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An 87-year sedimentary record of mercury contamination in the Old Yellow River Estuary of China

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ABSTRACT

A sediment core, spanning from the year 1925 ± 3.03 to 2012, was collected for analyzing historical distribution of mercury (Hg) in the Old Yellow River Estuary (OYRE), China. The Hg concentrations in the sediment core ranged from 14 to 351 ng g^{-1}, with the high values occurred in the middle layers (1960–1996), which may be resulted from intensive human activities during this period, such as oil exploitation and booming of petrochemical industry, salt chemical industry and chlor-alkali plants. A significant positive correlation was found between THg and loss on ignition (LOI). The main fraction of Hg existed in residual part while the fraction that was easy to leach out from sediments accounted for only a small portion according to the results of BCR sequential extraction procedure. Multiple ecological risks indices and guidelines of Hg indicated that the sedimentary record presented an "intermediate state" for Hg contamination in the OYRE.

1. Introduction

Mercury (Hg) is classified as a high priority pollutant by many international agencies due to its persistence in environment, great poisonousness to living beings and bioaccumulation through food chains (Sellers et al., 1996; Jiang et al., 2006; Todorova et al., 2015). When Hg is released into aquatic systems, it is easy to deposit into sediments (Lorey and Driscoll, 1999). However, mercury absorbed in sediments may also desorb into aquatic environment and cause secondary contamination when the physical and chemical properties of the environment change (Biester et al., 2000). Moreover, the sediment is deemed as the main production place for inorganic mercury to be transformed into methylmercury (MeHg) (Shi et al., 2005), which is a well-known neurotoxin(Myers et al., 1998; Rush et al., 2012), and can accumulate through food chains, placing people who consume predatory fish at great risks.

Estuarine system not only provides unique habitats for a diversity of species (Benoit et al., 1998; Yu et al., 2012), but also acts as a passage for terrestrial materials including Hg to be discharged into the sea (Vicente-Martorell et al., 2009; Han et al., 2017). Since 90% of the trace metals in estuarine system are reserved in the sediments (Sarkar, 2017), the sediment core has been frequently researched to reconstruct the historical contamination status of trace metals in estuarine environments (Valette-Silver, 1993; Ruiz-Fernández et al., 2002; Xu et al., 2014).

Many literatures have made efforts to explore the Hg contamination in sediments in the main estuaries of China, such as researches on the Pearl River Estuary and Yangtze River estuary of China (Yu et al., 2012; Wang et al., 2015; Tao et al., 2016; Chen et al., 2001; An et al., 2009). However, few literatures have studied on the contamination level of Hg in the Yellow River Estuary, especially on the Hg historical contamination and ecological risk assessment. The Old Yellow River Estuary (OYRE), which was the estuary for the water in Yellow River (the second longest river in China) flowed into Bohai Sea during 1976–1996, is an important estuary that has went through various anthropogenic disturbance, such as oil exploration and production, artificial diversions of the channel of Yellow River, and booming of industry. Therefore, it is significant to figure out the influence of human activities on the historical Hg variation and evaluate the ecological risk in the OYRE.

The objectives of this work are to (1) investigate Hg historical contamination level in sediments of the OYRE; (2) recognize the critical factors affecting the Hg distribution; (3) determine the bioavailable property of Hg using the BCR-sequential extraction method; (4) estimate the contamination level and ecological risks of Hg in sediments of the OYRE using multiple indices and guidelines.

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2. Materials and method

2.1. Study area and sampling site

The Estuary of Yellow River has received significant attentions for large amount of silt sedimentation. About 1.4 billion tons of silt annually are washed down from the Loess Plateau, transported by flowing water of Yellow River (the second longest river in China), and carried into the shallow Bohai Gulf through the Yellow River Estuary (Cui et al., 2009). The Old Yellow River Estuary (OYRE) is located in Qingshuigou course of Dongying City, Shandong Province, China. Great changes have taken place there over the last century. In 1960, Shengli Oilfield, the second largest oilfield in China, was discovered near the OYRE. Human activities that came with the oil exploitation and subsequent booming of petrochemical industry, salt chemical industry and chlor-alkali plants posed severe threats to the OYRE ecological system and adjacent coastal area (Zhuang and Gao, 2015). To ensure the safety and development of local agriculture, industry and oil exploitation, the government adopted measures to rechannel the Yellow River twice in 1976 and 1996, respectively (Yuan et al., 2014). During 1976 to 1996, the Yellow River fed into the Bohai Sea through the OYRE, and then changed into the new Yellow River Estuary since 1996. Subsequently, the OYRE became an abandoned estuary. In recent decades, great attention has been paid to ecological protection. To protect the local Wetland ecological system and rare and endangered birds, the Nature Reserve of Yellow River Delta was established in 1992. Frequent human activities and environmental changes over the last century have caused great effects on the local environment.

In July 2012, a 41-cm long sediment core was sampled near the mouth of the OYRE (37°39′5.48″ N, 119°16′19.15″ E) (Fig. 1). The sediment core was collected using a gravity corer. The corer was driven vertically into the undisturbed sediment and then pulled up. The sediment core was retained in the coring tube (PVC material, 80 mm in diameter). At the sampling site, three sediment cores were collected randomly from the same area and the longest and most intact core was selected for use. The PVC coring tube was sliced open immediately after collection. The entire sediment core was divided into sub-samples at 1 cm intervals along the profile using a stainless-steel cutter. All the sectioned samples were wrapped in aluminium foil and then transported to the laboratory on ice. All samples were freeze-dried to constant mass, then ground, and sieved with a nylon sieve of 100 meshes per inch, and stored in polyethylene bags in desiccators for later analysis.

