Contents, Enrichment, Toxicity and Baselines of trace elements in the estuarine and coastal sediments of the Daliao River System, China

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The Daliao River System (DRS) estuary in the Liaodong Bay has a highly industrial, urbanized, and agricultural catchment. The objective of this study was to investigate the multi-elemental geochemistry in the estuarine and coastal sediments, including enrichment, sources, toxicity, and geochemical baselines. Thirty-five sediment samples were collected from the estuarine and coastal area and analyzed for As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Sc, V, Y, Zn, P, Mn, Ti, Al, Fe, Ca, Mg, Na, and K. The average content (mg/kg) was 11.4 for As, 0.34 for Cd, 10.2 for Co, 60.8 for Cr, 20.0 for Cu, 0.05 for Hg, 22.6 for Ni, 26.6 for Pb, 71.8 for Zn, and 0.68 for Sb. The enrichment factor (EF) values of the trace elements, relative to the upper continental crust (UCC), ranged from 7.06 for As to 1.04 for Co, using Fe as a reference element. In general, As, Cd, and Sb were significantly or moderately enriched, while the other trace elements were not or were minimally enriched. The As and Ni in the sediments may pose potential toxicity to biota, while the Cd, Cr, Cu, Hg, Pb, and Zn might rarely or not pose toxicity. All elements except Ca, K, and Na were significantly and positively correlated with one another, with correlation coefficients of 0.523 to 0.994. Principal component analysis (PCA) revealed three groups of elements in association with secondary clay minerals, primary minerals, and carbonate minerals. Generally, the Cr, Cu, Hg, Ni, Pb, and Zn in the sediments originated from natural sources and their regional geochemical baselines (RGBs) were developed using Fe as a reference element. These RGBs may help identify the origins of these metals in the sediments of the Liaodong Bay and document their change over time.

Keywords: estuary sediment, trace element, enrichment, toxicity, regional geochemical baseline

INTRODUCTION

Aquatic sediments react as traps for trace elements, especially for pollutant elements. Thus, the contamination of estuarine sediments by trace elements is a worldwide problem (Bloxam *et al.*, 1972; Thompson *et al.*, 1980; Akagi and Haraguchi, 1994; Krupadam *et al.*, 2006). Consequently, geochemical sediment surveys are important to illustrate the distribution, source, and enrichment of elements or contaminants in estuaries.

The estuary of the Daliao River System (DRS) has a highly urbanized and industrialized catchment. The DRS is the most important watercourse in the Liaoning Province of China. These rivers drain large industrial, urban and agricultural areas. The average annual outputs of Cu, Pb and Zn in the province were 70.3×10^3 , 40.3×10^3 and 265.9×10^3 t, respectively, from 1990 to 2006 (Statistical Bureau of Liaoning Province (SBLP), 2008). In addition, the output of pig iron reached 37.6×10^6 t in 2006 (SBLP, 2008). The large industrial cities include

Fushun, Shenyang, Benxi, Anshan, Liaoyang, Panjin, and Yingkou, with populations of 2.24, 6.98, 1.56, 3.47, 1.82, 1.25, and 2.30 million, respectively, in 2005 (SBLP, 2008). During the past few decades, large amounts of various synthetic and geogenic pollutants have been discharged into the DRS with a stream of wastewater from industries and municipalities and runoff from agriculture. However, studies on the geochemistry of trace and minor elements in the estuarine sediments of the DRS have not been conducted so far. We previously reported the contents and chemical forms of Cd, Cr, Ni, Mn, and P in the estuarine sediments of the DRS (Wang *et al.*, 2009; Wu *et al.*, 2011a).

The present study aims to determine the levels of trace, minor, and major elements in the estuarine and coastal sediments of the DRS; to identify the enrichment and sources of trace elements; to estimate the ecological risk; and to assess the regional geochemical baselines of heavy metals in the estuarine and coastal sediments of the DRS.

MATERIALS AND METHODS

In August 2007 (flood season), surface sediment samples were collected at 35 sites in the Daliao River's estu-

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Fig. 1. Schematic graph of the Daliao River System (Daliao River, Hun River, Taizi River) and its estuary and the sampling sites in the estuarine area.

