

ADSORPTION PROCESSES AND HYDRODYNAMIC CONDITIONS IN ESTUARIES

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(Received in final form 20 July 1980)

ABSTRACT

In estuaries the decrease in adsorption of dissolved metals to suspended particulate matter is counteracted by more or less simultaneous increases in turbidity, pH and by the formation of new particulate matter. Experiments on the behaviour of cadmium and zinc under artificial estuarine conditions show that the processes in the region of 0-5 ‰ chlorinity are most important.

1. Introduction

Both physical and chemical processes cause large variations in the concentrations of particulate and dissolved trace metals in estuaries. An important physical process is the mixing of relatively uncontaminated marine sediments with contaminated fluvial sediments, which results in a decrease in metal concentrations in the seaward direction. This process, first suggested for the Elbe estuary¹, has been studied with the aid of natural tracers in the Ems, Rhine and Scheldt estuaries^{2,3}. However, superimposed on the mixing process addition and/or removal processes are taking place^{4,5}. There is strong evidence that removal processes are predominant⁶. One of the processes which may be responsible for the removal of dissolved trace metals is adsorption. From the various field investigations and laboratory studies reported in the literature we conclude that the following variables influence adsorption under estuarine conditions:

- Chlorinity. Adsorption experiments in which both seawater and riverwater were used, showed in general less adsorption in seawater^{7,8,9}.
- Turbidity. The suspended matter concentrations vary in estuaries. Often a turbidity maximum is found^{10,11}, which may extend into the fresh-

water tidal area. It has been found that the amount of suspended matter is a major factor for the removal of dissolved metals from solution 7,12,13.

- pH. The pH varies in a systematic way in estuaries¹⁴. It has been found that the pH is of major importance for the adsorption of trace metals. Generally the adsorption increases sharply over a pH range of a few units. The path of the curve is characteristic for each metal.
- New particulate matter. (e.g. the precipitation of iron and manganese). Studies^{15,16} have shown that iron and manganese hydroxides are scavengers for dissolved trace metals. The flocculation of organic matter¹⁷ may also provide new surfaces for adsorption.

Although many experiments on adsorption to suspended matter have been carried out, few have been done under estuarine conditions. In this communication we report results of our experiments on the adsorption of trace metals under artificial estuarine conditions taking into account the influence of chlorinity, pH, suspended matter concentrations and the formation of new particulate matter. Adsorption experiments have been carried out with radioactive cadmium, zinc, chromium, nickel, copper and arsenic. In order to make the results of the large number of experiments comparable, it was not possible to use one batch of "wet" sediment, due to changes during storage. Therefore, we had to use one batch of freeze-dried Rhine sediment. To determine the influence of freeze-drying on the extent of the adsorption, a number of experiments with both "wet" and freeze-dried sediments were carried out. Although differences in the amount of trace metals removed from solution were observed, these differences (0-20 %) are rather small and do not affect the general conclusions drawn from the experiments.

For the discussion of the relationship between hydrodynamic conditions and adsorption processes, we selected the results for cadmium and zinc.

2. Results

The simultaneous influence of chlorinity and pH on the adsorption is shown in figure 1A. The pH was varied during the experiments by controlling the partial pressure of CO₂. The chlorinity was varied by mixing artificial river- and seawater in the appropriate ratios. Concentrations of cadmium and zinc in the experiments were 5 and 50 µg/l respectively. With an increase in chlorinity the amount of added metal which adsorbs onto the suspended sediment (100 mg/l) decreases; the ratio of dissolved to particulate metal increases. Especially for cadmium an increase in

