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CONTENTS AND BEHAVIOUR OF MERCURY AS COMPARED WITH OTHER HEAVY METALS IN SEDIMENTS FROM THE RIVERS RHINE AND EMS

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ABSTRACT

Mercury is one of the various waste substances transported by the river Rhine across the German-Dutch border. Together with a number of other heavy metals mercury is present in large quantities. Upstream these metals are predominantly fixed to the suspended solids in the water and may be deposited on river flats and flood plains. From the fresh-water tidal area of the river onward, however, these elements are more or less solubilized during their transport as organo-metallic complexes. The mobilization of mercury is most pronounced in this respect. leading to more normal amounts of this element in sediments from the Wadden Sea. This article deals with the behaviour of mercury through the whole Rhine estuary as compared with a number of other heavy metals.

As a counterpart of the Rhine the same processes are described for the river Ems. The latter may be regarded as a classic example of an unpolluted stream.

INTRODUCTION

One of the main problems of environmental pollution in our highly industrialized society is the production of persistent wastes. A considerable part of these are carried by the sediments of rivers and can accumulate in (water) ecosystems along the river and in the sea.

Among the heavy metals mercury has received much attention because of fatalities that occurred in Japan and Sweden.

In this study the contents and behaviour of mercury, compared with a number of other heavy elements, in the suspended matter of the highly polluted river Rhine are described, together with the situation in the unpolluted estuary of the river Ems.

The chemistry of heavy metals in suspended matter (mud) in dependence on the location of sedimentation can only be studied efficiently, if the ways of transport of the material from the rivers to the marine coastal areas are well-known. As an introduction to our problem we therefore give some details on these displacements of the material especially referring to the rivers Rhine and Ems. We shall focus our attention in this paper to those solid constituents having a diameter < 16 microns. These particles are transported over large distances in rivers and the sea even with relatively weak currents. Deposition of this material takes place when the water movement is only slight: where the river is considerably broadening, in harbours and along the coast in shallow areas of the sea.

All experiments in this study have been carried out with freshly deposited material from the different locations.

ORIGIN AND TRANSPORT OF MUD

The mud transported by the longshore currents, along the western European coast, originates mainly from the rivers. A detailed insight into the movements of this material could be obtained on the basis of the comparison of the considerably diverging

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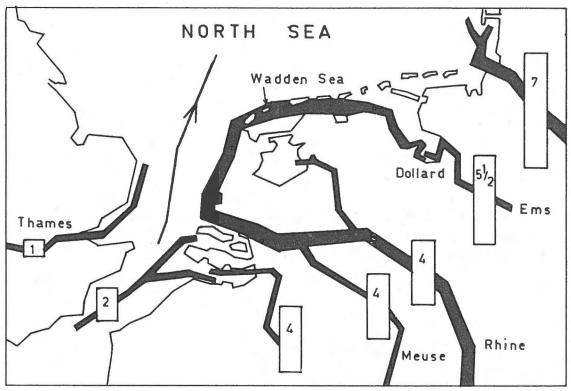

Fig. 1
Manganese contents and movements of mud in Western Europe (schematic).

Mn-contents of the sediments from different origins (fig. 1, in which the mud of the river Thames has been chosen as a standard and the Mn-contents of the sediments originating from the other rivers have been presented as a multiple, d e G r o o t, 1964).

Within the scope of this paper we confine ourselves to the behaviour of the mud of the rivers Rhine and Ems. The Rhine material (fig. 1), mixed with a less important amount of Meuse sediment is, after leaving the river outlets by the Haringvliet and Nieuwe Waterweg, transported mainly in a north-easterly direction in a narrow zone along the coast of the provinces of South and North Holland. Then the material reaches the western Wadden Sea, from where it is transported further towards the east over the Wadden Sea flats. A part of the Rhine mud finally reaches the Dollard area. The river 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.

EXPERIMENTAL

Due to a preferred occurrence of the heavy metals in the finest grain-size fractions, linear relationships are always found between the contents of the heavy metals and the fraction of particles < 16 microns (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 per unit of weight causes a higher content of the relevant metal). In fig. 2 these relationships are shown for a number of elements in sediments of the river 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 obtained by extrapolation to 100% of the fraction < 16 microns (d e G r o o t, 1964).

The analyses of metals have been carried out by different techniques: spectrophotometry, Röntgen-fluorescence and non-destructive as well as destructive activation analysis (d e G r o o t et al., 1968; d e G r o o t, 1970).

