

Molecular Fingerprint-regulated Cu(II) Adsorption in Acidic Soil by Biomass Burning Smoke-derived DOM: Feedstock Specificity and Aging Effects

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Abstract

Purpose

Biomass burning smoke-derived dissolved organic matter (BBS-DOM) is annually deposited in massive quantities into terrestrial ecosystems, yet its impacts on heavy metal geochemistry in acidic soils remain poorly characterized.

Methods

We investigated the 3-month dynamic effects of six BBS-DOMs derived from alfalfa, pinewood, and corn straw combustion on Cu(II) adsorption in an acidic soil, combining UV-Vis, EEM-PARAFAC and FT-ICR MS.

Results

Feedstock-specific bidirectional effects strongly modulated by aging: alfalfa-BBS-DOM consistently promoted Cu(II) adsorption, with $4648 \text{ L} \cdot \text{kg}^{-1} K_d$ in unaged soil and remaining 7.8 ~ 8.4-fold higher than control throughout incubation; pinewood/corn straw-BBS-DOM initially inhibited or had no significant promotive effect on soil Cu(II) adsorption, with K_d increasing by 187.2%~206.8% in the first month but returning to control levels after 3 months. Molecular characterization revealed alfalfa-BBS-DOM was dominated by nitrogen-enriched large humic-like matters (CHON and CHONP compounds), while pinewood/corn straw-BBS-DOM mainly consisted of oxygen-rich polyphenol-like matters dominated (CHO compounds). Mechanistically, these divergent effects arise from the coupled regulation of aqueous-phase complexation and soil-surface interactions on Cu(II) adsorption: protonated amino ($-\text{NH}_2$) groups in alfalfa-BBS-DOM inhibit soluble DOM-Cu(II) complex formation in the aqueous phase, while negatively charged $-\text{SO}_3^-$, $-\text{H}_2\text{PO}_3^-$, and $-\text{COO}^-$ groups enable alfalfa-BBS-DOM to strongly adsorb to soil surfaces; the adsorbed alfalfa-BBS-DOM retains these negatively charged functional groups, which attract Cu(II) ions. Conversely, $-\text{COOH}$ and phenolic-OH groups in pinewood/corn straw-BBS-DOM form soluble aqueous complexes with Cu(II).

Conclusion

This study provides a mechanistic basis for heavy metal risk assessment in wildfire-affected ecosystems.

1. Introduction

Global climate change and intensive agricultural activities have led to a marked increase in the frequency and scale of biomass burning events, including wildfires and uncontrolled crop residue combustion, which emit massive amounts of biomass burning smoke-derived dissolved organic matter (BBS-DOM) (Senande-Rivera et al., 2022; Xue et al., 2024; Zhu et al., 2025), which accounts for 40%~92% of the total organic aerosols in the atmosphere (Liu et al., 2022; Ponczek et al., 2022). While existing studies have predominantly focused on the atmospheric environmental effects of BBS-DOM, such as solar radiation absorption (Li et al., 2020; Tomaz et al., 2018), haze formation (Wu et al., 2013; Wu et al., 2019), transportation of pollutants (Ghetu et al., 2022; Rice et al., 2023) and human health hazards (Aguilera et al., 2021), the atmosphere is not the ultimate sink for BBS-DOM. Annually, approximately $0.53 \sim 0.95 \times 10^{12}$ kg of BBS-DOM is deposited into surface environments via atmospheric deposition, with nearly 50% entering soil ecosystems (Huang et al., 2022; Jurado et al., 2008). Accordingly, BBS-DOM exhibits a distinct cross-media environmental behavior, and its deposition into soil may profoundly alter the geochemical behavior and environmental risk of heavy metals in terrestrial ecosystems (Chen et al., 2022; Ren et al., 2015).

Exogenous DOM is widely recognized as a key regulator of heavy metal adsorption, migration, and bioavailability in soil (Lian et al., 2022; Zhang et al., 2024). DOM is rich in oxygen-containing functional groups (e.g., -COOH, Phenolic-OH) and aromatic structures, which can form stable complexes with heavy metal cations, thereby directly affecting their solid-liquid partitioning in soil (Cheng et al., 2024; Wu et al., 2025; Ye et al., 2025). However, the effects of DOM on heavy metal adsorption are highly controversial: numerous studies have reported that DOM promotes heavy metal adsorption via surface complexation (Tan et al., 2017; Wei et al., 2026; Wu et al., 2025), while others have demonstrated inhibitory effects due to site competition and the formation of soluble DOM-metal complexes (Chen et al., 2025; Qin et al., 2025; Wang et al., 2020). This controversy largely stems from the high heterogeneity of DOM molecular composition, which is determined by its source and formation process. Compared with natural soil DOM and biochar-derived DOM, BBS-DOM exhibits unique molecular characteristics: higher aromaticity, smaller average molecular weight, and higher abundance of polyphenolic and protein-like matters, oxygen/nitrogen-enriched aromatic compounds (Chen et al., 2025; Zhang et al., 2023; Zhang et al., 2022). These distinct features suggest that BBS-DOM may exert differential effects on soil heavy metal adsorption compared with conventional DOM sources. However, the direction and extent of the influence of BBS-DOM on the adsorption of heavy metals in the soil, as well as the key controlling factors, remain largely unclear.

Acidic soils cover approximately 30% of the global land area and more than 50% of potential arable land, supporting 40%~50% of global crop production (Liu et al., 2023; Meena et al., 2019; Ye et al., 2026). In China, acidic red soil accounts for over 20% of the total land area, and soil acidification and heavy metal (especially Cu(II)) contamination have become increasingly prominent environmental issues in this region (Hou et al., 2025; Wang et al., 2017). Cu(II) is a typical heavy metal widely detected in agricultural soils, with strong biotoxicity, accumulation potential, and high binding affinity to organic matter (Huang et al., 2021; Yan et al., 2023). In acidic soils, high H^+ concentration intensifies the competition for

adsorption sites with Cu(II), making the adsorption of Cu(II) highly sensitive to changes in soil organic matter properties and pH (Wang et al., 2024). Nevertheless, current research on the effects of BBS-DOM on acidic soil properties and Cu(II) adsorption behavior is still in its infancy.

Importantly, the molecular composition and physicochemical properties of BBS-DOM are inherently feedstock-dependent (Zhang et al., 2021; Zhang et al., 2023). Biomass feedstocks differ dramatically in their elemental stoichiometry (C/N/P/S ratios), lignocellulosic structure, and secondary metabolite content, which are faithfully transmitted to the combustion products (Yu et al., 2026). These molecular-level differences directly determine the reactivity of BBS-DOM with heavy metals and soil minerals (Cheng et al., 2024; Zhong et al., 2024), leading to potentially divergent effects on Cu(II) adsorption. Furthermore, once deposited into soil, BBS-DOM does not remain chemically inert but undergoes a dynamic aging process involving microbial mineralization, abiotic oxidation, adsorption-desorption, and intermolecular polymerization (Hu et al., 2017; Luo et al., 2019). Concurrently, BBS-DOM aging modulates key soil physicochemical properties including pH, cation exchange capacity, and surface area, which collectively reshape the soil's adsorption capacity for heavy metals over time. Specifically, two critical scientific gaps remain to be addressed: (1) How do BBS-DOM derived from different feedstocks affect Cu(II) adsorption in acidic red soil, and what is the underlying molecular-level mechanism governing these divergent effects? (2) How does the aging process dynamically regulate the effects of BBS-DOM on Cu(II) adsorption in acidic soils?

