

Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay, China

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Abstract

This work investigated the distribution and speciation of Cd, Cu, Pb, Fe and Mn in the shallow sediments of Jinzhou Bay, Northeast China, which has been heavily contaminated by nonferrous smelting activities. The concentrations of Cd, Cu and Pb in sediments were found to be 100, 13 and 7 times, respectively, being higher than the national guideline (GB 18668-2002). Sequential extraction test showed that 39%–61% of Cd were exchangeable fractions, indicating that Cd in the sediments posed a high risk to local environments. While Cu and Pb were at moderate risk levels. According to the relationships between percentage of metal speciation and total metal concentration, it was concluded that the distributions of Cd, Cu and Pb in some geochemical fractions were dynamic in the process of pollutants migration and the stability of metals in sediments of Jinzhou Bay decreased in the order of Pb > Cu > Cd.

Key words: heavy metals; sediment pollution; fractionation; Jinzhou Bay; risk assessment

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Introduction

Since the Industrial Revolution, tremendous amounts of toxic pollutants have been discarded into coastal environment and the sediments of bays and estuaries have represented huge sinks of heavy metals (Fukue et al., 1999; Turner, 2000; Billon et al., 2002; Fan et al., 2002). Toxic heavy metals are adsorbed onto organic matter and mineral surfaces in inorganic or organic forms. Extraction and disturbance processes altering redox potential of sediments and chemical forms of heavy metals can accelerate the emission flux of heavy metals from sediments to water and organism (Gambrell et al., 1980; Zhuang et al., 1994; Fan et al., 2002). One way of understanding geochemical effects on metal bioavailability is based on total metal concentrations in sediments collected across a widely spatial scale and metals speciation extracted by various acid and digestion methods (Tessier et al., 1993; Rule and Alden, 1996; Du Laing et al., 2002). Previous studies have generally shown that (1) labile metals (such as those extracted easily by MgCl_2 , acetate acid and diluted HCl) are more bioavailable to benthic biota (Du Laing et al., 2002); (2) metals associated with the amorphous Fe-Mn oxides are unavailable for benthic organisms; (3) acid volatile sulfur concentration strongly influences the bioavailability of metals to the benthic animals (Ankley et al., 1991; Di Toro et al., 1992; Chen and Mayer, 1999);

and (4) the influence of organic coating on metal assimilation from sediment is inconsistent (Schlekat et al., 1999; Griscom et al., 2000; Lee et al., 2000). However, these relationships are not invariable along with the variation of environmental parameters; such as salinity, pH and redox potential. Despite that metal sulfides are very insoluble in anaerobic environment, once exposed to enough oxygen some metal sulfides like CdS will be transformed into soluble CdSO_4 (Di Toro et al., 1996). Gallon et al. (2004) also suggested that reductive dissolution of hydrous Fe-Mn oxides could release Pb from sediments to interstitial water. Therefore, the distribution, mobility and bioavailability of heavy metals may be greatly different in various aquatic environments.

A great mass of toxic metal-containing wastewater and solid wastes directly has been disposed into Wuli River and Jinzhou Bay since 1937. As a huge sink of various heavy metals, Jinzhou Bay is drawing increasing attention from government and researchers nationwide (Ma et al., 1989; Qiao, 1991; Zhu et al., 1992; Shao et al., 1993; Fan et al., 2002). It was reported, for instance, that the concentration of Cd and Cr in some commercial mollusks collected from Jinzhou Bay was as high as 6.54 and 6.64 mg/kg wet weight, respectively, which is about 65 and 3.3 times that of national guideline values for seafood safety (GB 18406.4-2001) (He, 1996). High concentration of Hg ((2.19 ± 1.17) mg/kg) and Cd ((0.46 ± 0.32) mg/kg) in piscatorial hairs was also reported (Fu et al., 1992). In

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general, sediments of Jinzhou Bay contributed massive heavy metals to seawater and organisms. In spite of some previous surveys, the behavior of heavy metals in Jinzhou Bay is not well understood yet. The aims of present work were: (1) to explore the relationship between elements migration and geochemical phases of Cd, Cu and Pb; (2) to assess mobility and ecological risk of these metals in the sediments of Jinzhou Bay.

1 Materials and methods

1.1 Study area

Jinzhou Bay, located in northwest of Liaodong Gulf ($40^{\circ}43' - 40^{\circ}53'N$, $120^{\circ}55' - 121^{\circ}05'E$), northeast China, is a semi-closed shallow water area with the average depth of 3.5 m and total area of 120 km^2 (Fig. 1). The area of intertidal belt accounts for about 40% of the bay due to relatively flat seafloor and shallow water in this area. Six rivers including Wuli River, Lianshan River, Cishan River, Lao River, Tashan River, and Zhouliu River flow into Jinzhou Bay. Extensive lead-zinc smelting activities are found along the southwest bank of Wuli River, which constitute major sources of heavy metal pollution to surrounding environments due to fluedust emission, wastewater discharge and tailings discarding. Land reclamation from sea by landfill of soils and solid wastes has been undertaken, which has created 20 km^2 of new land along the west coast of Jinzhou Bay (Fig. 1). This also contributes to the worsening pollution of the sedimentary environments in this area.

1.2 Sampling and pretreatment

From 17 to 18 of August 2007, surface sediment samples at site HLD-1 and six sediment cores at site HLD-3 to HLD-8 were collected using a stainless gravity corer (Fig. 1). The cores were sectioned at 1 cm intervals and each core section was sliced into 50 mL polyethylene centrifuge tubes. All the sediment samples were carried to laboratory and preserved in a refrigerator at $3 - 4^{\circ}\text{C}$. Before determination of elements concentration, sediment samples were

freeze-dried and homogenized using a mechanical agate mortar.

1.3 Determination of cadmium, copper, lead, iron and manganese

The sediment samples were digested using concentrated analytical grade HNO_3 and HClO_4 . Approximate 0.5 g of dry sediment sample was put into a glass vessel and 5 mL of concentrated HNO_3 was added. In succession, the glass vessel was heated on an electrothermal board at 150°C until the mixture was nearly dried. Another 5 mL of concentrated HNO_3 and 3 mL of concentrated HClO_4 were added into the glass vessel and maintained at 150°C for 3 hrs. During the digestion process, a tundish was used to cover the mouth of glass vessel for preventing acid splashing. After cooling, the digested sample was decanted into a glass tube and diluted to 25 mL with 2% HNO_3 . The metal concentrations were determined using an atomic absorption spectrophotometer (Varian AA240, USA). Deuterium background correction was used. The detection limits for Cd, Cu, Pb, Fe and Mn were 0.01, 0.02, 0.02, 0.05 and 0.05 mg/L, respectively.

