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In situ high-resolution evaluation of labile arsenic and mercury in sediment of a large shallow lake

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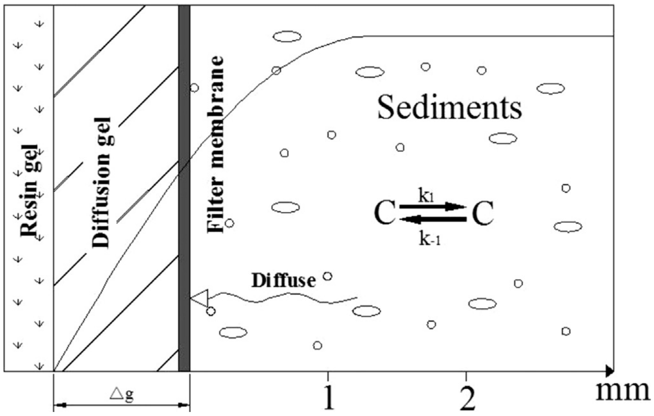
HIGHLIGHTS

- In situ measurement of As and Hg by DGT was applied on a large scale.
- Zr-O DGT for As and 3-mercaptopropyl functionalized silica gel DGT for Hg were used.
- DGT-labile As/Hg in sediment profiles exhibited considerable variation at mm scale.
- Sediment acted as a sink and source of As and Hg to the lake.
- DGT technique is an effective and robust tool that could be widely applied.

GRAPHICAL ABSTRACT



The principle of DGT is based on the diffusion of dissolved species through a well-defined gel and subsequent accumulation on an ion-exchange resin. A diffusion gel and a filter membrane (to protect the gel) are commonly used as the diffusive layer. The resin gel, which serves as a binding agent, is incorporated into a second polyacrylamide gel. The concentrations of the target elements are measured, including the fractions in pore water near the device surface and the fractions resupplied from solution, as well as that continuously released from the sediments.

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ABSTRACT

The precise evaluation of arsenic (As) and mercury (Hg) bioavailability in sediment is crucial to controlling As and Hg contamination, but traditional ex situ measurements hamper comprehensive analysis of labile As and Hg in sediment. In this study, we characterized in situ labile As and Hg in sediment of Lake Hongze using the zirconium (Zr) oxide diffusive gradients in thin films (DGT) technique and 3-mercaptopropyl functionalized silica gel DGT, respectively. The concentrations of DGT-labile As and Hg in the sediment profiles were found to exhibit considerable variation, ranging from 0.15 to 4.15 $\mu g\ L^{-1}$ for As and from 0.04 to 1.35 $\mu g\ L^{-1}$ for Hg. As and Hg flux values, calculated based on the concentration gradients measured from the DGT profiles for both the overlying water and sediment close to the sediment–water interface, were used to determine the contamination status of As and Hg. Flux values of As and Hg were between −0.066 and 0.067 $ng\ cm^{-2}\ d^{-1}$ and between −0.0187 and 0.0181 $ng\ cm^{-2}\ d^{-1}$, respectively. The GNU's Not Unix R (GNU R) programming language was used to identify outliers of As and Hg at various depths at the sampling sites. The results indicate that the sites with the most outliers were all located in the regions that were seriously affected by contaminants from the Huai River. The DGT-labile As and Hg concentrations in the 0–30 mm layer were found to be significantly correlated with

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concentrations of labile As and Hg, total dissolved As and Hg, and total As and Hg in the overlying water, as indicated by ex situ measurements. Results show that DGT is a reliable and high-resolution technique that can be used for in situ monitoring of the labile fractions of As and Hg in sediment in fresh water bodies.

1. Introduction

Anthropogenic activities, such as electroplating, smelting, fossil fuel combustion, and arsenic (As) and mercury (Hg) ore mining, are major contributors to As and Hg contamination of fresh waters (Cameron et al., 2004; Verplanck et al., 2008). Arsenic and mercury are notorious toxins that are on the United States Management Committee blacklist (Beryllium, Lyon: IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 1993). The World Health Organization has declared that at least 50 million people face threats from endemic arsenism (Williams et al., 2007). The situation is similarly serious for Hg contamination (McCormack, 2014). As is chemical species that may be bioaccumulated throughout the aquatic food chain, which is of concern from the perspective of human exposure (Bryan and Langston, 1992; Waring and Maher, 2005; Casado-Martinez et al., 2010). Previous work has indicated that Hg had an irreversible influence on organisms of the trophic food chains due to biomagnification (Fisher et al., 1984; Mathews and Fisher, 2008). Accordingly, monitoring As and Hg contamination in fresh water is of great significance.

Previous studies have shown that sediment plays an extremely important role in controlling the concentration of elements in fresh water (Søndergaard et al., 2007). Sediment is a major sink that can entrap and accumulate exogenous elements, and release of these elements influences daily and seasonal cycling. Release may occur from sediment into water (cf. Jiang et al., 2008; Smith et al., 2011). Studies indicate that the rates at which elements such as P, N, and Fe are released from sediment depend on several chemical, physical, and biological factors, such as the pH, dissolved oxygen, redox potential, and temperature of the water (Namiesnik et al., 2005; Condron and Newman, 2011; Sun et al., 2015). Consequently, investigation of labile As and Hg in sediment is crucial to managing As and Hg contamination in the aquatic ecosystem.

