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Soil organic carbon characteristics affected by peanut shell biochar in saline-sodic paddy field

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Abstract: Biochar exhibits a profound impact on soil organic carbon (SOC) turnover and dynamics, but the underlying mechanism under field conditions is still unclear. A three-year field experiment was performed to evaluate the impact of peanut shell biochar applied at rates of 0, 33.75, 67.5, and 101.25 t/ha (referred to as B0, B1, B2, and B3, respectively) on SOC content and chemical composition in a saline-sodic paddy field using stable carbon isotope composition and ^{13}C nuclear magnetic resonance technology. With increasing rates of biochar, SOC and aromatic carbon contents and alkyl carbon/oxygen-alkyl carbon and hydrophobic carbon/hydrophilic carbon ratios increased, while alkyl carbon and oxygen-alkyl carbon contents and aliphatic carbon/aromatic carbon ratio decreased. The new carbon from biochar and rice residues accounted for 26.5% of SOC under B0 and increased to above 80.0% under B2 and B3. The decay rate of old carbon was faster in biochar-amended than in unamended soil. SOC content was positively correlated with alkyl carbon/oxygen-alkyl carbon and hydrophobic carbon/hydrophilic carbon ratios but negatively correlated with aliphatic carbon/aromatic carbon ratio. The results suggest that biochar can increase SOC content by increasing its humification, aromaticity, and hydrophobicity. However, negative priming is not the main mechanism for SOC accumulation during the short-term period.

Keywords: carbon accumulation; biochar rate; saline-alkali soil; priming effect; *Oryza sativa* L.

Saline-alkali soil is widely distributed on the earth and occupied approximately 9.5×10^8 ha at present (Li et al. 2021). The Songnen Plain in northeast China are the main saline-alkali area around the world and covers approximately 2.39×10^6 ha (Gong et al. 2021). The saline-alkali soil (referred to as saline-sodic soil) in this plain is characterised by high pH, excessive Na^+, poor structure, low nutrients levels, and limited microbial activity (Yao et al. 2021), which consequently inhibited crops growth and yield. It has been well known that soil organic carbon (SOC) is of great importance in maintaining soil productivity and ecosystem sustainability because of its positive contribution to various soil properties including pH buffering, structural stability, nutrient retention and availability, and biological activity (Ramesh et al. 2019, Han et al. 2020). Therefore, it is necessary to raise SOC accumulation for the reasonable ameliorate and exploitation of saline-alkali soil.

Biochar, known as new black gold, is produced through pyrolysis of biomass materials under oxygen-deficient conditions. Due to its great surface area, high charge density, stable porous structure, and rich carbon content (Zhang et al. 2021), biochar

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Table 1. Basic properties of soil and peanut shell biochar used in this experiment

	pH	SOC	Total C	Total N	Total P	Total K	Na	Ca	Mg	Total PAHs (mg/kg)
		(g/kg)								
Soil	10.1	3.71	–	0.27	0.12	1.73	–	–	–	–
Biochar	7.94	–	540.6	15.9	0.74	12.5	1.17	2.01	0.25	3.40

SOC – soil organic carbon; PAHs – polycyclic aromatic hydrocarbons

application displayed a profound influence on SOC accumulation (Han et al. 2020). But the underlying mechanism of SOC accumulation following biochar amendment under a realistic field condition is still unclear. Some researchers reported that biochar inhibited native SOC mineralisation (i.e., negative priming), while some other researchers observed that biochar stimulated (i.e., positive priming) or had no impact on native SOC degradation (Ding et al. 2018). The contradictory results could be attributed to many factors like soil type, biochar property, biochar rate, and duration period.