To fill these gaps, we proposed the following scientific hypotheses: (1) BBS-DOM derived from different feedstocks will exert different effects on soil Cu(II) adsorption, which is determined by their intrinsic molecular and spectral characteristics, chemical complexation mediated by the distinct molecular fingerprints of various BBS-DOM is the dominant mechanism driving these divergent effects. (2) The aging process will dynamically regulate the effects of BBS-DOM via selective mineralization of labile components and enrichment of recalcitrant humic-like matters. To verify these hypotheses, we prepared six BBS-DOM samples from three typical biomass raw materials (alfalfa, pine wood, and corn stalks), and subjected them to pyrolysis under both smoldering and flaming combustion conditions, characterized their molecular and spectral properties via UV-Vis, Fluorescence excitation-emission matrix (EEM), and FT-ICR MS. We then conducted a 3-month aging incubation experiment to investigate the dynamic changes in soil physicochemical properties, DOM characteristics, and Cu(II) adsorption behavior after BBS-DOM input, to elucidate the molecular-level mechanisms. This study aims to advance the understanding of the cross-media environmental effects of BBS-DOM and provide a theoretical basis for heavy metal pollution risk assessment and control in wildfire-affected acidic soil ecosystems.

2. Materials and Methods

2.1 Preparation and characterization of BBS-DOM

In this study, three types of biomass feedstocks were selected to produce BBS-DOM: pinewood (PW, representative of wood combustion), corn straw (CS, representative of agricultural straw combustion),

and alfalfa (AF, representative of herbaceous combustion). All biomass materials were cut into pieces of < 1 cm in length, rinsed with ultrapure water, and dried in an oven at 80 °C for 12 h. Subsequently, combustion was performed in a muffle furnace at target temperatures of 300 °C (smoldering) and 600 °C (flaming), with a heating rate of 20 °C/min and a holding time of 3 h at the set temperature. The generated smoke first passed through an empty glass buffer bottle, then into a second glass buffer bottle containing 500 mL of ultrapure water. Both buffer bottles were immersed in an ice-water bath to enable rapid cooling of the smoke and facilitate efficient collection of BBS-DOM. After 3 h of combustion, the collected BBS-DOM solution was ultrasonicated for 30 min at 100 W to dissolve organic matter adsorbed on water-insoluble particulates into the aqueous phase. The solution was then filtered through a 0.45 µm membrane filter (Chen et al., 2025; Zhang et al., 2022; Zhang et al., 2025). The final BBS-DOM samples (PW300, PW600, CS300, CS600, AF300, and AF600) were stored in a refrigerator at 4 °C until further use, the number in the name of BBS-DOM represents the burning temperature.

2.2 UV-vis and Fluorescence spectroscopic determination

BBS-DOM samples were measured using the UV-Vis spectrophotometer (Shimadzu, Japan) with the detailed procedure shown in **Text S1**. The UV-Vis spectral curves of BBS-DOM samples are shown in **Fig. S1**. Spectral indices including specific UV absorbance at 254 nm ($SUVA_{254}$) and molecular weight index ($S_{275-295}$) were calculated with their specific calculation methods shown in **Text S1**. $SUVA_{254}$ was positively correlated with DOM aromaticity (Li et al., 2017; Zhang et al., 2023). Furthermore, $S_{275-295}$ is the spectral slope obtained by linear fitting of the exponential absorption coefficient in the 275–295 nm wavelength range, with values inversely proportional to DOM molecular size (Xu et al., 2017; Yu et al., 2023).

The BBS-DOM solutions were used to perform fluorescence spectroscopic analysis. The samples were initially diluted to a DOC concentration below 10 mg-C/L to correct inner-filter effects (Zhang et al., 2021; Zhang et al., 2023). The EEM-PARAFAC analysis of the data set was performed using MATLAB R2023a (the DOMFluor Toolbox) (Quan et al., 2020). The concrete determination and EEM-PARAFAC process was provided in **Text S1**. After EEM-PARAFAC analysis, four fluorescent components (C1 ~ C4 in Fig. 1a) were obtained.

2.3 FT-ICR MS analysis of BBS-DOM

Prior to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis, BBS-DOM samples were desalted and concentrated via solid phase extraction (SPE) using Bond Elut PPL cartridges (300 mg, 3 mL, Agilent Technologies, USA). BBS-DOM was then eluted with 2 mL of HPLC-grade methanol into amber glass vials and stored at -20 °C until analysis. Molecular characterization of BBS-DOM was performed using a 9.4 T Solaris X FT-ICR MS system (Bruker Daltonics, USA) equipped with an electrospray ionization source operated in negative ion mode. Molecular formulas were assigned to peaks with a signal-to-noise ratio > 6, with elemental constraints set as $C \geq 1$, $H \geq 1$, $O \geq 0$, $N \leq 6$, $P \leq 3$, $S \leq 3$. H/C vs. O/C van Krevelen diagrams of the identified molecules are provided in **Fig. S3**. Compounds

were classified into groups based on elemental composition (e.g., CHO, CHON, CHONP, CHONS, CHONSP, CHOS, CHOP, and other compounds), as detailed in **Text S2**. Molecular parameters including H/C ratio, O/C ratio, double bond equivalent (DBE), modified aromaticity index (AI_{mod}), DBE/C ratio, and molecular weight were calculated based on the assigned molecular formulas, with interpretations of these indices provided in **Table S1**. Detailed operating parameters of the FT-ICR MS and calculation methods for molecular parameters are described in **Text S2**.

2.4 Soil selection and aging incubation experiment

In this study, unpolluted red soil collected from a pine forest in Xinyu, Jiangxi Province, China, was used as the test acidic soil. The physicochemical properties of the original soil are presented in **Table S2**. To systematically investigate the effects of BBS-DOM on Cu(II) adsorption by soil over different aging durations, the as-prepared BBS-DOM solutions were mixed with soil at a mass ratio of 1:1000 (BBS-DOM to soil). Two aging time points, 1 month and 3 months, were set to simulate the short-term and medium-term aging processes of BBS-DOM in the natural environment. Initially, 100 g of soil was thoroughly mixed with each type of BBS-DOM solution respectively. The original soil treatment without BBS-DOM addition was set as the control group. The mixed soil samples were transferred into Erlenmeyer flasks, and an appropriate volume of deionized water was added to maintain the soil moisture content at 60% of the field water-holding capacity. Subsequently, the Erlenmeyer flasks were placed in a constant temperature and humidity incubator for aging incubation at 25 °C. During the incubation period, soil moisture content was monitored regularly, and deionized water was supplemented as needed to maintain 60% field water-holding capacity, ensuring the stability of soil microbial activity and the BBS-DOM aging process. Subsamples of soil were collected from each treatment group after 1 month and 3 months of aging incubation, respectively. Immediately after sampling, the soil samples were freeze-dried to preserve their original physicochemical properties. The freeze-dried samples were used for subsequent determination of physicochemical properties and Cu(II) adsorption experiments. All treatments were performed in triplicate.

2.5 Characterization of soil and BBS-DOM-soil properties

The dissolved organic carbon (DOC) content of BBS-DOM was measured using a total organic matter analyzer (TOC-VCPH; Shimadzu, Japan). The total organic carbon content, DOC content, pH values, and the specific surface area (SSA), micropore surface area (MSA), soil cation exchange capacity (CEC) of soil samples were detected; the specific methods are shown in **Text S3**. BBS-DOMs-added soil-DOM was extracted at a soil-to-water mass ratio of 1:10. Briefly, a weighed mass of soil sample was mixed with deionized water in a 40 mL amber glass vial, then shaken continuously at 150 rpm for 24 h at 25 °C in a constant temperature shaker to ensure complete dissolution of BBS-DOMs-added soil-DOM. After shaking, the suspension was centrifuged at 2500 rpm for 10 min, and the supernatant was filtered through a 0.45 µm membrane filter to obtain the BBS-DOMs-added soil-DOM solution. The characterization of BBS-DOMs-added soil-DOM is consistent with the methods described in Section 2.2.