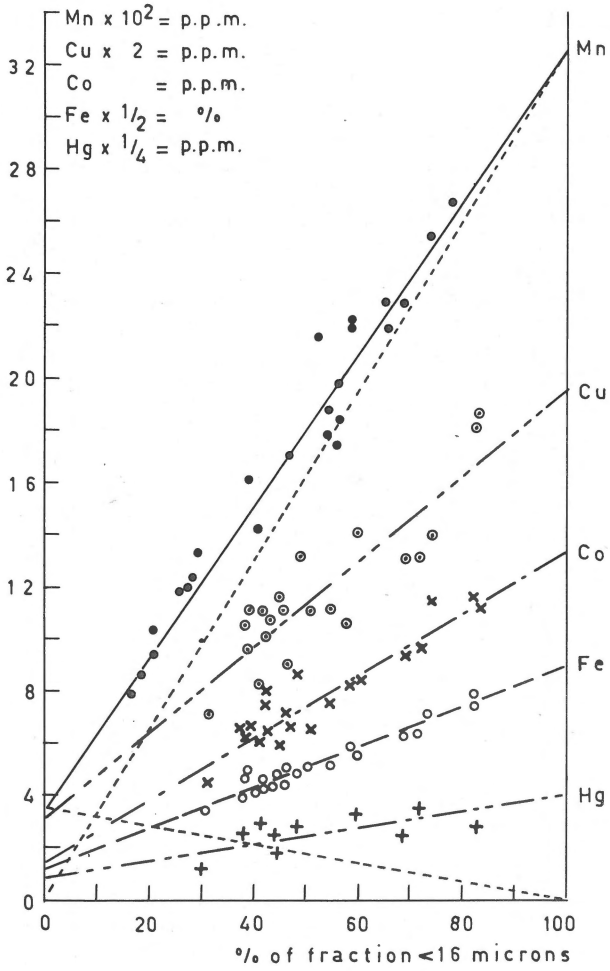

Fig. 2
Linear relationships between metal contents and percentage of fraction < 16 microns (Ems sediments).

The procedure of the activation-analytical determination of Hg is as follows:

From the homogenized sediments 100-300 mg samples were taken for analyses. The samples were irradiated in quartz vials for 1 - 5 hours in a neutron flux of about 10^{13} neutrons per cm^2 per second. After a decay period of 2-5 days the vials were cleaned outside with aqua regia, cooled by dipping in liquid nitrogen, wrapped in paper tissue and broken in a pneumatic press. The sample, quartz and paper tissue, together with 10 mg of mercury nitrate as a carrier, were carbonized by heating with 20 ml of concentrated sulphuric acid. The sample was subsequently oxidized by dropwise addition of hydrogen peroxide. After raising the temperature to 200°C the mercury was distilled off as mercury bromide by addition of 10 ml hydrogen bromide at a rate of 1 ml per minute. The distillate was collected in a solution of 20 ml water containing 13.5 g of sodium acetate. After addition of 0.2 ml of metallic mercury to the distillate, the mixture was stirred magnetically; the metallic mercury forms many small droplets, thus increasing the interface and ensuring a good and rapid isotopic exchange. After 1 hour, when all mercury activity has reached the metallic phase, the mixture was passed through a sintered glass filter. The remaining mercury was washed with water and acetone. Finally, the mercury was dissolved in nitric acid and counted in a 3 inch X 3 inch NaI (Tl) – scintillation crystal connected to a 400-channel analyser. For the measurement the combined 68-77 keV peak of Hg-197 was used.

Under standard conditions the sensitivity of the method lies between 10^{-9} and 10^{-10} g of mercury. By the use of an automatic apparatus for the chemical treatment of the samples after irradiation, a sample changer for counting the samples and a computer for data handling, many samples per day can be processed.

CONTENTS OF MERCURY AND OTHER HEAVY METALS IN RHINE AND EMS SEDIMENTS

The Rhine is the prototype of a river in which industrial wastes and other pollutions are drained in large quantities. The river Ems and its tributaries, on the contrary, flow through a scarcely populated area with only a restricted amount of industry. The composition of sediments from the fresh part of both rivers with regard to mercury and a number of other heavy metals has been analysed. The results for the Rhine (samples from the Biesbosch area, fig. 3) and for the Ems (samples from the location of Diele, fig. 4) are given in table 1.

The figures in this table concern samples which have been collected from the rivers during the years 1958-1960. It proves that, besides Hg, 5 other elements, Zn, Cr, Pb, Cu and As, are present in excessive quantities in sediments from the river Rhine.