1.4 Total organic carbon analysis

Total organic carbon (TOC) content was assessed after sample oxidation in potassium dichromate (VI) according to the Tiurin method.

1.5 Sequential extraction

Sediment samples from sites HLD-3, HLD-5 and HLD-8 were sequentially extracted according to modified Tessier method (Ure et al., 1993). The detailed procedures are described as below:

(1) Exchangeable fraction. A 20-mL of magnesium chloride solution (1 mol/L MgCl_2 , pH 7.0) was added in each 50 mL centrifuge tube containing 0.5 g dry sediment sample. The sediment was extracted at room temperature for 16 hr with vigorous agitation using a rotary bed at 160 r/min.

(2) Fraction bound to carbonates. The residue from step (1) was agitated in 20 mL acetic acid (0.11 mol/L) for 16

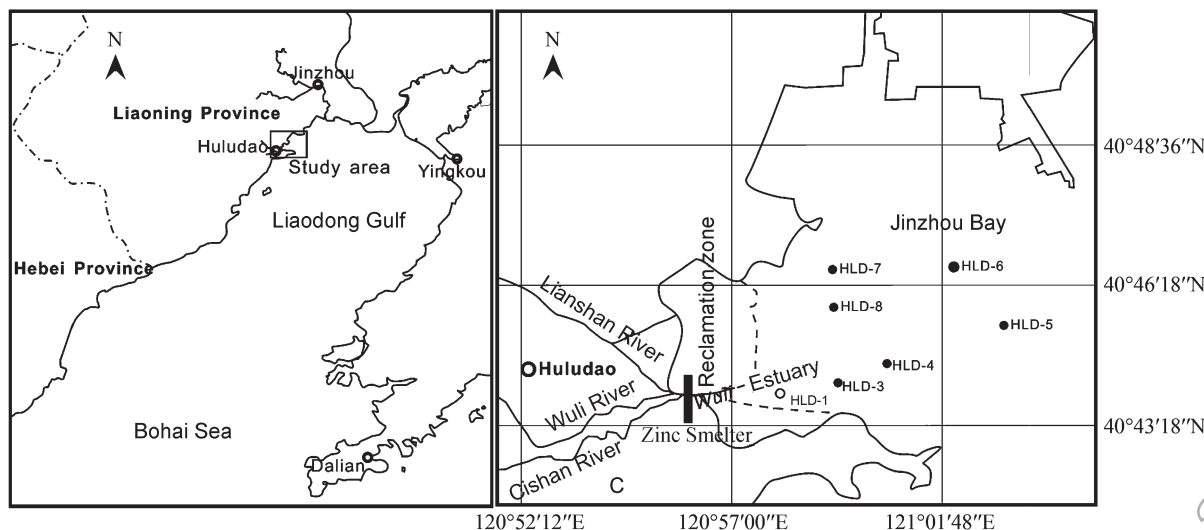


Fig. 1 Schematic maps of sampling location in Jinzhou Bay.

hr at ambient temperature.

(3) Fraction bound to hydrous Fe-Mn oxides. The residue from step (2) was mixed with 20 mL hydroxylamine hydrochloride (0.1 mol/L, pH 2, adjusted by HNO_3) and agitated for 24 hr at room temperature.

(4) Fraction bound to organic matter and sulfides. The residue in the centrifuge tube of step (3) was mixed with 10 mL of H_2O_2 (8.8 mol/L, pH 2–3), loosely covered with a small glass funnel and digested at room temperature for 1 hr with occasional shaking. Thereafter, the tube was allowed to stand for 1 hr in a 85°C water bath. The solution volume was reduced to a few milliliters by heating the uncovered tubes in a boiling water bath. This procedure was repeated twice. Then, 50 mL of ammonium acetate (1 mol/L, adjusted to pH 2 with HNO_3) was added and the tube was shaken for 16 hr at room temperature.

(5) Residual fraction. The residue from step (4) was digested using a mixture of HNO_3 and HClO_4 as described in Section 2.3.

After centrifugation for 10 min at 4000 r/min, the supernatant of each step was separated for the analysis of Cd, Cu, Pb, Fe and Mn.

1.6 QA/QC

The quality assurance and quality control were controlled by method blanks, sample duplicates, and certified

Table 1 Method precision and credibility of Cd, Cu, Pb, Fe and Mn (GBW 08301)

Element	Certified value (mg/kg) ^a	Measured value (mg/kg)
Cd	2.45 ± 0.15	1.9 ± 0.31
Cu	53 ± 3	47 ± 3.4
Pb	79 ± 6	69 ± 2.8
Fe	39400 ± 600	34100 ± 610
Mn	975 ± 17	776 ± 55.5

^a Certified value of reference materials were determined by digestion using HClO_4 , HNO_3 and HF.

Data are expressed as mean ± standard deviation, $n = 4$.

reference material (GBW 08301, river sediment). The results showed that all elements concentrations in method blanks were below the detection limits of the FAAS. The recovery efficiency was > 77% for all metals using acid extraction when compared with certified values of total metals concentrations in reference sediment which was determined using HNO_3 , HClO_4 and HF (Table 1). The relative variation factors of duplicates were < 17%. Four sets of TOC duplicate digests lead results consistent within 10%.

2 Results and discussion

2.1 Spatial and temporal distribution of heavy metals and TOC

2.1.1 Cadmium, copper and lead

Table 2 summarizes the concentrations of Cd, Cu and Pb in sediments from Jinzhou Bay. It is obvious that average concentrations of Cd, Cu and Pb decreased systematically from Wuli Estuary to offshore sites. The concentrations of Cd, Cu and Pb in the sediment at site HLD-1 reached 64, 400, and 460 mg/kg, respectively, which exceeded the national guideline values (GB 18668-2002) by 100, 13, and 7 times, respectively. The lightest contamination was detected at site HLD-5 which is about 8 km away from Wuli Estuary. The concentrations of Cu ((26 ± 8.3) mg/kg) and Pb ((41 ± 5.7) mg/kg) in the sediment at site HLD-5 were below the national guideline value (GB 18668-2002), but Cd concentration ((1.5 ± 0.2) mg/kg) was 2 times higher than the guideline value.

