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Contamination level, chemical fraction and ecological risk of heavy metals in sediments from Daya Bay, South China Sea

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ABSTRACT

Contamination level, chemical fraction and ecological risk of heavy metals in sediments from Daya Bay (DYB) were conducted in this study. The results revealed that the concentration of Cr, Cu, Zn, As, Cd and Pb in sediments were in the range of 36.38–90.33, 9.54–61.32, 33.54–207.33, 7.80–18.43, 0.13–0.43 and 15.89–30.01 mg kg^{-1}, respectively, with bioavailable fractions of 13.29, 54.16, 47.60, 32.74, 68.14, 26.59%, respectively. A modified potential ecological risk index (MRI) was used for the ecological risk assessment, with ecological risk contribution ratios of 75.73, 14.29, 5.47, 1.74, 1.57 and 1.21% for Cd, As, Cu, Cr, Pb and Zn, respectively. The main contaminants were Cd and As, with their ecological risks "High" and "Moderate" levels, and their enrichment degrees "Moderately Severe" and "Moderate", respectively. The multivariate statistical analysis suggested that the various anthropogenic activities along the bay might contribute mainly to the heavy metals contamination in DYB.

Heavy metals contamination has aroused great concerns due to their toxic effects and potentials for substantial and long-term accumulation in sediments and organisms (Oursel et al., 2013; Chen et al., 2016; Zhang et al., 2016a; Zhang et al., 2016b). It is well known that heavy metals from industrial, urban, and agricultural sources were discharged into rivers, and ultimately immobilized in marine sediments under current action (Machado et al., 2016; Wu et al., 2017). Therefore, coastal zones like estuaries and bays tend to suffer from more seriously anthropogenic heavy metals contamination (Wang et al., 2013; Aiman et al., 2016), and the sediments in estuaries and bays generally tend to be a reservoir for heavy metals discharged into marine environment (Fujita et al., 2014; Machado et al., 2016). Actually, heavy metals in sediments could migrate upward to the sediment-water interface, and be released into the overlying waters when environmental conditions (e.g., current, pH, DO, redox potentials and temperature) changed, leading to potential threats to aquatic environments and organisms (Zhao et al., 2013; Dhanakumar et al., 2015; Machado et al., 2016; Chen et al., 2017).

In addition, the release of heavy metals in sediments greatly depends on their different chemical forms, which generally exhibit different physical and chemical behaviors in terms of chemical interaction, potential toxicity, bioavailability and mobility (Sun et al., 2016; Gabarrón et al., 2017; Kang et al., 2017). According to the European "Community Bureau of Reference" (BCR) sequential extraction procedure (Quevauviller et al., 1997), chemical forms of heavy metals in sediments are classified into four parts, that is, the exchangeable, reducible, oxidizable and residual parts. Usually, the bioavailable fractions are composed of the former three parts, which could be released into overlying water so that a secondary contamination occurred (Cheng and Yap, 2015; Kang et al., 2017). Thus, the chemical fractions of heavy metals, especially those with high bioavailability, should be analyzed for the evaluation of ecological risk of heavy metals in sediments.

Generlly, the ecological risk of heavy metals in sediments is evaluated by the risk assessment code (RAC) (Perin et al., 1985) and the potential ecological risk index (PERI) (Hakanson, 1980), both of which have been used for the assessment of ecological risk of heavy metals in estuaries (Dhanakumar et al., 2015), bays (Gao et al., 2010) and coastal lines (Zhang et al., 2016a; Zhang et al., 2016b). However, RAC only considered the bioavailable fractions of heavy metals, while the PERI considered the toxicities and total concentrations of heavy metals. Recently, a modified potential ecological risk index (MRI), which simultaneously considered the influences of toxicities, total concentrations and bioavailability of heavy metals, was proposed (Kulikowska

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et al., 2015; Wang et al., 2016). This new index introduced a coeffieient on bioavailabiliy into the traditionally used PERI. However, its application has seldom been used in heavy metals contamination, especially in marine environment. In addition, it is known that the actual contamination levels of heavy metals and the contribution ratio of total heavy metals from human activities could be evaluted by the geo-accumulation index (I_{geo}) and enrichment factor (EF), respectively (Diop et al., 2015; Liu et al., 2017). Thus, it would be interesting to simultaneously apply the multiple indices such as I_{geo}, EF, RAC, PERI and MRI for assessment of heavy metals contamination in marine environment.

Daya Bay (DYB) is a semi-enclosed embayment in the northwestern part of the South China Sea. It is located between Shenzhen and Huizhou of Guangdong Province, China (Yang et al., 2014). The DYB is composed of many sub-basins, including Aotou Harbor and Yaling Bay in the northwest, Dapeng Cove in the southwest and Fanhe Harbor in the northeast. There are no major rivers discharged into DYB, while there are three tributaries discharged into Dapeng Cove. With the rapid development of industrilization and urbanization, large-scale anthropogenic activities have been appeared along its coastline in recent decades, such as the mariculture, port, nuclear power station and petrochemical business (Yu et al., 2010; Yu et al., 2016). Various kinds of contaminants, including heavy metals, have entered the DYB and caused serious heavy metal contamination (Gu et al., 2016).

