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## Mobility of heavy metals in harbour sediments: an environmental aspect for the reuse of contaminated dredged sediments

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**Abstract** Different methods to determine the source strength of two harbour sediment fractions were applied and are discussed with a focus on As, Cd, Cr, Co, Cu, Mo, Ni, Pb, and Zn. Four different batch experiments were performed with both the sandy and the silty fractions of harbour sediments sampled at the disposal site for dredged material in Bremen Seehausen, north Germany. In addition to the batch experiments a modified centrifugation tube was used in order to obtain pore water from the unsaturated silty fraction. Column experiments were run with the sandy fraction of the material under saturated and unsaturated conditions, irrigated with artificial acid rain water. The results show that the legal threshold value applying to Mo and Pb is not exceeded in any of the methods applied to the sandy or the silty fractions. As for the sandy fraction, Cr and Co were also below this limit. Cd, Ni,

Cu and Zn exceeded the threshold values in some of the batch experiments applied to both fractions, depending on the pH value and the elution agent used in the experiment. All results obtained from saturated column leaching were below the respective threshold values; however, it should be noted that the pH was between 7 and 8 throughout the entire experiment. This pH also applied to the unsaturated column, with the exception of the 'first flush'. This first sample had a pH value of 3.8, which was due to sulphide oxidation at the beginning of the experiment and led to strong leaching of all the elements under study. As a consequence, arsenic, Cu and Ni values exceeded their respective threshold values.

**Keywords** Contaminated dredged material · Heavy metals · Batch experiment · Column experiment

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### Introduction

The sediments of harbours and waterways have to be dredged to maintain the water depth for shipping and naval traffic. In the Netherlands, and in Germany, the responsible authorities have to deal with 30–50 million m<sup>3</sup> annually. Due to contaminants some fractions of the dredged material cannot be relocated to the river, the estuary or the sea, but have to be treated or deposited on land. In the Germany, annually 2–3 million m<sup>3</sup> are deposited on land each year.

The sediment management concept in Bremen is based on three main principles: Firstly, to identify the sources of pollution in the catchment area of the Weser River and reduce sedimentation in the harbour (Nasner 1992) in order to minimise the amount of sediment which has to be managed; secondly, to deposit the material if environmentally justifiable (Biener et al. 1999); and thirdly, to investigate and compare treatment techniques as potential alternatives to land disposal. Technologies discussed are subaqueous disposal (Jacobs and Förstner 1999), brick production (Hamer and Ka-

rius 2002), use as containment or cover layer in landfills (von Lührte et al. 1996; Tresselt et al. 1998), and production of light-weight aggregates (Derman and Schlieper 1999; Hamer et al. 2003).

According to German law (Federal Bulletin 1998) such reuse of dredged material requires an environmental assessment, which considers the mobility of pollutants. The investigation procedure according to the Federal German Soil Protection and Contaminated Site Ordinance (Federal Bulletin 1999) considers both bulk and eluate concentrations. If the bulk concentrations allow a reuse of the sediments, the focus will lie on the mobility of the pollutants measured in various eluate tests. Within this context, the so-called “source-strength” is important. The Federal German Soil Protection Act (Federal Bulletin 1998) defines the source strength as the total mass flow caused by natural leaching. If the threshold value defined for various inorganic and organic contaminants (Table 4) is exceeded, a transport prognosis, has to be made to determine that the concentration leached from the material under investigation by natural precipitation does not exceed threshold values on its way into the groundwater. Ultimately, this prognosis leads to a calculated value of the contaminant concentration at the boundary between the vadose and the saturated zone. This interface between vadose and saturated zone is the ‘place of assessment’. If threshold values are not exceeded in the place of assessment, reuse of dredged material will be possible (Fig. 1; Oberacker and Eberle 2003; Lager et al. 2003).

