EFFECT OF DIFFERENT PROPORTIONAL MIXTURES OF CORN STRAW AND PEAT ON HUMUS COMPOSITION AND HUMIC ACID STRUCTURE OF BLACK SOILS

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Abstract. In order to mitigate the degradation of black soil organic matter, this paper designed a field microplot experiment with different proportional mixtures of corn straw and peat with an equal carbon amount. Treatments included (ⅰ) no organic materials applied (CK), (ⅱ) Application of peat (P), (ⅲ) Peat and corn straw are 2:1(2/3P), (ⅳ) Peat and corn straw are 1:2(1/3P) and (ⅴ) Application of corn straw (0P). The humus composition and humic acid (HA) structural characteristics of black soil were studied using elemental analysis, Fourier transform infrared (FTIR) spectroscopy, fluorescence spectrum and thermogravimetric analysis. The results demonstrated that water-soluble substances carbon (WSS-C) content increased with the increase of straw application amount, SOC, humification rate (PQ) and carbon content of other humus fractions increased with the increase of peat application amount. In addition, the higher peat applied, the stronger the aromatic nature of HA structure, the more stable and complex the structure of HA, the higher corn straw applied, the stronger the aliphatic nature of HA structure, and the simpler the structure of HA. With the consideration of the humus composition and HA structural characteristics of black soil, the appropriate ratio of the application of corn straw and peat deemed 2:1.
Keywords: *organic materials, soil organic matter, humic acid structure, elemental analysis, fluorescence spectrum*

Introduction

Humic substances (HS) is an important portion of soil organic matter, which represents the key function of soil fertility. The major fractions of HS are humic acids (HA), fulvic acids (FA), and humin (Hm). Humic acid (HA) is an active substance in HS. Its structure and properties directly affect soil fertility (Dou et al., 2020). In northeast China, the black soils are the main grain-producing area in China. Recently, in the cultivated soils, the soil organic carbon content (SOC) decreased and the deterioration of HA due to the successive production and the unsustainable use of organic matter resources (Xu et al., 2010; Zhao et al., 2018a; Gu et al., 2018). Using organic material instead of inorganic fertilizer is one of the most effective methods of improvement (Luan et al., 2019; Wang et al., 2019). Several studies have shown that the application of organic materials could significantly improve the content of humus and the structure of HA in soil (Dou and Jiang, 1988). And improving soil HA structure can improve soil fertility and soil C stock (Amoah-Antwi et al., 2020).

Corn straw and peat are two representative organic materials. However, the two organic materials have different effects on the soil due to their own characteristics. Corn

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straw is a rich organic material, rich in cellulose, hemicellulose, lignin and other polymers (Chen et al., 2019; Huang et al., 2018). Studies have shown that returning corn straw to the field can improve crop yield and SOC content (Xu et al., 2019), reduce the oxidation degree of HA and improve the humification degree of HA (Gao et al., 2019), increase the carbon component of soil HS. The aliphatic, hydroxyl, methoxy and carboxyl compounds in HA molecules are increased, which simplifies the molecular structure of HA (Ndzelu et al., 2020).

Peat is a precious natural resource (Zaccone et al., 2018), It is a highly humic organic material formed by the long-term accumulation of plant residue that cannot be wholly decomposed under anaerobic conditions (Rydin et al., 2013). The formed HS has a higher degree of condensation, aromatization and more complex molecular structure, which has excellent potential to enhance soil organic matter (SOM) (Zheng et al., 2019). Studies have shown that the application of peat can be used for nutrient retention to maintain and improve soil fertility (Zhang et al., 2017), increase the carbon composition of soil HS and enhance the degree of humification and the aromaticity of HA (Wu et al., 2020).

Current researches suggest that both corn straw and peat can increase soil humus component and improve HA structure. At present, there are many researches about improving soil quality and fertility by corn straw and peat, but there are few researches on soil HA structure. Therefore, this paper designs the corn straw and peat different mixing proportion in field microplot experiment, the objectives were to (i) Compare the effect of applied corn straw and peat on soil improvement (ii) evaluate changes in HA structural characteristics under different mixing ratios of two organic materials applied (iii) comprehensive considering the change of soil humus composition and HA structure, find the optimum mix proportion of corn strow and peat for black soil fertilizing. In order to provide a scientific basis for organic material mixed fertilization black soil.

