

## BIOGEOCHEMICAL PROCESSES AFFECTING METAL CONCENTRATIONS IN LAKE SEDIMENTS (IJSELMEER, THE NETHERLANDS)

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### ABSTRACT

The IJsselmeer originated in 1932 when a former coastal lagoon was shut off from the North Sea. Its main source of water and sediments is from the highly polluted river Rhine. The lake acts as a sink not only for particulate trace metals, but also for the dissolved metals; especially dissolved zinc, chromium and cadmium are held back in the lake. For these metals field and laboratory experiments revealed a correlation between pH and element concentrations where adsorption strongly depends on the pH within the range 7–9 observed in the IJsselmeer. Algae account for about 4–14% of the removal cadmium, chromium, zinc and copper. In the mouthing area of the river IJssel, metal concentrations in the sediments are determined by physical (mixing of lake and river sediments) and by chemical processes (adsorption). Mixing of the sediments has been quantitatively studied with the aid of natural stable isotope tracers. Between 1932 and 1974 trace metal concentrations in the sediments show increases between 25% (chromium) and 600% (cadmium). Organic matter concentrations increased by 140%, calcium carbonate by 300% and phosphorus by 600%.

### INTRODUCTION

Large amounts of trace metals are transported by the river Rhine and its affluent the river IJssel to the North Sea. Before reaching the North Sea the river water from the IJssel spends about 6 months in the artificial lake IJsselmeer, formed in 1932 when the Zuiderzee was separated from the North Sea (Fig. 1). The surface area of the shallow lake has gradually decreased as a consequence of reclamation projects. The present surface area of the lake is 1230 km<sup>2</sup>, including the Ketelmeer (the mouthing area of the river IJssel), which originated in 1955. The mean depth of the lake is 4.5 m and the

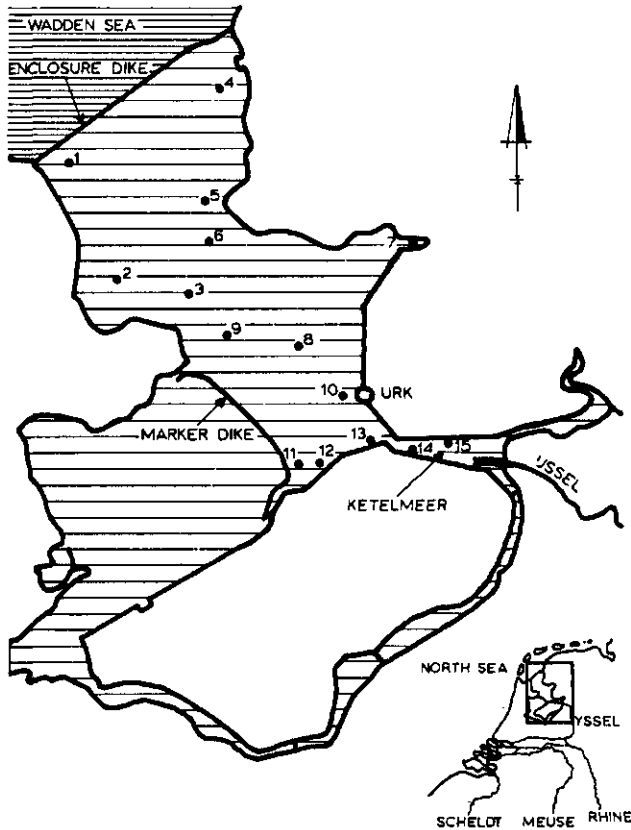


Fig. 1. Map of the IJsselmeer showing the sampled localities for the deposited sediments.

volume of the water body is  $5.5 \text{ km}^3$ . The river IJssel is the main water source and is largely responsible for the heavy metal phosphorus input to the lake (trace metals: about 1700 tons/year). The aim of our research program is to construct a model of the biogeochemical processes affecting the dissolved and particulate metal concentrations in the IJsselmeer. This study has now provided a qualitative picture of the processes affecting the metal content of the sediments.

