

Characterisation, Availability, and Risk Assessment of the Metals in Sediment after Aging

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Abstract The behavior of metals in sediments after their disposal to land has important implications for the environmental management. The sediment from the Carska Bara (Serbia) was polluted with adequate metal salts in order to reach severe contamination based on the pseudo-total metal content of Pb, Cd, Ni, Zn, Cu, and Cr according to the corresponding Dutch standards and Canadian guidelines. The toxicity and fate of the metal in sediment depend on its chemical form, and therefore, quantification of the different forms of a metal is more meaningful than the estimation of its total concentration. In this study, fractionation of metals in sediment has been investigated to determine its speciation and ecotoxic potential, as well as evaluation of metal potential toxicity based on the simultaneously extracted metals (SEMs) and acid volatile sulfides (AVSs)

analysis at the beginning of the experiment and after 5 weeks of sediment aging. The investigations suggest that Cd, Pb, and Zn have a tendency to associate with labile fraction, the most mobile and most dangerous fraction for the environment. Risk assessment code revealed their high risk. Copper and chromium showed low to medium risk to the aquatic environment. Nickel showed no risk to the aquatic environment. This was the case at the beginning and after 5 weeks of aging. Aging yielded an increased mobility of all metals based on the increased proportion in mobile fractions. The $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio was found to be >1 both at the beginning and after 5 weeks of aging, with the ratio showing an increase with time. This ratio indicates the potential availability/toxicity and, according to the US EPA criteria, the samples belong to the group with probable negative effect. If particular metals are considered, only the $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio for zinc was >1 at the beginning. After 5 weeks, the ratio was >1 for zinc, lead, and copper. Comparison of the results of sequential extraction and the results of SEM and AVS analysis showed good agreement for lead and zinc.

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1 Introduction

Surface water and sediment represent a complex system of natural and anthropogenic substances.

Numerous physical, chemical, and biochemical processes affect the distribution of substances in the sediment–water system. Pollution by metals is a serious problem because of their toxicity and ability to accumulate in biota with a negative impact on the environment and human health. It is now widely accepted that the role of aquatic sediments as a sink or as a source of pollutants cannot fully be assessed by measuring total metal concentrations. In addition, the determination of total elements does not give an accurate estimate of the likely environmental impact. Instead, it is desirable to have information on the potential availability of metals (whether toxic or essential) to biota under various environmental conditions. Since the mobility of trace metals and their bioavailability and related ecotoxicity to plants depend critically on the chemical form in which a metal is present in the sediment, considerable interest exists in element speciation (Davidson et al. 1994).

Single and sequential extraction schemes have been designed for the determination of binding forms of trace metals in sediments (Sahuquillo et al. 1999). Many of the sequential extraction methods are in fact variants of the Tessier procedure (Tessier et al. 1979), in which the exchangeable metals and those nominally associated with carbonate, Fe–Mn oxides, organic material, and silicate residues are extracted with different reagents (Tessier et al. 1979). Based on Tessier's procedure, the Community Bureau of Reference of the Commission of the European Union produced the definition of an extraction protocol (the BCR protocol) and a purely operational definition of sequential fractionation. This method partitions the heavy metals into four fractions: exchangeable and carbonate bound, iron and manganese oxides bound, organic matter bound, and residual metal. Metals in labile forms usually refer to exchangeable and carbonate fractions, and they generally represent the environmentally available components. The Fe–Mn oxides fraction includes the metal oxides/hydroxides soluble under slightly acidic pH, as well as the metals associated with reducible amorphous Fe–Mn oxyhydroxides. Organic fraction may be associated with various forms of organic material such as living organisms, detritus, or coatings on mineral particles through complexation or bioaccumulation processes. This form of metals can exist in sediment for longer periods and can also be released with organic matter decomposition. Residual fraction, that is, the metals still remaining in sediment after the above extraction

procedures, is usually present as consolidated oxides, coprecipitates, and strongly held complexes, which remain relatively stable and do not show significant transformation under various conditions. The main limitations of sequential extraction procedures are that they are extremely time-consuming; thus, they are rarely used for routine analysis.

The distribution of metals in different fractions obtained by sequential extraction procedure offers an indication of their availability, which, in turn, allows the assessment of the risk of their presence in the aquatic environment. Risk assessment code (RAC) gives an idea of the possible risk by applying a scale to the percentage of metals present in exchangeable and carbonate (i.e., labile) fractions. According to RAC, if this fraction is <1%, there is no risk for the aquatic system; at 1–10%, it exhibits low risk; at 11–30%, it exhibits medium risk; at 31–50%, it exhibits high risk; and at >75%, it exhibits very high risk (Jain 2004).

