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THEMATIC ISSUE

Seasonal variation of enrichment, accumulation and sources of heavy metals in suspended particulate matter and surface sediments in the Daliao river and Daliao river estuary, Northeast China

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Abstract Suspended particulate matter (SPM) and sediment samples were collected from the Daliao river and Daliao river estuary (Northeast China) to clarify the changes of metal concentrations, enrichment and accumulation during the medium season, wet season and dry season, respectively. The results showed that concentrations, enrichment factor (EF) values and geo accumulation (I_{geo}) values for metals significantly changed during the time. Generally, metal concentrations in sediments during the dry season were higher than those during the medium season and wet season. SQGs results revealed that potential toxicity for aquatic organisms may frequently happen for most of the metals during the dry season, while during the wet season and medium season, adverse effects for aquatic organisms may occasionally happen. Enrichment factor values (EF values) showed that various range of EF values for metals were found and Cd, Pb, As and Zn showed the most sever enrichment among the studied metals. Seasonal mean EF values for metals in SPM showed the following orders: Pb (2.82) > Cd (2.53) > As (2.07) > Zn (2.05) > Mn (1.94) > Co (1.23) > Fe (1.20) > Ni (1.15) > Cr (1.12) > Cu (1.00) and showed the following decreasing order: medium season > dry season > wet season, while for Mn, Cd and Pb, it shows that dry season > medium season > wet season, indicating minor enrichment for all the elements. For sediments, seasonal mean EF values for metals are showed as follows: Cd (12.80) > Pb (9.62) > As (4.11) > Zn (3.15) > Co (2.32) > Cr (2.27) > Mn (2.05) > Fe (1.87) > Ni (1.46) > Cu (1.43), indicating severe enrichment for Cd, moderate severe enrichment for Pb, moderate enrichment for As and Zn and minor enrichment for Co, Cr, Mn, Fe, Ni and Cu, respectively. Geo-accumulation index (I_{geo}) results indicated that mean I_{geo} values for most of metals in sediment samples were below 0 which was classified as unpolluted except for Cd whose I_{geo} values was classified as unpolluted to moderately polluted sediment samples during the wet season and dry season, respectively. I_{geo} values in SPM for metals also showed seasonal variation and Cd, Pb, As and Zn displayed the highest seasonal mean I_{geo} values. Sources analysis for metals in sediments indicated that natural and anthropogenic sources both contributed to the metal accumulations in sediments and industrial and municipal sewage effluents discharged from the upstream cities may be the main anthropogenic sources for metals in the Daliao river and Daliao river estuary.

Keywords The Daliao river · Suspended particulate matter · Sediment · Metals · Enrichment factor · Geo accumulation

Introduction

Sediment pollution with heavy metals has been a worldwide problem and metals originating from anthropogenic sources are frequently detected in sediments in water environment (Peng et al. 2009). On one hand, sediment is one of the most important sinks for trace metals. Metals in water column or suspended particulate matter (SPM) can be precipitated and adsorbed in sediment under certain conditions. On the other hand, sediment also acts as a source for trace metals as metals can be released or

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desorbed from sediment and back into water column when water disturbance happens. Sediment quality is considered as an indicator of water pollution and various researches have been conducted to assess water pollution by studying sediment quality such as Kaohsiung Harbor (Chen et al. 2007), Hudson river estuary (Feng et al. 2002) and the Rawal lake reservoir (Zahra et al. 2014).

Concentrations of metals in SPM are generally several to dozens times higher than those in sediment, and SPM is recognized as the most important carrier of trace metals in water (Bilos et al. 1998; Feng et al. 2002; Dumas et al. 2014). Generally, sources of metals in SPM are both from natural or anthropogenic origin. For anthropogenic origin, industrial and municipal sewage effluents are recognized as the most important anthropogenic sources for metals, while dry and wet deposition or traffic emissions are assignable. Besides, in agricultural land, it is the application of substances like insecticides, herbicides, rodenticides and fungicides, in addition to erosion of soils and irrigation, which affect the water quality (Fu et al. 2014; Reis et al. 2014). For natural sources, parent rock materials transported by surface runoff are the main source. Moreover, sediment resuspension process also contributes to the metal concentrations in SPM especially in estuary areas where tidal cycle can remarkably change hydrodynamic condition (Feng et al. 2002).

The Daliao river system is one part of the Liao River system which is located in Liaoning province in northeast China, and it consists the main stream of Daliao river, two main tributaries of the Hun river and Taizi river, with a watershed area of 27,700 km^2 and 510 km in length. The Daliao river flows into Liaodong Bay of the Bohai Sea in Yingkou city which is dominated by a semi-moist monsoon climate and with a width of 210–1202 m and a depth of 2.97–9.98 m, respectively. The Daliao river has a large seasonal variation in discharge and sediment load as the rainfall in the Daliao river basin mainly occurs in summer and concentrates from June to September (Zhao et al. 2011). It has been reported that, without considering the freeze period from the late November to March, the annual mean precipitation of the Daliao river in May (medium season), August (wet season) and November (dry season) was 53.9, 149.4 and 21.5 mm, respectively (http://www.weather.com.cn/html/cityintro/101070801.shtml). Song et al. (1997) has reported that the annual discharge amounts of water and sediment of the Daliao river were 42 $\times 10^8$ m^3 and 9 $\times$ 10^6 ton, respectively. Besides, the Daliao river estuary, with a depth of up to 20 m, has also been influenced by significantly tidal currents that can reach up to 94 km upstream from the river mouth to Sanchahe during the dry season (spring and autumn).

