

Pyrolysis-driven molecular reorganization controls photon absorption and reactive-intermediate formation in sewage sludge biochar-derived dissolved organic matter

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Abstract

Biochar-derived dissolved organic matter (BDOM) can affect aquatic carbon cycling and contaminant transformation, but how pyrolysis jointly regulates its release, molecular composition, and photochemical behavior remains unclear. Here, water-extractable BDOM from sewage-sludge biochars produced at 200–700 °C was characterized by DOC analysis, UV–visible and excitation–emission matrix fluorescence spectroscopy, high-performance size-exclusion chromatography, and negative-ion Orbitrap high-resolution mass spectrometry, and photochemically produced reactive intermediates (PPRIs) were quantified. DOC release decreased from 13.52 to 0.38 mg C g⁻¹ biochar (97.2%), whereas SUVA₂₅₄ and the absorbed-photon rate (Ra) peaked at 400 °C. HRMS revealed a formula-rich pool at 200 °C, pronounced CHON enrichment at 300 °C, and maximum unsaturation and aromaticity-compatible CRAM-/lignin-like formula-space enrichment at 400 °C. The 400–500 °C interval showed the greatest formula turnover (Jaccard similarity = 0.133), with preferential disappearance of unsaturated CHON-rich formulas and newly detectable, more saturated CHO/CHOS formulas. BDOM₄₀₀ produced the highest steady-state PPRI concentrations primarily through superior photon absorption rather than uniformly higher efficiencies. Although f_{TMP} and Φ_{OH} increased at 500–700 °C, they only partially compensated for weak absorption, while ¹O₂ formation remained below reliable quantification. Pyrolysis therefore decoupled carbon mobilization, photon absorption, and photon-normalized conversion, creating distinct controls on realized PPRI exposure.

1. Introduction

Thermochemical conversion is increasingly used to reduce sewage-sludge volume, stabilize organic matter, and recover carbon in the form of biochar (Cao et al., 2024; Du et al., 2022). However, the environmental behavior of sludge biochar is not determined solely by its solid-phase properties because biochar-derived dissolved organic matter (BDOM) can be mobilized after application (Du et al., 2022; Li et al., 2026; Sun et al., 2021). Once released, BDOM can alter nutrient and metal transport, microbial activity, sorption, redox chemistry, and contaminant transformation, making both its released quantity and chemical reactivity relevant to environmental assessment (El-Naggar et al., 2019; Huang et al., 2021; Tang et al., 2024). This issue is particularly important for sewage-sludge biochar because its dissolved fraction originates from thermochemical transformation of proteinaceous biomass, microbial residues, extracellular polymeric substances, heteroatom-rich organic matter, and mineral-associated phases (He et al., 2026; Zhu et al., 2026). Its molecular evolution may therefore differ substantially from that of lignocellulosic biochars.

Pyrolysis temperature strongly affects both the amount and composition of extractable BDOM, although the magnitude and direction of the response depend on feedstock composition, thermal history, atmosphere, and extraction conditions (Cao et al., 2026; Rajapaksha et al., 2019; Wozniak et al., 2020; Zhu et al., 2026). DOC release generally decreases as pyrolysis temperature increases, whereas specific UV absorption, fluorescence composition, apparent molecular size, and molecular-formula distributions can vary nonmonotonically (He et al., 2026; Huang et al., 2021; Li et al., 2022). Consequently, a low

BDOM yield does not necessarily indicate weak optical or chemical reactivity per unit of dissolved carbon (Cao et al., 2026; Li et al., 2026; Xie et al., 2026). Resolving this quantity–quality decoupling requires complementary analytical approaches. UV–visible absorption and fluorescence EEMs describe chromophoric and fluorophoric properties, respectively, but neither uniquely identifies molecular structures (Chen et al., 2003; Huang et al., 2020; Quan et al., 2020). High-performance size-exclusion chromatography (HPSEC) provides an operational retention-size distribution and high-resolution mass spectrometry (HRMS) resolves elemental formulas within the extractable and ionizable fraction (Guo et al., 2022; Koch and Dittmar, 2006; Tian et al., 2022). These analytical windows describe different dimensions of BDOM and cannot be treated as interchangeable measurements of molecular structure or molecular size.

Upon irradiation, BDOM chromophores can generate photochemically produced reactive intermediates (PPRIs), particularly excited triplet states ($^3\text{BDOM}^*$), singlet oxygen ($^1\text{O}_2$), and hydroxyl radicals ($\cdot\text{OH}$), which participate in aquatic redox reactions and contaminant transformation (Fu et al., 2015; Tang et al., 2024; Wan et al., 2021; Wang et al., 2020). PPRI steady-state concentrations depend jointly on the number of photons absorbed and the formation efficiency per absorbed photon, whereas common optical indices do not predict all PPRI pathways uniformly (Berg et al., 2023; Maizel and Remucal, 2017; McKay et al., 2017; Wang et al., 2023). Thermal aromatization has been associated with altered photosensitization, but its direction varies with feedstock, functional groups, and preparation pathway (Li et al., 2024; Luo et al., 2023; Wang et al., 2025a; Zuo et al., 2024). Moreover, weakly absorbing fractions may retain high apparent quantum yields (Li et al., 2025; Liu et al., 2024; Luo et al., 2025). Reliable comparison therefore requires spectrum-matched photon accounting and probe-specific interpretation rather than equating probe transformation directly with the total production of a single PPRI (Du et al., 2025; Laszakovits et al., 2017; Milstead et al., 2023).

Previous sludge-biochar studies have primarily related pyrolysis temperature to DOC release, optical properties, molecular composition, or biological effects, whereas direct integration of molecular characterization with experimentally quantified PPRI formation across a continuous sludge-biochar temperature series remains limited (He et al., 2026; Hou et al., 2025; Li et al., 2026; Zhu et al., 2026). More importantly, previous DBC/BDOM studies have rarely separated four quantities within one sludge-derived system: carbon release, photons absorption, PPRI formation efficiency, and the resulting steady-state PPRI concentrations (Fu et al., 2015; Li et al., 2024; Wang et al., 2023). This distinction is mechanistically important because enhanced photon absorption may sustain high PPRI concentrations despite unchanged or declining photon-normalized efficiency, whereas high apparent efficiency may be insufficient to overcome weak absorption (Li et al., 2025; Wang et al., 2025a; Yang et al., 2025).

To address this gap, sewage-sludge biochars were produced at 200–700°C, and their water-extractable BDOM was evaluated on an equal-biochar-mass basis and at a standardized DOC concentration. DOC release, UV–visible absorption, fluorescence regional integration, HPSEC, and Orbitrap HRMS were combined with absorbed-photon measurements and probe-based determination of $^3\text{BDOM}^*$, $^1\text{O}_2$, and $\cdot\text{OH}$. The objectives were to (i) resolve temperature-dependent changes in BDOM release, optical

properties, apparent size distribution, and molecular composition; (ii) identify the principal molecular-transition interval across the pyrolysis series; and (iii) determine how photon absorption and apparent photon-normalized formation efficiency jointly shape steady-state PPRI exposure. We hypothesized that the pyrolysis temperature maximizing steady-state PPRI concentrations would not necessarily maximize the corresponding apparent efficiency per absorbed photon. This design explicitly separates BDOM mobilization, photon capture, photon conversion, and realized PPRI exposure.

2. Materials and methods

2.1. Preparation of sludge-derived biochars

Sewage sludge was collected from the secondary sedimentation tank of a municipal wastewater treatment plant operated with an anaerobic–anoxic–oxic (A^2/O) process in Chuzhou, China. The sludge was dewatered, freeze-dried, ground, and passed through a 100-mesh sieve. Aliquots (30.0 g) were pyrolyzed in a tubular furnace under a continuous flow of high-purity N_2 . The furnace temperature was increased at $10^\circ\text{C min}^{-1}$ to 200, 300, 400, 500, 600, or 700°C , maintained at the target temperature for 2 h, and cooled to room temperature under N_2 . The resulting biochars were ground and passed through a 100-mesh sieve. The biochars were designated SBC200, SBC300, SBC400, SBC500, SBC600, and SBC700 according to their respective pyrolysis temperatures. Their corresponding water-extractable dissolved organic matter fractions were designated BDOM200–BDOM700.

2.2. BDOM extraction and DOC quantification

BDOM was extracted with ultrapure water following previously reported sludge-biochar procedures with minor modifications (Du et al., 2022; Zhu et al., 2026). Briefly, 2.000 ± 0.001 g of biochar was mixed with 40.0 mL of ultrapure water (1:20, w/v) and shaken in the dark at 200 rpm for 24 h at room temperature. The suspension was centrifuged at 4000 rpm for 30 min and filtered through a 0.45- μm membrane. Filtrates were stored in amber bottles at 4°C until analysis. Dissolved organic carbon (DOC) was quantified as non-purgeable organic carbon using a TOC-VCPH analyzer (Shimadzu, Japan). BDOM solutions were diluted with ultrapure water to 10 mg C L^{-1} for spectroscopic characterization.

