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Spatial distribution and pollution assessment of heavy metals in the surface sediments of the Bohai and Yellow Seas

Xiaoda Xu [a,b], Zhimin Cao [a], Zhixun Zhang [b], Rihui Li [b], Bangqi Hu [b,*]

[a] College of Geo-Marine Sciences, Ocean University of China, Qingdao 266100, China
[b] Key Laboratory of Marine Hydrocarbon Resources and Environmental Geology, Ministry of Land and Resources, Qingdao Institute of Marine Geology, China Geological Survey, Qingdao 266071, China

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ABSTRACT

A total of 141 surface sediments were collected and analyzed for their geochemistry, total organic carbon, and grain size to assess the heavy metal pollution in the Bohai and Yellow Seas. The enrichment factor (EF) and geoaccumulation index (I_{geo}) of Cu, Pb, Zn, Cr, Cd, Ni, As, and Hg were calculated to assess anthropogenic contamination, and the results suggest that moderate Pb, Cd, and As contamination occurs in the study area. Sediment quality guidelines were applied to assess the adverse biological effects of these metals. The spatial distribution of the mean Effects Range-Median quotient for the vast majority of the study area is between 0.1 and 0.5, indicating low impact and potential negative biological effects. Multivariate analysis indicates that Cu, Pb, Zn, Cr, and Ni resulted primarily from lithogenic sources, whereas As, Cd, and Hg were mainly attributed to anthropogenic sources.

With rapid urbanization and industrialization, heavy metals are continuously delivered to the estuarine and coastal areas through aeolian and alluvial processes and have caused severe environmental crises in marine ecosystems (Gao and Chen, 2012; Hu et al., 2013a; Hu et al., 2013b; Li et al., 2013; Pan and Wang, 2012). The sediment of an aquatic system is not only an important reservoir of heavy metals but it is also an important source of heavy metals for aquatic organisms when the environmental conditions (e.g., pH, redox potential, salinity, and resuspension) are changed (Hill et al., 2013; Roberts, 2012; Sundelin and Eriksson, 2001). Due to their persistence in the environment, bioaccumulation and high toxicity, the increasing pollution from heavy metals has received considerable attention (Rainbow, 2007; Wang and Rainbow, 2008). Thus, spatial surveys of metal concentrations at a large scale are often used to provide basic information for the assessment of environmental health risks and to investigate anthropogenic impacts on marine ecosystems (Long et al., 2006; Long et al., 1995).

The Yellow and Bohai Seas are bordered by China and the Korean Peninsula. The two seas have a total area of 460×10^3 km^2 and a total volume of 18.1×10^3 km^3. The Yellow and Bohai Seas have been affected by human activities and population growth and annually receive large amounts of fluvial materials (including anthropogenic metals) from surrounding rivers. Most of previous studies about the heavy metal pollution statues of the Yellow and Bohai seas were only available in the river outlets and/or estuary areas and thus lack spatial resolution (Gao and Chen, 2012; Hu et al., 2013a; Hu et al., 2013b; Huang et al., 2014; Li et al., 2013; Yuan et al., 2012). This limits our understanding of the transport or fate of such contaminants and their potential adverse environmental impacts. Specifically, the objectives of this study were: (1) to determine the levels of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) in the sediments from the Yellow and Bohai Seas at large scale; (2) to assess the contamination status of heavy metals using the enrichment factor (EF), geoaccumulation index (I_{geo}), and the sediment quality guidelines (SQG) method; and (3) to identify the possible sources of these metals via multivariate analysis.

A total of 141 surface sediment (0–2 cm) samples were collected in 2012 using a Van-Veen grab sampler according to a spatial grid of 20 km × 20 km (Fig. 1). All samples were stored in refrigerators at 4 °C until analysis. An evaluation of the sediment grain size distribution was performed directly using a Mastersizer 2000 laser particle

* Corresponding author at: Qingdao Institute of Marine Geology, Fuzhou South Road 62#, Qingdao, Shandong 266071, China.
E-mail address: bangqihu@gmail.com (B. Hu).

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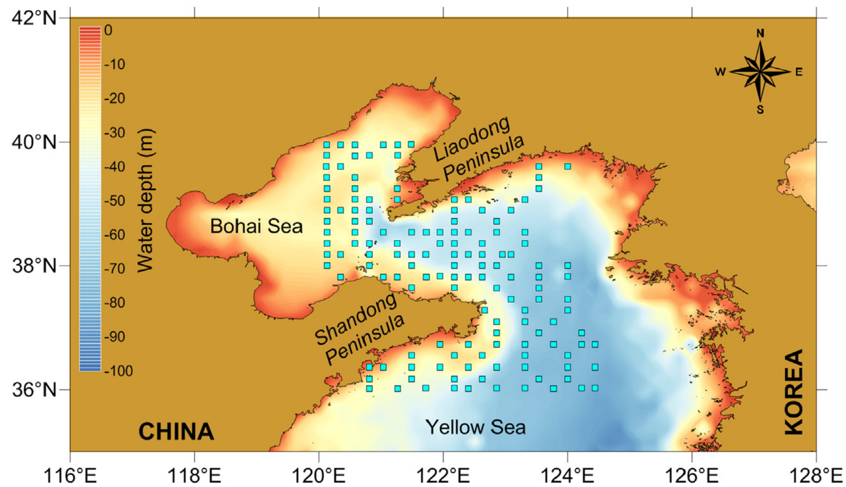

Fig. 1. Geographic location of the study area and sampling sites.

analyzer (Malvern Instruments Ltd., UK), which was capable of measurements ranging from 0.02 to 2000 μm, with a repeatability error of <3%. Before the analysis, all of the samples were treated with 10% H_2O_2 and 0.5 M HCl to remove organic matter and carbonate. Textural classification of the sediment samples was based on the relative percentages of clay (<0.004 mm), silt (0.004–0.063 mm), and sand (0.063–2 mm).

