

BIOGEOCHEMICAL STUDIES ON THE DISTRIBUTION OF HEAVY METALS IN THE ELBE ESTUARY

Wolfgang Ahlf, Wolfgang Calmano and Ulrich Förstner

Arbeitsbereich Umweltschutztechnik, TUHH Hamburg-Harburg,
Eissendorferstr. 40, D-2100 Hamburg 90, FRG

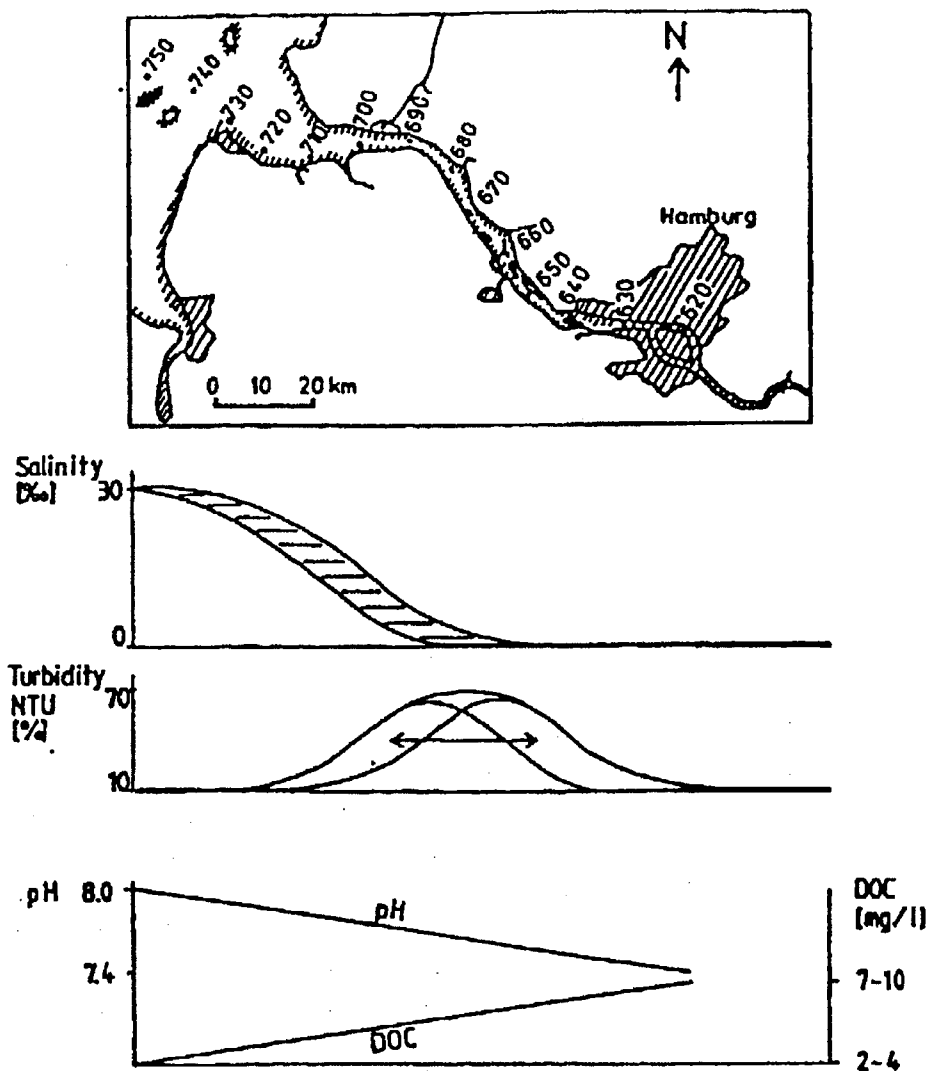
Introduction

The mixing of riverwater and seawater in an estuary is accompanied by a large number of biogeochemical and physical processes which change the distribution, partitioning and bioavailability of contaminants. Superimposed on this physical mixing process, removal or release processes from the particulates may take place, which cause deviations from the theoretical mixing curve between dissolved metal ions and salinity. Seasonal fluctuations and year-to-year variations in concentrations of trace metals must be considered in characterizing the importance of biogeochemical processes for the distribution of anthropogenic metals in estuaries. We undertook the present study to interpret the time and space variability of metal concentrations within the Elbe estuary and its relationship with physical and biogeochemical processes of metal distribution. The data also provided information on the role of particulate components in the distribution process.

