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Distribution and contamination of heavy metals in surface sediments of the Daya Bay and adjacent shelf, China

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ABSTRACT

Heavy metal (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), and zinc (Zn)) concentrations from the Daya Bay and adjacent shelf were determined to evaluate their levels and spatial distributions. The measured concentrations ranged from 1.94–13.67 mg/kg for As, 0.03–0.13 mg/kg for Cd, 10–85 mg/kg for Cr, 1–39.5 mg/kg for Cu, 0.01–0.09 mg/kg for Hg, 11–56 mg/kg for Pb, and 13–125 mg/kg for Zn. The spatial distributions exhibited a gradual decrease from west to east, and the concentrations of the seven heavy metals met the China Marine Sediment Quality criteria. Both metal enrichment factor (EF) and geo-accumulation index (Igeo) values showed that Cd, Cr, Cu, Hg, and Zn were not at pollution levels in the region. Multivariate analysis (PCA) revealed that lithogenic factors dominated the distribution of most of the metals, whereas As and Hg were clearly influenced by anthropogenic input.

Contamination of heavy metals in aquatic environments has recently drawn attention due to their high toxicity, persistence, and bioaccumulation (Bastami et al., 2015a; Bastami et al., 2015b; Hu et al., 2013a; Li et al., 2013a; Li et al., 2013b; Liu et al., 2015; Ravisankar et al., 2015; Song et al., 2014; Suresh et al., 2015; Wang et al., 2015; Xu et al., 2015; Zhang et al., 2015a; Zhang et al., 2015b). With rapid industrialization and economic development in coastal regions worldwide, heavy metals have been continuingly introduced to coastal environments through rivers, runoff, and land-based point sources where metal refinishing by-products are produced. When metals enter the marine environment, most settle and become incorporated into sediment, together with organic matter, iron/manganese (Fe/Mn) oxides, sulfides, and clay (Wang and Chen, 2000). Accumulated heavy metals in sediment can be chemically altered by organisms and converted into organic complexes, some of which may be hazardous to animal and human life via the food chain (Bastami et al., 2014). Therefore, it is important to understand the distribution of heavy metals in sediments to develop strategies and approaches for pollution control (Dou et al., 2013).

Coastal bays, which are regions of active land-ocean interaction, are sensitive to natural processes and anthropogenic activities (Li et al., 2007). Heavy metal contamination in sediments of these areas poses an environmental problem due to potential metal transfer to aquatic biota (Filgueiras et al., 2002). Daya Bay (DYB) is a semi-enclosed shallow bay located in the north-east part of the Pearl River Estuary. Since the 1980s, there has been a rapid expansion in aquacultural, industrial, and agricultural activities in the area, with simultaneous development in harbor construction, transportation, and tourism. Such dramatic changes have adversely affected the water quality in the bay (Zhou et al., 2001). The population nearly doubled from 1986 to 2002, and total industrial output of the main townships along the DYB coast increased 7.8 times from 1993 to 2001 (Wang et al., 2008). Although several heavy metal contamination studies in the DYB have been conducted in recent years (Gao et al., 2010; Yu et al., 2010), sampling density has been insufficient and heavy metal indices incomplete. In addition, as most of the water in the DYB originates from the South China Sea, water from the Pearl River Estuary affects the DYB via the South China Sea during flood seasons (Yu et al., 2010). Thus, high-resolution and improved heavy metal index sampling in the DYB and adjacent shelf are urgently needed. In this study, we aimed to (1) quantify and investigate the spatial distribution of heavy metals in surface sediments from the DYB and adjacent shelf; (2) assess the state of heavy metal contamination using the enrichment factor (EF) and geo-accumulation index (Igeo); and (3) analyze the sources and transport pathways of heavy metals.

The DYB has a surface area of 650 km^2 and coast line of 92 km. No large river discharges directly into the bay, but there are over 10 seasonal streams running into it along the coast (Han, 1995). The tidal current in the DYB is dominated by an irregular semidiurnal tide, and the mean

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tidal range is 1.01 m with a maximum of 2.57 m. Surface water of the DYB has an average resident time of 3.2 d (Wang et al., 1996). The annual mean precipitation is 1827 mm, and dry and rainy seasons can be easily distinguished (Han, 1995). The water depth ranges from 6 m to 15 m, with the average of 10 m (Du et al., 2008; Wang et al., 1996; Xu, 1989). The climate is mild, wet subtropical, with annual variations in water temperature from 14.0 °C (winter) to 32.8 °C (summer) and an average of 23.5 °C. Salinity is usually between 22.7 and 33.8, and fluctuates little, except in the typhoon season (Wang et al., 2008; Wang et al., 2006).

We collected 159 surface sediment (0–5 cm) samples from the DYB and adjacent shelf using grab samplers in January 2008 (Fig. 1). In the sampling process, each sample was placed in a clean cloth bag and then enclosed in a polyethylene bag in the field. At encampment, the samples in the cloth bags were removed from the polyethylene bags and air-dried at room temperature for several days. The fully air-dried samples were then sieved with a 10 mesh (<2 mm) nylon sieve and enclosed in new polyethylene bags individually, before being submitted to the laboratory for chemical analysis.