Table 1. Analytical results of certified and obtained values of geochemical standard substances (GSS1 and GSS2) from the Institute of Geophysical and Geochemical Exploration (IGGE), Chinese Academy of Geological Sciences

	Unit	Certified value		Measured value				Measured value			
		GSS1	GSS2	GSS1	GSS1	Mean	Error %	GSS2	GSS2	Mean	Error %
As	mg/kg	34.00	13.70	33.95	33.63	33.79	-0.62	13.62	13.44	13.53	-1.24
Cd	mg/kg	4.300	0.071	4.210	4.212	4.211	-2.07	0.069	0.069	0.07	-3.28
Co	mg/kg	14.20	8.70	13.13	13.25	13.19	-7.11	8.25	7.99	8.12	-6.67
Cr	mg/kg	62.00	47.00	62.80	69.40	66.10	6.61	43.10	46.87	44.99	-4.29
Cu	mg/kg	21.00	16.30	20.12	19.69	19.91	-5.20	15.40	15.17	15.29	-6.22
Hg	mg/kg	0.032	0.015	0.031	0.031	0.031	-3.37	0.016	0.014	0.01	-0.96
Mn	mg/kg	1760.00	510.00	1769.80	1868.00	1818.90	3.35	509.30	514.90	512.10	0.41
Ni	mg/kg	20.40	19.40	18.77	19.11	18.94	-7.16	19.13	18.26	18.70	-3.63
P	mg/kg	735.00	446.00	790.69	782.20	786.44	7.00	451.08	432.70	441.89	-0.92
Pb	mg/kg	98.00	20.00	100.81	98.78	99.79	1.83	20.72	20.20	20.46	2.30
Sb	mg/kg	0.87	1.30	0.96	0.82	0.89	1.85	1.28	1.23	1.26	-3.18
Sc	mg/kg	11.20	10.70	10.38	10.23	10.31	-7.98	10.73	10.33	10.53	-1.61
Ti	mg/kg	4830.00	2710.00	4690.21	4726.00	4708.10	-2.52	2751.83	2597.00	2674.41	-1.31
V	mg/kg	86.00	62.00	79.00	86.71	82.85	-3.66	61.64	61.65	61.65	-0.57
Zn	mg/kg	680.00	42.00	673.07	641.10	657.09	-3.37	39.05	46.52	42.79	1.87
Al ₂ O ₃	%	14.18	10.31	14.06	14.35	14.21	0.18	10.71	10.49	10.60	2.83
Fe ₂ O ₃	%	5.19	3.52	5.52	5.27	5.39	3.93	3.46	3.44	3.45	-1.95
MgO	%	1.81	1.04	1.80	1.83	1.82	0.33	1.25	1.02	1.14	9.13
CaO	%	1.72	2.36	1.76	1.77	1.77	2.78	2.37	2.36	2.36	0.18
Na ₂ O	%	1.66	1.62	1.69	1.64	1.66	0.05	1.93	1.54	1.74	7.12
K ₂ O	%	2.59	2.54	2.64	2.51	2.57	-0.65	2.61	2.41	2.51	-1.22

ary and coastal area, the Liaodong Bay, using Van Veen grab (Eijkkelkamp, Netherlands) cable-operated sediment samplers (Fig. 1). The samples were placed in plastic bags and brought back to the laboratory, where they were freeze-dried, slightly crushed, passed through a 2 mm sieve, and stored in glass bottles. The salinity and dissolved oxygen of the water of the studied area, measured in the field using a portable spectrophotometer (DR2400, Hach), ranged from 0.28 to 2.83‰ and 1.2 to 7.5 mg L⁻¹, respectively. The pH value of sediment samples, analyzed in the suspension of 1:10 solid:liquid ratio, ranged 6.0 to 8.0, with an average of 7.6. The dissolved Fe and Mn concentration in the porewater of sediment profiles, measured *in-situ* by the diffusive gradients in thin films (DGT), showed the weak reduction zone (0 to 3 cm depth), strong reduction zone (3 to 4 cm depth) and moderate reduction zone (4 to 13 cm depth) (Wu *et al.*, 2011b).