2.3. Spectroscopic characterization

2.3.1. UV-visible absorption spectroscopy

UV–visible absorption spectra were recorded from 200 to 700 nm using a UV-2600 spectrophotometer (Shimadzu, Japan). Specific UV absorbance at 254 nm (SUVA_{254}) was calculated by normalizing absorbance at 254 nm to DOC concentration (Luo et al., 2023; Weishaar et al., 2003), and E_2/E_3 was calculated as A_{250}/A_{365} (Helms et al., 2008; Yan et al., 2023). These indices were interpreted as operational optical proxies rather than direct structural measurements.

2.3.2. EEM fluorescence spectroscopy

Excitation–emission matrices (EEMs) were acquired using an F-4600 fluorescence spectrophotometer (Hitachi, Japan). Excitation wavelengths ranged from 200 to 400 nm and emission wavelengths from 290 to 520 nm, both at 5-nm increments. The scan rate was 12,000 nm min⁻¹, and the photomultiplier-tube voltage was 700 V. Ultrapure-water blanks were subtracted, and Rayleigh- and Raman-scattering regions were masked before analysis. Fluorescence regional integration (FRI) was performed using the EFC platform (<https://nomresearch.cn/efc/indexCN.html>) (Zhu et al., 2025). The excitation–emission boundaries of Regions I–V are provided in **Table S1** (Chen et al., 2003; Wang et al., 2025b). The integrated fluorescence volume of each region was normalized to the summed integrated volume across all five regions and expressed as a percentage of the total regional fluorescence response. These regions were treated as operational fluorescence domains and were not interpreted as discrete molecular components.

The humification index (HIX) was calculated as the ratio of the integrated emission intensity from 435 to 480 nm to that from 300 to 345 nm at Ex = 254 nm (Chen et al., 2022; Tang et al., 2024). The biological index (BIX) was calculated as the ratio of emission intensity at 380 nm to that at 430 nm at an excitation wavelength of 310 nm (Yan et al., 2023; Zhu et al., 2026). Results were reported as not determined (n.d.) when corrected fluorescence was insufficient for reliable regional integration or index calculation.

2.4. Apparent molecular-size analysis by HPSEC

Apparent molecular-size distributions were characterized by HPSEC coupled with diode-array detection (HPSEC-DAD). Samples were filtered through 0.22-μm membranes and separated on a Polysep-GFC-P3000 column with a matching guard column (Phenomenex, USA). The mobile phase consisted of methanol/water (1:9, v/v) containing 25 mmol L⁻¹ ammonium acetate and was delivered isocratically at 1.0 mL min⁻¹. Chromatograms recorded at 254 nm were integrated over six fixed retention domains (F1–F6). For descriptive cross-scale comparison, F1, F2 + F3, and F4 + F5+F6 were grouped as larger, intermediate, and smaller apparent-size domains, respectively. Because SEC retention can also reflect conformation, association, detector wavelength, and non-size-exclusion interactions, these labels are operational and do not represent calibrated molecular-weight ranges (Fan et al., 2024; Xiao et al., 2018). Additional conditions are provided in **Text S1**.

2.5. Orbitrap high-resolution mass spectrometry

BDOM was concentrated using Bond Elut PPL cartridges (500 mg, 6 mL; Agilent) before molecular analysis (Du et al., 2024; Tian et al., 2022). Methanolic extracts were introduced by direct infusion into an Exactive Plus Orbitrap high-resolution mass spectrometer equipped with heated electrospray ionization (Thermo Fisher Scientific, Bremen, Germany). Spectra were acquired in negative-ion mode over m/z 90–900 at a resolving power of 140,000 at m/z 200. Molecular formulas containing C, H, O, N, and S were assigned using the TRFu workflow (Fu et al., 2020) and grouped by elemental composition and operational Van Krevelen regions (Fan et al., 2024; Koch and Dittmar, 2006; Xu et al., 2025). Formula-assignment criteria, mutually exclusive classification boundaries, molecular indices, and overlap calculations are described in **Text S2** and **Table S2**.

2.6. Photochemical experiments and PPRI determination

Photochemical experiments were conducted in an HF-GHX-VI reactor (Hefan, China) equipped with a 1000-W xenon lamp and a 290-nm cutoff filter. The relative lamp spectrum was measured using a USB2000 + spectrometer (Ocean Optics, USA), and absolute photon irradiance was calibrated with a p-nitroanisole/pyridine actinometer (Laszakovits et al., 2017). The integrated incident photon irradiance over 290–400 nm was 2.26×10^{-8} einstein $\text{cm}^{-2} \text{s}^{-1}$. Actinometric and absorbed-photon-rate (R_a) calculations are provided in **Text S3**.

BDOM solutions were standardized to 5 mg C L^{-1} . Aliquots were irradiated in quartz tubes in the presence of 2,4,6-trimethylphenol (TMP), furfuryl alcohol (FFA), or terephthalic acid (TPA) to probe reactive triplet BDOM ($^3\text{BDOM}^*$), singlet oxygen ($^1\text{O}_2$), and hydroxyl radicals ($\cdot\text{OH}$), respectively. The photochemical solutions were maintained at pH 7.0 with 5 mM phosphate buffer solution at 25°C. Probe loss or product formation was quantified by HPLC, and irradiated probe blanks were analyzed under otherwise identical conditions. Probe-specific interpretation and blank correction followed current photochemical guidance (Du et al., 2025; Milstead et al., 2023). Probe concentrations, kinetic treatment, analytical conditions, and calculations of absorbed-photon rates, steady-state concentrations, and photon-normalized descriptors are provided in **Text S4** and **Table S3**.

2.7. Quality assurance, data processing, and integrative visualization

Unless otherwise stated, independent BDOM extractions and photochemical experiments were conducted in triplicate, and results are presented as mean $\pm$ standard deviation. Probe-loss rate constants were obtained by linear regression of $\ln(C_t/C_0)$ against irradiation time, whereas hTPA formation rates were determined from the initial linear formation region.

For molecular-formula overlap analysis, assigned C/H/O/N/S formulas were converted into binary presence–absence patterns across BDOM200–BDOM700. When multiple rows with an identical formula occurred within a sample, their signal intensities were summed before set membership was defined. The UpSet plot displays the 20 largest exact intersections, whereas each sample set size was calculated from all valid nonempty intersections (Gomez et al., 2023). For adjacent temperature sets A and B, formulas were classified as retained ($N_{A \cap B}$), lost ($N_A - N_{A \cap B}$), or newly detected ($N_B - N_{A \cap B}$). Jaccard similarity was calculated as (Lu et al., 2016):

$$J(A,B) = \frac{|A \cap B|}{|A \cup B|} = \frac{N_{\text{retained}}}{N_{\text{retained}} + N_{\text{lost}} + N_{\text{new}}}$$

The retention and novelty fractions were calculated as N_{retained}/N_A and N_{new}/N_B , respectively.

For cross-scale visualization, selected release, photon absorption, fluorescence, apparent molecular-size, molecular-composition, photon-normalized efficiency, and steady-state-exposure variables were

standardized independently across the available temperature-level means using population row-wise z-scores:

$$z_{ij} = \frac{x_{ij} - \mu_i}{\sigma_i}$$

where x_{ij} is the value of metric i at temperature j , and μ_i and σ_i are the mean and population standard deviation, respectively, of the available temperature-level values for that metric. Values reported as n.d. were excluded from the calculation and were not imputed as zero. The heatmap therefore compares relative temperature patterns within each metric; its colors do not represent absolute differences among metrics. Because the series contained only six temperature levels and several variables included n.d. values, no formal cross-variable correlation or multivariate model was fitted.

Conventional plots were prepared using OriginPro 2021 (OriginLab Corporation, Northampton, MA, USA), whereas the UpSet and cross-scale visualizations were generated using custom Python scripts with pandas, NumPy, and Matplotlib.

