METAL INTERACTIONS WITH ORGANIC SOLIDS IN ESTUARINE WATERS - EXPERIMENTS ON THE COMBINED EFFECTS OF SALINITY AND ORGANIC CHELATORS

U. Förstner*, W. Ahlf*, W. Calmano* and C. Sellhorn*

ABSTRACT

In order to estimate the possible influence of nitrilotriacetic acid (NTA) on the sorption of metals in the estuarine environment (Hamburg Hr./ Elbe River Estuary as a critical example containing strongly polluted sediments) laboratory experiments were performed using an organic substrate, which was prepared from cell walls of the algae Scenedesmus quadricauda. While the concentration of sodium chloride, calcium chloride and magnesium chloride exhibits relative small effects on the sorption of copper, lead and zinc, a significant influence was measured for the sorption edges of cadmium and silver. For cadmium the combination of salinity and NTA affects lower sorption rates than does either one of both factors. On the other hand, the data for lead and copper indicate that with increasing salinity the mobilizing effect of higher NTA-concentrations is counteracted by the increase of calcium and magnesium. These findings suggest complex competition between various organic and inorganic ligands in the different stages of estuarine mixing affecting metal interactions with particulate matter.

INTRODUCTION

River-borne metals entering the estuarine environment can be affected by changes in the pH ($< 7.2 - 8.1$), chlorinity, the turbidity maximum and the formation of new particulate matter (ref 1). While the removal of iron and in some estuaries manganese at low salinities is well established (ref 2) release of metals from particulate matter has been reported from Scheldt Estuary (ref 3), Savannah/Ogeechee Estuaries (ref 4), Weser Estuary (ref 5), Elbe Estuary (ref 6) and Gironde Estuary (ref 7) and has been interpreted by intensive breakdown of organic matter, complexation with chloride ions, or by competition with calcium and magnesium ions for sorption sites.

It seems that natural dissolved organic matter, such as humic material or amino acids, present usually in inland waters and in the sea, is insufficient to make any significant contribution to the speciation of dissolved Cd, Pb or Zn (ref 8); only the distribution of Cu species as affected markedly by natural organic chelators (ref 9). Significant effects, however, on most heavy metals can be expected in inland waters from strong synthetic chelators, such as nitrilotriacetic acid (NTA), which is used in some countries already in detergents to substitute polyphosphates. In the actual discussion on the introduction of NTA into detergents for the West Germany market major emphasis has been given to the possible implications with river sediments strongly polluted with heavy metals (ref 10). For seawater conditions, it is expected that dilution effects and - in particular - competition of the alkaline earth ions Ca and Mg should reduce the concentrations of heavy-metal complexes with NTA or EDTA (ref 11).

*Environmental Protection Technique Division, Hamburg-Harburg Technical University, Eissendorfer Strasse 38, P.O.Box 90 14 03, D-2100 Hamburg 90, F.R.Germany.

However, in the critical example of Hamburg Harbour, significant re-mobilization of nickel and copper was observed from sediments at NTA-concentrations as low as 100 µg/l (ref 12). It has been argued that this situation might be particularly unfavourable, because (i) a large portion of the waste water effluents in the Hamburg area is still insufficiently treated; (ii) the sediments of the harbour area are strongly enriched in heavy metals from both upstream and local sources; (iii) considerable pro-portions of polluted sediments are deposited in the tidal section of the Elbe River as the stream is broadening (this effect causes large problems from dredged sediments but is beneficial for the German Bight of south-eastern North Sea). If there would exist a mechanism to mobilize metals from the harbour sediments, these components could escape into the lower estuary and eventually into the North Sea.

METHODS

In the present work, the combined effect of salinity and strong or-ganic chelators on the mobilization of characteristic heavy metals (zinc, lead, cadmium, copper and silver) from an organic substrate has been stu-died. We have used cell walls of the algae Scenedesmus quadricauda; to remove the plasma contents the algae were heated with KOH-solutions and later extracted with ethanol. These materials have previously been ap-plied to estimate the possible influences of NTA on the sorption of trace metals in sewage treatment plants and in freshwater systems (ref 13).

Cell walls have a high anionic charge density and consequently are strongly interacting with the electropositive metal ions dissolved in the environment to accumulate large quantities of bound metals (ref 14). An-other advantage of this procedure was that the application of the cell walls of Scenedesmus quadricauda for the first time enabled the quanti-tative recovery and analysis of the organic solid matter in such experi-ments.

The experiments on different pH-conditions/NTA-concentrations were performed with ~ 90 mg/l cell wall suspensions; the effect of salinity was studied on suspensions containing 100 mg/l of cell wall material.

