Ecotoxicology and Environmental Safety 104 (2014) 143–151

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Ecological risk and pollution history of heavy metals in Nansha mangrove, South China

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ARTICLE INFO

Article history:
Received 15 October 2013
Received in revised form
26 January 2014
Accepted 20 February 2014
Available online 25 March 2014

Keywords:
Ecological risk assessment
Heavy metal
Pollution
Mangrove
Sediment
Phytoremediation

ABSTRACT

Owing to the Industrial Revolution in the late 1970s, heavy metal pollution has been regarded as a serious threat to mangrove ecosystems in the region of the Pearl River Estuary, potentially affecting human health. The present study attempted to characterize the ecological risk of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) in Nansha mangrove, South China, by estimating their concentrations in the surface sediment. In addition, the pollution history of heavy metals was examined by determining the concentrations of heavy metals along the depth gradient. The phytoremediation potential of heavy metals by the dominant plants in Nansha mangrove, namely *Sonneratia apetala* and *Cyperus malaccensis*, was also studied. Results found that the surface sediment was severely contaminated with heavy metals, probably due to the discharge of industrial sewage into the Pearl River Estuary. Spatial variation of heavy metals was generally unobvious. The ecological risk of heavy metals was very high, largely due to Cd contamination. All heavy metals, except Mn, decreased with depth, indicating that heavy metal pollution has been deteriorating since 1979. Worse still, the dominant plants in Nansha mangrove had limited capability to remove the heavy metals from sediment. Therefore, we propose that immediate actions, such as regulation of discharge standards of industrial sewage, should be taken by the authorities concerned to mitigate the ecological risk posed by heavy metals.

1. Introduction

Mangroves, which are distributed in the intertidal zone within circumtropical regions, provide various ecological services and sustain the integrity of coastal areas (Robertson and Duke, 1987; Harty, 1997; Krauss et al., 2008). Unfortunately, they have been globally menaced by urbanization and industrialization that their total area has been dwindling over the last few decades (Alongi, 2002; Bosire et al., 2008). In South China, for example, the health and integrity of mangroves are aggravated due to substantial discharge of industrial sewage into the Pearl River Estuary (PRE) from the coastal cities (Chen et al., 2006; Chen et al., 2013). It is estimated that the annual amount of industrial sewage has reached approximately 200 million tons (Chen et al., 2006). Among different types of pollutants in the sewage, heavy metals are of special concern since alarming levels of cadmium, lead and zinc were annually discharged into the Pearl River (Li et al., 2006), potentially causing far-reaching ramifications on human health and ecosystems. Since sediment in coastal areas is generally regarded as the primary sink for heavy metals (Montouris et al., 2002), it is surmised that heavy metals have insidious effects on mangrove ecosystems due to their toxicity, non-biodegradability and potential to bioaccumulation (Chaudhuri et al., 2014; Nath et al., 2013; Usman et al., 2013). Therefore, monitoring and assessment of heavy metals in sediment should be launched regularly to evaluate their ecological risk. To do so, a classical method is to calculate the potential ecological risk index (Hakanson, 1980), in which the concentrations of heavy metals in the study site are compared to those in the reference site (i.e. background level). For better monitoring and assessment, however, understanding the historical or pre-anthropogenic record of heavy metal pollution is also important. The pollution history of heavy metals can be reflected by the depth of sediment as long as the sedimentation rate is known (Abrahim and Parker, 2008; Rezaee et al., 2010; Liu et al., 2011). Elucidating the spatial and

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http://dx.doi.org/10.1016/j.ecoenv.2014.02.017
0147-6513

temporal variations of heavy metals in sediment can offer precious information for policy makers or environmentalists to manage mangrove habitats more effectively.

