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Source identification and risk assessment based on fractionation of heavy metals in surface sediments of Jiaozhou Bay, China

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ABSTRACT

To identify sources and evaluate ecological risks of heavy metals in sediments of Jiaozhou Bay, contents and chemical fractions of Cd, Cr, Cu, Pb, Zn, Ni, Sb and Sn were studied. Results suggested that higher metal contents appeared at inner bay and near marine dumping area. Labile fractions of heavy metals accounted for 0.5–77% (~36%) of total contents indicating their significant anthropogenic sources. The enrichment levels of Cd and Sb were relatively higher. Cu, Ni, Cd and Zn were at low to medium risks. Cr, Pb, Sn and Sb were at no or low risks. Total contents of heavy metals were mainly controlled by natural sources, while anthropogenic inputs were important sources of labile fractions of heavy metals in sediments of Jiaozhou Bay with industrial and domestic activities as main contributors for Cu, Pb, Zn, Cr, Ni and Sn, and agricultural activities for Cd and regional coal combustion for Sb.

Due to the accumulation processes of chemical adsorption and physical precipitation, heavy metal contents in sediments are significantly higher compared with those in the water body (Leung et al., 2014; Scheibye et al., 2014). In natural state, heavy metals in sediments have no threat to ecosystems. However, ubiquitous use of metals in human society (industry, traffic, agriculture and infrastructure construction) causes the excessive release of heavy metals, inducing the enrichment of heavy metals in sediments, which can be a second source of heavy metals in water and potential threat to aquatic flora, fauna, and microorganisms (Zhang et al., 2016). Besides, heavy metals are regarded as important indicators for anthropogenic activities, e.g., a group of heavy metals including Zn, Cu and Pb is the indicator for automobile traffic in urban environment, while Cr, Zn and Ba for leather industry, V and Ni for marine traffic, Cu, Te and Hg for antifouling paint (Lewan, 1984; Moffett et al., 1997; Tamim et al., 2016; Wei and Yang, 2010). Therefore, the study of heavy metals in sediment is significant in assessing anthropogenic impact on aquatic environments. In recent years, heavy metal pollution in sediments of rivers, lakes and bays has been widely studied (Gao and Chen, 2012; Ra et al., 2014). Previous researches showed that heavy metal accumulation in semi-enclosed bays may cause continual harm to the aquatic ecosystem due to its closure compared with outlying bays (González-Fernández et al., 2011).

Jiaozhou Bay is a typical semi-enclosed bay surround by the city of Qingdao, one of the leading cities in Shandong Peninsula Blue Economic Core Area (Fig. 1). In the past, the city of Qingdao experienced significantly economic development, with the total agricultural output value increasing from 25 million to 9501 million and the total industrial output value from 43 million to 263,05 million between 1949 and 2014 (MSBQ, 2016). There are significant possible metal sources at Jiaozhou Bay area, including Qingdao Port, one of the most important international trading and maritime transportation hub in China, as well as industrial activities including mining (15 plants), tanning (11 plants), petroleum processing (9 plants), metal product industry (380 plants) and electrical machinery manufacturing (217 plants) (MSBQ, 2016). Previous studies on heavy metals in sediments of Jiaozhou Bay mainly focused on the total contents of heavy metals (Wang et al., 2007; Xu et al., 2016). However, the total metal contents in sediments are influenced by not only anthropogenic activities, but also some other nature factors, e.g., TOC contents and grain sizes (Duan et al., 2010), indicating that the total metal contents may obscure the signal of human activities. It has been widely recognized that specific chemical forms of heavy metals in sediments can reveal much more information on different anthropogenic activities, as well as their release potentials under various conditions (Gleyzes et al., 2002; Perin et al., 1997).

In this study, sequential extraction procedure was conducted to

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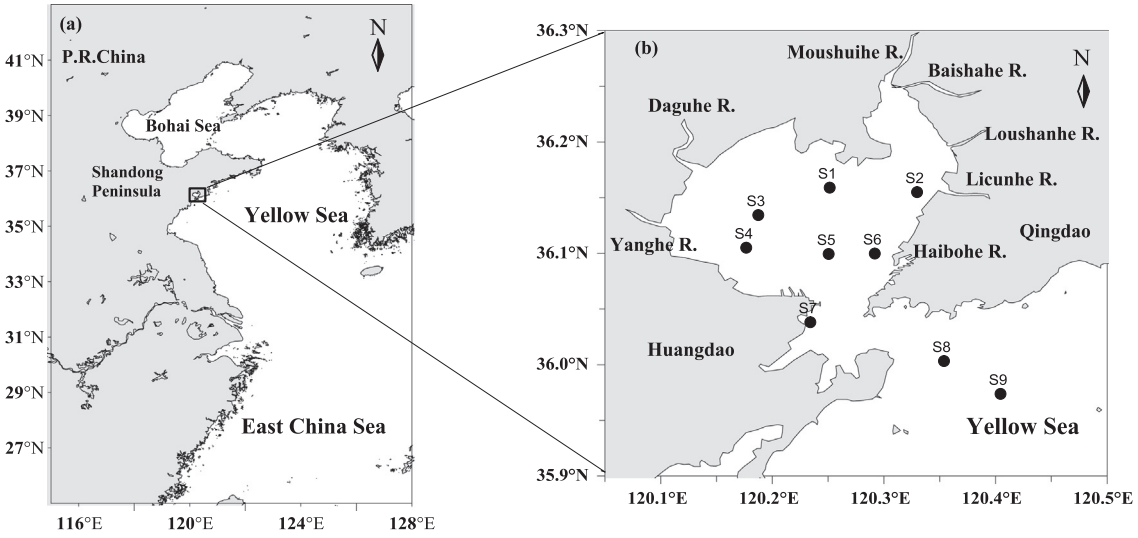

Fig. 1. Locations of Jiaozhou Bay (a) and sampling sites of surface sediments (b).

comprehensively understand the fractional characteristics of heavy metals in surface sediments of Jiaozhou Bay. The objectives of this study were to (1) recognize the chemical characteristics of heavy metals in sediments; (2) assess the enrichment levels and environment risks of heavy metals using different indices; (3) target the potential sources and further identify indicator that best respond to different anthropogenic pressures.

