

Manganese Oxides Drive Divergent Fates of Litter-Derived DOM via pH-Regulated Oxidative Decomposition and Polymerization

Feng Jiang, Hong Su, Qing-long Fu, Zi Yang, Xiaoming Wang, Hui Yin, Wenfeng Tan, Bruno Lanson, and Xionghan Feng*



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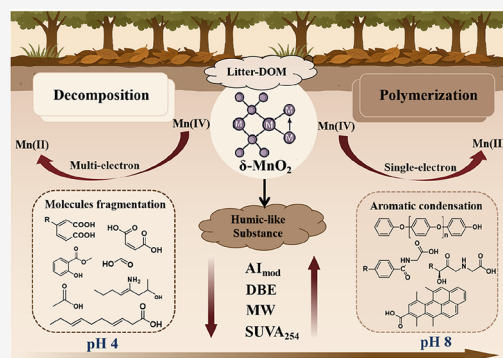
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ABSTRACT: Manganese (Mn) redox cycling critically regulates soil organic carbon (SOC) turnover, especially in the forest litter layer. However, the molecular-level mechanisms underlying the Mn oxide-mediated decomposition and polymerization of dissolved organic matter (DOM) from litter remain poorly understood. Integrating excitation–emission matrix spectroscopy (EEM) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), we investigated molecular mechanisms of δ -MnO₂-driven transformations of natural leaf litter-derived DOM samples across an ambient pH gradient (4, 6, 8). Results reveal that δ -MnO₂ simultaneously drives decomposition and polymerization of DOM, with pH modulating their relative contributions. At higher pH (pH 8), δ -MnO₂ facilitates aromatic condensation and coupling involving Mn(IV) $\rightarrow$ Mn(III)-mediated single-electron transfer, forming highly aromatic humic-like polymers and reducing electron-donating capacity, thereby enhancing oxidative resistance. Under lower pH (pH 4), δ -MnO₂ drives depolymerization and aromatic ring-opening by selectively cleaving oxygen-rich aromatic species. This process is dominated by multielectron transfer, with Mn(IV) reduced to Mn(II) via successive electron donation from DOM. Additionally, initial DOM composition impacts its transformation pathway. Specifically, high-aromaticity, high-molecular-weight fractions preferentially decompose, whereas low-aromaticity DOM tends to polymerize. These findings highlight the dual roles of Mn oxides in stabilizing organic matter, driving both the breakdown and reassembly through pH-regulated redox reactions.

KEYWORDS: manganese oxides, dissolved organic matter, abiotic humification, Mn–OC interaction mechanisms, FT-ICR MS



1. INTRODUCTION

Soils constitute the largest carbon reservoir on Earth, harboring more carbon than the atmosphere and vegetation combined.¹ The persistence of this critical carbon pool is governed by a dynamic equilibrium between decomposition and stabilization processes.^{2,3} Recently, microbial catabolism was regarded as the principal mechanism driving soil organic matter (SOM) production and sequestration,⁴ a concept encapsulated in the microbial carbon pump (MCP).⁵ However, emerging studies highlight the role of mineral surfaces in promoting the formation of recalcitrant organic matter through abiotic mechanisms such as adsorption, occlusion, redox reactions, and polymerization.^{6–12} This framework, recently conceptualized as the soil mineral carbon pump (MnCP), complements the MCP by emphasizing the importance of mineral-facilitated abiotic pathways in long-term carbon stabilization.⁸

Among mineral–organic interactions, growing evidence suggests that mineral-mediated molecular transformations, facilitated by redox reactions and surface catalysis, critically influence the stability of organic matter.^{6,7,13} Such processes can result in either oxidative degradation and mineralization of organic carbon or the polymerization of small organic

molecules into larger, more recalcitrant structures, with the latter pathway increasingly recognized as critical for carbon stabilization.^{6,7,12–14} Clay minerals (e.g., kaolinite, montmorillonite) and metal (oxyhydr)oxides (e.g., iron and Mn oxides) have been reported to catalyze polymerization reactions that yield high molecular weight, humic-like substances.^{6–12} However, mechanistic insights remain limited by reliance on simple model compounds (e.g., catechol, glucose, glycine), which inadequately capture the molecular diversity of natural organic matter.^{6–11} Consequently, the dynamic equilibrium between oxidative polymerization and decomposition of natural organic matter, as well as the molecular-scale transformation pathways mediated by reactive minerals, remains inadequately understood.¹⁴

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Among reactive minerals, Fe and Mn oxides are ubiquitous in soil and play key roles in regulating redox cycling of environmental elements.^{15–20} Although less abundant than Fe oxides, Mn oxides possess higher redox potentials, enabling more efficient transformation of organic molecules through redox reactions.^{21,22} Mn is enriched in foliage through plant uptake and subsequently accumulates in surface organic layers at levels comparable to or exceeding those of Fe.^{23,24} Field studies in forest ecosystems have revealed strong correlations between Mn abundance and organic carbon degradation rates, identifying Mn redox cycling as a major control on long-term litter decomposition.^{24–26} In this context, litter-decomposing fungi mediate Mn(II) oxidation to soluble Mn(III)–ligand complexes, enhancing the oxidative breakdown of lignin and other aromatic litter components as a critical mechanism contributing to litter decomposition.^{24–26} Concurrently, under limited ligand availability, Mn(II) is preferentially oxidized to insoluble Mn(III/IV) oxides during litter decay, contributing to Mn accumulation in surface soils.^{18,24,27} These Mn transformations occur within a leaf litter matrix rich in humic precursor, including phenolic compounds (e.g., tannins, lignin derivatives) and carbohydrates, which leach into soils and constitute an important source of DOM.^{18,28–32} While laboratory studies with model systems have demonstrated that Mn(IV) oxides promote the formation of humic-like polymers via oxidative coupling of phenols and Maillard reactions,^{8–10,18} direct molecular evidence for such abiotic pathways in natural litter remains scarce. Given the critical role of litter-derived DOM as a reactive carbon pool in biogeochemical cycling and carbon flux regulation,³² molecular-level elucidation of Mn oxide-driven abiotic transformation is essential to understanding mineral-induced organic matter stabilization.

Here, we investigated the abiotic transformation of DOM leached from four types of fresh leaf litter upon reactions with δ -MnO₂ under ambient pH conditions (4, 6, and 8). Although forest litter layers are typically acidic, pH 8 was included to reflect naturally occurring alkaline environments in certain forest soils and adjacent aquatic systems,^{33–36} and to enable comparison with previous studies on Mn oxide–DOM interactions, particularly those involving organic matter polymerization.^{6,9,10,37,38} The complementary application of FT-ICR MS and three-dimensional fluorescence excitation–emission matrix-parallel factor analysis (EEM-PARAFAC) revealed molecular polymerization and decomposition patterns of DOM and their potential molecular transformation pathways. Changes in Mn oxidation states in both solid and liquid phases were concurrently analyzed to reveal the relationship between electron transfer processes and DOM transformation. Electron-donating capacity (EDC) assays were further employed to evaluate shifts in the redox properties of the reaction products. This work aims to (1) confirm the existence of abiotic polymerization reactions driven by Mn oxides in natural litter systems, (2) characterize pH-dependent decomposition and polymerization patterns, and (3) decipher the relationship between interfacial electron transfer pathways and organic molecule transformations. Together, these findings advance our mechanistic understanding of MnCP-driven carbon stabilization at Mn oxide–organic interfaces.

2. MATERIALS AND METHODS

Information about chemicals used is given in Text S1.

2.1. Preparation of Litter-Derived DOM and δ -MnO₂. Freshly senesced leaves of four representative deciduous

species—*Liquidambar formosana* Hance (LF), *Quercus acutissima* Carruth (QA), *Lindera glauca* Blume (LG), and *Acer buergerianum* Miq. (AB)—were collected in June 2023 from a mixed evergreen–deciduous broad-leaved forest at the Dabie Mountain Forest Ecosystem State Field Scientific Observatory, Henan Province, China (32°06′46″N, 114°02′23″E). Newly fallen leaves were intercepted using sterilized nylon mesh traps (1 mm pore size, 1 m² area) elevated 15 cm above the ground to prevent soil contamination. Weekly collections were performed using sterile forceps, and samples were rinsed with ultrapure water (18.2 M Ω ·cm) to remove surface particulates. Leaves were oven-dried at 60 °C for 48 h to constant weight, cut into 1 cm $\times$ 1 cm fragments using sterilized stainless-steel scissors, and subjected to aqueous extraction at a 40:1 ultrapure water-to-biomass ratio under agitation (180 rpm, 25 °C, 24 h). The suspensions were filtered through 0.22 μ m poly(ether sulfone) membranes (Millipore) to obtain species-specific DOM extracts, designated LF-DOM, QA-DOM, LG-DOM, and AB-DOM. Further details regarding the selection and representativeness of these species are provided in Text S2.

δ -MnO₂ was synthesized via the reaction between Mn²⁺ and MnO₄[−] according to a previously reported protocol (Text S3).³⁹ Material characterization confirmed its mineral phase by X-ray diffraction (XRD), its mesoporous structure by Brunauer–Emmett–Teller (BET) analysis (surface area: 123.0 m² g^{−1}; average pore diameter: 14.5 nm), and its aggregated, amorphous morphology by scanning and transmission electron microscopy (SEM/TEM), as shown in Figure S1.

2.2. Kinetic Experiments of DOM Reactions with δ -MnO₂. Reactions were carried out in 250 mL amber serum bottles at 25 $\pm$ 1 °C under continuous magnetic stirring (300 rpm) in the dark. The reaction system consisted of 0.8 g L^{−1} δ -MnO₂ and various litter-derived DOM solutions containing 80 mg L^{−1} total organic carbon, with 10 mM NaCl as the background electrolyte. The solution pH was adjusted to 4, 6, or 8 using 0.1 M HCl or NaOH, with pH fluctuations controlled within $\pm$ 0.1 throughout the 30-day reaction period. To suppress microbial activity, 0.02% (w/v) sodium azide (NaN₃) was added.⁴⁰ At predetermined intervals, aliquots were filtered through 0.22 μ m membranes for analysis. Postreaction minerals were isolated via high-speed centrifugation, washed three times with ultrapure water, freeze-dried, and ground, then sieved through a 100-mesh screen for further characterization.⁴¹

2.3. Characterization of the Reaction Solution and Solid. The dissolved organic carbon (DOC) concentration was measured using a multi-N/C 2100 analyzer (Analytik Jena, Germany). UV–Vis spectra (200–800 nm, 1 nm interval) were recorded using an Agilent Cary 8454 spectrophotometer, and the specific UV absorbance at 254 nm (SUVA₂₅₄) was calculated as absorbance at 254 nm normalized to DOC (mg L^{−1}).⁴² Mn concentrations were determined by atomic absorption spectrometry (AAS; Agilent Technologies 200 series), and the absence of Mn(III) in the filtrates was confirmed by the Leucoberbelin Blue (LBB) method.^{43,44} The excitation–emission matrix (EEM) fluorescence spectra were acquired at room temperature using a Hitachi F-7100 fluorescence spectrophotometer with excitation wavelengths (Ex) from 220 to 450 nm and emission wavelengths (Em) from 250 to 600 nm. The EEM data ($n = 120$) were decomposed using parallel factor analysis (PARAFAC) with

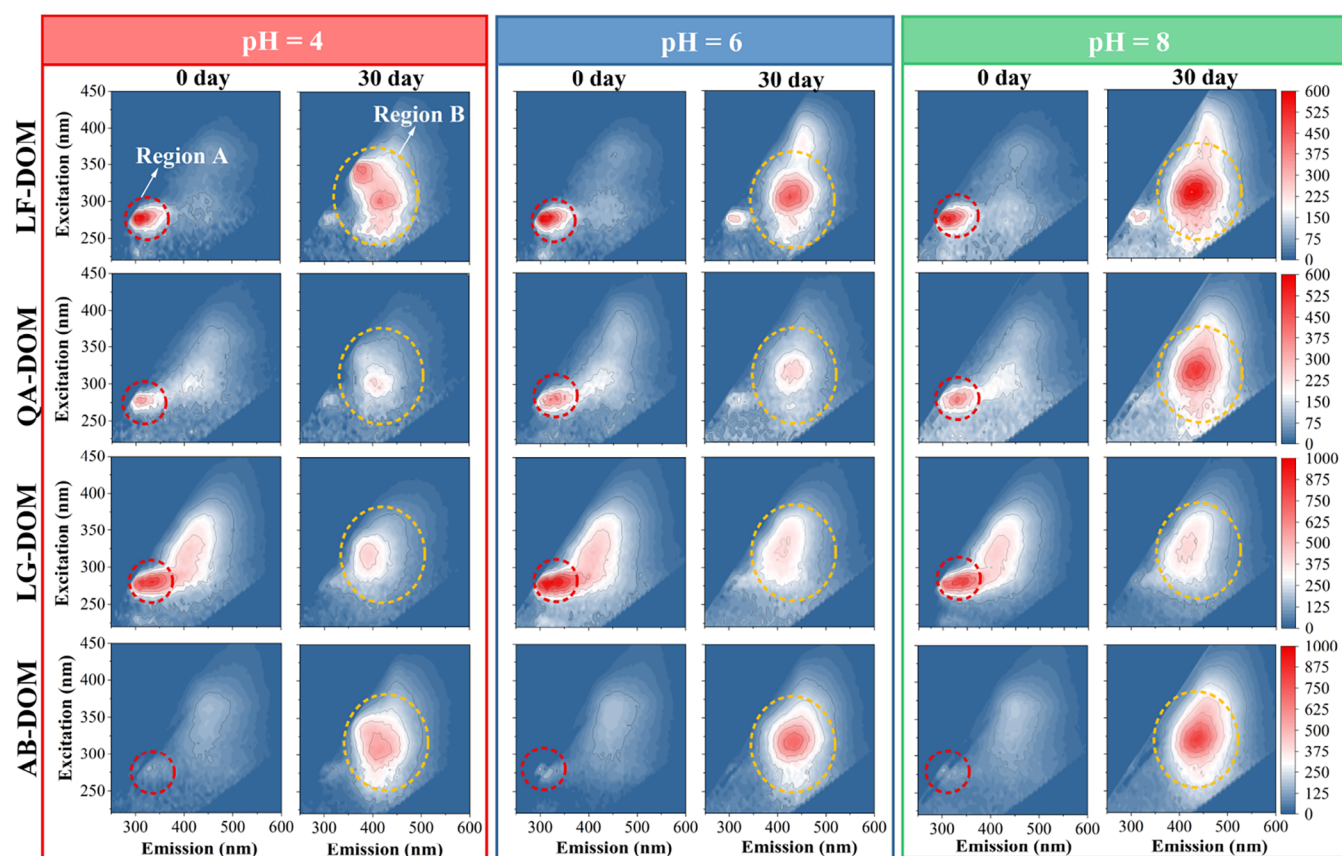


Figure 1. EEM fluorescence spectra of four litter-derived DOM samples (LF-DOM, QA-DOM, LG-DOM, AB-DOM) before (0 day) and after (30 days) reaction with δ -MnO₂ at pH 4, 6, and 8. Regions A and B are highlighted by red and yellow circles, respectively.

the EEMFlour toolbox in MATLAB R2024,⁴⁵ yielding three components (C1, C2, C3) validated by split-half validation and residual analysis. Fluorescence indices, including the fluorescence index (FI), humification index (HIX), and biological index (BIX), were calculated following previous reports.^{46,47} The influence of Mn²⁺ on UV and fluorescence measurements was assessed by varying its concentration from 0 to 500 mg L⁻¹, showing negligible effects on the EEM spectra, HIX, and UV absorbance at 254 nm (Figure S2). Low molecular weight organic acids (LMWOAs, e.g., formic, acetic acid, and malic acids) were quantified using ion chromatography (IC; Metrohm 930 Compact IC Flex) equipped with a Metrosep Organic Acids column (250 mm × 7.8 mm, 9 μm particle size) maintained at 30 °C. Total phenolic content was quantified via the Folin-Ciocalteu colorimetric assay (Text S4),⁴⁸ and protein-like components were quantified using the Bradford method (Text S5). The EDC within DOM was quantified by measuring the number of electrons transferred from the DOM to the radical cation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS^{•+}) (Text S6).^{49,50} Mineral phase evolution and Mn valence states were analyzed by XRD, electron spin resonance (EPR), and X-ray photoelectron spectroscopy (XPS), respectively. Details of the relevant analyses are presented in Texts S7–S9.

2.4. FT-ICR MS Analysis. Molecular composition of DOM before and after reaction was analyzed using a 7 T FT-ICR MS instrument (Solarix 2xR, Bruker, Germany) with an electrospray ionization (ESI) source in the negative ion mode. Aqueous samples were isolated by solid-phase extraction (SPE) before MS measurement (Text S10 for extraction

details).^{51,52} Data collection covered a mass-to-charge ratio (m/z) range of 100–1000 Da with 450 scans and 0.05 s ion accumulation time. Formulas for peaks with a signal-to-noise ratio above 4 were assigned within a mass tolerance of <1.0 ppm. Additional constraints included $0 < O/C \leq 1.2$, $0.3 \leq H/C \leq 2.5$, and $-10 \leq DBE-O$ (double bond equivalent minus oxygen) ≤ 10 .⁵³ The optimum formula for each peak was further determined with the minimum number of heteroatoms ($N + S + P$). All detected ion peaks, the number of successfully assigned molecular formulas, and the intensity-based formula assignment ratio are summarized in Table S1. The molecular weight (MW), H/C ratio, O/C ratio, modified aromaticity index (AI_{mod}), nominal oxidation state of carbon (NOSC), and DBE were used to describe the molecular properties (Text S11 for calculation details). Detected compounds were classified into major biochemical classes based on O/C and H/C ratios, according to established criteria (Table S2).⁵⁴ Notably, although FT-ICR MS offers high resolution and mass accuracy, inherent limitations such as partial analyte loss during sample preparation and ion suppression during electrospray ionization may result in underestimation of certain molecular components. To determine the changes in DOM composition after the reaction, detected DOM compounds were categorized into the following three pools: persistent (present before and after reaction), removed (detected only before reaction), and formed (detected only after reaction).^{37,55,56} Precursor–product pairs were identified by comparing exact mass differences between initial and newly formed molecules corresponding to characteristic transformations—including $-H$, $-2H$, $+O$, $+O-2H$, $+2O-2H$, $+3O$, $+O-SC-4H$, and

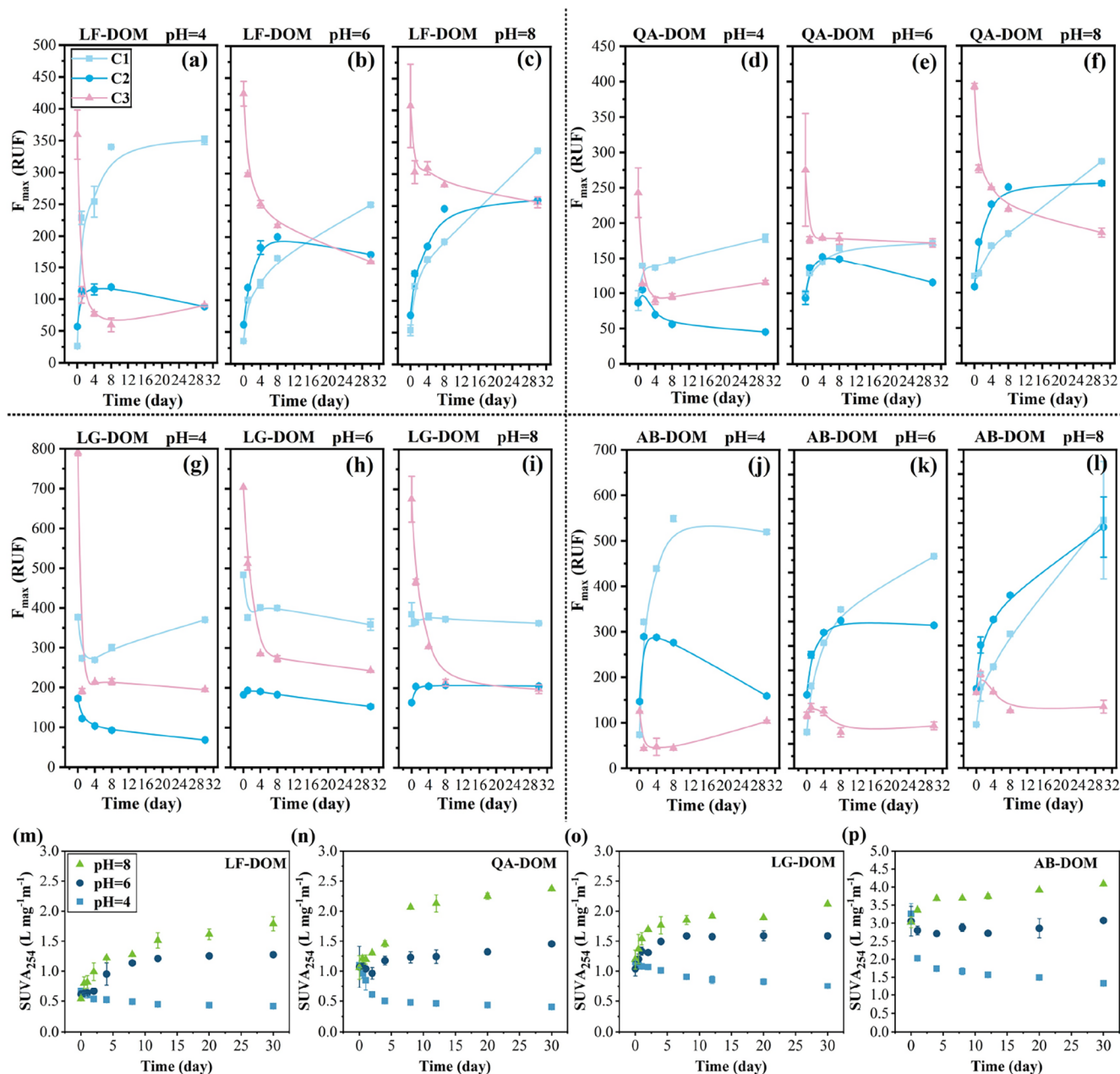


Figure 2. Temporal variations in $F_{\max}$ of PARAFAC-derived fluorescent components (C1, C2, C3) and $SUVA_{254}$ of four litter-derived DOM types (LF-DOM, QA-DOM, LG-DOM, AB-DOM) during reactions with δ -MnO₂ under pH 4, 6, and 8. Panels (a–l) show $F_{\max}$: (a–c) LF-DOM, (d–f) QA-DOM, (g–i) LG-DOM, and (j–l) AB-DOM. Panels (m–p) show $SUVA_{254}$: (m) LF-DOM, (n) QA-DOM, (o) LG-DOM, and (p) AB-DOM.