Portions of the sediment samples were digested with HNO₃-HF-HClO₄ (Lin *et al.*, 2008). The Al, Fe, Mg, Ca, Na, K, Ti, Mn, P, Cr, and V in the extracts were measured with ICP-AES (IRIS Intrepid II, Thermo Electron), while the Cd, Co, Cu, Ni, Pb, Sb, Sc, and Y were measured with ICP MS (X Series II, Thermo Electron). Portions of the soil samples were digested with aqua regia, a 1% KMnO₄ solution, and 1% oxalic acid. The As and Hg in the supernatant were determined by hydride generation atomic fluorescence spectrometry (HGAFS) and cold

vapor atomic fluorescence spectrometry (CVAFS), respectively. The accuracy of the method was assessed by replicate analyses of the elements in the certified reference materials GSS1 and GSS2 (Institute of Geophysical and Geochemical Exploration (IGGE), Chinese Academy of Geological Sciences). The results are shown in Table 1 and demonstrate that the analytical error (accuracy) ranged from -7.98% for Sc to 9.13% for Mg.

Natural variations in the abundance of mineral matter generally have an important effect on elements in soils and sediments (Loring, 1991; Sutherland, 2000). Therefore, enrichment factors relative to the upper continental crust (UCC) were calculated to evaluate the effect of human activities and weathering. Al or Fe is often used as a normalizing element to calculate the enrichment factor of trace elements (TEs) (Mil-Homens *et al.*, 2007). In this study, the enrichment factor (EF) was calculated for all trace elements as

$$EF = ([TE]/[Al \text{ or } Fe])_{\text{Sample}} / ([TE]/[Al \text{ or } Fe])_{\text{UCC}} \quad (1)$$

where the concentrations of TE, Al, and Fe in the UCC were taken from Wedepohl (1995) (Table 2). EF < 2, EF = 2 to 5, EF = 5 to 20, EF = 20 to 40, and EF > 40 suggest no or minimal, moderate, significant, strong, and extreme enrichment or pollution, respectively (Sutherland, 2000).

Table 2. Average contents of elements in the estuarine and coastal sediments of the Diaoliao River System (DRS), the upper continental crust (UCC), and worldwide sediment (WS)

Element	Unit	DRS*						Globe**	
		Mean	Std	CV%	Max	Min	Median	UCC	WS
As	mg/kg	11.41	4.66	40.9	19.13	4.61	10.68	2.00	7.70
Cd	mg/kg	0.34	0.20	57.4	0.67	0.05	0.39	0.10	0.17
Co	mg/kg	10.17	4.15	40.9	16.02	3.61	10.60	11.60	14.00
Cr	mg/kg	60.83	16.87	27.7	85.80	15.40	65.20	35.00	72.00
Cu	mg/kg	20.04	11.57	57.7	43.80	2.77	21.06	14.30	33.00
Hg	mg/kg	0.05	0.03	63.8	0.10	0.01	0.06	0.06	0.19
Ni	mg/kg	22.60	10.80	47.8	38.62	5.47	23.47	18.60	52.00
Pb	mg/kg	26.62	7.44	27.9	39.18	16.57	26.19	17.00	19.00
Zn	mg/kg	71.80	36.50	50.8	125.93	16.53	76.62	52.00	95.00
Sb	mg/kg	0.68	0.25	37.0	1.12	0.27	0.70	0.31	1.20
Sc	mg/kg	8.70	3.63	41.7	14.38	2.60	9.16	7.00	10.00
V	mg/kg	58.64	17.74	30.3	81.92	14.79	62.37	53.00	105.00
Y	mg/kg	22.74	5.11	22.5	30.13	10.17	23.77	20.70	40.00
P	mg/kg	548.5	132.4	24.1	840.9	229.7	561.3	665.0	670.0
Mn	mg/kg	623.9	238.6	38.2	1073.0	264.7	622.8	527.0	770.0
Ti	mg/kg	3186	821	25.8	4052	765	3470	3117	3800
Al	%	6.72	1.09	16.2	7.97	3.77	7.29	7.74	7.20
Fe	%	2.61	1.02	39.2	4.19	0.67	2.91	3.09	4.10
Ca	%	1.20	0.27	22.2	2.02	0.75	1.11	2.95	6.60
Mg	%	1.24	0.37	29.9	1.67	0.34	1.40	1.35	1.40
Na	%	2.39	0.41	17.2	3.22	1.63	2.28	2.57	0.57
K	%	2.46	0.12	4.9	2.87	2.29	2.43	2.87	2.00

