SESSION III
TRANSPORT MECHANISMS (1)

FIELD OBSERVATIONS ON THE TRANSPORT OF HEAVY METALS IN SEDIMENTS

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INTRODUCTION

The pollution of rivers with degradable organic wastes, persistent materials such as heavy metals and chlorinated hydrocarbons, as well as oil, is a pressing problem, in particular for the Rhine in western Europe. For the Netherlands delta this also applies, to a lesser extent, for the rivers Meuse and Scheldt. Of the substances mentioned above, the heavy metals are probably the most harmful. Compared with the natural uncontaminated environment, the heavy metals can occur in relatively high concentrations and influence the fluvial ecosystem and, after their transport to the sea, also influence the food chains in the marine environment. The harmful effects are linked to the accumulation in biological systems, even in their lowest forms of development.

For the Dutch delta, information could be obtained on the occurrence and the chemical behavior of nine heavy metals. Notwithstanding the rather low concentrations of suspended matter in river water (generally 40–80 mg/l), many metals are predominantly bound to the suspended material rather than being dissolved. It is therefore important, when considering the contamination of rivers with heavy metals, to pay detailed attention to the elements fixed onto the suspended matter.

In this study the contents and behavior of heavy metals in a number of types of suspended matter will be described. Special attention will be given to the changes which the heavy metal composition of some types of suspended matter undergoes upon the displacement of the material from the rivers through their estuaries to the open sea. The fate of heavy metals in suspended matter can only be studied efficiently, however, if the transport paths of the material from the rivers to the marine coastal areas are well known. As an introduction to the problem, some details on these displacements of material, especially referring to the Dutch delta, are given. In this paper, those solid constituents having a diameter $< 16\ \mu m$ are studied. All experiments refer to freshly deposited material from the different locations.

Further, some data shall be given on the contents of a few heavy metals in filtered river and sea water. By combining the amounts of fine-grained material and water discharged by the river with the metal contents of these components, an estimate can be made of the total load of a river with heavy metals.

ORIGIN AND TRANSPORT OF SEDIMENTS

The fine-grained material (often called mud) transported along the western European coast, originates mainly from the rivers. A detailed insight into the movements of this material was obtained on the basis of the comparison of the considerably divergent Mn contents of sediments from different origins, as shown in Fig. 1, in which the mud of the River Thames was chosen as a standard.[1]

In this paper we confine ourselves to the transport behavior of the mud within the Netherlands delta (Fig. 2). This delta is mainly influenced by the Rhine, Meuse, Scheldt, and Ems. The suspended matter of the Scheldt has only a restricted sedimentation area and is deposited chiefly within the eastern part of the Western Scheldt. The mouthing area of the Western Scheldt receives its fine-grained material mainly

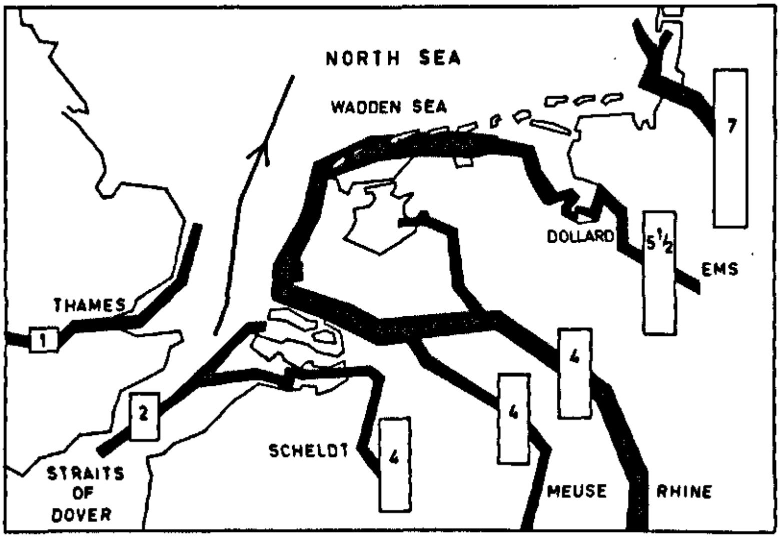

FIG. 1. Manganese contents and movements of mud in western Europe (schematic).

