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Insights into complexation of dissolved organic matter and Al(III) and nanominerals formation in soils under contrasting fertilizations using two-dimensional correlation spectroscopy and high resolution-transmission electron microscopy techniques

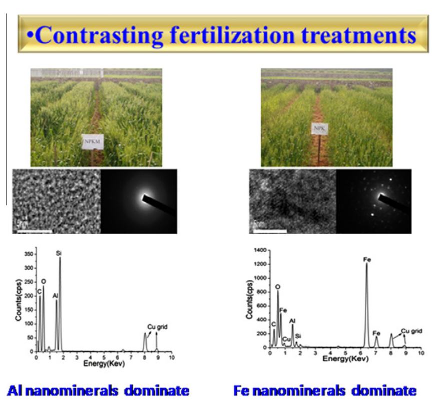
Yongli Wen [a,b,1], Huan Li [a,b,1], Jian Xiao [a,b], Chang Wang [a,b], Qirong Shen [a,b], Wei Ran [a,b], Xinhua He [c,d], Quansuo Zhou [a,b], Guanghui Yu [a,b,e,*]

[a] National Engineering Research Center for Organic-Based Fertilizers, Nanjing Agricultural University, Nanjing 210095, China
[b] Jiangsu Collaborative Innovation Center for Solid Organic Waste Utilization, Nanjing Agricultural University, Nanjing 210095, China
[c] NSW Department of Primary Industries, West Pennant Hills, NSW 2125, Australia
[d] School of Plant Biology, University of Western Australia, Crawley, WA 6009, Australia
[e] State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China

HIGHLIGHTS

- Understanding the organomineral associations in soils is of great importance.
- Fertilization modified the binding characteristics of organic ligands to Al(III).
- The binding of organic ligands to Al(III) altered in the turnover of SOM.
- Crystalline nanominerals were predominant in soil DOM under NPK.
- Amorphous nanominerals were dominant in soil DOM under Control and NPKM.

GRAPHICAL ABSTRACT



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ABSTRACT

Understanding the organomineral associations in soils is of great importance. Using two-dimensional correlation spectroscopy (2DCOS) and high resolution-transmission electron microscopy (HRTEM) techniques, this study compared the binding characteristics of organic ligands to Al(III) in dissolved organic matter (DOM) from soils under short-term (3-years) and long-term (22-years) fertilizations. Three fertilization treatments were examined: (i) no fertilization (Control), (ii) chemical nitrogen, phosphorus and potassium (NPK), and (iii) NPK plus swine manure (NPKM). Soil spectra detected by the 2DCOS Fourier transform infrared (FTIR) spectroscopy showed that fertilization modified the binding characteristics of organic ligands to Al(III) in soil DOM at both short- and long- term location sites. The CH deformations in aliphatic groups played an important role in binding to Al(III) but with minor differences among the Control, NPK and NPKM at the short-term site. While at the long-term site both C–O stretching of polysaccharides or polysaccharide-like substances and aliphatic O–H were bound to Al(III) under the Control,

* Corresponding author at: College of Resources and Environmental Sciences, Nanjing Agricultural University, 1 Wei Gang, Nanjing 210095, China. Tel./fax: +86 25 8439 6221.
E-mail addresses: yuguanghui@njau.edu.cn, henan223@163.com (G. Yu).
[1] Yongli Wen and Huan Li contributed equally to this work.

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Two-dimensional correlation (2DCOS) spectroscopy

whereas only aliphatic O–H, and only polysaccharides and silicates, were bound to Al(III) under NPK and NPKM, respectively. Images from HRTEM demonstrated that crystalline nanominerals, composed of Fe and O, were predominant in soil DOM under NPK, while amorphous nanominerals, predominant in Al, Si, and O, were dominant in soil DOM under Control and NPKM. In conclusion, fertilization strategies, especially under long-term, could affect the binding of organic ligands to Al(III) in soil DOM, which resulted in alterations in the turnover, reactivity, and bioavailability of soil organic matter. Our results demonstrated that the FTIR-2DCOS combined with HRTEM techniques could enhance our understanding in the binding characteristics of DOM to Al(III) and the resulted nanominerals in soils.

1. Introduction

As the link between the geosphere and hydrosphere, the small proportion of soil dissolved organic matter (DOM) plays various ecological roles in binding xenobiotics (Zsolnay, 1996), physical stability (Rilling and Steinberg, 2002) and carbon sequestration (Guggenberger and Kaiser, 2003). Moreover, soil DOM is the reactive fraction of soil organic matter (SOM) (Yu et al., 2012). Meanwhile, fertilization could affect the size and composition of DOM (McDowell et al., 1998; Chantigny et al., 2000; Yu et al., 2012), leading to alterations in the formation of complexes between organic ligands and metals, and the SOM sequestration (Yu et al., 2012). However, information on the mechanisms of fertilization on the formation of complexes between organic ligands with metals in soil is limited.

