Marine Pollution Bulletin 88 (2014) 155–161

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Influence of early diagenesis on the vertical distribution of metal forms in sediments of Bohai Bay, China

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ARTICLE INFO

Article history:
Available online 26 September 2014

Keywords:
Metal pollution
Different forms
Vertical distribution
Early diagenesis
Bohai Bay

ABSTRACT

The influence of early diagenesis on the vertical distribution of metal forms in the sediments of Bohai Bay was discussed in this paper. The results showed that the concentrations were: Al > Fe ≈ Ca > Mn > Cr > Zn > Cu > Pb > Cd. In vertical distribution, the forms of Cr and Pb were stable from the top to the bottom. However, the exchangeable forms and acid-extracted forms of Cd, Cu and Zn presented an obvious declining trend. The metals would be transformed to more stable forms during the early-diagenesis process. Further analysis found that early diagenesis can change the sedimentary environment, affecting pH, oxidation–reduction potential (ORP), total dissolved solid (TDS) and the structure of organic matter (OM), all main factors influencing metal forms in the sediments of Bohai Bay.

1. Introduction

Heavy metal pollution of aquatic environments has become a severe problem, especially in developing countries (Tao et al., 2012; Yu et al., 2012; Meng et al., 2008). Sediments are both a source and a sink for metals in aquatic environments, significantly influencing the behavior and bioavailability of metals (Chen et al., 2007; Singh et al., 2005). It has been reported that the concentration of metals in sediments usually exceeds that of overlying water by three to five orders of magnitude (Bryan and Langston, 1992). Of the pollutants found in sediments, metals are among the most persistent because they cannot be degraded in the natural environment. However, they can accumulate in sediments and pose a risk to the environment (Duong et al., 2009). They are also useful as markers of environmental change (Arnason and Fletcher, 2003). In coastal areas with rapid economic development, metals derived from anthropogenic sources continuously accumulate in estuarine and coastal zones through aeolian and/or alluvial processes (Roussiez et al., 2011; Pan and Wang, 2012). As a result, a large majority of land-derived metals accumulate in sediments.

Although the total concentration of metals in sediments can reflect the degree of pollution of the overlying aquatic environment, it is not a good indicator of the bioavailability of metals (Gorski et al., 2008), which directly affects aquatic organisms. In the sediments, metals can exist in various forms; for example, they can be occluded in amorphous materials, adsorbed on clay surfaces or iron/manganese oxyhydroxides, present in lattice of carbonates, sulfates or oxides, and complexed with OM or silicates (Yu et al., 2001; Peng et al., 2009). Each form has a different remobilization potential, which affects its bioavailability and toxicity. Currently, the Tessier method is generally applied to study the forms of metals. This method divides metals in sediments into various forms: the exchangeable forms (EF), the acid-extractable forms (AF), the iron and manganese bound forms (IF), the organic and sulfide bound forms (OF), and the residual forms (RF) (Tessier et al., 1979). However, these forms are also affected by the environmental conditions of the sediment, such as salinity, pH, redox potential, OM content, and cation exchange capacity (Peng et al., 2009).

In the study of metal forms in sediments, researchers should pay attention to the dynamic environmental conditions of the sediments. One of the most important changes is the early diagenesis of sediments. Sediments are an important reservoir of OM, and the mineralization of OM is a central issue in water ecology, because early diagenesis, along with element recycling, are essential processes for sustaining primary and secondary production in aquatic ecosystems (Nascimento et al., 2012). During early diagenesis of sediments, the OM structure, pH, microbial activities, and redox conditions change, directly influence the forms of metals dependent on these environmental factors (Zhu et al., 2010).

Bohai Bay, surrounded by the Bohai Economic Ring, is one of the three most densely populated and industrialized zones in China,

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http://dx.doi.org/10.1016/j.marpolbul.2014.09.011
0025-326X/

and is located in the western part of the Bohai Sea. The bay has a mean depth of 12.5 m, and is a typical semi-enclosed coastal bay. The bay has limited water exchange with the ocean and receives industrial and domestic sewage from two megacities of China (Beijing and Tianjin). The heavy metal pollution status in Bohai Bay has attracted considerable attention from both scientific and regulatory communities, and many studies have focused on assessing the heavy metal pollution status of the river outlets and coastal areas of the bay (Feng et al., 2011; Gao and Chen, 2012; Gao and Li, 2012). Some studies also focus on metal forms in surface sediments of Bohai Bay because it is a good indicator of bio-available metals, which can directly affect aquatic organisms (Zhu et al., 2010).