The seepage water is exposed to a variety of chemical and physical processes on its way through the contaminated deposit and the underlying soil to the boundary between the vadose and the saturated zones. The concentration of the seepage water at this point is strongly dependent on the type of contaminant and the composition and texture of both the concerned recycling material and the subsoil. On their way through the underground, the contaminants can be transformed or immobilised, and organic substances might become

decomposed (van der Sloot et al. 1997; Scheffer and Schachtschabel 1998). These processes can lead either to a delayed discharge or a reduction of the concentration of contaminants (Wild 1993). Focussing on inorganic contaminants, the most important processes are sorption and precipitation (van der Sloot et al. 1997). Both strongly depend on the conditions of pH and  $E_H$  prevalent in the unsaturated zone. Therefore, it is crucial to take these conditions inclusive of their temporal development into account for selecting the adequate method to determine the source strength.

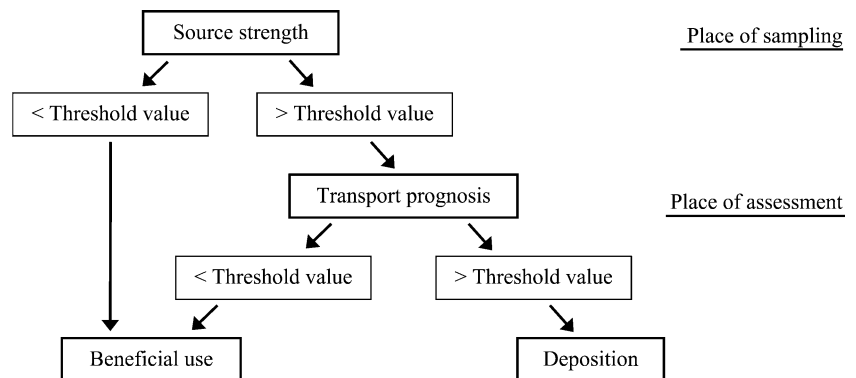
In the following, the results of the different methods will be discussed with respect to the suitability of the respective methods for the determination of the source strength. Furthermore, conclusions will be drawn specifying the circumstances under which the sandy and the silty fractions of the harbour sediments could be reused, considering soil and groundwater quality.

## Material

The sediment samples investigated were collected at the disposal deposit site for dredged material located at Bremen Seehausen, northern Germany. Here, the sediment material dredged from the harbour basins of Bremen and Bremerhaven is deposited after a dewatering process of about one year. This is done by dredging ships pumping the material via pipelines onto drainage fields (Biener et al. 1999). A grain-size separation of the former dredged sediments takes place in the course of this field flushing process. The sandy fraction accumulates close to the outlet of the pipeline (von Lührte et al. 1996). Aggregates of clayey material are found in the sandy fraction, whereas clayey, slightly sandy silt deposits are dispersed throughout the rest of the field.

The accumulated material was sampled by taking 20–30 kg of both fractions at five different locations. As regards homogeneity of the analysis of the elements, calcium, potassium, magnesium, sodium, strontium, and

**Fig. 1** Beneficial use versus deposition: Process design as described in the German Federal Soil Protection Act (Federal Bulletin 1998)



zinc in the pore water displayed deviations of less than 10%. However, five samples of both fractions were each homogenised to a single sample and used in all subsequent investigations. The grain-size distribution of the sandy fraction and the silty fraction was determined according to DIN 18123 (1996) either by sieving or with an areometer, respectively (Fig. 2).  $E_H$  and pH values were determined in situ, all other parameters were performed in the laboratory (Table 3).

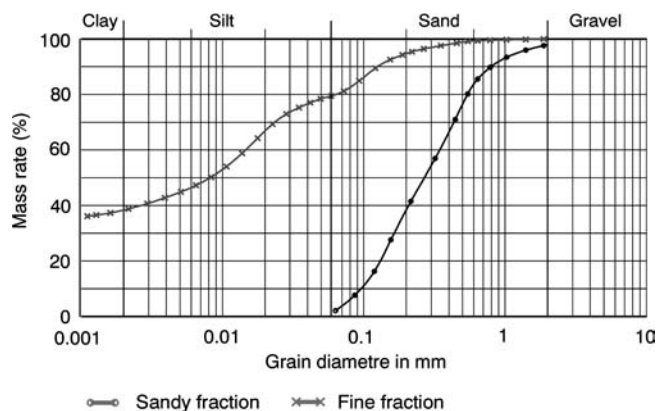
## Methods

Various batch experiments were employed to investigate both grain-size fractions of the investigated material:

