Ecotoxicology and Environmental Safety 140 (2017) 48–54

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Assessing remobilization characteristics of arsenic (As) in tributary sediment cores in the largest reservoir, China

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ARTICLE INFO

Keywords:
Arsenic
Sediment cores
Tributaries
Three Gorges Reservoir
Diffusive gradients in thin films (DGT)

ABSTRACT

The environmental impact of the Three Gorges Reservoir (TGR) in China has raised widespread concern especially in relation to metal pollution. The diffusive gradient in thin films (DGT) technology was applied to investigate arsenic (As) remobilization in sediment cores collected from the main stream and a tributary in the TGR during July 2015. The results showed that the horizontal and vertical distributions of C_{DGT}-As varied among the four sampling sites. For the same DGT probe, the horizontal distributions of C_{DGT}-As (0–6 mm, 6–12 mm, 12–18 mm) exhibited similarity in the overlying water and different tendencies in the sediment profiles; the vertical variations of C_{DGT}-As showed different mobilization tendencies. Moreover, the mobility patterns of As in the sediment profile showed the diffusion potential of As from the deep sediment to the surface sediment and overlying water were in the order of MX-2 < MX-1 < CJ < MX-3. In addition, similar distribution characteristics and correlation analysis showed that the mechanisms of As mobility were associated with Fe and Mn. The results also showed that sulphide and As were simultaneous remobilization in the tributary sediment core in the TGR.

1. Introduction

Sediments subject to anthropogenic disturbances act as efficient reservoirs for all kinds of pollutants. Early diagenetic processes may liberate dissolved species that diffuse to the overlying waters increasing toxicity levels (Duester et al., 2008; Gorny et al., 2015a). Trace element pollutants in the sediments such as arsenic (As) have drawn particular concern because of their potential toxicity and prevalence (Gorny et al., 2015b; Yang et al., 2015). In fact, arsenic has been ranked as a group I carcinogen by the International Agency for Research on Cancer (IARC) (Straif et al., 2009). The accumulation and chemical speciation of As in the sediments are a potential threat to water resources and aquatic organisms, especially benthonic organisms. Currently, considerable researches are focused on unraveling the complexity and role of As in sediments (Gorny et al., 2015a). It is an accepted fact that the toxicity of metals depends on their chemical forms, sediment geochemical properties and not on their total concentrations (Zhang et al., 2014). Therefore, monitoring the bioavailability of As in sediments is crucial for managing As contamination in the aquatic ecosystem and assessing sediment quality.

In the past decades, ex situ chemical methods such as the sequential extraction procedure have been used to measure the bioavailability of As in sediments (Wenzel et al., 2001). Equilibrium partitioning approach is another widely accepted ex situ method for studying the concentration of mobile or potentially mobile species in the sediment that are available to biota (Di Toro et al., 1991). Ex situ measurements provide partial information on the labile fractions of elements on a measurable scale but fail to describe the dynamic interaction between the pore water and the sediment. Moreover, As chemical speciation may be modified during the multiple steps of these sequential experiments (Österlund et al., 2010; Wang et al., 2016a, 2016b). Diffusive gradients in thin films (DGT) is an in suit technique that has drawn the attention of researchers in recent years. It enables high-resolution measurement of labile metal cations and oxyanions in the sediment, water and soil (Davison et al., 1997; Davison and Zhang, 2012; Davlson and Zhang, 1994; Ding et al., 2016a, 2016b). The analyte diffuses through a diffusive gel and is captured by a binding gel. DGT has been found to represent a dynamic supply of metal from the solid phase regardless of the binding agent (e.g., sulphide, Fe/Mn oxide or natural organic matter) (Fan et al., 2013; Yin et al., 2014) and can be used to assess the bioavailability of metals for benthonic organisms (Amato et al., 2016). Moreover, DGT using ferrihydrite-binding gel, metsorb and Zr-oxide gel

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http://dx.doi.org/10.1016/j.ecoenv.2017.01.050
Received 4 August 2016; Received in revised form 5 January 2017; Accepted 30 January 2017
Available online 27 February 2017

have been used successfully for direct determination of labile As content (Österlund et al., 2010; Bennett et al., 2010; Sun et al., 2014; Guan et al., 2015; Ding et al., 2016a, 2016b). However, previous field experiments about the measurement of labile metals in a core sediment using DGT have focused only on vertical variations of the DGT-labile metals, neglecting horizontal variations (Gao et al., 2006; Wu et al., 2015a). In fact, sediment is characterized by distinct heterogeneity in chemical and biological distributions at the millimetre to submillimeter scale (Stockdale et al., 2009).

The Three Gorges Dam (TGD) is the world's largest man-made river engineering project (Shen and Xie, 2004). With the completion of TGD in 2003, the Three Gorges Reservoir (TGR) became the largest reservoir with 1080 km^2 in 2009 (Ye et al., 2011). The TGR critically affects the Yangtze River ecosystem and national drinking water resources. Following water impoundment of the TGR, the backwater area of the TGR (the region with water being held or pushed back by the dam) has been transformed from a riverine system into a lacustrine system resulting in an increase in the water levels and decrease in the flow velocity (Yan et al., 2015). Periodically fluctuations of water levels during summers and winters have formed a water-level-fluctuation zone in the TGR area (Tang et al., 2014) and changed the natural transport balance of the upstream sediments of the TGR (Bing et al., 2016). During dry season, heavy metals in the riparian zone generally originated from natural weathering and anthropogenic activities, such as riverine discharge, industrial wastewater and large volumes of domestic sewage (Feng et al., 2004; Ye et al., 2011). During wet season, increased shipping transportation, industrial waste and human activities in the upstream of the TGR deposited metals into the riparian zone through flooding and rainwater (Gao et al., 2015a; Ye et al., 2011). Thus, the TGR has triggered the evolution of a new unique ecosystem that significantly influences the local ecological environment (Yang et al., 2012). Consequently, contamination of trace metals in the TGR has drawn particular attention. As a toxic pollutant, the geochemical fate or processing process of As have received extensive concern. However, bioavailable As in the main stream and tributaries of the T GR had not been reported.

