Spectral characteristics of dissolved organic matter in various agricultural soils throughout China

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HIGHLIGHTS

- DOM in various agricultural soils of China was characterized by EEMs-PARAFAC.
- DOC extracted from various soils ranged from 17.39 to 86.01 mg L^{-1}.
- DOM mainly contained humic-like substances and tyrosine-like materials.

GRAPHICAL ABSTRACT
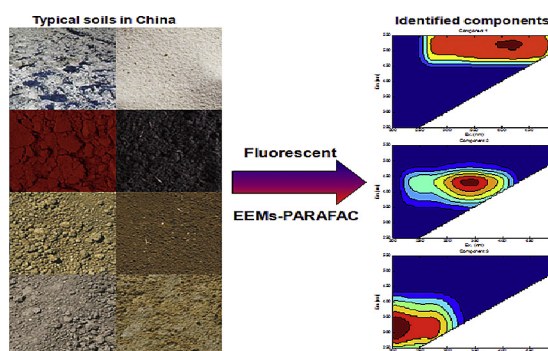
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ABSTRACT

Dissolved organic matter (DOM) plays an essential role in many environmental processes, particularly in soil ecosystems. In the present study, ultraviolet–visible (UV–Vis) spectroscopy and parallel factor analysis (PARAFAC) of three-dimensional fluorescence excitation-emission matrices (3D-EEMs) were used to characterize DOM extracted from various agricultural soils across four climate regions of China. The maximum (86.01 mg L^{-1}) and minimum (17.39 mg L^{-1}) dissolved organic carbon (DOC) concentrations were found in soils from Jiangsu and Yunnan, respectively. Specific UV–Vis absorption at 254 nm ($SUVA_{254}$) for soil DOM from the temperate continental climate (TCC) region was higher than that of soil DOM in other climate regions. Three fluorescence components including UVC humic-like substances (excitation peak at 400 nm, emission peak at 525 nm), UVA humic-like substances (250(330)/430 nm), and tyrosine-like materials (220(275)/320 nm) were identified in soil DOM using PARAFAC analysis. However, there were no significant differences in the distributions of these three components for soil DOM from different climate regions. Positive correlations were found among the humification index (HIX), fluorescence index (FI), and autochthonous index (BIX). Our results demonstrate that EEMs-PARAFAC could be a feasible approach for characterizing DOM in agricultural soils from different crop systems and can be used to further study complex DOM in agricultural environments.

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1. Introduction

As a major source of carbon and nutrients, dissolved organic matter (DOM) plays a significant role in soil–water systems (Cory and McKnight, 2005; Ishii and Boyer, 2012) and its degradation fuels microbial activities (Abdi and Williams, 2010). Derived from the breakdown of bacteria, algae, and plants, DOM consists of a complex mixture of aromatic and aliphatic organic compounds (Ishii and Boyer, 2012). Approximately 25%–50% of DOM is comprised of humic acid and fulvic acids, and the remaining consists of proteins, polysaccharides, and hydrophilic organic acids (Grasso et al., 1990), which are crucial for the absorption and desorption of acid anions and ion leaching (Magill and Aber, 2000). The characteristics of DOM in soil are influenced by microbial degradation, which is strongly related to soil physicochemical properties and the structural composition of DOM (Saadi et al., 2006). Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) reflect the activities of soil microorganisms, and their ratio influences the rate of DOC mineralization (Zak et al., 1990). DOM is also a main parameter for evaluating soil fertility and quality, and it is more sensitive than total organic matter (TOM) for indexing soil physicochemical properties and biological activities. According to the previous studies, mostly due to various vegetation types, DOM concentrations vary in the order forest soils > grassland soils > cultivation soils (Chantigny, 2003). However, management practices such as liming, organic improver, mineral fertilization also influenced soil organic matter pool (Chantigny et al., 2000; Chantigny, 2003). Moreover, due to active chemical fractions, DOM has a large impact on environmental quality. To a large extent, DOM can influence the transport and toxicity of organic and inorganic contaminants (Barriuso et al., 1992; Hu et al., 2016).

