

ABSTRACT

Structure-reactivity Mechanisms of Organic Matter Sorption and Photochemical Transformation in Aqueous Environments

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Black carbon produced from vegetation fires accounts for 15% of soil organic carbon and the dissolved component makes up 10% of organic carbon transported by rivers to the oceans annually. The association of organic carbon with metal oxides and its photochemical transformation are critical factors controlling C turnover in soils and aquatic systems. However, the influence of chemical structure on photodegradation of dissolved organic matter and its sorption to metal oxides remains questionable. The original research in this dissertation is aimed towards better understanding structure-reactivity mechanisms that control organic matter sorption to metal oxides and its photodegradation in aquatic environments.

The molar heat of sorption of lignin monomers onto ferrihydrite was 1.17 kJ mol^{-1} and occurred via an outer-sphere mechanism involving multiple points of attachment. Sorption of lignin monomers was characterized by an exchangeable fraction that was bound to surface sites and within unblocked intraparticle pores and an unexchangeable fraction that was not accessible and/or removable by simple ion exchange. Plant biomass

type and its processing via charring were significant drivers of dissolved organic matter (DOM) photolability and its sorption to nano-crystalline boehmite. The photo-bleaching behavior of DOM was captured by a three-component energy-based model. The first component was resistant to photobleaching, whereas the second and third components required a mean energy flux of 42-204 kJ m⁻² and 168-1540 kJ m⁻², respectively. Model predictions showed that an increase in vegetative fires would decrease photodegradative contributions to DOM cycling in the conifer-dominated east Texas, increase contributions in the hardwood shrub-dominated west, but have no effect in the grass-dominated central regions. The sorption of DOM to nano-crystalline boehmite was related to the preponderance of alkyl attachments to the aromatic backbone. Photolysis of DOM reduced the complexity and total energy of sorption for DOM thereby suggesting that solar-exposed DOM will be less prone to being sorbed, sorbed strongly and hence preserved via sorptive preservation on metal oxide colloids.

Structure-reactivity Mechanisms of Organic Matter Sorption and Photochemical Transformation in
Aqueous Environments

by

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Chapter Two – B.C.L. completed the investigation and visualization, wrote, and revised the manuscript, and contributed to the methodology, formal analysis, resources, and funding acquisition. W.C.H. contributed to the formal analysis, resources, revising the manuscript and supervision. M.M.M. contributed to the resources and revising the manuscript. A.N.M. contributed to the resources and revising the manuscript. ORH conceptualized the work, and contributed to the methodology, investigation, formal analysis, resources, supervision, funding acquisition and revising the manuscript. All authors have read and agreed to the published version of the manuscript.

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CHAPTER ONE

Introduction

Global change, such as land-use, cover and management and changes in climate (e.g., wildfire activity), have perturbed the abiotic systems within the critical zone which has significant implications for the turnover potential of carbon. This work was conducted to improve our understanding of two important abiotic processes that influence organic matter transformation in aqueous environments — sorption and photolysis. Special emphasis is also placed on the role of fire in carbon cycling dynamics and how climatic and anthropogenic alterations in wildfire regimes will affect carbon stocks. The literature background and motivation for the research presented herein, is summarized in the introductory chapter. The subsequent chapters address uncertainties regarding the influence of organic matter structure on its photochemistry and sorption to metal oxides. Chapter Two evaluates the influence of oxygen-containing functional groups on the sorption dynamics and energetics of lignin monomers onto ferrihydrite. Chapter Three examines the structure-reactivity mechanisms of DOM photodegradation as relates to solar energy input. Chapter Four presents a more holistic approach to understanding the abiotic interactions of organic matter by assessing the photochemical alteration of dissolved organic matter from plant biomass (and pyrolyzed counterparts) and comparing their sorption dynamics and energetics onto nano-crystalline boehmite. Chapter Five concludes with general insights and environmental implications of this research.

Organic Matter in Aqueous Environments

Organic matter (OM) in terrestrial and aquatic environments is a product of plant and animal tissue decay and is a critical component of the global carbon cycle. Dissolved organic matter (DOM) is comprised of the constituents of OM that can pass through a 0.45 μm filter pore, whereas particulate organic matter does not (Zsolnay, 2003). Hence, by definition, the term ‘dissolved organic matter’ is misleading in that DOM does not exist exclusively as a chemical solution, but as a fine colloidal suspension of relatively small molecular structures ranging from 100-2,000 Daltons (Stenson et al., 2002; Sutton and Sposito, 2005). These primary molecules may aggregate into macromolecular structures (up to 100,000 Daltons) by non-polar interactions, hydrogen bonding and poly-covalent cation interactions facilitated by ketone, amide, carboxyl, hydroxyl and other minor functional groups (Leenheer and Croué, 2003; Piccolo, 2002). Surface charge and functional group reactivity is especially relevant for DOM interactions with microorganisms and other geomeia including solutes and surfaces (Bauer and Bianchi, 2011). For example, dissolved organic matter can form metal-ligand complexes thereby altering the solubility, reactivity, and transport of metals (Aiken et al., 2011; Hernandez-Soriano and Jimenez-Lopez, 2012). Additionally, DOM also affects the transport of organic pollutants such as PAHs; inorganic nutrients such as nitrate and phosphate; cations and anions released by mineral weathering; and can change the optical properties of surface waters thereby influencing aquatic photochemical reactions (Chen et al., 2005; De Paolis and Kukkonen, 1997; Vähätalo et al., 2003).

The different reactivities of OM compounds has implications for both fast and slow cycling of carbon with residence times ranging from days to millennia (Lorenz et

al., 2007; Marín-Spiotta et al., 2014). Allochthonous sources of DOM such as decomposing leaf litter and roots, microbially decomposed soil organic matter, as well as metabolic by-products of plants and soil biota are the primary suppliers of DOM to the organic carbon pool in aquatic systems where the biomass of primary producers is low (Bolan et al., 2011; McDowell, 2003). Of the 2200 gigatons of carbon stored in plants and soils, an estimated 250 megatons C yr⁻¹ is transported by rivers to the ocean (Bauer and Bianchi, 2011; Hedges et al., 1997). Compounds identified in freshwater systems include: i) carbohydrates, ii) soluble fatty acids and terpenoid derivatives such as carboxylic-rich alicyclic molecules, iii) lignin- and tannin-derived polyphenols, iv) amino acids/sugars, peptides and peptidoglycan derivatives, and v) condensed aromatic structures (Lam et al., 2007; Nebbioso and Piccolo, 2013; Seidel et al., 2015; Stubbins et al., 2010). Despite a shared provenance in land plants, DOM dynamics are different between land and freshwater ecosystems. Photodegradation and other light-mediated reactions may play a more prominent role in the fate of DOM in aquatic systems, whereas abiotic interactions with reactive solid components are more dominant in soils (Bolan et al., 2011).

Organic Matter in Aqueous Environments: Dissolved Black Carbon

Wildfires and prescribed fires create a diverse thermal environment in which lignocellulosic tissues (leaf, stem, root, wood, bark, detritus, etc.) are exposed to a range of temperatures, durations, gases, and vapors. Variation in feedstock properties (lignin to cellulose ratios) and pyrolysis conditions (fire temperature and duration, oxygen availability, pressure) produce a continuum of thermally derived molecular components that are collectively referred to as black carbon (BC). In general, pyrolysis of plant

biomass lowers the H/C and O/C ratio, shortens alkyl chain length, and increases aryl carbon content thereby shifting the structure of OM to one that is more recalcitrant than its unburnt predecessor (Baldock and Smernik, 2002; Cheng et al., 2006; Harvey et al., 2012b; Knicker, 2011). Annual terrestrial production of BC ranges from 40-250 megatons and is largely retained in soils where it makes up roughly 13% of soil organic carbon (Jaffé et al., 2013; Reisser et al., 2016). Counterintuitive to the apparent hydrophobicity of BC, roughly 10% of bulk dissolved organic carbon in global riverine systems is comprised of dissolved black carbon (DBC) structures (Dittmar et al., 2012; Jaffé et al., 2013; Roebuck et al., 2018). Nonetheless, the stability and fate of DBC is not well-characterized despite evidence that it is a critical component of carbon cycling between the land, water, and atmosphere (Aufdenkampe et al., 2011; Masiello and Louchouart, 2013).

Sorption of Organic Matter in Aqueous Environments

The sorption of selected constituents of DOM—selective sorption—occurs when the external forces of attraction between DOM and the mineral surface (e.g., electrostatic forces) are stronger than the intermolecular forces between DOM constituents (Lv et al., 2016). Sorption mechanisms of amphiphilic compounds such as DOM include: ligand exchange, hydrophobic forces, electrostatic and van der Waals interactions, cation bridging, surface ion chelation and hydrogen bonding (Philippe and Schaumann, 2014). In acidic environments, Al and Fe oxyhydroxides can impart a positive surface charge to the mineral surface whereas DOM is negatively charged. Under these conditions, compounds in DOM with the highest electron density or net negative charge are attracted to positively charged oxide surfaces by strong electrostatic forces, thus facilitating the

formation of organo-mineral aggregates. Furthermore, micro and mesopores of Fe/Al oxyhydroxides surfaces can increase the reactive surface area by providing internal sorption sites (Kaiser and Guggenberger, 2003). More than 20% of OM found in soil and sediment is attributable to interactions with iron minerals (Kleber et al., 2005; Lalonde et al., 2012; Wagai and Mayer, 2007). While the linkage between amorphous iron and the preservation and stabilization of DOM is well-studied (Lalonde et al., 2012; Riedel et al., 2013), the influence of DOM chemistry on sorption strength and efficiency remains unresolved.

