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Impact of macrozoobenthic bioturbation and wind fluctuation interactions on net methylmercury in freshwater lakes

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ABSTRACT

The methylmercury (MeHg) as the toxic fractions has presented significant threats to biota in freshwater ecosystems. Hg methylation process is demonstrated to be manipulated by biota process (benthic disturbance and algae bloom existence) as well as the abiotic influence (wind fluctuation and illumination intensity) in freshwater ecosystems. However, the mechanisms influencing Hg methylation are still unclear, and the coupled influences of the biotic and abiotic process with the shifts in variation on methylmercury remain unexplored. Accordingly, an annular flume experiment which simulated the freshwater ecosystem, was conducted for 108 days to examine the influences of typical disturbance by chironomid larvae and wind fluctuations on MeHg variation in sediment profiles. The *in-situ*, passive sampler technique of revealing diffusive gradients in thin films (DGT) encompassed the special resin, based on referenced extraction and coloration-computer imaging densitometry, were employed to obtain labile MeHg, Fe, and S concentrations at high resolution. The results indicate that larval bioturbation during the initial period of the experiment could diminish bioavailable MeHg concentrations and change the diffusion direction of MeHg fluxes. However, this inhibitive effect on MeHg concentrations ceased with larvae eclosion. Compared to bioturbation, wind fluctuation exerted slow but sustained inhibition on MeHg release. Furthermore, the eight parameters (dissolved organic carbon (DOC), DO, labile Fe and S concentrations, pH, sulfate-reducing bacteria (SRB) abundance in sediment, oxidation-reduction potential (ORP) and EC) could explain more of variation in MeHg concentrations which indicated by the canonical correspondence analysis. And these eight parameters manifest higher explanatory power for MeHg distributed in newly formed sediment. More notably, the comparison results of the multiple and simple regression directly demonstrated the DOC was the fundamental and robust factor to control the MeHg variation in the freshwater ecosystem.

1. Introduction

Mercury (Hg) is relatively rare in the earth's crust. However, due to the atmospheric deposition and weathering of the cinnabar as well as the anthropogenic activities i.e., runoff from factories and abandoned mines, Hg contamination of aquatic environments has become a global concern (World Health Organization, 2008; Cardenas et al., 2015). Studies have revealed the toxicity of MeHg is much higher than any other Hg fractions i.e., mercuric component (Hg (II)) and elements fractions (Hg (0)) (Xiong et al., 2009; Parks et al., 2013). Accordingly, the toxicity of mercury is largely dependent on the conversion percentage of the inorganic Hg fractions to organic Hg fractions such as methylmercury (MeHg), which is a typical neurotoxin that could affect the central nervous system of biota through bioaccumulation and biomagnification (Herrero et al., 2005; Zhang et al., 2005). Moreover, the sediment has been in general recognized as the area mercury methylation occurred. Consequently, the net yield of methylmercury in sediment is the most important consideration for evaluating mercury bioavailability in aquatic ecosystems.

It is generally accepted that anaerobic or hypoxic conditions in sediments or hypolimnetic water (Jeong et al., 2008; Eckley and Hintelmann, 2006), as well as the presence of methylation

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microbe are critical for methylation in aquatic ecosystems (Rickard, 1995; Gray and Hines, 2009). Sediments act as the a regulator in aquatic system, they are deemed to be a major sink for entrapping and accumulating allochthonous fractions, subsequently releasing these fractions under the influences of daily and seasonal cycling (Chen et al., 2015; Wang et al., 2016). Moreover, sediment also acted as the "container" for methylation microbes (Bravo et al., 2015). Consequently, the precise measurement of methylation microbes abundance and net methylmercury yields in sediment and the overlying water, are essential for the overall understanding of mercury methylation processes in freshwater ecosystems.

