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Heavy metals in surface sediments along the Weihai coast, China: Distribution, sources and contamination assessment

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ABSTRACT

The Weihai coast is a representative zone with fifty-year history of mariculture in China. Algae and shellfish are the main cultured species, other species including fish and sea cucumber are also cultivated. In this study, heavy metals in surface sediments, sampled along the Weihai coast during May yearly between 2009 and 2013 were investigated in terms of their contents and spatiotemporal variation. The contents of Zn, Cr, Cu, Cd, Pb and As showed different spatiotemporal variations and ranged between 11.6 and 115.9, 4.15–51.3, 5.2–21.9, 0.02–0.33, 6.0–54.2, and 2.9–18.7 μg g^{-1}, respectively. Among them, Zn, Cu and As declined during the five years. Ecological risk assessment revealed that Cd posed a moderate risk, as compared to other five elements, which were relatively low risks in surface sediments. Source analysis revealed that Zn, Cr and Cd were mainly from lithogenic contribution, while As was likely from anthropogenic discharges.

Heavy metal pollution is a serious threat to marine environment due to their high toxicity, non-degradability, bioaccumulation and biomagnification (Bryan and Langston, 1992; Wong et al., 2002; Diagomanolin et al., 2004; Luoma and Rainbow, 2008). To date, 12 species of heavy metals have been classified as priority pollutants, including As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Ti, and Zn (Protano et al., 2014; Li et al., 2015a, 2015b). Marine sediment is a large reservoir for heavy metals, monitoring heavy metals in sediment is considered as an approbatory approach for environmental quality assessment (Bellucci et al., 2002; Ianni et al., 2010; Collier et al., 2012).

The Weihai coast is a representative mariculture region in northern China (Guo et al., 1999). The annual production of kelp, shellfish, sea cucumber and fish cultured here, were 5.0×10^5 tons (dry weight), 9.1×10^5 tons (wet weight), 1.8×10^4 tons (wet weight) and 4.1×10^4 tons (wet weight), respectively during 2014 (the Bureau of Statistics of Weihai city, http://www.stats-wh.gov.cn/), which were largely responsible for people's increasing demand for marine food supplies. In recent years, with the booming industrialization and urbanization of the Weihai city, increasing heavy metals are brought to the coastal waters annually with industrial wastewaters, agricultural discharges, municipal sewage and surface run-off (Cui et al., 1997; Jiang et al., 2008). For example, Muzhu (122.0°E) and Rushan (121.5°E) Rivers are the largest two rivers that flow through the Weihai city, which discharged 8.63 t y^{-1} of heavy metals (including Zn 3.51 t y^{-1}, Cr 3.05 t y^{-1}, Cu 0.82 t y^{-1}, Pb 0.33 t y^{-1}, Cd 0.20 t y^{-1}, As 0.72 t y^{-1}) into the Weihai coastal water during 2011 (MEB, 2011). If anthropogenic heavy metal residues in the underwater surface sediments accumulate in the cultured organisms, metals may enter into the food chain and consequently result in human health problems, even the death, growth reduction, impaired reproduction of aquatic organisms (Olivares-Rieumont et al., 2005; Praveena et al., 2007). Whether the mariculture environment along the Weihai coast is polluted by heavy metals needs to be investigated so as to assess their potential risk to seafood security and human health.

The present study is designated to examine the spatiotemporal variation, pollution status, possible sources and potential ecological risks of heavy metals (Zn, Cr, Cu, Cd, Pb and As) in surface sediments, *via* analyzing five cruises data along the Weihai coast during May yearly, 2009–2013.

The Weihai coast is located in the most eastern part of Shandong Peninsula, China (36°30′–37°45′ N, 121°15′–122°50′ E), which is belonging to the Yellow Sea (Fig. 1). The average water depth is 12.8 m, and the maximum water depth is 45 m (Li and Gao, 2014). Six primary bays along the Weihai coast, *i.e.* the Weihai Bay, Rongcheng Bay, Sanggou Bay, Jinghai Bay, Wulei Bay and Rushan Bay, have been

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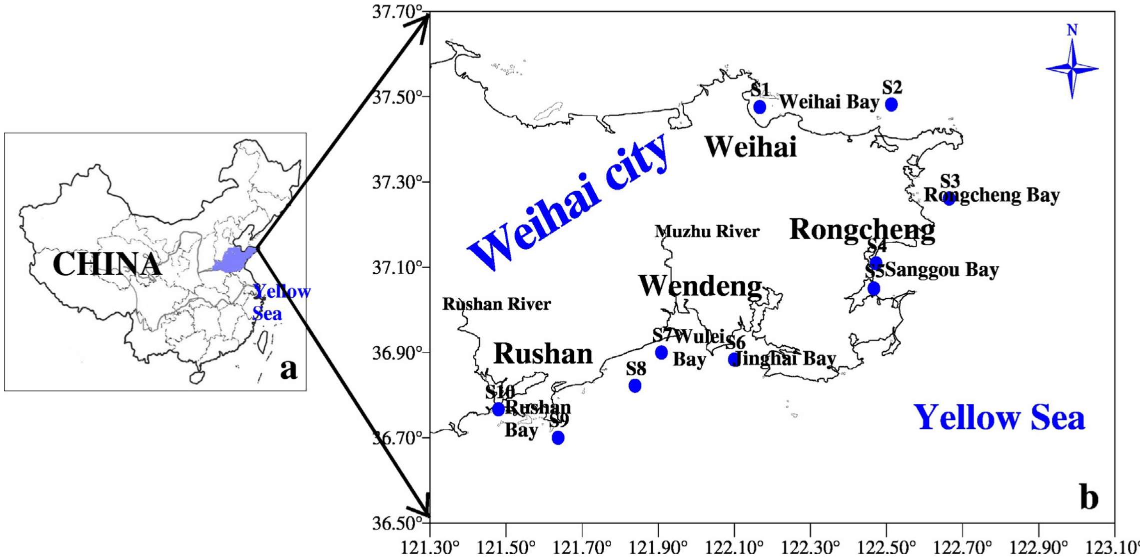

