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Using new hetero-spectral two-dimensional correlation analyses and synchrotron-radiation-based spectromicroscopy to characterize binding of Cu to soil dissolved organic matter[☆]

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ABSTRACT

Understanding the binding characteristics of copper (Cu) to different functional groups in soil dissolved organic matter (DOM) is important to explore Cu toxicity, bioavailability and ultimate fate in the environment. However, the methods used to explore such binding characteristics are still limited. Here, two-dimensional correlation spectroscopy (2DCOS) integrated with Fourier transform infrared (FTIR), ²⁹Si nuclear magnetic resonance (NMR), ²⁷Al NMR, and synchrotron-radiation-based FTIR spectromicroscopy were used to explore the binding characteristics of Cu to soil DOM as part of a long-term (23 years) fertilization experiment. Compared with no fertilization and inorganic fertilization (NPK), long-term pig manure fertilization (M) treatment significantly increased the concentration of total and bioavailable Cu in soils. Furthermore, hetero-spectral 2DCOS analyses demonstrated that the binding characteristics of Cu onto functional groups in soil DOM were modified by fertilization regimes. In the NPK treatment, Cu was bound to aliphatic C, whereas in the manure treatment Si–O groups had higher affinity toward Cu than aliphatic C. Also, the sequence of binding of functional groups to Cu was modified by the fertilization treatments. Moreover, synchrotron-radiation-based FTIR spectromicroscopy showed that Cu, clay minerals and sesquioxides, and C functional groups were heterogeneously distributed at the micro-scale. Specifically, clay-OH as well as mineral elements had a distribution pattern similar to Cu, but certain (but not all) C forms showed a distribution pattern inconsistent with that of Cu. The combination of synchrotron radiation spectromicroscopy and 2DCOS is a useful tool in exploring the interactions among heavy metals, minerals and organic components in soils.

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1. Introduction

In China, excessive amounts of inorganic fertilizers and various types of manures are used to increase soil fertility and obtain high yield (Bolan et al., 2004; Zhao et al., 2015; Zhou et al., 2015). However, overuse of inorganic fertilizers causes significant soil acidification in major China croplands, whereas application of animal manures may contaminate soil with heavy metals derived from additives in the animal feeds (Nicholson et al., 1999; Ogiyama et al., 2005; Sager, 2007). For example, copper (Cu) is used as a feed additive; many reports indicated that the concentration of Cu in soil to which manure was applied often exceeded the acceptable limits

for food production (Asada et al., 2012; Chen et al., 2005; Zhao et al., 2015). Despite moderate doses of Cu being beneficial for all living organisms, excessive Cu would have a negative effect (Ramos, 2006). Therefore, understanding the binding characteristics of Cu after its addition to soil via fertilization is essential for predicting its toxicity, distribution and migration.

Inherently stable and chemically unique compounds are important components of soil organic matter (SOM) and play a crucial role in binding Cu (McBride et al., 1997; Römken and Dolfing, 1998). Carbonate minerals, clay minerals, and iron, manganese and aluminum oxides are also important sinks for metals in soils. Moreover, soil dissolved organic matter (DOM) is one of the most reactive fractions of SOM (Yu et al., 2012). Soil DOM is known to form strong complexes with Cu, thus influencing its distribution, toxicity, bioavailability, and ultimate fate in the environment (Cabaniss, 2009, 2011; Chen et al., 2015; Sauvé et al., 2000).

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Recently, several investigators showed that fertilization regimes could affect the proportion and composition of DOM (Asada et al., 2012; Wen et al., 2014a), leading to alterations in the formation of complexes between organic ligands and metals, as well as a change in soil redox conditions by improving soil structure (Al Mamun et al., 2016; Asada et al., 2012). However, the approaches to explore the interaction between soil DOM and Cu are still limited.

Owing to optical spectroscopy responses of the abundant light-absorbing and light-emitting groups in the metal-DOM complexes, the most frequently used tools for metal-DOM interaction analysis are fluorescence excitation-emission matrix (EEM) spectroscopy, differential absorbance titration, and size-exclusion chromatography (Bai et al., 2008; Wu et al., 2011; Yan and Korshin, 2014; Yu et al., 2011b). Two limitations of these methods are their highly overlapping responses during the binding process and incapacity to characterize the complexes of metals with non-fluorescent substances (i.e., polysaccharides, lipids and lignin that are abundant in soil) (Chen et al., 2015; Yu et al., 2012).

Fourier transform infrared (FTIR) spectroscopy combined with two-dimensional correlation spectroscopy (2DCOS) has been developed to assess the complexes of organic ligands with metals in soil DOM (Wen et al., 2014a; Yu et al., 2012). 2DCOS is capable of resolving overlapped peaks by extending spectra along the second dimension as well as providing information about the relative directions, determining the binding characteristics of both fluorescent and non-fluorescent complexes and sequential orders of structural variations (Chen et al., 2015; Xu et al., 2013; Yu et al., 2012). This combination of techniques has recently been used to probe the interactions of some environmentally-relevant heavy metals and DOM. However, the range of wavelength sensitivity of FTIR makes it difficult to assign particular elements to the soil minerals. Complementary techniques to FTIR include ^{29}Si or ^{27}Al nuclear magnetic resonance (NMR) (Li et al., 2012). These powerful modern techniques can address the local coordination state of the mineral elements in the soil compounds (Li et al., 2014; Strawn and Baker, 2008). In addition, combination of synchrotron-radiation (SR)-based FTIR spectroscopy and electron probe micro-analysis (EPMA) can simultaneously characterize the distribution of organic functional groups, clay minerals, and heavy metals in geosamples (Luo et al., 2014). It is expected that studies using these two complementary techniques may provide direct evidence for the distribution of Cu in soils at the molecular level, which cannot be achieved with 2DCOS techniques. To date, no attempt has been made to combine 2DCOS, SR-based FTIR spectroscopy, and EPMA in exploring the binding characteristics of Cu with organic functional groups and clay minerals in soils.