The potential mobility and toxicity of metal ions could be directly related to the $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio for the sediment (Di Toro et al. 1992; Berry et al. 1996; US EPA 2001, 2004). Acid volatile sulfide (AVS) is one of the major chemical components that control the activities and availability of metals in the interstitial waters of sediments. Sulfide reacts with several divalent transition metal cations (cadmium, copper, nickel, lead, and zinc) to form highly insoluble compounds that are not bioavailable (Allen et al. 1993; Ankley et al. 1996; Berry et al. 1996; US EPA 2004). It has been verified (Di Toro et al. 1990) that divalent transition metals do not begin to cause toxicity in sediment until the reservoir of sulfide is used up (i.e., until the molar concentration of metals exceeds the molar concentration of sulfide), typically at relatively high dry-weight metal concentrations. This observation has led to a laboratory measurement technique for calculating the difference between the simultaneously extracted metal (SEM) concentration and AVS concentration in field samples, to determine potential toxicity. To evaluate the potential effects of metals on benthic species, the molar concentration of AVS ($[\text{AVS}]$, $\mu\text{mol g}^{-1}$) is compared to the sum of SEM molar concentrations ($[\text{SEM}_i]$, $\mu\text{mol g}^{-1}$) for five metals: cadmium, copper, nickel, lead, and zinc; when $\Sigma[\text{SEM}_i]/[\text{AVS}] < 1$, acute toxicity due to heavy metals is not probable. On the other hand, the sediment may be considered potentially toxic when this ratio is > 1 (Di Toro et al. 1990; Ankley et al. 1996).

One of the objectives of this study was to examine the distribution of metals in sediment due to continuous discharges of wastewaters contaminated with heavy metals or after an accidental spill, which would rapidly lead to increased concentrations of metals. Sediments in Vojvodina (part of Serbia where the sediment sampling was done) are still under impact by metals from point sources of pollution since only 15% of wastewaters are treated. Although it is not expected that the sediment polluted in laboratory conditions is the same as the sediment polluted in natural environment, with this kind of experiment, it is possible to demonstrate the type of mechanism and behavior that will be applicable in such conditions (Rodriguez and Reynoldson 1999).

In some cases, due to the different factors, sediment may need dredging and landfilling. The behavior of metals in sediments after their disposal to land has important implications for the environmental management of dredging activities. The effects of changes such as oxidation and aging on the sediment must be investigated. When anoxic sediments are oxidized, metals are initially released, but adsorption and (co)precipitation processes could result in the new binding of metals.

In view of the above, the objectives of this study were (1) to define metal speciation and to evaluate environmental risk at the beginning of experiment and after 5 weeks of aging, (2) to evaluate potential bioavailability and toxicity based on the results of the SEM and AVS analysis at the same time points, and (3) to find out whether the release of metals from contaminated sediment was significantly affected by the time since they were exposed to oxidizing conditions.

2 Materials and Methods

2.1 Sample Collection and Preparation

Fresh sediment was collected, using an Eijkelkamp core sampler, from the middle of a sediment reach, Carska Bara (Serbia), and was placed in a sealed plastic, acid-rinsed box (base=15×15 cm and 20 cm deep) immediately after sampling. In laboratory conditions, sediment was polluted with adequate metal salts to the concentration that require sediment remediation according to the Dutch national evaluation scheme and above Canadian probable effect levels (PELs). The results of sediment

metal pseudo-total concentrations are discussed in reference to Dutch regulation standards (Ministry of Housing, Spatial Planning and Environment Directorate-General for Environmental Protection 2000), since Serbia has neither an established system of continual monitoring of sediment quality nor regulations concerning the quality standards. The degree of pollution with priority substances was classified from 0 (clean) to 4 (heavily polluted) on the basis of chemical analyses according to the method prescribed by the Ministry of Transport and Public Works (Ministry of Housing, Spatial Planning and Environment Directorate-General for Environmental Protection 2000). Sediment quality was also assessed based on the Canadian guidelines (CCME 1995). Sediment was allowed to equilibrate undisturbed in anaerobic conditions for 1 year.

