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Assessment of metal contamination in estuarine surface sediments from Dongying City, China: Use of a modified ecological risk index

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ABSTRACT

Surface sediments and clam *Meretrix meretrix* were collected from a northern estuarine region in Dongying City, China. Sediments were analysed for heavy metals (Hg, As, Cd, Cr, Cu, Pb, and Zn) and the clams were tested for metallothioneins (MTs) and lysosomal membrane stability (LMS). The heavy metal total concentrations decreased in the order of Cr > Zn > Cu > Pb > As > Cd > Hg. The results of Bureau Communautaire de Référence (BCR) sequential extraction of heavy metals showed that the geochemical speciation of all heavy metals was dominated by residual fraction. According to the responses of biomarkers in *M. meretrix*, the modified potential ecological risk index (*PERI-B*) can more accurately reflect heavy metals pollution. *PERI-B* showed all sediment samples have low or moderate risk, except at site S10 (considerable risk), and the main contribution of ecological risk heavy metals were Cd and Hg.

1. Introduction

With the development of industry, agriculture, and urbanisation, heavy metals discharged into the marine environment through surface runoff have continuously increased. Heavy metals are highly toxic, non-biodegradable, and easily enriched in aquatic organisms. They may cause harm to the marine ecosystem and human health when their concentrations in the marine environment reach a certain level (Diagomanolin et al., 2004; DeForest et al., 2007; Zhang and Gao, 2015). When entering coastal waters, metals are readily scavenged by particulate matter and then deposited to coastal bottom sediments. Hence, sediments represent the major component of metal storage in marine environments (Pan and Wang, 2012). Although total heavy metal contents in sediments can be a good indicator of historical anthropogenic input of metals, such measures provide little information about the mobility and bioavailability of the heavy metals therein (Nemati et al., 2011). In fact, the mobility and bioavailability of heavy metals in sediments mainly depend more on their chemical forms. Usually, the non-residual metal, i.e., the sum of a metal's content in acid-soluble, reducible, and oxidisable forms was considered to be bioavailable (Rauret et al., 1999; Pérez-López et al., 2008). Therefore, geochemical speciation of metals in sediments has been increasingly recognised as an important step in predicting actual environmental impacts (Delgado et al., 2011).

The potential ecological risk index (*PERI*) method was developed by Hakanson (1980) and has been commonly applied as a diagnostic tool for heavy metal pollution in sediments because it considers both contents, and toxic response factors, of heavy metals (Ntakirutimana et al., 2013); however, the levels of risk may be overestimated due to using total contents rather than data associated with speciation. So, the calculation of *PERI* should be modified (Paterson et al., 2011; Zhao et al., 2012).

Dongying city, located in the northwest of Shandong Peninsula in China and the south coast of Bohai Bay, is a typical petrochemical city. The industrial wastewater discharged in the northern part of the city mainly flows into the sea through several seasonal rivers. These rivers run through the city from south to north, and there are a large number of enterprises, such as the salt chemical industry, petroleum exploitation, petrochemical industry, machinery manufacturing, and metal processing, as well as several livestock farms and farmland on both sides of the rivers. The estuarine waters, with a water depth < 5 m, are ecologically and economically important due to their biological diversity including a variety of anadromous fishes, plankton, benthos (commercial shellfish species, etc.), and other organisms of economic and ecological value (Oursel et al., 2013; Vilar et al., 2017). Since 2008, the west of this area has been declared as a China Marine Special Conservation Area (MSCA) for the protection of its estuary shellfish ecosystem, with a watershed area of 396.23 km^2. Therefore,

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understanding the status of the pollution by heavy metals in sediments is related to the healthy growth of marine organisms, and shellfish in particular; however, no information is available in the literature on the contamination of heavy metals in sediments of this estuarine area.

Thus, the present work aimed to (i) investigate the total contents, spatial distribution, and sources of seven heavy metals (Cu, Pb, Zn, Cr, Cd, Hg, and As) in surface sediments; (ii) discover the relationships between the heavy metals levels and sediment physico-chemical characteristics; (iii) analyse the chemical speciation and bioavailability of metals; (iv) assess the ecological risk level associated with metal contamination in sediments using of original and modified *PERI* methods, respectively, and (v) validate the efficacy of original and modified *PERI* methods according to the responses of biomarkers in *M. meretrix*.

2. Material and methods

2.1. Study area and sample collection

The study area is located in the northern estuarine region of Dongying City within the range of about 20 km from the shore, and its coastal type belongs to silt mud coast. The average water depth of study area is about 2 m, but the maximum water depth is > 5 m. The study area has the features of semidiurnal and diurnal currents, and the tidal currents are dominated by reciprocating flow (Li et al., 2011). Several small seasonal rivers with sediments loads and various water discharge into this area, namely, Chaohe, Maxinhe, Zhanlihe, Tiaohe, and Caoqiaogou Rivers (Fig. 1). This area has an important economic and ecological status because it possesses abundant shallow water and tidal flats resources, and has been considered as a famous culture base of economic shellfish in sea of northern China (Guo et al., 1999; Liu et al., 2017).

