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Analysis of the fluorescence spectral characteristics of dissolved organic matter in a black soil with different straw return amounts

Jiuming Zhang[1,3], Yan Li[1,3], Jiahui Yuan[1], Fengqin Chi[1], Enjun Kuang[1], Yingxue Zhu[1], Lei Sun[1], Dan Wei[2]✉ & Jie Liu[1]✉

Straw return improves soil carbon pool and dissolved organic matter (DOM) characteristics in black soil. Optimal straw return rate is the key to promoting straw return practices in farmland in Northeast China. The experiment was conducted at the Science and Technology Park of China Grain Storage and Northern Corporation in NenJiang, Heilongjiang Province, straw return at 0 kg hm^{-2}, 3000 kg hm^{-2}, 4500 kg hm^{-2}, and 9000 kg hm^{-2}. In the seventh year of the experiment, we used three-dimensional excitation-emission matrices combined with Parallel Factor analysis to characterize the fluorescence characteristics of DOM of black soils. The results showed substantial improvement in soil physical characteristics and soil organic matter (SOM) following straw return, SOM content rises in proportion to the amount of straw returned, and a significant positive correlation coefficient between water-holding capacity (WHC) ($p < 0.001$, r = 0.82) and dissolved organic matter (DOC) ($p < 0.01$, r = 0.77). Moreover, straw return significantly increased the richness of three fluorescent components, namely fulvic acid (UV and visible fulvic acids), humic-like acid, and protein-like (short and long-wavelength tryptophan). The fluorescence intensities of these components were lower in straw treatments than in no straw return. The fluorescence intensities of fulvic and humic acids showed decreasing and increasing trends, respectively, with increasing straw return amount. The fluorescence spectroscopy data of DOC demonstrated the key role of high straw return amounts in enhancing substantially the metabolic activity of soil microorganisms. Overall, straw-returning practices improve soil fertility and can be beneficial for black soil farmlands, with the optimal return rate observed at 4500 kg hm^{-2}.

Keywords Straw return, Residual amount, Soil dissolved organic carbon, Three-dimensional fluorescence, Parallel factor analysis

Straw-returning practices are essential for improving soil fertility, mitigating agricultural surface pollution, and achieving dual-carbon goals[1,2]. The utilization rate of crop straw nationwide has been increasing steadily, gradually demonstrating its ecological benefits. Indeed, the total straw amount collected in 2021 reached 400 million tons, of which the contribution of corn straw is estimated at 126 million tons, representing 42.6% of the total amount collected in China. Numerous studies have shown that straw return to fields can regulate the contents of soil organic matter (SOC). The increase in the SOC contents can effectively improve the water-holding capacity (WHC) and total porosity of soils, which can significantly reduce soil weights and improve the distribution of soil water, nutrients, gas, and heat, thereby creating favorable environmental conditions for improving crop yields[3–5]. Straw-returning is often applied following crop harvests in the northern regions of China at air temperatures

[1]Key Laboratory of Black Soil Protection and Utilization, Ministry of Agriculture and Rural Affairs, Heilongjiang Academy of Black Soil Conservation and Utilization, Heilongjiang Academy of Agricultural Sciences, Harbin 150086, China. [2]Institute of Plant Nutrition, Resources and Environment, Beijing Academy of Agricultural and Forestry Sciences, Beijing 100097, China. [3]These authors contributed equally: Jiuming Zhang and Yan Li. ✉email: wd2087@163.com; liujie16777@163.com

lower than 10 °C under inhibited microbial decomposition, resulting in a long complete natural decay of straw into organic matter crop over 400–600 days or more. Therefore, the application of optimal straw return rates is the key to promoting straw return practices in farmland in Northeast China.

Dissolved organic matter (DOM) is an important and very active component of the Earth's carbon cycle, energy flow in ecosystems, and material cycling, and it is the most dominant component of organic matter composition. This component DOM has a carbon-based soluble organic matter with different structures and molecular weight sizes, containing many types of functional groups. However, DOM is highly mobile and unstable in soil, thus impacting soil nutrient migration and transformation[6,7]. Therefore, it is important to study the structural properties of soil DOM following straw return to fields to understand the effects of this practice on the redistribution of soil carbon (C) and to evaluate soil fertility[8]. Soil DOM is a component of soil total organic matter (TOM), characterized by rapid turnover rates and more sensitivity to agricultural cultivation practices[9], making it of particular interest to researchers and scholars. Several studies have pointed out that DOM is a key factor in controlling the soil carbon aggregation process, promoting soil aggregate formation, nutrient transfers, and microbial abundance and diversity [10–12].