The Study Area

The Elbe is the largest German tidal river. The watershed is 1143 km in length and the catchment area is 148.500 km². The annual mean discharge is 800 m³/s. A weir divides the 973 km, tideless river, from the 170 km long tidal Elbe. The Elbe estuary is a coastal plain estuary and has the characteristics of a moderately layered estuary. The salt wedge front is situated between river km 670 and 700, depending on the water discharge from upstream catchment area. We focused our attention on the area below Hamburg where the impact due to urban and industrial contaminants is very

Fig. 1. Schematic diagram of the variations of typical parameters in a longitudinal section of the tidal Elbe River (Forstner et al., 1989).



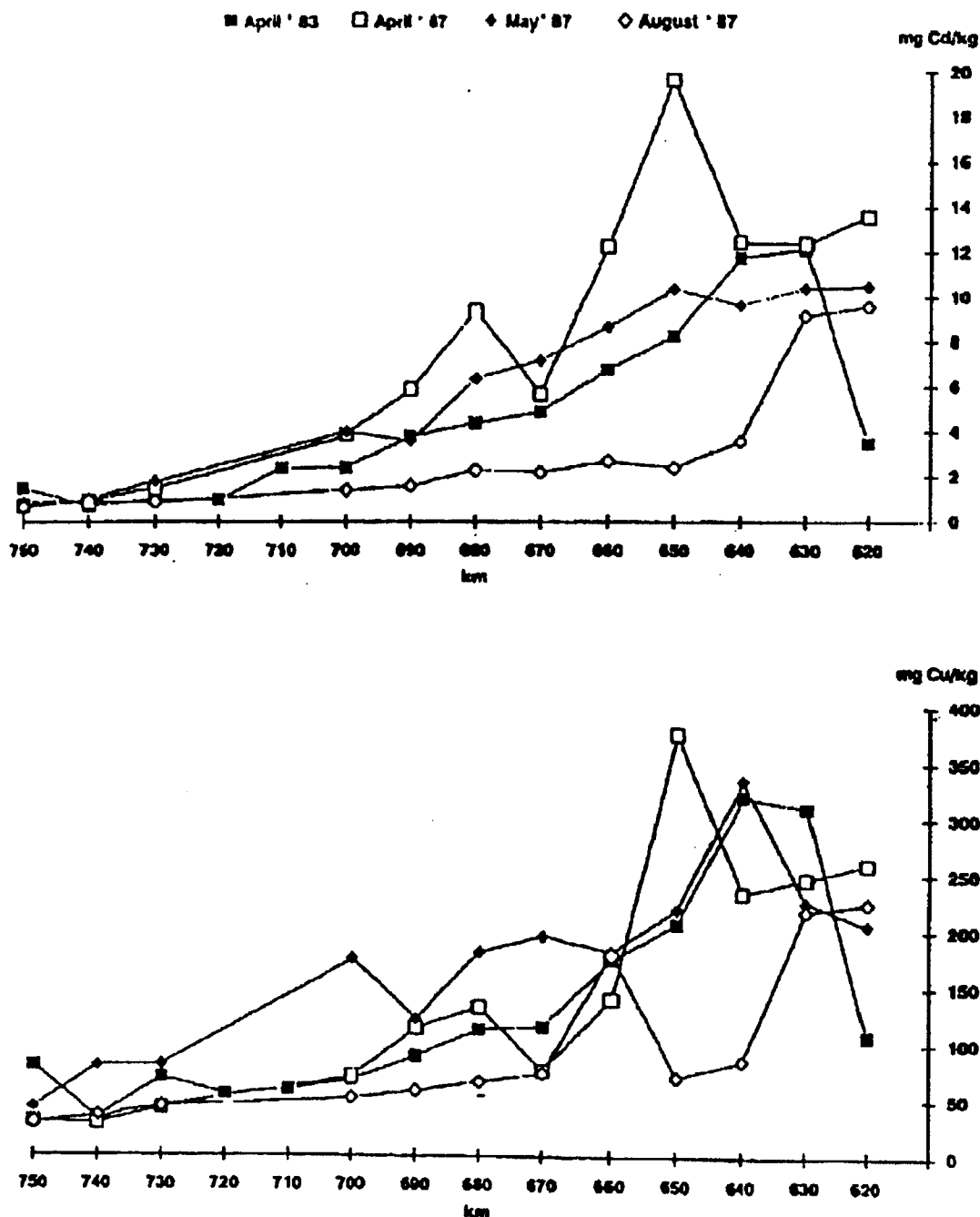
marked. Fig.1 is a schematic diagram of the variations of typical parameters in this longitudinal section of the tidal Elbe River. The position of the salinity gradient and dependent parameters, such as turbidity, are predominantly determined by water discharge. pH varies between 7.4 and 8.1; and dissolved organic carbon (DOC) concentrations vary between 7-10 and 2-4 mg/l.