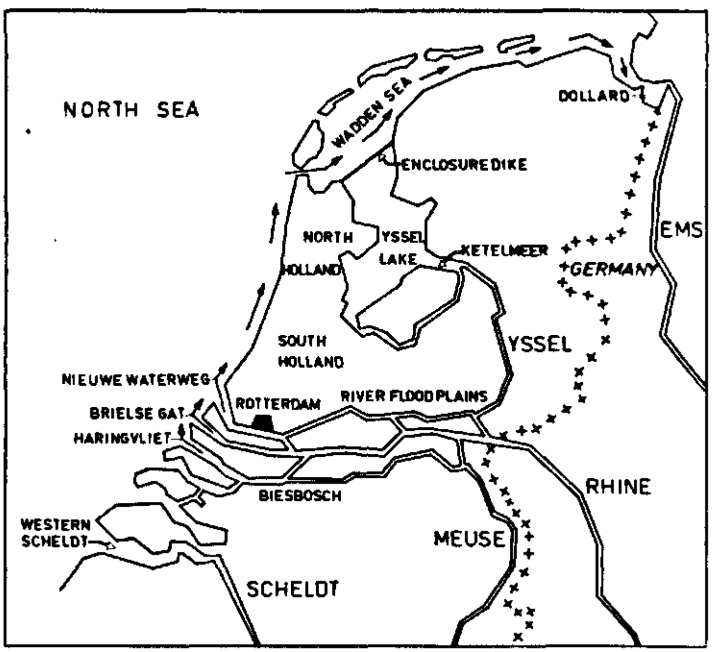

FIG. 2. Movements of sediments in the Rhine estuary, North Sea, and Wadden Sea.

from the south, coming through the Straits of Dover to this part of the Netherlands coast. The main source of mud in the Dutch delta is the Rhine, transporting yearly 3.5 Mtons of fine-grained material in 75 km^3 of water. From this material 10% is transported via the distributary IJssel to Lake IJssel. After leaving the river outlets by the Haringvliet and Nieuwe Waterweg, the Rhine material (Figs. 1 and 2), mixed with a smaller contribution of Meuse sediment, is transported mainly in a northeasterly direction in a narrow zone along the coast of the provinces of South and North Holland (average speed 0.05–0.10 m/s). Then the material reaches the western Wadden Sea from which it is transported further towards the east over the Wadden Sea flats. A part of the Rhine mud finally reaches the Dollard area. The Ems carries much less suspended matter than the Rhine, so its deposition is restricted to a part of the Dollard, especially along the German border of this area.

Although the preceding sediment transport studies were carried out according to the manganese method, based upon the property of this element to remain fixed to the suspended matter during transport in aerated water, nowadays more advanced techniques are available. Our knowledge of the behavior of metals in suspended matter is more detailed now and much progress has been achieved in the analytical techniques to determine these metals. So lanthanum, scandium, and a number of rare earths were found to behave like manganese and can be easily determined by nondestructive *neutron activation analysis*. Furthermore, we use, especially for sediment transport studies over shorter distances, tracer techniques (in connection with siltation problems of harbors and navigation channels). Therefore an element, which either does not occur in the sediment or only occurs in minute quantities, is fixed to the mud from the river or sea arm. After the material is marked it is returned to the water course where it mixes with the solids moving naturally. At specified points throughout the water course sediment samples are taken to determine the marking element by activation analysis. This gives an insight into the flow path of the suspended matter. As a marking element, tantalum was found to be successful in this respect.[2,3]

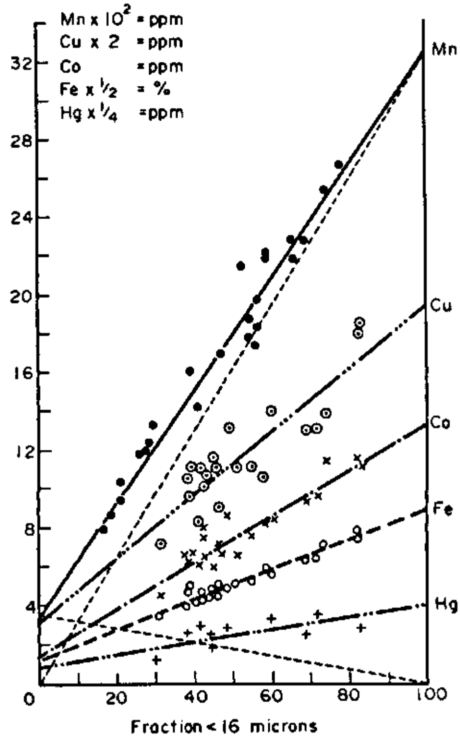

FIG. 3. Linear relationships between metal contents and percentage of fraction < 16 μm (Ems sediment).