2.6 Adsorption experiments

Adsorption experiments were conducted in 20 mL centrifuge tubes, with 0.2 g of soil sample mixed with 20 mL of $\text{Cu}(\text{NO}_3)_2$ solution prepared in 0.01 M NaCl background electrolyte. Initial $\text{Cu}(\text{II})$ concentrations were set as 5, 10, 20, 40, 60, 80, and 120 mg/L. The pH of the suspension was adjusted to 5.8 ± 0.2 using 0.01 M NaOH. The tubes were shaken continuously at 200 rpm for 48 h at 25 °C to reach adsorption equilibrium. After equilibration, the suspensions were centrifuged at 2500 rpm for 10 min to completely separate soil particles, and the supernatant was filtered through a 0.22 μm membrane filter. The filtrate was acidified with 1% HNO_3 , and the equilibrium $\text{Cu}(\text{II})$ concentration was determined via inductively coupled plasma optical emission spectrometry (ICP-OES). Blank controls without soil were included in each batch to account for $\text{Cu}(\text{II})$ loss via sorption to tube walls. The equilibrium pH of each suspension was measured after the experiment. All treatments were performed in triplicate.

To quantify the $\text{Cu}(\text{II})$ adsorption performance of different treatments, adsorption data were fitted to the Freundlich and Langmuir isotherm models (Xu et al., 2019):

$$\text{Freundlich, } Q_e = K_F \cdot C_e^n \quad (1)$$

$$\text{Langmuir, } Q_e = Q_m \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \quad (2)$$

$$K_d = Q_e / C_e \quad (3)$$

Where Q_e (mg/g) is the equilibrium $\text{Cu}(\text{II})$ adsorption capacity of soil; C_e (mg/L) is equilibrium aqueous $\text{Cu}(\text{II})$ concentrations; n (dimensionless) is the Freundlich linearity index; Q_m (mg/g) is the maximum adsorption capacity from the Langmuir model; K_F ($\text{mg}^{1-n} \cdot \text{L}^n/\text{g}$) and K_L (L/mg) are the Freundlich affinity coefficient and Langmuir adsorption equilibrium constant, respectively. The solid-liquid distribution coefficient K_d (L/kg) is a core metric for evaluating the heavy metal adsorption capacity of soils and predicting the mobility and bioavailability of heavy metals. A higher K_d value indicates a stronger $\text{Cu}(\text{II})$ adsorption capacity of the soil and a lower environmental risk of the heavy metal (Wu et al., 2026; Yang et al., 2021). Based on realistic soil scenarios with varying levels of $\text{Cu}(\text{II})$ contamination in the natural environment, K_d values were calculated at three concentration gradients: low-level contamination ($C_e = 0.01 \pm 0.001$ mg/L, denoted as K_{d1}), medium-level contamination ($C_e = 0.1 \pm 0.01$ mg/L, denoted as K_{d2}), and high-level contamination ($C_e = 1.0 \pm 0.1$ mg/L, denoted as K_{d3}).

2.7 Data analysis

Analysis of variance (ANOVA) for significant differences was performed with variance analysis (a significant result of $p < 0.05$) using SPSS (version 27.0). The Pearson correlation analysis and plotting were performed using Origin 2021, with a significant result of $p < 0.05$. Redundancy analysis (RDA) was carried out using Canoco 5.

3. Results

3.1 The molecular and spectral characteristics of BBS-DOM

Four fluorescent components (Fig. 1a) were identified via EEM-PARAFAC analysis: C1 (Ex = 235 nm and 290 nm/Em = 374 nm, large humic-like matters), C2 (Ex = 265 nm and 350 nm/Em = 446 nm, fulvic-like matters), C3 (Ex = 235 nm and 325 nm/Em = 398 nm, large humic-like matters), and C4 (Ex = 215 nm and 275 nm/Em = 314 nm, polyphenol-like matters) (**Table S3**), with component interpretations consistent with previous studies (Gu et al., 2020; Qin et al., 2020; Ye et al., 2020). The relative abundance of fluorescent components varied significantly among different BBS-DOM samples (Fig. 1b). AF-BBS-DOM was dominated by humic-like fluorescent components (C1 + C3, 63%~65% of total fluorescence), while PW- and CS-BBS-DOM were predominantly composed of fluorescent component of polyphenol-like matters (C4, 58%~84% of total fluorescence). For PW and CS, BBS-DOM generated under flaming had higher C4 abundance than that under smoldering, while pyrolysis temperature had little effect on the component composition of AF-BBS-DOM, consistent with previous findings (Zhang et al., 2021; Zhang et al., 2022).

SUVA₂₅₄, a robust indicator of DOM aromaticity, showed that at the same pyrolysis temperature, the aromaticity of BBS-DOM followed the order of CS > PW > AF (Fig. 1c). For PW and CS, BBS-DOM generated under smoldering had significantly higher SUVA₂₅₄ than that under flaming ($p < 0.05$), while pyrolysis temperature had no significant effect on the aromaticity of AF-BBS-DOM. $S_{275-295}$, which is negatively correlated with DOM molecular weight, followed the order of CS > PW > AF, indicating that the molecular weight of BBS-DOM followed the order AF > PW > CS (Fig. 1d). For CS and AF, 600 °C BBS-DOM had significantly lower $S_{275-295}$ than 300 °C BBS-DOM, meaning flaming produced larger molecular weight DOM for these two feedstocks.

FT-ICR MS analysis revealed distinct differences in the molecular composition of BBS-DOM from different feedstocks (Fig. 1e, Table 1 and **Table S7**). PW- and CS-BBS-DOM were dominated by CHO compounds (relative intensity 0.67 ~ 0.80), with significantly higher abundance of CHOP and CHONSP compounds than AF-BBS-DOM ($p < 0.05$). These CHO molecules possess relatively high O/C ratios (up to 0.49 in PW600), indicating a high density of oxygen-containing functional groups, predominantly -COOH and phenolic-OH groups (Table 1). In contrast, AF-BBS-DOM had extremely high abundance of CHON (0.36 ~ 0.37) and CHONP (0.20 ~ 0.28) compounds, which were 4 ~ 18-fold higher than those in PW- and CS-BBS-DOM, the specific elemental constraints and relative molecular weights of these nitrogen-bearing molecules in AF-BBS-DOM point to a significant presence of nitrogen-containing functional groups, particularly amido(-NH₂) groups (Table 1), interwoven with oxygen-containing structures. This difference is directly attributed to the elemental composition of the raw feedstocks: the nitrogen content of AF (3.85 wt.%) is 3.4-fold that of CS (1.14 wt.%) and 55-fold that of PW (0.07 wt.%) (**Table S4**), and AF also has higher phosphorus content than CS and PW (Trubetskaya et al., 2016). Pyrolysis temperature had a negligible effect on the overall molecular composition of BBS-DOM compared with feedstock type.