RESULTS

(a) pH/salinity dependencies

pH-values are variable to some extent during estuarine mixing – in the example of Scheldt Estuary (ref 3) values were measured from pH 7.5 in the river water via pH 7.2 at ~15‰ salinity to pH 8.1 in seawater. Initial adsorption experiments at different pH-values with distilled water have been performed primarily to estimate the relative binding strength of the individual metal examples with the organic substrate (Figure 1). Here, however, one has to take into account that the adsorbent concentration sig-nificantly affects the position of the "adsorption edges" (ref 15); there-fore, additional experiments will be undertaken on different concentrations of cell walls in suspension. According to the data in Figure 1 adsorption of Cu, Pb, Cd and Zn takes place within a narrow pH-interval, whereas the curve of silver covers a broad section between pH 2 (30% adsorbed) to pH 7 (100% adsorption); the different behaviour of the metal pair Zn/Cd (higher mobility) and Cu/Pb (relatively immobile under normal pH-conditions) has been observed from natural sediments and soils (ref 16) and mono-mineralic substrates (refs 17 and 18).

Figure 2 shows that the influence of increasing concentrations of dis-solved salts is relatively small for the sorption of Cu (Pb, Zn), whereas adsorption of Cd and Ag is strongly affected (see section DISCUSSION).
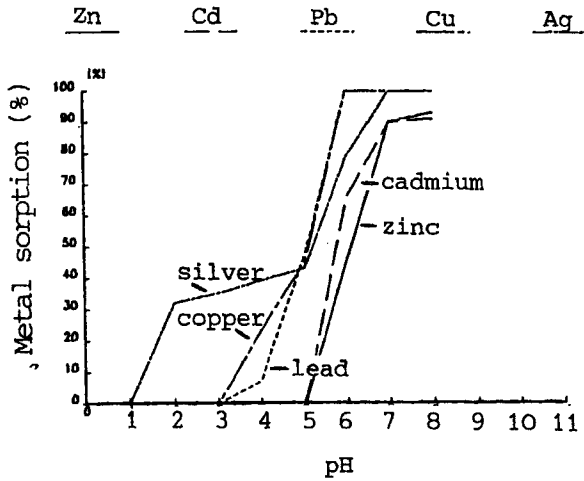
Sorption of Heavy Metals on Algal Cell Walls

Zn   Cd   Pb   Cu   Ag

Figure 1

Adsorption experiments at different pH-values with distilled water. pH-values were adjusted with HCl and NaOH.
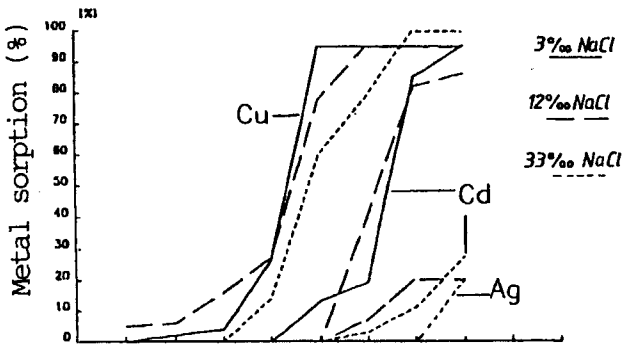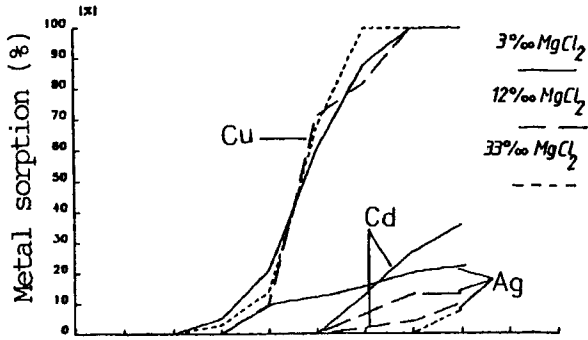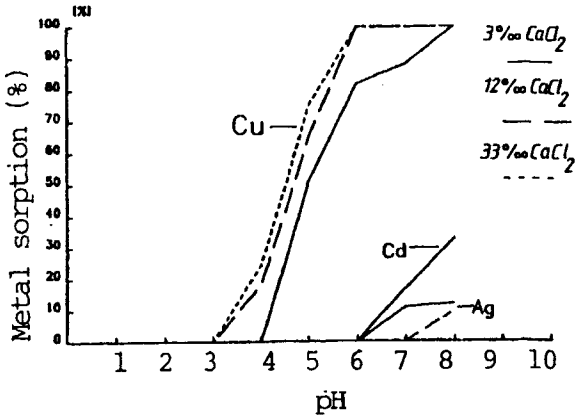

