Catena 126 (2015) 43–52

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Spatial variations and bioaccumulation of heavy metals in intertidal zone of the Yellow River estuary, China

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ARTICLE INFO

Article history:
Received 7 June 2014
Received in revised form 26 October 2014
Accepted 31 October 2014
Available online 19 November 2014

Keywords:
Heavy metals
Sediments
Plants
Intertidal zone
Yellow River estuary

ABSTRACT

Nine units in new-born intertidal zone of the Yellow River estuary, China were examined for concentrations of heavy metals (Pb, Cr, Cu, Zn and Ni) in sediments and plants. Heavy metal levels in surface sediments were in the order of Zn > Pb ≈ Cr > Cu ≈ Ni and generally increased in a seaward direction except for Z6 (*Tamarix chinensis-Suaeda salsa* zone) and Z7 (*S. salsa-T. chinensis* zone) units. Significant differences in metal concentrations of the 9 units were observed in the profiles ($p < 0.01$). Heavy metal levels in the shoots or roots of different plants decreased in the order of Zn > Cu > Pb > Ni > Cr and differed among plants or tissues. The roots at Z2 (*Calamagrostis pseudophragmites* zone), Z3 (*Imperata cylindrical* zone) and Z4 (*Phramites australis* zone) units accumulated greater metals than shoots [TFs (translocation factors) < 1], while the shoots at Z1 (*Sparganium minimum-Potentilla supina* zone), Z7 and Z8 (*S. salsa* zone) units accumulated greater metals than roots (TFs > 1), implying that intertidal plants showed different pathways in metal accumulation and internal transportation. Except for Pb, the concentrations of Cr, Cu, Zn and Ni in sediments were lower than the criteria of Class I recommended by the Environmental Quality Standard for Soils of China. Although heavy metal levels in intertidal zone were generally the lowest (Cr, Cu, Zn and Ni) or relatively moderate (Pb) compared with other estuaries or bays in Asia and Europe, high eco-toxic risk of Pb and Ni exposure still could be observed at Z4, Z6 and Z9 (mudflat zone) units. *S. salsa* was more suitable for the potential biomonitor or phytoremediation of all five heavy metals if intertidal sediments was seriously contaminated with increasing of pollutants loading in the Yellow River estuary.

1. Introduction

Heavy metals are serious pollutants due to their toxicity, persistence in natural conditions and ability to be incorporated into food chains (Armitage et al., 2007; Sakan et al., 2009; Wang et al., 2013). Estuaries are zones of complex interaction between fluvial and marine processes that may act as a geochemical trap for heavy metals bonded in the sediments. The mixing of continental river water and marine salt water usually leads to flocculation and accumulation processes of heavy metals, which are mainly controlled by water/particle interactions and solution chemistry, such as sedimentation, flocculation, organic and inorganic complexation, adsorption and sediment resuspension (Flegal et al., 1991; Moran et al., 1996). In addition, evolution of the composition of the particle in the mixing zone of the estuary indicates that heavy metals do not behave conservatively and that they are also affected by the changing physico-chemical conditions, such as salinity, pH and redox (Calmano and Hong, 1993; Comans and van Dijk, 1988). Heavy metals released into coastal marsh are generally bound to particulate matter, which eventually settle down and be incorporated into sediments. Marsh plants can take up large quantities of sediment-bound metals, releasing them as they decay (Baldantoni et al., 2004). In general, factors affecting metal accumulation by plants can be biological (e.g., species, growth stage, generation) and non-biological (e.g., temperature, season, salinity, pH, metal concentration) (Bonanno and Giudice, 2010). In recent years, there has been an ever-increasing interest in discussing the fate of heavy metals in coastal marshes (Comans and van Dijk, 1988; Griscom et al., 2000; Turner, 2000) and the metal-accumulation plants for environmental remediation application (termed as 'phytoremediation') (Chaney et al., 1997; Deng et al., 2004; Peng et al., 2008). Previous studies have showed that coastal marshes were generally recognized to be important reservoirs or sinks as filters, retaining heavy metals that exist in water, sediments, plants and other organisms (Arias et al., 2005; Prokisch et al., 2009). The

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http://dx.doi.org/10.1016/j.catena.2014.10.037
0341-8162/

heavy metals retained in marsh may also have significantly toxic effects on wildlife (Zhang et al., 2010a). Thus, studies on distribution and geochemical behavior of heavy metals in sediments and plants are significant for interpreting the geochemistry of heavy metals in the estuaries and elucidating the physical, chemical and biological processes that happen between the land and the ocean (Wang and Liu, 2003).