Previous studies on soil DOM in China and worldwide have focused mainly on its sources, distributions, compositions, structural characteristics, migration and transformation patterns, and biological toxicity. These studies have used several techniques to achieve their objectives, including individual or integrated application of ultraviolet–visible spectroscopy (UV–vis), three-dimensional fluorescence spectroscopy (3D-EEM), nuclear magnetic resonance (NMR), and Fourier transform infrared spectroscopy (FTIR), as well as multivariate statistical methods for quantitative and qualitative characterization of DOM. In recent years, fluorescence spectroscopy technology has been widely used to study the stability of soil carbon components following straw returns to fields. The results of indoor simulation experiments on straw returns to fields showed that straw DOM is mainly composed of tryptophan-like, tyrosine-like, and fulvic acid-like substances, with its photochemical activity closely related to the straw decomposition time[13]. In addition, the compositions of soil samples from straw-returned fields showed that soil DOM is mainly composed of humus-like and protein-like substances of microbial origins, with unaffected and significantly affected relative abundances by short-term straw returns, respectively[14]. Other researchers have shown that DOM from soil samples of tropical farmland is mainly composed of terrestrial-like humus, microbial-derived humus, and protein-like substances and that different fertilizer application practices (straw return to fields, chemical fertilizers, and straw-fertilizer composite) over five consecutive years significantly altered the molecular diversity and relative abundance of soil DOM components[15].

Currently, most research centered on the impact of various straw return methods on soil organic carbon composition, storage, and crop yield. The specific short-term redistribution effects on soil organic matter components due to varying straw return amounts and their influence on the active composition and structure of soil organic carbon remain unclear. In this context, the present study aims to assess the fluorescence characteristics of DOM in the tillage horizon (0–20 cm) of black soils with different straw return amounts and to explore the effects of the straw return proportion on the composition and structure of the black soil DOM using three-dimensional excitation-emission matrices (3D-EEMs) combined with Parallel Factor (PARAFAC) analysis. The results of this study provide further insights into the migration and changing rules of DOM in soil with different straw return amounts, as well as important theoretical and practical significance for implementing effective measures of straw return practices, choosing optimal straw proportions, and improving agricultural practices to increase SOC contents.

Materials and methods

Experiment design

The experiment was conducted at the Science and Technology Park of China Grain Storage and Northern Corporation in NenJiang, Heilongjiang Province, between longitude and latitude of 125°27′5″N and 49°33′35″E, respectively. According to the Chinese soil classification, the study area is characterized by a black soil type, which is a soft soil (black soil) type based on the classification system of the United States Department of Agriculture. This soil type consists of a thick layer of humus and a clay texture. On the other hand, the climate in the study area is a mid-temperate continental monsoon, with an average annual temperature range, annual rainfall amount range, frost-free period, and effective accumulated temperature of 1.0–2.0 °C, 450–500 mm, 115 days, and 2150 °C, respectively. The physicochemical properties of the tillage horizon are reported in Table 1. Each treatment consisted of six plots, covering a total area of 39 m^2 (6 m × 10 m × 0.65 m). The experiment was initiated in 2012 through a systematic plantation of corn. In addition, mechanical crushing and rotary plowing were employed in the experiment to ensure a straw return to the field during the autumn season. Nitrogen (N), phosphorus (P_2O_5), and potassium (K_2O) mineral fertilizers were applied in the experiments at rates of 150, 75, and 75 kg hm^{-2}, respectively, to regulate the C/N ratio of the applied straw. In addition, other treatment scenarios were considered in this study, namely root stubble return (T1), 3000 kg hm^{-2} of the straw return amount (T2), 4500 kg hm^{-2} of the straw return amount (T3), and 9000 kg hm^{-2} of the straw return amount (T4).

Organic matter	Total N	Total P	Total K	Available N	Available P	Available K
g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
45.9	2.5	2.0	22.7	211.9	78.6	226.7

Table 1. Some chemistry properties of the 0–20 cm soil depth in the experimental site.

Sample collection and measurement methods

Sample collection

In this study, soil samples were collected in October 2019 from the 0–20 cm soil layer in different treatment plots using a ring knife with a 100 cm^3 volume immediately after harvesting the Demeria 2 corn variety. Indeed, the soil samples were collected in cloth bags from five different points in each plot, then thoroughly mixed to obtain a composite soil sample, sealed with tape, and transported to the laboratory. This sampling approach was conducted in triplicate. The collected soil samples were first cleared of plant roots and other debris, then dried indoors, crushed, sieved through a 2 mm sieve, and stored at room temperature.

Determination of soil physicochemical indicators

The soil organic matter (SOM) contents were determined through the oxidation of potassium dichromate with ferrous sulfate titration. The ring-knife immersion method was employed to determine the bulk density (BD), porosity and water-holding capacity(SP) of the soil[16].