The molecular fractionation of OM at the mineral-water interface and its deposition can have major implications for carbon storage and flux in terrestrial ecosystems and its export to marine environments. Amorphous oxides such as Fe^{3+} and Al^{3+} have a higher affinity for OM than other metals (Luider et al., 2003; McKnight et al., 1992; Riedel et al., 2012; Riedel et al., 2013) and influence the removal of OM from aquatic systems by degradation processes and/or sedimentation (Helms et al. 2013; Porcal et al., 2013; Sowers et al., 2019). In the case of terrestrial DOM, especially that originating from plants, carboxylic groups attached to aromatics are preferentially adsorbed, which causes the surrounding solution to become enriched in aliphatic compounds (Kang and Xing, 2008). Kaiser (Kaiser, 2003) reported the stronger sorption of lignin-derived compounds rich in aromatic and carboxylic C onto goethite, relative to carbohydrate-derived compounds rich in O,N-alkyl C. These results were similar to that reported by Adhikari and Yang (Adhikari and Yang, 2015) for the sorption of alkali-soluble peat extracts onto hematite. However, non-aromatic carbon was more resistant to reduction reactions. The preferential preservation of non-aromatic moieties was ascribed

to steric effects that favored the inner layer complexation of more flexible aliphatic components, relative to the more rigid aromatic rings. The aromatic rings were consequently “pushed” to the outer surface of the organic matter-mineral complex making them more susceptible to desorption triggers.

Fundamentally, the concentration and the composition of DOM exported from soils to receiving oceans is contingent on metal oxide content and the reversibility of the bond formation. Redox reactions can compromise the stability of mineral-bound DOM thereby influencing the cycling of DOM and the molecular composition of that exported to marine ecosystems. For example, in surface estuaries, DOM is mostly removed by adsorption to mineral phases. Under such a scenario, the mineral surface provides ballast and protection of the OM from oxidants, including microbial enzymes, thus facilitating preservation of OM in sedimentary environments (Lalonde et al., 2012; McKnight et al., 1992). Consequently, the selective sorption of DOM by metal oxides may be more important in the stabilization and preservation of OC in terrestrial systems than the characteristics of the microbial community (Naisse et al., 2015). To this end, Chapter Two, assesses the influence of electro-steric effects on the thermodynamics and stability of hydroxycinnamate sorption onto ferrihydrite.

Phototransformation of Organic Matter in Aqueous Environments

Unlike the soil environment, photochemical degradation can be more dominant than microbial processes in aquatic systems with significant terrestrial sources (Marschner and Kalbitz, 2003; Minor et al., 2007) While, the microbial acquisition of bioavailable C is inhibited by conjugation and condensation of OM molecules (Harvey et al., 2016) and by the strong sorption of organic carbon to mineral surfaces. The more

aromatic nature of DBC compared to DOM from non-pyrogenic sources has been reported to increase its photo-reactivity and is a major contributing factor to the production of more labile compounds favored by microbes (Stubbins et al., 2012; Ward and Cory, 2016). In Arctic lakes and rivers, the rate of photodegradation is 3-19 times the rate of dark respiration by bacteria and accounts for up to 95% of C processed during the summer months (Cory et al., 2014). Stubbins et al. (Stubbins et al., 2012) observed increased photo-lability with increasing aromatic condensation in DOM from a marine environment but were not able to clearly define a reason for this preferential breakdown of aromatic compounds. Nonetheless, results indicated that DBC with a larger proportion of aromatic structures, decreased by 95% of initial concentration after 28 days of artificial irradiation (UV-A 340 nm), whereas non-pyrogenic DOM decreased by 76% during that same period (Stubbins et al., 2012).

Despite speculation regarding the mechanisms controlling photodegradation, the production of reactive intermediates and radicals such as hydrogen peroxide and singlet oxygen from light absorption by aromatic C is the proposed first step in the direct and indirect breakdown of DOM (Page et al., 2014; Stubbins et al., 2010). However, aromatic content is not the only control on photo-lability of DOM. Recent studies have reported that other moieties can control photodegradation by interactions with radicals during indirect photochemical reactions that occur after light absorption (Cory et al., 2013; Johannessen and Miller, 2001; Powers and Miller, 2015; Ward and Cory, 2016). For example, Ward et al. reported increased photo-lability in permafrost DOM of lower aromatic character than shallow soil DOM. This increased photo-lability was attributable to a reduced ability to quench reactive oxygen species due to a lower abundance of

phenolic compounds (Ward and Cory, 2016). Chapter Three examines the structure-reactivity mechanisms that govern the photodegradation of DOM and presents an energy-based model to predict the change in photodegradative cycling of DOM across Texas in response to a vegetative fire.

Sorptive Fate of Phototransformed Organic Matter

Photodegradation of DOM and its adsorption to metal oxides have been shown to be the primary controls on DOM processing in sunlit (Cory et al., 2014; Ward et al., 2014) and sediment-rich waters (McKnight et al., 1992), respectively. The effect of photoirradiation on the sorption of DOM onto mineral surfaces is important where a combination of these processes might occur such as estuarine systems (Kieber et al., 2006). Pullin et al. (Pullin et al., 2004) reported a 60% decrease in equilibrium adsorption concentrations for DOM onto goethite that had been previously exposed to solar-simulated light. They concluded that the complete loss or photodecarboxylation of DOM in the 1251-3750 Dalton range was primarily responsible for the decrease in adsorption affinity. However, photodegradation is not a major direct process of organic C mineralization but rather produces a suite of smaller more oxidized photoproducts (Bertilsson and Stefan, 1998; Ward and Cory, 2016). On shorter time scales (< 24 h) photodegradation may result in the initial production of carboxylic groups as DOM becomes more oxidized (Xie et al., 2004). Changes to sorption behavior of DOM on metal oxides will depend on the net effect of photodegradation processes which are primarily: i) the preferential breakdown of higher molecular weight components, ii) the decrease in proportion of aromatic compounds and degree of condensation, iii) a decrease in carboxylic groups and iv) an increase in oxidized compounds (Stubbins et al., 2012;

Wagner and Jaffé, 2015; Ward et al., 2014). Unravelling the additive or antagonistic effects of sorption and photodegradation on the molecular composition of DOM is critical in elucidating the chemistry of carbon deposited to an intermediate long-term carbon storage reservoir in inland waters. Chapter Four assesses the importance of aromatic substituents on the photochemical activity of DOM and evaluates the sorption dynamics of DOM onto nano-crystalline boehmite in response to photolysis.

CHAPTER TWO

Sorption Dynamics and Energetics of Cinnamic Acid and its Derivatives at the Ferrihydrite–Water Interface Determined by Flow-Adsorption Microcalorimetry

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Abstract

Lignin-derived aromatic structures are stabilized in soils and soil clay-rich fractions by iron oxyhydroxides. However, the dynamics and energetics of sorption have not been determined and are challenging to study directly in soil matrices due to complex mineralogy and organic molecular diversity of soils. Flow adsorption microcalorimetry experiments conducted using cinnamate and its hydroxylated derivatives (coumarate, ferulate and sinapate) were used to assess the impact of the position and type of R-group substituent (OH and OCH₃) on the sorption behavior at the ferrihydrite–water interface. The molar heat of sorption of (hydroxy)cinnamates was 1.17 kJ mol⁻¹ and was consistent with an outer-sphere mechanism that comprised both electrostatic and physisorption interactions. Cinnamate sorption was endothermic and entropy-driven whereas sorption of the hydroxylated derivatives was exothermic. While the OH substituent shifted the enthalpic response to exothermic, it had minimal effect on the duration and total energy of the reaction. With each OCH₃ substituent added, both the energy and duration of reaction were greater. Compared to OH, the OCH₃ substituent contributed significantly less to the molar heat of sorption, suggesting that OCH₃ facilitated the formation of

intermolecular bonds between sorbate molecules. The OH and OCH₃ substituents increased the energy of sorption by 54% but had minimal effect on the proportion of sorbate that was desorbed by nitrate—54% for cinnamate versus 51% for ferulate. These findings suggest that a significant fraction of (hydroxy)cinnamate interactions with iron oxyhydroxides are weak electrostatic forces and unless protected within the mineral framework, is highly susceptible to shifts in environmental conditions.

Introduction

The sorption of organic matter to mineral surfaces is a dominant carbon stabilization mechanism in soils and sediments globally. Lignin-derived aromatic structures make up roughly 20% of plant litter input into soil and are enriched in soil and clay-rich fractions where it is associated with iron (oxyhydr)oxide minerals.¹⁻⁴ The molecular composition of lignin compounds in soil is reflective of the macromolecular diversity of plant groups that arises from various combinations and proportions of *p*-coumaryl, coniferyl and sinapyl alcohol. For example, gymnosperm wood is mainly comprised of coniferyl units while that of angiosperms have equal amounts of coniferyl and sinapyl units associated with *p*-coumaryl units.⁴ Interaction of organic molecules with iron (oxyhydr)oxide is a dynamic processes involving diffusion of molecules from bulk solution to the surface of mineral particles, competition and exchange reactions, and intraparticle diffusion.⁵ Within the pore network, sorption of organic molecules can occur by multiple ligand attachments which causes pores to become clogged and restricts accessibility of micropores.⁶ Despite this knowledge, the bond-forming or sorption mechanisms are challenging to study directly in soil matrices due to complex mineralogy and organic molecular diversity.