*Std, standard deviation; CV, coefficient of variance; Max, maximum; Min, minimum.

**Data sources: UCC (Wedepohl, 1995), WS (Bowen, 1979).

RESULTS AND DISCUSSIONS

Contents of major, minor, and trace elements in the estuarine and coastal sediments

The averages, standard deviations, and ranges of major, minor, and trace elements in the estuarine and coastal sediments of the DRS are summarized in Table 2.

Major and minor elements As shown in Table 2, Al was the most abundant major element in the sediment (3.8–8.0%), followed by Fe (0.7–4.2%), Na (1.6–3.2%), K (2.3–2.9%), Mg (0.3–1.8%), and Ca (0.8–2.0%). The Ti, Mn, and P contents were within the range of 230–841, 265–1073, and 765–4052 mg kg⁻¹, respectively. The lowest fluctuation (spatial variation), indicated by the coefficient of variance (CV%), was observed for K (4.9%), while the largest was observed for Fe (39.5%) and Mn (38.2%). Fe and Mn are generally present in the secondary oxides, which may lead to their high spatial variation in content. The composition of major and minor elements in the estuarine and coastal sediments of the DRS is similar to that for the UCC, but quite different from that for sediments throughout the world. Therefore, it is reasonable to judge the enrichment of trace elements in the estuarine and coastal sediments of the DRS relative to the UCC.

Trace elements The average contents of trace elements ranged from 0.05 mg kg⁻¹ for Hg to 71.8 mg kg⁻¹ for Zn. The contents of some trace elements in the estuarine and coastal sediments (Table 2) were highly variable: Hg, Cu, Cd, and Zn accounted for more than 50% of CV. The lowest fluctuation was observed for Y, with 22.5% of CV. The contents of Cd, As, and Sb in the estuarine and coastal sediments were much higher than those in the UCC, while the contents of other trace elements in the estuarine and coastal sediments was similar to those in the UCC.

Accornero *et al.* (2008) summarized sediment concentrations of trace metals for world estuaries and coasts. They showed that the contents (in mg/kg) in the estuarine sediments were within the range of 3.3–244 for As, 0.2–42.8 for Cd, 38–428 for Cr, 1.8–466 for Cu, 0.4–98 for Hg, 18–56 for Ni, 3–1890 for Pb, and 0.4–16880 for Zn. Thus, whereas the contents of these trace metals in the estuarine sediment of DRS were within the range observed for other estuarine sediments, the maximal contents of these trace elements were much lower than the reported upper limits. For example, the Co, Sb, and Sc contents in the estuarine sediments of the DRS were similar to those for the Ganges-Brahmaputra estuarine sediment in India (Stummeyer *et al.*, 2002), while the V content was similar to that for Baltic Sea sediments (Szefer

Fig. 2. Comparison of trace element contents in the estuarine and coastal sediments of the DRS with those in the estuarine sediments of the Pearl River ($n = 38$) and the Yangtze River ($n = 59$).