Table 1
Properties of the main elemental molecules in various BBS-DOM

Compound	Properties	AF300	AF600	PW300	PW600	CS300	CS600
CHO	H/C	1.27	1.42	1.21	1.21	1.16	1.19
	O/C	0.46	0.45	0.49	0.49	0.49	0.49
	Al _{mod}	0.28	0.22	0.29	0.29	0.32	0.31
	DBE	6.44	4.97	7.22	7.19	7.32	7.03
	Mass	289.6	264.6	318.4	319.4	305.8	303.1
CHON	H/C	1.39	1.46	1.32	1.32	1.24	1.28
	O/C	0.32	0.33	0.45	0.51	0.42	0.41
	O/N	3.20	2.87	5.78	5.34	5.49	5.31
	Al _{mod}	0.25	0.20	0.28	0.31	0.31	0.29
	DBE	7.17	6.35	7.69	8.36	7.80	7.53
	Mass	319.4	306.0	347.1	360.6	320.8	324.4
CHONP	H/C	1.51	1.48	1.37	1.37	1.34	1.43
	O/C	0.25	0.20	0.27	0.27	0.29	0.38
	O/N	2.28	1.45	1.25	0.99	1.67	3.30
	Al _{mod}	0.18	0.21	0.34	0.34	0.34	0.23
	DBE	8.05	9.07	11.81	12.57	12.18	8.96
	Mass	387.3	401.8	429.6	450.0	431.0	384.8

The molecular characteristic parameters further confirmed the differences among BBS-DOM samples (Fig. 2 and **Fig. S2**). CS-BBS-DOM had the lowest molecular weight, while PW- and CS-BBS-DOM had lower H/C ratios, higher O/C ratios (polarity), DBE (unsaturation), Al_{mod} (aromaticity), and DBE/C ratios than AF-BBS-DOM. These results indicate that PW- and CS-BBS-DOM have lower aliphaticity, higher polarity, and higher unsaturation than AF-BBS-DOM, which is related to the higher cellulose and hemicellulose content in PW and CS (Trubetskaya et al., 2016; Yu et al., 2026). For CS and AF, BBS-DOM generated under smoldering had higher O/C ratio, Al_{mod}, and DBE/C ratio, and lower H/C ratio than that under flaming, indicating that smoldering produces BBS-DOM with higher polarity, aromaticity, and lower aliphaticity for these two feedstocks.

Based on Pearson correlation analysis, we clarified the coupling relationship between fluorescent components and molecular composition (**Fig. S4** and **S5**): the relative abundance of fluorescent

components of humic-like matters (C1 and C3) was extremely significantly positively correlated with the relative intensity of CHON/CHOS/CHONP/CHONS-class aromatic macromolecules (these molecules having high AI_{mod} , high DBE, and high O/C) ($p < 0.001$); while the relative abundance of fluorescent component of polyphenol-like matters (C4) was extremely significantly positively correlated with the relative intensity of CHO-class monocyclic/bicyclic aromatic small molecules with low molecular weight and low unsaturation ($p < 0.001$).

Overall, the molecular and spectral characteristics of BBS-DOM are strongly feedstock-specific: AF-BBS-DOM is characterized by high pH (5.06–8.38, **Table S5**), large molecular weight, high abundance of humic-like matters, and CHON/CHOS/CHONP/CHONS compounds with $-NH_2$, $-SO_3H$ and $-H_2PO_3^-$ groups; while PW- and CS-BBS-DOM are characterized by low pH (3.19–3.39, **Table S5**), small molecular weight, high aromaticity, and high abundance of polyphenol-like matters and $-COOH$ -/phenolic-OH-containing CHO compounds. These intrinsic differences in molecular characteristics are the fundamental basis for the divergent effects of different BBS-DOM on soil $Cu(II)$ adsorption.

3.2 BBS-DOM exerts effects on soil $Cu(II)$ adsorption with aging time dependence

The adsorption isotherms of $Cu(II)$ on pristine and BBS-DOM amended soils at different aging times are shown in Fig. 3. The adsorption isotherm fitting results (**Table S6**) showed that the Freundlich model ($R^2 = 0.96 \sim 1.00$) provided a better fit for all treatments than the Langmuir model ($R^2 = 0.81 \sim 0.98$). This indicates that $Cu(II)$ adsorption on both pristine and BBS-DOM amended acidic red soil is dominated by multilayer adsorption on heterogeneous surfaces, which is consistent with the adsorption behavior of heavy metals on soil organo-mineral complexes reported in previous studies (Chen et al., 2025; Li et al., 2022; Tian et al., 2026).

The solid-liquid partition coefficient (K_d) was used to quantitatively evaluate the effects of BBS-DOM on soil $Cu(II)$ adsorption capacity (Fabregat-Palau et al., 2025). To reflect the environmental relevance of the results, K_d values were calculated at three typical $Cu(II)$ concentration levels (Fig. 3). Our results clearly revealed that BBS-DOM exerted bidirectional (promotive/inhibitory) effects on soil $Cu(II)$ adsorption, which were strongly feedstock-specific and aging-dependent. In the unaged stage (0 month), AF-BBS-DOM exhibited a significant promotive effect on $Cu(II)$ adsorption, while PW- and CS-BBS-DOM showed no significant promotion or even inhibitory effects. At low $Cu(II)$ concentration ($C_e = 0.01 \pm 0.001$ mg/L), the K_d value of AF600 treatment reached $4648 \text{ L} \cdot \text{kg}^{-1}$, which was 8.41-fold higher than that of pristine soil ($552 \text{ L} \cdot \text{kg}^{-1}$, $p < 0.05$); the K_d value of AF300 treatment was $1292 \text{ L} \cdot \text{kg}^{-1}$, also significantly higher than the control. In contrast, the K_d value of PW300 treatment was only $474 \text{ L} \cdot \text{kg}^{-1}$, which was 14.2% lower than that of pristine soil ($p < 0.05$), showing a significant inhibitory effect; the K_d values of CS300, CS600, and PW600 treatments had no significant difference from the control ($p > 0.05$).

The aging process significantly regulated the effects of BBS-DOM on soil Cu(II) adsorption, with a general trend of rapid increase in K_d values in the first month of aging, followed by stabilization in the second to third months. During the 0 ~ 1 month aging period, the K_d values of all treatments increased significantly: the K_d values of PW300 and CS600 treatments increased by 206.8% and 187.2%, respectively, compared with the unaged stage, and the K_d values of all PW/CS treatments exceeded or approached the level of pristine soil. During the 1 ~ 3 months aging period, the increase in K_d values slowed down and stabilized: the K_d values of AF-BBS-DOM treatments remained significantly higher than that of pristine soil, while the K_d values of PW/CS treatments decreased slightly and returned to levels not significantly different from the control. This aging process is directly related to the molecular-spectral coupling characteristics of BBS-DOM. The CHO-class small molecules coupled with fluorescent component of polyphenol-like matters, which dominate PW-/CS-BBS-DOM, decreased rapidly in abundance during aging, with their initial inhibitory effects eliminated accordingly; while the CHON/CHOS/CHONP/CHONS aromatic macromolecules coupled with fluorescent components of humic-like matters, which dominate AF-BBS-DOM, persisted stably during aging, maintaining the promotive effect on Cu(II) adsorption throughout the 3-month incubation period.

3.3 The soil physicochemical properties and DOM characteristics after BBS-DOM input during the aging process

BBS-DOM input significantly altered the physicochemical properties of acidic red soil, and the effects gradually weakened with the extension of aging time (**Table S8**). At the unaged stage, BBS-DOM input significantly increased soil organic carbon content (from $7.45 \text{ mg} \cdot \text{g}^{-1}$ to $8.18 \sim 8.78 \text{ mg} \cdot \text{g}^{-1}$, $p < 0.05$), decreased soil specific surface area and micropore area, and altered soil pH. AF-BBS-DOM with high pH significantly increased soil pH, while PW- and CS-BBS-DOM with low pH further decreased the pH of the already acidic red soil. During the aging process, soil organic carbon content showed a trend of first increasing and then decreasing. Soil specific surface area and micropore area gradually increased with aging time, as the pore-blocking BBS-DOM molecules were gradually mineralized, and new pores were formed via microbial activities (Dong et al., 2017). Soil pH showed an overall upward trend during aging, and the pH difference between different treatments gradually narrowed.

