

A 50-year sedimentary record of heavy metals and their chemical speciations in the Shuangtaizi River estuary (China): implications for pollution and biodegradation

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Abstract Two parallel sediment cores collected from tidal flat located in the Shuangtaizi River estuary were analyzed for heavy metal concentrations and chemical speciations. Based on the ^{137}Cs activity profile, mean sedimentation rate at the sampling site during the past 50 years was estimated to be $1.3\text{ cm}\cdot\text{a}^{-1}$. Correlation analyses show that almost all the metals are associated with each other, suggesting that these metals might be derived from same sources and/or affected by same geochemical processes. Influence of total organic carbon (TOC) content on the concentrations of Cr, Ni, Cu and Cd is evident. Silt and clay contents, instead of sand content, play an important role in the distribution of these metals. The dominant binding phases for most of the metals (except for Cd) are the residual. The relative decrease of the residual fraction of Cd and Pb in the upper 66 cm of the core is striking. The distribution of chemical fraction confirms that the residual fractions of these metals have a natural origin, while only the non-residual fractions of Cd and Pb increased upward the core due to pollution in the past five decades. Pollution assessment on these heavy metals based on Index of Geoaccumulation (I_{geo}) also demonstrates that most of the metals are unpolluted. The weak pollution as observed in the sediments is perhaps related to a local plant, the *Suaeda heteroptera* Kitag, which may have played a significant role in the biodegradation of these metals and the metal distribution in the estuary.

Keywords Shuangtaizi River estuary, sediment core, heavy metals, pollution

1 Introduction

Coastal and estuarine regions are the important sinks for many persistent pollutants which accumulate in organisms and bottom sediments [1]. Heavy metals in aquatic systems could be transported rapidly into sediments, where they could be released out of sediments in case of environmental conditions changed, resulting in a secondary pollution source affecting the ecosystems in the estuary and the marginal sea. Therefore, sediments are both heavy metal carrier and potential pollution sources in an aquatic system.

The Shuangtaizi River, located in the downstream of the Liao River and the North-east of Liaodong Bay, discharges into the Bohai Sea in Panjin City, Liaoning Province, China. On average, the drainage area ($5.7\times 10^5\text{ km}^2$), the water discharge ($4.3\times 10^9\text{ m}^3\cdot\text{a}^{-1}$) and the sediment load ($2\times 10^{10}\text{ m}^3\cdot\text{a}^{-1}$) carried by the Shuangtaizi River account for 4.3%, 5.4% and 1.7%, respectively, of nationwide river systems [2]. The Shuangtaizi estuarine wetland, as a national level nature preserve zone, has been ranked as the second biggest swamp and the biggest bulrush wetland in the world and listed in “The Record of Important International Wetland Conservation District” in December 2004. The wetland makes great sense in ecological protection to both the Shuangtaizi River and the areas. However, with fast economic growth and an increasing population in the area in recent years, pollutants, especially heavy metals, are increasingly discharged into the local aquatic environments. According to State Ocean Bureau of China (2008) [3], the discharge of pollutants in the estuary has risen to 15062 tons in 2008, especially, the discharge of heavy metals reaching 54 t. Consequently, the Shuangtaizi River estuary has become one of most potentially polluted estuaries in China.

However, our understanding of the Shuangtaizi River

estuary pollution is limited due to the short history of research in this area. A few studies on the geochemistry of trace metals in the estuary only focus on the concentration of some chemical elements (mainly Cu, Pb, Zn and Cd) either in the surface sediments [4–6] or water [7,8]. There are few studies on the heavy metals' distributions and enrichments in sediment core of the estuary. Especially, few studies focus on heavy metals V, Cr, Co and Ni in the sediments of the estuary.

There are two main goals of the present study. The first is to investigate the trace metal concentration and chemical form distributions in a tidal flat sediment core in the estuary. The second is to assess the condition and environmental impacts of heavy metal pollutants in the sediments within the estuarine area. The research on the distribution of the heavy metals using sediment core samples will reveal the heavy metal pollution history leading to a better understanding of the ecological system in the region.

2 Materials and methods

2.1 Study area and sample collection

The study area is located in the national level nature preserve zone, Panjin, China. In this study, two parallel sediment cores (PJI and PJII) were collected in a tidal flat in the nature preserve zone in July 2008 (Fig. 1). The cores showed undisturbed mud–water interfaces, and no evidence of bioturbation was observed along the sequences. The cores were 80 cm long and taken using a PVC tube. The cores PJI and PJII were 0.4 m apart. The inner diameter of the coring tube was 50 mm. The sediment was immediately sliced in thin sections with a plastic cutter at 4 cm resolution for the core PJI and at 6 cm resolution for

the core PJII. The samples were transported to laboratory in sealed polyethylene bags at 4°C–6°C and stored in a freezer until being analyzed. For physical and chemical analysis, the samples were air-dried at room temperature and sieved through a 2-mm nylon sieve to remove coarse debris. For the heavy metals analyses, the samples were then ground with a pestle and mortar until all particles passed a 200-mesh nylon sieve.

2.2 Analyses

For the trace metal analyses, 500 mg of sediment was digested with 1 mL HNO_3 , 3 mL HF and 3 mL HCl at a temperature of 90°C–190°C for 16 h. The resulting sample was diluted to 10 mL with deionized water and then analyzed for eight trace elements (Cu, Pb, Zn, Co, Ni, Cr, Cd and V) on inductively coupled plasma-mass spectrometry (ICP-MS; Finnigan MAT, Germany). Chinese national standard sediment sample GBW07303 was used to monitor the analyses. The recovery rates for heavy metals in the standard reference material were around 90%–110% (Table 1). Moreover, reagent blank and replicate samples were also inserted into the analyses procedure at random. The results showed that there was no contamination during analyses and the relative standard deviation (RSD) of all replicate samples was less than 10%.