The molecular structure of organic matter directly affects the mechanisms and bonding forces controlling sorption and desorption on iron-bearing minerals. Strong inner-sphere ligand exchange reactions with surface hydroxyl groups are responsible for the preferential sorption of aromatic lignin-like compounds relative to other compounds.⁷⁻

⁹ Whereas weak outer-sphere complexes through van der Waals forces, electrostatic interactions and hydrogen bonding by aliphatic fractions make them easily desorbable.^{3,10-12} Reactions may occur concurrently giving rise to myriad sorption sites, sorption mechanisms, and conformational changes. Recently, Coward et al.⁷ proposed that the rapid sorption (≤ 15 min) of aromatic compounds onto goethite via ligand exchange facilitated the subsequent multi-layer sorption of lignin-like compounds via hydrophobic/charged interactions, followed by tertiary aliphatic compounds via outer-sphere interactions. Notably, less-substituted aromatic compounds were preferentially adsorbed over polycyclic aromatic compounds within the first 5 min and suggested that sorption of the larger compounds onto the surface of goethite was less thermodynamically favorable due to steric hindrances. Other evidence shows that for humic acid sorption onto hematite, although aromatic fractions are disproportionately favored over aliphatic fractions,¹³ preservation was influenced by steric effects that favored the inner layer complexation of the more flexible aliphatic components relative to the more rigid aromatic components that were present. The aromatic compounds were consequently “pushed” to the outer surface of the organic matter–hematite complex making them more susceptible to desorption. Thus, the combined electro-steric effects of molecular volume and functional groups are pivotal in determining the thermodynamics

and stability of organic–iron association^{10,14,15} and the sorbed organic matter at the iron (oxyhydr)oxide-water interface can be viewed as dynamic and evolving.

The dynamics of bond formation between organic matter and metal oxides has been observed experimentally as an attenuation of heat evolved with higher loading. This was interpreted as a progression from enthalpy-driven ligand and/or electrostatic interactions to an entropy-driven process primarily involving hydrophobic attraction and H-bonding,^{16,17} as well as conformational changes of the sorbates.¹⁸ However, sorption isotherms commonly used in studies assessing binding energetics are constrained by assumptions that are invalid in most environmental systems. For example, the required assumptions of the Langmuir isotherm such as the attainment of equilibrium conditions, reversibility, and preservation of the sorbent surface, fail to account for the heterogeneous nature of interactions¹⁹ and results may be inconsistent for the same sorbent and sorbate.^{8,10} Flow adsorption microcalorimetry (FAMC) can be used to measure sorption thermodynamics of simple ions and organic molecules onto metal oxide surfaces, with the sensitivity to detect entropy-driven processes and negligible enthalpic contributions.¹⁸ The FAMC is particularly useful for measuring the evolution of heat associated with different stages of the sorption process, changes in the mechanism and multiple reactions occurring simultaneously but at different rates.²⁰⁻²² Other features of FAMC include: temporal resolution on the order of seconds and the ability to distinguish reversible and irreversible processes through the application of multiple sorption and desorption cycles.^{22,23}

While lignin monomers are known to be stabilized through interaction with iron oxyhydroxides, the dynamics and energetics of sorption and desorption have not been

determined. The primary objective of this study was to investigate the sorption of lignin monomers to ferrihydrite, and furthermore, to assess electro-steric effects (molecular volume and polarizability) due to the influence of oxygen-containing side chains. To this end, we used FAMC to study the dynamics and energetics of cinnamate and its hydroxylated derivatives onto ferrihydrite. The hydroxylated derivatives, *p*-coumarate, ferulate and sinapate are precursor molecules to *p*-coumaryl, coniferyl and sinapyl alcohol, respectively. Both the size and electron distribution of cinnamate is changed by the addition of a hydroxyl group (OH) for *p*-coumarate, and the stepwise addition of methoxy groups (OCH₃) for ferulate and sinapate, respectively. An increase in the number of substituents will increase the likelihood of intermolecular attractive forces such as hydrogen bonding at bottle-neck sites such as the mouths of micropores. We hypothesized that the additional OH and OCH₃ groups would influence the sorbed amount and the energy of sorption, and therefore the nature of the bonding interactions would be dictated by the size of the molecule and its polarizability. Differences in the evolution and total energy of sorption of cinnamate and its hydroxylated derivatives were used to assess the influence of OH and OCH₃ groups on sorption dynamics and energetics. The number of moles sorbed and the energy evolved were used to calculate the molar heat of sorption. Experimental quantification of the molar heat of sorption provides valuable information regarding the stability of organic carbon interactions at the ferrihydrite-water interface and can improve predictions of sorption behavior as relates to organic carbon chemistry. To our knowledge, this is the first study to use flow calorimetry to systematically investigate the influence of oxygen-containing functional groups on the sorption dynamics and energetics of simple organic molecules.

Materials and Methods

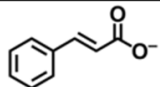
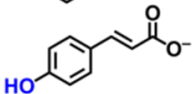
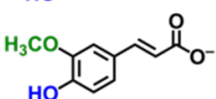
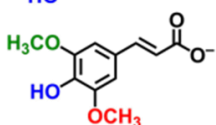
(Hydroxy)cinnamate Solutions

In all experiments, solutions were made using nanopure water (18.2 M Ω ; ThermoScientific, Waltham, MA), *trans*cinnamic acid (99% purity; CAS No. 501-52-0), *p*-coumaric acid (98% purity; CAS No. 501-98-4), ferulic acid (99% purity; CAS No. 1135-24-6), and sinapic acid (98% purity; CAS No. 530-59-6). Table 2.1 lists their relevant physicochemical properties.

Synthesis and Characterization of Ferrihydrite

Ferrihydrite was synthesized according to the method by Villacís-García et al.²⁴ and was slightly modified for this study. Briefly, a solution of 7.5 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 200 mL of deionized water was adjusted to a pH of 7.5 by the drop-wise addition of 1M NaOH in a 500 mL conical flask at room temperature. The resulting suspension was washed and centrifuged repeatedly to an ionic concentration of $<80\mu\text{S cm}^{-1}$ before drying in an oven at 80 °C. After drying, solids were stored at room temperature for use in subsequent experiments. The formation of two-line ferrihydrite was confirmed by x-ray diffraction analysis that displayed the presence of two bands centered at a 2θ of 34° and 61° (Figure A.1). Scanning Electron Microscope images showed that ferrihydrite grains had an average size of $186 \pm 86 \mu\text{m}$ (Figure A.2). Surface charge of ferrihydrite was assessed using the ion-probe flow adsorption microcalorimetry method of Harvey et al.²⁵ Probing experiments were conducted at pH 4, 5, 6, 7, 9, and 10 using K^+ and Na^+ as the cationic probes whereas the anionic probes were Cl^- and NO_3^- (Figure A.3).

Table 2.1. Calorimetric measurements and physicochemical properties for cinnamate (CIN), coumarate (COU), ferulate (FER) and sinapate (SIN) sorption onto ferrihydrite at pH 5. Details on the calculation of E_{total} , Q_s and ΔH_{sorp} are provided in Section 2 of Appendix A.

	Chemical structure	Cumulative energy, E_{total} (J g ⁻¹)	Adsorbed amount, Q_s (mmol g ⁻¹)	Molar heat of sorption, ΔH_{sorp} (kJ mol ⁻¹)	Length of reaction (min)	*Carboxyl pKa	*Phenol pKa	*Percent carboxylate	**Polarizability ($\times 10^{24}$ cm ³)	**Molar volume (cm ³)
CIN		1.12	0.70	1.57	70	4.09	-	89	17.3	125
COU		1.29	0.83	1.56	55	3.89	9.15	93	18.1	123
FER		1.73	1.78	0.97	100	3.99	8.71	91	20.7	147
SIN		3.30	2.74	1.21	140	4.05	8.47	90	23.4	172

*Calculated using Chem3d v. 16.0

**Properties predicted using ACD/Labs Percepta Platform – PhysChem Module (<http://www.chemspider.com>)

Flow Adsorption Microcalorimetry Experiments

Flow adsorption microcalorimetry was used to study the sorption characteristics of cinnamate (CIN), coumarate (COU), ferulate (FER), and sinapate (SIN) onto NO₃-saturated ferrihydrite. The energy of sorption was measured on a FAMC built in-house. Details on its design and operation are described elsewhere²² and within Section 2 of Appendix A. All sorption reactions were conducted in duplicate and carried out at a solution flow rate of 0.50 mL min⁻¹; ionic strength of 10 mM; pH of 5; and using 150 mg of ferrihydrite. Before the sorption experiments, ferrihydrite was hydrated in 10 mM NaNO₃, packed into the calorimeter, and flushed with 10 mM NaNO₃ until a stable baseline was obtained, indicating complete NO₃ saturation and thermal equilibrium. The sorption characteristics of (hydroxy)cinnamates on the NO₃-saturated ferrihydrite were evaluated using 0.5 mM CIN, COU, FER, and SIN in a 9.5 mM background of NaNO₃. Sorption of (hydroxy)cinnamate onto NO₃-saturated ferrihydrite was initiated by switching the pump valve from NaNO₃ solution to 0.5 mM (hydroxy)cinnamate solution. The simultaneous transfer of sorbate from solution to the ferrihydrite surface was monitored by measuring the changes in the evolution or absorption of heat in the sensing unit and the UV-Vis absorbance of the effluent. The UV-Vis absorbance measurements were acquired in quartz cuvettes (10 mm pathlength) at an excitation wavelength of 260 nm until the thermal signal returned to baseline and no further change in effluent concentration was detected (i.e., absorbance returned to the absorbance of stock solution/remained constant). Regression analysis was used to calculate (hydroxy)cinnamate concentrations from absorbance measurements of a stock dilution series. The coefficient of determination was used to select the best-fit regression line. The

concentrations obtained using this method and the corresponding volume of solution flowed over the surface were used to calculate the number of moles of (hydroxy)cinnamate sorbed to ferrihydrite (Q_s). The cumulative energy (E_{total}) for the duration of the experiment was calculated as the integral of the thermogram converted to energy units per mass of sorbent (J g^{-1}) using the calibration curve in Figure A.5. The values for Q_s (mmol g^{-1}) and the corresponding E_{total} were used to calculate the molar heat of sorption (ΔH_{sorp} ; kJ mol^{-1}). Details on calculation of parameters are provided in Section 2 of Appendix A. Comparison of the ΔH_{sorp} for different sorption reactions provided insight into the mechanism of bonding under the experimental conditions.²⁶

