Spatial and temporal dynamics of heavy metal pollution and source identification in sediment cores from the short-term flooding riparian wetlands in a Chinese delta

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Abstract: Sediment samples were collected to a depth of 60 cm along a 350-m sampling belt in a short-term-flooding riparian wetland in the Yellow River Delta of China in three sampling seasons. Contents of heavy metals were determined to investigate their spatial and temporal distributions, sources and ecotoxicities. Our results showed that As contents in the top 20 cm sediments increased before decreasing along the sampling belt in summer, whereas they kept stable before increasing in fall and spring. Cd contents increased along the sampling belt in three sampling seasons, whereas Ni and Cr generally exhibited a decreasing tendency. Comparatively, Cu, Pb and Zn consistently increased at the first 50 m distance and then decreased before increasing from the distance of 150 m in summer and fall and increased to the maximum at the distance of 250 m and then showed a decrease in spring. Two “hotspots” of heavy metal accumulation in sediment cores along the belt were observed at the distance from 50 to 100 m in summer and at the distance from 200 to 300 m in spring. Most of sediment samples contained higher heavy metals in excess of threshold effect levels except for Zn and Pb in three sampling seasons and the values of toxic units in more than 30% of sediment samples exceeded 4 in

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summer. As, Ni and Cr had relatively higher contribution to the values of toxic units compared with other heavy metals in three sampling seasons. Multivariate analysis showed that As and Cd might originate from the same source and Cu, Zn, Cr, Pb and Ni might derive from another similar source. Cd was significantly correlated with salinity ($p < 0.01$) and pH ($p < 0.05$). Meanwhile, these heavy metals were also significantly correlated with other properties such as S, Al, TP, SOM and Silt+Clay.

Key Words: Riparian wetlands; Heavy metals; Spatial distribution; Temporal dynamic; Ecotoxicity; Multivariate analysis

Capsule: We observed the “hotspot” of heavy metal accumulation in sediment cores along the belt in summer and spring.

1. Introduction

Riparian wetlands are located in river floodplains, which can provide an important transition zone from the terrestrial to the aquatic ecosystem. Riparian wetlands often act as important sinks for heavy metals from river water or upland by the process of adsorption and sedimentation (Du Laing et al., 2009; Zhang et al., 2011), thus they can protect water quality of rivers by capturing and storing heavy metals and chemicals through preventing these pollutants from entering the water cycle. Therefore, there are increasing concerns on riparian wetland sediments though less studies have been carried out compared to terrestrial soils (Romic et al., 2012).

Despite the great ecological service functions, river floodplains in most industrialized countries have been polluted by heavy metals and become potential pollution sources as particulate anthropogenic pollutants (e.g., fly ash and dust) are transported and disseminated more efficiently by rivers than by the atmosphere (Grygar et al., 2013). The agricultural input to these

wetlands by surface runoff has also been identified to be an important source (Heim et al., 2004). Zhang et al. (2011) found that the tidal channels received wastewater discharged from industrial, agricultural and domestic activities, which contributed to heavy metal accumulation in reclaimed tidal riparian wetlands. Heavy metal pollution has become a critical issue because heavy metals can be retained and accumulated in soils/sediments for a long time (Bai et al., 2010; Bai et al., 2011b). Once heavy metal contents in the riparian wetland sediments exceed environmental quality standards, they will pose potential ecotoxic risks for the organisms in these riparian wetlands (Leuven et al., 2005; Bai et al., 2011a). Schipper et al. (2011) found that plant species richness and diversity showed a significant decrease with the levels of heavy metals pollution in a lowland Rhine River floodplain wetland. Therefore, it is necessary to investigate the distribution and ecotoxic risks of heavy metals in riparian wetlands.

The flood event and sediment sorting can greatly impact heavy metal distribution in riparian wetlands (Ibragimow et al., 2013; Grygar et al., 2013) through changing sediment physical-chemical properties, as sediment properties may have a strong influence on heavy metal accumulation (Violante et al., 2008). Moreover, heavy metals would undergo post-depositional mobilization in wetland sediments with changing hydrological conditions (Du Laing et al., 2009; Grygar et al., 2013). Bai et al. (2012) presented that the flow and sediment regulation could elevate heavy metal levels in tidal freshwater wetlands due to the redistribution of sediments. Walling et al. (2003) also pointed out that about 90% of the heavy metals in the aquatic environment was connected with the suspension and fluvial sediments. Most researchers have focused on historical trend in heavy metals in wetland sediments as affected by intense anthropogenic activities using ^{14}C or $^{137}\text{Cs}/^{210}\text{Pb}$ dating techniques (Grygar et al., 2013; Lokas et

al.; 2010; Heim et al., 2004), as the floodplain sediment contains quite a lot information on regional environmental changes (de Moor et al., 2008; Grygar et al., 2010). However, few studies have been carried out on spatial and seasonal distributions of heavy metals in riparian wetlands along a distance gradient to the river bank in the coastal region.

