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Fate modeling of mercury species and fluxes estimation in an urban river

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ABSTRACT

The fate and transfer of mercury in urban river is an important environmental concern. In this study, QWASI (Quantitative Water–Air–Sediment Interaction) model was selected to estimate the levels of total mercury and three mercury species in water and sediment, and was used to quantify the fluxes of mercury at water/air and sediment/water interfaces of an urban river. The predicted mercury levels in water and sediments were closed to the measured values. Water inflow, re-suspension of sediment and diffusion from sediment to water are major input sources of mercury in water. The net mercury transfer flux from water to air was 0.16 ng/(m^2 h). At the sediment/water interface, a net total mercury transfer of 1.32 ng/(m^2 h) from water to sediment was seen. In addition to the existing dynamic flux chambers measurement, this model method could provide a new perspective to identify the distribution and transfer of mercury in the urban river.

1. Introduction

Mercury could be emitted to the air through many ways such as coal combustion (Streets et al., 2005). Mercury has also been widely used in numerous industrial products and related fields, such as chlor-alkali production, batteries, fluorescent lamps and thermometers. These factors cause the mercury pollution to be one of the biggest environmental concerns in China (Li et al., 2001; Feng and Qiu, 2008; Yin et al., 2009). China is believed to be the largest atmospheric mercury emission source in the world. Wu et al. (2006) calculated the total mercury emissions from all anthropogenic sources in China and found that emissions increased at an average annual rate of 2.9%, reaching 696 ± 307 metric tons in 2003. Due to the rapid development of industries and the lack of waste treatment facilities, a considerable amount of mercury is transported to aquatic systems through sludge, fertilizers, lime and manures as well as atmospheric deposition. Global background total mercury (THg) concentrations in water were reported to be below 5 ng/L (Fujii, 1976; Sullivan and Mason, 1998). The mercury levels in many waters of China are far beyond this level. For example, mercury concentration in Yitong River, Changchun City, was 208 ng/L during the normal period (Li, 2003), and in Cishan River, Huludao City, was 3630–9580 ng/L (Zhang and Wong, 2007). Besides, serious mercury pollution incidents caused by direct waste discharges from chemical plants near the Jiyun River (Zhang et al., 1981) and Songhua River (Zhang and Wong, 2007) also highlighted the urgency to pay attention to the mercury pollution of the aquatic system.

In the aquatic systems, another primary environmental concern associated with mercury is that, sediments can serve as a mercury source for the aquatic organisms. Inorganic mercury can be transformed into methylmercury (MeHg) by methylation, leading to bioaccumulation of MeHg in the aquatic food chain, and exposing the humans to mercury risks by direct consumption of contaminated fish finally (Compeau and Bartha, 1985; Mason et al., 1999). Generally, the major sources of mercury in the aquatic system include direct waste discharges, atmospheric deposition and inflows from upstream water (Mason et al., 1999; Rolfhus et al., 2003; Kim et al., 2004; Balcom et al., 2008). However, in the industrial areas with a long pollution history, mercury in the water may bind with suspended particles, and settle down to the sediment, so that the sediment becomes one of the main long term sinks of mercury pollution. In such conditions, even if no mercury containing waste is directly discharged into the water, the mercury in the sediment

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can be transported into the water through sediment re-suspension and water/sediment surface diffusion (Bloom et al., 2004; Mackay and Toose, 2004; Either et al., 2012). Our previous study reported that the mercury concentrations in surface sediments of the Haihe River, North China, were up to 375 ng/g (Tong et al., 2013). In Lake Taihu, concentrations of THg were in a range of 23–168 ng/g in superficial sediments, significantly higher than the established baseline levels of the lake (Chen et al., 2013). Hence, understanding and quantifying the processes governing mercury cycling in the river and lake is an important step for assessing the risks of mercury exposure to wildlife and humans.

Mercury source identification and fluxes quantification between different interfaces (such as air/water interface and sediment/water interface) have become an interesting topic for researchers. A great deal of researches has been conducted to identify the fate and flux of mercury discharges in aquatic systems by dynamic flux chambers (DFCs). DFCs have been deployed for the measurement of non-point source mercury emissions from a wide range of surfaces. The measurements of mercury emissions depend on the differences of air mercury concentrations entering and exiting the chamber (Eckley et al., 2010). The release flux of mercury from surface water to the atmosphere in Chongqing was measured using a DFC, and the mercury flux was always less than 10 ng/(m^2 h) (Wang et al., 2006). The mercury discharge from aquatic systems to air in coastal areas of the Mediterranean Basin was about 0.1 ± 0.2 ng/(m^2 h) (Ferrara and Mazzolai, 1998). In addition to the air/water interface, the flux of mercury and MeHg from estuarine sediments to water has also been studied (Rossmann, 1999; Muresan et al., 2007). However, a standard DFC protocol does not exist and a large diversity existed in the design and operating conditions that have been applied (Eckley et al., 2010). Uncertainty about the appropriate airflow rates through the chamber and chamber exposure to ambient wind could be major sources of potential errors during the applications of DFCs (Gillis and Miller, 2000).

In this paper, the QWASI model was selected to estimate the distribution of the mercury species and emission fluxes at different interfaces in the Haihe River, a typical urban river of China. The predicted mercury levels in the water and sediments were compared with the measured mercury concentrations (Tong et al., 2013). The mercury fluxes at the air/water and sediment/water interfaces were calculated to determine the role of different phases in the fate of mercury. The model results also presented the major mercury inputs and identified important processes that could affect the transfer of mercury in the aquatic system. This easily operated QWASI model could be a useful supplement to the current DFCs method in quantifying the mercury transport in the environment.

