

POLLUTION HISTORY OF TRACE METALS IN SEDIMENTS,
AS AFFECTED BY THE RHINE RIVER

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INTRODUCTION

In industrialized countries the trace metal concentrations in fluvial sediments reflect the industrial activity in the drainage areas of the relevant rivers. In Western Europe the river Rhine is an outstanding example of a stream in which large quantities of metals are discharged. In its lower courses the dissolved and particulate metals are transported to some artificial freshwater lakes, which are a result of enclosure works (see Figure 1, Haringvliet and Lake IJssel), to the Rotterdam harbor area, and to the North Sea. In recent years numerous studies have dealt with the concentrations of trace metals in the sediments (De Groot, 1973; De Groot and Allersma, 1975), as well as with the dissolved and particulate trace metals (Duinker *et al.*, 1974; Duinker and Nolting, 1976, 1977). In this chapter we shall describe the development of the trace metal concentrations in the sediments with time and discuss briefly some processes of these metals in freshwater bodies.

OCCURRENCE OF TRACE METALS IN SEDIMENTS

The grain size composition of the sediments in sedimentation areas may vary considerably. Because trace metals are associated with the finely grained particles, a wide range in trace metal concentrations is found, too. The concentrations correlate positively with the amount of finely grained particles,

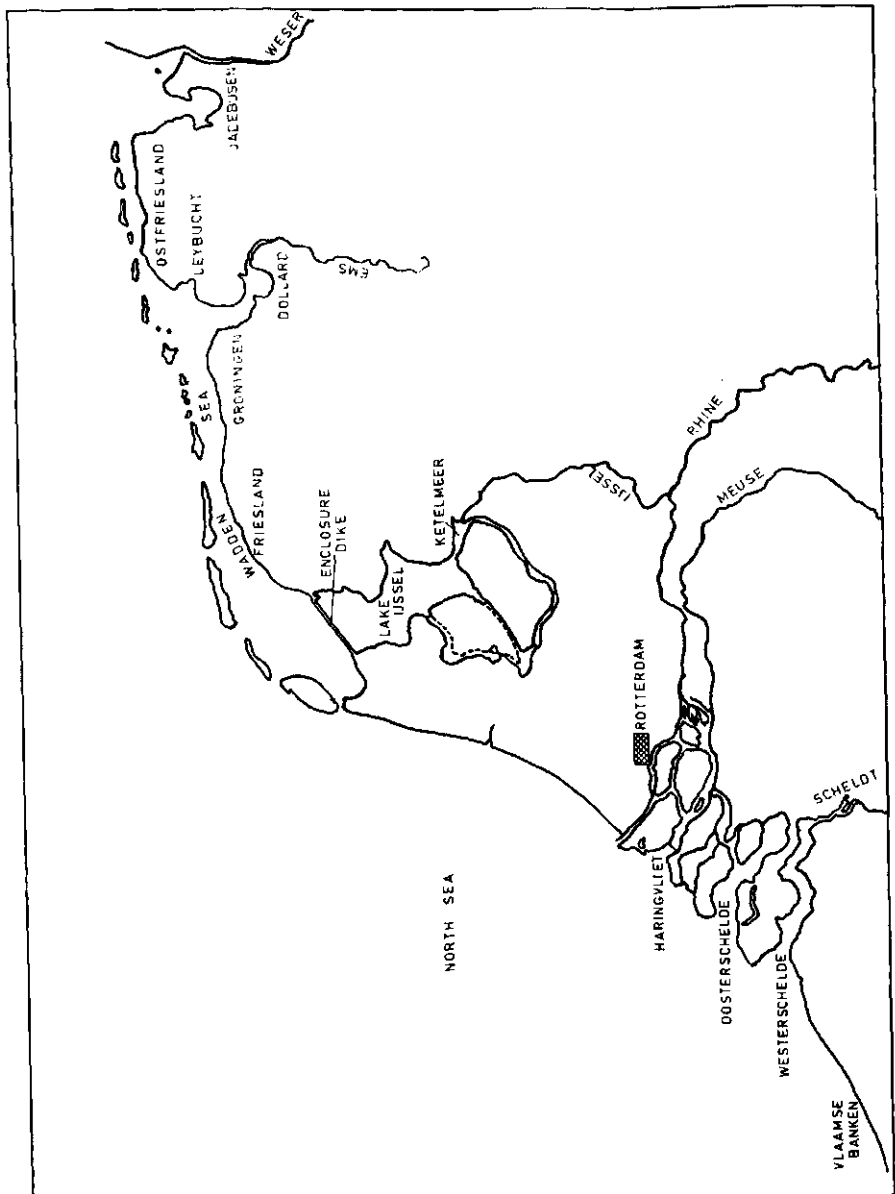


Figure 1. The area studied.

as expressed by the percentage of particles less than $16 \mu\text{m}$ in diameter (Figure 2C). The mineralogical composition (Figure 2B) as well as the major element composition (Figure 2A) also correlate with this parameter.

To compare the composition of sediments from different sedimentation areas and to determine the development of trace element concentrations with time, the concentrations at 50% $<16 \mu\text{m}$ will be used. This value corresponds with the mean grain size composition of estuarine sediments from the Rotterdam harbor, a major sedimentation area in The Netherlands.