The samples were treated and concentrations determined according to analytical elements as follows: (1) Samples were dissolved by evaporating to dryness with a mixed acid of $HF + HNO_3 + HClO_4$. The residue was redissolved with aqua regia. The supernatant was pipetted and diluted with HNO_3 (3 + 97). Measurement was carried out using a VG Elemental ICP–MS for Cd and Cu and atomic fluorescence spectrometry (AFS) for As and Hg; (2) For Cr, Pb, Zn, Al_2O_3, and Fe_2O_3, samples were pelletized and determined by wavelength dispersive X-ray fluorescence spectrometry (PANalytical AXIOS PW4400). Calibration was made using certified reference materials and α correction applied to correct for matrix interferences; (3) Organic carbon (Corg) 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. All chemicals were of analytical reagent grade and contained very low concentrations of heavy metals. Normal precautions for heavy metal analysis were observed throughout the experiment. All glassware and Teflon vessels were previously soaked overnight with 20% HNO_3 and then rinsed thoroughly with deionized water. Sediment Reference Materials (GBW07317, GSS1, GSS2, and GSS8) were used as analytical quality controls. Recoveries were between 90% and 99% for all metals, with a precision of 10%.

Table 1
Analytical methods and detection limits.

Indicator	Analytical method	Detection limit	Unit
As	AFS	1	μg/g
Cd	ICP-MS	0.02	μg/g
Cr	XRF	5	μg/g
Cu	ICP-MS	1	μg/g
Hg	AFS	0.003	μg/g
Pb	XRF	2	μg/g
Zn	XRF	2	μg/g
Al_2O_3	XRF	0.05	%
Fe_2O_3	XRF	0.05	%
Corg	Electric potential	0.10	%

For sediment grain size analysis, an appropriate amount of sample was placed into a beaker, with 15 mL of H_2O_2 solution (30%) added to soak the sample for 24 h to remove organic matter. The sample was then bathed in 5 mL of HCL solution (3 mol/L) for 24 h to remove calcareous cement and shell materials. All samples were fully desalted and dispersed before measurements. Grain size analysis was performed using a Mastersizer 2000 instrument (Malvern Ltd., UK), with a measurement range of 0.02–2000 μm, resolution of 0.01 Φ, and repeated measurement error of <3%.

Results of mean grain size and heavy metal (As, Cd, Cr, Cu, Hg, Pb, and Zn), Al_2O_3, and Corg concentrations of the surface sediment samples from the DYB and adjacent shelf are listed in Table 2. The surface sediments were primarily composed of silt with a mean size of 6.24 φ. The percentage of mud (silt and clay fractions) varied between 18.2% and 99.6%, with a mean value of 86.4%. The concentrations of Corg ranged from 0.14% to 1.51%, with an average value of 0.77%, which is higher than that of the eastern Beibu Bay (0.49%) (Dou et al., 2013) and the Yangtze River Estuary (0.7%) (Zhang et al., 2009). Comparisons of the heavy metals in the study area with those of other regions worldwide are listed in Table 3. Results showed that the average concentrations of Cu, Pb, and Zn were lower than those previously determined

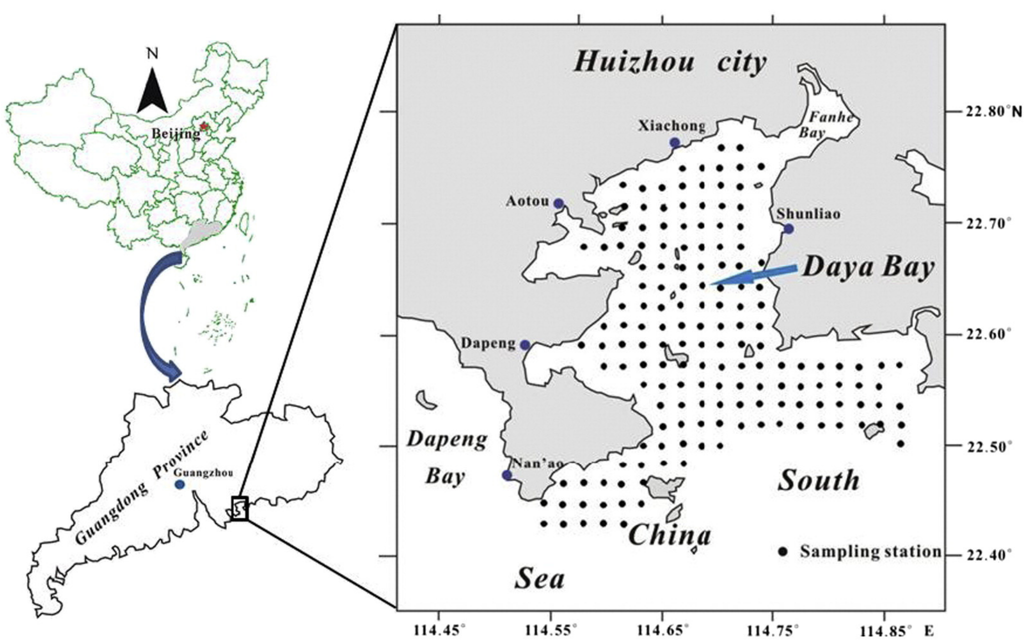

Fig. 1. Location of the study area and sampling sites.

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