Baseline

Assessment of nutrient and heavy metal contamination in the seawater and sediment of Yalujiang Estuary

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ABSTRACT

Yalujiang River is a famous border river between China and North Korea. In this study, 22 sample sites (seawater and sediments) were investigated to determine the concentrations of nutrients (dissolved inorganic nitrogen and soluble reactive phosphorus) and trace elements (Hg, As, Pb, Cu, Cd, Cr, and Zn) during the flood season (August). Generally, the concentration of nutrients were higher in the entrance of the estuary than that in the downstream region and the trophic index ranged from moderate to high production, indicating a potential eutrophication risk. With the exception of Cd, the mean concentrations of most metals attained the first level of seawater quality. Sediment pollution assessment was undertaken using contamination factor (CF) and geoaccumulation index (I_{geo}). The CF values of the seven trace elements were in the following order: Cd > Hg > Pb > As > Cu > Zn > Cr. Both CF and I_{geo} values indicated the elevated Cd and Hg concentrations in the region. Cluster analysis indicated that the sources of Cu, Cd, Cr, and Zn were mainly derived from copper mine and coastal industrial effluents, whereas Pb, Hg, and As were mainly from vehicle emissions and oil combustion. This study could provide a basis for the sustainable management of the marine ecosystem in this region.

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As the confluence area of land runoff and seawater, an estuary transports terrestrial matter to the sea. With the rapid economic development of coastal, estuaries receive substantial amounts of anthropogenic inputs from both point and non-point upstream sources of pollution from industrialization and urbanization activities, and ecological problems have become severe as a result. Consequently, the estuarine ecosystem is one of the most heavily used and globally threatened natural systems (Lotze et al., 2006; Liu et al., 2016a, b). Estuaries often act as nurseries to numerous forms of aquatic life; thus, estuaries are important to aquaculture and fisheries. The intertidal areas of estuaries attract a variety of birds, and these zones are often globally important sites for migratory species. Thus, assessing the contamination in estuaries and its biological influence is crucial.

Heavy metal pollution in the marine environment has received global attention because of the ubiquity, difficult degradation, and easy accumulation of heavy metal pollutants. In estuarine and coastal regions, sediments have been regarded as both carriers and sinks of various contaminants originating from industrial and agricultural processes (Gan et al., 2013; Yang et al., 2012). As a result, sediment contamination is recognized as a major source of marine ecosystem health stress (Chapman and Wang, 2001). Sediments release more heavy metals into the seawater when local environmental conditions (e.g., salinity, pH, and redox

potential) change (Valdés et al., 2005; Hill et al., 2013). Consequently, the transfer of metals from sediment to water columns and the subsequent bioaccumulation along the food chain are detrimental to the marine environment and public health (Pan and Wang, 2012; Zhang et al., 2012).

Yalujiang Estuary is located in the Northern Yellow Sea, Liaoning Province, China. This estuary is known for being the boundary river between China and North Korea. Yalujiang River originates from Tianchi Lake in Changbaishan Mountain and flows a distance of approximately 790 km from northeast to southwest through Jilin Province and Liaoning Province. This river supplies the most important sources of drinking water for the surrounding cities. With the rapid urbanization and industrialization in recent years, Yalujiang River suffers from industrial, agricultural, and domestic pollution, which results in potential ecological risks (Gao et al., 2008). Some industrial enterprises (e.g., automobile, papermaking, printing, and textile) are concentrated in the cities of Dandong and Donggang. Substantial amounts of industrial effluents have been taken to the sea by the river, particularly during the flood season. The average water discharge is $3.02 \times 10^8 \text{ m}^3/\text{a}$, of which 70%–80% occurs during the flood season. However, only few pollution investigations have been conducted in Yalujiang Estuary (Wu et al., 2003; Gao et al., 2008; Cheng et al., 2011); as a result, the understanding of the influence of human activities on the marine ecosystem in this region is limited. In the current study, the spatial distribution of heavy metals during the flood season in Yalujiang Estuary is determined, and the

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sources of these pollutants are identified to provide basic information for future pollution monitoring and environmental management.