Peanut shell is an abundant and inexpensive byproduct of peanut production. One of the most promising ways to utilise peanut shells is through pyrolysis to produce biochar, which can be used as a desired amendment for soil fertility improvement (Wang et al. 2020, Dominchin et al. 2021). In a previous study, Yao et al. (2021) have observed that the application of peanut shell biochar had a positive influence on rice yield, soil nutrients, and soil enzyme activity but exhibited a negative influence on the Na^+/K^+ ratio in a saline-sodic paddy field. This study aimed to further examine the impact of peanut shell biochar on SOC content and chemical composition in a field experiment. Meanwhile, the contents of SOC from peanut shell biochar and native soil were individually quantified to evaluate positive or negative priming of biochar on native SOC degradation. We hypothesised that biochar application can enhance SOC accumulation by inhibiting native SOC mineralisation and altering SOC chemical composition in this experimental soil.

MATERIAL AND METHODS

Field experimental design. This experiment was initiated in April 2017 at the Sheli County (45°35'N, 123°50'E), Jilin province, China. This site featured a temperate semi-arid continental monsoon climate. The mean annual temperature is 4.7 °C with rainfall of approximately 413.7 mm. The saline-sodic soil is developed from Fluvial and Lacustrine Deposits and has a loamy clay texture. The peanut shell biochar used in this study was prepared *via* pyrolysis of the peanut shell in a kiln (350–550 °C, 4 h). Prior to this experiment, the field had been continuously cultivated with rice for three years without fertilisation. The soil and biochar characteristics can be found in Yao et al. (2021) as well as in Table 1. Solid-state ^{13}C cross-polarisation magic-angle-spinning (CPMAS) NMR (nuclear magnetic resonance) analysis showed that aromatic C was the predominant component in the biochar (Figure 1).

In this study, a completely randomised block experiment consisting of four treatments and three repetitions was selected: no biochar application (B0), and biochar application rates at 33.75 (B1), 67.5 (B2), and 101.25 (B3) t per hectare, respectively. An alone irrigation and drainage outlet was set for each plot (5 m × 6 m), and all plots were separated from each other through a buffer row. The rice cultivar cultivated was Changbai9. Before rice transplantation, biochar was evenly spread on the soil surface and then ploughed to approximately 15 cm depth. However, biochar was not applied afterwards. The rice seedlings

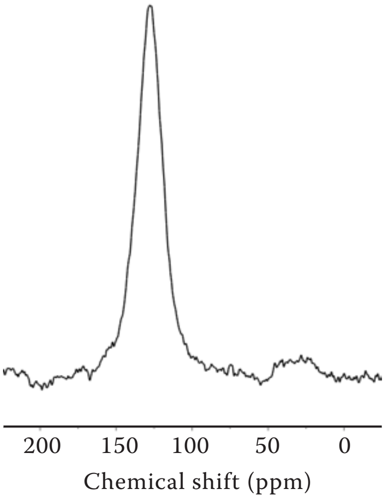

Figure 1. Solid-state ^{13}C NMR (nuclear magnetic resonance) spectra of peanut shell biochar

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40 days after sowing were manually transplanted from the greenhouse to the field at 16.5 cm × 30 cm spacing with three seedlings per hill in May 2017. For each treatment, mineral fertilisers were applied in the forms of ammonium sulfate (or urea), diammonium phosphate, and potassium sulfate. The annual application rates and timings of mineral fertilisers were 90.0 kg N, 30.1 kg P, and 31.0 kg K per hectare before rice transplanting, 69.0 kg N per hectare at the tilling stage, and 27.6 kg N and 20.7 kg K per hectare at the panicle stage. After harvesting, rice straw was removed but root and stubble residues were left in the field. More details on this field experiment can be found in Yao et al. (2021).

Soil sampling and analysis. After rice harvest in 2019, composite soil samples (0–20 cm) were taken from five randomly selected sites in each replicated plot. The soil samples were air-dried and sieved through a 2 mm sieve.