Fluorescent sample handling and measurement methods

To determine the DOM contents, double distilled water (Milli-Q, resistivity 18.2 MΩ cm) was added to 5 soil samples at 1:10 [W(g): V(mL)], then stirred at 200 r·min^{-1} and room temperature for 24 h, followed by centrifugation at 4 °C and 12 000 r min^{-1} for 20 min. The obtained supernatants were subsequently filtered through 0.45 μm membrane filters to separate DOM in the filtrate. The obtained solution was analyzed using a multiN/C 2100 TOC meter (Analytik Jena AG, Germany). The soil DOC contents were standardized to 15 mg L^{-1}.

The spectral fluorescent characteristics of soil DOM were determined using an F-7000 fluorescence spectrometer (Hitachi, Japan) equipped with a powerful 450W xenon arc lamp for excitation light. The voltage, signal-to-noise ratio, bandpass for excitation and emission, and scanning speed were set to 700V, over 110, 5 nm, and 1200 nm min^{-1}, respectively, with an automatic instrument correction response time during spectrum scanning. In addition, the excitation and emission scanning ranges of the 3D fluorescence spectrum were 200–600 nm and 200–600 nm, respectively. To avoid any interference from second-order Rayleigh scattering, it was imperative to incorporate a 290 nm cutoff filter on the fluorescence emission light. The collected data were processed using FL WinLab software provided by the instrument. Furthermore, to eliminate the effects of Raman scattering, PARAFAC was performed by subtracting the measured fluorescence data of the sample from that of the deionized water.

Statistical analysis

In this study, Origin 2016 and Matlab 2011 software were used to draw three-dimensional fluorescence spectra and perform PARAFAC analysis. In addition, correlation analysis and redundancy analysis (RDA) were performed to assess the relationship between fluorescence indexes and soil physicochemical properties using SPSS 19.0 and Canoco 4.5, respectively.

Results

Soil organic matter and physical indexes

The obtained results showed significant increases in the SOM contents and WHC following straw return compared with not return ($p < 0.05$) (Table 2). In contrast, straw return significantly decreased the soil bulk density. However, no significant increases in the soil porosity were observed following straw return. The SOM content was 47.3 g kg^{-1} in the CK treatment, then increased by 1.1–3.8% following straw return. Notably, the highest straw application to the field (T4) significantly increased the SOM contents from 47.3 to 49.1 g kg^{-1}. In addition, straw return to the field affected the physical characteristics of the soil, significantly decreasing the bulk density of the soil from 1.17 to 1.08 g cm^{-3} in the CK and T2 treatment scenarios, respectively. The WHC significantly increased following straw return, reaching the highest value of 40.84% in the T3 treatment scenario, while no significant changes in the soil porosity were observed in the experiments.

Fluorescence spectral index of DOM

The fluorescence spectral indices (FI, BIX, and HIX) were used in this study to characterize the soil DOM under different straw return treatment scenarios. The FI values of the straw return methods ranged from 1.4 to 1.9 (Table 3). In this study, straw return exhibited great influences on the exogenous SOM compared to the CK treatment scenario. In addition, the T1 treatment scenario revealed the highest effect on the autogenous SOM, showing an FI value of 1.53. It was clear that the use of external sources of humus enhanced with increasing straw

Treatment	T1	T2	T3	T4
SOM (g kg^{-1})	47.3 ± 4.02 c	47.8 ± 3.98 bc	48.3 ± 1.66 b	49.1 ± 3.21 a
BD (g cm^{-3})	1.17 ± 0.04 a	1.08 ± 0.05 b	1.09 ± 0.06 ab	1.13 ± 0.05 ab
WHC (%)	37.86 ± 2.34 b	39.72 ± 1.47 ab	40.84 ± 0.60 a	40.17 ± 1.04 ab
SP (%)	46.13 ± 2.85 a	50.68 ± 4.02 a	52.42 ± 4.49 a	49.17 ± 3.35 a

Table 2. Soil physicochemical properties in upper soil 7 years after straw manuring. SOM:soil organic matter; BD:bulk density; WHC: water-holding capacity; SP:water-holding capacity of the soil. The data reported in the table are means ± standard deviations. Lowercase letters represent significant differences at the $p < 0.05$ level.

Treatment	T1	T2	T3	T4
FI	1.53	1.51	1.52	1.52
BIX	0.63	0.65	0.66	0.64
HIX	4.83	5.00	5.32	5.58

Table 3. Results of the soil DOM fluorescence spectral indices. The data listed in the table are means ± standard deviations.

return amount without showing significant differences between the treatments. In this study, the DOM contents in the treatment scenarios were characterized by the BIX values. Indeed, a BIX range of 0.6–0.7 suggests a smaller autogenous component. The BIX values in this study ranged from 0.63 to 0.66 without indicating significant differences in the autochthonous SOM between the treatment scenarios. On the other hand, HIX can be used to assess DOM across different treatments. In this study, the HIX values suggested strong humic characteristics and weak nektonic autochthonous sources, ranging from 3.0 to 6.0. The highest HIX value was observed in the T4 treatment scenario. In addition, the decomposition size of humus followed the order of T4 > T3 > T2 > T1. The soil humification level significantly increased following straw return. In summary, the FI, BIX, and HIX characterization results were consistent. The impact of microbial decomposition on the soil organic humification degree increased with increasing straw return amount to the field.