Although it is beyond the scope of this article some attention may be given to the significance of these high amounts of heavy metals for cultivated soils, reclaimed by embankment of flood plains. Our primary concern is the pollution of grass vegetation with Hg and its toxic effect on cattle consuming this crop. Of the other elements Zn and As may be mentioned. High amounts of Zn induce Mn-deficiency symptoms in different arable crops, high As-contents of the soil cause undesirable As-levels in e.g. potato tubers with regard to human consumption.

TABLE 1
Contents of metals, expressed in p.p.m., in sediments from the rivers Rhine and Ems (extrapolated to 100% of the fraction < 16 microns).

	Rhine	Ems
Fe x 10^{-3}	54	112
Mn	2600	3300
Zn	3900	700
Cr	760	180
Pb	850	100
Cu	470	150
As	310	60
La	80	80
Co	43	40
Hg	18	3
Sc	12	12
Sm	7	9

All the above-mentioned figures refer to sediments transported under normal flow conditions of the river. The suspended matter then originates to a large extent from the river-source area. Under conditions

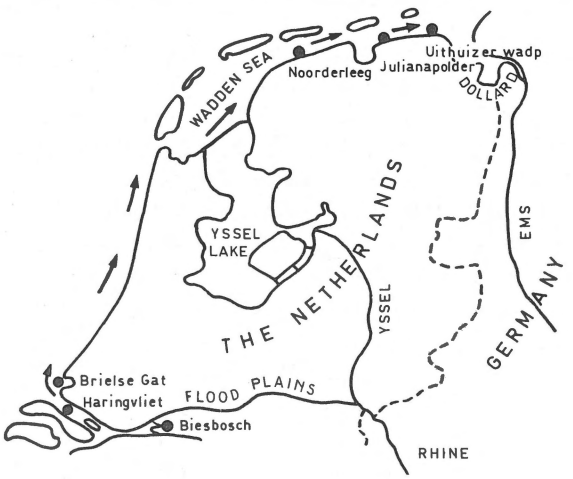

Fig. 3
Rhine estuary; movement of sediments in the Rhine estuary, North sea, and Wadden sea.

TABLE 2
Contents of mercury, expressed in p.p.m., in sediments from the Rhine estuary and the Wadden Sea (extrapolated to 100% of the fraction < 16 microns).

Location	1958–1960			1969–1970		
	Sediments			Sediments		
	Water ‰ Cl	p.p.m. Hg	% Mobilized	Water ‰ Cl	p.p.m. Hg	% Mobilized
Biesbosch	0	18.1	0	0	23.3	0
Haringvliet	2	5.6	69	2	–	–
Brielse Gat	–	4.8	73	–	–	–
Noorderleeg	16	1.6	91	16	2.7	89
Julianapolder	16	–	–	16	3	94
Uithuizerwadpolder	16	1.2	93	16	1.6	93

of high water discharge, however, erosion of the river bed takes place, causing the suspension of a kind of suspended matter with other chemical and sedimentation characteristics. Generally, the degree of contamination is lower. For Hg the contents of these Rhine sediments, taken from the whole area of river-flood plains, are in the order of 8 p.p.m. (varying from 4 to 14 p.p.m.), which is a high value. This "erosion mud" may cover very large areas of flood plains (for the Rhine courses about 8,000 ha, fig. 3), which are generally in use for grazing cattle.

MOBILIZATION OF MERCURY AND OTHER 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. It may be said that the total amounts of heavy metals in solution are appreciably lower than the quantities bound to the solid phase under these conditions, even if allowance is made for the relatively small concentration of the solids in the water. Downstream from the fresh-water tidal area of the river, however, a number of metals is mobilized more or less, going into solution in the surrounding water as organometallic complexes (de Groot, 1966; de Groot et al., 1968; de Groot, 1970).

For Hg in the Rhine distributaries these mobilization processes are demonstrated in table 2. The analyses have been carried out in 2 series of sediments, taken with an interval of 10 years from the distributaries in order to establish an eventual increase in the gravity of the pollution. The inaccuracy of the presented figures due to extrapolation to 100% of the fraction < 16 microns amounts to 10-20%.

From the Biesbosch (fresh-water tidal area) to the Haringvliet (see table 2 and fig. 3) a very intensive mobilization of Hg takes place, followed by a further release of the element from the suspended matter on its way from the Haringvliet to the Dutch Wadden Sea (Noorderleeg, Juliana- and Uithuizerwadpolder, respectively under marine conditions). There is no considerable difference in Hg-contents and degrees of mobilization between the two periods of sampling.