Figure 2a

Figure 2b

Figure 2c

(b) pH/NTA-dependencies

The pH-conditions were adjusted with additions of NaOH and HCl, respectively, to distilled water; during the shaking period (24 hrs) the original pH-conditions (pH 6 and pH 8) shiftet towards the neutral point, i. e. from pH 6 to pH 6.8-7.0, and from pH 8 to pH 7.9-7.7. In Figure 3 the data for the two experimental sets were given for the NTA-concentrations of O.O mg/l, O.3, 1, 3, and 10 mg/l. At pH 7 there is a similar decrease of metal sorption for all metal examples from 70-95% sorption at O mg/l NTA to less than 20% at 3 mg/l NTA. At pH 8 two different developments can be distinguished: While the decrease of metal sorption for cadmium and zinc is similar to that in the pH 7 experiment, the reduction of sorption for copper and lead is much lower at higher NTA-concentrations, and approx. 50% of the original metal contents in solution is still adsorbed onto the cell wall material at NTA-concentrations of 10 mg/l for copper and lead.

(c) Salinity/NTA-dependencies

In Figure 4 the data of the combined effects of increasing salinity (natural river water and estuarine water as mixture of artificial seawater with distilled water) and increasing NTA concentrations were summarized for the metal examples cadmium (Fig. 4a), lead (Fig. 4b), copper (Fig. 4c) and zinc (Fig. 4d). The data for Cd indicate that the combination of NTA and salinity affects lower sorption rates for this metal than either one of both factors. On the other hand, the values for lead show that with increasing salinities the mobilizing effect of higher NTA-concentrations is clearly counteracted. This is valid to some extent also for copper; The "anormal" behaviour of the river water system is possibly related to the presence of other chelating components, which would particularly affect this element (see above). Widely unexpected is the development of the zinc-curves, where with the increase of salinity in the lower salinity range there is a characteristic increase of Zn-sorption (as for Pb and Cu); however with 10‰ salinity the sorption rates are again reduced.

DISCUSSION

The sorption of metals on sediments is complicated because the various organic and inorganic ligands in solution and the various components in the the sediments all compete for complexation of the trace metals. To simplify the system with the substrate factor, we have used cell walls as a well-defined organic sorbent. With regard to competing ligands in solution, two situations can be envisaged (ref 19):

- The complexing ligand (for instance: chloride) is not adsorbed onto the sedimentary components, and thus it competes with surfaces for coordination of the metal ion. Increased concentration of the ligand causes a decrease in adsorption as exemplified for cadmium with a chlorinity increase in estuaries (note effect of suspended matter; ref 3).

- The complexing ligand is adsorbed onto surfaces. If this is the case, the adsorption of metal ions can be significantly enhanced. This is the case for EDTA (ref 19) and NTA (ref 20); the latter study (ref 20) has shown this effect at lower pH-values. In this way the speciation of trace metals in solution determines the particulate metal speciation.

Our experiments have shown considerable differences between the individual metal examples. In this respect, the effect of salinity on metal speciation can be estimated in a first approximation by the comparison of the respective stability constants for hydroxide and chloride complexes (ref 21). Silver and cadmium form relative stable chloro-complexes, while hydrolysis is enhanced for zinc, lead and copper; the respective chloro-complexes are particularly weak for the latter metals.
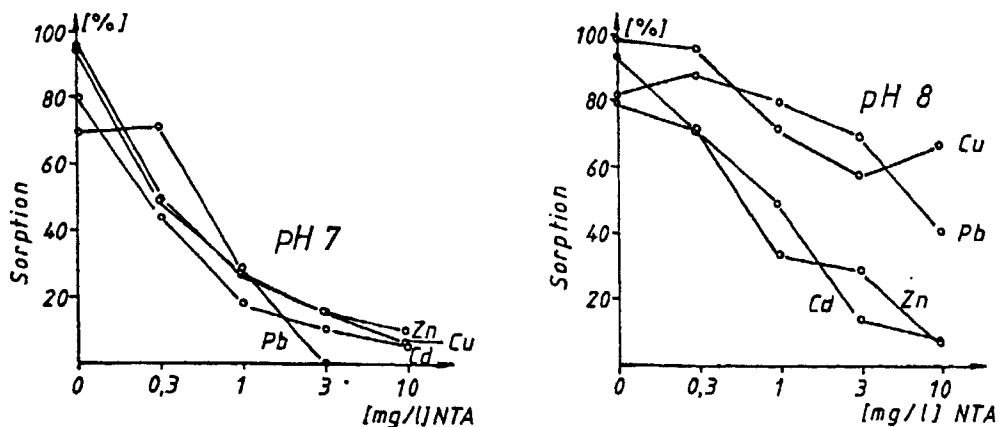
Figure 3