The Daliao river watershed is one of the most important industrial bases of China, and runs through many industrial cities in northeastern part of China such as Fushun, Benxi, Anshan, Shenyang, Yingkou, etc. In recent years, the Daliao river system has been one of the most contaminated rivers in China, and it received about 60 % pollutant discharge load in the whole Liao River watershed (Tan et al. 2009; Liu et al. 2007). It has been reported that water qualities especially the concentrations of nutrients in the Daliao river often exceeded the standards of Category V of China surface water environmental quality standard (Zhang et al. 2008a, b) and sediments in the Daliao river system has been found to be polluted by organic pollutants (Zhao et al. 2011; Zhang et al. 2008a, b; Liu et al. 2007). Besides, concentrations and sources of heavy metals in the Daliao river also have been concerned. Wu et al. (2011, 2012) have reported the comparatively low concentrations of several metals (Cd, Cr, Mn, Ni, Co, Cu, Pb and Zn) in surface sediments from the Daliao river estuary, and found that pollution level of the studied metals are in "unpolluted" class except for several sampling sites. However, the changes and sources of metal contaminants in the Daliao river and Daliao river estuary during seasonal time are still unclear. The purpose of this study is to focus on the enrichment and sources of metals in the Daliao river and Daliao river estuary, and aims to clarify the changes of metal sources in suspended particulate matter (SPM) and sediments in the studied area over time.

Materials and methods

Sampling

Surface sediment samples were collected during 3 sampling campaigns in areas of the Daliao river and Daliao river estuary in May, April and November, reflecting the medium season, wet season and dry season, respectively (Fig. 1). Sites L01-L17 represented the main stream of the Daliao river, sites E1–E13 represented the Daliao river estuary. At each site, 1500 ml of overlying water (0–20 cm) were gathered in polyethylene flasks directly for the collection of suspended particulate matter (SPM) in lab. Surface sediments were collected using a grab sampler and putting in polyethylene bags. All the samples were stored in an isothermal freezer at 4 °C and then taken to the laboratory and analyzed immediately to minimize possible oxidation or microbial action.

Reagents and chemicals

All reagents used in the experiments were of analytical grade or better. High quality ultrapure water from a Michcm system (18.23 MO, MW-20D) was used for all solutions.

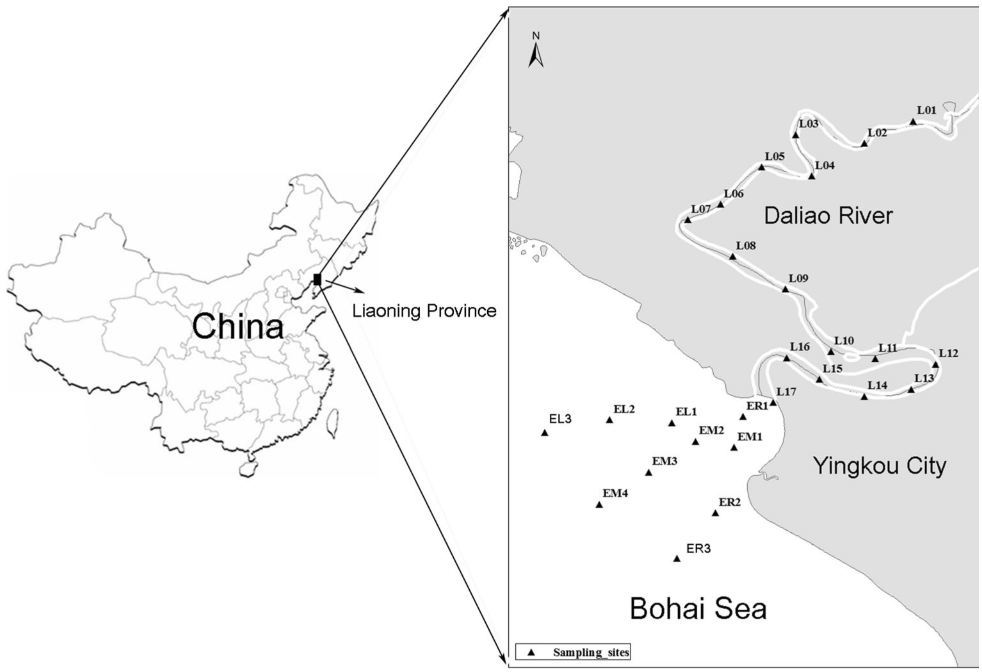

Fig. 1 Study location map and sampling sites of the Daliao river and Daliao river estuary

Sample treatment

Preparation of SPM

About 1 L of water sample was filtered through a weighed 0.45 µm filter (Waterman), and then the filter was freeze dried, weighed, and digested as follows.

Pretreatment of SPM and sediment samples for metal analysis

Sediment samples for total metal analysis were freeze dried, homogenized, and crushed to pass through a 150 µm nylon sieve (100 mesh) for chemical analyses. The total metal concentrations in sediments were determined by the following procedure: Aliquots (0.1 g) of sediment samples were decomposed in a digestion vessel with a mixture of 5 ml nitric acid and 3 ml hydrofluoric acid. The mixture was heated in a MARS microwave digestion system (CEM Corporation, USA) for 20 min at 190 °C. After cooling, the digest was quantitatively transferred into a 50 ml PTFE crucible and evaporated to dryness at 320 °C in a fume hood until the acid solution was evaporated completely. After then, 2 ml nitric acid was injected into solution and then transferred into a 100 ml glass tube, filled up by super purified water, homogenized and stored at 4 °C until measured by ICP-MS.