The time required for sediment equilibration following additions of metals to sediments is poorly documented (Simpson et al. 2004). According to literature data (Simpson et al. 2004; Fairbrother et al. 2007), a period greater than 1 year is sufficient to attain pseudo-equilibration status. That is why we used a 1-year period and assumed it was enough to establish (pseudo-) equilibration period. In the present study, the aging of the sediments is defined starting from the time the contaminated sediment was disposed in the air that could appear with possible landfilling or by dredging. Thus, contaminated sediment after 1 year of equilibration presented the initial sample. In laboratory conditions (18–20°C), the initial sample of sediment was left to air dry for 5 weeks. The sample was taken from top (0–10 cm) and represented the sediment sample after 5 weeks of aging. Pseudo-total content, SEM and AVS analysis, and sequential extraction procedure were done in the initial sample and after 5 weeks of aging.

2.2 Analytical Methods

Fractional analysis of initial sediment samples (particles < 2 µm, fraction in the range of 2–63 µm and sand content) was carried out according to the sedimentation method. The size of particles in the sediment fraction was defined according to DIN 4022 standard values. The sediment samples consisted of 29% clay (particles less than 2 µm), 51% silt (the fraction of 2–63 µm), and 20% sand (the fraction > 63 µm).

Contents of dry and organic matter were determined by drying 5–10 g of samples at 105°C to a

constant mass and then by heating to 550°C to determine the ignition loss according to the so-called NEN procedures of the Netherlands Normalisation Institute (NNI): NEN 5754:1994. Dry matter was 65±5% and organic matter was 15.5±0.3. The given values represent the means of three measurements ± standard deviation.

Initial top sediment samples and top sediment sample after 5 weeks of aging were analyzed using aqua regia digestion (Alloway 1995) for pseudo-total metal content. Pseudo-total metal contents were assessed on sample triplicate after aqua regia digestion (ISO 11466:1995) and mean values were used. The standard deviations (% R.S.D.) obtained ($n=3$) were below 10%.

Samples were subjected to the sequential extraction procedure and the analyses of SEMs and AVSs.

The extracting solutions were prepared from analytical-grade reagents. The hydroxylammonium chloride solution was prepared prior to use. All glassware and plastic materials used were previously treated for 24 h in 2 M nitric acid and rinsed with deionized water. Extraction was carried out using 100-mL acid-washed polyethylene centrifuge tubes, while 100-mL polyethylene vessels were used for storage of the extracts.

The sequential extraction procedure used was the improved version of the original BCR three-step procedure after an exhaustive study of possible sources of uncertainty (Sahuquillo et al. 1999). Step 1 (labile, exchangeable fraction): 40 mL of acetic acid, 0.11 mol L⁻¹, was added to 1 g of sediment in a centrifuge tube. The tube was then shaken in an ‘end-over-end’ shaker for 16 h (overnight) at room temperature. The extract was separated from the solid residue by centrifugation and the supernatant liquid was decanted into a polyethylene container and stored at 4°C for the analysis. Step 2 (reducible fraction): 40 mL of hydroxylamine hydrochloride, 0.5 mol L⁻¹ (pH 1.5 with the addition of HNO₂ mol L⁻¹), was added to the residue from step 1 in the centrifuge tube, and the extraction was performed as above. Step 3 (oxidizable fraction): 10 mL of hydrogen peroxide, 8.8 mol L⁻¹, was added carefully. The tube was then covered loosely with a stopper, and digestion was allowed to proceed for 1 h at room temperature with occasional manual shaking. The digestion was continued by heating the covered tube for 1 h at 85°C in a water bath, and then the volume was reduced to a few

milliliters by further heating of the uncovered tube. A further aliquot of 10 mL of hydrogen peroxide was added to the residue. The tube was covered again and heated at 85°C for 1 h. Then, the stopper was removed and the volume was reduced to almost dryness. After cooling, 50 mL of ammonium acetate, 1.0 mol L⁻¹, was added to the residue and the tube was then shaken in an ‘end-over-end’ shaker for 16 h (overnight) at room temperature. The remaining operations for separation of the extract were as above. Step 4 (residual fraction): The residue from step 3 was digested in aqua regia as for the pseudo-total sediment metal content. The sum of the four-step sequential procedure and pseudo-total metal content differed less than 10%, which is in accordance with the literature data (Fytianos and Lourantou 2004). The good agreement observed with the results obtained as the sum of the four steps and the pseudo-total content shows that the laboratory working conditions were under control. The results of pseudo-total metal concentration are given as the mean for three different samples of the same sediment and standard deviations were less than 10%.