Results and Discussion

Field Studies

Estuaries are inherently variable. Spatial variation of heavy metal distribution in the Elbe river resulted in a metal content decrease towards the

Fig. 2. Concentrations of Cd and Cu in suspended matter (mg /kg dry weight).



sea as a rough description for suspended matter (Fig. 2). The data are summarized from different publications (Ahlf, 1983; Ahlf & Wellershaus, 1984; ARGE-Elbe, 1988).

The distinct decrease of metal concentrations in sediment samples downstream from Hamburg, when the estuary is widening, was subject to additional investigations. A joint study by the GKSS Research

Centre Geesthacht, Delft Hydraulics Laboratory and the Technical University of Hamburg-Harburg (Salomons et al., 1987; Schwedhelm et al., 1988) have been performed in order to prove the mixing theory, which postulated a mixing of highly polluted river sediments with still relatively clean marine sediments. Different natural tracers were used for the determination of the origin of particulate matter from the Elbe estuary. Here is only the clay mineral composition presented, which seemed to be promising a good indicator, because the smectite concentrations in the sediments of the inner German Bight are higher and the kaolinite concentrations are minor compared to the ones in the sediments of different middle European rivers (Schwedhelm, 1984). In Fig. 3 longitudinal profiles of heavy metal concentrations in the sediment fraction $< 2 \mu\text{m}$ related to 100% at the location upstream of Hamburg are presented together with the smectite:kaolinite ratio as natural trace indicator for limnic or marine sediment material.

Fig. 3. Summary of the results showing the clay-ratio in relationship to the heavy metal decrease in sediments

