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Heavy metal contamination and ecological risk in *Spartina alterniflora* marsh in intertidal sediments of Bohai Bay, China

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ABSTRACT

To investigate the effects of *Spartina alterniflora* on heavy metals pollution of intertidal sediments, sediment cores of a *S. alterniflora* salt marsh and a mudflat in Bohai Bay, China were analyzed. The results showed that *S. alterniflora* caused higher total C and P, but lower bulk density and electrical conductivity. The levels of Cd, Cu and Pb were higher in *S. alterniflora* sediment. Both Cd and Zn were higher than the probable effect level at both sites, indicating their toxicological importance. The geo-accumulation and potential ecological risk indexes revealed higher metal contamination in *S. alterniflora* sediment. Multivariate analysis implied that anthropogenic activities altered mobility and bioavailability of heavy metals. The percentage of mobile heavy metals was higher in *S. alterniflora* sediment, indicating improvement of conversion from the immobilized fraction to the mobilized fraction. These findings indicate that *S. alterniflora* may facilitate accumulation of heavy metals and increase their bioavailability and mobility.

1. Introduction

The ubiquitous use of anthropogenic heavy metals associated with rapid economic development has significantly changed their original distribution patterns in the natural environment, enabling their delivery to intertidal zones from river catchments via fluvial transport, atmospheric deposition, and local wastewater discharge (Qiao et al., 2007; Li et al., 2013; Golestaninasab et al., 2014). Unlike biodegradable organic pollutants, heavy metals have the potential for bioaccumulation and biomagnification, resulting in potential long-term effects on human health and ecosystems (Pan and Wang, 2012). Bohai Bay, which is the second largest bay in the Bohai Sea, a semi-closed shallow sea in North China, receives industrial and domestic sewage from Beijing and Tianjin. Owing to the large amount of contaminant inputs and poor physical self-cleaning capacity, Bohai Bay has become one of the most degraded marine systems in China. Thus, the impact of urbanization and economic development on sediment quality of the intertidal zone of Bohai Bay is of concern. Accordingly, many recent studies have been conducted to investigate the heavy metal pollution status of river outlets and northwestern coastal areas in Bohai Bay (Li et al., 2011; Zeng et al., 2013; Gao et al., 2014).

When environmental conditions change (pH, cationic exchange capacity, nutrient status, redox potential, etc.), some of the sediment-bound heavy metals may be remobilized and released back into the water, where they can have adverse effects on living organism (Morillo et al., 2002; Peng et al., 2009). In fact, the mobility of metals in the environment depends strongly on their chemical forms or types of the binding of the element (Cuong and Obbard, 2006; Yu et al., 2010). Numerous analytical techniques have been used to identify the key factors that control distribution and speciation of heavy metals in the coastal and estuarine sediment in order to understand their mobility and potential ecological risks (Tessier et al., 1979; Kersten and Förstner, 1986; Cuong and Obbard, 2006). One of the most common methods is the three-stage sequential extraction procedure proposed by the European Community Bureau of Reference (BCR) (Cappuyns et al., 2007). This method, which illustrates the acid extractable, reducible, oxidizable and residual fractions of metals in sediment, might provide a great deal of useful information regarding the chemical nature or potential mobility and bioavailability of a particular element, thereby offering a more realistic estimate of actual environmental impact (Cuong and Obbard, 2006; Chakraborty et al., 2014). As for total heavy metal accumulation in sediment, a number of indices have also been developed in the last decade to assess heavy metals contamination and its ecological effects, including the threshold effect level (TEL) and probable effect level (PEL) guidelines (MacDonald et al., 2000), geo-accumulation index (I_{geo})

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(Müller, 1981), and potential ecological risk index (Hakanson, 1980; Shi et al., 2010).

Spartina alterniflora, an invasive halophyte from North America, was intentionally introduced to the coastal region of China in 1979 (Wan et al., 2009). This species now occupies the naked mudflat and has formed dense monospecific stands in the intertidal zone in Bohai Bay, China. The negative effects of *S. alterniflora* on the native ecosystems have become increasingly obvious in the coastal wetlands of South China, such as landscape change, impact on endangered species, decrease in abundance of native species, degradation of native ecosystems and considerable economic loss (Tian et al., 2008; Li et al., 2009). However, some studies have shown positive effects of *S. alterniflora* in preventing erosion and promoting sediment accretion, absorbing nutrients, improving the growth of mollusks and attracting many regional waterfowl (Zhang, 2007; Wan et al., 2009; Li et al., 2010). Previous studies have shown that *S. alterniflora* can facilitate organic carbon and nitrogen storage (Zhang et al., 2010; Yang et al., 2013) and influence cycles of sulfur (Li et al., 2009; Nie et al., 2009) in salt marsh sediment. Furthermore, this species may have significant effects on the biogeochemical redox processes and bacterial sulfate reduction, thereby enabling it to control the chemical speciation, bioavailability, toxicity and mobility of many heavy metals in salt marshes (Wang et al., 2013). Many studies have suggested that *S. alterniflora* can greatly influence the mobility of heavy metals in sediment and has the potential for use in heavy metals remediation (Hempel et al., 2008; Salla et al., 2011; Nalla et al., 2012; Chai et al., 2013).