Temporal variation of metal concentrations in sediment cores is illustrated in Fig. 2. It can be seen that from bottom to top of the sediment cores at sites HLD-3, HLD-4, HLD-6 and HLD-8, the concentration of Cd, Cu and Pb increased gradually to a peak at 9 cm, and then reached the second peak at around 6 cm. In succession, a sharp decreasing of metal concentrations was found from 6 to

Table 2 Statistics of Cd, Cu, Pb, Fe and Mn concentrations and TOC contents in sediments at all sampling sites of Jinzhou Bay

Site	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Fe (mg/g)	Mn (mg/kg)	TOC (%)	<i>n</i>
HLD-1	64	400	460	23	260	2.0	1
HLD-3	25 ± 8.5 (13–36)	150 ± 47 (110–240)	260 ± 43 (230–340)	33 ± 2.9 (31–39)	540 ± 110 (410–740)	1.9 ± 0.24 (1.8–2.4)	6
HLD-4	4.7 ± 1.4 (2.4–7.6)	41 ± 6.1 (32–53)	64 ± 12 (49–86)	26 ± 5.1 (21–38)	460 ± 91 (380–680)	1.3 ± 0.2 (1.0–1.7)	10
HLD-5	1.5 ± 0.2 (1.2–1.9)	26 ± 8.3 (15–42)	41 ± 5.7 (31–47)	21 ± 4.7 (15–29)	430 ± 67 (320–530)	0.99 ± 0.09 (0.84–1.1)	9
HLD-6	3.5 ± 0.7 (2.5–5.1)	41 ± 7.6 (26–51)	56 ± 11 (46–80)	25 ± 6.9 (18–42)	550 ± 120 (370–730)	1.3 ± 0.11 (1.1–1.4)	11
HLD-7	15 ± 3.5 (8.2–20)	79 ± 30 (41–130)	120 ± 21 (76–140)	28 ± 12 (9.4–43)	400 ± 100 (210–560)	1.3 ± 0.15 (1.1–1.5)	8
HLD-8	16 ± 6.6 (6.9–27)	72 ± 24 (30–110)	150 ± 52 (80–260)	32 ± 5.4 (22–40)	430 ± 67 (310–550)	1.7 ± 0.34 (1.2–2.4)	14
Bay of Güllük ^a	0.56	25	20				
Mediterranean Sea ^b	0.1–13.5	1.1–51.3	1.3–394				
France SW Coast ^c	0.29–1.91	46–97	44.6–106				
Ria de Aveiro lagoon ^d	7 (max)	203 (max)	84 (max)				
Kaohsiung Estuary ^e	0.1–4.64	48.2–505	34.3–140				
Jinzhou Bay ^f	2.6–488						

^a Dalman et al., 2006; ^b Alomary and Belhadj, 2007; ^c Fichet et al., 1999; ^d Monterroso et al., 2003; ^e Chen and Wu, 1995; ^f Fan et al., 2002.

Data are expressed as mean concentration ± standard deviation (range).

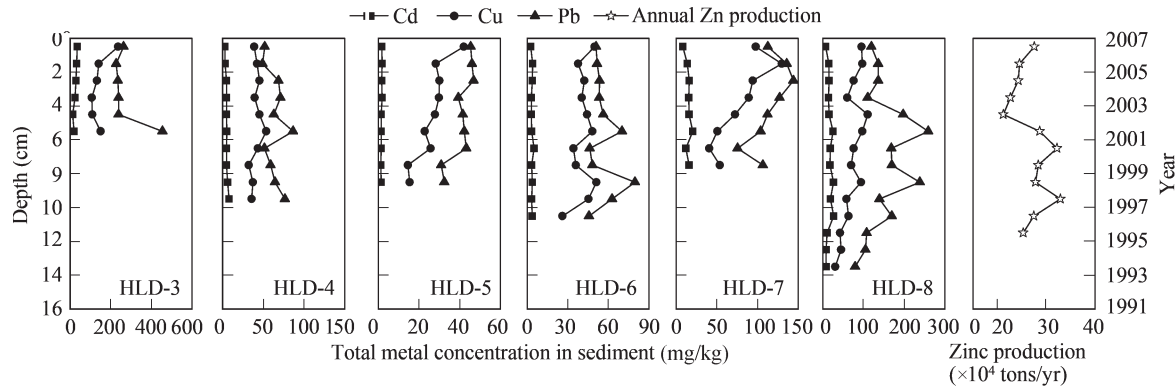


Fig. 2 Vertical distribution of Cd, Cu and Pb in sediment cores collected from Jinzhou Bay and annual Zn production from Zinc Smelter.

4 cm. Temporal metal concentrations at sites HLD-5 and HLD-7 showed different pattern from other sampling sites because the effect of pollutants imported from Wuli River was relatively weak at these two sites. According to the sedimentation rate of about 1.0 cm/yr (Ma and Shao, 1994), the comparison between temporal variations of heavy metals in sediment cores and annual Zn production from 1995 to 2006 showed that two peaks pattern of metal concentrations in sediment cores was similar to annual Zn production of local Zn smelter (Fig. 2). This is conclusive evidence that Zn smelting operation was the dominant pollution source of aquatic environment in Jinzhou Bay.

Heavy metal concentrations in sediments from other areas in the world are also shown in Table 2. Fan et al. (2002) reported a very high concentration of Cd (488 mg/kg), which is about 7 times higher than the maximum value found at sampling site HLD-1 in the present work. The sediment sample with much elevated concentration of Cd obtained by Fan et al. (2002) was probably collected from the most heavily polluted estuarine area which has been reclaimed by landfill (Fig. 1).

2.1.2 Iron, manganese and TOC

As shown in Table 2, average concentrations of Fe, Mn and TOC are in the range of 21–32 mg/g, 260–540 mg/kg and 0.84%–2.4% in the sediments, respectively. Similar to Cd, Cu and Pb, average TOC content decreases from 2.0%

to 0.99% with increasing distance away from Wuli Estuary. Vertical distributions of Fe, Mn and TOC are illustrated in Fig. 3 and no temporal regularity is observed in all sediment cores.

2.1.3 Relationships between Cd, Cu, Pb, Fe, Mn and TOC

Pearson’s correlations between the mean value of Cd, Cu, Pb, Fe, Mn and TOC were investigated (Table 3). Apparently, Cd, Cu and Pb correlated with each other very significantly ($p < 0.01$), indicating that heavy metals were released from the same source. It was also found that relationships between TOC and Cd, Cu and Pb were significant and the Pearson’s correlation coefficients achieved 0.82 ($p < 0.05$), 0.77 ($p < 0.05$) and 0.88 ($p < 0.01$), respectively. It showed that both organic carbon and metals originated from terrestrial sources. At

Table 3 Pearson correlation coefficients (r) between the mean values of Cd, Cu, Pb, Fe, Mn and TOC from all sampling sites, respectively

	Cd	Cu	Pb	Fe	Mn
Cu	0.99**				
Pb	0.99**	0.98**			
Fe	−0.04	−0.15	0.05		
Mn	−0.76*	−0.80*	−0.70	0.27	
TOC	0.82*	0.77*	0.88**	0.48	−0.50

* Correlation is significant at the 0.05 level (2-tailed); ** correlation is significant at the 0.01 level (2-tailed).