SOC content was determined by $K_2Cr_2O_7$ and the H_2SO_4 oxidation method. Carbon (C) stable isotope composition ($\delta^{13}C$) of soil samples after removing carbonate using 1 mol/L HCl solution were measured with Finnigan MAT-253 isotope ratio mass spectrometer (Thermo Fisher, Bremen, German). The proportion of new C (f_{new}, C from peanut biochar and rice residues) and the decay rate constant for old C (k, C from native soil) were calculated as follows (Balesdent and Mariotti 1996, Dou et al. 2018):

$$f_{new} = [(\delta_{new} - \delta_{old})/(\delta_{br} - \delta_{old})] \times 100\% \qquad (1)$$

$$k = -\ln (f_{old})/t \qquad (2)$$

where: δ_{new} – $\delta^{13}C$ values of SOC in biochar-amended soil; δ_{old} – $\delta^{13}C$ values of SOC in native soil (–21.4‰); δ_{br} – average $\delta^{13}C$ value (–26.0‰) of biochar (–24.4‰) and rice residues (–27.5‰); f_{old} (i.e., $1 - f_{new}$) – proportion of old C; t – duration of field experiment (three years).

Solid-state ^{13}C CPMAS NMR spectra were acquired on Avance III 400 WB spectrometer (Bruker BioSpin, Fallanden, Switzerland) at 100.57 MHz and applied a spinning speed of 8 kHz, a 20 ms acquisition time, and a 2 ms contact time. Semi-quantification was conducted by integrating each chemical shift region through MestReNova 5.3.1 package (Mestrelab Research, Santiago de Compostela, Spain). The alkyl C to O-alkyl C (A/O-A), aliphatic C to aromatic C (Ali/Aro), and hydrophobic C to hydrophilic C (HB/HI) ratios were calculated (Zhang et al. 2019).

Statistical analysis was done with SPSS 16.0 (Chicago, USA). A one-way ANOVA following Fisher's *LSD* (least significant difference) test was applied to compare differences among treatment means at $P < 0.05$. The relationships between SOC content and its chemical composition were evaluated with Pearson correlation at $P < 0.05$ and $P < 0.01$.

RESULTS AND DISCUSSION

Rice yield. The rice grain yields during 2017–2019 are presented in Figure 2. Compared with the B0 treatment, rice yields were significantly higher under B1, B2, and B3 treatments during the three years field experiment. Although rice yields were not significantly different among B1, B2, and B3 treatments during the first year of this experiment, significantly higher rice yields under B2 and B3 than under B1 treatment were observed. There were no significant differences between B2 and B3 treatments during the three years experiment.

SOC content and carbon stable isotope composition. The SOC content was not significantly different between the B0 and B1 treatments. However, SOC content was significantly higher in B2 and B3 compared to B1 treatment. As expected, the B3 treatment exhibited the highest SOC content among all the treatments. The $\delta^{13}C$ value in B1 was significantly lower than that in B0 treatment. With increasing biochar rates, $\delta^{13}C$ value further declined, but no significant differences were found between B2 and B3 treatments. After three years of field experiment, the proportion of new C was 26.5% in B0 treatment and increased to above 80.0% in B2 and B3 treatments. On the contrary, the proportion of old C was 73.5%

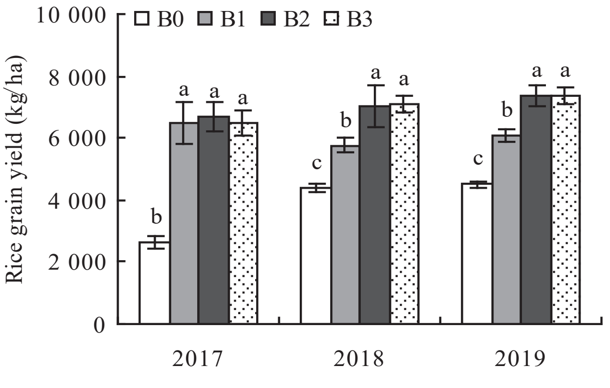

Figure 2. Rice grain yield during 2017–2019 in a saline-sodic paddy field amended with peanut shell biochar: B0 – 0, B1 – 33.75, B2 – 67.5, B3 –101.25 t/ha. Vertical bars represent the standard deviation of means ($n = 3$). Different small letters indicate significant differences among treatments ($P < 0.05$)