Materials and methods

Study site

The test site is located in the teaching and research base of Jilin Agricultural University in Jilin Province China (N43°48′43.57″, E125°23′38.50″). It is a temperate continental humid climate with an annual precipitation of 600-700 mm, a frost-free period of 140-150 days and an annual freezing period of 5 months. The soil type is black soil, belonging to Argiudolls according to the American soil classification system. The basic chemical soil properties are presented in *Table 1* (Zhang et al., 2020). All the specification of treatments’ plots is 1 m × 1 m, surrounded by bricks, with 1.5-m intervals between the treatments’ plots. The experimental corn straw was collected from the teaching and research base of Jilin Agricultural University in September 2019, and the peat was collected from the cultivated land of peat soil in Da qiao Town, Dun hua City in October 2019. The two kinds of organic materials are air-dried and smash into 2-3-cm pieces before the application, and their initial basic elemental composition is shown in *Table 2*.

Experimental design

The experiment was designed in a plot experiment in May 15th, 2020. The organic materials were applied at equal carbon mass and C/N ratio. The carbon amount was

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calculated according to the total carbon amount of corn straw returned to the field (10000 kg/hm^2) and C/N was 20/1. Five treatments were designed as follows: (ⅰ) CK (untreated control), (ⅱ) P (1.19 kg of peat and 12.73 g of urea), (ⅲ) 2/3P (793.7 g of peat + 333.3 g of corn straw + 10.26 g of urea), (ⅳ) 1/3P (396.9 g of peat + 666.6 g of corn straw + 7.81 g of urea), and (ⅴ) CS (1 kg of corn straw + 5.37 g of urea). The specific operation is taking out 20 cm of soil within the treatment and put it on the plastic film, and then mix it with organic matter evenly and return it. Each treatment plot was set with four planting points and two corn seeds were sown per point and 2 weeks after emergence one of the poor growing corn was uprooted in each point. Each treatment was repeated 3 times. The experiment was harvested in September 20th, 2020.

Table 1. *Basic soil chemical soil properties*

Soil type	Organic matter (g/kg)	pH	Total nutrient (g/kg)			Available nutrient (mg/kg)		
			N	P	K	N	P	K
Argiudolls	17.22	6.89	1.74	0.41	11.48	86.74	33.76	121.98

The total nutrient is total nitrogen, total phosphorus, and total potassium. Available N is nitrogen extracted by NaOH; Available P is phosphorus extracted by activated charcoal, and available K is potassium extracted by Ammonium acetate

Table 2. *Initial basic elemental composition of the organic materials in study*

Organic materials	Element content (g.kg^{-1})				C/N (mol)	O/C (mol)	H/C (mol)
	C	N	H	O			
Peat	403.45	18.58	49.55	528.41	25.33	0.87	1.47
Corn straw	480.34	25.53	58.76	435.36	21.95	0.60	1.47

C, N, H and O represent the content of carbon, nitrogen, hydrogen and oxygen elements in organic materials; C/N, O/C and H/C represent the mole ratios of elements

Soil sampling and analysis

Five soil samples (0-20 cm) were taken from different places of each plot, and then mixed to form a representative sample. The soil samples were air-dried, then pass through a 2-mm sieve for chemical analysis.

Soil organic carbon

SOC was directly determined by the potassium dichromate external heating method (Dou, 2010). Briefly, 0.2 g of pass through 60 mesh soil weighed into a 50-mL volumetric flask was treated with 10 mL of 0.4 N $K_2Cr_2O_7$-H_2SO_4 solution and covered with a curved funnel. The soil-solution mixture was heated at 180 °C until the first drop appeared from the funnel. The heating was maintained for another 5 min. After cooling to room temperature, it was titrated with 0.2 N $FeSO_4$ after drop two drops of o-phenanthroline indicator.

Sequential extraction of soil humus fractions carbon

Water-soluble substance (WSS), water floating substances (WFS), and humic substances (HS) were sequentially extracted following the modified method as

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described by (Dou, 2010). Briefly, 5 g of air-dried soil sample was sequentially extracted with 30 mL of distilled water to extract WSS. After filtrate of WSS, the water floating substance was dried and calculated. The C content of WSS was measured by using a TOC analyzer (Shimadzu TOC-Vcph, Japan). Thereafter, the remaining part of sample was treated with 30 mL of a mixture solution of 0.1 M of NaOH + $Na_4P_2O_7$ under continuous shaking at 70 ℃ for 1 h to extract HS. After acidification with 1 M of H_2SO_4, the coagulated fraction represents humic acids (HA), while the supernatant represents fulvic acids (FA). The HA part was dissolved with warming 0.05 M NaOH and transferred into 50 ml volumetric flask. As well, FA was completed by 0.05 N H_2SO_4 into 50 ml volumetric flask. The residual fraction represents the humin (HM). The C content of HA, FA, and HM was determined by dichromate method. Humification rate (PQ) was computed as *Equation 1*.

$$PQ = HA - C/(HA - C + FA - C) \quad \text{(Eq.1)}$$

Isolation and purification of humic acid

The HA was extracted and purified using the International Humic Substances Society method (IHSS) (Kuwatsuka et al., 1992). Briefly, 50 g of air-dried soil sample was extracted with 0.1 m NaOH for HS extraction. This step was repeated three times. HS solution was acidified with 1M HCl to precipitate HA. After high-speed centrifugation of acidified suspension, electro-dialyzed, rotary evaporation and freeze-drying, solid pure HA was obtained.