Pseudo-total sediment metal content and metal content in sequential extraction procedure steps after aqua regia digestion were analyzed by AAS (Perkin Elmer AAnalyst™ 700) or ICP-MS (Perkin Elmer Sciex Elan 5000) according to the standard NEN procedures—NEN 5762:1990 (Cd), NEN 5767:1991 (Cr), NEN 5758:1990 (Cu), NEN 5765:1991 (Ni), NEN 5761:1990 (Pb), and NEN 5759:1990 (Zn)—and according to the ISO procedures—ISO 11466-95 (Fe) and ISO 11047-98 (Mn). All the results are expressed with respect to sediment dry matter.

The procedures for AVS and SEM analyses were adopted from the method described by Allen et al. (1993). The experimental setup consisted of a round-bottom reaction flask connected to a trapping vessel containing 100 mL of 0.5 M NaOH solution. After sparging for 10 min with N₂, the wet sediment sample (about 10 g) was added and sparged for another 10 min with N₂. The sediment suspension was acidified with 20 mL of 6 M HCl and stirred for 45 min at room temperature (cold extraction) to form H₂S, which was subsequently collected in a NaOH solution at a continuous N₂ flow. The dissolved sulfide concentration in the NaOH solution was measured spectrophotometrically using the methylene blue method (Allen et al. 1993). The remaining acid

solution was filtered (Whatman 0.45 μm) prior to analysis for dissolved metal (SEM). Known amounts of sulfide and metals were added to wet sediment. The mean recovery for AVS was 96% and metal recoveries were 94%. All results are expressed with respect to sediment dry matter.

3 Results and Discussion

3.1 Pseudo-Total Metal Content in the Initial Sediment Sample

The results presented in Table 1 are discussed in reference to Dutch regulation standards (Ministry of Housing, Spatial Planning and Environment Directorate-General for Environmental Protection 2000) and Canadian guidelines (CCME 1995).

Dutch regulation standards include two numerical levels: target and intervention values. The target value is the lower level, the baseline concentration value below which compounds and/or elements are known or assumed not to affect the natural properties of the sediment. The intervention value is the higher level, the maximum tolerable concentration above which remediation is required. The target values and intervention values for metals (Cd, Cu, Ni, Zn, Cr, and Pb) depend on the clay and/or organic matter content. According to the Dutch system, the class limits are defined for “standard sediment”, with 10% organic matter and 25% clay. In assessing sediment quality, the values for a standard sediment are converted to the values applying to the actual sediment concerned on the basis of the measured organic material (measured by percentage weight lost by volatilization, on the total dry weight of the sediment) and clay content (the percentage by weight of the total dry material comprising mineral particle matter with a

diameter of less than 2 μm). Metal concentrations of the sediment were first corrected to standard sediment based on correction formulas and then classified according to the Dutch system. The sediment quality at the beginning of the experiment was established using the “worst class” sediment parameter(s).

As can be seen in Table 1 according to Dutch regulation standards, sediment is polluted with all metals, except nickel. In the present Dutch system of sediment assessment, classification of only one of the listed components into the highest pollution class will generally be sufficient to place the sediment into that particular class. According to Dutch regulations, class 4 sediments are of unacceptable quality and need highest urgency situation, dredging, disposal in special storage reservoirs, and, if possible, sediment clean-up measures (Roeters 1998; Kelderman and Drossaert 1999).

Compared with Canadian Sediment Quality Guidelines (CCME 1995) for aquatic life protection, metal contents are above the PEL. Sediment concentrations above PEL values are expected to be frequently associated with adverse biological effects. Although PEL is considered to be applicable to a variety of sediment types, it cannot define uniform values of sediment pollution as the bioavailability (and hence toxicity) of contaminants may be different (CCME 1995).

Concentration of metals in the initial sample of sediment decreased following the order $\text{Pb} > \text{Zn} > \text{Cr} > \text{Cu} > \text{Cd} > \text{Ni}$, which does not necessarily mean that such order is from the aspect of their mobility in the sediment. Mobility, toxicity, bioavailability, and sediment vary, depends on which phase metals are associated in the sediment. Data on the pseudo-total metal content does not provide a clear picture of their possible origin or of their binding to sediment. The determination of total elements does not give an accurate estimate of the likely environmental impact. Instead, it is desirable to have information on the potential availability of

Table 1 Sediment classification according to the Dutch national evaluation scheme (Ministry of Housing, Spatial Planning and Environment Directorate-General for Environmental Protection 2000)

	Cd	Cu	Cr	Mn	Fe	Ni	Pb	Zn
Pseudo-total concentration of metals (mg kg^{-1})	43.4 \pm 4.1	631 \pm 62	849 \pm 81	627 \pm 60	38,700 \pm 450	42.6 \pm 4	4,140 \pm 410	1,340 \pm 125
Class	4	4	4	ND	ND	3	4	4

Class 0 not polluted, *class 1* slightly polluted, *class 2* moderately polluted, *class 3* heavily polluted, *class 4* extremely polluted
ND not defined

metals (whether toxic or essential) to biota under various environmental conditions.