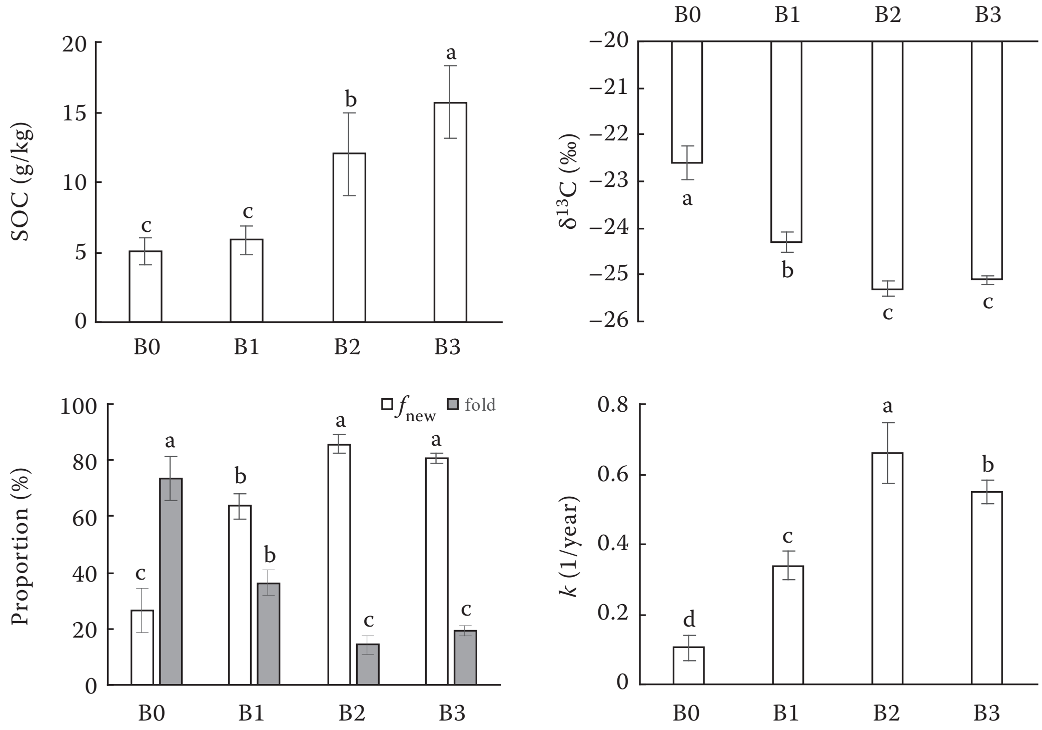

Figure 3. Soil organic carbon (SOC) content, stable carbon isotope composition ($\delta^{13}C$), the proportion of new C from biochar and rice residues (f_{new}), and proportion (fold) and decay rate constant (k) of old C from native soil in a saline-sodic paddy field amended with peanut shell biochar: B0 – 0, B1 – 33.75, B2 – 67.5, B3 –101.25 t/ha. Vertical bars represent the standard deviation of means (n = 3). Different small letters indicate significant differences among treatments ($P < 0.05$)

in the B0 treatment and decreased to below 20.0% in B2 and B3 treatments. Accordingly, the decay rate of old C was faster for biochar-amended than for unamended soil (Figure 3).