Although some studies on heavy metals contamination in sediments of the Daya Bay could be found, the total concentrations of metals without their chemical fractions in sediments could not well reflect their actual contamination status (Gu et al., 2016; Han et al., 2013; Gu et al., 2012). Some studies conducted chemical fractions of heavy metals in sediments (Gao et al., 2010; Yu et al., 2010), however, heavy metals contamination caused by increased human population and anthropogenic activity, such as mariculture, petrochemistry and port around this area in recent years and their potential ecological risk have not been reported. Although some studies on concentrations, chemical fractions and ecological risk of heavy metals had been conducted (Cao et al., 2014; Yang et al., 2014), their risk assessment method just considered the chemical fractions of heavy metals, ignoring the concentration levels and toxicities of heavy metals. Therefore, the latest comprehensive study, considering concentrations, chemical fractions and ecological risk assessment of heavy metals in sediments from Daya Bay, was necessary and realistically significant.

In this study, the main objectives were to: (1) investigate the spatial distribution characteristics of heavy metals (Cr, Cu, Zn, As, Cd and Pb) in sediments from DYB; (2) quantify the chemical fractions and bioavailability of heavy metals by BCR sequential extraction procedure; (3) evaluate the heavy metals contamination of DYB with indices of the I_{geo}, EF, PERI, RAC and MRI.

Samples of the surface sediment were collected in Nov 2016 from 14 sampling sites in the Daya Bay (Fig. 1). The surface sediments (top 5 cm) were collected by using steel box grabs, and then sealed in polyethylene plastic bags. Samples of the sediments were collected in triplicates and combined homogeneously as a sample at each site. All the samples were directly placed on ice in a cryogenic storage container and transported to the laboratory. In the laboratory, the sediment samples were firstly ice-dried at −20 °C, then stones and plant fragments were removed. The samples were subsequently ground with a pestle and mortar until all particles passed through a 150 nylon mesh sieve. All samples were finally stored at 4 °C in the dark for the subsequent treatment.

Chemical fractions of Cr, Cu, Zn, As, Cd and Pb in sediments were extracted according to the European "Community Bureau of Reference" (BCR) sequential extraction procedure (Quevauviller et al., 1997), and the residual parts of the heavy metals were digested by a mixture of acid (HNO_3 + HF + $HClO_4$) (Bai et al., 2011). All supernatants were decanted into polyethylene containers and refrigerated prior to analysis. Between each extraction, samples were washed using 10 mL ultrapure water. Finally, all concentrations of heavy metals were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500cx, USA).

Quality assurance and quality control were ensured using the analysis of duplicate samples, method blanks, and standard reference materials. The total concentrations of heavy metals in sediments were estimated by summing up the four fractions by BCR procedure. After the mobile fractions were extracted, the concentration of residual fraction was verified by recovery measurements on the standard reference material of the sediment in South China Sea (GBW07334). Five replicates were conducted for the determination of total concentration of the heavy metals in reference materials. The results were consistent with the reference values, and the differences were all within 10%, with recoveries ranging from 95 to 105 (n = 5). The precision, expressed as the relative standard deviation, ranged from 5 to 12%. In addition, all the glassware and polypropylene wares were soaked overnight in diluted nitric or hydrochloric acid. Then they were rinsed with deionized water prior to use. All the reagents and standard solutions used were of guarantee grade.

In this study heavy metals contamination in sediments was evaluated by the geo-accumulation index (I_{geo}), enrichment factor (EF), risk assessment code (RAC), potential ecological risk index (PERI) and a modified potential ecological risk index (MRI), respectively.

The index I_{geo} has been demonstrated to be a useful tool for assessing contamination levels of heavy metals. The I_{geo} is calculated by the following equations:

$$I_{geo} = \log_2[C_n/(1.5 \times B_n)]$$

where C_n is the concentrations of heavy metals in sediments; B_n is the geochemical background contents of heavy metals. The background values of heavy metals in sediments proposed by Zhang (1991) were selected as the geochemistry background value (B_n) in this study (Table 1). According to the I_{geo} values, categories of contamination levels were defined (Table S2).

The index EF has been used to evaluate the contamination degree of anthropogenic heavy metals in sediments. The calculation formula of EF is showed as follows:

$$EF = (Metal_{Sample}/Fe_{Sample})/(Metal_{Background}/Fe_{Background})$$

where $Metal_{Sample}$ is the concentrations of heavy metals in sediments; $Metal_{Background}$ is the geochemical background contents of heavy metals; Fe_{Sample} is the concentrations of Fe in sediments; $Fe_{Background}$ is the geochemical background contents of Fe. According to the EF values, enrichment degree of heavy metals in sediments could be defined as seven categories (Table S3).

The index RAC has been applied to assess the heavy metals mobility according to their chemical fractions. The RAC is expressed by the following equation:

$$RAC = C_m/C_{total} \times 100\%$$

where C_m is the metal concentration of B1; C_{total} is the total metal concentration in sediment. According to the values of RAC, the classification of ecological risk about RAC was shown in Table S4.

The index PERI has been widely used to evaluate the potential ecological risk of single heavy metal and total heavy metals in sediments or soils, while the value of PERI can be calculated by the following formula:

$$PERI_i = \sum_{i=1}^{m} EI_i = T_i \times C_d^i/C_r^i$$

where EI_i is the potential risk of individual heavy metal; $PERI_i$ is the sum of all EI_i values; C_d^i is the present concentrations of heavy metals in sediments; C_r^i is the background values that determined by Zhang (1991); T_i is the toxic response factor. According to the classification of potential ecological risk index (Hakanson, 1980), five categories of