Seawater and sediment samples for metal analysis were collected from 22 sites in Yalujiang Estuary during the flood season (August 2016) (Fig. 1). The surface seawater samples were collected from 0.5 m below the surface at each site with 5 L Niskin bottles. The surface sediment samples (top 5 cm of the surface) were obtained using a van Veen collector (0.05 m²). The bulk sediment samples were divided into three subsamples for the determinations of trace metals, total organic carbon (TOC), and grain size. The seawater salinity and temperature were measured in situ with a multiparameter sensor (YSI6600), and the pH values were determined with a pH meter. The seawater for dissolved oxygen (DO) analysis was collected with a tube reaching the bottom of the bottle until the water overflowed. Suspended particulate material samples were filtered through pre-weighed Whatman GF/F fiber filters (25 mm). The samples for metal determination were immediately filtered through Whatman GF/F fiber filters (0.45 mm),

acidified with 10% HNO₃, placed in an icebox, and then transported to the laboratory.

The concentrations of NO₃, NO₂, NH₄, and PO₄ in seawater were determined following to the methods described by Grasshoff et al. (1983). DO was determined using the Winkler titration method. Chlorophyll-*a* (Chl*a*) was determined by filtering 100–200 mL of seawater through a GF/F fiber filter with a cascading filtering device under a low vacuum pressure. After extraction with 90% acetone, Chl*a* was determined using a Turner Designs fluorometer (TD Trilogy). The concentrations of the dissolved heavy metals were determined by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X series) for Cd, Pb, Zn, Cu, and Cr, whereas the contents of Hg and As were determined using an atomic fluorescence spectrometer (AFS-920).

The grain sizes of the sediment samples were determined using a Mastersizer 2000 laser particle size analyzer (Malvern, UK). The samples were divided into four fractions according to particle size: clay (<2 μm), silt (2–40 μm), fine sand (40–200 μm), and coarse sand

Fig. 1. Location map of sample sites in Yalujiang Estuary.

(>200 µM) (Ip et al., 2007). Approximately 20 g of sediment samples for element analysis were oven-dried (<60 °C) and then ground to powder (<63 µm). Approximately 0.2 g of powdered samples were totally digested in a Teflon vessel with a mixed solution of HNO₃ + HCl + HF (5:4:1) on a heating plate and heated (<150 °C) to dryness. Afterward, the residue was extracted with HNO₃ and diluted to a specific volume. The TOC was measured with an elemental analyzer.

The environmental data of seawater and sediment were analyzed using SPSS 18.0. Pearson correlation analysis was employed to test the relationship among sediment grain size, TOC, sulfide, and trace elements. Cluster analysis (CA) was performed to determine the analyzed parameters and their possible sources (natural or anthropogenic). A hierarchical CA was performed using the hclust function in the R package pvcust (Suzuki and Shimodaira, 2006), which automatically computes the *p*-value (AU and BP types) for all clusters of the original data.

Eutrophication in marine ecosystems has become a deleterious environmental problem worldwide. In this study, the ecological risks of nitrogen and phosphorus were assessed by the trophic index (TRIX) (Vollenweider et al., 1998):

$$\text{TRIX} = \frac{\log(\text{Chla} \times [\% \text{DO}] \times \text{DIN} \times \text{SRP}) + 1.5}{1.2}$$

Chla, DIN, and SRP are the concentrations of Chla (mg/m³), dissolved inorganic nitrogen (mg/m³), and soluble reactive phosphorus (mg/m³), respectively; %DO is the absolute value of the oxygen saturation deviation (|100 – %DO|). TRIX is classified into four levels: low production (TRIX < 4), moderate production (4 < TRIX < 5), between moderate and high production (5 < TRIX < 6), and high production (TRIX > 6).

The eutrophication risk of the nutrients ranged from moderate to high production in Yalujiang Estuary (Fig. 2), indicating that the overall condition in the study area was eutrophic. Generally, the worst water quality conditions (in trophic terms) were found at the upper estuary sites (S1, S2, S3, and S4), which were exposed to the highest influence of anthropogenic activities, while better water conditions were detected in the downstream regions (S13–S22). These results indicated that industrial, agricultural, and urban effluent inputs resulted in the elevated nutrient levels in the study area, and such levels are conducive to phytoplankton growth.

