneum B diploma aan het Pius X College te Almelo. In september van dat jaar begon hij zijn bodemkunde studie aan de toenmalige Landbouwhogeschool te Wageningen.

Met groot enthousiasme heeft hij de klassieke geologie, geomorfologie en veldbodemkundige vakken in de kandidaatsfase gevolgd. Uiteindelijk heeft hij gekozen voor een milieuchemische specialisatie in de doctoraal fase. De drie hoofdvakken in deze fase waren veldbodemkunde, bodemverontreiniging en cultuurtechniek. Achtereenvolgens werd onderzoek verricht naar de effecten van mestoverschotten op de bodem in Limburg en Brabant, naar nitraat in het grondwater rondom Lunteren en naar veranderingen die de atmosferische depositie in de stooisellaag te Hackford bracht. Hij heeft zijn praktijktijd in de zomer van 1984 vervult in Saskatoon, Saskatchewan te Canada, alwaar hij specifiek onderzoek deed aan gronden op hellingen tijdens de bodemkarteringen van de universiteit van Saskatoon van deze provincie. In januari 1986 heeft hij het doctoraal diploma ontvangen van de vakgroep Bodemkunde en Bemestingsleer van de Landbouwhogeschool, inmiddels omgedoopt tot Landbouwuniversiteit. Nog dat zelfde jaar is hij tijdelijk werkzaam geweest als docent aan de Hogere Bosbouw en Cultuurtechnische School te Velp als docent Algemene Geologie en Bodemkunde.

Op 1 januari werd hij als onderzoeksmedewerker bodemkunde aangesteld bij de Subafdeling Bodemkunde van de Rijksdienst voor de IJsselmeerpolders. Om de specifieke inrichtingskennis van de onderzoeksafdeling niet geheel te laten verdwijnen werd in 1989 hij en zijn collega's onderdeel van Rijkswaterstaat, Directie Flevoland. De bodemkundige en milieukundige onderzoekstaken, die tot dat moment geheel op de bodem van Zuidelijk Flevoland gericht waren, gingen zich nu op de bodem van de Rijkswateren richten. Binnen Rijkswaterstaat was zijn bodemkundige kennis zeer bruikbaar tussen die van de civiele ingenieurs. Hij werd dan ook benoemd tot hoofd van de Afdeling Bodemkunde in 1991. Zijn onderzoek naar de waterbodems in het IJsselmeergebied bleef niet onopgemerkt en met Prof. S.B. Kroonenberg werd hij belast met de organisatie van de PAON-cursus Waterbodemkunde. Inmiddels is via een reorganisatie binnen Rijkswaterstaat hij en zijn afdeling onderdeel gaan vormen van het Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling (RIZA) te Lelystad. Hier heeft hij ook zijn huidige werkkring als taakveldleider Bodemkunde op de afdeling Onderzoek bij de hoofdafdeling Inrichting en Herstel.