- German standard method DEV S4, a leaching experiment with deionised water (DIN 1984)
- Ammonium-nitrate extract (DIN 1997b)
- Soil saturation extract (Federal Bulletin 1999)
- pH-stat test at pH 4, 5, 6, 7, and 11 (Obermann and Cremer 1992; Karius and Hamer 2001b)

The acid consumption of each pH-stat test performed at pH 4, 5, 6 and 7 was recorded within the 24-h test and used to calculate the acid or base neutralisation capacity (ANC<sub>24</sub>).

A modification of the centrifugation technique for gaining pore water from unsaturated material was applied to the fine fraction of the harbour sludge, while the sandy fraction was applied in column experiments conducted under saturated and unsaturated conditions. The saturated column, made of Perspex, was 48 cm in length and 5 cm in diameter. The wet material weighing 1.82 kg was saturated with water upon being loaded into the column. The flow rate was set to 0.1 mL/min. The unsaturated column, also made of Perspex, was 48 cm in length and 10 cm in diameter. 5.88 kg of the wet material was incorporated and slightly compacted. The col-



**Fig. 2** Grain-size distribution of the sandy and fine fractions of harbour sludge

umn was irrigated once a day for over an hour with 50 mL artificial rainwater (Table 1) applied through six precipitation cocks. Tap water was diluted with deionised water to yield a water hardness of 0.0895 mmol/L. Acid rain was simulated by application of an average pH of 4.1 (Table 2).

Table 2 shows the test conditions and several factors controlling the release of contaminants in the methods applied. A detailed description of the methods can be found in Lager et al. (2003).

Bulk concentrations of the sediments were determined by total digestion induced by microwave heating (DIN 1983). All samples were filtered through a 0.2  $\mu\text{m}$  cellulose-acetate membrane filter and acidified with nitric acid for conservation. The concentration of lead was determined by GF-AAS measurement (Unicam Solaar 989QZ). The detection limit for lead was 4  $\mu\text{g/L}$ . The concentrations of the main elements were determined by ICP-OES measurement (Perkin Elmer, Optima 3000), the apparatus being connected to a cross-flow nebulizer. The concentrations of arsenic, cadmium, chromium, cobalt, copper, molybdenum, nickel and zinc were also obtained by ICP-OES measurement. Here, however, an ultra sonic nebulizer (CETAC USN) was connected. The detection limit of arsenic was 10  $\mu\text{g/L}$ , 4  $\mu\text{g/L}$  in the case of cadmium, and 2  $\mu\text{g/L}$  for chromium, cobalt, copper, molybdenum, nickel and zinc. Measuring the artificial rainwater the detection limits were lower for some trace elements (Table 1). This is because some of the samples derived from the experiments had to be diluted. The ICP-OES connected with the ultra sonic nebulizer was not able to measure bulk contents higher than 1 g/L.

PHREEQC (version 2.8) (Parkhurst and Appelo 1999) is a programme for speciation, saturation-index calculations, one-dimensional (1D) transport calculations and inverse modelling. It was used in this study to calculate the speciation and saturation-indices of copper in the batch experiments. The LLNL (Lawrence Livermore National Laboratory) dataset included was therefore complemented with the Gibbs free energies of the known copper amino complexes (Smith and Martell 1976). In order to calculate the pyrite weathering reac-

**Table 1** of the artificial rainwater

Element	Unit	Concentration	Element	Unit	Concentration
Al	$\mu\text{g/L}$	3	Mn	$\mu\text{g/L}$	< 5
Ba	$\mu\text{g/L}$	3	Mo	$\mu\text{g/L}$	< 2
Ca	mg/L	3	Na	mg/L	1
Cd	$\mu\text{g/L}$	< 2	Ni	$\mu\text{g/L}$	1
Co	$\mu\text{g/L}$	< 2	S	mg/L	3
Cr	$\mu\text{g/L}$	< 2	Si	$\mu\text{g/L}$	450
Cu	$\mu\text{g/L}$	13	Sr	$\mu\text{g/L}$	9
Fe	$\mu\text{g/L}$	3	V	$\mu\text{g/L}$	< 10
K	$\mu\text{g/L}$	270	Zn	$\mu\text{g/L}$	24
Mg	$\mu\text{g/L}$	320			