The flow-sediment regulation is implemented from June to July of each year to control the discharge of water and sediments from the Xiaolangdi Reservoir in the upper stream of the Yellow River Delta since 2002 (Bai et al., 2012). A strong hydrological influence on heavy metals in wetland ecosystems in the Yellow River Delta has been identified (Li et al., 2009; Bai et al., 2012). Bai et al. (2012) presented that some heavy metal levels in coastal wetland soils were elevated after flow-sediment regulation than before in the Yellow River Delta. Therefore, we hypothesized that the heavy metal levels decreased with depth and along the sampling belt and higher heavy metal levels in summer than in fall and spring due to the input of the flow-sediment regulation in the early summer. The primary objectives of this study were: (1) to investigate spatial and seasonal distributions of heavy metals (i.e., As, Cd, Cr, Cu, Ni, Pb and Zn) in sediment cores along the distances from the river bank in the Yellow River Delta; (2) to assess the ecotoxic risks of these heavy metals; and (3) to identify pollution sources of these heavy metals using multivariate analysis.

2. Materials and Methods

2.1 Study area

The study area is located in the northern bank of the lower reach of the Yellow River in the Yellow River Delta (37°35' to 38°12' N and 118°33' to 119°20' E, Figure 1). It has a warm-temperate and continental monsoon climate, with annual precipitation of 640 mm and

annual mean evaporation of 1962 mm. The annual mean air temperature is 11.9 °C, with 196 frostless days. The estimated average sedimentation rate might have been 7.58 cm/a in the estuarine area since 1976 (Wei et al., 2015). The flow-sediment regulation scheme is implemented from June to July of each year by the Yellow River Conservancy Commission to control the discharge of water and sediments from the Xiaolangdi Reservoir since 2002 (Bai et al., 2012). Thus the study area will suffer from short-term flooding (less than 30 days) during the flow and sediment regulation regime each year. The dominant vegetation include *Phragmites australis*, *Suaeda salsa* and *Tamarix chinensis* (He et al., 2007). The sediments are mainly derived from the loess material of the Quaternary period, which was carried by surface runoff from the Loess Plateau (Zhang et al., 2007; Yu et al., 2011).

2.2 Sediment collection and analysis

A 350-m sampling belt including five sampling sites were selected along the direction perpendicular to the river bank of the Yellow River. We selected 0 m, 50 m, 150 m, 250 m and 350 m as typical sampling plots far away from the river bank according to the wetland plant types (Figure 1). Plant communities at five sites are *Phragmites australis* (0 to 50 m)-*Phragmites australis* +*Suaeda salsa*+*Tamarix chinensis* (from 50 to 250 m)- *Suaeda salsa* (from 250 to 350 m). Sediment cores with three replicates were collected to a depth of 60 cm and stratified at 20 cm intervals (i.e., 0-20 cm, 20-40 cm and 40-60 cm) at each sampling site. In total 135 sediment samples were collected in August of 2007 (Summer), November of 2007 (Fall) and April of 2008 (Spring). All sediment samples were placed in polyethylene bags and brought to the laboratory and then air dried at room temperature for three weeks. Some air-dried sediment samples were sieved through a 2-mm nylon sieve to remove coarse debris and stones, and then

ground with a pestle and mortar until all particles passed a 0.149-mm nylon sieve for the determination of sediment chemical properties. The rest of air-dried sediments were used to determine sediment particle size. Additionally, a single 4.8-cm diameter sediment core was collected from each sediment layer of each sampling site for the determination of bulk density (BD) and moisture.

