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Distribution of cadmium, chromium, copper, lead and zinc in marine sediments in Hong Kong waters

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Abstract Partitioning of heavy metals (Cd, Cr, Cu, Pb, Zn) in marine sediments collected from various sites in Hong Kong waters were determined using sequential extraction method. Sediments from Kellette Bank, located in Victoria Harbour, had higher metal concentrations especially Cu and Zn than most other sites. Slightly over 20% of total Cu and Cr existed as readily available forms in Peng Chau and Kellette Bank. At most sampling sites, over 15% of the Cu existed as the exchangeable form indicating that Cu could be readily released into the aqueous phase from sediments. A significantly higher percentage of Pb and Zn was associated with the three non-residual fractions. Hence, there is a greater environmental concern for remobilization of Pb and Zn compared with Cr. The high amount of residual Cd (> 50%) and the relatively lower Cd content indicate that little environmental concern is warranted for the remobilization of Cd. Distribution of metals in sediments collected from different depth at Kellette Bank shows that metal concentrations decreased with profile depth. The levels of Pb and Zn associated with the two readily available fractions increased sharply in the surface sediment. These metals represented the pollutants, which were introduced into the area in the mid-eighties through early nineties as a result of rapid economic and industrial development in the territory. As significant portions of these metals were bound to the readily available phases in the surface sediments, metal remobilization could be a concern.

Keywords Dredging · Metal pollution · Sequential extraction · Metal speciation

Introduction

Heavy metals discharged into a marine system by natural or anthropogenic sources during their transport are distributed among the aqueous phase, suspended solids and sediments. Sediments can be, depending on the environmental conditions, either a sink or a source for heavy metals in aquatic environment. Changing environmental conditions, such as pH, redox potential or the presence of organic chelators may render the remobilization of metals from sediments (Bernhard et al. 1986; Calmano et al. 1990; 1993; Nystrom et al. 2003; Guevara-Riba et al. 2004; Lager et al. 2005).

Marine sedimentary particulate matter consists of different phases, including crystalline minerals, carbonates, hydrous metal oxides and organic matters (Szefer et al. 1995). The distribution of heavy metals in the different phases of sediment determines their mobility (Rauret et al. 1988), bioavailability (Szefer et al. 1995) and toxicity (Borovec 1996) in the aquatic environment. Thus, to assess the environmental impact of polluted sediments, the determination of the total metal concentration is not sufficient. Sequential extraction techniques have been used to examine the partitioning of sediment-associated metals among the various "operationally defined geochemical phases" in the sediment.

Since the early eighties, large amounts of different pollutants have been discharged into the coastal regions in Hong Kong with the advent of industrial and commercial activities (Environmental Protection Department 1998; Li et al. 2000). The main sources of industrial effluents include the electroplating, dying, printing, metal finishing and chemical industries (Sin et al. 2001). Increased dredging, reclamation and site formation activities have also caused a significant disturbance to the already contaminated sea bed sediments. These activities may expose anoxic sediments to oxic conditions. Changing environmental conditions, such as redox potential may render the remobilization of metals from sediments. This motivated us to assess the extent of metal contamination in dredging and reclamation sites in Hong Kong. In the present study, the characteristics and distribution of cadmium, chromium, copper, lead and zinc of marine sediments were determined using sequential extraction method (Tessier et al. 1979) in order to assess the availability of these metals in six major sampling sites. Significant dredging and reclamation will be carried out in these sites.

Methods

Sampling areas and sample treatments

Six locations were selected for this study. They were: (1) Sham Tseng; (2) Peng Chau Typhoon Shelter; (3) Kellette; (4) Tolo Harbour; (5) Cheung Sha Wan; and (6) Southeast Kowloon (Fig. 1). Fifty sediment core samples were collected from these areas and they were retrieved in thick-walled (0.25 in), 3-in inside diameter tubes (Lexan) using a vacuum-action piston corer. Sample contact with oxygen was avoided to obtain meaningful extraction results from redox-sensitive solid phases. These sediment cores were immediately packed in nitrogen-pruged delivered-boxes and stored at 4°C for transport back to the laboratory. All subsequent sediment preparation and extraction steps in the laboratory were performed in an acrylic glovebox or polyethylene glovebag purge with high-purity nitrogen gas.

