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Predicting remobilization characteristics of cobalt in riparian soils in the Miyun Reservoir prior to water retention

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ABSTRACT

The Middle Route of the South-to-North Water Diversion Project is a significant water diversion project intended to alleviate water shortages in the north China plains, especially for the capital (Beijing). After water retention, the potential ecological risk of metal contamination in the riparian soils of the Miyun Reservoir (MYR) to water quality has raised public concern. The remobilization characteristics of cobalt (Co) in MYR riparian soils are still unknown. Riparian soil samples (considering five different land use types and three vertical elevations) were collected from the MYR prior to water impoundment. Total Co concentrations, soil properties, total Co in soil solution, Co chemical fractions and labile Co measured by diffusive gradients in thin films (DGT) are applied to investigate the Co remobilization characteristics. The results showed that the total concentrations of Co (C_{total}-Co) were approximately equal to background values of Co in Beijing and China at most of the sites. The highest values of C_{total}-Co were observed at 140 m and 145 m in recreational land (S3), which may be influenced by the anthropogenic activities. No obvious differences in C_{total}-Co and DGT-labile Co (C_{DGT}-Co) were found with the variation of land use types and vertical elevations in the soils of the MYR. C_{DGT}-Co made up 9%-52% of the total dissolved Co, with an average value of 25%, indicating that Co in the soil solution was partially sustained by the solid phase. The highest C_{DGT}-Co were observed in grassland and mountain land, indicating that the previous intensive mining in the upstream areas of the MYR is responsible for the release of Co. The results of the sequential extraction showed that Co is mainly bound to the residual fraction. DGT-labile Co had no correlation with non-residual fractions measured by sequential extraction, but had a significantly positive relationship with C_{DGT}-Mn, indicating that Co trapped by DGT mainly came from the dissolution of MnO_x. When the MYR riparian soils are submerged, a reducing environment will be formed. In this case, Co associated with MnO_x may be also released into the water.

1. Introduction

Cobalt (Co) is an essential element for human health (Wendling et al., 2009; Hooda, 2010). However, at elevated concentrations Co has been demonstrated to cause irreversible damages to plant cells, and to have genotoxic and carcinogenic effects to human beings (Lison et al., 2001). Co is widely utilized in many crucial industries (Zeng and Li, 2015) and is mainly an associated product or a by-product metal of ores of iron, copper and nickel (Karuppanapandian and Kim, 2013; Pourret et al., 2016). Therefore, Co contamination in soils is becoming a severe issue for environmental safety and human health. Since Co can be ingested by humans, it is imperative to decrease Co(II) in groundwater to levels that are not harmful to human health (Wang et al., 2011). It is universally accepted that total metal concentration is a poor indicator of bioavailability, since the toxicity is related to the chemical forms of a metal (Collins and Kinsela, 2010; Rinklebe et al., 2016). *Ex situ* methods such as sequential extraction and the equilibrium partitioning method have been used to evaluate the bioavailability of heavy metals (Pueyo et al., 2008; Yin and Fan, 2011). Nevertheless, the *ex situ* methods can not evaluate the available metals accurately, because the speciation of metals may be modified during transport or during the course of the labor-intensive procedure (Zhang et al., 2001). In comparison, the diffusive gradients in thin films (DGT) technique is developed as an *in situ* passive sampling technique for trace metal measurements (Davison and Zhang, 1994; Zhang and Davison, 1995). It has been demonstrated to be a convenient and rapid way to assess metal bioavailability (Amato et al., 2016; Luo et al., 2014; Guan et al., 2015). It can reflect the degree of metal pollution over a period of time.

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Beijing is the capital of China, with a population of more than 20,000,000 (Ding et al., 2016). Drinking water safety is of high priority for urban development. As the only surface water source for drinking water in Beijing, the quality and quantity of water in Miyun Reservoir (MYR) is key to socio-economic development and the water security of Beijing (Ding et al., 2016; Qin et al., 2014). To solve the problem of water shortages in Beijing, the government has undertaken the Middle Route of the South-to-North Water Diversion Project (MRSNDP). The project diverts water from the Danjiangkou reservoir to Beijing and Tianjin (Wang and Ma, 1999; Wei et al., 2016b). The MRSNDP is km long, and crosses the Yangtze, the Yellow, Huai and Hai river basins. The annual diversion capacity of the region is 15 billion m^3 (Wang and Ma, 1999). Upon completion, this project is expected to relieve the severe water shortages and recharge groundwater in Beijing.

Therefore, the remobilization characteristics of Co in the riparian soils around the MYR were investigated prior to the impoundment of water during the construction of the MRSNDP. The primary objectives of the present study are: (1) to provide useful information on the variation of DGT-labile Co in the riparian soils relevant to the land use types and vertical elevations; (2) to predict the mobility of Co using DGT, dissolved Co concentration and traditional BCR sequential extraction; (3) to explain the relationship between DGT-labile Co and different chemical speciations.