+ $n(C_6H_4O)$ ($n \geq 1$), following the previously reports of DOM oxidation by Mn oxides (Table S3).^{37,51,57–59} The mass difference networks were visualized using the Gephi software (0.9.4) to illustrate precursor–product relationships. The precursors and products of the dehydration condensation reaction are identified by mass spectrometry-matched molecular formulas (Text S12). Spearman correlation analysis ($p < 0.05$, $|r| > 0.7$) was performed to assess the associations between FT-ICR MS-derived molecular formulas and the fluorescent components (C1, C2, and C3) resolved by PARAFAC (Text S13).^{60–62}

3. RESULTS AND DISCUSSION

3.1. pH-Regulated Transformation of DOM: Polymerization and Decomposition by δ -MnO₂. EEM spectroscopy

was employed to track changes in fluorescent components of litter-derived DOM during reaction with δ -MnO₂. Initially, the four DOM samples (LF-, QA-, LG-, and AB-DOM) showed prominent fluorescence in the Ex/Em = 250–300/280–350 nm range (Region A), characteristic of tyrosine-like proteins and phenolic compounds (e.g., lignin phenols and tannins) (Figure 1).^{63–67} Upon reaction with δ -MnO₂, fluorescence in Region A diminished, while a broad, red-shifted band accumulated in the Ex/Em = 250–450/350–500 nm (region B), consistent with humic-like fluorescence.⁶³ HIX derived from EEM spectra showed significant elevation under all pH conditions after reaction (Figure S3), indicating Mn oxide-mediated abiotic humification. Quantitative assays confirmed a substantial depletion of protein-like (Figure S4) and phenolic-like components (Figure S5) across all DOM

samples, corroborating the fluorescence observations. These findings suggest the conversion of protein-like or phenolic precursors into humic-like substances, consistent with previously established polyphenol–Maillard and oxidative coupling mechanisms.^{6,8,14} Additionally, LF-, QA-, and AB-DOM systems exhibited a pH-dependent increase in humic-like fluorescence intensity (Region B), suggesting that higher pH conditions may be conducive to the formation of humic-like substances (Figure 1). In the LG-DOM system, labile short-wavelength components (Region A) were selectively removed, while humic-like substances (Region B) were retained. This preferential removal of low-aromatic species could also increase the humification degree via a relative enrichment of aromatic constituents.

To resolve the dynamic evolution of DOM fluorophores, three distinct components were resolved via PARAFAC analysis: a lower-aromaticity humic-like component (C1; $E_{\text{max}}/E_{\text{max}} = 315/410$ nm), a higher-aromaticity humic-like component (C2; $E_{\text{max}}/E_{\text{max}} = 365(320)/455$ nm), and a labile low-molecular-weight component (C3; $E_{\text{max}}/E_{\text{max}} = 280/325$ nm) (Figure S6), which exhibits spectral signatures of protein-like compounds (e.g., tyrosine), phenolic moieties, and other small metabolites.^{63–65,68–70} Time-resolved analysis uncovered pronounced pH-dependent dynamics in component behavior. The maximum fluorescence intensity (F_{max}) (Figure 2a–l) and relative abundance of C3 (Figure S7) declined markedly over time, with a faster depletion at lower pH, reflecting enhanced interfacial processes, such as surface adsorption and oxidative transformation. Concurrently, the humic-like components (C1 and C2) exhibited progressive accumulation, signifying humification-driven conversion of labile compounds, such as phenolic and tyrosine-like substances (C3), to humic-like macromolecules. Interestingly, the F_{max} of the higher aromaticity component (C2) demonstrated significant biphasic behavior in LF-DOM, QA-DOM, and AB-DOM systems under acidic conditions (pH 4), showing an initial F_{max} increase followed by a gradual decline, accompanied by concurrent increases in the less aromatic components (C1 and C3), suggesting selective adsorption and subsequent oxidative degradation of highly aromatic fractions. This transformation was progressively suppressed with increasing pH, reflecting the enhanced resilience of C2 to surface-mediated processes. As shown in Figure S7, the relative abundance ratio of C2 to C1 increased with pH across all DOM types after 30 days of reaction, reflecting preferential preservation of higher aromatic humic-like substances (C2) under alkaline conditions. By the end of the reaction, different pH conditions lead to distinct F_{max} accumulation profiles for three components (C1, C2, and C3) across all DOM (Figure 2a–l). At pH 4, the lower aromaticity component (C1) dominated over C2, indicating the selective accumulation of less aromatic humic substances. At pH 6, compared to pH 4, C1 decreased while C2 increased, indicating a shift toward the formation of higher aromatic humic-like substances. At pH 8, C1 and C2 accumulated synergistically, resulting in maximal humic substance preservation. These findings collectively suggest that Mn oxide-mediated polymerization and decomposition occur concurrently, with pH regulating the selective preservation of aromatic moieties. Further analysis of the three fluorescent components combined with FT-ICR MS was discussed in Section 3.4.

The DOM aromaticity changes during the reaction were monitored through time-resolved SUVA₂₅₄ measurements

(Figure 2m–p), a well-established indicator of molecular aromaticity and humification degree.⁷¹ Throughout incubation in the presence of δ -MnO₂, SUVA₂₅₄ increased under alkaline conditions (pH 8) and decreased under acidic conditions (pH 4) across all DOM types. At pH 6, SUVA₂₅₄ increased in LF-, QA-, and LG-DOM (+108%, +36%, and +53%, respectively), while AB-DOM showed minimal change (+0.65%), indicating limited aromatic enrichment. Under alkaline conditions, AB-DOM also showed a smaller increase (+35%) compared to LF- (+233%), QA- (+123%), and LG-DOM (+77%). The divergence likely stems from inherently high initial aromaticity (SUVA₂₅₄ = 3.26 L·mg^{−1}·m^{−1}) compared to other DOM types (0.67–1.15 L·mg^{−1}·m^{−1}), limiting polymerizable low-aromaticity precursors. Concurrently, the δ -MnO₂-mediated selective adsorption and oxidative decomposition of the highly aromatic fraction in AB-DOM likely cause a net loss of aromatic structures, thereby offsetting any polymerization-driven increase in SUVA₂₅₄.^{37,55} Thus, the observed SUVA₂₅₄ trajectory reflects the balance between these competing surface processes. After the reaction, SUVA₂₅₄ consistently followed the trend pH 8 > pH 6 > pH 4, indicating that alkaline conditions favor aromatic enrichment, whereas acidic conditions promote aromatic depletion, likely via preferential adsorption and oxidative breakdown. Control experiments conducted in the absence of δ -MnO₂ showed only minimal changes in SUVA₂₅₄ over 30 days (0.25–7.6%), confirming that the observed alterations in aromaticity were primarily mediated by δ -MnO₂ (Figure S8).

As shown in Figure S9, formic acid, acetic acid, and malic acid were identified, with their varying carbon chain lengths reflecting the extent of organic matter decomposition. At pH 4, formic and acetic acids predominated, while malic and acetic acids became the main products at pH 6 and 8. The higher relative abundance of shorter-chain acids at lower pH may reflect increased decomposition of DOM under acidic conditions. The above findings reveal that reaction pH governs Mn oxide-mediated organic matter transformation, with high pH favoring polymerization and low pH favoring decomposition, while the intrinsic chemical characteristics of DOM modulate this balance.

3.2. Molecular-Level Responses of DOM to pH Revealed by FT-ICR MS. FT-ICR MS analysis was employed to elucidate the pH-dependent transformation pathways of two contrasting DOM types—low-aromatic LF-DOM (SUVA₂₅₄ = 0.67 L·mg^{−1}·m^{−1}) and high-aromatic AB-DOM (SUVA₂₅₄ = 3.26 L·mg^{−1}·m^{−1})—upon reaction with δ -MnO₂. Compared to LF-DOM, the initial molecular features of AB-DOM were characterized by higher values of MW_w, AI_{modw}, DBE_w, O/C_w, and NOSC_w, reflecting its inherently more condensed and oxygen-rich aromatic structure (Table S4). Under alkaline conditions (pH 8), LF-DOM exhibited an increase in MW_w (378.35 → 412.26), DBE_w (5.70 → 6.35), O/C_w (0.37 → 0.39), and AI_{modw} (0.16 → 0.17), consistent with polycondensation reactions occurring during humification.^{72–75} In contrast, AB-DOM exhibited a dual response: increases in AI_{modw} (0.39 → 0.41) and NOSC_w (0.17 → 0.24), coupled with slight decreases in DBE_w (10.13 → 10.10) and MW_w (412.40 → 400.80), imply simultaneous polycondensation and oxidative cleavage. At neutral pH (pH 6), LF-DOM continued to exhibit signs of polymerization (MW_w: 378.35 → 404.43; DBE_w: 5.70 → 6.57; AI_{modw}: 0.16 → 0.18), whereas AB-DOM began to show more apparent degradation, with declines in DBE_w (10.13 → 8.96), MW_w (412.40 → 386.40), and AI_{modw}

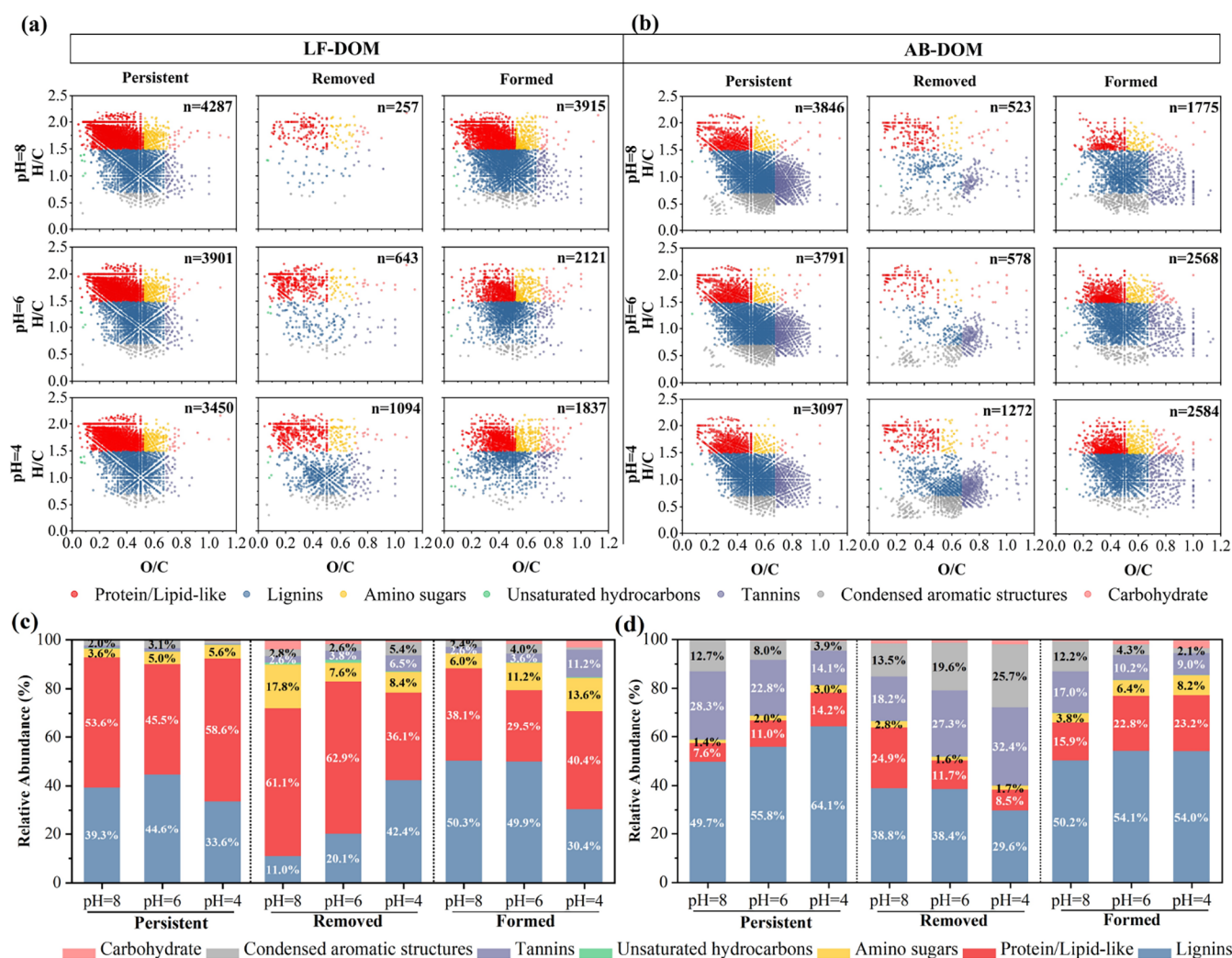


Figure 3. Van Krevelen diagrams showing persistent, removed, and newly formed molecular species in (a) LF-DOM and (b) AB-DOM after reaction with δ -MnO₂ at pH 4, 6, and 8. Relative abundances of biochemical categories in LF-DOM (c) and AB-DOM (d), corresponding to the molecular pools shown in (a, b), respectively.

(0.39 $\rightarrow$ 0.35). Under acidic conditions (pH 4), molecular fragmentation became dominant for both DOM types. LF-DOM showed reduced aromaticity (DBE_w : 5.70 $\rightarrow$ 5.48; AI_{modw} : 0.16 $\rightarrow$ 0.13) and a slight increase in H/C_w (1.52 $\rightarrow$ 1.54), indicating hydrolytic disruption and a shift toward more aliphatic character. For AB-DOM, degradation was more pronounced, with concurrent declines in MW_w (412.40 $\rightarrow$ 376.78), DBE_w (10.13 $\rightarrow$ 7.90), AI_{modw} (0.39 $\rightarrow$ 0.29), NOSC_w (0.17 $\rightarrow$ -0.09), and O/C_w (0.58 $\rightarrow$ 0.52), and an increase in H/C_w (1.01 $\rightarrow$ 1.20), suggesting cleavage of condensed aromatics, accompanied by hydrolytic disruption, and depletion of oxygen-rich moieties. These divergent responses suggest that AB-DOM is inherently more prone to oxidative decomposition, likely due to its higher unsaturation and abundance of oxygen-rich functional groups, whereas LF-DOM tends to undergo polymerization.

3.3. pH-Modulated Molecular Dynamics: Unraveling Patterns of Removal, Formation, and Persistence. Van Krevelen diagrams classify molecules into persistent, removed, and newly formed pools, with biochemical categories shown in Figure 3a,b. Weighted average molecular indices (Figure S10) and relative frequency distributions (Figures S11 and S12) further illustrate compositional shifts across pH. For both

DOM types, decreasing pH intensified the removal of aromatic/unsaturated components, evidenced by an increase in removed molecule counts and distribution shifts toward lower H/C regions (Figure 3a,b). Furthermore, at lower pH, the removed molecules in both DOM types exhibited elevated MW_w , AI_{modw} , DBE_w , NOSC_w , and O/C_w , coupled with reduced H/C_w (Figure S10). Similar patterns appeared in the frequency distributions of these indices (Figures S11 and S12), which collectively shifted toward higher MW, AI_{mod} , DBE, NOSC, and O/C values, and lower H/C values, indicating the preferential removal of oxygenated, highly unsaturated, aromatic polymers under acidic conditions. Specifically, in LF-DOM, the dominant removal shifted from protein/lipid-like compounds plus amino sugars (78.9% to 44.5%) to lignin (11.0% to 42.4%) as pH declined from 8 to 4 (Figure 3c). In AB-DOM, removal shifted from proteins/lipids (24.9% to 8.5%) and lignins (38.8% to 29.6%) to condensed aromatic structures (13.5% to 25.7%) and tannins (18.2% to 32.4%) (Figure 3d). Notably, removed molecules in AB-DOM showed higher MW_w , AI_{modw} , DBE_w , O/C_w , and NOSC_w and lower H/C_w than those in LF-DOM (Figure S10), indicating a greater loss of aromatic and oxygen-rich structures. This likely results from the preferential removal of tannins and condensed

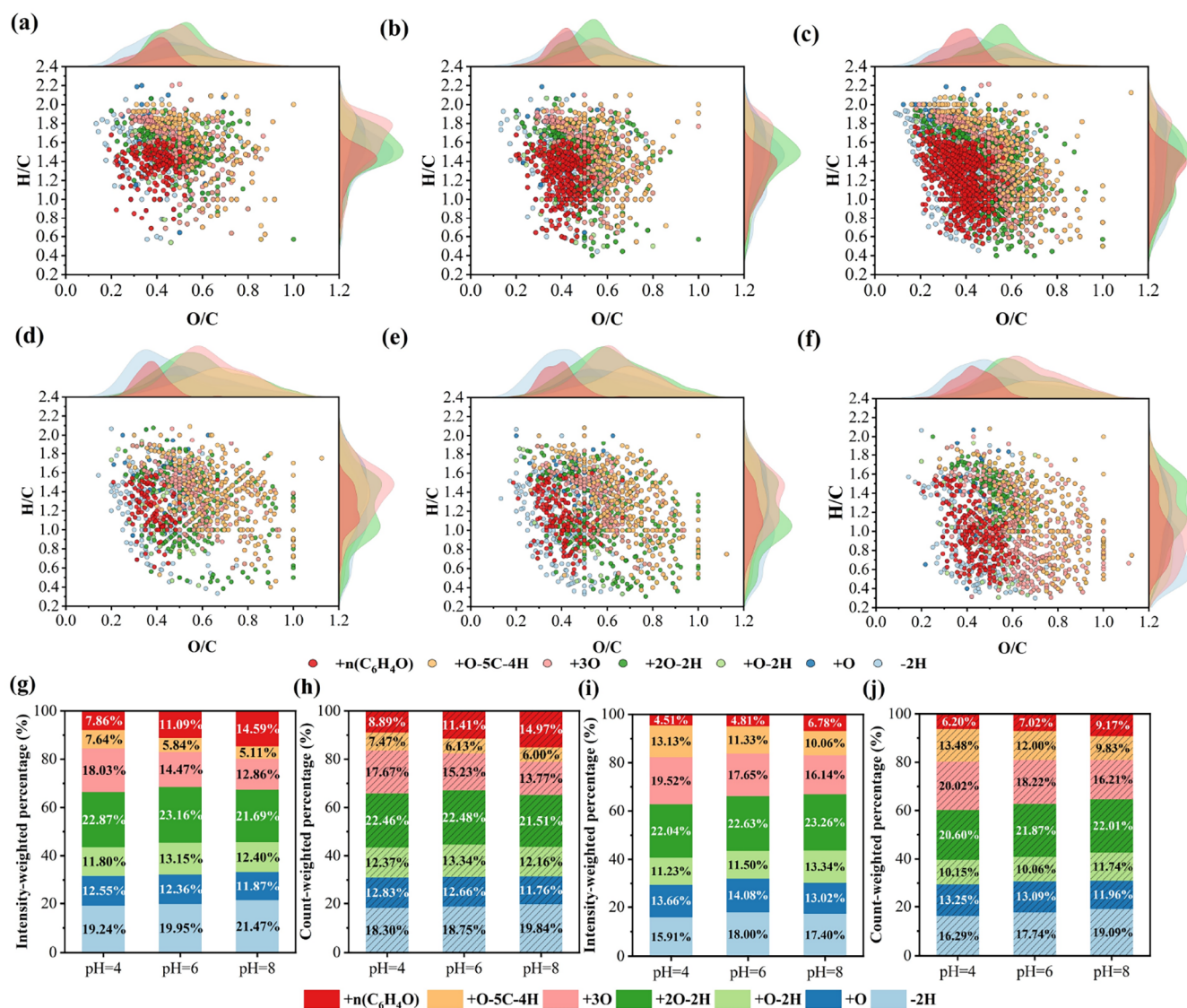


Figure 4. Van Krevelen diagrams of molecular products from different reaction pathways of LF-DOM at pH 4 (a), 6 (b), 8 (c), and AB-DOM at pH 4 (d), 6 (e), 8 (f); Panels (g, i) present intensity-weighted relative percentages of products, while panels (h, j) show molecule count-weighted relative percentages for LF-DOM (g, h) and AB-DOM (i, j), respectively.

aromatics in AB-DOM, which possess higher aromaticity, unsaturation, and oxygen content (particularly phenolic $-OH$ and carboxylic $-COOH$ moieties) than the protein/lipid-like compounds primarily removed from LF-DOM, as reflected by their frequency distributions of AI_{mod} , DBE, and O/C (Figure S13). These structural features confer enhanced redox activity, rendering them more susceptible to oxidative degradation.⁵⁵

For newly formed molecules, both DOM types exhibited increases in MW_w , $AI_{mod,w}$, DBE_w, and a decline in H/C_w with rising pH (Figure S10), indicating that higher pH favors the formation of aromatic polymers.^{72–75} This could be further supported by shifts in the frequency distributions of MW, AI_{mod} , DBE, toward higher values, and H/C toward lower values (Figures S11 and S12), consistent with the enrichment of unsaturated, aromatic compounds.^{72–75} The O/C_w of LF- and AB-DOM showed opposite pH-dependent trends, with LF-DOM increasing under acidic conditions likely due to oxygen incorporation via ring-opening and oxygenation, whereas AB-DOM decreased potentially via oxygen loss from decarboxylation and mineralization. In LF-DOM systems, the

relative abundance of lignin fractions within newly formed molecules exhibited a pH-dependent increase from 30.4% to 50.3%, which potentially contributes to the increased aromaticity (Figure 3c). In AB-DOM, although lignin remained the main newly formed component, its abundance decreased at higher pH, while condensed aromatic structures (rising from 2.1% to 12.2%) and tannins (from 9.0% to 17.0%) became more abundant, suggesting that enhanced aromaticity of AB-DOM under alkaline conditions is largely attributable to tannin and condensed aromatics formation (Figure 3d). These aromatic species—such as lignin, tannins, and condensed aromatic structures—likely serve as nuclei for the formation of humic-like substances.⁷⁴

Collectively, these results reveal a pH-dependent selectivity in δ -MnO₂-mediated DOM transformation pathways, as also observed in previous reports.^{37,38,55} Under acidic conditions, δ -MnO₂ preferentially interacts with highly oxygenated, aromatic molecules—particularly tannins and polyphenols—leading to their degradation and redistribution of molecular weight toward lower, aliphatic-rich modes. In contrast, under alkaline

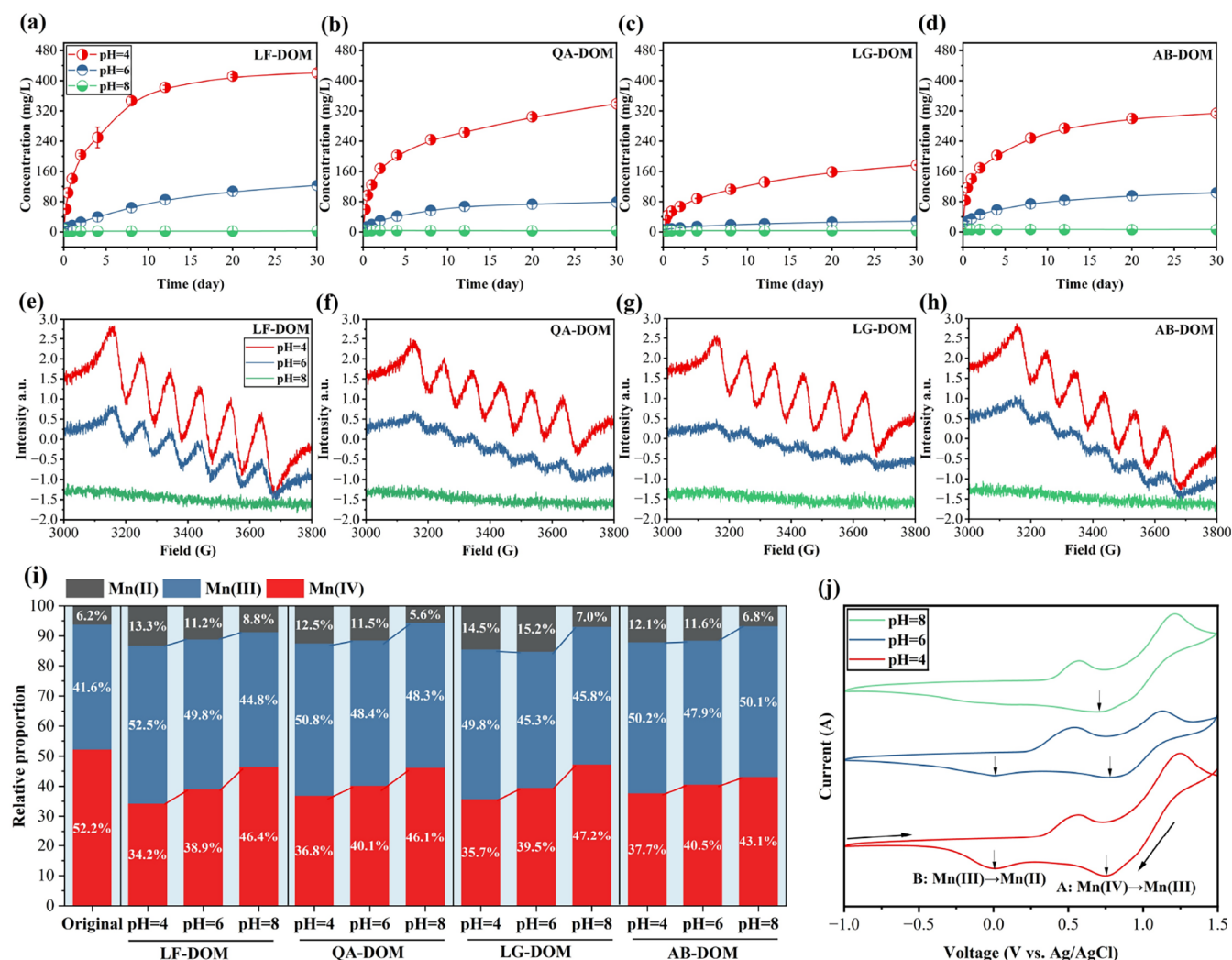


Figure 5. (a–d) Dissolution kinetics of Mn^{2+} from δ -MnO₂ during interaction with LF-DOM (a), QA-DOM (b), LG-DOM (c), and AB-DOM (d). (e–h) EPR spectra of δ -MnO₂ after reaction with LF-DOM (e), QA-DOM (f), LG-DOM (g), and AB-DOM (h). (i) Relative proportions of Mn(IV), Mn(III), and Mn(II) in δ -MnO₂ before and after reaction, determined by high-resolution Mn 3p XPS fitting. (j) Cyclic voltammetry curves of δ -MnO₂ under different pH conditions, using Ag/AgCl as the reference electrode.

conditions, δ -MnO₂ favors the removal of relatively less aromatic, low-MW molecules, while concurrently catalyzing polymerization reactions, yielding aromatic macromolecules.