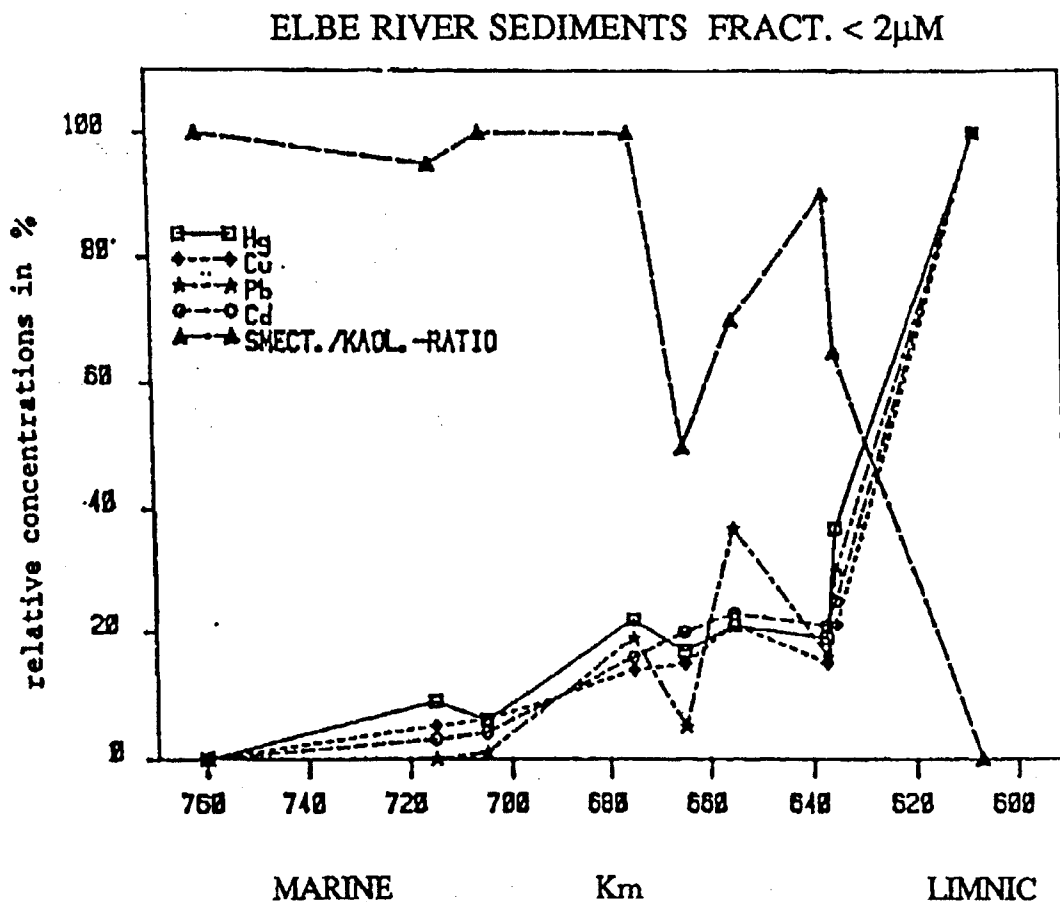
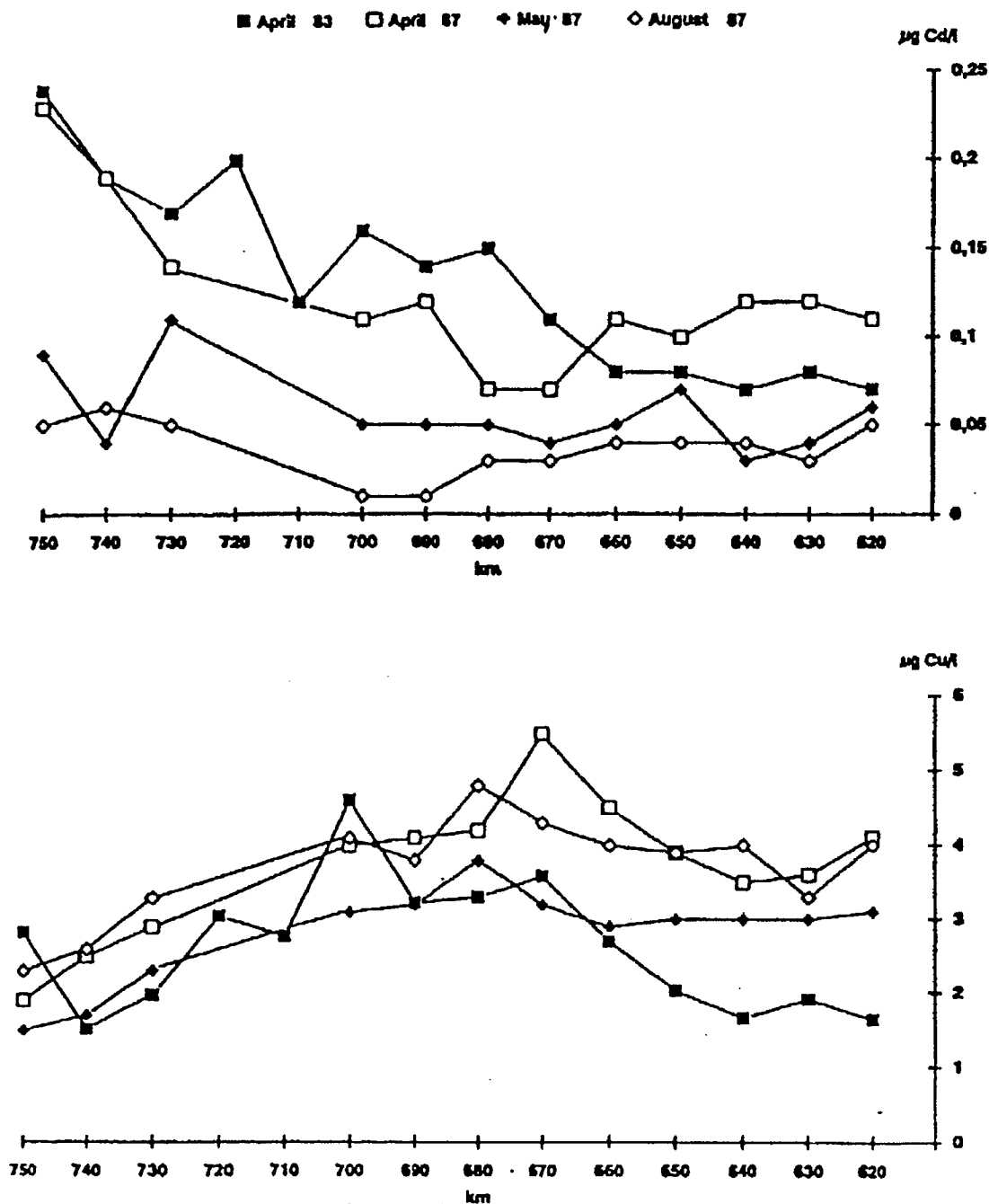