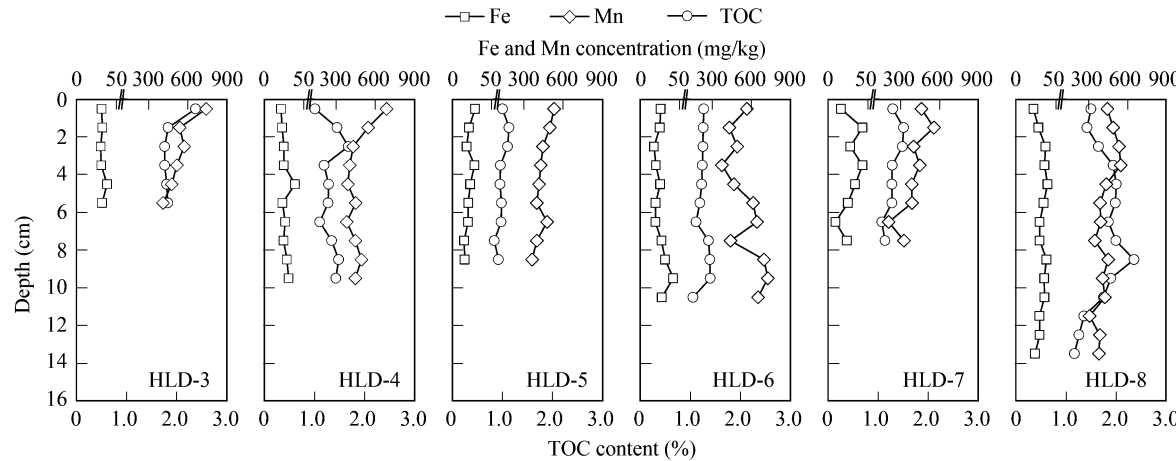


Fig. 3 Vertical variation of Fe, Mn and TOC in sediment cores collected from Jinzhou Bay.

the same time, strong association between metals and organic carbon induced similar characteristics of migration in aquatic environment (Ottosen and Villumsen, 2006). No significant relationship between the concentrations of trace metals (Cd, Cu and Pb) and Fe were observed. Mn has significant negative relationship with Cd and Cu. The possible reason for this difference is that Cd and Cu mainly originate from anthropogenic activities whereas Fe and Mn were controlled by natural geochemical process.

2.2 Metal speciation in sediments

It has been demonstrated that metal speciation and solubility affect the mobility, bioavailability and toxicity of metals significantly (Griscom et al., 2000; Yap et al., 2002; Amiard et al., 2007). Although the sequential extraction method elaborated by Tessier et al. (1979) and modified by other researchers (e.g., Ure et al., 1993; Mossop and Davidson, 2003) has some shortcomings for identifying metal speciation (Martin et al., 1987; Zhang et al., 2001), it has been widely employed to study the geochemical occurrence of metals in suspended and deposited sediments (e. g., Pueyo et al., 2001; Svete et al., 2001; Martinez et al., 2002; Peng et al., 2005). To access the mobility and bioavailability of Cd, Cu and Pb, five-step sequential extraction method was performed to determine the geochemical distribution of Cd, Cu, Pb, Fe and Mn in sediments collected from sites HLD-3, HLD-5 and HLD-8 according to the modified Tessier method (Ure et al., 1993).

2.2.1 Exchangeable fraction

It has been widely accepted that the exchangeable metal in sediments is labile, highly toxic and the most bioavailable fraction. Our study showed that the exchangeable fraction of Cd accounted for 61%, 39% and 57% of total Cd content in the sediments at site HLD-3, HLD-5 and HLD-8, respectively (Table 4). Elevated percentage of exchangeable Cd indicates that Cd has posed a great threat to benthic biota in the bay and local residents. At the same time, only 3.7%–7.9% of Mn was extracted by $MgCl_2$ solution and the amounts of exchangeable Cu, Pb and Fe were negligible (Table 4).

2.2.2 Fraction bound to carbonate

Because metals bound to carbonate minerals are bioavailable for gut environment of benthic organisms, metals bound to carbonate was extracted together with exchangeable fraction according to some methods (such as BCR). Previous studies relative to the geochemical behavior of some heavy metal ions (such as Cd^{2+} , Cu^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+}) reported that these metallic ions can be adsorbed onto the surfaces of carbonate minerals followed by incorporation into the crystal lattice to form $Cd_xCa_{1-x}CO_3$ solid solution (Billon et al., 2002). From Table 4, it can be seen that approximately half (46%–54%) of Mn and 10%–25% of Cd, Cu and Pb were associated with carbonate minerals and only a small fraction of Fe (1.3%–2.1%) was found in this phase. This reveals that calcite has a strong affinity for all the investigated metals (especially for Mn) but Fe. From the electron spin resonance investigations of Mn in calcite, Billon et al. (2002) contended that most Mn bound to carbonate mineral was well dispersed on sedimentary calcite surface. However, this cannot explain how other metals bind to carbonate minerals and why such large a fraction of Mn is adsorbed by sedimentary calcite in Jinzhou Bay.

2.2.3 Fraction bound to hydrous Fe-Mn oxide

Due to the large surface area, amorphous hydrous Fe-Mn oxides are one of the most important geochemical phases impacting the mobility and behavior of trace metals (Swallow et al., 1980; Petersen et al., 1993; Turner, 2000). Large numbers of studies have been conducted to remove organic or inorganic pollutants by utilizing the strong adsorption capacity of hydrous Fe or Mn oxides (Jackson and Bistricki, 1995; Wang et al., 1997; Choo and Kang, 2003; Root et al., 2007). Due to their chemical characteristics, Fe and Mn extracted by hydroxylamine hydrochloride solution are regarded as amorphous hydrous Fe-Mn oxides in sediments or soils (Ariza et al., 2000). Our results showed that 7.6%–12% of Fe and 9.7%–13% of Mn occurred as amorphous Fe-Mn oxides in sediments of Jinzhou Bay; and 4.6%–6.9% of Cd was found to be associated with Fe-Mn oxides. It has been proved that

Table 4 Average percentage of five sequentially extracted phases of Cd, Cu, Pb, Fe and Mn in the sediment (%)