Fluorescence excitation–emission matrix (EEM) spectroscopy has been employed to determine binding characteristics between fluorescent groups (i.e., proteins-, humic- and fulvic- acid -like substances) and metals in DOM (Plaza et al., 2006; Ohno et al., 2008; Wu et al., 2011, 2012). The limitation of this method is its incapacity of characterizing the complexes of non-fluorescent substances (i.e., polysaccharides, lipids, and lignin) with metals, which are the predominant components in soil (Yu et al., 2012). Fourier transform infrared (FTIR) spectroscopy combined with two-dimensional correlation spectroscopy (2DCOS) analysis (FTIR-2DCOS) has been recently developed to address the complexes of organic ligands with metals in soil DOM (Yu et al., 2012). This method could (i) determine the binding characteristics of both fluorescent and non-fluorescent substances; (ii) solve the problems of overlapping peaks by distributing the spectral intensity within a data set over a second dimension; and (iii) probe the specific sequencing/ordering of spectral intensity changes through asynchronous analyses (Hur and Lee, 2011; Xu et al., 2013). Soil nanominerals will form with the complexes of organic ligands with metals (Yu et al., 2012). However, FTIR-2DCOS alone could not provide the information about the morphology/appearance of soil nanominerals. High resolution-transmission electron microscopy (HRTEM) coupled to selected area electron diffraction (SAED) technique could be a promising tool to observe the morphology/appearance of nanominerals in soil DOM.

The binding of organic ligands in the IR (infrared) region of 1800–900 cm^{-1} to Al(III) in DOM of soils that endured a 21-years long-term fertilization has been reported (Yu et al., 2012). However, the IR region of 3600–3200 cm^{-1} has not been studied, in spite of the importance as one of critical component of soil nanominerals (i.e., allophane and imogolite). Meanwhile, it is unclear how compost fertilization affects the binding of organic ligands to Al(III) in soil DOM and if the binding characteristics of organic ligands to Al(III) is different in soil under a short- and long- term fertilization. In addition, the binding of H-bond network (i.e., 3600–3200 cm^{-1} in the FTIR spectrum) to Al(III) in soil DOM under either a short- or long- term fertilization has not been explored, which is very important for the formation of Al nanominerals, i.e., allophane $[Al_2O_3(SiO_2)_{1-2}(H_2O)_{2.5-4}]$ and/or imogolite $[(OH)_3Al_2O_3SiOH]$. These soil nanominerals possess unique properties that are not found in bulk samples of the same mineral, e.g., binding up more organic matter than their bulk minerals and organic carbon bound to nanominerals persisting for much longer than that bound to bulk minerals (Yu et al., 2012).

Under three fertilization treatments (no fertilization, Control; chemical nitrogen, phosphorus and potassium, NPK; and NPK plus manure, NPKM) at both a 3-years short-term and a 22-years long-term fertilization site, using the promising FTIR-2DCOS and HRTEM techniques, the objectives of this study were thus to (i) investigate the intensity and sequence of organic ligands binding to Al(III) in soil DOM and (ii) study how fertilization affects the morphology of nanominerals or organomineral associations in soil DOM. Understanding in the binding characteristics of DOM to Al(III) and the morphology of nanominerals in soils could provide insights into the turnover, reactivity, and bioavailability of soil organic matter.

2. Materials and methods

2.1. Site description, sampling, and extraction

The long-term fertilization experiment has been established since September 1990 at Qiyang (26°45′N, 111°52′E, 120 m above the sea level), Hunan, China with an annual double cropping system of wheat and corn. The short-term fertilization experiment locates at Jintan (31°74′N, 119°56′E), Jiangsu, China and was started in October 2009. Three fertilization treatments from both sites have been selected for this study: (i) no fertilization (Control), (ii) chemical nitrogen, phosphorus and potassium (NPK), and (iii) NPK plus manure (NPKM). Swine manure, compost of swine manure and wheat straw was applied in NPKM at Qiyang and Jintan fertilization experiment, respectively. Each treatment has two replicates with a size of 20 m × 10 m for each replicate. Soils (Ferralic Cambisol at Qiyang and Paddy soil at Jintan) at 0–20 cm depths from two locations of each replicate were collected with a 5 cm internal diameter auger in May 2012. Each plot was evenly separated into three regions and 10 cores were then randomly sampled from each region. In total, each treatment had 6 composites of 10 random cores. Characteristics of soils under Control, NPK, and NPKM at 2012 are listed in Table 1.

Soil DOM was extracted with deionized water (1:5 w/v) on a horizontal shaker (170 rpm) at 25 ± 1 °C for 24 h and then centrifuged for 8 min at 2800*g* (Yu et al., 2012). The supernatant suspension was passed through a 0.45 μm membrane filter and further diluted until the dissolved organic carbon(DOC) was <10 mg L^{-1} and then stored in the dark at 4 °C for further analysis.

2.2. Al(III) titration test

The Al(III) titration was conducted in a brown sealed bottle that contained 30 ml DOM fraction solution. Prior to the titration test, the DOM extracts was passed through a H+-saturated cation