Structural composition of HA

An elemental analyser (Vario-EL-III Hanau, Germany) was used to assess C, H, N and O contents of solid HA.

Fourier transform infrared (FTIR) spectra was obtained using 1.5–2 mg of solid HA sample mixed with potassium bromide (KBr). The obtained pellet was analyzed with FTIR (Spectrum Two PerkinElmer, USA), covering a frequency range of 4000–400 cm^{-1}, under 4 cm^{-1} wave number resolution, 16 scans and pure KBr spectra as a background.

Fluorescence spectra of the soil HA was obtained using Perkin Elmer FL-6500 fluorescence spectrophotometers. Two mg of the solid HA sample was dissolved by 0.05 mol/L NaHCO3 and constant volume to 50 ml for measuring. Fluorescence spectra in the form of excitation/emission matrices (EEM) were recorded over the emission wavelength range of 250–750 nm and excitation wavelength range of 250–650 nm. Em and Ex slits were fixed at 10 nm. Scanning speed was 2400 nm/min. The voltage of PMT was 550 mV.

Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) analysis of solid HA samples were performed using STA 2500 Regulus thermogravimetric analyzer (Netzsch, German). About 4–6 mg of solid HA sample was heated to 750 ℃ at a constant heating rate of 15 ℃/min.

Data analysis

Data processing was performed using Microsoft Excel and statistical analyses were performed using SPSS software (IBM Statistics 20.0). One-way analysis of variance with the least significant difference (LSD) test was applied to test the significance of

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difference at $p < 0.05$ among treatments. Spectra and graphs were compiled using the Origin 2018 software. TG and DTA charts were analyzed using TA Universal Analysis software.

Results

Effects of different treatments on SOC content and humus composition

After six months of field microplot experiment, the contents of SOC and WFS-C increased in the order of: CK < 0P < 1/3P < 2/3P ≤ P (*Table 3*). Compared to CK, the SOC in P, 2/3P, 1/3P and 0P treatments increased by 52.2%, 46.4%, 34.8% and 17.4%, respectively. And no significant difference between 2/3p and P treatment. The 0P treatment possessed significantly greater WSS-C than other treatments following the order of: CK < P < 2/3P < 1/3P < 0P (*Table 3*). Furthermore, the difference between treatments was significant.

Similar to SOC, the contents of HA-C, FA-C and HM-C increased in the order of: CK < 0P < 1/3P < 2/3P < P (*Table 3*). The P treatment possessed significantly greater HA-C than other treatments. No significant difference was observed in FA-C content between P and 2/3P, and a significant difference was observed in HM-C content between the 0P treatment and other treatments. Compared with CK (54.18%) treatment, P (62.80%), 2/3P (61.23%), 1/3P (58.81%) and 0P (56.51%) treatments all increased PQ significantly (*Table 3*).

Table 3. *Effects of different proportional mixtures of corn straw and peat on SOC content and humus carbon content*

Treatment	(g.kg^{-1})						PQ (%)
	SOC	WFS-C	WSS-C	HA-C	FA-C	HM-C	
P	15.23 ± 0.160a	0.901 ± 0.035a	0.239 ± 0.003d	3.35 ± 0.009a	1.99 ± 0.021a	8.75 ± 0.122a	62.80 ± 0.003a
2/3P	14.66 ± 0.291a	0.810 ± 0.023b	0.258 ± 0.005c	3.06 ± 0.032b	1.94 ± 0.039a	8.60 ± 0.226a	61.23 ± 0.004b
1/3P	13.50 ± 0.126b	0.728 ± 0.062c	0.269 ± 0.003b	2.56 ± 0.035c	1.79 ± 0.030b	8.15 ± 0.113a	58.81 ± 0.007c
0P	11.75 ± 0.534c	0.602 ± 0.013d	0.283 ± 0.005a	2.26 ± 0.037d	1.74 ± 0.040bc	6.87 ± 0.543b	56.51 ± 0.003d
CK	10.01 ± 0.425d	0.502 ± 0.020e	0.206 ± 0.002e	2.00 ± 0.015e	1.69 ± 0.017c	5.62 ± 0.415c	54.18 ± 0.004e