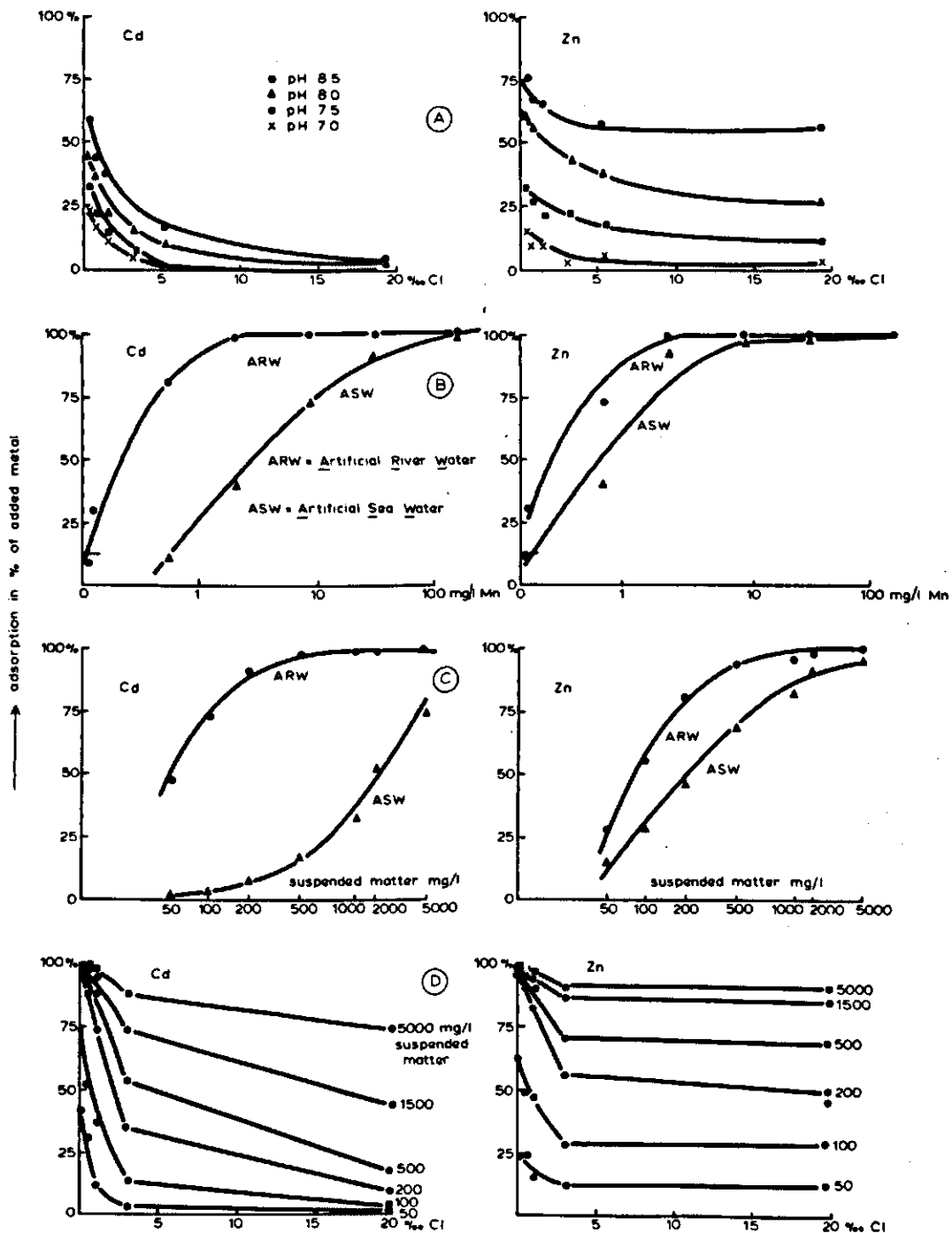


Figure 1. Adsorption of Cd (5 $\mu\text{g/l}$) and Zn (50 $\mu\text{g/l}$) on sediment from the river Rhine.

A. Influence of chlorinity and pH

B. Adsorption on hydrous manganese oxides in ARW and ASW

C. Influence of the suspended matter concentration

D. Influence of chlorinity and suspended matter concentration

chlorinity causes at all pH-values a drastic decrease in the adsorption. With an increase in the pH the adsorption increases.