Ultraviolet–Visible (UV–Vis) spectroscopy has been used to evaluate the physicochemical features and molecules weight fractions of DOM, which indirectly reflect degree of humification and aromaticity (Weishaar et al., 2003). Previous studies showed that UV absorbance at 254 nm ($SUVA_{254}$) reflected the aromaticity level of DOM, with higher absorbance indicating higher aromaticity (Dilling and Kaiser, 2002). In addition, other studies reported that the proportion of hydrophobic components could be characterized by UV absorbance at 260 nm (Chin et al., 1994; Dilling and Kaiser, 2002; Granskog et al., 2007). Similarly, fluorescence spectroscopy could provide useful information regarding DOM characteristics and has been used for tracing DOM sources and assessing DOM quality in various environmental systems (Marhaba et al., 2000; Baker, 2001; Chen et al., 2003). However, it should be noted that DOM fluorescence would be affected by solution pH and ionic strength, and various interactions between DOM molecules and organic or inorganic matter should be considered when interpreting fluorescence data (Saadi et al., 2006; Wang et al., 2011; Gao et al., 2014; Li et al., 2014). Recently, many studies have focused on DOM characterization by combining excitation emission matrices (EEMs) with parallel factor analysis (PARAFAC) (Stedmon et al., 2003; Cory and McKnight, 2005; Stedmon and Markager, 2005). Using EEMs-PAFAFAC approach, Ohno and Bro found that five fluorescing components were identified and fluorescence approach could well model the chemical profile of terrestrial DOM (Ohno and Bro, 2006). Moreover, EEMs-PARAFAC was employed by Gao et al. to investigate the characteristics of DOM released from Minjiang River and two humic-like substances and one protein-like component were found (Guo et al., 2011). Tadini et al. reported humin extracted from Amazonian soils could be well characterized by EEMs-CP/PARAFA (Tadini et al., 2015). Additionally, PARAFAC analysis was also utilized to explore the soil pore water samples with biological degradation experiments and they releaded that climate warming could decreased riparian DOC concentration

(Selvam et al., 2016). Therefore, a hypothesis that DOM derived from different agricultural soils in various climate regions existed variations was raised in the present study.

To understand the characteristics of soil DOM in various cultivated regions with different soil types and crops in China, the DOM content and properties of various agricultural soils were analyzed by combining UV absorbance and fluorescence spectroscopy. Furthermore, the components of DOM and their distributions were identified to clarify the properties of DOM derived from various agricultural soils in China.

2. Materials and methods

2.1. Study area and sample collection

Farmland soils (0–20 cm) were collected from 18 provinces (autonomous regions) from the four main climate regions of China. Sites with typical soil types, in which diverse crops including maize, wheat, and rice were grown, were selected as our study locations (Fig. 1). Detailed physical and chemical properties of the soil samples determined by conventional methods are given in Table 1. Soil pH was measured with a glass electrode in a soil to water ratio of 1:2.5. Soil organic matter (SOM) was processed in an oil bath, and cation exchange capacity (CEC) content was determined using 1 mol L^{-1} NH_4COOH in a solution with pH of 7. Finally, the contents of clay and calcium carbonate ($CaCO_3$) were evaluated with standard and gaso-metric methods, respectively (Clark et al., 1998).

2.2. Extraction of water extractable DOM

All soils were air-dried and passed through a 0.25-mm sieve. Five grams of soil was weighed into 50 mL centrifuge tubes, and 30 mL of deionized water was added for a soil and water ratio of 1:6. After shaking the tubes for 24 h at room temperature, the samples were centrifuged at a speed of 4000 r min^{-1} for 20 min, and then filtered through 0.45-μm filters. The liquid suspension, i.e., the extracted DOM solution, was preserved in the dark at −20 °C until further use.

2.3. Spectroscopic data analysis

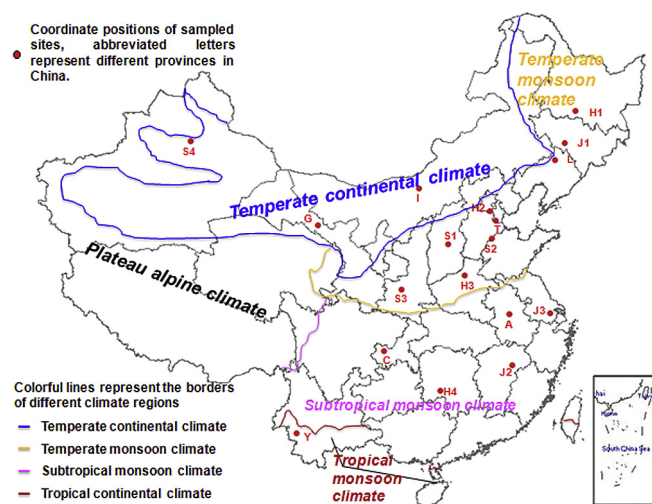DOM concentration was represented as dissolved organic

Fig. 1. Locations of all the sampling sites in different climate regions in China. The figure specifically decribles the sampled sites from different provinces (autonomous regions) and the typical climate regions in China.