

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

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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 (SUVA₂₅₄) 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.

Keywords: agricultural soils; dissolved organic matter; ultraviolet-visible; fluorescence; parallel factor analysis

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 et al., 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 2000 et al., 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 (SUVA₂₅₄) 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 Markger, 2005). Using EEMs-PARAFAC 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

humins extracted from Amazonian soils could be well characterized by EEMs-CP/PARAFAC (Tadini et al., 2015). Additionally, PARAFAC analysis was also utilized to explore the soil pore water samples with biological degradation experiments and they revealed that climate warming could decrease 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 NH₄COOH in a solution with pH of 7. Finally, the contents of clay and calcium carbonate (CaCO₃) were evaluated with standard and gaso-metric methods, respectively (Clark et al., 1988).

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 carbon (DOC), which was measured with a total organic carbon analyzer (Shimadzu, TOC-L, Japan). A UV spectrometer (Shimadzu, UV-1780, Japan) was employed to measure specific UV absorbance (SUVA₂₅₄) using a 10-mm quartz cell with a scanning wavelength ranging from 250-400 nm, and SUVA₂₅₄ was calculated as the UV absorbance at 254 nm per 1 mg·C⁻¹·m⁻¹. The description and significance of DOM optical indices and parameters used in this study were

presented in Table 2 detailedly. A fluorescence spectrometer (F97 Pro, Lengguang Tech., China) was used to create EEMs by measuring fluorescence intensity across excitation wavelengths ranging from 200 to 500 nm and emission wavelengths ranging from 250 to 550 nm. The scanning frequency and interval were $1000 \text{ nm} \cdot \text{min}^{-1}$ and 5 nm, respectively.

2.4 PARAFAC modeling

Deionized water was used as a blank comparison for measured samples and calculated data. PARAFAC modeling was conducted using the PLS_toolbox version 7.0 in MATLAB. PARAFAC can distinguish overlapping fluorescence spectra, decompose data into scores, and determine the concentration of relative components automatically (Stedmon and Markger, 2005). Once selected, the percent distribution of each of component was determined by quantifying the relative content of each component (Fellman et al., 2008). The core consistency diagnostic score can be used to determine the validity of the component number.

2.5 Statistical analysis

Data in this study were presented as mean \pm standard deviation. Differences among different soil types were analyzed with ANOVA in SPSS 20.0, and all the figures were made using Origin 9.0. Significance levels were reported as non-significant ($p > 0.05$), significant ($0.05 < p < 0.01$), or highly significant ($p <$

0.01).

3. Results and discussion

3.1 Variations in content of soil DOM

Crop types, tillage mode, soil types and related management practices affect soil properties, and thereby influence soil DOM content (Chantigny, 2003). DOC concentrations of 18 soil samples are shown in Fig. 2. Mean DOC values ranged from 17.39 mg·L⁻¹ (Yunnan) to 86.01 mg·L⁻¹ (Jiangsu). DOC concentrations for soils from the tropical monsoon climate (TrMC) region were approximately 2.4-times lower than those for soils from the other three climate regions. However, mean DOC concentrations (39.23 mg·L⁻¹, 47.39 mg·L⁻¹ and 38.81 mg·L⁻¹) did not differ significantly among temperate monsoon climate (TMC), subtropical monsoon climate (subTMC), and temperate continental climate (TCC) soils, respectively. Temperature, precipitation, and solar radiation, which significantly differ among the four regions, may affect the content, composition, and structure of soil DOM in a long-term cultivation (Chantigny, 2003). In the TMC region, the DOC concentration for black soil from Jilin (51.41 mg·L⁻¹) was higher than that for black soil from Heilongjiang (36.27 mg·L⁻¹). This difference may be due to different cropping patterns or crop types. Previous studies have reported that the amount and type of C input to soil was dependent on crop rotation, as roots exude labile material (Xu and Juma, 1993). It is possible that the clay content in the top 20 cm influenced the

soil DOM between Heilongjiang and Jilin (Chantigny, 2003). Seashore saline soil from Tianjin, which was similar to marine sediment with a higher pH (8.29) and CaCO_3 content ($53.57 \text{ g}\cdot\text{kg}^{-1}$), had a higher DOC concentration compared with soils from other regions, except Heilongjiang. High Ca^{2+} concentrations in calcareous soils could affect DOM concentrations, possibly through the influence of cations on flocculation and adsorption (Karlik 1995). The DOC concentration in brown soil from Liaoning was $40.41 \text{ mg}\cdot\text{L}^{-1}$, and that in cinnamon soil from Shanxi was $31.24 \text{ mg}\cdot\text{L}^{-1}$ ($p < 0.05$). Different cropping patterns and various soil types might affect the soil DOM content in these two sites. Large differences existed among soils from the subTMC region, with maximum and minimum DOC concentrations in Wushan soil from Jiangsu ($86.01 \text{ mg}\cdot\text{L}^{-1}$) and krasnozems from Hunan ($24.11 \text{ mg}\cdot\text{L}^{-1}$), respectively. However, there was no significant difference ($p > 0.05$) between DOC concentrations in krasnozems from Jiangxi ($30.80 \text{ mg}\cdot\text{L}^{-1}$) and Hunan ($24.11 \text{ mg}\cdot\text{L}^{-1}$), which may be attributed to similar soil type and texture (Marhaba et al., 2000; Chantigny, 2003). DOC concentrations increased successively in Gansu ($26.38 \text{ mg}\cdot\text{L}^{-1}$), Sinkiang ($40.56 \text{ mg}\cdot\text{L}^{-1}$), and Inner Mongolia ($49.48 \text{ mg}\cdot\text{L}^{-1}$), which may indicate that degree of calcium and clay content can influence soil DOM concentrations. The lowest DOC concentration was found in latosolic red soil from Yunnan (TrCC region), where the major agricultural crop is rice and the significance of this factor should not be overlooked. Overall, the contents of DOM differed among soil types cultivated with various crops, however,

additional research would be required to better understand how plant species and soil type influence DOM content and composition.