P, all peat; 2/3P, peat and corn straw are 2:1; 1/3P, peat and corn straw are 1:2; 0P, all corn straw; CK, no organic materials applied; SOC, soil organic carbon; WFS-C, water floating substance carbon; WSS-C, water soluble substances carbon; HA-C, humic acid carbon; FA-C, fulvic acid carbon; HM-C, humin carbon; PQ, humification rate calculated as HA-C/(HA-C + FA-C). The values represent the means ± standard error (SE), Means that do not share the same letter superscript within a column are significantly different ($p < 0.05$)

Elemental composition of HA

Table 4 shows the elemental composition of soil HA across all treatments, the contents of C and N in all treatments in the order of CK < 0P < 1/3P < 2/3P < P, and the difference between P and 2/3P treatments was not significant. Compared with CK treatment, the content of H in HA under 0P, 1/3P, 2/3P and P treatments increased by 2.8%, 2.4%, 1.9% and 1.3%, respectively, while the content of O decreased by 1.3%, 2.3%, 2.9% and 3.2%, respectively (*Table 4*). The H/C ratio across all treatments followed this order: 2/3P < P < CK < 1/3P < 0P, while the O/C ratio followed the order of: CK < 0P < 1/3P < 2/3P = P (*Table 4*).

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***Table 4.** Effects of different proportional mixtures of corn straw and peat on the elemental composition of soil humic acid*

Treatment	Element content (g.kg^{-1})				Ratio (mol)	
	C	N	H	O	O/C	H/C
P	534.1±1.72a	25.71±0.30a	47.22±0.17b	393.0±1.39d	0.552±0.004c	1.061±0.006b
2/3P	532.7±1.33a	25.70±0.21a	47.50±0.43ab	394.1±1.87cd	0.555±0.004c	1.070±0.007b
1/3P	529.8±0.98b	25.58±0.18ab	47.73±0.27ab	396.9±1.00c	0.562±0.002c	1.081±0.007b
0P	525.0±1.09c	25.24±0.05b	47.95±0.12a	400.8±1.18b	0.572±0.003b	1.094±0.003a
CK	522.7±1.44d	24.68±0.15c	46.61±0.39c	406.0±1.90a	0.583±0.004a	1.070±0.006b

P, all peat; 2/3P, peat and corn straw are 2:1; 1/3P, peat and corn straw are 1:2; 0P, all corn straw; CK, no organic materials applied. Mean elemental values ± SE that do not share the same letter superscript within a column are significantly different ($P < 0.05$)

FTIR spectra of HA

The FTIR spectrum of soil HA for different treatments is shown in *Figure 1*. All treatments exhibited similar peak characteristics, differing only in their absorption intensities (*Table 5*). The P treatment showed higher absorption intensity at 1620 cm^{-1} peak, and the 0P treatment showed more abundant peaks at 2920 cm^{-1} and 2850 cm^{-1} (*Table 5*). Compared with CK, the ratio of I2920/I1720 was significantly increased in all treatments, following the order of: CK < 0P < 1/3P < 2/3P < P. Besides, the ratio of I2920/I1620 was decreased in P and 2/3P treatments, while 1/3P and 0P treatments were opposite (*Table 5*).

***Table 5.** Effect of different proportional mixtures of corn straw and peat on the relative intensity of the main absorption peaks from Fourier transform infrared spectra of soil humic acid*

Treatment	Relative intensity (%)				Ratio	
	2920 cm^{-1}	2850 cm^{-1}	1720 cm^{-1}	1620 cm^{-1}	I_{2920}/I_{1720}	I_{2920}/I_{1620}
P	2.80±0.21c	0.88±0.03c	6.18±0.08d	13.18±0.28a	0.597±0.046a	0.279±0.013d
2/3P	3.07±0.12bc	1.00±0.09b	6.91±0.20c	12.83±0.33a	0.589±0.031ab	0.317±0.018c
1/3P	3.38±0.22ab	1.06±0.04b	7.92±0.10b	10.57±0.51b	0.561±0.035abc	0.420±0.015b
0P	3.52±0.24a	1.15±0.04a	8.83±0.09a	10.02±0.21b	0.529±0.028bc	0.466±0.026a
CK	2.15±0.09d	0.81±0.02c	5.78±0.30e	9.11±0.03c	0.513±0.027c	0.325±0.009c

