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Characterization of metal kinetics and bioavailability using diffusive gradients in thin films technique in sediments of Taihu Lake, China

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For an improved understanding of the metal behavior between the sediment and overlaying water of Taihu Lake, the technique of diffusive gradients in thin films (DGT) was used to characterize the DGT measured concentration in sediments and release kinetics of Cr, Ni, Cu, Zn, Cd and Pb in representative lake parts. Spatially, the DGT-measured concentration of heavy metals showed that Zn, Cu, Ni, Cr, and Pb had higher concentrations in the northern lake than in the eastern Lake Taihu. The order of the release flux for the studied metals from sediments to overlaying water was Zn > Cu > Ni, Cr > Pb > Cd ($p < 0.05$). DGT devices were deployed over a series of time (0.5, 1, 2, 4, 8, 12, 24 and 48 h) in sediment cores from the two typical lake parts (northwest algae dominant area and southeast macrophyte dominant area) to explore the dynamics in the sediment/DGT system, and the best fitted regression model was selected to characterize the release of metals in the two lake parts. The fitted results showed that the equilibration time of the metal release was approximately 24 h and Zn had a higher release capacity than other metals. Further analyses indicated that significant correlation existed between the DGT-measured metal concentrations in sediments and metal concentrations in lake organisms ($r = 0.943$ and 0.996 for zoobenthos and *coilia ectenes*, $p < 0.05$), suggesting that DGT technique is more effective to predict the metal bioavailability in lake sediments.

1. Introduction

Heavy metal pollution has attracted significant attention all over the world, especially in developing countries including China (Chen et al., 2007; Vardanyan and Ingole, 2006; Zheng et al., 2008). With China's urbanization and industrialization accelerating, heavy metal emissions have become increased. In aquatic systems, heavy metals are mostly adsorbed by various adsorbents and settled to and accumulated in the sediment (Roosa et al., 2014; Xia et al., 2011), so sediments have become a major metal pollutant pool in water environments (Vdović et al., 2006; Yi et al., 2011). Accumulation of heavy metals in sediments posed threats to ecosystem and human health through food chains and the cumulative effects (Song and Li, 2015; Yi et al., 2011), which has become a major concern worldwide.

It is generally recognized that trace metal toxicity and bioaccumulation are primarily associated to their bioavailabe fractions rather than to the total concentration (Di Toro et al., 1992; Ren et al., 2015; Roulier et al., 2008; Yin et al., 2014). The technique of diffusive gradients in thin films (DGT) has been developed as a promising tool to study metal bioavailability in sediments (Wegener et al., 2002; Zhang et al., 1995). DGT can be used not only to measure the active metal concentration of porewater in sediments but also the metal flux from solid phase to solution (Bade et al., 2012; Tankéré-Muller et al., 2012). The magnitude of the flux is dependent on diffusion in solution and the exchange rate of metals between solid and solution (Ernstberger et al., 2005). The DGT measurement can reflect metal kinetic and bioavailable capacity of the sediment, as well as the mean concentration in porewater during the standing time (Ren et al., 2013).

Some studies have suggested that a significant relationship between the DGT-measured metal concentration and metal concentration in organisms (Nolan et al., 2005; Zhang et al., 2004, 2001); while others obtained the opposite result (Almås et al., 2006; Koster et al., 2005; Nowack et al., 2004). Therefore, a comprehensive evaluation of the DGT technique is required to clarify its feasibility for the prediction of metal bioavailability and kinetics in the sediment.

Although there have been some studies to report the metal contamination in Taihu Lake (Yin et al., 2014; Yu et al., 2012b, 2012c), few focused on bioavailable fraction (Ren et al., 2015; Wu et al., 2010; Yin et al., 2014), and hardly studies on the kinetics of metal release from the lake sediment. Our work is designed to use the DGT technology to evaluate metal bioavailability and kinetics

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in Lake Taihu sediments from representative lake parts. The objectives of the study are to: (1) investigate bioavailability of six metals (Cu, Zn, Cr, Ni, Cd and Pb) in sediments in the typical lake parts; (2) characterize the dynamics and flux release measured by DGT technology; and (3) evaluate the effectiveness of DGT technology for lake sediments. Our results provide support for the metal pollution monitoring, toxicity assessment and metal criteria development for Taihu Lake.

2. Materials and methods

2.1. Study area

The Taihu region is well known for its advanced economy in China and its high eutrophication in science community (Qin et al., 2007). Taihu Lake, located in the Yangtze Delta, is the third largest fresh water lake in China, with a water area of approximately 2428 km^2 and an average depth of 2 m. As an important drinking water source for local large cities such as Wuxi and Suzhou, its water quality, including heavy metal pollution, received wide concerns. Generally, there was no pristine sediments in the entire lake, and our previous study showed that lake sediments were to some degree polluted with heavy metals (Yu et al., 2012b), although metals in water column of the lake were generally in compliance with the quality standard. Also, there was a clear pollution gradient from the influx rivers (such as Caoqiao river, Fig. 1) to the lake and the metal pollution was generally heavier in the northwest part than in the southeast part of the lake (Yu et al., 2012b).