Fig. 4. Dissolved concentrations of Cd and Cu in the Elbe estuary



The typical decrease in the heavy metal concentrations, which is similar for Hg, Cu, Pb, and Cd clearly suggests a uniform process, in that it corresponds with an increase in the natural tracer parameter, quantifying the part of marine-borne material which dilutes the contaminated limnic material far upstream of the salinity gradient. The mixing process was also demonstrated with suspended matter. However, it does not explain the seasonal variations. There are many indications, that, for the understanding of natural situations, it is necessary to consider time series and estimate the

degree of variability. In an additional investigation aimed at the origin of the heavy metal gradients, temporal variations of the suspended matter composition were measured near Hamburg harbour (Irmer et al., 1988). Since the interest is focussed on the fine-grained material, which can both be transported over longer distances and exhibits higher concentrations of persistent pollutants such as heavy metals, samples were collected (bi-weekly from March to November 1985) at slack-water time during the ebb-tide. The authors concluded, that there was a significant positive correlation between suspended matter and phytoplankton and a significant negative correlation of Cd in suspended matter and amounts of suspended matter, which means a "dilution effect" induced by phytoplankton. These findings explain the low concentrations of Cd in suspended matter in August 1987 (Fig. 2). Variations on different temporal scales are on the one hand surprisingly uniform, on the other hand there is a marked difference between summer and winter concentrations of Cd in the dissolved phase (Fig. 4).

From field investigations, indication on metal release has only been given from the increase of dissolved cadmium concentrations near the salinity gradient. This effect can be explained by the formation of relative stable soluble chloro-complexes with Cd and competition of earth alkali ions Mg and Ca for sorption sites on solid substrates. However, in summer a "suspended solid effect" could reverse the solid/solution equilibria by sorption processes. In order to look closer to this process, we carried out an experimental study in laboratory.

