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Baseline

Spatial variation, fractionation and sedimentary records of mercury in the East China Sea

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ABSTRACT

Surface and core sediments were collected to study distributions, phases and potential environmental risk of Hg and to reconstruct anthropogenic Hg change over the past one hundred years in the East China Sea (ECS). Hg contents in surface sediments displayed a decreasing gradient from the Changjiang Estuary to the outer sea. Sequential extraction analysis showed that Hg mainly existed as residual fraction (70.18% of total), and while organic matter fraction (22.96% of total) was the main component of labile fraction, indicating the strong adsorption of organic matters on Hg. Enrichment factor and sediment quality guidelines suggested that Hg in sediments of ECS were at minor enrichment and low adverse effect. Temporal distributions of total Hg content, labile fraction, burial flux and anthropogenic Hg flux showed that anthropogenic Hg input increased since the 1960s, which was related to riverine input and atmospheric transport.

Mercury (Hg) is considered to be one of the most harmful pollutants for marine environment, and is recognized to be extremely toxic even at trace levels because its transfer along the trophic chains is associated with bioconcentration and biomagnification processes (Ullrich et al., 2001; Covelli et al., 2012). The negative effects of Hg on ecosystems and human health are mostly related to its transformation into the more toxic and mobile organic form, methyl-Hg (MeHg; Ullrich et al., 2001). MeHg is a neurotoxin and lipophilic organic compound which readily crosses biological membranes and accumulates to harmful concentrations in expose organisms, which then biomagnifies in aquatic food webs to concentrations of toxicological concern. Thus, Hg is listed as a priority pollutant by international agencies in charge of marine environmental protection due to its high toxicity, biomagnification and difficulties on its control (Beiras et al., 2002; García-Rico et al., 2006).

Hg is a naturally occurring element that is widespread in environment (e.g., Hg abundance in the crust is approximately 7 ng/g, Chi, 2004; Hg background in marine sediments is 50–80 ng/g, Fujii, 1976), but there also are anthropogenic Hg released to air and water as byproducts of various industrial processes, including coal burning, fossil fuel combustion and chloroalkali production (Chakraborty and Babu, 2015; Cristol et al., 2008). Once entering into waters, Hg has a high tendency to be sorbed on organic and inorganic particles and eventually settles down and accumulate in sediments (Ullrich et al., 2001), making deposition three to five times larger than preindustrial deposition in the northern hemisphere (Selin, 2009; Yang et al., 2010). Thus, sediments can represent efficient Hg traps and archives of past contamination (Castelle et al., 2007; Stupar et al., 2014).

However, besides the role of sink, contaminated sediments can also serve as a long-term source of Hg because their stability and fate are strongly influenced by environmental conditions (e.g., pH, redox condition, sulfide concentration; Baig et al., 2009). When environmental conditions change, the labile Hg associated with sediments is released to overlying waters, threatening the aquatic biota (Prica et al., 2008). Sequential extraction procedure proposed by Tessier et al. (1979) is commonly used to distinguish the binding forms of trace elements in sediment and better estimate their potential mobility and ecotoxicological effect under different environmental conditions. It partitions trace elements into five fractions including exchangeable, carbonates, Fe–Mn oxides, organic matter and residual fractions. The exchangeable metals are likely to be affected if water ionic composition changes, the metals bound to carbonates are susceptible to changes of pH. Metals bound to Fe–Mn oxides and organic speciation are susceptible to the redox conditions, and while the residual metals are not expected to be released in solution under natural conditions (Duan et al., 2010; Feng et al., 2014). Extraordinarily high proportions of labile fractions (exchangeable, carbonates, Fe–Mn oxides and organic matter fractions) are usually deemed as an indication of anthropogenic input, while residual fraction represents natural lithogenic input (Ram et al., 2009; Acquavita et al., 2012).