Sediment samples were digested with an $\text{HClO}_4\text{-HNO}_3\text{-HF}$ mixture in Teflon tubes to analyze total contents of S, P, Al, As, Cd, Cr, Cu, Ni, Pb and Zn. The solutions of the digested samples were determined using the inductively coupled plasma atomic absorption spectrometry (ICP-AAS). Quality assurance and quality control were assessed using duplicates, method blanks and standard reference materials (GBW07401) from the Chinese Academy of Measurement Sciences with each batch of samples (1 blank and 1 standard for each 10 samples). The recoveries of samples spiked with standards ranged from 95 to 106 %. Sediment organic matter (SOM) was determined using the method presented by Walkley and Black (1934). Sediment pH (H_2O) and conductivity (EC) were measured using a pH meter and a conductivity meter, respectively (sediment: water =1:5). The sediments were oven dried at 105°C for 24 h and weighed for sediment bulk density and moisture. Sediment particle size was analyzed on a Laser Particle Size Analyzer (Microtrac Inc., USA).

2.4 Statistical analysis

One-way ANOVA analysis was performed to identify significant differences in heavy metals among different sampling periods. Pearson correlation analysis was performed to reveal the relationships between heavy metals and selected sediment properties. Factor analysis (FA) analysis among heavy metals was conducted to further identify the pollution source. Difference

was considered to be significant if $p < 0.05$. Data analysis was carried out using SPSS 13.0 and Suffer 7.0 software packages.

3. Results and Discussion

3.1 Spatial and seasonal distributions of heavy metals in top 20 cm sediments

Figure 2 shows seasonal dynamic of heavy metals in top 20 cm sediments along the sampling belt. Generally, As contents increased with increasing distances far away from the river bank and reached the maximum level at the distance of 250 m, and then decreased at the distance of 350 m in summer. However, in fall and spring, As levels kept stable at the distance from 0 to 150 m and then increased gradually from 150m. Higher As levels were observed in summer than in fall and spring ($p < 0.05$; Table 1). In contrast, Cd contents increased gradually with increasing distance away from the river bank in three sampling seasons, which is significantly related to increasing salinity levels ($p < 0.05$; Table 2). However, Balls et al. (1994) observed increasing Cd desorption from particulate phase with increasing salinities in the forth estuary. This was likely related to higher sulfide levels in these sediments due to the formation of CdS precipitation (Du Laing et al., 2009). We also observed the significant correlations between Cd and S levels in this study ($p < 0.05$; Table 2). Similar to As, Cd levels were also significantly higher in summer than fall and spring ($p < 0.05$; Table 1). This was associated with the flow and sediment regulation which could elevate heavy metals due to sediment deposition (Bai et al., 2012). Interestingly, Cu, Pb and Zn showed similar spatial and seasonal distributions. They increased from 0 to 50 m and then decreased from 50 to 150 m, after that a monotonous increase was observed from 150 to 350 m in summer and fall. In contrast, they generally exhibited an increase along the sampling belt in spring. However, no significance differences in Cu, Pb and Zn were observed among sampling seasons ($p > 0.05$; Table

1). Generally, the seasonal changes in As and Cd supported the hypothesis that heavy metal levels were higher in summer, whereas the spatial distributions of As, Cd, Cu, Pb and Zn in top 20cm sediments denied the hypothesis that heavy metal levels decreased along the sampling belt.

As shown in Table 3, higher mean levels of Cd and Pb and lower As, Cu and Zn were observed in riparian wetlands than those in salt marshes in the YRD (Bai et al., 2014). The riparian wetland sediments in the YRD contained lower heavy metal levels than those in the Pearl River Delta (Bai et al., 2011a). With the exception of higher Cu and Zn levels, heavy metals showed lower levels in the Yangtze River Delta than those in the Yellow River Delta (Zheng et al., 2016). Meanwhile, both Niger Delta and Parnaíba River Delta exhibited lower heavy metal levels compared to the YRD (Table 3). Additionally, higher Cd levels in the Tamirabarrani River Estuary and higher Cr, Cu, Ni and Zn levels in the Kavak Delta were observed than those in the YRD (Table 3).

SOM and sulfur contents exhibited similar distributions to those of Cu, Pb and Zn (Figure 2 and Table 4), implying that they might dominantly affect the spatial distributions of Cu, Pb and Zn as organic matter could act as a major sink for heavy metals due to its strong complexing capacity for metallic contaminants (Bai et al. 2010) and the formation of insoluble metal-sulfides (Du Laing et al., 2009). The results of correlation analysis also showed significant correlations among SOM, sulfur, and Cu, Pb and Zn for all the sediments ($p < 0.05$; Table 2). We noted that the lowest levels of heavy metals such as As, Cd, Cu, Pb and Zn occurred in the sediments adjacent to the river bank, whereas higher levels were observed at the distance of 50 m and 250 m or 350 m, respectively. The possible explanation was that much lower SOM, S, water content and salinity levels in sediments adjacent to the river bank than those in sediments away from the river bank

($p < 0.05$, Table 4) make this site to become a less favorable one for heavy metals. Lower sulfur levels could decrease the formation of insoluble metal-sulfides (Du Laing et al., 2009). Meanwhile, lower salinity could enhance plant uptake of heavy metals in sediments (Fritioff et al., 2005), leading to lower heavy metal levels in sediments (Figure 2). Additionally, spatial differences were also related to hydraulic flushing of heavy metals away from the sites in high-energy regimes (Roychoudhury, 2006).