The additional analyses of $SUVA_{254}$, $SUVA_{260}$ and S_R indices were used to further study the chemical characteristics of DOM released from various soils by UV-visible spectrophotometry (Table 3). Over all study sites, S_R values ranged from 2.24 (Gansu) to 3.26 (Heilongjiang), with an average difference value of 1.02. This indicates that soil DOM in Heilongjiang was mainly composed of macromolecular substances, whereas soil DOM in Gansu primarily consists of materials with smaller molecular weights. There were no differences in S_R among soils from TMC (2.72^{bc}), subTMC (2.89^{ab}), and TrMC (3.04^a) regions, but a significant difference existed between TrMC (3.04^a) and TCC (2.53^c) regions ($p < 0.05$). For TCC region, the minimum S_R value occurred in soil from Gansu, where vegetables are the dominant crop, and the maximum S_R value was in low-fertility desert soil from Sinkiang. Local residents applied organic fertilizer to vegetable plots in this region, but the contribution of fertilizers to the aromatic composition of soil DOM was minimal because this type of exogenous organic matter consists of proteins, polysaccharides, and organic acids (Puget and Drinkwater, 2001). However, latosolic soil in Yunnan was mainly cultivated with rice paddies, which have a relatively high S_R value. It is possible that the crop residuals including abundant nutrients such as organic proportion, nitrogen, phosphorous and potassium in the process of agricultural production might accelerate soil

humication and increase the fraction of aromatic compounds (Marinari et al., 2010). Basing on the SUVA₂₅₄ and SUVA₂₆₀ values (Table 3), we could know soil DOM in the TCC and TrMC regions displayed strong aromatic and hydrophobic properties. Moreover, the correlations between SUVA₂₅₄ and SUVA₂₆₀ were significant ($p < 0.01$) (Table 6).

3.2 EEM-PARAFAC components of DOM in soil

PARAFAC components also have been observed and described throughout the previous literature of DOM fluorescence, and a number of matching peaks were found from database of fluorescence components (Uchimiya et al., 2016). As is shown in Table 4, three common PARAFAC components (labeled 1, 2, and 3) were identified in the soil samples. These components were characterized as humic-like and tyrosine-like molecules, and they typically were observed in the EEMs landscapes of humic acids and protein substances in soil and aquatic DOM. Details of DOM classification via PARAFAC for the present study and previous studies are shown in Table 5. The component 1 was characterized by the peak at 400 nm excitation with 525 nm emission wavelength, which indicated high molecular (Coble et al., 1990; Van Heusden et al., 1998; Parlanti et al., 2000). Stedmon et al. found that this component was often abundant in DOM originating from terrestrial sources such as soil leachates and solutions (Stedmon et al., 2003). The component 2 was characterized by the peak at 250 nm excitation with 430 nm emission

wavelengths, which was defined as a UVA-humic-like substances with low molecular and could be found in marine, wastewater, wetlands and agricultural lands (Van Heusden et al., 1998; Parlanti et al., 2000; Stedmon and Markger, 2005; Santín et al., 2009; Abdi et al., 2010). The component 3 was characterized by the peak at 220 nm excitation with 320 nm emission wavelengths, which was confirmed as tyrosine-like compound. This compound could indicate the diversity of amino acids and abundance of proteins (Van Heusden et al., 1998; Parlanti et al., 2000; Stedmon and Markger, 2005).

To better understand the variability of DOM from different agricultural soils, component distributions in all samples were evaluated. The relative distributions of the three components for different sites are shown in Fig. 3. Component 1 was comprised approximately 30% of all soils DOM, and no significant differences were found among samples. A slight difference in the abundance of Component 2 was found among different sites, with the maximum in Shandong (42.83%) and the minimum in Anhui (36.95%), indicating that DOM has more low molecular weight substances in soil from Shandong compared with Anhui. Soils from Anhui and Shandong had the minimum (31.97%) and maximum (25.78%) of Component 3, respectively, indicating that the content of amino acids or degraded peptide material in soil DOM from Anhui was higher than that in Shandong. Similarly, a previous study by Sierra et al. (2005) reported that humic substances in subtropical environments may contribute to an abundance of proteinaceous materials,

which is consistent with our results. Overall, for various soils from different agricultural lands, Component 2 is the most abundant, followed by Component 1, and finally Component 3. This trend may be indicative of the low decomposition rate of proteinaceous materials or not-fully degraded peptide materials with relatively lower contents of tyrosine-like substances.

Furthermore, there were no significant differences in the contents of the three components among the four climate regions with the exception of Anhui and Shandong ($p < 0.05$).