Characterization of the DOM fluorescent components

In this study, PARAFAC was used to analyze the three-dimensional fluorescence spectral components of soil DOM under the treatment scenarios. The fluorescence component results of the four treatments and literatures of Huguet et al., Li et al., He et al., Li et al., and Baker et al.[17–21], including the peak types, are reported in Table 4. The three-dimensional fluorescence spectral components of soil DOM are shown in Fig. 1.

The three fluorescent fractions of DOM were similar in the four treatment scenarios. The C1 component represented fulvic acid-like substances. The material content of C1 increased with increasing straw return amount. Among them, C1 in the T1 and T2 treatments contained one excitation peak and one emission peak, representing the fulvic acid-like substances in the UV region. In contrast, C1 in the T3 and T4 treatments contained two excitation peaks and one emission peak, representing the UV and visible regions of fulvic acid, respectively. Fulvic acids are related to hydroxyl and carboxyl groups in humic substance structures, corresponding to Peak A and Peak C. The C2 component represented humic acid, corresponding to Peak F. Among them, fraction C2 in the T1 treatment contained one excitation peak and one emission peak, while fraction C2 in the T2, T3, and T4 treatments contained two excitation peaks and one emission peak. The C3 component contained two excitation peaks and one emission peak, indicating tryptophan-like substances. These substances belong to protein-like substances and are related to carboxyl functional groups, corresponding to Peak T and Peak T1. Peak T and T1 indicate short and long-wavelength tryptophan, respectively.

In summary, straw return significantly changed the fluorescent fractions, namely fulvic acid (UV and visible fulvic acid), humic acid, and protein-like substances (short and long-wavelength tryptophan).

Fluorescence intensities and correlation analysis of the DOM components

In order to analyze the effects of the straw return amounts on soil DOM, the fluorescence intensities and relative proportions of the different DOM fractions were analyzed (Table 5). The fluorescence intensities of the DOM fractions were lower in the straw-returned treatments than those in the CK treatment. The fluorescence intensities of the fulvic acid and humic acid-like substances showed decreasing and increasing trends with an increase in the straw return amount, following the orders T1 > T2 > T4 > T3 and T1 > T3 > T4 > T2, respectively. The differences in the fluorescence intensity of the protein class were not significant between the straw return treatments, following the order of T1 > T2 = T3 = T4. The total fluorescence intensity (C1 + C2 + C3 + C4) showed an increasing–decreasing trend with increasing straw return amount. The highest total fluorescence intensity was 3547.20 relative units (R.U.) following the T3 treatment. On the other hand, the relative proportion trends of

DOM fluorescent component	Grouping Type	λEx/λEm (nm) values of this study	Fluorescent Peak	λEx/λEm (nm) in the literatures
C1	UV region class fulvic acid	230/415–430	A	230–260/370–460, 250–300/380–480
	Visible area of fulvic acid	300–325/415	C	310–360/370–480, 320–370/420–480
C2	Humic acid	250–275/455, 340–370/455	F	250–370/430–530
C3	Short-wave tryptophan (protein-like)	225/330–345	T	270–285/322–340, 225–237/340–350
	Long-wave tryptophan	275/330–345	T1	270–290/300–310, 380/330, 275/340

Table 4. Characteristics of the DOM fluorescence components in the straw return treatment scenarios.

