Mobilization of pollutants from river sediments

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1   Mobility of contaminants

In the surface layer of riverbank sediments, contaminants accumulate in the interstitial water and may be released by changing hydrological, biological, and hydrochemical conditions. The present study examines interstitial waters and river sediments using the River Odra as example to quantify the non-point inputs of priority contaminants.

In previous studies, increased levels were observed in pore-waters [Müller & Heininger 1996; Müller et al. 2002]; results on the relations between concentrations in surface waters and in sediments depend on several conditions. The results of these studies gave information about the priority pollutants according to HELCOM [HELCOM 1998]. With regard to the quality of the surface water, the release potential of sediments and the different sources of mobilized contaminants are of interest.

For the analysis of material fluxes in ecological systems, it is decisive which releases are to be reckoned with in the case of hydrological extreme situations in order to quantify non-point contributions of pollutants.

The study is focused on organic fine-grain sediments which show higher concentrations of nutrients and contaminants in the interstitial water.

In dependence on the buffering capacity of the sediments, anaerobic decomposition of organic carbon into organic acids lowers the pH from 8 to 6 or even lower;

2 Area and methods

Generally, Odra sediments, which were analyzed in 37 samples from three example areas - the headwaters, the region around Glogow, and the area near Widuchowa downstream of the inflow of the River Warta [Müller et al. 2002] - showed different elution behaviour regarding P and N compounds and toxic elements in dependence on the method applied. Usually, the heavy metal portion that can be mobilized is determined according to the German Standard DIN [DEV 2000] to decide on the usability of dredged sediment material. As the mobility of metals depends strongly on the matrix of the sediment or the solids, it is reasonable to compare the results of several elution methods.

In dependence on the buffering capacity of the sediments, anaerobic decomposition of organic carbon into organic acids lowers the pH from 8 to 6 or even lower, associated with the mobilization of contaminants such as trace metals [Paschke et al. 1999]. For this reason, the pH-stat method [Obermann & Cremer 1992] is used additionally. For the standard elution analyses, the DEV 2000 is used applying supra pur water and surface water from the sampling site as elution agents.

3 Results

The results correspond to the situation in three example areas in 1999 and 2000 using averaged values with regard to each river reach. The data basis consists of 37 samples.
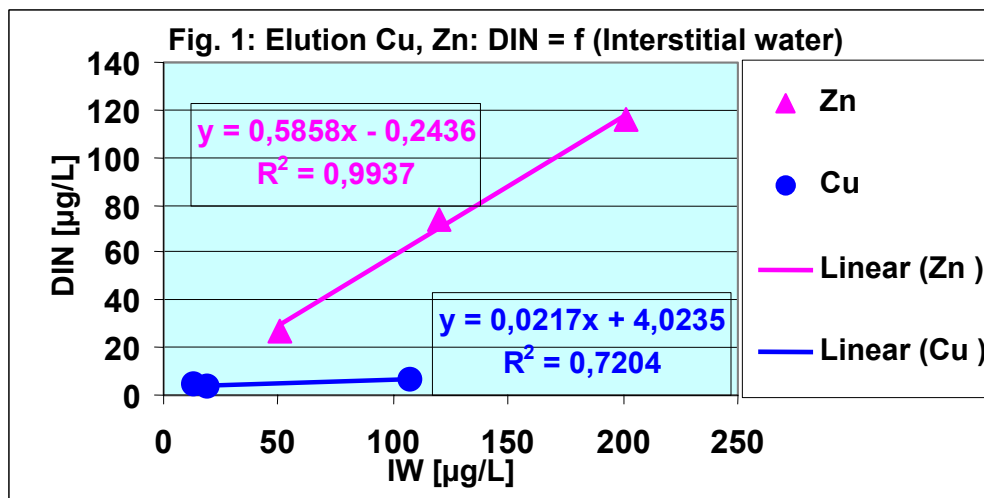
3.1 Relation between surface water and interstitial water

Generally, the nitrogen content in the interstitial waters is around 2-4 times higher than in the surface water at same site. On the other hand, the phosphorus contents in interstitial and surface waters were similar.