The sediment cores were then subsectioned into 5-cm increments using a hacksaw, and the sediment that came in contact with the hacksaw was removed with a Teflon spatula and was discarded. Each increment was then placed into 250-mL polycarbonate Sep-Cor centrifuge bottles, and the porewater was removed by centrifugation at 11,000 *g* for 25 min. Sediment samples were freeze-dried and were then homogenized with mortar and pestle until near uniform consistency, preferably to pass through a series of plastic sieve (1,180, 300, 150, 63 μm). All samples used in the study except the grain size effect were passed through the 63-μm ASTM sieve.

Wet sediment samples from both highly contaminated Tolo Harbour and less metal-rich sandy sediment from Sham Tseng were used to test the extraction procedure for intramethod reproducibility. In addition, intermethod variability between the sequential extraction procedure and a single-step acid digestion by aqua regia was investigated. Samples for inter- and intramethod reproducibility experiments were frozen until needed, and then thawed.

A necessary validation step for the extraction procedure was quantifying recovery of metal-bearing spikes added to sediment matrixes. Homogenized freeze-dried sediment was used as the matrix for spike recovery assessment. To minimize potential redox alterations in the freeze-dried sediment, the sediments were prepared in a nitrogen atmosphere and the samples were then loaded into a nitrogen-purged desiccator for freeze-drying. The freeze-dried matrix sediments used for the standardization were able to quantitatively determine spike recoveries.

Apparatus and reagents

All glassware and plasticware used for this experiment were previously soaked twice in 10% HNO_3 (v/v) for at least 24 h and rinsed with deionized-distilled water five times before used. Volumetric flasks were of Class A. A Perkin Elmer Optima 3300 DV inductively coupled plasma-atomic emission spectrometry (ICP-AES) instrument was used to determine the metal concentrations in the sample extracts.

All reagents used were of 'Analytical Grade' or 'Suprapur' quality. Deionized-distilled water (Millipore, 18.3 Mohm/cm resistivity) was used. Stock standard solutions (1,000 mg/L) acidified with nitric acid were used. All standard and reagent solutions were stored in polypropylene bottles.

Sequential extraction procedures

The leaching scheme used mainly followed that proposed by Tessier et al. (1979) with a change in the final step. This procedure defines the following fractions: exchangeable metal (extracted with $MgCl_2$ solution), bound to carbonates (leached by NaOAc/HOAc), bound to Fe-Mn oxides (extracted by $NH_2OH{\cdot}HCl$), bound to organic matter/sulfides (released from sample by HNO_3 and H_2O_2, then NH_4OAc/HNO_3 extraction), and residual [digested by aqua regia (3:1 $HCl:HNO_3$)]. Then, the metal concentration in each fraction was

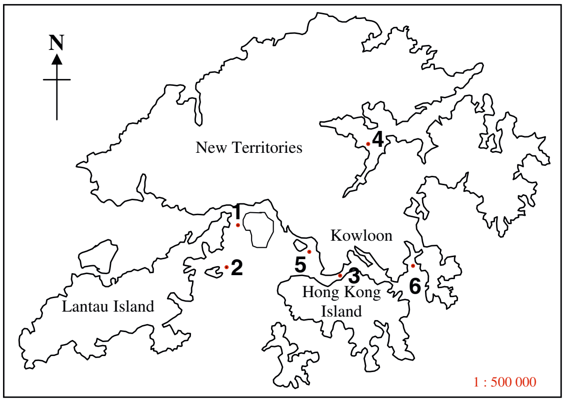

Fig. 1 Location of sampling sites (latitude/longitude)

1. Sham Tseng (22.360°/ 114.071°)
2. Peng Chau Typhoon Shelter (22.293° / 114.048°)
3. Kellette Bank (22.297° / 114.195°)
4. Tolo Harbour (22.431° / 114.208°)
5. Cheung Sha Wan (22.320° / 114.136°)
6. Southeast Kowloon (22.297° / 114.260°)

determined by ICP-AES. Seven standard solutions were prepared for calibration of each metal concentration. Calibration curves for each heavy metal were prepared prior to every batch of sample determinations. For accuracy, triplicates were analysed per sample. A standard reference material from the National Institute for Science and Technology, USA, was used for quality control purposes.