BBS-DOM input also significantly altered the content and characteristics of soil DOM, with distinct dynamic changes during the aging process (Fig. 4). BBS-DOM input significantly increased soil DOC content, and the increase was more pronounced for BBS-DOM generated at flaming than smoldering, indicating that flaming pyrolysis BBS-DOM releases more soluble organic matter after entering the soil. During aging, soil DOC content decreased significantly in all treatments, which is mainly due to the mineralization of labile DOM components by soil microorganisms and the adsorption and fixation of DOM by soil (Yang et al., 2022; Wu et al., 2023). For soil DOM molecular weight, PW-BBS-DOM input decreased soil DOM molecular weight (increased $S_{275-295}$), AF-BBS-DOM input increased soil DOM molecular weight, while CS-BBS-DOM input showed a trend of first decreasing and then increasing. The

molecular weight of soil DOM in all treatments increased with aging time, as small molecular weight components were preferentially utilized and decomposed by microorganisms (Li et al., 2023). For soil DOM aromaticity (SUVA₂₅₄), only AF600 treatment significantly increased soil DOM aromaticity in the unaged stage, while other treatments had no significant effect. The aromaticity of soil DOM in all treatments increased with aging time, as labile components with low aromaticity were rapidly decomposed, while recalcitrant components with high aromaticity were preserved and enriched (Ge et al., 2024; Qiu et al., 2025).

The fluorescent component composition of soil DOM was directly determined by the input of BBS-DOM, and showed distinct selective dynamic changes during aging (Fig. 4 and S6), which were highly coupled with the evolution of molecular composition. BBS-DOM input significantly increased the content of all four fluorescent components in soil DOM. AF-BBS-DOM input mainly increased the content of fluorescent components of humic-like matters (C1 + C3), corresponding to a significant increase in the relative intensity of CHON/CHOS/CHONP/CHONS-class aromatic macromolecules; while PW- and CS-BBS-DOM input mainly increased the content of fluorescent component of polyphenol-like matters (C4), corresponding to a significant increase in the relative intensity of CHO-class small molecules. During aging, the abundance of fluorescent component of polyphenol-like matters (C4) decreased rapidly within 1 month, and its content in all treatments decreased to a level not significantly different from pristine soil after 3 months of aging, corresponding to a significant sharp decrease in the relative intensity of CHO-class small molecules in FT-ICR MS results. This indicates that polyphenol-like matters have extremely high bioavailability and are preferentially transformed by soil microorganisms in the early stage of aging (Huang et al., 2023). In contrast, the fluorescent components of humic-like matters (C1 + C3) showed strong resistance to transformation: after 3 months of aging, the residual content of humic-like matters in AF-BBS-DOM treatments ($0.15 \sim 0.19 \text{ mg} \cdot \text{g}^{-1}$) was still significantly higher than that in PW/CS treatments ($0.08 \sim 0.10 \text{ mg} \cdot \text{g}^{-1}$) and pristine soil ($0.03 \text{ mg} \cdot \text{g}^{-1}$), corresponding to no significant decrease in the relative intensity of CHON/CHOS/CHONP/CHONS-class aromatic macromolecules, and a relative enrichment trend in AF-derived treatments. This confirms that the humic-like matters and their coupled aromatic macromolecules in AF-BBS-DOM have high stability in soil.

Additionally, we quantified the solid-phase adsorption content of each fluorescent component of BBS-DOM in soil, calculated by the difference between the theoretical input value of each component in BBS-DOM and its actual residual value in soil aqueous solution. The quantitative results of solid-phase adsorption of each fluorescent component are shown in **Fig. S7**. The quantitative results revealed a significant feedstock-specific selective adsorption of BBS-DOM fluorescent components by acidic red soil. For AF-BBS-DOM treatments, the soil solid phase preferentially adsorbed and fixed large humic-like matters. The total adsorption content of humic-like matters in AF600 treatment reached 2.06 mg/g , which was 6.6-fold that of PW300 treatment and 9.0-fold that of CS300 treatment, and the adsorption amount of C1 and C3 in AF600 was significantly higher than that in AF300 ($p < 0.05$). In contrast, for PW- and CS-BBS-DOM treatments, the main component adsorbed by soil solid phase was polyphenol-like matters. The polyphenol-like matters adsorption amount of PW600 and CS600 treatments reached 1.51

mg/g and 1.16 mg/g, respectively, which were significantly higher than those of AF series treatments ($p < 0.05$).

4. Discussion

4.1 Feedstock specificity effects of BBS-DOM on Cu(II) adsorption

Pearson correlation analysis and RDA were performed to elucidate the dominant factors and molecular-level mechanisms governing Cu(II) adsorption in BBS-DOM amended acidic red soil (Fig. 5). The results revealed that the K_d value of Cu(II) was extremely significantly positively correlated with the abundance of large humic-like matters (C1 + C3) in soil DOM ($p < 0.001$), and significantly negatively correlated with soil specific surface area ($p < 0.01$) and micropore area ($p < 0.001$). This inverse relationship between K_d and soil specific surface area is seemingly contradictory to the traditional physical adsorption theory, but it clearly demonstrates that chemical complexation mediated by organic functional groups, rather than physical adsorption by soil minerals, is the dominant mechanism governing Cu(II) adsorption in this acidic organo-mineral system.

AF-BBS-DOM exhibited a significant and immediate promotive effect on Cu(II) adsorption. Mechanistically, AF-BBS-DOM is uniquely characterized by an extremely high abundance of nitrogen-containing compounds (CHON: 0.36 ~ 0.37; CHONP: 0.20 ~ 0.28), which are 4 ~ 18-fold higher than those in PW-/CS-BBS-DOM (Fig. 1e). These nitrogen-bearing molecules are predominantly embedded in large humic-like matters (C1 + C3, 63%~65% of total fluorescence) and functionalized with abundant amino ($-NH_2$) groups (Table 1). In the acidic matrix (initial pH 4.14), $-NH_2$ groups undergo rapid protonation to form positively charged $-NH_3^+$ moieties (Chen et al., 2023; Hu et al., 2024). This protonation generates strong electrostatic repulsion between AF-BBS-DOM macromolecules and positively charged Cu(II) cations in the aqueous phase, effectively inhibiting the formation of soluble BBS-DOM-Cu(II) complexes. Consequently, Cu(II) remains predominantly in the free ionic state, available for adsorption onto soil solid phases. Concurrently, acidic red soil exhibits preferential adsorption of AF-BBS-DOM humic-like matters, as evidenced by **Fig. S7**. The solid-phase adsorption content of humic-like components (C1 + C3) in AF600 treatment reached 2.06 mg/g, which was 6.6-fold higher than that in PW300 and 9.0-fold higher than that in CS300. This selective adsorption is driven by the presence of negatively charged functional groups ($-SO_3^-$, $-H_2PO_3^-$, and $-COO^-$) on AF-BBS-DOM (adsorbed onto the soil surface) humic macromolecules (Table 1 and **Table S7**), which form strong electrostatic interactions with positively charged Cu(II) under acidic conditions, increasing the total adsorption capacity of the soil (Ahmad et al., 2018; Chen et al., 2023; Yang et al., 2026).