Results and Discussion

Chloride–Nitrate (Cl/NO₃) versus Cinnamate–Nitrate (CIN/NO₃) Interactions at the Ferrihydrite–Water Interface

The thermograms for Cl/NO₃, CIN/NO₃ and the reverse reactions on the surface of ferrihydrite at pH 5 are presented in Figure 2.1. Comparison of CIN/NO₃ and Cl/NO₃ thermograms showed that the cinnamate sorption mechanism with NO₃-saturated ferrihydrite was different from the simple anion exchange reaction of Cl/NO₃. Both Cl and CIN reacting with the NO₃-saturated ferrihydrite were endothermic with a E_{total} of $+3.15 \text{ J g}^{-1}$ and $+1.12 \text{ J g}^{-1}$, respectively. By comparison, the complementary reverse reactions (i.e., NO₃ replacing Cl or CIN) were exothermic with a E_{total} of -3.10 J g^{-1} and -0.51 J g^{-1} , respectively. The similarity in the energetics between Cl/NO₃ ($+3.15 \text{ J g}^{-1}$) and NO₃/Cl (-3.10 J g^{-1}) is congruent with flow adsorption microcalorimetry studies of simple ion exchange reactions; which is completely reversible and occur via outer-sphere, electrostatic interactions of anions (or cations) with metal oxides^{23,27} and other charged

surfaces.^{21,25} The endothermic response of Cl/NO₃ relative to the exothermic response of NO₃/Cl is reflective of the smaller ionic radius of Cl.^{21,28} The unimodal shape and comparable reaction duration (30–35 minutes) of the Cl/NO₃ and NO₃/Cl thermograms were also consistent with the simple reaction dynamics of outer-sphere ion exchange.

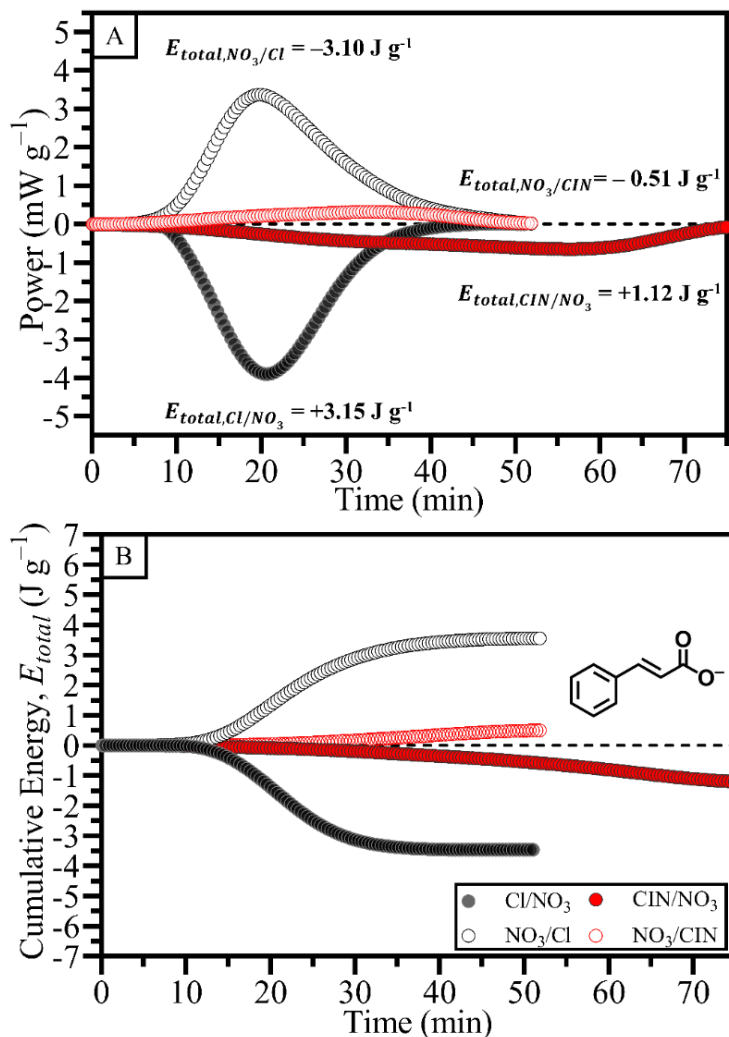


Figure 2.1. Calorimetric thermograms of mass-normalized energy (A) for chlorine replacing (Cl/NO₃) and vice versa (NO₃/Cl); and cinnamate replacing nitrate (CIN/NO₃) and vice versa (NO₃/CIN). Cumulative energy transfer (E_{total}) during the sorption reaction (B).

In contrast to the simple ion exchange of Cl reacting with NO₃-saturated ferrihydrite (and vice-versa), the energetics and evolution of CIN interactions pointed to more complex reaction dynamics and mechanism(s). The bi-modal nature of the thermogram for CIN interacting with the NO₃-saturated ferrihydrite is reflective of a multi-step/multi-phase reaction. The doubling of the reaction duration for CIN (70 minutes) versus Cl (35 minutes) thermograms indicated much slower interaction kinetics for CIN with the NO₃-saturated ferrihydrite (compared to Cl on the same surface). Furthermore, the significantly lower E_{total} for CIN (+1.12 J g⁻¹) on the NO₃-saturated ferrihydrite (compared to +3.15 J g⁻¹ for Cl on the same surface) also point to CIN interactions being less energetic than simple ion exchange. The even lower E_{total} for the NO₃/CIN (−0.51 J g⁻¹) suggests that NO₃ is unable to completely desorb and replace the previously sorbed CIN.

The multi-modal sorption, slower sorption kinetics, and irreversibility apparent in CIN interactions at the ferrihydrite–water interface have also been observed for sulfate^{29,30} and phosphate^{23,27,31} sorption on various Al(III) and Fe(III) oxides. Gale et al.²⁷ attributed multi-modal thermograms for phosphate sorption on boehmite to sorption occurring on differentially coordinated surface hydroxyls. Slower sorption kinetics has been attributed to steric hindrances and intra-particle diffusion.^{5,13,32} Irreversibility of sulfate and phosphate sorption by ion exchange with NO₃ or Cl has been attributed to the phosphate being sorbed onto the same sites as NO₃ or Cl but via ligand rather than ion exchange.²³ While the basis for the involvement of differentially coordinated surface hydroxyls, steric hindrances, and intra-particle diffusion in CIN/ferrihydrite interactions could not be ruled out, the premise for irreversibility due to ligand exchange was not well

supported. Specifically, ligand exchange is an inner-sphere interaction with a much higher heat of sorption than simple ion exchange; an outer-sphere interaction. Harvey and Rhue²³ as well as Gale et al.,²⁷ found that ligand exchange for phosphate had a ΔH_{sorp} that was an order of magnitude higher than simple ion exchange (i.e., 20-30 kJ mol⁻¹ for ligand exchange versus 2-3 kJ mol⁻¹ for simple ion exchange). The ΔH_{sorp} for CIN to NO₃-saturated ferrihydrite was 1.6 kJ mol⁻¹; more in-line with physisorption or more appropriately a mixture of physisorption and ion exchange.³⁰

The likely involvement of both physisorption and ion exchange in CIN/ferrihydrite interactions at the experimental pH of 5 is further supported by the fact that 89% of the carboxyl groups in CIN (pKa = 4.09) would be deprotonated/dissociated and available to participate in ion exchange (Table 2.1).³³ The remaining 11% of undissociated carboxyl would be available to participate in physisorption reactions. The most plausible explanation for the irreversibility of CIN by NO₃ is a pore-filling mechanism where CIN becomes entrapped within the intra-particle pores/structure of the ferrihydrite and renders some intra-particle sites inaccessible to subsequent solutes (e.g., NO₃). In such a scenario, only sites on the surface or in unblocked intraparticle pores of the ferrihydrite would be available for further sorption. This inaccessibility would explain both the lower E_{total} and shorter duration of the NO₃/CIN versus CIN/NO₃ cycle in Figure 2.1. Given that E_{total} is directly proportional to the quantity sorbed,²³ we can estimate that only about 46% (0.51/1.12) of sorption sites remained accessible for NO₃/CIN exchange after the first CIN/NO₃ cycle (Table 2.1 and Figure 2.1). Further evidence of a pore-filling irreversibility will be discussed later for FER.

