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The complexation of rhizosphere and nonrhizosphere soil organic matter with chromium: Using elemental analysis combined with FTIR spectroscopy

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ABSTRACT

Complexation is a main mechanism controlling the reactions between soil organic matter (SOM) and heavy metals, which still have not been fully understood up to date. The objective of this study was to compare the SOM composition of nonrhizosphere and rhizosphere in low Cr treatment with that in high Cr treatment and to find out how metal concentrations affect the complexation with SOM. The results revealed that both the hydroxyl and the carboxyl were significantly different under different Cr treatment groups. For nonrhizosphere samples, the high Cr treatment tended to have less hydroxyl contents and more structural changes on hydroxyl (3389–3381 cm^{-1}) than the low Cr treatment (3389–3388 cm^{-1}), while in the rhizosphere samples the reverse happened. The gap of the different Cr treated band area in the rhizosphere samples (44 a.u of the gap) was greatly smaller than that in the nonrhizosphere samples (576 a.u of the gap). In both the rhizosphere and nonrhizosphere samples, the high Cr treatment showed greater structural changes on carboxylic acids (11, 12 a.u changes based on the control) than the low Cr treatment (4, 6 a.u). The unsaturated carboxylic acids could account for downward frequency shift and the contents in the nonrhizosphere samples were slightly greater than that in the rhizosphere samples. This study used elemental analysis combined with FTIR spectroscopy to explore the effects of metal concentrations on the complexation of Cr with SOM and the composition of SOM. These findings give a way to understanding part of the complexation mechanisms between the metal and SOM.

1. Introduction

Health authorities and environmental protection agencies are getting increasingly concerned about the harm of heavy metals to environment and human health (Huang et al., 2015a, 2015b; Weil et al., 2016). However, heavy metal pollution in soil environment is invisible and metals can be accumulated gradually and results in the outbreak of toxicity eventually (Chen et al., 2010; Huang et al., 2014; Zhang et al., 2017). Chromium usually comes from factories such as metal smelting, electronic products and leather tanning (Azaman et al., 2017; Galvin, 1996; Srivastava et al., 1979). The toxicity of hexavalent Cr is the highest among all of the states and is more unstable compared to trivalent Cr. The retention of Cr in the soil mainly results from the reaction with different soil components through precipitation, adsorption, and especially, complexation (Goldberg and Sposito, 1984; Kumar et al., 2010). Complexation is of great importance for the mobility of metals in soil. For example, soil surface contains various hydroxyl groups whose reactivity are concerned with the dissociation of H^+, therefore the soil acidification affects the availability of Cr (Gorny et al., 2016; Nie et al., 2018). Among these soil components, soil organic matter (SOM) is considered to play an important role in controlling heavy metal mobility (Kwiatkowska-Malina, 2017; Lee and Scholz, 2006). SOM embodies all non-humic solutes and humus including OM connected to the soil minerals and dissolved organic matter (DOM) (Baldock and Nelson, 2000; Kallenbach et al., 2016). According to the distance from plant roots, SOM can be divided into nonrhizosphere and rhizosphere SOM (Azimzadeh et al., 2016; Hu et al., 2007), both of which have obvious difference in compositions and physicochemical characteristics (Chu et al., 2017; Cotton et al., 1999; Waite et al., 1994). SOM contains various functional groups such as hydroxyl and carboxyl on its surface. These functional groups usually show high affinity for metal ions in soil solution (Huang et al., 2016).

The complexation mechanisms between the SOM and heavy metals have been well explored. Some studies found that increased DOM content can promote the formation of organo-metal complexes, thus enhancing metal mobility and toxicity (Mesquita and Carranca, 2005;

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Sauve et al., 1998; Touceda-González et al., 2017). However, other studies observed that increasing SOM content can increase the proportion of HA-metal among the total immobilized metal and promote the metal binding capacity on soil (Fan et al., 2016). The contradictory results indicated that the effects of SOM on metal complexation in soil still have not been fully understood (Hinz and Selim, 1999; Pan et al., 2016).

In the past decades, the widespread use of Fourier transform infrared (FTIR) spectroscopy on OM has achieved many useful contributions. Dupuy and Douay (Dupuy and Douay, 2001) studied the different complexations with OM between Pb and Zn by using FTIR and chemometrics, and pointed out that FTIR is a potential technique for qualitatively and quantitatively detecting the difference in SOM functional groups by using the wave number location of peak intensities, band areas and frequency shifts of SOM samples. Hydroxyl, carboxyl, methyl, and mononuclear aromatic hydrocarbons are the most distinctive functional groups in the FTIR spectra (Ellerbrock et al., 2005; Sawalha et al., 2007). In this study, five organic functional groups were selected. As it was difficult to analysis the difference between the control and treatment groups based on all of the five functional groups, principal component analysis (PCA) method was used for factors reduction to identify one or two principal factors from multivariable initial variables (Jolliffe, 1986; Jolliffe and Cadima, 2016). The application of PCA combined with FTIR spectroscopy was uncommon in the complexation of SOM with Cr. However, for complexation analysis, along with FTIR spectroscopy some other methods should also be included. SOM characteristics should be learned about more such as elemental compositions and ratios (%C, %N, %O, %S, C/N, etc.) so that the specific functional groups and general trends occurred among different SOM samples could be obtained more accurately (Sleighter and Hatcher, 2011). The elemental analysis can provide the information about elemental compositions of SOM samples. Hence this study provided a new way in exploring the complexation mechanism between SOM and metals to control metal mobility eventually.

