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Sedimentary mercury (Hg) in the marginal seas adjacent to Chinese high-Hg emissions: Source-to-sink, mass inventory, and accumulation history

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ABSTRACT

We comprehensively investigated sedimentary Hg in Yellow and East China Seas (YECSs), which constitute potentially important depocenters for large anthropogenic Hg emissions from mainland China. A large dataset of Al-TOC-Hg concentrations led to an in-depth understanding of sedimentary Hg in the entire YECSs, including distribution and its determinants, source-to-sink, background levels, inventory in flux and budget, and accumulation history. Especially, the net atmospheric Hg flux to the sediments was estimated to be 1.3×10^{-5} g/m^2/yr, which corresponded reasonably well to that calculated using a box model. About 21.2 tons of atmospheric Hg (approximately 4% of the total anthropogenic atmospheric Hg emissions from China) were buried annually in the YECS basin. This result implies that most of atmospheric Hg from China is transferred to the surface of the Pacific (including the East/Japan Sea and South China Sea) by the westerlies and, consequently, can play a critical role in open-sea aquatic ecosystems.

1. Introduction

Mercury (Hg) is one of the most hazardous, persistent, and toxic contaminants that can be globally transported by the atmosphere from an emission source, resulting in worldwide contamination and biomagnification in aquatic environments (Fitzgerald et al., 1998). Globally, Hg levels in the atmosphere and sediments/soils have been continually increasing; for example, atmospheric Hg deposition has increased approximately threefold since preindustrial times (Lamborg et al., 2002; Lindberg et al., 2007), and the amount of riverine Hg buried in marginal seas has been increasing by 40–400% since the 1900s, particularly in China and India (An et al., 2010; Shi et al., 2010; Lim et al., 2012; Amos et al., 2014).

East Asia (mainly China and India) is one of the largest Hg emission source regions in the world, contributing approximately 54% of global anthropogenic emissions (Pacyna et al. 2006 and 2010; Holmes et al., 2010; Fig. 1a). In particular, China contributes about 30 and 50% of global and Asian anthropogenic Hg emissions, respectively, which potentially increases the input of Hg to adjacent seas via wet/dry deposition because of the short lifetime of reactive gaseous and particulate Hg (Ci et al., 2011). Several studies have shown that Hg emitted from the East Asian region was recently transported long-range to the North American continent due to a large-scale atmospheric transport event, a springtime Asian dust episode (Jaffe et al., 2005; Obrist et al., 2008). The riverine input, approximately 2030 Mg yr^{-1} to the North Pacific (including marginal seas), is mainly derived from the major Chinese rivers and accounts for 37% of the global riverine inventory (Holmes et al., 2010; Amos et al., 2014). Thus, Hg from mainland China probably plays a leading role in regional (North Pacific marginal seas) and global Hg balances. Accordingly, studies of sedimentary Hg in Chinese marginal seas may yield important information about regional and global Hg cycles, as well as the behavior of anthropogenic Hg.

The Yellow and East China Seas (YECSs), which are adjacent to Chinese high Hg emission source regions, might be vulnerable to the impact of anthropogenic Hg, and their sediments are probably important reservoirs for Chinese land-based Hg via atmospheric and riverine transport. There have been several recent studies of the distribution and flux of sedimentary Hg, mostly in the estuarine, coastal, and/or inner shelf zones of the East and South China Seas, mainly

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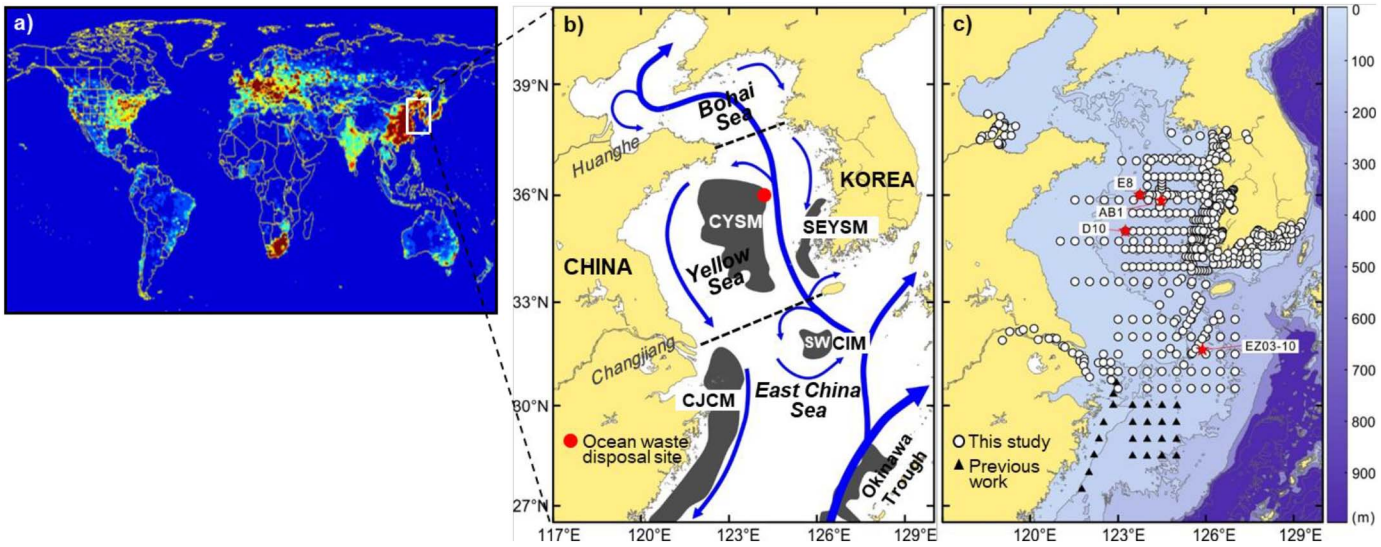