In contrast, PW-/CS-BBS-DOM showed no significant promotive effect or even inhibitory effect on Cu(II) adsorption in the unaged stage, which stems from their oxygen-enriched molecular characteristics and the dominant formation of soluble DOM-Cu(II) complexes in the aqueous phase. PW-/CS-BBS-DOM are

dominated by CHO compounds (relative intensity 0.67 ~ 0.80) associated with polyphenol-like matters (C4, 58%~84% of total fluorescence) (Fig. 1e). These CHO molecules have extremely high O/C ratios, indicating a high density of -COOH and phenolic-OH groups (Table 1). Even in the strongly acidic environment of PW-/CS-BBS-DOM-amended soils (pH 3.72 ~ 3.87 in the unaged stage), these strong acidic functional groups undergo partial dissociation to form negatively charged -COO⁻ moieties (Ahmad et al., 2018; Yang et al., 2026). These negatively charged -COO⁻ moieties exhibit high binding affinity for Cu(II) cations, readily forming stable, water-soluble BBS-DOM-Cu(II) complexes in solution. This process sequesters Cu(II) in the aqueous phase rather than promoting its adsorption to the soil solid phase, directly reducing the solid-liquid distribution coefficient (K_d) of Cu(II). This is the core reason for the significant inhibitory effect observed in the PW300 treatment, whose K_d value was 14.2% lower than that of the unamended control (Fig. 3). Two additional mechanisms further exacerbate this inhibitory effect. First, the strongly acidic nature of PW-/CS-BBS-DOM (pH 3.19 ~ 3.39) further acidified the already acidic red soil, increasing H⁺ activity and intensifying competition between H⁺ and Cu(II) for adsorption sites (Pinilla-Sanchez et al., 2026; Yang et al., 2026). Second, polyphenolic-like matters preferentially occupy high-energy adsorption sites on soil surfaces (Atkins et al., 2025), blocking Cu(II) access to these sites and further reducing adsorption capacity. This “bridge effect” of AF-BBS-DOM between soil and Cu(II) cations is the primary pathway for enhanced Cu(II) immobilization.

4.2 Aging effects of BBS-DOM on Cu(II) adsorption

For AF-BBS-DOM treatments, the promotive effect showed a characteristic pattern of “significant enhancement at 1 month followed by stabilization at 3 months”, which is driven by the combined effects of pH increase and selective adsorption/mineralization of DOM components. Specifically, AF300 treatment exhibited a marked increase in K_d value (from 1292 L·kg⁻¹ to 3876 L·kg⁻¹) during the first month of aging (Fig. 3). This enhancement is attributed to two key factors: (1) Soil pH increased from 4.20 to 5.01 (**Table S8**), which reduced H⁺ competition for adsorption sites and promoted partial deprotonation of -NH₃⁺ groups to the more Cu(II)-reactive neutral -NH₂ form (Yang et al., 2026). (2) Soil DOC content decreased significantly (Fig. 4a), while soil organic carbon content increased from 8.36 mg/g to 8.86 mg/g (**Table S8**). This inverse relationship indicates that a large proportion of aqueous-phase AF-BBS-DOM was adsorbed onto the soil solid phase during the first month, further increasing the density of Cu(II)-binding functional groups (sulfonate, phosphate, etc.) on soil surfaces and enhancing adsorption capacity. For AF600 treatment, the promotive effect remained exceptionally stable throughout the 3-month aging period, with K_d values consistently 7.8 ~ 8.4-fold higher than the control. This stability is explained by the balanced mineralization of both adsorbed and unadsorbed DOM components. During aging, total SOC content decreased from 8.72 mg/g to 8.12 mg/g, and soil DOC content also decreased significantly (**Table S8** and Fig. 4a), indicating that both solid-phase adsorbed and aqueous-phase dissolved AF-BBS-DOM underwent partial mineralization. However, the core nitrogen-containing functional groups embedded in the aromatic backbones of humic-like matters are highly recalcitrant to microbial degradation. As evidenced by Fig. 4, the absolute content of humic-like matters (C1 + C3) in AF600 treatment remained at 0.19 mg/g after 3 months of aging, which was 6.3-

fold higher than that in the control. This persistence of key functional groups ensures the long-term stability of the promotive effect.

For PW-/CS-BBS-DOM treatments, Cu(II) adsorption showed a three-stage dynamic pattern driven by the transformation of their dominant polyphenolic-like matters. Initially, polyphenolic-like matters formed stable soluble Cu(II) complexes via cation- π interaction of phenolic-OH groups and synergistic chelation with partially dissociated -COOH groups (Di et al., 2025; Meng et al., 2025; Yang et al., 2026).

Concurrently, the low pH of PW-/CS-BBS-DOM further acidified the soil, intensifying H^+ competition for adsorption sites, and polyphenolic-like matters preferentially occupied high-energy mineral sites (Pinilla-Sanchez et al., 2026; Yang et al., 2026). These combined effects resulted in significant inhibition. During 0 ~ 1 month, the absolute content of polyphenolic-like matters decreased by 42.7%~56.3%, while the average molecular weight of soil DOM increased significantly, and soil DOC decreased with a concurrent increase in OC. These results collectively indicate that polyphenolic-like matters underwent oxidative polymerization, converting from low-molecular-weight, water-soluble compounds into high-molecular-weight, insoluble polymers. This transformation substantially reduced their ability to form soluble Cu(II) complexes, and the insoluble polymers instead adsorbed onto soil surfaces to provide additional Cu(II)-binding sites. Meanwhile, soil pH increased by 0.2 ~ 0.55 units, alleviating H^+ competition. Consequently, K_d values increased by 187.2%~206.8% and the initial inhibitory effect was fully eliminated. During 1 ~ 3 months, the absolute content of polyphenolic-like matters in all PW/CS treatments decreased to levels indistinguishable from the pristine soil, and soil organic carbon content showed a continuous decreasing trend, confirming that polyphenolic-like matters and their polymers were largely diminished. Therefore, K_d values gradually returned to the control level.

5. Conclusion

This study provides a comprehensive molecular-level investigation of the aging effects of BBS-DOM derived from different feedstocks and combustion temperatures on Cu(II) adsorption in acidic red soil. Our findings demonstrate that feedstock type is the primary determinant of BBS-DOM's geochemical influence on heavy metal mobility in acidic soils, and that BBS-DOM regulates Cu(II) adsorption through the combined effects of aqueous-phase complexation and soil-surface interactions, with functional group-mediated chemical complexation, rather than physical adsorption by soil surface, governing the divergent net effects. Alfalfa-derived BBS-DOM exerts a sustained and significant promotive effect on Cu(II) immobilization, which is mainly attributable to its uniquely high nitrogen and phosphorus content. These elements are incorporated into large humic-like matters that possess a dual functional group architecture: $-NH_3^+$ groups that inhibit soluble DOM-Cu(II) complex formation in the aqueous phase, and negatively charged $-SO_3^-$, $-H_2PO_3^-$, and $-COO^-$ groups that enable strong electrostatic adsorption to positively charged soil surfaces under acidic conditions. This dual functionality facilitates the formation of highly stable ternary complexes: soil, BBS-DOM and Cu(II), while the near-neutral to alkaline pH of AF-BBS-DOM further alleviates intense H^+ competition for adsorption sites in the acidic soil matrix. In contrast, pinewood and corn straw-derived BBS-DOM exhibit initial inhibitory or non-promotive effects,