EXPERIMENTAL

Due to a preferred occurrence of the heavy metals in the finest grain-size fractions, linear relationships are found between the contents of the heavy metals and the fraction of particles less that 16 μm in size (expressed as a percentage of the $CaCO_3$-free mineral constituents in the oven-dry sediment) in samples from the same location. The metals are generally present as a coating around the particles, so a larger surface area per unit of weight causes a higher content of the relevant metal. In Fig. 3 these relationships are shown for a number of elements in sediments of the Ems.

These linear relationships make it possible to characterize the content of a specific metal of a whole group of co-genetic sediments by a single value, the content being obtained by extrapolation to 100% of the fraction < 16 μm.[1] These types of values will now be used in this paper for the description of the heavy metal composition at different localities.

The analysis of metals has been carried out by different techniques. Originally many metals were estimated by classical spectrophotometry. This technique has now been replaced by atomic absorption for the estimation of cadmium, chromium, copper, nickel, lead, and zinc. For mercury, arsenic, and antimony, as well as for a number of elements estimated in connection with sediment transport studies activation analysis is used.[4,5]

HEAVY METALS IN RIVER DEPOSITS

Immediately following, a treatise is given on the contents of heavy metals in deposits from the Rhine, Meuse, Scheldt, and Ems. A few words will further be devoted to metals in sediments deposited on river flood plains as a consequence of high water discharge of the river. Finally, some details on the suspended matter composition of some tropical rivers will be given.

Rhine, Meuse, Scheldt, and Ems

Within western Europe the Rhine is the prototype of a river in which industrial wastes and other pollutants are drained in large quantities. From the four rivers governing the Dutch deltaic area, the Rhine is therefore predominant from a viewpoint of pollution. The Ems and its tributaries, on the contrary, flow through a sparsely populated area with only a limited amount of industry. The Meuse and the Scheldt are intermediate between the Rhine and Ems.

The composition of sediments from the freshwater part of the Rhine, Meuse, and Ems with respect to a number of heavy metals have been analyzed. For the Scheldt the deposits originated from the brackish-water tidal area of this river. The results are given in Table 1.

From Table 1 it is obvious that the sediments of the Rhine, compared with those of the Ems, have very high contents of zinc, chromium, and copper. This applies to a lesser extent to nickel. Although it has not been mentioned in Table 1, it was already found before 1970 that the contents of lead, mercury, and arsenic are also much higher in the Rhine deposits that in those of the Ems.[5] The contents of heavy metals in the Meuse sediments are also high, although the values are lower than for the Rhine. Striking are the high cadmium values for the Meuse, which are as high as those for the Rhine.

The Scheldt sediments generally have no higher contents of metals than the Ems, with the exception of chromium. We should take into account, however, that the Scheldt deposits have been taken from the brackish-water tidal area of the river. Wollast[6] found that farther upstream in the river the heavy metal contents of the mud are appreciably higher. This is in accordance with the findings to be mentioned later in this paper about the solubilization of metals from sediments in the estuarine part of a river (section on the mobilization of metals).

During the last few years attention has been focused, mainly in the daily press, on a steady increase of the heavy metal pollution of our rivers, especially of the Rhine. We were able to compare in this respect some rivers for the years 1960 and 1970. For the Rhine the results have been given in Table 2.

Except for cadmium, there is, on the average, no strong increase in the contents of the heavy metals during the past decade. The contents of arsenic, zinc, and lead decreased; copper, chromium, and nickel, on the other hand, increased. Alarming is the very strong increase of the cadmium contents of the Rhine sediments. This increase is continuing after 1970, now being more than twice as high as the mercury contents. The industrial use of cadmium seems to increase as a constituent of rubber, dyes, alloys, batteries, etc.

River flood plains

The contents of heavy metals in Rhine sediments, as mentioned in the preceding sections, refer to sediments as they are transported under normal flow conditions of the river. The suspended matter then mainly originates from the source areas of the river. After deposition we characterize this material as "original mud."