Fig. 3. EF values of trace elements in the estuarine and coastal sediments of the DRS using Al and Fe as reference elements. (The error bars represent the spatial variation of EF values in the studied area, $n = 35$).

et al., 2009). In addition, the contents of Co, Cr, Cu, Ni, Pb, and Zn were lower in the estuarine sediment of DRS than in the estuarine sediments of the Pearl River (Wang *et al.*, 2008) and the Yangtze River (Zhang *et al.*, 2009) (Fig. 2). The Hg content in the estuarine sediment of DRS was slightly higher than that (0.01 to 0.03 mg kg^{-1}) in the sediments of the Huanghe (Yellow River) estuary (Lu *et al.*, 1990), but much lower than that (0.05 to 2.57 mg kg^{-1}) in the sediments of coastal British Columbia near Vancouver (Thompson *et al.*, 1980). Therefore, the estuarine sediments of the DRS generally contained lower Co, Cr, Cu, Ni, Pb, Zn and Hg than the abovementioned sediments in other estuaries or coasts.

To quantify the possible anthropogenic impacts, the EF values relative to the UCC were calculated for each element using equation (1) (Fig. 3). The average EF value ranged from 6.39 for As to 0.97 for Co or from 7.06 for As to 1.04 for Co using Al or Fe as normalizing elements, respectively. The EF values decreased in the following order: As, Cd, Sb, Cr, Pb, Cu, Zn, Sc, Ni, V, Y, Hg, and

Fig. 4. Principal component score plots of major, minor, and trace elements in the estuarine and coastal sediments of the DRS.

Co. In general, As was significantly enriched, while Cd and Sb were moderately enriched. However, Cr, Pb, Cu, Zn, Sc, Ni, Y, V, Hg, and Co were not or were only minimally enriched.

However, the origin (i.e., natural or anthropogenic) of an element can be distinguished based on the EF value (Liu *et al.*, 2003). Elements having EF values <1 might indicate enrichment due to anthropogenic inputs (Mil-Homens *et al.*, 2006). The mean EF for the elements in the estuarine and coastal sediments in Fig. 4 showed that the poorly enriched elements, Cr, Pb, Cu, Zn, Sc, Ni, Y, V, Hg, and Co, might be of natural origin, whereas the moderately and significantly enriched elements, As, Cd, and Sb, might partly originate from anthropogenic sources associated with industrial effluents and atmospheric deposition. For example, 1.410 kg of As and 5150 of Cd were

Fig. 5. Contents of Cr, Cu, Hg, Ni, Pb, and Zn were plotted against Fe content in the estuarine sediments of the DRS. Linear regression lines and $\pm 95\%$ prediction limits are superimposed on the data.

discharged into the Liao River System with industrial effluents in 1985 (Su *et al.*, 2010). Emission from coal combustion was about 15400 kg for Sb in 2009 and 6870 kg for Cd in 2008 in the Liaoning province (Tian *et al.*, 2012a, b), while As emission from coal-fired power plants was 40,000 kg in 2007 (Tian *et al.*, 2011).

Element interrelations and sources

Correlation (Pearson) and principal component analy-

sis (PCA) have often been performed to assess element interrelations and origins (Li *et al.*, 2000). The correlation coefficient matrix for the element content in the estuarine and coastal sediments of the DRS is listed in Table 3.

The correlation between any two trace elements (As, Cd, Co, Cr, Hg, Ni, Pb, Sb, Sc, V, Y, and Zn), minor elements (P, Mn, and Ti) and major elements (Al, Fe, and Mg) was significant at a 0.01 level, with a maximal cor-

Table 4. Regression parameters for trace metal vs. Fe in the estuarine and coastal sediments of the DRS. All relationships were significant at $p < 0.0001$

	Formula for RGB	R^2	n
Cr	$\text{Cr (mg/kg)} = 15.38 \times \text{Fe(\%)} + 19.84$	0.932	31
Cu	$\text{Cu (mg/kg)} = 10.27 \times \text{Fe(\%)} - 7.49$	0.942	33
Hg	$\text{Hg (mg/kg)} = 0.030 \times \text{Fe(\%)} - 0.025$	0.893	34
Ni	$\text{Ni (mg/kg)} = 10.64 \times \text{Fe(\%)} - 5.41$	0.965	34
Pb	$\text{Pb (mg/kg)} = 6.60 \times \text{Fe(\%)} + 9.41$	0.875	33
Zn	$\text{Zn (mg/kg)} = 34.75 \times \text{Fe(\%)} - 19.00$	0.949	35