Oppositely, Ni and Cr generally exhibited a decreasing tendency along the distances far away from the river bank in three sampling seasons, which supported the hypothesis on horizontal distribution of heavy metals along sampling belt. Ni contents did not show significant differences between sampling seasons, whereas significant differences in Cr contents between summer and spring were observed, showing that the seasonal distribution of Ni denied the hypothesis. However, Cr and Ni showed similar changing tendencies with higher levels in the sediments close to the river bank.

3.2 Seasonal dynamics of depth distribution of heavy metals

As shown in Figure 3, As and Cd exhibited higher levels in the whole sediment cores in summer compared to fall and spring. However, Roychoudhury (2006) observed a minor increase in depth-integrated trace metal contents in tidal wetland sediments in winter compared to summer due to plant assimilation and accumulation in growing seasons and plant return to sediment through plant litters in the late fall. The As and Cd input affected by the flow-sediment regulation might explain their higher levels in summer (Bai et al., 2012). Lower levels of As and Cd occurred in sediments adjacent to the river bank, whereas higher levels were observed in sediments far away from the river bank. A similar patch with lower levels of As and Cd were observed in deeper

sediments at the distance of 250 m in summer. Like the top 20 cm sediments, Cu, Pb and Zn showed similar profile distributions in each of the three sampling seasons. Obviously, a patch with higher levels of Cu, Pb and Zn was observed in upper sediments at the distance of 50 m and 350 m away from the river bank, whereas a larger zone with lower levels occurred in deeper sediments from 150 to 250 m in summer. In spring, a large zone with higher levels appeared in deeper sediments at the distance from 200 to 300 m. Higher SOM contents in these sediments could explain higher accumulations in these sediment cores ($p<0.05$; Table 4). Compared to summer, levels of Cu, Pb and Zn decreased in deeper sediments at the distances from 0 to 150 m, whereas they increased at the distances from 150 to 300 m in fall and spring due to the leaching of the soluble fraction of heavy metals (Beesley et al. 2010). In contrast, the depth distribution of Ni was similar to that of Cr in each of the three sampling seasons. Higher accumulation was observed in sediments at the distances from 50 to 100 m and from 300 to 350 m in summer, and higher levels of Ni and Cr mainly occurred in these sediments at the distances from 50 to 350 m in fall. Comparatively, the zone with lower levels in deeper sediments expanded from 0 to 200 m in spring. Generally, sediment cores adjacent to the river bank consistently contained lower levels of heavy metals in three sampling seasons due to the influence of freshwater of the Yellow River. Among three sampling seasons, higher accumulation occurred in sediment cores at the distances from 50 to 100 m in summer due to the overbank flood from the flow and sediment regulation (Bai et al., 2012), whereas higher levels at the distance from 200 to 300 m in spring was associated with the influx of tidal water from tidal ditches at high tides as no major anthropogenic sources in this region. Additionally, the clay minerals might influence the depth distribution of these heavy metals due to similar distribution (Wang et al., 20003) and heavy metal-adsorption by Clay

minerlas (Gier and Johns, 2000). Generally, the depth distributions of these heavy metals supported the hypothesis that heavy metals decreased with depth except for some patches with higher heavy metal levels in deeper sediments.

3.3 Ecotoxicity assessment of heavy metals

Two sets of SQGs developed for marine ecosystems (Long and MacDonald, 1998) were applied to evaluate the ecotoxicology caused by heavy metal in sediments in this study: (a) the effect range low (ERL)/effect range median (ERM) and (b) the threshold effect level (TEL)/probable effect level (PEL) values (Table 1; Zheng et al., 2008; Bai et al., 2011b). ERLs and TELs represent the low threshold concentrations below which adverse effects upon sediment dwelling fauna would be infrequently expected. However, the ERMs and PELs represent high threshold concentrations above which adverse effects are likely to occur (MacDonald et al., 2000).