3.4. Linking Molecular Composition with EEM Components. To elucidate the molecular characteristics underlying PARAFAC-derived fluorescent components, Spearman correlation analysis ($p < 0.05$, $|r| > 0.7$) was performed by integrating normalized fluorescence and FT-ICR MS data, identifying molecular formulas significantly associated with each component, as visualized in Van Krevelen diagrams (Figure S14a–c). Molecules positively correlated with labile low-molecular-weight component (C3) ($r > 0$) clustered in regions characterized by the highest H/C and lowest O/C ratios, corresponding to lipid/protein-like metabolites. In contrast, lower aromaticity humic-like component (C1)-correlated formulas occupied intermediate regions, while higher aromaticity humic-like component (C2)-associated formulas were enriched in domains with low H/C and high O/C ratios, indicative of highly unsaturated, oxygen-rich compounds. Kinetic analyses (Figure 2a,d and Section 3.1) revealed pH-dependent Mn oxide-driven humification: labile C3 is converted into humic-like C1 and C2, with C1

dominating under acidic conditions (pH 4) and C2 accumulating selectively at higher pH. Accordingly, the frequency distribution of AI_{mod} DBE, and NOSC increased progressively from C3 to C1 to C2, indicating rising aromaticity, unsaturation, and carbon oxidation state (Figure S14d–f). These molecular distinctions corroborate the assignment of C1 and C2 as humic-like substances with increasing aromaticity. These observations support the interpretation presented in Section 3.1 that higher aromaticity molecules formed during polymerization are more likely to be preserved under alkaline conditions, whereas selectively removed under acidic conditions. This selective removal is likely attributable to the markedly higher degree of unsaturation and abundance of oxygen-containing functional groups in C2-correlated molecules compared to C1. As demonstrated in Section 3.3, at lower pH, Mn oxides preferentially remove the highly aromatic, oxygen-rich molecules, leading to their enhanced decomposition.

3.5. Molecular Transformation Pathways of DOM Driven by δ -MnO₂ Oxidation. Based on previous studies,^{37,51,57–59} δ -MnO₂-mediated transformation of aromatic DOM can be summarized into four primary pathways (Table

S3): (i) oxidative conversion of phenol to *p*-benzoquinone, (ii) aromatic ring carboxylation, (iii) aromatic ring-opening, and (iv) oxidative coupling. Potential precursor–product pairs were identified via comprehensive mass difference analysis and visualized using a molecular network diagram (Figure S15). The corresponding reaction products were further illustrated in the Van Krevelen diagrams (Figure 4a–f). No molecular pairs corresponding to $-H$ were identified, likely due to the rapid coupling of phenoxy radicals. Quantitative analysis of transformation products was performed using both signal intensity-weighted and count-weighted molecular percentages, as shown in Figure 4g–j. Increasing pH significantly promoted the formation of coupling products ($+n(C_6H_4O)$), while suppressing the generation of ring-opening products ($+3O$, $+O-5C-4H$) in both DOM types. Comparative analysis further revealed that LF-DOM consistently exhibited a higher proportion of coupling products and a lower proportion of ring-opening products than AB-DOM, reflecting its stronger polymerization potential and lower decomposition tendency. Moreover, under lower pH conditions (notably pH 4 vs 6 and 8), both DOM types demonstrated increased contributions from $+O$ pathways, indicating an increased hydroxyl ($-OH$) groups. This enrichment in electron-donating functionalities may enhance the reductive potential of DOM.⁷⁶ To further characterize the molecular transformations, Figure S16 presents distributions of AI_{mod} and DBE, along with intensity-weighted averages of products derived from different reaction pathways. In both types of DOM, ring-opening products ($+3O$, $+O-5C-4H$) were shown to exhibit the lowest DBE and AI_{mod} in almost all reaction pathways. These findings suggest that ring-opening reactions may predominantly drive the reduction in aromaticity. Moreover, coupling products exhibited the highest DBE values for both DOM types, along with the greatest AI_{mod} for LF-DOM and the second-highest for AB-DOM. This consistent pattern demonstrates that oxidative coupling could serve as an important pathway enhancing molecular aromaticity and unsaturation during δ -MnO₂-mediated DOM transformation. In AB-DOM, the $-2H$ product showed slightly higher AI_{mod} than the coupling product, likely due to the abundance of highly aromatic phenolics (e.g., tannins) whose conversion to quinones preserved greater aromaticity than newly formed coupling products.

Condensation reactions constitute a pivotal mechanism in polymerization processes, playing a central role in soil humus formation.⁷⁷ These reactions facilitate the directed assembly of organic molecules, including phenols, aldehydes, alcohols, amines, and carbohydrates through dehydration (Figure S17a).⁷⁸ A typical dehydration condensation reaction is the Maillard reaction of reducing sugars and amino acids, which has been proven to be catalyzed by Mn oxides.⁷⁹ Systematic identification of dehydration-induced polymeric products via molecular formula matching (detailed in Text S12) revealed distinct pH-dependent characteristics in both LF-DOM and AB-DOM systems. As shown in Figure S17b–g, elevated pH significantly enhances the proportion of condensation products with low H/C ratios, accompanied by progressive accumulation of aromatic compounds such as lignins, tannins, and condensed aromatic structures. This phenomenon indicates that elevated pH may facilitate the generation of condensation products with increased aromaticity and unsaturation. These conclusions are corroborated by progressive increases in the $AI_{mod,w}$ and DBE_w , coupled with a systematic decline in H/C_w

(Figure S17h–m), collectively illustrating that elevated pH enhances Mn-driven aromatic condensation.

3.6. Interfacial Interaction between δ -MnO₂ and Litter-Derived DOM. The reductive dissolution of δ -MnO₂ during the interaction with four types of DOM exhibited pronounced pH dependence (Figure 5a–d), with Mn^{2+} release decreasing from 96.3%–40.5% at pH 4 to 28.3%–6.58% at pH 6, and further to 1.43%–0.63% at pH 8. EPR spectra of reacted δ -MnO₂ (Figure 5e–h) displayed the characteristic six-line hyperfine splitting of hydrated Mn^{2+} at $g \approx 2.005$, indicative of a high-spin d^5 center.^{80,81} EPR signal intensities increased in the order $pH\ 8 < 6 < 4$, consistent with greater Mn^{2+} release under acidic conditions and implying partial readsorption of Mn^{2+} onto δ -MnO₂ surfaces.⁸² Concurrently, DOC removal was significantly enhanced under acidic conditions (Figure S18a–d), indicating that both DOM adsorption and oxidation were promoted at lower pH. This synergy can be attributed to the enhanced DOM– δ -MnO₂ interfacial affinity arising from the reduced negative surface charge and an elevated redox potential of δ -MnO₂, which promotes organic carbon oxidation via direct electron transfer. Meanwhile, pH governs the protonation state of the oxygen bridges connecting Mn atoms on the MnO₂ surface, specifically, the $-O$, $-OH$, and $-OH_2$ groups.^{21,55} At lower pH, these oxygen bridges become increasingly protonated, which weakens the Mn–O bonds and facilitates the reductive release of Mn^{2+} from δ -MnO₂.⁴⁴

XRD patterns indicated that unreacted δ -MnO₂ exhibited low-intensity peaks at $2\theta = 23.5^\circ$ and 66.2° (Figure S18e–h), attributed to the (002) and (005) planes, without the (001) reflection at 12.5° , suggesting poor stacking along the *c*-axis.^{83,84} A broad peak near $2\theta = 37.0^\circ$ confirmed its turbostratic phyllosilicate structure.⁸⁵ Upon reaction with DOM, new diffraction peaks emerged at $2\theta = 42.4^\circ$ and 56.3° , especially under acidic and neutral conditions (Figure S18e–h). These features do not match known Mn mineral patterns, suggesting no secondary mineral formation.⁸⁴ These two peaks, also reported in previous studies involving the reaction of δ -MnO₂ with organic matter, are hypothesized to indicate the ordering of a mixture of sheets with hexagonal and orthogonal 2-dimensional symmetry.^{83,84} These features likely reflect structural modifications resulting from interactions with organic matter, leading to a more ordered phase. At lower pH, the enhanced reductive dissolution of Mn^{2+} from δ -MnO₂ by DOM may act as a bridging cation, potentially coordinating with edge hydroxyl groups and Mn vacancies on the basal plane to promote the ordered stacking of δ -MnO₂ nano-sheets.^{86,87}

The average oxidation state (AOS) of the surface Mn atoms was calculated based on the XPS spectra of Mn 3s (Figure S19a).⁸⁸ Following reaction with the four DOMs, AOS declined by 0.31–0.40, 0.26–0.32, and 0.10–0.16 at pH 4, 6, and 8, respectively. The more pronounced decline at lower pH further suggests enhanced direct electron transfer from DOM to δ -MnO₂. Mn 3p XPS deconvolution (Figure S19b) revealed that pristine δ -MnO₂ consisted of 52.2% Mn(IV), 41.6% Mn(III), and 6.2% Mn(II) (Figure S1). Postreaction, the reduction of Mn(IV) exhibited pronounced pH-dependent variability, with the most substantial decrease observed at pH 4 (14.5%–18.0%), followed by pH 6 (11.7%–13.3%), and the least reduction at pH 8 (5.0%–9.1%), with corresponding increases in Mn(III). These results indicate that Mn(IV) in δ -MnO₂ acts as the primary electron acceptor from DOM. Notably, under alkaline conditions (pH 8), Mn(II) formation

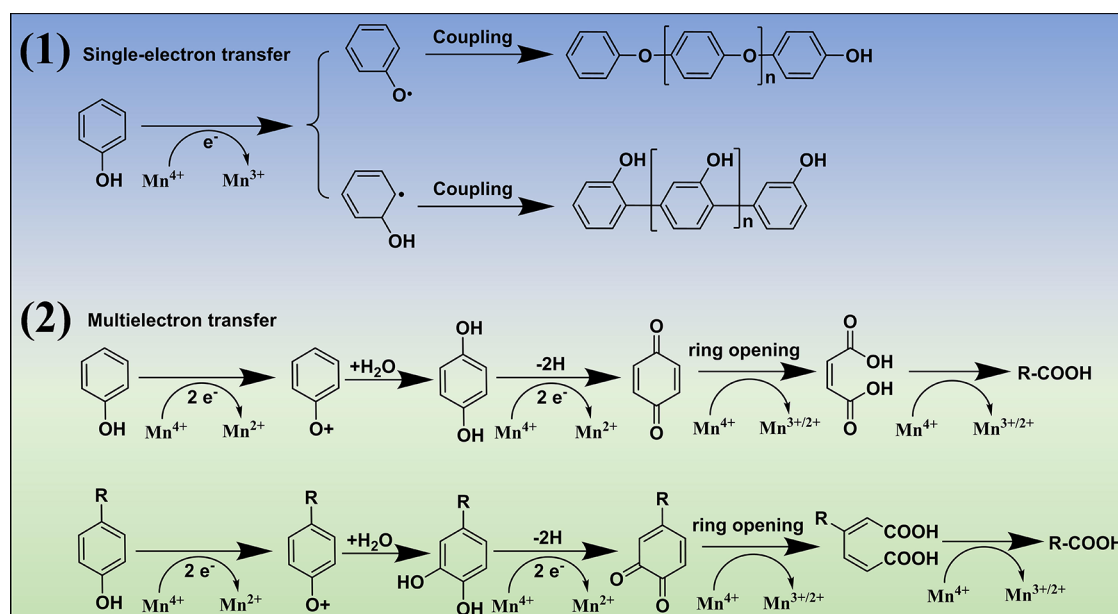


Figure 6. Conceptual schematic of single- and multielectron transfer processes driving distinct pathways of organic matter transformation.

was negligible in both the aqueous phase and on the mineral surface, whereas substantial accumulation occurred under acidic conditions (pH 4) (Figure 5a–i). The significant accumulation of Mn(II) at pH 4 reflects the extensive two-electron reduction of Mn(IV) to Mn(II), likely proceeding via rapid conversion of transient Mn(III) intermediates. In contrast, negligible Mn(II) formation alongside an increase in Mn(III) at pH 8 suggests that the reduction proceeds predominantly via a single-electron transfer pathway from Mn(IV) to Mn(III). The pH-dependent selectivity highlights an elevated proportion of Mn(IV)-to-Mn(III) transformation relative to Mn(IV)-to-Mn(II) reduction as pH increases.

Cyclic voltammetry was used to probe the pH-dependent redox behavior of δ -MnO₂ (Figure 5j). At pH 4, two cathodic peaks appeared at ~ 0.75 V (Peak A) and ~ 0 V (Peak B), corresponding to the stepwise reductions of Mn(IV) to Mn(III) and Mn(III) to Mn(II), respectively, consistent with the established redox hierarchy.^{59,89} Notably, as the pH increased from 4 to 8, the intensity of Peak B progressively diminished and nearly vanished at pH 8. This trend indicates enhanced stability of Mn(III) under alkaline conditions, thereby suppressing further reduction to Mn(II).⁸⁹ Consequently, the Mn(III) to Mn(II) transition constitutes the rate-determining step in the overall Mn(IV) to Mn(II) redox cascade. Notably, single-electron transfer processes are favorable for generating organic radicals (e.g., phenoxyl and semiquinone radicals), which are key intermediates in covalent bond formation, such as coupling and addition reactions.^{12,18,90–92} The pH-dependent stability of Mn intermediates likely modulates organic radical dynamics. Mn(III) species exhibit enhanced stability at higher pH levels, potentially allowing single-electron transfer from DOM to Mn(IV) to produce organic radicals with extended lifetimes that increase the probability of radical–radical coupling before further oxidation. This observation aligns with the increased proportion of oxidative coupling products observed at pH 8 (Figure 4g–j). Conversely, at lower pH levels, the oxidative reactivity of Mn(III) is enhanced, leading to rapid sequential electron transfers from DOM to Mn(IV) and subsequently to

Mn(III), culminating in the formation of Mn(II). This accelerated electron transfer sequence may rapidly consume organic radicals before they can form stable covalent bonds and further promote the fragmentation of organic molecules.

To probe the electron transfer regimes, EDC was quantified via ABTS^{•+} consumption ($\Delta_{\text{ABTS}^{•+}}$), reflecting the oxidation resistance of organic matter (Figure S20).⁴⁹ For all DOMs, the $\Delta_{\text{ABTS}^{•+}}$ decreased after the reaction, indicating the net depletion of native electron-donating moieties (Figure S20a). However, at pH 4 and 6, the EDC of LF-, QA-, and LG-DOM increased after the reaction (Figure S20b), with greater increases at lower pH, indicating the potential generation of newly formed electron-donating species.⁷⁶ This increase may result from δ -MnO₂-driven oxidation of otherwise ABTS^{•+}-resistant components, given the higher redox potential of δ -MnO₂ ($E^\circ = 1.23$ V) relative to ABTS^{•+} ($E^\circ = 0.68$ V).^{49,59,93} Specifically, δ -MnO₂-mediated depolymerization and ring-opening of aromatics may generate oxygen- and nitrogen-rich intermediates (e.g., carboxylated, hydroxylated, aminated species), which could serve as electron donors contributing to ABTS^{•+} consumption.^{18,76,94} More importantly, the increased EDC may reflect the transformation of certain organic compounds into more strongly reducing species, which could further contribute to Mn(IV/III) reduction within a redox-cycling process. In contrast, AB-DOM showed a consistent decrease in EDC across all pH levels, indicating that the consumption of native electron-donating moieties exceeded the formation of new redox-active species. Under alkaline conditions, the reduction in EDC may result from oxidative C–O–C coupling and condensation reactions involving phenolic and other electron-donating moieties, thereby increasing oxidation resistance.

Combining the molecular transformation pathways of DOM discussed in Section 3.5, it is implied that the oxidative transformation of DOM is fundamentally regulated by the pH-dependent electron transfer pathway. Under alkaline conditions, single-electron transfer predominates, generating organic radicals (e.g., phenoxyl and semiquinone radicals) that drive polymerization via radical coupling (C–O/C–C

bond formation) (Figure 6; eq (1)).⁵⁹ This process enhances the oxidation resistance of organic matter by forming cross-linked networks that inhibit further Mn(IV/III) reduction. In contrast, under acidic conditions, a multielectron transfer process dominates, involving the Mn(IV) → Mn(II) reduction through successive electron donation from DOM to MnO₂ and sequential oxidation of reactive organic intermediates. A representative pathway initiates with the two-electron oxidation of phenolic moieties to phenoxonium ions (Ar–O⁺), followed by nucleophilic water addition to form hydroquinone, which is further oxidized via another two-electron transfer to form benzoquinone.^{51,59,91} These intermediates then undergo further oxidation-mediated ring cleavage, ultimately yielding low-molecular-weight carboxylic acids (Figure 6; eq (2)).⁹¹ These findings highlight that the electron transfer pathway critically dictates DOM transformation trajectories—toward polymerization (radical recombination) or decomposition (structural breakdown)—depending on the prevailing redox conditions.

3.7. Environmental Implication. This study offers fundamental insights into the pH-dependent dual functionality of Mn oxides in regulating the fate of litter-derived DOM. By integrating fluorescence spectroscopy (PARAFAC) with FT-ICR MS analyses, specific molecular formulas were linked to resolved fluorescence components, providing complementary, cross-validated molecular-level evidence for the simultaneous occurrence of oxidative decomposition and polymerization. These complementary techniques collectively corroborate that Mn oxides function as key abiotic catalysts within the MnCP.⁵ Under alkaline conditions, Mn oxides act as molecular “builders”, promoting oxidative coupling and condensation reactions accompanied by single-electron transfers between Mn oxides and organic matter, which favor the formation of aromatic, humic-like geopolymers. This abiotic humification could enhance long-term carbon sequestration, especially in mineral-rich or microbially constrained environments. In contrast, under acidic conditions, Mn oxides shift to a “breaker” role, where multielectron transfers dominate, selectively cleaving aromatic compounds via ring-opening reactions and generating low-molecular-weight (LMW) organics. This pathway likely contributes to enhanced CO₂ emissions and the mobilization of Mn²⁺ through ligand-driven dissolution, offering a partial explanation for field-observed correlations between Mn abundance and litter decomposition.^{24–26} Notably, polymerization persists even under low-pH regimes, though its efficiency is suppressed by competing decomposition pathways. Collectively, these findings indicate that interfacial electron transfer between Mn oxides and natural organic matter fundamentally governs both the transformation behavior and structural stability of organic molecules.

Our findings address two critical knowledge gaps: (1) the molecular mechanisms underlying Mn oxide-mediated interactions with multiple natural plant-derived DOMs, rather than model compounds, and (2) the synchronized decomposition and polymerization processes that create competing carbon fluxes—simultaneously consuming labile carbon through oxidative decomposition while stabilizing carbon via abiotic humification. By situating these molecular mechanisms within the MnCP paradigm, this insight underscores the importance of incorporating mineral-driven polymerization and decomposition kinetics into Earth system models to improve

predictions of long-term carbon pool stability and carbon–climate feedbacks.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.5c08244>.