driven by their dominance of oxygen-rich CHO compounds containing abundant -COOH and phenolic-OH groups associated with polyphenol-like matters. These compounds readily form soluble DOM-Cu(II) complexes in the aqueous phase that retain Cu(II) in solution rather than promoting its fixation to soil solids; furthermore, their strongly acidic nature (pH 3.19 ~ 3.39) further intensifies soil acidification, enhances H⁺ competition, and blocks native high-energy soil adsorption sites for Cu(II). We further demonstrate that the aging process dynamically regulates these divergent effects through selective microbial decomposition of labile polyphenol-like matters and humic-like matters. This mechanism explains the transient inhibitory effect of PW-/CS-BBS-DOM and the persistent promotive effect of AF-BBS-DOM observed in this study. The stability of AF-BBS-DOM's promotive effect stems from the resistance of its nitrogen- and phosphorus-containing humic-like macromolecules to microbial degradation, ensuring the long-term persistence of -NH₃⁺, -SO₃⁻, -H₂PO₃⁻, and -COO⁻ functional groups in the soil system. This work fills a critical gap in understanding the cross-media environmental effects of BBS-DOM on soil heavy metal behavior, revealing the molecular fingerprint-regulated mechanisms by which different BBS-DOMs modulate Cu(II) adsorption in acidic soils through integrated aqueous and soil-surface processes. This study is limited to Cu(II) as a representative heavy metal and a single type of acidic red soil under laboratory incubation conditions. Future research should extend to other heavy metals and composite heavy metal pollution, investigate BBS-DOM effects under complex field conditions (e.g., wet-dry cycles, temperature fluctuations), and explore the impacts of BBS-DOM on heavy metal bioavailability and ecological risk in terrestrial ecosystems. Nevertheless, our findings have important implications for improving heavy metal pollution risk assessment and developing targeted remediation strategies in wildfire-affected acidic soil ecosystems worldwide.

Declarations

Author Contribution

Zhigeng Wang: Writing-Original Draft, Investigation; Ruxin Tong: Software; Weifeng Chen: Writing-review & editing, Supervision, Conceptualization; Yanling Deng: Writing-review & editing, Resources, Validation; Huiying Zhang: Investigation, Software; Jinzhi Ni: Validation; Hui Jia: Methodology, Investigation; Frimpong Dapaah: Validation; Abdallah Abdelfattah: Validation. All authors reviewed the manuscript.

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Figures

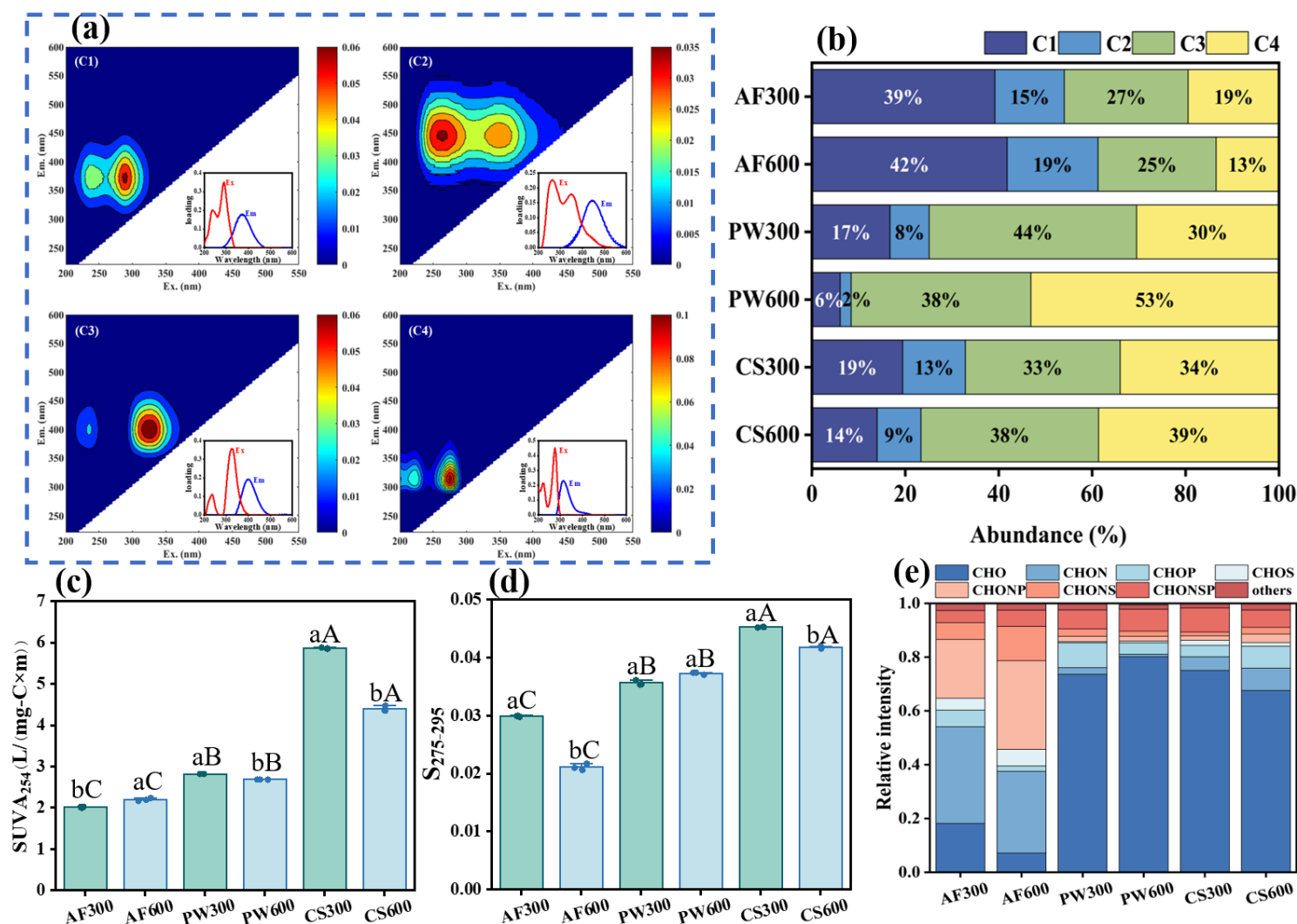


Figure 1

Fluorescence organic component spectra (a), abundance of four components (b), spectral indicators including SUVA₂₅₄ (c), S₂₇₅₋₂₉₅ (d) and relative intensity of different compounds (e) of BBS-DOM. Different capital letters indicate significant differences in spectral indicators among different BBS-DOMs from a same combustion temperature, and different lowercase letters indicate significant differences in spectral indicators among different combustion temperatures of a same biomass-derived BBS-DOM ($p < 0.05$). The suffixes “300” and “600” indicate the smoldering and flaming conditions.

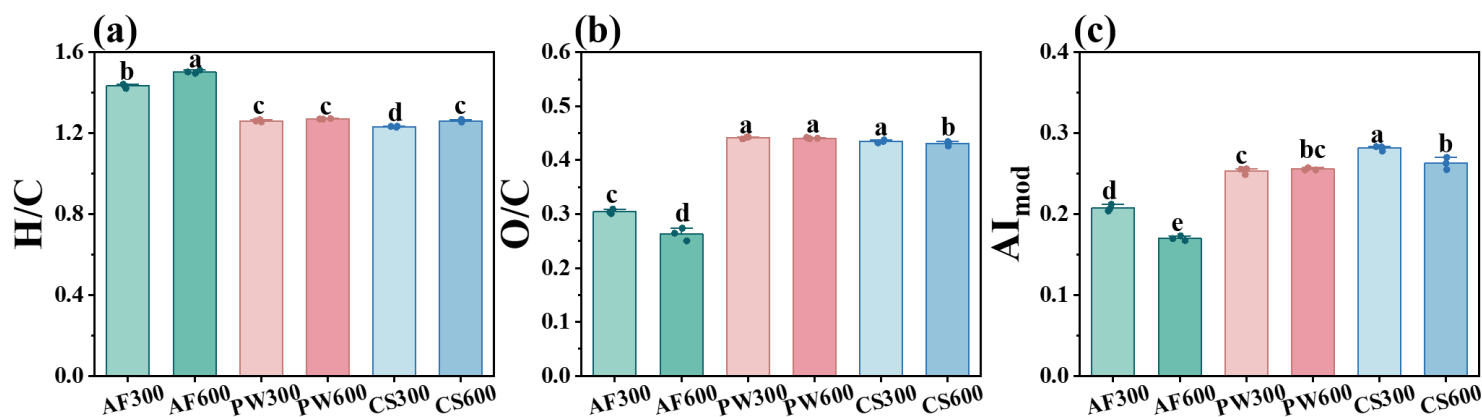


Figure 2

Molecular characteristics of BBS-DOM, including H/C (a), O/C (b) and Al_{mod} (c). Different lowercase letters indicate significant differences among different BBS-DOMs ($p < 0.05$). The suffixes “300” and “600” indicate the smoldering and flaming conditions.