3. Results and discussion

3.1. BDOM release and UV–visible absorption properties

Pyrolysis progressively reduced the release of water-extractable carbon from the sludge biochars (Table 1). DOC release decreased from 13.52 ± 0.21 mg C g⁻¹ biochar for SBC200 to 8.77 ± 0.87 , 1.40 ± 0.05 , and 0.38 ± 0.01 mg C g⁻¹ biochar for SBC300, SBC400, and SBC700, respectively. The overall decrease was 97.2%, and the largest stepwise loss occurred between 300 and 400°C (84.0%). This interval therefore marks the strongest decline in BDOM extractability, rather than necessarily a universal compositional transition. Comparable temperature-dependent losses of extractable DOC have been reported for sludge- and fecal-derived biochars, although their magnitude depends on feedstock and extraction conditions (Cao et al., 2026; He et al., 2026; Xie et al., 2026). The decline is consistent with thermal removal or transformation of soluble protein-, carbohydrate-, lipid-, and microbial-residue-derived constituents and their incorporation into a less water-extractable carbon matrix (Du et al., 2022; Hou et al., 2025; Zhu et al., 2026).

Table 1
DOC release from SBC and optical characteristics of the corresponding BDOM.

Pyrolysis temperature (°C)	DOC (mg C g ⁻¹ biochar)	UV indices		Fluorescence indices	
		SUVA ₂₅₄ (L mg C ⁻¹ m ⁻¹)	E ₂ /E ₃	HIX	BIX
200	13.52 ± 0.21	2.03 ± 0.10	6.61 ± 0.16	1.57 ± 0.02	1.27 ± 0.03
300	8.77 ± 0.87	2.29 ± 0.04	10.85 ± 0.28	4.32 ± 0.08	1.45 ± 0.01
400	1.40 ± 0.05	3.08 ± 0.08	7.69 ± 0.12	2.09 ± 0.01	2.07 ± 0.01
500	0.72 ± 0.01	0.74 ± 0.03	10.67 ± 0.25	1.27 ± 0.10	3.14 ± 0.06
600	0.50 ± 0.01	0.36 ± 0.03	7.70 ± 0.42	n.d.	n.d.
700	0.38 ± 0.01	0.27 ± 0.13	3.51 ± 0.14	n.d.	n.d.
Note: n.d. represents not determined.					

All BDOM samples showed strong UV-vis absorption followed by a featureless decline toward visible wavelengths (**Fig. S1**), a common spectral pattern for heterogeneous chromophoric DOM with overlapping electronic transitions (Cheng et al., 2024; Helms et al., 2008; Wang et al., 2025a). SUVA₂₅₄ increased from 2.03 ± 0.10 L mg C⁻¹ m⁻¹ for BDOM200 to 2.29 ± 0.04 for BDOM300 and reached a maximum of 3.08 ± 0.08 L mg C⁻¹ m⁻¹ for BDOM400 (Table 1). Thus, relative to BDOM200, BDOM400 was released at an 89.6% lower DOC yield but exhibited 51.7% higher DOC-normalized absorption. Release quantity and light absorption per unit DOC therefore did not vary in parallel. The BDOM400 maximum indicates relative enrichment and/or greater carbon-normalized absorptivity of UV-absorbing conjugated chromophores. Above 400°C, SUVA₂₅₄ decreased sharply to 0.74 ± 0.03 mg C⁻¹ m⁻¹ for 500°C, and declined further to 0.36 ± 0.03 and 0.27 ± 0.13 L mg C⁻¹ m⁻¹ for BDOM600 and BDOM700, respectively. Together with the low DOC yields, these values define the high-temperature extracts as low-yield and weakly UV-absorbing dissolved pools. This interpretation applies to the water-extractable fraction and does not imply decreasing carbonization of the bulk biochar. Because published biochar series show increasing, decreasing, or nonmonotonic SUVA₂₅₄ responses (He et al., 2026; Huang et al., 2021; Li et al., 2022), the 400°C maximum should be regarded as specific to the present sludge and preparation conditions rather than a universal temperature optimum.

E₂/E₃ showed a more complex response, increasing from 6.61 ± 0.16 at 200°C to 10.85 ± 0.28 at 300°C, decreasing to 7.69 ± 0.12 at 400°C, increasing again to 10.67 ± 0.25 at 500°C, and then decreasing to 7.70 ± 0.42 and 3.51 ± 0.14 at 600 and 700°C, respectively (Table 1). Lower E₂/E₃ values are often associated with greater apparent chromophore size or condensation (Du et al., 2024; Fu et al., 2015). The lower value for BDOM400 than for BDOM300 and BDOM500 is therefore consistent with its stronger long-wavelength absorption and maximum SUVA₂₅₄. The low BDOM700 value, however, should not be

interpreted as renewed enrichment of large or aromatic chromophores: $SUVA_{254}$ was minimal, and its relative standard deviation approached 48%, so uncertainty in the weak A365 signal could be strongly amplified in the ratio. E_2/E_3 is consequently used here as a descriptive spectral index, especially for BDOM600–BDOM700, rather than as a direct measure of molecular size.

3.2. Fluorescence characteristics of BDOM

EEM fluorescence provided a complementary view of the emissive BDOM fraction (Fig. 1 and Table 1). Corrected signals were sufficient for quantitative FRI and fluorescence-index analysis for BDOM200–BDOM500 but not for BDOM600–BDOM700 (Fig. 1a). Regions I–II, III, IV, and V are operationally described as protein-like, fulvic-like, soluble microbial byproduct-like, and humic-like, respectively (Chen et al., 2003; Zhu et al., 2025). These labels denote fluorescence regions and do not identify discrete compounds.

BDOM200 had the greatest relative contribution from protein-like regions: Regions I + II accounted for 45% of integrated fluorescence, whereas Regions III + V accounted for 34% (Fig. 1b), and HIX was 1.57 ± 0.02 (Table 1). Together with the high DOC yield, this distribution is consistent with extraction of incompletely transformed microbial- and proteinaceous-residue-associated fluorophores after mild pyrolysis, but it does not demonstrate the presence of intact proteins (Du et al., 2022; He et al., 2026; Hou et al., 2025). A pronounced redistribution of fluorescence occurred at 300°C. The combined contribution of Regions III + V increased to 52%, Regions I + II decreased to 31%, and HIX reached 4.32 ± 0.08 . BDOM300 therefore exhibited the highest relative contribution of fulvic- and humic-like fluorescence within the investigated temperature series. Because the transformation was thermochemical rather than biological, this response is described as humic-like fluorescence enrichment rather than humification (Chen et al., 2003; Liu et al., 2022; Wang et al., 2025b).

BDOM400 showed the strongest EEM signal, despite a lower HIX (2.09 ± 0.01) and a smaller Regions III + V contribution (44%) than BDOM300. This difference is not contradictory: EEM intensity describes signal magnitude, whereas HIX and FRI represent an emission ratio and a relative regional distribution, respectively (Huguet et al., 2009; Quan et al., 2020; Yan et al., 2023). The concurrence of maximum EEM intensity and $SUVA_{254}$ at 400°C indicates enrichment of both emissive and more broadly UV-absorbing chromophores. Conversely, the distinct BDOM300 maxima in HIX and humic-like FRI contribution demonstrate that fluorescence composition and bulk UV absorption are not interchangeable descriptors.

At 500°C, both the EEM intensity and $SUVA_{254}$ decreased sharply, whereas the relative contribution of Regions I + II increased to 40% and BIX reached 3.14 ± 0.06 . These percentage and ratio increases do not indicate recovery of an absolute protein-like pool or renewed biological production. Instead, they reflect spectral redistribution within a depleted fluorescent pool because a component can increase proportionally while its absolute signal declines (Chen et al., 2003; Helms et al., 2008; Liu et al., 2022). The weak signals of BDOM600–BDOM700 precluded reliable regional integration and index calculation. Overall, the fluorescence sequence progressed from protein-like dominance at 200°C, to maximum

relative humic-like character at 300°C, to maximum emission at 400°C, followed by severe optical depletion at $\geq 500^\circ\text{C}$.

3.3. Apparent molecular-size distributions determined by HPSEC

HPSEC–UV₂₅₄ resolved broad, multimodal chromatographic profiles for BDOM200–BDOM500, demonstrating that the UV-absorbing fraction was distributed across several retention domains (Fig. 2). Six fixed operational regions (F1–F6) were applied to all chromatograms (Fig. 2a). Under ideal size-exclusion behavior, earlier and later elution correspond to larger and smaller apparent hydrodynamic sizes, respectively; detector wavelength, molecular conformation, and stationary-phase interactions can also affect the observed profiles (Hanson et al., 2022; Xiao et al., 2018; Zhu et al., 2025). Accordingly, F1, F2 + F3, and F4 + F5+F6 were treated as larger, intermediate, and smaller apparent-size domains. The fractional contribution $P_i = A_i/\Sigma A_i \times 100\%$ therefore describes the within-sample distribution of UV₂₅₄-active BDOM rather than an absolute concentration or calibrated molecular-weight distribution.