Previous studies showed that SOC content gradually increased with increasing peanut shell biochar application rates (Bhaduri et al. 2016, Liu et al. 2019), in agreement with our present finding. The increment in SOC content following biochar addition was generally ascribed to the input of C-rich biochar, the high stability of biochar C (Han et al. 2020), the negative priming influence of biochar on native SOC degradation (Liu et al. 2018), and the adsorption affinity of biochar for some C fractions such as humic acids (Kasozi et al. 2010). However, our present results supported the positive rather than negative priming of biochar for SOC degradation. The possible mechanisms for the positive priming influence included the stimulation of biochar to soil microbes for C decomposition (Zheng et al. 2021) and the inducement of labile C fractions from biochar to soil microbial activity (Maestrini et al. 2015). It was generally suggested that positive priming occurred in a short term, but negative priming occurred in the long term (Ding et al. 2018). A longer-term experiment was needed to verify the positive or negative priming influence under this field condition.

SOC chemical composition. The NMR spectra (Figure 4) were comprised of alkyl C (0–50 ppm), O-alkyl C (50–110 ppm), aromatic C (110–160 ppm), and carboxyl C (160–190 ppm). Compared with B0 treatment, B1 treatment exhibited significantly lower proportions of alkyl C, O-alkyl C, and carboxyl C whereas a significantly higher proportion of aromatic C. With increasing biochar rates, the proportions of alkyl C, O-alkyl C, and carboxyl C further decreased, while the proportion of aromatic C further increased in B2 and B3 than in B1 treatment. No significant differences were found between B2 and B3 treatments. When expressed in terms of content, alkyl C and O-alkyl C contents were also generally lower whereas aromatic C content was higher after biochar application (Figure 5). The chemical composition of biochar has a profound impact on that of SOC in native soil amended with the biochar (Zhang et al. 2019). In this study, peanut shell biochar was

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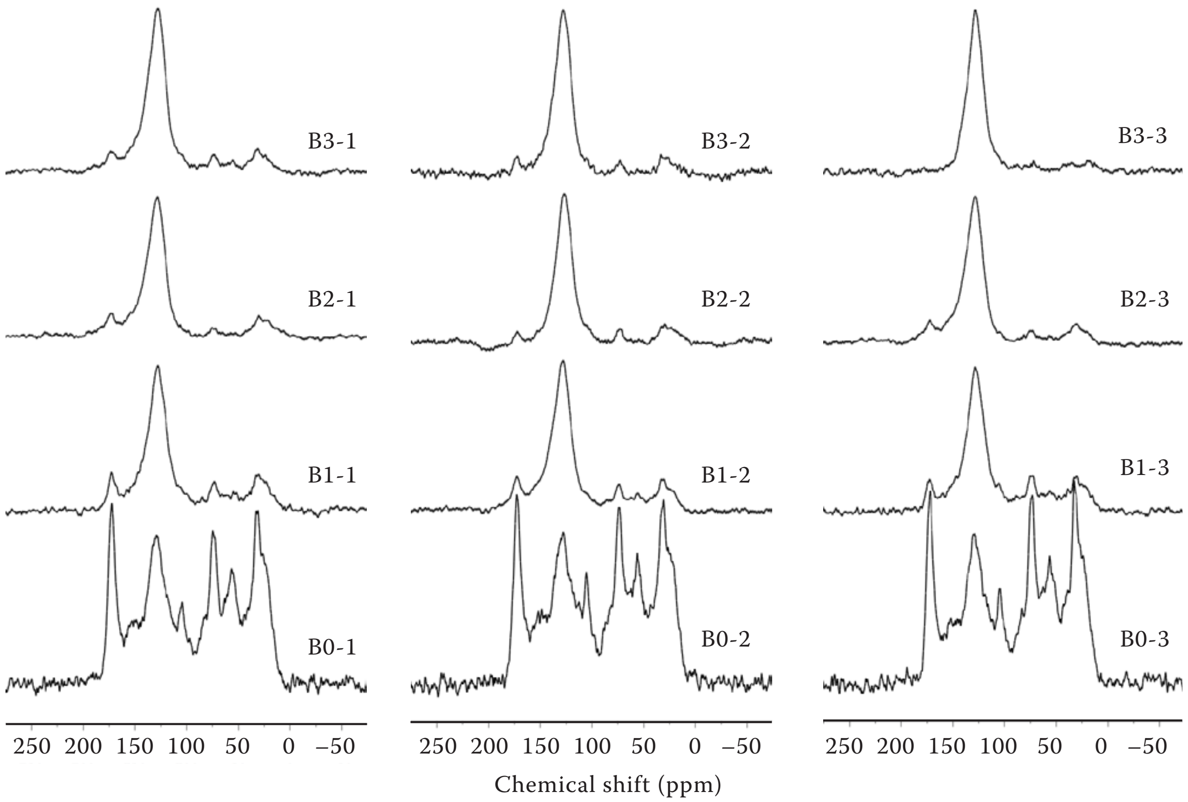