The distribution of trace metals over the various chemical compounds and minerals in sediments (including discrete minerals, which may be formed by the metals themselves) is described as elemental partition. Various leaching techniques have been used to determine the elemental partition of trace metals in sediments. Our routine procedure consists of two successive extraction procedures by which three different fractions of heavy metals can be distinguished:

1. Acid-reducible fraction. An extraction with $0.1 M$ hydroxylamine-HCl (pH 2) is carried out. This extraction releases presumably those metals which are associated with hydrous oxides of manganese and those which occur as carbonates, hydroxides and sulfides. By substitution of hydroxylamine-HCl for HCl at the same pH of 2, acetic acid (33%) or a mixture of $1 M$ hydroxylamine-HCl and 25% (v/v) acetic acid comparable results for the relevant sediments have been found.
2. Acid-oxidizable fraction. An extraction is performed with a solution of hydrogen peroxide (30%) at a pH of 2.5. This extraction probably releases that part of the metals which is associated with organic solids.
3. Resistant fraction. This fraction is obtained by subtracting from the total amount of trace metal in the sample, the amounts found in the two preceding extractions.

Results have been obtained in this respect for the metals manganese, zinc, copper, lead, cadmium and nickel in fluvial sediments from the rivers Rhine, Meuse, Ems and Scheldt and in marine sediments from the Wadden Sea and the Oosterschelde (Figure 3).

Although the distribution of the trace metals over the various fractions is variable, some trends can be recognized. Compared with the fluvial sediments, the trace metals in marine sediments tend to occur to a larger extent in the resistant fraction. The amounts of the trace metals (except Cu), which are associated with the acid-oxidizable fraction, is relatively constant; this trend is quite pronounced in the fluvial sediments.

In both marine and fluvial sediments nickel is predominantly associated with the resistant fraction. Zinc occurs in