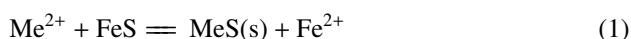
Element	Site	Exchangeable	Bound to carbonate	Bound to Fe-Mn oxide	Bound to organic matter and sulfide	Residual
Cd	HLD-3	61 (59–62)	16 (14–18)	4.6 (3.7–5.1)	13 (18–16)	4.9 (3.8–6.7)
	HLD-5	39 (34–48)	22 (15–36)	6.9 (3.3–9.5)	13 (9.0–18)	19 (13–24)
	HLD-8	57 (37–77)	21 (11–40)	6.3 (0.3–12)	9.4 (5.8–15)	5.7 (2.8–9.6)
Cu	HLD-3	1.3 (0.9–1.6)	25 (18–32)	19 (16–21)	14 (13–19)	41 (32–49)
	HLD-5	0.6 (0–1.7)	9.9 (6.3–13)	21 (16–23)	4.5 (2.9–6.3)	64 (58–74)
	HLD-8	0.9 (0–2.1)	18 (11–27)	22 (17–27)	8.5 (4.9–14)	51 (30–67)
Pb	HLD-3	N.D.	17 (16–20)	41 (53–48)	16 (12–21)	25 (22–30)
	HLD-5	N.D.	16 (11–24)	51 (47–56)	11 (7.0–14)	23 (19–27)
	HLD-8	N.D.	16 (11–20)	47 (42–54)	16 (10–20)	21 (12–26)
Fe	HLD-3	N.D.	2.1 (1.2–2.9)	12 (8.3–15)	0.7 (0.6–0.9)	86 (83–89)
	HLD-5	N.D.	1.3 (0.7–1.7)	7.6 (5.2–10)	0.8 (0.5–1.0)	90 (88–93)
	HLD-8	N.D.	2.1 (1.2–2.9)	11 (8.0–17)	0.8 (0.6–1.1)	86 (79–90)
Mn	HLD-3	7.9 (5.2–11)	49 (46–52)	11 (10–12)	3.9 (2.5–5.0)	29 (26.1–33)
	HLD-5	3.7 (2.3–4.9)	54 (47–62)	9.7 (7.1–12)	3.9 (3.5–4.4)	29 (25–34)
	HLD-8	6.1 (3.3–12)	46 (16–53)	13 (5.7–20)	4.8 (4.1–7.4)	30 (21–51)

Data are expressed as average percentage (range). N.D.: not detected.

Cd^{2+} has a strong affinity for chloride ion but a weak affinity for organic matter compared to many other trace metals in seawater (Tipping et al., 1998). Thus, cadmium intends to exist as various chlorocomplexes forms rather than free Cd^{2+} in seawater. As a result, the adsorption on Fe-Mn oxides and coordination with organic matter are appreciably hindered due to the decreased availability of free Cd^{2+} ions despite that these materials have a strong affinity for Cd^{2+} (Turner et al., 2008). Moderate amount of Cu was found binding to Fe-Mn oxides (average 19%, 21% and 22% at sites HLD-3, HLD-5 and HLD-8, respectively). About half of Pb ions (41%–51%) were found residing in hydrous Fe-Mn oxides which was significantly higher than that of Cd and Cu. This suggests that hydrous Fe-Mn oxides may play a major role in controlling the fate and transport of Pb in the sediments of Jinzhou Bay. Previous investigation demonstrated that reductive dissolution of iron oxyhydroxides and subsequent release of adsorbed Pb was a potential source of Pb in porewaters (Gallon et al., 2004). Thus, under anoxic condition, Pb bound to hydrous Fe-Mn oxides may contribute a fraction to that in interstitial or above water in Jinzhou Bay.

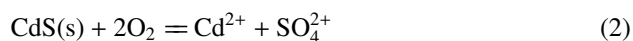
2.2.4 Fraction bound to organic matters and sulfides

Organic matter and sulfides are important factors controlling the mobility and bioavailability of heavy metals. Current opinions differ on the toxicity of heavy metals influenced by organic matters. For example, Hoss et al. (2001) proposed that Cd complexation by organic matter, serving as food, might elevate the toxicity of Cd to nematode in sediment. In contrast, Besser et al. (2003) thought that amendments of humus shifting the partitioning of Cd and Cu towards greater concentrations in sediments and lesser concentrations in porewaters reduced the toxicity of Cd and Cu. In our study, relatively low percentage of metals was found to bind to organic matters and sulfides in spite of higher TOC contents (0.99%–2.0%) in the sediments (Table 4). This indicates that organic matter is not the primary factor impacting the behavior of heavy metals in the study area. Heavy metals can substitute Fe in FeS to form metal sulfides precipitate according to Reaction (1) (Di Toro et al., 1992):



Sulfides are the major solid phases controlling the concentration of dissolved heavy metals. The sediments with an excess of acid volatile sulfur (AVS) usually have very low concentration of dissolved metals in their porewaters due to the precipitation of hardly soluble heavy metal sulfides (Di Toro et al., 1992, 1996; Simpson et al., 2000). However, sequential extraction results revealed that trace metals bound to organic matter and sulfide were minor (9.4%–13%). Simpson et al. (2000) thought that, in anthropogenically metal-contaminated, sulfide enriched estuarine sediments, Pb and Zn contaminants might not occur as metals sulfides but metal powders, oxides or solid metal salts. The occurrence and transformation of cadmium may be different from other metals. Simpson et al. (2000) found that cadmium sulfide was resistant

to oxidation during resuspension in oxygenated seawater. However, earlier investigations concluded that Cd bound to AVS can be liberated rapidly as a result of aeration of sediments and elevated oxygen level can significantly increase the bioavailability of Cd for *A. filiformis* and *M. edulis* in sediments (Zhuang et al., 1994; Schaanning et al., 1996). Therefore, a possible interpretation of high proportion of exchangeable Cd is that Cd precipitate was partially/entirely oxidized to soluble CdSO_4 during aerobic extraction processes as the following Reaction (2):



This reaction is very likely to happen in the sediments of shallow Jinzhou Bay because strong disturbance of tide and riverflow may alter the redox potential of sediment as suggested by Zhuang et al. (1994) and Schaanning et al. (1996). Hence, the present extraction results indicate a high toxicity of Cd for benthic invertebrate regardless of how much Cd was presented as CdS in the original sediment.

Relatively low percentages of Cu (4.5%–14%) and Pb (11%–16%) bound to organic matter and sulfide contributed very low toxicity to benthic biota because these fractions are stable in sediments.

2.2.5 Residual fraction

Residual phases of metals are generally much less toxic for organisms in aquatic environment. In Jinzhou Bay, dominant fractions of Fe (86%–90%) and Cu (41%–64%) were found residing in residual fraction while the percentage of Cd, Pb and Mn associated with residual fraction was 4.9%–19%, 21%–25% and 29%–30% respectively (Table 4).