The dissolved heavy metal concentrations and other environmental factors in seawater are listed in the Supplement Table S1. The concentrations of Cu, Pb, Zn, Cr, As, Cd, and Hg were 2.86 ± 0.81 , 0.68 ± 0.34 , 14.93 ± 3.05 , 0.13 ± 0.13 , 1.80 ± 0.15 , 1.18 ± 0.14 , and

0.029 ± 0.013 µg/L (Table 1), respectively, which are ranked following the order of Zn > Cu > As > Cd > Pb > Cr > Hg. Table 1 provides a comparison of the concentrations of trace elements in some typical regions in China and those in the study area. The concentrations of trace elements in Yalujiang Estuary were higher than those in the Northern Yellow Sea, particularly for Cr, Zn, and Hg, indicating that the riverine input carried metal pollutants. However, the metal concentrations in Yalujiang Estuary were lower than those in Jinzhou Bay and Tianjin Bay, which are two inner bays of the Bohai Sea. With the exception of Cd, the concentration levels of most metals reached the first level according to the National Seawater Quality Standard of China (GB 3097-1997), indicating that the concentrations were within the range of clean water. Consequently, Cd was the main pollutant element in the seawater of Yalujiang Estuary.

In this study, the median grain size (Mz) varied between 2.0φ and 5.2φ, with a mean value of 3.0φ, indicating that the sediments of Yalujiang mainly comprised fine sand-sized components. The TOC ranged from 0.02% to 0.60%, with an average of 0.22%. The metal concentrations (mg/kg) ranged from 0.008 to 0.184 (average 0.05) for Hg, from 5.3 to 15.1 (average 9.37) for Cu, from 26.0 to 53.8 (average 37.86) for Zn, from 12.2 to 37.7 (average 24.3) for Cr, from 0.05 to 0.41 (average 0.20) for Cd, from 12.3 to 29.9 (average 17.95) for Pb, and from 3.8 to 11.3 (average 6.36) for As (Table 2, Supplement Table S2).

A comparison of the metal concentrations in the sediments of Yalujiang Estuary and those in some typical estuaries in China is provided in Table 2. The mean contents of Hg, Cd and As in Yalujiang Estuary were higher than their corresponding average values in the East China, while the contents of Cu, Zn, Cr and Pb were lower. The mean concentration of Hg in the study area was higher than that of other representative estuaries in China, including Liaohe Estuary (Li et al., 2007), Perl River Estuary (Zhou et al., 2004), Changjiang Estuary (Zhang et al., 2009), and Luanhe Estuary (Liu et al., 2016a, b). With regard to Cu, Zn, and Cr, their contents in Yalujiang Estuary were lower than those in other representative coastal regions in China. In addition, with regard to the other three elements (i.e., Cd, Pb, and As), their average contents were comparable to those in Liaohe Estuary and Luanhe Estuary. The concentration levels of all metals attained the first level according to the Chinese Marine Sediment Quality Standard Criteria (GB 18668-2002), indicating that the concentrations of metals in the study area were within the range of clean sediment.

Fig. 2. The variations of the trophic index (TRIX) in Yalujiang Estuary. Moderate production: $4 < \text{TRIX} < 5$; moderate and high production: $5 < \text{TRIX} < 6$; high production: $\text{TRIX} > 6$.

Table 1

Comparison of dissolved heavy metal concentrations in the surface seawater of some typical area (μg/L).

Region	Cu	Zn	Cr	Hg	Cd	Pb	As	Reference
Yalujiang Estuary	1.80–4.70	9.20–19.60	0.113–0.14	0.006–0.049	0.83–1.33	0.40–1.80	1.60–2.05	This study
	2.86	14.93	0.13	0.03	1.18	0.68	1.80	
Southern Yellow Sea	1.12	3.44	nd	0.0086	0.053	0.30	1.66	He et al. (2008)
Jinzhou Bay	3.06	11.87	nd	0.03	0.92	0.61	2.19	Wang et al. (2012)
Tianjin Bay	2.54	26.9	0.40	0.04	0.12	7.18	1.26	Meng et al. (2008)
Dingzi Bay	2.02	23.62	4.10	0.05	0.36	1.07	1.33	Pan et al. (2014)
The Pearl River Estuary	1.64	13.54	nd	nd	0.12	1.61	2.55	Zhang et al. (2013)
Changjiang Estuary	0.96	7.56	0.39	nd	0.06	0.68	nd	Sun et al. (2009)
SWQ-1	5	20	50	0.05	1	1	20	AQSIQ (1997)
SWQ-2	10	50	100	0.20	5	5	30	AQSIQ (1997)

SWQ-1 and SWQ-2 are included in Chinese Sea Water Quality standard criteria (GB 3097-1997) issued by Administration of Quality Supervision, Inspection and Quarantine (AQSIQ).
nd: no data.