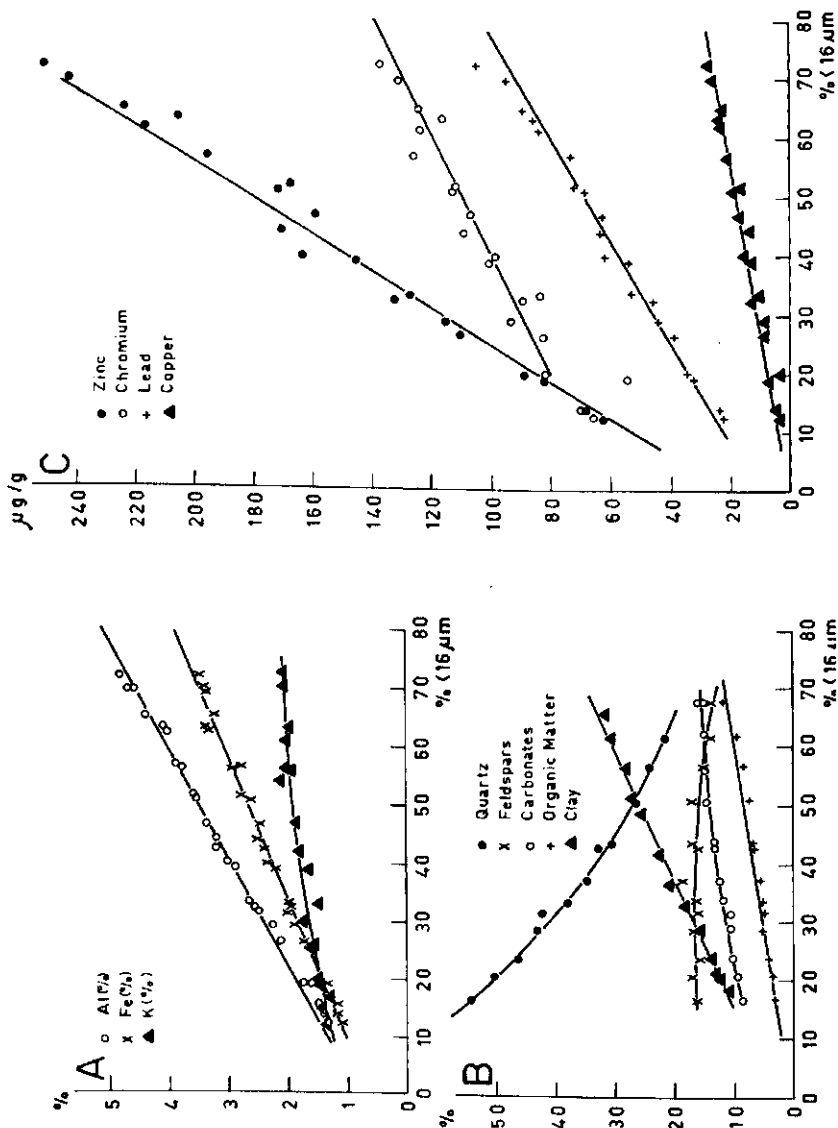


Figure 2. Composition of the sediments studied. Correlations with the amount of finely grained particles in sediments (< 16 μm) and (A) major element composition, (B) mineralogical composition, (C) trace metal composition.

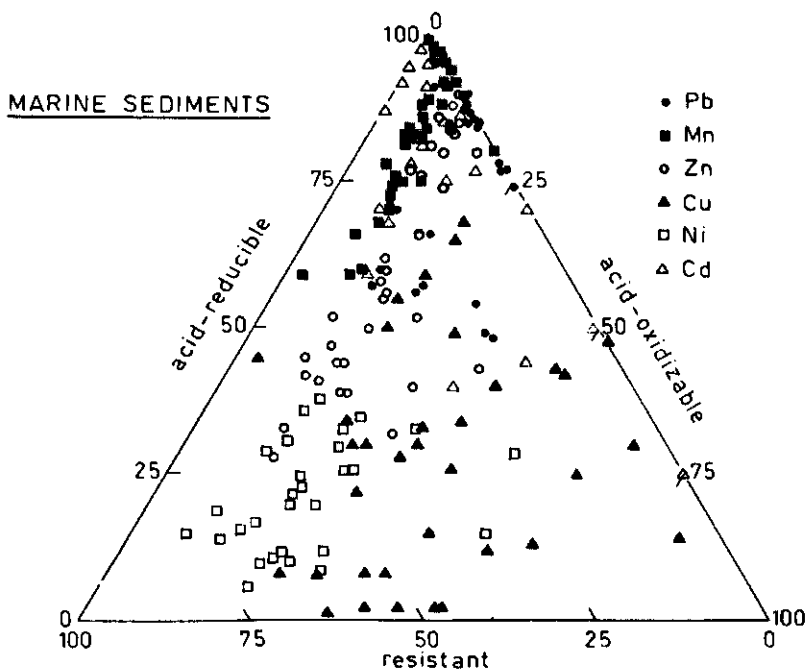
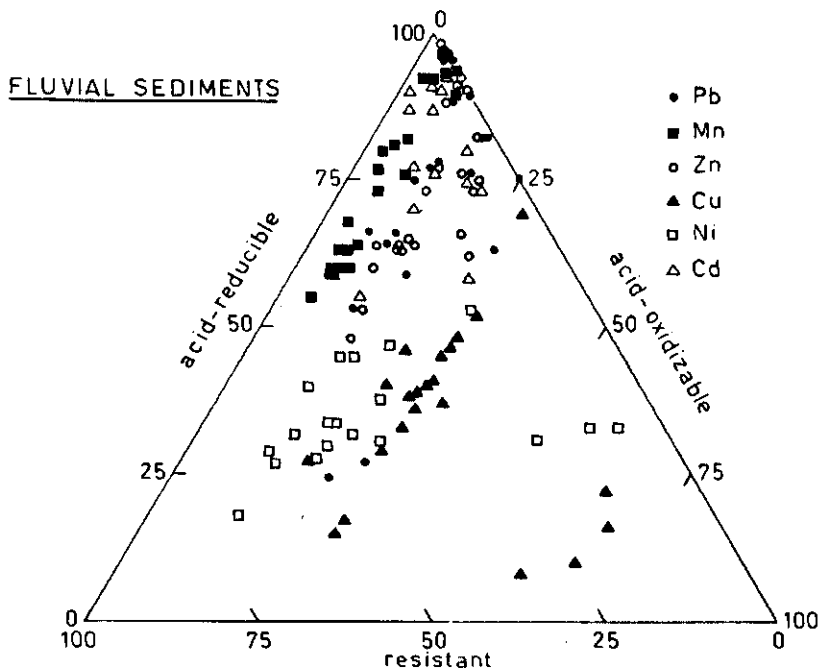