Results and discussion

General distribution of cadmium, chromium, copper, lead and zinc

The total metal concentrations (Cd, Cr, Cu, Pb, Zn) of marine sediments collected from various sites are shown in Table 1. The results are expressed as milligrams of metal extracted per kilogram of dry sediment, and are the mean value of three replicates.

Compared with other estuarine and coastal sediment, the results show similar range of metal concentration to that in Barcelona Harbour, Spain.

Sham Tseng Among all the selected locations, this area showed the lowest heavy metal concentration. It could be because there have not been too many industrial and commercial discharges into that area. By comparing with the selected background and other areas in this study, the pollution of this area was relatively low.

Peng Chau Typhoon Shelter Although there are only 32 industrial sources of discharges found in that part of Hong Kong, the metal concentrations were much higher than those in Sham Tseng. This could be due to the weak tidal flushing inside the typhoon shelter. The sediment in the typhoon shelter could be vulnerable to the accumulation of heavy metals.

Kellette Bank Sediments from this water had higher metal concentrations, especially Cu and Zn contents, than most other sites. The results indicate that significant pollution problem exists in this area. Kellette Bank is located in Victoria Harbour and some major urban areas are included in this water control zone, which received about 1.3 million m^3/day of mostly untreated sewage effluents from 12 sewage outfalls during 1997. Electroplating and metal finishing factories around the area were also the likely major sources of metal contamination.

Tolo Harbour The levels of copper, zinc and lead were relatively high. There are many industrial estates that discharge heavy metals from textiles, electroplating, galvanizing and plastic fabrication industries into the Harbour.

Cheung Sha Wan Copper concentration was very high among all the selected locations. This high concentration is expected as there are many electroplating, textile and clothing industries in this area too.

Southeast Kowloon As this sampling point was near Junk Bay, the results would be affected by the eastern buffer control zone to a certain extent. Relatively high concentration of copper was found in the sediment, which was mainly due to the industrial effluents discharged from Kwun Tong and Wan Chi. There are also many electroplating factories in this area.

Metal speciation

Heavy metals in sediments can be bound in different forms. The distribution of metal is mainly influenced by the competition of ligands in the sediment in a narrow range of pH, but wide range of redox potential (Oakley et al. 1981). On the surfaces of the sediments, the main ligands are, of course, Mn and Fe oxides (as $Mn{\cdot}MnO_2$), reactive Fe or $Fe{\cdot}MnO_2$, amorphous Fe oxides or $Fe{\cdot}Fe_2O_3$ (Horowitz et al. 1989), clay, sulfides and organic matter (as humic acids). In a sulfide-poor environment, the adsorption could be treated as competition between metals and protons for surface

Table 1 Comparisons of heavy metal content (mg/kg) in selected estuarine and coastal surface sediments in industrial areas

Description	Chromium	Copper	Lead	Zinc	Cadmium
Rotterdam Harbour, The Netherlands (van den Hurk et al. 1997)	NA	10–40	20–60	60–190	0.6–1.8
Portovesme Harbour, Italy (Schintu and Degetto 1999)	NA	NA	1–3	5–25	20–250
Barcelona Harbour, Spain (Guevara-Riba et al. 2004)	45–95	70–195	85–130	180–300	0.4–1.4
Peng Chau Typhoon Shelter	57.5	146	37.4	108	2.5
Kellette Bank	51.4	202	96	225	1.8
Tolo Habour	39.7	152	108	167	1.8
Cheung Sha Wan	57.6	195	41	111	2.3
SE Kowloon	42.1	153	20	77	1.9
Sham Tseng	34.9	112	47	93	1.5

NA not available

sites. Table 2 shows the concentrations of Cd, Cr, Cu, Pb and Zn in the various operationally defined geochemical phases of the sediment samples obtained from six selected locations in Hong Kong.