**Table 2** Test conditions and some release controlling factors of the applied methods (modified after Lager et al. 2003)

Method	Grain-size	pH value	Liquid-solid ratio (L/kg)/ flow conditions	Elution time	Elution agent	Parallel tests
DEV S4 test	< 1 cm original	Dependent on material	10/overhead shaker	24 h	Deionised water	3
Soil saturation extract (SSE)	< 2 mm	Dependent on material and $\text{NH}_4\text{NO}_3$	~1/kneading and stirring for 15 min respectively	48 h	Deionised water	3
Ammonium-nitrate extract	< 2 mm	4, 5, 6, 7, 11	4/overhead shaker	3 h	1 M $\text{NH}_4\text{NO}_3$	3
pH-stat test	< 2 mm	4	10/stirrer	24 h	Deionised water	3
Saturated column	< 2 mm	4	Variable/0.1 mL/min	Weeks to month	Artificial rainwater	1
Unsaturated column	< 2 mm	4	Variable/50 mL/day in 1 h	Weeks to month	Artificial rainwater	1
Centrifugation	original	Dependent on material	adequate to natural/none	1 h	Pore water	3

tions in the unsaturated column experiment, the MINTEQ dataset was employed.

## Results

### Material characterisation

The main sandy harbour-sediment fraction is composed of quartz. Minor constituents are potassium-feldspar, plagioclase, muscovite, and zircon. Quartz is also the major constituent of the fine fraction of harbour sediments. Minor components are potassium-sodium-feldspar, muscovite, clinocllore, calcite, and dolomite. The soil physical properties (Table 3, Fig. 2) of the fine fraction allow its use as building material in noise-protection embankments and dikes or as a mineral sealing agent in landfill surface sealing (von Lührte et al. 1999; Biener et al. 2003). The sandy material could be used for road construction or as landfill drainage sand.

In the following section, the concentrations of the heavy metals arsenic and molybdenum are compared with the threshold values as defined inter alia for the source strength by the Federal Soil Protection and Contaminated Sites Ordinance (Federal Bulletin 1999) for each fraction of the harbour sediments.