The Yellow River is the second largest river in China and is well known as a sediment-laden river in the world. In recent years, approximately 1.68×10^8 tons of sediment is carried to the estuary and deposited in the slow flowing delta, which forms an extensive intertidal zone and special marsh landscape (Xu et al., 2002). Meanwhile, approximately 4.40×10^5 tons of pollutants (including 1,110 tons of heavy metals) from the cities and industrial and mining enterprises in the Yellow River basin were carried to the estuary (State Oceanic Administration of China, 2013). Presently, the Yellow River Delta is an important economic development area in Shandong Province of China. With the rapid development of industrialization, urbanization and agricultural practices in the coastal zone of the Yellow River Delta, the ecological health of estuarine ecosystem are threatening by loading excessive pollutants (especially threatened by heavy metals) (Tang et al., 2010). The coastal marsh in the Yellow River estuary is predominantly composed of silts and clayey silts, reflecting the fact that the suspended materials discharging into the estuarine region are dominated by fine grained particles (about 73.6% is <32 μm during flood season) (Deng et al., 2008). The plants in the coastal marsh also contribute to the spatial distribution of sediment grain size due to the influence of vegetation in attenuating tide energy (Yang, 1999). Previous studies have showed that particle size significantly influenced the fate and accumulation of heavy metals in coastal marsh sediments (Breslin and Sanudo-Wilhelmy, 1999; Gao and Li, 2012; Zhang et al., 2001, 2011). Fine grained sediments often show higher concentrations of heavy metals due to their greater surface to volume ratio and enrichment of organic matter and Fe-Mn oxides (Rae, 1997; Williams et al., 1994), but how the sediment grain-size influences the spatial distribution of heavy metals in marsh sediments of the Yellow River estuary remains scarce. Since coastal marshes are generally recognized as an important filter for retaining heavy metals, the distribution, variation and transportation of the heavy metals in sediments and plants, to a great extent, affects the accumulation and chronic poisoning of wild animals or human by food chains (Prokisch et al., 2009; Tang et al., 2010). However, insufficient information is available in the Yellow River estuary concerning the distribution of heavy metal concentrations in sediments and plants and the abilities of different plants or tissues to absorb and transport metals. Understanding the related knowledge will provide insight into choosing suitable plants for marsh phytoremediation systems in the future.

In this paper, heavy metal concentrations (Pb, Cr, Cu, Zn and Ni) in intertidal zone of the Yellow River estuary were determined by *in situ* sampling and ICP-MS (Inductively coupled plasma mass spectrometry) analysis. The primary objectives of this study were *i*) to investigate the spatial distribution of heavy metals in sediments across the intertidal zone, (*ii*) to determine the differences in heavy metal levels accumulated by shoots or roots of different intertidal plants, and (*iii*) to discuss the potential use of intertidal plants for biomonitor or phytoremediation.