Overall, the analyzed trace elements in the Yalujiang Estuary sediment generally showed similar distribution patterns (Fig. 3). In general, the sample sites with lower metal concentrations were located in the downstream regions, while the higher content sites were distributed near the mouth of the estuary. As and Cr exhibited similar distributions. These two elements presented high concentration levels in the western part of the study area, near the mouth of the Dayang River. These results suggested that the riverine input was an important source of metal pollution in this area. All metal elements (except As and Cr) exhibited high concentration levels around sites S05 and S06 because these sites are located near the shipping channel, where wastewater is frequently discharged.

The Pearson correlation coefficients among the trace elements, TOC, sulfide, and Mz in the sediments are shown in Table 3. Significant positive correlations existed between TOC and Mz ($r = 0.732$, $P < 0.01$), indicating that the sediment grain size is the main factor influencing TOC accumulation. The significant correlation between TOC and Cr ($r = 0.56$, $P < 0.05$) suggested that TOC might be a major influencing factor on the abundance of Cr, which was obviously influenced by anthropogenic sources. Cu showed significant correlations with Zn ($r = 0.78$, $P < 0.01$), Cr ($r = 0.53$, $P < 0.05$), and Cd ($r = 0.48$, $P < 0.05$), indicating that these metals might have a common natural or anthropogenic source. The poor correlation between Mz and heavy metals suggested that Mz was not the main factor controlling the concentrations of metals.

The contamination factor (CF) and pollution load index (PLI) were used to assess the degree of anthropogenic metal contamination. The CF is calculated as the ratio of the measured concentration in the sediment to the background value, that is, $CF = Me_{\text{sample}}/Me_{\text{baseline}}$.

CF is classified into four levels: low degree ($CF < 1$), moderate level ($1 \leq CF < 3$), considerable degree ($3 \leq CF < 6$), and high degree ($CF \geq 6$) (Loska et al., 1997). The CF values of heavy metal in this study varied as follows: 0.72–6.31 (mean of 3.07) for Cd, 0.32–7.24 (mean of 2.19) for Hg, 0.61–1.50 (mean of 0.90) for Pb, 0.49–1.47 (mean of 0.83) for As, 0.35–1.00 (mean of 0.62) for Cu, 0.40–0.83 (mean of 0.58) for Zn,

and 0.20–0.63 (mean of 0.41) for Cr (Fig. 4A). These results suggested that Cd was the foremost contaminant in the sediment of Yalujiang Estuary, with the CF values of all sample sites > 1 (Fig. 5). The CF values of the seven trace elements were found to be in the following order: $Cd > Hg > Pb > As > Cu > Zn > Cr$. The CF values of the other six elements indicated that S11, S13, S14, S15, S16, S17, S18, and S20 were the cleanest sites as their CF values were < 1 . By contrast, the sediments collected at S1 and S8 were considerably polluted with Cd and Hg, with CF values of > 3 .

The PLI was applied to compare the integrated pollution status at different sample sites because heavy metals always occur in sediments as complex mixtures with great variation: $PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$.

The PLI is determined as the n th root of the multiplications of CF. $PLI > 1$ indicates a polluted condition, whereas $PLI < 1$ indicates no metal pollution (Tomlinson et al., 1980). In the study area, the PLI values ranged from 0.44 to 1.27, with an average of 0.86 (Fig. 6). Among all sample sites, 7 of 19 values were > 1 , indicating that 36.8% of the sites were metal contaminated to some extent. Furthermore, the contaminated sites were located near the mouth of the estuary. This finding is similar to that observed from the CF index.