2.3 Risk assessment

The distribution of metal speciation associated with different geochemical fraction is a critical parameter to assess the potential mobility and bioavailability of heavy metals in sediments. Risk assessment code (RAC) established by Perin et al. (1985) was used to evaluate the risk of Cd and Cu and Pb in sediments of Jinzhou Bay. RAC is mainly applies the sum of exchangeable and carbonate-bound fractions for assessing the availability of metals in sediments (Table 5). From Table 4, it can be seen that the sum of exchangeable and carbonate-bound fraction of Cd, Cu and Pb was 61%–79%, 11%–26% and 16%–17%, respectively. This suggests that Cd has posed a very high risk to local environment, and Cu and Pb were at medium risk level. Much more Cd distributing in labile phases (exchangeable and bound to carbonate) than Cu and Pb in the sediments illuminated that Cd was more bioavailable

Table 5 Classification of risk assessment code (RAC)

RAC	Criteria (%)
No risk	< 1
Low risk	1–10
Medium risk	11–30
High risk	31–50
Very high risk	> 50

for benthic organisms. This may be a reason why Cd concentration in mollusc was 65 times that of national safety guideline for seafood and Cu and Pb concentrations in organisms were at safe level (He, 1996).

2.4 Relationships between the distribution of metal speciation and total metal concentration

Our results showed that total metal concentrations at sites HLD-3, HLD-5 and HLD-8 were significantly different. In a sense, this difference can represent the migration distance of pollutants from estuary to offshore site. Therefore, dynamic variation and stability of metal speciation can be investigated in seaward migration process of pollutants through analyzing the relationships between percentage of metal speciation and total metal concentration in sediments of Jinzhou Bay.

The results showed that some speciation of metals correlated significantly with total metal concentrations in sediments (Fig. 4). On one hand, the percentage of

exchangeable Cd, Cu bound to carbonate and organic matters, and Pb associated with organic matters decreased with the reduction of total Cd, Cu and Pb concentrations in sediments. On the other hand, along with the decrease of total Cd, Cu and Pb, residual fractions of Cd and Cu, and Pb adsorbed on amorphous hydrous Fe-Mn oxides increased in different degrees. Above relationships may indicate that in the migration process of pollutant in JinZhou Bay, (1) exchangeable Cd, Cu bound to carbonate and organic matters, and Pb adsorbed onto organic matters could be liberated from these geochemical fractions; and (2) a fraction of Cd and Cu will enter into residual phase and Fe-Mn oxides will fix more Pb. Except above metal speciation, percentages of other metal speciation did not fluctuate with the change of total metal concentration in sediments (Fig. 4). This may suggest that these speciation in solid phase were comparatively stable in Jizhou Bay system.

According to varying degree of metal speciation shown

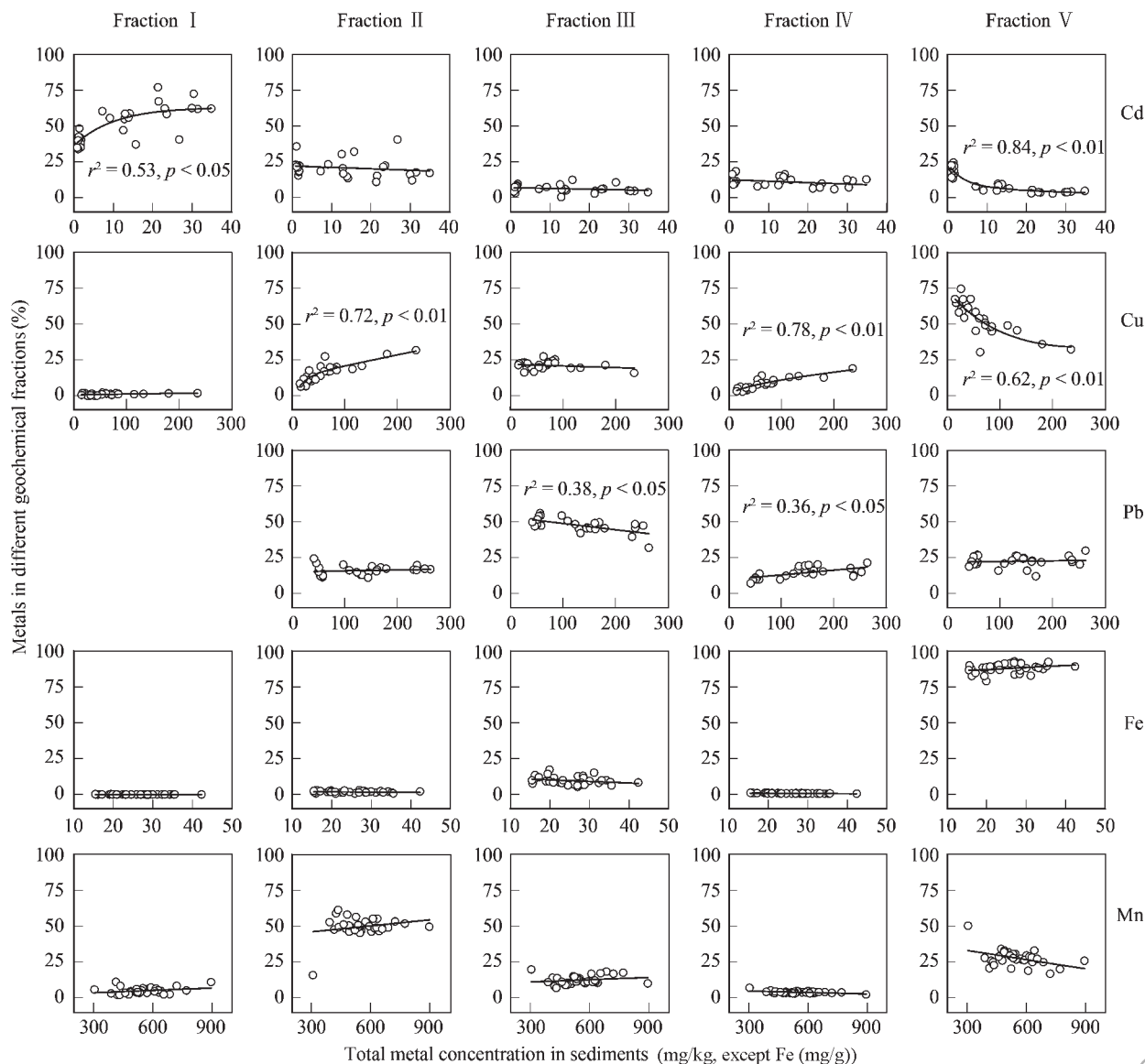


Fig. 4 Relationships between metals in different geochemical fractions and total metal concentration in sediments. Fraction I: exchangeable fraction; Fraction II: fraction bound to carbonate minerals; Fraction III: fraction bound to Fe-Mn oxides; Fraction IV: fraction bound to organic matter and sulfide; Fraction V: residual fraction.

in Fig. 4, it can be inferred that the stability of metals decreased in the order of Pb > Cu > Cd in sediments of Jinzhou Bay.