Figure 4. Solid-state ^{13}C NMR (nuclear magnetic resonance) spectra of soil samples in a saline-sodic paddy field amended with peanut shell derived biochar: B0 – 0, B1 – 33.75, B2 – 67.5, B3 –101.25 t/ha. The numbers 1 to 3 after B0, B1, B2, and B3 in the subplots represent three replicates from each treatment

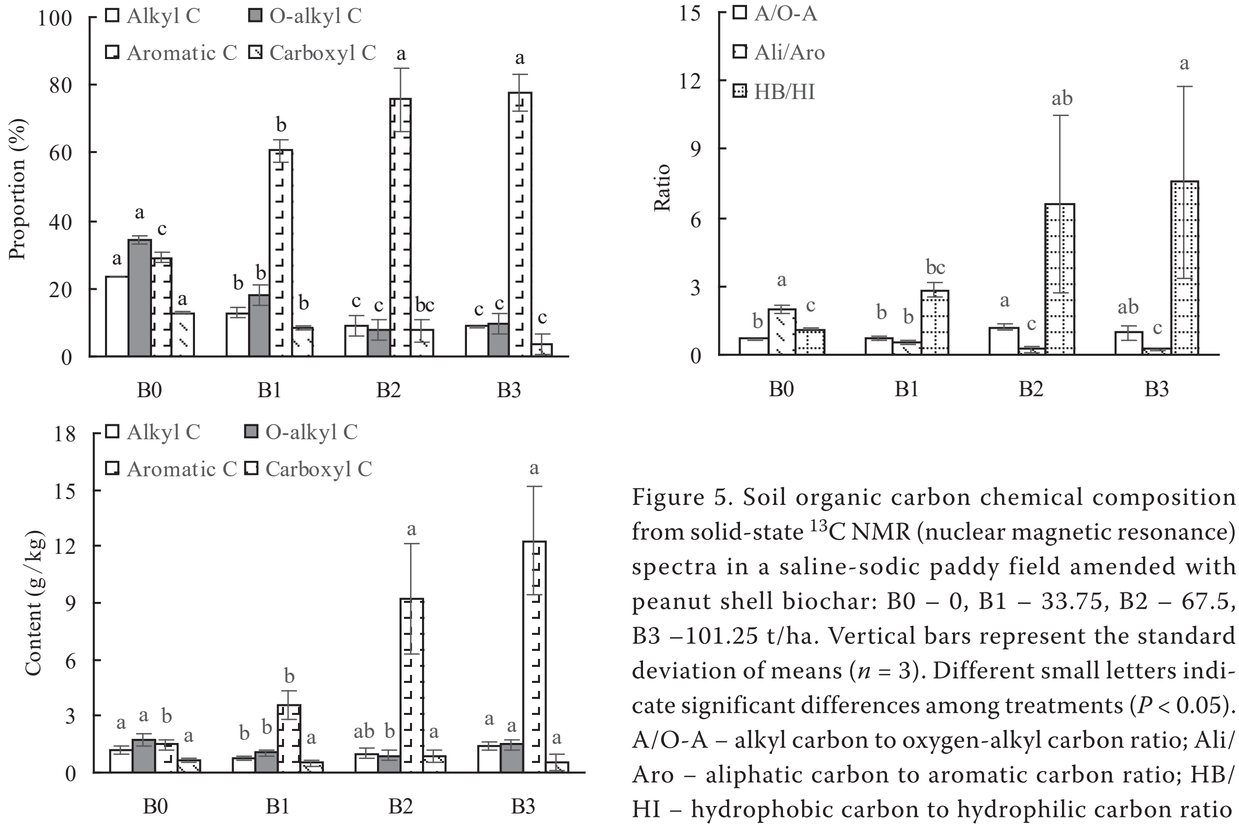

Figure 5. Soil organic carbon chemical composition from solid-state ^{13}C NMR (nuclear magnetic resonance) spectra in a saline-sodic paddy