Under conditions of high water discharge the erosion of the river bed and of the shores of the river gives rise to the formation of a suspension with different sedimentation characteristics, referred to as "erosion mud." This material forms aggregrates of sufficient size to easily settle again when the high flow velocities are reduced somewhat. This mainly happens where the river enters the area of the river flood plains. These flood plains consist of meadows and are occasionally flooded during wintertime. In

TABLE 1

Metal contents, expressed in ppm, in sediments from the Rhine, Meuse, Scheldt, and Ems in 1970 (extrapolated to 100% of the fraction $< 16\,\mu m$)

	Rhine	Meuse	Scheldt	Ems
Zn	2900	2500	800	1100
Cr	1240	620	380	180
Cu	600	340	140	160
Ni	100	83	53	79
Pb	800	600	—	—
Cd	45	45	—	—
Hg	23	—	—	—
As	220	—	—	—
Sb	18	—	—	—

TABLE 2

Comparison of metal contents in Rhine sediments in 1960 and 1970, expressed as percentages of the amounts in 1960

	1960	1970
As	100	66
Zn	100	77
Pb	100	85
Sb	100	89
Cu	100	110
Cr	100	125
Hg	100	129
Ni	100	147
Cd	100	194

the summer season these plains are used for grazing cattle.

In 1970 samples of this erosion mud were taken from the river flood plains of the Rhine after extremely high water levels of the stream. In Table 3 the contents of a number of metals in this erosion mud are given, compared with the contents of these metals in original mud (the latter sampled under normal flow conditions of the river).

From this table it is obvious that the metal contents in erosion mud are lower than in the original Rhine mud. From these lower contents it must be concluded that these materials had less contact with pollutants, introduced into the river, than the original mud. It is further remarkable that the erosion mud shows large regional differences in the metal contents (indicated in parentheses in Table 3). At one location, however, the sediments have a uniform composition. We have not yet found the cause of the regional differences in the sediment composition of the river flood plains. It must be attributed, however, to any process of selective sedimentation.

Tropical rivers

Some attention has been paid to the natural contents of heavy metals in sediments from tropical rivers. Generally these contents are low. In Table 4 this has been demonstrated for the River Chao Phya in Thailand[4] and for the River Tji Tarum on the island of Java, Indonesia,[7] compared with the Ems.

It is obvious that the level of the metals, which act as trace metals in agriculture (zinc, copper, and cobalt), is critical. In this connection attention should be paid to the very low zinc contents of the sediments of the River Chao Phya. This river irrigates the central rice area in Thailand.

The most striking value in Table 4 is the very high natural mercury content of the sediment from the River Tji Tarum. This value is as high as that of the very polluted Rhine. The high mercury contents of this tropical river must be attributed to the volcanic deposits in the drainage area of this river.

Tropical river sediments not only deviate in their metal contents from those deposited under temperate climatic conditions, but also the behavior of the metals in the estuarine part of the river is different. Later on in this paper we will pay attention to this aspect.

TABLE 3

Contents of zinc, copper, chromium, and mercury, expressed in ppm, in original mud and in erosion mud from the Rhine (extrapolated to 100% of the fraction < 16 μm)

	Zn	Cu	Cr	Hg
Original mud	2900	600	1240	23
Erosion mud	1300	270	530	9
(Flood plains)	(900–1500)	(140–370)	(280–760)	(3–13)

TABLE 4

Metal contents, expressed in ppm, in sediments from the rivers Ems, Chao Phya, and Tji Tarum (extrapolated to 100% of the fraction < 16 μm)

	Zn	Cu	Cr	Co	Pb	Hg	As
Ems	1100	160	180	40	100	3	60
Chao Phya	30	50	100	20	30	—	50
Tji Tarum	80	37	40	27	—	20	7

DISCHARGE OF HEAVY METALS BY THE WATTER AND BY THE SUSPENDED MATTER OF THE RHINE

The discharge of a number of heavy metals by the Rhine water can be calculated from the mean water discharge (2200 m^3/s) and the mean contents of the relevant metals in the filtered river water. The latter were obtained from the Government Service for Public Health in the Netherlands. The results of these calculations, expressed as tons per year, have been given in Table 5.

In the same table the discharges of heavy metals by the suspended matter have been given. These estimates could be made by combining water discharge, concentration of suspended matter in the river water (38 mg/l of the fraction less than 16 μm) and the contents of heavy metals in the suspended matter. From the ratios metal in water/metal in sediments it is obvious that upstream in the river there is for lead, chromium, copper, arsenic and mercury, a more pronounced occurrence in the

TABLE 5

Discharge of heavy metals by the water and by the suspended matter of the Rhine

	In the water (tons/year)	Fixed to sediments (fraction < 16 μm) (tons/year)	Metal in water/ metal in sediments
Pb	695	1830	1:2.6
Cr	1250	2820	1:2.3
Cu	765	1355	1:1.8
As	375	500	1:1.3
Hg	42	53	1:1.3
Cd	125	105	1:0.8
Zn	11380	6705	1:0.6
Ni	765	235	1:0.3

suspended material. So the transport of these metals mainly takes place in a solid form.

