



## Assessment of labile Zn in reservoir riparian soils using DGT, DIFS, and sequential extraction

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### ABSTRACT

The middle route of the South-to-North Water Diversion project alleviates drought in northern China, especially reducing water shortage pressure in Beijing. However, after submersion, the potential release risk of metals in newly submerged soils into the water in the receiving reservoir remains unclear. Here, we assess the labile Zn in the riparian soils of Miyun Reservoir (MYR) using the diffusive gradients in thin films (DGT), DGT-induced fluxes in soils (DIFS) model, and Community Bureau of Reference (BCR) sequential extraction. The results showed that the average Zn concentrations at three sampling sites (S2, S3, and S5) exceeded soil background value (74.8 mg/kg), indicative of Zn accumulation in the MYR. The concentrations of DGT-labile Zn varied within 39.7–62.4 µg/L (average: 56.7 µg/L), with the greatest value observed at 145 m at sampling site S3, attributed to anthropogenic activities in recreational areas. The DGT-labile Zn showed no correlation with classes of land, elevations, or soil properties. Sequential extraction results demonstrated that Zn predominantly existed in the residual fraction, but still showed a strong capability for resupply from the solid phase ( $R > 1$ ). The DIFS model simulation results showed that Zn underwent irreversible diffusion of intra-particle metals from the solid phase to the soil solution. Therefore, the potential release risk of labile Zn in riparian soils in MYR cannot be ignored, especially for areas experiencing human disturbance.

### 1. Introduction

The South-to-North Water Diversion Project (SNWDP) is a fundamental water resource strategy in China, and the Chinese government has invested 500 billion yuan (USD 62.5 billion) on the project to effectively alleviate water resource scarcity in North China (Chen et al., 2013; Sun et al., 2017). Three routes have been constructed to divert 44.8 billion m<sup>3</sup> of water from the Yangtze River to northern cities such as Beijing, Tianjin, Henan and Hebei Province (Bagla et al., 2006). One of the destinations of the middle route of the SNWDP is the Miyun Reservoir (MYR), the only surface drinking water source in the capital of China. The impoundment is expected to raise water levels and lead to changes in the physicochemical environment of the MYR. Simultaneously, the water quality of the MYR has attracted substantial attention, since it is the main surface water source of more than 21 million people in Beijing.

Metals are the primary contaminants and the most persistent pollutants in aquatic environments due to their resistance to decomposition and accumulation in biota (Li et al., 2015). Sediments are both sinks and sources of trace metals. After land submersion, riparian soils

become sediments and have the risk of releasing toxic elements into the water and directly altering drinking water quality (Han et al., 2016). Zn is the 24th most abundant element on earth, and its contents range from 5 to 770 mg/kg (average: 64 mg/kg) in soil. As an essential element and the second-most abundant transition metal in organisms (Broadley et al., 2007), Zn deficiency is associated with numerous chronic illnesses (e.g., diabetes and cancer). However, it is also a toxic trace metal in excess concentrations. Therefore, maximum limits of Zn in drinking water have been established in China (MHPRC, 2006), the United States (USEPA, 1983), and the European Union (CEC, 1980), with concentrations of 1.0 mg/L, 9.0 mg/L, and 0.1 mg/L, respectively. Moreover, Zn is a common element in the riparian soils of the MYR (Li et al., 2014), anthropogenic activities in the upstream region of the MYR (e.g. mining activities) can input Zn-containing particles into the MYR (Li et al., 2014). Zn is also highly enriched in the MYR soils (Wu et al., 2017) and MYR soils are moderately polluted with Zn (Ji et al., 2016; Qiao et al., 2013; Zhu et al., 2013). After the water levels rise in the MYR, it is unclear whether Zn in the newly submerged soils will have the potential to be released into the water body and pose a risk to the water quality. Therefore, the mobilization of Zn must be predicted

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to evaluate the contamination level and release risk of Zn in the MYR after impoundment.