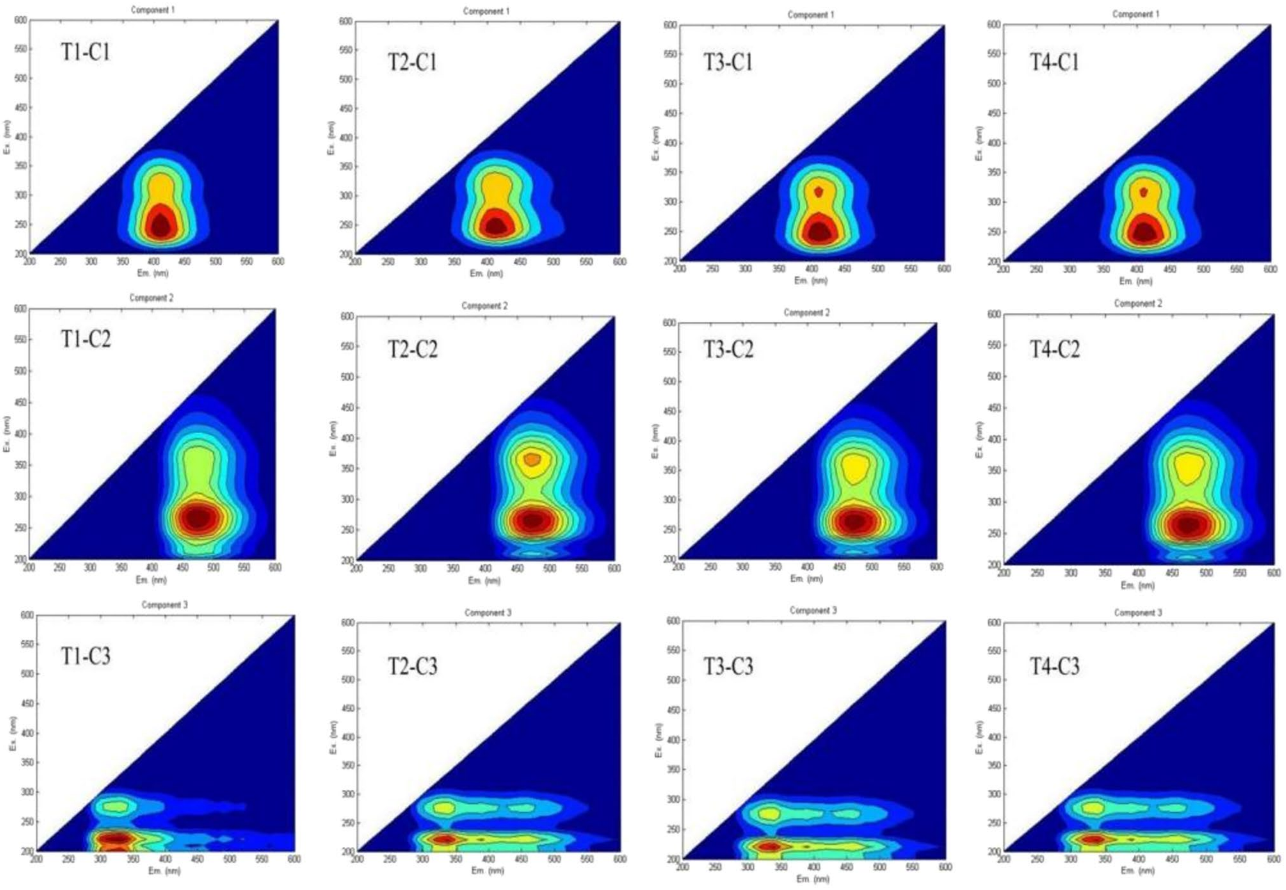

Fig. 1. Three-dimensional fluorescence fractions of soil DOM in the treatment scenarios.

	Fluorescence intensity (R.U.)			Relative proportion (%)			
Treatments	**C1**	**C2**	**C3**	**C1**	**C2**	**C3**	**Total fluorescence intensity (R.U.)**
T1	1950.05	1256.50	932.03	47.12	30.36	22.52	4138.58
T2	1796.93	860.09	790.97	52.12	24.94	22.94	3448.00
T3	1768.00	988.37	790.83	49.84	27.86	22.29	3547.20
T4	1770.42	977.23	790.73	50.03	27.62	22.35	3538.38

Table 5. Fluorescence intensities of the DOM components in the straw return treatment scenarios.

the three fluorescence fractions were not consistent with those of the fluorescence intensity. Indeed, the relative proportions of the fulvic acid, humic acid, and protein-like substances followed the order of T2 > T4 > T3 > T1, T1 > T3 > T4 > T2, and T2 > T1 > T4 > T3, respectively.

The relationships between the fluorescence intensities of the DOM components and soil physicochemical properties were analyzed using correlation analysis (Fig. 2). According to the obtained results, fulvic acid showed a positive correlation coefficient with tryptophan ($p < 0.001$, $r = 0.87$), while humic acid showed positive correlation coefficients with fulvic acid and tryptophan of 0.80 ($p < 0.01$) and 0.79 ($p < 0.01$), respectively. In addition, the SOM contents showed positive correlation coefficients with WHC ($p < 0.001$, $r = 0.82$), soil porosity ($p < 0.01$, $r = 0.77$), and soil bulk density ($p < 0.05$, $r = 0.64$). In contrast, the results showed a lack of correlation between the SOM contents and fluorescence intensities of the DOM components. Whereas a significant positive correlation was found between the tryptophan fluorescence intensities and soil bulk density values ($p < 0.05$, $r = 0.63$).