Quality assurance and quality control of metal analyses were assessed using duplicates, reagent blanks and standard reference materials (GSD-9, GBW-07309, Drainage Sediment, Geochemical Standard Reference Sample, IGGE). The heavy metals recoveries for the standard reference material were controlled between 80–120 %.

Enrichment factor (EF)

Enrichment factor is often used to assess sediment quality and to differentiate metal source originating from anthropogenic and natural sources (Zahra et al. 2014; Chen et al. 2007). Generally, this involves the normalization of metals with a reference element such as Al, Fe, Mn and Li (Acevedo-Figueroa et al. 2006; Daskalakis and O'Connor 1995; Windom et al. 1989; Schropp et al. 1990; Zahra et al. 2014; Loring 1991). EF of normalized metals was calculated using the following equation:

$$EF = (Cx/Bn)sample/(Cx/Bn)reference$$

where, (Cx/Bn) sample is the ratio of concerned metal concentration to that of reference elements concentration in sample; (Cx/Bn) reference is the ratio of concerned metal concentration to that of reference elements concentration in reference sample. In this study, world river average suspended particulate matter (WRSPM) (Viers et al. 2009) and world average concentration of metals for the shale were used as background values (reference sample) for metals in SPM and sediment, respectively. Based on chemical composition of the earth crust, assuming minor contributions of pollutant Aluminum (Al) (Gao et al. 2002), Al was used as reference element to calculate metal enrichment factor since it represents the aluminasilicates, the predominant contents of costal sediments (Chen et al. 2007), and on the basis of the calculated EF values, the sampling

Table 1 Enrichment factor (EF) and I_{geo} classes in relation to sediment quality

EF classes	Sediment quality	I_{geo} classes	Sediment quality
EF < 1	No enrichment	$I \leq 0$	Unpolluted
EF < 3	Minor enrichment	$0 < I \leq 1$	Unpolluted to moderately polluted
EF 3–5	Moderate enrichment	$1 < I \leq 2$	Moderately polluted
EF 5–10	Moderate severe enrichment	$2 < I \leq 3$	Moderately to highly polluted
EF 10–25	Sever enrichment	$3 < I \leq 4$	Highly polluted
EF 25–50	Extremely severe enrichment	$4 < I \leq 5$	Highly to very highly polluted
		$I > 5$	Very highly polluted

Zahra et al. (2014); Chen et al. (2007)

sites were categorized into five main classes (Table 1) (Zahra et al. 2014; Chen et al. 2007).

Geo-accumulation index (I_{geo})

Geoaccumulation index (I_{geo}) developed by Muller (1979) was used to quantify the degree of heavy metal pollution in SPM and sediments in the Daliao river and Daliao river estuary, I_{geo} was calculated according to the following equation:

$$I_{geo} = (\log 2\mathrm{Cn}/1.5\mathrm{Bn})$$

where Cn is the concerned metal concentration in SPM or sediments, Bn is the geochemical background value of metal in WRSPM and the shale for SPM and sediment, respectively, and the factor 1.5 is used to account the possible variations in the background values. The results were interpreted according to Table 1.

Results and discussion

Metal concentrations in SPM and surface sediments

Concentrations of Fe, Mn, Co, Cr, Cd, Cu, Ni, As, Zn and Pb in SPM and surface sediments in the Daliao river and Daliao river estuary were showed in Table 2. It can be seen that metal concentrations in SPM were generally several to dozens times higher than those in surface sediments, and the seasonal mean concentrations of metals in SPM and surface sediments followed the order: Fe > Mn > Zn > Pb > Cr > Ni > Cu > As > Co > Cd and Fe > Mn > Zn > Cr > Pb > Ni > Cu > As > Co > Cd, respectively.

SPM

For metals in SPM, most of metals except for Fe, Cr, Cd during the three sampling campaign showed the following decreasing order: dry season > medium season > wet season. The lower metal concentrations in SPM during the wet season may be attributed to dilution during rainwater input at this time (Zahra et al. 2014). We can see from Fig. 2 that water samples during the wet season contained most of the SPM. Besides, most of metal concentrations showed significant difference between samples during the medium season and dry season and samples during the wet season and dry season ($p < 0.05$), but showed no difference between samples during the medium season and wet season (data not shown).

The SQGs (Sediment quality guidelines) provide us a way to identify the potentially adverse biological effects in sediment (MacDonald et al. 2000; Choueri et al. 2009; McCauley et al. 2000). In this study, the threshold effect level (TEL)/probable effect level (PEL) and the effect range low (ERL)/effect range median (ERM) are introduced to evaluate the ecotoxicology caused by heavy metals in SPM and surface sediments in the Daliao river and Daliao river estuary, and the results were showed in Table 2. Values below TEL or ERL are considered that adverse effects on aquatic biology would rarely happen, whereas concentrations above PEL and ERM represent that adverse effects are expected to occur frequently. The results showed that mean concentrations of Cr, Cd, Cu, As, Zn, and Pb in SPM during the medium season and wet season were higher than ERL and TEL, but below ERM and PEL, however, during the dry season, Cr and Cu content in SPM was above PEL but below ERM, indicating that potential toxicity for aquatic organisms may occasionally happen. Cd, As, Zn and Pb concentrations in SPM during the dry season and Ni content in SPM during the three sampling campaigns were above ERM and PEL, showing that adverse effects for aquatic organisms are expected to occur frequently.

