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Heavy metals pollution in soil profiles from seasonal-flooding riparian wetlands in a Chinese delta: Levels, distributions and toxic risks

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ABSTRACT

Soil profile samples were collected in seasonal-flooding riparian wetlands in the Yellow River Delta (YRD) of China in autumn and spring to investigate the levels, distributions and toxic risks of heavy metals in soil profiles. Total elemental contents of Al, As, Cd, Cr, Cu, Ni, Pb and Zn were determined using inductively coupled plasma atomic absorption spectrometry (ICP-AAS). Results indicated that the contents of determined heavy metals showed non-negligible depth variations (coefficient of variation $> 10\%$), and their distribution patterns were irregular. Compared with other heavy metals, both As and Cd presented higher enrichment factors (EF) based on the classification of EF values (moderate enrichment for As while significant enrichment for Cd). Cluster analysis (CA) and principal components analysis (PCA) revealed that Cr, Cu, Ni, Pb and Zn might derive from the common source, while As and Cd shared another similar source. The toxic unit (TU) values of these heavy metals did not exceed probable effect levels (PEL) except for Ni. Both As and Ni showed higher contributions to the sum of TU ($\sum$TUs), which indicated they were the primary concerns of heavy metals pollution. Generally, As, Cd and Ni should be paid more attention for wetlands managers and policy makers to avoid potential ecotoxicity in the study area. The findings of this study could contribute to the prevention and control of heavy metals pollution in estuarine wetlands.

1. Introduction

Estuarine and coastal wetlands are complex and important ecosystems, which provide multitudinous habitats for a diverse array of flora and fauna (Bai et al., 2012; Mitsch and Gosselink, 2007). Meanwhile, the fragility of these ecosystems make them more easily destructed by the anthropogenic activities in these areas.

Estuarine wetlands may act as geochemical traps for heavy metals bonded in the sediments and soils due to the complex interaction between fluvial and marine processes (Sun et al., 2015). With the rapid development of agriculture and industry, pollutants including metallic elements are continuously discharged into rivers without effective treatment, more and more intense human activities would also aggravate heavy metals pollution in these zones. Soils or sediments in riparian wetlands do not only act as the main precipitator for trace metals, but are also potential secondary sources of heavy metals when hydrological conditions change in these wetlands (Xie et al., 2014; Chen et al., 2016). Polluted sediments transported onto the river terrace due to flooding, contribute significant quantities of heavy metals to riparian soils (Bai et al., 2012).

The riparian zone consists of different landscape units characterized by different hydro-geomorphological site conditions, which is determined by flooding frequency and duration, distance to river channels, elevation, and water flow velocity (Graf-Rosenfellnera et al., 2016). Hydrological conditions such as intensity and duration of flooding and groundwater level, would significantly affect the migration and transformation of metals in riparian wetlands soils (Pavlović et al., 2016).

The Yellow River delta (YRD) is one of the most rapid sedimentation areas on earth, it is estimated that approximately 1.05×10^7 tons of sediments per year are carried and deposited in this delta (Xu et al., 2002; Zhang et al., 2016). The severe hydrological fluctuations would significantly change biogeochemical processes (e.g., heavy metals pollution) in the adjacent area. And

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Bai et al. (2012) has demonstrated that the flow-sediment regulation regime could contribute to some heavy metals accumulation (As and Cd) in this region. However, few study has focused on the profile distribution of heavy metals in seasonal-flooding riparian wetlands soil, and the information of seasonal dynamic changes for heavy metals pollution in needed for better understanding the ecological toxic risks caused by heavy metals. Therefore, The primary objectives of this study were: (1) to investigate the profiles distribution of heavy metals (including As, Cd, Cr, Cu, Ni, Pb and Zn) in riparian soils from seasonal-flooding wetlands of YRD, China; (2) to assess the pollution levels based on the enrichment factor (EF) and toxic risks by toxic units (TUs); (3) to reveal the association among heavy metals using cluster analysis (CA) and principal components analysis (PCA).

2. Materials and methods

2.1. Study area

The study area is located in the new born wetlands of Yellow River Delta (37°38′-37°48′ N and 119°05′-119°17′ E, Fig. 1), Shandong province, China. It has a warm-temperate and continental monsoon climate, with annual mean precipitation of 640 mm and annual mean evaporation of 1962 mm. The annual mean air temperature is 11.9 °C, with 196 frostless days. Soil type in this region is typical Fluvisols, originating from the sediment and the parent materials of loess soil. The dominant vegetation primarily comprises *Phragmites australis*, *Suaeda salsa* and *Tamarix chinensis*.