Selected sediment samples were also analyzed for chemical partitioning at the Analytical Laboratory of Institute of Geophysical and Geochemical Exploration in the Chinese Academy of Geological Sciences, using a four-step modified BCR (Community Bureau of Reference) sequential extraction method [9]. This method gave partitioning in four chemical phases as follows: 1) exchangeable fraction (exchangeable ions and carbonate phase) (20 mL of 0.11 mol·L⁻¹ HOAc), 2) Fe/Mn oxides (20 mL of 0.5 mol·L⁻¹ $\text{NH}_2\text{OH}\cdot\text{HCl}$, pH 1.5), 3) organic matter/ sulfides (10 mL of 8.8 mol·L⁻¹ H_2O_2 + 25 mL of 1.0 mol·L⁻¹ NH_4OAc , pH 2), and 4) residual metal forms. The same quality control scheme was adopted in the sequential extraction. The ratios of cumulative concentrations of the four fractions to the independent total metal concentrations of Cu, Pb, Zn, Cr, Cd, Co, Ni and V ranged between 80% and 120%.

Particle size of sediment was determined on a Malvern Mastersizer 2000 type laser particle analyzer. The particle sizes of the sediment samples were separated into fractions on the basis of particle size: 1) greater than 63 μm , 2) 4–63 μm , and 3) less than 4 μm . The three fractions with particles sized greater than 63 μm , 4–63 μm , and less than 4 μm , represent sand, silt, and clay, respectively. The pH values of the sediments were determined in the deionized water with a ratio of 1:5 (sediment to water) by using a pH meter. The chemical oxygen demand (COD) was measured by titration with potassium dichromate, and has been used as a proxy for total organic carbon (TOC) [10].

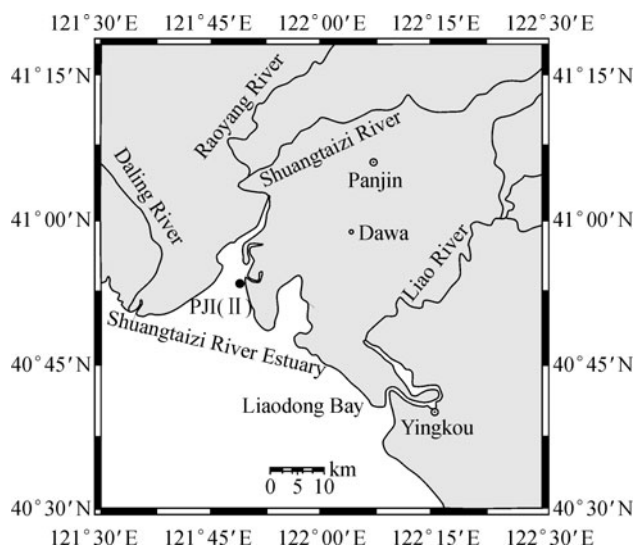


Fig. 1 Geographic map showing study area and sampling location map

Table 1 Method accuracy and recovery of measured heavy metals in standard sediment (GBW 07303)

element	certified value/(mg·kg ⁻¹)	measured value/(mg·kg ⁻¹)	recovery/%
V	120	121.4	101.2
Cr	87	92.19	106.0
Co	11.7	10.8	92.3
Ni	26	32.1	123.5
Cu	177	173.3	97.9
Zn	52	50.38	96.9
Cd	0.1	0.115	115.0
Pb	40	40.71	101.8

Note: Data are expressed as mean, $n = 2$

¹³⁷Cesium radionuclide records were only measured on the sediment core PJII. These measurements were done on 6–10 g dry samples with a low background noise γ -ray spectrometer, using a germanium detector. The precision of this method is typically better than 10% [11].

3 Results and discussion

3.1 Sediment core chronology

¹³⁷Cesium found in marine and fluvial sediments is an anthropogenic radionuclide introduced in the environment, due mainly to the nuclear weapon tests. Global dispersion of ¹³⁷Cs began in 1954 AD, with marked maxima in the deposition of ¹³⁷Cs occurring in the northern hemisphere in 1958 AD, 1963 AD (from nuclear weapons testing) and 1986 AD (from the Chernobyl accident) [12].

Vertical variations in ¹³⁷Cs in the upper section of the

profile were shown in Fig. 2. The ¹³⁷Cs profile displays three well defined peaks at 58, 34 and 22 cm, respectively, and activities increase from 22 cm toward the surface.

The ¹³⁷Cs activities rapidly increase to detectable activities at 70 cm, which might mark the first widespread dispersion of ¹³⁷Cs in 1954. The deepest peak at 58 cm might be associated with the first fallout maximum in 1958, while the 34 cm peak may correspond to the atmospheric radioactive fallout maximum in 1963. However, the last peak related to the Chernobyl accident (1986) could not to be identified clearly in the upper 22 cm. The significant increase of ¹³⁷Cs activities from 10 to 4 cm depth may be related to enhanced soil erosion due to intensive rainfall over the Shuangtaizi river drainage basin since the late 1990s [14,15]. It was possible that under the abundant rainfall, ¹³⁷Cs previously deposited in the deeper soil layers is re-eroded and transported to the estuarine area and deposited there, resulting in the significant increase of ¹³⁷Cs toward the surface of the core [13].

If the peaks at 34 cm and 58 cm correspond to ages of 1963 and 1958, respectively, and the surface at 4 cm and base at 70 cm correspond to ages of 2006 and 1954, respectively, a mean sedimentation rate of 0.7 cm·a⁻¹ for the upper 4–34 cm sections, 4.8 cm·a⁻¹ for 34–58 cm and 1.3 cm·a⁻¹ for 58–70 cm can be obtained. The average sedimentation rate in the region during the past 50 years is 1.3 cm·a⁻¹.

The high sedimentation rate from 1959 to 1964 may have been derived from higher erosion from the drainage basin, resulted from abundant rainfall during the period in the Shuangtaizi river catchment [14].