δ -MnO₂ synthesis and characterization (XRD, XPS, SEM, TEM, BET); solid-phase extraction of DOM; quantification of phenolic, protein-like compounds, organic acids, and EDC; identification of FT-ICR MS formulas linked to fluorescence PARAFAC components; identification and visualization of molecular transformation pathways and condensation products; and evaluation of DOC removal and δ -MnO₂ transformation (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Xionghan Feng — Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China; Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China; orcid.org/0000-0001-5499-7174; Phone: +86 27 87280271; Email: fxh73@mail.hzau.edu.cn; Fax: +86 27 87288618

Authors

Feng Jiang — Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China; Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China

Hong Su — Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China; Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China

Qing-long Fu — School of Environmental Studies, China University of Geoscience, Wuhan 430074, China; orcid.org/0000-0002-7125-6877

Zi Yang — Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China; Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China

Xiaoming Wang — Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China; Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China; orcid.org/0000-0002-5484-3922

Hui Yin — Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan

430070, China; Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China;
orcid.org/0000-0003-3060-7025

Wenfeng Tan – Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural Affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China; Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China;
orcid.org/0000-0002-3098-2928

Bruno Lanson – University Grenoble Alpes, CNRS, University Savoie Mont Blanc, IRD, University Gustave Eiffel, ISTERre, F-38000 Grenoble, France; orcid.org/0000-0003-1187-3221

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.est.5c08244>

Notes

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REFERENCES

- (1) Köchy, M.; Hiederer, R.; Freibauer, A. Global distribution of soil organic carbon – Part 1: Masses and frequency distributions of SOC stocks for the tropics, permafrost regions, wetlands, and the world. *Soil* **2015**, *1* (1), 351–365.
- (2) Bradford, M. A.; Berg, B.; Maynard, D. S.; Wieder, W. R.; Wood, S. A. Understanding the dominant controls on litter decomposition. *J. Ecol.* **2016**, *104*, 229–238.
- (3) Schmidt, M. W. I.; Torn, M. S.; Abiven, S.; Dittmar, T.; Guggenberger, G.; Janssens, I. A.; Kleber, M.; Kögel-Knabner, I.; Lehmann, J.; Manning, D. A. C.; Nannipieri, P.; Rasse, D. P.; Weiner, S.; Trumbore, S. E. Persistence of soil organic matter as an ecosystem property. *Nature* **2011**, *478* (7367), 49–56.
- (4) Kallenbach, C. M.; Frey, S. D.; Grandy, A. S. Direct evidence for microbial-derived soil organic matter formation and its ecophysiological controls. *Nat. Commun.* **2016**, *7* (1), No. 13630.
- (5) Liang, C.; Schimel, J. P.; Jastrow, J. D. The importance of anabolism in microbial control over soil carbon storage. *Nat. Microbiol.* **2017**, *2* (8), No. 17105.
- (6) Moore, O. W.; Curti, L.; Woulds, C.; Bradley, J. A.; Babakhani, P.; Mills, B. J. W.; Homoky, W. B.; Xiao, K.-Q.; Bray, A. W.; Fisher, B. J.; Kazemian, M.; Kaulich, B.; Dale, A. W.; Peacock, C. L. Long-term organic carbon preservation enhanced by iron and manganese. *Nature* **2023**, *621* (7978), 312–317.
- (7) Kleber, M.; Bourg, I. C.; Coward, E. K.; Hansel, C. M.; Myneni, S. C. B.; Nunan, N. Dynamic interactions at the mineral–organic matter interface. *Nat. Rev. Earth Environ.* **2021**, *2* (6), 402–421.
- (8) Xiao, K.-Q.; Zhao, Y.; Liang, C.; Zhao, M.; Moore, O. W.; Otero-Fariña, A.; Zhu, Y.-G.; Johnson, K.; Peacock, C. L. Introducing the soil mineral carbon pump. *Nat. Rev. Earth Environ.* **2023**, *4* (3), 135–136.
- (9) Shindo, H.; Huang, P. M. Significance of Mn(IV) oxide in abiotic formation of organic nitrogen complexes in natural environments. *Nature* **1984**, *308* (5954), 57–58.
- (10) Shindo, H.; Huang, P. M. Role of Mn(IV) oxide in abiotic formation of humic substances in the environment. *Nature* **1982**, *298* (5872), 363–365.
- (11) Wang, M. C.; Huang, P. M. Humic macromolecule interlayering in nontronite through interaction with phenol monomers. *Nature* **1986**, *323* (6088), 529–531.
- (12) Johnson, K.; Purvis, G.; Lopez-Capel, E.; Peacock, C.; Gray, N.; Wagner, T.; März, C.; Bowen, L.; Ojeda, J.; Finlay, N.; Robertson, S.; Worrall, F.; Greenwell, C. Towards a mechanistic understanding of carbon stabilization in manganese oxides. *Nat. Commun.* **2015**, *6* (1), No. 7628.
- (13) Babakhani, P.; Dale, A. W.; Woulds, C.; Moore, O. W.; Xiao, K.-Q.; Curti, L.; Peacock, C. L. Preservation of organic carbon in marine sediments sustained by sorption and transformation processes. *Nat. Geosci.* **2025**, *18* (1), 78–83.
- (14) Zhao, Y.; Jia, J.; Liu, C.; Feng, X. Carbon preservation in sedimentary deposits: Beyond mineral protection. *Innovation* **2024**, *5* (2), No. 100576.
- (15) Post, J. E. Manganese oxide minerals: Crystal structures and economic and environmental significance. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96* (7), 3447–3454.
- (16) Ying, C.; Lanson, B.; Wang, C.; Wang, X.; Yin, H.; Yan, Y.; Tan, W.; Liu, F.; Feng, X. Highly enhanced oxidation of arsenite at the surface of birnessite in the presence of pyrophosphate and the underlying reaction mechanisms. *Water Res.* **2020**, *187*, No. 116420.
- (17) Liao, S.; Wang, X.; Yin, H.; Post, J. E.; Yan, Y.; Tan, W.; Huang, Q.; Liu, F.; Feng, X. Effects of Al substitution on local structure and morphology of lepidocrocite and its phosphate adsorption kinetics. *Geochim. Cosmochim. Acta* **2020**, *276*, 109–121.
- (18) Li, H.; Santos, F.; Butler, K.; Herndon, E. A critical review on the multiple roles of manganese in stabilizing and destabilizing soil organic matter. *Environ. Sci. Technol.* **2021**, *55* (18), 12136–12152.
- (19) Wang, C.; Ying, C.; Wang, W.; Zhou, S.; Wan, B.; Tan, W.; Feng, X. Sunlight-driven transformation of ferrihydrite via ligand-to-metal charge transfer: The critical factors and arsenic repartitioning. *Environ. Sci. Technol.* **2025**, *59* (13), 6567–6578.
- (20) Wang, X.; Wang, Q.; Yang, P.; Wang, X.; Zhang, L.; Feng, X.; Zhu, M.; Wang, Z. Oxidation of Mn(III) species by Pb(IV) oxide as a surrogate oxidant in aquatic systems. *Environ. Sci. Technol.* **2020**, *54* (21), 14124–14133.
- (21) Remucal, C. K.; Ginder-Vogel, M. A critical review of the reactivity of manganese oxides with organic contaminants. *Environ. Sci.: Process. Impacts* **2014**, *16* (6), 1247–1266.
- (22) Chorover, J.; Amistadi, M. K. Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces. *Geochim. Cosmochim. Acta* **2001**, *65* (1), 95–109.
- (23) Kaste, J. M.; Bostick, B. C.; Heimsath, A. M.; Steinnes, E.; Friedland, A. J. Using atmospheric fallout to date organic horizon layers and quantify metal dynamics during decomposition. *Geochim. Cosmochim. Acta* **2011**, *75* (6), 1642–1661.
- (24) Keiluweit, M.; Nico, P.; Harmon, M. E.; Mao, J.; Pett-Ridge, J.; Kleber, M. Long-term litter decomposition controlled by manganese redox cycling. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112* (38), E5253–E5260.
- (25) Berg, B.; Davey, M. P.; De Marco, A.; Emmett, B.; Fauri, M.; Hobbie, S. E.; Johansson, M. B.; Liu, C.; McClaugherty, C.; Norell, L.; Rutigliano, F. A.; Vesterdal, L.; De Santo, A. V. Factors influencing limit values for pine needle litter decomposition: a synthesis for boreal and temperate pine forest systems. *Biogeochemistry* **2010**, *100* (1), 57–73.
- (26) Berg, B.; Steffen, K. T.; McClaugherty, C. Litter decomposition rate is dependent on litter Mn concentrations. *Biogeochemistry* **2007**, *82* (1), 29–39.
- (27) Herndon, E. M.; Martinez, C. E.; Brantley, S. L. Spectroscopic (XANES/XRF) characterization of contaminant manganese cycling in a temperate watershed. *Biogeochemistry* **2014**, *121* (3), 505–517.
- (28) Krishna, M. P.; Mohan, M. Litter decomposition in forest ecosystems: a review. *Energy Ecol. Environ.* **2017**, *2* (4), 236–249.

- (29) De Nobili, M.; Bravo, C.; Chen, Y. The spontaneous secondary synthesis of soil organic matter components: A critical examination of the soil continuum model theory. *Appl. Soil Ecol.* **2020**, *154*, No. 103655.
- (30) Bernhard-Reversat, F.; Main, G.; Holl, K.; Loumeto, J.; Ngao, J. Fast disappearance of the water-soluble phenolic fraction in eucalypt leaf litter during laboratory and field experiments. *Appl. Soil Ecol.* **2003**, *23* (3), 273–278.
- (31) Xu, J.-W.; Ding, Y.-D.; Li, S.-L.; Mao, R. Amount and biodegradation of dissolved organic matter leached from tree branches and roots in subtropical plantations of China. *For. Ecol. Manage.* **2021**, *484*, No. 118944.
- (32) Wang, M.; Tian, Q.; Liao, C.; Zhao, R.; Liu, F. Effect of litter-derived dissolved organic carbon addition on forest soil microbial community composition. *Front. Soil Sci.* **2021**, *1*, No. 733431.
- (33) Chen, Y.; Jiang, C.; Wang, Y.; Song, R.; Tan, Y.; Yang, Y.; Zhang, Z. Sources, environmental fate, and ecological risks of antibiotics in sediments of Asia's longest river: a whole-basin investigation. *Environ. Sci. Technol.* **2022**, *56* (20), 14439–14451.
- (34) Ganbat, B.; Tsenden-Ish, B. Characteristics and properties of soil reaction (pH) in Mongolian forests. *Mong. J. Geogr. Geocol.* **2024**, *61* (45), 208–217.
- (35) Dai, W.; Li, Y.; Fu, W.; Jiang, P.; Zhao, K.; Li, Y.; Penttinen, P. Spatial variability of soil nutrients in forest areas: a case study from subtropical China. *J. Plant Nutr. Soil Sci.* **2018**, *181* (6), 827–835.
- (36) Poghosyan, L.; Lehtovirta-Morley, L. E. Investigating microbial and environmental drivers of nitrification in alkaline forest soil. *ISME Commun.* **2024**, *4* (1), No. ycae093.
- (37) Ding, Z.; Ding, Y.; Liu, F.; Yang, J.; Li, R.; Dang, Z.; Shi, Z. Coupled sorption and oxidation of soil dissolved organic matter on manganese oxides: nano/sub-nanoscale distribution and molecular transformation. *Environ. Sci. Technol.* **2022**, *56* (4), 2783–2793.
- (38) Wu, P.; Fu, Q.-L.; Zhu, X.-D.; Liu, C.; Dang, F.; Müller, K.; Fujii, M.; Zhou, D.-M.; Wang, H.-L.; Wang, Y.-J. Contrasting impacts of pH on the abiotic transformation of hydrochar-derived dissolved organic matter mediated by δ -MnO₂. *Geoderma* **2020**, *378*, No. 114627.
- (39) Villalobos, M.; Toner, B.; Bargar, J.; Sposito, G. Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. *Geochim. Cosmochim. Acta* **2003**, *67* (14), 2649–2662.
- (40) Lichstein, H. C.; Soule, M. H. Studies of the effect of sodium azide on microbial growth and respiration: I. The action of sodium azide on microbial growth. *J. Bacteriol.* **1944**, *47* (3), 221–230.
- (41) Huang, Y.; Li, S.; Song, K.; Yang, J.; Liang, J.; Zheng, P.; Zheng, Y.; Tang, L.; Nan, C.; Sun, S. Oxygen vacancies on ferrihydrite promote surface polymerization of decomposing straw-derived dissolved organic matter: implications for soil carbon sequestration. *Environ. Sci. Technol.* **2025**, *59* (32), 16959–16971.
- (42) Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **2003**, *37* (20), 4702–4708.
- (43) Jones, M. R.; Luther, G. W.; Mucci, A.; Tebo, B. M. Concentrations of reactive Mn(III)-L and MnO₂ in estuarine and marine waters determined using spectrophotometry and the leuco base, leucoberberlin blue. *Talanta* **2019**, *200*, 91–99.
- (44) Ye, H.; Hu, Z.; Yin, R.; Boyko, T. D.; Liu, Y.; Li, Y.; Li, C.; Lu, A.; Li, Y. Electron transfer at birnessite/organic compound interfaces: mechanism, regulation, and two-stage kinetic discrepancy in structural rearrangement and decomposition. *Geochim. Cosmochim. Acta* **2025**, *388*, 253–267.
- (45) Stedmon, C. A.; Bro, R. Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. *Limnol. Oceanogr.: Methods* **2008**, *6* (11), 572–579.
- (46) Lin, H.; Guo, L. Variations in colloidal DOM composition with molecular weight within individual water samples as characterized by flow field-flow fractionation and EEM-PARAFAC analysis. *Environ. Sci. Technol.* **2020**, *54* (3), 1657–1667.
- (47) Korak, J. A.; McKay, G. Meta-analysis of optical surrogates for the characterization of dissolved organic matter. *Environ. Sci. Technol.* **2024**, *58* (17), 7380–7392.
- (48) Del Vecchio, R.; Schendorf, T. M.; Blough, N. V. Contribution of quinones and ketones/aldehydes to the optical properties of humic substances (HS) and chromophoric dissolved organic matter (CDOM). *Environ. Sci. Technol.* **2017**, *51* (23), 13624–13632.
- (49) Walpen, N.; Houska, J.; Salhi, E.; Sander, M.; von Gunten, U. Quantification of the electron donating capacity and UV absorbance of dissolved organic matter during ozonation of secondary wastewater effluent by an assay and an automated analyzer. *Water Res.* **2020**, *185*, No. 116235.
- (50) Wang, W.; Fang, X.; Fu, Q.-L.; Huang, C.; Fang, L.; Zhang, J.; Feng, X.; Tan, W.; Liu, F.; Li, J.; Yin, H. Iron(II/III) alters the relative roles of the microbial byproduct and humic acid during chromium-(VI) reduction and fixation by soil dissolved organic matter. *Environ. Sci. Technol.* **2025**, *59* (5), 2778–2790.
- (51) Trainer, E. L.; Ginder-Vogel, M.; Remucal, C. K. Selective reactivity and oxidation of dissolved organic matter by manganese oxides. *Environ. Sci. Technol.* **2021**, *55* (17), 12084–12094.
- (52) Dittmar, T.; Koch, B.; Hertkorn, N.; Kattner, G. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnol. Oceanogr.: Methods* **2008**, *6* (6), 230–235.
- (53) Zhou, Z.; Fu, Q.-L.; Fujii, M.; Waite, T. D. Complementary elucidation of the molecular characteristics of groundwater dissolved organic matter using ultrahigh-resolution mass spectrometry coupled with negative- and positive-ion electrospray ionization. *Environ. Sci. Technol.* **2023**, *57* (11), 4690–4700.
- (54) Fu, Q.-L.; Fujii, M.; Riedel, T. Development and comparison of formula assignment algorithms for ultrahigh-resolution mass spectra of natural organic matter. *Anal. Chim. Acta* **2020**, *1125*, 247–257.
- (55) Zhang, J.; McKenna, A. M.; Zhu, M. Macromolecular characterization of compound selectivity for oxidation and oxidative alterations of dissolved organic matter by manganese oxide. *Environ. Sci. Technol.* **2021**, *55* (12), 7741–7751.
- (56) Ma, H.; Wang, P.; Thompson, A.; Xie, Q.; Zhu, M.; Teng, H. H.; Fu, P.; Liu, C.; Chen, C. Secondary mineral formation and carbon dynamics during FeS oxidation in the presence of dissolved organic matter. *Environ. Sci. Technol.* **2022**, *56* (19), 14120–14132.
- (57) Ding, Z.; Hu, S.; Zhu, L.; Xiao, J.; Ye, Q.; Liu, T.; Shi, Z. Multiple effects of iron oxides on the adsorption and oxidation of dissolved organic matter by manganese oxides. *Geochim. Cosmochim. Acta* **2024**, *384*, 213–227.
- (58) Liu, H.; Li, Y.; Huangfu, Z.; Lu, Q.; Yang, B.; Liu, Y. Structure and molecular-level transformation for oxidation of effluent organic matters by manganese oxides. *Water Res.* **2024**, *262*, No. 122082.
- (59) Stone, A. T. Reductive dissolution of manganese(III/IV) oxides by substituted phenols. *Environ. Sci. Technol.* **1987**, *21* (10), 979–988.
- (60) Stubbins, A.; Lapierre, J. F.; Berggren, M.; Prairie, Y. T.; Dittmar, T.; del Giorgio, P. A. What's in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada. *Environ. Sci. Technol.* **2014**, *48* (18), 10598–10606.
- (61) Wang, Y.-H.; Zhang, P.; He, C.; Yu, J.-C.; Shi, Q.; Dahlgren, R. A.; Spencer, R. G. M.; Yang, Z.-B.; Wang, J.-J. Molecular signatures of soil-derived dissolved organic matter constrained by mineral weathering. *Fundam. Res.* **2023**, *3*, 377–383.
- (62) Kellerman, A. M.; Guillemette, F.; Podgorski, D. C.; Aiken, G. R.; Butler, K. D.; Spencer, R. G. M. Unifying concepts linking dissolved organic matter composition to persistence in aquatic ecosystems. *Environ. Sci. Technol.* **2018**, *52* (5), 2538–2548.
- (63) Chen, W.; Westerhoff, P.; Leenheer, J. A.; Booksh, K. Fluorescence excitation–emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* **2003**, *37* (24), 5701–5710.
- (64) Bosco, M.; Callao, M. P.; Larrechi, M. S. Resolution of phenol, and its di-hydroxyderivative mixtures by excitation–emission fluorescence using MCR-ALS: Application to the quantitative

monitoring of phenol photodegradation. *Talanta* **2007**, 72 (2), 800–807.

(65) Leenheer, J. A.; Croué, J.-P. Peer Reviewed: Characterizing aquatic dissolved organic matter. *Environ. Sci. Technol.* **2003**, 37 (1), 18A–26A.

(66) Hernes, P. J.; Bergamaschi, B. A.; Eckard, R. S.; Spencer, R. G. M. Fluorescence-based proxies for lignin in freshwater dissolved organic matter. *J. Geophys. Res.: Biogeosci.* **2009**, 114 (G4), No. G00F03.

(67) Maie, N.; Scully, N. M.; Pisani, O.; Jaffé, R. Composition of a protein-like fluorophore of dissolved organic matter in coastal wetland and estuarine ecosystems. *Water Res.* **2007**, 41 (3), 563–570.

(68) Mahamuni, G.; Rutherford, J.; Davis, J.; Molnar, E.; Posner, J. D.; Seto, E.; Korshin, G.; Novosselov, I. Excitation–emission matrix spectroscopy for analysis of chemical composition of combustion generated particulate matter. *Environ. Sci. Technol.* **2020**, 54 (13), 8198–8209.

(69) Doskočil, L.; Burdíkova-Szewieczková, J.; Enev, V.; Kalina, L.; Wasserbauer, J. Spectral characterization and comparison of humic acids isolated from some European lignites. *Fuel* **2018**, 213, 123–132.

(70) Fu, P.-Q.; Liu, C.-Q.; Yin, Z.-Y. Characterization of humic acid by three-dimensional excitation emission matrix fluorescence spectroscopy. *Geochimica* **2004**, 33 (3), 301–308.

(71) Traina, S. J.; Novak, J.; Smeck, N. E. An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids. *J. Environ. Qual.* **1990**, 19 (1), 151–153.

(72) Yu, Z.; Liu, X.; Chen, C.; Liao, H.; Chen, Z.; Zhou, S. Molecular insights into the transformation of dissolved organic matter during hyperthermophilic composting using ESI FT-ICR MS. *Bioresour. Technol.* **2019**, 292, No. 122007.

(73) Liu, J.; Wang, N.; Fujii, M.; Bao, Z.; Wei, J.; Hao, Z.; Fu, Q.-L.; Gao, R.; Liu, J.; Wei, Y. Insights into the roles of DOM in humification during sludge composting: Comprehensive chemoinformatic analysis using FT-ICR mass spectrometry. *Chem. Eng. J.* **2023**, 475, No. 146024.

(74) Cai, S.; Liu, M.; Zhang, Y.; Hu, A.; Zhang, W.; Wang, D. Molecular transformation of dissolved organic matter and formation pathway of humic substances in dredged sludge under aerobic composting. *Bioresour. Technol.* **2022**, 364, No. 128141.

(75) Song, J.; Li, M.; Jiang, B.; Wei, S.; Fan, X.; Peng, P. Molecular characterization of water-soluble humic-like substances in smoke particles emitted from combustion of biomass materials and coal using ultrahigh-resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Environ. Sci. Technol.* **2018**, 52 (5), 2575–2585.

(76) Yang, P.; Jiang, T.; Cao, D.; Sun, T.; Liu, G.; Guo, Y.; Liu, Y.; Yin, Y.; Cai, Y.; Jiang, G. Unraveling multiple pathways of electron donation from phenolic moieties in natural organic matter. *Environ. Sci. Technol.* **2023**, 57 (44), 16895–16905.

(77) Collins, M. J.; Bishop, A. N.; Farrimond, P. Sorption by mineral surfaces: Rebirth of the classical condensation pathway for kerogen formation? *Geochim. Cosmochim. Acta* **1995**, 59 (11), 2387–2391.

(78) Flory, P. J. Fundamental principles of condensation polymerization. *Chem. Rev.* **1946**, 39 (1), 137–197.

(79) Hardie, A. G.; Dynes, J. J.; Kozaka, L. M.; Huang, P. M. Abiotic Catalysis of the Maillard and Polyphenol–Maillard Humification Pathways by Soil Clays from Temperate and Tropical Environments. In *Molecular Environmental Soil Science at the Interfaces in the Earth's Critical Zone*; Xu, J.; Huang, P. M., Eds.; Springer: Dordrecht, 2010; pp 26–28.

(80) Gong, Y.; Shen, J.; Wu, Y.; Shen, L.; Zhao, S.; Zhou, Y.; Li, Y.; Cui, L.; Kang, J.; Chen, Z. Ligands-Triggered Evolution of Catalytic Intermediates during Periodate Activation via Soluble Mn(II) for Organic Contaminants' Abatement. *Appl. Catal., B* **2023**, 322, No. 122093.

(81) Reed, G. H.; Markham, G. D. EPR of Mn(II) Complexes with Enzymes and Other Proteins. In *Biological Magnetic Resonance: Vol. 6*; Berliner, L. J.; Reuben, J., Eds.; Springer US: Boston, MA, 1984; pp 73–142.

(82) Wang, Q.; Yang, P.; Zhu, M. Structural transformation of birnessite by fulvic acid under anoxic conditions. *Environ. Sci. Technol.* **2018**, 52 (4), 1844–1853.

(83) Wang, Z.; Jia, H.; Zhao, H.; Zhang, R.; Zhang, C.; Zhu, K.; Guo, X.; Wang, T.; Zhu, L. Oxygen limitation accelerates regeneration of active sites on a MnO₂ surface: Promoting transformation of organic matter and carbon preservation. *Environ. Sci. Technol.* **2022**, 56 (13), 9806–9815.

(84) Flynn, E. D.; Catalano, J. G. Reductive transformations of layered manganese oxides by small organic acids and the fate of trace metals. *Geochim. Cosmochim. Acta* **2019**, 250, 149–172.

(85) Villalobos, M.; Lanson, B.; Manceau, A.; Toner, B.; Sposito, G. Structural model for the biogenic Mn oxide produced by *Pseudomonas putida*. *Am. Mineral.* **2006**, 91, 489–502.

(86) Yang, P.; Post, J. E.; Wang, Q.; Xu, W.; Geiss, R.; McCurdy, P. R.; Zhu, M. Metal adsorption controls stability of layered manganese oxides. *Environ. Sci. Technol.* **2019**, 53 (13), 7453–7462.

(87) Yang, P.; Wen, K.; Beyer, K. A.; Xu, W.; Wang, Q.; Ma, D.; Wu, J.; Zhu, M. Inhibition of oxyanions on redox-driven transformation of layered manganese oxides. *Environ. Sci. Technol.* **2021**, 55 (5), 3419–3429.

(88) Ding, D.; Zhou, Y.; He, T.; Rong, S. Facet selectively exposed α -MnO₂ for complete photocatalytic oxidation of carcinogenic HCHO at ambient temperature. *Chem. Eng. J.* **2022**, 431, No. 133737.