Figure 3. Mode of occurrence of trace metals in fluvial and in marine sediments.

the acid-reducible fraction and partly in the resistant fraction. Lead and cadmium occur mainly in the acid-reducible fraction. The distribution of copper over the various fractions is extremely variable in marine sediments. The data show, however, that this metal appears to be more associated with the acid-oxidizable fraction than the other metals studied.

RESULTS AND DISCUSSION

Generally, the concentrations of trace metals in river sediments reflect the occurrence and abundance of certain rocks or mineralized deposits in the drainage area of the river. At present, however, the anthropogenic input of certain trace metals into the environment equals or exceeds the amounts released by weathering. Often it is difficult to make a direct quantitative estimate of the anthropogenic contribution to the trace metal concentrations in sediments. By analyzing sediments actually collected about 50 years ago, we have been able to trace the development of trace metal concentrations in fluvial, marine and lagoon sediments. Samples from the following three areas have been investigated for trace metals:

1. Fluvial samples from the river Rhine taken on its flood plain in 1922 (Masschaupt and Hissink, 1924). Two areas have been sampled, one area regularly flooded by the Rhine and without vegetation (area A), the other irregularly flooded and grown over with willows (area B). In both areas, samples from depths of 0-25 cm and 25-50 cm had been taken. The regularly flooded area represents the most recent material; the layer 0-25 cm was deposited probably around 1920. The samples from the irregularly flooded area were deposited close to the beginning of the 20th century.
2. Marine sediments from the Dollard (Figure 1) collected in 1921. Both the tidal flat and the salt marsh have been sampled up to depths of 100 cm (Masschaupt, 1923). No differences in trace metal concentrations were found along the profiles and between the tidal flat and salt marsh samples.
3. Lagoon sediments from the Zuiderzee, sampled in 1933.

Trace Metals in Sediments from the River Rhine

The development of trace metal concentrations in sediments from the river Rhine could be studied by means of samples collected on its flood plain in 1922 and of bottom sediments collected in 1958, 1970 and 1975. Additionally, soil samples have been analyzed from polders reclaimed in 1788 and in the 15th and 16th centuries. The results of the analyses are given in Table I.