In table 3 a similar sequence of the mobilization of Hg is shown for the river Ems (see also fig. 4). There is no essential difference between the Rhine and Ems systems, except for the low contents of the element

TABLE 3
Contents of mercury, expressed in p.p.m., in sediments from the Ems estuary (extrapolated to 100% of the fraction < 16 microns).

Location	1958–1960		
	Sediments		
	Water ‰ Cl	p.p.m. Hg	% Mobilized
Diele	0	3.3	0
Leerort	< 0.3	1.3	60
Ditzum	6	1.0	69
German Dollard	> 6	1.4	58

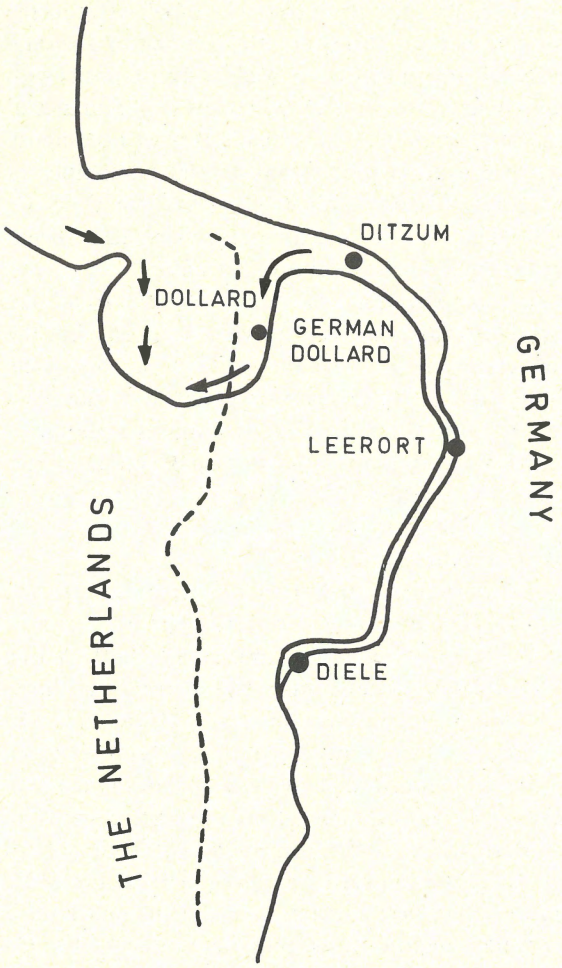

Fig. 4
Ems estuary and Dollard; movement of sediments.

in the unpolluted Ems.

There is a large difference between the several metals in the degree of mobilization, varying from more than 90% of the total quantity originally present in the sediment to complete immobility (see for different metals, except Hg, de Groot et al., 1968; de Groot, 1970). For the Rhine distributaries this is demonstrated in fig. 5. The most striking in this respect is Hg, followed by Zn, Pb, Cr and As. Mobilization at an intermediate level takes place with Co and Fe (it should be remembered in this connection that the natural Fe-contents of sediments are high, so the absolute amount of the element mobilized is appreciable.) The elements La, Sc, Sm and Mn are not subject to solubilization processes (the usefulness of Mn for sediment transport studies is emphasized by this observation).

The cause of these mobilization processes is the intensive decomposition of the organic matter related to the sediments from the fresh-water tidal area, especially as far as the mouth of the estuary. This organic matter also changes in a qualitative respect: the C/N-ratios in 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 sediments. The degree of mobilization depends on the stability constant of the relevant metal with the organic ligand (the group in a molecule able to form a metal complex). The mobilization processes in the Rhine distributaries are so intensive that the extreme quantities of Hg, Zn, Cr, Pb, Cu and As in the sediments from the upper reaches of the estuary are reduced to normal quantities in the lower courses of this area.

For the river Ems the processes occurring from the fresh-water tidal area to the deposition area of the sediment in the Dollard are similar to the situation in the Rhine area, as far the solubilization of the metals is concerned, apart from the fact that the Ems sediment does not contain an excessive amount of heavy metals. The kind of decomposition products of the organic matter responsible for the mobilization processes, however, is different for the two river systems. For the river Rhine these are mainly aliphatic compounds, while the mobilizing compounds of the Ems largely proved to consist of natural phenols, the latter being the result of the peaty character of the drainage basin.