Figure 1B shows the adsorption of cadmium and zinc on various amounts of precipitated manganese hydroxide suspended in artificial seawater and in riverwater. The pH during the experiment was 7.9 ± 0.3 , similar to estuarine conditions. In riverwater about 0.25 mg/l of precipitated manganese takes up 50 % of the added cadmium (7.7 $\mu\text{g/l}$). In seawater 30 times as much manganese is required to take up the same amount of cadmium. The influence of chlorinity on the adsorption is smaller for zinc as compared with cadmium.

The amount of suspended matter strongly influences the adsorption (figure 1C). In riverwater 50 mg/l of suspended matter is able to adsorb nearly 50 % of the added cadmium ions. In seawater the adsorption of both cadmium and zinc is reduced. To obtain a 50 % removal of the added cadmium, the concentration of suspended matter has to be increased 40 fold to 2000 mg/l. Again the adsorption of zinc is less strongly reduced in seawater compared with cadmium.

In figure 1D the combined influence of chlorinity and suspended matter on the adsorption of cadmium and zinc is shown. Already a small increase in the chlorinity causes a large decrease in the amount of metals removed from solution. Again the decrease is larger for cadmium compared with zinc. Between chlorinities of 3 and 19 ‰, the adsorption of zinc is nearly independent of chlorinity; cadmium shows a further decrease in adsorption.

The question now arises whether the adsorption process is reversible; e.g. are the adsorbed trace metals likely to become desorbed with an increase in chlorinity.

Desorption was studied by adding cadmium and zinc to suspended matter in riverwater. After adsorbing periods of 1, 3, 8, 24 and 60 days, NaCl was added to the suspension to increase the chloride concentrations to 19 ‰. In a parallel experiment NH_4Ac (1 N) was added to the suspension (a common method for determining the amount of exchangeable cations). The amount of desorbed metal ions is different for treatment with either NaCl or with ammoniumacetate, the latter removed more cadmium but less zinc from the suspended matter (table 1). After an adsorption period of only one day, 24 % of the adsorbed cadmium and 60 % of the adsorbed zinc remains bound to the sediment, for NH_4Ac the percentages are 31 and 37 respectively. The amount of non-desorbable metal increases with time;