P, all peat; 2/3P, peat and corn straw are 2:1; 1/3P, peat and corn straw are 1:2; 0P, all corn straw; CK, no organic materials applied. I2920/I1720, absorption intensity ratio of 2920 cm^{-1} and 1720 cm^{-1} calculated as (2920 + 2850)/1720; I2920/I1620, absorption intensity ratio of 2920 cm^{-1} and 1620 cm^{-1} calculated as (2920 + 2850)/1620. Values are means ± SE and means that share the same letter superscript within a column of a given depth are not significantly different ($P < 0.05$)

Fluorescence spectra of HA

The fluorescence spectra of HA revealed three fluorophores (peaks A, B and C) across all treatments (*Fig. 2*). Peak A (400-490/475-575 nm), peak B (310-400/475-560 nm) and peak C (260-310/460-550 nm) were all approximately situated in fluorescent regions belonged to HA component. Indicated that three organic substances in HA could emit fluorescence. The difference is the fluorescence intensity of the peak.

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Compared with CK, the fluorescence intensity of peak A, peak B and peak C under P and 2/3P treatment was decreased, while that under 1/3P and 0P treatment were increased (*Fig. 2*).

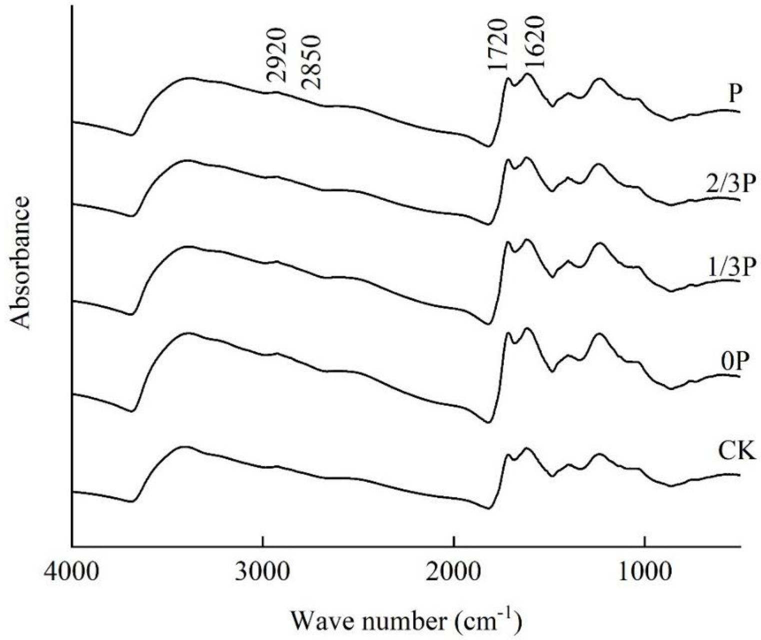

Figure 1. *Fourier transform infrared spectrum of soil humic acid under different proportional mixtures of corn straw and peat*