Similar results have been found by Gibbs[8] for the Amazon and Yukon rivers, where the ratios were even more extreme.

Mobilization of metals in the tidal area of the delta

As long as a river does not undergo the influence of the sea, the metals remain fixed to the suspended matter. Downstream of the freshwater tidal area of the river, however, a number of metals are mobilized to a greater or lesser extent, going into solution into the surrounding water, partly as organo-metallic complexes.[4, 5, 9] For the Rhine these mobilization processes, measured according to the conditions in 1960, have been demonstrated in Fig. 4. Compare Fig. 2 for the relevant localities.

There are large differences among the several metals in their degree of mobilization, varying from more than 90% of the total quantity originally present in the sediment to complete immobility. The most striking elements in this respect are cadmium and mercury, followed by copper, zinc, lead, chromium, and arsenic. Mobilization at an intermediate level takes place with nickel. The elements lanthanium, scandium, samarium, and manganese are not subject to solubilization processes. The usefulness of manganese and also of lanthanium, scandium, and samarium for sediment transport studies is emphasized by these observations.

The main cause of these mobilization processes is the intensive decomposition of the organic matter in the sediments from the freshwater tidal area, especially as far as the mouth of the estuary. This organic matter also changes in its carbon/nitrogen ratios (the Biesbosch, Haringvliet, and Wadden Sea are 21, 14, and 11, respectively). In laboratory experiments, evidence has been obtained that decomposition products of the organic matter form soluble organometallic complexes with the metals from the suspended matter. The degree of mobilization depends on the stability constant of the metal under consideration with the organic ligand (the group in a molecule able to form a metal complex). For some metals (copper and mercury) the mobilization can be promoted by the possibility of forming stable complexes with both positively and negatively charged organic ligands. Finally, inorganic ions also, such as Cl^-, can play a role in the mobilization processes.[5] It is well known in this respect that mercury forms very stable complexes with Cl^- ions (e.g. $HgCl_2$ and $HgCl_4^{2-}$). The stability of these complexes can compete with several organic mercury compounds. The mobilization processes in the Rhine distributaries are so intensive that great quantities of a number of metals in the sediments from the upper reaches of the estuary are reduced to normal quantities in the lower courses of this area.

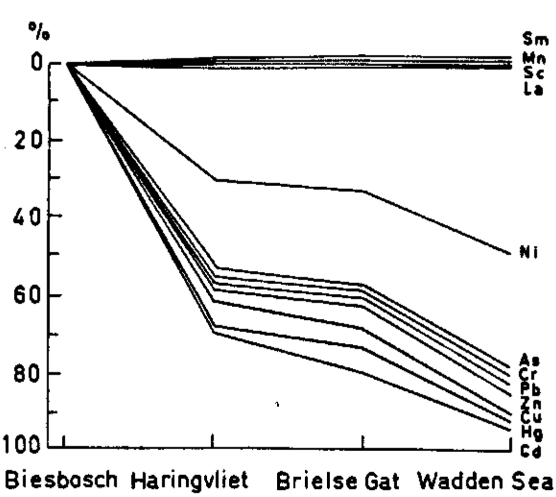

FIG. 4. Mobilization of metals in the Rhine estuary, North Sea, and Wadden Sea, expressed as percentages of the original contents (1960).

For the Ems and the Scheldt the processes occurring from the freshwater tidal area to the deposition area in the Dollard are similar to those in the Rhine, as far as the solubilization of the metals is concerned, apart from the fact that the Ems sediment does not contain an excessive amount of heavy metals.

A number of investigations have been carried out to characterize the organic compounds responsible for the mobilization of the metals. Freshly deposited sediments from the freshwater tidal regions of the Rhine and Ems were incubated with distilled water and from the dissolved organic matter the fulvic and humic acid fractions were isolated according to Kononova[10] (fulvic acid soluble in acid and alkali, humic acids insoluble in acid and soluble in alkali). A calculation based on iron and organic-matter contents of the fractions pointed out that the fulvic acid fraction is mainly responsible for the metal mobilization.

The fulvic acid fractions subsequently have been subjected to gel filtration column-chromatography on Sephadex and to functional group analysis.