Sediments

In sediments, metal concentrations in surface sediments showed the decreasing order of dry season > wet season > medium season except for As whose concentrations in surface sediments showed as follows: dry season > medium season > wet season. The mean concentrations of Cr, Cu, Ni, Zn and Pb in sediments during the

Table 2 Metal concentration in SPM and sediments in different seasons (μg/g)

μg/g	Fe	Mn	Co	Cr	Cd	Cu	Ni	As	Zn	Pb
SPM										
Medium season										
Mean	57,717	2281	24.13	117.92	2.02	65.37	71.49	73.3	350.4	123.68
Min	5295	107	2.07	12	0.16	12.65	6.5	4.42	0	8.57
Max	225,287	7505	93.35	444.15	10.21	224.57	228.35	328.88	884.69	671.34
Wet season										
Mean	70,240	1712	21.32	124.1	4.25	54.82	61.86	52.15	209.22	113.85
Min	8312	502	4.36	19.11	0.31	10.53	13.84	13.2	79.46	9.86
Max	133,200	2849	41.15	245.1	11.83	99.44	113.5	89.44	406	253.5
Dry season										
Mean	157,851	9092	65.67	318.26	14.22	161.42	190.81	132.29	926.39	637.98
Min	77,390	3055	34.54	189.7	3.81	93.56	91.85	42.44	676.4	177.1
Max	211,500	20,030	86.53	384.1	40.47	344	342.2	231.5	1522	1230
Seasonal mean concentrations	95,269	4362	37.04	186.76	6.83	93.87	108.05	85.91	495.34	291.84
Sediments										
Medium season										
Mean	11,806	221	5.53	25.42	0.45	6.84	13.2	8.87	27.65	15.11
Min	4461	60	2.23	10.59	0.12	0	4.65	0.29	2.43	0
Max	28,269	510	11.85	61.17	1.05	24.38	32.35	22.78	102.99	59.37
Wet season										
Mean	11,879	244	6.23	30.64	0.61	11.86	14.05	5.66	53.06	21.33
Min	1678	28	0.81	4.43	0.07	1.8	1.92	0.65	7.09	2.21
Max	22,844	501	11.72	56.99	0.9	27.68	35.72	12.2	109.12	31.21
Dry season										
Mean	18,123	469	8.01	40.00	0.81	14.89	17.78	9.2	60.98	22.39
Min	7555	159	4.02	15.85	0.4	3.69	6.54	3.42	28.77	14.18
Max	29,250	991	12.57	70.96	1.2	30.31	31.4	20.79	103.25	58.76
Seasonal mean concentrations	13,936	311	6.59	32.02	0.62	11.20	15.01	7.91	47.23	19.61
ERL	–	–	–	81	1.2	34	20.9	33	150	47
ERM	–	–	–	370	9.6	270	51.6	85	410	218
TEL	–	–	–	52	0.7	19	n.a.	5.9	124	30
PEL	–	–	–	160	4.2	108	n.a.	17	271	112

three seasons, the mean concentrations of Cd during the medium season and wet season and the mean content of As during the wet season were all below ERL and TEL, suggesting no adverse effect to aquatic organisms. The mean concentration of Cd during the dry season and the mean concentrations of As during the medium season and dry season were above TEL but below ERL and PEL, indicating that potential toxicity for aquatic organisms may occasionally happen.

Enrichment factor (EF)

SPM

EF values for metals with respect to WRSPM in SPM during different seasons were presented in Table 3, respectively. Generally, the change of EF values for metals along the Daliao river and Daliao river estuary did not show significant roles and the maximum and minimum EF values are 3.04 and 0.52 for Fe, 7.74 and 0.12 for Mn, 2.98 and 0.39 for Co, 4.44 and 0.41 for Cr, 9.67 and 0.66 for Cd, 3.36 and 0.30 for Cu, 4.15 and 0.56 for Ni, 11.65 and 0.31 for As, 7.82 and 0.00 for Zn, 8.16 and 0.56 for Pb, respectively. Seasonal mean EF values for metals are showed as follows: Pb (2.82) > Cd (2.53) > As (2.07) > Zn (2.05) > Mn (1.94) > Co (1.23) > Fe (1.20) > Ni (1.15) > Cr (1.12) > Cu (1.00) and showed the following decreasing order: medium season > dry season > wet season, while for Mn, Cd and Pb, it shows that dry season > medium season > wet season, indicating minor enrichment for all the elements. Gordeev et al. (2004) calculated the EF enrichment of heavy metals in SPM in the Irtysh river, and found that only 2 elements (As and Cd) had an enrichment factor of more than 2. It is reported that As and Cd EF values for the middle Irtysh SPM and lower Irtysh SPM were 7.5 and 16.1, 3.5 and 2.9, respectively, and the EF values for As and Cd in our study was lower than that of the Irtysh river.

