



## Occurrence and fate of colloids and colloid-associated metals in a mining-impacted agricultural soil upon prolonged flooding

Bing Xia<sup>a,b,c,1</sup>, Hao Qiu<sup>b,d,\*,1</sup>, Klaus-Holger Knorr<sup>e</sup>, Christian Blodau<sup>e</sup>, Rongliang Qiu<sup>a,\*\*</sup>

<sup>a</sup> School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou, China

<sup>b</sup> School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, China

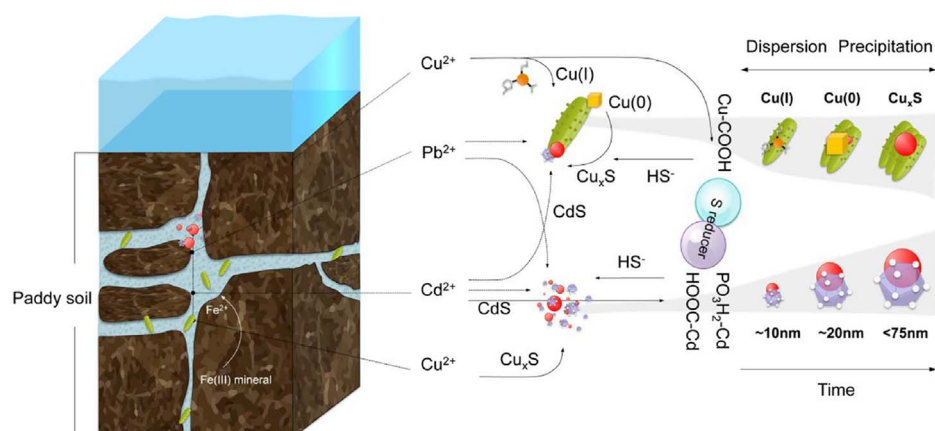
<sup>c</sup> Anhui Academy of Environmental Science Research, Hefei, China

<sup>d</sup> Key Laboratory of Original Agro-Environmental Pollution Prevention and Control, Ministry of Agriculture/Tianjin Key Laboratory of Agro-Environment and Safe-Product, Tianjin, China

<sup>e</sup> Institute of Landscape Ecology, University of Münster, Münster, Germany



### GRAPHICAL ABSTRACT



### ARTICLE INFO

**Keywords:**  
Colloids  
Metals  
Flooding  
Sulfide  
EXAFS

### ABSTRACT

Colloids formed during soil flooding can potentially facilitate the mobilization of metal contaminants. Here, laboratory batch incubations with a contaminated soil were performed to monitor temporal changes in the porewater dynamics of metals, the morphology and composition of colloids, and the speciation of colloid-associated metals during 30 days of flooding. The concentrations of colloidal and dissolved metals increased initially and peaked at a certain time, but then decreased with the on-going sulfate reduction. The combined analysis of spectrometric, spectroscopic, and size-fractionation results revealed that the dynamics of Cu were dominated by microbe-associated colloids and were mediated largely by Cu(0) biomineralization and subsequent sulfidation, while the microbe-associated and freely dispersed colloids were equally relevant for governing the dynamics of Cd and Pb. Mobilization of Zn, on the other hand, was dominated by its dissolved form, probably due to the low thermodynamic stability of Zn-sulfide. Additionally, adsorption via organic functional groups was another mechanism for metal incorporation into colloids. We also provided direct spectroscopic evidence for the formation and persistence of dispersed heterocolloids consisting of Cu<sub>x</sub>S and CdS during flooding. Our findings

\* Corresponding author at: School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, China.

\*\* Corresponding author.

E-mail addresses: [haoqiu@sjtu.edu.cn](mailto:haoqiu@sjtu.edu.cn) (H. Qiu), [eesqr@mail.sysu.edu.cn](mailto:eesqr@mail.sysu.edu.cn) (R. Qiu).

<sup>1</sup> Co-first authors.

suggest that colloids-induced metal mobilization should be considered in assessing bioavailability and risks of metals in contaminated soils upon flooding.

## 1. Introduction

Anthropogenic input of heavy metals into the subsurface environment is widespread and has received much concern with regard to their adverse impact on soil and groundwater quality [1]. Metals that are sparingly soluble or strongly adsorbed to a solid phase were traditionally deemed to be largely immobile in soils and aquifers [2]. This viewpoint has been challenged recently by ample evidence demonstrating that nanoparticles, or more general, colloids can act as carriers to facilitate the transport of adsorbed metals through porous media [3–5]. Failure to account for colloid-enhanced metal mobilization may cause a severe underestimation of the transport potential and the actual risks of these metals. Therefore, it is essential that the occurrence and fate of mobile colloids and their associated metals be investigated for the adequate risk assessment of metal-contaminated soils.

Natural nanoparticles or colloids are composed of inorganic, organic, or microbial material. Due to their high specific surface area and reaction activity, colloids can be effective sorbents for metals present in soil [6]. The mobility of metals is therefore affected by the formation and release of colloids and metal-colloid adsorption phenomena. Much research has been dedicated to delineating colloid-facilitated mobilization of a single contaminant in simplified systems (e.g., engineered nanoparticles as carrier and water-saturated quartz sand as porous media) [3,7]. In contrast, little attention has been paid to the naturally occurring colloidal particles and their implications for the fate of multiple metal contaminants in soil. Further, the occurrence and stability of colloids in soil may vary with variations in soil chemistry triggered by certain circumstances such as seasonal flooding [8] and freeze–thaw cycles [9], which in turn could cause fluctuations in metal mobility and bioavailability.