With respect to the molecular weight distribution it can be reported that the fulvic acid fraction is composed of three groups: one having molecular weights less than 1000; the second, from 1000 to 10,000; and the third, larger than 10,000. Only the second group, which comprises by far the greatest part of the fulvic acid fraction, possesses metalchelating properties. The major oxygen-containing functional groups in these compounds were carboxyls, phenolic hydroxyls, and carbonyls.

A comparison between the fulvic acid fractions of Ems and Rhine sediments demonstrated further that the Ems has a greater mobilizing capacity than the Rhine. In this connection it can be remarked that the fulvic acids responsible for the mobilization show some differences for the two river systems. For the Rhine these fulvic acids have a predominantly aliphatic character, while the mobilizing compounds of the Ems largely proved to consist of phenols, the latter being the result of the peaty character of the drainage basin of this river.

In a preceding section it has been reported that generally the contents of heavy metals in deposits from tropical rivers are low. Another important difference compared with the Rhine, Scheldt, and Ems is the behavior of the metals in the suspended matter on their way from the freshwater tidal region of the river to the sea. For the River Chao Phya it was found that no mobilization of the heavy metals took place. The contents of all the metals in the sediments remained constant. The cause of this immobility is the lack of organic matter in such a river. Even in the freshwater tidal region of the river, the organic contents of the sediments are very low and no significant decomposition takes place on the way to the marine area.

HEAVY METALS IN RHINE AND COASTAL WATERS

The heavy metals, separating from the suspended matter as a consequence of mobilization processes, are solubilized into the water. For the freshwater tidal area this means that the water is burdened with these metals, almost without dilution. In the brackish-water tidal area, however, dilution with salt water from the sea takes place. So the water in the mouthing area of the Rotterdam harbour contains about 75% of sea water.

At sea a further mixing with the water of the North Sea takes place. Under the influence of the tides and the wind, the sea water is constantly in motion. Through the Straits of Dover 1500 to 2000 km^3 of water enters the North Sea annually.[11] This amount of water moves at an average speed of 0.05–0.1 m/s along the eastern shores of the North Sea.

The velocity with which dissolved substances are spread throughout the coastal waters of the North Sea can be derived from some tracer experiments.[12] It was found that an injection of 1 kg of tracer was spread in 12 h over an area of about 1 km^2 with a maximum concentration of 10^{-6} kg/m^2. This concentration further diminishes with time (estimated range t^{-2} to t^{-3}), whereas the surface of the area increases proportionally.

The dilution of the river water (Rhine water, 75 km^3/year) with the sea water (the latter coming in via the Straits of Dover) will not be smaller than the ratio of their discharges 75: 1750 = 1:23. After a few weeks a further mixing with the total water mass of the North Sea takes place.

The large amounts of metals added to the water in consequence of mobilization processes are not found back in the coastal water in the North Sea, as may be seen from Table 6. The strong dilution of the river water with sea water is responsible for this.

The metal contents in the North Sea water are generally much lower than in the river water (Table 6). The high copper contents in the coastal water may be the result of dumping in the investigated area.

INFLUENCE OF CIVIL ENGINEERING PROJECTS ON THE BEHAVIOR OF HEAVY METALS IN SEDIMENTS

The mobilization of heavy metals, as has been described in a previous section, is related to the existence of the tidal effects in the fluvial and marine regions, especially in the estuaries of rivers. The intensive decomposition of the organic matter in estuaries will be caused by an optimum microbial activity in these fresh- and brackish-water tidal areas.

TABLE 6
Metal contents in filtered water, expressed in μg/l

Location	Ref.	Zn	Cu	Cr	Ni	Pb	Cd	Hg
Rhine		164	11	18	11	10	1.8	0.6
North Sea (coast)		31	21	—	—	—	0.9	0.1
North Sea	13	6	6	—	—	2	0.3	0.1
Wadden Sea		30	2	—	1	2	<0.1	—
Sea water (mean value)	14	5	3	1	2	<0.1	<0.1	<0.1

Large civil engineering projects are carried out in the mouthing areas of the Rhine in connection with the well-known Delta Plan. This means that by the end of 1970 the action of the tides was stemmed in one of the most important Rhine outlets—the Haringvliet. In several respects the hydrology is disturbed as a consequence of such actions.

Such a situation has existed even longer in Lake IJssel, which was separated 40 years ago from the Dutch Wadden Sea by the construction of the Enclosure Dike. Under these circumstances, 10% of the Rhine water is flowing into Lake IJssel without passing of a tidal area.