HIX is an indicator of the degree of condensation of aromatic structures in soil DOM or the degree of the conjugation of unsaturated aliphatic chains (Hur et al., 2011). As is shown in Fig. 4, HIX values ranged from 1.02 (Anhui) to 1.09 (Shanxi) and the mean HIX values for the TMC, TCC, and TrMC regions were 1.08, 1.07, and 1.08, respectively. Mean HIX was relatively lower (1.04) in soils from the subTMC region. In addition, the degree of humification of soil DOM from all sites was relatively high compared with the typical range of 0–1 (Ohno, 2002). FI is typically employed to distinguish the sources of DOM and negatively related to aromatic content (McKnight et al., 2001). The distribution of FI was similar to that of HIX, ranging from 1.08 (Anhui) to 1.31 (Shanxi), and there was a positive correlation between FI and HIX ($p < 0.01$) (Table 6). As our values are similar to ranges reported in previous studies (e.g., 1.2 to 1.5; McKnight et al., 2001), we could infer that the soil DOM from different agricultural lands in our study was derived from terrestrial and allochthonous

sources. BIX ranged from 0.81 in Shanxi to 0.96 in Jiangxi, and the value for the subTMC region (0.91) was higher than that in the TMC (0.85), TCC (0.84), and TrMC (0.82) regions. This indicates that protein-like materials are more prevalent in the subTMC region, possibly because farmland in this region is treated with crop straw and/or organic fertilizer, which resist degradation during long-term tillage.

4. Conclusions

EEMs-PARAFAC was used to characterize soil DOM in various agricultural soils in China. The results showed that the highest and lowest DOC concentrations were found in soil from Jiangsu and Yunnan, respectively, where rice was main crop. However, there was no significant difference among the four climate regions about soil DOC content. Moreover, according to UV spectral results, Wushan soils in Jiangsu had relatively strong aromatic properties. EEMs-PARAFAC modeling revealed three spectral components present in all soil samples that are indicative of humic-like and tyrosine-like materials. A significant relationship between HIX and FI indicated that soil DOM was mainly derived from terrestrial and autochthonous sources. Future studies should be conducted to elucidate the interactions between soil DOM and metals, microorganisms, and nutrients in soil–water environments.

Acknowledgements

We gratefully acknowledge financial support by the National Science Foundation of China (NSFC, Project No. 51508466), Fundamental Research Funds for the Central Universities (No. 2452016067) and National Key e

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Table 1 Physicochemical properties of soil samples

Climate types	Soil type, Main crop, Site	OC (g·kg ⁻¹)	TN (g·kg ⁻¹)	TP (g·kg ⁻¹)	CEC (cmol·kg ⁻¹)	CaCO ₃ (g·kg ⁻¹)	pH	Clay(%) (<0.002mm)
Temperate monsoon climate (TMC)	Black soil, Wheat Maize, Heilongjiang(H1)	35.69	1.74	0.48	28.59	-	6.27	0.19
	Black soil, Maize, Jilin(J1)	32.85	1.75	0.35	31.11	-	6.82	0.30
	Brown soil, Rice, Liaoning(L)	25.84	1.00	0.73	12.19	-	5.74	0.17
	Cinnamon soil, Wheat Maize, Shanxi(S1)	23.17	1.13	0.95	16.80	25.15	8.24	0.18
	Moisture soil, Wheat Maize, Hebei(H2)	8.57	0.68	0.53	8.12	17.62	7.98	0.11
	Seashore saline soil, Wheat, Tianjin(T)	22.02	1.42	0.92	24.67	53.57	8.29	0.08
	Moisture soil, Wheat Maize, Henan(H3)	17.79	1.07	0.75	16.01	27.50	8.07	0.18
	Moisture soil, Wheat Maize, Shandong(S2)	11.84	0.93	0.97	13.09	31.69	8.65	0.17
	Loess soil, Wheat Maize, Shaanxi(S3)	16.49	1.36	0.98	22.37	35.60	7.90	0.26
Subtropical monsoon climate (subTMC)	Purple soil, Rice, Chongqing(C)	17.48	1.00	0.55	21.34	-	5.74	0.25
	Krasnozem, Wheat Maize, Hunan(H4)	15.52	1.14	0.47	10.85	-	4.90	0.43
	Yellow brown soil, Wheat Maize, Anhui(A)	20.04	0.99	0.35	19.08	-	6.25	0.17
	Krasnozem, Wheat, Jiangxi(J2)	11.69	0.51	0.52	8.70	-	6.01	0.37
	Wushan soil, Rice, Jiangsu(J3)	47.69	2.44	0.69	26.20	-	6.93	0.46
Temperate continental climate (TCC)	Anthropogenic-alluvial soil, Vegetables, Gansu(G)	19.27	1.05	0.74	11.23	38.51	8.37	0.07
	Desert soil, Wheat Maize, Sinkiang(S4)	19.43	1.32	0.78	25.25	15.06	8.12	0.10
	Chestnut soil, Wheat Maize, Inner Mongolia(I)	16.30	0.96	0.38	11.61	11.51	8.80	0.11
Tropical monsoon climate (TrMC)	Latosolic red soil, Rice, Yunnan(Y)	34.26	2.01	0.81	11.10	-	5.92	0.28

- indicates the content of CaCO₃ was not detected.