3.2 Sediment geochemical characteristics

The variations of particle size, pH and TOC in the core were shown in Fig. 3. Mean grain size in the sediment was calculated using the formulae of Folk and Ward [16]. There is a gradually decreasing trend of mean grain size from the bottom to the top of the sediment core. The silt content of sediments is relatively high (ranging from 56.5% to 74.0%), followed by the clay (ranging from 10.9% to

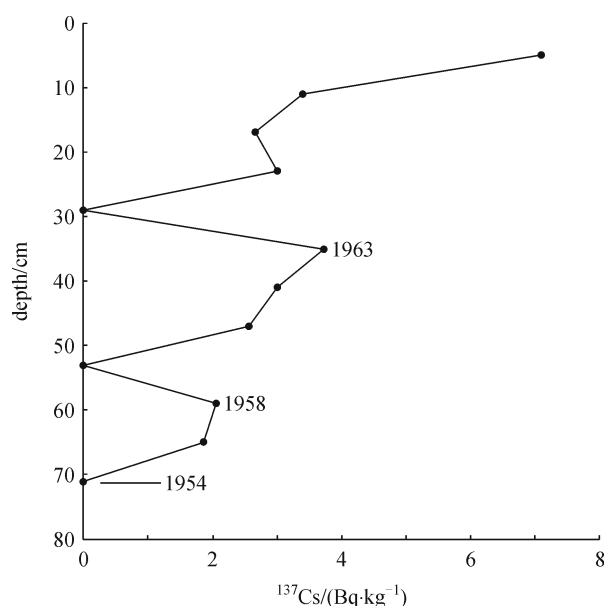


Fig. 2 Down core variations of ¹³⁷Cs in the sediment core PJII (the data come from [13])

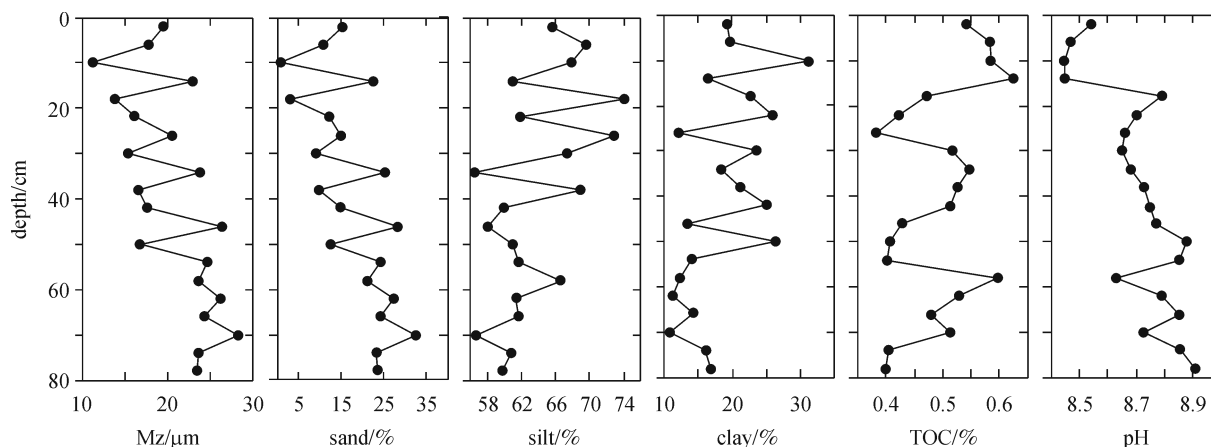


Fig. 3 Down core variations of mean grain size (Mz), contents of sand, silt and clay, pH and TOC in the sediment core PJI (the particle size data come from Ref. [13])

31.4%) and sand (ranging from 0.7% to 32.5%). The pH values of the sediments vary from 8.45 to 8.91, with a gradual decrease from the bottom to the top of the profile. Overall, the TOC profile shows a relatively stable trend. The TOC content ranges between 0.39% and 0.63%, with a mean of 0.49%.

3.3 Heavy metal concentrations

The means and ranges of heavy metal concentrations in the Shuangtaizi River estuary sediments obtained in this study and some other references were summarized in Table 2.

Except for Zn, Cd and Pb, the concentrations of most metals in the core PJI are lower than soil background values in Liaoning Province [17] and sediment background in the Liaodong Bay [18], indicating that most metals are depleted in the core. Compared to the national coastal area background values of China [19], the sediments in the Shuangtaizi River estuary are depleted in Pb, Zn and Cu. However, the mean Cd concentration in the core PJI is as high as 5.0 times of the background values in Liaodong Bay marine sediments. The results suggest that although most metals are depleted in the core, Cd is enriched in the sediments.

3.3.1 Downcore patterns of heavy metal concentrations

The downcore profiles of heavy metal concentration in PJI were shown in Fig. 4. Generally, two downcore patterns (1 and 2) can be identified in the core.

Pattern 1: Cu, Pb, Zn, Cr, V, Co and Ni gradually increase from the bottom to 25 cm in the core, except for an evident decrease between 45 and 55 cm. From 25 cm to the surface of the core, the concentrations of these metals gradually decrease.

Pattern 2 (gradual increase distribution): A consistent increase from the bottom to the core top was observed for Cd.

Generally, almost all the metals show a gradually increasing trend from the bottom to 25 cm of the core. The trend might be consistent with increasing pollutant inputs resulted from anthropogenic activities in the region due to local economic development since the last century suggested by previous studies on the heavy metals [4,5].