3.2 Assessment of Sediment Toxicity Based on the Results of SEM and AVS Analysis

The parameters that determine the bioavailability/toxicity of sediment metals (results of SEM and AVS analyses) of samples from the surface of sediment sample in the beginning of the experiment and after 5 weeks of aging are presented in Table 2. After aging, the $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio increased from 2.54 to 8.53, which indicates potential bioavailability/toxicity of the metals since the ratio exceeds 1.

The predominance of the SEM(Zn) over all other metals is evident in both samples (13.65–19.85 $\mu\text{mol g}^{-1}$). As can be seen from Table 2, the $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio was >1 for zinc in the beginning and at the end of the experiment. This ratio for lead and copper was >1 only at the end of the experiment, which indicates that these two metals are most readily found in pore water and that they will be potentially bioavailable. For all the metals, this ratio increased with aging (by 60% to 74%), the increases being highest for lead. Despite the high metal concentration, there was no case of $\Sigma[\text{SEM}_i]/[\text{AVS}] < 1$, which was observed in our previous studies (Dalmacija et al. 2006; Prica et al. 2008). The initial sample with the $\Sigma[\text{SEM}_i]/[\text{AVS}] > 1$ was already recognized as place of high risk based on Dutch standards.

The AVS concentration decreased with time from 15.87 $\mu\text{mol g}^{-1}$ to 4.10 $\mu\text{mol g}^{-1}$, which is in agreement with the literature data (Åstrom 1988; Alloway 1995; Stephens et al. 2001).

According to USEPA, the assessment of metal toxicity is based on the difference between the corresponding SEM and AVS molar concentrations. In this approach, each sample falls into one of three categories (tiers): associated adverse effects on aquatic life are probable (Tier 1), associated adverse effects on

aquatic life are possible (Tier 2), or no indication of associated adverse effects (Tier 3). According to the USEPA evaluation, when $\Sigma[\text{SEM}_i]/[\text{AVS}]$ is greater than 5, the sampling site is classified as Tier 1. If $\Sigma[\text{SEM}_i]/[\text{AVS}]$ is between 0 and 5, the sampling site is classified as Tier 2. If $\Sigma[\text{SEM}_i]/[\text{AVS}]$ is less than 0, the sampling site is classified as Tier 3. Table 2 shows that $\Sigma[\text{SEM}_i]/[\text{AVS}]$ is higher than 5 and both samples are classified as Tier 1 with possible negative effects on aquatic life.

According to the US EPA criteria, a sample with $\Sigma[\text{SEM}_i]/[\text{AVS}] > 5$ belongs to group 1, with “probable negative effect on aquatic life” (US EPA 2004). The value of this ratio increased by aging from 24.5 to 30.9 is in agreement with the literature data (Stephens et al. 2001).

Because of the limitations of the available sediment quality measures and assessment methods, USEPA characterizes this evaluation as a screening-level analysis. A screening-level analysis typically identifies many potential problems that prove not to be significant upon further analysis. Thus, classification of sampling locations in this analysis is not meant to be definitive but is intended to be inclusive in respect of potential problems arising from persistent metal contaminants.

Although this method can be used for the detection of potential problems in the polluted sediments, sediment classification on the basis of this analysis should not be final. Relation $\Sigma[\text{SEM}_i]/[\text{AVS}] > 1$ is not showing the actual bioavailability and toxicity, because there are bound metals in sediment in different forms with iron and manganese (Ankley et al. 1996). The ratios of Fe to AVS (from 32.03 to 124) are much higher compared with other metals. This might indicate that $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratios overestimate the availability of metals (Allen et al. 1993; Ankley et al. 1996; Fang et al. 2005). When $\Sigma[\text{SEM}_i]/[\text{AVS}] > 1$, other binding forms for metals in sediment should be considered to assess the bioavailability of metals. The