The mobility and bioavailability of trace metals in soil depend highly on chemical speciation. Therefore, understanding speciation is instrumental in predicting and interpreting metal toxicity in aquatic systems (Han et al., 2005). Ex-situ methods (e.g. sequential extraction) have been used to obtain bioavailable metals (Tessier et al., 1979). However, redissolution, redistribution, and reabsorption of metals during transportation can change their chemical speciation (Zhang et al., 2001). To circumvent these limitations, the in-situ DGT technique, simulating the process of organism uptake of metals (Bradac et al., 2009), has been adopted to quantitatively measure bioavailable fractions of trace metals in water, sediment, and soil (Davison and Zhang, 2012; Santner et al., 2015). Meanwhile, the DGT-induced fluxes in soils (DIFS) model has been demonstrated to be effective for clarifying the dynamic diffusion process of metals between the solid phase and soil solution (Harper et al., 1998). The pool size of the soil and kinetic parameters were also determined (Chen et al., 2014). DGT is a passive in-situ sampling technique that shows unparalleled performance in measuring the labile forms of Zn (Degryse et al., 2003; Zhao et al., 2017). Combining the traditional ex-situ extraction method with the in-situ DGT and DIFS will provide a better way to understand the dynamic process of labile metals in the soil.

In this study, DGT, DIFS, and Community Bureau of Reference (BCR) sequential extraction were used to investigate the Zn remobilization characteristics in riparian soils of the MYR before water storage. The primary aims of this study are to (1) provide useful information of the DGT-labile fractions of Zn in the MYR riparian soils, (2) obtain a better approach to evaluating the mobility of Zn by comparing DGT and BCR sequential extraction, and (3) clarify the mechanism and remobilization kinetics of Zn using the DIFS model.

## 2. Materials and methods

### 2.1. Sample collection

Riparian soil samples were collected from the MYR before its impoundment in July 2015. The samples were collected from five main classes of land in the MYR: shoal land (S1), grassland (S2), recreational land (S3), forestland (S4), and mountain land (S5). After the water impoundment, water level of the MYR was estimated as 130–150 m (Han et al., 2016). Hence, samples were also collected at three vertical elevations of 130, 140, and 145 m. Fig. 1 shows the locations of the sampling sites. The sampling sites were distributed all around the MYR, including two upstream inflow regions along the Chao River (S2) and Bai River (S5), a downstream outflow region (S1), the central zone of the MYR (S4), and a holiday resort (S3). Soil samples were collected based on a sampling grid, and all samples were sealed in polyethylene bags and immediately transported to the laboratory. Then, the samples were air-dried, ground with an agate mortar and sifted through a 65-mesh nylon sieve to obtain homogenized particles for the sequential analysis.

The total Zn concentration at all sites was measured using  $\text{HNO}_3 + \text{HF} + \text{H}_2\text{O}_2$  digestion method. Aliquots of each sample (0.04 g) were weighed in 10-mL Teflon acid digestion bombs, and then sequentially treated with 2 mL of concentrated  $\text{HNO}_3$  and 0.2 mL of concentrated  $\text{H}_2\text{O}_2$ . Organic matter was removed after the bombs were left on a hot plate for 24 h. The residue samples were dried at 120 °C, and then 1 mL of concentrated  $\text{HNO}_3$  and 2 mL concentrated HF were added to the mixture and ultrasonic treatment was conducted for 20 min. Next, the samples were transferred to sealed bombs and placed in an oven at 190 °C for 48 h to generate clear solutions. The product was subjected to evaporation at 120 °C, the samples were treated by ultrasound treatment for another 30 min and dissolved in 1%  $\text{HNO}_3$  (v:v). Finally, total Zn concentrations in the soils were determined by inductively coupled plasma-mass spectrometry (ICP-MS; Agilent

7700 ×). Certified reference materials for soils (GSS-9, GBW07423) were analyzed as part of the quality assurance and quality control. A Vario MACRO cube CHNS analyzer (Elementar Analysensysteme, Germany) was used to measure the total organic carbon. The particle size of samples was determined with a particle size analyzer (S3500; Microtrac, USA), which divided particles into three fractions: < 2 μm (clay), 2–20 μm (silt), and > 20 μm (sand). Sample pH values were acquired using a pH meter (Mettler Toledo, Switzerland) with dilution to a soil:water ratio of 1:5.