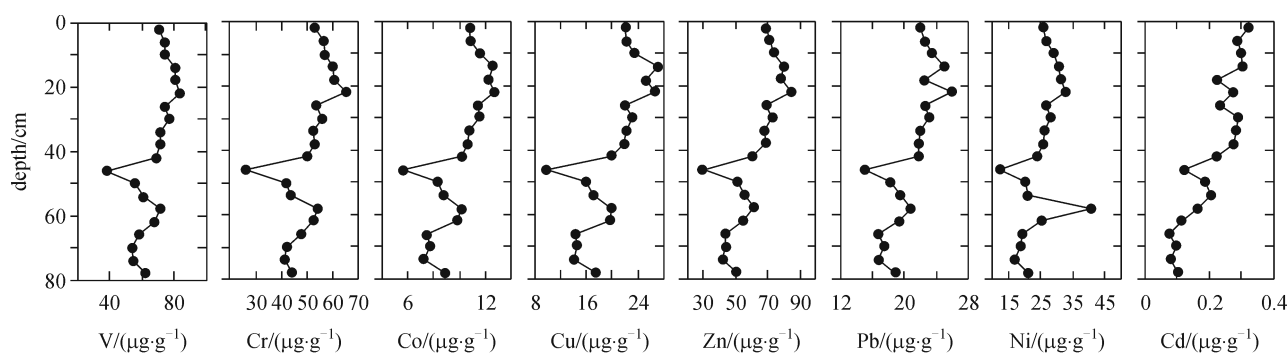
Based on the sedimentation rate calculated on ^{137}Cs activity profile, 49 cm of the core represents the period about 1961–1962. According to the annual precipitation data of Liaoning Province for the past 60 years, a maximum of rainfall (950 mm) occurred between 1961 and 1962 [14]. It is presumed that, in a year with the extremely heavy rainfall, fresh water discharging into the Shuangtaizi River is significantly increased, resulting in heavy metals concentrations in the water diluted strongly, and therefore, low metal concentrations occur in the sediments [13]. In addition, sand content reaches 30% at 49 cm in the grain size profile (Fig. 3), suggesting much strong soil erosion caused by the heavy rainfalls which carried more sands into the estuary, and therefore, led to a dilution effect of heavy metal contents.

3.3.2 Influence of sediment properties on the heavy metal concentrations

To better understand the influence of sediment properties on these heavy metal distribution profiles in the sediment, Pearson's correlation analyses among the concentrations of heavy metal, grain size, pH and TOC were performed (Table 3). Strong positive correlations among heavy metals were observed (except for Cd), with their correlation coefficients being higher than 0.78. This indicates that these metals are associated with each other, suggesting that these metals might be derived from same sources and/or affected by same geochemical processes. Cd shows a middle positive correlation with other metals, suggesting that there is an additional source and/or different migration

Table 2 Concentrations of heavy metals in the sediment core (PJI) from the Shuangtaizi River estuary and their corresponding background values/ ($\text{mg} \cdot \text{kg}^{-1}$)

sediment sample	V	Cr	Co	Ni	Cu	Zn	Cd	Pb
D1	70.9	53.1	10.8	25.7	22.1	68.6	0.32	21.9
D2	73.8	56.2	10.9	26.5	22.2	71.5	0.29	22.5
D3	74.5	57.3	11.5	29.1	23.4	73.7	0.30	23.5
D4	80.9	60.1	12.6	30.6	27.2	80.1	0.31	24.9
D5	80.9	60.7	12.3	31.4	25.2	77.7	0.23	22.5
D6	83.9	65.0	12.8	32.6	26.7	85.0	0.28	25.9
D7	73.8	53.4	11.4	26.9	22.1	69.2	0.23	22.5
D8	76.6	55.6	11.6	27.8	23.1	72.8	0.29	23.2
D9	71.5	52.5	10.8	26.3	22.2	67.6	0.28	22.1
D10	71.1	53.2	10.6	25.6	21.7	68.5	0.28	21.8
D11	68.2	49.8	10.2	23.8	19.9	60.0	0.23	21.8
D12	37.5	26.5	5.6	12.3	9.9	30.3	0.12	15.1
D13	55.9	41.7	8.3	20.4	16.0	50.6	0.19	18.3
D14	61.0	43.4	8.8	21.0	17.0	56.0	0.20	19.6
D15	71.4	54.3	10.2	40.8	20.0	61.7	0.16	20.9
D16	68.0	52.4	9.8	25.1	19.6	54.8	0.12	19.4
D17	58.2	47.7	7.4	19.2	14.4	43.4	0.07	16.8
D18	53.5	41.8	7.7	18.8	14.6	43.3	0.10	17.6
D19	54.8	41.1	7.3	17.0	14.2	42.0	0.08	16.8
D20	61.7	44.3	8.9	21.0	17.6	50.4	0.10	18.8
mean (20)	67.4	50.5	10.0	25.1	19.9	61.4	0.21	20.8
maximum	83.9	65.0	12.8	40.8	27.2	85.0	0.32	25.9
minimum	37.5	26.5	5.6	12.3	9.9	30.3	0.07	15.1
STD	11.4	8.8	2.0	6.4	4.6	14.6	0.08	2.9
background of marine sediments in the Liaodong Bay [18]	NA	NA	NA	NA	19.2	57.0	0.042	11.5
background in China's coastal areas [19]	NA	NA	NA	NA	30	80	NA	25
background of soil in Liaoning Province [17]	86	59	17	27	21	59	0.1	20

**Fig. 4** Down core variations of heavy metals in the sediment core PJI (the data come from Ref. [13])

behavior for Cd. In addition, significantly positive correlations were observed for almost all the heavy metals (except for Cd) and silt content, with their correlation

coefficients being between 0.47 and 0.57. This indicates that these metals are associated with silt. Significantly positive correlations between Cd, Pb, Zn, Co, Cu and clay

Table 3 Correlation matrix among the heavy metals concentrations, grain size, pH and TOC ($n = 20$) of the sediments