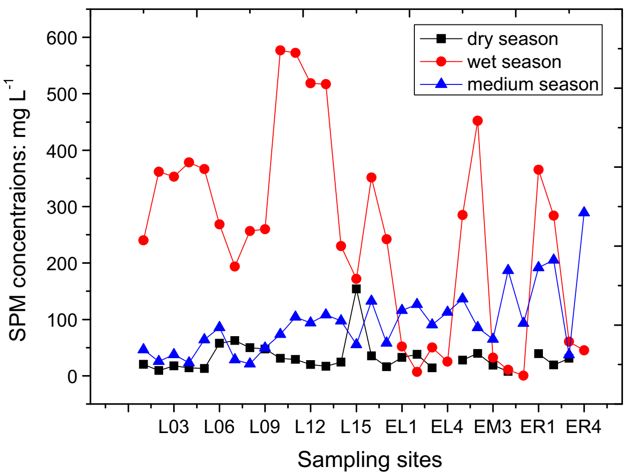

Fig. 2 SPM concentrations in water samples from different seasons

Sediments

Seasonally, mean values of EF for Fe, Mn, Co, Cr, Ni, As, Pb in sediment samples showed the following decreasing order: medium season > wet season > dry season, while for Cd, Cu and Zn, the decreasing order for EF values were as follows: wet season > medium season > dry season (Table 3). Seasonal mean EF values for metals in sediments showed the following decreasing order: Cd (12.80) > Pb (9.62) > As (4.11) > Zn (3.15) > Co (2.32) > Cr (2.27) > Mn (2.05) > Fe (1.87) > Ni (1.46) > Cu (1.43). It has been reported that the mean EF factors for Cd, Pb, Cr, Cu, and Zn in sediments of Kaohsiung Harbor were 16.45, 7.98, 2.45, 3.93 and 8.32, respectively (Chen et al. 2007), we can therefore conclude that EF factors of Cd, Cr, Cu and Zn in our study were lower than that of Kaohsiung Harbor, however, Pb EF factor in our study area was

Table 3 Enrichment factor (EF) for metals in SPM and sediments in different seasons

EF	Fe	Mn	Co	Cr	Cd	Cu	Ni	As	Zn	Pb
SPM										
Medium season										
Mean	1.45	1.99	1.55	1.37	1.73	1.43	1.52	3.29	3.18	2.51
Min.	0.82	0.64	0.94	0.71	1.05	0.66	0.68	0.54	0	1.34
Max.	2.85	3.75	2.98	2.64	2.79	3.36	2.98	11.65	7.82	5.07
Wet season										
Mean	0.93	1.10	0.78	0.76	1.85	0.60	0.70	1.31	0.88	1.33
Min.	0.52	0.12	0.39	0.41	0.66	0.3	0.35	0.31	0.34	0.56
Max.	3.04	2.92	2.4	2.59	4.5	1.94	2.18	4.89	2.25	3.66
Dry season										
Mean	1.23	2.72	1.35	1.24	4.02	0.98	1.24	1.62	2.09	4.63
Min.	0.69	0.82	0.7	0.66	1.32	0.56	0.56	0.6	1.27	1.32
Max.	1.65	7.74	1.82	4.44	9.67	2.09	4.15	2.75	4.35	8.16
Seasonal mean values	1.20	1.94	1.23	1.12	2.53	1.00	1.15	2.07	2.05	2.82
Sediments										
Medium season										
Mean	2.74	2.66	3.35	3.07	16.03	1.44	2.14	7.35	3.49	17.58
Min.	1.34	1.17	1.66	1.6	5.43	0	0.85	0.31	0.49	5.43
Max.	8.98	6.73	12.3	9.27	47	4.57	7.39	21.48	20.31	34.28
Wet season										
Mean	2.08	2.34	2.72	2.82	16.72	2.16	1.69	3.51	4.63	8.93
Min.	1.26	1.38	1.79	1.55	7.95	0.84	0.76	0.87	2.45	6.38
Max.	3.44	4.19	4.38	4.5	24.2	3.95	3.73	7.84	8.17	13.96
Dry season										
Mean	0.8	1.16	0.88	0.93	5.66	0.68	0.54	1.47	1.34	2.36
Min.	0	0	0	0	0	0	0	0	0	0
Max.	1.6	3	1.7	1.85	9.4	1.54	1.19	3.35	2.48	6.37
Seasonal mean values	1.87	2.05	2.32	2.27	12.80	1.43	1.46	4.11	3.15	9.62

higher than that of Kaohsiung Harbor. It is noticeable that EF values for Cd, Pb, As and Zn displayed remarkably enrichment when compared with other metals. The seasonal mean EF values for Cd, Pb, As and Zn in sediments were 12.80, 9.62, 4.11 and 3.15, indicating severe enrichment for Cd, moderate severe enrichment for Pb and moderate enrichment for As and Zn, respectively. Metals of Cd, As, Pb and Zn are always typical anthropogenic metals associated with human activities, and they are common components of industrial and municipal sewage. Pb has also been reported that it mainly arise from atmospheric deposition (Praveena et al. 2007). Wu et al. (2012) has reported relatively higher sequence of pollution extent and potential ecological risk of Pb in the surficial sediments in Daliao river estuary. In this study, Pb was found to be the most enrichment elements in SPM, and this may caused the higher enrichment of Pb than other metals in sediment as the results of precipitation process.

Geo-accumulation index (I_{geo})

SPM

In SPM, I_{geo} values for metals showed large variance between sites. The mean I_{geo} values for most metals indicated no pollution during medium season and wet season (with the occasional exception), while their mean I_{geo} values during the dry season ranged from 0.45 to 2.65 and shows the following decreasing order: Pb (2.65) > Cd (2.44) > Mn (1.62) > Zn (1.54) > As (1.16) > Co (0.94) > Ni (0.88) > Fe (0.81) > Cr (0.75) > Cu (0.45), indicating moderately to highly polluted SPM samples for Pb and Cd, moderately polluted SPM samples for Mn, Zn and As and unpolluted to moderately polluted SPM samples for Co, Ni, Fe, Cr and Cu during the dry season, respectively. Seasonal mean I_{geo} values for metals in SPM showed the order of Pb (Mean I_{geo} 0.72) > Cd (Mean I_{geo} 0.65) > As (Mean I_{geo} 0.20) > Zn (Mean I_{geo} 0.14) > other metals (Mean $I_{geo} < 0$) and this is consistent with EF values reported above (Table 4).