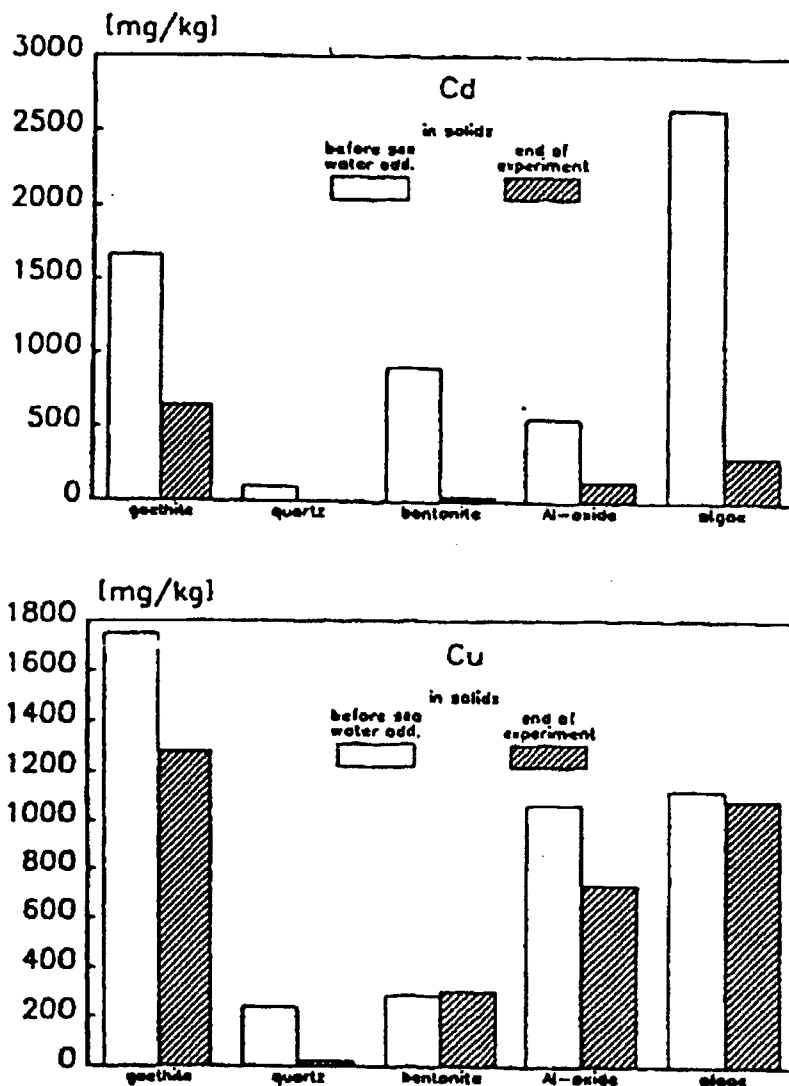
Laboratory Studies

The sorption/desorption of heavy metals should be confirmed by analyses of the particulate components. It seemed to be favourable to keep the individual components of suspended matter separated to study the competition between the different sedimentary phases.

The system we used is a multi-chamber device in which membranes of 0.45 μm pore diameter separated the solid components, but allowed the transfer of dissolved elements (Calmano et al., 1988). The device was filled with algal cell walls, bentonite (a clay mineral with high ion exchange capacity), Al-oxide (neutral, 400 mesh) or Mn-oxide, goethite (synthetically made), and quartz powder. Figure 5 show the sorption of Cd and Cu on the sediment components. We found a strong affinity of Cd to algal cell walls. If we altered the ionic strength of the medium by adding salts which corresponded to the composition of sea water, desorption of heavy metal occurred (Fig. 5.)

Cd is clearly remobilized from all components. Displacement of sorbed Cd ions by cation competition and formation of dissolved Cd-chloro complexes may be the main reasons for observed mobilization, which

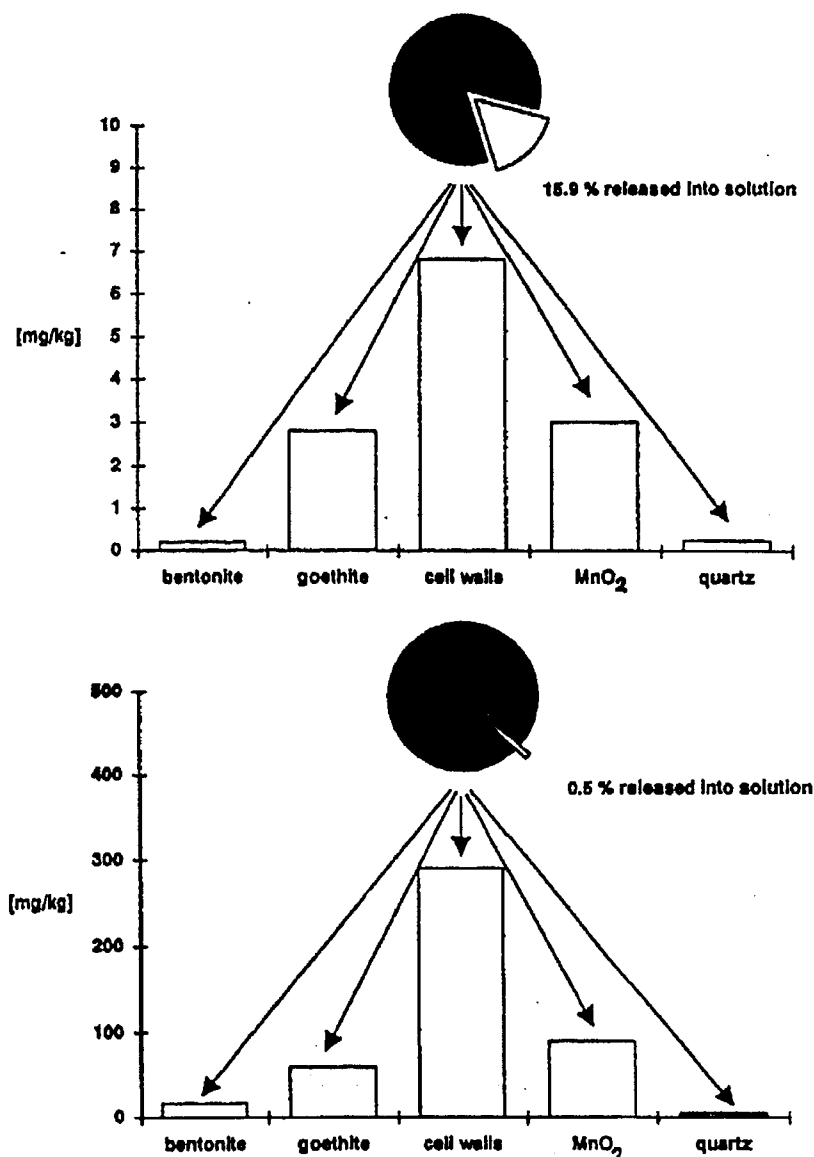
Fig. 5. Sorption and desorption of Cd and Cu before and after addition of seawater