	V	Cr	Co	Ni	Cu	Zn	Cd	Pb	Clay	Silt	Sand	TOC	pH
V	1.00												
Cr	0.98	1.00											
Co	0.98	0.95	1.00										
Ni	0.85	0.85	0.82	1.00									
Cu	0.98	0.95	1.00	0.80	1.00								
Zn	0.97	0.94	0.99	0.80	0.99	1.00							
Cd	0.73	0.67	0.81	0.55	0.81	0.86	1.00						
Pb	0.95	0.91	0.98	0.78	0.97	0.98	0.86	1.00					
clay	0.41	0.40	0.46	0.24	0.46	0.51	0.58	0.51	1.00				
silt	0.57	0.55	0.56	0.53	0.52	0.57	0.44	0.47	0.25	1.00			
sand	-0.61	-0.60	-0.64	-0.47	-0.61	-0.68	-0.65	-0.63	-0.82	-0.76	1.00		
TOC	0.43	0.48	0.42	0.53	0.45	0.41	0.46	0.43	0.11	0.12	-0.14	1.00	
pH	-0.55	-0.55	-0.61	-0.54	-0.62	-0.63	-0.73	-0.66	-0.24	-0.36	0.37	-0.76	1.00

Note: Significant p -values ($p < 0.05$) corresponding to high coefficient values marked in bold

were observed, suggesting that sediment clay contents have a significant control on the distribution of these metals in the sediments. All metals strongly negatively correlate with sand content, suggesting that sand content do not play an important role in the distribution of these metals. Especially, with the increase of silt and clay contents, Cr, Cu, Zn, Pb and Ni concentrations increase accordingly, reflecting stronger adsorption capabilities of fine grained materials to these metals.

The metals Cr, Ni, Cu and Cd show significant positive correlations with the TOC content, suggesting the TOC might also play a role in controlling the distribution of these metals in sediments. Significant negative correlations were observed between the pH values and heavy metals, indicating that the metals might mobilize at low pH value, and stabilize in the sediment at high pH value.

3.4 Chemical partitioning of heavy metals

The chemical partitioning of heavy metals in the sediment among the exchangeable, Fe/Mn oxides, organic matters/sulfide, and residual fractions, was plotted in Fig. 5.

The dominant binding phases for almost all the metals except for Cd is the residual fraction, which is generally regarded as relatively stable or inert under normal conditions.

Cr, V and Ni are mostly concentrated in the residual fraction. The percentage of Cr, V and Ni associated with different fractions is in the order: residual > organic/sulfide. Other studies also showed that Cr, Ni and V were found in association with residual material [9,20–22]. These results indicate that Cr, V and Ni have the strongest association with the crystalline structures of sediments.

Co, Zn and Cu were found in all of the four operationally defined chemical phases. Their dominant phase is the

residual fraction, which accounts for more than 70% of the total concentration of metals for most layers, followed by the Fe/Mn oxides fraction and exchangeable fraction. The dominant proportion of residual fraction for Co is in agreement with the literatures [22,23]. The high proportion of Cu in residual fraction is likely due to that Cu is chemisorbed on or incorporated in clay minerals [22,24]. Most Zn is present in the residual fraction being also consistent with observations of Li et al. [25].

The predominant chemical phases of Pb are residual and Fe/Mn oxides fractions. The percentage of Pb fractions is in the following order: residual > Fe/Mn oxides > organic/sulfide > exchangeable. This is in agreement with results reported by Morillo et al. that Fe and Mn hydrous oxides are important scavengers of Pb in sediments [20]. Pb can form stable forms with Fe hydroxide and Mn dioxide [26].

Cd in the sediments is strongly associated with exchangeable fractions. The percentage of Cd associated with different fractions is in the following order: exchangeable fraction > Fe/Mn oxides > residual > organic/sulfide. The average percentage of Cd exchangeable fraction is as high as 50%, which indicates that most of Cd in the sediments is exchangeable and bound to carbonates (soluble to acid). This might be related with the high concentration of Cl^- in the estuary sediments, which could form various chlorocomplexes forms and increase the mobility and bioavailability of Cd [27]. High Cd content in the exchangeable fraction was also found in the river sediments by Morillo et al. [28] and in marine sediments by Guevara-Riba et al. [21].

Bird et al. have suggested that anthropogenically sourced metals preferentially partition to the non-residual phase of the sediment, and that the residual phase generally reflects background geochemical conditions [29]. Accordingly, in our study, the relative decrease of the residual