For the majority of elements, linear functions between surface water and pore water could be calculated with coefficients of determination above 0.8 and sensitivity factors between 0.4 (Zn, Ni), 2-7 (Hg, Cu) and 29 (As).
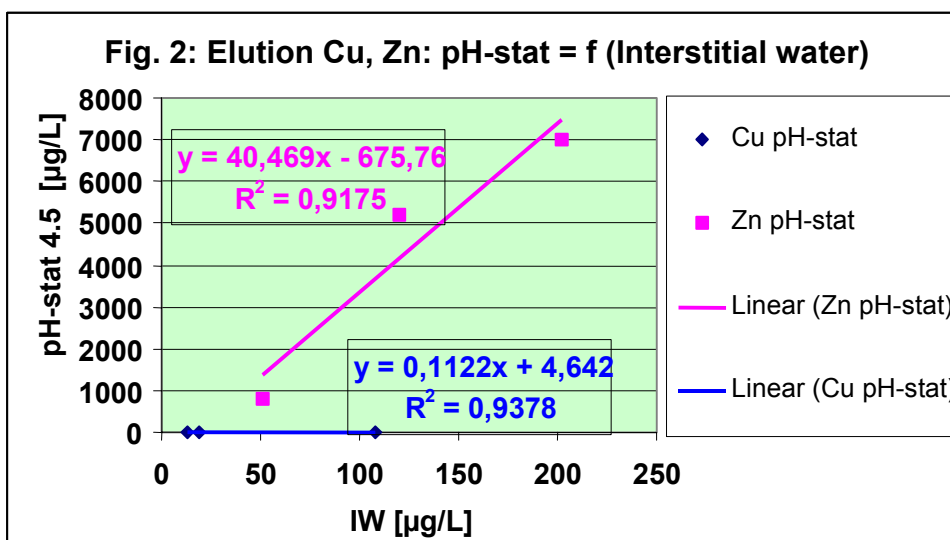
3.2 Relation of concentrations found by elution according to DIN and in interstitial water

The relation between the elution concentration according to DIN and the pore-water concentration shows for the elements functions with a coefficient of determination above 0.7. However, the sensitivity factors vary between 0.02 for Cu and 0.9 for Ni (ref. Fig. 1).

Fig. 1: Elution Cu, Zn: DIN = f (Interstitial water)

$y = 0{,}5858x - 0{,}2436$
$R^2 = 0{,}9937$

$y = 0{,}0217x + 4{,}0235$
$R^2 = 0{,}7204$

3.3 Relation of concentrations found by elution according to pH-stat and in interstitial water

The consideration of the relation between pH-stat concentrations and interstitial-water concentrations yielded coefficients of determination above 0.8 for the elements and nutrients, with factors between 0.002 for P and 40 for Zn (cf. Fig. 2).

Fig. 2: Elution Cu, Zn: pH-stat = f (Interstitial water)

$y = 40{,}469x - 675{,}76$
$R^2 = 0{,}9175$

$y = 0{,}1122x + 4{,}642$
$R^2 = 0{,}9378$

3.4 Relation of concentrations found by elution according to DIN and pH-stat

The relation between the DIN and the pH-stat method was estimated for the priority contaminants with a coefficient of determination above 0.8. In Fig. 3 examples are presented for Zn and Cu. An exception from this general relation is phosphorous, where the pH-stat method is disturbed due to precipitation effects by metal cations forming metal phosphates.

Fig. 3: Elution Cu, Zn : pH-stat = f (DIN)
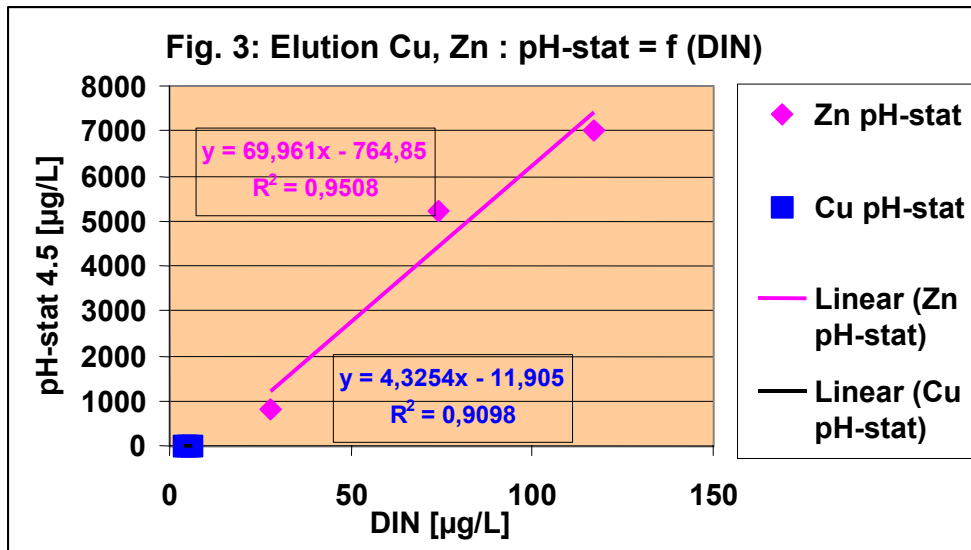
3.5 Mobilization in dependence on pH

