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Characterization of atrazine binding to dissolved organic matter of soil under different types of land use

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ABSTRACT

Atrazine is widely used in agriculture. In this study, dissolved organic matter (DOM) from soils under four types of land use (forest (F), meadow (M), cropland (C) and wetland (W)) was used to investigate the binding characteristics of atrazine. Fluorescence excitation-emission matrix-parallel factor (EEM-PARAFAC) analysis, two-dimensional correlation spectroscopy (2D-COS) and Stern-Volmer model were combined to explore the complexation between DOM and atrazine. The EEM-PARAFAC indicated that DOM from different sources had different structures, and humic-like components had more obvious quenching effects than protein-like components. The Stern-Volmer model combined with correlation analysis showed that log K values of PARAFAC components had a significant correlation with the humification of DOM, especially for C3 component, and they were all in the same order as follows: meadow soil (5.68) > wetland soil (5.44) > cropland soil (5.35) > forest soil (5.04). The 2D-COS further confirmed that humic-like components firstly combined with atrazine followed by protein-like components. These findings suggest that DOM components can significantly influence the bioavailability, mobility and migration of atrazine in different land uses.

1. Introduction

Atrazine, a broad-leaf weed control herbicide, is widely used in agriculture, and it has a long residual time in the environment (Ali et al., 2016; Gupta and Ali, 2006; Ali and Aboul-enein, 2001). The environmental behavior and bioavailability of atrazine have become a hotspot in the field of controlling soil organic pollution. Atrazine can also be transformed into other ecosystems through wet and dry atmospheric deposition, application drift, surface runoff, and deposition of wind/eroded soil (Xu et al., 2009). It is also reported that atrazine does harm to reproductive function of males. Hayes et al. (2002) reported that atrazine could stop the production of testosterone in tadpoles. Therefore, the levels of atrazine in the environment should be effectively controlled.

It has been widely reported that dissolved organic matter (DOM) plays an important role in biochemistry cycling of organic contaminant in the environment. It is generally accepted that DOM significantly affects the bioavailability of organic pollutants (Xia et al., 2013, 2015). There are many kinds of pollutants in soils. Atrazine is a widely existing persistent organic pollutant. Therefore, the recognition, detection, transport of atrazine should be further studied owing to its carcinogenic, teratogenic and mutagenic effects. Atrazine can bind to DOM and affect its migration, transformation, sedimentation and degradation. Therefore, it is very necessary to characterize the dynamic of atrazine in soil environment.

The types of land use can regulate the quantity, quality, and dynamics of DOM in soils (Roberts et al., 2009; Lu et al., 2012). Therefore, it is necessary to study the binding characteristic of DOM in different soils. The content of DOM presents different level under different types of land use. The structure and property of DOM could be affected by the vegetation types, the pesticide application and the degree of soil humus. Forest soil, meadow soil, cropland soil and wetland soil were selected in this study due to its typical representative of northeast of China. DOM is composed of the dissolved component of influent organic matter and the degradation of composite organic compounds (Yekta et al., 2012). The bioavailability, mobilization and distribution of atrazine in the environment are generally influenced by the binding characteristics of DOM (Cabaniss, 2009, 2011; Yan and Korshin, 2014). Study methods for characterizing the properties of organic pollutants binding with DOM are quite diverse, including equilibrium dialysis, size exclusion chromatography, differential absorbance titration, and excitation and emission matrix-parallel factor (EEM-PARAFAC) analysis (Cabaniss, 2011; Bai et al., 2008; Chen et al., 2014; Yan et al., 2013). In this study, EEM-PARAFAC analysis

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was employed to investigate the fate of DOM and know about its environmental behaviors in soils (Borisover et al., 2009; Ishii and Boyer, 2012; Stedmon et al., 2003; Yang et al., 2015).

To investigate the sequential orders of atrazine binding with organic ligands, two- dimensional correlation spectra (2D-COS) was obtained by the synchronous fluorescence spectra with different concentrations of atrazine. Furthermore, recent studies demonstrated that 2D-COS can be used to resolve peak overlapping problems by extending spectra along the second dimension. In addition, it is also an efficient way to study the atrazine-DOM interactions (He et al., 2015). Therefore, it is widely used to investigate the interaction mechanisms of environmental-related substances (Chen et al., 2014; Hur and Lee, 2011a; Nakashima et al., 2008; Xu et al., 2013). EEM-PARAFAC analysis combined with 2D-COS can provide an effective method to understand the binding characteristics between DOM and atrazine deeply.

Based on the introduction above, it is necessary to investigate the atrazine binding properties of DOM from different soils, but there is little information on it. In this paper, the binding properties of DOM under different types of land use were studied by characterizing structures of DOM, humification degree and vegetation cover. The experiences were carried out in Suihua, China, where it was a rare black soil region and a perfect place for plant growing. This study could provide a theoretical basis for the prevention and control of black soil pollution.

The objectives of the study were: (1) to investigate binding characteristics of DOM-atrazine under different types of land use; (2) to give the binding sequencing and capabilities during the complexation process between DOM components and atrazine; and (3) to understand the environmental significance of DOM binding with atrazine.