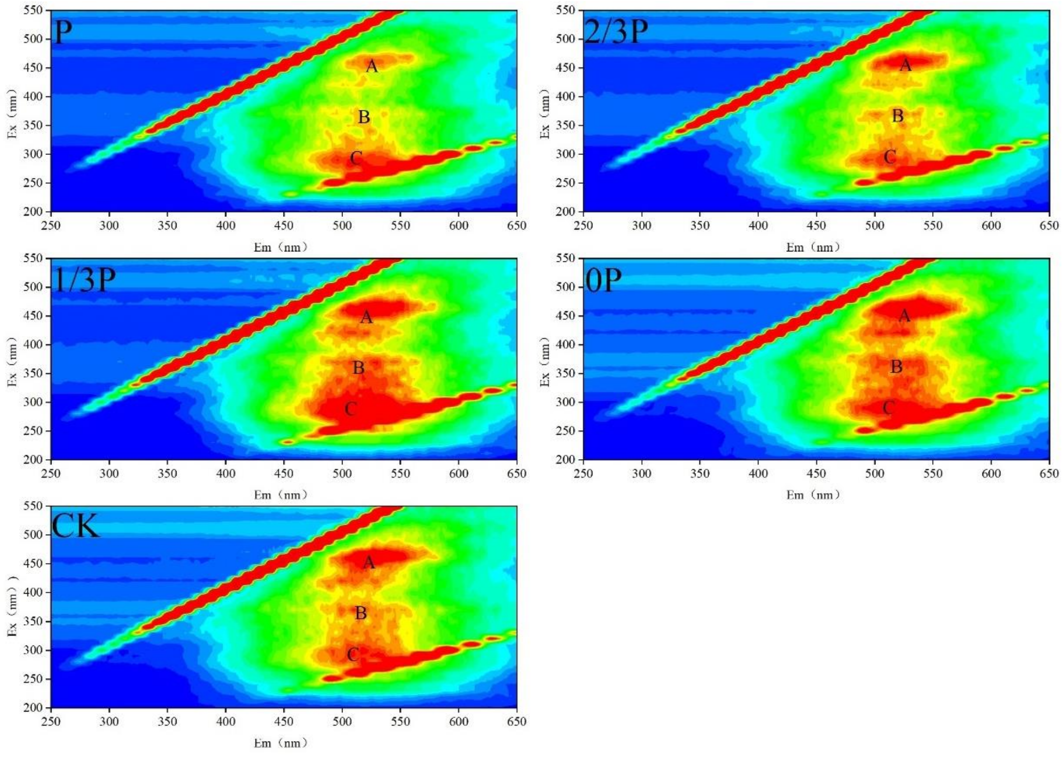

Figure 2. *The excitation/emission matrices fluorescence spectra of soil humic acid under different proportional mixtures of corn straw and peat*

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Thermal analysis of HA

The DTA and TG curves of soil HA under all treatments are shown in *Figures 3* and *4*. During the pyrolysis process. HA samples showed heat release and weight loss at moderate temperature (302.35 ℃ ~ 322.86 ℃) and high temperature (490.08 ℃ ~ 521.34 ℃). Compared with CK, the medium and high temperature under 2/3P and P treatment increased, while that under 1/3P and 0P treatment decreased (*Fig. 3*). Moreover, heat release and weight loss were increased in all treatments at moderate and high temperatures (*Table 6*). The heat release and weight loss were highest under the 0P treatment at moderate temperature, following CK < P < 2/3P < 1/3P < 0P. The P treatment was highest at high temperature, following CK < 0P < 1/3P < 2/3P < P (*Table 6*).

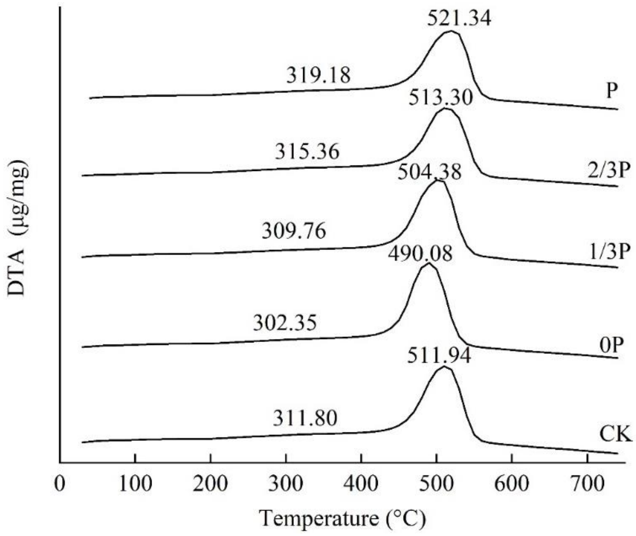

Figure 3. *The thermogravimetric analysis (DTA) curve of soil humic acid under different proportional mixtures of corn straw and peat*

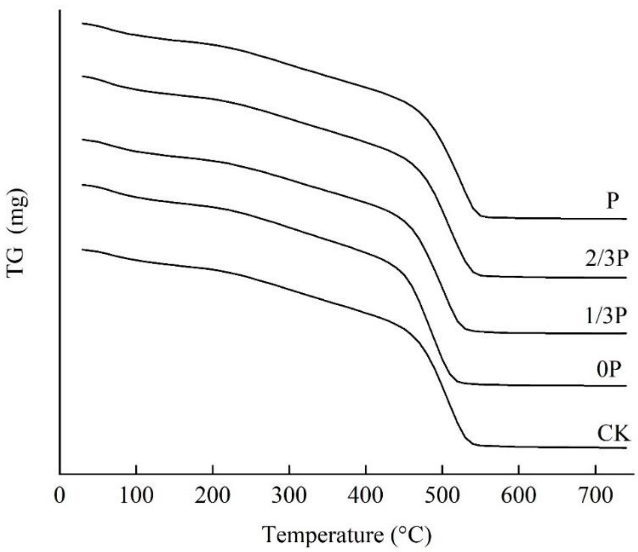

Figure 4. *The thermogravimetric (TG) curve of soil humic acid under different proportional mixtures of corn straw and peat*

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***Table 6.** Effects of different proportional mixtures of corn straw and peat on heat release and weight loss of soil humic acid*