2.2. ^{210}Pb dating and mercury analysis

The sediment core date was determined using the ^{210}Pb dating techniques. The calculating method of dates and uncertainty associated with the dating method were described by Sanchez-Cabeza and Ruiz-Fernández (2012). ^{137}Cs chronology was also determined for calibration. Before the analysis, 5 g samples were introduced into the centrifuge tubes and sealed for over three weeks to allow radioactive equilibration of ^{226}Ra and its daughter isotope ^{214}Pb. The activities of ^{210}Pb, ^{226}Ra and ^{137}Cs in sediment were measured by an Ortec HPGe GWL series well-type coaxial low background intrinsic Ge detector manufactured by AMETEK at 46.5 keV, 352 keV and 662 keV, respectively. The activity of excess ^{210}Pb (^{210}Pb$_{ex}$) was obtained by subtracting ^{226}Ra activities from total ^{210}Pb activities. The chronology and the sedimentation rate of the sediment core were calculated using a constant rate of supply (CRS) dating model (Appleby, 2002):

$$t(i) = \frac{1}{\lambda} \ln\left[\frac{A(0)}{A(i)}\right]$$

$$r(i) = \lambda \frac{A(i)}{C_i}$$

where t(i) is the time elapsed since formation of sediment at depth (i), A(i) is the accumulated deposit of ^{210}Pb$_{ex}$ below depth (i), A(0) is the inventory of ^{210}Pb$_{ex}$ in the whole core, C_i is the concentration of ^{210}Pb$_{ex}$ in section i, λ is the decay constant of ^{210}Pb (λ = 0.031 yr^{-1}).

The concentrations of mercury solution were determined by cold vapor atomic fluorescence spectrometry (AFS-9600, Haiguang Instrument Co. Ltd., Beijing, China). Approximately 0.3 g of dried sediments were acid digested by 12 mL of aqua regia in a narrow-mouth Erlenmeyer flask covered with a watch glass for approximately 12 h (until the formation of brown nitrous gases had ceased) on a hot plate, which was gradually elevated from room temperature to 110 °C. To oxidize all forms of Hg to Hg(II), 0.1 mL bromine monochloride (BrCl) was added to the cooled digested solution (Bloom and Crecelius, 1983). Then the solution was diluted to 25 mL with Milli-Q water and stored at 4 °C until analysis.

Reagent blanks, sample replicates and standard reference materials (GSD-9, GSS8, GSS9, China) were digested with the same protocol. The recovery rates of standard reference materials ranged from 90% to 106%. Duplicate samples were measured to estimate reproducibility, the difference was not > 10%.

2.3. Sequential extraction

The three-step BCR sequential extraction procedure was proposed by the Community Bureau of Reference (Ure et al., 1993). Its modified version which was successfully used by Chakraborty et al. (2014) for Hg speciation in estuarine sediments was applied in this work (Table 1). Four kinds of Hg fractions were extracted: step 1, the sum of ion-exchangeable, water soluble and carbonate fraction of Hg (F1); step 2, reducible fraction of Hg (F2); step 3, oxidizable fraction of Hg (F3); and digested solution of the residue from Step 3, residual fraction of Hg (F4). The Hg concentrations in each extracted solution and in digestion solution of residual fraction were analyzed in duplicate by AFS. The values of (F1 + F2 + F3 + F4) / total Hg (THg) for certified reference materials (GSD-9, GSS8, GSS9, China) were used to verify the accuracy of the method, which ranged from 86% to 118%.

3. Result and discussion

3.1. Historical distribution of mercury concentrations in core sediments

The ^{210}Pb$_{ex}$ dating results and its uncertainty associated with the CRS dating model were shown in Fig. 2. The dating results indicated that ages of the core from the OYRE spanned 87.22 ± 3.03 years, from the year 1925 ± 3.03 to 2012, and the average sedimentation rate of the sediment core was 0.46 cm yr^{-1}. Similar dating results of sediment core from the adjacent Bohai Sea were reported by Hu et al. (2011). They applied ^{210}Pb dating method to study the chronologies of the sediment core at site BC2 (near the estuary of Yellow River), and found that the age of the bottom sediment (at depth of 40 cm) of the core was around the year 1920 and the average sedimentation rate of the whole core was 0.47 cm yr^{-1}.

The concentrations of total mercury (THg) in this sediment core ranged from 14 to 351 ng g^{-1}, with an average value of 200 ng g^{-1}. Compared with the results of other estuarine and coastal sediments worldwide (Table 2), the Hg values in this sediment core were comparable to those from the Pearl River Estuary of China (Yu et al., 2012), and much higher than those from the Berg River Estuary of South Africa (Kading et al., 2009), the Yellow Sea and the East China Sea (Meng et al., 2014), but much lower than those from the Seine Estuary of France (Mikac et al., 1999). It's worth noting that the average THg concentration in the sediments from the OYRE is approximately ten times of the background value in sediments of the Yellow River and in the soil of Shandong Province (CNEMC, 1990; Zhao and Yan, 1992), suggesting an important role of anthropogenic sources of Hg. However, the average value of surface sediments (0–10 cm, from year