Table 2 Definition and significance of the DOM optical indices and parameters used in the present study

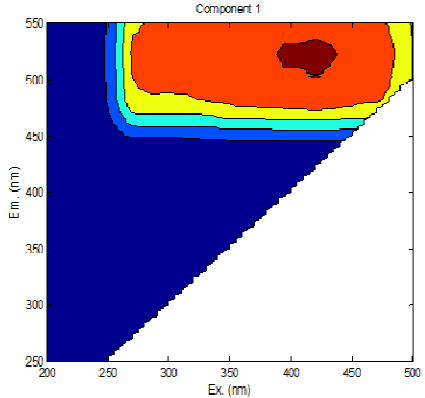
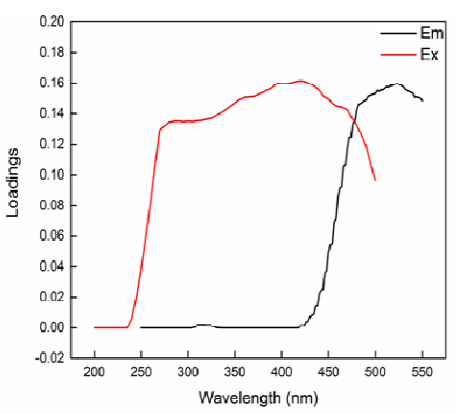
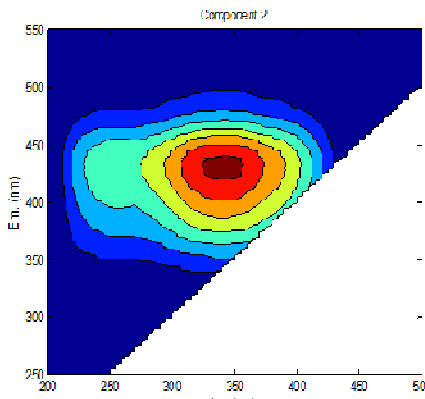
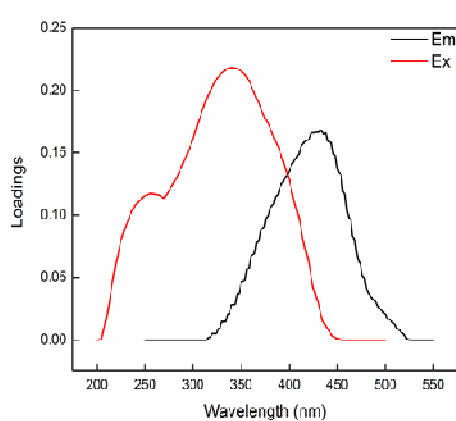
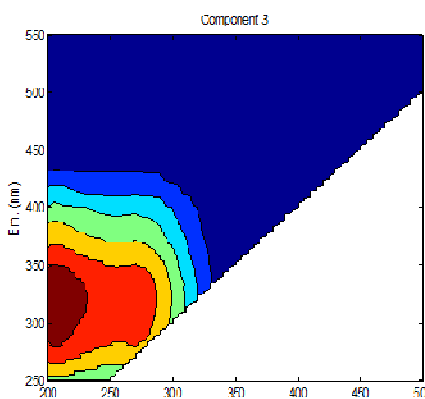
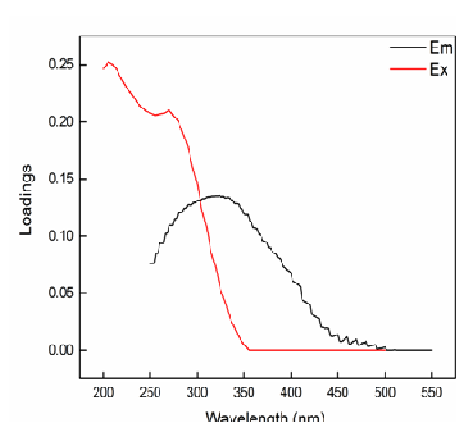
DOM quality index	Definition and significance	Reference
Absorption coefficient : $a(\lambda) = 2.303D(\lambda)/l$	$D(\lambda)$ is the absorbance at wavelength $\lambda(m^{-1})$ and l is the path-length of the optical cell in meters (10 mm).	(ElBishlawi and Jaffe, 2015)
Specific UV absorbance: $SUVA = a(\lambda)/c(DOC)$	$a(\lambda)$ is the absorption coefficient at wavelength λ and $c(DOC)$ is the concentration of extractable dissolved organic matter ($mg \cdot L^{-1}$).	(ElBishlawi and Jaffe, 2015)
Slope ratio: $S_R = (S_{(275-295)}/S_{(350-400)}) a(\lambda) = a(\lambda_0) \exp[S(\lambda_0 - \lambda)]$	$S_{(275-295)}$ and $S_{(350-400)}$ are the S values for 275–295 nm and 350–400 nm wavelengths, respectively, $a(\lambda)$ is the absorption coefficient at wavelength λ , and λ_0 is the reference wavelength.	(Helms et al., 2007)
Humification index: $HIX = (\sum I_{435-480})/(\sum I_{300-345})$	I is the fluorescence intensity at each wavelength HIX value reflects the degree of humification and the complexity of the DOM structure.	(Ohno, 2002)
Fluorescence index : FI	FI is determined as the ratio ($f_{470/520}$) of fluorescence intensity at emission wavelengths of 470 nm and 520 nm and an excitation wavelength of 370 nm. Microbial activity is the main source of DOM for $1.7 < FI < 2.0$, and the contribution of organisms is lower when $1.2 < FI < 1.5$.	(McKnight et al., 2001)
Biological index: BIX	The ratio of fluorescence intensity between wavelengths of 380 nm and 430 nm (emission) and 310 nm (excitation). BIX value reflects the ratio of albuminoid and biological components.	(Wilson and Xenopoulos, 2009)