The compositional differences of SOM between the rhizosphere and nonrhizosphere samples have great influence on controlling the metal mobility in the micro domain and still have not been fully understood (Shuman, 1975; Trehan and Sekhon, 1977). The objective of this study was to compare the SOM composition of nonrhizosphere and rhizosphere soil in low Cr treatment with that in high Cr treatment by using elemental analysis combined with FTIR spectroscopy, and thereby to enhance the characterization and understanding of behavior of Cr in soil.

2. Material and methods

2.1. Experiment materials

A 1 mg/L concentration of $Cr(NO_3)_3$ solution was prepared. The SOM samples from both the rhizosphere and nonrhizosphere soil were selected as the objects of study. About 500 g undivided soil sample was collected in April 2017 from a washland along the Xiangjiang River, Hunan province, China (28° 15′ 41″ N, 112° 57′ 27″ E). The place was chosen with the Cr concentrations 68.6 mg/kg in the nonrhizosphere and 129.2 mg/kg in the rhizosphere, living up to the secondary standard. The soil sample was divided into rhizosphere and nonrhizosphere subsamples by hand according to the distance of 1 cm from the roots. The pH values of the nonrhizosphere and rhizosphere soils were 7.2 and 7.07, respectively. Once transported to the laboratory, the samples were extracted with 5% methanol aqueous solution under a moist solid: water ratio of 1:5 (w/v). All the suspensions were shaken at 200 rpm for 30 min at 25 °C on a reciprocal shaker and then centrifuged at 5000 × *g* for 5 min and filtered. The filtrate of each sample containing SOM was frozen for 30 min and then drought in a freeze drier until it was completely drought. These solid SOM samples were prepared for complex experiments and other analysis.

2.2. Complexation experiments

Each rhizosphere and nonrhizosphere SOM sample (1 mg) was weighed and put into a 10 ml polyethylene centrifuge tube. Each tube was added with 1 ml or 3 ml 1000 mg/L $Cr(NO_3)_3$ solution, making the solid: liquid ratio 1:1 (low Cr treatment) and 1:3 (high Cr treatment), respectively. The design of the two different concentrations was to detect the influence of metal content on complexation between SOM and Cr. The SOM samples for control groups were prepared without any addition of $Cr(NO_3)_3$ solution. All the tubes were shaken on a reciprocal shaker at 240 rpm for 21 h at 25 °C and then frozen and drought in a freeze drier for 24 h. These solid samples were prepared for further FTIR and elemental analysis.

2.3. FTIR spectroscopy

FTIR spectroscopy was obtained from IR Affinity-1 spectrometer (Shimadzu, Japan), with the range of 4000–400 cm^{-1} scanned to detect the functional groups of SOM. About 1 mg solid sample was mixed with 100 mg KBr and was ground in an agate mortar. The powder was made into a pressed disc before analysis. A total of 25 scans were processed for each sample. The absorbance region of SOM could be divided into five primary characteristic peaks as follows: 3500–3200 cm^{-1} – -OH (hydroxyl), 3000–2800 cm^{-1} – $-CH_3$ (methyl), 2800–2260 cm^{-1} – =C-H (on the benzene ring), 1820–1750 cm^{-1} – -C=O (carboxylic acid), 1650–1626 cm^{-1} – -C=C (on the mononuclear aromatic hydrocarbons) (Hussein et al., 2016; Ouchi et al., 2016). The samples were made with three replicates. The collected spectra data were further analyzed by origin 9.0 software.

2.4. Statistical analysis

PCA was conducted using the factor reduction method. Six samples with three replicates were used to implement the PCA. The input absorption values of the sample were used as original data and then all of the variables including the control samples were transformed to two or three new independent abstract variables called principal components. The PCA processed the original data as scores and loadings which depicted the characteristics of principal components. The two-factor or three-factor loadings were plotted to collect most of the original information of the selected variables from the FTIR data. A one way analysis of variance was used to illustrate the significant difference between the treated groups and the control. All the statistical analysis was carried out with SPSS 20.0 software.

2.5. Elemental analysis

Many elemental analysis techniques such as electron ionization high-resolution mass spectrometry (Aiken et al., 2007), plasma emission spectroscopy (Jones, 1977), and time-of-flight mass spectrometry (Mahoney et al., 1997), have been applied to provide information about elemental compositions and ratios. However, due to the high degree of accuracy, high-sensitivity, and large amounts of information, electrospray ionization–Fourier transform ion cyclotron resonance–mass spectrometry (ESI-FTICR-MS) was used to study the specific elemental properties of rhizosphere and nonrhizosphere SOM (Hughey et al., 2001). The purified SOM samples were infused into an ESI ion source equipped in a Bruker Daltonics 7T SolariX FTICR-MS instrument. The specific procedures have been shown in the previous studies (Kaplan et al., 2016a; Kujawinski et al., 2002; Tfaily et al., 2015). All the m/z data with the signal-to-noise (S/N) ≥10 were selected for further elemental analysis. Then each m/z datum was correspondent to a specific formula by using the previous technique (Koch et al., 2005). The information about elemental composition was then figured out through mathematical analysis.