(89) Larabi-Gruet, N.; Peulon, S.; Lacroix, A.; Chaussé, A. Studies of electrodeposition from Mn(II) species of thin layers of birnessite onto transparent semiconductor. *Electrochim. Acta* **2008**, 53 (24), 7281–7287.

(90) Zhang, N.; Samanta, S. R.; Rosen, B. M.; Percec, V. Single electron transfer in radical ion and radical-mediated organic, materials and polymer synthesis. *Chem. Rev.* **2014**, 114 (11), 5848–5958.

(91) Gao, X.; Yang, Z.; Zhang, W.; Pan, B. Carbon redirection via tunable Fenton-like reactions under nanoconfinement toward sustainable water treatment. *Nat. Commun.* **2024**, 15, No. 2808.

(92) Snider, B. B. Mechanisms of Mn(OAc)₃-based oxidative free-radical additions and cyclizations. *Tetrahedron* **2009**, 65 (52), 10738–10744.

(93) Scott, S. L.; Chen, W. J.; Bakac, A.; Espenson, J. H. Spectroscopic parameters, electrode potentials, acid ionization constants, and electron exchange rates of the 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate) radicals and ions. *J. Phys. Chem. A* **1993**, 97 (25), 6710–6714.

(94) Reardon, P. N.; Chacon, S. S.; Walter, E. D.; Bowden, M. E.; Washton, N. M.; Kleber, M. Abiotic protein fragmentation by manganese oxide: implications for a mechanism to supply soil biota with oligopeptides. *Environ. Sci. Technol.* **2016**, 50 (7), 3486–3493.

Supporting Information for

**Manganese Oxides Drive Divergent Fates of Litter-Derived DOM via
pH-Regulated Oxidative Decomposition and Polymerization**

Feng Jiang^{1,2}, Hong Su^{1,2}, Qing-long Fu³, Zi Yang^{1,2}, Xiaoming Wang^{1,2}, Hui Yin^{1,2},

Wenfeng Tan^{1,2}, Bruno Lanson⁴, Xionghan Feng^{1,2*}

¹Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtse River), Ministry of Agriculture and Rural affairs, College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China

²Hubei Key Laboratory of Soil Environment and Pollution Remediation, Wuhan 430070, China

³School of Environmental Studies, China University of Geoscience, Wuhan 430074, China

⁴University Grenoble Alpes, CNRS, University Savoie Mont Blanc, IRD, University Gustave Eiffel, ISTerre, F-38000 Grenoble, France

*Corresponding author: Xionghan Feng, Tel: +86 27 87280271; fax: +86 27 87288618; E-mail: fxh73@mail.hzau.edu.cn

This file contains 43 pages, 14 texts, 4 tables, and 20 figures.

Text S1. Chemical Agents

Manganese(II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\geq 99\%$, Sinopharm Chemical Reagent, China); potassium permanganate (KMnO_4 , $\geq 99\%$, Sinopharm Chemical Reagent, China); Folin–Ciocalteu reagent (Sigma-Aldrich, USA); sodium carbonate (Na_2CO_3 , $\geq 99\%$, Sinopharm Chemical Reagent, China); hydrochloric acid (HCl , AR, Chron Chemicals, China); gallic acid (GA, $\geq 99\%$, Sigma-Aldrich, USA); sodium hydroxide (NaOH , $\geq 96\%$, Sinopharm Chemical Reagent, China); Bradford protein assay kit (BL524A, BioSharp, China); bovine serum albumin (BSA, Sigma-Aldrich, USA); 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS, $\geq 99\%$, Sigma-Aldrich, USA); methanol (HPLC grade, Thermo Fisher Scientific, USA); sodium azide (NaN_3 , $\geq 99\%$, Sinopharm Chemical Reagent, China); leucoberbelin blue (LBB, $\geq 65\%$, Sigma-Aldrich, USA); sodium hypochlorite (NaClO , $\geq 10\%$, Sinopharm Chemical Reagent, China).

Text S2: Selection of Representative Leaf Species for DOM Analysis

In this study, four deciduous species—*Liquidambar formosana* (LF), *Quercus acutissima* (QA), *Lindera glauca* (LG), and *Acer buergerianum* (AB)—were selected as representative sources for leaf-derived DOM to capture both ecological relevance and functional diversity. These species are either constructive or dominant in East Asian subtropical forest ecosystems, with extensive geographical distribution and significant ecological functions.¹ Taxonomically, they belong to four distinct families—Altingiaceae, Fagaceae, Lauraceae, and Sapindaceae—that represent phylogenetically diverse lineages within angiosperms.² This phylogenetically diverse selection ensures that the sampled

DOM captures maximal chemical diversity arising from divergent plant genetic backgrounds.³ *Liquidambar formosana* (LF), representing the Altingiaceae family, produces resinous substances and yields DOM rich in carbohydrates, flavonoids, and simple phenolics (e.g., gallic acid and p-hydroxybenzoic acid).⁴ These compounds are highly reactive, likely contributing to relatively rapid decomposition under environmental conditions. *Quercus acutissima* (QA), a representative species of the Fagaceae family, produces leathery leaves rich in lignin and condensed tannins.⁵⁻⁷ These structurally complex constituents contribute to strong resistance against microbial attack, resulting in slower decomposition rates.⁸ *Lindera glauca* (LG), from the Lauraceae family, contains abundant hydrophobic monoterpenes and sesquiterpenoid volatile oils, such as (E)- β -ocimene, β -caryophyllene, and nerolidol, which are generally recalcitrant to rapid microbial degradation.⁹ *Acer buergerianum* (AB), as a representative species of the Sapindaceae (*Acer*) lineage, exhibits traits typical of the genus.^{10,11} Leaves of *Acer* species are often rich in polyphenolic compounds, and their litter releases substantial amounts of readily degradable components (e.g., soluble carbohydrates and proteins) during the initial decomposition process.^{10,11} This chemical diversity gradient enables a comprehensive assessment of how leaf litter with varying properties contributes to the DOM pool and influences interactions with soil minerals.

Text S3. Synthesis of δ -MnO₂

δ -MnO₂ was synthesized via the reaction between Mn²⁺ and KMnO₄ according to a previously reported protocol.¹² In a typical one-pot procedure, 80 mL of 100 mM KMnO₄

and 160 mL of 100 mM NaOH were combined in 1.5 L of ultrapure water. Separately, 3.07 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 100 mL of ultrapure water and then added dropwise to the solution. The reaction mixture was allowed to proceed for 3 h at room temperature. The resulting suspension was washed repeatedly with 1.0 L aliquots of ultrapure water until the conductivity of the supernatant dropped below $10 \mu\text{S cm}^{-1}$. The solid product was then collected by centrifugation, freeze-dried for 4 h, ground, and sieved through a 100-mesh screen to obtain the synthesized $\delta\text{-MnO}_2$.

Text S4. Determination of Total Phenol Contents

Total phenolic content was determined using a modified Folin-Ciocalteu assay adapted for Mn(II)-containing systems.¹³⁻¹⁵ To eliminate Mn(II) interference, 10 mL of reaction mixture was pretreated by passing through a 6 cm column of Na-form cation-exchange resin three times, followed by filtration through a $0.22 \mu\text{m}$ membrane, achieving a removal efficiency of greater than 99.5% for Mn^{2+} .¹⁴ For analysis, 1 mL aliquots of the sample were sequentially mixed with 50 μL of Folin-Ciocalteu reagent and 150 μL of 20% Na_2CO_3 (w/v) solution, followed by a 60 min incubation at 25°C in light-protected conditions. Absorbance measurements at 750 nm were conducted on a Spark 10M multimode microplate reader (TECAN Infinite 200 PRO). A calibration curve (0–20 μM) was established using gallic acid (GA) standards, analyzed in duplicate to validate linearity ($R^2 > 0.995$). Total phenolic contents were normalized to dissolved organic carbon (DOC) concentration and expressed as millimolar gallic acid (GA) per gram of organic carbon ($\text{mmol GA (g OC)}^{-1}$).

Text S5. Determination of Protein-like Component

Protein-like components in DOM were quantified using the Bradford assay kit (BL524A, BioSharp). Briefly, 150 μL aliquots of DOM samples were mixed with 150 μL of Coomassie Brilliant Blue G-250 reagent and incubated for 10 min at 25 ± 0.5 $^{\circ}\text{C}$ under light-protected conditions. Absorbance was measured at 595 nm using a Spark 10M multimode microplate reader (TECAN Infinite 200 PRO). A calibration curve ($0.1\text{--}10$ mg L^{-1}) was established using bovine serum albumin (BSA) standards and validated for linearity ($R^2 > 0.995$).

Text S6. Determination of Electron-Donating Capacity (EDC)

The Electron-donating capacity (EDC) of DOM was quantified using a modified ABTS radical cation ($\text{ABTS}^{\bullet+}$) decolorization assay.^{16,17} Stock solutions were prepared as follows: (1) 1 mM ABTS dissolved in 7.5 mM H_2SO_4 (pH 2.0); (2) 1 mM NaClO ; and (3) 500 mM phosphate buffer (pH 7.0) composed of NaH_2PO_4 and Na_2HPO_4 . $\text{ABTS}^{\bullet+}$ working solution was generated by mixing 350 μL of NaClO (1 mM) with 1 mL of ABTS (1 mM). For sample analysis, 100 μL of DOM (serially diluted to 100%, 80%, 50%, 25%, 0% with ultrapure water) was reacted with 100 μL of phosphate buffer and 300 μL of $\text{ABTS}^{\bullet+}$ reagent for 15 min (25 ± 0.5 $^{\circ}\text{C}$, dark). To account for potential interference from Mn^{2+} , DOM-free blanks containing matched Mn^{2+} concentrations were subtracted from sample measurements. The absorbance at 728 nm was recorded and used to calculate the $\text{ABTS}^{\bullet+}$ concentration based on a molar extinction coefficient of $14,000 \text{ M}^{-1} \text{ cm}^{-1}$ (728 nm, pH 7.0).¹⁶ The net depletion of $\text{ABTS}^{\bullet+}$ ($\Delta_{\text{ABTS}^{\bullet+}}$) was calculated as the difference between the

blank and sample measurements, representing the total electrons donated from DOM to ABTS^{•+}. Final EDC was calculated by normalizing $\Delta_{\text{ABTS}^{\bullet+}}$ to the DOC concentration.

Text S7. EPR Measurement

For Mn²⁺ speciation analysis on solid-phase samples, 1 mg of material was loaded into a quartz EPR tube under ambient conditions. Electron spin resonance (EPR) spectroscopy was conducted using a Bruker ESR5000 spectrometer (Bruker BioSpin GmbH, Germany) operating at X-band frequency (9.85 GHz). Spectra were acquired with the following parameters: 100 kHz modulation frequency, 0.2 mT modulation amplitude, 10 mW microwave power, 100 s sweep time, and a magnetic field sweep range of 3000-3800 G (0.3-0.38 T).

Text S8. XRD Measurement

The powder X-ray diffraction (XRD) patterns of the reaction deposit were obtained using a Rigaku D/max-1200 diffractometer with CuK α radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA). Data were collected over a 2θ range of 5–85° at a scan speed of 10° min⁻¹ to characterize the crystalline phases and structures.

Text S9. XPS Measurement

X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250XI spectrometer (Thermo Fisher Scientific, USA) equipped with an Al K α X-ray source to analyze the surface elemental composition and valence states. The average oxidation state (AOS) of Mn was calculated using the equation $\text{AOS} = 8.956 - 1.126 \times \Delta E_{\text{Mn}}$, where ΔE_{Mn} denotes the energy separation between the two splitting peaks in the Mn 3s spectrum.¹⁸

Additionally, the Mn 3p spectrum was subjected to multi-peak fitting to determine the relative proportions of Mn(II), Mn(III), and Mn(IV), based on previously reported literature.¹⁹

Text S10. Solid-Phase Extraction (SPE) of DOM

Aqueous samples were diluted with deionized water to achieve a DOC concentration of 3 mg L⁻¹, resulting in a final volume of 300 mL. Solid-phase extraction (SPE) was conducted using 500 mg/6 mL C18 cartridges (Agilent Bond Elut), which were sequentially preconditioned with 18 mL of HPLC-grade methanol followed by 18 mL of 0.01 M HCl to activate the sorbent. Samples were acidified to pH 2.0 ± 0.1 using 6 M HCl and passed through the SPE columns at a controlled flow rate of 1 mL min⁻¹. Following sample loading, the cartridges were rinsed with 18 mL of 0.01 M HCl to remove residual ionic impurities and then dried under a stream of nitrogen gas for 30 min to eliminate residual moisture. Organic constituents retained on the sorbent were eluted with 6 mL of methanol. The methanolic extracts were stored at -20 °C until analysis by FT-ICR MS. Before analysis, the extracts were diluted 1:100 (v/v) with a 50% methanol aqueous solution. To assess DOC recovery during SPE, 1.0 mL of the DOM eluate was dried under vacuum at 25 °C and 1,300 rpm for 180 min using a centrifugal concentrator (CV200, Beijing JM Instrument Co., Ltd., China).²⁰ The dried residue was subsequently re-dissolved in 7 mL of ultrapure water for further analysis. Based on DOC recoveries, this method achieved DOM extraction efficiencies exceeding 58% for all samples.

Text S11. Calculation of parameters related to the molecular properties of the

reaction product based on FT-ICR MS

O/C ratio, H/C ratio, double bond equivalent (DBE), modified aromatic index (AI_{mod}), and nominal oxidation state of carbon (NOSC) were calculated as follows:

$$O/C = o/c$$

$$H/C = h/c$$

$$DBE = (1 + (2c - h + n)/2)$$

$$AI_{mod} = (1 + c - o/2 - h/2 - s)/(c - o/2 - n - s)$$

$$NOSC = 4 - [(4c + h - 3n - 2o - 2s)/c]$$

NOSC was calculated from the chemical formula, assuming that all elements are in their initial oxidation states ($H = +1$, $O = -2$, $N = -3$, and $S = -2$).

The intensity-weighted average O/C_w , H/C_w , $NOSC_w$, MW_w , DBE_w , and AI_{modw} were calculated as follows:

$$O/C_w = \Sigma [O/C_i \times (I_i/\Sigma I_i)]$$

$$H/C_w = \Sigma [H/C_i \times (I_i/\Sigma I_i)]$$

$$NOSC_w = \Sigma [NOSC_i \times (I_i/\Sigma I_i)]$$

$$MW_w = \Sigma [MW_i \times (I_i/\Sigma I_i)]$$

$$DBE_w = \Sigma [DBE_i \times (I_i/\Sigma I_i)]$$

$$AI_{modw} = \Sigma [AI_{modi} \times (I_i/\Sigma I_i)]$$

The relative abundance (RA_i) of the molecule is calculated as follows:

$$RA_i = I_i/\Sigma I_i$$

where I_i represents the intensity of an individual molecule.

Text S12. Identification of Condensation Products via Molecular Formula Pairing

To identify potential condensation-derived products, molecular formulas of pre-reaction compounds were algorithmically analyzed. Each formula (e.g., C₆H₁₂O₆) was decomposed into elemental compositions (C:6, H:12, O:6) using a regular expression-based parser. All unique pairwise combinations of precursor formulas (Formula₁ + Formula₂) were computationally generated, and their summed elemental counts were adjusted to simulate stoichiometric water loss (H₂O: -2H, -1O), following the condensation equation: Product Formula=Formula₁+Formula₂-H₂O.

Resultant formulas with non-positive elemental counts were discarded; valid outputs were reconstructed into standardized notation and cross-referenced against newly formed molecular after reaction inventories to validate condensation products empirically. Validated products were mapped to precursor pairs, and duplicates were removed to ensure specificity. The above work was conducted using Python.

Text S13. Spearman Correlation Analysis Between EEM and FT-ICR-MS Data

Fluorescence intensities of individual PARAFAC-derived components were normalized to the total fluorescence intensity within each sample. Similarly, FT-ICR-MS peak intensities were normalized to the total intensity of all peaks assigned to molecular formulas in each sample. Spearman's rank correlation was used to evaluate associations between the relative abundances of molecular formulas and normalized fluorescence intensities using LF-DOM and AB-DOM samples collected before and after reactions at pH 4, 6, and 8.²¹⁻²³ Molecular formulas showing statistically significant correlations with

individual fluorescent components ($p < 0.05$, $|r| > 0.7$) were identified as potential contributors to fluorescence variability. To minimize source-specific biases and enhance analytical robustness, only molecules detected in both AB-DOM and LF-DOM groups (i.e., present in at least one sample from each group) were retained.

Text S14. Cyclic Voltammetry (CV) Measurement

To prepare the working electrode, δ -MnO₂ (10 mg) was ultrasonically dispersed in a 1:1 (v/v) mixture of 10 mM naphthol solution and anhydrous ethanol (total volume: 500 μ L). Subsequently, 100 μ L of the resulting suspension was drop-cast onto a polished glassy carbon electrode (GCE) and dried at 60 °C for 30 min. CV measurements were conducted at 25 °C using a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) in a conventional three-electrode configuration, consisting of the modified GCE (working electrode), an Ag/AgCl (reference electrode), and a platinum wire (counter electrode). The supporting electrolyte was 0.1 M KCl, adjusted to pH 4, 6, or 8. Before measurements, the electrolyte solution was purged with high-purity nitrogen for 10 min to remove dissolved oxygen. CV scans were recorded from -1.0 V to +1.5 V (vs. Ag/AgCl) at a scan rate of 0.1 V s⁻¹, and the second of two successive cycles was analyzed for each pH condition.

Table S1. The number of detected ion peaks, total intensity of all detected peaks (I_{total}), number of assigned molecular formulas, total intensity of assigned formulas (I_{assigned}), and the fraction of total intensity successfully assigned (Ratio = $I_{\text{assigned}} / I_{\text{total}}$) for each DOM determined by FT-ICR-MS. Sample IDs include the initial LF-DOM (LF₀) and AB-DOM (AB₀), as well as samples after 30 days of reaction with δ -MnO₂ at pH 4, 6, and 8 (LF/AB–pH 4, LF/AB–pH 6, LF/AB–pH 8).

Sample ID	Peaks	I_{total}	Assigned	I_{assigned}	Ratio (%)
LF ₀	12053	5.43E+10	4881	4.14E+10	76.26
LF-pH 8	16512	1.19E+11	8978	1.02E+11	86.24
LF-pH 6	13818	7.06E+10	6651	5.78E+10	81.93
LF-pH 4	13690	6.66E+10	6318	5.27E+10	79.11
AB ₀	16000	8.83E+10	4717	6.66E+10	75.44
AB-pH 8	18032	1.19E+11	5903	9.37E+10	78.85
AB-pH 6	18546	1.41E+11	6634	1.20E+11	84.89
AB-pH 4	15717	1.04E+11	5956	8.87E+10	85.08

Table S2. Classification of molecular compounds into major biochemical classes.

Molecular class	Criteria
Carbohydrate	H/C:1.5-2.4; O/C:0.71-1.2
Amino sugars	H/C:1.5-2.2; O/C:0.52-0.71
Protein/Lipid-like	H/C:1.5-2.2; O/C:0-0.52
Tannins	H/C:0.5-1.5; O/C:0.67-1.2
Lignins	H/C:0.7-1.5; O/C:0.1-0.67
Unsaturated hydrocarbons	H/C:0.7-1.5; O/C:0-0.1
Condensed aromatic structures	H/C:0.2-0.7; O/C:0-0.67

Note: The classification method was adopted from a previous study.²⁴

Table S3. Classification of δ -MnO₂-mediated DOM transformation pathways and representative mass shifts. Based on previous studies,^{14,25-28} the transformation of aromatic DOM mediated by δ -MnO₂ can be classified into four primary pathways: (i) Oxidative conversion of phenols to *p*-benzoquinones (ii) Aromatic ring carboxylation, (iii) Aromatic ring-opening (e.g., +3O, +O-5C-4H), (iv) Oxidative coupling (e.g., +n(C₆H₄O), $n \geq 1$).

Reaction	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Change	+O	+O-2H	-2H	+2O-2H	+3O	+O-5C-4H	-H	+n(C ₆ H ₄ O)
Mass shift	+15.994914	+13.9792645	-2.01565	29.9741792	47.9847438	-48.0363854	-1.007825	+n(92.0262146), $n \geq 1$

(i)

(ii)

(iii)

(iv)

Table S4. Molecular characterization of the initial LF-DOM (LF₀) and AB-DOM (AB₀), and the samples after 30 days of reaction with δ -MnO₂ at pH 4, 6, and 8 (LF/AB–pH 4/6/8), based on FT-ICR MS.