Table 2 Parameters indicating bioavailability/toxicity of metals in the initial sample and sediment sample after 5 weeks of experiment

Sample	$[\text{SEM}_{\text{Ni}}]/R$	$[\text{SEM}_{\text{Cd}}]/R$	$[\text{SEM}_{\text{Zn}}]/R$	$[\text{SEM}_{\text{Pb}}]/R$	$[\text{SEM}_{\text{Cu}}]/R$	[AVS]	$\Sigma[\text{SEM}_i]$	R_1	R_2	R_3	R_4
Initial	0.52/0.03	0.50/0.03	19.85/1.25	9.77/0.62	9.73/0.61	15.87	40.37	2.54	24.50	32.03	0.69
After 5 weeks	<0.00/0.00	1.39/0.34	13.65/3.33	9.73/2.37	6.10/1.49	4.10	34.97	8.53	30.9	124	1.16

$[\text{SEM}_i]$ ($\mu\text{mol g}^{-1}$); $R = [\text{SEM}_i]/[\text{AVS}]$; [AVS] ($\mu\text{mol g}^{-1}$); $\Sigma[\text{SEM}_i] = \text{SEM}(\text{Cd}) + \text{SEM}(\text{Cu}) + \text{SEM}(\text{Ni}) + \text{SEM}(\text{Pb}) + \text{SEM}(\text{Zn})$ ($\mu\text{mol g}^{-1}$); $R_1 = \Sigma[\text{SEM}_i]/[\text{AVS}]$; $R_2 = \Sigma[\text{SEM}_i]/[\text{AVS}]$; $R_3 = [\text{Fe}]/[\text{AVS}]$; $R_4 = [\text{Mn}]/[\text{AVS}]$

sequential extraction procedure must be used as an additional tool for assessing the potential bioavailability and toxicity of metals in sediment. Although the role of AVS is to transform the metals from biologically available chemical species into insoluble sulfides, the sedimentary sulfide system is of highly dynamic nature. Metals that are associated with AVS may be released within sediments through storms, dredging activities, oxidation, etc., and may have adverse environmental impacts (Fang et al. 2005).

3.3 Results of Sequential Extraction

The distribution of heavy metals at the beginning and after 5 weeks of aging in different fractions extracted according to modified BCR fractionation scheme is shown in Fig. 1. First fraction is the most dangerous for the environment. Metal mobilities decreased in the following order: Zn>Cd>Pb>Cu>Cr>Ni. Percentages of extracted metals in this most available, mobile step were in the range from 50.1% (Pb), to 53.4% (Cd), to 55.2% (Zn), while for Cu, Cr, and Ni, they were much lower: 0.7% (Ni) to 15.8% (Cd).

The dominant proportion of Pb, Cd, and Zn found in the soluble fraction indicates their main occurrence in exchangeable forms and their being bound to carbonates. Other studies also reported lead and zinc association with labile fractions in sediments (Cloutier and Dubé 1998; Stephens et al. 2001; Guevara-Riba et al. 2004; Jain 2004; Pertsemli and Voutsas 2007).

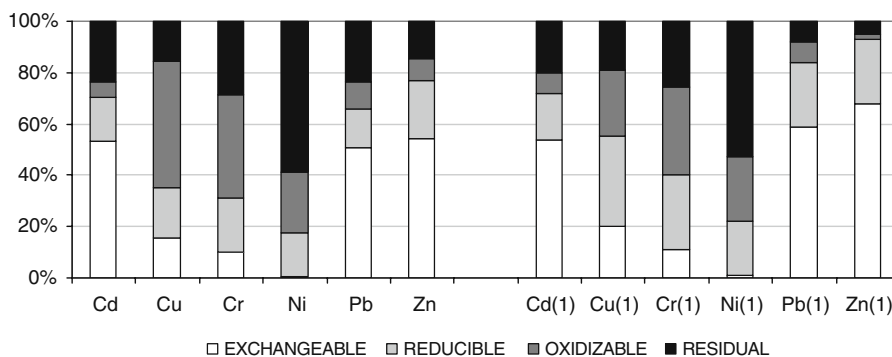
The ranking of metals in the other modified BCR fractions according to their relative contents is as follows:

- Zn>Cu>Cd>Ni>Cr>Pb in reducible fraction,
- Cr>Cu>Ni>Pb>Cd>Zn in oxidizable form, and
- Ni>Cr>Pb>Cd>Cu>Zn in residual fraction.