relation coefficient of 0.994 for Co vs. Ni and a minimal correlation coefficient of 0.523 for As vs. Ti. The correlation coefficients between trace element contents ranged from 0.756 to 0.994. All trace elements were positively and significantly correlated with Al and Fe, with average correlation coefficients of 0.868 (0.793 to 0.924) and 0.934 (0.856 to 0.934), respectively. In addition, the correlation coefficients of Fe vs. As (0.856) and Cd (0.886) were lower than those for Fe vs. other trace elements, indicating that As and Cd in the estuarine and coastal sediments might be impacted by anthropogenic sources. Ca, Na, and K were negatively correlated with other elements. Na was positively and significantly correlated with K. A positive correlation of trace elements with Fe and a negative correlation of trace elements with Ca were observed for the estuarine and coastal sediments of the Pearl River (Li *et al.*, 2000; Liu *et al.*, 2003). The high correlation between trace elements and Fe, Al, and Mn might be due to their adsorption, co-precipitation, and isomorphous substitution on/in Fe, Al, and Mn minerals (Sparks, 2003).

Principal component analysis (PCA) is used to reduce a large number of variables to a few component variables that explain most of the variability. In the PCA of elemental contents, the first two principal components account for 85.4% of the total variance, with the first principle component (F1) accounting for 79.3% of the total variance. The PCA factor loadings of the different elements are plotted in Fig. 4.

The PCA results show there were three groups of elements: the first group (As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Sc, Zn, Y, P, Mn, Ti, Al, Fe, and Mg), the second group (Na and K), and the third group (Ca) (Fig. 4(a)).

The first group (79.3% of the total variance) includes most of the elements. The loading values for this element group on F1 ranged from 0.76 for Ti to 0.99 for Fe. This group generally represents secondary clay minerals and the trace elements associated with them. Whereas Al and Ti were included in the first group, their positions in Fig. 4(b) were relatively far from the other elements in this group. Al generally occurs in both secondary minerals

Fig. 6. Ratios of average elemental contents in the estuarine sediment of DRS to the threshold effect level (TEL) and effects range low (ER-L) benchmarks (MacDonald *et al.*, 1996).

(e.g., aluminum oxides and silicate clay) and primary minerals (e.g., feldspars) (Sparks, 2003). Thus, the loading of Al on the second factor (F2) was relatively high (0.22). However, Ti generally forms minerals in primary igneous and metamorphic rocks, which, because of their resistance to weathering, persist in the derived soils and sediments as resistant heavy minerals (Fitzpatrick and Chittleborough, 2002). Previous studies documented that secondary clay colloid minerals are usually the major factor controlling and binding trace elements in the estuarine and coastal sediments of the Pearl River (Li *et al.*, 2000; Liu *et al.*, 2003).

The secondary group (6.1% of the total variance) includes Na and K, with relatively high negative loading (−0.73 and −0.48) on F1 and relatively high positive loading on F2 (0.44 and 0.64). This group may represent primary minerals, such as feldspars and muscovite, because they are the major primary minerals in the soils of this area.

The third group (5.4% of the total variance) only includes Ca, with negative loading on both F1 and F2. Ca occurs in the secondary carbonate minerals and organism relics (e.g., shell pieces) in the estuarine and coastal environment.

Regional geochemical baselines of selected trace elements

Scatter plots of the metals against the reference element for non-contaminated samples within a geographically coherent area allow the definition of regression lines representing the regional geochemical baseline (RGB). The natural population can be defined by the 95% confidence interval of the plotted population (Loring and Rantala, 1992). The correlation between Fe or Al and trace metal concentrations has been used to develop the RGB model in other estuarine sediments around the world (Schropp *et al.*, 1990; Mil-Homens *et al.*, 2007; Newman and Watling, 2007; Lin *et al.*, 2007).