	LF ₀	LF-pH 8	LF-pH 6	LF-pH 4	AB ₀	AB-pH 8	AB-pH 6	AB-pH 4
Molecular count	4544	8202	6022	5287	4369	5621	6359	5681
MW_w	378.35	412.26	404.43	396.14	412.40	400.80	386.40	376.78
DBE_w	5.70	6.35	6.57	5.48	10.13	10.10	8.96	7.90
O/C_w	0.37	0.39	0.42	0.40	0.58	0.59	0.55	0.52
H/C_w	1.52	1.48	1.43	1.54	1.01	0.98	1.08	1.20
AI_{modw}	0.16	0.17	0.18	0.13	0.39	0.41	0.35	0.29
NOSC_w	-0.76	-0.68	-0.57	-0.72	0.17	0.24	0.08	-0.09
CHO	86.89% (3731)	89.78% (6365)	88.42% (4756)	85.59% (3963)	85.86% (2967)	82.72% (3330)	78.06% (3409)	73.95% (2941)
CHON	7.90% (443)	6.81% (1187)	7.48% (748)	8.42% (775)	8.55% (1082)	15.38% (2061)	18.61% (2538)	21.59% (2346)
CHOP	1.55% (193)	1.34% (311)	2.30% (332)	3.18% (361)	0.83% (100)	0.21% (44)	0.37% (82)	1.56% (219)
CHOS	3.65% (177)	2.07% (339)	1.80% (186)	2.80% (188)	4.76% (220)	1.69% (186)	2.96% (330)	2.90% (175)
Amino sugars	4.08% (310)	3.96% (519)	5.77% (497)	6.81% (453)	1.04% (127)	1.56% (182)	2.46% (240)	3.84% (256)
Carbonhydrate	0.37% (35)	0.29% (48)	0.55% (53)	0.87% (78)	0.36% (32)	0.33% (35)	0.57% (52)	1.14% (67)
Condensed aromatic structures	3.95% (105)	2.09% (208)	3.19% (155)	1.07% (66)	11.99% (436)	12.51% (598)	7.50% (442)	3.60% (255)
Lignins	32.83% (1886)	40.84% (3806)	45.24% (2831)	33.10% (2045)	41.24% (2365)	49.02% (3171)	55.42% (3701)	62.32% (3364)
Protein/Lipid-like	57.39% (2101)	51.30% (3394)	43.45% (2331)	55.83% (2506)	12.51% (691)	8.19% (773)	12.25% (1133)	15.63% (1109)
Tannins	1.07% (92)	1.39% (203)	1.70% (141)	2.10% (113)	31.66% (682)	27.00% (799)	21.15% (746)	13.27% (609)
Unsaturated hydrocarbons	0.27% (11)	0.10% (13)	0.09% (11)	0.15% (15)	0.04% (2)	0.02% (4)	0.02% (4)	0.01% (2)

Note: Intensity-weighted average values are presented for molecular weight (MW_w), nominal oxidation state of carbon ($NOSC_w$), modified aromaticity index (AI_{modw}), double bond equivalence (DBE_w), H/C ratio (H/C_w), and O/C ratio (O/C_w). Molecular formulas are grouped into elemental classes (CHO, CHON, CHOS, CHOP), and the “Molecular count” represents the total number of compounds across these four elemental classes. The percentage distributions of compound classes were abundance-weighted. In parentheses are the numbers of compounds in each compound class

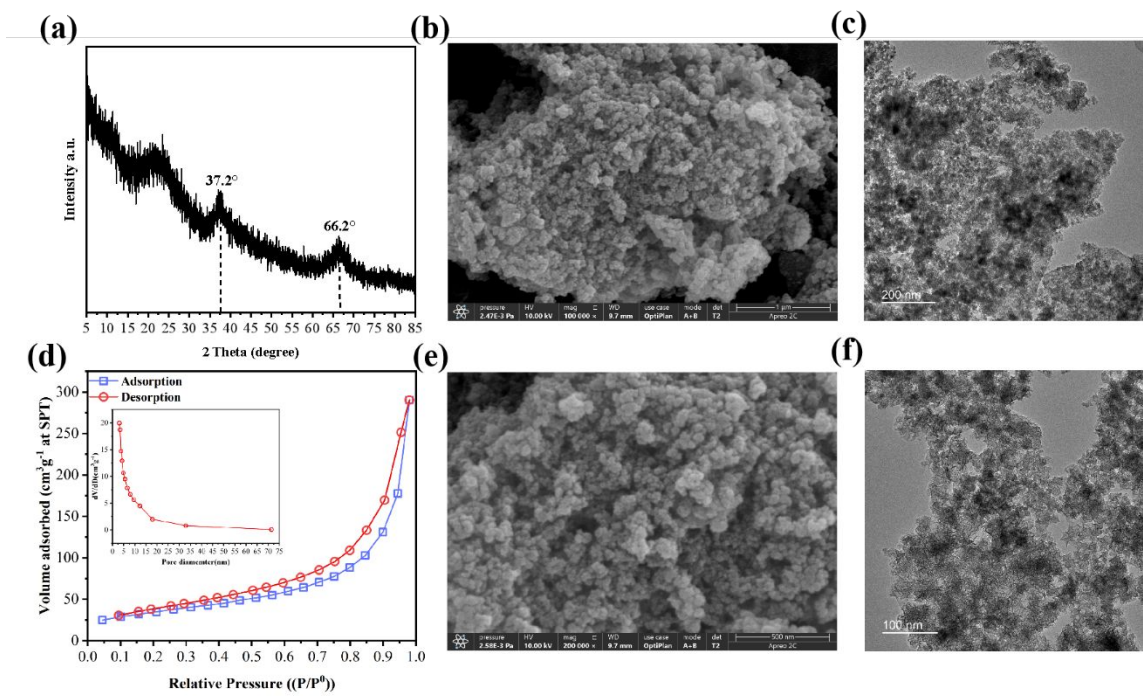


Figure S1. Structural characterization of synthesized δ -MnO₂: (a) XRD pattern; (b, e) SEM images; (c, f) TEM images; and (d) N₂ adsorption–desorption isotherm and the corresponding pore size distribution (inset).

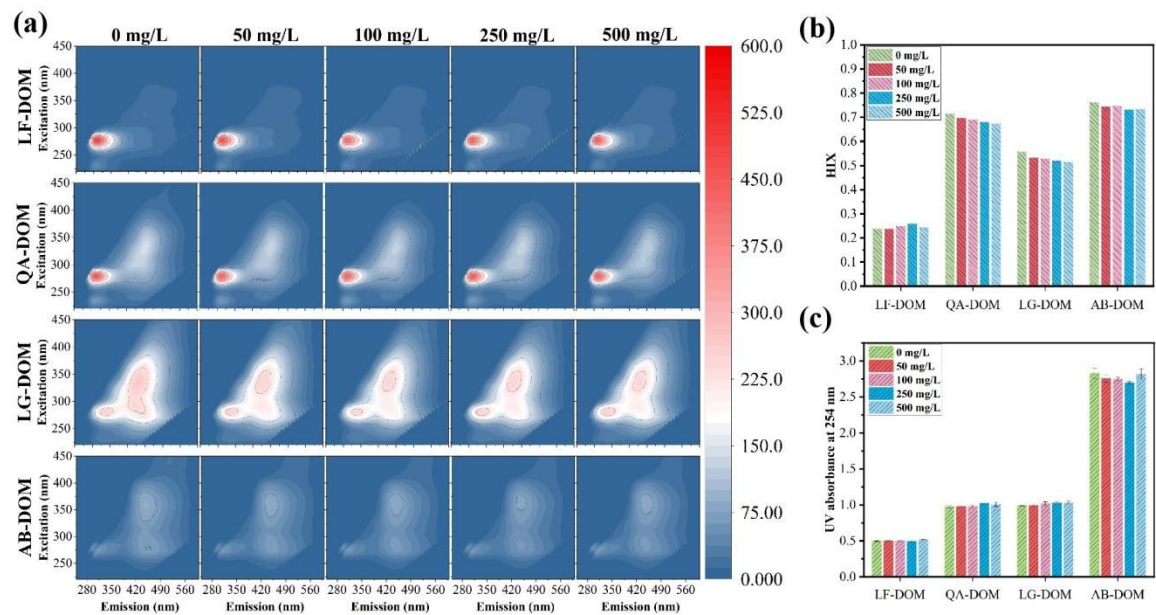


Figure S2. Influence of Mn^{2+} addition (0–500 mg L⁻¹) on (a) EEM spectra, (b) humification index (HIX), and (c) UV absorbance at 254 nm for four types of DOM (LF-DOM, QA-DOM, LG-DOM, and AB-DOM).

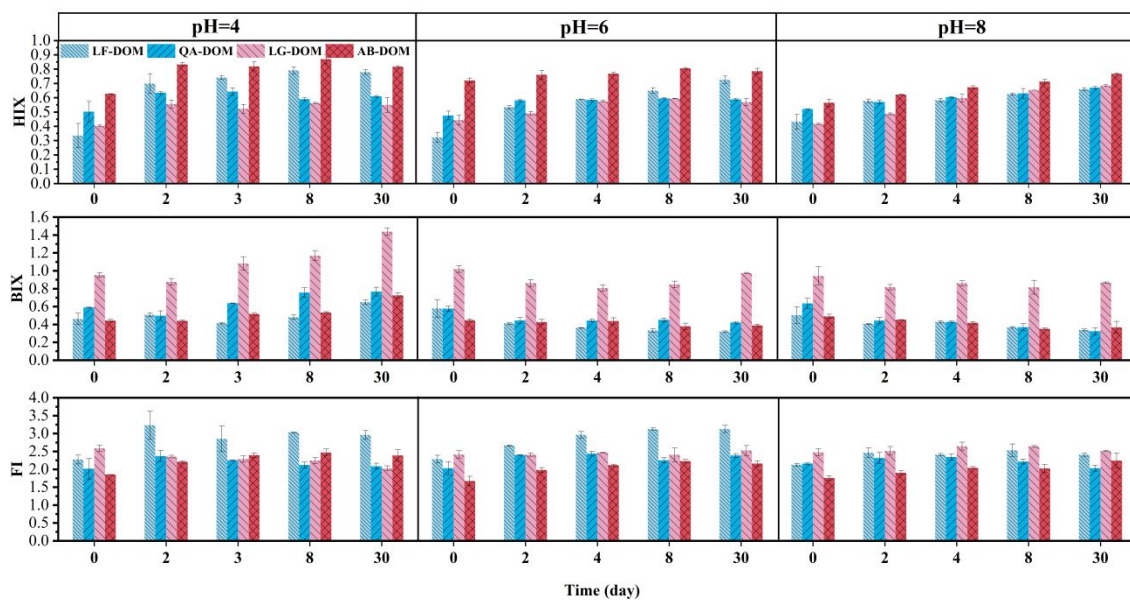


Figure S3. Temporal variations in the humification index (HIX), biological index (BIX), and fluorescence index (FI) of four DOM types (LF-DOM, QA-DOM, LG-DOM, and AB-DOM) during 30-day incubation with δ -MnO₂ at pH 4, 6, and 8.

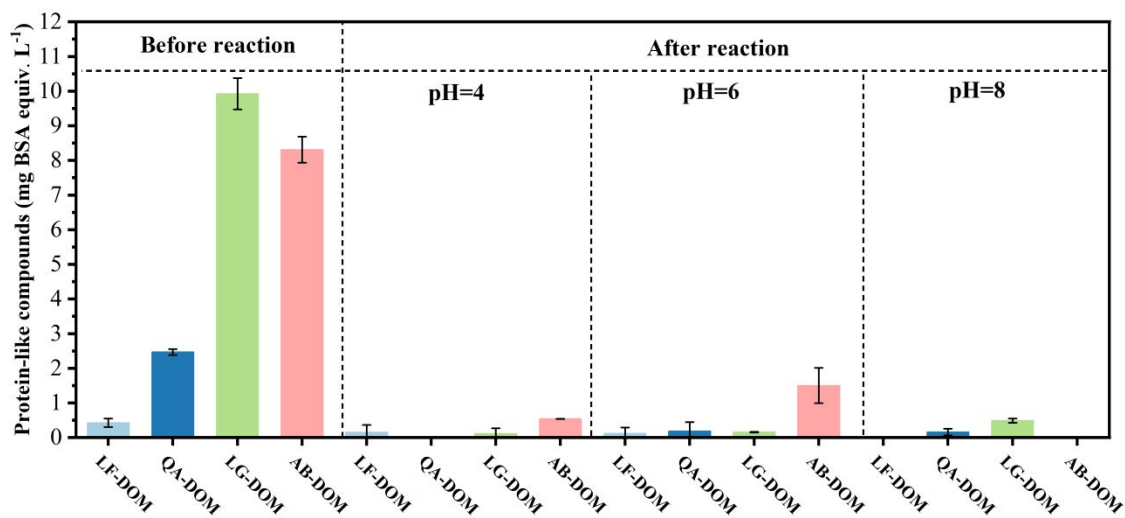


Figure S4. Protein-like compound contents in four DOM types (LF-DOM, QA-DOM, LG-DOM, and AB-DOM) before and after reaction with δ -MnO₂ at pH 4, 6, and 8, as quantified by the Bradford method.

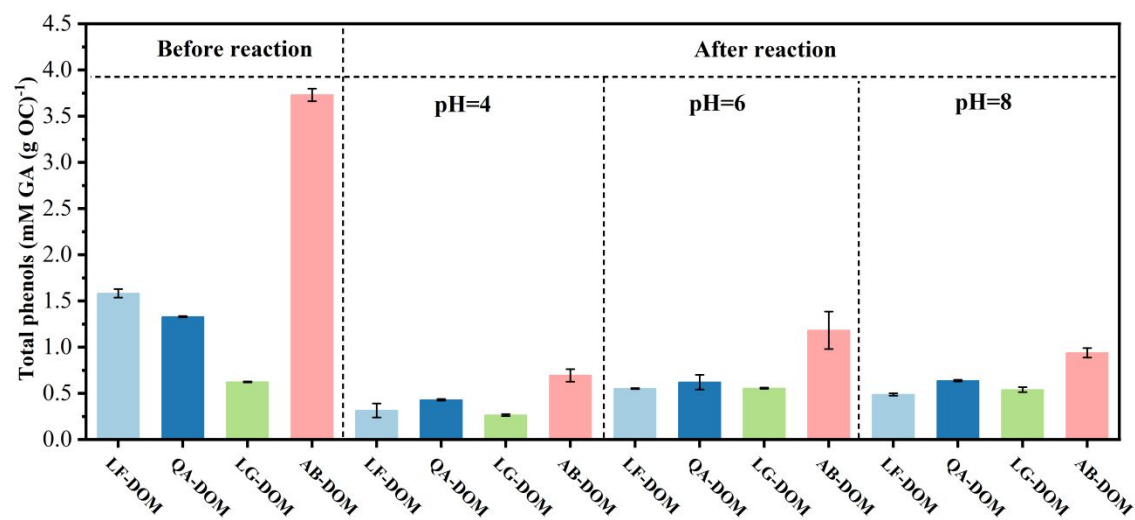


Figure S5. Total phenolic contents in four DOM types (LF-DOM, QA-DOM, LG-DOM, and AB-DOM) before and after reaction with δ -MnO₂ at pH 4, 6, and 8, as determined by the Folin–Ciocalteu assay.

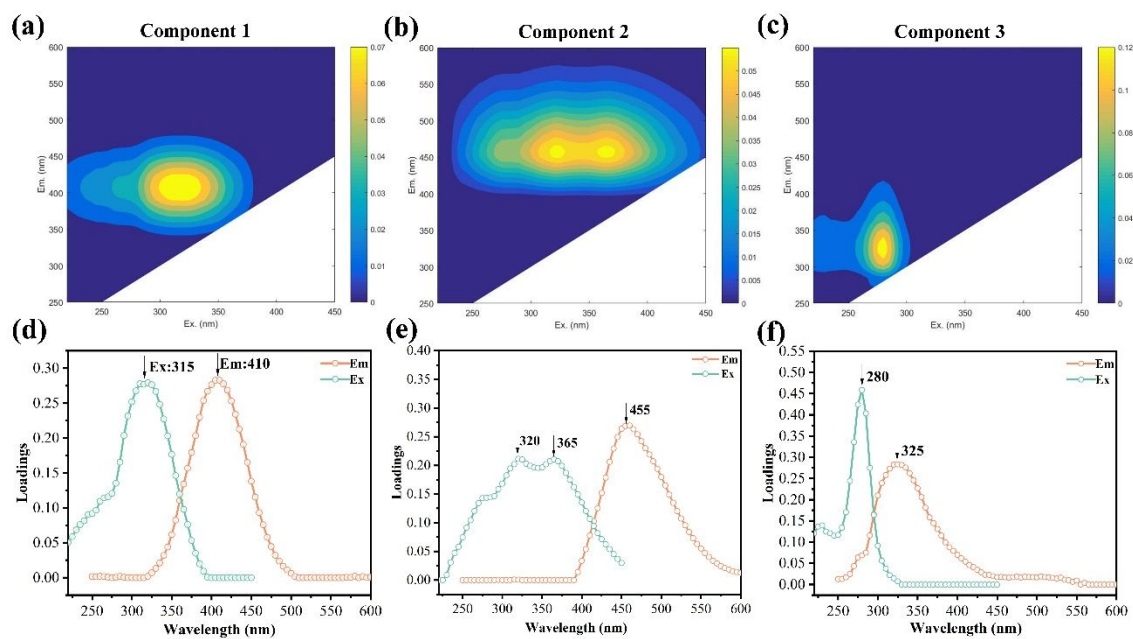


Figure S6. Contour plots (a–c) and corresponding loadings (d–f) of three PARAFAC-derived fluorescent components: C1 (a, d), C2 (b, e), and C3 (c, f).

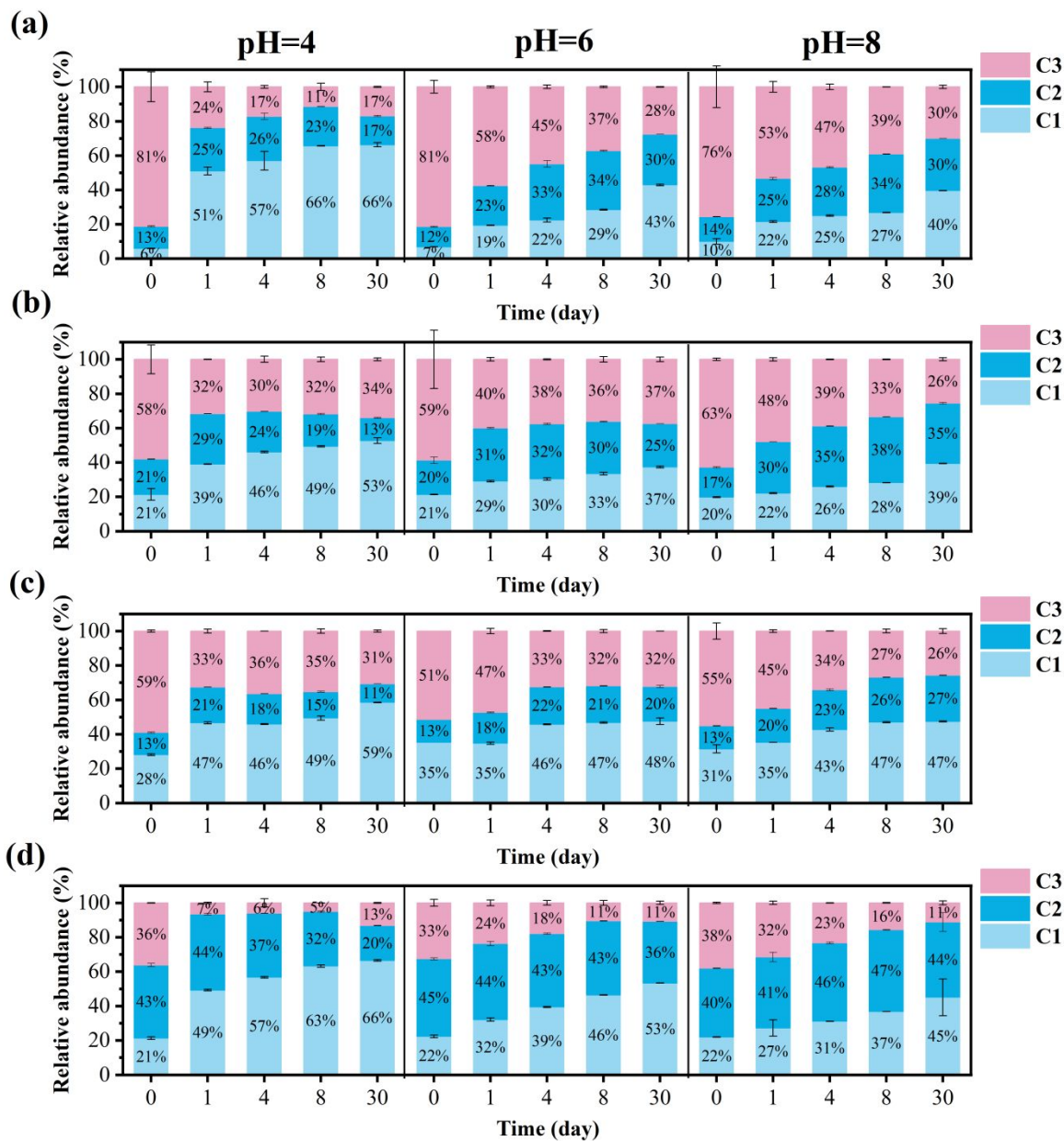


Figure S7. Relative abundance changes of PARAFAC-derived fluorescence components (C1, C2, C3) in (a) LF-DOM, (b) QA-DOM, (c) LG-DOM, and (d) AB-DOM during reaction with δ -MnO₂ at pH 4, 6, and 8.

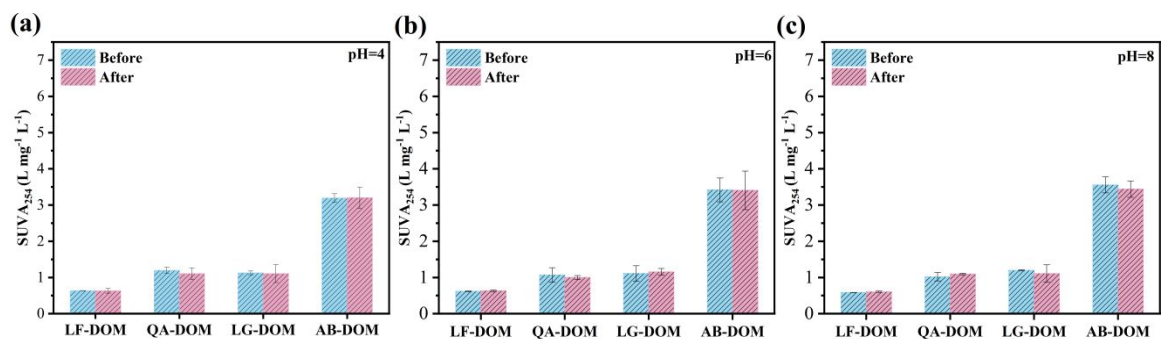


Figure S8. SUVA₂₅₄ of LF-DOM, QA-DOM, LG-DOM, and AB-DOM at pH 4 (a), pH 6 (b), and pH 8 (c) before and after 30 days of incubation in the absence of δ -MnO₂.

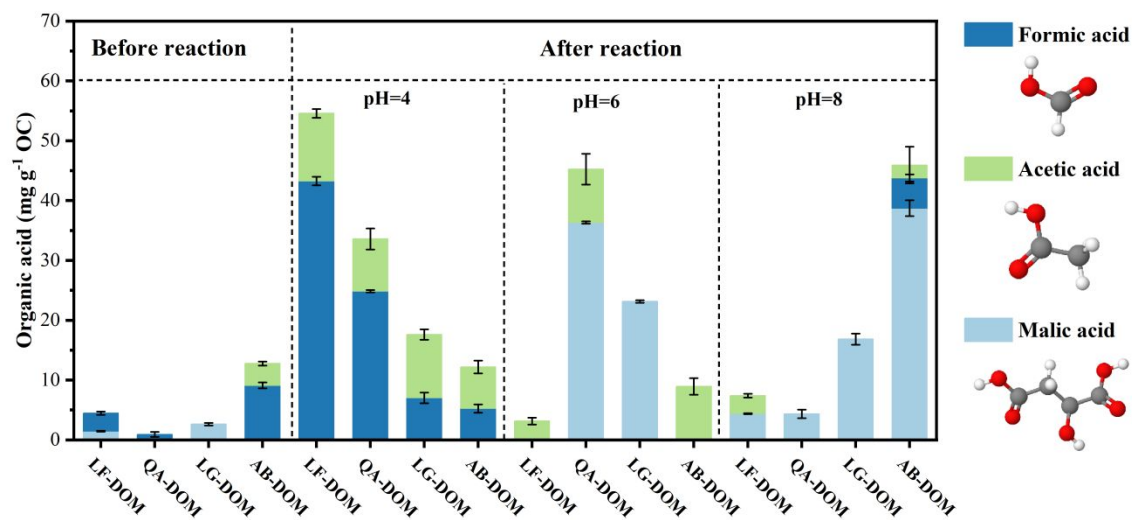


Figure S9. Concentrations of low-molecular-weight organic acids (formic, acetic, and malic acids) in four DOM types (LF-DOM, QA-DOM, LG-DOM, and AB-DOM) before and after reaction with δ -MnO₂ at pH 4, 6, and 8.