## EXPERIMENTAL METHODS

### *Sampling*

*Surface waters* were sampled in a poly-ethylene bucket and filtered under pressure over an acid-washed membrane filter ( $0.45 \mu\text{m}$ ) in all-teflon filtration apparatus. The filtration equipment of Duinker and Nolting (1977) has been slightly modified for this purpose. After filtration the samples were acidified to a pH of 0.5–1 and kept frozen prior to analysis.

*Suspended matter* was sampled with the aid of a teflon-coated continuous centrifuge with a capacity of about 1.0 l/min. The efficiency for the removal of suspended matter was determined by comparison with filtration through 0.45  $\mu\text{m}$  membrane filters and varies between 85 and 95%. Low efficiencies were found for areas containing large amounts of algae.

*Algae* were sampled using plankton net with a mesh-size of 50  $\mu\text{m}$  and the material was immediately frozen in dry ice on board ship and later freeze-dried in the laboratory.

*Deposited sediments* were collected with the aid of a normal van Veen grab. In a few cases use was made of a modified Jenkins-mud sampler.

#### *Analytical methods*

*Dissolved heavy metals.* Water samples were gently boiled for 10 min in a covered beaker and were then split into five subsamples. To each known amount of all determinants were added (standard addition method). The metals were subsequently extracted into an APDC-MIBK mixture and back-extracted into a HCl solution. The metal concentrations were finally determined with a heated graphite atomizer in conjunction with an atomic absorption spectrophotometer.

*Heavy metals in the sediments and algal material* were determined by atomic absorption after digesting the sample in a mixture of hot  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  (Zn, Cu, Cr) or in concentrated  $\text{HNO}_3$  (Cd, Pb).

#### *Statistical methods*

The grain size composition of the sediment deposited in the IJsselmeer varies considerably. Because trace metals and also phosphorus are preferentially associated with the finely grained particles, a wide range in trace metal concentrations is found at one locality. In order to compare the composition of sediments from different sedimentation areas within the lake and to determine the development of trace metal concentrations in time, corrections had to be made to allow for local variations in grain size. This was done by using the correlation between the metal concentrations and the amount of particles with diameters less than 16 microns (Fig. 2) and normalizing to 50% < 16  $\mu\text{m}$  (Salomons and De Groot, 1978).

*Isotope analysis.* For isotope analysis the sediment samples were treated with 95%  $\text{H}_3\text{PO}_4$ . The resulting  $\text{CO}_2$  was measured mass spectrometrically with a Varian M86 according to standard procedures (Mook and Grootes, 1973).

The isotopic ratios are given as relative deviations from that of a standard (PDB):

$$\delta(\text{‰}) = [(R_s - R_{st})/R_{st}] \times 1000$$

where  $R = {}^{18}\text{O}/{}^{16}\text{O}$ ,  ${}^{13}\text{C}/{}^{12}\text{C}$ ; s = sample; st = standard. Results are primarily based on  $\delta_{\text{PDB}}^{13}$  and  $\delta_{\text{PDB}}^{18}$  for NBS-20 of  $-1.06$  and  $-4.14\text{‰}$  respectively.

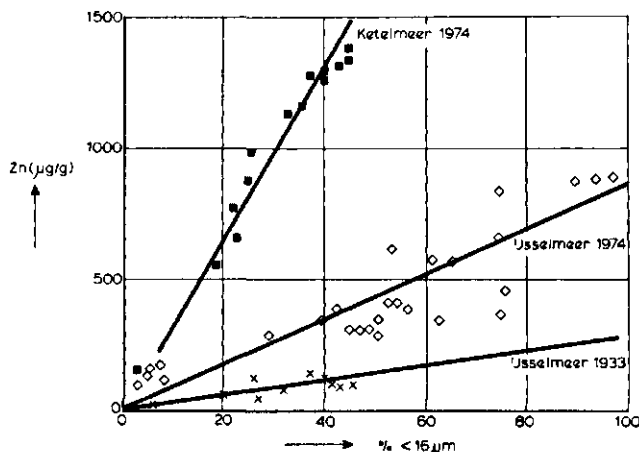


Fig. 2. Correlation between the grain size ( $\% < 16 \mu\text{m}$ ) and the zinc concentrations.

## RESULTS AND DISCUSSIONS

### *Heavy metals in the sediments*

The suspended matter transported by the river IJssel into the lake is partly deposited in its mouthing area, the Ketelmeer.