Interactions of Cinnamate Derivatives at the Ferrihydrite–Water Interface

Thermograms for COU/NO₃, FER/NO₃ and SIN/NO₃ also reflected the involvement of multiple sorption mechanisms, and the influence of OH and OCH₃ substituents on sorption dynamics and energetics (Figure 2.2). Most striking was that unlike the endothermic response of CIN/NO₃, the addition of an OH group resulted in an exothermic reaction for COU/NO₃ and a slightly higher E_{total} of -1.29 J g^{-1} . The exothermic response persisted with the addition of OCH₃ groups and similar to COU, FER and SIN sorption was more energetic than that of the unsubstituted CIN. However, the OCH₃ groups of FER and SIN had a greater effect on the absolute magnitude of E_{total} than the OH group of COU. While only a 13% difference was observed between the E_{total} of CIN (1.12 J g^{-1}) and COU (1.29 J g^{-1}), the E_{total} of FER (1.73 J g^{-1}) was 54% higher than that of CIN. Furthermore, the E_{total} of SIN was 3.30 J g^{-1} —three times higher than that of CIN. This suggested that both the functional groups present and perhaps also their position on the aromatic ring can influence the rates and mechanisms of sorption at the ferrihydrite–water interface.

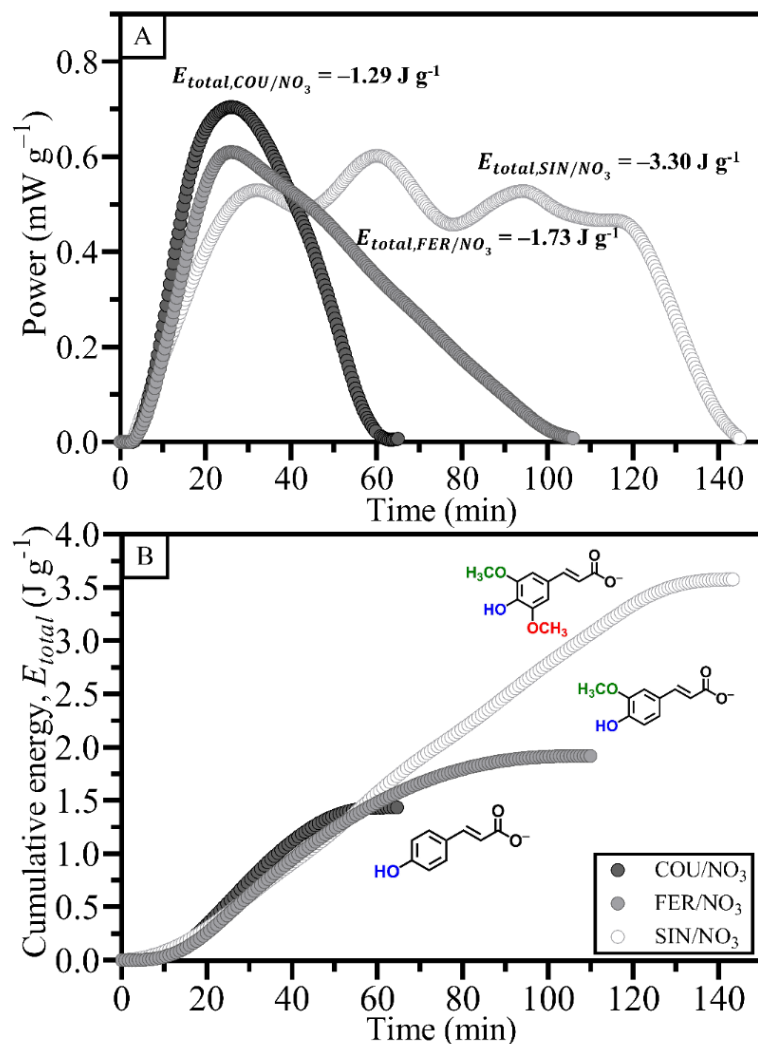


Figure 2.2 Calorimetric thermograms of mass-normalized energy (A) for coumarate (COU/NO₃), ferulate (FER/NO₃), and sinapate (SIN/NO₃) sorption onto nitrate-saturated ferrihydrite. Cumulative energy transfer (E_{total}) during the sorption reaction (B).

Norén and Persson³⁴ found that sorption of monocarboxylates (acetate, benzoate, and cyclohexanecarboxylate) at the goethite–water interface corresponded to the pK_a of the sorbate and occurred strictly via outer-sphere coordination. They proposed two modes of attachment of the carboxylate group to the hydrated oxide surface. The first was facilitated by the solvation of the carboxylate group of the sorbate, whereas the second was stabilized by hydrogen bonds between the oxygen atoms of the carboxylic group and

the surface coordinated water molecules or hydroxyl groups. While the importance of compound acidity could not be ruled out, we found no correlation between the E_{total} and the pK_a (Table 2.1). Moreover, both the number and orientation of water molecules within the carboxyl group as well as the strength of hydrogen bonds are influenced by the structure of the R group and the electronic charge distribution of the compound.³⁵ More plausible, was that the relative size, polarity, and polarizability of the cinnamate compounds significantly influence sorption through thermodynamic contributions of the hydration sphere, giving rise to the measured differences in E_{total} . The (hydroxy)cinnamates used in our study consist of a carboxylic group connected to the phenyl ring by an ethylenic group (Table 2.1). Thus, any changes to E_{total} would be reflective of the additional OH and OCH₃ groups attached to the phenyl ring. CIN which had the fewest substituents, lowest molecular weight, and smallest volume, would encounter the least resistance during diffusion to the surface. The endothermic response would be reflective of a greater loss of hydration waters at the mineral surface and/or the loss of confinement within a water cluster.^{36,37} Furthermore, the hydrophobic effect of the unsubstituted phenyl ring in CIN would have larger endothermic and entropic contributions.^{8,38} In contrast, the shift in electronic distribution from the para-positioned OH group in COU would increase its polarizability compared to CIN (Table 2.1). This higher polarizability in COU would favor its interaction with the surface via dipole-type interactions and would explain the exothermic response in the hydroxycinnamates. Congruently, the increased hydration/hydrated radius and proximal distance between dipoles and the surface would explain variations in bonding strength. That is, as polarizability and hydration radius of the hydroxycinnamates increase, bonding strength/

molar heats of sorption (ΔH_{sorp}) becomes weaker. Altogether, the change in enthalpic sign was indicative of a more thermodynamically favorable reaction for COU, FER, and SIN on the NO_3 -saturated surface than the entropy-driven mechanism of CIN/ NO_3 .

The absolute magnitude of E_{total} was greater with each OH and OCH_3 substitution in proportion to the total amount sorbed (Q_s ; mmol g^{-1} ; Figure 2.3). The average ΔH_{sorp} for all samples obtained from the slope of the regression line was 1.17 kJ mol^{-1} . The ΔH_{sorp} was lower for FER (0.97 kJ mol^{-1}) and SIN (1.21 kJ mol^{-1}) compared to CIN (1.57 kJ mol^{-1}) and COU (1.56 kJ mol^{-1}) and pointed to an OCH_3 -induced increase in moles of sorbate per exchange site. The lower ΔH_{sorp} , and greater sorbed amount with larger molecule volume, are inconsistent with sorption occurring via a single mechanism only at surface sites. Rather, higher sorbed amounts for FER and SIN may be related to their higher polarizability ($\text{CIN} < \text{COU} < \text{FER} < \text{SIN}$; Table 2.1). Molecular polarizability is the response of the electron cloud to weak external fields induced by solvent molecules and charged surfaces. Higher polarizability can increase the strength/likelihood of charged interactions such as H-bonding and π electron-donor interactions between sorbate molecules.³⁹

The shape of thermograms provided insight into the effects of OH and OCH_3 substituents on the sorption dynamics of CIN and was supportive of the involvement of multiple mechanisms that included intermolecular bonding. For example, COU sorption was 15 minutes shorter and peaked 15 minutes earlier than CIN sorption (Table 2.1; Figures 2.1 and 2.2). The steeper initial slope of COU relative to CIN was indicative of the ferrihydrite surface having a higher affinity for COU than CIN that is directly related to the addition of an OH group. This OH-induced increase in affinity may also be

responsible for the steeper initial slope of FER and SIN relative to CIN. In comparison, the length of reaction for FER (100 min) was twice that of COU (55 min). Furthermore, the addition of a second OCH₃ group increased the length of reaction for SIN to 140 min. This lengthening of the reaction with increasing molar volume is consistent with an associative mechanism of sorption whereby access to surface sites is restricted by steric crowding.^{9,40}

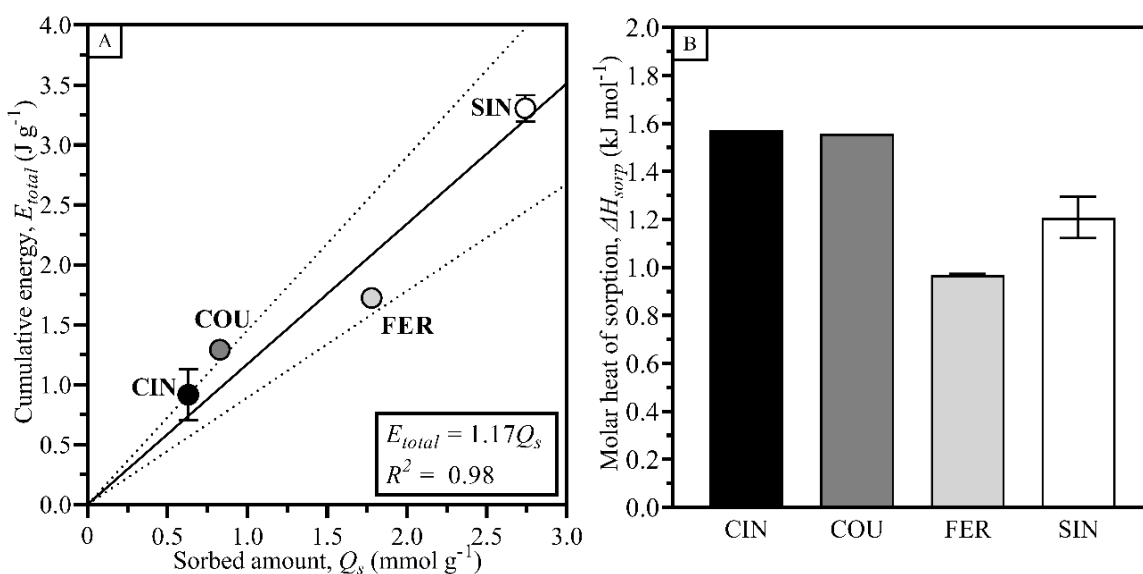


Figure 2.3. Relationship between cumulative energy (E_{total}) and sorbed amount (Q_s) of cinnamate (CIN), coumarate (COU), ferulate (FER), and sinapate (SIN) onto nitrate-saturated ferrihydrite (A). Comparison of molar heat of sorption (ΔH_{sorp}) for CIN, COU, FER and SIN (B). Error bars represent Standard Error of the Mean for all replicates ($n=2$).