The EF values indicated that Cr, Cu, Hg, Ni, Pb, and Zn in the estuarine and coastal sediments of the DRS gen-

erally originate from natural sources. In addition, their contents are significantly correlated with the contents of the mineral matrix elements, such as Fe and Al. Furthermore, the correlation coefficients of trace metals vs. Fe are higher than those for trace metal vs. Al. Therefore, the dataset can be used to develop the RGB of these six trace metals using Fe as a reference element.

The plots between trace metals Cr, Cu, Hg, Ni, Pb, and Zn and Fe are presented in Fig. 5. All points that fall inside the 95% confidence band of metal versus Fe concentrations are characterized as natural sediments, whereas the sampling points that fall above the 95% confidence limit are considered a metal-enriched population. The data points falling outside the 95% confidence band were removed, and the remaining data points were used to develop the RGB of the trace metals in the estuarine and coastal sediments of the DRS (Table 4). The correlation coefficients for the formula ranged from 0.875 to 0.965. All relationships were significant at $p < 0.0001$. These RGB models provide the basis for future assessments of the metal contamination in other estuarine and coastal sediments of the DRS.

Potential level of biological risk

To define the potential level of biological risk associated with the contents of trace metals in the estuarine sediments of DRS, our data were compared with the threshold effect level (TEL) and effects range low (ER-L) benchmarks (MacDonald *et al.*, 1996). These indexes can be used to estimate the contents of trace metals that are most likely causing toxicity and to identify sites where adverse biological effects are possible. The TEL is the geometric mean of the 15th percentile in the effects data set and the 50th percentile in the no effects data set. The ER-L is the 10th percentile in the effects data set. Generally, sediments were considered “nontoxic” when the contents were lower than the ER-L and TEL values, “rarely toxic” when the contents were lower than the ER-L but higher than the TEL, and “potentially toxic” when the contents were higher than both the TEL and ER-L (MacDonald *et al.*, 1996; Accornero *et al.*, 2008). The ratios of the average contents of trace metals to the TEL and ER-L are shown in Fig. 6 for the estuarine sediments of DRS.

The ratios of the As and Ni contents in the sediment to the TEL and ER-L were >1.0 , indicating that the As and Ni in the sediment might pose potential toxicity to biota such as amphipods (MacDonald *et al.*, 1996). The ratios of the Cr and Cu contents in the sediment to the TEL were >1.0 , while their ratios to the ER-L were <1.0 . Thus, Cr and Cu in the sediment would rarely pose toxicity to biota. The ratios of the Cd, Hg, Pb, and Zn contents to the TEL and ER-L were <1.0 , showing that these four metals would not pose toxicity to biota.

CONCLUSIONS

In general, the composition of the major and minor elements, except Ca, in the estuarine and coastal sediments of the DRS was similar to that of the upper continental crust (UCC). The contents of Fe and Mn, mainly in the secondary minerals, had the largest degree of spatial variance. The contents of As, Cd, and Sb in the estuarine and coastal sediments of the DRS were much higher than those in the UCC, while the contents of the other trace elements were similar to those in the UCC.

The EF values decreased in the following order: As, Cd, Sb, Cr, Pb, Cu, Zn, Sc, Ni, V, Y, Hg, and Co. The poorly enriched elements (Cr, Pb, Cu, Zn, Sc, Ni, V, Y, Hg, and Co) may be of natural origin, while the significantly or moderately enriched elements (As, Cd, and Sb) may have partly originated from anthropogenic sources, such as industrial effluents and atmospheric deposition.

The trace elements, minor elements, and Al, Fe, and Mg were positively correlated with one another, while they negatively correlated with Ca, Na, and K. PCA analysis revealed three groups of elements: the elements in or associated with the secondary clay minerals, the elements in the primary minerals, and the elements in carbonate minerals.

Fe was successfully used as a normalizing tracer to develop RGBs of Cr, Cu, Hg, Ni, Pb, and Zn in the estuarine and coastal sediments of the DRS. These RGBs help identify the origins of these metals in the sediments of the Liaodong Bay and document their change over time.

As and Ni in the sediments may pose toxicity to the biota, while Cd, Hg, Pb, and Zn would not pose toxicity.

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