Surface sediments were collected from 9 stations in Jiaozhou Bay using a box grab sampler in May 2015 (Fig. 1). Sub-samples (0–2 cm) were taken from the center of the sediments with a polyethylene spoon. Immediately after collection, samples were kept in pre-cleaned polyethylene bags, sealed and frozen until lab analysis. Sediment samples were dried in an oven at 60 °C for 72 h. Aliquots of dried samples were ground using an agate mortar and pestle for homogenization. Position of sediment sample was recorded by the global positioning system (GPS) technology.

About 0.05 g dry sample was digested for total element contents in a closed Teflon digestion vessel with a mixture of HNO_3-HF-$HClO_4$ (1:3:1) at 150 °C for 48 h. The residue in the vessel was transferred into 50 ml colorimetric tube and the solution was diluted with Milli-Q water to 50 ml. A modified BCR sequential extraction procedure (Yu et al., 2014) was performed on 0.1 g of dried samples. Acid-soluble fraction (F1) was extracted by 20 ml of 0.11 mol·l^{-1} acetic acid (room temperature, 16 h). The residue from the first extraction step was leached with 20 ml of 0.5 mol·l^{-1} hydroxylamine hydrochloride (pH 1.5; room temperature for 16 h) to receive reducible fraction (F2). The residue from the second extraction step was treated twice with 5 ml of 8.8 mol·l^{-1} hydrogen peroxide (pH 2; room temperature for 1 h and then 80 °C for 1 h). After cooling down, 20 ml of 1.0 mol·l^{-1} ammonium acetate was added (pH 2; room temperature, 16 h) to extracted oxidizable fraction (F3). The difference between total element content and the sum of first three extracted fractions was the residual fraction (F4).

Heavy metals (Cr, Cu, Ni, Pb, Sn, Cd, Zn and Sb) and lithophile elements (Al, Th, Sc, Cs and Ti) contents in digestion solution were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; SCIEX Elan 5000). Major elements (Fe, Mn, Ca, Sr and Ba) contents were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; PerkinElmer Optima 3000). The analytical accuracy was guaranteed using standard reference sediments (GBW07309 and GBW07429), with recoveries ranging from 89 to 118% (Table 1). Total organic matter (TOC) contents in sediments were determined by the Walkey-Blake method (Gaudette et al., 1973). The percentages of three grain size groups (< 4 μm for clay, 4–63 μm for silt and > 63 μm for sand) were analyzed by a Laser Particle Size Analyzer (Cilas 940 L).

Table 1
Analytical results of measured and certified contents of heavy metals in standard reference materials (GBW07309 and GBW07429).

Element	GWB07309		GWB07429	
	Measured values	Certified values	Measured values	Certified values
Cr	75.9	85 ± 7	80.4	87 ± 4
Ni	31.0	32 ± 2	37.0	41 ± 1
Cu	29.8	32 ± 2	34	37 ± 2
Pb	21.0	23 ± 3	29.9	38 ± 2
Sb	0.834	0.81 ± 0.15	2.25	1.9 ± 0.2
Sn	2.37	2.6 ± 0.4	4.12	4.5 ± 0.05
Cd	0.334	0.26 ± 0.04	0.340	0.21 ± 0.02
Zn	77.4	78 ± 4	91.9	94 ± 4

The measurement repeatability error of the Laser Particle Size Analyzer was < 3%.

The percentages of sand fraction (> 63 μm), silt fraction (4–63 μm) and clay (< 4 μm) were in ranges of 0.2–64.5%, 35.0–78.8% and 4.5–28.6%, respectively. The highest clay content presented at the central bay (i.e., S5) and the coarse-grained sediments mainly appeared at the bay mouth and outer bay (i.e., S7, S8, and S9). TOC contents ranged from 0.2 to 0.98% and decreased from the inner bay to the outer bay with the higher content at Licunhe estuary, indicating that Licunhe River was an important source of TOC to the inner bay. Major elements of Al, Fe, Ca, Sr and Ba varied from 6.1% to 8.8%, 2.0% to 4.3%, 0.98–1.9%, 166–283 mg·kg^{-1} and 561–811 mg·kg^{-1}, with average values of 7.3%, 3.0%, 1.3%, 218 mg·kg^{-1} and 658 mg·kg^{-1}, respectively. Correlation analysis was applied for contents of TOC, clay, Al, Fe, Ca, Sr and Ba. Results showed that, Al was well correlated with Fe (r = 0.916, p < 0.01), which could be attributed to their common terrestrial sources. Clay contents had significantly positive correlations with Al and TOC contents (r = 0.711, p < 0.05; r = 0.821, p < 0.05), indicating that the spatial distributions of Al and TOC in sediments were affected by sediment type. Ca, Sr and Ba had positive correlations with each other and negative correlations with Al, Fe and clay, suggesting that Ca, Sr and Ba in sediments of Jiaozhou Bay were not from terrestrial sources, and more associated with biological deposition.

Total contents of heavy metals in surface sediments of Jiaozhou Bay displayed different ranges between elements. It possibly reflected their natural abundances, which is not related to anthropogenic activities. For instance, the background values of Sn, Sb and Cd in Chinese soils were lower than 10 mg·kg^{-1} which could be described as relatively low