Lowering of pH in the pH-stat method affects in particular the mobility of Zn, Ni and As. Their mobility is increased by the factors 50, 25, and 10, respectively, against those found by the DIN S4-Method.

Fig. 4: Element concentration in dependence on pH
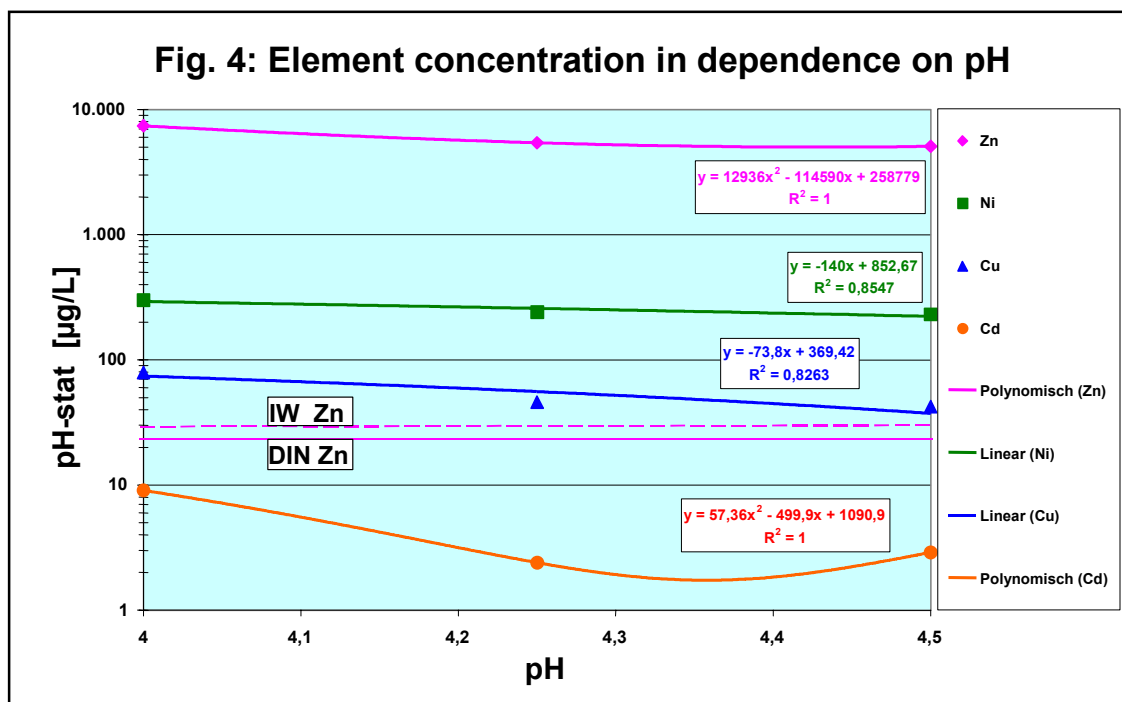
With lowering pH, the mobility of mobile elements increases and surpasses the concentrations in pore water and the release according to DIN by some orders of magnitude. Under acid conditions, increase of concentrations by 50% has to be expected for nitrogen and a decrease by 50% for phosphorous (ref. Fig. 4).