Fig. 1. Maps showing the global anthropogenic emissions (ton/year, Dastoor and Larocque, 2004) (a), the shelf mud patches, and current systems (arrows) in the Yellow and East China Seas (YECSs) (b), and the surface and core sampling sites (c). CYSM: central Yellow Sea mud, SEYSM: southeastern Yellow Sea mud, SWCIM: southwestern Cheju Island mud, CJCM: Changjiang coastal mud.

associated with the Changjiang (Yangtze) River and Pearl River depositional systems (Liu et al., 1990; Shi et al. 2005 and 2010; Fang and Chen, 2010; Meng et al., 2014; Liu et al., 2017). The total deposition budget of Hg in the Changjiang coastal and inner shelf zones was reported as approaching 52 ton/yr, with a deposition rate of 6–120 ng/cm^2/yr, suggesting that this zone was a major sink for Changjiang-derived anthropogenic Hg (Meng et al., 2014; Liu et al., 2017). More recently, there have been some efforts to simulate and calculate Hg export from mainland China to the adjacent seas on the basis of the box model (Ci et al., 2014; Liu et al., 2016). However, these previous studies of sedimentary Hg were conducted locally, mainly in the river-dominated coastal and inner shelf zones (particularly the eastern Chinese coastal zone) of YECSs, which are associated with riverine Hg inputs. Due to uncertainties and the limited availability of data, the model provides relatively rough calculations and predictions (Ci et al., 2014; Liu et al., 2016). In fact, the quality and quantity of available sedimentary Hg data, on which we rely for mass inventories of Hg in marginal seas, are limited. More importantly, literature is lacking on source-to-sink, flux, budget, and mass inventory of sedimentary Hg for the entire YECS basin. The ocean waste-disposal site, located in the central part of the Yellow Sea (Fig. 1b), is considered to be another potential point source of anthropogenic Hg, together with several large and small rivers. However, there is no observational evidence of the influence of ocean waste disposal, particularly with regard to Hg accumulation.

In this study, we present the first comprehensive dataset for sedimentary Hg, as well as aluminum (Al) and total organic carbon (TOC), for the YECS shelf area, including riverine, estuarine, and coastal environment systems. On the basis of this large dataset, we examine the source-to-sink processes, mass inventory (flux and budget), and accumulation history (including the background value) of sedimentary Hg in the YECSs. Our results may contribute significantly to a better understanding of the behavior of Hg from Chinese sources, and will help to further refine global estimates of Hg discharge to ocean margins and open oceans in East Asia.

2. Analytical methods

A total of 492 surface sediments and four sediment cores were taken from the YECS shelf, including Korean and Chinese rivers, estuaries, and coastal zones (Fig. 1c). For Hg, Al, lead (Pb), and TOC contents, the sediment samples were freeze-dried and then ground. Total Hg (THg) concentrations of the sediments, together with a standard reference material (MESS-3), were measured using a Hydra II C direct Hg analyzer (Teledyne Leeman Labs Inc., Hudson, NH, USA), which utilizes the serial processes of thermal composition, catalytic reduction, amalgamation, desorption, and atomic absorption spectroscopy. The analytical accuracies were within 5%, based on the certified accuracy of the reference material, and the analytical precision error was < 10% in all THg analyses, based on replication of several standard materials and sediment samples.

For Al and Pb concentrations, the powdered sediment samples, including a standard reference material (MAG-1), were dissolved in a mixture of hydrofluoric and perchloric acids, and these solutions were then analyzed to determine elemental concentrations using inductively coupled plasma atomic emission spectroscopy. The analytical accuracy and precision errors were between 5 and 10%, indicating satisfactory data acquisition. Total carbon (TC) and total inorganic carbon (TIC) content in the sediments were measured using an elemental analyzer (FLASH 2000: Thermo Fisher Scientific, Waltham, MA, USA) and a CO_2 coulometer (model CM5014: UIC, Joliet, IL, USA), respectively. The analytical accuracies and precision for these elements were within 5%, based on the analysis of standard reference materials (L-cysteine in the TC analysis and calcium carbonate with 12.00% C in the TIC analysis) and/or replicate samples. TOC content was calculated as the difference between TC and TIC content.

To reconstruct the ages of the three box cores (AB1, D10, and E8, see Fig. 1c), sedimentation rates were determined using excess ^{210}Pb ($^{210}Pb_{ex}$) activity values, which are equivalent to the total ^{210}Pb activity ($^{210}Pb_{tot}$) minus the supported ^{210}Pb activity that is in equilibrium with sedimentary ^{226}Ra. The analytical method used to determine ^{210}Pb activity has been described in detail in many previous studies of YECS core sediments (e.g., Lim et al. 2007a and 2012). The ^{210}Pb-derived linear sedimentation rates calculated from the gradient of $^{210}Pb_{ex}$ activity in each core were estimated to be 0.09, 0.14, and 0.10 cm/yr in cores AB1, D10, and E8, respectively, from the central Yellow Sea mud (CYSM) area of the Yellow Sea shelf. These rates are similar to those previously reported for this area (approximately 0.10 cm/yr; Lim et al., 2007a and references therein). The sedimentation rate of core EZ03-10 sediments from the southwestern Cheju Island mud (SWCIM) area of the East China Sea (ECS) was calculated on the basis of the accelerator mass spectrometry (AMS) ^{14}C age (1030 ± 40 yr BP) of foraminifera identified at a core depth of 150 cm (Dou et al., 2015). The linear sedimentation rate of the core was estimated at approximately 0.15 cm/yr, which is slightly lower than that (0.2–0.5 cm/yr) reported in a