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Assessment of heavy metal contamination in surface sediments of the west Guangdong coastal region, China

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ABSTRACT

Heavy metals (As, Cd, Cr, Cu, Hg, Pb, Zn), organic carbon and grain size of 237 surface sediment samples and one sediment core, taken from the west Guangdong coastal region in January 2008, were analyzed to evaluate the spatial distribution and pollution status. Results show that the ranges of the measured heavy metal concentrations in sediments are as follows: 8.33–39.49 mg/kg for As, 0.1–1.49 mg/kg for Cd, 33–108 mg/kg for Cr, 11.5–78.8 mg/kg for Cu, 0.04–0.26 mg/kg for Hg, 21–73 mg/kg for Pb, 56–248 mg/kg for Zn. The heavy metal enrichment is closely associated with Corg and grain size. Both the metal enrichment factor and geoaccumulation index indicate that there was no detected pollution on metals As, Cr, Cu, Pb in our study area and a slight to moderate contamination of Cd, Hg and Zn. However, As, Cr and Cu have showed a certain risk.

Heavy metals are among the most serious pollutants within the natural environment and can be a serious threat to ecosystems at a global scale, due to their toxicity, persistence and potential to bioaccumulate (Ghaderi et al., 2012; Haruna et al., 2011; Tam and Wong, 2000). With the rapid industrialization and economic development in coastal region, heavy metals are continuing to be introduced to estuarine and coastal environment through river discharge, oceanic dumping and aeolian processes (Bastami et al., 2015; Suresh et al., 2015; Wu et al., 2014a, b; Yang et al., 2015a). Sediments are enumerated as sources of heavy metals in marine environments and play a key role in transmission and deposition of metals. Accumulated heavy metals in sediment can be chemically altered by organisms and converted into organic complexes, some of which may be more hazardous to animal and human life, via the food chain (Bastami et al., 2014). The spatial distributions of heavy metals in sediments are of primary significance in locating pollution sources (Birch et al., 2001; Liu et al., 2003; Zhou et al., 2007).

As one of the most developed industrial areas in China and the manufacturing base in the world, during the past several decades, the economic growth has resulted in the excessive release of heavy metals to the coastal waters in Guangdong Province, which caused severe heavy metal contamination in sediments, water and marine organisms (Ip et al., 2007; Kwok et al., 2014; Zhang et al., 2015a; Zhang et al., 2015b). Nevertheless, previous studies mostly focused on Pearl River Estuary, and few work on large-scale environmental assessments for west Guangdong coastal regions have been reported so far. Many rivers surrounding the west Guangdong coastal region, have provided a large amount of agricultural, residential and industrial wastewater. Heavy metal discharge into coastal regions by these rivers through the Pearl River Estuary, Modao Gate, Jiti Gate, Huangmaohai Estuary, Guanghai Bay, and Zhenhai Bay probably has exerted an effect on the marine environment. In this study, we present the distribution and pollution degree of heavy metal in the west Guangdong coastal region. Our main objectives are: (1) to reveal the spatial distribution of heavy metals (As, Cd, Cr, Cu, Hg, Pb, and Zn) in the study area; (2) to determine the background values of heavy metals by ^{210}Pb; and (3) to evaluate the metal contamination using the enrichment factor (EF) and geoaccumulation index (Igeo).

Two hundred and thirty-seven surface sediment (0–5 cm) samples and one sediment core (SSZ21) with 204 cm in length were collected from the west Guangdong coastal region in January 2008 (Fig.1). Each of the surface sediment samples was put in clean cloth bags and enclosed by polyethylene bag in the field. At encampment the samples in cloth bags were taken out from polyethylene bags to be air-dried at room temperature for several days. These samples which have been fully air-dried were sieved with a 10 mesh

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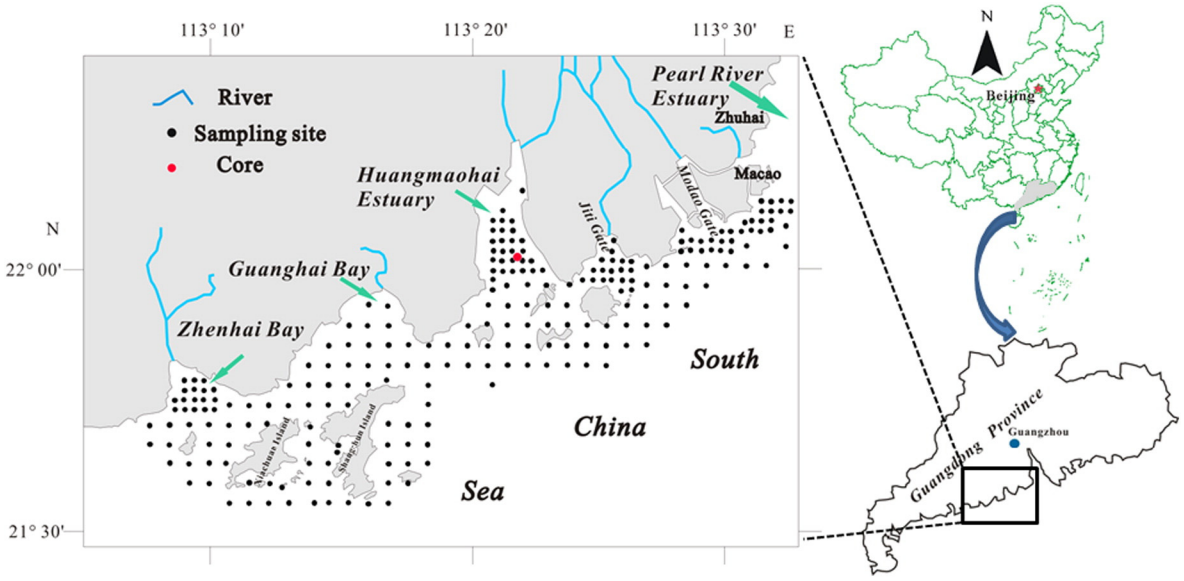

Fig. 1. Location of the study area and sampling sites.