From differences in suspended matter concentrations in the river IJssel (40 mg/l) and at the end of the Ketelmeer 20 mg/l, it can be estimated that about half of the sediment load of the river (200,000 tons) is deposited in the mouthing area, the remainder is deposited in the IJsselmeer. Due to the shallowness of the lake (mean depth 4.5 m) an intense reworking of the deposited sediments takes place, and recent, contaminated sediments are mixed with older less contaminated deposits.

Sediments samples from the Ketelmeer were taken in 1972 and 1974, and from the IJsselmeer in 1974. The samples were analysed for heavy metals and their grain size distribution ( $\% < 16 \mu\text{m}$ ). Determination of the grain size distribution is essential in order to eliminate its influence on metal concentrations (see Experimental methods). Results, calculated metal concentrations at  $50\% < 16 \mu\text{m}$ , are presented in Table 1.

TABLE 1

CONCENTRATIONS OF HEAVY METALS (values in  $\mu\text{g/g}$  at  $50\% < 16 \mu\text{m}$  calculated from curves as shown in Fig. 1).

*N* refers to the number of samples analysed. The spread in the data is about 10%.

	<i>N</i>	Zn	Cd	Cu	Cr	Pb
IJsselmeer 1933	10	150	0.4	19	88	39
IJsselmeer 1974	40	500	2.8	39	106	88
Ketelmeer 1972	40	2115	31	300	680	360
Ketelmeer 1974	10	1750	24	209	460	240

TABLE 2

METAL CONCENTRATIONS (RHINE 1970 = 100) IN THE KETELMEER AND THE IJSSELMEER AND THE ISOTOPIC COMPOSITION (IN ‰) OF CARBONATE IN THE SEDIMENTS

	Zn	Cd	Cu	Cr	Pb	$\delta_{\text{PDB}}^{13}$	$\delta_{\text{PDB}}^{18}$
Rhine	100	100	100	100	100	-2.7	-7.9
Ketelmeer 1972	114	115	92	86	81	-2.6	-8.1
Ketelmeer 1974	90	89	62	56	54	-1.4	-7.0
IJsselmeer 1974	25	10	12	13	20	+ 0.8	-7.8

Sediments from the IJsselmeer are less contaminated compared with those from the Ketelmeer as a result of reworking the sediments in the lake.

The metal concentrations in the Ketelmeer sediments differ from those in the river, and furthermore significant differences are observed for the two surveys (1972 and 1974). One might expect metal concentrations in the Ketelmeer to be equal to those in the river IJssel. However, both in 1972 and 1974 this is not the case (Table 2). In 1972, the concentrations of copper, chromium and lead were slightly lower as compared with the river IJssel, while concentrations of zinc and cadmium were slightly higher. The trace metal concentrations in 1974 were much lower compared to 1972. However, again the same pattern emerges: high concentrations for zinc and cadmium, and low concentrations for copper, chromium and lead.

Two phenomena have to be explained for the Ketelmeer area:

- (i) the difference in trace metal concentrations between 1972 and 1974
- (ii) the difference in behaviour between Cu, Cr, Pb on the one hand and Zn, Cd on the other.

#### *Physical process affecting trace metal concentrations*

The heavy metal load between 1972 and 1974 of the river Rhine did not change significantly (Salomons and De Groot, 1978). Therefore, the differences, cannot be explained by a different input of trace metals in 1972 and 1974.

The low concentrations in 1974 may be caused by a transport of less contaminated sediments from the lake into the Ketelmeer area. This mixing of sediments from two different sources can be determined quantitatively with the aid of suitable natural tracers (for a discussion see Salomons et al. 1978). For the Ketelmeer, the carbonate fraction can be used as a natural tracer to distinguish between sediments from the lake and from the river. In the IJsselmeer an extensive precipitation of calcium carbonate takes place at pH values exceeding 8.8, which are common in summer as a consequence of algal blooms.