BDOM200 had the largest F1 contribution (34% of total UV₂₅₄ area). F2 and F3 contributed 11% and 16%, whereas F4–F6 contributed 26%, 9%, and 4%, respectively (Fig. 2b). Accordingly, the larger, intermediate, and smaller apparent-size groups represented 34%, 27%, and 39% of the integrated area. This broad distribution indicates a heterogeneous, readily extractable pool containing a substantial early-eluting and/or more strongly associated UV-active fraction. Together with the high DOC yield and protein-like fluorescence described in Sections 3.1–3.2, the result characterizes BDOM200 as release-rich and compositionally broad.

A marked redistribution toward later elution occurred at 300°C. The smaller apparent-size group (F4 + F5+F6) increased to 71%, while F1 and F2 + F3 decreased to 11% and 19%, respectively (Fig. 2b). This later-eluting dominance was even more pronounced at 400°C, where F5 and F6 alone accounted for 39% and 27%, and the full smaller apparent-size group reached 75%. The shift is consistent with fragmentation, disaggregation, and/or selective release of later-eluting UV-active products, although retention data alone cannot distinguish among these possibilities (Hanson et al., 2022; Xiao et al., 2018; Zhu et al., 2025). BDOM400 simultaneously exhibited the highest SUVA₂₅₄, showing that late elution and strong DOC-normalized UV absorption can coexist. Apparent hydrodynamic size, chromophore absorptivity, and E_2/E_3 remain related but non-equivalent properties; their agreement therefore provides qualitative cross-support rather than repeated measurement of a single molecular-weight variable (Hanson et al., 2022; Helms et al., 2008).

A second redistribution occurred at 500°C. F1 and F2 + F3 increased to 27% and 36%, respectively, whereas F4 + F5+F6 decreased to 37% (Fig. 2b). This partial return toward earlier and intermediate elution does not prove production of larger molecules. It may instead reflect preferential loss of the late-eluting chromophore pool, proportional enrichment of residual fractions as UV absorption and fluorescence declined, or changes in association and conformation (Hanson et al., 2022; Xiao et al.,

2018). The total UV₂₅₄ responses of BDOM600 and BDOM700 were close to baseline (Fig. 2a), thus their F1–F6 percentages were not considered reliable.

Wavelength-resolved HPSEC–DAD maps provided additional qualitative evidence (**Fig. S2**). BDOM200 showed a broad early/intermediate-eluting absorbance domain, whereas BDOM300 and BDOM400 displayed several more distinct late-eluting bands, and BDOM500 retained only a few narrower bands. Signals were concentrated mainly at shorter UV wavelengths and attenuated toward longer wavelengths, indicating that the retention regions also differed in spectral response. The weak, horizontally striped BDOM600–BDOM700 maps are best interpreted as low-signal or baseline behavior rather than resolved chromatographic components (Hanson et al., 2022).

Overall, HPSEC revealed nonmonotonic reorganization of UV-active BDOM: a broad distribution with a prominent F1 fraction at 200°C, strong enrichment of smaller apparent-size domains at 300–400°C, redistribution toward larger and intermediate domains at 500°C, and insufficient signal for robust fraction analysis at 600–700°C. This sequence should not be simplified to a monotonic change in molecular weight because retention integrates apparent hydrodynamic size, association, conformation, and possible non-size-exclusion interactions.

3.4. Molecular composition and formula turnover revealed by Orbitrap HRMS

Negative-ion ESI Orbitrap HRMS spectra and Van Krevelen diagrams are shown in **Figs. S3 and S4**, respectively. The number of assigned formulas decreased from 2,099 in BDOM200 to 1,664, 1,563, 724, 552, and 450 in BDOM300–BDOM700. Detectable formula richness in the BDOM fraction therefore declined by 78.6%, with the largest stepwise contraction between 400 and 500°C (53.7%). This result indicates narrowing of the analytically accessible formula pool, not necessarily an equivalent decline in the total molecular diversity of unextracted BDOM (Cui et al., 2026; Dittmar et al., 2008; Fu et al., 2020).

Low- and intermediate-temperature BDOM was dominated by N-containing formulas (Fig. 3a). CHON formulas accounted for 40% of unique formulas and 36% of assigned-peak intensity in BDOM200, increased to 71% and 87% in BDOM300, and remained dominant in BDOM400 (68% and 71%, respectively). CHON enrichment is plausible for protein-rich sludge, but interactions among proteins, carbohydrates, lipids, and mineral-associated organic matter also influence N-containing thermochemical products (Du et al., 2022; Hou et al., 2025; Zuo et al., 2024). Thus, this trend cannot be assigned to protein pyrolysis alone. The CHON-intensity maximum at 300°C coincided with maximum HIX and humic-like FRI contribution, whereas BDOM400 combined a CHON-rich formula pool with maximum SUVA₂₅₄. These aligned trends support sequential reorganization but do not make CHON formulas equivalent to humic fluorophores or UV chromophores (Dittmar et al., 2008; Fu et al., 2020; Xu et al., 2025).

BDOM400 exhibited the strongest unsaturation- and aromaticity-compatible formula signature. The operational CRAM-/lignin-like region represented 76% of formulas and 86% of assigned intensity

(Fig. 3b). DBE_w and Almod_w reached 7.12 and 0.41, respectively, whereas H/C_w reached a minimum of 1.13 (**Table S4**). These internally consistent descriptors accord with the SUVA₂₅₄ maximum and indicate enrichment of unsaturated, strongly absorbing formula space (Fan et al., 2024; Li et al., 2024; Zhu et al., 2025). Nevertheless, “CRAM-/lignin-like” is an elemental-ratio classification, not proof of lignin or CRAM structures, and Almod_w constrains possible aromaticity without identifying molecular structures.

Formula-overlap analysis identified 400–500°C as the principal molecular transition interval (Fig. 4a-b). Of the 1,563 formulas detected in BDOM400, only 268 were retained in BDOM500, whereas 1,295 were no longer detected and 456 became newly detectable. The resulting Jaccard similarity was 0.133, compared with 0.293–0.452 for the other adjacent-temperature pairs (Fig. 4c). The transition therefore involved extensive formula replacement rather than only intensity changes within a conserved pool. Comparable temperature-dependent contraction and compositional reorganization have been reported for sludge-derived BDOM, although the exact transition window remains preparation-dependent (Cao et al., 2026; Du et al., 2022; He et al., 2026). FTIR spectra of freeze-dried BDOM provided qualitative bulk support, in which BDOM500 developed a sharper band near 1395 cm⁻¹ and more resolved features in the 1200–1095 cm⁻¹ fingerprint region (**Fig. S5**). Because these bands contain overlapping vibrations, they support a change in bulk functional-group distribution but do not identify the structures responsible for individual molecular formulas.

Differential formula analysis clarified the direction of molecular replacement (**Fig. S6**). Among the 1,295 formulas no longer detected at 500°C, 71% were CHON formulas and 79% occupied the operational CRAM-/lignin-like region. They had low H/C_w (1.11), high DBE_w (7.71), and high Almod_w (0.43), confirming preferential loss of the unsaturated and aromaticity-compatible formula pool enriched in BDOM400. In contrast, the 456 newly detectable formulas were dominated by CHO (43%) and CHOS (28%) compositions and were distributed mainly in the aliphatic/protein-like (30%) and lipid-like (27%) regions. They showed higher H/C_w (1.87), lower DBE_w (2.24), lower Almod_w (0.05), and lower NOSC_w (–0.80) than the no-longer-detected formulas. The 268 shared formulas also underwent marked intensity redistribution: 115 decreased by at least twofold and were predominantly CHON (84%) and CRAM-/lignin-like (88%), whereas 73 increased by at least twofold and were mainly CHO or CHOS formulas (84% combined). Thus, the transition involved directional replacement of an unsaturated, CHON-rich detectable pool by a more saturated and reduced CHO/CHOS-containing assemblage rather than a simple decline in formula richness. These are detection- and intensity-based patterns and should not be interpreted as direct evidence of compound formation or absolute enrichment in bulk BDOM.

At the aggregate class level (Fig. 3), the CHON contribution decreased from 68% to 31% by formula number and from 70% to 12% by assigned intensity between BDOM400 and BDOM500, while the CRAM-/lignin-like intensity contribution decreased from 86% to 26%. In parallel, H/C_w increased from 1.13 to 1.77, whereas DBE_w and Almod_w decreased from 7.12 to 2.79 and from 0.41 to 0.10, respectively. CHOS formulas represented 28% of unique formulas but 59% of assigned intensity at 500°C, and S/C_w reached 0.075. This number–intensity divergence indicates that a restricted subset of CHOS formulas dominated the negative-mode ESI response. It does not establish their absolute

abundance, functional-group identity, or formation pathway in the complete BDOM pool (Hou et al., 2025; Xu et al., 2025; Zuo et al., 2024).