Table 3 Description and statistics of UV parameters SUVA₂₅₄ ,SUVA₂₆₀ , and S_R

Climate types	Soil type, Main crop, Sites	SUVA ₂₅₄ (L·mg ⁻¹ ·m ⁻¹)	Variation coefficient%	SUVA ₂₆₀ (L·mg ⁻¹ ·m ⁻¹)	Variation coefficient%	S _R	Variation coefficient%
Temperate monsoon climate (TMC)	Black soil, Wheat Maize, Heilongjiang(H1)	1.01±0.06	5.81	0.96±0.06	5.90	3.26±0.10	3.07
	Black soil, Maize, Jilin(J1)	1.12±0.02	1.59	1.04±0.02	1.69	2.69±0.05	1.70
	Brown soil, Rice, Liaoning(L)	0.84±0.03	3.92	0.79±0.03	4.05	2.96±0.01	0.24
	Cinnamon soil, Wheat Maize, Shanxi(S1)	1.08±0.03	2.65	1.01±0.03	2.73	2.48±0.02	0.79
	Moisture soil, Wheat Maize, Hebei(H2)	0.74±0.08	10.94	0.70±0.07	10.62	2.65±0.03	1.31
	Seashore saline soil, Wheat, Tianjin(T)	1.19±0.04	2.97	1.13±0.03	2.89	2.57±0.01	0.22
	Moisture soil, Wheat Maize, Henan(H3)	0.49±0.08	16.88	0.46±0.08	16.87	2.60±0.02	0.65
	Moisture soil, Wheat Maize, Shandong(S2)	0.66±0.08	11.72	0.62±0.07	11.73	2.73±0.01	0.39
	Loess soil, Wheat Maize, Shaanxi(S3)	0.73±0.08	11.36	0.69±0.08	11.31	2.48±0.02	0.75
Subtropical monsoon climate (subTMC)	Purple soil, Rice, Chongqing(C)	0.51±0.01	1.66	0.49±0.01	1.56	3.27±0.06	1.74
	Krasnozem, Wheat Maize, Hunan(H4)	0.40±0.03	7.59	0.38±0.03	7.82	2.98±0.14	4.71
	Yellow brown soil, Wheat Maize, Anhui(A)	0.50±0.06	12.84	0.47±0.06	12.77	2.85±0.07	2.50
	Krasnozem, Wheat, Jiangxi(J2)	0.26±0.07	28.40	0.25±0.07	28.15	2.85±0.32	11.22

Temperate continental climate (TCC)	Wushan soil, Rice, Jiangsu(J3)	0.75±0.06	8.18	0.71±0.06	8.38	2.52±0.05	2.09
	Anthropogenic-alluvial soil, Vegetables, Gansu(G)	1.04±0.03	2.97	0.96±0.04	4.01	2.24±0.04	1.59
	Desert soil, Wheat Maize, Sinkiang(S4)	1.28±0.04	3.21	1.20±0.03	2.40	2.80±0.03	1.17
	Chestnut soil, Wheat Maize, Inner Mongolia(I)	1.37±0.05	3.88	1.29±0.05	3.88	2.55±0.03	1.05
Tropical monsoon climate (TrMC)	Latosolic red soil, Rice, Yunnan(Y)	1.23±0.06	4.51	1.16±0.05	4.42	3.04±0.01	0.47

Table 4 EEM locations, representative EEMs, and florescence spectral loadings of the three components identified by PARAFAC analysis for all soil samples from different climate regions.

Component	Approximate EEMs location	EEMs	Spectral loadings
1	Ex:400 nm Em:525 nm		
2	Ex:250(330) [#] nm Em:430 nm		
3	Ex:220(275) [#] nm Em:320 nm		

()[#] Excitation wavelengths given in parentheses are secondary peaks.

Table 6 Correlations analysis for DOC concentrations, S_R, SUVA₂₅₄, SUVA₂₆₀, FI, HIX and BIX

	DOC	S _R	SUVA ₂₅₄	SUVA ₂₆₀	FI	HIX	BIX
DOC	1						
S _R	-.143	1					
SUVA ₂₅₄	-.001	-.222	1				
SUVA ₂₆₀	.006	-.213	1.000 ^{**}	1			
FI	-.018	-.165	.106	.107	1		
HIX	-.215	-.146	.465 ^{**}	.464 ^{**}	.669 ^{**}	1	
BIX	.272 [*]	.054	-.352 ^{**}	-.352 ^{**}	-.600 ^{**}	-.775 ^{**}	1

* Indicates significant correlation at the 0.05 level.

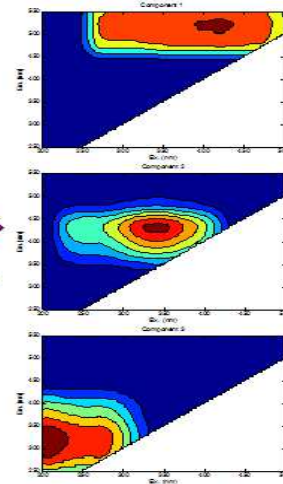
** Indicates significant correlation at the 0.01 level.