Figure 3 shows the seasonal cycle of the calcium concentrations for the northern part of the lake. Low values occur in summer as a consequence of

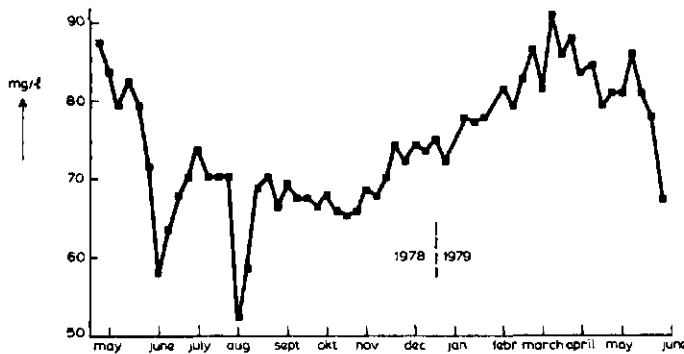


Fig. 3. Calcium concentrations in the Northern part of the lake (May 1978—May 1979).

calcium carbonate precipitation. The high values in the winter and spring period are similar to values in the river IJssel. With the onset of the algal blooms in May, the calcium carbonate concentrations decrease sharply. In the autumn period they gradually increase as a consequence of the decrease in pH (no more algal blooms) and a replenishing of the water in this part of the lake by water from the river. After six months (which is in fact the residence time of the water in the lake) the values reach again the concentrations observed in the river IJssel. The total amount of calcium carbonate which precipitates annually in the lake is about 400,000 tons.

The carbon isotopic composition of this newly formed calcium carbonate in the suspended matter is  $+2.2\text{‰}$ . The newly formed carbonates are mixed with those already present in the lake (derived from the North Sea before 1932) resulting in an observed average isotopic composition of  $\delta^{13} = +0.8\text{‰}$  and  $\delta^{18} = -7.8\text{‰}$ . The carbon isotopic composition of the carbonates in the lake thus differs by about  $3.4\text{‰}$  from the carbonates in sediments from the river IJssel (Table 2). This difference is sufficiently large to warrant its use as a natural tracer.

The isotopic composition of the carbonates in the sediments of the Ketelmeer in 1972 is close to the value for the river Rhine. The slightly lower value (Table 2) may point to a small admixture of sediments from the lake, which also explains the slightly lower concentrations of copper, chromium and lead in the sediments.

In 1974 the carbon isotopic composition ( $-1.4$ ) is intermediate between the value for the river ( $-2.6$ ) and for the lake ( $+0.8$ ). Apparently a mixing of sediments has taken place. The mixing ratio of lake to fluvial sediments as deduced from the isotopic data is about 1 : 1, in agreement with the observed concentrations of copper, chromium and lead. This transport of sediments into the Ketelmeer may be a result of the construction of the Markerdike (completed in 1975, see Fig. 1), which has affected the sediment transport pattern in the lake. Formerly the predominant N-E winds transported the eroded material into the southern part of the lake. However, after the construction of the Markerdike, the sediments are more likely to be forced into the Ketelmeer area.

### Chemical processes affecting trace metal concentrations

The high concentration of zinc and cadmium must be caused by an input of these two metals from the solution into the sediments. No industry is located in the immediate vicinity of the Ketelmeer area, so that industrial input can be ruled out. The higher concentrations can, therefore only be explained by adsorption of dissolved metals on the suspended matter.

The differences in concentrations between the incoming water from the river IJssel and the water leaving the lake through the sluices in the enclosure dike indeed show that the lake acts as a sink for dissolved zinc, cadmium and chromium and, to a smaller extent, for copper (Table 3). Chromium and copper are, however, transported mainly in particulate form (Fig. 4), so that adsorption processes will not significantly influence the metal concentrations in the sediment. Moreover, the removal of copper is to a large extent caused by algae; in the Ketelmeer area and its immediate vicinity, this process is not yet significant.

Field investigations carried out in 1977 and 1978, in most cases, showed a decrease in chromium and zinc concentrations from the IJssel in the direction of the enclosure dike correlated with pH (Fig. 5). The small increase in pH in the Ketelmeer of about 0.3 units, appears to result in a decrease in the dissolved cadmium concentrations from about 0.8  $\mu\text{g/l}$  to below 0.1  $\mu\text{g/l}$ . In the laboratory pH-dependent adsorption processes have also been studied by adding radioactive cadmium and zinc to suspended matter from the lake

TABLE 3  
MEAN CONCENTRATIONS (DETERMINED DURING 1977 (8-WEEKLY SAMPLING) AND 1978 (FOUR-WEEKLY SAMPLING) OF TRACE METALS AND ORTHO-PHOSPHORUS IN THE IJssel, AND CLOSE TO THE ENCLOSURE DIKE. ALL DATA IN  $\mu\text{g/l}$ .

