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Baseline

Heavy metal fractionation and ecological risk implications in the intertidal surface sediments of Zhelin Bay, South China

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ABSTRACT

Intertidal surface sediments collected from Zhelin Bay, the largest mariculture base of eastern Guangdong Province of China, were analyzed for total metal concentrations and chemical speciation. Average total metal concentrations (mg/kg) were 0.063 (Cd), 35.69 (Pb), 23.07 (Cr), 7.50 (Ni), 7.95 (Cu), 74.95 (Zn), and 751.32 (Mn). Concentrations of Cd, Cu, Zn, and Mn were significantly higher than the corresponding background values of Zhelin Bay. All studied metals were dominated by residual fractions, whereas the second relatively higher average portions of Cd (24.10%) and Mn (15.17%) were strongly associated with the acid-soluble fraction. Overall, the intertidal surface sediments of Zhelin Bay were only slightly polluted based on the pollution load index (PLI), with a 21% probability of toxicity based on the mean effects range–median quotient. The metals Cd and Mn posed medium to high risk levels based on the method of risk assessment code (RAC).

Estuarine and marine embayments supporting different habitats and providing significant economic benefits are complex and dynamic aquatic environments. (Thrush et al., 2004; Morelli and Gasparon, 2014; Jonsson et al., 2017). Heavy metals used in all kinds of human activities are one of the main ecosystem threats for estuarine waters, and often associated with sediments transported from the catchments (Ip et al., 2007; Souza Machado et al., 2016). Heavy metals are associated with sediments by means of particle surface adsorption, ion exchange, co-precipitation, and complexation with organic matter (Peng et al., 2009; Passos et al., 2010; Dong et al., 2014). In intertidal zones, physical, chemical, and biological interactions between terrestrial and marine systems have a profound influence on the transport and fate of heavy metals (Spencer, 2002; Ip et al., 2007; Trant et al., 2016). Compared with that of other marine areas, the distribution of heavy metals in estuaries and their surrounding tidal areas is generally heavily affected by various human activities, riverine and atmospheric inputs, coastal and seafloor erosions, and biological activities (Zhang and Gao, 2015; Trant et al., 2016). Some of the sediment-bound metals can be released into the water column, thereby becoming bioavailable and potentially toxic to marine organisms (Macdonald et al., 1996; Teuchies et al., 2012; Gu et al., 2015). A complete assessment of the anthropogenic metal contribution to the environment should therefore consider both the total and the exchangeable metal concentrations.

Guangdong, located in South China, is the province with the most highly developed economy and the largest aquaculture production in China (Gu et al., 2017; NBSC, 2017). Zhelin Bay, covering an area of about 70 km^2, is a bay of the South China Sea on the northeastern coast of Guangdong (Fig. 1). It is the largest mariculture zone and the most intensively managed coastal aquaculture pond areas in eastern Guangdong (Gu et al., 2017; Fig. S1). Mariculture has taken up half areas of the seawater in Zhelin Bay and substantially promoted the local economy; however, its development has also caused rapid deterioration of the aquatic ecosystem in recent years. Besides pollution associated with aquaculture, rapid economic development and urbanization in recent decades have deteriorated the bay environment by increased industrial pollution, agricultural activities, and domestic sewage discharge (Gu et al., 2014b; Gu et al., 2017). There is evidence that the concentrations and potential mobility of some heavy metals in the surface sediments from some spots of the fish cage culture areas of in the Bay adversely impact marine organisms (Wang et al., 2013; Gu et al., 2014b; Gu and Lin, 2016). However, there is currently no information be found about the heavy metal concentrations in the intertidal sediments of this area.

In this context, we investigated the intertidal zone of Zhelin Bay in regard to the concentrations of heavy metals. The objectives of this study were to evaluate concentrations of Cd, Pb, Cr, Ni, Cu, Zn, and Mn in the intertidal surface sediments of the bay, establish their exchangeable fractions to assess their potential bioavailability, and estimated their pollution degree and ecological risk assessment.

Based on the extent of intertidal areas and the physical property of

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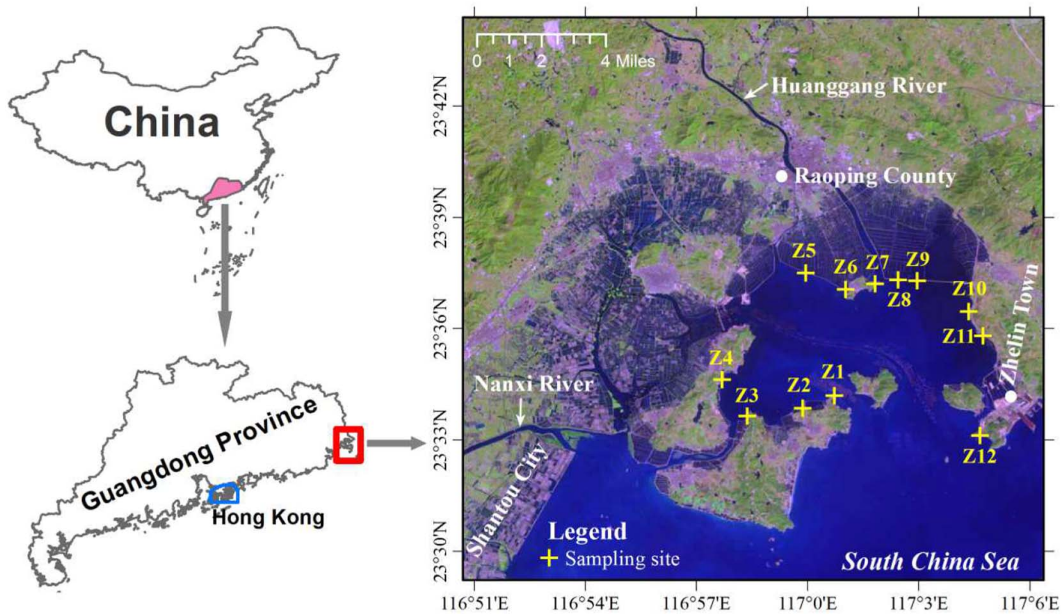

