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Flux and source-sink relationship of heavy metals and arsenic in the Bohai Sea, China☆

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ABSTRACT

This study conducted a field campaign to collect atmospheric deposition samples of heavy metals and arsenic, a metalloid element with typical chemical-physical characteristics (HMA), from 12 sampling sites and water samples from 37 rivers across the Bohai Sea (BS) and North Yellow Sea (NYS) in China. The HMA budgets in the BS and NYS were quantified by a budget model, which was developed based on the HMA inputs from atmospheric deposition and riverine discharge, sequestration to sediment, and interexchange among the BS's four subareas and the NYS. Statistical analyses of 76 deposition samples and 109 water concentration samples showed that atmospheric deposition was a main pathway of Pb entering the BS and NYS, whereas riverine discharge dominated the input of Cr, Cu, Zn, Cd, and As into the marine environment. Modeled results showed that the fractions of HMA in the water bodies compared with their total burdens were 86.6 ± 4.55% in the Liaodong Bay, 60.5 ± 10.5% in the Bohai Bay, 20.9 ± 9.05% in the Laizhou Bay, 95.1 ± 2.06% in the Central BS, and 94.3 ± 1.93% in the NYS. The lowest fraction of HMA in the Laizhou Bay was attributed to high sedimentation rates and higher suspended particulate matter concentrations due to inputs from the Yellow River. The modeled 1-, 10- and 100- year mass budgets indicated that the Liaodong Bay in the north of the BS was a sink of HMA, the Bohai Bay and Laizhou Bay in the west and south of the BS acted as sources, and the Central BS and NYS were a transition area for most HMA.

1. Introduction

The Bohai Sea (BS) watershed is one of the most populated and industrialized regions in China. With rapid economic development and urbanization over the past few decades around the BS, the marine ecosystem has been heavily contaminated by the input and discharge of toxic chemicals through the atmosphere, runoff, and surrounding rivers. Considerable attention has been paid to the environmental pollution of the BS due to the significance of the BS Rim to China (Duan and Li, 2017; Gao et al., 2014). In the coastal area of the BS, which is known as the BS Economic Rim (BSER), there are four key national economic zones, including the Tianjin Binhai New Area, Liaoning Coastal Economic Zone, Yellow River Delta Eco-economic Zone, and Blue Economic Zone of Shandong

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Peninsula, as of 2000 (Liu et al., 2014). The establishment of these economic zones has led to rapid population aggregation and intensive expansion of urbanization and industrialization in the BSER (Wu et al., 2016), thereby putting the BSER at risk to environmental stress (SOA(State-Oceanic-Administration-of-China) 2017). A number of surveys demonstrated that the estuary and bay ecosystems in the BS have been in sub-healthy and unhealthy states in recent years (Gao et al., 2014) and heavy metals and arsenic (HMA) were some of the most important pollutants (Hu et al., 2017, SOA(State-Oceanic-Administration-of-China) 2017, Zhang and Gao 2015).

Identification of the flux and source-sink relationship of HMA in the BS is vital in order to design effective programs and strategies to regulate and restore its ecosystem (Fang ets al. 2015). To improve the BS's environmental condition, the Chinese government made great efforts and launched national programs, such as the 'Bohai Blue Sea Action Plan' in 2001 (Gao et al., 2014). However, the programs have not achieved sufficient success (Gao et al., 2014). The flux and source-sink relationship of pollutant in the BS were also not established. Nevertheless, many sampling campaigns under the umbrella of this program and other national programs were launched to assess the BS's environmental condition. These campaigns measured various chemical markers, including nutrients, organic compounds, and toxic heavy metals in the water column, biota, and sediments of the BS (Gao et al., 2014; Meng et al., 2017; Zhang et al., 2009). Of the many pollutants identified, HMA have been identified as the most prevalent pollutants leading to the degeneration of the BS ecosystem (SOA(State-Oceanic-Administration-of-China) 2017). HMA are often used as tracers in the assessment of source-sink relationship of pollutant because they are the most persistent and do not decompose in the environment (Liu et al., 2017; Pan and Wang, 2012).