Exchangeable (I) and carbonate phases (II) These two phases represent the readily available fraction. The binding of metals onto these phases is vulnerable to pH changes and salinity fluctuations. Therefore, these phases are the most hazardous for the environment.

Reducible phase (III) This phase theoretically represents the contents of each metal bound to iron and manganese oxides that would be released if the sediment is subjected to more reductive conditions (Panda et al. 1995).

Oxidable phase (IV) This phase shows the amount of metal bound to the organic matter and sulfurs, which would be discharged into the environment if conditions change to oxidative. Such a change could occur during dredging (Förstner 1989).

Residual phase (V) In this phase, the metals, which are associated strongly to the crystalline structures of the minerals, are extracted and are therefore the most difficult to separate from the sediments (Kersten and Förstner 1991).

The idea of metal 'availability' to plants and animals is well known, and there are many empirical chemical extractants used on a routine basis to estimate the metal components in sediment and soil available for plant as well as animal uptake under varying environmental conditions (Förstner 1983, 1985; Usero et al. 1998). Figure 2 gives the metal speciation of the sediment collected from the various sites. The readily available fraction includes the exchangeable phase (I), carbonate phase (II) and the reducible phase (III). The binding of metal onto these three fractions is vulnerable to pH changes, salinity fluctuations and variations in redox potential.

Slightly over 20% of total Cu and Cr existed as readily available forms in Peng Chau and Kellette Bank. Cu and Cr present in the phase would remobilize rather easily in the seawater. At some sampling sites, over 15% of the Cu existed as the exchangeable form. This fraction would be readily released if pH is lowered in the aqueous phase. Significant amounts of Cu and Cr were associated with the oxidable phase at most sampling sites. This agrees with the result of other studies, which reported that a high portion of Cu became bound to the organic matter in the sediment (Pardo et al. 1990). Stumm and Morgan (1981) proposed that copper can easily form complexes with organic compounds that make them rather stable in the aquatic environment. The complex binding with the organic matter and the high affinity of the metal-sulfide bond provide a strong and stable binding under anoxic conditions. However, a change of oxidation state will convert organic-bound metals into mineralized metals that could cause a significant effect on the environment. Such a change could occur during dredging and thus metals would remobilize from sediments.

A significantly higher percentage, over 50%, of Pb and Zn, were associated with the three non-residual fractions at most sampling sites. Zn and Pb were mainly associated with Fe-Mn oxides, as they formed stable complexes with Fe-Mn oxides. A typical example is with Zn, which could be adsorbed on Mn/Fe-oxy-hydroxide: $Zn^{2+} + 2\ Fe^{3+} + 4H_2O \rightarrow ZnFe_2O_4 + 8H^+$ (Pulford and Bakhsh 1989). A substantial amount of zinc was found in carbonate phase (20.5 and 20.1%) at Tolo Harbour and Kellette Bank, as calcium carbonate is a strong absorbent to form complexes with zinc as double salts $CaCO_3{\cdot}ZnCO_3$ in the sediment (Zhou et al. 1998). The zinc associated with the carbonate phase would remobilize and redissolve into the seawater if the pH is changed. Hence, a greater environmental concern is warranted for the remobilization of Pb and Zn compared with Cr.

The percentage of metal extracted in each step of the sequential extraction procedure is represented as bar diagrams (Fig. 2). More than 50% of Cd existed in residual form, except for samples collected from Tolo

Table 2 Chromium, copper, lead, zinc and cadmium (mg/kg) partitioning in the sediment samples