Like CIN, the sorption of COU, FER and SIN is expected to occur by outer-sphere mechanisms that consisted of a mixture of electrostatic interactions of carboxylate ions and protonated hydroxyls on the surface and physisorption (e.g., van der Waals). As such, the reactivity would be determined by the resonance, inductive and steric effects of OH and OCH₃ substituents. Although, the Hammett equation (and the resultant Hammett

constant) has been used by previous authors to quantify structure-reactivity relationships of substituted aromatics,^{41,42} we did not calculate Hammett constants for the (hydroxy)cinnamates as the steric effects at the sorption site by the rigid aliphatic chain would confound estimates of OH and OCH₃ substituent parameters.⁴³ This is supported by the fact that the addition of OH had a negligible effect on the molar volume of COU (123 cm³) relative to CIN (125 cm³). In comparison, the molar volume of FER (147 cm³) and SIN (172 cm³) was higher than that of COU by 18% and 38%, respectively. Zhu et al.⁴⁰ found that the total available pore space of thermochemically altered wood char was sterically restricted for single-ring aromatic compounds with three substituents (1,3,5 configuration) or more. They concluded that polar interactions of oxygen-containing functional groups were not the sole driving force for sorption. Instead, water molecules formed interconnected clusters at sorption sites, thereby blocking access of other molecules and reducing surface area of pore space. Additionally, polar compounds had higher sorption to thermochemically altered wood chars than apolar compounds that was attributed to π - π electron-donor acceptor interactions with the graphene rings.⁴⁰ While it is unlikely that π - π electron-donor acceptor interactions occur at the surface, ferrihydrite is rich in surface water⁴⁴ and it is not unreasonable to speculate that similar steric exclusion mechanisms could be responsible for the slower sorption of FER and SIN relative to CIN and COU.

Pore-Filling Irreversibility of Ferulate Sorption

We conducted three exchange cycles on the same ferrihydrite surface using FER and NO₃ to assess the influence of OH and OCH₃ on the irreversibility of sorption (Figure 2.4). Similar to NO₃ replacing CIN, the absolute magnitude of E_{total} was lower for

NO₃/FER (0.89 J g⁻¹) than the preceding FER/ NO₃ cycle (1.73 J g⁻¹). This meant that NO₃ could only exchange with 51% (0.89/1.73) of the sites that were accessible by FER, or in other words, FER restricted access to 49% of sites that were previously available for NO₃ sorption. It has been proposed that the non-removable fraction of organic matter bound to goethite consisted of molecules that form multiple strong attachments, mainly involving carboxyl groups, at the mouths of micropores.⁴⁵ This unexchangeable fraction may be hindered by intraparticle diffusive mass transfer limitations, steric hindrance, or a higher activation energy.^{32,45-47} Additionally, previous calorimetric assessment of oxyanion sorption irreversibility^{23,27,29,30} concluded that the fraction of oxyanions that were non-exchangeable with monovalent ions that predominantly sorb via electrostatic interactions in outer-sphere complexes (e.g., chloride ions) was bound via inner-sphere complexation. For instance, Namayandeh and Kabengi³⁰ postulated that roughly 55% of sulfate on the surface of ferrihydrite was not exchangeable for Cl at pH 5.6. This fraction was kinetically interpreted as a “slow reversible pool” whereas the fraction that was exchangeable with Cl was labeled the “fast reversible pool.” They also noted that the increase in the slow reversible pool (and concurrent decrease in the fast reversible pool) with decreasing pH and increasing Al substitution was attributable to the preponderance of inner sphere vs. outer sphere complexation. Interestingly, for the pristine ferrihydrite surface at pH 5.6, the enthalpy of sulfate sorption was considerably low (−0.30 kJ mol⁻¹) and suggested that although inner-sphere interactions may occur, they were not the dominant mechanism.³⁰ Furthermore, the charge distribution on the sulfate-treated ferrihydrite surface was restored to pre-sulfate conditions after multiple successive NO₃/Cl exchange cycles. These lines of evidence could also be interpreted as the

progressive removal of sulfate entrapped deeper within the pore network of ferrihydrite and suggest that sulfate could be completely desorbed by simple ion exchange.

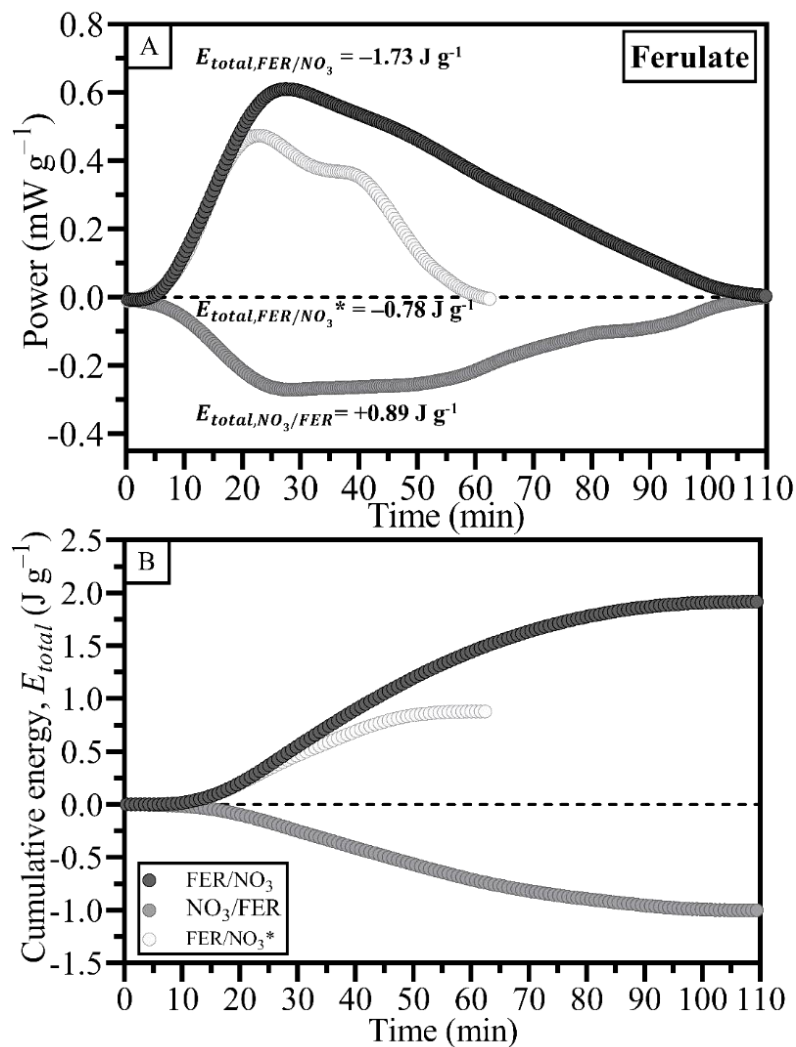


Figure 2.4. Calorimetric thermograms of mass-normalized energy obtained for ferulate replacing nitrate (FER/NO₃), followed by nitrate replacing ferulate (NO₃/FER), and a final cycle of ferulate replacing nitrate (FER/NO₃^{*}) on ferrihydrite. Cumulative energy transfer (E_{total}) during the sorption reaction (B). Cycles were run consecutively on the same ferrihydrite surface. Microbial decay was considered negligible on the timescale of the experiments (~6 hours).