Sediments

I_{geo} values for metals in sediments in the Daliao river and Daliao river estuary were presented in Table 4. It can be seen that mean I_{geo} values for most of metals in sediment samples were below 0 which was classified to be unpolluted except for Cd whose mean I_{geo} values were −2.59 during the medium season, 0.29 during the wet season and 0.79 during the dry season, suggesting unpolluted sediment samples for medium season and unpolluted to moderately polluted sediment samples for wet season and dry season, respectively. Seasonal mean I_{geo} class for metals in sediments were lower than that of Kaohsiung Harbor (Chen et al. 2007) and seasonal mean I_{geo} values for metals showed the following decreasing order: Cd (Mean I_{geo} 0.29) > others (Mean $I_{geo} < 0$). Among the metals, seasonal mean I_{geo} values for Cd in sediment showed the highest accumulation.

It can be seen that Cd and Pb showed the highest accumulation either in SPM or in surface sediments and this is consistent with EF values reported above. Li et al. (2012), Shao and Zhao (2012) and Wu et al. (2012) have reported the higher accumulation of Cd and Pb in sediments in the Taizi river (upstream of the Daliao river) and Daliao river estuary, Fan et al. (2008) and Zhang et al. (2008a, b) declared that metals in sediments of the Daliao river may partly derived from the transported SPM from upstream rivers, i.e., the Hun river and Taizi river, partly emitted from industrial and municipal effluents discharged from Yingkou city. We can conclude that SPM transferred from upstream of the Daliao river and the resuspension of sediment may be the main source of Cd and Pb pollution in sediments and SPM of the Daliao river and Daliao river estuary, as well as other metals.

Sources of metals in SPM

Comparison of normalized metal between SPM and sediments

Comparison of normalized metal between SPM and sediments has been used to understand the exchange of metal contaminants between water column and sediment and to estimate the anthropogenic impacts as well. It is considered that metal/reference ratios in SPM and sediments in same ranged is derived from the same source. Feng et al. (2002) compared the metal/Fe ratios in SPM with those in surface sediments to clarify the metal sources in water, and they declared that sources of metal contaminants to the water column were both from local sediment resuspension and lateral advection. In this study, Al was used as reference element to normalize metals and comparable metal/Al ratios in SPM to those in surface sediments was showed in Table 5. During the medium season, ratios of Cr, Fe, Co, Cr and Pb to Al in SPM were significantly lower than those in sediments ($p < 0.05$), ratios of Mn, Cu, Zn to Al in SPM were remarkably higher than those in sediments ($p < 0.05$), while ratios of Ni and As to Al in SPM showed no difference with sediments ($p > 0.05$). We can see that metals of Cr, Fe, Co, Cr, Ni, As and Pb to Al rations in SPM during the medium season were within the range of those in sediments, therefore these metals in SPM during the medium season may mainly derived from the resuspension of surface sediment in the Daliao river and Daliao river estuary, while metals of Mn, Cu and Zn in SPM not only originated from surface sediment but also may derived from anthropogenic sources.

Table 4 I_{geo} values for metals in SPM and sediments in different seasons

I_{geo}	Fe	Mn	Co	Cr	Cd	Cu	Ni	As	Zn	Pb
SPM										
Medium season										
Mean	−1.17	−0.80	−1.07	−1.26	−0.90	−1.29	−1.14	−0.17	−0.15	−0.28
Min.	−4.04	−4.56	−4.03	−4.02	−3.86	−3.17	−4.10	−3.62	−3.50	−3.42
Max.	1.37	1.58	1.47	1.19	2.14	0.98	1.03	3.34	1.50	2.87
Wet season										
Mean	−1.10	−0.99	−1.01	−1.12	0.40	−1.46	−1.24	−0.38	−0.95	−0.22
Min.	−17.31	−12.32	−6.41	−8.95	−2.91	−8.5	−8.33	−6.91	−9.78	−7.17
Max.	0.61	0.85	0.29	0.33	2.98	−0.2	0.02	1.41	0.38	1.58
Dry season										
Mean	0.81	1.62	0.94	0.75	2.44	0.45	0.88	1.16	1.54	2.65
Min.	−0.17	0.28	0.03	−0.04	0.71	−0.28	−0.28	−0.36	1.12	0.95
Max.	1.28	2.99	1.36	2.57	4.12	1.60	4.95	2.09	2.29	3.75
Seasonal mean values	−0.49	−0.06	−0.38	−0.54	0.65	−0.76	−0.50	0.20	0.14	0.72
Sediments										
Medium season										
Mean	−2.76	−2.80	−2.49	−2.59	−0.22	−4.03	−3.16	−1.46	−2.72	0.04
Min.	−3.99	−4.41	−3.68	−3.67	−1.97	−7.14	−4.46	−6.10	−5.88	−1.98
Max.	−1.32	−1.32	−1.27	−1.14	1.22	−1.47	−1.66	0.22	−0.47	0.98
Wet season										
Mean	−2.73	−2.56	−2.33	−2.30	0.29	−2.75	−3.12	−2.09	−1.60	−0.60
Min.	−5.40	−5.52	−5.13	−4.93	−2.78	−5.23	−5.73	−4.90	−4.33	−3.76
Max.	−1.79	−1.52	−1.47	−1.34	1.00	−1.29	−1.88	−0.68	−0.68	0.06
Dry season										
Mean	−2.07	−1.57	−1.91	−1.87	0.79	−2.39	−2.67	−1.25	−1.33	−0.51
Min.	−3.23	−3.01	−2.82	−3.09	−0.16	−4.19	−3.96	−2.51	−2.31	−1.08
Max.	−1.28	−0.36	−1.18	−0.93	1.41	−1.15	−1.70	0.09	−0.46	0.97
Seasonal mean values	−2.52	−2.31	−2.24	−2.25	0.29	−3.06	−2.98	−1.60	−1.88	−0.35