If we take into account the spread in the calculated

Table I
Trace Metal Concentrations in $\mu\text{g/g}$ (values at 50% < 16 μm)
in Sediments from the River Rhine

| | Cu | Zn | Ni | Pb | Cr | Cd | Hg | As |
|---|-----|------|----|-----|-----|-----|------|------|
| <u>Rhine Polders Reclaimed in:</u> | | | | | | | | |
| 15th-16th century | 21 | 93 | 33 | 31 | 77 | 0.5 | 0.14 | 12.2 |
| 1788 | 25 | 100 | 39 | 29 | 89 | 0.3 | 0.21 | 12.5 |
| <u>River Flood Plain Sampled in 1922:</u> | | | | | | | | |
| Area A 0-25 cm | 68 | 1051 | 36 | 273 | 107 | 4.4 | 2.6 | 45.9 |
| 25-50 cm | 69 | 779 | 32 | 232 | 106 | 4.7 | - | - |
| Area B 0-25 cm | 41 | 378 | 36 | 141 | 84 | 1.6 | 0.91 | 32.7 |
| 25-50 cm | 33 | 174 | 36 | 87 | 85 | 0.7 | - | - |
| <u>Bottom Sediments Sampled in:</u> | | | | | | | | |
| 1958 | 294 | 2420 | 54 | 533 | 642 | 14 | 10.5 | 198 |
| 1970 | 323 | 1855 | 62 | 447 | 789 | 27 | 14.5 | 136 |
| 1975 | 325 | 1905 | 81 | 399 | 820 | 31 | 10.1 | 54 |

values, which in this case is about 10 percent, the differences in trace metal concentrations between the two polders is not significant (Table I). With the exception of copper, the trace metal concentrations are comparable with those found in sediments from the Dollard (1921) and from the Zuiderzee (1933). As can be concluded from Table II the similarity suggests that these concentrations are close to the original contents in Rhine sediments and may be regarded as a baseline level.

The samples from the river flood plain have high concentrations of copper, zinc, lead, cadmium and mercury. The nickel and chromium values are close to the baseline. Apparently, the concentrations of copper, zinc, lead, cadmium and mercury were already anthropogenically influenced at that time. This fact is further substantiated by the variations in trace metal concentrations with depth and by the differences between the younger depositions area A and the overgrown area B. With increasing age of the sediments the trace metal concentrations decrease. We may conclude, therefore, that already in the beginning of the 20th century the river Rhine was polluted with a considerable number of trace metals.

Between 1920 and 1958 all trace element concentrations studied have increased in the sediments from the river Rhine (Figure 4). Between 1958 and 1975 this rise in the concentrations continued for cadmium, phosphorus, copper and chromium. The concentrations of lead, zinc and mercury, however, decreased, and the concentration of copper tended to level off. The decline in the arsenic concentrations is striking, and is probably caused by a ban on the use of arsenic-containing pesticides.

The anthropogenic contribution to the total metal concentrations in sediments from the Rhine exceeds the background value by an order in magnitude, in some cases. It can even be estimated that less than 1 percent of the cadmium found in Rhine sediments in 1975 originated from natural sources.

Trace Metals in Nearshore Sediments

Nearshore sediments have been sampled along the Belgian, the Dutch and part of the German coast. The localities sampled are shown in Figure 1. Sources for the sediments in this area are the rivers Rhine, Meuse and Scheldt, as well as material transported by a northward current through the English Channel. The overall transport of sediments in the coastal areas of Belgium and The Netherlands is directed to the north. The contribution of fluvial material to the sediments deposited in the nearshore environment is relatively small (Salomons, 1975; Salomons *et al.*, 1975).

The trace metal concentrations (values at 50% < 16 μm) in the relevant sediments are given in Table II and shown for some metals in Figure 5. The metal contents in the Dollard sediments from 1921 can be regarded as baseline levels in this