Typical soils in China



Fluorescent
EEMs-PARAFAC

Identified components



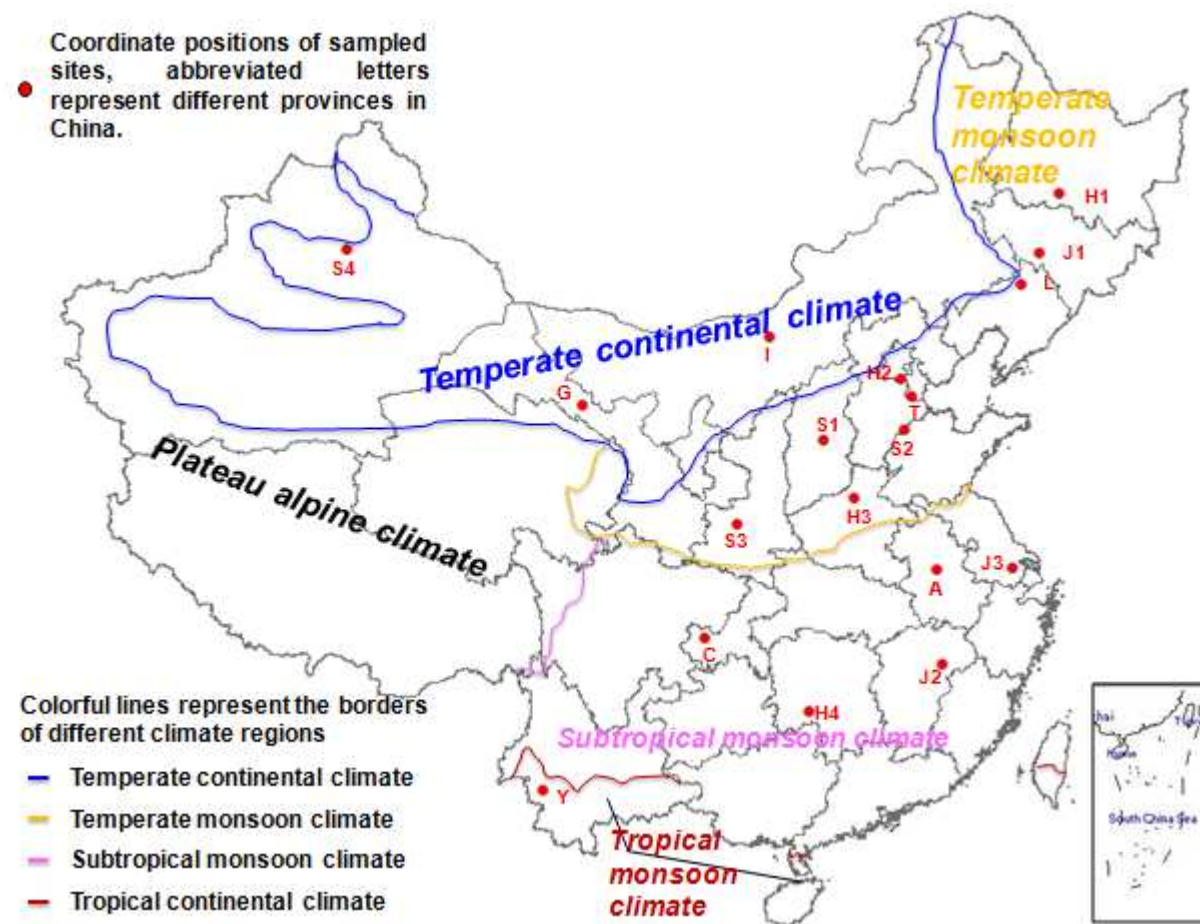


Fig.1 Locations of all the sampling sites in different climate regions in China. The figure specifically describes the sampled sites from different provinces (autonomous regions) and the typical climate regions in China.

Table 5 Characteristics of the three components identified with fluorescence PARAFAC modeling in this study and comparison with previously identified components

Components	This study		Previous study			
	Excitation maxima(nm)	Emission maxima(nm)	Fluorescent compounds	Descriptions and assignments	Possible origin	References
1	400	525	UVC Humic-like	High molecular weight and widely in environments	Terrestrial or soil organic matter	(Coble et al., 1990; Van et al., 1998; Parlanti et al., 2000; Ohno and Bro, 2006)
2	250(330) [#]	430	UVA Humic-like	Low molecular weight, can be found in marine, wastewater, wetlands and agricultural lands	Terrestrial or soil organic matter	(Van et al., 1998; Parlant et al., 2000; Stedmon and Markger, 2005; Santín et al., 2009; Abdi et al., 2010)
3	220(275) [#]	320	Tyrosine-like	Amino acids, free of bound in proteins	Terrestrial or Autochthonous production or Microbial process	(Van et al., 1998; Parlanti et al., 2000; Stedmon and Markge, 2005)

()[#] Excitation wavelengths given in parentheses are secondary peaks.