(<2 mm) nylon sieve and enclosed in new polyethylene bags individually, and then were submitted to the laboratory for chemical analysis. Core sample was taken with a vibrating sampler and sliced in 4 cm long sections for further grain size, element analysis and radionuclide measurement.

The sediment samples were pretreated with 10% H_2O_2 to digest the organic matter. The excessive H_2O_2 solution was removed by heating and evaporation. After that, 0.5% of sodium hexameta-phosphate was added to the samples, making the sediments completely dispersed, and then the mixture was analyzed with a Mastersize 2000 laser particle size analyzer at the Qingdao Institute of Marine Geology, China Geological Survey (QIMG, CGS).

Sediment samples were dried at a constant temperature (<60 °C) and ground through a 250 mesh for elemental analysis. The samples were treated and determined according to analytical elements as follows: (1) Measurement was carried out using the inductive coupled plasma mass spectrometry (ICP-MS) for Cd, Cu. The sample was dissolved by evaporating to dryness with a mixed acid of HF + HNO_3 + $HClO_4$. The residue was redissolved with aqua regia. The detailed procedure followed the method described by Xia et al. (2011); (2) Arsenic (As) and Hg were analyzed using Atomic Fluorescence Spectrometry (AFS); (3) The sample was pelletized and determined by wavelength dispersive X-ray fluorescence spectrometry PANalytical AXIOS PW4400 for Cr, Pb, Zn and Al_2O_3, according to the method described by Xia et al. (2008). Calibration was made using certified reference materials and α correction applied to correct for matrix interferences; and (4) organic carbon was determined by wet oxidation in an acid dichromate solution, followed by back titration of the remaining dichromate using a ferrous ammonium sulfate solution. The analytical methods and detection limits of element determinations are listed in Table 1. Quality was ensured by duplicate analysis and comparison with standard reference materials (see Zhou et al., 2014 for details). The differences in concentrations between the determined and certified values were required to be less than 5%. The precisions (RSD%) of the reference materials range from 4.53% to 8.73% (Table 1).

Table 1
Analytical methods and detection limits.

Indicator	Analytical method	Detection	Unit	RSD%
As	AFS	1	μg/g	7.2
Cd	ICP-MS	0.02	μg/g	7.95
Cr	XRF	5	μg/g	4.66
Cu	ICP-MS	1	μg/g	5.8
Hg	AFS	0.003	μg/g	8.73
Pb	XRF	2	μg/g	7.01
Zn	XRF	2	μg/g	5.97
Al_2O_3	XRF	0.05	%	4.53
Corg	Electric potential	0.10	%	7.8

^{210}Pb and ^{226}Ra were analyzed using the BE3830 gammaray spectrometer (made in Canberra Company of USA) at the Testing Center of QIMG, CGS, following a procedure similar to that of Xia et al. (2011). The counting uncertainties associated with sample measurements were typically less than 10% based on triplicate samples. Supported ^{210}Pb activities were assumed to be equal to the measured ^{226}Ra activities, and ^{210}Pb activities (^{210}Pbxs) were calculated by subtracting supported ^{210}Pb activities from total ^{210}Pb activities (^{210}Pbtot) (San Miguel et al., 2004). The apparent sediment accumulation rates were calculated by the CRS model (Appleby and Oldfield, 1992). The ^{210}Pb geochronology was calculated using the equation.

$$T = \lambda^{-1} \cdot \ln(A_0/A_h). \quad (1)$$

where A_0 and A_h are the ^{210}Pbxs accumulation fluxes below the sediment–water interface and the depth h, respectively. λ is the ^{210}Pbxs radioactive decay constant (0.03114 y^{-1}).

Heavy metal concentrations and the basic physic-chemical parameters (percentages of Corg and clay) in the surface sediments from the west Guangdong coastal region, are summarized in Table 2. The ranges of Corg and the fine fraction (clay, <2 μm) contents of analyzed sediments are 0.23%–1.65% and 0%–41.35%, respectively. Their average values are 0.84% and 22.01%, respectively. The concentrations of As, Cd, Cr, Cu, Hg, Pb, and Zn range between 8.33 and 39.49, 0.1 and 1.49, 33 and 108, 11.5 and 78.8, 0.04 and 0.26, 21 and 73, and 56 and 248 mg/kg, respectively. The mean value of heavy metal concentrations in the study area follows a descending order as: Zn (139.93 mg/kg) > Cr (86.97 mg/kg) > Pb (44.29 mg/kg) > Cu (43.83 mg/kg) > As (20.83 mg/kg) > Cd (0.38 mg/kg) > Hg (0.13 mg/kg). The spatial distribution of Cd differs largely, and variable coefficient of Cd is 60.91%, demonstrating that it may be from the point source input in several sites.

The heavy metal concentrations obtained in this investigation and heavy metal concentrations published by previous studies in the Pearl River estuary, Daya Bay and some other estuaries are listed in Table 3. The mean values of heavy metal concentrations in the study areas are higher than those in the Daya Bay, southern Bohai Bay, Liaodong Bay,

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