Table II
Trace Metal Concentrations in $\mu\text{g/g}$ (values at 50% < 16 μm)
in Near Shore Sediments and in Sediments from
Lake IJssel (Zuiderzee)^a

| | Cu | Zn | Ni | Pb | Cr | Cd |
|--------------------------------|----|-----|----|----|-----|-----|
| <u>Wadden Sea</u> | | | | | | |
| Dollard 1921 | 10 | 88 | 26 | 32 | 74 | 0.3 |
| Dollard 1958 | 24 | 150 | 27 | 47 | 85 | 0.7 |
| Dollard 1975 | 10 | 135 | 27 | 45 | 91 | 0.6 |
| Groningen 1957 | 25 | 175 | 21 | 65 | 100 | 0.6 |
| Groningen 1970 | 17 | 180 | 22 | 68 | 105 | 0.9 |
| Groningen 1975 | 22 | 160 | 25 | 67 | 92 | 0.9 |
| Friesland 1958 | 29 | 235 | 22 | 80 | 100 | 0.8 |
| Friesland 1970 | 32 | 250 | 29 | 86 | 115 | 0.9 |
| Leybucht 1975 | 18 | 140 | 27 | 53 | 89 | 0.6 |
| Ost-Friesland 1969 | 17 | 150 | 25 | 55 | 104 | 0.6 |
| Jadebusen 1969 | 13 | 125 | 25 | 43 | 88 | 0.4 |
| <u>Southern Areas</u> | | | | | | |
| Oosterschelde | 25 | 160 | 25 | 55 | 90 | 0.9 |
| Westerschelde | 29 | 170 | 23 | 62 | 97 | 1.0 |
| Vlaamse Banken | 26 | 190 | 19 | 75 | 92 | 0.6 |
| <u>Zuiderzee (Lake IJssel)</u> | | | | | | |
| 1933 | 19 | 133 | 39 | 39 | 88 | 0.4 |
| 1974 | 39 | 460 | 37 | 88 | 106 | 2.8 |

^aThe sampled localities are shown in Figure 1.

respect. Except for Cu, these values are close to the metal contents that were regarded as baseline levels for the river Rhine (compare Rhine polders in Table I). Compared with the Dollard sediments from 1921, the chromium and nickel concentrations in 1970 increased only slightly. The concentrations of cadmium, zinc, lead and copper, on the other hand, increased considerably.

No clear-cut trend in trace metal concentrations is observed during the last 20 years in the Wadden Sea area. A slight increase is found in Friesland, whereas the concentrations remained at a constant level in the Dollard and in the Groningen area. The concentrations found in the areas south of the Rhine-Meuse estuary (Oosterschelde, Westerschelde and Vlaamse Banken) are comparable to those found in the Groningen area. The trace metal concentrations in the Dutch Wadden Sea

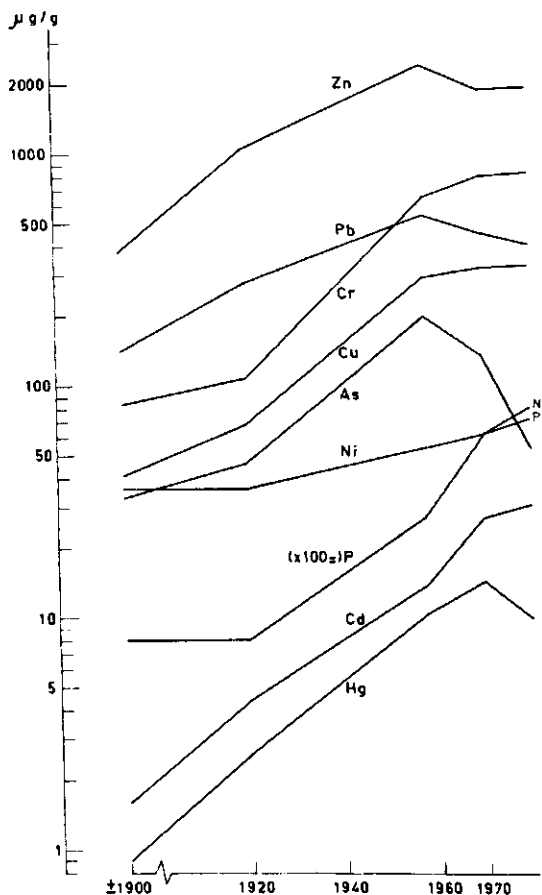


Figure 4. History of trace metals in Rhine sediments.

decrease in an easterly direction (Figure 2), apparently caused by a diminishing influence of the river Rhine. A similar trend is found along the German coast (Leybucht, Ost-Friesland and Jadebusen).