Adsorption of cadmium, zinc, lead and copper on cell walls at different
NTA-concentrations (0, 0.3, 1, 3, 10 mg/l NTA) for pH-values of approxi-
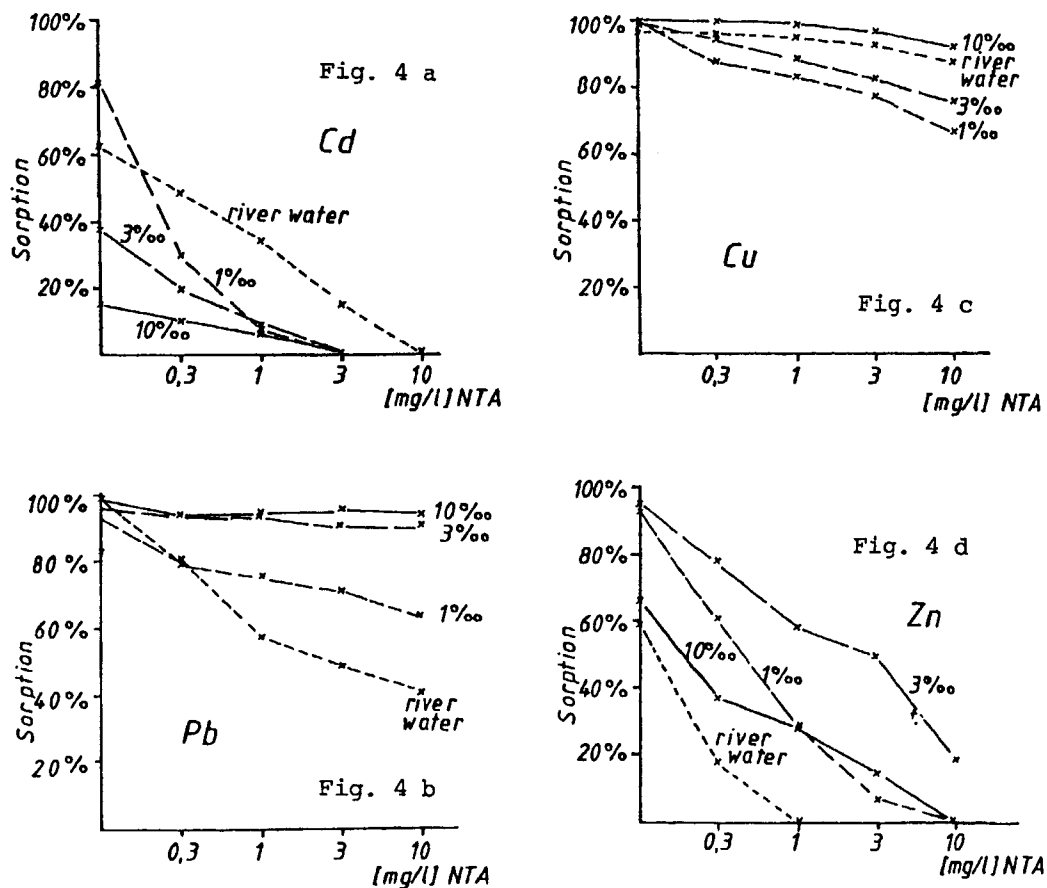mately 7 and 8, resp.

Figure 4

Effect of different salinities (river water; 1 permil, 3 permil and 10
permil salinity) and different NTA-concentrations (0, 0.3, 1, 3, 10 mg/l
NTA) on the sorption of cadmium (Fig. 4a), lead (Fig 4b), copper (Fig. 4c)
and zinc (Fig. 4d). Original solutions contained 100 µg/l.

It has been suggested by Millward & Moore (ref 22) from adsorption experiments on iron hydroxides that even more significant effects would arise from the earth alkaline cations in seawater. While adsorption isotherms of copper were found to behave independently from salinity, those for zinc indicated an increase in the pH of the adsorption "edge" with increase in salinity (reflecting reduced sorption strength of the metal onto the solid). This is confirmed from our data in Figure 2, where the cations Na, Mg and Ca in different concentrations are only insignificantly affecting sorption of copper onto the cell wall material, whereas adsorption of cadmium (and silver) is characteristically influences by higher salt contents, in particular, by the earth alkaline cations.

With the introduction of NTA (Figure 4), a strongly chelating agent, into the system, calcium and magnesium will play a major role in displacing heavy metals in their NTA-complexes at higher salinities. The "free" metal ions may either hydrolize to become increasingly adsorbed onto the solid substrate, such as for the examples of copper and lead, or may form chloro-complexes, of which at least the negatively charged species are preferentially kept in solution, such as for cadmium (e.g. $CdCl_3^-$). The behaviour of zinc lies between these two extremes and may be affected by the interrelations between chloride/NTA-competition and concentrations of cations, mainly of alkaline earth metals (Figure 4 d).

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