As shown in Figure 3, all sediments (from 0 to 60 cm depth) contained higher As levels in excess of TELs in each of the three sampling seasons, moreover, higher As levels exceeding PELs were observed in most sediment samples far away from the river bank in summer. Cd levels exceeded TELs in a large number of sediment samples at the distances from 50 to 350 m in summer and spring, whereas they were below TELs in most sediment samples in fall. Almost all sediment cores contained higher Cu, Cr and Ni levels in excess of TELs or ERLs in three sampling seasons, moreover, most sediments exhibited higher Ni levels exceeding PELs, even ERMs, in each of the three sampling seasons. Comparatively, Zn levels were below TELs in almost all sediment samples in three seasons, and Pb also showed less toxicity except for higher Pb levels in excess of TELs in some sediments in summer and spring. According to the Sediment Quality Guidelines of China (Table 1), As, Cd and Cr levels exceeded the Class I criteria

(suitable for fisheries and natural waters), but they were below the Class II criteria (used for industrial and tourism sites) in approximately 84%, 89% and 100% of sediment samples, respectively. All other heavy metals (i.e., Pb, Zn, Ni and Cu) were below the Class I criteria except for 3 sediment samples with Cu levels in excess of Class I criteria.

Toxic units were used to normalize the toxicity caused by various heavy metals and thus allowed the comparison of their relative effects which are defined as the ratio of the determined concentration to PEL value (Pedersen et al., 1998). The sum of TUs ($\sum TU$) for sediments from the 350 m belt based on the contents of As, Cd, Cr, Cu, Ni, Pb and Zn is illustrated in Figure 4. Generally, the TUs in almost all sediment samples in fall and spring were lower than 4, indicating low toxicity (Pedersen et al., 1998). However, the TUs values in more than 30% of sediment samples exceeded 4 in summer. This implies the moderate toxicity in these sediment samples far away from the river bank in summer due to higher levels of heavy metals (i.e. As, Cr and Ni) as affected by the flow-sediment regulation (Bai et al., 2012). Therefore, further research is needed to identify and control the higher toxicity of these heavy metals in this zone far away from the river bank. The average toxic units of these heavy metals followed the order As > Ni > Cr > Zn > Cu > Cd > Pb in summer, and the followed order was Ni > Cr > As > Zn > Cu > Pb > Cd in fall, whereas they decreased following the order Ni > As > Cr > Zn > Pb > Cu > Cd in spring. This indicates that As, Ni and Cr had relatively higher contributions (As, 27.4%; Ni, 27.2%, Cr, 18.1% in summer and As, 18.7-20.9%; Cr, 19.4-22.6%; Ni, 30.6-32.3% in fall and spring) to $\sum TU$ compared to other heavy metals. Slightly alkaline conditions (pH ranging from 7.49 to 8.77) in this region increased the toxic risk of As (VI) transformation to As (III) and Cr (III) to Cr (VI) and as As (III) and Cr (VI) are more mobile and toxic (Kumpiene et al.; 2008). However, lower

contributions of Cd (4.4-6.5%) to $\sum_{TU}$ were observed though higher Cd levels in these sediments.

3.4 Potential sources of heavy metals and important influencing factors

3.4.1 Principal component analysis (PCA)

PCA analysis was applied to assist the source identification of heavy metals. Table 5 shows the factor loadings with a VARIMAX rotation and the eigenvalues. The eigenvalues (eigenvalue > 1) indicated that 73.4% of the data variance could be explained by the first two components. The PC1 accounting for 56.2% of the total variance was strongly correlated with As and Cd. The PC2 explaining 17.2% of the total variance showed highly positive factor loadings on Cu, Pb, Zn, Cr and Ni. In this case, the Cr loading (0.519) is not as high as the loadings of the other elements of the group, which might, therefore, imply a quasi-independent behavior within the group (Han et al., 2006). This might be associated with slightly alkaline environment in this region (Table 4). Kumpiene et al. (2008) also presented that slightly alkaline environment could improve the mobility of Cr due to the oxidation of Cr (III) to Cr (VI), whereas other heavy metals (e.g., Cu, Pb and Zn) were more stable in slightly alkaline conditions. These degrees of covariance are strongly suggestive of common sources for the metals (Bai et al., 2011a). Cr and Ni are often identified as immobile elements as they tended to occur in trivalent oxide or co-precipitated with Fe hydrous oxide that had low mobility and bioavailability in soils/sediments and retained stable for a long time (Bai et al. 2010; Kumpiene et al. 2008). Thus the PC1 could be defined as an anthropogenic component due to the presence of high levels in sediments, whereas PC2 as a lithogenic component seemed to be controlled by parent rocks (Mico et al., 2006).