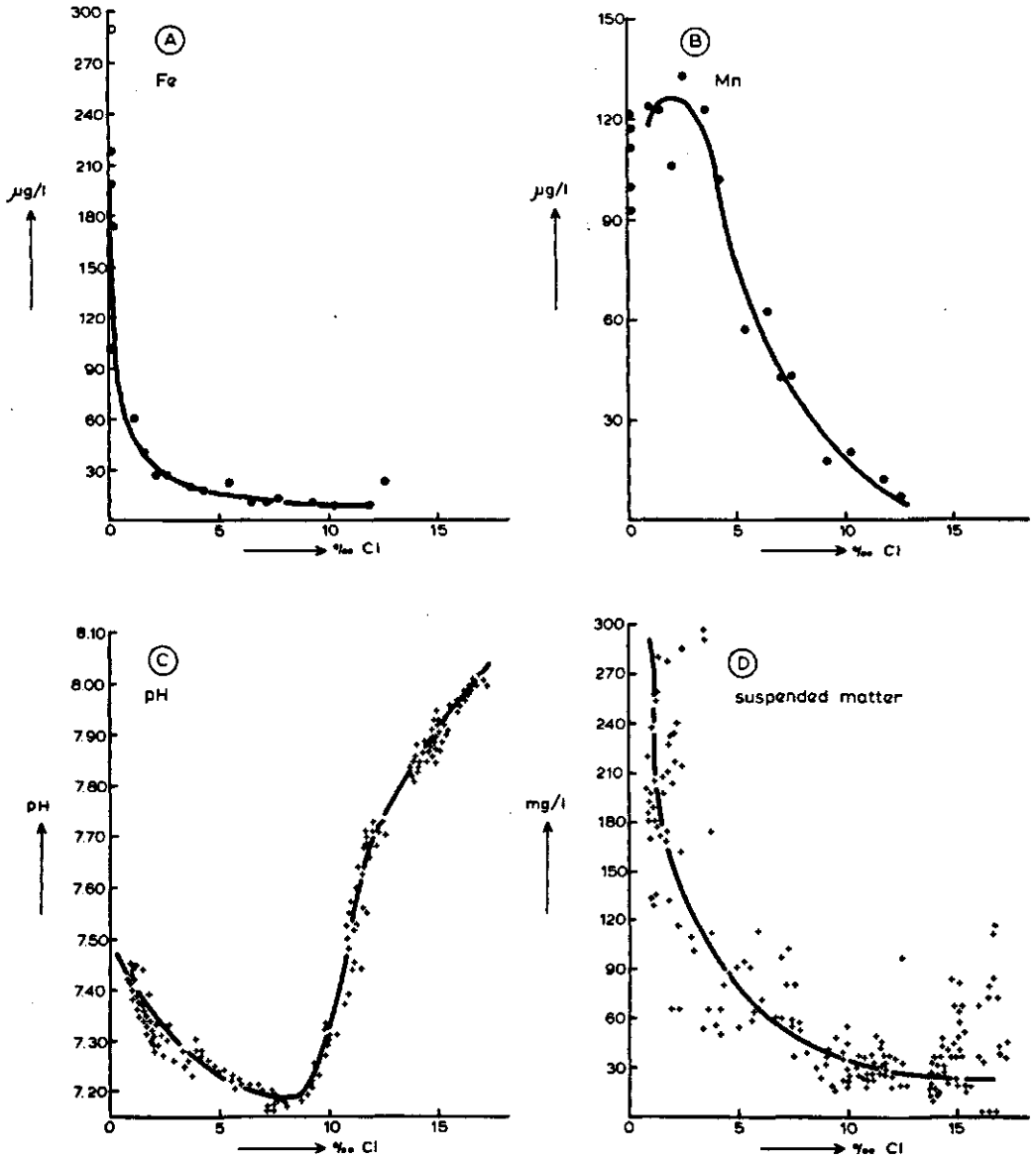


Figure 2. Variables which influence the adsorption in estuaries.

A. Removal of iron (A) and manganese (B) from solution (Ems-
estuary, W-Germany)

B. Changes in pH (C) and suspended matter concentrations (D)
(Scheldt estuary, Belgium).

after 60 days 40 % of the cadmium and 88 % of the zinc bound to the sediment is not released after NaCl treatment. Apparently, the adsorbed zinc and cadmium become more strongly bound to the sediment with increase in time. Similar observations have been reported for the adsorption of cobalt on montmorillonite ¹⁸. A second experiment was performed for the adsorption of cadmium and zinc on suspended matter in seawater. After an adsorption period of one day 24 % of the adsorbed zinc remains bound to the sediment, after an adsorption period of 60 days this increases to 64 %.

Adsorption period	1 day	3 days	8 days	24 days	60 days
<u>NaCl (35 ‰)</u>					
Cadmium	24	30	33	37	40
Zinc	60	67	70	74	88
<u>1N NH₄Ac</u>					
Cadmium	31	36	38	45	52
Zinc	37	42	43	56	75

Table 1. Percentage of cadmium and zinc not released from suspended matter in riverwater after treatment with NaCl or ammoniumacetate.

3. Discussion

If no changes take place in the pH and suspended matter concentrations and if there is no formation of new particulate matter, the adsorption in an estuary will always be smaller compared with the river, due to the increase in chlorinity. However, this will be only the case for a limited number of estuaries. In most estuaries significant changes take place (figure 2). The discussion of the results in relation to conditions in estuaries is facilitated with the aid of figure 3, which shows the major features of water and sediment movement in a stratified estuary. The freshwater discharge generates a residual seaward flow in the upper layer (figure 3). The seawater which is entrained from the lower layer by this flow is compensated by a residual landward flow along the bottom. Since the suspended sediment concentrations near the bottom generally are greater than near the surface this causes a residual landward sediment