The primary objectives of the present study are to (1) provide useful information on the contamination status of DGT-labile As in sediment cores of the main stream and Meixi river, a typical tributary in the TGR, during dry season; (2) investigate horizontal and vertical variations of the DGT-labile As concentrations (C_{DGT}-As) in sediment cores, and diffusion trend at the sediment-water interface (SWI) at the millimetre scale; (3) explain the mechanisms of As remobilization and relationship between DGT-labile As and other elements (S, Fe and Mn).

2. Materials and methods

2.1. Sampling procedure

Four sampling sediment cores were collected from the main stream (CJ) and a tributary (Meixi River (MX)) in the TGR during July 2015. Locations of the sampling sites on a map are shown in Fig. 1. Sediment samples were taken using a core sampler (K-B type, Wildco, USA) near the middle of the river at the main stream and three sampling sites in the tributary. Then sediment cores were protected with nitrogen (N_2) and sealed immediately to exclude the interference of oxygen in the air. The cores were covered with two layers of black plastic bags to keep them in dark and immediately taken to the laboratory. During the transportation, sediment cores were maintained upright to minimize the disturbance. In the laboratory, the sediment cores were stabilized for at least 24 h at 25 °C prior to deployment of the DGT probes.

2.2. General DGT procedures

2.2.1. DGT probe preparation

The assembled DGT probes (DGT Research Ltd, Lancaster, UK) had 150 mm × 18 mm windows. Two different types of DGT probes were used for cations and anions, respectively. A 0.4 mm thick Fe-oxide gel was used for measuring As and a 0.4 mm Chelex-100 gel was used for measuring Fe and Mn. The estuary of the tributary (MX-3) was selected as the representative to measure the variation of sulphide. A thin gel layer containing a silver iodide (AgI) resin gel was in the front of the Fe-oxide gel. The probes were stored at 4 °C in the clean plastic bags prior to deployment.

2.2.2. DGT deployment and retrieval

DGT probes were deoxygenated for 24 h by immersing in a 0.01 M NaCl solution and bubbled with N_2 before being deployed at 25 °C ± 0.5 °C. A reference line for SWI was inscribed prior to use. Thereafter, two different deoxygenated DGT probes were gently inserted into the sediment back to back. The whole procedure was performed in the dark. DGT probes were retrieved from the sediment cores after 24 h and rinsed with Milli-Q water to remove particles. The DGT probes were opened and filters and diffusive gels were removed. In order to investigate the vertical and horizontal variation of DGT-labile As in the overlying water and sediment profile, each Chelex-100 or Fe-oxide gel was cut into 5 mm (vertically) × 6 mm (horizontally) slices using Teflon-coated razor blades in a glove box filled with N_2. The binding gel was divided into three parts transversely, we called it 0–6 mm, 6–12 mm, 12–18 mm. Each gel slice was then placed in a polyethylene vial and eluted in 0.3 mL 1 M super-pure HNO_3 for 24 h. Extracted metals were diluted ten times and analyzed using ICP-MS (Agilent 7700x, Agilent Technologies, USA).

2.2.3. Calculation of C_{DGT}-As, C_{DGT}-Fe and C_{DGT}-Mn

The accumulated mass (M, mg) and the concentrations of pollutants measured using DGT (C_{DGT}, μg/L) following a specific deployment time (t, s) can be calculated using Eq. (1) and Eq. (2).

$$M = \frac{C_e(V_{gel} + V_{acid})}{f_e} \quad (1)$$

where C_e (mg/L) is the concentration of metals in the elution solution, V_{gel} (L) is the volume of the binding gel, V_{acid} (L) is the volume of the acid for elution, and f_e is the elution factor for metals (Zhang, 2003; Luo et al., 2010).

$$C_{DGT} = \frac{M \times \Delta g}{D \times A \times t} \quad (2)$$

M is the accumulated mass (M, mg), A is the area of the gel (cm^2), △g is the thickness of the diffusive layer and filter layer, D is the diffusion coefficient of metals at 25 °C (Zhang, 2003; Luo et al., 2010).

2.3. Laboratory analysis

After the retrieval of DGT probes, sediment cores were sliced into 5-cm intervals in a glove box filled with N_2. Thereafter, each surface sediment subsample was placed in a centrifuge tube filled with N_2. Interstitial water was obtained by centrifuging the sediment at 4000 rpm for 20 min, and filtering through a 0.45-μm membrane. As concentrations in the pore water were measured using ICP-MS. The remaining sediment samples were wet-sieved through an acid-cleaned 63 μm mesh nylon sieve. Then sediment samples were dried at 40 °C to constant weight and ground in an agate mortar to ensure homogeneity. Total concentrations of trace elements in sediments were measured using the established method (Wei et al., 2016).

2.4. Statistical analysis

The basic statistical analysis and correlations were carried out using SPSS 19.0 and Sigmaplot 10.0 for Windows. The Pearson correlation coefficient was used at the significant level of $p < 0.05$ and $p < 0.01$ to elucidate the correlation in this study.