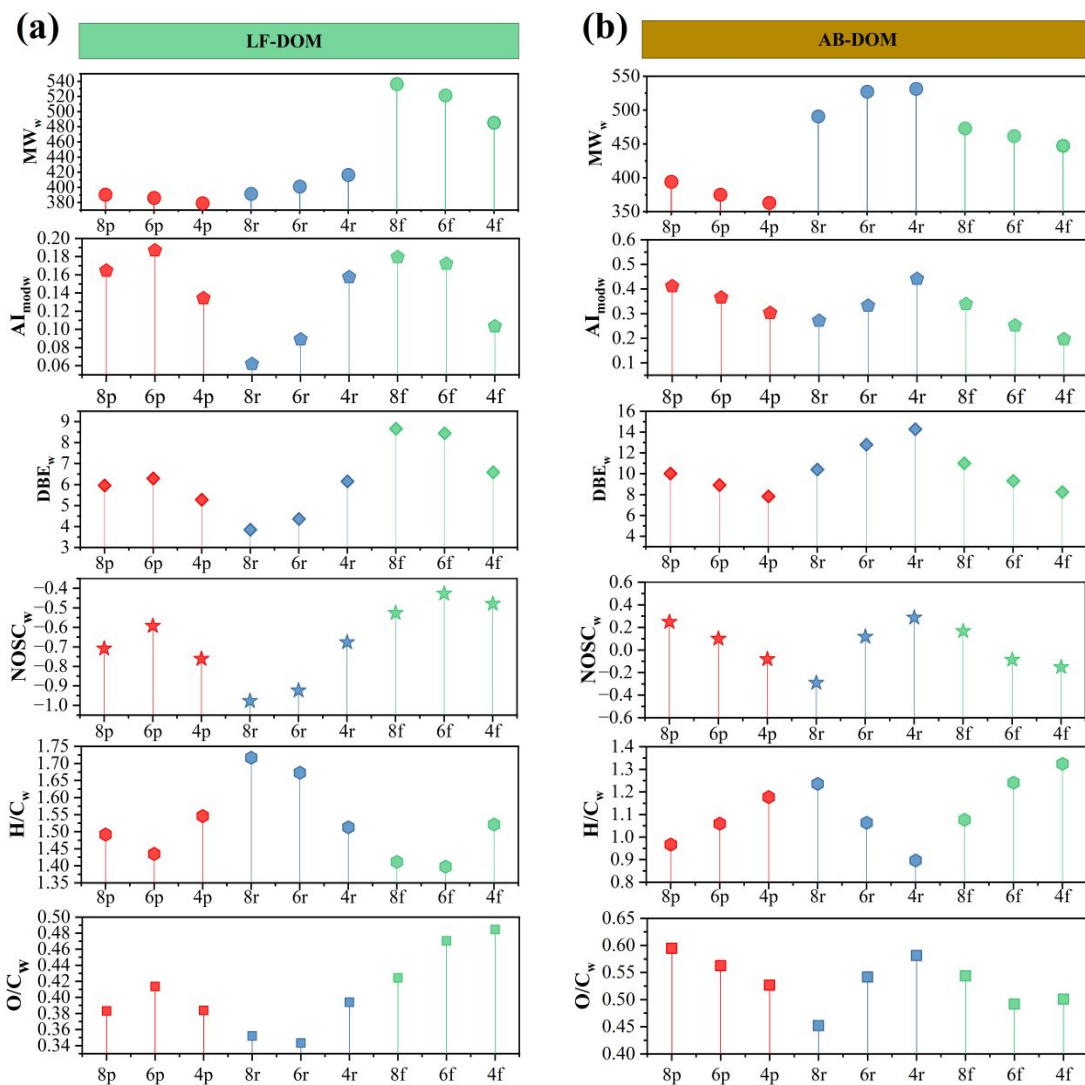


Figure S10. Intensity-weighted average values of MW, AI_{mod}, DBE, NOSC, H/C, and O/C for molecules in LF-DOM (a) and AB-DOM (b) following reaction with δ -MnO₂ at pH 4, 6, and 8. Molecular categories include: persistent (8p, 6p, 4p), removed (8r, 6r, 4r), and newly formed (8f, 6f, 4f).

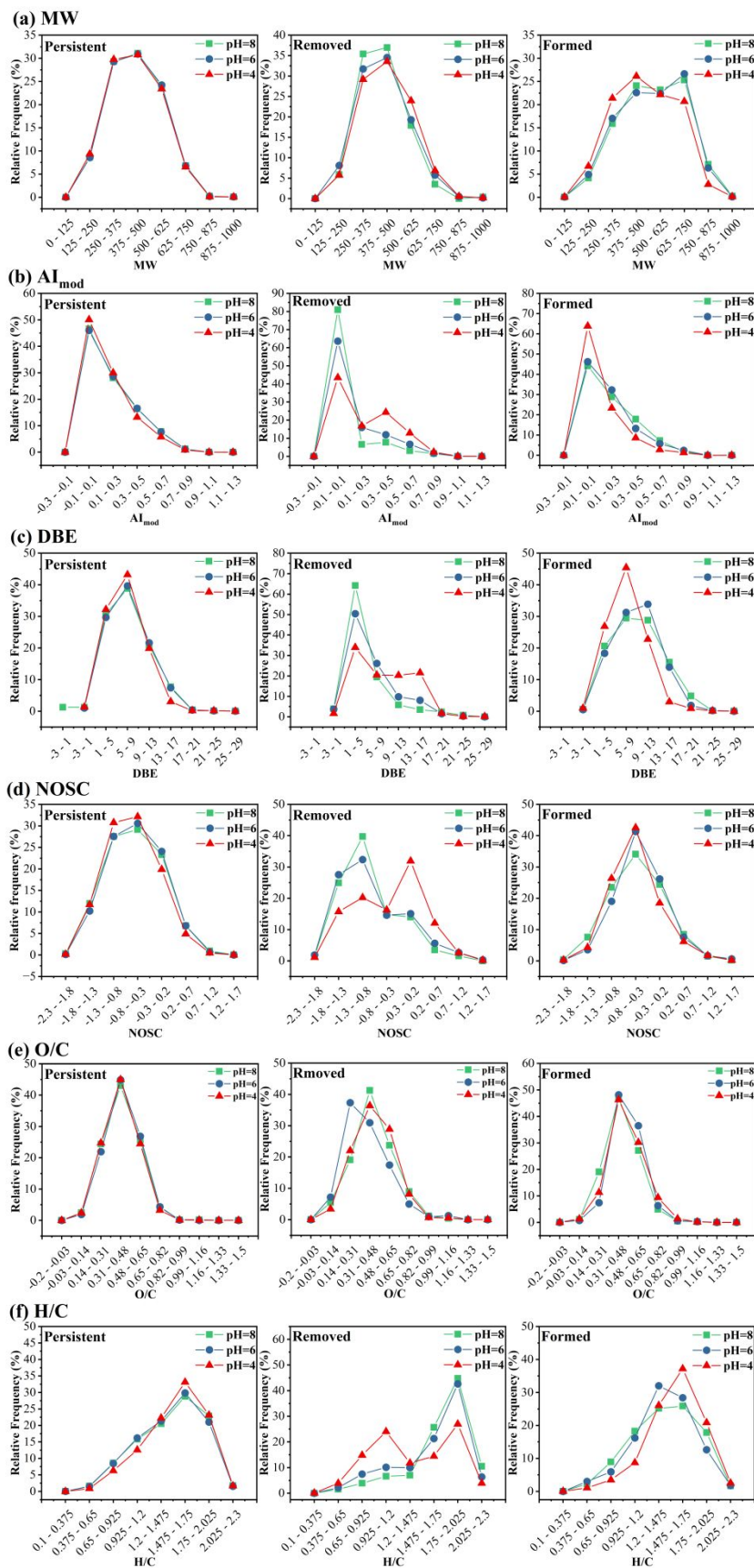


Figure S11. Relative frequency distributions of (a) MW, (b) AI_{mod} , (c) DBE, (d) NOSC, (e) O/C, and (f) H/C for persistent, removed, and newly formed molecules in LF-DOM after reaction with $\delta\text{-MnO}_2$.

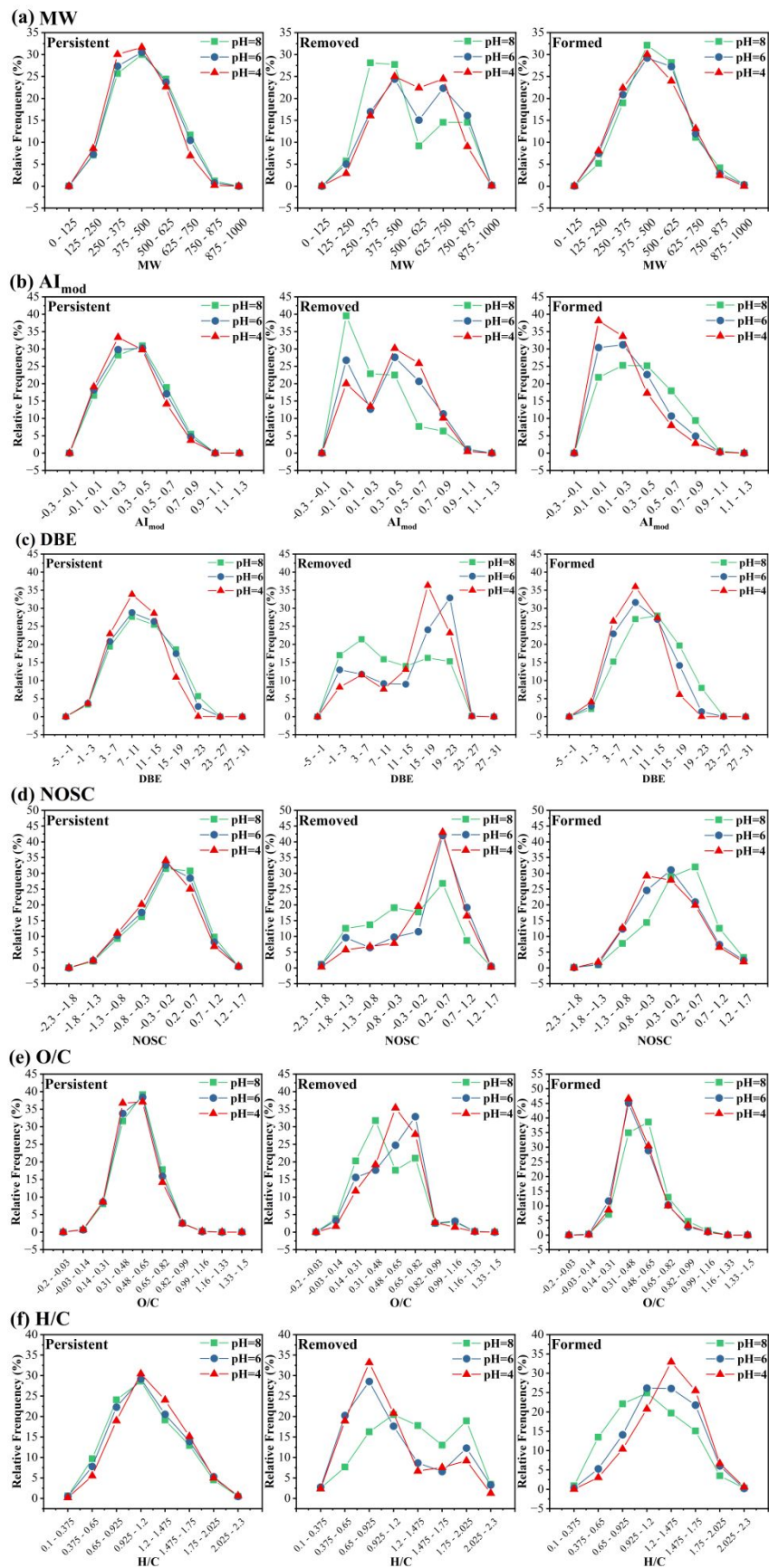


Figure S12. Relative frequency distributions of (a) MW, (b) AI_{mod} , (c) DBE, (d) NOSC, (e) O/C, and (f) H/C for persistent, removed, and newly formed molecules in AB-DOM after reaction with $\delta\text{-MnO}_2$.

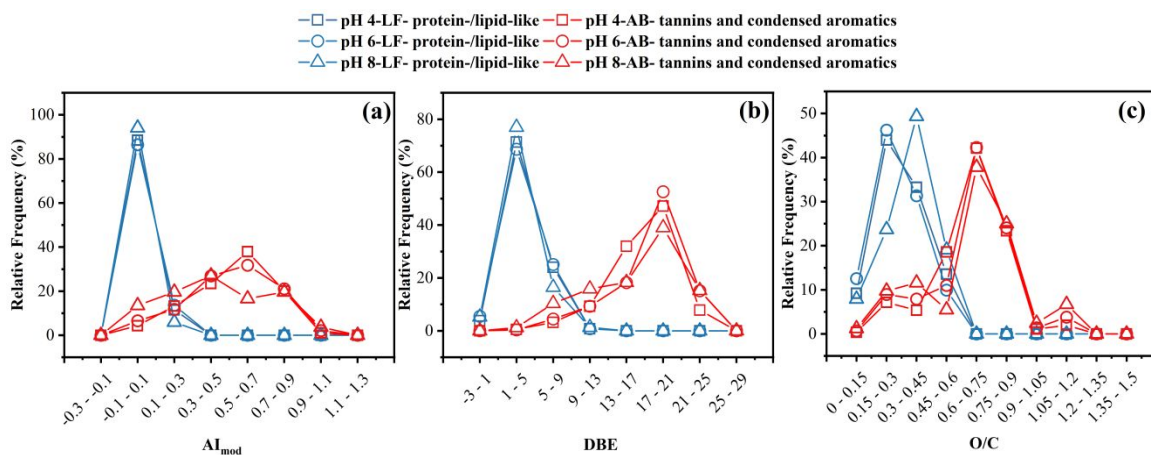


Figure S13. Relative frequency distributions of (a) AI_{mod} , (b) DBE, and (c) O/C ratio for removed protein-/lipid-like compounds from LF-DOM versus removed tannin and condensed aromatic compounds from AB-DOM.

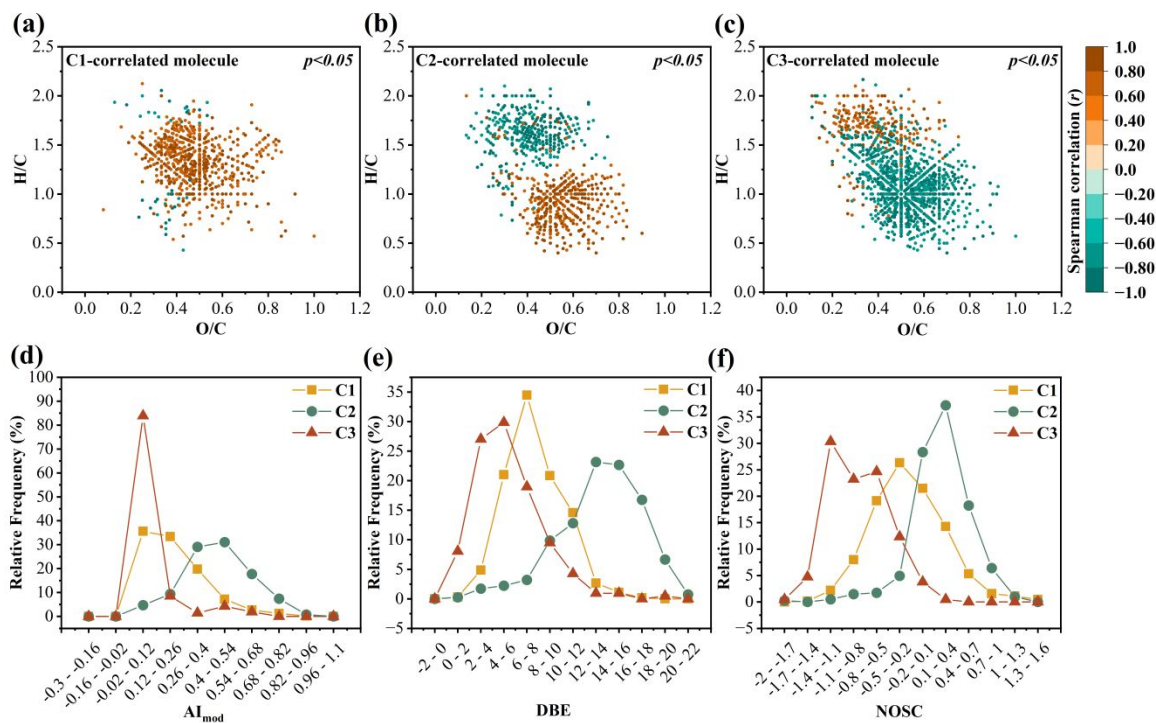


Figure S14. (a–c) Van Krevelen diagrams of FT-ICR MS–assigned molecular formulas significantly correlated with EEM–PARAFAC components C1 (a), C2 (b), and C3 (c), based on Spearman correlation ($p < 0.05$, $|r| > 0.7$). Positively ($r > 0$) and negatively ($r < 0$) correlated formulas are shown in brown and green, respectively. (d–f) Relative frequency distributions of AI_{mod} (d), DBE (e), and NOSC (f) for positively correlated formulas.

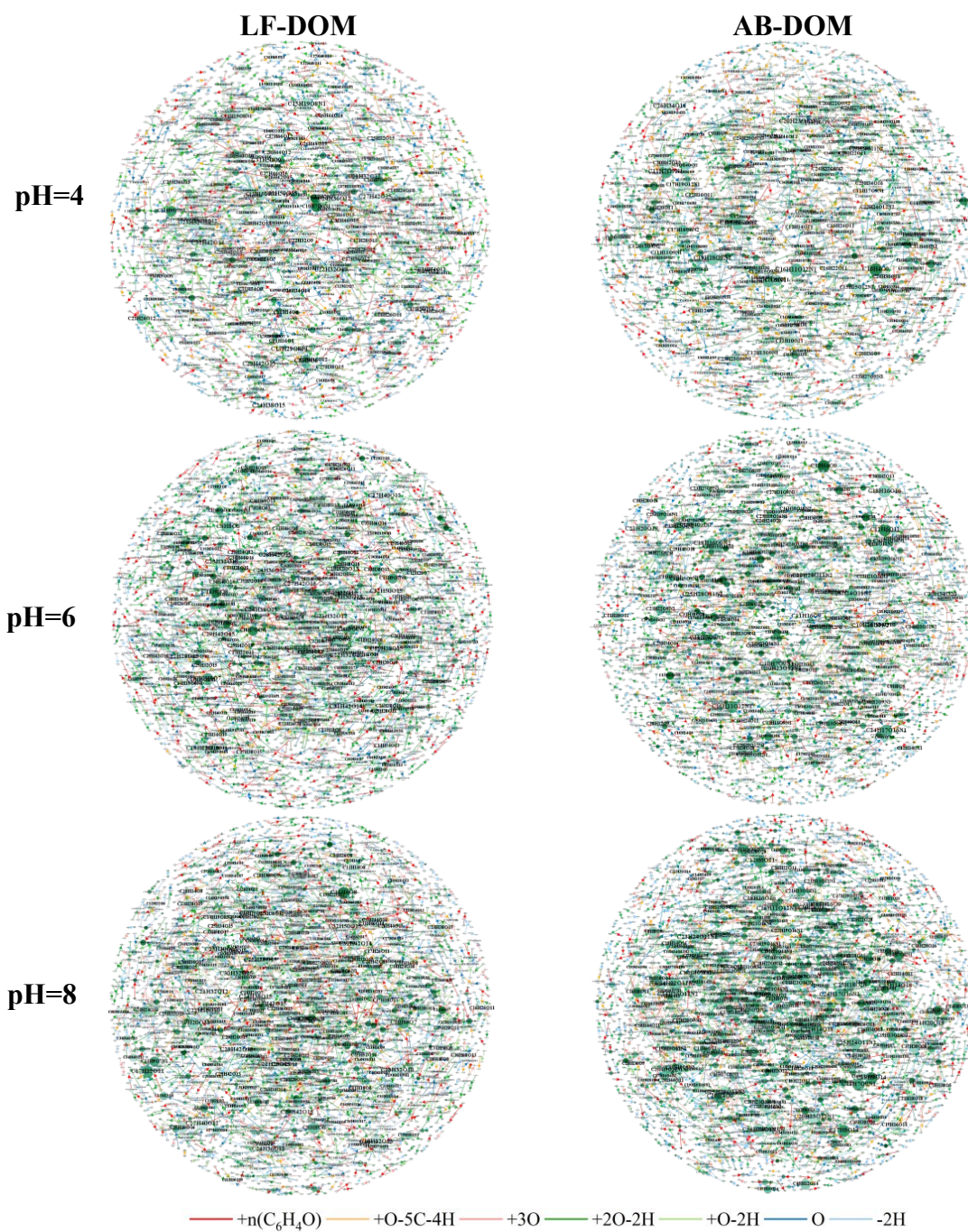


Figure S15. Molecular networks showing precursor–product pairs involved in key transformation pathways (+n(C₆H₄O), +O–5C–4H, +3O, +2O–2H, +O–2H, +O, –2H) during the reactions of δ -MnO₂ with LF-DOM and AB-DOM at pH 4, 6, and 8. Node size indicates connectivity; edge color denotes transformation type.

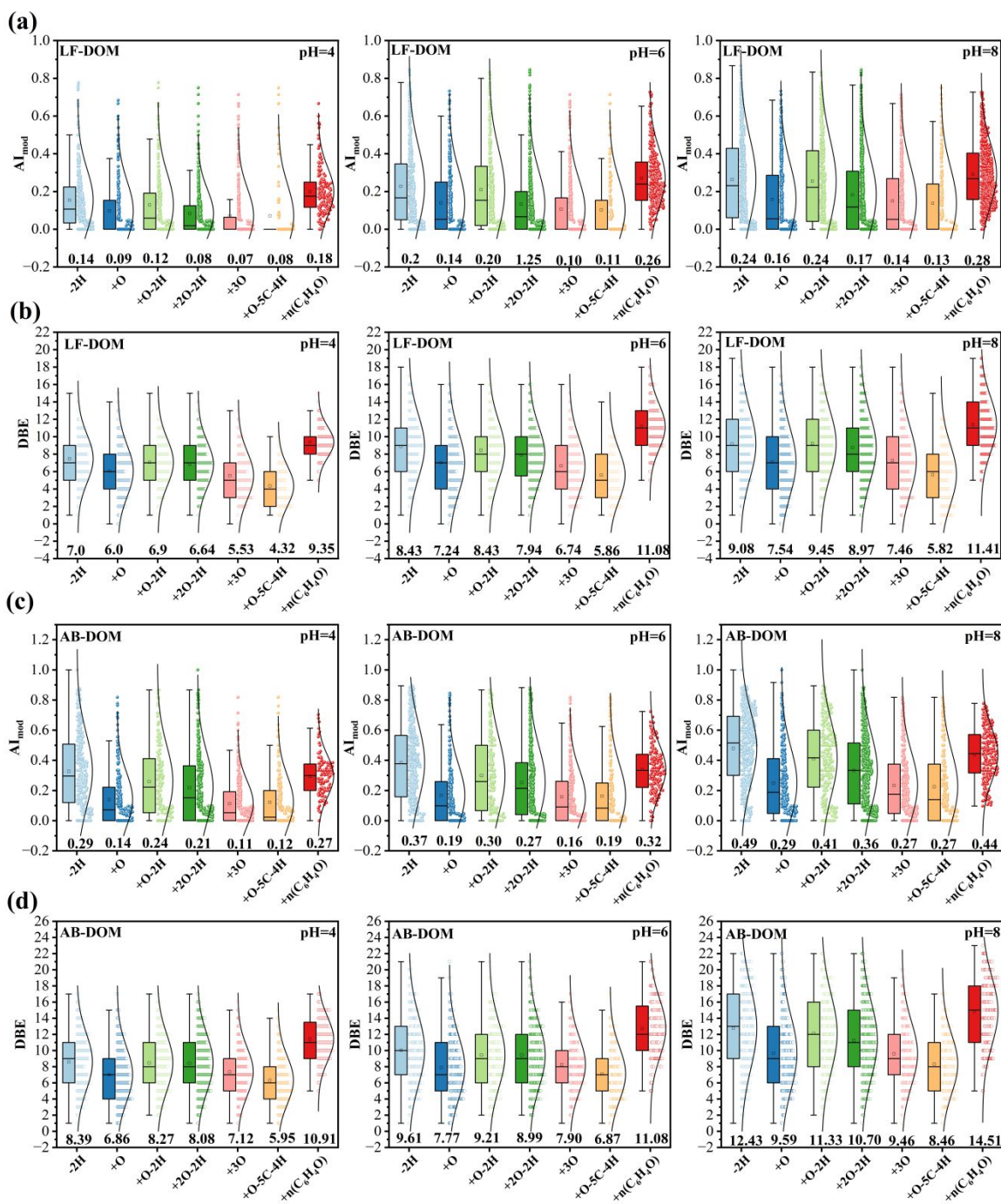


Figure S16. Distribution and intensity-weighted AI_{mod} (a, c) and DBE (b, d) of reaction products from distinct transformation pathways at pH 4, 6, and 8 for LF-DOM (a, b) and AB-DOM (c, d) systems. Numerical values below each violin plot indicate intensity-weighted average AI_{mod} or DBE for each transformation pathway.