	Sham Tseng	Peng Chau	Kellette Bank	Tolo Harbour	Cheung Sha Wan	SE Kowloon
Chromium, Cr						
I	0	0	0	0	0	0
II	0	0.2	0.4	0.7	0.1	0
III	1.2	6.9	11.1	6.3	5.9	3.3
IV	1.9	7.9	11.7	15.6	9.8	5.6
V	31.8	42.4	28.2	17.2	41.8	33.3
Total	34.9	57.4	51.4	39.8	57.6	42.2
Copper, Cu						
I	16.6	25	18.2	16	27.8	20.5
II	7.2	9.5	19.2	1.2	3.6	1.1
III	6.5	0	6.1	0	1.1	15.7
IV	9.2	31.2	54.7	38.3	58.7	15.6
V	72.9	80.1	103.7	96.7	103.6	99.7
Total	112.4	145.8	201.9	152.2	194.8	152.6
Lead, Pb						
I	0	0	0	0	1	0.2
II	7.7	4.6	21.1	4.7	1.5	0.6
III	16.5	15.2	48.1	37.1	15.5	7.5
IV	8.6	5.6	4.9	10.8	2.4	3.4
V	13.8	12.1	22	54.9	20.2	7.8
Total	46.6	37.5	96.1	107.5	40.6	19.5
Zinc, Zn						
I	0.6	0.1	0.9	1.2	0.8	0.4
II	9.4	9.5	45.2	34.3	4.2	1.1
III	15.5	31.9	71.3	53.3	36.5	26.4
IV	3.6	14	19.6	18.2	15.3	8.3
V	63.4	52.5	88.2	60.2	54.1	40.3
Total	92.5	108	225.2	167.2	110.9	76.5
Cadmium, Cd						
I	0	0	0	0	0.1	0
II	0	0	0	0.1	0	0
III	0	0.2	0	0.2	0.1	0.5
IV	0	0.3	0.5	0.9	0.4	0.1
V	1.5	2	0.8	0.5	1.7	1.3
Total	1.5	2.5	1.3	1.7	2.3	1.9

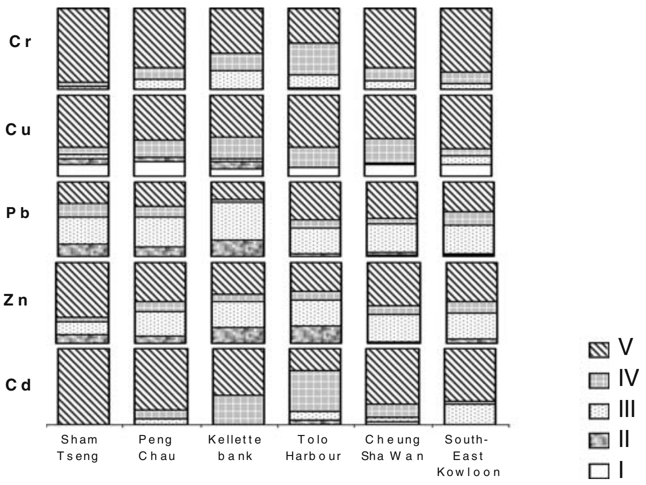

Fig. 2 Chromium, copper, lead, zinc and cadmium partitioning in the collected samples

Harbour, which were dominated by the oxidable phase. The high amount of residual Cd and the relatively lower Cd content indicate that little environmental concern is warranted for the remobilization of Cd.

Effect of depth

Figure 3 shows the distribution of metals in sediments collected from different depths at the Kellette Bank. In general, it shows that metal contents in the surface sediments were generally higher than those in the deeper layers. However, the difference in concentration between top and bottom sediment layers was not significant for Cu, Cr and Cd. The levels of Pb and Zn associated with phases II and III in the surface sediment increased sharply. These metals represented the pollutants that were introduced into the area not too long time ago as a