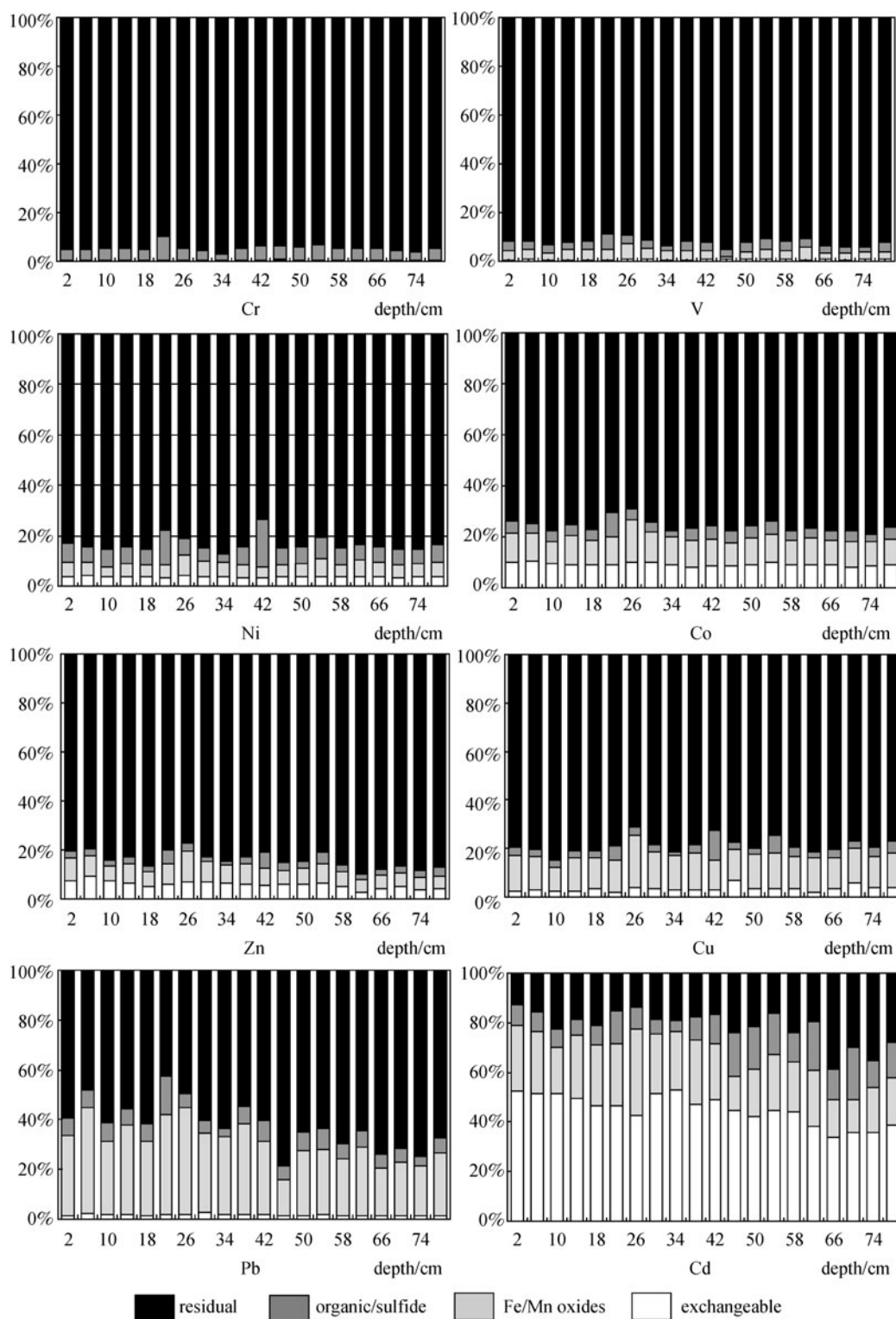


Fig. 5 Chemical fraction variations of heavy metals in the sediment core PJJ

fraction of Cd and Pb in the upper 66 cm is striking. In contrast, below 66 cm, the concentration of Pb and Cd in various fractions remains relatively constant along the profile, which may reflect the background levels of the metals in the sediment. The change in fraction distribution in the upper 66 cm, which is contrasting to the one at larger

depths, therefore suggests that in the upper of the core, the increase of the non-residual fractions (mainly the Fe/Mn oxides and exchangeable fractions) was because of the increasing pollutant input into the sediments in the past five decades.

Among the non-residual fractions of Pb and Cd, the Fe/

Mn oxide fraction exhibits the most pronounced increase in the upper 66 cm, followed by the exchangeable fraction. The results suggest that the main mechanisms of anthropogenic Pb and Cd accumulation in the upper core may be related to precipitation and co-precipitation with Fe/Mn oxides.

3.5 Assessment of the heavy metal pollution

Index of geoaccumulation (I_{geo}) introduced by Müller was also used to assess the heavy metals' pollution in the sediment core PJI in the Shuangtaizi River estuary [30]:

$$I_{\text{geo}} = \log_2[C_n/(1.5 \times B_n)], \quad (1)$$

where C_n is the measured concentration of the examined metal “ n ” in the sediment and B_n is the geochemical background concentration of the metal “ n .” The I_{geo} is associated with a qualitative scale of pollution intensity, samples may be classified as unpolluted ($I_{\text{geo}} \leq 0$), unpolluted to moderately polluted ($0 \leq I_{\text{geo}} \leq 1$), moderately polluted ($1 \leq I_{\text{geo}} \leq 2$), moderately to strongly polluted ($2 \leq I_{\text{geo}} \leq 3$), strongly polluted ($3 \leq I_{\text{geo}} \leq 4$), strongly to extremely polluted ($4 \leq I_{\text{geo}} \leq 5$), and extremely polluted ($5 \leq I_{\text{geo}}$).

Although I_{geo} was originally devised for use with the global standard shale values as background metal levels, Rubio et al. had shown that the use of regional background values yielded more appropriate results [31]. In this study, I_{geo} was calculated using background values for crustal average metal concentrations of eastern China as presented in Gao et al. [32].

The index of geoaccumulation indicates that most of the heavy metals (except for Cd) shows negative I_{geo} values throughout the core, suggesting these metals are generally in unpolluted level during the past 50 years.

Various pollution levels of Cd were observed in the core profile. Cd shows a positive value ($I_{\text{geo}} = 0.12$) from 60 cm of the core, and then keeps in a moderately polluted level from 16 cm ($I_{\text{geo}} = 1.02$) to the top of the core. The increase of non-residual fraction of Cd in the upper 66 cm is consistent with vertical change of I_{geo} of Cd, which further confirms the pollution of Cd.

Based on the estimated sediment rate above, the sediment layers of the 60 and 16 cm can approximately represent the depositions in the years of 1958 and 1992, respectively. Therefore the downcore variation of pollution of Cd possibly indicates that anthropogenic activities resulted in the increase of Cd concentration since the last 1950s. Moderate pollution of Cd occurred from the early 1990s to the present. Furthermore, as discussed in Sect. 3.4, Cd in the sediments is strongly associated with exchangeable fraction. Cd might have a high potential of creating hazardous effects on the local wetland ecosystem since the exchangeable fraction was the most plant-available form [33].

The study area is located in the semi-close Liaodong

Bay. Major pollution industries of North-east China, such as mining, metal smelting, petroleum chemical industry, are situated inside the drainage areas of the Liao Rivers [34]. Most of the industrial wastes were directly discharged into the rivers and flowed into the Liaodong Bay without any treatment until the end of the last century [35]. The high Cd concentration in seawater and sediment in the Liaodong bay was also reported by many literatures [4,5,8,34]. The possible sources for Cd are attributed to the increasing municipal and industrial wastewater discharges, agricultural runoff and rapid urbanizations [4,34]. As to Pb pollution as suggested by chemical partitioning data (Sect. 3.4), there are two possible end number sources for Pb, the regional geogenic background and anthropogenic input [36]. Anthropogenic input (automobile exhaust, Pb-Zn deposit) was greatly intensified after 1980 [36].