corresponds to the observed field data. For Cu only small amounts were desorbed and nearly no remobilization could be found on algal cell walls. This metal forms very stable chelating complex compounds on organic surfaces. The strong binding intensity of Cu with organic material explains the conservative behaviour in the Elbe estuary.

In an additional experiment we simulated the resuspension of sediment from Hamburg harbour into sea water. In the presence of the uncontaminated sedimentary phases re-adsorption was demonstrated (Fig. 6). About 16 % of total Cd from the sediment is remobilized and found in solution, the mobilized part of Cu is > 1 percent. Algal cell walls were the

Fig. 6. Mobilization of Cd and Cu from sediment and re-adsorption on different model sediment components in artificial sea water



most important sorption sites for Cd and Cu in this model system, though sorption takes place also on the other components.

Re-adsorption may occur for metal species whose strength of binding to model components exceeds their strength of binding to suspended material. This may occur in nature at times with high organic content in suspended particulate matter, e. g. in summer. Therefore the dissolved concentrations of Cd in summer are decreased in comparison with winter data and the laboratory studies confirmed the interpretation of seasonal variations of Cd distribution in the Elbe estuary.

Acknowledgements

Financial assistance by the German Research Council and cooperation in the framework of the "Sonderforschungsbereich 327" is gratefully acknowledged.

References

- Ahlf W. (1983). The River Elbe: behaviour of Cd and Zn during estuarine mixing. *Environ. Technol. Lett.*, 4: 405-410.
- Ahlf W. and Wellershaus S. (1984). Trace metals in the Elbe River Estuary. *Proc. Conf. Sediment and Water Interactions, Geneve*, 257-260.
- ARGE-Elbe (1988). Wassergutedaten der Elbe.
- Calmano W., Ahlf W. and Forstner U. (1988). Study of metal sorption/desorption processes on competing sediment components with a multi-chamber device. *Environ. Geol. Water Sci.*, 11: 77-84.
- Forstner, U., Ahlf, W. and Calmano, W. (1989). Studies on the transfer of heavy metals between sedimentary phases with a multi-chamber-device: combined effects of salinity and redox variation. *Mar. Chem.*, 28: 145-158.
- Irmer U., Knauth H.-D. and Weiler K. (1988). Influence of suspended particulate matter regime on the heavy metal pollution of the tidal river Elbe at Hamburg. *Z. Wasser-Abwasser-Forsch.* 21: 236-240.
- Salomons W., Schwedhelm E., Schoer J. and Knauth H.-D. (1987). Natural tracers to determine the origin of sediments and suspended matter from the Elbe estuary. *Proc. Conf. Coastal and Estuarine Pollution, Fukuoka*, 119-132.
- Schwedhelm E. (1984). Schermetalle-Bioelemente in den Nordseewatten und der Jadeund die Tonmineralverteilung in den Sedimenten der südlichsten Nordsee. diss. Univ. Heidelberg. 177p.
- Schwedhelm E., Salomons W., Schoer J. and Knauth H.-D. (1988). Provenance of the sediments and the suspended matter of the Elbe estuary. GKSS, 76p.