3 Conclusions

From our investigation, the following conclusions can be obtained. (1) Due to serious contamination of heavy metals from nonferrous smelting activities, the highest concentration of Cd, Cu and Pb in the sediments collected from Jinzhou Bay was up to 64, 400 and 460 mg/kg, which was 100, 13 and 7 times higher than national guideline values (GB 18668-2002), respectively. (2) Spatial distribution of Cd, Cu and Pb showed a systematical decrease from Wuli Estuary to offshore area and temporal variations of Cd, Cu and Pb concentrations in sediment profiles were well consistent with the annual Zn production of Huludao Zinc Smelter. (3) Relationships between metals speciation and total metals concentrations reflected that the stability of metals was in the order of Pb > Cu > Cd. (4) According to RAC, Cd was at very high risk level while Cu and Pb were at medium risk level for local ecosystem in Jinzhou Bay.

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References

- Alomary A A, Belhadj S, 2007. Determination of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) by ICP-OES and their speciation in algerian mediterranean sea sediments after a five-stage sequential extraction procedure. *Environmental Monitoring and Assessment*, 135: 265–280.
- Amiard J C, Geffard A, Amiard-Triquet C, Crouzet C, 2007. Relationship between the lability of sediment-bound metals (Cd, Cu, Zn) and their bioaccumulation in benthic invertebrates. *Estuarine Coastal and Shelf Science*, 72: 511–521.
- Ankley G T, Phipps G L, Leonard E N, Benoit D A, Mattson V R, Kosian P A, 1991. Acid-volatile sulfide as a factor mediating cadmium and nickel bioavailability in contaminated sediments. *Environmental Toxicology and Chemistry*, 10: 1299–1307.
- Ariza J L G, Giraldez I, Sanchez-Rodas D, Morales E, 2000. Metal sequential extraction procedure optimized for heavily polluted and iron oxide rich sediments. *Analytica Chimica Acta*, 414: 151–164.
- Besser J M, Brumbaugh W G, May T W, Ingersoll C G, 2003. Effects of organic amendments on the toxicity and bioavailability of cadmium and copper in spiked formulated sediments. *Environmental Toxicology and Chemistry*, 22: 805–815.
- Billon G, Ouddane B, Recourt P, Boughriet A, 2002. Depth variability and some geochemical characteristics of Fe, Mn, Ca, Mg, Sr, S, P, Cd and Zn in anoxic sediments from Authie Bay (Northern France). *Estuarine Coastal and Shelf Science*, 55: 167–181.
- Chen M H, Wu H T, 1995. Copper, cadmium and lead in sediments from the Kaohsiung River and its harbour area, Taiwan. *Marine Pollution Bulletin*, 30: 879–884.
- Chen Z, Mayer L M, 1999. Assessment of sedimentary Cu availability: A comparison of biomimetic and AVS approaches. *Environmental Science & Technology*, 33: 650–652.
- Choo K H, Kang S K, 2003. Removal of residual organic matter from secondary effluent by iron oxides adsorption. *Desalination*, 154: 139–146.
- Dalman O, Demirak A, Balci A, 2006. Determination of heavy metals (Cd, Pb) and trace elements (Cu, Zn) in sediments and fish of the Southeastern Aegean Sea (Turkey) by atomic absorption spectrometry. *Food Chemistry*, 95: 157–162.
- Di Toro D M, Mahony J D, Hansen D J, Berry W J, 1996. A model of the oxidation of iron and cadmium sulfide in sediments. *Environmental Toxicology and Chemistry*, 15: 2168–2186.
- Di Toro D M, Mahony J D, Hansen D J, Scott K J, Carlson A R, Ankley G T, 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environmental Science & Technology*, 26: 96–101.
- Du Laing G, Bogaert N, Tack F M G, Verloo M G, Hendrickx F, 2002. Heavy metal contents (Cd, Cu, Zn) in spiders (*Pirata piraticus*) living in intertidal sediments of the river Scheldt estuary (Belgium) as affected by substrate characteristics. *Science of the Total Environment*, 289: 71–81.
- Fan W H, Wang W X, Chen J S, 2002. Geochemistry of Cd, Cr, and Zn in highly contaminated sediments and its influences on assimilation by marine bivalves. *Environmental Science & Technology*, 36: 5164–5171.
- Fichet D, Boucher G, Radenac G, Miramand P, 1999. Concentration and mobilisation of Cd, Cu, Pb and Zn by meiofauna populations living in harbour sediment: their role in the heavy metal flux from sediment to food web. *Science of the Total Environment*, 244: 263–272.
- Fu Y N, Chen Z L, Fu Y Z, Xu H Z, 1992. The investigation of Cd and Hg accumulation in human hairs in the area of Jinzhou Bay. *Marine Environmental Science*, 11: 61–63, 67.
- Fukue M, Nakamura T, Kato Y, Yamasaki S, 1999. Degree of pollution for marine sediments. *Engineering Geology*, 53: 131–137.
- Gallon C, Tessier A, Gobeil C, Alfaro-De La, Torre M C, 2004. Modeling diagenesis of lead in sediments of a Canadian shield lake. *Geochimica et Cosmochimica Acta*, 68: 3531–3545.
- Gambrell R P, Khalid R A, Patrick W H, 1980. Chemical availability of mercury, lead, and zinc in Mobile Bay sediment suspensions as affected by pH and oxidation-reduction conditions. *Environmental Science and Technology*, 14: 431–436.
- Griscom S B, Fisher N S, Luoma S N, 2000. Geochemical influences on assimilation of sediment-bound metals in clams and mussels. *Environmental Science & Technology*, 34: 91–99.
- He G, 1996. Levels of heavy metals in molluscs from the coastal region of Bohai Sea and Huanghai Sea. *China Environmental Science*, 16: 96–100.
- Hoss S, Henschel T, Haitzer M, Traunspurger W, Steinberg C E W, 2001. Toxicity of cadmium to *Caenorhabditis elegans* (Nematoda) in whole sediment and pore water – The ambiguous role of organic matter. *Environmental Toxicology and Chemistry*, 20: 2794–2801.
- Jackson T A, Bistricki T, 1995. Selective scavenging of copper, zinc, lead, and arsenic by iron and manganese oxyhydroxide coatings on plankton in lakes polluted with mine and