The input and output fluxes of HMA are crucial information for building their source-sink relationship in the BS. Usually, atmospheric deposition and river runoff are considered the primary input pathways of HMA entering the BS (Duan and Li, 2017). Their burial in sediments can be treated as the dominant output pathway (Fang et al., 2015) and their exchange between the BS and the North Yellow Sea (NYS) can be viewed as the dominant output or input pathway (Fang et al., 2015; Wang et al., 2007). However, the knowledge about the HMA source-sink relationship gained from previous studies was disproportionate. Data on the HMA environmental loadings in the BS sediments are the most abundant. For instance, a recent review article summarized more than 3000 HMA concentration records in the BS sediments (Duan and Li, 2017). The second amplest data are the HMA concentrations in the water bodies of the BS and its estuaries (Wang and Wang, 2007; Xu et al., 2013a). Regarding these estuaries, more concern has been paid to large rivers, such as the Yellow River (Bi et al., 2014; Tang et al., 2010; Wang et al., 2016) and Liao River (Yang et al., 2015). While there are more than 40 rivers entering the BS (Gao et al., 2014), a systematic and comprehensive HMA survey of estuaries has not been conducted. In particular, there is a large knowledge gap regarding HMA atmospheric deposition to the BS due to scarce measurements.

This study conducted a sampling campaign to collect atmospheric deposition samples and riverine water samples across the BS and NYS to fill knowledge and data gaps of HMA. A model was developed to quantify HMA source-sink relationship, which took into account the measured land-source input, burial into sediments, and transport by water exchange among the BS's four subareas and the NYS. The major objectives of the present study were (1) to examine the spatiotemporal patterns of atmospheric deposition rates and river concentrations of HMA, (2) to assess the HMA fluxes via atmospheric deposition and river discharge and their respective contributions to the total budget, and (3) to establish source-sink relationship of HMA in the BS and NYS.

2. Materials and methods

2.1. Sampling site and sample collection

The BS is a semi-enclosed and shallow marginal sea of the northwestern Pacific Ocean on the northern coast of China. Administratively, the BS is adjacent to the Liaoning, Hebei and Shandong Provinces, as well as the Tianjin Municipality. The BS can be geographically divided into four parts, including the Liaodong Bay in the north, Bohai Bay in the west, Laizhou Bay in the south, and the Central BS. The BS is connected to the NYS on its east edge through the Bohai Strait, as shown in Fig. 1. The NYS is separated from the South Yellow Sea to the south by a boundary from Chengshantou at the east edge of the Shandong Peninsula to Changsangot on the Korean Peninsula (Li et al., 2016). The NYS and Bohai Strait are the major channels of matter exchange between the BS and open seas (Liu et al., 2009).

The sampling area in the present study covered the BS and NYS in China. Atmospheric bulk deposition samples (mixture of dry and wet deposition) were collected seasonally from summer 2014 to winter 2015 at 12 sampling sites, as shown in Fig. 1. A total of 76 bulk deposition samples were collected during the sampling period. The details are described in Text S1 and Table S1 of Supporting Information (SI). Water samples were collected from 37 major rivers around the BS and NYS in 2015. The total water volume of the 37 rivers accounts for more than 98% of the total river discharge into the BS and NYS (Wang et al., 2015). The samples in normal, rainy, and dry seasons were collected from late May to early June, from late August to early September, and from late November to early December 2015, respectively. Three or five water samples collected along one transect were mixed to form a single sample, which was then immediately filtered through an acid-treated microporous filter (0.45 mm mesh) into pre-cleaned high-density polyethylene containers in the field. The filtered samples were acidified to $pH < 2$ with HNO_3 and then delivered to our laboratory, where they were kept at 4 °C before further analyses. A total of 109 water samples were collected. The detailed information is presented in Text S1 and Table S2 of SI.

2.2. Sample analysis

Bulk deposition samples were presented as water solutions, and the same method was used to analyze HMA in deposition samples and river water samples (Sharma et al., 2008). Before analysis, some of the insects and large biological debris were removed from samples. Original water samples were filtered using a sand core filter with a polyether sulfone (PES) membrane filter (0.2 μm). The filtrate was collected in a glass bottle and was directly measured for soluble HMA using Inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer ELAN DRC II). PES membranes were subjected to 24-h equilibration at 25 °C ± 1 °C temperature and 50% ± 2% relative humidity before and after use. Loaded filters were put into a Teflon digestion tank and 5 mL of high-purity HNO_3 were added for microwave digestion. The supernatant of the digested solution was used to measure the particle fraction of HMA using ICP-MS. Six HMA, including Lead (Pb), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd), and arsenic (As) in the field samples were determined in the field samples. Atmospheric deposition rates (μg m^{-2} day^{-1}) were calculated using the measured total amount of HMA divided by the area of the sampler mouth and the sampling times.

Duplicate blanks and standard reference materials (Chinese