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Predicting trace metal bioavailability to chironomids in sediments by diffusive gradients in thin films

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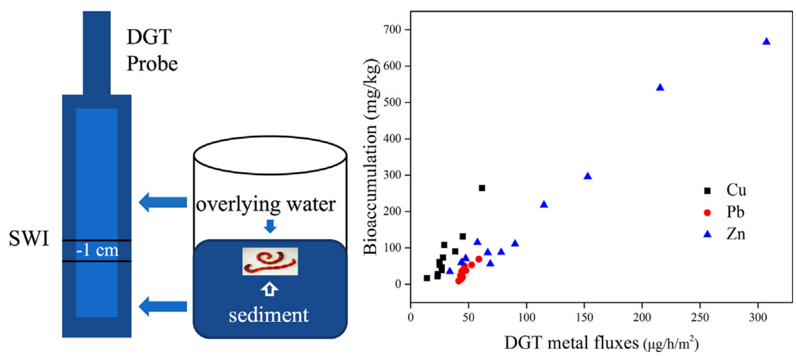
HIGHLIGHTS

- DGT was an effective alternative to assess metal bioavailability to chironomids.
- Peaks in DGT-metal fluxes located approximately 1 cm below the SWI.
- Significant accumulation in chironomids was observed with the order of Zn > Cu > Pb.
- Metal bioaccumulation can be predicted by TRM concentrations and DGT fluxes.

GRAPHICAL ABSTRACT



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ABSTRACT

The technique of diffusive gradients in thin films (DGT) has been developed as a promising tool to assess metal bioavailability in sediment. However, it has yet to be determined whether the DGT-labile metal in sediment is representative of bioavailable fraction for benthic organisms. In this study, the performance of DGT for predicting metal bioavailability was evaluated by exposing DGT and chironomids *Chironomus tentans* to a series of metal-contaminated natural sediments in the laboratory. Conventional methods, including acid-volatile sulfides and simultaneously extracted metals method, and total recoverable and dilute-acid extractable metal concentrations were also used to assess the availability of Zn, Cu and Pb to chironomids. The bioassay results showed that >70% of the larvae ($73 \pm 1.7\%$–$98 \pm 0.5\%$) survived in all sediment samples, however, an enhanced uptake of Zn, Cu and Pb by *C. tentans* in contaminated sediments was observed compared to control sediments. The correlation analyses indicated that the total recoverable metal concentrations and DGT-metal fluxes in the surficial sediment (−1 cm) were all significantly associated with metal bioaccumulation in *C. tentans* ($p < 0.01$). Given the advantages of DGT devices for in situ and time-averaged measurement of the potentially bioavailable fraction, DGT-metal fluxes were proved to be a better surrogate to predict *C. tentans* response to metal contamination. The results further supported the applicability of the DGT technique as an alternative method to assess the bioavailability of metals in sediment to benthic invertebrates.

1. Introduction

Trace metals as ubiquitous environmental contaminants are of great concern due to their toxicity and non-biodegradable nature. In aquatic systems, sediment is a major sink for trace metals resulting from natural

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geochemical processes and anthropogenic activities (Varol, 2013). The accumulated metals may pose a threat to aquatic organisms, especially for benthic invertebrates, which are closely associated with surficial sediment. These metals may cause toxicity to benthic organisms when uptake rates are high, and may be transferred to higher trophic-level organisms via the food chain, causing ecotoxicological risks to the aquatic ecosystems (Pertsemli and Voutsa, 2007; Ferreira et al., 2013; Islam et al., 2015). To determine the extent to which sediment-bound metals will enter the aquatic food chain, the measurement of bioavailable metals in sediment is important and necessary.

Metal bioavailability is generally controlled by organic matter, acid-volatile sufides (AVS), iron and manganese oxides, carbonates, and clay content, and the behavior and physiology of the organisms (Chapman et al., 1999; Simpson and Batley, 2007). In the assessment of metal bioavailability in sediment, total metal concentrations are not necessarily related to the biologically available fractions (Zhang et al., 2014; De et al., 2009; Tan et al., 2013). In contrast, pore water measurement gives a more realistic estimation of the bioavailable metals, but it provides non time-integrated concentrations and does not reflect the supply of metals from the particulate phase (Bervoets et al., 1997; Hare et al., 2003). During the past decades, sequential extraction method has been frequently used to assess the chemical speciation of metals and their bioavailability (Pueyo et al., 2008). However, this procedure has been long questioned because of the poor precision and selectivity resulting from the alteration of metal speciation during the extraction process (Zhang et al., 2001; Nolan et al., 2005). Furthermore, whether the extracted metals can be used to represent the bioavailable fraction is still the subject of debate (Tian et al., 2008). AVS are known to react with divalent metals and form insoluble metal sulfides, which reduce the concentration of free metal ions and thus metal availability (Di Toro et al., 1992). The amount of AVS and simultaneously extracted metals (SEM) has been proposed as a predictor for toxicity of certain metals in sediment (USEPA, 2005). However, the AVS-SEM measurement may overemphasize the importance of the AVS binding phase, and other sediment phases such as iron and manganese oxides, are not considered (Simpson et al., 2012a, 2012b). Given the uncertainty as to the available methods, it appears necessary to develop new techniques to better estimate the metal bioavailability.