The structure of OM and mineral species in soil as influenced by the long-term fertilization regimes has been reported (Wen et al., 2014a; Yu et al., 2012). However, it is unclear whether long-term fertilization practices can influence the binding mechanisms and distribution of Cu in soils at the micro-scale. Hence, the objectives of this study were (i) to investigate the interaction between functional groups and Cu in soil DOM using 2DCOS technique combined with FTIR, ^{29}Si NMR and ^{27}Al NMR; (ii) to explore the binding sites and distribution of functional groups, mineral elements and Cu in soils by combining SR-based FTIR and EPMA; and (iii) to provide a new insight into Cu speciation for improved risk analysis and enhanced remediation strategies.

2. Materials and methods

2.1. Soil samples and DOM extraction

The treatments of no fertilization (control), inorganic

fertilization (NPK), pig manure (M) fertilization, and inorganic fertilizer plus manure (NPKM) fertilization were selected in a long-term (23-year) fertilization experiment ($26^{\circ}45'\text{N}$, $111^{\circ}52'\text{E}$, 120 m above sea level) located at the experimental station of the Chinese Academy of Agricultural Sciences, Qiyang, Hunan Province, China. The experiment comprised an annual double-cropping system of wheat and corn. The red soil was classified as Ferralic Cambisol. A detailed description of the long-term fertilization experiment site has been provided previously (Yu et al., 2012; Zhang et al., 2009). Surface soil (0–20 cm) samples were collected in September 2013 using a 5-cm internal diameter auger. Each sample was a composite of 10 random cores collected from a single plot. The fresh soil was thoroughly mixed, air-dried, and sieved through a 2-mm and 0.15-mm screens for further analysis.

Soil DOM was extracted with deionized water (solid-to-water ratio of 1:5 w/v) on a horizontal shaker (170 rpm) for 24 h at room temperature and then centrifuged at 3000 g for 10 min. The supernatant suspension was passed through a 0.45- μm polytetrafluoroethylene filter and then stored in the dark at 4 °C for further study.

2.2. Soil pH, SOC and total nitrogen (TN) content

Soil pH was measured with deionized water (solid-to-water ratio of 1:5 w/v). SOC and TN contents in the control, NPK, NPKM and M treatments were measured by a CN analyzer (VarioEL, Elementar GmbH, Hanau, Germany).

2.3. Total and bioavailable Cu

To determine the total amount of heavy metals in the soils, corn stalks and wheat straws, a concentrated acid mixture (HNO_3 , HClO_4 and HF) were used for digestion (Zhou et al., 2007). Inductively Coupled Plasma-Atomic Emission Spectrometry (710/715 ICP-AES, Agilent, Australia) was employed to analyze the total Cu concentration in solution. Diffusive gradients in thin films (DGT) were prepared by placing the Chelex-100 disc on the support, followed by a diffusive gel disc (DGT Research Ltd, Lancaster, UK), and then filtered through a membrane filter. The upper cover, with a window exposed to the sample, was affixed lightly (Ahumada et al., 2014). The calculated C_{DGT} represents the effective available concentration of Cu in soil (Supporting Information Methods).

2.4. Titration of DOM with Cu^{2+}

The Cu^{2+} titration was conducted in a culture bottle that contained 100 mL of the soil DOM fraction with 100 μg $\text{Cu}(\text{NO}_3)_2/\text{mL}$ introduced using an automatic syringe. The Cu concentrations in the final solutions ranged from 0 to 800 $\mu\text{g}/\text{L}$ in the 100- $\mu\text{g}/\text{L}$ steps. All titrated solutions were shaken at 100 rpm for 24 h at 25 °C to allow equilibrium to be reached (Xu et al., 2013; Yu et al., 2012). The freeze-dried samples of DOM- Cu^{2+} complexes were analyzed by FTIR, ^{29}Si NMR and ^{27}Al NMR.

2.5. Using 2DCOS to combine FTIR, ^{29}Si NMR and ^{27}Al NMR spectroscopy analyses

FTIR spectra were performed by adding 1 mg of DOM- Cu^{2+} complex to 100 mg of potassium bromide (KBr, IR grade), and then the mixture was ground and homogenized to reduce light scatter (Yu et al., 2011a). The FTIR spectra were collected by using a Nicolet 370 FTIR spectrometer at 4 cm^{-1} of resolution with 200 scans over the range from 4000 to 400 cm^{-1} . The chemical speciation of Si and Al in the freeze-dried DOM fractions and the DOM- Cu^{2+} complexes was detected on a Bruker Avance III 400 spectrometer at 79.5 MHz,

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