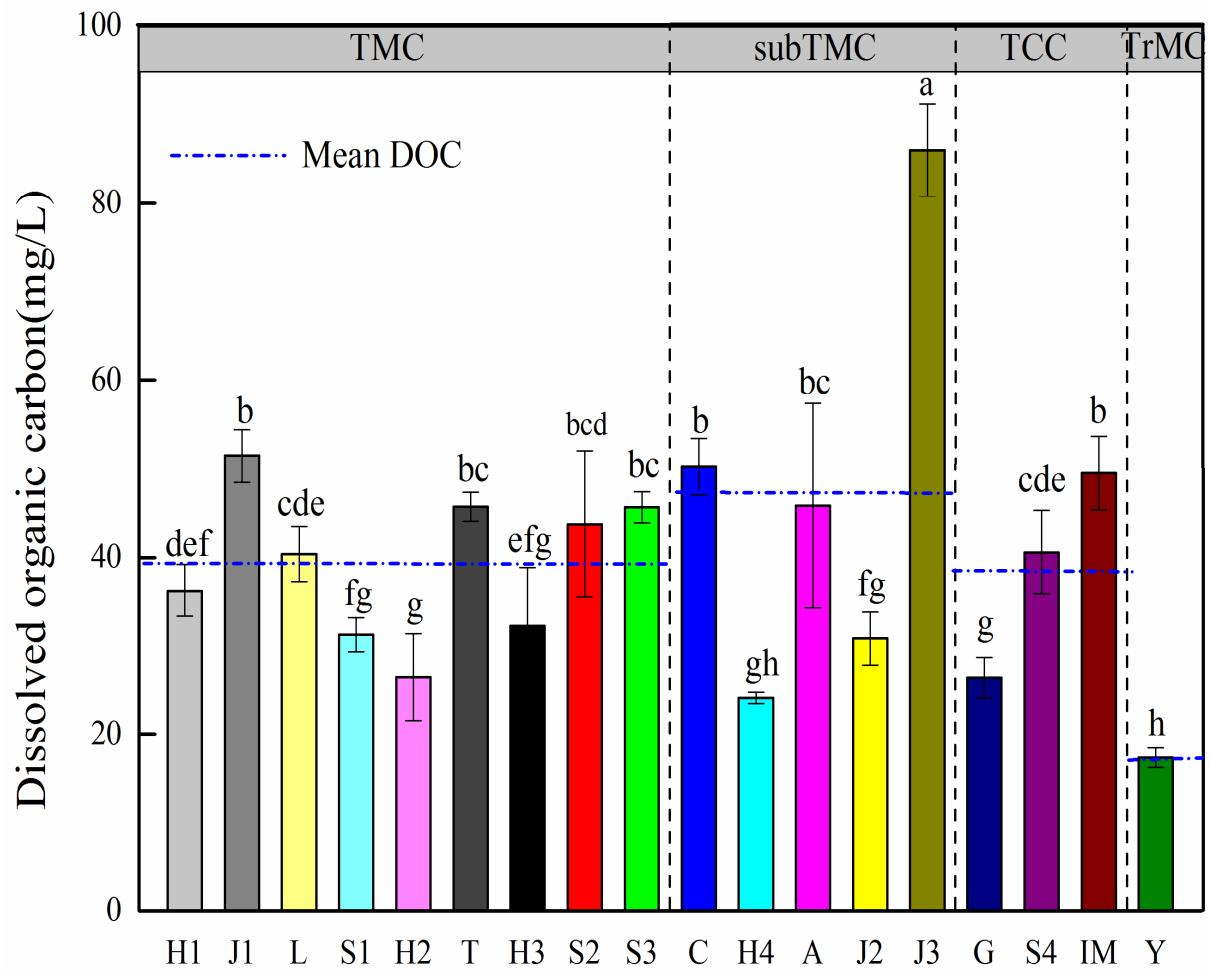


Fig.2 Mean DOC concentrations observed in all soils from different climate regions (\pm SD). Different letters indicate difference ($p < 0.05$) in measurements taken in different soils.