Treatment	Exothermic heat (kJ g^{-1})		Exothermic heat ratio of moderate and high temperature	Mass loss (mg g^{-1})		Ratio of high and moderate mass loss
	Moderate temperature	High temperature		Moderate temperature	High temperature	
P	0.056 ± 0.004a	9.83 ± 0.46a	177.1 ± 5.8a	138.5 ± 4.0cd	687.4 ± 6.6a	4.97 ± 0.18a
2/3P	0.060 ± 0.003ab	9.46 ± 0.11ab	159.0 ± 8.8b	144.1 ± 4.1bc	677.3 ± 6.2a	4.70 ± 0.09b
1/3P	0.064 ± 0.002bc	8.90 ± 0.34bc	138.4 ± 6.6c	151.4 ± 2.7b	657.1 ± 6.4b	4.34 ± 0.05c
0P	0.069 ± 0.002c	8.29 ± 0.29cd	120.3 ± 4.9d	162.8 ± 7.1a	633.2 ± 4.9c	3.89 ± 0.15d
CK	0.049 ± 0.002d	7.71 ± 0.44d	158.7 ± 6.0b	131.3 ± 1.7d	615.7 ± 4.2d	4.69 ± 0.05b

P, all peat; 2/3P, peat and corn straw are 2:1; 1/3P, peat and corn straw are 1:2; 0P, all corn straw; CK, no organic materials applied. Values are means ± SE and means that share the same letter superscript within a column of a given depth are not significantly different (P < 0.05)

Discussion

Effect of different proportional mixtures of corn straw and peat on soil SOC and humus composition

Multiple studies have shown that organic materials or green fertilizers can significantly improve the SOC and humus contents in the soil (Wu et al., 2021; Zhang et al., 2019b; Yu et al., 2020). This is the same as the research results of this paper, compared with CK, the SOC, carbon content of humus fractions and PQ of P, 2/3P, 1/3p and 0P were significantly increased (*Table 3*). Corn straw and peat are C-rich substance and contains specific quantities of humus fractions (Han et al., 2020a; Rydin et al., 2013). Therefore, their application increased the SOC and carbon content of soil humus fractions. Compared with CK, except WSS-C, the increase of SOC and carbon content of other humus fractions are in the order of 0P < 1/3P < 2/3P < P. This is broadly consistent with the results of other researchers (Zhao et al., 2018b; Zhang et al., 2020). The result is related to the nature of organic materials (Tamura et al., 2017). Compared with corn straw, the degree of humification is greater, and the content of unstable organic carbon in peat is relatively less (Xu et al., 2020). Therefore, the content of WSS-C was increased with the increase of corn straw application amount, while the C of peat was more easily transformed into the soil after being applied to the soil. Moreover, peat can increase the diversity of soil microorganisms (Xiang et al., 2020; Cong et al., 2020), and is more conducive to increase SOC content. (Xu et al., 2017) believes that the way to transform organic materials into soil humus is to transform to HM first, followed by HA and FA fractions. Compared with peat, corn straw decomposition is slower (Tang et al., 2020), so SOC, HM-C, HA-C, FA-C and PQ were increased with the increase of peat application amount.

Effect of different proportional mixtures of corn straw and peat on HA structural characteristics

The application of organic materials can change the structure of HA in soil, but the change of HA structure depends on the nature of materials, soil properties and soil microorganisms (El-Naggar et al., 2018; Han et al., 2020b; Brunetti et al., 2007). The proportion of unsaturated lipids and lignin-derived compounds in soil with high SOC content was higher. On the other hand, a lower SOC level was associated with a higher proportion of saturated lipids (Jimenez-Gonzalez et al., 2020). The results of this paper showed that the aromaticity of HA was increased with the increase of peat application

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amount, the aliphaticity and the length of aliphatic chain hydrocarbon of HA were increased with the increase of corn straw application amount. Compared with CK, the H/C ratio (*Table 4*), I_{2920}/I_{1620} ratio (*Table 5*) and peak fluorescence intensity (*Fig. 2*) of P and 2/3P treatments were reduced, the 0P and 1/3P treatments are the opposite, specifically, following the order of: P < 2/3P < CK < 1/3P < 0P. And the P treatment showed higher absorption intensity at the aromatic peak and the 0P treatment showed more abundant aliphatic peaks (*Fig. 1*). The H/C ratio represents the molecular complexity of HA, while the O/C ratio represent the oxidation degree of HA (Xiaoli et al., 2008; Zhang et al., 2015). The values of I2920/I1720 and I2920/I1620 were used to indicate the oxidation degree and aromaticity of HA structure (Gao et al., 2018; Pospisilova et al., 2020). Peak fluorescence intensity can indicate the aromaticity and the content of aliphatic compounds of HA in fluorescence spectra (Chen et al., 2003; Liu et al., 2020b; Hu et al., 2019). This is because the highly aromatic soil humic acid structure is mainly derived from black carbon, while the carboxy-rich aliphatic structure is mainly derived from natural organic matter (DiDonato et al., 2016; Haumaier and Zech, 1995). Moreover, the leading functional group in HA is the carboxylic acid formed by the bonding of alicyclic and aromatic molecules, both of them are derived from the oxidation of lignin in organic materials (DiDonato and Hatcher, 2017). In addition, both peat and corn straw can reduce the oxidation degree of HA, and the degree of decrease increased with the increase of peat application, because compared with CK, the O/C ratio of all treatments is reduced (*Table 4*), while the I_{2920}/I_{1720} ratio is increased (*Table 5*), manifested explicitly as P < 2/3P < 1/3P < 0P < CK.