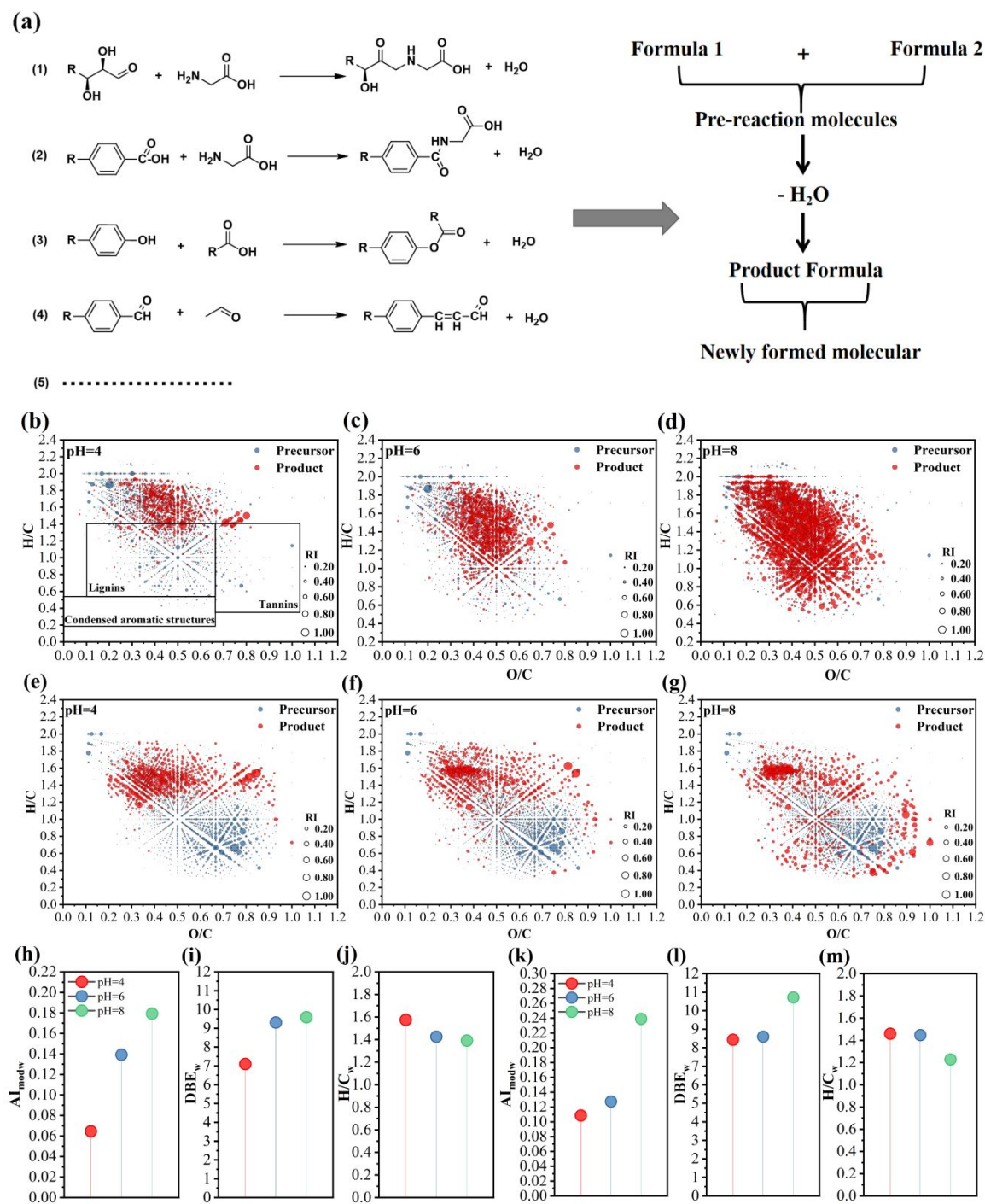


Figure S17. (a) Schematic representation of representative dehydration condensation reactions—Maillard reaction (1), amidation (2), esterification (3), and aldol condensation (4)—along with the computational workflow used to identify condensation products based

on FT-ICR MS data. (b–g) Van Krevelen diagrams of condensation precursors and products in LF-DOM (b–d) and AB-DOM (e–g) at pH 4 (b, e), 6 (c, f), and 8 (d, g). Symbol size denotes relative intensity (RI), calculated as the peak intensity of each molecular formula normalized to the maximum intensity within its respective group (precursors or products). (h–m) Intensity-weighted average values of AI_{mod} (h, k), DBE (i, l), and H/C (j, m) for the condensation products of LF-DOM (h–j) and AB-DOM (k–m) at pH 4, 6, and 8.

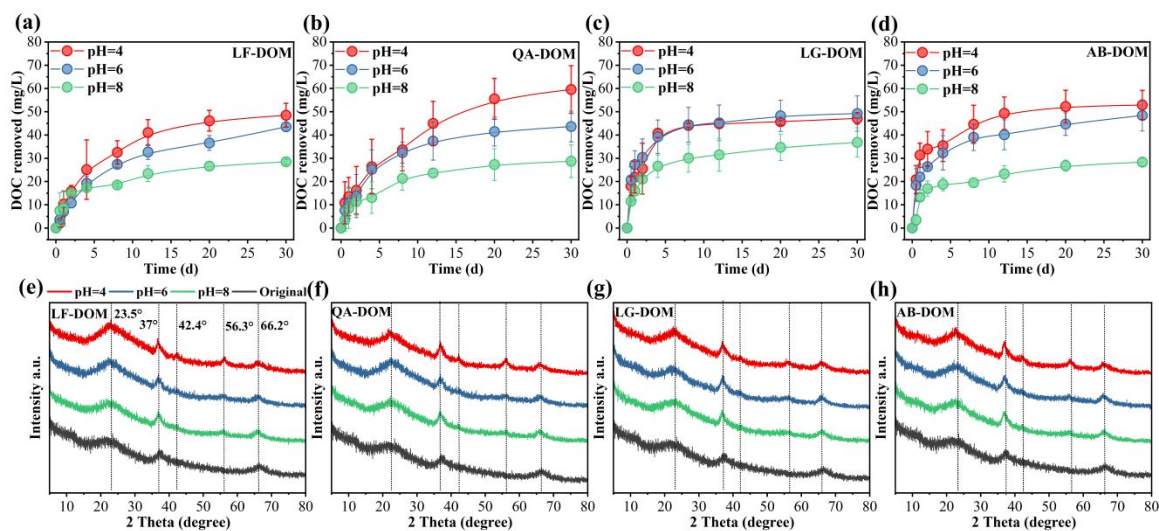


Figure S18. (a–d) DOC removal during reaction of δ -MnO₂ with (a) LF-DOM, (b) QA-DOM, (c) LG-DOM, and (d) AB-DOM at pH 4, 6, and 8. (e–h) XRD patterns of δ -MnO₂ before and after reaction with (e) LF-DOM, (f) QA-DOM, (g) LG-DOM, and (h) AB-DOM at pH 4, 6, and 8.

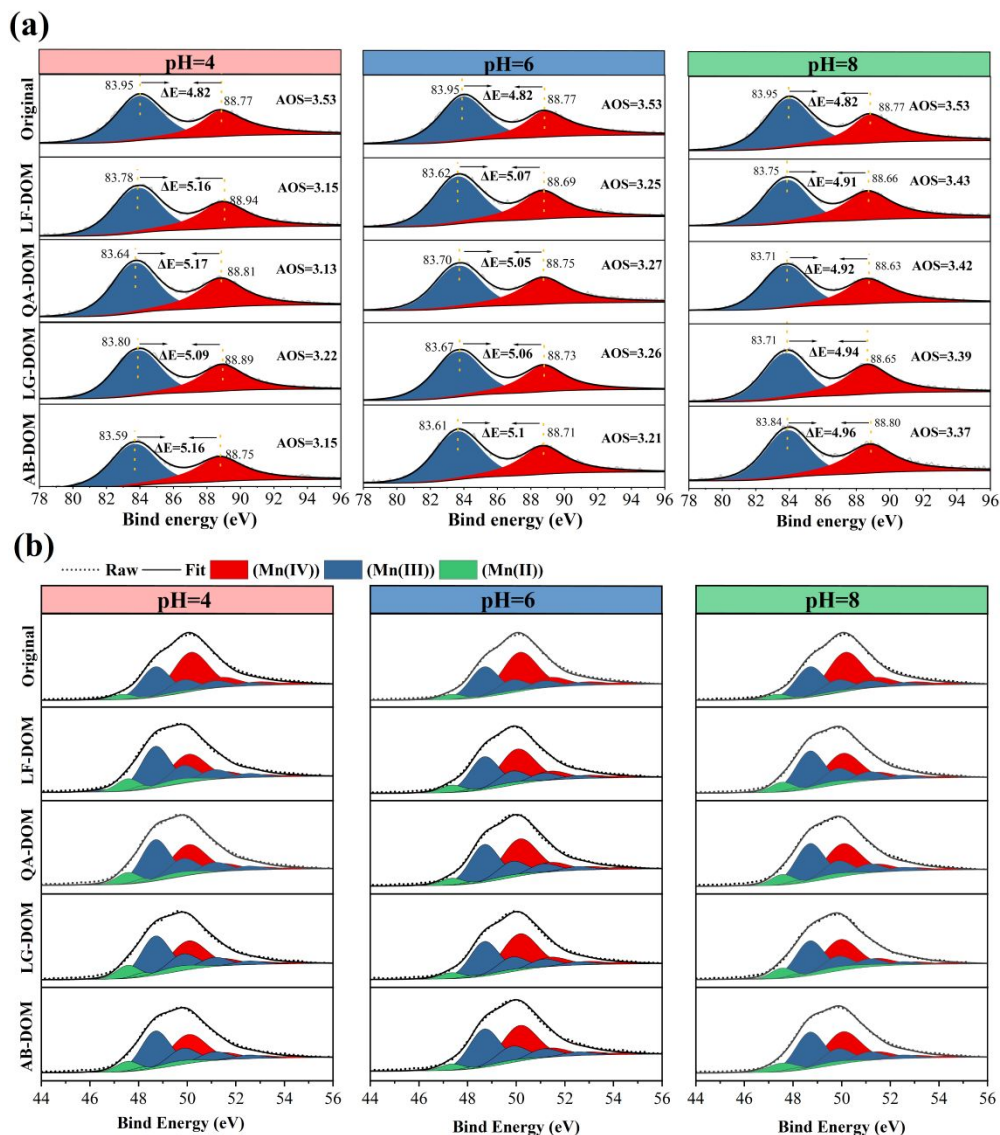


Figure S19. (a) High-resolution Mn 3s XPS spectra of δ -MnO₂ before and after reaction with LF-DOM, QA-DOM, LG-DOM, and AB-DOM at pH 4, 6, and 8. The energy separation (ΔE) between two splitting peaks was utilized to calculate the average oxidation state (AOS) of Mn using the empirical equation: $AOS = 8.956 - 1.126 \times \Delta E$. (b) High-resolution Mn 3p XPS spectra and corresponding peak deconvolution results for δ -MnO₂ before and after reaction with LF-DOM, QA-DOM, LG-DOM, and AB-DOM at pH 4, 6, and 8.

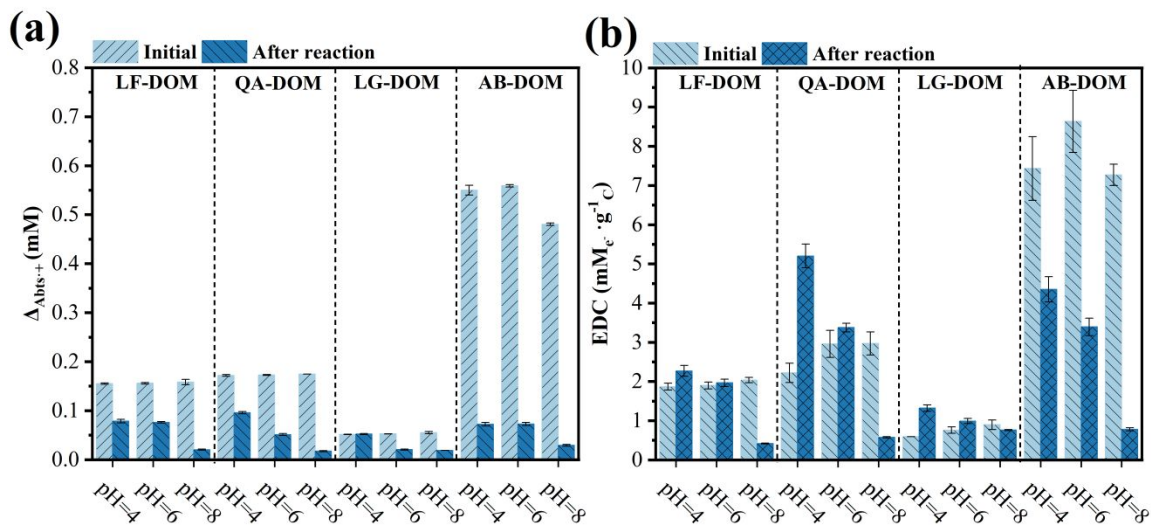


Figure S20. ABTS^{•+} consumption ($\Delta_{\text{ABTS}^{\bullet+}}$) (a) and EDC (b) of four types of DOM (LF-DOM, LG-DOM, QA-DOM, and AB-DOM) upon reaction with $\delta\text{-MnO}_2$ at the initial stage (0 day) and after 30 days. EDC was calculated by normalizing $\Delta_{\text{ABTS}^{\bullet+}}$ to the DOC concentration. $\Delta_{\text{ABTS}^{\bullet+}}$ represents the total electrons donated from DOM to ABTS^{•+}.

REFERENCE

- (1) Version, E.; Li, L.; Yang, Q.; Li, F. *Vegetation of China*; China Agricultural University Press: Beijing, **2020**.
- (2) Byng, J.; Chase, M.; Christenhusz, M.; Fay, M.; Judd, W.; Mabberley, D.; Sennikov, A.; Soltis, P.; Stevens, P. An update of the angiosperm phylogeny group classification for the orders and families of flowering plants: APG IV. *Bot. J. Linn. Soc.* **2016**, *181* (1), 1–20.
- (3) Angst, Š.; Angst, G.; Mueller, K. E.; Lange, M.; Eisenhauer, N. Un(der)explored links between plant diversity and particulate and mineral-associated organic matter in soil. *Nat. Commun.* **2025**, *16*, 5548.
- (4) Liao, Y. Y.; Fu, H. Z.; Zhou, G. P.; Zhong, R. J.; Yuan, H.; Guo, Q.; Yan, Q. W. [Chemical constituents from leaves of *Liquidambar formosana*]. *J. Chin. Med. Mater.* **2014**, *37* (11), 2219–2221.
- (5) Cornwell, W. K.; Cornelissen, J. H. C.; Amatangelo, K.; Dorrepaal, E.; Eviner, V. T.; Godoy, O.; Hobbie, S. E.; Hoorens, B.; Kurokawa, H.; Pérez-Harguindeguy, N.; Quested, H. M.; Santiago, L. S.; Wardle, D. A.; Wright, I. J.; Aerts, R.; Allison, S. D.; Van Bodegom, P.; Brovkin, V.; Chatain, A.; Callaghan, T. V.; Díaz, S.; Garnier, E.; Gurvich, D. E.; Kazakou, E.; Klein, J. A.; Read, J.; Reich, P. B.; Soudzilovskaia, N. A.; Vaieretti, M. V.; Westoby, M. Plant species traits are the predominant control on litter decomposition rates within biomes worldwide. *Ecol. Lett.* **2008**, *11* (10), 1065–1071.
- (6) Jiang, L.; Yin, S.; Wang, G.; Shao, X.; Wang, Y.; Li, Y.; Ding, Y. The genus *Quercus*:

metabolites, biological activity and mechanisms of action. *Phytochem. Rev.* **2025**, *24*, 259–302.

(7) Hernes, P. J.; Hedges, J. I. Tannin signatures of barks, needles, leaves, cones, and wood at the molecular level. *Geochim. Cosmochim. Acta* **2004**, *68* (6), 1293–1307.

(8) Park, B. B.; Han, S. H.; Hernandez, J. O.; An, J. Y.; Youn, W. B.; Choi, H.-S.; Jung, S. Leaf litter decomposition of deciduous *Quercus acutissima* Carruth. and evergreen *Quercus glauca* Thunb. in an inter-site experiment in three contrasting temperate forest stands in South Korea. *Ann. For. Sci.* **2021**, *78*, 34.

(9) Zhu, B.; Hou, X.; Niu, J.; Li, P.; Fang, C.; Qiu, L.; Ha, D.; Zhang, Z.; Sun, J.; Li, Y.; Lin, S. Volatile constituents from the fruits of *Lindera glauca* (Sieb. et Zucc.) with different maturities. *J. Essent. Oil-Bear. Pl.* **2016**, *19* (4), 926–935.

(10) Wong, B. L.; Baggett, K. L.; Rye, A. H. Seasonal patterns of reserve and soluble carbohydrates in mature sugar maple (*Acer saccharum*). *Can. J. Bot.* **2003**, *81*, 780–788.

(11) Yeasmen, N.; Orsat, V. Advanced separation of phytochemical and bioactive attributes from various morphological components of sugar maple (*Acer saccharum*) tree. *Food Biosci.* **2023**, *19*, 103260.

(12) Villalobos, M.; Toner, B.; Bargar, J.; Sposito, G. Characterization of the manganese oxide produced by *Pseudomonas putida* strain MnB1. *Geochim. Cosmochim. Acta* **2003**, *67* (14), 2649–2662.

(13) Coq, S.; Souquet, J.-M.; Meudec, E.; Cheynier, V.; Hättenschwiler, S. Interspecific variation in leaf litter tannins drives decomposition in a tropical rain forest of French

Guiana. *Ecology* **2010**, *91* (7), 2080–2091.

(14) Ding, Z.; Hu, S.; Zhu, L.; Xiao, J.; Ye, Q.; Liu, T.; Shi, Z. Multiple effects of iron oxides on the adsorption and oxidation of dissolved organic matter by manganese oxides. *Geochim. Cosmochim. Acta* **2024**, *384*, 213–227.

(15) Del Vecchio, R.; Schendorf, T. M.; Blough, N. V. Contribution of quinones and ketones/aldehydes to the optical properties of humic substances (HS) and chromophoric dissolved organic matter (CDOM). *Environ. Sci. Technol.* **2017**, *51* (23), 13624–13632.

(16) Walpen, N.; Houska, J.; Salhi, E.; Sander, M.; von Gunten, U. Quantification of the electron donating capacity and UV absorbance of dissolved organic matter during ozonation of secondary wastewater effluent by an assay and an automated analyzer. *Water Res.* **2020**, *185*, 116235.

(17) Wang, W.; Fang, X.; Fu, Q.-l.; Huang, C.; Fang, L.; Zhang, J.; Feng, X.; Tan, W.; Liu, F.; Li, J.; Yin, H. Iron(II/III) alters the relative roles of the microbial byproduct and humic acid during chromium(VI) reduction and fixation by soil-dissolved organic matter. *Environ. Sci. Technol.* **2025**, *59* (5), 2778–2790.

(18) Liu, J.; Su, H.; Hu, Y.; Gong, C.; Lu, J.; He, D.; Zhu, W.; Chen, D.; Cao, X.; Li, J.; Gligorovski, S.; Luo, Y. Highly efficient degradation of sulfur-containing volatile organic compounds by amorphous MnO₂ at room temperature: Implications for controlling odor pollutants. *Appl. Catal., B* **2023**, *334*, 122877.

(19) Ilton, E. S.; Post, J. E.; Heaney, P. J.; Ling, F. T.; Kerisit, S. N. XPS determination of Mn oxidation states in Mn (hydr)oxides. *Appl. Surf. Sci.* **2016**, *366*, 475–485.

- (20) Wu, S.; Feng, Y.; Chen, X.; Fu, Q.-L.; Dong, H.; Yang, X.; Ma, R.; Fu, P.; Wang, Y. Deciphering the effects of quenching on the chemodiversity of low- and non-volatile disinfection byproducts in drinking source water using ESI(-)-FT-ICR MS. *Environ. Sci. Technol.* **2025**, *59* (33), 17834–17845.
- (21) Stubbins, A.; Lapierre, J.-F.; Berggren, M.; Prairie, Y. T.; Dittmar, T.; del Giorgio, P. A. What's in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada. *Environ. Sci. Technol.* **2014**, *48* (18), 10598–10606.
- (22) Wang, Y.-H.; Zhang, P.; He, C.; Yu, J.-C.; Shi, Q.; Dahlgren, R. A.; Spencer, R. G. M.; Yang, Z.-B.; Wang, J.-J. Molecular signatures of soil-derived dissolved organic matter constrained by mineral weathering. *Fundam. Res.* **2023**, *3*, 377–383.
- (23) Kellerman, A. M.; Guillemette, F.; Podgorski, D. C.; Aiken, G. R.; Butler, K. D.; Spencer, R. G. M. Unifying concepts linking dissolved organic matter composition to persistence in aquatic ecosystems. *Environ. Sci. Technol.* **2018**, *52* (5), 2538–2548.
- (24) Fu, Q.-L.; Fujii, M.; Riedel, T. Development and comparison of formula assignment algorithms for ultrahigh-resolution mass spectra of natural organic matter. *Anal. Chim. Acta* **2020**, *1125*, 247–257.
- (25) Ding, Z.; Ding, Y.; Liu, F.; Yang, J.; Li, R.; Dang, Z.; Shi, Z. Coupled sorption and oxidation of soil dissolved organic matter on manganese oxides: Nano/sub-nanoscale distribution and molecular transformation. *Environ. Sci. Technol.* **2022**, *56* (4), 2783–2793.
- (26) Liu, H.; Li, Y.; Huangfu, Z.; Lu, Q.; Yang, B.; Liu, Y. Structure and molecular-level transformation for oxidation of effluent organic matters by manganese oxides. *Water Res.*

2024, 262, 122082.

(27) Trainer, E. L.; Ginder-Vogel, M.; Remucal, C. K. Selective reactivity and oxidation of dissolved organic matter by manganese oxides. *Environ. Sci. Technol.* **2021**, 55 (17), 12084–12094.

(28) Stone, A. T. Reductive dissolution of manganese(III/IV) oxides by substituted phenols. *Environ. Sci. Technol.* **1987**, 21 (10), 979–988.