### Leaching tests

#### *Sandy fraction*

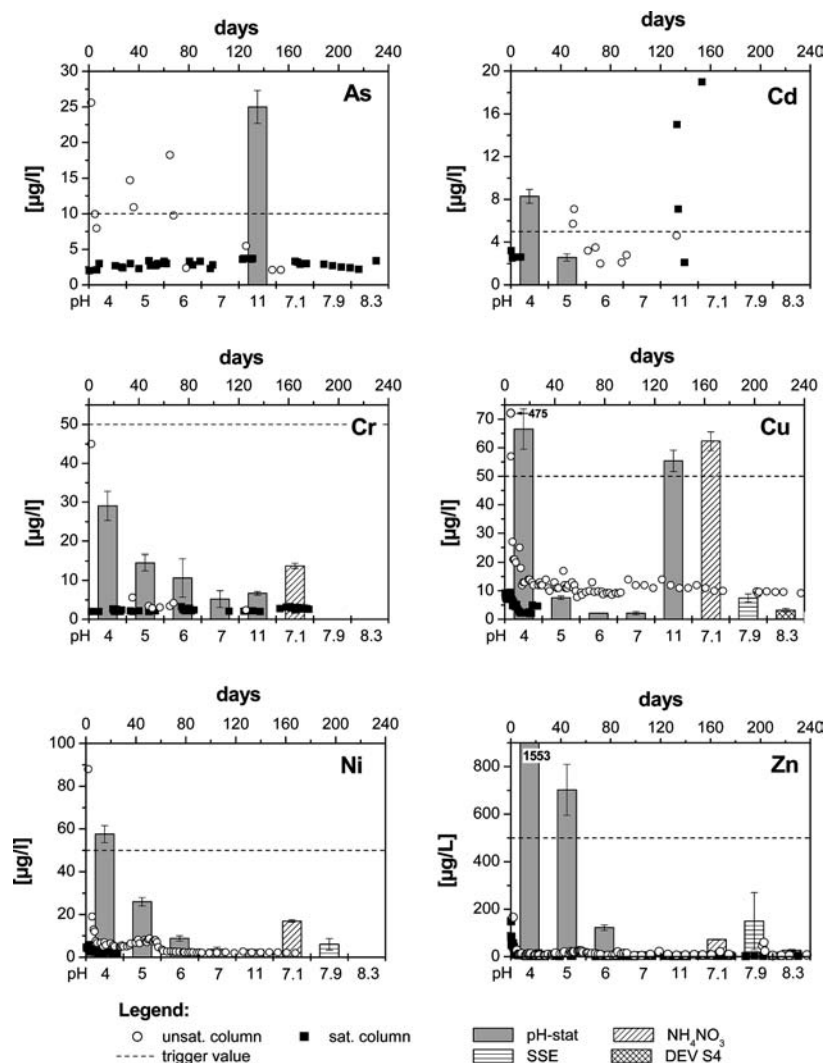
In none of the applied experiments with the sandy fraction of harbour sludge did cobalt, chromium (Fig. 3) and molybdenum exceed the threshold value of 50  $\mu\text{g/L}$ , which is defined for these three elements. Neither did lead exceed the threshold value of 25  $\mu\text{g/L}$ .

Cadmium, copper, nickel and zinc exceeded their respective threshold values (Fig. 3) in the pH4-stat test, zinc also in the pH5-stat test. Arsenic and copper showed strong leaching behaviour at pH 11 exceeding their respective threshold values. Enhanced leaching properties that led to concentrations higher than the

**Table 3** Material properties of the sandy and fine fraction of harbour sediments

	Sandy Fraction	Fine Fraction
Water content [% weight] (DIN 1989)	~ 5	~ 34
Specific weight [ $\text{g/cm}^3$ ] (DIN 1997a)	2.61	2.42
Specific surface area ( $\text{m}^2/\text{g}$ )	2.4	16.2
pH (in situ)	~ 8.3	7.0 – 7.6
$E_H$ [mV] (in situ)	~ 250	30 – 420
El. conductivity (mS/cm)	1.5	0.54
Total carbon (%)	0.3	4.6
Inorganic carbon (%)	0.07	0.46
Organic carbon (%)	0.23	4.14

**Fig. 3** Concentrations of arsenic, cadmium, copper, nickel, and zinc in the sandy fraction of harbour sludge as determined by various batch experiments and at the outlet of the saturated and unsaturated column. The respective threshold values are shown (Federal Bulletin 1999)



respective threshold value of copper could also be seen in the ammonium-nitrate extract.

Arsenic, copper and nickel exceeded the threshold value in the first flush of the unsaturated column. As for cadmium, only few values in the two column experiments were measured above the detection limit of 5 µg/L. Two concentrations in the saturated column distinctly exceeded the threshold value, one after 132 and the other after 151 days, whereas a concentration of 7 µg/L was reached in the unsaturated column after 50 days.

#### *Fine fraction*

The concentrations of lead and molybdenum were not found to be above their respective threshold values after application of all the test methods (Table 4). An enhanced leaching at low pH values could be observed in the case of cadmium, cobalt, chromium, copper, nickel and zinc. Thus the respective threshold values of these

elements were exceeded in the pH-stat test at low pH values (Table 4). Arsenic and copper also exceeded the threshold value at pH 11. In addition, the concentration of copper in pore water was higher than the threshold value. The same applied to cadmium in the ammonium-nitrate extract. Zinc showed very high concentrations in the pH-stat test at pH 4–6 which was a result of the very high bulk concentrations. The bulk concentrations were about six times higher than the highest background value measured in soils in Germany (Scheffer and Schachtschabel 1998) (Table 5).