At 600–700°C, the residual formula pool shifted further toward O-containing, N-free and lipid-like formula space (Fig. 3). From BDOM600 to BDOM700, CHO formulas increased from 41% to 53% of unique formulas and from 39% to 46% of assigned intensity; lipid-like contributions increased from 25% to 36% by formula number and from 24% to 30% by intensity. Condensed-aromatic formulas accounted for 11% of intensity at 700°C, whereas $Al_{mod,w}$ was 0.21, well below the BDOM400 maximum. The residual pool was therefore compositionally mixed rather than uniformly aliphatic or condensed aromatic (He et al., 2026; Hou et al., 2025; Zuo et al., 2024). Because only 552 and 450 formulas remained detectable, these percentages denote relative enrichment rather than absolute production. NOSC_w values of – 0.72 and – 0.76 indicate a more reduced average formula space than BDOM400 (– 0.16) (Fan et al., 2024; Li et al., 2024; Wang et al., 2025a).

The intensity-weighted mass of assigned formulas decreased from 284 Da in BDOM200 to 253 and 252 Da in BDOM400 and BDOM500, respectively, and then increased to 288 and 333 Da in BDOM600 and BDOM700 (**Table S4**). This trajectory should not be expected to reproduce the HPSEC distribution. Orbitrap mass describes individual detected ions, whereas HPSEC retention integrates hydrodynamic size, conformation, association, stationary-phase interactions, and UV₂₅₄ response. The two methods therefore resolve complementary, non-interchangeable molecular dimensions (Fan et al., 2024; Harir et al., 2022; Xiao et al., 2018).

Overall, Orbitrap HRMS resolved three compositional regimes: (i) a formula-rich, CHON-dominated pool at 200–300°C; (ii) maximum enrichment of unsaturated and aromaticity-compatible CRAM-/lignin-like formula space at 400°C; and (iii) a sharply contracted residual pool after the 400–500°C transition, marked by intense CHOS response at 500°C and increasing relative CHO/lipid-like contributions at 600–700°C. The exceptionally low 400→500°C Jaccard similarity, together with directional formula replacement and coherent changes in elemental classes and weighted indices, identifies this interval as the principal molecular-reorganization window within the detectable BDOM fraction.

3.5. Photochemical formation of PPRIs upon irradiation of BDOM

The absorbed-photon rate (R_a), steady-state PPRI concentrations, and apparent photon-normalized formation descriptors are summarized in Table 2, whereas probe kinetics and irradiated controls are shown in **Fig. S7**. At 5 mg C L⁻¹, R_a increased from 5.16×10^{-7} einstein L⁻¹ s⁻¹ for BDOM200 to 6.97×10^{-7} for BDOM300 and 13.84×10^{-7} for BDOM400, then decreased to 2.99, 1.85, and 1.31×10^{-7} einstein L⁻¹ s⁻¹ for BDOM500–BDOM700. Its ordering matched SUVA₂₅₄, and the BDOM400 maximum coincided with the highest DBE_w and $Al_{mod,w}$ and enrichment of unsaturated, CRAM-/lignin-like formula space. BDOM400 was therefore an absorption-dominated photoreactive pool. Strong absorption, however, does

not guarantee high formation efficiency because chromophores differ in intersystem crossing, excited-state energy, and quenching (Berg et al., 2023; Du et al., 2024; Maizel and Remucal, 2017).

Table 2
Steady-state concentrations and apparent quantum-yield descriptors of photochemically produced reactive intermediates generated by BDOM.

Sample	Ra (10 ⁻⁷ Einstein L ⁻¹ s ⁻¹)	Steady-state concentrations (M)			Apparent quantum-yield descriptors		
		[³ BDOM*] _{ss} (× 10 ⁻¹⁴)	[¹ O ₂] _{ss} (× 10 ⁻¹³)	[·OH] _{ss} (× 10 ⁻¹⁶)	f _{TMP} (M ⁻¹)	Φ _{1O₂} (× 10 ⁻²)	Φ _{·OH} (× 10 ⁻⁴)
BDOM200	5.16 ± 0.23	2.25 ± 0.05	0.57 ± 0.01	4.74 ± 0.32	131.10 ± 3.07	3.90 ± 0.04	1.52 ± 0.10
BDOM300	6.97 ± 0.48	3.83 ± 0.01	1.31 ± 0.07	5.94 ± 0.39	165.02 ± 0.30	6.57 ± 0.33	1.41 ± 0.09
BDOM400	13.84 ± 0.23	7.64 ± 0.29	1.83 ± 0.06	6.09 ± 0.46	165.65 ± 6.26	4.63 ± 0.14	0.73 ± 0.06
BDOM500	2.99 ± 0.45	1.24 ± 0.03	n.d.	3.98 ± 0.14	124.37 ± 2.98	n.d.	2.20 ± 0.08
BDOM600	1.85 ± 0.52	0.94 ± 0.07	n.d.	3.64 ± 0.19	151.84 ± 11.84	n.d.	3.25 ± 0.17
BDOM700	1.31 ± 0.13	1.01 ± 0.11	n.d.	3.02 ± 0.02	231.92 ± 24.27	n.d.	3.80 ± 0.02
Note: n.d. represents not determined.							

[³BDOM*]_{ss} increased from (2.25 ± 0.05) × 10⁻¹⁴ M for BDOM200 to (3.83 ± 0.01) × 10⁻¹⁴ M for BDOM300 and reached (7.64 ± 0.29) × 10⁻¹⁴ M for BDOM400. By contrast, f_{TMP} increased from 131.10 ± 3.07 M⁻¹ at 200°C to 165.02 ± 0.30 M⁻¹ at 300°C and remained unchanged at 400°C (165.65 ± 6.26 M⁻¹). The 99.5% increase in [³BDOM*]_{ss} from BDOM300 to BDOM400 thus matched the 98.6% increase in R_a, demonstrating an absorption-driven triplet-state maximum (McNeill and Canonica, 2016; Wan et al., 2021; Wang et al., 2020). Importantly, f_{TMP} is a TMP-reactivity-weighted coefficient, not the absolute quantum yield of all BDOM triplets (Du et al., 2025; Du et al., 2024; Milstead et al., 2023).

At higher temperatures, photon-normalized triplet reactivity partly compensated for declining absorption. From BDOM500 to BDOM700, f_{TMP} increased by 86.5% (124.37 ± 2.98 to 231.92 ± 24.27 M⁻¹), whereas R_a decreased by 56.2%. Consequently, [³BDOM*]_{ss} decreased by only 18.5% over this interval and increased slightly from BDOM600 to BDOM700. Relative to BDOM400, however, BDOM700 absorbed 90.5% fewer photons, despite a 40.0% higher f_{TMP} and its [³BDOM*]_{ss} remained 86.8% lower. The residual high-temperature BDOM was therefore comparatively efficient toward TMP but strongly absorption-limited,

precluding a simple monotonic temperature–photoreactivity relationship (Luo et al., 2023; Wang et al., 2023; Yang et al., 2025).

Quantifiable $^1\text{O}_2$ formation was observed for BDOM200–BDOM400. $[\text{}^1\text{O}_2]_{\text{ss}}$ increased from $(0.57 \pm 0.01) \times 10^{-13}$ M for BDOM200 to $(1.31 \pm 0.07) \times 10^{-13}$ M for BDOM300 and $(1.83 \pm 0.06) \times 10^{-13}$ M for BDOM400. The corresponding apparent $\Phi_{\text{}^1\text{O}_2}$ values were $(3.90 \pm 0.04)\%$, $(6.57 \pm 0.33)\%$, and $(4.63 \pm 0.14)\%$, respectively, consistent in magnitude with reported pyrogenic-DOM values (Fu et al., 2015; Wang et al., 2020; Wang et al., 2023). From 200 to 300°C, R_a and $\Phi_{\text{}^1\text{O}_2}$ increased by 35.1% and 68.5%, respectively. From 300 to 400°C, $\Phi_{\text{}^1\text{O}_2}$ decreased by 29.5%, yet $[\text{}^1\text{O}_2]_{\text{ss}}$ increased by 39.7% because R_a nearly doubled. Maximum $^1\text{O}_2$ exposure at 400°C therefore did not indicate maximum sensitization efficiency, which occurred at 300°C. For BDOM500–BDOM700, FFA loss was indistinguishable from that in the corresponding irradiated probe blank. This denotes production below the reliable quantification capability of the FFA method, not absence of $^1\text{O}_2$ (McNeill and Canonica, 2016; Milstead et al., 2023). The “n.d.” results are compatible with high f_{TMP} because TMP reports a reactivity-weighted triplet subset, whereas $^1\text{O}_2$ formation also depends on photon absorption, triplet energy, oxygen quenching, and energy transfer (Du et al., 2025; Du et al., 2024).

