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Original research article

Evaluating the bioavailability of heavy metals in natural-zeolite-amended aquatic sediments using thin-film diffusive gradients

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ABSTRACT

The effectiveness of natural zeolite amendment of sediments as a restorative material was studied, as was the feasibility of utilizing thin-film gradient diffusion (DGT) as a proxy for the accumulation of heavy metals in *Venerupis philippinaram*. The results showed that addition of natural zeolite to sediment, significantly decreased the equilibrium partitioning of Cu, Pb, Cd, Cr and As between the sediment pore water and natural zeolite over 24 h by 67%, 81%, 72%, 62% and 71%, respectively. Furthermore, the accumulation of Cu, Pb, Cd, Cr and As in *V. philippinaram* in the zeolite-amended sediments decreased by 44%, 37%, 54%, 30% and 59%, respectively after 28 days and the absorption rates also declined. The amount of heavy metals enriched into the DGT film and *V. philippinaram* over 28 days showed a significant correlation ($P < 0.001$) and indicated that DGT has the potential as a proxy to predict the bioaccumulation of heavy metals in benthic organisms in sediments amended by natural zeolite. Further studies focused on the modification of natural zeolite and the predictive ability of DGT in different sediments/organism scenarios are warranted.

1. Introduction

China is a major producer and consumer of aquatic products, and the expansion of the related industry has given it an important status in the national economy (Li et al., 2009). Aquatic products are an important source of high quality protein, and are beneficial for consumer health (Zhang & Jiang, 2010), but the accumulation of heavy metals in aquatic products is a cause for concern (Wu et al., 1999; Yang, Yao, & Xu, 2012). Previous research showed that heavy metals can be readily enriched in aquatic organisms (Tao et al., 2012; Turkmen, Turkmen, & Tepe, 2009). The heavy metals ingested by human consumption of aquatic products represent a health risk as they accumulate in the body (Järup, 2003). Kwok, Liang, and Wang (2014) found that the level of Cd and Pb in the muscle of the fish from the Pearl River estuary exceeded the permissible limits proposed by the Food and Agriculture Organization (FAO). The same was true for the contents of Cd (as high as 0.27–0.29 mg/kg) in the shellfish from Yangkou Port, China (Liu, Wang, & Yu, 2010). Relatively higher levels of Zn and Cu in the fish from the Luoyang area was also reported by Quan, Gong, and Cui (2010). Wang, Zhao, and Chen (2007) also reported that the amount of Hg accumulated in the fish was 1000 times higher than that of the surrounding water in Baiguishan Reservoir, China. Futhermore, numerous studies have indicated that the source of heavy metals in aquatic products is closely related to the sediment type (Yi, Yang, & Zhang, 2011; De et al., 2004; Kalantzi, Shimmield, & Pergantis, 2013). Therefore, it is important to remediate the contaminated sediments by reducing the bulk burden and the bioavailability of heavy metals.

There are several techniques available for remediation of heavy-metals in sediments, including the utilization of the specific cell morphology and physiological metabolism of actinomycetes (Alvarez, Saez, & Costa, 2017), the absorption and chelation of heavy metals by plant roots (Sarwar, Imran, & Shaheen, 2016), the high surface activity of biosurfactants (Gnanamani et al., 2010) and the high porosity of large-surface bio-carbons (Li, Wu, & Zhang, 2015). Natural zeolite is one kind of alkali-metal- or alkaline-earth-metal-framed aluminosilicate mineral, which has selective adsorptive properties, a high ion-exchange performance and a large adsorption capacity and so has been deployed in environmental remediation. Natural zeolite can also be used to control the release of nitrogen and phosphorus from the sediments (Montalvo et al., 2011; Nakhla, Zhu, & Cui, 2007).

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Recent studies have focused on the feasibility of natural zeolite for heavy-metal remediation in sediments. Motsi, Rowson, and Simmons (2009) reported a removal rate of 99% for Hg using a natural zeolite-molecular seive. Hui, Chao, and Kot (2005) explored the ability of synthetic natural zeolite to remove heavy metals in water and found that the removal rate of heavy metals was above 99% when the dosage was 1g/L. However, most studies have failed to consider strategies to reduce the bioavailiability of heavy metals, and have concentrated on the reduction of the bulk content of heavy metals in sediments. In this context, diffusive gradient in thin-film technology (DGT) was introduced to evaluate how it changes the bioavailiability of heavy metals in the sediments treated with natural zeolites in the present study.

DGT consists of a diffusion phase and a bonding phase and is a new type of in-situ passive sampling tool. The diffusion phase is a hydrogel or semipermeable membrane of a certain pore size. The binding phase is a polymer which is capable of providing the functional groups for coordination electron pairs. The role of the binding phase is to coordinately bind the diffusing metals, so that the partitioning of the metals between the diffusive phase and the bonding phase is reduced to a minimum (Gimpel, Zhang, & Hutchinson, 2001). Empirically, the concentrations of heavy metals in the pore water of the sediments after immersion of a DGT device for 24 h is used for calculating the metal concentrations (Ding, Xu, Sun, Yin, & Zhang, 2010). Therefore, DGT has been widely used for determining the reactive (free-dissolved) heavy metal content both from pore water and sediment (Davison & Zhang, 1994; Xu et al., 2013). Traditional procedure used to determine the free-dissolved heavy metals includes centrifugation, and flocculation (Hawthorne, Grabanski, Miller, & Kreitinger, 2005), which is far more laborious and less reliable than the DGT method. Moreover, DGT can be employed in the field without disturbing the formation of the sediment, providing in-situ monitoring data.