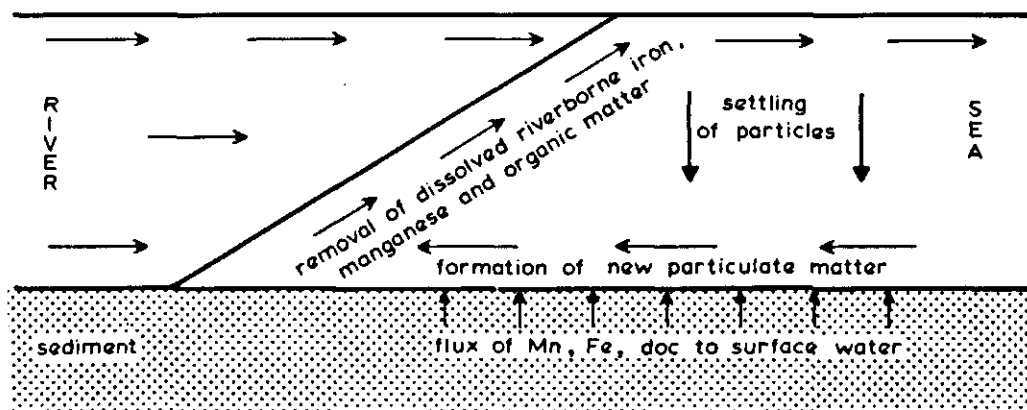


Figure 3. Main features of water and sediment movement and the formation of new particulate matter in a stratified estuary.

transport in the transition region between salt and freshwater. Accumulation of mud occurs until a state of (dynamic) equilibrium is reached between sediment supply along the bottom, removal of silt from the lower layer to the upper layer by mixing, seaward transport in the upper layer and sinking of silt from the upper layer back to the lower layer. The maximum silt concentrations of the water appear to occur at the tip of the salt-water wedge in the estuary (figure 3). The turbidity maximum may extend into the freshwater tidal area ^{10,11}. The recirculation of mud causes a longer residence time for the suspended matter compared with the water: water from the river with its dissolved components is in fact flowing through the turbidity maximum. Dissolved trace metals, therefore, encounter a change in environmental conditions already in the freshwater tidal area. Due to the increase in suspended matter concentration the dissolved metal concentrations decrease to reach a new equilibrium with the suspended matter (figure 1C). When the remaining dissolved metals pass the freshwater boundary, the chloride ions compete with the particulate matter for their complexation. Depending on hydrodynamic conditions (relation between suspended matter concentrations and chlorinity) the decrease in adsorption may be cancelled out by a further increase in suspended matter concentration. To show these effects more clearly, we have superimposed on figure 1D the adsorption caused by a hypothetical turbidity maximum (figure 4). The adsorption of cadmium up to about 5 ‰ chlorinity is larger compared with the river upstream from the turbidity maximum.

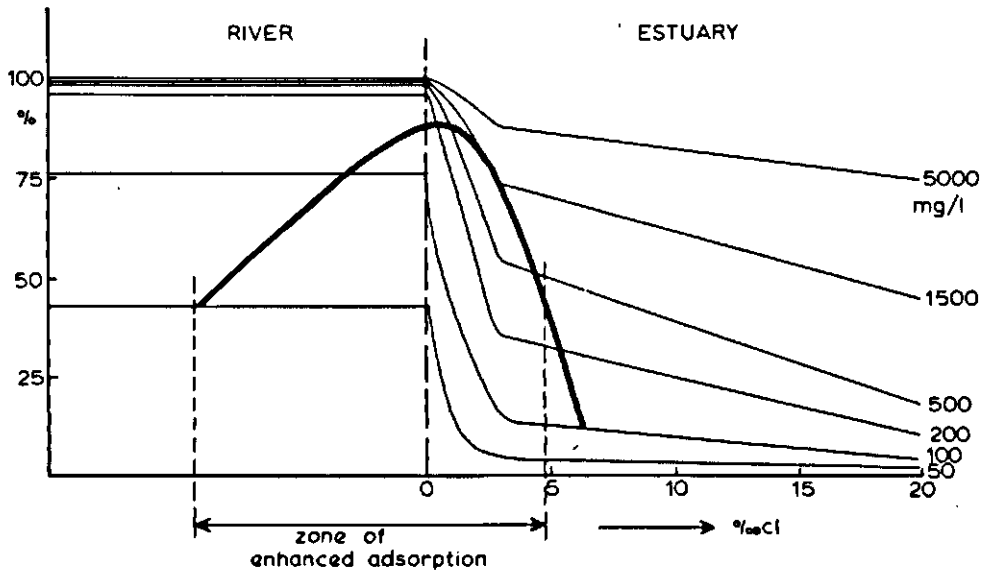


Figure 4. Adsorption (heavy line) caused by a hypothetical turbidity maximum in an estuary.

