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# Aging shapes the distribution of copper in soil aggregate size fractions<sup>☆</sup>



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## ABSTRACT

Soil aggregates are often considered the basic structural elements of soils. Aggregates of different size vary in their ability to retain or transfer heavy metals in the environment. Here, after incubation of a sieved (<2 mm) topsoil with copper, bulk soil was separated into four aggregate-size fractions and their adsorption characteristics for Cu were determined. By combining nano-scale secondary ion mass spectrometry and C-1s Near Edge X-ray Absorption Fine Structure Spectroscopy, we found that copper tends to bind onto organic matter in the <2 μm and 20–63 μm aggregates. Surprisingly, Cu correlated with carboxyl-C in the <2 μm aggregates but with alkyl-C in the 20–63 μm aggregates. This is the first attempt to visualize the spatial distribution of copper in aggregate size fractions. These direct observations can help improve the understanding of interactions between heavy metals and various soil components.

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## 1. Introduction

Anthropogenic activities such as sewage irrigation, waste utilization and fertilization (Williams et al., 2009; Wei and Yang, 2010) have resulted in continuous release of heavy metals into soil ecosystems over the past years (Burkitt et al., 1972; Zhao et al., 2014). The immobilization and mobility of heavy metals in soil environments depends strongly on their interactions with solid soil components, primarily minerals and organic matter, which are the basic constituents of soil aggregates (Sauvé et al., 2000; Weng et al., 2002). In soil systems, single organic and inorganic aggregates including clay minerals, humic substance and microorganisms tend

to form various aggregates with different sizes. Apart from soil physical and chemical properties such as pH, soil texture, mineral composition and organic content, the accumulation and distribution of heavy metals after introduction into the soil are also dependent on the size fraction of soil aggregates (Ajmone-Marsan et al., 2008; Acosta et al., 2009; Xiao et al., 2016). It has been shown that clay-sized aggregates affect the availability and toxicity of heavy metals differently from larger sized ones (Hochella et al., 2008; Plathe et al., 2013). Moreover, fine soil aggregates have a higher ability to retain heavy metals due to their larger surface area, higher clay mineral and organic matter content, and the presence of Fe-Mn oxide phases that act as sorbents for heavy metal ions (Bi et al., 2013; Huang et al., 2014). Aging is another factor that influence the chemical behaviors of heavy metals when they are introduced to soil environments (Sayen et al., 2009; Wang et al., 2015; Li et al., 2016). Soil aging may result in the decomposition and humification of organic matter, changes of oxyhydroxide forms and aggregation of organo-mineral complexes. Moreover, aging also facilitates the diffusion of Cu into the inner part of aggregates, and precipitation of Cu with minerals and so forth. These processes will ultimately influence the binding, transformation and stability

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of Cu species in soil.

To date, indirect methods such as sequential extraction procedures suffer from several unavoidable shortcomings such as incomplete extraction of the targeted species, potential re-adsorption of extracted elements and destruction of the natural structure of soil aggregates (Sutherland, 2010). Direct observation of elements distribution in soil components have attracted increasing attention in recent years. However, such observations remain challenging because there are few techniques that can simultaneously measure light elements (e.g., C, N, etc.) and heavy metals. Recently, limited investigations on soil organo-mineral associations by NanoSIMS showed the feasibility of this technique to distinguish soil minerals and organic matter by their corresponding elements, e.g., C, N, Fe, Al (Vogel et al., 2014; Höschel et al., 2015; Rumpel et al., 2015). This technique was also used to directly visualize heavy metal distribution in microorganism and plant cells (Behrens et al., 2012; Moore et al., 2014; Hong-Hermesdorf et al., 2014). Since imaging is able to detect both light and heavy elements, we hypothesized that NanoSIMS could directly observe trace metal distribution in soil aggregates, obtaining their interaction with minerals and organic matter simultaneously.

This work aimed to use NanoSIMS to study the spatial distribution of copper in soil aggregates of different size. An incubation experiment with the arable top layer of an Ultisol was performed to obtain various organo-mineral associations at different aging periods. In combination with macroscopic and synchrotron data, NanoSIMS was employed to quantify the distribution of copper in size-dependent soil aggregates during aging. To the best of our knowledge, this paper is the first attempt to visualize the spatial distribution of copper in different size of soil aggregates, offering valuable information on the correlation between copper and the inorganic/organic substances.