It is evident from the results of the fractionation study that the metals in the sediments are bound to different fractions with different strengths. The strength can, therefore, give a clear indication of sediment reactivity, which, in turn, indicates the risk associated with the presence of metals in an aquatic environment. These criteria, RAC, indicate that a sediment that can release in exchangeable and carbonate fractions less than 1% of the total metal will be considered safe for the environment. On the contrary, sediment releasing in the same fraction more than 50% of the total metal has to be considered highly dangerous and can easily enter the food chain (Jain 2004). The RAC as applied to the present study reveals that Cd, Pb, and Zn mostly exist in labile fractions and therefore are coming under the high-risk category and can easily enter the food chain. Because of their toxicity and availability, they can pose serious problems to the ecosystem. The total content of these metals in the sediments is quite high and its association with labile fractions may cause deleterious effects. Speciation pattern of Cu and Cr shows low to medium risk to the aquatic environment. Nickel does not show any risk to environment.

Fractionation profile of copper and chromium shows a similar trend—low percentage in the first two steps of sequential extraction procedure. Copper is mainly presented in the oxidizable fraction (49.4%) due to its pronounced tendency for complexation with organic matter and sulfides (Pardo et al. 1990; Tokalioglu et al. 2000; Chartier et al. 2001; Jain 2004; Morillo et al. 2004; Caplat et al. 2005). The dominant proportions of nickel (59.1%) were found in the residual fraction, which indicates its low availability. The residual fraction of metals is most strongly associated to the crystalline structures of the

Fig. 1 Distribution of metals in the sediment fractions according to modified BCR sequential extraction scheme at the beginning of the experiment and after 5 weeks (1) of aging



minerals, presenting small risk to the environment, and this holds for Ni. This is in accordance with literature data (Kartal et al. 2006).

Generally, aging yielded the redistribution of the metals from the “immobilized” to more mobile fractions (Stephens et al. 2001; Zoumis et al. 2001; Peijnenburg and Jager 2003; Simpson and Batley 2003; Simpson et al. 2004). Sequential extraction carried out after 5 weeks of sediment aging showed an increased mobility of all metals.

This increase is especially characteristic for zinc. The zinc proportion in the exchangeable fraction at the beginning of the experiment was 55.3%, and after 5 weeks, it amounted to 68.2%, becoming thus more mobile and more available. There was an increase in the concentrations of lead, nickel, copper, and zinc in the reducible fraction.

The increase in the content in this fraction may be due to the capturing with iron oxo-hydroxide, which is readily formed during sediment oxidation. Hydrated iron oxide captures metals from the sediment, due to the change in pH (Alloway 1995). Three common hydrated iron oxides, ferrihydrite, hematite, and goethite, exhibit adsorption potential for certain metals. Thus, ferrihydrite adsorbs metals in the order: $Pb > Cu > Zn > Ni > Cd$; hematite ($\alpha\text{-Fe}_2\text{O}_3$): $Pb > Cu > Zn > Ni$; and goethite (-FeOOH): $Cu > Pb > Zn > Cd$ (Alloway 1995). Coprecipitation of metals with iron/manganese oxide may explain the increase of the concentrations of Pb, Zn, and Ni in the reducible fraction, due to their coprecipitation with iron oxide (Alloway 1995, Stephens et al. 2001).

During sediment aging, metal sulfides are probably oxidized to sulfates. The metals that were bound to the sulfide surface in the anoxic sediment get released and then adsorbed on the newly formed sulfate surfaces and/or are coprecipitated as oxides. In some cases, metal oxides are less soluble than the corresponding metal sulfides, yielding a lower availability. Since the sulfide is oxidized during aging, a smaller portion of the metal is available on the surface of the organic matter (Sposito 1984). The organic matter itself becomes structurally less complex with aging, that is, with drying and oxidation (Gambrell and Patrick 1978). At the same time, the metals are released from the association with organic matter, which increases their availability. Oxidation of sulfides (to sulfates) and organic matter that takes place in the disposed sediment after its dredging yields the release of metals

bound to the oxidizable fraction and especially influence the behavior of zinc and nickel (Åström 1988; Stephens et al. 2001). This is in agreement with our findings from the SEM and AVS analysis.

Since some metals during aging are redistributed from the less to the more available forms, this has to be especially taken into account when considering dredging operation and disposal of such sediment, because the migration of these metals can increase their availability. Additional investigations are needed to characterize the operational processes occurring after the disposal on the soil (Stephens et al. 2001; Zoumis et al. 2001; Peijnenburg and Jager 2003; Simpson and Batley 2003; Simpson et al. 2004).