2.2. Soil sampling and analysis

Soil samples were collected using a soil auger (4.8 cm diameter) from four sampling sites in autumn (November 2007), and spring (April 2008). In each sampling site, the top 100 cm soils (sectioned into 0–10, 10–20, 20–40, 40–60, 60–80, and 80–100 cm) were collected with three replicates, and three replicates were mixed uniformly into one sample in the same soil profile. All soil samples were placed in polyethylene bags and brought to the laboratory, then air dried at room temperature for three weeks. Some air-dried soils at each site in each sampling season were used for soil particle size analysis. All the other air-dried soil samples were sieved through a 2-mm nylon sieve to remove coarse debris, and then ground with a pestle and mortar until all particles passed a 0.149-mm nylon sieve for the determination of soil chemical properties. Soil bulk density cores were also correspondingly collected using a 184 cm^3 cylinder from each soil layer of each soil profile, oven dried at 105 °C for 24 h, and weighed for the determination of bulk density (BD) and soil water content (SWC).

Soil samples were digested with an $HClO_4$-HNO_3-HF mixture in Teflon tubes to determine the contents of total sulfur (TS), total phosphorous (TP), Al, As, Cd, Cr, Cu, Ni, Pb and Zn. The digested solutions of soil samples were analyzed 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%. Soil organic matter (SOM) was measured using dichromate oxidation (Page et al., 1982). Soil pH and soil salt content (SSC) were determined in the supernatants of 1:5 soil and water mixtures using a Hach pH meter (Hach Company, Loveland, CO, USA) or salinity meter (VWR Scientific, West Chester, Pennsylvania, USA). Soil particle size was analyzed on a Laser Particle Size Analyzer (Microtrac Inc., USA).

2.3. Assessment methods

In our study, enrichment factor (EF) was selected to assess the pollution levels and the possible anthropogenic impact of each of the observed heavy metals. Aluminum (Al) was used as the reference element for geochemical normalization. EF is defined as $EF = (M/Al)_{sample}/(M/Al)_{background}$ (Bai et al., 2014), where M_{sample} and $M_{background}$ are the determined contents of targeted elements (e.g., As, Cd, Cr, Cu, Ni, Pb and Zn) in soil samples and their background values, respectively; Al_{sample} and $Al_{background}$ are the measured Al content in soil samples and the $Al_{background}$ value, respectively. Pollution levels were classified into five categories based on EF values: (1) $EF < 2$, deficiency to minimal enrichment; (2) $EF = 2–5$, moderate enrichment; (3) $EF = 5–20$, significant enrichment; (4) $EF = 20–40$, very high enrichment; and (5) $EF > 40$, extremely high enrichment (Han et al., 2006). Background values of heavy metals were from the China National Environmental Monitoring Center (CNEMC, 1990).

Toxic units (TUs) were used to normalize the toxicities of various

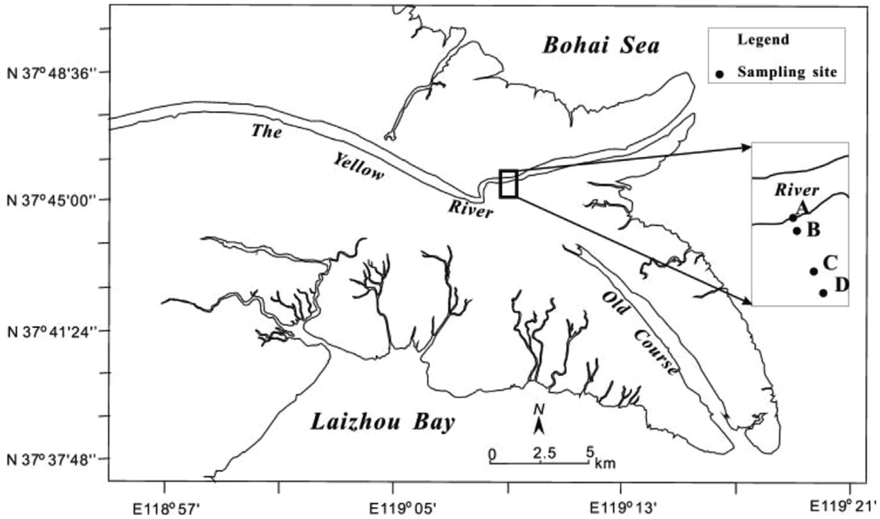

Fig. 1. Location map of the study area and sampling sites. The distances for site A, B, C and D from the river south bank were 0 m, 50 m, 250 m and 350 m, respectively. The vegetation types for site A, B, C and D were freshwater *Phragmites australis*, *Tamarix chinensis-Suaeda salus*, *Suaeda salus* and saltwater *Phragmites australis*, respectively.

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