### 2.2. BCR sequential extraction

The modified three-step BCR sequential extraction method (Ure et al., 1993) was adopted in the present study to obtain the Zn fraction proportions at each sampling site. BCR sequential extraction divides metals into four parts based on environmental conditions: F1 (acid extractable/exchangeable fraction), F2 (easily reducible fraction), F3 (oxidizable fraction), and F4 (residual fraction) (Nemati et al., 2011). Briefly, this extraction procedure included weighing 0.5 g of dried soil into a set of 50-mL centrifuge tubes and subjected to a series of extractions and measuring the Zn contents in the extraction solution with ICP-MS. BCR Reference Material (BCR 701) was used to assess the accuracy of the procedure. The recovery values were 95.0–120%.

### 2.3. DGT preparation and application

DGT devices were purchased from DGT Research Ltd. (Lancaster, UK). The assembled DGT device had an exposure window of 3.14 cm<sup>2</sup> and a diffusive layer with a thickness of 0.078 cm. Chelex 100 was used as the resin layer. A protective cellulose nitrate filter (0.14 mm thickness) separated the diffusive gel from the soil. Before using the DGT devices, deionized water was added into 60 g of homogenized, air-dried, and 2-mm-sieved soil until reaching 60% of the maximum water holding capacity and incubated for 2 days, which was then raised to 90% maximum water holding capacity for 24 h.

The deployment of DGT followed standard procedures described previously (Luo et al., 2014). Each soil sample was analyzed in triplicate. The DGT devices were applied by gently pressing them onto the soil paste to ensure complete surface contact between the filter membrane of the device and the soil and kept at 25 °C for 40 h. Then, the DGT devices were retrieved and rinsed with Milli-Q water (Millipore) to remove stained soil particles (Luo et al., 2014). Next, 1 mL of 1 M  $\text{HNO}_3$  was used to elute the resin gels for 24 h, and soil solutions were centrifuged at 3000 r/min for 15 min at room temperature. Finally, soil solutions were filtered through a 0.45-μm membrane filter and acidized with  $\text{HNO}_3$  for ICP-MS analysis.

The Zn, Fe, and Mn concentrations ( $C_{\text{DGT-Zn}}$ ,  $C_{\text{DGT-Fe}}$ , and  $C_{\text{DGT-Mn}}$ ) measured by DGT were calculated using the following equation.

$$C_{\text{DGT}} = \frac{M \times \Delta g}{D \times A \times T} \quad (1)$$

where M is the accumulated metal mass in the DGT binding layer,  $\Delta g$  is the total thickness of the diffusive gel and the filter membrane, D is the diffusion coefficient of Zn in the diffusive gel ( $6.08 \times 10^{-6}$  cm<sup>2</sup>/s) at 25 °C, A is the surface area of the DGT sampling window (3.14 cm<sup>2</sup>), and T is the deployment time.

R values reflect the capabilities of metals remobilize from the solid phase into soil solution, and higher values represent a greater possibility of diffusing into the aqueous phase. The R value can be represented as the ratio of concentration of DGT-labile Zn ( $C_{\text{DGT}}$ ) to Zn concentration in soil solution ( $C_{\text{sol}}$ ), as described in Eq. (2).

$$R = \frac{C_{\text{DGT}}}{C_{\text{sol}}} \quad (2)$$

$R_{\text{diff}}$  is the ratio of  $C_{\text{DGT}}$  to  $C_{\text{sol}}$  in the hypothetical case that the consumed Zn is only resupplied from porewater diffusion and not from

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