	Zn	Cu	Cr	Pb	Cd	o-P
IJssel	40	5.5	2.3	1.5	0.8	295
Enclosure dike	4.3	2.7	0.3	1.6	<0.1	71

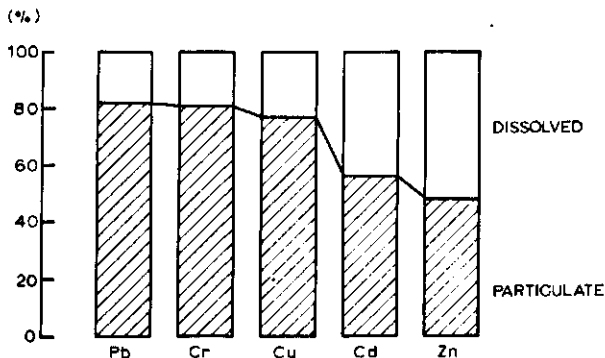


Fig. 4. Mode of transport of trace metals by the river Rhine (Anonymous, 1974).

and measuring the adsorption as a function of pH. Some results for suspended matter from the Ketelmeer area are presented in Fig. 6A. The adsorption is seen to depend strongly on the pH, especially over the range observed in IJsselmeer. The conclusion that the adsorption of copper is pH independent in the range of 7–9 (O'Connor and Kester, 1975; Grimme, 1968) explains the observation that the lake is not an important sink for dissolved copper.

The adsorption of metals is not only influenced by pH, but also by concentrations of suspended matter (Fig. 6B). As the lake is very shallow, and the bottom is subject to a frequent erosion, this results in a high concentration of suspended matter with values already greater than 100 mg/l at about Beaufort 7. The high suspended matter concentrations during periods of high wind velocity may cause a further adsorption of dissolved metals.

The river Rhine carries a large chloride load due to the discharge of salt into the river system; concentrations are at present about 200 mg/l. Chloride forms strong dissolved complexes with cadmium and to a smaller extent with zinc which reduces the adsorption of these two metals (Fig. 6C). Without chloride the IJsselmeer, and also the comparable Haringvliet area in the Western part of the Netherlands, might provide an even more efficient sink for dissolved trace metals. Also, the introduction of complexing agents, such as NTA, into the environment may negatively influence the adsorption of trace metals, causing enhanced dissolved metal levels. The extent of this influence of course depends on the actual concentrations.

#### *Biological processes affecting metal concentrations*

Algae not only indirectly influence the dissolved metal concentrations by raising the pH, but also by uptake of metals from the solution. This accumulation may be either passive (adsorption on the outside of cells) or active

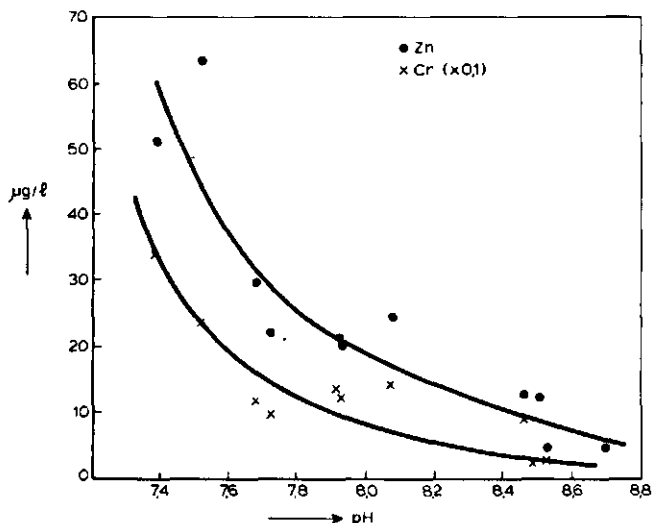


Fig. 5. Correlation between dissolved zinc and chromium and the pH.



