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Baseline

Historical trends of anthropogenic metals in sediments of Jiaozhou Bay over the last century

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ABSTRACT

Reconstructing heavy metal historical trends are essential for better understanding anthropogenic impact on marine ecosystems. In this work, the ecological risk and sources of Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb in Jiaozhou Bay were studied and the anthropogenic metal emissions was also quantified. The ecological risk was mainly caused by Cd, As and Cu, which presented an increasing trend with increased anthropogenic activities since the 1950s. The statistical analysis show that Cr, Mn, Ni, Cu and Zn were primarily from natural sources. Cadmium and Mn might originate from both natural and anthropogenic sources. Arsenic and Pb were sourced from agricultural activities and atmospheric precipitation, respectively. The anthropogenic flux of Cr, Mn, Ni, Cu, Zn, As, Cd and Pb were 138, 586, 63, 66, 161, 35, 0.31 and 44 mg/m^2/a since the 1950s. Over 40.0% of Cu and As were quantified from anthropogenic emissions since the 1950s.

Heavy metal have been emitted by anthropogenic activities and dispersed into the environment since the beginning of metallurgy (Bao et al., 2017). The accumulation of heavy metals in marine environment can cause serious problems to ecosystems due to their toxicity, persistence and bioaccumulation (Gao et al., 2014). The major sources of heavy metals in marine sediments including natural processes in the ocean and anthropogenic processes such as industrial manufacturing, the incineration of urban and industrial wastes (Chen et al., 2014; Cao et al., 2015; Guo and Yang, 2016). The relative contributions of anthropogenic sources to global emissions of heavy metals have considerably varied with time. Sediments in marine environments usually act as sink for metals and provide an excellent proof of anthropogenic impacts (Bao et al., 2017; Wang et al., 2017). Heavy metal signals recorded in dated sediment cores have shown to be an excellent tool for reconstructing the effects of anthropogenic activities and natural processes on marine environments. A number of researches have used sediment cores from marine, lake, wetland and peat bog environments to investigate and reconstruct historical records of contaminant inputs in these environments (Vleeschouwer et al., 2009; Bing et al., 2011, 2016; Guo and Yang, 2016; Bao et al., 2017; Wang et al., 2017).

Jiaozhou Bay is a semi-enclosed bay, which is located on the western Yellow Sea, cover a total area of approximately 390 km^2, and with the mean depth of 6–7 m (Dai et al., 2007). More than ten small rivers, including the Yanghe, Daguhe, Moshuihe, Baishahe and Licunhe rivers, discharge wastewater and sediments into Jiaozhou Bay (Wang et al., 2017). In recent decades, the Jiaozhou Bay is severely disturbed by anthropogenic activities (Yuan et al., 2016), with the development of industry and rapid urbanization in Qingdao city (a city adjacent to Jiaozhou Bay). As a result, the concentration of heavy metals generated by industrial and agricultural activities has substantially increased (Li et al., 2011; Wang et al., 2017). Thus, it is of great significance to evaluate the impact of anthropogenic activities on the heavy metal pollution in this area.

Most of the studies, so far, have been focused on understanding the temporal and spatial distributions of heavy metal in Jiaozhou Bay (Dai et al., 2007; Wang et al., 2017). Nevertheless, the previous studies present the results before the year of 2003 (Dai et al., 2007). There was a lack of research to reveal detailed evolution of the heavy metals during the last decade. In fact, the heavy metal pollution in Jiaozhou Bay was serious in recent decade. Although Wang et al. (2017) report the results before 2009, whose sampling station was located at the costal of Jiaozhou Bay. It is insufficient to represent the entire bay when

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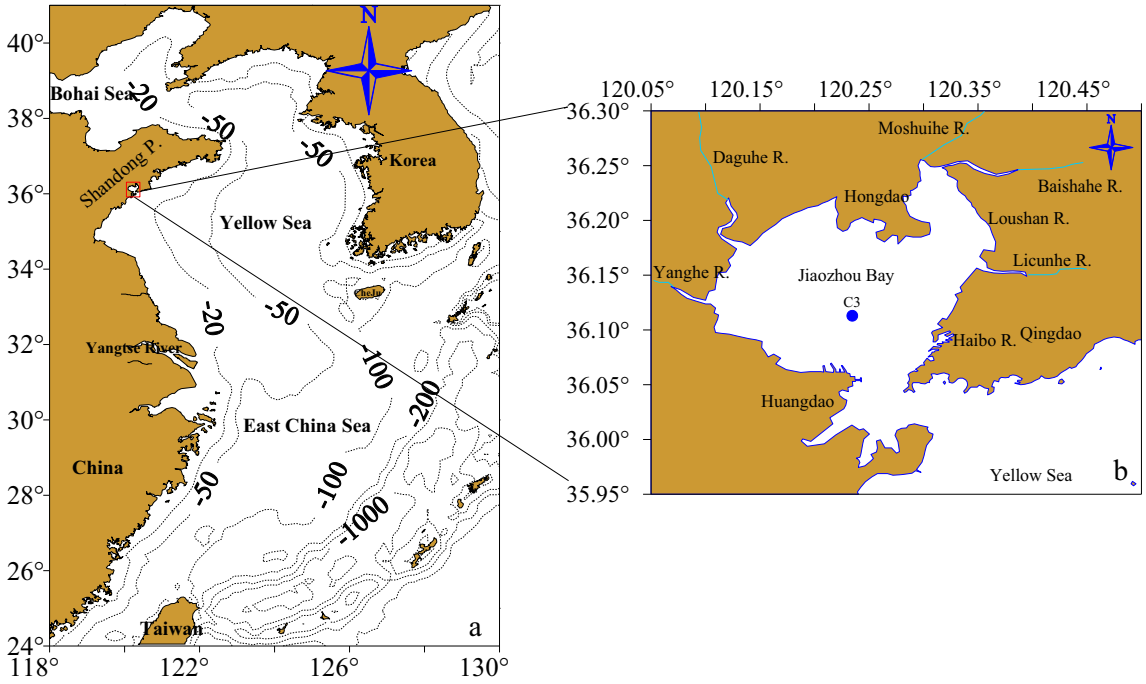