The $\cdot\text{OH}$ results showed the clearest efficiency–exposure divergence. $[\cdot\text{OH}]_{\text{ss}}$ increased from $(4.74 \pm 0.32) \times 10^{-16}$ M for BDOM200 to (5.94 ± 0.39) and $(6.09 \pm 0.46) \times 10^{-16}$ M for BDOM300 and BDOM400, respectively, and then decreased to (3.98 ± 0.14) , (3.64 ± 0.19) , and $(3.02 \pm 0.02) \times 10^{-16}$ M for BDOM500–BDOM700. Conversely, apparent Φ_{OH} decreased from $(1.52 \pm 0.10) \times 10^{-4}$ at 200°C to a minimum of $(0.73 \pm 0.06) \times 10^{-4}$ at 400°C before increasing to (2.20 ± 0.08) , (3.25 ± 0.17) , and $(3.80 \pm 0.02) \times 10^{-4}$ at 500–700°C (Berg et al., 2023; McKay et al., 2017; Wang et al., 2023; Liu et al., 2024). The 201% increase in Φ_{OH} from BDOM400 to BDOM500 did not prevent a 34.6% decrease in $[\cdot\text{OH}]_{\text{ss}}$ because R_a decreased by 78.4%. From BDOM400 to BDOM700, Φ_{OH} increased by approximately 421%, but $[\cdot\text{OH}]_{\text{ss}}$ still decreased by 50.4% as R_a fell by 90.5%. High apparent $\cdot\text{OH}$ efficiency at 500–700°C therefore represented compensation for weak absorption, not greater exposure.

The PPRI measurements consequently resolve three photochemical regimes. From 200 to 300°C, stronger photon absorption and greater $^1\text{O}_2$ sensitization efficiency jointly increased PPRI exposure. At 400°C, maximum R_a outweighed unchanged or lower photon-normalized efficiencies, producing absorption-driven maxima in $[\text{}^3\text{BDOM}^*]_{\text{ss}}$, $[\text{}^1\text{O}_2]_{\text{ss}}$, and $[\cdot\text{OH}]_{\text{ss}}$. At 500–700°C, increasing f_{TMP} and Φ_{OH} only partially compensated for the collapse in R_a . Absorbed-photon input and photon-normalized efficiency must therefore be evaluated separately when interpreting steady-state PPRI exposure (Berg et al., 2023; Maizel and Remucal, 2017; Wang et al., 2023).

3.6. Cross-scale synthesis of BDOM characteristics and photochemical reactivity

Because the series comprised only six temperature levels and several descriptors contained “n.d.” values, the cross-scale synthesis was based on aligned temperature patterns rather than formal cross-variable correlations or multivariate modeling. Figure 5 presents row-wise z-scores for release, photon absorption, fluorescence, apparent molecular size, molecular composition, apparent photon-normalized efficiency, and steady-state PPRI exposure, together with adjacent-temperature formula-overlap metrics. Each heatmap row is standardized independently, and colors therefore indicate whether a value is relatively high or low within that metric, not the magnitude of differences among metrics. The following comparisons are descriptive and do not establish statistical association or causal control.

The first major decoupling was observed between BDOM mobilization and DOC-normalized photon absorption. DOC release decreased monotonically, whereas $SUVA_{254}$ and R_a peaked at BDOM400. This absorption maximum coincided with the highest DBE_w and Almod_w, the lowest H/C_w, enrichment of CHON and CRAM-/lignin-like formulas, and predominance of the smaller apparent-size HPSEC fraction. Together, these measurements define an unsaturated, aromaticity-compatible, and strongly UV-absorbing analytical pool, but they do not identify a discrete molecular sensitizer class. The 300→400°C comparison provides the clearest functional evidence: R_a increased by 98.6%, f_{TMP} changed by only 0.4%, and $[^3BDOM^*]_{ss}$ increased by 99.5%. The BDOM400 triplet maximum was therefore absorption-driven. In contrast, the coincident BDOM300 maxima in HIX, humic-like FRI contribution, and Φ_{1O_2} indicate a distinct fluorescence-associated sensitization state, although the three quantifiable Φ_{1O_2} observations support only qualitative comparison.

The sharpest coupled transition occurred from 400 to 500°C. Differential formula analysis showed that the no-longer-detected pool was predominantly CHON and CRAM-/lignin-like, whereas newly detectable formulas were more saturated and dominated by CHO/CHOS compositions. This directional replacement coincided with redistribution away from the smaller apparent-size HPSEC fraction, a 78.4% decrease in R_a , and decreases of 83.8% and 34.6% in $[^3BDOM^*]_{ss}$ and $[^{\bullet}OH]_{ss}$, respectively. The simultaneous 201% increase in Φ_{OH} was insufficient to maintain $\bullet OH$ exposure. CHOS enrichment in BDOM500 is therefore best interpreted as a marker of the molecular transition rather than evidence for a sulfur-mediated $\bullet OH$ pathway: CHOS contributions subsequently declined while Φ_{OH} continued to increase, and molecular formulas cannot resolve sulfur functional groups or radical precursors (Luo et al., 2023; Zuo et al., 2024).

At 600–700°C, the residual BDOM occupied a photon-efficient but absorption-limited regime. Relative to BDOM400, BDOM700 had a 90.5% lower R_a but a 40.0% higher f_{TMP} and an approximately 421% higher Φ_{OH} . Nevertheless, $[^3BDOM^*]_{ss}$ and $[^{\bullet}OH]_{ss}$ remained 86.8% and 50.4% lower, respectively. The increased efficiencies therefore provided only partial compensation for diminished photon absorption. The high f_{TMP} of BDOM700 also does not imply efficient $^1O_2$ sensitization because TMP probes a reactivity-weighted triplet subset, whereas oxygen sensitization additionally depends on triplet energy and oxygen-quenching kinetics (McNeill and Canonica, 2016; Milstead et al., 2023; Yang et al., 2025).

Accordingly, $[^1\text{O}_2]_{\text{ss}}$ and $\Phi_{^1\text{O}_2}$ for BDOM500–BDOM700 remain “n.d.” rather than being interpreted as zero.

Collectively, pyrolysis shifted the dominant limitation from carbon release at 200–300°C, to photon capture at the BDOM400 exposure maximum, and finally to severe absorption limitation despite partial efficiency compensation at 600–700°C. This distinction is the principal advance of the study: pyrolysis controls not simply whether sludge BDOM is photoreactive, but whether carbon mobilization, photon absorption, or photon conversion limits realized PPRI exposure. Because all photochemical comparisons were conducted at a standardized DOC concentration and under a defined irradiation spectrum, the results establish comparative photochemical potential rather than field PPRI concentrations (Du et al., 2024; McKay et al., 2017; Yang et al., 2025).

4. Conclusions

Pyrolysis decoupled the release, composition, and photochemical performance of sludge BDOM. DOC release decreased by 97.2% from SBC200 to SBC700, whereas DOC-normalized light absorption was maximal for BDOM400. Fluorescence, HPSEC, and Orbitrap HRMS further identified 400–500 °C as the principal transition interval. Differential formula analysis showed preferential loss of unsaturated CHON and CRAM-/lignin-like formulas and the newly detectable appearance of a more saturated CHO/CHOS-containing assemblage at 500 °C. Residual BDOM at 600–700 °C was weakly absorbing and fluorescent and showed increasing relative contributions from CHO and lipid-like formula space.

BDOM400 produced absorption-driven maxima in the steady-state concentrations of $^3\text{BDOM}^*$, $^1\text{O}_2$, and $\cdot\text{OH}$. Conversely, higher f_{TMP} and $\Phi_{\cdot\text{OH}}$ at 600–700 °C only partially compensated for weak photon absorption, while $^1\text{O}_2$ formation by BDOM500–BDOM700 remained below reliable quantification using the FFA method. Carbon release, light harvesting, photon-normalized formation efficiency, and realized PPRI exposure are therefore distinct quantities and should not be used interchangeably. Validation across environmentally relevant DOC concentrations, irradiation spectra, oxygen conditions, particulate matrices, and scavenger loads is required before these laboratory trends are extrapolated to field PPRI exposure.