field amended with peanut shell biochar: B0 – 0, B1 – 33.75, B2 – 67.5, B3 –101.25 t/ha. Vertical bars represent the standard deviation of means ($n = 3$). Different small letters indicate significant differences among treatments ($P < 0.05$). A/O-A – alkyl carbon to oxygen-alkyl carbon ratio; Ali/Aro – aliphatic carbon to aromatic carbon ratio; HB/HI – hydrophobic carbon to hydrophilic carbon ratio

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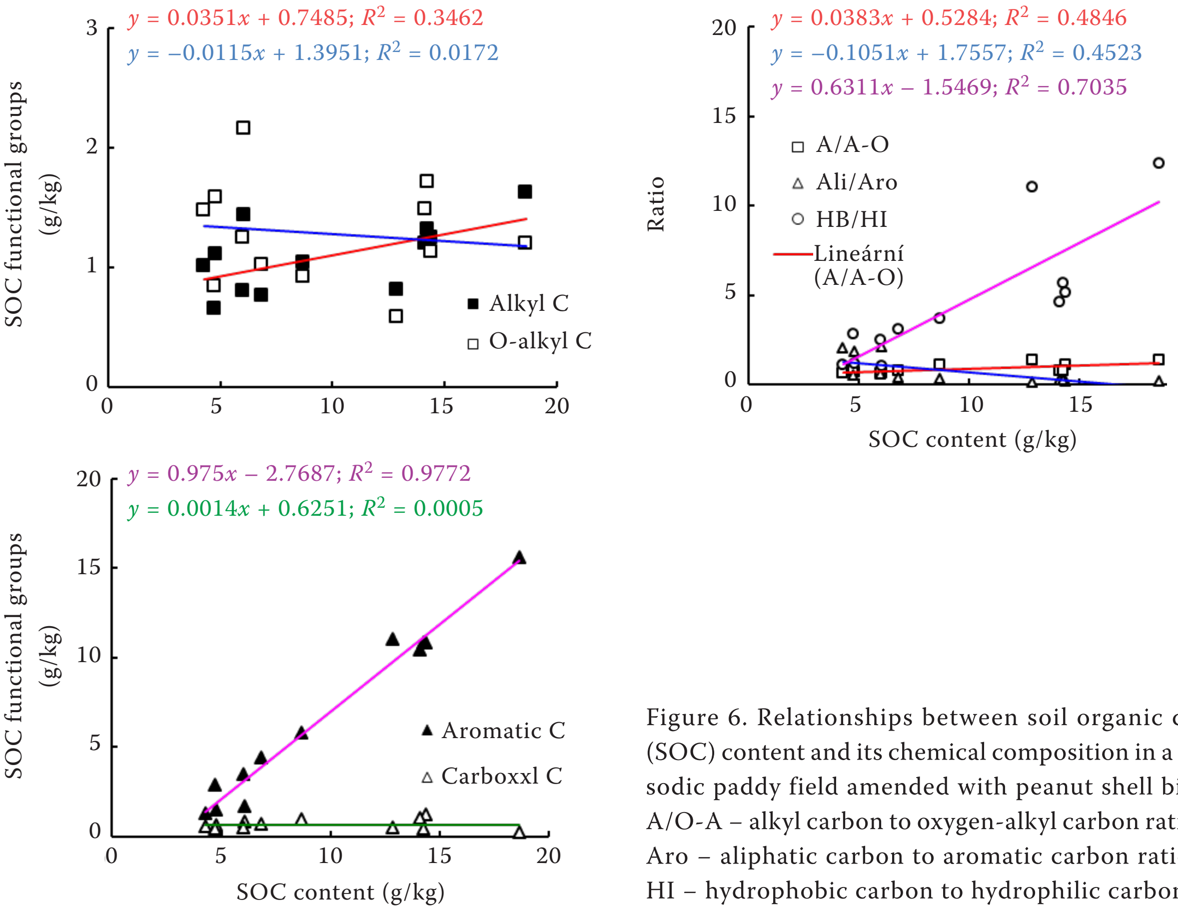