Several processes are responsible for the relatively small increase, as compared with the river Rhine, in trace metal concentrations:

1. The sediments from the river Rhine, the most important source of highly contaminated sediments, are deposited for the greater part in the Rotterdam harbor area and in the artificial freshwater lakes. The sediments from the Rotterdam harbors are continuously dredged and used partly for landfilling. The latter sediments and those deposited in the Haringvliet and in Lake IJssel are taken out of the "system" permanently.
2. Studies on the origin of sediments found in the Wadden Sea area have shown that the rivers Rhine and Meuse are

- not the major source for these sediments (Salomons, 1975; Salomons *et al.*, 1975). In the North Sea the contaminated fluvial sediments are mixed with large amounts of relatively clean marine sediments.
3. In the Wadden Sea area an erosion and mixing of older, relatively uncontaminated sediments with more recent polluted material takes place, causing a dilution of trace metal contents.
 4. The erosion of deposited layers and the subsequent re-lease of heavy metals, which are present in the pore waters, to the surface water may also contribute to a decrease in the heavy metal contents of the sediments (Duinker *et al.*, 1974).

Trace Metals in Lake IJssel (Zuiderzee)

Lake IJssel came into existence in 1933, when the Zuiderzee was shut off from the Wadden Sea by the Enclosure Dike. Since then the lake's main source for sediments is the river IJssel, a distributary of the Rhine. The water discharge of the river IJssel is estimated at 8.5 km³/yr, the sediment load at 400,000 tons/yr, and the water discharge of Lake IJssel to the Wadden Sea is about 12 km³/yr. The residence time of the water in the lake is about six months. The main depositional area for the contaminated sediments of the river IJssel is the Ketelmeer (Figure 1); the remainder is spread out over the

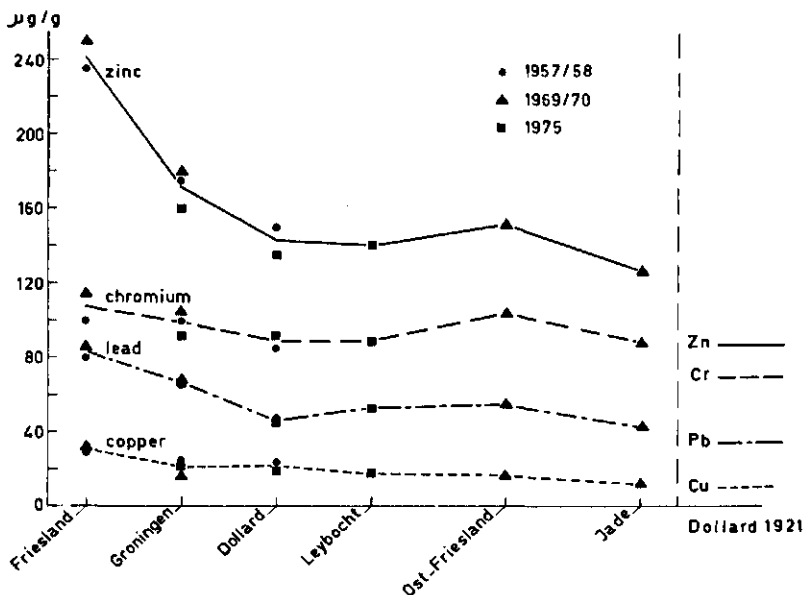


Figure 5. Trace metals in the Wadden Sea.

lake. The shallowness of the lake allows frequent erosion of bottom sediments to occur. The recent, contaminated sediments are mixed intensively with the older sediments. Consequently, hardly any gradients in trace metal concentrations in the sediments of Lake IJssel are found.