3.4.2 Correlation analysis

Sulfur exhibited significant correlations with heavy metals except for As (Table 2), which

was associated with the formation of insoluble sulphides (e.g. CuS, ZnS, PbS and CdS) in these sediments (Du Laing et al., 2009). Al was significantly correlated with all these heavy metals (Table 2), which indicates that these heavy metals and Al in this region were greatly associated with the upstream loess materials with higher Al contents (62700 mg kg^{-1} ; CNEMC, 1990). TP was significantly correlated with these heavy metals because P can immobilize these heavy metals though forming the precipitation of phosphate (Kumpiene et al. 2008). Also, this implies that these heavy metals and TP might have common source. SOM can retain heavy metals due to its strong complexing capacity for metallic contaminants (Gonzalez et al., 2006). In this study, significant positive correlations were also observed between SOM and these heavy metals (i.e., Pb, Cu, Zn and Ni). Silt+Clay contents were significantly positively correlated with these heavy metals (i.e., Pb, Cu, Zn, Cr and Ni) (Table 2) as fine sediment particles could adsorb heavy metals (Gonzalez et al., 2006; Bai et al., 2014). Conversely, sand contents were significantly negatively correlated with these heavy metals (Table 2). This also suggests these heavy metals (i.e., Pb, Zn, Cu, Cr and Ni) might originate from the same natural source.

Cd was significantly positively correlated with sediment salinity ($p < 0.01$, Table 2), whereas no significant correlations were observed between other heavy metals and salinities ($p > 0.05$, Table 2). Higher Cd levels were also observed in the sediments far away from the river bank than sediments nearby the river bank, as did salinity levels (Table 4). It is also noted that only Cd was negatively correlated with sediment pH values (ranging from 7.49 to 8.77) in all these sediments. However, Ololade et al. (2009) observed a positive correlation between sediment pH values and Cd in Ondo coastal sediments with pH ranging from 5.6 to 6.9. Boekhold et al. (1993) presented that Cd sorption was highly sensitive to pH as each 0.5 unit increase in pH resulted in twice as

much sorption of Cd in strong acid environment (pH ranging from 3.8 to 4.9). This indicates that Cd would occur different transfer processes under acid and alkaline conditions.

3.4.3 Hybrid redundancy analysis (Hybrid RDA)

The correlation structure between heavy metals and other sediment properties among different sampling seasons was illustrated in a hybrid RDA correlation biplot map (Figure 5). The first axis explained 44% of the total variance and 10% for the second axis. The contents of Al, S, Slit+Clay and SOM were closely correlated with the first axis with the correlation coefficients of more than 0.5. TP and water contents were strongly correlated with the second axis ($r=0.480$ and $r=0.4796$, respectively). Additionally, the results also exhibited the relationship between sediment samples in three sampling seasons. These sediment samples were collected in three sampling seasons and clearly grouped into three plates. Sediments collected in summer were closely associated with As, Cd and TP, indicating the flow-sediment regulation might contribute to As, Cd and TP pollution in summer. Comparatively, sediments collected in autumn were significantly correlated with Zn, Ni, Cu, Pb, water, S, SOM, Al and Silt+Clay, which implies that water, S, SOM, Al and Silt+Clay were the important factors influencing these four heavy metals. However, sediments collected in spring were closely linked to water, suggesting sediment water contents would be the important factor in this season.

4. Conclusions

We investigated the spatial and temporal distributions of heavy metals (i.e., As, Cd, Cr, Cu, Ni, Pb and Zn) in sediment cores along a 350 m belt in the short-term flooding riparian wetlands in the Yellow River Delta of China. Ni and Cr in the top 20cm sediments exhibited consistent changes as did Cu, Pb and Zn, with the obvious seasonal changes in three sampling sites.

