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Baseline

Distribution and contamination assessment of heavy metals in surface sediments of the Luanhe River Estuary, northwest of the Bohai Sea

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ABSTRACT

33 surface sediment samples from the Luanhe River Estuary have been analyzed for heavy metals to evaluate the spatial distribution pattern and their potential ecological risk. Higher metal concentrations were found in the river mouth and southern areas where being covered by fine particulate matters. In comparison with the threshold effect level and the probable effect level, Cu, Pb, Cr, Ni, and As had occasionally adverse biological effects on the aquatic ecosystems. Both the enrichment factor and geoaccumulation index values show that all the regions have been weakly polluted by Pb, Hg, As, and Cd with an exception of being moderately to strongly polluted by Hg in the river mouth and southern areas. The sources of Zn, Ni, Cd, Hg, and Cr were mainly from the river input and coastal discharge, whereas Cu, Pb, and As were mainly derived from vehicle emissions, coal and oil combustion.

Heavy metals have become a worldwide environmental problem because of their toxicity, ubiquity, persistence, non-biodegradability and bioaccumulation (Forstner and Wittmann, 1979; Beijer and Jernelov, 1986; Bryan and Langston, 1992; Diagomanolin et al., 2004). In estuary and coastal areas, sediments have been regarded as the main sink for various pollutants due to largely uncontrolled contaminants being discharged during industrial and agricultural processes (Matthiessen and Law, 2002; Ip et al., 2007; Gan et al., 2013). Marine sediments release more pollutants into the seawater if the environmental conditions have changed (Sin et al., 2001, Valdés et al., 2005; Hill et al., 2013). Therefore, investigation of the spatial distribution of heavy metals in the sediments is critical to assess pollution in the coastal environment. Previous studies mainly focused on estuaries of major large rivers, such as the Yangtze River, the Yellow River and the Pearl River. However, few attempts were made to carry out such related studies on estuaries of small rivers when in fact, small rivers play an important role in regional economic development and ecological environment.

The Luanhe River Estuary is located on the northwest coast of the Bohai Sea with water depths of <20 m (Fig. 1). The total length of the Luanhe River is approximately 888 km, with a drainage area of approximately 44,750 km^2. The river originates from the Mongolian Plateau of Inner Mongolia and flows southeast into the Bohai Sea (Zhang and Liu, 2002; Wang et al., 2015). Freshwater and sediment discharges have decreased greatly since the 1980s due to large dams and reservoirs built across the Luanhe River. The mean sediment load of 21.9×10^6 t yr^{-1} for 1929–1979, fell to 1.7×10^6 t yr^{-1} for 1980–2003, and the mean water discharge fell from 4.2×10^9 m^3 yr^{-1} for 1950–1979 to 1.1×10^9 m^3 yr^{-1} for 1980–2003. Furthermore, in recent years, the river is often drying up downstream. The tidal range in the nearshore area is 1–2 m with the NE-SW direction currents of 0.5–1.0 m s^{-1}. The sediments from the Luanhe River are mainly transferred southward into Bohai Bay and also partially transferred northward into Liaodong Bay (Qin et al., 1990).

The Luanhe River plays an important role in watershed economic development, which is the most important water source and aquaculture base of cities, including Tianjin, Tangshan and Chengde. Both sides of the estuary have a large-scale mariculture area with approximately 9000 hm^2 of beach culture and 70,000 hm^2 shallow culture. With rapid industrialization and urbanization along the Luanhe River Basin in recent decades, large amounts of industrial, agricultural and domestic sewage have been discharged directly into the river, resulting in severe risk to the environment (Wang et al., 2015). A large number of industrial and mining enterprises are concentrated in the cities of Qianxi, Qian'an, and Luanxian in the middle-lower reaches of the Luanhe River. Large amounts of industrial effluents produced during industrial activities have been taken into the sea by the river. Particularly in the flood season, heavy rainfall has led to a large number of terrigenous pollutants entering the estuary through surface runoff. Moreover, water environmental capacity has been decreased due to plummeted river flows of the Luanhe River in recent years, resulting in more pollutants deposited in the estuary. In addition, the city of Tangshan is one of the most important energy and raw materials bases in China, as well as one of the most industrialized zones. The Tangshan port, proximal to the