3.6 Implications for biodegradation of heavy metal pollution

According to our results, the heavy metal pollution seems not to be as serious as expected based on the pollution estimates from heavy metal pollutant discharges in the studying area. The Shuangtaizi River estuarine wetland is the second biggest swamp in the world, it is thus reasonable to assume that there are some self-repairing mechanisms in the wetland ecosystem. Zhu et al. has suggested that, a local plant *Suaeda heteroptera* Kitag, which is widely distributed in tideland ecosystem of the Shuangtaizi River estuary, has an obvious accumulation effect for Cu, Pb, Zn and Cd, if compared to their background concentrations in the tidal flat sediments [37]. However, as reported by Zhu et al., degradation and death of *S. heteroptera* have occur widely in the Shuangtaizi River estuary due to influence of anthropogenic activities since 2000 [38]. The degeneration or death of *S. heteroptera* Kitag in some local areas of the estuary has even led to weakening of biodegradation for the metals in the wetland (including Cu, Zn, Pb, Cr and Ni) and a more serious pollution of some metals in the seawater [7]. So, it is likely that the *S. heteroptera* Kitag plays a significant role in the biodegradation of some metals (such as Cu, Pb and Zn) and in the metal distribution in the estuary.

4 Conclusions

Two downcore concentration patterns of the heavy metals were identified in the sediment profile and most of the heavy metals are enriched at the top of the sediment core. The dominant binding phases for most of the metals (except for Cd) are the residual. Cd in all sediments is mainly associated with exchangeable fraction. Correlation analyses were performed to well understand the main controlling factors for the downcore distributions of

metals. Initial results suggest that, except for specific elements, silt and clay contents seem to be an important controlling factor on the concentration distributions of most heavy metals. In addition, the sediment pH does not have an important influence on the heavy metals concentrations. The influence of TOC content on the concentrations of almost all the metals is evident.

The relative decrease of the residual fraction of Cd and Pb in the upper 66 cm of the core is striking. The change in fraction distribution, which is contrasting to the one at larger depths, confirms that the residual fraction is related to the natural origin of these metals, whereas in the upper core, the increase of the non-residual fractions (mainly the Fe/Mn oxides fraction) is because of the increasing pollutant input into the sediments in the past five decades. The profile of index of geoaccumulation (I_{geo}) shows that V, Cr, Co, Ni, Cu, Pb and Zn are generally in unpolluted level, while Cd is in various pollution levels throughout the core.

It is presumed that the pollution of Cd is possibly related to the increasing anthropogenic pollutant due to the rapid economy development in the region. Since Cd in the sediments is strongly associated with exchangeable fraction, Cd may have a high potential of creating hazardous effects to the local wetland ecosystem.

The heavy metal pollution seems not to be as serious as expected based on the pollution estimates from heavy metal pollutant discharges in the studying area. It is likely that a local plant, the *S. heteroptera* Kitag, plays a significant role in the biodegradation of such as Cu, Pb and Zn and their distribution in the estuary.

Acknowledgements This study was supported by the National Natural Science Foundation of China (Grant No. 40940027), Fundamental Research Funds for the Central Universities (No. 2010ZY19), Special Fund for Public Welfare Industrial Research of the Ministry of Land and Resources of China (No. 200811014-02 and 201011019-05), and Important National Science & Technology Specific Projects (No. 2009ZX05009-002).