2. Materials and methods

2.1. Sample collection

Riparian soil samples were collected from the MYR prior to the water from the Danjiangkou reservoir entering into the MYR in July 2015. Samples S1–S5 were collected in the downstream outflow region of the reservoir, upstream reservoir inflow region along the Chao River, a holiday resort, the center of the reservoir and the upstream reservoir inflow region along the Bai River. Five different use types (shoaly land (S1), grassland (S2), recreational land (S3), forestland (S4), mountain land (S5)), and three vertical elevations (130, 140, and 145 m) of soils were considered. The sampling locations are shown in Fig. 1. At each sampling site, samples were collected using a sampling grid. Soil samples were stored in labeled polyethylene bags and transported to the laboratory. Samples were air-dried, gently crushed and sieved at 2 mm with a nylon sieve. Subsequently, samples were ground, homogenized with an agate mortar and passed through a 65 mesh nylon sieve for laboratory analyses.

2.2. Chemical analysis

The total Co concentrations (C_{total}-Co) in the soils were measured after being digested with HNO_3, HF and H_2O_2 (Wei et al., 2016a). Firstly, 0.04 g dry soil samples were weighed into 10 mL Teflon bombs. Approximately 2 mL concentrated HNO_3 and 0.2 mL concentrated H_2O_2 were added to the samples and the bombs were left on a hot plate for 24 h to remove organics. Thereafter, the samples were dried at 120 °C before 1 mL concentrated HNO_3 and 2 mL concentrated HF were added to the bombs and they were subjected to ultrasonic treatment for 20 min. Then the samples were put into sealed bombs and placed in an oven at 190 °C for 48 h. This procedure generated clear solutions from the samples. After evaporation at 120 °C, the samples were subjected to ultrasound treatment for another 30 min and dissolved in 1% HNO_3 (v:v). Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x) was used to determine total Co concentrations in the soils. The certified reference materials (CRMs) for soils (GSS-9, GBW07423) were analyzed as the quality assurance and quality control (QA/QC).

Samples were partitioned into three size fractions < 2 μm (clay), 2–20 μm (silt), and > 20 μm (sand) using a particle size analyzer (Microtrac S3500, USA). The total organic carbon (TOC) was analyzed using a Vario MACRO Cube CHNS analyzer (Elementar Analysensysteme, Germany). Soil pH was measured using a pH meter (Mettler Toledo, Switzerland) with a 1:5 soil to water ratio.

2.3. BCR sequential extraction procedure

Eight steps sequential extraction (Laveuf et al., 2009) and the AA-EDTA extraction methods (Faucon et al., 2009; Pourret et al., 2015) are often used for the estimation of Co mobility. In this study, in order to compare our Co fraction and DGT results with other studies, the modified three-step European Community Bureau of Reference (BCR) sequential extraction method was used to determine metal speciation in the soils (Rauret et al., 2001). Briefly, about 0.5 g of dried soil was weighed into a set of 50 mL centrifuge tubes and subjected to a series of extractions. The four fractions and extractants are listed below:

F1: acid-exchangeable (acetic acid)
F2: reducible (hydroxylamine hydrochloride; pH 1.5)
F3: oxidizable (hydrogen peroxide; pH 2, ammonium acetate).
F4: residual (total concentration-F1-F2-F3).

Cobalt concentrations in soils and solution extracts were determined by ICP-MS. BCR Reference Material (BCR 701) was used to check the accuracy of the analytical procedures. The recovery values were in the range of 95.5%–112.9%.

2.4. DGT preparation, deployment and data interpretation

Piston DGT devices with an exposure window of 3.14 cm^2 were purchased from DGT Research Ltd. (Lancaster, UK). The diffusion layer was polyacrylamide gel and the resin layer was Chelex 100. A protective filter separates the diffusive gel from the soil. Three DGT devices were kept for DGT blank determination.

Deployment in the soil followed the standard procedures for using DGT in soils (Zhang et al., 1998). 60 g of each homogenized, air-dried and 2 mm sieved soil was wetted to 60% maximum water holding capacity (MWHC) with ultrapure water and incubated for 2 days, then raised to 90% MWHC for 24 h prior to DGT deployment (Liang et al., 2014). Each soil treatment was analyzed in triplicate. DGT devices were carefully pressed onto the soil paste to ensure complete contact between the filter membrane of the device and the soil surface and kept at 25 °C for 40 h. Upon retrieval, DGT devices were washed with Milli-Q water (Milli-Q, Millipore) to remove soil particles, and then disassembled (Luo et al., 2014). The resin gels were removed from the DGT devices, and eluted with 1 mL of 1 mol/L HNO_3 for 24 h prior to analysis. After the retrieval of DGT devices, soil solutions were extracted by centrifugation at 3000 r/min for 15 min at room temperature. Then soil solutions were filtered through 0.45 μm membrane filter and acidized with HNO_3 prior to analysis (Ernstberger et al., 2005).

DGT-measured concentrations of Co (C_{DGT}-Co) and Mn (C_{DGT}-Mn) were calculated using Eq. (1).

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

where M is the mass accumulated on the binding gel, $\triangle g$ is the thickness of the diffusive layer and the filter membrane (0.078 cm), D is the diffusion coefficient of the Co (5.94×10^{-6} cm^2/s) and Mn (5.85×10^{-6} cm^2/s) at 25 °C (Zhang, 2003), A is the exposure window area of the DGT device (3.14 cm^2) and t is the deployment time.

The ratio of the C_{DGT} to metal concentration in the soil solution (C_{sol}) is termed as the R-value:

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

R reflects the ability of soil to resupply an element from the soil solid phase to the solution phase. A larger R-value means the soil's ability to resupply metal to the soil solution is greater (Guan et al., 2016, 2017).