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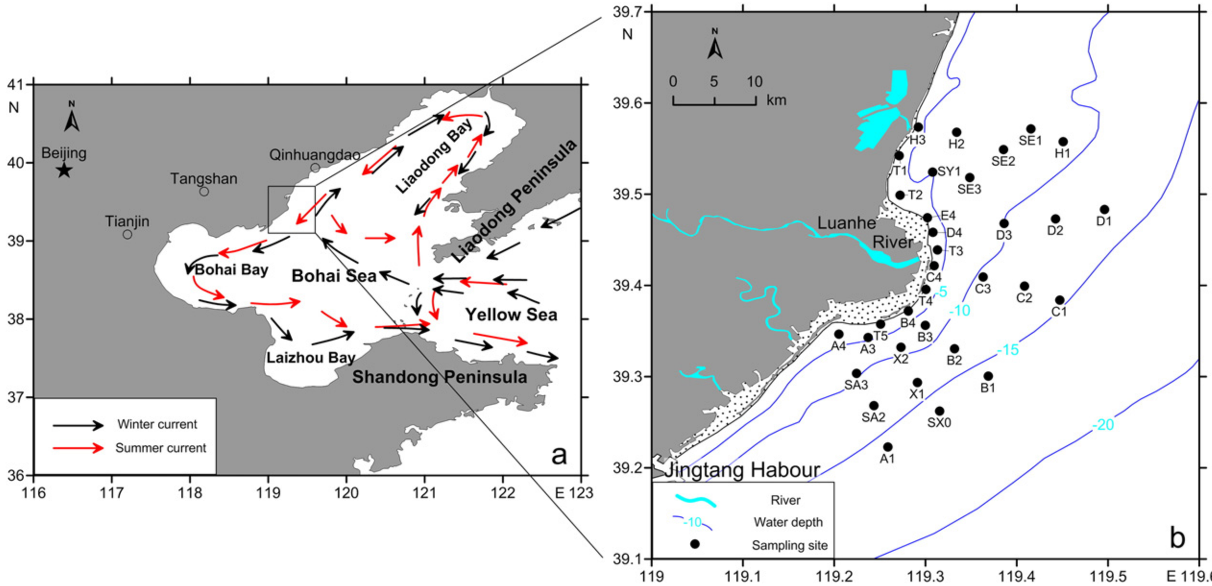

Fig. 1. Location of surface sediments in the Luanhe River Estuary, northwest coast of Bohai Sea. The seasonal circulation system were modified after Guan (1994) and Fang et al. (2000).

southern study area, has become one of the busiest ports in the Bohai Sea, with a cargo throughput of >5 billion tons in 2014. Additionally, ship electroplating, fuel burning, oil spilling, and waste dumping have also led to heavy metal pollution. These contaminants within sediments can therefore affect aquatic organisms, and cause harm to human health. Therefore, we aim to determine the spatial distribution and assess the contamination status of these metals in the Luanhe River Estuary. This study will also provide basic information for costal pollution control and environmental management.

A total of 33 samples were collected from the surface sediments (0–2 cm) in the Luanhe River estuary using a grab sampler in 2013 (Fig. 1). All sediment samples were stored in a plastic vessel and frozen at −20 °C.

Grain size analysis for the surface sediments were performed with a Mastersizer-2000 laser particle size analyzer (Malvern, UK) after removal of the organic matter with 10% H_2O_2 and the dispersion with sodium hexametaphosphate. Grain size parameters were calculated following the formula of Folk and Ward (1957).