During the wet season, ratios of Cr, Fe, Co, Ni, Cu, Zn, Cd and Pb to Al in SPM were significantly lower than those in sediments, while there were no difference between the ratios of Mn and As to Al in SPM with those in sediments, implying that all the studied metals in SPM may mainly derive from the resuspension of sediment during this time. Besides, plenty of farmland soil was found distributing along the Daliao river, as the effects of soil weathering during the wet season (in summer) are much stronger than those during the dry season and medium season, metals released from the geochemical weathering of soil and metals in soil particulates were easily transferred to the downstream water during rainstorm events, these metals may either indwell in SPM or precipitated to sediments, finally leading to a dynamic equilibrium between SPM and sediments, this may also result in the same variation range of metals/Al ratios in SPM and sediments.

During the dry season, all the metal/Al ratios in SPM were significantly higher than those in sediments, indicating that anthropogenic sources for metals contributed to metal concentrations in SPM. It has been reported that some important industrial cities of China, i.e., Shenyang city and Anshan city etc., are located upstream of the Daliao river, therefore industrial or municipal wastewater may be discharged into the Daliao river at this time. Besides, Cd, Pb, As and Zn displayed the highest EF values and Igeo values in SPM, and showed the most severe enrichment and accumulation. Fu et al. (2012) reported that wastewater discharged from electroplating, dyeing, smelting, mining, beneficiation and battery etc. activities are recognized as the most important anthropogenic sources for Cd, Pb, As and Zn in the Liao river basin, Anshan city, Shenyang city and Yingkou city were considered discharging most of the metal-contained industrial effluents to the downstream waters in recent years (Su et al. 2010). Therefore, metal sources in SPM during the medium season may partly derive from the effluents of above human activities and partly come from the resuspension of sediment.

Table 5 Metal/Al rations for metals in SPM and sediments in different seasons (10^{-4})

Metals/Al ratios	Fe	Mn	Co	Cr	Cd	Cu	Ni	As	Zn	Pb
SPM										
Medium season										
Mean	9649.08	383.76	4.01	20.47	0.31	12.47	12.96	13.70	75.89	17.60
Min.	5468.50	122.61	2.42	10.65	0.19	5.73	5.84	2.23	0.00	9.36
Max.	18,961.88	722.65	7.68	39.39	0.50	29.25	25.49	48.48	186.52	35.51
Wet season										
Mean	6215.78	211.50	2.01	11.38	0.32	5.19	6.00	5.44	21.07	9.11
Min.	3443.25	23.90	1.01	6.08	0.12	2.57	2.99	1.27	8.20	3.89
Max.	20249.15	562.14	6.20	38.60	0.80	16.85	18.61	20.34	53.56	25.64
Dry season										
Mean	8175.07	522.75	3.47	18.47	0.71	8.49	10.63	6.73	49.77	32.43
Min.	4609.20	157.97	1.80	9.91	0.24	4.89	4.80	2.48	30.31	9.25
Max.	10,964.68	1489.63	4.68	66.15	1.72	18.18	35.50	11.43	103.73	57.17
Seasonal mean values	8013.31	372.67	3.16	16.77	0.45	8.72	9.86	8.62	48.91	19.71
Sediments										
Medium season										
Mean	13,306.42	257.40	6.44	28.78	0.50	7.38	14.83	10.85	30.13	39.94
Min.	7180.57	113.26	3.59	16.40	0.19	0.00	6.54	0.46	5.34	12.34
Max.	28,679.91	650.19	13.20	59.26	0.95	23.40	32.44	31.73	86.30	77.90
Wet season										
Mean	11,156.44	226.23	5.87	28.82	0.57	11.03	13.02	5.18	49.96	20.30
Min.	6765.12	133.25	3.86	15.87	0.27	4.30	5.90	1.28	26.44	14.50
Max.	18,454.31	405.01	9.46	46.04	0.83	20.20	28.86	11.59	88.16	31.73
Dry season										
Mean	4616.22	119.82	2.05	10.18	0.21	3.74	4.51	2.34	15.55	5.76
Min.	2284.94	47.99	1.22	4.79	0.12	1.10	2.04	1.01	7.63	3.79
Max.	8560.14	290.08	3.68	18.90	0.32	7.87	9.19	4.94	26.74	14.47
seasonal mean values	9693.03	201.15	4.78	22.60	0.43	7.38	10.79	6.12	31.88	22.00

PCA

Multivariate techniques like the principal component analysis (PCA) have been shown useful to identify sources of metals and interpret the relationships existing amongst the elements in sediments (Duan et al. 2014; Ries et al. 2014; Fu et al. 2014; Zahra et al. 2014). In this study, PCA was employed to identify possible sources of metals in SPM in the Daliao river and Daliao river estuary during different time. The PCA was performed with the total concentrations of metals in SPM, the Chlorophyll a concentration in surface water, the silicate concentration in surface water and the water salinity, to clarify the relationships among these parameters (Fig. 3). The two first components explain 76.92, 82.93 and 61.87 % of the data variation during the medium season, wet season and dry season, respectively.