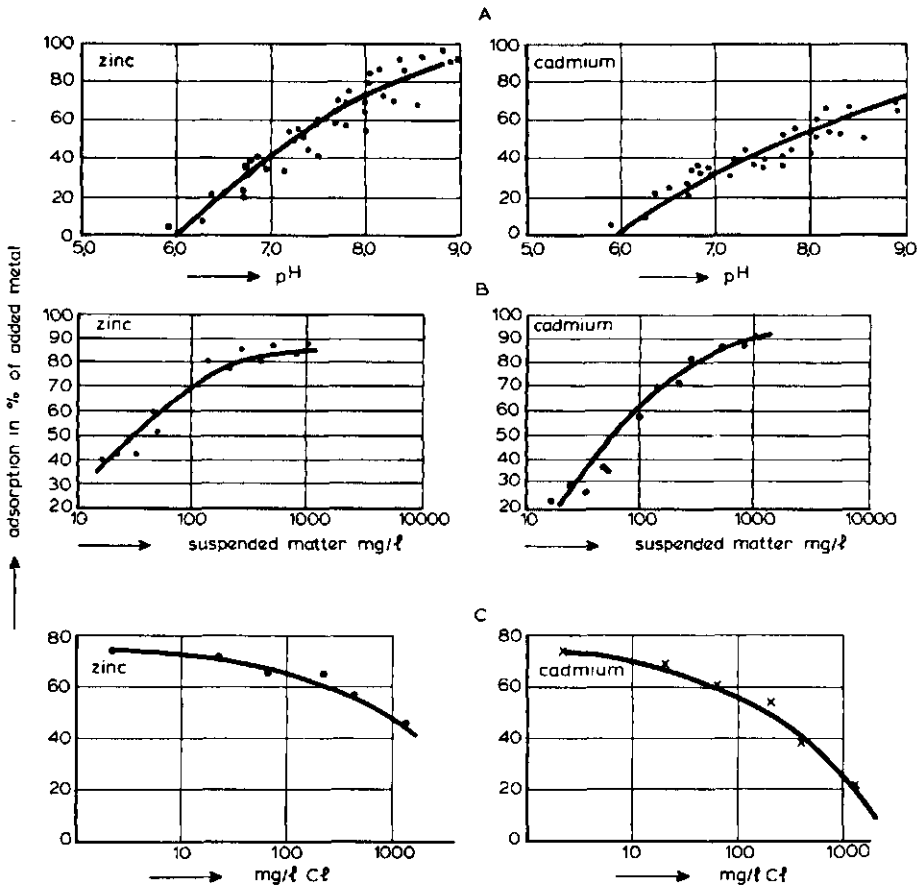


Fig. 6. Adsorption of cadmium and zinc on suspended matter from the lake. (A) Influence of pH. (B) Influence of sediment concentration. (C) Influence of chlorinity.

(incorporation in the cell tissue). A distinction between these two modes is not yet possible, so that only the overall effect can be estimated.

To determine the influence of algae on the composition of the sediments, the net flux of algae to the bottom and their metal content should be known.

Therefore algae were collected at four weekly intervals at 5 localities in the lake over a period of more than one year. Material collected with a plankton net is invariably contaminated with inorganic suspended matter. However, it is possible to make a distinction between algae and inorganic matter on the basis of the aluminum content; aluminum is a major constituent of clay minerals and feldspars but occurs only in minor amounts in algae. In Fig. 7 the relationship between the zinc and cadmium concentrations in algal material and the aluminum concentrations are shown. High metal concentrations are associated with high aluminum concentrations, showing that the concentrations in the algae are lower compared with those in the inorganic suspended matter. We have considered those samples which contain < 0.5%