Declarations

CRedit authorship contribution statement

Xufang Yu: Writing-original draft, Visualization, Formal analysis, Methodology. **Siyu Liu:** Investigation, Formal analysis, Data curation, Visualization. **Yichun Wang:** Investigation, Data curation. **Siyu Hang:** Data curation. **Limeng Shao:** Investigation. **Wenchao Ji:** Writing-review and editing. **Xingjun Fan:** Methodology, Supervision, Funding acquisition, Writing-review and editing. **Jianzhong Song:** Supervision, Funding acquisition, Writing-review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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Figures

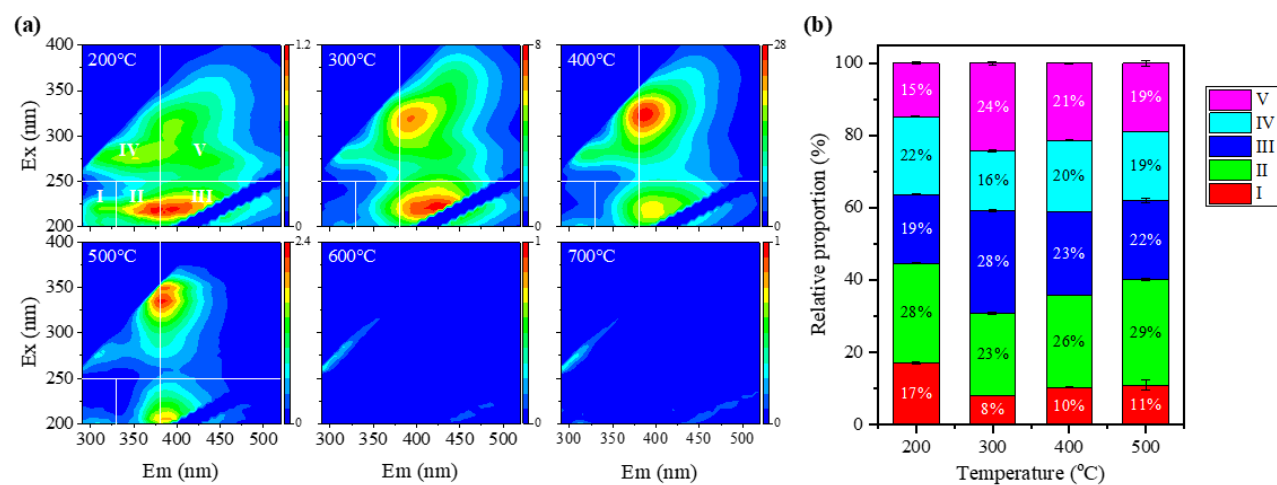


Figure 1

Temperature-dependent fluorescence characteristics of BDOM extracted from sludge-derived biochars produced at different pyrolysis temperatures. (a) EEM spectra of BDOM from SBC200-SBC700. (b) Relative contributions of fluorescence regional integration Regions I-V for BDOM200-BDOM500.

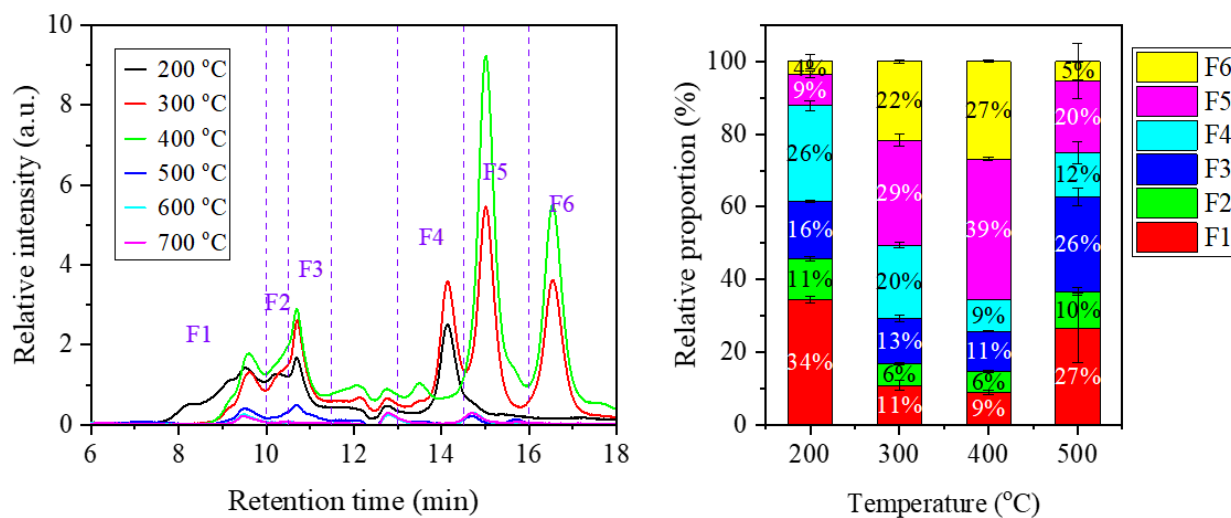


Figure 2

Operational HPSEC retention-time distributions of UV₂₅₄-active BDOM extracted from SBC200-SBC700. (a) HPSEC-UV₂₅₄ chromatograms, with vertical dashed lines defining six operational retention-time regions (F1-F6). (b) Contributions of F1-F6 to the total integrated HPSEC-UV₂₅₄ peak area of BDOM200-BDOM500.

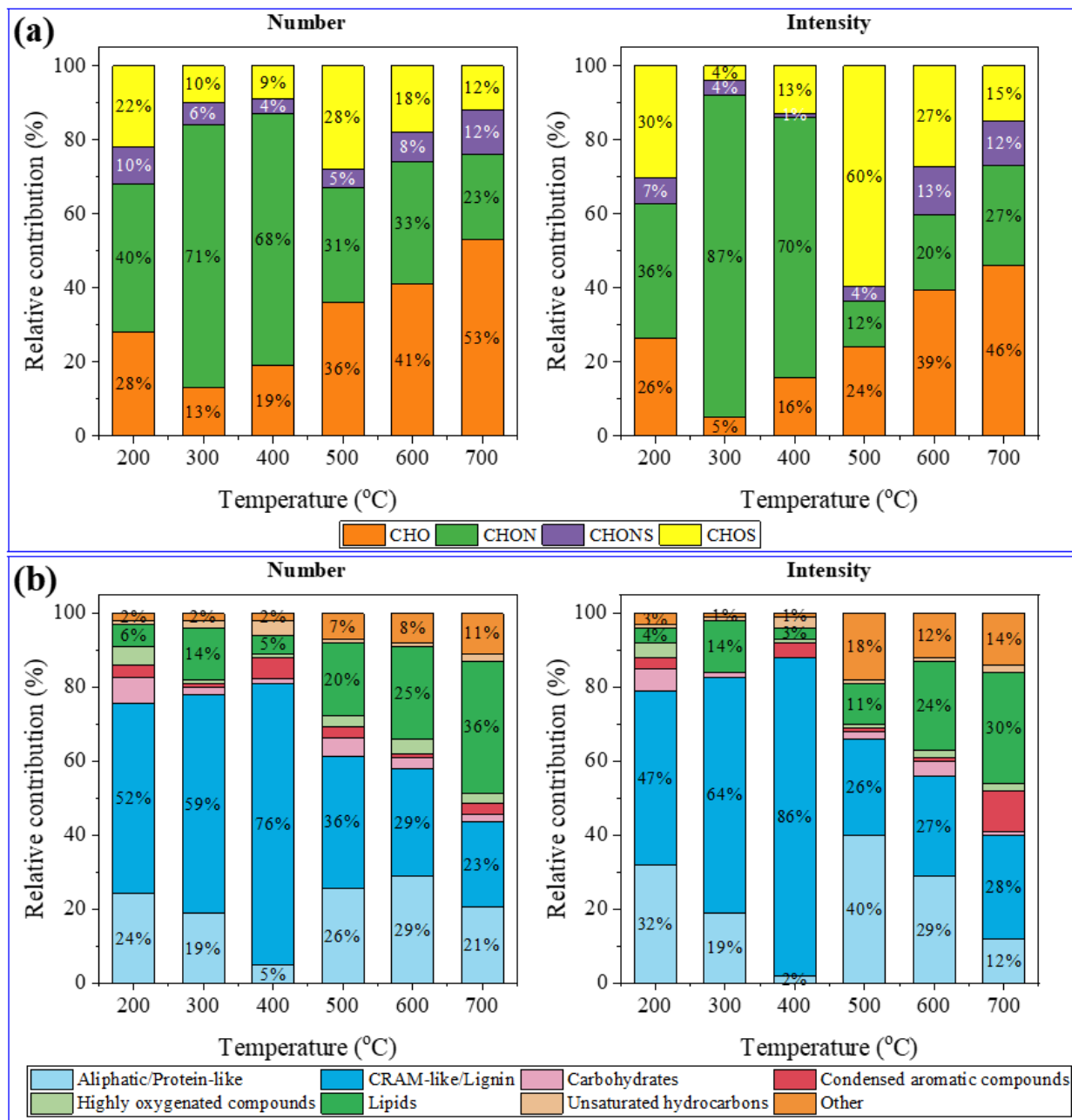


Figure 3

Temperature-dependent molecular-composition profiles of BDOM identified by Orbitrap HRMS. Relative contributions based on formula number (left) and summed assigned-peak intensity (right) are shown for (a) elemental groups and (b) operational Van Krevelen formula regions.