During the medium season, the first principal component was positively determined by most metal concentrations in SPM, suggesting the common source for these metals. The second principal component was positively determined by water salinity and negatively determined by Chlorophyll a and silicate concentrations in water. During the wet season, the first principal component, with a relative inertia of 72.21 %, was negatively determined by silicate concentration and most of metals except for Mn, while the second principal component, with a relative inertia of 10.72 %, was negatively determined by Mn and water salinity. During the dry season, the first principal component, with a relative inertia of 40.78 %, was positively determined by Fe, Co, Cu, Cd, As and Pb concentrations in SPM, but negatively determined by Chlorophyll a concentration in water, Ni and Zn concentrations in SPM. The second principal component, with a relative inertia of 20.21 %, was positively determined by silicate concentration in water and Cr and Mn concentrations in SPM but negatively determined by water salinity. Silicate is a typical component associated with parent rock materials and it is clear that the accumulation of most metals in SPM are strongly

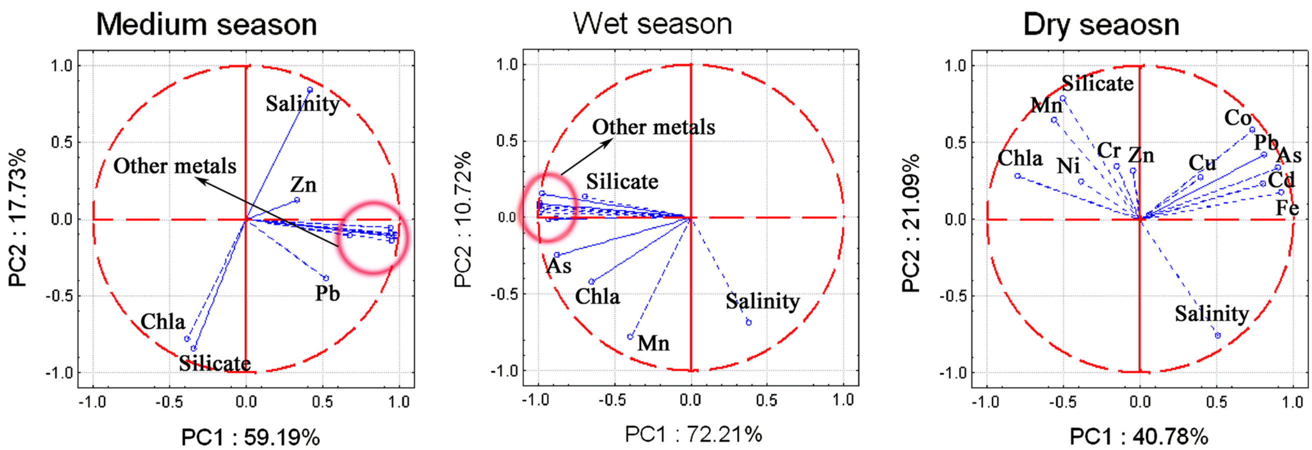

Fig. 3 Plot of the first two principal components obtained from the PCA of water salinity, water silicate, water Chlorophyll a and SPM metals (Cu, Pb, Zn, Cr, As, Fe, Mn, Ni, Co, Cd) during the dry season, wet season and medium season, respectively

affected or controlled by silicate during the wet season, indicating that these metals may mainly derive from natural sources such as surface runoff during this time. During the medium season, there were no correlations between silicate and metals, suggesting that metals during this time may mainly originated from the resuspension of sediment or anthropogenic sources as well. While the plot during the dry season suggests a combined source for metals, and natural and anthropogenic sources both contributed to the metals in SPM.

Figure 3 Plot of the first two principal components obtained from the PCA of water salinity, water silicate, water Chlorophyll a and SPM metals (Cu, Pb, Zn, Cr, As, Fe, Mn, Ni, Co, Cd) during the dry season, wet season and medium season, respectively.

Conclusions

Variation of metal concentrations, enrichment and accumulation in sediment samples in the Daliao river and Daliao river estuary significantly changed during years. The concentrations of various metals in SPM are several to dozens times higher than those in sediments, most of metals in SPM showed the following order: dry season > medium season > wet season, while in sediments, it showed as: dry season > wet season > medium season. SOGs results showed that most severe potential toxicity for aquatic organisms may happen either in SPM or in sediments during the medium season except for certain elements. Sources of metals in SPM and sediments may both derived from natural source and anthropogenic sources, and industrial and municipal sewage effluents transported from the upstream waters were considered as the most important anthropogenic sources for metals.

The Daliao river is a typical irregular semidiurnal tide river. The Daliao river estuary, has been influenced by significantly tidal currents that can reach up to 94 km upstream from the river mouth to Sanchahe during the dry season (spring and autumn). Besides, The Daliao river has a large seasonal variation in discharge and sediment load as the rainfall in the Daliao river basin mainly occurs in summer and concentrates from June to September. Therefore, the accumulation and behavior of heavy metals in SPM and sediments may be complicated by the above processes and show significant variation during time. This study will help us clarifying the change of metal sources and accumulation in SPM and sediment in the Daliao river and Daliao river estuary during time.

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