## 2. Materials and methods

### 2.1. Soil and incubation experiment

Soil samples were collected at a depth of 0–20 cm from Changsha, Hunan Province, China. The soil is an Ultisol based on the US Soil Taxonomy (Soil Survey Staff, 2014). The soil was air-dried and passed through a 2-mm nylon sieve prior to the analysis of various physical-chemical properties. An incubation experiment was conducted with 1 kg soil sample in ceramic containers. Copper was added as Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in aqueous solution at 200 mg kg<sup>-1</sup> rates, which exceeds class II of soil environmental quality according to the Ministry of Environmental Protection of China (GB 15618-1995). Then thoroughly mixed with the soil material. The pots were placed in the green house and maintained at about 60% water holding capacity by periodically weighing the pots and adjusting the weight by addition of distilled water. The soils were incubated for 4, 12, 28 months, each treatment was repeated in duplicate. The physicochemical properties of the soils were analyzed according to Bao (2000). The mineral composition of the clay fraction was determined by X-ray diffraction (Fig. S1). Soil total carbon (TOC) and nitrogen (N) were measured by catalytic high-temperature oxidation using a CN auto-analyzer (Vario PYRO cube, Elementar, Germany). Total soil Cu was digested by HNO<sub>3</sub>-HF-HClO<sub>4</sub> and determined by AAS analysis (AA240 Duo, Agilent, USA). The free and amorphous Fe and Al oxides were evaluated by the dithionite-citrate-bicarbonate (DCB) and oxalate (pH 3.0) methods, respectively (Lu, 1999). The concentrations of Fe/Al was measured with ICP-OES (Optima 8000, PerkinElmer, USA). These soil properties are presented in Table S1.

### 2.2. Physical soil fractionation

To extract the organo-mineral associations, we conducted an aggregate size fractionation (Vogel et al., 2014). Dry soil material (30 g, <2 mm) was saturated with 300 mL of deionized water and allowed to settle overnight. Subsequently, the dispersed sample was wet-sieved at 63 μm mesh sizes to separate the sand. The soil material fraction of <63 μm was separated into coarse silt fractions (20–63 μm) and fine silt (2–20 μm) and clay (<2 μm) via sedimentation. All fractions were dried (40 °C) and weighed to obtain the mass proportion of each fraction relative to the bulk soil. The TOC, total Cu, Fe and Al of each aggregate size fractions were analyzed according to the methods described above.

### 2.3. C NEXAFS measurement

The carbon 1s-NEXAFS spectra were obtained at the soft X-ray spectroscopy beamline (4B7B) of the Beijing Synchrotron Radiation Facility (BSRF). This light source produces a soft X-ray beam from the 2.5 GeV electron storage ring. Samples of the clay and silt size separates were mounted on to the sample disc using a double sided adhesive Cu tape. The samples were measured in a vacuum under 10<sup>-6</sup> Pa. The C-1s NEXAFS signal was simultaneously recorded in total electron yield (TEY) and C spectra were obtained from 280 to 310 eV. The energy spacing was chosen as follows: 0.5 eV steps from 280 to 282 eV; 0.05 eV steps from 283 to 293 eV and 0.5 eV steps from 294 to 310 eV. The stack measurements were obtained with dwell times of 1–1.5 ms to avoid potential beam damage. The spot size of the beam under the operating conditions was approximately 1 mm × 0.1 mm. Before scanning, the background spectra were collected through the sample free region of the same Cu tape. The IFFEFIT Athena version 0.8.056 was used for background subtraction, normalization and fitting of NEXAFS spectra.

### 2.4. NanoSIMS analysis

Soil aggregate size fractions at the time points of 4, 12 and 28 months were analyzed by means of NanoSIMS (Cameca NanoSIMS 50L, France) located at the Institute of Geology and Geophysics, Chinese Academy of Sciences, China. Clay and silt aggregates in a powder state were thoroughly mixed with deionized water (1mg/20 mL of water/solid ratio) to yield a homogeneous suspension. One droplet of the resulting solution (20 μL) was dispersed on a Si wafer (10 mm diameter), which was dried overnight in a desiccator. The homogeneous distribution of the aggregates was checked with scanning electron microscopy (JSM-6390LV, NTC, Japan). Prior to SEM observation, the samples were coated with a thin, electrically conductive gold film to avoid charging. For NanoSIMS analysis, the Cs<sup>+</sup> primary ion probe was used with a primary ion impact energy of 16 keV. Before analysis, contaminants and an additional gold coating layer (~30 nm) were sputtered away by a high primary beam current (pre-sputtering). During the pre-sputtering, the reactive Cs<sup>+</sup> ions were implanted into the sample to enhance the secondary ion yields. The primary beam (~1 pA) was focused at a lateral resolution of 100–200 nm and was scanned over the samples. The secondary ion images of <sup>12</sup>C<sup>-</sup>, <sup>27</sup>Al<sup>16</sup>O<sup>-</sup>, <sup>56</sup>Fe<sup>16</sup>O<sup>-</sup> and <sup>63</sup>Cu<sup>16</sup>O<sup>-</sup> were collected on electron multipliers with an electronic dead time fixed at 44 ns. We compensated for the charging due to the non-conductive mineral aggregates by employing the electron flood gun of the NanoSIMS instrument. All measurements were conducted in imaging mode. The ion images were obtained using a dwell time of 1–3 ms/pixel. All the image referred in this paper are 256 × 256 pixels, recorded in ~15 min. The roughness of specimens can be a potential source of bias because sample topography affects the NanoSIMS yield for ions. Our samples were coated with gold

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