Figure 6. Relationships between soil organic carbon (SOC) content and its chemical composition in a saline-sodic paddy field amended with peanut shell biochar. A/O-A – alkyl carbon to oxygen-alkyl carbon ratio; Ali/Aro – aliphatic carbon to aromatic carbon ratio; HB/HI – hydrophobic carbon to hydrophilic carbon ratio

dominated by aromatic C (Figure 1), which could be responsible for the significant increase in aromatic C after the peanut shell biochar amendment.

The A/O-A and HB/HI ratios tended to increase but Ali/Aro ratio tended to be decreased with increasing biochar rates. Significant differences were found between B0 and B1 with B2 treatments for A/O-A ratio, between B0 with B1, B2, and B3 and between B1 with B2 and B3 treatments for Ali/Aro ratio, and between B0 with B2 and B3 and between B1 and B3 treatments for HB/HI ratio (Figure 5). The ratios of A/O-A, Ali/Aro, and HB/HI have been considered as indicators to evaluate the degrees of humification, aliphaticity, and hydrophobicity of SOC (Zhang et al. 2017). In this study, the changes in these ratios suggested that the molecular structure of SOC became more humified (or decomposed), less aliphatic, and more hydrophobic after peanut shell biochar amendment. At this experimental site, Yao et al. (2021) found that peanut shell biochar application could enhance soil catalase, alkaline phosphatase, urease, and sucrose activities, which could explain the larger decomposition degree of SOC in this study. Previously, Bi et al. (2020) observed that rice straw biochar addition increased the A/O-A ratio in Yellow river alluvium paddy soil while decreasing this ratio in quaternary red clay paddy soil. The influences of soil properties on SOC functional groups compositions needed to be further studied in the further study.

Relationships between SOC content and its chemical composition. Pearson correlation showed that SOC content was positively correlated with alkyl C (r = 0.588, $P < 0.05$) and aromatic C (r = 0.989, $P < 0.01$) contents and A/O-A (r = 0.696, $P < 0.05$) and HB/HI (r = 0.839, $P < 0.01$) ratios but negatively correlated with Ali/Aro ratio (r = –0.673, $P < 0.05$) (Figure 6). It suggested that the increases in humification, aromaticity, and hydrophobicity were responsible for the increment of SOC content. A main mechanism for SOC accumulation in the biochar-amended soil was through the biochemical protection from recalcitrant SOC functional groups.

In conclusion, peanut shell biochar amendment can increase SOC content by increasing its humification, aromaticity, and hydrophobicity. The biochemical protection by recalcitrant SOC functional groups (i.e., alkyl C and aromatic C) is considered the main mechanism of SOC accumulation in the biochar-amended soil. However, negative priming is not the main mechanism for SOC accumulation during the short-term period. A longer-term experiment was needed to confirm the present conclusions. It is notable that the biochar used contains a certain amount of polycyclic aromatic hydrocarbons (PAHs) (Table 1). The potential threats of PAHs in the biochar to soil environment need to be evaluated before they can be used on a widespread scale.

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