Fig. 1. Intertidal surface sediment sampling sites in the Zhelin Bay, South China.

the sediments due to hydrodynamics, 12 sampling sites were selected along the Zhelin Bay (Fig. 1). Among these sites, some have a wider intertidal zone and demonstrated notably differences in sediment texture and composition. Based on the greater sediment heterogeneity, more stations were selected in these sites. In contrast, other sites are narrow and the sediments are more homogenous and fewer stations in these narrow intertidal area sites were selected. On 9 and 10 May 2017, sediment samples from the surface layer (0–5 cm) were collected during ebb tide in the intertidal areas. Sediment redox potential (Eh) and pH were measured in situ immediately after sampling with redox and pH electrodes (FJA-6 ORP depolarization method automatic measuring system, Nanjing Chuan-Di Instrument & Equipment CO., LTD, China), respectively. At each site, five surface sediment (0–5 cm) samples were collected using a plastic spatula within an area of 2.5 m^2 and mixed thoroughly to get a representative sample. The samples were placed in clean polyethylene bags, preserved with ice during transport to the laboratory, and stored at − 20 °C until further analysis. Each sample was divided into two sub-samples. One was defrosted the determination of particle size, the other one was oven-dried at 50 °C, large calcareous debris and rock and plant fragments were removed, and carefully homogenized, sieved through a 200-mesh stainless steel mesh (< 74 µm), and stored for determination of sediment organic matter (SOM), inorganic carbonate ($CaCO_3$), and heavy metals.

Pretreatments for the determination of particle size were undertaken in accordance with our previous study (Gu et al., 2016a), and the particle size of each sample was determined with a Malvern Mastersizer 2000 (Malvern Instruments Co., Ltd. UK). Concentrations of SOM and $CaCO_3$ were measured by the loss-on-ignition method. Specifically, the samples were placed in a muffle furnace (CWF1100, Carbolite, UK) and heated to 550 °C for SOM and, for a further 2 h, at 950 °C for $CaCO_3$ determination (Gu et al., 2016b).

Each sediment sample was sequentially extracted to achieve information about the heavy metal speciation, following an optimized BCR procedure (Sutherland, 2010; Gu et al., 2014b). In this procedure, the heavy metals are separated into four operationally defined geochemical fractions, the acid-soluble, reducible, oxidizable, and residual fractions. The optimized microwave-assisted sequential extraction method applied in this study has been described in our previous study (Li et al., 2017). The metals remaining in a sample residue were digested following the United States Environmental Protection Agency (USEPA) method 3050B (microwave digestion).

Concentrations of Cd, Pb, Cr, Ni, Cu, Zn, and Mn were determined using an atomic absorption spectrometer (AAS, Z2000, Hitachi, Japan). The Chinese national standard sediment sample GBW07436 was analyzed to check the accuracy of the sequential extraction procedure and to monitor the performance of the analytical method. The Cd, Pb, Cr, Ni, Cu, Zn, and Mn recovery rates were 87–92% in the acid-soluble fraction, 89–97% in the reducible fraction, 88–103% in the oxidizable fraction, and 91–107% in the residual fraction.

The distribution of particle size and SOM content are two important factors influencing metal distributions in sediments (Gu et al., 2016b; Zhang et al., 2017). In addition, CaCO3, Eh, and pH also play a role in metal distribution (Nielsen et al., 2010; Gu et al., 2016b). Our results show that the sediment texture follows a distinct spatial distribution pattern (Fig. 2). Generally, sites Z1–Z6, Z8–Z9, and Z11–Z12 were predominated by sand, while silt was the main component at Z7 and Z10. The average sand content of Z1–Z6, Z8–Z9, and Z11–Z12 was 58.81%, while the average silt composition of Z7 and Z10 was 73.62%. The SOM content varied from 1.07 to 6.34% of the dry sediment weight, with an average of 2.68%, and was more variable than the $CaCO_3$ content, which accounted for 1.24 to 3.42% of the dry sediment weight, with an average of 2.22%. The Eh varied from 265.00 to 977.40 mV, with an average of 362.55 mV. The pH was slightly alkaline, ranging from 7.22 to 7.47, with an average of 7.35.

Mean, standard deviation (SD), median, and ranges of the heavy metal concentrations in the intertidal surface sediments of the Zhelin Bay are summarized in Table 1, while the spatial distributions of metals are illustrated in Fig. 3. Generally, total metal concentrations decreased in the order Mn > Zn > Pb > Cr > Cu > Ni > Cd. Relatively higher heavy metal concentrations were found at sites Z7 and Z2, with Mn having the highest concentrations in the sediment samples. Mean total Ni concentration was 7.50 mg/kg, while the mean total Cd concentration was below 0.063 mg/kg. The Cd, Cu, Zn, and Mn concentrations were significantly higher than their corresponding background values ($p < 0.01$; determined using the one-sample *t*-test), which strongly suggests that sediment enrichment due to human activities has taken place. The relatively higher metal concentrations at Z7 are probably due to runoffs and sewage discharges into the rivers, in addition to industrialization and other human activities (Figs. 1 and 3). The high metal concentrations at site Z2, near the fish cage culture areas, may be ascribed to fish farming (Gu et al., 2014b; Gu et al., 2017).