In the thermal stability analysis, the pyrolysis of HA is dominated by aliphatic and aromatic compounds (Guo et al., 2020a). Heat release at medium temperature is the decomposition decarboxylation of the acidic group, carbohydrate and fatty acid in the sample structure (Schulten and Leinweber, 1996). A high temperature is the destruction of aromatic structure and the cleavage of the C-C bond’s cleavage (Francioso et al., 2005). Compared with CK, the peak temperature of the medium and high temperature under 2/3P and P treatments increased, while that under 1/3P and 0P treatments decreased (*Fig. 3*). Indicated that the application of peat could enhance the thermal stability of the HA structure and make the structure of HA more complex and stable. In contrast, corn straw was on the contrary, this is related to the content of aromatic C (Kim et al., 2020). P treatment had the highest ratio of heat release and weight loss at high temperature (CK < 0P < 1/3P < 2/3P < P), and 0P treatment had the highest ratio at medium temperature (CK < P < 2/3P < 1/3P < 0P) (*Table 6*). Indicates that the application of peat is more conducive to increasing the aromatic compounds in the HA structure, while the application of straw makes the aliphatic compounds in the HA structure more abundant. This result also confirms the results of elemental analysis (*Table 4*) and infrared spectroscopy (*Table 5*).

The optimum ratio of straw and peat to fertilize black soil

Multiple studies have shown that soil organic matter’s quantity, quality, and stability are essential indexes of soil fertility, which should be comprehensively considered when fertilizing soil (Bi et al., 2020; Guo et al., 2020b; Simansky et al., 2019). In the research results of this paper, compared with CK, SOC, WFS-C, HM-C, HA-C, and FA-C contents in P and 2/3P treatments increased more, and WSS-C contents increased less, the 0P and 1/3P treatments are the opposite. Simultaneously, the HA structure of the soil showed a stronger aromaticity and stability under the treatment of P and 2/3P, But

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the humic acid with high aromaticity has strong complexing ability and can increase the content of some heavy metals in the soil (Fan et al., 2020; Zhang et al., 2019a). Moreover, WSS-C is the most active carbon in the soil, and its content and structure are near related to the soil microbial community and mineralization of SOC (Liu et al., 2020a; Ma et al., 2019). Although WSS-C content under 0P treatment increased the most, its SOC and carbon content of other humus fractions increased less, and the stability of HA structure decreased and showing strong aliphaticity. Humic acids with more aliphatic and decomposable structure showed greater fungistatic activities, and thus reduced the ecological risk of crop infection by phytopathogenic fungi (Wu et al., 2019). Careful consideration, SOC and carbon content of each fraction of humus under 1/3P treatment increased significantly, and HA structure stability, aromaticity, and aliphatic ratio were appropriate, which was more suitable for black soil fertilization.

Conclusion

(ⅰ) Applied different proportional mixtures of corn straw and peat, all ratios can increase SOC and the carbon content of each humus fractions of black soil. WSS-C content is increased with the increase of corn straw application amount; SOC, PQ and carbon content of other humus fractions are increased with the increase of peat application amount.

(ⅱ) Applied different proportional mixtures of corn straw and peat, the more the proportion of peat, the stronger the aromatic nature of HA structure, the more stable and complex the structure of HA, and the more the proportion of corn straw, the stronger the aliphatic nature of HA structure, and the simpler the structure of HA.

(ⅲ) Comprehensive consideration of the changes of humus composition, and HA structural characteristics of black soil, the 2:1 ratio of corn straw and peat was appropriate. Under this ratio, SOC and WSS-C contents increased by 34.8% and 30.6%, respectively, and the HA structural aromaticity and aliphatic proportional were appropriate.

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