Furthermore, DGT has been used to predict the uptake of heavy metals by freshwater snails, and has the potential to predict the content of heavy metals in shellfish (Yin, Cai, & Duan, 2014). It was also reported that the enrichment effect of mussels and DGT on heavy metals was significantly relevant (Webb & Keough, 2002). To our knowledge, DGT has not been used as a passive sampling tool for evaluating the bioavailability of heavy metals in aquatic ponds during sediment remediation, or as a biomimetic tool to infer the accumulation of heavy metals in bethic organisms.

Therefore, in the present study, DGT devices were used as passive samplers, *Venerupis philippinaram* was used for heavy metal bioaccumulation experiments, and natural zeolites were used as the remediative material in sediments. In this study we explore; (1) the effect of natural zeolite on reducing the bioavailability of heavy metals in sediments and their bioaccumulation in *V. philippinaram* and, (2) the feasibility and reliability of using DGT to predict the bioaccumulation of heavy metals in benthic organisms.

2. Materials and methods

2.1. Sediment and natural zeolite

Surface sediment samples from Dafeng of Jiangsu Province (N33°16′34.45″, E120°50′47.64″) and Yangshan Port of Shanghai (N30°38′35.59″, E122°03′22.72″) in China were collected using a Peterson sampler (PSC-1/16). The samples were put in foil bags and placed on ice, then delivered to the lab and stored at −20 °C until analysis. Natural zeolite was purchased from Jinyun, Zhejiang Province, China. The cation exchange capacity of this natural zeolite is 1300–1800 mmol/kg, the molar ratio of Si/Al is 4.25–5.25, and the chemical composition is: SiO_2 (70%), Al_2O_3 (12%), Fe_2O_3 (0.87%), K_2O (1.1%), CaO (2.6%), MgO (0.13%) and Na_2O (2.6%). X ray diffraction analysis revealed that the natural zeolite contained 66% clinoptilolite, 19% mordenite and 15% silica. The natural zeolite was grounded and seived to obtain particles of 0.15–0.18 mm diameter, and then washed 5 times with deionized water prior to the experiments.

The samples collected from Dafeng coastland were used for the natural zeolite adsorption experiment and bioaccumulation experiment, while the samples from Yangshan Port were used as the blank controls. The bioaccumulation experiments were divided into two groups: a natural zeolite-amended group and a natural zeolite-free group. Each group had two replicates.

2.2. Subject organism and DGT device

V. philippinaram were purchased from Shanghai Luchao aquatic market and were acclimated to laboratory conditions for more than three weeks before using them for experiments. During *V. philippinaram* acclimation, the salinity and temperature of the seawater was 25 ± 2 and 20 ± 1 °C respectively, and the water was aerated continuously. The photoperiod was 16 h light followed by 8 h dark, and *V. philippinaram* was fed daily with a regular amount of *Phaeodactylum* (2 g per tank) (Ngo, Pinch, & Bennett, 2016).

The DGT device were purchased from Nanjing Intelligent Environment Technology Co., Ltd.. The three components of the DGT, i.e. a ZrO-Chelex fixed film, an agarose diffusion film and a PVDF filter, were superimposed on a new flat plastic case. The thickness of the DGT fixed film and diffusion layer was 0.40 and 0.90 mm, respectively, and the device window area was 150 mm × 20 mm (length × width). The DGT device was cut into six pieces and one piece (0.0065 g) represented one DGT in the present study.

2.3. Use of natural zeolite for adsorbing the free-dissolved heavy metals in sediment

Approximately 2 kg (wet weight with 30% water content) of the surface sediments collected in the Dafeng coastland was placed in a 5 L glass tank, and the natural zeolite was then added at a dry weight ratio of 10% and homogenized (Aggeliki, Anthimos, & Ioannis, 2001). We previously examined the influence of the amount of the zeolite on the survival of benthic organisms and found that at zeolite concentrations of less than 10%, the survival rate was above 95%, but as the dosage was increased the survival rate dropped sharply to less than 80% (data not shown). Thus, the dosage of zeolite used was 10% since it yields the best adsorption with a high survival rate of organisms. The temperature of the sediments was recorded and two DGT devices were inserted into the natural zeolite-amended sediments every 12 h, and then taken out without breaking or pressing the exposure window. The surface of the DGT device was then rinsed with deionized water and the fixed films were removed from the cases and the membrane was discarded. Excess water was wiped from the fixed film, and then the fixed film was placed into a 30 mL glass tube and immersed in 10 mL NaOH (1 mol/L) for 24 h and then in 10 mL HNO_3 for a further 24 h. The extracts were then filtered using a 0.22 μm glass filter before analysis. The chemical reagents used in the experiments were all analytical grade.

2.4. Calculation of the free-dissolved concentration of heavy metals in the sediment using DGT

The accumulation of heavy metals in the fixed film M (ng) of the DGT was calculated after introducing an extraction factor f_e, i.e. the extraction rate of heavy metals (Wang, Ding, & Gong, 2016). The equation is shown below.