Fig. 1. Maps of the study area. (a) Map of China, including the entire Shangdong peninsula (blue region); (b) the Weihai coast. Blue circle symbols (S1–S10) represent sampling stations that were investigated during May yearly from 2009 to 2013. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

employed for mariculture activities for >50 years (Troell et al., 2009) (Fig. 1b). Among them, Rongcheng Bay and Sanggou Bay are usually featured with integrated mariculture by shellfish and kelp (Jiang et al., 2015), whereas Wulei Bay and Rushan Bay are dominated by the single shellfish farming. Only limited areas are for sea cucumber or fish farming in these bays.

Sediment samples were collected from ten stations during 8–16 May yearly, 2009–2013. The ten stations were separately located at the six mariculture bays in the study area (Fig. 1b). Surface (top 2 cm) sediments were collected with a Peterson grab, then were taken with a polyethylene spatula and placed in acid-rinsed polyethylene zipper bags. Duplicate samples were collected at each station. All samples were stored in a cooler at 4 °C, then were frozen at −20 °C after being transferred to the laboratory immediately for further analysis (Lasorsa and Casas, 1996). Before analysis, the sediments were defrosted at room temperature, dried at 50 °C to constant weight (~24 h) (Hyun et al., 2007), and ground in an agate mortar (Zhao et al., 2016).

For acid digestion, ~0.10 g of each dried and homogenized sample was put in a Teflon bomb containing 8 ml of mixed acid solution (HNO_3:$HClO_4$:HF = 5:4:1, in volume) (Loring and Rantala, 1992). The solution was heated at 120 °C for 12 h on an electric heating thermostat. The above steps of acid digestion were repeated until there was no brown fume. Afterwards, the mixture was evaporated to semi-dryness. The contents of Zn, Cr, Cu, Cd, Pb metals were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo Fisher Scientific, XSeries II, USA). The As content was measured using Atomic Fluorescence Spectrometry (AFS, Beijing Haiguang Instrument Co.AFS-2202). The digestion solution was reduced by thiourea–HCl mixture before measuring the As content (Fu et al., 2014). Total organic carbon (TOC) in sediments was obtained by a Perkin-Elmer 2400 Series II CHNS/O Analyzer (Perkin Elmer Inc., USA) after inorganic carbon was removed with 1 M HCl. The grain size measurements of sediment samples were performed with a laser granulometer (Malvern Mastersizer 2000) to calculate the percentages of its clay (<4 μm), silt (4–63 μm) and sand (>63 μm) fractions.

For quality control and assurance, reagent blanks and standard reference materials (Sediment from Yellow Sea, GBW 07333) were used for each of the testing items. All sediment samples were analyzed in triplicate to guarantee the analytical precision. Our obtained contents of heavy metals were consistent with the reference values (Table 1), the differences were all within ±10%, and the analytical precision ranged from 5% to 10%. Recoveries for six heavy metals were between 93% and 104%.

Pearson's Correlation Coefficients (PCC) and Principal Component Analysis (PCA) are two statistical approaches that widely used for analyzing the sources of heavy metal in sediments (Facchinelli et al., 2001; Tariq et al., 2006; Wang et al., 2015). PCC was performed to assess if there was a significant relationship between pairs of variables. Significant difference was considered when $P < 0.05$. PCA was used to distinguish the association between contents of heavy metals, grain size and TOC. Both of the PCC and PCA analysis were conducted by software SPSS 16.0 (Shine et al., 1995).

Additionally, the contamination factor (*CF*) and geoaccumulation index (I_{geo}), as common quantitative geochemical indexes, were employed to estimate the pollution status of heavy metals in sediments. Meanwhile, the potential ecological risk index (*ER*) was used to evaluate the ecological risk posed by heavy metals (Villaescusa-Celaya et al., 2000; Çevik et al., 2009; Dou et al., 2013; Wang et al., 2015). Due to lack of relevant background data for unpolluted marine sediment in the study area, the national soil background values in China were used for the calculation of the above three parameters (*CF*, I_{geo} and *ER*): Zn, 67 μg g^{-1}; Cr 54 μg g^{-1}; Cu, 20 μg g^{-1}; Cd, 0.08 μg g^{-1}; Pb, 24 μg g^{-1}; As, 9.20 μg g^{-1} (Chen et al., 1991), as performed by previous studies (Cheng et al., 2013; Li et al., 2013b).

The *CF* was calculated using the Eq. (1), which was the ratio of the measured content in the samples (C_{sample}) to background abundance ($C_{background}$) of a given metal:

$$CF = (C)_{Sample}/(C)_{background} \quad (1)$$

Table 1
Analytical results of certified and obtained values (μg g^{-1}) of elements in standard reference materials of GBW07333.

Element	Measured values	Certified reference values
Zn	115.8	114 ± 6
Cu	29.5	29.1 ± 1.1
Pb	30.1	29.0 ± 1.6
Cr	104	107 ± 4
Cd	0.26	0.28 ± 0.03
As	7.9	7.6 ± 0.5

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