In previous decades, bioavailability of target elements in sediment has most often been measured by ex situ chemical methods, such as sequential extraction and single-step extraction methods (Menzies et al., 2007; Soriano-Disla et al., 2010). These equilibrium-based methods are based on operationally defined procedures, and they provide information on the concentrations of mobile or potentially mobile species in sediment that are available to biota. However, it has been reported that ex situ measurements can result in analytical errors, such as those in association with redissolution, redistribution, and readsorption, as well as changes in the chemical species of the element during measurement (Zhang et al., 2001; Nolan et al., 2005). Ex situ measurements cannot describe the dynamic interaction between the pore water and sediment, but provide information on the labile fractions of elements at the cm scale. But studies indicate that sediment is characterized by distinct heterogeneity in chemical and biological distributions at the mm scale (Stockdale et al., 2009). In addition, previous investigation showed two basic processes predominated in assessment of the dynamic release of elements from sediment into overlying water. One is pore water diffusion, by which the amounts of elements in the pore water are determined from the concentration gradients in the vicinity of the sediment–water interface (SWI). The other is the resupply process from the solid phase, by which the decreased concentration of elements in the pore water leads to the release of components from the binding located in the sediment (Wu et al., 2001; Xu et al., 2012). Bioavailable elements in the sediment are in dynamic equilibrium with the pore water elements, and bioavailable fractions vary with subtle changes in the biogeochemical environment. Consequently, these phenomena demand a robust and accurate measurement of bioavailable fractions that can simultaneously reflect the dynamic interaction between sediment and pore water. The diffusive gradients in thin films (DGT) technique has drawn the attention of researchers for its ability to determine the bioavailable fractions of elements in sediment, water and soil (Davison and Zhang, 1994; Zhang and Davison, 1995). DGT is based on Fick's first law, and adynamical, high-resolution technique which has the potential to satisfy the requirements to monitor the diffusion flux of solute species i.e., P, Cd, Zn and Pb as well as As and Hg in sediment (Zhang et al., 2001, 2004; Clarisse and Hintelmann, 2006; Clarisse et al., 2009; Tandy et al., 2011; Huynh et al., 2012; Qiu et al., 2012). The concentration information obtained includes the fractions that come from the pore water and that released from sediment solids that resupply pore water (Zhang et al., 2004; Qiu et al., 2012). Recently, the high-capacity zirconium (Zr) oxide DGT technique has been applied to the measurement of total dissolved As using a long-shelf-life binding gel impregnated with hydrous Zr oxide. The Zr oxide DGT technique has advantages over ferrihydrite and Metsorb DGT with respect to As evaluation (Ding et al., 2011; Sun et al., 2014). Satisfactory results for evaluation of Hg bioavailability can also be obtained using 3-mercaptopropyl functionalized silica gel DGT (Lomonte et al., 2008; Fernández-Gómez et al., 2010). Despite the advantages of DGT, its use is still limited mostly to laboratory trials; it is seldom applied in situ on a large scale in aquatic ecosystems. This has hindered the holistic analysis of the distribution of labile As and Hg in sediment, and their cycling in fresh water.

Lake Hongze is a shallow lake in China with a surface area of 1960 km^2, a mean water depth of 1.77 m, a maximum depth of 4.37 m, and a water volume of 28×108 m^3. The northwestern side of the lake basin is higher in elevation than the southeastern side, and the average elevation of the lake basin is 4–8 m higher than the plain. The rivers that empty into Lake Hongze are mainly distributed along the western side of the lake. The Huaihe River is the largest contributor, accounting for more than 70% of the total flow into the lake, and controls the water quality (Li et al., 2011). Significant differences in total As and Hg concentration of sediment of Lake Hongze have been reported by previous investigation (Yu et al., 2010). The internal loading of As and Hg is believed to be the main factor that influences the water quality of the lake, and this hypothesis is supported by ex situ measurements (Zhang et al., 2004).

In this study, changes in concentration of labile As and Hg in the sediment profiles of Lake Hongze were systematically investigated using the Zr oxide DGT technique for As, and 3-mercaptopropyl functionalized silica DGT for Hg. A flat DGT probe was used in situ to collect information on the distribution of labile As and Hg at the mm level from 21 sites considered representative of Lake Hongze. The standard DGT devices for water were hung by buoys (about 15 cm higher above the sediment–water interface) at the location that corresponded to the sediment probe for evaluation of the labile As/Hg concentration in water. And the ex situ technique i.e., $CaCl_2$, DTPA, HCl as well as the electricity plate digestion were applied to measure the concentration of As/Hg in sediment of 21 sites. The apparent fluxes of As and Hg across the sediment–water interface were calculated based on the DGT-measured As and Hg concentrations in the water and sediment. GNU R programming language was applied to detect outliers of As and Hg at the mm level. Finally, the relationships between DGT-labile As and Hg concentrations in the lake sediment and in the overlying water were investigated and compared to the relationships suggested by simple equilibrium-based ex situ extraction methods.