To combat moderate level of heavy metal pollution in mangrove habitats, phytoremediation has been recommended in view of its eco-friendliness and cost-effectiveness (reviewed by Cheng, 2003; Weis and Weis, 2004). While many heavy metals, such as Pb, in the anoxic sediment are often not readily bioavailable, plants can remobilize them and hence promote their bioavailability (De Lacerda et al., 1993), through oxidation by aerenchyma tissues of roots (Moorhead and Reddy, 1988) or acidification by plant exudates (Doyle and Otte, 1997). Consequently, the remobilized heavy metals can be removed by plants through various processes such as phytoextraction (reviewed by Ali et al., 2013). The plants are then harvested to prevent heavy metals from re-entering into the sediment when they have accumulated certain amount of heavy metals in their tissues. Nevertheless, plants cannot ad infinitum extract heavy metals from sediment because pernicious effects would be incurred if their threshold tolerance value is exceeded. In this regard, suitable candidates for phytoremediation of heavy metals should have high tolerance, accumulation capability, growth rate and above-ground biomass (reviewed by Ali et al., 2013).

In the present study, the spatial and temporal variations of heavy metals in the sediment in Nansha mangrove, the second largest mangrove forest in the region of the PRE, were examined to characterize the ecological risk and pollution history of heavy metals, respectively. Moreover, the concentrations of heavy metals accumulated in different dominant plants in Nansha mangrove were measured to estimate their phytoremediation potential. The findings could shed light on the degree of heavy metal pollution in the PRE as well as provide crucial information for monitoring, management and conservation of coastal environments.

2. Materials and methods

2.1. Study site

Nansha mangrove (113°33'00"E, 22°39'14"N) was chosen as the study site with an estimated area of 55 hm^2 in Sanmin Island, South China (Fig. 1). This mangrove was highly dominated by the introduced, mature, true mangrove plants *Sonneratia apetala* (average height: 8 m; average diameter at breast height: 11.8 cm), which were uniformly distributed with density of approximately 230 ind hm^{-2}. Apart from mangrove plants, sedge *Cyperus malaccensis* was ubiquitously distributed in the open forest gap, while water hyacinth *Eichhornia crassipes* was a rare species in the study site.

2.2. Collection of sediment and plant samples

In November 2012, the study site was uniformly divided into twenty sampling points along the Island with a distance of about 200 m between two consecutive sampling points (Fig. 1). At each sampling point, three random samples of surface sediment were collected by a rectangular sampler (10 cm long × 10 cm wide × 15 cm deep). To analyze the pollution history of heavy metals in the mangrove, three core sediment samples were collected by a PVC core (10 cm in diameter × 66 cm deep) in the unvegetated area at sampling points N5, N10 and N15 to minimize the effect of root uptake (Fig. 1). According to the previous results of 210Pb dating, the sedimentation rate in Nansha mangrove is approximately 2 cm yr^{-1} (Chen and Luo, 1991). Thus, the sediment sample in each core was cut into 33 layers from the top at 2 cm depth interval by a PVC knife to represent the pollution history from 1979 to 2011.

Roots, stems and leaves of the dominant plants, namely *S. apetala* and *C. malaccensis*, were also collected from sampling points N5, N10 and N15. Stems and leaves of *S. apetala* were collected by cutting. Roots of *S. apetala* were collected together with sediment using the PVC core, followed by washing away the sediment. *C. malaccensis* was collected by carefully removing the whole individual from sediment and each collected individual was then separated into roots and leaves. At each sampling point, three individuals were collected for each plant species.