DISCUSSION ON THE MOBILIZATION OF HEAVY METALS

Mercury forms complexes with high stability constants. In the order of the relative stabilities of metal complexes (rule of Irving and Williams, 1948) it is placed after trivalent iron: Fe (III) > Hg (II) > Cu (II) > Pb (II) > Zn (II), Co (II) > Mn (II). Especially with ligands containing N or S atoms as electron donors mercury forms strong complexes. Moreover, the ability of mercury to form complexes is greater than that of most other metals, because it not only forms stable complex ions with a negative

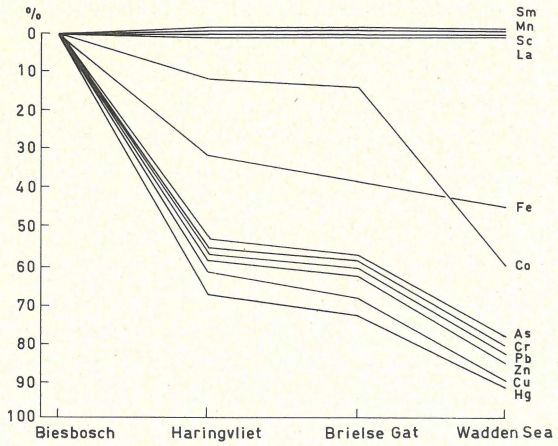

Fig. 5
Mobilization of metals in the Rhine estuary, North sea and Wadden sea, expressed as percentages of the original contents.

charge but also with a positive charge. Besides the above-mentioned properties, the chloride concentration of the water may also influence the mobility of mercury in the sediments. Chloride ions with mercury can form stable inorganic complexes (e.g. $HgCl_2$ and $HgCl_4''$) which may compete with several organic mercury complexes. In view of these considerations it is clear that the chemical conditions for mercury mobilization are more favourable than for any other of the above-mentioned metals.

In this paper the mobilization of Hg in the Rhine distributaries has been described for the periods 1958-1960 and 1969-1970. The solubilization processes for the other heavy metals were only examined in the sediments collected during 1958-1960. From the fact that the mobilization of Hg in the lower courses of the Rhine distributaries was as effective in recent years as in the preceding period it must not be concluded that the other metals, generally with a lower ability to form complexes than Hg, are still solubilized to an appreciable extent. During the past ten years a drastic change in the organic matter regime of the Rhine sediments took place. As a result of higher N contents of the organic matter (possibly as a result of the rapidly increasing ammonia and nitrate contents of the Rhine water) the breakdown of the organic material in sediments moving to the lower courses of the delta has considerably diminished, leading to a higher content of organic matter in Wadden Sea deposits. This may mean a decreasing ability of mobilization of toxic amounts of heavy metals (except for the extremely mobile Hg) in the estuarine part of the river, thus leading to a certain degree of contamination of Wadden Sea deposits with heavy metals. We refer to the situation in estuaries of tropical rivers, where a complete lack of decomposition of organic matter means a total immobility of the metals (de Groot et al., 1968; de Groot, 1970). The study of the mobility of metals in recent Rhine material has now our full attention.

The mobilization of heavy metals from the suspended matter appears to be associated with the tidal effects in the estuaries and in the open sea. About 10% of the Rhine water, however, flows via the Yssel into the Lake Yssel, without the passage of a tidal area. Moreover, the suspended matter transported by this Rhine distributary does not reach the open sea, but settles within the southern area of the Lake Yssel (fig. 3).

A comparable situation has been created at the end of 1970 by closing the Haringvliet by a dam of the well-known Delta Plan, thus stemming the action of the tides in a second important Rhine distributary.

In the near future our main effort must be focussed on the study of the heavy-metal composition of sediments from these areas: the southern part of Lake Yssel and the original sea inlet stretching from the Haringvliet to the Biesbosch. With our present knowledge we can hardly predict the behaviour of Hg and the other heavy metals in sediments under these unnatural conditions; we suppose, however, that the mobility will decrease considerably.

REFERENCES

Groot, A.J. de (1964) – Origin and transport of mud in coastal waters from the Western Scheldt to the Danish frontier. In: Developments in Sedimentology, Amsterdam, p. 91-103.

—— (1966) – Mobility of trace elements in deltas. Trans. Comm. II and IV, Int. Soc. Soil Sci, Aberdeen, p. 267-279.

Groot, A.J. de, K.H. Zschuppe, M. de Bruin, J.P.W. Houtman and P. Amin Singgih (1968) – Activation analysis applied to sediments from various river deltas. The 1968 Int. Conf. Modern Trends in Activstion Analysis, Gaithersburg (USA), p. 62-71.

Groot, A.J. de (1970) – Geochemisch onderzoek in deltagebieden. Natuurkundige Voordrachten, Nieuwe Reeks, Diligentia 's-Gravenhage, 48, p. 61-75.

Irving, H. and R. Williams (1948) – Order of stability of metal complexes. Nature, 162, p. 746-747.