References

1. Szefer P, Glassby G P, Pempkowiak J. Extraction studies of heavy metal pollutants in surficial sediments from the southern Baltic Sea off Poland. *Chemical Geology*, 1995, 120: 111–126
2. Zhang J, Liu C L. Riverine composition and estuarine geochemistry of particulate metals in China—weathering features, anthropogenic impact and chemical fluxes. *Estuarine, Coastal and Shelf Science*, 2002, 54: 1051–1070
3. State Ocean Bureau. *Bulletin of Marine Environment Quality of China in 2008*. Beijing, 2009 (in Chinese)
4. Zhou X Y, Wang E D, Zhu E J. Evaluation on heavy metal pollution in the sediments at the river mouths around Liaodong Bay. *Environmental Chemistry*, 2004a, 23(3): 321–325 (in Chinese)
5. Zhou X Y, Wang E D, Liu X Y, Wang W M. Environmental geochemistry of heavy metals in bottom sediments of river mouths in Liaodong Bay. *Geochimica*, 2004b, 33(3): 286–290 (in Chinese)
6. Feng M H, Long J P, Yu L, Li J J. Ecological risk evaluation of heavy metals of marine sediment in Liaodong Bay shallow waters. *Marine Sciences*, 2003, 27(3): 52–56 (in Chinese)
7. Sun S H, Wang D Y, Hu K, Yang J P, Wei N. Evaluation on pollution of heavy metal in the water and its analysis of ecological effect in Shuangtaizi estuary district. *Global Geology*, 2007, 26(1): 75–79 (in Chinese)
8. Wan L, Wang N B, Li Q B, Zhou Z C, Sun B, Xue K, Ma Z Q, Tian J, Du N. Estival distribution of dissolved metal concentrations in Liaodong Bay. *Bulletin of Environmental Contamination and Toxicology*, 2008, 80(4): 311–314
9. Cuong D T, Obbard J P. Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. *Applied Geochemistry*, 2006, 21(8): 1335–1346
10. Gaudette H E, Flight W, Tones L, Folger D. An inexpensive titration method for the determinations of organic carbon in recent sediments. *Journal of Sedimentary Research*, 1974, 44(1): 249–253
11. Jouanneau J M, Castaing P, Grousset F, Buat-Ménard P, Pedemay P. Recording and chronology of a cadmium contamination by ^{137}Cs in the Gironde estuary (SW France). *Comptes Rendus de L'acadé mie des Sciences—Series IIA—Earth and Planetary Science*, 1999, 329(4): 265–270
12. Cundy A B, Sprague D, Hopkinson L, Maroukian H, Gaki-Papanastassiou K, Papanastassiou D, Frogley M R. Geochemical and stratigraphic indicators of late Holocene coastal evolution in the Gythio area, southern Peloponnese, Greece. *Marine Geology*, 2006, 230(3–4): 161–177
13. Liu B L, Hu K, Xu X L, Liu X M, Fang F. Sedimentary record of heavy metal pollution in the Shuangtaizi estuary. *Marine Sciences*, 2010, 34(4): 84–88 (in Chinese)
14. Zhao C Y, Liu Q M, Li J. Studies on climate in Liaoning Province in recent 48 years. *Meteorological Monographs*, 2000, 26(5): 32–35 (in Chinese)
15. Liu C, He Y, Zhang H Y. Trend analysis of the water and sediment loads of the main rivers in China using water-sediment diagram. *Advances in Water Science*, 2008, 19(3): 317–324 (in Chinese)
16. Folk R L, Ward W C. Brazos River bar: a study in the significance of grain size parameters. *Journal of Sedimentary Research*, 1957, 27(1): 3–26
17. China Environmental Monitoring Station. *Natural Background Values of Soil Elements in China*. Beijing: China Environmental Science Press, 1990 (in Chinese)
18. Hao J, Li S Y, Zhou Y Z, Liu J. Preliminary study on the background of Cu, Pb, Zn and Cd in sediment of the Liaodong bay in the Bohai Sea. *Acta Oceanologica Sinica*, 1989, 11(6): 742–748 (in Chinese)
19. Zheng Q H, Liang Z Q, He Y Q, Wen W Y. Geochemical behaviour of the pollutants in surface sediments of Daya Bay. *Journal of Tropical Oceanography*, 1992, 11(1): 65–71 (in Chinese)
20. Morillo J, Usero J, Gracia I. Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, 2004, 55(3): 431–442
21. Guevara-Riba A, Sahuquillo A, Rubio R, Rauret G. Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. *Science of the Total Environment*, 2004, 321(1–3): 241–255

22. Yuan C G, Shi J B, He B, Liu J F, Liang L N, Jiang G B. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environment International*, 2004, 30(6): 769–783
23. Budimir S, Marko B. Distribution of Cd, Pb, Cu and Zn in carbonate sediments from the Krka River estuary obtained by sequential extraction. *Science of the Total Environment*, 1995, 170(1–2): 101–118
24. Pickering W F. Metal ion speciation—soil and sediments (a review). *Ore Geology Reviews*, 1986, 1: 83–146
25. Li X D, Shen Z G, Wai O W H, Li Y S. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River estuary. *Marine Pollution Bulletin*, 2001, 42(3): 215–223
26. Ramos L, Hernandez L M, Gonzalez M J. Sequential fractionation of copper, lead, cadmium and zinc in the soil from or near Donana National Park. *Journal of Environmental Quality*, 1994, 23(1): 50–57
27. Norvell W A, Wu J, Hopkins D G, Welch R M. Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. *Soil Science Society of America Journal*, 2000, 64(6): 2162–2168
28. Morillo J, Usero J, Gracia I. Partitioning of metals in sediments from the Odiel River (Spain). *Environment International*, 2002, 28(4): 263–271
29. Bird G, Brewer P A, Macklin M G, Serban M, Balteanu D, Driga B. Heavy metal contamination in the Aries river catchment, western Romania: implications for development of the Rosia Montana gold deposit. *Journal of Geochemical Exploration*, 2005, 86: 26–34
30. Müller G. Index of geoaccumulation in sediments of the Rhine River. *GeoJournal*, 1969, 2(3): 108–118
31. Rubio B, Nombela M A, Vilas F. Geochemistry of major trace elements in sediments of the Ria de Vigo (NW Spain) an assessment of metal pollution. *Marine Pollution Bulletin*, 2000, 40(11): 968–980
32. Gao S, Luo T C, Zhang B R, Zhang H F, Han Y W, Zhao Z D, Hu Y K. Chemical composition of the continental crust as revealed by studies in East China. *Geochimica et Cosmochimica Acta*, 1998, 62(11): 1959–1975
33. Nriagu J O. Human influence on the global cycling of trace metals. In: Farmer J D, ed. *Heavy Metals in the Environment*, Vol 1. Edinburgh: CEP Consultants, 1991, 1–5
34. Xu B, Yang X B, Gu Z Y, Zhang Y H, Chen Y F, Lv Y W. The trend and extent of heavy metal accumulation over last one hundred years in the Liaodong Bay, China. *Chemosphere*, 2009b, 75(4): 442–446
35. Zhang X L. Investigation of pollution of Pb, Cd, Hg, As in sea water and deposit of Bohai sea area. *Heilongjiang Environmental Journal*, 2001, 25(3): 87–90 (in Chinese)
36. Xu B, Gu Z Y, Han J T, Zhang Y H, Chen Y F, Lu Y W. Sequential extractions and isotope analysis for discriminating the chemical forms and origins of Pb in sediment from Liaodong Bay, China. *Archives of Environmental Contamination and Toxicology*, 2009a, 57(2): 230–238
37. Zhu M H, Ding Y S, Zheng D C, Tao P. Accumulation and tolerance of Cu, Zn, Pb and Cd in plant Suaeda heteroptera Kitag in tideland. *Marine Environmental Science*, 2005, 24(2): 13–16 (in Chinese)
38. Zhu H Z, Hou W F, Li Z B, Zhu Q H. Suaeda heteroptera degradation in the estuary of Shuangtaizi River. *Chinese Journal of Soil Science*, 2006, 37(6): 1191–1194 (in Chinese)