Using this logic, we ascribed the fast pool to readily exchangeable FER removed during the NO₃/FER cycle whereas the slow pool represented FER trapped within the

pore structure by attachment to multiple sorption sites and/or occluded by water molecules. Thus, the FER sorbed to the surface of ferrihydrite comprises a slow and fast pool in roughly equal proportions (Figure 2.4). However, unlike Namayandeh and Kabengi,³⁰ only one exchange cycle (NO₃/FER) was conducted for removal of entrained FER during the FER/NO₃ exchange cycle. Additionally, whether or not FER could be completely removed by simple ion exchange was not addressed using multiple exchange cycles. In comparison to FER, that consisted of equal proportions of a slow and fast reversible (Figure 2.4), the proportions of the slow and fast pool for CIN were 54% and 46% respectively (Figure 2.1). Hence, the addition of OH and OCH₃ substituents caused the distribution of sorbate to shift slightly from the slow to the fast reversible pool. Unlike the NO₃ and FER exchange cycles that both returned to baseline after 100 min, NO₃/CIN took roughly half the time of CIN/NO₃ thereby indicating that NO₃/FER was kinetically different from NO₃/CIN. Interestingly, the second FER/NO₃ cycle (FER/NO₃^{*}) was exothermic with a E_{total} of -0.78 J g^{-1} and was complete after 50 minutes. The brevity of the second FER/NO₃ cycle and the similar E_{total} to that of NO₃/FER points to FER replacing the NO₃ sorbed during the NO₃/FER cycle and is consistent with the greater activation energy required for desorption of organics.⁴⁶ The fact that OH and OCH₃ groups increased the Q_s and E_{total} for sorption but had little effect on the proportion of molecules desorbed suggested that other factors may be controlling the release of lignin monomers at the ferrihydrite–water interface. The kinetic hysteresis observed for FER exchange cycles coupled with the low ΔH_{sorp} are consistent with sorption occurring predominantly via weak electrostatic interactions and shows that a

significant fraction of FER remains trapped within pore structures due to intermolecular interactions as well as multiple points of attachment within the pore space.^{32,45,46}

Conclusions

This study is the first to use FAMC to assess how the number and position of oxygen-containing functional groups attached to cinnamate impact their sorption and retention by iron (oxyhydr)oxides. The collective results of this study, including the size and polarizability dependence of (hydroxy)cinnamate sorption onto ferrihydrite and the low ΔH_{sorp} , were consistent with sorption occurring exclusively via an outer-sphere mechanism that was more complex than simple ion exchange and reflected a multi-step/multi-phase reaction that likely involves a mixture of electrostatic and physisorption interactions. There was no overwhelming evidence pointing to inner-sphere interactions.

The OH and OCH₃ substituents had contrasting effects on the sorption properties of CIN. Cinnamate sorption onto the NO₃-saturated ferrihydrite was endothermic and was 2.7 times less energetic than the simple ion-exchange reaction of Cl replacing NO₃. These results are in stark contrast to the inner-sphere complexation models that are routinely reported for organic matter and metal oxide interactions and emphasizes the importance of fragile, transient bonding interactions on the retention of organic matter at the ferrihydrite–water interface. The addition of an OH substituent shifted the enthalpic response to exothermic but had a minimal effect on the length of reaction and the E_{total} . Microbial degradation was considered negligible on the timescale of the experiments (~6 hours). Both the length of reaction and E_{total} increased with each OCH₃ substituent added. However, the ΔH_{sorp} decreased and suggested that OCH₃ groups facilitated the formation

of multiple points of attachment within micropores and intermolecular attractions such as hydrogen bonding between sorbate molecules.

The reverse reaction involving the removal of (hydroxy)cinnamate from the surface was not completely reversible and showed that roughly half of the CIN and FER sorbed to ferrihydrite was not exchangeable with NO_3 . Hence sorption was classified into two phases, an exchangeable fraction that was removable by NO_3 and ascribed to surface sites and those within unblocked intraparticle pores, and an unexchangeable fraction that was not accessible and/or removable by NO_3 . Comparison of sorption energies for CIN and FER exchange cycles indicated that the addition of substituents makes CIN more accessible to desorption via simple ion exchange and changes to the size and electron distribution of CIN have a more profound effect on sorption versus desorption dynamics. Consequently, the observed environmental preservation of lignin-derived aromatic structures by metal oxides that is largely attributed to strong ligand exchange reactions on the surface, may contain a significant portion that is held via weak electrostatic forces. Although this fraction is kinetically hindered within the ferrihydrite pore structure, it may still be accessible by microbes and is highly susceptible to shifts in environmental conditions such as pH and ionic strength.

This study also demonstrates the high potential of FAMC for the fine-scale temporal investigation of interactions between low molecular weight organic molecules and metal oxides. Future studies will aim to combine temporal measurements from FAMC in tandem with optical spectroscopy to track the evolution of bond formation for reactions of organic molecules that may occur simultaneously and/or concurrently at the ferrihydrite interface. This will improve our understanding of the thermodynamic

stability and reversibility of organic molecule sorption to metal oxides and are essential for a better holistic understanding of the transport and fate of organic molecules in response to abiotic and biotic environmental perturbations.

Acknowledgments

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CHAPTER THREE

Structure-Energy-Photochemical Activity Relationships in Fluorophoric Water-Extracted Organic Matter from (un)charred Plant Materials

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Abstract

Photo-bleaching experiments of water-extracted dissolved organic matter (wDOM) from uncharred or charred grass (SG25 and SG400), softwood (EC25, AJ25, EC400 and AJ400) and hardwood (HM25 and HM400) biomass revealed that photodegradation proceeds along an energy-dependent, component-specific trajectory dictated by the nature of the aliphatic attachments associated with single-ring aromatic domains. Trends in wDOM photo-bleaching for both uncharred [EC25 = AJ25 (94%) > SG25 (46%) ≥ HM25 (41%)] and charred [EC400 = AJ400 (76%) > HM400 (55%) ≥ SG400(44%)] biomass pointed to biomass type/chemistry and its response to processing (here, charring) as key factors controlling photodegradation. Specifically, photo-bleaching was lower in wDOM where aliphatic attachments to the aromatic backbone had shorter alkyl chain lengths, was involved in heterocyclic ring formation or was more oxidized. Photo-bleaching behavior, across the wDOMs, was captured by a three-component, UVA photoenergy (E_{UVA-V})-based model comprising a fast, $wDOM_f$, component requiring mean E_{UVA-V} flux of 42-204 kJ m⁻² for photo-bleaching; a slow, $wDOM_s$, component requiring a 3-24 times higher E_{UVA-V} flux; and a photo-bleaching

resistant, $wDOM_{res}$ component. Combining long-term daily E_{UVA-V} across the State of Texas, the statewide distribution of vegetation types used in this study and our photobleaching model suggested that an increase in vegetation fires is likely to decrease photodegradative contributions to $wDOM$ cycling in the conifer-dominated east, have no effect in the grass-dominated central regions but increase in the hardwood shrub-dominated west.

Introduction

Globally, wildland and prescribed vegetation fires produce pyrogenic organic matter (*pyOM*: the physicochemically diverse organic residue of incomplete biomass burning) to the tune of 136 g OC m^{-2} and a total of $196\text{-}340 \text{ Tg OC y}^{-1}$.¹⁻³ Fire data for the conterminous United States indicate that the average size of fires have tripled since 1985 and is projected to increase through this century.^{4,5} A key overarching question of many current research efforts is; how will increasing *pyOM* inputs affect the biogeochemical cycling of carbon and what role(s) this increasingly important carbon source will play in key ecosystem functions such as climate regulation, contaminant transport and nutrient cycling?

Central to understanding the role and potential effect of *pyOM* on the functioning and biogeochemical cycling of carbon is a systematic unraveling of key structure-reactivity relationships of both the particulate and dissolved fractions of *pyOM*, in response to biotic and abiotic perturbations. Pyrogenic OM is known for 1) its general higher resistance to biotic degradation compared to unpyrolyzed OM and 2) its heterogeneous nature as a continuum of organic structures, ranging from disorganized lignocellulose fragments to more ordered condensed structures.^{6,7} Structural

heterogeneity in both the particulate and dissolved fractions of *pyOM* controls the functioning of *pyOM* in the environment and is a function of the source material chemistry (arising from taxa-specific variations in plant biomolecules) and pyrolysis conditions (e.g., temperature and duration of pyrolysis).⁷⁻¹⁰ For example, *pyOM* produced at increasingly higher pyrolysis temperatures or from hard tissues (e.g., wood) show higher resistance to biotic degradation largely because of a more condensed structure, and specifically higher activation energies for biodegradation.^{6,8,11}

Structure-reactivity relationships for abiotic transformations of *pyOM*, in general and dissolved *pyOM* (*pyDOM*) in particular, are far less understood than for biotic transformation. Current mechanistic understanding of DOM photodegradation suggests that the aromatic DOM fraction initiates transformation of a given compound either directly by absorbing photons; or indirectly via photo-production of reactive oxygen species (e.g., hydroxyl radicals).^{12,13} While there is evidence from field-collected samples linking higher photodegradative losses to more structural condensation in the *pyDOM*,¹⁴⁻¹⁶ other evidence show that photodegradation is only partially controlled by aromatic character and is predominantly driven by the number of oxygen-containing substituents and the production of reactive intermediates and oxygen radical species.^{12,17} Given the comparative bond dissociation energies for C-C (348 kJ mol⁻¹) versus C=C (614 kJ mol⁻¹), the equivalent wavelength of light containing that energy (344 versus 195 nm), and the fact that the UV-light reaching Earth from the sun is ~0% UV-C (200–280 nm) but ~95% UV-A (315–400 nm) it would be reasonable to expect alkyl domains attached to the light absorbing aromatic domain of the *pyDOM* to be more susceptible to non-catalytic solar-induced photodegradation, than condensed domains.¹⁸⁻²² Moreover, prior to sampling, field

samples are often subjected to various degrees of environmental processing as they are aged/weathered and transported through a watershed. Consequently, different mechanisms/drivers dictating photochemical reactivity across a processing/aging/weathering continuum can be reasonably expected. For instance, compared to well processed/aged samples, fresh/unaged *pyDOM* would contain a preponderance of aliphatic/alkyl domains.²³ Additionally, for lignin subunits that differ primarily in alkyl side chain character (e.g., additional methoxy group of sinapyl versus coniferyl alcohol) it can be expected that the quantity and nature of alkyl domains within the *pyDOM* will significantly influence total photodegradative loss and the net energy input required to initiate such losses.

