



## Speciation of heavy metals in different grain sizes of Jiaozhou Bay sediments: Bioavailability, ecological risk assessment and source analysis on a centennial timescale



Xuming Kang<sup>a,b</sup>, Jinming Song<sup>a,b,\*</sup>, Huamao Yuan<sup>a,b</sup>, Liqin Duan<sup>a,b</sup>, Xuegang Li<sup>a,b</sup>, Ning Li<sup>a,b</sup>, Xianmeng Liang<sup>a,c</sup>, Baoxiao Qu<sup>a,b</sup>

<sup>a</sup> CAS Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

<sup>b</sup> Laboratory for Marine Ecology and Environmental Sciences, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China

<sup>c</sup> University of Chinese Academy of Sciences, Beijing 100049, China

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### ABSTRACT

Heavy metal contamination is an essential indicator of environmental health. In this work, one sediment core was used for the analysis of the speciation of heavy metals (Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb) in Jiaozhou Bay sediments with different grain sizes. The bioavailability, sources and ecological risk of heavy metals were also assessed on a centennial timescale. Heavy metals were enriched in grain sizes of < 63 μm and were predominantly present in residual phases. Moreover, the mobility sequence based on the sum of the first three phases (for grain sizes of < 63 μm) was Mn > Pb > Cd > Zn > Cu > Ni > Cr > As. Enrichment factors (EF) indicated that heavy metals in Jiaozhou Bay presented from no enrichment to minor enrichment. The potential ecological risk index (RI) indicated that Jiaozhou Bay had been suffering from a low ecological risk and presented an increasing trend since 1940s owing to the increase of anthropogenic activities. The source analysis indicated that natural sources were primary sources of heavy metals in Jiaozhou Bay and anthropogenic sources of heavy metals presented an increasing trend since 1940s. The principal component analysis (PCA) indicated that Cr, Mn, Ni, Cu and Pb were primarily derived from natural sources and that Zn and Cd were influenced by shipbuilding industry. Mn, Cu, Zn and Pb may originate from both natural and anthropogenic sources. As may be influenced by agricultural activities. Moreover, heavy metals in sediments of Jiaozhou Bay were clearly influenced by atmospheric deposition and river input.

### 1. Introduction

Heavy metal contamination is an environmental problem today in the world due to their toxicity, widespread sources and accumulative behaviors (Li et al., 2014; Xu et al., 2014; Gu et al., 2015; Liu et al., 2015). When metals enter the marine environment, most of them will sink into sediments. Sediments act as source/sink for metals and provide an excellent proof of anthropogenic impacts (Wang et al., 2017). Many coastal bays have been suffering from severe heavy metal pollution caused by anthropogenic activities with the rapid economic development (Sun et al., 2012; Chen et al., 2014; Gao et al., 2014; Wang et al., 2017).

Previous studies indicated that the measurement of total concentrations of heavy metals in sediments was necessary for the evaluation of the overall pollution level (Gao et al., 2014). However, it has been proved that the determination of total metal concentrations alone is

insufficient for the study of the environment impact of contaminated sediments, which critically depends on the specific chemical forms and the relative mobility (Filipek and Owen, 1979; Yu et al., 2014; Gu et al., 2015). The European Community Bureau of Reference (BCR) standard method is a widely used sequential extraction scheme for the determination of the chemical forms of heavy metals (Gu et al., 2015; Zhang and Gao, 2015). This scheme partitions elements into four operationally defined geochemical fractions including: acid-soluble fractions (exchangeable and bound to carbonates), reducible fractions (bound to Fe/Mn oxyhydroxides), oxidizable fractions (bound to organic matter and sulfides) and residual fractions (contained within lithogenic minerals). Up to now, many studies have been carried out on heavy metal pollution using the BCR sequential extraction method in samples such as sediments (Fytianos and Lourantou, 2004; Gao et al., 2014; Li et al., 2014; Gu et al., 2015; Zhang and Gao, 2015; Ma et al., 2016), suspended particulated matter (Gao et al., 2015), soils (Guillén et al.,

\* Corresponding author at: CAS Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China.  
E-mail address: [jmsong@qdio.ac.cn](mailto:jmsong@qdio.ac.cn) (J. Song).