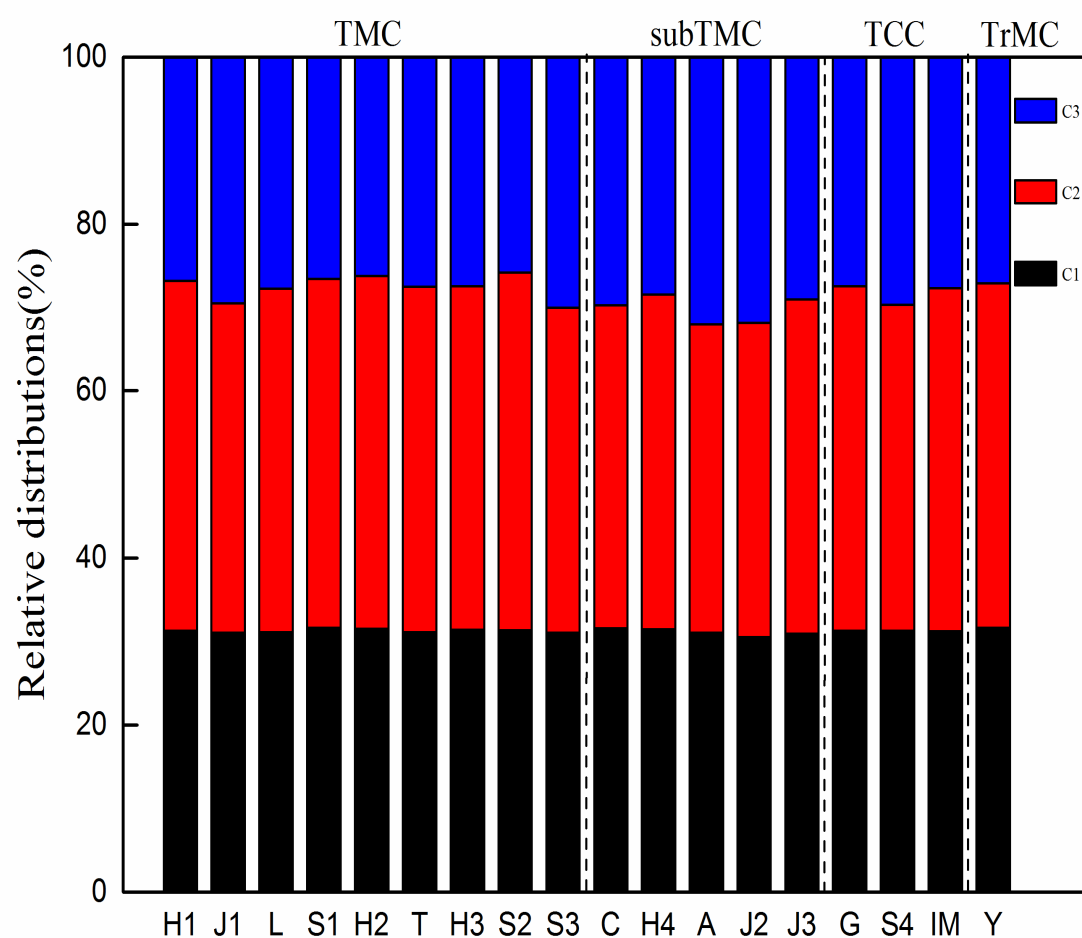


Fig.3 Mean relative distributions of component 1, 2, 3 calculated by PARAFAC modeling in all soils from different climate regions.

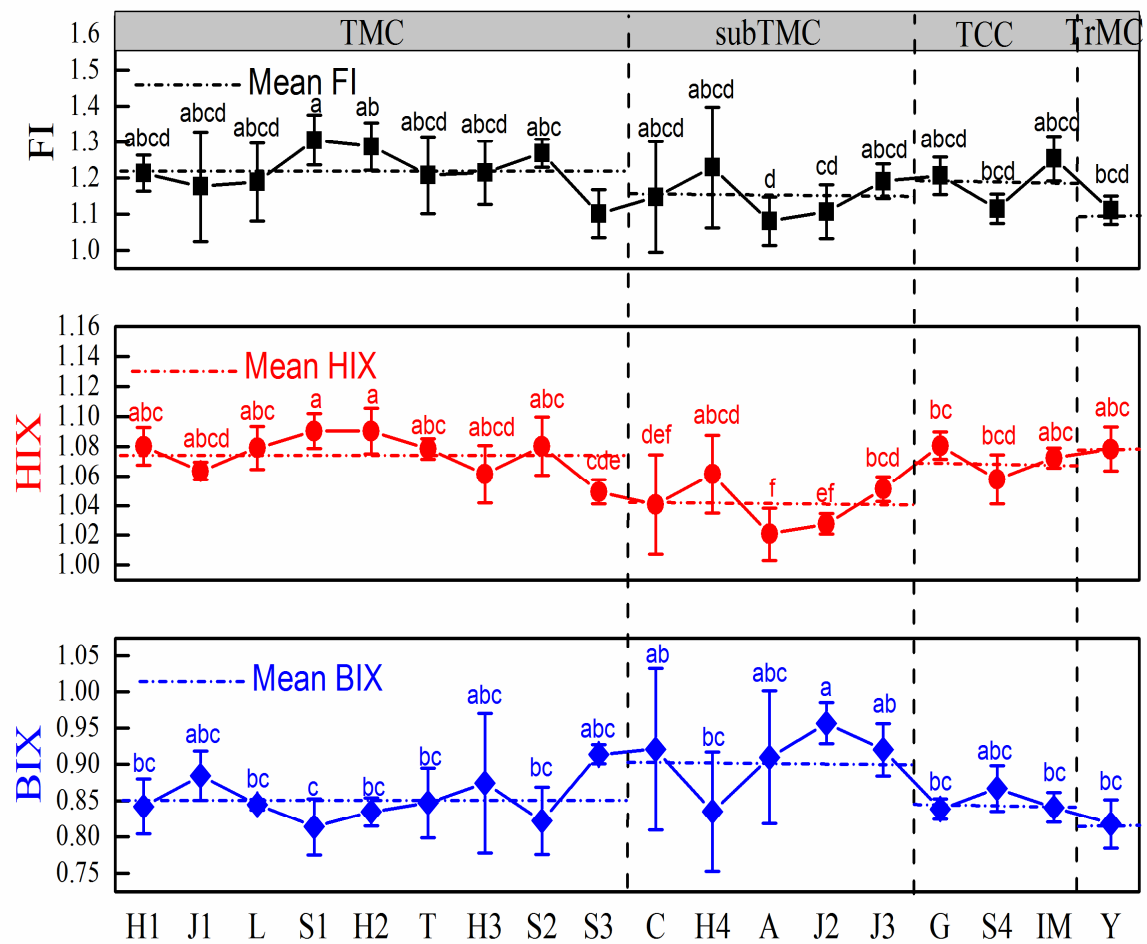


Fig. 4 Fluorescence parameters of FI, HIX and BIX calculated by PARAFAC modeling in all soils from different climate regions.