It is now possible to define a zone of enhanced adsorption: a zone in an estuary in which the adsorption is larger compared with the river upstream from the turbidity maximum. In the freshwater tidal area this zone coincides with the increase in turbidity, however, in the brackish part this zone does not cover completely the area of higher turbidity. Up to now the discussion has been limited to the influence of suspended matter concentrations on the adsorption. But, not all estuaries exhibit a pronounced turbidity maximum, and as was shown above more variables influence the adsorption. It can therefore be concluded that more metals are removed from solution if the formation of new particulate matter is taken into account (e.g. the precipitation of iron and manganese hydroxides and the flocculation of organic matter¹⁷). Sources for these components are the river water and the interstitial waters of the estuarine sediments. Flocculation of organic matter and precipitation of iron and manganese take place at low chlorinities in general. The newly formed particulate matter (or the formation of coatings on the suspended particles) causes additional adsorption sites and therefore an increase in adsorption. Additional sources for new particulate matter are the dissolved components in the pore waters¹⁹. The concentration of iron, manganese and dissolved organic matter are high in pore waters. Typical values for the Rhine estuary, measured over a three year period, vary

between 20-50 mg/l, 2-10 mg/l and 34-60 mg/l respectively²⁰. More important, however, is the flux of dissolved components from the pore waters to the surface waters. Information in this respect has been obtained from a large-scale field experiment conducted in the Rhine estuary. Three large pits (80x30x6 m) have been dug and were filled with fluvial, estuarine and marine sediments. The changes in the composition of the pore waters and the consolidation rate were measured over a period of 600 days. Especially iron concentrations increase rapidly with the onset of reducing conditions but decrease after 50 days (onset of sulfate reduction). Concentrations in the pore waters after 50 days, the period with the highest consolidation rate, were 46 mg/l, 6 mg/l and 31 mg/l for iron, manganese and dissolved organic carbon respectively. This shows that already in freshly deposited material large amounts of dissolved components from the pore waters may enter the surface waters. Apart from consolidation processes, the erosion of bottom deposits by tidal currents results in a release of components from the pore waters. Once the dissolved (reduced) iron and manganese encounter the oxygenrich surface water a reprecipitation takes place²¹. The newly formed particulate matter (or coatings) adsorbs or co-precipitates trace metals. The influence of pH variations on the adsorption is complicated. The small decrease in pH at low chlorinities (figure 2C) causes a decrease in adsorption. This effect, however, is probably cancelled out by the high turbidity and the formation of new particulate metals in the low chlorinity region. At higher chlorinities the increase in pH, causing an increase in the adsorption, is at least for cadmium, cancelled out by the competition of chloride ions for complexation of the cadmium. On the other hand, for zinc the competition by chloride ions is less and in this case the increase in pH may cause a further removal of dissolved zinc from solution.

The estuarine circulation pattern (figure 3) enhances the adsorption by transporting the sinking particles again to the area of low salinity and high turbidity, where the competition with chloride ions for complexation of metal ions is smaller. Additionally, newly formed particles (flux of pore water) may be taken up during the landward bottom transport. Whether adsorption in estuaries causes removal of dissolved trace metals depends not only on the processes in the low-chlorinity region but also on the sedimentation pattern and on the reversibility of the adsorption process. Sedimentation in the zone of enhanced adsorption

means a permanent removal of the adsorbed metals from the estuarine system. However, part of the suspended matter may not be deposited and may escape the estuarine circulation pattern. In this case a partial desorption may take place (table 1). A long residence time of the suspended matter, however, favours the fixation of the trace metals.

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