2012) and street dust (Yildirim and Tokaloğlu, 2016).

Previous studies found that the translocation ability is indicated by the acid-soluble fractions, and the bioavailability of heavy metals is the sum of acid-soluble fractions, reducible fractions and oxidizable fractions, while the residual fractions are not available (Ma et al., 2016). The chemical forms and mobility of heavy metals are controlled by the environmental conditions, such as pH, redox potential and other environmental parameters (Gu et al., 2015). Moreover, grain size is an essential property of sediments, as it affects the physicochemical behavior in terms of remobilization, erosion, sedimentation, adsorption capacity, and the distribution of metals (Devesa-Rey et al., 2011). Significant effects of grain size on the concentration of heavy metals in sediments have been reported, which indicated that the behavior of heavy metals in the environment was different due to grain size fractions with various composition and properties (Brook and Moore, 1988; Devesa-Rey et al., 2011; Guillén et al., 2012; Yao et al., 2015; Yıldırım and Tokaloğlu, 2016). Therefore, it is significant to distinguish and quantify the geochemical forms of heavy metals in sediments with different grain sizes in order to predict the mobility and bioavailability of metals and develop heavy metal pollution control strategies.

Jiaozhou Bay is a typical bay in coastal China. Due to urbanization and industrial development, heavy metal pollution in Jiaozhou Bay has become serious and attracted much attention. Previous studies reported the distribution of heavy metals in surface or core sediments from Jiaozhou Bay, and most of these evaluated the metal pollution according to the total metal concentrations alone (Dai et al., 2007; Wang et al., 2017). However, to our knowledge, the speciation of heavy metals with different grain sizes was neglected. In addition, the effects of sediment grain size on the accumulation of heavy metals and its bioavailability were never reported. Therefore, an integrated speciation research of heavy metals considering the effects of grain sizes is required in the assessment of the heavy metal pollution for the protection of Jiaozhou Bay. The purposes of this work were to assess the effects of grain size on the accumulation of heavy metals and their bioavailability. We also aimed to address the possible sources and ecological risk of heavy metals to Jiaozhou Bay on a centennial timescale.

## 2. Materials and methods

### 2.1. Study area

Jiaozhou Bay is a semi-enclosed bay, which is located in the western Yellow Sea (Fig. 1), occupying a total area of approximately 390 km<sup>2</sup>, and with the mean depth of 6–7 m (Dai et al., 2007). More than ten small rivers, like Yanghe, Daguhe, Moshuihe, Baishahe and Licunhe rivers, discharge industrial and domestic wastewater and sediments into Jiaozhou Bay (Wang et al., 2017). The concentration of heavy metals generated by anthropogenic activities including shipbuilding, industrial sewage and agricultural activities has substantially increased due to the development of industry, rapid urbanization in Qingdao city (a city adjacent to Jiaozhou Bay) (Li et al., 2011; Wang et al., 2017).

### 2.2. Sediment sampling and grain size separation

One sediment core was obtained in June 2015 from the inner area of Jiaozhou Bay using a gravity sampler deployed on the *R/V Kexue 3* (Fig. 1). The length of core C4 was 82 cm. The sediment core was sectioned at 2 cm intervals. The subsamples were immediately placed in plastic zip lock bags with air being excluded. All samples were stored in the dark at –20 °C for further analysis at the lab.