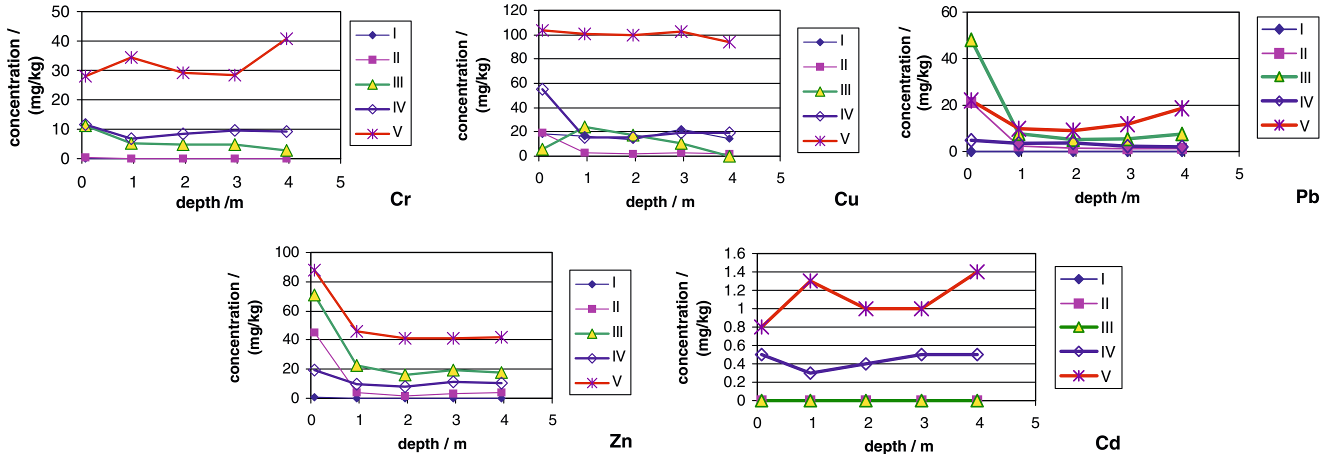

Fig. 3 Effect of depth on metal partitioning demonstrated by sediments at the Kellette Bank

result of rapid economic and industrial development. As these metals were bound to the readily available phases of the surface sediments, metal remobilization could be a concern. The metal distribution in the profile could be affected by many factors including the water input, sediment properties and dredging activities. Hence, this can also reflect the natural dynamic conditions and the disturbance by dredging activities in this area.

Conclusions

The results obtained in this project showed that the behaviours of heavy-metal partitioning onto the sediments were quite different at various locations in the Hong Kong waters. This reflected different degrees of pollution among the areas studied. Sediments from the Kellette Bank had higher metal concentrations, especially Cu (202 mg/kg) and Zn (225 mg/kg) contents, compared with most other sites in Hong Kong. Tolo Harbour and Cheung Sha Wan also had high levels of Pb and Cu in the sediments. Slightly over 20% of total Cu and Cr existed as readily available forms in Peng Chau and Kellette Bank. At most sampling sites, over 15% of the Cu existed as the exchangeable form indicating that this fraction may be readily released into the aqueous phase. A significant higher percentage of Pb and Zn were associated with the three non-residual fractions. These metals, which were bound to the first three phases, were relatively more mobile than the others, thus increasing their bioavailability. More than 50% of Cd existed in the residual form, except for samples from Tolo Harbor, which were dominated by the organic fraction. The high amount of residual Cd and the relatively lower Cd content indicate that little environmental concern is warranted for the remobilization of Cd. Distribution of metals in sediments collected from different depths at the Kellette Bank shows that metal concentrations decreased with profile depth. The levels of Pb and Zn associated with phases II and III increased sharply in the surface sediment compared with the deeper layer. These metals represented the pollutants that were introduced into the area in the mid-eighties through the early nineties as a result of rapid economic and industrial development. As these metals were bound to the readily available phases of the surface sediments, metal remobilization could be a concern.

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References

Bernhard M, Brinckman FE, Itgolic KJ (1986) Why "speciation?" In: Bernhard M, Brinckman FE, Sadler PJ (eds) The importance of chemical "speciation" in environmental processes. Springer, Berlin Heidelberg New York, pp 7–14

Borovec Z (1996) Evaluation of the concentrations of trace elements in stream sediments by factor and cluster analysis and the sequential extraction procedure. Sci Total Environ 177:237–250

Calmano W, Hong J, Förstner U (1993) Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. Wat Sci Technol 28:223–235

Calmano W, Wolfgang A, Förstner U (1990) Exchange of heavy metals between sediment components and water. In: Broedaert AC, Gucer S, Adams F (eds) Metal speciation in the environment. NATO ASI Series G: Ecological Science, vol 23. Springer, Berlin Heidelberg New York, pp 503–522