Approximately 20 g of the subsamples for element analysis were oven-dried (<60 °C), and then ground to powder (<63 μm). Approximately 0.2 g powered samples were totally digested in a Teflon vessel with a mixed solution of HNO_3 + HCl + HF (5:4:1) on a heating plate, and heated (<150 °C) to dryness. Afterwards, the residue was extracted with HNO_3 and diluted to volume. The total organic carbon (TOC) was measured with an elemental analyzer (Vario EL-III). Al, Fe and Mn were measured with an X-ray fluorescence spectrometer (XRF, Axios PW4400). Cu, Pb, Zn, Cd, Cr and Ni were measured with inductively coupled plasma mass spectrometry (ICP-MS, Thermo X series). As and Hg were measured with an atomic fluorescence spectrometer (AFS-920). Blanks and China Stream Sediment Reference Materials (GBW07345, GSD9, and GSD4) were included in the analyses for data QA/QC (see Hu et al., 2013a and Dou et al., 2013 for detail). Replicated samples were measured with a variation of <10%.

The mean grain size (Mz) varied between 1.6Φ and 6.6Φ, with a mean value of 3.7Φ, indicating that the sediments were mainly composed of fine sand-sized components. The TOC contents varied between 0.03 and 0.9%, with an average of 0.28%. As shown in Table 1, the concentrations (mg kg^{-1}) of the heavy metals varied from 9.6 to 35.6 (average 18.8) for Cu, 22.6 to 43.7 (average 31.0) for Pb, 12.9 to 94.7 (average 44.6) for Zn, 11.6 to 76.2 (average 41.1) for Cr, 3.5 to 35.8 (average 15.6) for Ni, 0.02 to 0.24 (average 0.092) for Cd, 3.4 to 13.6 (average 7.2) for As, and 0.002 to 0.065 (average 0.19) for Hg.

Comparisons of the mean values of the heavy metals concentrations in this study with those in the other regions are also listed in Table 1. Except for the lower values of Cr from Southern Bohai Bay and the lack of Cd data observed from Liaodong Bay and Pearl River Estuary, the mean concentrations of Cu, Zn, Cr, Ni, and Cd from the Luanhe River estuary were lower than from the Bohai Bay (Feng et al., 2011; Gao and Li, 2012; Gao and Chen, 2012; Hu et al., 2013b), Liaodong Bay (Hu et al., 2013a), Laizhou Bay (Xu et al., 2015), Pearl River Estuary (Zhou et al., 2004), and Changjiang Estuary (Zhang et al., 2009). The Pb concentration in this study was higher than that of the Bohai Bay, Laizhou Bay and Changjiang Estuary. The concentration was comparable to Liaodong Bay but was far lower than Pearl River Estuary. The As concentration

Table 1
Comparison of heavy metal concentrations in the surface sediments of the Luanhe River Estuary and other representative areas (unit: mg·kg^{-1}).

Locations	Cu	Pb	Zn	Cr	Ni	Cd	As	Hg	References
Luanhe River Estuary	9.6–35.6	22.6–43.7	12.9–94.7	11.6–76.2	3.5–35.8	0.020–0.240	3.4–13.6	0.002–0.065	This study
	18.76	30.98	44.63	41.14	15.60	0.09	7.21	0.02	
Southern Bohai Bay, China	22.7	21.7	71.7	33.5	30.5	0.14	na	na	Hu et al. (2013b)
Western Bohai Bay, China	27.9	20.5	83.6	53.1	31.4	0.13	na	na	Feng et al. (2011)
Intertidal Bohai Bay, China	24	25.6	73	68.6	28	0.12	na	na	Gao and Li (2012)
Coastal Bohai Bay, China	38.5	34.7	131.1	101.4	40.7	0.22	na	na	Gao and Chen (2012)
Liaodong Bay, China	19.4	31.8	71.7	46.4	22.5	na	8.3	0.04	Hu et al. (2013a)
Laizhou Bay, China	22	21.9	60.4	60	na	0.12	12.7	na	Xu et al. (2015)
Pearl River Estuary, China	46.2	59.3	150.1	89	41.7	na	na	na	Zhou et al. (2004)
Changjiang Estuary, China	30.7	27.3	94.3	78.9	31.8	0.26	na	na	Zhang et al. (2009)
MSQ-1	35	60	150	80	na	0.5	20	0.2	AQSIQ (2002)

MSQ-1 is Chinese Marine Sediment Quality standard criteria (GB 18668-2002) issued by Administration of Quality Supervision, Inspection and Quarantine (AQSIQ).