The geoaccumulation index (I_{geo}) is another parameter to assess the metal contamination in sediments with a corresponding natural background level as a reference (Müller, 1969):

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right),$$

where C_n is the concentration of a metal (n) in the sample and B_n is the geochemical background concentration of the metal (n). The factor (1.5) is a background matrix correction factor attributed to lithogenic effects (Müller, 1979). I_{geo} is classified into seven levels: unpolluted ($I_{geo} \leq 0$), unpolluted to moderately polluted ($0 < I_{geo} \leq 1$), moderately polluted ($1 < I_{geo} \leq 2$), moderately to strongly polluted ($2 < I_{geo} \leq 3$), strongly polluted ($3 < I_{geo} \leq 4$), strongly to extremely polluted ($4 < I_{geo} \leq 5$), and extremely polluted ($I_{geo} > 5$). The I_{geo} values of the surface sediments from the Yalujiang Estuary decreased in the following

Table 2

Comparison of heavy metal concentrations in the surface sediments of the Yalujiang Estuary and other representative coastal regions in China (mg/kg).

Locations	Cu	Zn	Cr	Hg	Cd	Pb	As	References
Yalujiang Estuary	5.3–15.1	26.0–53.8	12.2–37.7	0.008–0.181	0.05–0.41	12.3–29.9	3.8–11.3	This study
	9.37	37.86	24.3	0.05	0.20	17.95	6.36	
Liaohu Estuary	14.94	nd	49.0	0.039	0.175	12.86	6.54	Liu et al. (2016a, b)
Perl River Estuary	46.2	150.1	89	nd	nd	59.3	nd	Zhou et al. (2004)
Changjiang Estuary	30.7	94.3	78.9	nd	0.26	27.3	nd	Zhang et al. (2009)
Luanhe Estuary	18.76	44.63	41.14	0.02	0.09	30.98	7.21	Liu et al. (2016a, b)
Southern Bohai Bay	22.7	71.7	33.5	nd	0.14	21.7	nd	Hu et al. (2013)
Laizhou Bay	22	60.4	60	nd	0.12	21.9	12.7	Xu et al. (2015)
Average upper crust of East China	27	66	99	0.0094	0.091	15	5.6	Gao et al. (1998)
MSQ-1	35	150	80	0.2	0.5	60	20	AQSIQ (2002)

MSQ-1 is included in Chinese Marine Sediment Quality Standard Criteria (GB 18668-2002) issued by Administration of Quality Supervision, Inspection and Quarantine (AQSIQ).
nd: no data.

Fig. 3. Spatial distribution of heavy metals (As, Cr, Cd, Hg, Cu, Pb and Zn, mg/kg) and total organic carbon (TOC, %) of surface sediments in Yalujiang Estuary.

Table 3

Pearson's correlation matrix for the analyzed parameters in the sediments of Yalujiang Estuary.

	Cu	Pb	Zn	Cr	Cd	As	Hg	TOC	Sulfide	Mz
Cu	1									
Pb	−0.019	1								
Zn	0.78**	0.14	1							
Cr	0.53*	−0.13	0.18	1						
Cd	0.48*	0.17	0.28	0.21	1					
As	−0.42	−0.21	−0.31	−0.48*	−0.23	1				
Hg	0.19	0.29	0.19	0.25	−0.023	−0.26	1			
TOC	0.42	−0.29	0.072	0.56*	0.10	−0.10	−0.21	1		
Sulfide	0.49*	−0.082	0.45*	0.34	0.18	−0.095	0.45*	0.36	1	
Mz	0.636**	−0.229	0.286	0.560*	0.405	−0.132	−0.322	0.732**	0.281	1

* Correlation is significant at the 0.05 level (two-tailed).

** Correlation is significant at the 0.01 level (two-tailed).

Fig. 4. Box-and-whisker plots for of heavy metals in the surface sediments of Yalujiang Estuary. A: enrichment factor (CF); B: Geoaccumulation index (I_{geo}).