In the following we pay some attention to the influence of the above-mentioned projects in the behavior of the heavy metals in Lake IJssel, the Delta area (main mouthing area of the Rhine), and the harbors of Rotterdam.

Lake IJssel

Since the origin of Lake IJssel (after the enclosure of the former Zuider Sea, 40 years ago) the main deposition area of the river IJssel is the Ketelmeer, directly in the vicinity of the mouth of the river. Recently, the heavy metal composition of the Rhine deposits in the Ketelmeer has been examined. The results of these investigations, compared with the composition of the original Rhine, have been given in Table 7.

From Table 7 it is obvious that the composition of the freshly deposited material (superficial layer) in the Ketelmeer and even of the underlying more consolidated sediments is very close to the Rhine sediments deposited in 1960 and 1970. There is no evidence of any mobilization process. The lead and cadmium contents in the Ketelmeer deviate somewhat from those in the Rhine river. In this connection we should be aware of the fact that the lead contents of the Rhine sediments have been further decreasing since 1970; the cadmium contents, on the other hand, still showed a considerable rise from 1970 to 1972.

Any suspended matter from the River Yssel which is not deposited in the Ketelmeer is spread out over Lake IJssel. Probably this material is settling out in the former tidal channels of the lake. Only slight amounts of the suspended matter escape through the sluices of the Enclosure Dike to the Wadden Sea.

TABLE 7

Heavy metals in Ketelmeer deposits (1972), expressed as percentages of the Rhine deposits in 1970

	Zn	Cu	Cr	Pb	Cd
Rhine, 1960	130	91	80	118	52
Rhine, 1970	100	100	100	100	100
Ketelmeer (superficial layer)	114	92	86	81	115
Ketelmeer (consolidated layer)	112	86	87	81	104

Delta area

At the end of 1970 the Haringvliet was closed by a dam, as a part of the Delta Plan, thus stemming the action of the tides in a second important Rhine distributary.

The first consequence of this enclosure dam is that large quantities of mud, originally discharged via the Haringvliet to the North Sea, are now settling in the area between Biesbosch and Haringvliet. The experience obtained in the Ketelmeer gives rise to the expectation that the heavy metals in these deposits are also not mobilized as a consequence of the stemming of the action of the tides. At this moment a good deal of our effort is focused on the study of these sediments.

Rotterdam harbors

Originally there were two main outlets of the Rhine—the Haringvliet and the Nieuwe Waterweg (compare Fig. 2). The latter distributary flows through the Rotterdam harbor area. Since the enclosure of the Haringvliet, the main part of the Rhine water is discharged via the Waterweg. As a consequence of the great depth of the harbors, intensive siltation processes occur. The deposited material

TABLE 8

Heavy metals in dredged sediments from the Rotterdam harbors (1972), expressed as percentages of the Rhine deposits in 1970

	Zn	Cu	Cr	Pb	Cd	Dredged quantities (Mton/year)
Inner harbors	74	74	70	68	79	0.4
Intermediate harbors	45	41	35	38	42	2.1
Outer habors	12	9	15	12	6	1.0

contains more, or less, heavy metals, depending on the location of the relevant harbor. In consequence of the siltation, large-scale dredging operations are necessary. A review of the quantities of dredged sediments and the contamination of these materials has been given in Table 8.

From Table 8 it is apparent that the degree of contamination depends on the measure of exposure of the relevant harbors to effects of the sea. The mud of the inner harbors must be regarded as severely contaminated, although the contents of the heavy metals are lower than farther upstream in the Rhine. The sediments from the outer harbors, on the other hand, must be regarded as uncontaminated. The low contents of heavy metals in the latter sediments are partly caused by mobilization processes of the heavy metals from the suspended matter in the river. Introduction of uncontaminated material from the sea into the mouthing area of the Nieuwe Waterweg may also play a role.

At this time an exact discrimination between materials of fluvial and marine origin in the Rotterdam harbor area is not yet possible. We are convinced, however, that the main portion of the deposited material comes from the Rhine.

For the dredged materials, deposition areas have to be found. The mud is deposited either at sea (about 10 miles outside of the harbor mouth) or on the land. The latter deposits are later used for suburban development or are used as arable land. Insofar as the deposits are contaminated with heavy metals and other pollutants (chlorinated hydrocarbons and oil) serious problems arise for the disposal of these materials. Much attention has to be paid to these problems in the near future.