2. Materials and methods

2.1. Sample collection and DOM extraction

Four types of land use taken from Suihua, China, including forest soil, meadow soil, cropland soil and wetland soil were collected to study the characterization of DOM binding to atrazine. DOM samples were extracted by mixing one part of dried soil sample with five parts of ultrapure water and continuously shaking them for 24 h. The liquid was centrifuged at 10,000 rpm for 20 min at 4 °C and filtered through a pre-washed 0.45-mm membrane. Then the filtered liquid was used for the fluorescence analysis. Details of sample collection are described in the literature (Yuan et al., 2015). The concentration of DOM was measured by the total organic carbon analyzer (TOC-Vcph). The TOC values of DOM are summarized in Table 1.

2.2. Quenching titration experiment

To avoid the inner filter effects, the concentrations of all DOM samples were diluted to 10 mgC/L before the fluorescence scanning. After that, the pH of DOM samples was adjusted to 7.0 by adding 0.1 M HCl or NaOH solution. Take a 10-mL aliquot of this solution and put them into 50-mL brown sealed vials. Quenching titration was carried out by adding atrazine solutions into DOM samples. The final atrazine concentrations of the total solutions were 0, 10, 20, 30, 40, 50, 60 and 70 μg/L for the eight soil DOM samples. To prevent the concentration change, no more than 5% of total volume of the solution was added. All solutions after titration were continuously shaken at 25 °C for 5 min to ensure an equilibrium binding between atrazine and DOM Then the solutions were used for the determination of synchronous fluorescence spectra and EEM fluorescence spectra.

Table 1
TOC values, specific UV absorbance ($SUVA_{254}$) and fluorescence characteristics of DOM under four land uses.

	TOC (mg/L)	$SUVA_{254}$ (L/ (m·mg))	C1 (%)	C2 (%)	C3 (%)	C4 (%)
F	245	0.0492	22.0%	52.9%	25.1%	–
M	286	0.0852	14.9%	28.1%	31.7%	25.4%
C	227	0.0607	19.0%	53.3%	27.8%	–
W	298	0.0714	16.9%	39.6%	30.4%	13.1%

(F forest, M meadow, C cropland, W wetland).

2.3. Fluorescence spectra

The synchronous fluorescence spectra and EEM fluorescence spectra were recorded by F-7000 fluorescence spectrometer (Hitachi High Technologies, Japan) at room temperature (20 ± 2 °C). The synchronous spectra over the range from 200 to 600 nm were collected in 1 cm increment at the scan speed of 240 nm min^{-1} with a constant offset Δλ of 18 nm. Fluorescence EEM spectra were measured with both excitation and emission ranges of 200–600 nm, at 5 nm increments respectively. The spectral were recorded at a scan rate of 2400 nm min^{-1}.

2.4. PARAFAC analysis

PARAFAC model is a generalization of bilinear principal component analysis (PCA) to higher order arrays, which disintegrates N-way arrays into N loading matrices. Thus, the model statistically decomposes the overlapped peaks of the fluorescence EEM spectra into individual fluorescence components. For example, if fluorescence EEMs are arrayed in a three-way array X of dimensions I×J×K, where I is the number of samples, J is the number of Ex wavelengths, and K is the number of Em wavelengths, PARAFAC disintegrates them into three matrices A (the score matrix), B and C (loading matrices) with elements a_{if}, b_{jf}, and c_{kf}. The relative concentration of each component is reflected by fluorescence intensity which is represented by F_{max} (Stedmon and Bro, 2008; Stedmon and Markager, 2005; Bro, 1997; Ohno et al., 2008; He et al., 2014), while the contribution of each component to the total fluorescence (i.e., %C1, %C2, %C3 and %C4) is considered as DOM quality indices (Table 1).

The PARAFAC modeling was carried out in MATLAB 2010b using the free-download DOM Fluor toolbox (www.models.life.ku.dk). In the PARAFAC analysis, 2 to 8 components can be computed, and split half analysis and residual analysis were used to identify the number of components (Stedmon and Bro, 2008; Bro, 1997; Ohno et al., 2008; He et al., 2014; Yu et al., 2013). The EEM data for the PARAFAC analysis were obtained from four land uses of soil samples before and after binding with atrazine (the number of each type of land use=80).

2.5. Complexation modeling

To calculate the binding ability between DOM and atrazine, Stern-Volmer equation was used in this study. The equation is given as follows (Bernard, 2001; Lakowicz and Masters, 2008).

$$\frac{F_0}{F} = 1 + K_{oc}[Q] \quad (1)$$

where F_0 and F are the fluorescence intensity of DOM with and without the addition of atrazine respectively and both of the two values are F_{max} values from PARAFAC analysis. K_{OC} is the binding constant which represents the binding ability between DOM and atrazine, and Q is the concentration of atrazine (μg/L). The equation is based on the assumption of the formation of 1:1 atrazine/ligand complexes.

2.6. 2D fluorescence correlation spectroscopy

To obtain the substances variation information on DOM-bound