order: -1.07 to 2.07 (average 0.88) for Cd, -2.23 to 2.27 (average -0.18) for Hg, -1.29 to 0 (average -0.78) for Pb, -1.60 to -0.03 (average -0.90) for As, -2.09 to -0.58 (average -1.33) for Cu, -1.91 to -0.86 (average -1.40) for Zn, and -2.88 to -1.25 (average -1.93) for Cr (Fig. 4B). On the basis of the Müller scale (Müller, 1979), except Cd, the I_{geo} values indicated no metal pollution in Yalujiang Estuary as a whole. However, minimal deviations were observed across metals and sample sites. The average I_{geo} value of Cd was between 0 and 1, suggesting that slight to moderate Cd pollution occurred in Yalujiang Estuary. As shown in Fig. 7, the I_{geo} values of As, Cr, Cu, Zn, and Pb in all the sample sites were categorized as class 0, indicating that the sediments

Fig. 6. The spatial variations of pollution load index (PLI) of the heavy metals in the sediment of Yalujiang Estuary.

in all the sites were unpolluted by these metals. Six sites and eight sites were unpolluted to moderately polluted, one site and eight sites were moderately polluted, and three sites and one site were moderately to strongly polluted with Hg and Cd, respectively.

CA was used to group the similar sampling sites and determine the specific areas of contamination. Hierarchical CA was performed on the normalized data set using Ward's method (Ward, 1963) based on AU/BP values. Spatial CA produced a dendrogram, which clustered two clades (Fig. 8). Cluster 1 contained 7 sites in the downstream regions, which corresponded to the low-contamination sites. Cluster 2 comprised the other 13 sites in the upper estuary, which corresponded to the high-contamination sites. The cluster classifications varied with the significance level because the sites in these clusters had similar characteristic features and anthropogenic/natural background source types. These results indicated that the geographical regions presented different degrees of contamination in Yalujiang Estuary, suggesting that anthropogenic activities with wastewater discharge were possible significant sources of pollution.

Based on Ward's normalized data, CA was employed to determine the relationships among the analyzed trace elements and their possible sources. The rendered dendrogram (Fig. 9) produced two clusters. Cluster 1 included Cr, Cd, Cu, and Zn, which mainly represented the riverine input and coastal industrial discharge. The upstream region of Yalujiang River has the largest copper reserves in Asia, and this region has been heavily mined since the nineteenth century (Gao et al., 2008). The Cu and Zn accumulation in the sediment of the estuary might have been derived from the discharges of the copper mine plant. By contrast, the

Fig. 5. The spatial variations of the contamination factor (CF) of seven trace elements in the sediment of Yalujiang Estuary.

Fig. 7. Spatial variations of the geoaccumulation index (I_{geo}) of seven trace elements in Yalujiang Estuary.

environmental occurrence of Cd can be attributed to its considerable usage in electroplating, pigment production, and the manufacture of plastic stabilizers and batteries (Eisler, 2007). Some industrial enterprises are concentrated in the cities of Dandong and Donggang, including automobile, papermaking, printing, and textile companies. Consequently, substantial amounts of industrial effluents have been discharged into the sea, and these effluents could have contributed to the accumulation of Cd in the sediment of the Yalujiang Estuary. Cluster 2 contained As, Hg, and Pb, which are primary sources of metal contamination from the precipitation of aerosols (Liu et al., 2016a, b). Shipping activities with vehicle emissions and oil combustion could be other sources of metal contamination in this region.

In conclusion, this field study assessed the levels of the nutrients and seven trace elements (Hg, As, Pb, Cu, Cd, Cr, and Zn) in both the seawater and sediment of Yalujiang Estuary. The results showed that the overall condition of the study area was eutrophic, with the eutrophication risk of the nutrients ranging from moderate to high production. With the exception of Cd, the concentration levels of most metals attained

the first level according to the National Seawater Quality Standard of China (GB 3097-1997), indicating that the concentrations were within the range of clean water. High concentrations of nutrients and heavy metals in seawater samples were located at the mouth of Yalujiang Estuary; this finding indicated that riverine inputs were possible significant sources of pollution. Sediment pollution assessment was undertaken using CF and I_{geo} , which indicated elevated Cd and Hg concentrations in the region. The sources of Cu, Cd, Cr, and Zn were mainly derived from copper mine and coastal industrial effluents, whereas Pb, Hg, and As were mainly from vehicle emissions and oil combustion.

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Fig. 8. Dendrogram showing clustering of sediment sample site in the Yalujiang Estuary.

Fig. 9. Dendrogram showing clustering of the analyzed trace elements in sediment samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marpolbul.2017.01.069>.

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