- smelter wastes: Results of energy dispersive X-ray micro-analysis. *Journal of Geochemical Exploration*, 52: 97–125.
- Lee B G, Griscom S B, Lee J S, Choi H J, Koh C H, Luoma S N, 2000. Influences of dietary uptake and reactive sulfides on metal bioavailability from aquatic sediments. *Science*, 287: 282–284.
- Ma J R, Shao M H, 1994. Variation in heavy metal pollution of offshore sedimentary cores in Jinzhou Bay. *China Environmental Science*, 14: 22–29.
- Ma J R, Zhang F R, Ma D Y, 1989. The distributive characteristics of chemical speciation of heavy metals in the sediments in Jinzhou Bay. *Journal of Liaoning Normal University*, 1: 48–57.
- Martin J M, Nirel P, Thomas A J, 1987. Sequential extraction techniques: Promises and problems. *Marine Chemistry*, 22: 313–341.
- Martinez G, Rodriguez L, Senior W, 2002. Cd, Zn, Cr and Pb speciation in sediment nuclei in the Bergantin Bay, Anzoategui State, Venezuela. *Interciencia*, 27: 173–179.
- Monterroso P, Pato P, Pereira E, Vale C, Duarte A C, 2003. Distribution and accumulation of metals (Cu, Cd, Zn and Pb) in sediments of a lagoon on the northwestern coast of Portugal. *Marine Pollution Bulletin*, 46: 1200–1205.
- Mossop K F, Davidson C M, 2003. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. *Analytica Chimica Acta*, 478: 111–118.
- Ottosen L M, Villumsen A, 2006. High Cu and Cd pollution in sediments from Sisimiut, Greenland. Adsorption to organic matter and fine particles. *Environmental Chemistry Letters*, 4: 195–199.
- Peng S H, Wang W X, Chen J S, 2005. Relationships between Cd and Zn partitioning and geochemical composition in sediments from Chinese rivers. *Environmental Toxicology and Chemistry*, 24: 294–303.
- Perin G, Craboledda L, Lucchese M, Cirillo R, Dotta L, Zanetta M L *et al.*, 1985. Heavy metal speciation in the sediments of northern Adriatic Sea. A new approach for environmental toxicity determination. In: Heavy Metals in the Environment (Lakkas T D, ed). CEP Consultants Edinburg.
- Petersen W, Wallmann K, Schroer S, Schroeder F, 1993. Studies on the adsorption of cadmium on hydrous iron(III) oxides in oxic sediments. *Analytica Chimica Acta*, 273: 323–327.
- Pueyo M, Rauret G, Luck D, Yli-Halla M, Muntau H, Quevauville P, 2001. Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. *Journal of Environmental Monitoring*, 3: 243–250.
- Qiao F Y, 1991. Monitoring of pollution status and prediction of trend on heavy metals in Jinzhou Bay. *Marine Environmental Science*, 10: 69–73.
- Root R A, Dixit S, Campbell K M, Jew A D, Hering J G, O'Day P A, 2007. Arsenic sequestration by sorption processes in high-iron sediments. *Geochimica et Cosmochimica Acta*, 71: 5782–5803.
- Rule J H, Alden R W, 1996. Interactions of Cd and Cu in anaerobic estuarine sediments. II. Bioavailability, body burdens and respiration effects as related to geochemical partitioning. *Environmental Toxicology and Chemistry*, 15: 466–471.
- Schaanning M T, Hylland K, Eriksen D O, Bergan T D, Gunnarson J S, Skei J, 1996. Interactions between eutrophication and contaminants. II. Mobilization and bioaccumulation of Hg and Cd from marine sediments. *Marine Pollution Bulletin*, 33: 71–79.
- Schlekat C E, Decho A W, Chandler G T, 1999. Dietary assimilation of cadmium associated with bacterial exopolymer sediment coatings by the estuarine amphipod *Leptocheirus plumulosus*: effects of Cd concentration and salinity. *Marine Ecology-Progress Series*, 183: 205–216.
- Shao M H, Wu Z Q, Jiang G F, 1993. Study on the existence and distribution of Zn, Pb and Cd in the water of Jinzhou Bay. *Environmental Protection Science*, 19: 40–46.
- Simpson S L, Apte S C, Batley G E, 2000. Effect of short-term resuspension events on the oxidation of cadmium, lead, and zinc sulfide phases in anoxic estuarine sediments. *Environmental Science & Technology*, 34: 4533–4537.
- Svete P, Milacic R, Pihlar B, 2001. Partitioning of Zn, Pb and Cd in river sediments from a lead and zinc mining area using the BCR three-step sequential extraction procedure. *Journal of Environmental Monitoring*, 3: 586–590.
- Swallow K C, Hume D N, Morel F M M, 1980. Sorption of copper and lead by hydrous ferric oxide. *Environmental Science & Technology*, 14: 1326–1331.
- Tessier A, Campbell P G C, Bisson M, 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, 51: 844–851.
- Tessier A, Couillard Y, Campbell P G C, Auclair J C, 1993. Modeling Cd partitioning in oxic lake-sediments and Cd concentrations in the fresh-water bivalve *anodonta-grandis*. *Limnology and Oceanography*, 38: 1–17.
- Tipping E, Lofts S, Lawlor A J, 1998. Modelling the chemical speciation of trace metals in the surface waters of the Humber system. *Science of the Total Environment*, 210–211: 63–77.
- Turner A, 2000. Trace metal contamination in sediments from U.K. estuaries: An empirical evaluation of the role of hydrous iron and manganese oxides. *Estuarine, Coastal and Shelf Science*, 50: 355–371.
- Turner A, Le Roux S M, Millward G E, 2008. Adsorption of cadmium to iron and manganese oxides during estuarine mixing. *Marine Chemistry*, 108: 77–84.
- Ure A M, Quevauviller P, Muntau H, Griepink B, 1993. Speciation of heavy-metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the commission of the European communities. *International Journal of Environmental Analytical Chemistry*, 51: 135–151.
- Wang L, Chin Y P, Traina S J, 1997. Adsorption of (poly)maleic acid and an aquatic fulvic acid by goethite. *Geochimica et Cosmochimica Acta*, 61: 5313–5324.
- Yap C K, Ismail A, Tan S G, Omar H, 2002. Correlations between speciation of Cd, Cu, Pb and Zn in sediment and their concentrations in total soft tissue of green-lipped mussel *Perna viridis* from the west coast of Peninsular Malaysia. *Environment International*, 28: 117–126.
- Zhang S Z, Wang S X, Shan X Q, 2001. Effect of sample pretreatment upon the metal speciation in sediments by a sequential extraction procedure. *Chemical Speciation and Bioavailability*, 13: 69–74.
- Zhu J S, Guan D M, Zhang F R, 1992. Mercury transformation and migration in the sediment of Jinzhou Bay. *China Environmental Science*, 12: 87–92.
- Zhuang Y Y, Allen H E, Fu G M, 1994. Effect of aeration of sediment on cadmium-binding. *Environmental Toxicology and Chemistry*, 13: 717–724.