Fig. 1. Study area. (a) East China marginal seas and the location of Jiaozhou Bay (inside the red rectangle). (b) The blue point indicated the sampling station of Jiaozhou Bay. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compared to sampling stations at the center of the bay. Moreover, to our knowledge, distinguish and document the temporal trends of natural versus anthropogenic heavy metals were neglected. The present study aims to reconstruct the heavy metal history and evaluate the possible source and ecological risk of heavy metals during the last century in Jiaozhou Bay. We also aimed to differentiate anthropogenic versus natural sources of heavy metals and quantitatively distinguish anthropogenic contribution to heavy metal accumulation.

A 60 cm sediment core (C3) was retrieved at 13 m depth on June 2015 from the central part of Jiaozhou Bay using a gravity sampler while aboard the *R/V Kexue 3* (Fig. 1). The core was sub-sampled at a 2 cm resolution. The subsamples were placed in plastic zip lock bags with air being excluded. All samples were stored in the dark at −20 °C prior to analysis. Sediments for heavy metal analysis were oven dried at 60 °C and ground to a fine powder with an agate mortar (Guo and Yang, 2016).

Briefly, about 50 mg of homogenized sediment were completely digested using the mixture of concentrated HF, HNO_3 and $HClO_4$ (5:2:1) and heated at 160 °C for 36 h (Gao et al., 2015). The concentrations of heavy metals (Cr, Mn, Ni, Cu, Zn, As, Cd and Pb) and the lithogenic metals (Al, Fe and Ti) were measured using an inductively coupled plasma mass spectrometry (Agilent7700X ICP-MS). Quality assurance and quality control were assessed in duplicates, with blanks samples and standard reference materials (Kang et al., 2017a). The quality of the analytical procedures was tested by recovery measurements on the Chinese national geo-standards GBW07309. Five replicates were conducted for the determination of the total content of the metals in reference materials. The results were consistent with the reference values, and the differences were all within 10%, with recovery ranging from 93 to 98% ($n = 5$). The precision, expressed as the relative standard deviation, ranged from 5% to 10%.

The core C3 was dated using ^{210}Pb radionuclide. The ^{210}Pb chronology and sedimentation rate were determined by measuring the ^{210}Pb activity through its granddaughter product ^{210}Po with ^{208}Po added as yield monitor. The activities of Po isotopes (i.e. ^{210}Po and ^{208}Po) were counted using α-spectrometry. The excess ^{210}Pb in each sample was obtained by subtracting the activity of ^{210}Pb in the background value from the total activity of ^{210}Pb. Then the excess ^{210}Pb was used to develop a chronology using the constant initial concentration (CIC) dating model (Dai et al., 2007). Geochronology of core C3 has been discussed by Li et al. (2003) and Kang et al. (2017b) in detail and the results were cited in this study. The sedimentation rate was 0.64 cm/a for core C3. It is obtained that the sediment core covered a period of 1923–2015.

To minimize the potential influence of sediment texture (e.g. grain size) on metal concentrations and identify sources and reflect the degree of heavy metal pollution in sediments, enrichment factors (EF) are used (Liu et al., 2015). The EF is calculated based the following formula:

$$\mathrm{EF} = \frac{(\mathrm{Me/Al})_{\mathrm{sample}}}{(\mathrm{Me/Al})_{\mathrm{background}}}$$

where $\mathrm{Me}_{\mathrm{sample}}$ and $\mathrm{Al}_{\mathrm{sample}}$ represent the concentrations of target heavy metals and Al in the sample, respectively, and $\mathrm{Me}_{\mathrm{background}}$ and $\mathrm{Al}_{\mathrm{background}}$ represent the average value of heavy metals and Al in sediments before the 1940s. Before the 1940s, the modern industrialization and urbanization of Qingdao city was relatively lower. Therefore, the mean concentrations of heavy metals prior to the 1940s were used as the relative reference concentration in order to discuss the modern anthropogenic contribution to the metal enrichment in the sediment.

Aluminum is typically a conserved element and mainly from natural source. Normalization of heavy metals to Al could minimize the variability of sediment profiles due to mineralogy and grain size effect (Chen et al., 2014; Gu et al., 2015). Therefore, we used Al as a reference element and calculated the EF. The EF below 1.5 usually indicated the metal was from natural weathering process. While, the EF > 1.5 suggested that the anthropogenic source may be an important contributor (Gu et al., 2015).

The potential ecological risk index (RI) was widely used to quantitatively assess the ecological risk induced by heavy metals (Hakanson, 1980; Chen et al., 2014). It is calculated by the following formula:

$$RI = \sum_{i=1}^{8} Er^i = \sum_{i=1}^{8} \frac{Tr^i \times C_i}{C_b}$$