## Discussion

### Grain-size and soil mechanics

Unlike former investigations (Hamer et al. 1995), the fine fraction of harbour sediments was found to be very homogeneous. The sandy fraction also displayed good

**Table 4** Concentration of trace elements in the applied batch experiments, measured in the fine fraction of harbour sediments. The respective threshold values (Federal Bulletin 1999) are shown for reasons of comparison in ( $\mu\text{g/L}$ ); concentrations underlined indicate that the threshold value was exceeded

	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn
pH4-stat	<10	112	118	102	64	<2	381	6.6	21186
pH5-stat	<10	35	30	53	8.3	<2	146	<5	7088
pH6-stat	<10	8.1	<2	16	5.3	<2	33	<5	1062
pH7-stat	<10	<4	<2	<2	4.8	<2	4.3	<5	68
pH11-stat	170	4.7	<2	8.0	393	3.3	29	<5	36
NH <sub>4</sub> NO <sub>3</sub> , pH 7.0	<10	6.0	<2	7.0	40	<2	24	<5	164
SSE, pH 7.2	<10	<4	<2	13	7.8	<2	8.9	<5	208
Cen, pH 7.3	<10	<4	<2	<2	60	<2	23	<5	299
DEV S4, pH 7.6	<10	<4	<2	<2	4.7	<2	2.3	4.6	79
Threshold value	10	5	50	50	50	50	50	25	500

**Table 5** Bulk concentrations and background values determined in soils in Germany listed in Scheffer and Schachtschabel (1998) in (mg/kg)

	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	Zn
Sandy fraction	1.4	0.9	4.2	11	9.3	1.5	<0.05	12	53
Fine fraction	12	4.1	20	90	65	1.5	41	75	490
Background values, soils	1–20	0.1–0.6	5–100	2–40	2–40	3–50	2–80	10–80	

homogeneity. Additionally, enough material is dredged annually to supply a construction project with building material. Homogeneity and capacity are important factors for the assessment of potential reuse and the substitution of primary resources. The beneficial use of harbour sediments has a lot of advantages. Primary resources like sand or clay can be saved and thus also natural landscapes. Secondly, the construction of new disposal sites including dewatering facilities, which consume space (Hamer and Karius 2002) and are thus often accompanied by the destruction of natural landscapes, can be prevented. In addition to common deposition or relocation, silty dredged material could be used as a substitute raw material in the production of bricks (Hamer and Karius 2002), applied as a containment or cover layer in landfills (von Lührte et al. 1996; Tresselt et al. 1998), or used in the production of light weight aggregates (Derman and Schlieper 1999; Hamer et al. 2003). A general overview of the current activities is given in Netzband et al. (2002).

Environmental aspects: mobility of heavy metals

#### Simple leaching tests

The release of most heavy metals increases with decreasing pH value (van der Sloot 1996; Paschke et al. 1999; Karius and Hamer 2001a; van Herreweghe et al. 2002). Thus cadmium, copper, nickel and zinc exceeded

their respective threshold values (Table 4, Fig. 3) in the eluates at pH values below 4. Arsenic and copper showed a strong leaching behaviour at pH 11 and exceeded their respective threshold limit values.

Arsenic(V) is the dominant dissolved arsenic-species in natural waters, i.e. under oxic and circum natural pH conditions. Arsenic(V) has a high adsorption affinity to oxides and hydroxides of Fe and Al (Langmuir et al. 1999; Sracek et al. 2004). Bowell (1994) found a maximum sorption of Arsenic(V) on goethite and lepidocrodite at pH 6 and on hematite between pH 7 and pH 8. A mobilisation of arsenic in the acidic and alkaline pH range therefore mainly occurs by dissolution of the adsorbing matrix (Dankwarth and Gerth 2002). The strong leaching of Al (1 mg/L) and Fe (0.3 mg/L) in the pH-stat test at pH 11 as compared to the pH-stat test conducted in the neutral to slightly acidic range led to the mobilisation of formerly adsorbed arsenic.