The diffusive gradients in thin films (DGT) technique were developed as an in-situ device for the time-integrated measure of the labile metal fluxes from pore water and sediment particulate phase (Zhang et al., 1995). The DGT measurement is able to reflect the dynamic supply of metals from solid phase regardless of the binding ligand and provide valuable insight into micro-scale biogeochemical heterogeneity of sediment. These advantages of DGT make it attractive for the bioavailability assessment of metals in sediment. In recent years, the potential application of DGT technique in evaluating the metal bioavailability to benthic invertebrates has been investigated. Many studies have reported strong correlations between the labile metal concentrations measured by DGT and the toxicity to benthic organisms. For example, Amato et al. (2015) demonstrated that DGT-metal fluxes (Cu, Pb and Zn) were significantly associated with body metal concentrations in bivalve *Tellina deltoidalis* under both laboratory and field conditions. Significant correlations were also obtained between the survival of bivalve *Tellina deltoidalis* or amphipod *Melita plumulosa* and DGT-labile metal fluxes (Simpson et al., 2012a, 2012b; Amato et al., 2014). However, in some cases, the DGT measurement was not necessarily a good predictor of the metal toxicity. For instance, Roulier et al. (2008) found DGT-measured metal concentrations were significantly correlated to the metal uptake in chironomid *Chironomus riparius* for Cu and Pb, but not for Cd. The study of Van der Geest and Paumen (2008) showed a notable correlation between labile Cu captured by DGT and Cu bioaccumulation by oligochate *Tubifex* in only the first three weeks of ten-week exposure. Dabrin et al. (2012) investigated the possible relations between DGT measurements and Cd bioaccumulation in three different benthic organisms, and results indicated that a significant correlation was only observed for mud snail *Potamopyrgus antipodarum*. Similarly, in terms of predicting invertebrate community response to sediment Ni, AVS-SEM measurements were superior to DGT-Ni concentrations (Costello et al., 2012). These studies have found inconsistencies among metals or taxa from the use of the DGT devices for the metal bioavailability assessment. It necessitates the investigations to assess the limitations of the DGT technique, and to determine the best application conditions to evaluate the available metal fractions, and to better predict metal toxicity to benthic invertebrates.

The primary aim of this study was to investigate the performance of the DGT technique for predicting metal bioavailability to the chironomid *Chironomus tentans* exposed to a series of metal-contaminated natural sediments in the laboratory. Chironomids, one of the most widely distributed benthic invertebrates in freshwater ecosystems, burrow in the upper layer of sediment and feed on particulate matter. They served as a food source for fish and thus represented a vector for the trophic transfer of metals (Arslan et al., 2010). The DGT-labile metal concentrations in different compartments of the sediment were measured and compared with chironomid bioassay. In addition, other traditional approaches including total recoverable and dilute-acid extractable metal concentrations and AVS-SEM measurements were also used to predict metal availability to chironomids. The results of this study are expected to address the question of whether DGT could provide an accurate predictor of metal bioavailability to sediment-dwelling organisms in naturally contaminated sediments, and improve the understanding of the relationship between DGT labile metal fractions and the toxicity to benthic invertebrates.

2. Materials and methods

2.1. Sample collection

Clean water was collected from the Jingmi Diversion Canal in Beijing, filtered through a 0.45 μm Whatman glass microfiber filter and stored at 4 °C in the refrigerator (metal contents were shown in Table S1). Eleven metal-contaminated sediment samples (0–10 cm) were collected from the upstream of Hunhe River (120° 20′-125° 15′ E, 41° 30′-41° 15′ N) in Liaoning Province, China (sites H1-H11, Fig. S1), where different types of mines including gold, iron and copper mines were distributed along the river. Control sediments were collected from Shisanling Reservoir in Beijing that had low background metal concentrations (designated as site H12). All sediments were sieved to <2 mm, homogenized and subsequently stored in dark at 4 °C for a maximum of one month before use in tests.

2.2. Chironomid bioassay

The chironomid, *Chironomus tentans* (*C. tentans*), was selected as the test species because of its prevalence in freshwater sediment. This species was obtained from laboratory cultures as described previously (He et al., 2016). Whole-sediment bioassays with chironomid were conducted according to standard protocols with some modifications (USEPA, 2000). In brief, 400 mL of sediment was placed in a 1-L beaker, and 500 mL of clean water was added slowly. All beakers were incubated at 23 ± 1 °C on a 16:8 h light: dark photoperiod with continuous aeration. Sediments were allowed to equilibrate for two weeks before tests to ensure re-establishment of physicochemical profiles within the sediment. Five replicates were used for each sediment sample and one replicate was void of organisms for sediment properties analysis. On day 0, the overlying water (80%) was gently syphoned off and replaced with clean water. Ten second-instar larvae were then randomly assigned to each beaker, and daily supplied with 6 mg of finely ground fish food. Over the 7-day test period, the overlying water was renewed every day and sampled for dissolved metals analyses. In addition, water parameters including pH, temperature, conductivity, dissolved oxygen and ammonia were monitored throughout the tests. On day 7, the