Discussion

Effects of straw return on the soil organic matter contents and physical indicators

Straw-returning practices are effective measures of conservation tillage, which can improve soil nutrients, structures, and microbiology[22]. Numerous researchers have highlighted substantial increases in the SOC contents by 7.81–17.18% following straw return to fields in different regions[23,24]. In this study, the straw return treatments increased the SOM contents by 1.1–3.8%, soil organic matter is positively correlated with the amount of straw

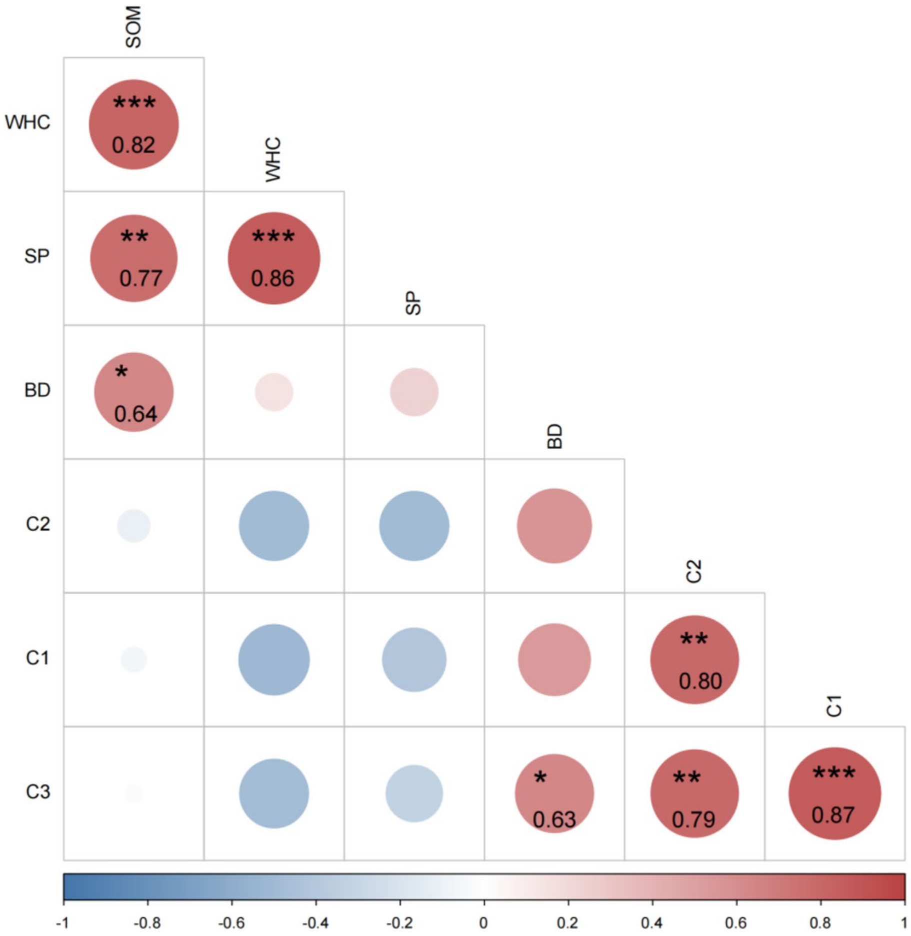

Fig. 2. Correlations between the DOM fluorescence components and soil physicochemical properties. *: $p < 0.05$; **: $p < 0.01$; ***: $p < 0.001$.

returned to the field, and the greatest increase in organic matter is achieved when all of the straw is returned to the field. This finding might be due to the low straw decomposition rates and weak organic carbon in the alpine region of Northeast China. Therefore, the T3 treatment scenario resulted in optimal soil characteristics. Slight increases in the SOM contents can improve soil water retention and porosity, decreasing the soil bulk weight and improving soil aeration, water permeability, soil structure, soil nutrient, air, and heat distributions, and, consequently, creating a favorable environment for improving crop yields[25–28]. Meta-analysis studies have indicated significant effects of straw return on the SOC contents in different regions[29,30]. Notably, the SOC contents after straw returns in North and Northwest China were about 2.20 and 1.54 times higher than those in Northeast China, respectively[23,24]. In addition, previous studies have shown that straw return significantly enhanced the soil bulk density, changing the soil WHC and porosity of the field without significant differences between the straw return amounts[31], which is consistent with the result obtained in this study. Straw return to fields in Northeast China reduced the bulk density by 3.87%[22]. Whereas in this study, the soil bulk density was reduced by 3.53 to 8.33%, showing a poor effect of the T4 treatment on the improvement of bulk density. This finding might be due to the indirect effects of the pedological and hydrothermal conditions in Northeast China on the straw decomposition rates by influencing the soil microbial environment[32]. The residual hemicellulose, cellulose, and lignin contents in corn stover under anaerobic decomposition conditions were higher than those under aerobic conditions[33]. The low temperatures in the winter season inhibited the physiological activities of soil microorganisms in Northeast China, decreasing the decomposition rates of the returned stover and, consequently, resulting in an insufficient release of available nutrients and insignificantly influencing the physical indicators of the soil[34,35].