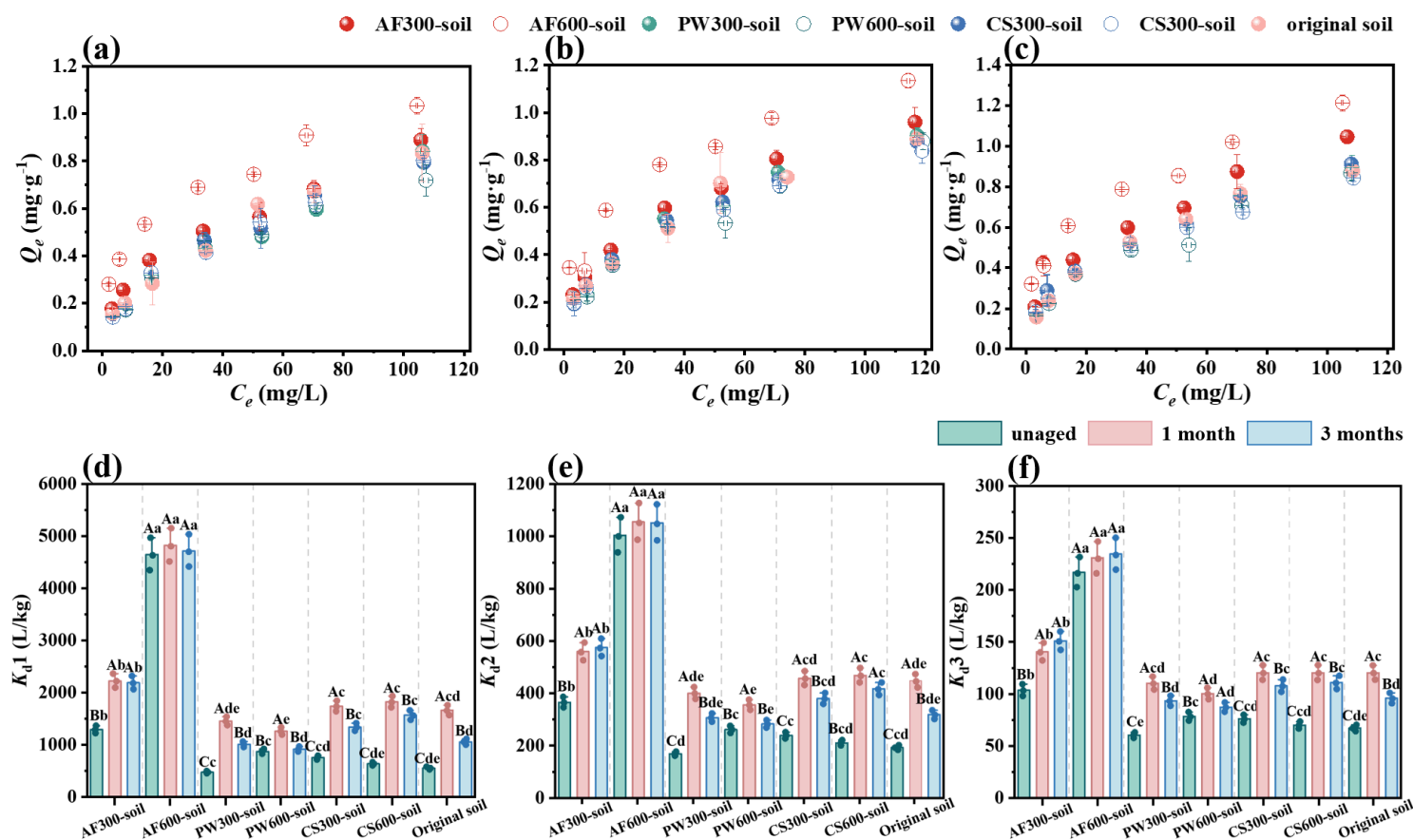


Figure 3

Adsorption capacity (a~c) and K_d value (d~f) of Cu(II) in BBS-DOM-soils and original soil after different aging times. Different capital letters indicate significant differences among different aging times for a

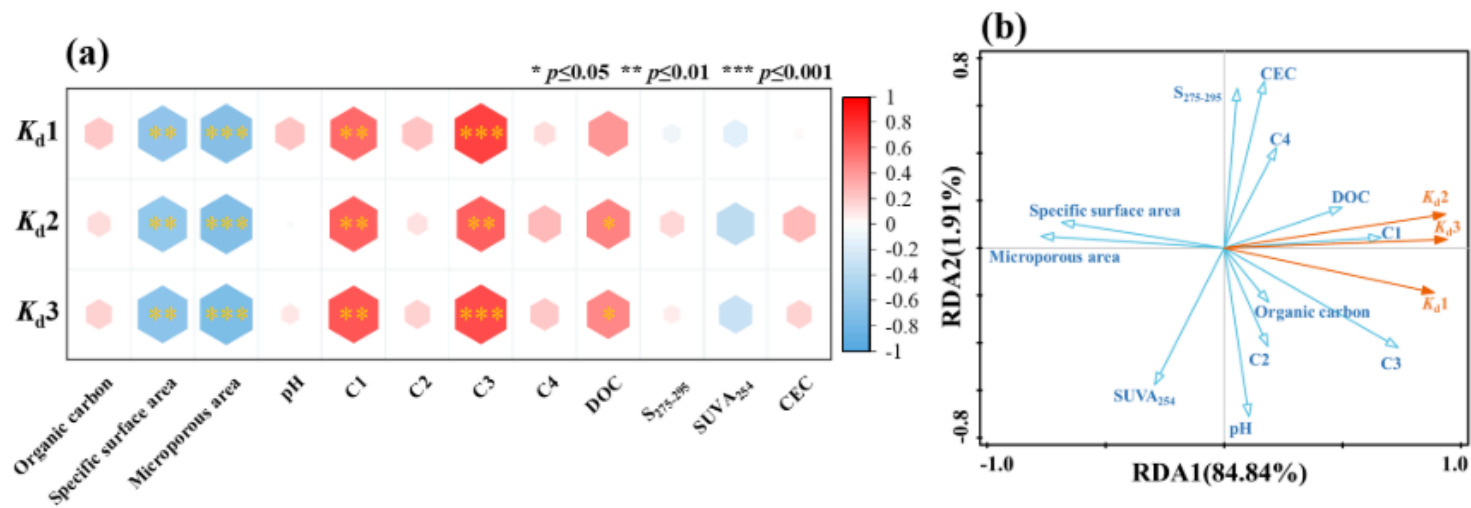


Figure 5

Pearson correlation heatmap (a) and redundancy analysis (RDA) ordination diagram (b) between soil properties and K_d values of Cu(II) adsorption.

Supplementary Files

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