Currently available data on heavy metals in Bohai Bay are not sufficient for evaluation of their total environmental impact because the chemical state of heavy metals in sediment needs to be known to evaluate their mobility, bio-availability and toxicity. Furthermore, little data is available regarding the effects of *S. alterniflora* on fractionation and bioavailability of heavy metals in the intertidal zone of Bohai Bay. Based on the above discussion, it was hypothesized that *S. alterniflora* may alter the sediment properties, and improve accumulation of heavy metals, thereby affecting heavy metal pollution. Consequently, this study was conducted (1) to quantify the influence of *S. alterniflora* on sediment properties and heavy metals accumulation in intertidal sediment in Bohai Bay; (2) to assess the potential ecological risk and sources of heavy metals and (3) to identify the speciation of heavy metals.

2. Materials and methods

2.1. Sediment sampling and analysis

Sediment cores were collected in August 2012 from the coastal wetland of Bohai Bay (39°0′N, 117°46′E) (Fig. 1). The climate in this study area belongs to warm and humid subtropical monsoon climate. The tidal regime is semidiurnal, with a maximum range of 2.92 m. Annual mean rainfall is around 622 mm and annual mean evaporation is around 1800 mm; annual mean temperature is 11.7 °C and mean temperatures of the coldest (January) and hottest (July) months are 3.5 and 26.2 °C, respectively (Yang, 2005). Six sample locations were selected along the coastline. In each sample location, three sediment cores in mudflats with and without *S. alterniflora* were collected (acid-washed PVC pipes, 100 cm length, 7.5 cm internal diameter), respectively. The unvegetated mudflat was considered as a control. Then, 18 sediment cores were immediately sliced at 0–10 cm, 10–20 cm, and 20–30 cm using a plastic cutter, after which the subsamples were immediately sealed with plastic bags, and transported back to the laboratory on the same day.

The sediment samples were air-dried for the analysis of the physicochemical parameters. Bulk density was determined by drying the sediment at 70 °C for 24 h. pH was determined in deionized water using mass ratios of 1:2.5 (sediment to water). Electrical conductivity (EC) was determined in deionized water using mass ratios of 1:5 (sediment to water). Total carbon (TC), total nitrogen (TN) and total phosphorus (TP) were measured using an elemental analyzer Vario EL Cube (Elementar, Germany).

2.2. Determination of heavy metals

To determine the total heavy metal concentrations, sediment samples were subjected to microwave digestion in a mixture of 9 ml HNO_3, 3 ml HF and 1 ml HCl. All reagents were of analytical grade or better. The concentrations of Cd, Zn, Pb and Cu in sediments were determined by inductively coupled plasma mass-spectrometry (ICP-MS).

Pollution levels of heavy metals could also be characterized by the geo-accumulation index (I_{geo}) put forward by Müller (1969). I_{geo} has commonly been cited by researchers in environmental studies (Abrahim and Parker, 2008; Shi et al., 2010), and could be defined by the following equation: $I_{geo} = \log_2 (C_n/1.5B_n)$, where, C_n is the measured content of the metal n and B_n is the background or pristine value of the metal. The constant factor 1.5 was introduced to analyze natural fluctuations in the contents of a given substance in the environment and very small anthropogenic influences (Loska et al., 2004). As shown in Table 1, seven classes of I_{geo} were proposed (Müller, 1981).

Ecological risks associated with heavy metals were assessed using the potential ecological risk index (R_I) developed by Hakanson (1980). R_I could be used to comprehensively evaluate the ecological risks posed by heavy metals, because it covers a variety of research domains, including biological toxicology, environmental chemistry, and ecology (Shi et al., 2010).

$$E_r^i = T_r^i \cdot c_f^i = T_r^i \cdot c_s^i/c_n^i \quad R_I = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \cdot c_s^i/c_n^i$$

where c_f^i is the contamination factor, c_s^i is the concentration of heavy metals in the sediment, and c_n^i is a reference value for heavy metals. The c_n^i values for Cd, Zn, Pb and Cu are 0.5, 80, 25 and 30, respectively (Hilton et al., 1985). T_r^i is a toxic-response factor for a given substance, which accounts for toxicity and sensitivity requirements. The T_r^i values for Cd, Zn, Pb and Cu are 30, 1, 5 and 5, respectively (Hilton et al., 1985). E_r^i is the monomial potential ecological risk factor, and R_I is calculated as the sum of all risk factors for heavy metals in sediment, which represents the sensitivity of the biological community to the toxic substances and illustrates the potential ecological risk caused by the overall contamination. Hakanson (1980) defines five categories of E_r^i and four categories of R_I values as shown in Table 2.

Multivariate analysis, such as principle component analysis (PCA) and hierarchical cluster analysis (HCA), has been shown to be an effective tool for understanding the significant groupings and dominant pathways. At both sites, PCA was performed to investigate sediment properties (bulk density, pH and EC), nutrient elements (TC, TN and TP), and heavy metals (Cd, Zn, Pb and Cu) with varimax rotation.

2.3. Sequential extraction of heavy metals

The sequential extraction procedure (SEP) used to analyze heavy metal speciation was the improved BCR three-step scheme (Guillén et al., 2012). The various fractions of heavy metals were determined by inductively coupled plasma-mass spectrometry (ICP-MS).