3.6 Relation between concentrations of surface water and sediments
The distribution equilibrium between solid and liquid phases is estimated in the example of the suspended matter obtained by means of flow-through centrifuge in 1999 and 2000. With suspended matter and diluted phase, it is a question of daily composite samples. The metal contents in the liquid phase were analyzed in the unfiltered centrifuged sequence.
For the estimation of the distribution of relevant heavy metals between particulate suspended matter and the centrifuged sequence, the partition coefficients were calculated in the order of $2,7 \bullet 10^4$ up to $8,14 \bullet 10^4$ [L / kg]

4 Summary
For the majority of elements and nutrients, the interstitial water concentration has a decisive function with regard to the contaminant release using DIN and pH-stat methods; especially for nitrogen and single elements, e.g. copper, a bioaccumulation effect with maximum factors of 10 and 4 respectively was observed.
- The portion of contaminant release from the solid phase can be assumed to approximately 50%.
- For the majority of elements and nitrogen, the relations between DIN method and pH-stat method have factors of determination above 0.7, but the sensitivity factors differ from element to element.
- With lowering pH, the mobility of elements increases and surpasses the concentrations in pore water and the release of the DIN method by some orders of magnitude.
- pH-stat examinations of nutrients indicated that a 10-15 % nitrogen release from sediments, deposited e.g. on dikelands or on the bank, is expected on a long-term basis, while phosphate is precipitated with other cations and is mobilized only to 50 %.
- Elution with surface water gave higher concentrations in dependence on the element comparing elution with supra pur water due to the different ion strengths;

Conclusions
- The elution results analyzed by DIN 38414-S4 should be corrected by the interstitial water content to obtain the releases from interstitial water and solid matter, respectively. For further differentiation of the chemical compounds, a sequential extraction can be used [Tack et al. 1996, Mester et al. 1998].
- With regard to N, a certain relation between interstitial water concentration and release potential was observed. In contrast to this, the conditions of the behavior of P should be clarified.
- The investigations regarding the mobilization-capability should be continued in selected materials with substrate-related methods. As well as organically characterized sediments, alluvial flood-plain soils and also sands should be included in the investigation.
- Material fluxes during high water periods, when pollutants are initially released by sediment transport should be estimated, and their fate has to be clarified.
- Comparative studies should be made between different river catchment areas in order to find a possible dependence on substrates and other factors influencing mobilization effects.

References

1. DEV 2000 Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Weinheim. DIN 38406-29 Kationen, Teil 29: Bestimmung von 61 Elementen durch Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS). DIN 38414-S4 Schlamm und Sedimente: Bestimmung der Eluierbarkeit mit Wasser
2. HELCOM 1998 Helsinki Commission. HELCOM objective with regard to hazardous substances. Recommendation 19/5, adopted 26 March
3. Mester, Z.; Cremisini, C.; Ghiara, E.; Morabito, R. 1998
4. Comparison of two sequential extraction procedures for metal fractionation in sediments
5. Analytica Chimica Acta 359 (1998) 133-142
6. Müller A. & P. Heininger 1996
7. Zur Schadstoffbelastung der Odersedimente
8. GDCh-Jahresversammlung Koblenz
9. Müller A., P. Heininger, M. Wessels, J. Pelzer, K. Grünwald, S. Pfitzner, M. Berger 2002
10. Contaminant Levels and Ecotoxicological Effects in Sediments of the River Odra
11. Acta hydrochim et hydrobiol 30 (2002) 5-6, 244-255
12. OBERMANN, P. AND CREMER, S. 1992: Mobilisierung von Schwermetallen in Porenwässern von belasteten Böden und Deponien: Entwicklung eines aussagekräftigen Elutionsverfahrens. Materialien zur Ermittlung und Sanierung von Altlasten, Band 6, Landesamt für Wasser und Abfall Nordrhein Westfalen, Düsseldorf
13. Paschke A., R. Wennrich and P. Morgenstern 1999: Comparison of 24 h and Long-term pH-stat Leaching Tests for Heavy Metals Mobilization from Solid Matrices
14. Acta hydrochim. hydrobiol 27 (1999) 4, 223-229
15. Tack, F.M.G; Vosius, H.A.H.; Verloo, M.G. 1996
16. A comparison between sediment metal fractions, obtainded from sequential extraction and estimated from single extraction
17. Int. J. Environ. Anal. Chem 63 (1996) 61-66