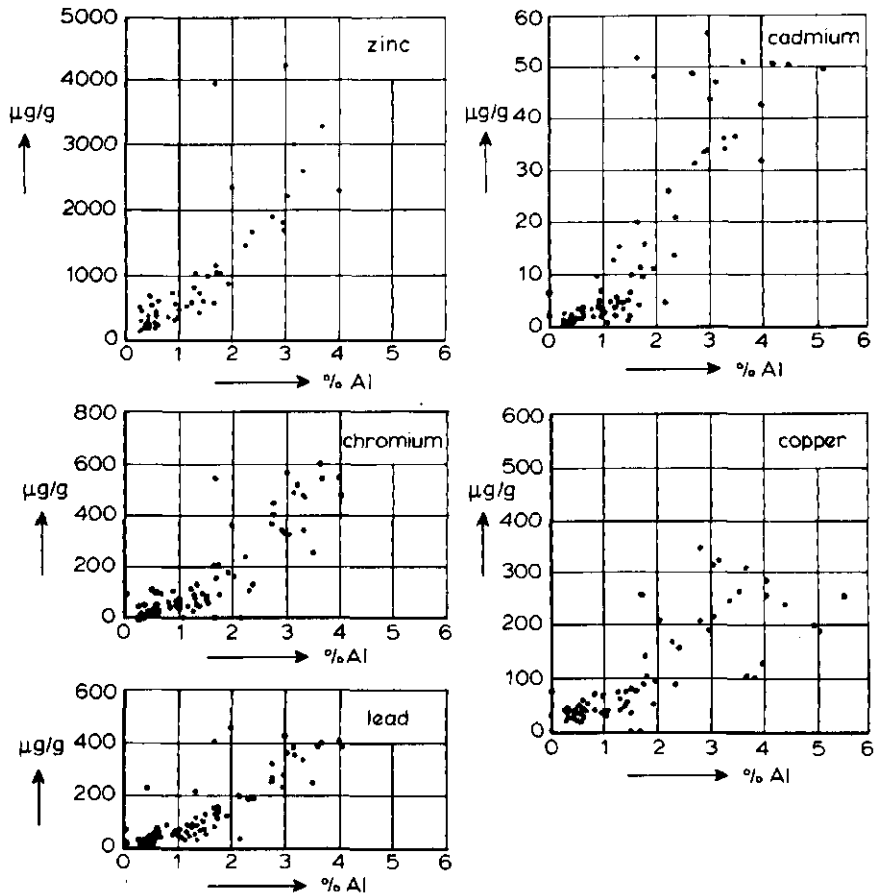


Fig. 7. Metal concentrations in algal material as a function of the aluminum content.

of Al as representative for the metal concentration in algae. The average values are shown in Table 4.

In order to determine the flux of dead algal material to the bottom, use was made of the phosphorus balance of the lake. The accumulation of dissolved ortho-phosphorus in the lake is about 1600 tons/year. If it is assumed that the major process causing this accumulation is the algal bloom (a fact which is supported by the high organic-P concentrations in the bottom sedi-

TABLE 4  
METAL CONCENTRATIONS IN ALGAE  
FROM LAKE IJSSEL ( $\mu\text{g/g}$ )

Zn	Cu	Cr	Pb	Cd
298	32	15	47	1,9

TABLE 5  
BALANCE FOR DISSOLVED METALS IN TONS/YEAR.  
BETWEEN (THE VALUES) ARE GIVEN IN % OF THE INPUT.

	Input	Output	Accumulation by algae	Accumulation by inorganic processes
Zinc	344	56 (16)	48 (14)	240 (70)
Copper	47	35 (74)	5.1 (11)	6.9 (15)
Cadmium	6.8	< 1.3 (19)	0.3 (4)	< 5.2 (> 76)
Chromium	20	3.9 (29)	2.4 (12)	13.7 (69)

ments, *viz.* 60% of the total-P; Salomons and Gerritse, 1980), and if it is further assumed that the phosphorus content of the settling material is 1%, then the accumulation of organic matter in the lake is 160,000 tons/year. Postma (1967) calculated that the total amount of organic matter accumulated in the lake between 1932 and 1965 was about  $4 \times 10^6$  tons.

With the aid of the metal concentrations in the algae and the net flux of algal material to the bottom, it is now possible to calculate the removal of metals by algae. Data are shown in Table 5 together with the amount of dissolved metal transported into the lake, the removal by inorganic processes and the amount of dissolved metals leaving the lake through the sluices. Algae appear to account for about 4–14% of the removal of dissolved metals. For copper, algae are seen to provide an important mechanism for removal, whereas for dissolved cadmium and zinc, and possibly also chromium, the pH-dependent adsorption is the major process.