PERSPECTIVES FOR FURTHER INVESTIGATIONS

Some important questions for further investigations in the near future on the occurrence and behavior of heavy metals in estuary regions and the nearby coast involve deeper insights into the mechanisms of the mobilization processes and into the sorption of metals to different kinds of suspended matter.[15] Although it is beyond the scope of this paper and we will not go into further details on this subject, we mention the severe gaps in our knowledge of the uptake and accumulation of the heavy metals in the biosphere.

Mobilization processes

The mobilization of metals, especially in the estuarine part of the river, is one of the most striking phenomena found in some estuaries of the temperate climatic region. It is doubtful, however, if these processes occur generally in estuaries around the North Sea. It is important to assemble evidence on the existence of estuaries contrasting in this respect, and to carry out intensive investigations in these estuaries.

Detailed investigations on the processes of mobilization of the metals may also throw more light on the constitution of organic and also inorganic metal compounds in the water of the various coastal regions. Also important in this respect is knowledge of the fates of trace materials after they have been solubilized (so far only iron has been studied in our investigations, and it again adheres to solid substances outside the estuarine region). These undeveloped fields of research must be considered to be of prime importance for studies of bioaccumulation of heavy metals.

Metal sorption on suspended matter

For bottom sediments, taken from the same location, a linear relationship is always found between the contents of the heavy metals and the fraction of particles less than 16 μm (Fig. 3). The granulometric composition was determined after destruction of the organic matter.

There are other factors which influence the metal contents of suspended material. In the first place, the type of the suspended matter depends on the velocity of the river currents. Under normal flow conditions of the river the main component of the suspended matter is the so-called original mud. For the Rhine this material originates mainly from its source area. It is this type of material, gathered under low tidal conditions as a freshly deposited, thin, superficial layer in estuarine and marine areas, from which the general conclusions in this publication have been drawn. But earlier it was mentioned that under conditions of high water discharge the erosion of the river bed gives rise to the formation of a suspension with different sedimentary characteristics, referred to as erosion mud. In consequence of processes of pedogenesis on the river bottom, this material forms aggregates of sufficient size to easily settle again when the high flow velocities are reduced at the place where the river enters the area of the flood plains. The latter is still upstream with respect to the freshwater tidal region.

The original mud, as it was collected from the main deposition areas in estuarine and coastal regions, has been regarded for many years as representative of the material present as a suspension in the river water under normal flow conditions.

However, it has been pointed out recently that the suspended matter contains components which do not settle out within the normal sedimentation areas. These components have a higher content of organic matter than those settling out normally. It is even possible that at least a part of these components never settles out at all.

The characteristics of the different forms of this suspended matter, apart from the granulometric composition after destruction of the organic matter, are of the highest importance. Besides differences in sedimentation characteristics, there exist appreciable differences in contents of heavy metals. For the Rhine it has been found that the metals supplied to the stream by industrial wastes adhere to the solids in decreasing contents in the following order: suspended matter, original mud (the main component settling in shallow areas), and erosion mud. The distribution of the solid substances in the environment diminishes in the same order (i.e., the erosion mud is deposited very locally on the river flood plains; a part of the suspended matter, on the other hand, moves very far). So those constituents which have been contaminated in the most severe way have the most widespread distribution in the aquatic environment.

A more detailed insight into the relations between contamination characteristics and physical properties of the solid constituents of the aquatic environment is urgently needed, especially in view of processes of bioaccumulation.

SUMMARY

In addition to their natural content of heavy metals, sediments transported by some rivers carry large amounts of these elements resulting from pollution.

The distribution of these elements between the suspended matter and the surrounding water, upstream with respect to the estuary, indicates for a number of elements a preferred adsorption to the solid phase. The composition of the fine-grained material from the rivers influencing the Netherlands delta (mainly the Rhine) is described, as well as that from some tropical river systems.

Under temperate climatic conditions the sediments on their way to the sea can undergo changes in their metal composition by mobilization of these elements as soluble metal-organic complexes. These processes lead to less-contaminated sediments in the lower courses of the delta. Special attention is paid to the influence of civil engineering projects (enclosure of river outlets) on these processes.

Finally, a treatise is given on the pollution with heavy metals of the diverse types of suspended matter. Dependent on the velocity of the river currents, different types of suspended matter are transported. These types differ in their sedimentation characteristics. It appears that those constituents, which have been contaminated in the most severe way, have the most widespread distribution in the aquatic environment.

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