The pH of the water in the lake increases from about 7.2 (river IJssel) to more than 8.5 at the Enclosure Dike. Two processes are responsible for this. First, the partial pressure of CO₂ in river water from the IJssel exceeds the partial pressure of CO₂ in the atmosphere. As a consequence, in the Ketelmeer and in Lake IJssel the excess of carbon dioxide escapes to the atmosphere, giving rise to an increase in pH. Second, the high phosphorus load of the river IJssel causes algal blooms in Lake IJssel. The consumption of CO₂ by these organisms causes an additional rise in the pH. The latter process is probably the most important.

Due to the high pH of Lake IJssel, calcium carbonate precipitates. The stable carbon isotopic composition of these newly formed carbonates differs from that of the carbonates in the sediments from the river IJssel, as can be seen from the data in Table III. In this way the carbon isotopic composition can be used to distinguish between sediments from Lake IJssel and those from the river IJssel.

Hydrodynamical and geochemical processes, as described before, determine trace metal concentrations in Lake IJssel. In order to illustrate these processes, we will discuss the trace metal concentrations in sediments from the Ketelmeer (the interface between the river IJssel and Lake IJssel).

If the dissolved and particulate trace metals behave conservatively and if there is no transport of sediments from Lake IJssel into the Ketelmeer, the composition of the sediments in the Ketelmeer will be similar to that of the Rhine. However, both in 1972 and in 1974 this was not the case (Table III). The stable carbon isotopic composition of the carbonates of the sediments sampled in 1972 shows that these are derived mainly from the river IJssel (Rhine). The concentrations of cadmium, zinc and nickel are higher than expected, whereas the concentrations of chromium, lead and copper are lower. The low

Table III
Trace Metal Concentrations in the Ketelmeer and Lake IJssel (Rhine 1970 = 100). The Stable Carbon Isotopic Composition of the Carbonates in the Rhine is -2.7 ± 0.4 .

| | Cu | Zn | Ni | Pb | Cr | Cd | $\delta_{PDB}^{13}C$ (‰) |
|------------------|----|-----|-----|----|----|-----|--------------------------|
| Ketelmeer 1972 | 92 | 114 | 111 | 81 | 86 | 115 | -2.6 |
| Ketelmeer 1974 | 62 | 90 | 100 | 54 | 56 | 89 | -1.4 |
| Lake IJssel 1974 | 12 | 25 | 63 | 20 | 13 | 10 | +0.8 ± 1.0 |

concentrations for these latter metals are probably caused by a small admixture of sediments from Lake IJssel. In 1974 the stable carbon isotopic composition shows that the sediments are composed of about equal mixtures of sediments from the lake and from the river. This mixing ratio explains the concentrations of copper, chromium and nickel. However, the concentrations of zinc, cadmium and nickel are higher.

Detailed investigations in progress (Salomons, unpublished results; Duinker, personal communication) show significant decreases in the concentrations of some dissolved trace metals. Apparently, adsorption or precipitation processes are taking place. These processes are able to influence the composition of the sediments only if a large part of a trace metal is transported in solution. The metals chromium and lead are transported for about 20 percent in solution; adsorption of these metals onto the sediments influences their composition only to a small extent. The concentrations of chromium and lead, therefore, could be explained by a simple mixing of sediments from the river IJssel with sediments from Lake IJssel.

Copper, cadmium, zinc and nickel, on the other hand, are transported for 40, 50, 60 and 70 percent, respectively, in solution. An adsorption of these metals causes a significant increase in the concentrations in the sediments. This increase is indeed found for cadmium, zinc and nickel, but not for copper. This discrepancy is probably caused by the dependence of the adsorption process on the pH.

Laboratory experiments have shown that the adsorption of zinc (O'Conner and Renn, 1964; Murray and Murray, 1973) and of cadmium and nickel (Salomons, unpublished results) is strongly dependent upon pH, especially over the pH range observed in the Ketelmeer and Lake IJssel. The adsorption of copper, however, is not dependent upon the pH between pH values of 7 and 9, which is the range observed in Lake IJssel (O'Conner and Kester, 1975; Grimme, 1968).

The results of these laboratory experiments are in qualitative agreement with the metal concentrations observed in the Ketelmeer. It appears from our data that the carbon cycle of Lake IJssel and of the Ketelmeer determines, indirectly, the concentrations of metals in the surface waters and in the sediments.

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