Surface sediment samples (0–10 cm) from twelve different sites (S1 to S12) in study area were collected using a Van-Veen grab sampler with an area of 0.1 m^2 in October 2016 (Fig. 1). In detail, these sites were distributed uniformly across the study area and formed six transects; each transect contained two sites extending from the near-shore to far-shore and sites S1 to S6 were located in MSCA. Each sediment sample was packed into a polyethylene bag and transported to the laboratory and stored at − 4 °C until further analysis. At the same time, > 10 individuals of *M. meretrix* (38.0 ± 1.2 mm) were sampled from each site. Five of them were rapidly dissected in situ, and gills and digestive glands were separated, respectively. For the other five individuals, haemolymph was withdrawn from the adductor muscle. All the samples were transported into the laboratory and stored at − 80 °C until biochemical analysis.

2.2. Determination of physico-chemical characteristics of sediments

Sediments samples for detecting granulometry and organic matter (OM) were air-dried to constant mass. The granulometry of sediment samples was analysed using a Malvern Particle Size Analyser (MS 2000, Malvern, UK). Before analysis, all of the samples were treated with 10% H_2O_2 and 0.5 mol L^{-1} HCl to remove organic matter and carbonates. The percentages of the following three grain size groups were determined: < 4 μm (clay), 4–63 μm (silt), and 63–2000 μm (sand) (Wentworth, 1922). For determination of organic matter (OM), the dried samples were digested with potassium bichromate followed by a titration with ferrous ammonium sulphate (Specification for Marine Monitoring (GB 17378.5-2007), State Oceanic Administration of China (SOA), 2007), and the contents were expressed as a percentage of the total sediment (dry mass).

2.3. Determination of heavy metals in sediments

According to the Specification for Marine Monitoring((GB17378.5-2007), SOA, 2007), the sediment samples were dried to a constant mass at 90 °C (samples for Hg determination were only air-dried by exposure to ambient air), and then ground in a mortar followed by sieving through a 96 μm mesh to obtain consistent physical properties.

For determining Cu, Pb, Zn, Cd, and Cr contents, the samples, approximately 0.2500 g of each, were digested with a mixed solution of HNO_3 + HCl + HF (9:3:5, v/v) in a microwave digestion instrument (GFAAS; M6 Series, Thermo Scientific, USA) ((Pre-treatment Guideline of Heavy Metals Analysis in the Marine Sediments and Organisms—Microwave Assisted Acid Digestion HY/T 132-2010), SOA, 2010), and the total contents for these metals were measured by a inductively coupled plasma emission spectrometer (ICP-AES) (ICAP-6300, Thermo Scientific, USA). Sediments for Hg and As analysis (0.5000 g each sample) were digested with *aqua regia* (HNO_3: HCl (3:1, v/v)) for 1 h ((GB17378.5-2007), SOA, 2007), and Hg and As were

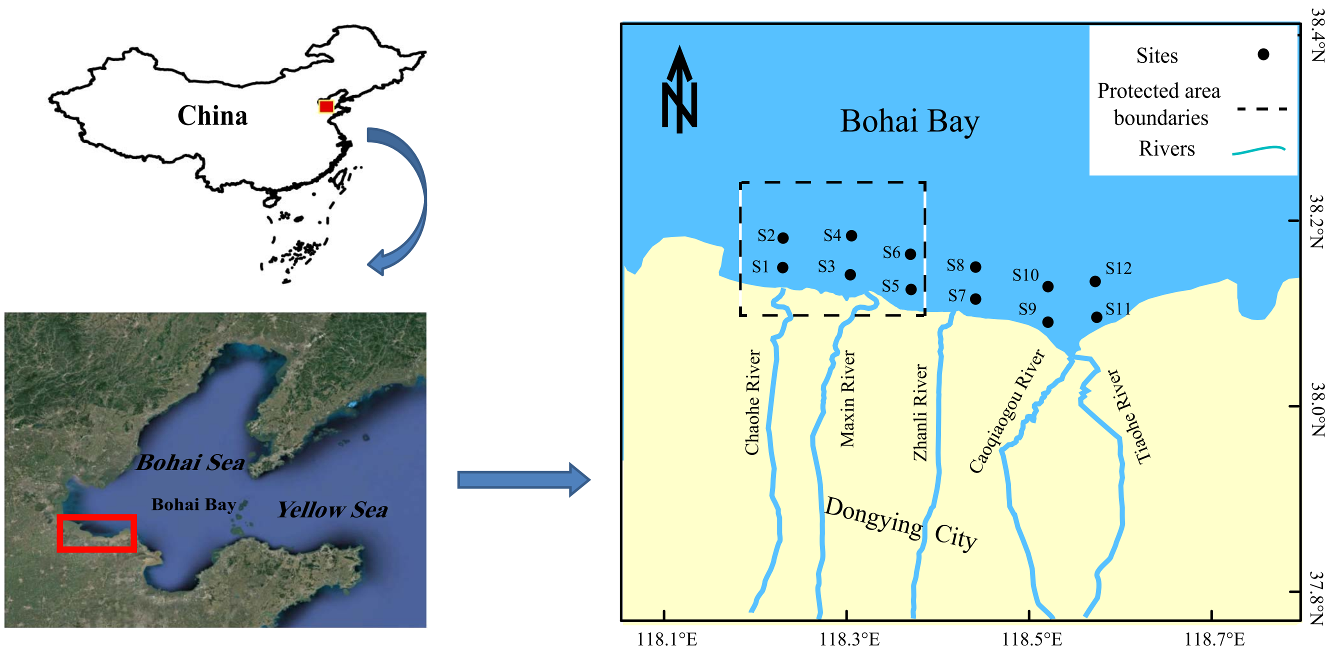

Fig. 1. Distribution of sediment and *M. meretrix* sampling sites.