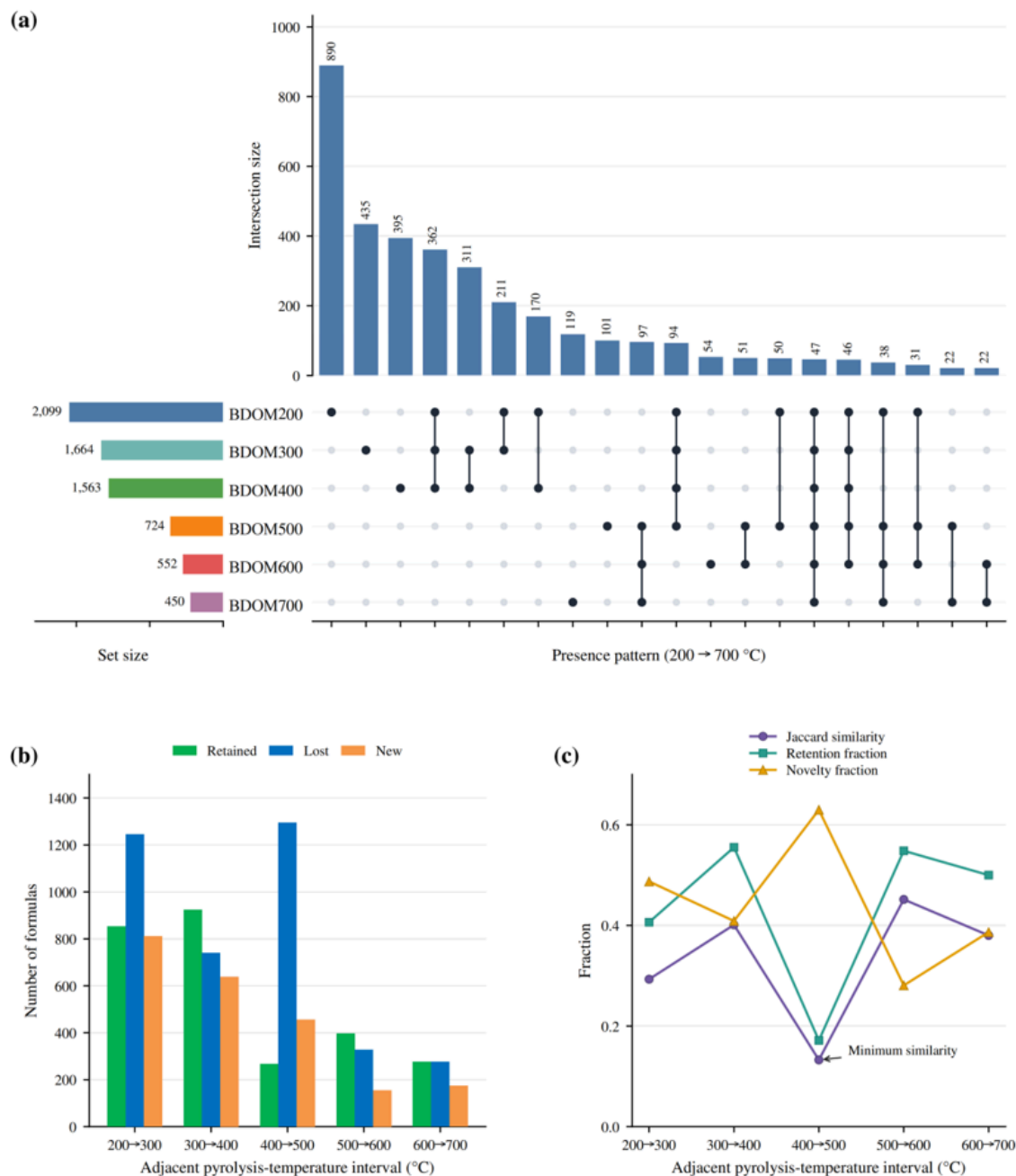


Figure 4

Overlap and turnover of exact molecular formulas in BDOM across the pyrolysis-temperature series. (a) UpSet plot showing the 20 largest intersections of identical C/H/O/N/S formulas among BDOM200-BDOM700; horizontal bars indicate the total number of formulas detected in each sample. (b) Numbers of retained, lost, and newly detected formulas between adjacent pyrolysis temperatures. (c) Jaccard similarity, retention fraction, and novelty fraction for adjacent temperature intervals.

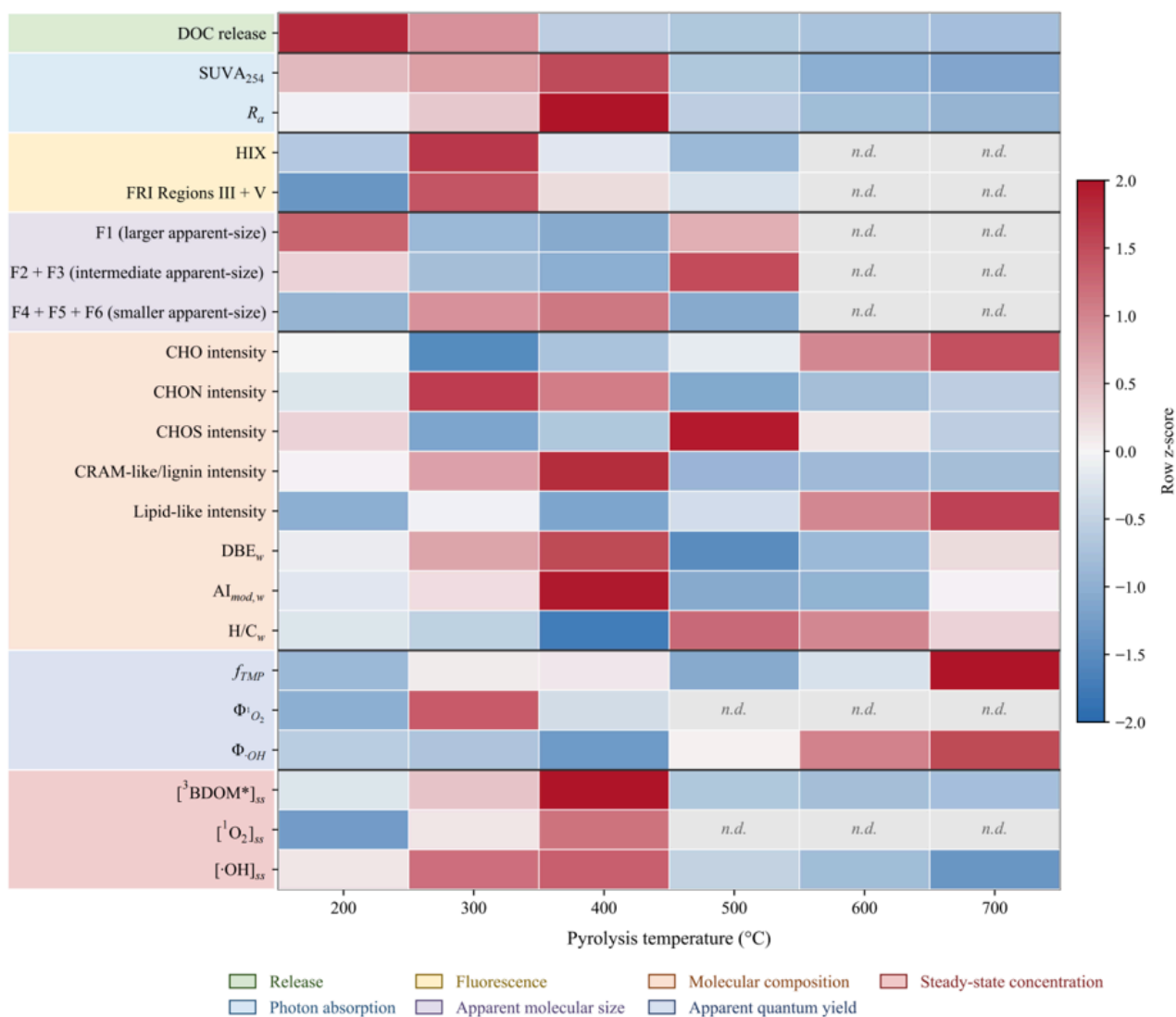


Figure 5

Cross-scale patterns of BDOM release, photon absorption properties, molecular composition, photon-normalized photochemical efficiency, and steady-state PPRI concentrations across the pyrolysis-temperature series. Gray cells marked n.d. were excluded from standardization.

Supplementary Files

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