Another feature of Taihu Lake is that it includes two distinctive lake parts: algae dominant northwest area and southeast macrophyte dominant area (Yin and Fan, 2011; Yin et al., 2011; Yu et al., 2012c). The generally water quality and metal pollution in these two parts differs significantly (Wenchuan et al., 1999; Yin et al., 2011; Yu et al., 2012b). Therefore, we selected sediments from theses two parts to characterize the metal dynamics in the sediment and DGT system.

2.2. Sample collection

Sediment cores were collected in Taihu Lake in the November 2013 at six representative sites (Fig. 1). The top 30 cm sediment were loaded in plexiglass tubes (with 11 cm in diameter) using a gravity core sampler. Two parallel sediment cores were taken at T1–T3, and T5, of which one was used for 24-h DGT deployment (discussed in Section 2.3), and the other for the measurement of the total metal concentration and sediment properties such as pH and conductivity. At T4 (representing algae dominant area) and T6 (representing macrophyte dominant area), nine sediment cores were taken respectively, of which eight were for the measurement of DGT dynamics with different deployment time; one for the measurement of other parameters mentioned above.

Except for sediment cores for DGT deployment, other sediment cores were segmented every 3 cm from top to bottom in situ. Two replicate sediment samples were taken at each site, and the

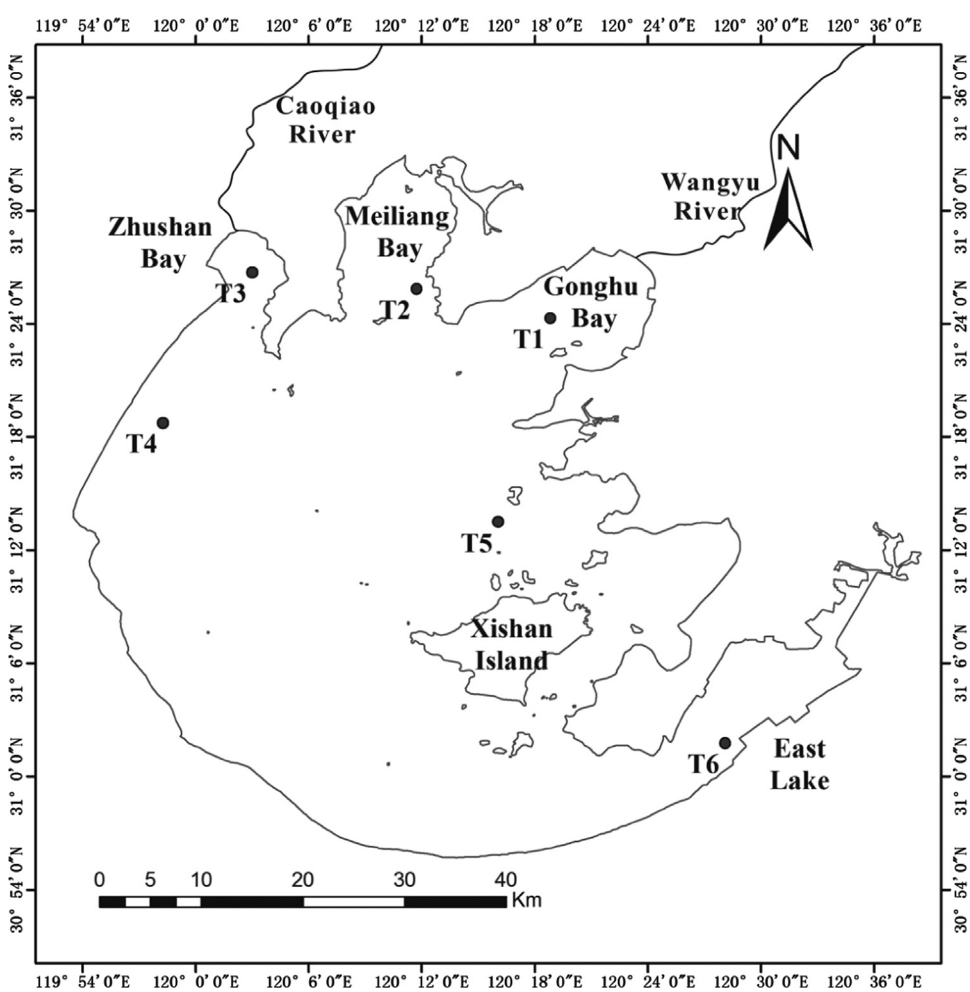

Fig. 1. Sampling sites in this study.