For the chemical analysis, all samples were oven-dried at 45 °C for 24 h. The samples were hermetically sealed and then decomposed by nitric acid, hydrofluoric acid, and perchloric acid in an open system in which hydrofluoric acid was removed by evaporation and then heated with dissolved salts of hydrochloric acid and converted to a nitric acid medium. A PerkinElmer's DV4300 inductively coupled plasma emission spectrometer (ICP-AES) was used for determining Al, Fe, and Mn, an inductively coupled plasma mass spectrometry (ICP-MS, Thermo X series) was used for Cd, Cr, Cu, Ni, Pb, and Zn analysis, and an atomic fluorescence spectrometer (AFS-920) was used for analyzing As and Hg. Blanks and China Stream Sediment Reference Materials (GBW07345, GSD9, and GSD4) were included in the QA/QC for data analyses (Table 1). Replicated samples were analyzed with a variation of <10%. Total organic carbon (TOC) was measured using an elemental analyzer (Vario EL-III). The measurement error was within 5% based on replicate sediment analysis.

It is well known that median grain size (Mz) and TOC are important factors that control the abundance of trace metals in the natural environment. Fine-grained sediments tend to have relatively high metal content due to a large specific surface area that favors surface adsorption and ionic attraction. In this study, the values of Mz for the sediments varied from 1.958–7.758 φ, with an average Mz of 5.19 ± 1.16 φ. The amount of TOC varied from 0.06–1.37%, with a mean of 0.53 ± 0.3%. Fig. 2 indicates that there is a significant linear correlation between the total TOC and Mz, and thus, Mz has a significant impact on TOC concentrations. There is a significant correlation between Mz and Al and Fe concentrations as a result of natural weathering; thus, Al and Fe concentrations are mainly controlled by the grain size (Fig. 2).

The metal concentrations in the study area range from 6.11–18.55% for Al, 2–7.06% for Fe, 4.2–40.6 mg/kg for Cu, 14.4–37.4 mg/kg for Pb, 20.7–133 mg/kg for Zn, 13.8–111 mg/kg for Cr, 6.69–49.2 mg/kg for Ni, 0.054–0.62 mg/kg for Cd, 3.85–33.2 mg/kg for As, and 0.0024–0.071 mg/kg for Hg. A comparison of heavy metal content in different areas reveals differences in heavy metals concentrations in the two seas of the study area (Table 2). The concentrations of Zn and Ni are low compared with their corresponding values in other areas/estuaries, while those of Cu, Pb, and Cr are at a moderate level compared to those in the other regions. Similar comparisons are not possible for Cd, As, and Hg because the data are limited. The concentrations of heavy metals in the study area are lower than those in Germany's Bremen Bay (Hamer and Karius, 2002) and South Korea's Masan Bay (Hyun et al., 2007), but most concentrations are higher than those in the Arabian Gulf (Basaham and El-Sayed, 1998) and Florida Bay (Caccia et al., 2003).

The spatial distributions of heavy metals in the Yellow and Bohai Seas are described in Fig. 3. The spatial distributions of Cu, Pb, Zn, Cr, Ni, and TOC are high mainly toward the center of the North Yellow Sea and north of the South Yellow Sea. These distributions coincide with the differing sizes of the distributions of surface sediments in the study area; there is a significantly positive correlation between Mz and Cu, Pb, Zn, Cr, Ni, and TOC concentrations. The concentrations of Cd, As, and Hg are noticeably dispersed throughout the study area, whereas the distribution of Cd is noticeably high in the central portion of the North Yellow Sea and the northern regions of the South Yellow Sea. The distribution of As is noticeably high near the Laotieshan watercourse and in the area northeast of Shandong Peninsula. The distributions of Hg are dispersed but high throughout the study area and occur primarily near the Changshan Islands, the southern bank of the Liaodong Peninsula, and the seas near Qinhuangdao. Fine Hg particle deposition zones can be observed toward the area north of the South Yellow Sea.

Table 1
Results (mean ± standard deviation) obtained from certified reference materials analysis.

	Certified value (mg/kg)	Measured value (mg/kg)	Reference materials
Cu	15 ± 3.8	15.6 ± 0.7	GBW07345 (n = 8)
Pb	28 ± 6.3	31.3 ± 1.1	
Zn	45 ± 9.4	44.6 ± 2.3	
Cr	85 ± 15.8	81.3 ± 3.4	GSD-9 (n = 10)
Ni	32 ± 7.0	31.2 ± 0.5	
Cd	0.18 ± 0.08	0.16 ± 0.06	
As	19.7 ± 4.7	18.7 ± 1.8	GSD-4 (n = 8)
Hg	0.044 ± 0.013	0.049 ± 0.001	

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