Analysis of the DOM fluorescence spectral indices

The FI, BIX, and HIX can be used to determine the source of humus[36], the proportion of autochthonous organic matter[37], and the humification degree of organic matter[38], respectively. The FI values of the straw return treatment scenarios ranged from 1.4 to 1.9, indicating that soil DOM was influenced by a combination of autochthonous and exogenous sources. In addition, DOM was derived both from the transformation of SOM and straw microbial decomposition, which is consistent with the fluorescence index results observed in other black soil areas following straw return[39,40]. The effect of the soil environment on soil carbon storage was changed following straw returns to the field. First, straw contains certain nutrients (nitrogen, phosphorus, potassium, and other nutrients), organic matter components (cellulose, hemicellulose, lignin, protein), and ash elements, thus further increasing soil nutrients and contributing to the formation of DOM. Second, the straw return can provide energy-rich organic materials for soil microorganisms, thereby increasing the number of microorganism species and their enzymatic activities. Furthermore, the microbial decomposition and transformation processes of cellulose, lignin, polysaccharides, humic acid, and other black colloidal substances produced can bind soil particles, increase soil humus and DOM contents, form organic and inorganic complexes with clay minerals, and promote the formation of soil aggregates. These benefits can reduce the capacity of the soil and improve the soil water, nutrient, air, and heat distributions, thereby improving the physicochemical properties of the soil.

The results of this study showed a lack of significant differences in the BIX values between the straw return treatments. Indeed, the effect of straw decomposition on soil physicochemical properties is a long process. The results of different straw return methods were different, which might be due to the soil hydrothermal and climatic conditions of the local farmland. In this study, the soil of the experimental site was subjected to tillage practices and was consistently affected by the hydrothermal conditions of the soil, resulting in inconclusive BIX results. In contrast, previous studies have highlighted obvious humification characteristics and increases in the BIX values with increasing straw-returning depth[39,40], demonstrating the effects of straw-returning depths on the microbial endogenous and exogenous humus derived from straw and plant roots, as well as on the humification process of SOM.

The DOM HIX results of the straw return treatments showed strong humus characteristics and low recent autogenic components. Returning high straw amounts may significantly change the physical structure of the soil and enhance the contact area between the straw and soil particles. Therefore, the strong putrefactive character enhancement might be due to the decomposition of the returned straw to the field to form DOM. It should be noted that the application of optimal straw amounts can enhance substantially the microbial decomposition rates of straw in the soil. Previous studies have used the HIX index and indicated weak humus characteristics at different straw-returning depths[39], which might be due to the weak microbial activities at different soil depths. In addition, microbial decompositions of simple and easily degradable substances in soils can generate more complex and stable humic acid substances using hard soil substances to decompose, thereby increasing the humification degree of soil dissolved organic carbon (DOC). Li et al. have indicated significant variations in the humification degree between different years of straw return to fields[41]. The FI, BIX, and HIX results were consistent in this study. The metabolic capacity of soil microorganisms increased with increasing straw return amount to the field. The higher the decomposition straw efficiency of microorganisms, the greater the impact on the soil organic matter humification degree, enhancing the formation of bioavailable elements and improving soil fertility.

Characteristics of the DOM fluorescence components

The straw return amounts significantly influenced the abundance of the fluorescent DOM components in the soil, including fulvic acid (UV and visible fulvic acid), humic acid, and protein-like substances (short and long-wavelength tryptophan). The C1 component (fulvic acid) increased with increasing straw return amount. Substances represented by Peak A were mainly derived from organic substances with large relative molecular mass and low biodegradability. Whereas substances represented by Peak C were mainly derived from more easily biodegradable organic matter with smaller relative molecular mass, characterized by good photochemistry, high fluorescence efficiency, and easy oxidative decomposition. Both types are humic acid-like substances and indicators of exogenous inputs. The C2 component (humic acid-like substances) increased substantially with increasing straw return amount compared with the CK treatment scenario. Humic acid is related to lignin in straw degradation, characterized by high molecular weight and humification degree, containing polycyclic aromatic hydrocarbons and benzene rings. The C3 component belongs to protein-like substances and is related to carboxyl functional groups. The short-wavelength tryptophan content was high in the CK treatment scenario, while the long-wavelength tryptophan content increased significantly following straw return. Tryptophan-like substances are soluble metabolites derived from the microbial degradation process, which are prone to energy transfer with tyrosine bound in the same protein and have a complex effect on the fluorescence peaks. Tryptophan-like substances are protein-like components related to the structure of aromatic ring amino acids in DOM, which is mainly free or protein-bound and can be used to reveal intact proteins, potentially from the produced microbial enzymes or proteins in biological residues. According to previous studies, the fluorescence fractions of soil DOM consisted of humus and protein-like fractions following straw return using different tillage practices, of which humus and protein-likes fractions were mainly characterized by fulvic acid and tryptophan-like substances, respectively, which is consistent with the results of PARAFAC analysis in the present study[39–41].