2. Methodology

2.1. Study area

The Haihe River (Fig. S1) is a typical urban river. It flows through the urban area of Tianjin City, and flows into the Bohai Sea at Dagukou. The Haihe River is one of the main water sources for Tianjin, and has played an important role in sustaining the rapid industrialization and urbanization in Tianjin. Tianjin is located approximately 100 km southeast of Beijing and is the second largest industrial and commercial city in North China (Fig. S1). Tianjin has an area of approximately 11, 200 km^2 and a population of 10 million. The average length, width and depth of the Haihe stem river are 33 km, 180 m and 11 m, with a surface area of 6×10^6 m^2. The rainy season is mainly concentrated in a very short period (the summer) in the Haihe River Basin, and the average annual precipitation is about 548 mm in this area. Another important water source for the Haihe River is from the Luanhe River, and the water input was 20, 000, 000 m^3 in 2009 (data from Tianjin Water Conservancy Bureau).

2.2. Multimedia modeling

The fugacity approach has been used to describe the multi-media behaviors of organic chemicals in aquatic systems (Mackay, 1991; Mackay and Arnot, 2011). However, this method is only applicable for chemicals with a measurable vapor pressure.

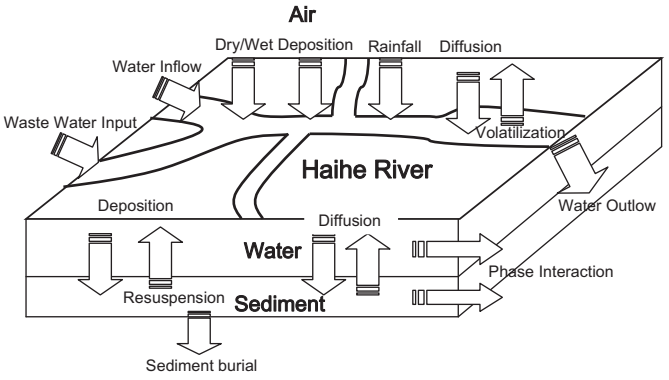

Fig. 1. Mercury transfer processes simulated in the model.

For most nonvolatile chemicals, such as heavy metals, another equilibrium criterion, aquivalence, is used. The details of the aquivalence approach are described in a previous study (Mackay and Diamond, 1989; Diamond, 1999; Diamond, 2000; Tong et al., 2012). Based on the QWASI and aquivalence approach, the behaviors and transfer fluxes of various mercury species (including Hg^{2+}, Hg^0, MeHg) of the water/air and water/sediment interface of the main stem of the Haihe River were described. The studied environmental processes, which are believed to be the major processes associated with the chemical fate of mercury in the river, are described in Fig. 1.

Chemical movement, transformation and species interconversion are expressed by flux (D) values (m^3/h). The definitions of the various mercury fluxes are listed in Table 1, and the calculations and parameters for determining the Z and D values are described in Tables S1–S4 of the supplementary material. Generally, the aquivalence capacity (Z) in the water was defined as "1", and Z values in the other phases were calculated based on the partition coefficient between water and the corresponding phase. The C (mol/m^3) and Q (mol/m^3) values represent the mass concentrations and aquivalence values, respectively, for the mercury species. The subscripts 0, 1, 2 and 3 represent the environment outside the study target, and the air, water and sediment phase, respectively. T_1 (mol/h) and T_2 (mol/h) represent the mercury inputs through water inflow and wastewater, respectively. T values were calculated by the mercury concentration in the water and its volume.

The chemical mass balance equations in the water and sediment phases, based on the input and output of mercury, were developed as follows.

For the water phase:

$$d(Q_2Z_2V_2)/dt = T_1 + T_2 + D_{12}M \times Q_1 + D_{12D} \times Q_1 + D_{12W} \times Q_1 + D_{12A} \times Q_1 + D_{32R} \times Q_3 + D_{32F} \times Q_3 - (D_{20} \times Q_2 + D_{21E} \times Q_2 + D_{23D} \times Q_2 + D_{23F} \times Q_2)$$

For the sediment phase:

$$d(Q_3Z_3V_3)/dt = D_{23D} \times Q_2 + D_{23F} \times Q_2 - (D_{32R} \times Q_3 + D_{32F} \times Q_3 + D_{30} \times Q_3)$$

Under steady-state conditions, the aquivalence values in water and sediment (Q_2 and Q_3) were calculated through mass balance equations. Then, the concentrations

Table 1
Definitions of mercury transfer processes in the studied environment.

	Mercury flux	Process
Input		
T02	D02 × C02	Water inflow
T03	D03 × C03	Direct waste input
Output		
T20	D20 × Q2	Water outflow (including water use)
T30	D30 × Q3	Sediment burial
Air/water interface		
T12M	D12M × Q1	Rainfall
T12D	D12D × Q1	Dry particle deposition
T12W	D12W × Q1	Wet particle deposition
T12A	D12A × Q1	Air to water diffusion
T21E	D21E × Q2	Volatilization
Sediment/water interface		
T23D	D23D × Q2	Deposition of suspended particles
T23F	D23F × Q2	Water to sediment diffusion
T32R	D32R × Q3	Sediment re-suspension
T32F	D32F × Q3	Sediment to water diffusion