For this study, three core sediment samples were collected from Bohai Bay. The basic physical and chemical properties of the sectioning sediments, and the concentration and forms of the metals were analyzed. The aims of this study were to: (1) study the sedimentary environment in sediments of various depths; (2) examine the vertical variation in metal forms in the core sediments of Bohai Bay; and (3) discuss the effects of changes in the sediment environment on metal forms. This information is expected to provide a new perspective on the vertical distribution of metal forms in sediments.

2. Materials and methods

2.1. Sample collection and treatment

Sampling was conducted in Bohai Bay in August, 2011. Sampling sites were located in the coastal areas of Bohai Bay, based on the depth of the water level (5 m, Fig. 1). The core sediments were collected with a cylindrical corer with a diameter of 10 cm. The sediment cores were usually 30–50 cm in length; each core was segmented every 2 cm from top to bottom to examine the variation in metals along the sediment profile. All samples were sealed in polythene bags in situ, then taken back to the lab and stored at 0–4 °C until further analysis.

2.2. Sample processing and analysis

In the laboratory, 5 g of each sample was set aside for particle size analysis (Mastersizer 2000) and the remaining samples were air-dried for 3 days. Dried samples were sieved through a nylon sieve (1 mm) to remove stones and shells. The samples were grounded using a mortar, then sieved through a nylon sieve for analysis. All sediment samples were sequentially extracted to examine metal forms using the Tessier method (Tessier et al., 1979).

The extracted sediments were freeze-dried and then digested using the Chinese National Standard Method (GB/T17140) with HCl-HNO_3–HF–$HClO_4$ acid. The mixed acids were added in the vessel for digestion until the supernatant became clear and brownish-colored fumes were no longer generated. When the solution became nearly dried, 1% HNO_3 was added and the solution was filtered through a 0.45 μm filter membrane into a 50 ml polyethylene bottle and this final solution was diluted to 50 ml with 1% HNO_3 for instrumental analysis. To ensure the analytical quality of metal measurements, the national certified material Offshore Marine Sediment (GB-W07314) and a blank sample for each test group was synchronously processed and analyzed alongside the sediment samples.

Metal analysis was conducted using an ICP-MS (Agilent 7500, Agilent Technologies, Santa Clara, CA, USA). OM was measured using the Chinese National Standard Method (GB 8834-1988).

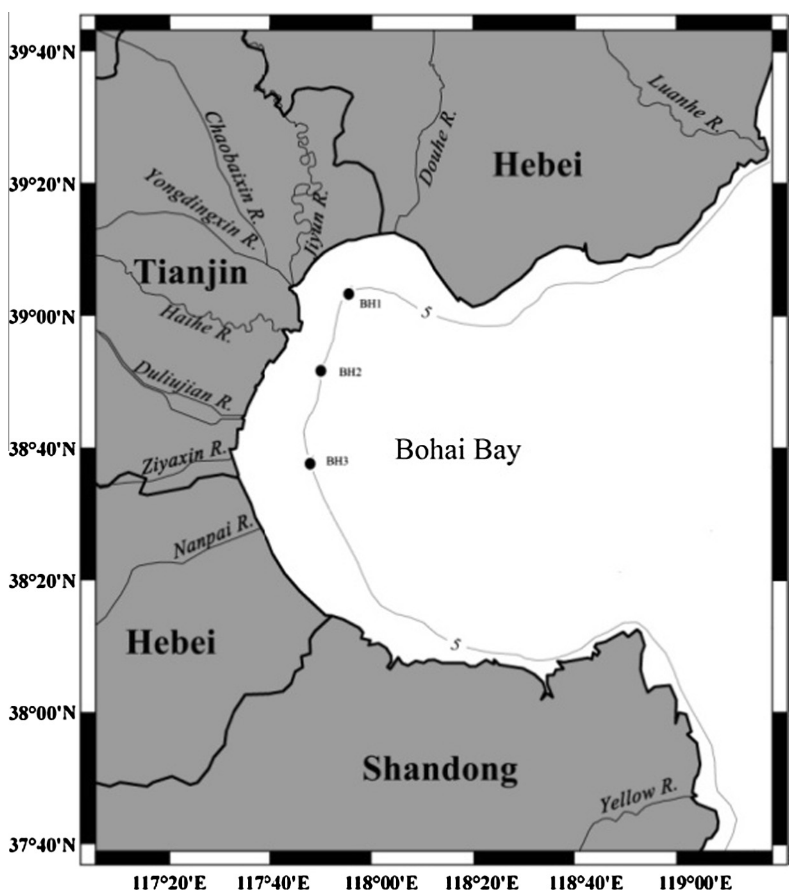

Fig. 1. Locations of sampling sites.