Fluorescence intensities of the DOM components and correlation analysis results

The fluorescence intensities of fulvic and humic acids showed decreasing and increasing trends with increasing the straw return amount, respectively. The total fluorescence intensity (C1 + C2 + C3 + C4) showed an increasing–decreasing trend with the increasing straw returned amount. The fluorescence intensities of the different components were related to the structure and functional groups of the straw decomposition products. Protein-like substances exhibited lower fluorescence intensity due to the presence of carboxyl and carbonyl groups with high relative molecular masses, while humus-like substances showed higher fluorescence intensity due to the presence of amino, methoxy, and hydroxyl groups. The straw decomposition efficiency decreased with increasing straw return amount. Microorganisms can decompose polysaccharides, proteins, and carbohydrates contained in straw, resulting in humus-like substances with a linear aromatic ring structure, simple composition, and small molecular mass. However, SOM exhibited high fluorescence intensities in this study following straw return to the field. Indeed, fluorescence intensities are closely related to the structure of DOM, indirectly revealing the active functional groups contained in DOM and its nature. Therefore, the straw return amounts influenced the fluorescence components.

The relative proportions of the three-dimensional fluorescence components were not consistent with the fluorescence intensity results. The relative proportions of the fluorescent components followed the order of fulvic acid > humic-like acid > protein in the T2, T3, and T4 treatment scenarios, respectively. The straw decomposition can release lignin-containing polysaccharides and lipids, which are favorable to the humification process and can increase the aromatic structural components. After fermentation, the humification and aromaticity degrees of the protein-like substances, as well as the humic-like acid content, increased significantly following straw return. Corn stover contains a large amount of fibrous materials (lignin and cellulose). Proteins can be transformed into fulvic acid and humic acid through microbial decomposition and humification processes. Indeed, humic acid can reflect the stability degrees of soils. The T3 treatment showed the highest relative proportion of humic-like acid fractions, indicating that this treatment was optimal for achieving good soil carbon pool stability.

The results of this study revealed a significant positive correlation coefficient between the WHC and DOC contents. This finding can be explained by the positive effect of WHC on the dissolution of DOC from DOM. The fluorescence intensity of the fulvic acid fractions of soil DOM decreased due to the light and temperature effects. The release of nutrients from the returned straw is a relatively slow process. Humus-like substances produced by straw decomposition can be directly absorbed and utilized by plants, resulting in a relatively minor effect on the soil carbon pool. After the application of straw to the fields, the soil organic carbon pool demonstrated notable stability. Within this, the light intensity of humic acid and fulvic acid-like compounds in the DOC exhibited significant stability despite variations in the soil environment. However, the fluorescence intensities of the tryptophan-like substances showed a significant positive correlation with the bulk density values, mainly due to the formation of small protein molecules in the soil following the microbial decomposition of the returned straw, increasing the fluorescence intensities of the protein-like substances. Therefore, although straw-returning practices can improve soil fertility, they exhibit minor effects on soil carbon pool stability.

Conclusion

The impact of straw-returning to the field on soil carbon storage is directly related to the agricultural production capacity of the soil. Straw-returning practices can provide numerous benefits, including increasing SOM contents, reducing soil bulk densities, and enhancing soil WHC and porosity characteristics. In this study, the fluorescence spectroscopy data demonstrated the key role of high straw return amounts in enhancing substantially the metabolic activity of soil microorganisms. In addition, the SOM humification degree was greatly influenced by the straw microbial decomposition, increasing the availability of bioavailable substances, which is consistent with the obtained FI, BIX, and HIX results. On the other hand, PARAFAC analysis showed three DOM-derived fluorescent components in the returned straw, namely fulvic acid (UV and visible fulvic acids), humic acid, and protein (short and long-wavelength tryptophan). The straw return amounts significantly increased the richness of the fluorescent components and resulted in lower fluorescence levels of various components compared to the CK treatment. Additionally, the fluorescence intensities of fulvic and humic acids showed decreasing and increasing trends with increasing straw return amount, respectively. In contrast, the total fluorescence intensity (C1 + C2 + C3 + C4) exhibited an increasing–decreasing trend with increasing straw return amount. It is noteworthy that the T3 treatment resulted in the highest total fluorescence intensity of 3547.20 R.U. and the highest proportion of the humic-like components of 27.86%, which was inconsistent with the relative proportions of the three fluorescence components of DOM. Indeed, the relative proportions of the fluorescence components followed the order of fulvic acid > humic-like acid > protein-like with increasing straw return amount. Therefore, it is strongly recommended to use straw return to black soil farmland at an application rate of 4500 kg hm^{-2} as a long-term return ratio to effectively stabilize the soil organic carbon pool.

Data availability

The data generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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Author contributions

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Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to D.W. or J.L.

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