2. Study area and methods

2.1. Study area

This study was carried out in intertidal zone of the northern Yellow River estuary, which is located in the Nature Reserve of the Yellow River Delta (37°35′N ~38°12′N, 118°33′E ~119°20′E) in Dongying City, Shandong Province, China. Both tides and waves influence sediment transportation and accumulation in intertidal zone. The tide in intertidal zone is irregular semidiurnal tide and the mean tidal range is 0.73–1.77 m (Li et al., 1991). Under fair weather conditions, the Yellow River estuary coast is less influenced by waves and tides play the dominant role in controlling sedimentation in intertidal zone. Coastal marsh is the main marsh type, with an area of 964.8 km^2, accounting for 63.06% of the total area of the Yellow River Delta (Cui et al., 2009). The marsh soil is dominated by salt soil and the main marsh vegetations include *Suaeda salsa*, *Phragmites australis* and *Tamarix chinensis* (Sun et al., 2013; Tian et al., 2005). The width of the coastal marsh in the Yellow River estuary ranged from 4 km to >10 km, and from the land to the sea, a well-developed intertidal zone typically contains 9 distinct units (Fig. 1): a *Sparganium minimum* and *Potentilla supina* zone (*S. minimum* is dominant species, Z1), a *Calamagrostis pseudophragmites* zone (Z2), a *Imperata cylindrical* zone (Z3), a *P. australis* zone (Z4), a *S. salsa* and *P. australis* zone (*S. salsa* is dominant species, Z5), a *T. chinensis* and *S. salsa* zone (*T. chinensis* is dominant species, Z6), a *S. salsa* and *T. chinensis* zone (*S. salsa* is dominant species, Z7), a pure *S. salsa* zone (Z8) and mudflat zone (Z9). The aboveground and belowground biomasses of the plants in intertidal zone are shown in Fig. 2 (Dong et al., 2010). This sequence of geomorphic units is complete in intertidal zone of the Yellow River estuary due to less human activities, which generally comprises three areas in a seaward direction: high marsh (Z1, Z2, Z3 and Z4), middle marsh (Z5, Z6 and Z7 units) and low marsh (Z8 and Z9), at the elevations of 2.4–3.5 m, 1.0–2.5 m and −1.0–0.9 m, respectively (Song et al., 2010). The physical and chemical properties of topsoil (0–10 cm) in high marsh, middle marsh and low marsh are shown in Table 1.

2.2. Study methods

2.2.1. Sample collection

Two typical transects perpendicular to the riverbank or extending from the vegetated marsh zones to the mudflat were laid in intertidal zone of the northern Yellow River estuary in May 2009. On each transect, the surface and profile samples were taken at the abovementioned Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8 and Z9 zones, respectively. At each zone, 4 surface samples were collected at a sampling depth of 0–5 cm and 2 profiles (0–60 cm) were simultaneously sampled at 10 cm interval. A total of 72 surface samples and 216 profile samples were collected. All sediment samples were air-dried, ground and sieved through a 100-mesh nylon sieve. Aboveground and belowground biomasses of plants (3 replications) were collected from the same position with sediment profile samples, with 96 samples in total. All plant samples were washed thoroughly with deionized water and then oven-dried at 80 °C for 48 h. After the measurement of dry weights, the samples were ground into fine powder (<0.25 mm).

2.2.2. Sample analysis

A 0.1000 g homogenized sediment sub-sample was digested with 2 mL HNO_3, 1 mL $HClO_4$ and 5 mL HF at 160–190 °C for 16 h. The residue was dissolved in 2 mL of 4 mol/L HCl and then diluted to 10 mL with deionized water for heavy metal analysis. A 0.2000 g plant sub-sample was digested in a mixture of 65% HNO_3 (2 mL) and 30% H_2O_2 (1 mL). The residue was diluted with deionized water to 10 mL for analyzing heavy metal concentrations. The concentrations of heavy metals (Pb, Cr, Cu, Zn and Ni) in all samples were determined by Agilent 7500 ICP-MS (Agilent Company, America). Quality assurance and quality control were assessed using duplicates, method blanks and standard reference materials (GBW07401 and GBW08513) from the National Research Center for Standards in China with each batch of samples (one blank and one standard for each 20 samples). Sediment organic matter (SOM) was measured by $K_2Cr_2O_7$ oxidation method (The Committee of Agro-chemistry of the Chinese Society of Soil Science, 1983). Moreover, 54 samples from the 9 units were selected for grain-size determination using Coulter Laser granulometer.

2.2.3. Calculations

To study the accumulation and transportation characteristics of heavy metals in plants, the bioaccumulation factor (BCF) and translocation