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Anthropogenic Hg beginning to discharge into coastal waters of China since 1960s due to the increasing economic growth has significantly altered the coastal Hg cycle (Gao and Chen, 2012; Pan and Wang, 2012). Potential risks of sedimentary Hg also existed since 1960s. Identification of long-term trends in Hg contamination can contribute to a better understanding of long-term risks of Hg and determining what anthropogenic activities have released Hg into the coastal waters, and can assist in evaluation of the effectiveness of environmental legislation aimed at reducing the impact of human activities. Heavy metal records in sediment core have been used to assess long-term enrichment and potential contamination risks of metals and reconstruct the history of human disturbance (Legesse et al., 2002; Duan et al., 2013). At present, most historical reconstruction of Hg accumulation in marine environments is based on total concentration, it does not provide any information on the changing rates of Hg accumulation in sediments. However, buried flux can be used as an effective proxy to reflect the changing rates of Hg accumulation in sediments due to it is influenced by several processes, including Hg flux from the sea surface to sea floor, and burial and preservation at the sea floor. These processes depend on different variables, such as sedimentation rate, sediment porosity, microbial activity, bioturbation rates and bottom water oxygen conditions (Schenau et al., 2005).

The East China Sea (ECS) is the largest marginal sea in the western Pacific Ocean, covering an area of approximately 5.0×10^5 km^2 (Fang et al., 2009). The Changjiang River is the major source of material to ECS, annually delivering 4.61×10^8 t sediment into ECS (Zhang and Liu, 2002). There are many developed cities along the coast, such as Shanghai and Ningbo, resulting in a large number of factories in the area. Due to a lack of waste control practices, many studies have indicated that heavy metal contamination exist in coastal area of ECS since 1960s (Huh and Chen, 1999; Yuan et al., 2004). It was recently reported that the amount of heavy metals (Cu, Pb, Zn, Cd and Hg) flowing into ECS from Changjiang River was 2.4×10^4 t/yr on average from 2002–2010 (Bulletin of China's Marine Environmental Status of China for the year of 2002 to 2010, 2002–2010). However, previous studies on Hg in the ECS is scarce and mainly focused on its total concentration in surface sediments (Fang and Chen, 2010; Liu et al., 2011). Chemical fractions of Hg, effective index of pollution status and potential risk of Hg in sediment were rarely studied in the ECS. Besides, the baseline data on long-term changing trends of Hg contamination in the ECS also is absent. Therefore, the objectives of the study were to (1) determine Hg distributions and its influencing factors in sediments; (2) analyze chemical fractions of Hg in sediments; (3) assess eco-environmental risks of Hg in the ECS; and (4) trace the historical changes of Hg in the ECS.

Thirty-eight surface sediments and two sediment cores from the ECS were sampled in May 2009 with the cruise of "Kexue 1" (Fig. 1). Surface sediments (0–2 cm) were collected using a box sampler. Immediately after collection, samples were placed in pre-cleaned polyethylene bags, sealed, and refrigerated. Two sediment cores (G1 and A5) were collected using a gravity corer (Fig. 1). Core G1 (122°31.05′E, 29°30.25′N) is located in the inner shelf coastal mud area with a water depth of 32 m; core A5 (124°59.66′E, 32°30.04′N) is located in the middle shelf mud area with a water depth of 59 m. Immediately after collection, the cores were sectioned at 2 cm intervals and stored in pre-cleaned polyethylene bags, sealed, and refrigerated until lab analysis. Both of surface and core sediments were transported to the laboratory within a month. All sediment samples were freeze-dried in lab. Dried aliquots were ground using an agate mortar and pestle for homogenization, and prepared for analysis.

The analytical technique for Hg was performed by modifying a method of Covelli et al. (2012). Briefly, total Hg content was determined on about 0.2 g of freeze-dried sample digested with a mixture of 10 ml of aqua regia in a closed Teflon digestion vessel heated in water bath for 2 h. The resulting solutions were analyzed by Cold-Vapor Atomic Fluorescence Spectrometry (CV AFS) using 0.7% KBH_4 with 0.05 M NaOH as a reducing agent.