A strong leaching effect of copper under alkaline conditions, which was probably due to the formation of hydroxo complexes, was also found by van Herreweghe et al. (2002). Copper is known to have a strong tendency to form hydroxo complexes (Tamura and Furuichi 1997).

An enhanced leaching in the ammonium-nitrate extract was recognized for cadmium, chromium, copper, nickel and zinc. Cadmium and copper even exceeded the threshold values when this method was applied. Despite the fact that dissolved ammonium-nitrate has a pH of 5, the pH adjusted to 7.1 in the experiment included the sandy fraction of harbour sludge. Thus the enhanced leaching observed in comparison to the pH-stat experiment is not due to the pH value. Compared to the pH-stat and the DEV S4 test, the liquid to solid ratio in the ammonium-nitrate extract was significantly lower (Table 2). However, if the leached amounts (in mg/kg) are compared, a higher leaching effect to still observed in the case of copper. Thermodynamic modelling with PHREEQC (Parkhurst and Appelo 1999) showed the formation of tetra-amino-complexes with copper ( $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ). Another reason why the concentrations measured in the ammonium-nitrate extract should be handled carefully as far as the validity of the source strength is concerned is that high ionic strength can lead to an increased retention of oxo-anion producers like arsenic and vanadium (Dankwarth and Gerth 2002).

#### Breakthrough curves of column experiments

The breakthrough curves of all the column experiments conducted showed a high initial concentration followed by a decrease. In general, this makes it obvious that an assessment based on simple leaching tests as previously discussed neglects much information, that might be important. Consequently, column experiments appear to

be essential for a detailed description of the leaching behaviour and thus for long-term risk assessment.

For example, the concentration of nickel in the unsaturated column was almost twice as high as the threshold value at the beginning of the leaching process, that of copper almost ten times higher. The far higher values compared to those derived from the pH4-stat test is imputable to the even lower pH of 3.8 which prevailed in the initial state in the column.

The pH value at the outlet of both columns varied between 7 and 8, except for the first sample of the unsaturated column. The so-called 'first flush' showed a pH value of 3.8 which is even lower than the pH of the artificial rainwater used to irrigate the column. This is possibly due to Fe(II)-oxidation, Fe(III)-precipitation ( $\text{Fe}^{2+} + 1/4\text{O}_2 + 3/2\text{H}_2\text{O} \Rightarrow \text{FeOOH} + 2\text{H}^+$ ) and the formation of sulphurous acid ( $2\text{S}^{2-} + 3.5\text{O}_2 + \text{H}_2\text{O} \Rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+$ ). To verify this hypothesis, thermodynamic calculation was performed with the model PHREEQC (version 2; Parkhurst and Appelo 1999). The conditions of pH and  $E_H$  of the initial solution (pure water) corresponded to the conditions in the first flush of the unsaturated column (pH 4.1, pe 10.232). The phases  $\text{Fe}(\text{OH})_3$  and kaolinite were allowed to react to equilibrium (saturation index equal to 0).  $\text{O}_2$  and  $\text{CO}_2$  partial pressures were maintained at  $10^{-0.67}$  and  $10^{-3.4}$  (atmospheric partial pressure). The weathering of 2.7 mmol pyrite resulted in a solution with a pH of 3.3. Buffering reactions with calcite were included in a second step. A pH of 3.8 was reached after adding 4.25 mmol calcite.

This phenomenon does not occur in the saturated column. Here, less  $\text{O}_2$  is present and available due to the water-saturated conditions.

Considering how sensitive the development of the pH is for the potential mobilisation of inorganic contaminants, the ANC should be accounted for. The  $\text{ANC}_{24}$  against infiltration of water with a pH of 4 was 624 meq/kg in the fine fraction, and only ~91 meq/kg in the sandy fraction (Table 6). Thus, in case of the fine fraction, it takes much longer until the ANC is consumed in a horizon of material, and consequently until the material is fully acidified and the enhanced leaching of heavy metals commences (Lager et al. 2003). Anticipating an annual infiltration rate of 300 mm of water at pH of 4, it will take less than 500 years until a horizon of 0.1 m of sandy fraction is fully acidified by means of acidic rain-water infiltration. Under the assumption of an infiltration rate of 50 mm/a, complete acidification of the fine fraction will be due after about 20,000 years (Lager et al. 2003).