#### *Changes in the composition of the sediments in the lake between 1933 and 1974*

Before the reclamation of various parts of the lake extensive soil surveys were carried out. Part of the original samples collected in 1933 have been kept in store. These samples offer a unique possibility to determine the changes in metal concentrations and in the mineralogy of the sediments between 1933 and 1974. The results of the analysis are presented in Table 6, the relative change in the composition of the sediments is shown in Fig. 8.

Large increases are observed for cadmium, zinc and phosphorus, smaller increases for copper and lead. The increase for chromium is small, probably reflecting the fact that this metal is a relatively recent addition to the field of industrial pollution. The mineralogical composition of the sediments has also drastically changed. As a consequence of the high phosphorus load of the river Rhine the lake is subject to massive algal blooms which are responsible for the increase in organic matter concentrations in the sediments by a factor of 2.4. The pH increase in the lake, due to algal blooms, causes a calcium carbonate precipitation which explains the high carbonate concentrations in the sediments.

Question may now arise such as what changes in metal concentrations and

TABLE 6  
CONCENTRATIONS OF TRACE METALS AND PHOSPHORUS (ALL IN  $\mu\text{g/g}$ ) IN  
SEDIMENTS FROM THE IJSELMEER AND THE WADDEN SEA

	Zn	Cu	Cr	Pb	Cd	P
IJsselmeer 1933	150	19	88	39	0.4	700
IJsselmeer 1974	500	39	106	88	2.8	2800
Wadden Sea 1970	248	32	116	88	1.0	1200

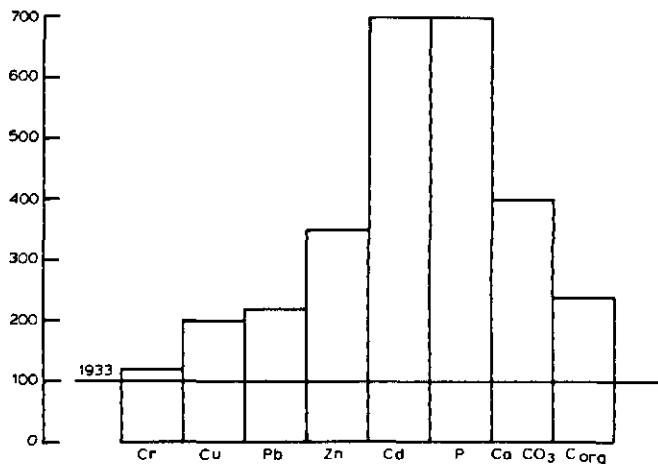


Fig. 8. The metal concentrations and the organic matter and carbonate content in sediments from the IJsselmeer in 1974 expressed in percentages of the concentrations in 1933.

mineralogy are caused by the enclosure of the former lagoon or, to put it differently, what would have been the metal concentrations and the mineralogy of the sediments if the area would still be open to the sea? Because the river IJssel would form some kind of an estuary, adsorption processes would still take place, as was shown by Duinker and Nolting (1977, 1978) by analysing the water phase and by Salomons and Mook (1977) by analysing the deposited sediments in the estuaries of the river Rhine and Ems. In both situations the incoming polluted sediments would be mixed with less contaminated sediments. In the case of the "open situation" this would concern marine sediments from the North Sea and older, less contaminated, deposits present in the IJsselmeer. It may be worthwhile to compare the composition of the sediments in the IJsselmeer (with the exception of the Ketelmeer) with sediments from the Wadden Sea area. The sediments in the Wadden Sea are derived for about 10–20% from the highly contaminated river Rhine and Meuse and for the remainder from relatively less polluted sediments from the North Sea (Salomons, 1975; Salomons et al., 1975). In Table 6, it may be seen that the concentrations of lead, chromium and copper are about equal, but the concentrations of cadmium and zinc are higher in the IJsselmeer. It

may be speculated that this is due to the fact that the IJsselmeer is subject to a supply of both dissolved and particulate trace metals from the river IJssel, whereas the Wadden Sea area is mainly subject to a supply of metals associated with particulates. The adsorption processes in the IJsselmeer cause the high zinc and cadmium levels.

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