2.3. Heavy metal analysis of sediment and plant samples

The sediment samples were freeze-dried, ground into powder and passed through a 2 mm sieve. To extract the heavy metals, 0.3 g sediment sample was digested by a mixture of concentrated hydrochloric acid (HCl) and nitric acid (HNO_3) (3:1, v/v) using microwave digestion method. As for plant samples, the roots were rinsed with deionized water and immersed in 20 mmol l^{-1} Na_2-EDTA for 20 min to remove the aluminum adhered on the surface. The plant samples were then dried in an oven at 80 °C for 72 h. 0.3 g plant sample, which was powdered using an agate mill, was digested by a mixture of concentrated HNO_3 and perchloric acid ($HClO_4$) (4:1, v/v). The concentrations of heavy metals in the extract, namely chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn), were determined by inductively coupled plasma-optima emission spectrometry (ICP-OES, Optima 5300DV, Perkin-Elmer Instruments, USA), while cadmium (Cd) was determined by an atomic absorption spectrometer (AAnalyst 800, Perkin-Elmer Instruments, USA). To estimate the accuracy of this method, a certified reference material from the State Oceanic Administration of China (GBW 07334) was used for recovery test. The recoveries for all the metals ranged from 90% to 97% (RSD: 3.81–5.75%).

2.4. Statistical analyses

The potential ecological risk coefficient (E_r^i) was calculated to evaluate the ecological risk of each heavy metal according to the following formula (Hakanson, 1980):

$$E_r^i = T_r^i \times C_f^i = \frac{T_r^i \times C_s^i}{C_n^i}$$

where T_r^i is the toxic-response factor of heavy metal i, which reflects the toxicity level and sensitivity of organisms to it; C_f^i is the contamination factor of heavy metal i; C_s^i is the measured concentration of heavy metal i in the sediment; C_n^i is the background value of heavy metals i, adopted from Li and Zheng (1988). The toxic-response factor for Cd, Cr, Cu, Mn, Pb and Zn was 30, 2, 5, 1, 5, and 1, respectively (Hakanson, 1980). The degree of ecological risk can be categorized as follows: $E_r^i < 40$: low risk, $40 \le E_r^i < 80$: moderate risk, $80 \le E_r^i < 160$: considerable risk, $160 \le E_r^i < 320$: high risk, and $E_r^i \ge 320$: very high risk.

The potential ecological risk index (RI), which represents the overall ecological risk of multiple heavy metals in the sediment, was calculated using the following formula (Hakanson, 1980):

$$\mathrm{RI} = \sum_{i=1}^{n} E_r^i$$

where n is the number of heavy metals analyzed in the sample (i.e. $n=7$ in the present study). RI can be classified into four levels: RI < 150: low risk, 150 ≤ RI < 300: moderate risk, 300 ≤ RI < 600: considerable risk, and RI ≥ 600: very high risk.

Bioconcentration factor (BCF) and translocation factor (TF) were calculated to estimate the efficiency of a plant to accumulate heavy metals from sediment and to translocate the heavy metals from its roots to its stems or leaves, respectively. BCF and TF are calculated by the following formulas (Wilson and Pyatt, 2007; Zacchini et al., 2009):

$$\mathrm{BCF} = \frac{C_{plant}}{C_{sediment}}; \quad \mathrm{TF} = \frac{C_{stem/leaf}}{C_{root}}$$

where C_{plant} and $C_{sediment}$ are the concentrations of a particular heavy metal in the plant and sediment, respectively; C_{stem}, C_{leaf} and C_{root} are the concentrations of a particular heavy metal in the stem, leaf and root, respectively.

Pearson correlation analysis was applied to examine the relationship among heavy metals in the surface sediment. Linear regression analysis was conducted to examine the correlation between concentration and sediment depth. One-way analysis of variance (ANOVA), followed by Tukey's test for pair-wise comparisons, was used to compare the concentrations of heavy metals in different plant organs of each plant species. Statistical analyses were performed using software SPSS 20.0 for Windows.

3. Results

3.1. Concentration and ecological risk of heavy metals in the surface sediment

The concentrations of heavy metals in the surface sediment at different sampling points are shown in Fig. 2. Four distinct patterns were observed based on spatial variation. Pattern 1 (Cd): a dramatic fluctuation in concentration appeared from N1 to N20 with an overall slightly decreasing trend (Fig. 2a); Pattern 2 (Cr and Cu): the concentrations decreased remarkably from N1 to