Comparatively, the top 60 cm sediments adjacent to the river bank contained lower levels of these heavy metals than other sampling sites. We observed the “hotspot” of heavy metal accumulation along the belt at the distance from 50 to 100 m in summer and at the distance from 200 to 300 m in spring, respectively. Our findings generally supported the hypothesis on the depth distributions of these heavy metals and denied the hypothesis on horizontal distributions along the sampling belt except for Ni and Cr. Meanwhile, the hypothesis on seasonal dynamics was only supported by the results of As, Cd and Cr. Generally, the toxicity of these heavy metals was lower in this region in three sampling periods except for higher toxicity in more than 30% of sediment samples in summer. As, Ni and Cr should be paid much more concerns especially in summer due to higher contributions to TUs than other heavy metals. Some steps (e.g., changing sediment properties such as pH, salinity, S and SOM) can be taken to control these heavy metals and maintain wetland ecosystem health, though the influencing mechanisms of these sediment properties on the distributions and fates of heavy metals are still needed to carry out in the future. It is also necessary to continuously monitor these heavy metals to better understand heavy metal pollution and thus reduce ecological risks in this region.

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Table 1 Mean contents of heavy metals in the top 20cm sediments in the riverine wetlands and sediment quality guidelines (SQGs) (mg kg⁻¹)

		As	Cd	Cr	Cu	Ni	Pb	Zn
Summer	Mean	45.3a	1.02a	114.9a	27.5a	46.7a	28.4a	77.0a
	SD	12.6	0.20	24.7	7.3	8.4	7.2	18.9
Fall	Mean	27.9b	0.78b	106.7ab	26.1a	43.3a	26.1a	72.9a
	SD	8.05	0.10	7.9	4.7	4.5	4.4	18.0
Spring	Mean	27.7b	0.58bc	97.0b	27.56a	43.0a	30.6a	75.9a
	SD	3.8	0.15	7.8	5.6	6.8	5.3	17.5
SQGs of China ^a	Class I	20	0.5	80	35	34c	60	150
	Class II	65	1.5	150	100	40c	130	350
	Class III	93	5	270	200	40c	250	600
	TEL	7.2	0.68	52.3	18.7	15.9	30.2	124.0
SQGs ^b	PEL	41.6	4.2	160.4	108.2	42.8	112.2	271.0
	ERL	8.2	1.2	81.0	34.0	20.9	46.7	150.0
	ERM	70.0	9.6	370.0	270.0	51.6	218.0	410.0

SD: standard deviation

^a SQGs of China: Sediment Quality Guidelines of China, National Standard of P.R. China (2002).

^b SQGs: Sediment Quality Guidelines for marine ecosystem; TEL: threshold effect level; PEL: probable effect level; ERL: effects range low; ERM: effects range median (Long and MacDonald, 1998).

^c Sediment quality benchmark in Hong Kong SAR (EPD, 2005)

abc Different letters in the same column represent significant differences in heavy metals between different sampling seasons (p<0.05)

Table 2 Correlation coefficients among heavy metals and selected sediment properties for all sediment samples

	As	Cd	Cu	Pb	Zn	Cr	Ni
S	-0.018	0.296 [*]	0.652 ^{**}	0.609 ^{**}	0.519 ^{**}	0.338 [*]	0.622 ^{**}
Al	0.375 [*]	0.722 ^{**}	0.651 ^{**}	0.385 ^{**}	0.522 ^{**}	0.492 ^{**}	0.622 ^{**}
Water	-0.285	-0.537 ^{**}	0.057	0.335 [*]	0.088	-0.419 ^{**}	-0.070
pH	0.005	-0.343 [*]	-0.023	0.187	0.116	-0.218	-0.131
Salinity	0.274	0.444 ^{**}	0.266	0.209	0.242	0.200	0.227
TP	0.522 ^{**}	0.582 ^{**}	0.302 [*]	0.132	0.357 [*]	0.498 ^{**}	0.281
SOM	0.048	0.173	0.587 ^{**}	0.585 ^{**}	0.409 ^{**}	0.248	0.468 ^{**}
Sand	0.079	-0.160	-0.614 ^{**}	-0.543 ^{**}	-0.350 [*]	-0.421 ^{**}	-0.479 ^{**}
Silt+Clay	-0.010	0.221	0.648 ^{**}	0.554 ^{**}	0.414 ^{**}	0.359 [*]	0.493 ^{**}

*represents significant correlation at $p<0.05$.