Previous studies used samples of a variety of grain sizes and different methods of sieving: Yao et al. (2015) used the < 8, 8–16, 16–32, 32–63 and > 63 µm fractions through a water elutriation apparatus. Brook and Moore (1988) used the < 17, 17–38, 38–63, 63–300, and > 300 µm fractions through wet sieving and centrifuga-

tion. Filipek and Owen (1979) used the < 3.9, 3.9–63 and > 63 µm fractions through wet sieving. Analysis of the fraction < 63 µm was recommended in sediment studies because clay and silt particles generally contain the highest concentrations of pollutants, and are most readily transported in suspension in natural waters (Fytianos and Lourantou, 2004). In addition, considering the mass loading of heavy metals exhibiting substantial accumulation in particle size fractions < 32 µm (Yao et al., 2015), and the diluting effect of the > 63 µm fraction, due to its higher content of quartz and feldspars (Devesa-Rey et al., 2011), the sediment samples were separated in to three grain size fractions (< 32 (clay and silt), 32–63 (coarse silt) and > 63 µm (sand)) for the determination of the relationship between grain size and metal contents. To ensure the dispersion and avoid excessive solubilization of sediments, the samples were dispersed in pre-filtered sea water (with 0.45 µm filter membrane) (Tessier et al., 1982). The fraction of > 63 µm was obtained by wet-sieving with nylon sieves. Fractions of < 63 µm were obtained by the precipitation method according to the Stokes Law (Peng and Guo, 2001). Considering the influence of different drying procedures (freeze-drying, oven-drying, air-drying, and the fresh sediment) on speciation analysis including potential artifacts, the reproducibility of analysis and other potential influence (Rapin et al., 1986; Bordas and Bourg, 1998; Baeyens et al., 2003; Huang et al., 2015), the separated fractions were dried at 60 °C for further analysis (Helali et al., 2016).

### 2.3. Elemental analysis

For each grain size fraction of sediment, three chemical fractions, including acid-soluble, reducible, and oxidizable of heavy metals were extracted using BCR procedure (Rauret et al., 1999). Briefly, about 0.20g of homogenized sediment was weighed and loaded into a 50 mL centrifuge tube, and acid-soluble fraction was extracted with 20 mL 0.11 M acetic acid, shaken for 16 h at 22 °C. The sediment residue was extracted with 20 mL 0.5 M hydroxylammonium chloride with continuous shaking for 16 h as reducible fraction. For oxidizable fraction, the residue from reducible fraction was extracted with 5 mL of 30% H<sub>2</sub>O<sub>2</sub> for 1 h, then the tube was covered and heated at 85 °C for 1 h in a water bath, and the volume was reduced to less than 2 mL by further heating of the uncovered tube. After that, another 5 mL of 30% H<sub>2</sub>O<sub>2</sub> was added and heated at 85 °C for 1 h, then the volume was reduced to about 1 mL, and subsequently 25 mL of 1 M ammonium acetate was added to the residue with continuous shaking for 16 h. For the residue fraction, the residue from the oxidizable fraction was digested using the mixture of concentrated HF, HNO<sub>3</sub> and HClO<sub>4</sub> (5:2:1) and heated at 160 °C for 36 h (Yu et al., 2014). Between steps, solid/liquid separation was achieved by centrifuging at 4000 rpm for 5 min, the resulting supernatant being decanted into polyethylene bottles and stored in a refrigerator at about 4 °C before analysis. Residues were then washed with 20 mL high purity water, shaken for 15 min, and centrifuged for 5 min at 4000 rpm, and the supernatant was discarded. Blank reagent solutions were prepared in the same way. The digest was diluted using nitric acid (HNO<sub>3</sub>, 2%) for heavy metal analysis using inductively coupled plasma mass spectrometry (ICP-MS).

### 2.4. Analytical equipment

Elemental analysis of Cr, Mn, Ni, Cu, Zn, As, Cd, Pb and Al was carried out using an inductively coupled plasma mass spectrometry (Agilent7700X ICP-MS) equipped with a high matrix introduction (HMI) system, micromist glass concentric nebulizer, quartz Scott-type Peltier-cooled spray chamber, Nickel cones and octopole reaction system (ORS<sup>3</sup>). Typical instrument operating conditions for ICP-MS spectrometer were: RF power–1550 W; plasma Ar flow rate–14.0 L min<sup>-1</sup>; nebulizer Ar flow rate–0.78 L min<sup>-1</sup> and auxiliary Ar flow rate–1.0 L min<sup>-1</sup>. For calibration curve construction, a mixed standard solution with contents of 100.00 µg mL<sup>-1</sup> for As and Zn and

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