For the mining-impacted paddy soils the investigation on the fate of metal-bearing colloidal particles under flooding conditions is particularly relevant, because these metal-rich soils are submerged in water during most of the time of rice growth. Flooding strongly limits molecular oxygen diffusion into the soil, driving soil-dwelling microorganisms to respire using sequentially  $\text{NO}_3^-$ ,  $\text{Mn}^{4+}$ ,  $\text{Fe}^{3+}$ , and  $\text{SO}_4^{2-}$  as electron acceptors [10]. The reductive dissolution of Mn/Fe oxides can give rise to the release of metals from soil matrix to the aqueous phase [11]. Microbial sulfate reduction may lead to the immobilization of chalcophile metals (e.g., Cu, Cd, Pb, and Zn) via sequestration into poorly soluble metal sulfide precipitates [12]. On the other hand, the formation of metal sulfide clusters (colloidal metal sulfides) that are resistant to aggregation and deposition may significantly enhance metal mobility in sulfate-reducing systems [8,13]. Besides, the newly-formed metal sulfide nanoparticles can serve as sites for adsorption or coprecipitation of other coexisting metals [14,15]. Previous studies on colloid-facilitated metal mobilization were mainly based on total concentrations of colloidal metals in the leachates and did not track the above-mentioned (possibly transient) processes [4,16]. Upon prolonged soil flooding, a clear picture of the formation, chemical composition and temporal dynamics of natural nanoparticles as well as their impact on metal mobilization is still lacking. Advanced analytical tools (e.g., synchrotron-based X-ray absorption spectroscopy, transmission electron microscopy, and ultrafiltration) provide the possibilities for accurate determination of speciation of metals and the type of colloids with which they are associated [17,18], thereby will aid in the efforts to understand the origin and fate of metal-bearing colloids.

The main objectives of the present study were to determine changes in dynamics of colloidal and dissolved metals (Cu, Cd, Pb, and Zn) in the porewater of a mining-impacted agricultural soil during flooding,

and to explore the molecular-level mechanisms that are responsible for the formation, persistence, and deposition of metal-bearing colloids in the reducing environment. Microcosm batch experiments were performed to mimic the flooded field conditions. The combined use of wet-chemical analyses, microscopic (transmission electron microscopy, TEM) and synchrotron-based spectroscopic techniques (extended X-ray absorption fine structure spectroscopy, EXAFS) were expected to provide new insights into the formation and transformation of colloids and the potential colloid-facilitated mobilization of metals in flooded soil.

## 2. Material and methods

### 2.1. Preparation of soil and synthetic river water

The top-layer soil (0–15 cm) was sampled in Shangba Village, along the Hengshi River, Guangdong, China. In this area, the agricultural lands were contaminated with multiple metals because of adjacent mining activities [19]. After sampling, soils were air-dried and sieved through a 2 mm polyethylene sieve before use. Selected physicochemical properties of the investigated soil are listed in Table A.1 (in Supplementary material). Synthetic river water was prepared by adding different amounts of  $\text{CaSO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$ , and  $\text{NaCl}$  salts to the Milli-Q ultrapure water. The resulting solution consisted of 1.0 mM  $\text{CaSO}_4$ , 0.5 mM  $\text{Mg}(\text{NO}_3)_2$ , and 1.9 mM  $\text{NaCl}$ , resembling the main composition of the Hengshi river water during the flooding season [20].

### 2.2. Microcosm experiments

The device for the microcosm experiment was a one-liter glass bottle (Schott Duran®, Germany), which was equipped with a porous suction cup (pore size: 10–16  $\mu\text{m}$ ) and connected to a Teflon shut-off valve (Fig. A.1 in Supplementary material). For each microcosm, 250 g air-dried soil was suspended in the aerated synthetic water (1000 mL) and the suspension was equilibrated by end-over-end shaking for 2 h under air. After equilibration, the soil slurry was centrifuged at 600g for 15 min. The supernatant was decanted and the soil paste recovered after centrifugation was directly placed into a microcosm. An additional amount of the synthetic water (250 mL) was added to the system to have a water-saturated soil layer with a 5–7 cm submergence depth, commencing the experiment. A series of microcosms were incubated in the dark at 25 °C for different time from 1 to 30 days (14 time points  $\times$  3 replicates). The incubation course was set based on the understanding that the chemical properties of the submerged paddy soils usually reach apparent equilibrium within 30 days [21]. Two control series were prepared by adding formaldehyde (0.04%, w/v) to inhibit microbial activity [22] and by aerating to maintain an oxic suspension, respectively.

Soil porewater at each time point (day 1–10, 15, 20, 25, and 30) was sampled by linking the suction cup to a syringe. A slow flow rate of 0.4 mL/min was chosen to minimize the impact of external forces on soil grains and to avoid the formation of colloidal Si, Mn or Fe [15]. Around 25 mL porewater was obtained from each microcosm (see notes to Fig. A.1 for details in Supplementary material). All the sampling procedures were carried out in a steel glovebox ( $p\text{O}_2 < 1$  ppm; Braun, Germany).

### 2.3. Size fractionation of colloids in the porewater

The 0.025  $\mu\text{m}$  cut-off value was used to define the colloidal-dissolved boundary [8,15]. Specifically, the colloidal and dissolved metal

Download English Version:

<https://daneshyari.com/en/article/6968925>

Download Persian Version:

<https://daneshyari.com/article/6968925>

[Daneshyari.com](https://daneshyari.com)