Environmental Protection Department (1998) Marine water quality in Hong Kong in 1997. Government Printer, Hong Kong

Förstner U (1983) Assessment of metal pollution in rivers and estuaries. In: Thornton I (ed) Applied environmental geochemistry. Academic, London, pp 395–423

Förstner U (1985) Chemical forms and reactivities of metals in sediments. In: Leshber R, Davis RD, L'Hermite P (eds) Chemical methods for assessing bio-available metals in sludges and soils. Elsevier, London, pp 1–30

Förstner U (1989) Contaminated sediments. In: Bhattacharji S, Friedman GM, Neugebauer HJ, Seilacher A, eds., Lecture Notes in Earth Sciences, vol 21. Berlin Heidelberg New York: Springer-Verlag

Guevara-Riba A, Sahuquillo A, Rubio R, Rauret G (2004) Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. Sci Total Environ 321(1–3):241–255

Horowitz AJ, Elrick KA, Hooper RP (1989) Prediction of aquatic sediment-associated trace element concentrations using selected geochemical factors. Hydrol Process 3:347–364

Kersten M, Förstner U (1991) Speciation of trace elements in sediments. In: Batley GE (eds) Trace element speciation: analytical methods and problems. CRC Press, Boca-Raton, pp 245–317

Lager T, Hamer K, Schulz HD (2005) Mobility of heavy metals in harbour sediments: an environmental aspect for the reuse of contaminated dredged sediments. Environ Geol 48(1):92–100

Li XD, Wai OW H, Li YS, Coles BJ, Ramsey MH, Thornton I (2000) Heavy metal distribution in sediment profiles of the Pearl River estuary, South China. Appl Geochem 15:567–581

Nystrom GM, Ottosen LM, Villumsen A (2003) The use of sequential extraction to evaluate the remediation potential of heavy metals from contaminated harbour sediment. J Physique IV 107(2):975–978

Oakley SM, Nelson PO, Williamson KJ (1981) Model of trace-metal partitioning in marine sediments. Environ Sci Technol 15:475–480

Panda D, Subramanian V, Panigrahy RC (1995) Geochemical fractionation of heavy metals in Chika Lake (east coast of India)—a tropical coastal lagoon. Environ Geol 26:199–221

Pardo R, Barrado E, Perez L, Vega M (1990) Determination and speciation of heavy metals in sediments of the Pisuerga River. Water Res 24:373–379

Pulford ID, Bakhsh A (1989) Uptake of zinc by soil: adsorption or precipitation? In: Proceedings ofinternational conference on heavy metals in the environments, vol 2, pp 193–196

Rauret G, Tubio R, Lopez-Sanchez JF, Casassas E (1988) Determination and speciation of copper and lead in sediments of a Mediterranean river (River Tenes, Catalonia, Spain). Water Res 22:449–455

Schintu M, Degetto S (1999) Sedimentary records of heavy metals in the industrial harbour of Portovesme, Sardinia (Italy). Sci Total Environ 241:129–141

Sin SN, Chua H, Lo W, Ng LM (2001) Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong. Environ Int 26(5–6):297–301

Stumm W, Morgan JJ (1981) Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters, 2nd edn. Wiley, New York

Szefer P, Glasby GP, Penpkowiak J, Kaliszan R (1995) Extraction studies of heavy-metal pollutants in surficial sediments from the Southern Baltic Sea of Poland. Chem Geol 120:111–126

Tessier A, Campbell PGC, Bison M (1979) Sequential extraction procedure for the speciation of particulate metals. Anal Chem 51:844–851

Usero U, Gamero M, Morillo J, Gracia I (1998) Comparative study of three sequential extraction procedures for metals in marine sediments. Environ Int 24:487–496

van den Hurk P, Eertman RHM, Strokhorst J (1997) Toxicity of harbour canal sediments before dredging and after off-shore disposal. Mar Pollut Bull 34(4):586–590

Zhou HY, Cheung RYH, Chan KM, Wong MH (1998) Metal concentrations in sediments and *Tila Pia* collected from inland waters of Hong Kong. Water Res 32:3331–3340