The formation and distribution of the MeHg in freshwater ecosystem were reported to be controlled and constrained by a wide variety of physicochemical parameters, including oxidation-reduction potential (ORP), dissolved oxygen (DO), pH, the total labile Hg concentration, the presence of the organic as well as the inorganic fractions, light intensity and temperature (Jiang et al., 2008; Bravo et al., 2013). However, a majority of previous investigations endeavored to address the mercury methylation process through the exogenous added MeHg which might be overestimated the MeHg bioavailability, and most studies attempted to illustrate the methylation process only under single influence (Hammerschmidt and Fitzgerald, 2004; Bravo et al., 2015). Thus, there existed considerable debate on the fundamental influence as well as the mechanism for controlling the MeHg presence and concentration. Together, couple the typical process with the shifts in the variation of freshwater MeHg, were the reasonable and essential parts for the overall understanding of the Hg methylation process. Previous studies reported that wind fluctuation was important for maintaining DO and for the transition of the organic and the inorganic fractions between overlying water and surface sediments in a freshwater environment (Verplanck et al., 2008; Bravo et al., 2015). Similarly, macrozoobenthos could also take oxygen from suspended phytoplankton within the oxygen-rich overlying water; altered the watershed characteristics such as pH, H_2S, EC; meanwhile, reconstructed DO and the organic and inorganic fractions distribution in surface sediments results in variation of redox conditions in the vicinity of macrozoobenthos burrows (Gao et al., 2009; Fernandez-Gomez et al., 2012). Furthermore, Ding et al. (2015) emphasized that this larval bioturbation was particularly significant for labile P, S redistribution, especially in a eutrophic lake. Chen et al. (2003), Black et al. (2012), and Wang et al. (2016) reported that MeHg tended towards demethylation in sediment due to the ventilate effects. Consequently, wind variation and bioturbation in freshwater aquatic systems might be the main abiotic and biotic transport processes for regrouping particles and digging burrows, thereby influencing the sediment matrices as well as MeHg concentration (Jiang et al., 2008; Yao et al., 2016b). However, the effects of these abiotic/biotic processes on the diffusion of labile MeHg fractions remain disputed. Wind fluctuation and the larval bioturbation were reported as the independent disturbance factors for overlying water and sediment, respectively. Owning to the presence of bacteria and biofilm in the vicinity of the sediment–water interface (SWI), SWI acts as an obstacle to the diffusion of labile fractions between overlying water and sediment (Ding et al., 2015; Yao et al., 2016a). Accordingly, the diffusion of elements between water and sediment might have a sharply bounce after the inconspicuous diffusion. Furthermore, wind disturbance and larval bioturbation are not sufficiently intensive to destabilize the relationship between the overlying water labile MeHg and sediment labile MeHg. Taken together, variations in wind intensity and larval bioturbation might be appropriate parameters for simulating their influence on labile MeHg concentrations in freshwater ecosystems. In addition, previous studies indicated that bioturbation intensity showed no significant difference in typical freshwater bodies such as Tai Lake and Lake Hongze (Jiang et al., 2008; Yao et al., 2016b). Accordingly, the density of the larvae addition was kept consistent under differing wind conditions in this study.

The increasing understanding of this topic has highlighted the important role of microorganisms for Hg methylation. As shown in Fig. S1 (Supplementary Information), many species of bacteria were mainly distributed in surface sediment, e.g., *Mycobacterium phlei, Bacillus megaterium, Clostridium cochlearium, Aerobacter aerogenes, Saccharomyces cerevisiae, Scopulariopsis brevicattlis*, are able to methylate labile mercury (Oremland et al., 1991; Stubner, 2004). However, not all species with the capacity for methylation occur in freshwater environments (Stubner, 2004; Achá et al., 2011). Related investigations revealed the Hg methylation process was mainly mediated by iron-reducing bacteria (IRB) and sulfate-reducing bacteria (SRB) (Fleming et al., 2006). Furthermore, the importance of IRB could only be manifested in sediments with extremely low sulfate concentration of freshwater ecosystem (Daniela et al., 2016). Although previous studies have revealed that sulfate reduction could be responsible for more than 50% of total bacterial respiration in sediment, and the pure culture work with SRB indicated their capability for methylation of mercury. Parks et al. (2013) and Avramescu et al. (2011) have reported the SRB could simultaneously methylate and demethylate Hg in the freshwater ecosystem. The SRB preferred the formation of MeHg under their lower activity and iron reducing condition through decreasing their demethylation rates. Accordingly, Accordingly, SRB are unequivocally efficient in influencing labile MeHg concentrations in complex freshwater ecosystems. Together, the relationship between sediment SRB abundance and MeHg concentration/diffusion fluxes was examined in our freshwater simulation experiment.

Since SWI have an important function in freshwater ecosystems, obtaining precise information on contamination gradients is essential for a comprehensive understanding of variations in its environmental ecology (Han et al., 2015). However, its physicochemical parameters might display dramatic variation within a range from less than 0.5 mm to finer scales (Ding et al., 2015). Accordingly, the technique of diffusive gradients in thin films (DGT) and the use of penetrating microelectrodes are employed for high-resolution recognition of SWI variations. Based on Fick's first law, this technique can evaluate the labile fluxes of soluble species through the binding phase, which could adsorb and accumulate the solute (Zhang and Davison, 1995). DGT has shown clearly superior determination characteristics. As a non-invasive tool, it could potentially overcome the limitations of *ex situ* measurements such as redissolution, readsorption, and redistribution (Yao et al., 2016a). Furthermore, Zhang et al. (2004) and Ding et al. (2015) applied this high-resolution method to calculate apparent diffusion fluxes between sediments and overlying water. Since the adoption of this technology, it was found that 3-mercaptopropyl-functionalized silica DGT and Chelex DGT were the effective routes for labile MeHg and bivalent cation accumulation, respectively, in aquatic ecosystems (Wang et al., 2016; Yao et al., 2016b). Recently, a two-dimensional (2D) DGT device impregnated with high capacity of AgI or ZrO particles in resin gel, combined with computer-imaging densitometry (CID), has been developed for high-resolution imaging of labile S and P, respectively. Furthermore, the 2D high-resolution imaging could effectively reflect the heterogeneity of labile fractions in sediment as the results of horizontal (wind fluctuation) and vertical (larval bioturbation) disturbance (Ding et al., 2011; Sun et al., 2015). Similarly, penetrating microelectrodes were also applied to improve the richness of the physicochemical index across the vicinity of the SWI.

Herein we describe a comprehensive investigation to explain Hg