A sequential extraction procedure of Tessier et al. (1979) was conducted to fractionate Hg phase. Briefly, exchangeable (F1), bound to carbonate (F2), bound to Fe–Mn oxide (F3), and bound to organic matter (F4) fractions of Hg were sequentially extracted with 1 M $MgCl_2$ (pH 7.0, room temperature, 1 h), 1 M NaOAc (pH 5.0, room temperature, 5 h), 0.04 M $NH_2OH \cdot HCl$ in 25% HOAc (96 °C, 5 h), and 0.02 M HNO_3 and 30% H_2O_2 (pH 2, twice, 85 °C, 2 h and 3 h each time) followed by 3.2 M NH_4OAc in 20% (v/v) HNO_3 (room temperature, 0.5 h). The extractants were treated with the same way as total Hg and then were determined by CV-AFS. Hg in F5 was obtained as the difference between total content and the sum of former four extracted phases.

Total organic carbon (TOC) was analyzed by the Walkley–Black method (Gaudette et al., 1974). $CaCO_3$ was measured by the method of Yu et al. (2013). Total Fe content was determined by the method of Karamanev et al. (2002). Sediment grain size was measured by a Laser

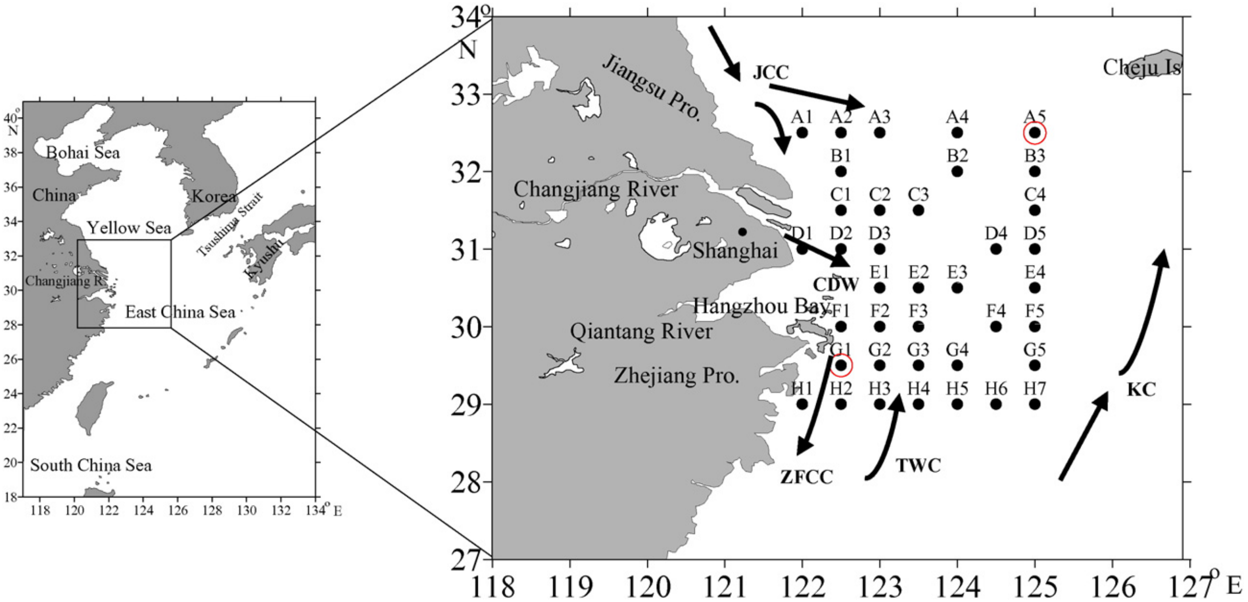

Fig. 1. Location of the stations in the East China Sea. ● indicates surface sediments, ○ indicates cores. The currents are pointed out by arrows. CDW: the Changjiang Dilute Water; KC: the Kuroshio Current; JCC: the Jiangsu Coastal Current; ZFCC: the Zhejiang–Fujian Coastal Current; TW: Taiwan Warm Current.