When this three-extractability order is examined (sum of F1+F2+F3), it seems that probably the most mobilizable elements are Cd, Pb and Zn. The non-residual fractions (exchangeable+reducible+oxidizable) of these metals were greater than 80% (80.1% for Cd, 91.1% for Pb, and 95.5% for Zn). This is also an indication that these metals in sediments are potentially available for exchange and/or release into the environment.

Comparison of the results of sequential extraction and the results of SEM and AVS analysis shows good agreement for Pb and Zn. Therefore, a single approach to quality assessment may be insufficient.

Modified BCR sequential extraction procedure can provide useful information for migration assessment in the landfill since the amounts of metals mobilizable under different changes in environmental conditions can be determined. This should be taken into consideration if the contaminated sediment is to be dredged.

BCR procedure could be useful also as a potential method to determine if the heavy metals can be removed by remediation techniques or predict removal efficiency is to determine speciation by selective extraction techniques (Mulligan et al. 2001). It is believed that exchangeable, carbonate, and reducible oxide fractions may be amenable to soil washing techniques (Li et al. 1995). Removal of the organically and residually bound fractions may be justified if, as in our case, one metal is easily available, that is, present in the exchangeable and reducible fractions (Cd), and the other is potentially not easily available (Pb). Gombert (1994) used sequential extraction to determine if cesium, cobalt, and chromium could be removed by soil washing. Since less than 20% was extracted after dissolving 20% of the soil mass, soil

washing was abandoned as an option. Mulligan et al. (1999) demonstrated that sequential extraction could be used prior to soil washing, to design and monitor the remediation process.

After 5 weeks of aging, applied RAC revealed that Pb, Cd, and Zn mostly exist in labile fractions and therefore are coming under the very high risk and high-risk category and can easily enter the food chain. Because of their toxicity and availability, they can pose serious problems to the ecosystem. The total content of these metals in the sediments is quite high and its association with labile fractions may cause deleterious effects. Speciation pattern of Cu, Ni, and Cr remained same as at the beginning of the experiment.

4 Conclusions

The modified BCR fractionation scheme was employed to determine exchangeable (soluble, labile), oxidizable, reducible, and residual metal fractions in contaminated sediment and upon 5 weeks of aging. Metals exhibited different fractionation profiles. While Pb, Zn, and Cd were found mostly in the mobile fraction, Cu and Cr were present mainly in the residual fraction. In this study, Pb, Cd, and Zn seem to pose a high risk due to their high availability based on the modified BCR sequential extraction and RAC at the beginning and after 5 weeks of aging. Speciation pattern of the other metals showed only low to medium risk to the aquatic environment. Nickel showed no risk to the environment based on the results of the sequential extraction procedure. Aging resulted in an enhanced mobility of all metals, with increased proportion of Cd, Pb, and Zn in most mobile fraction. Metal content in the first three fractions of sequential extraction increased and decreased in the residual fraction.

The $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio was found to be greater than 1 at the beginning and after 5 weeks of aging and increased with time. These results indicate potential bioavailability/toxicity of the metals, and based on this ratio, according to the US EPA criteria, the samples belong to the group with probable negative effect. As far as the particular metals are concerned, zinc, lead, and copper, the $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio exceeded 1 after 5 weeks of aging. For zinc, the $\Sigma[\text{SEM}_i]/[\text{AVS}]$ ratio exceeded 1 both in the begin-

ning and after 5 weeks of aging. Comparison of the results of sequential extraction and the results of SEM and AVS analysis showed good agreement for lead and zinc.

Based on the results, the release of metals from contaminated sediment was significantly affected since the time they were exposed to oxidizing conditions.

Successful application of these methods requires further investigation in the direction of detailed study of sediment quality and risk assessment, because only one approach is not enough for easy risk assessment for the environment. Sequential extraction can clearly define binding possibilities of metals in sediment with predictions of their mobility, potential toxicity, and bioavailability.

In this study, in fact, we wanted to mimic the “worst case” scenario that could appear in real sediment samples: to see what type of metal bonding and behavior of metals is possible after a sudden increase in metal concentration happens in the sediment system in which the metals are already present in certain concentrations. Although it is not expected that the sediment polluted in the laboratory conditions is the same as the sediment polluted in natural environment, the results we obtained are very useful in elucidating the type of metal bonding and behavior that might be applicable in real conditions and future studies.

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