**represents significant correlation at $p<0.01$.

Table 3 Mean contents of heavy metals in the top 20 cm sediments in the worldwide large river deltas (mg kg⁻¹)

Sampling sites		As	Cd	Cr	Cu	Ni	Pb	Zn	References
The Yellow River Delta	Riparine wetlands	28.89	0.79	106.20	27.05	44.33	28.37	75.27	This study
	Salt marshes	31.06	0.70	-	28.23	-	25.79	83.85	Bai et al., 2014
The Pear River Delta	Riparian wetlands	-	2.35	119.02	194.99	53.44	49.46	218.33	Bai et al., 2011a
The Yangtze River Estuary	Salt marshes	19.50	0.27	69.4	38.4	42.7	28.2	99.5	Zheng et al., 2016
The Niger Delta	Estuary	-	0.1	2.0	0.5	0.5	0.3	2.8	Onojake et al., 2015
The Tamirabarrani River Estuary	Estuary	-	2.61	97.16	7.76	11.85	7.30	27.53	Chandrasekaran et al., 2015
The Parnaíba River Delta	Estuary	-	-	18.0	6.8	-	5.9	13.4	De Paula et al., 2015
The Kavak Delta	Salt marshes	-	0.47	163.00	37.50	141.0	26.50	84.20	Sungur et al., 2015

“-” no data.

Table 4 Mean values of selected soil properties of all the top 20cm soils along the sampling belt

Distance to the bank	0 m		50 m		150 m		250 m		350 m	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
S (mg/kg)	366.86a	98.55	436.80ab	80.73	620.29b	229.08	601.08b	38.48	610.08b	77.13
Al (g/kg)	44.68a	13.15	58.37b	5.52	55.66ab	2.62	55.33ab	1.94	57.84b	6.96
Water (%)	22.23a	1.54	25.74b	2.69	24.04ab	0.23	25.43b	1.06	23.13ab	1.10
pH	8.28a	0.20	8.26a	0.38	7.85a	0.28	8.23a	0.25	8.13a	0.26
Salinity (‰)	0.23a	0.11	0.38ab	0.20	1.43b	0.25	0.98b	0.58	1.25b	0.23
TP (mg/kg)	613.83a	52.23	646.67a	87.45	630.77a	16.04	635.51a	55.25	685.64a	103.51
SOM (g/kg)	4.04a	2.31	5.74abc	1.48	4.65ab	2.00	8.44c	2.81	7.84bc	0.51
Sand (%)	56.89a	26.45	55.61a	20.12	27.21a	4.71	40.22a	34.58	41.26a	29.20
Slit+Clay (%)	43.11a	26.45	44.39a	20.12	72.79a	4.71	59.78a	34.58	58.74a	29.20

Comparisons between samling sites were tested by One - Way ANOVA analysis and LSD test

^{abc}Different letters represent significant differences among sampling sites along the belt.

Table 5 Total variance explained and rotated component matrix (two principal components selected) for heavy metal contents in all sediment samples

	Initial eigenvalues			Heavy metals	Rotated component matrix	
	Total	% of variance	Cumulative %		PC1	PC2
	Total variance explained				Component matrix	
1	3.934	56.195	56.195	As	0.127	0.920
2	1.204	17.207	73.402	Cd	0.329	0.889
3	0.925	13.213	86.615	Cu	0.907	0.277
4	0.511	7.293	93.908	Pb	0.889	0.047
5	0.194	2.771	96.679	Zn	0.723	0.236
6	0.157	2.245	98.924	Cr	0.519	0.235
7	0.075	1.076	100.000	Ni	0.860	0.205

PCA loadings >0.5 are shown in bold.

Figure Legends

Figure 1 Location map of sampling sites in the Yellow River Delta.

Figure 2 Seasonal dynamics of heavy metals, SOM and Clay contents in the top 20 cm sediments along a 350-m transect in the Yellow River Delta.

Figure 3 Spatial and temporal distributions of heavy metals in sediment cores along a 350-m transect of the Yellow River Delta.

Figure 4 TUs of heavy metals in sediment cores along a 350-m transect in the Yellow River Delta in (a). summer, (b) fall, and (c) spring). a represents 0-20 cm sediment layer, b represents 20-40 cm sediment layer and c represents 40-60 cm sediment. The blue solid line represents the moderate ecotoxicity ($TUs=4$)²⁴

Figure 5 Biplot map of hybrid RDA analysis for heavy metals and environmental factors. The blue arrows represent heavy metals and the red ones represent influencing factors. The length of these arrows represent the influencing degree of these selected sediment properties on heavy metals. Blue plate represents spring, brown plate represents autumn and green plate represents summer. Circles stand for soil samples. Samples 1-15 were collected in summer, samples 16-30 were collected in spring and samples 31-45 were collected in autumn.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5