## Conclusion

The effects that various elution agents may have on the mobilisation of contaminants have to be taken into ac-

**Table 6** Acid and base neutralisation capacities calculated from the acid or base consumption in the pH-stat tests

	$\text{ANC}_{24}$			
	pH4	pH5	pH6	pH7
Sandy fraction	91	50	21	17
Fine fraction	624	525	375	137

count when a method for the determination of the source strength is to be defined. Ammonium-nitrate was shown to enhance the leaching of copper due to the formation of amino-complexes. In addition, ammonium-nitrate, as compared to deionised water, which was used as the elution agent in all other batch experiments, is known to reduce the mobility of arsenic and vanadium.

With the exception of molybdenum and lead all other elements exceeded their threshold value when the methods were applied. This mainly depends on the pH value. An enhanced leaching at decreasing pH applies to all heavy metals. Arsenic and copper revealed an increased mobility at pH 11 as well. Arsenic is mainly adsorbed to oxides and hydroxides of Al and Fe. The enhanced leaching of Al and Fe in the pH-stat test at pH 11 therefore produced enhanced leaching of arsenic. Copper is more mobile at high pH values, probably due to the formation of hydroxo-complexes. These pH-dependent mobilisation mechanisms can be interpreted from the pH-stat tests. Furthermore, the ANC contributes to developing a time frame applying to the acidification of a horizon.

The observed strong and rapid increase of the concentrations in the breakthrough of the column experiments, the so-called 'first flush', a phenomenon that also occurs under natural conditions of deposition, can only be revealed in a column test. It was shown that leaching in the first flush will be potentially even stronger under unsaturated conditions, if sulphide oxidation occurs and results in a decrease of pH.

A similar approach consisting of a combination of pH-stat and column test should be applied to organic contaminants, e.g. TBT. Efforts are on within the BMBF-project to design a column test suitable for the examination of both inorganic and organic contaminants (e.g. North Rhine-Westphalian State Environment Agency (LUA NRW) in Essen). However, a sample volume of 1 L is necessary for measuring organic substances in a range of 10–100 ng/L. The analytical requirement of huge sample volumes leads to a decrease in time resolution in the breakthrough curves. Consequently, the first flush phenomenon is not easy to observe.

It is clear that a reuse of both fractions of harbour sediments, i.e. the silty sand and the clayey, slightly

sandy silt fractions, is only possible under conditions in which the pH-dependent degradation can be retarded or prevented. Considering the  $ANC_{24}$  and the various transport mechanisms within the two materials, it becomes obvious that the precautionary measure should be even more stringent for the sandy fraction as compared to the fine fraction. A possible scenario for the reuse of the fine fraction could consist in the substitution of natural clays in cover systems for wastes under an overlying soil layer (Tresselt et al. 1998). As previously shown, the buffer capacity of the fine fraction itself will last for about 20,000 years, anticipating an infiltration with rain at pH 4. Assuming preferential flow mechanisms to be negligible, diffusion will be the main transport mechanism within such a deposition of the fine fraction of harbour sludge, whereas advection will predominate in the sandy fraction.

The seepage water prognosis is defined as the estimation of the concentration of pollutants that will reach the groundwater together with the leachate in the foreseeable future. Including this time frame in the risk

assessment, the risk of polluting the underlying groundwater is much higher underneath a deposition of the sandy fraction. A potential scenario of reuse could consist in its implementation as a core in dikes, a situation in which advection is rather irrelevant, because such core would be enclosed in a very fine-grained material displaying a hydraulic conductivity in a range of less than  $10^{-8}$  m/s (von Lührte 1997). With such an overlying fine-fractioned material the surface discharge will even be enhanced. A layer consisting of the same material and situated underneath the embankment would inhibit the discharge into the underlying soil.

Next to the bulk concentration and the leachable concentration of the contaminants, we have to consider for reuse scenarios the development of the pH conditions, the buffer capacity of the material, and the flow conditions in a deposition of this material.

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