In an effort to contribute to the current fundamental understanding of abiotic transformation of *pyDOM*, we studied relationships between chemical structure, energy input and photochemical transformation in water-extracted DOM and *pyDOM* (herein referred collectively to as *wDOM*) from fresh uncharred and charred plant biomass. Specifically, we aimed to elucidate the influence of aromatic-alkyl character of *wDOM* on its photochemical reactivity and energy needed to initiate transformation via photo-bleaching. We hypothesized that while aromatic/condensed domains may drive energy absorption and direct photodegradation, the low bond dissociation energy associated with C-C will favor higher overall photochemical lability, via photo-bleaching, in *wDOM* with higher alkyl character (i.e., for *wDOMs* with comparable aromatic character, those with a higher preponderance of C-C will be more susceptible to abiotic degradation). To test this hypothesis, we assessed structure-energy input-photochemical lability relationships in *wDOM* with similar aromatic domain (and hence solar energy absorption abilities) but

varying alkyl character. Chemical structure information on wDOM was obtained via ^{13}C NMR spectroscopy. Information on photochemical lability was obtained from systematic steady-state fluorescence spectroscopy studies of the loss of the wDOMs' fluorophoric behavior in response to varying amounts of natural solar energy input (E_{solar}) and specifically, the absorbable portion of solar energy input—herein referred to as $E_{\text{UVA-V}}$.

Materials and Methods

Material Preparation and wDOM Extraction

The plant materials used in this study were selected to provide representative variability in taxonomy, vascular tissue (non-woody, softwood, hardwood) and by extension, chemical structure across wDOM within the study area (Texas, US). To this end, one grass [switchgrass (SG; *Panicum virgatum*)] two softwood conifers [eastern red cedar (EC; *Juniperus virginiana*) and ashe juniper (AJ; *Juniperus ashei*)] and one hardwood, shrub [honey mesquite (HM; *Prosopis glandulosa*)] were chosen. Only the aboveground portion, (namely, the stems and leaves/needles) of the plants were used. For SG, stems and needles were used. For EC and AJ, the needles were used while for HM, woody stem and bark material was used. Prior to pyrolysis and wDOM extraction, plant materials were cut into 1-inch (2.54 cm) pieces and oven dried at 80 °C to constant weight. For pyrolysis, samples were tightly packed into quartz tubes (diameter = 2.54 cm), wrapped in aluminum foil (to produce oxygen-limited conditions), and pyrolyzed in a furnace at a ramp rate of 25–30 °C/min from room temperature to 400 °C. Holding time at 400 °C was 1 hour with the resulting charcoals being allowed to cool back to room temperature before removal from the oven, grounding, sieving (<250 μm) and storage in

air-tight glass jars. It is worth mentioning that pyrolysis conditions were selected to be consistent with charring intensities for natural vegetation fires and to capture the thermal degradation point of cellulose (315–400 °C)—which is known to be associated with alteration in alkyl character, but not significant condensation/aromaticity, of the wDOM.^{1,23-25}

Extraction of wDOM was done using a solid: extractant ratio of 1: 40 with nanopure water as the extractant/solvent (18.2 MΩ; ThermoScientific, Waltham, MA). Two wDOM extraction approaches were initially tested: one with the 1: 40 suspensions shaken on a horizontal shaker for 24 h at room temperature (22.5 °C); and another using microwave-assisted extraction (8 °C/min to 80 °C and held for 1.5 h; EthosUP Microwave Digestion System, Milestone Inc., USA). The microwave-assisted extraction was found to be more effective at extracting wDOM—as shown by visually darker extracts—compared to non-microwave assisted (which showed no visible change in color after 24 hours of shaking). Increasing the shaking time of the room temperature extraction to 50 hours (as described by Bostick et al.¹⁶) increased wDOM recovery compared to 24 h but was still less efficient than microwave-assisted digestion (as compared by color intensity and wDOM recovery from freeze-drying of extracts). In addition, similarities in ¹³C-NMR spectra indicated that the fluorophores in wDOM were similar for both microwave-assisted and 48-h room temperature extracts (Figure B.1). This was consistent with evidence from other studies showing cold or warm water-extracts of organic matter having the same components,²⁶ and the use of warm water to accelerate the extraction of wDOM from charcoals,²⁷ and most plausibly doing so via accelerated hydration to overcome the hydrophobicity barrier and increase aqueous

partitioning of water-soluble components from charcoal into the water phase.²⁸ Because of the higher extraction efficiencies (and shorter extraction times), the microwave-assisted approach was chosen as the preferred method for wDOM extraction in this study. Following extraction, samples were vacuum filtered through glass fiber filters (0.7 μm) and the resulting wDOM extract freeze-dried and stored for further use in solid-state ^{13}C NMR characterization and photochemical lability experiments. Nomenclature for differentiating the wDOMs studied was plant material source (eastern red cedar; EC, switchgrass; SG, honey mesquite; HM and ashe juniper; AJ) and pyrolysis temperature (25 for uncharred sample versus, 400 $^{\circ}\text{C}$). For example, wDOM extracted from eastern cedar at 400 $^{\circ}\text{C}$ was referenced as EC400-derived wDOM while that from its uncharred counterpart was referenced as EC25-derived wDOM.

Solid-state ^{13}C NMR Characterization of the wDOM

For solid-state ^{13}C NMR characterization, freeze-dried wDOM samples were packed into a 4 mm zirconia rotor; and the spectra were acquired at a spinning rate of 12 kHz on a 300 MHz BrukerAvance III spectrometer. Cross polarization-magic angle spinning (CP-MAS) experiment, which makes use of polarization transfer ^1H - ^{13}C to enhance sensitivity, was used to obtain semi-quantitative information on the bonding environment of carbon. In addition, the ^1H - ^{13}C dipole-dephasing experiment of Harbison et al.²⁹ was used for spectral editing to suppress signals from non-quaternary (protonated) carbons. A total dipolar-dephasing delay of 70 μs was selected, based upon the analysis of external standards (glycine and vanillyl alcohol). The time-domain NMR data were processed by zero-filling to 18k, exponential multiplication, and Fourier transformed with 50 Hz line broadening.

The information from ^{13}C NMR includes the relative abundance of protonated and non-protonated functional groups. For their relevance to photon absorption, we were mainly interested in the aromatic ring carbons bonded to H, O, Alkyl C, and Aryl C. The algorithms developed by Solum et al.^{30,31} were used to calculate the average dimension and degree of substitution of aromatic structures in wDOM.

Photo-bleaching/Photochemical Activity Experiments

Experiments to assess the photochemical lability of the wDOMs were conducted on four separate days between February and September at two different locations. Experiments for EC-derived, and SG-derived samples were repeated on two clear-sky days (February 15th and March 1st) in North Texas (Lat: 32.75; Long: -97.33; altitude: 220 m). Experiments for AJ-derived and HM-derived extracts were conducted in Central Texas (Lat: 31.54; Long: -97.15; altitude: 127 m) on July 12th and September 15th, respectively. July 12th was a clear-sky day whereas July 15th was overcast. The solutions used in photo-bleaching experiments were prepared by re-dissolving freeze-dried wDOM in nanopure water and adjusting to a final pH of 5 ± 0.1 (via dropwise addition of 0.1 N HCL) and an absorbance of 0.18 ± 0.07 at 365 nm. For each wDOM, 100 mL of the solution was transferred to each of two custom-built, crimp-style quartz tubes (125 mL capacity; 21 mm internal diameter); that were then rubber-stoppered, crimped and cooled to room temperature. One quartz tube in each set was designated a dark control and the other a light-exposed treatment. Dark controls were completely wrapped in aluminum foil and placed with light-exposed treatments (no aluminum foil) in direct sunlight for a total of 8 hrs. During this period, 2 mL aliquots of wDOM were sampled through the crimp-sealed stopper in duplicate or triplicate at 1 or 2 h intervals, using a syringe with stainless

steel needle. Solar irradiance was simultaneously recorded in 5 min intervals using a solar irradiance meter (Seaward, Tampa, FL) and the data integrated to determine total solar irradiance, E_{solar} , at each sampling time. Associated location- and time-specific full solar spectrum³² was used to correct E_{solar} to yield the cumulative absorbable portion of solar energy (E_{UVA-V}) the sample was exposed to at each sampling time.

Steady-state fluorescence measurements were carried out concurrently with each triplicate sampling. All fluorescence measurements were made in quartz cuvettes (10 mm pathlength) at an excitation wavelength of 405 nm (λ_{exc} 405 nm) and with emission observations wavelengths of 440 nm to 650 nm (Cary Eclipse fluorescence spectrophotometer; Varian Inc., Palo Alto, CA). The fluorescence emission spectrum for water was used to correct the sample spectra for Raman scattering effects. The area under the raman-corrected emission spectra ($A_{em, E=i}$) at a given E_{UVA-V} normalized to the area of the respective dark control sample ($A_{em, E=0}$) were used to quantify photochemical lability of fluorophoric wDOM in the experiments. Normalized area reflected the fluorophoric wDOM remaining ($wDOM_r$) after exposure to i quantity of solar energy (i.e., $wDOM_r = A_{em, E=i} / A_{em, E=0}$; at λ_{em} between 440 and 650 nm). For dark controls, $wDOM_r$ were similar at the start and end of the experiment, reflecting little to no effect of temperature (air temperature = 23–44 °C) on photochemical lability of fluorophoric wDOM in our experiments. The photo-bleaching experiments and the associated fluorescence measurements for EC- and SG-derived extracts had a very similar E_{solar} and spectroscopic response which were not statistically different [paired t (18) = 1.5, p = 0.15]. Of such, the E_{solar} is herein presented as Day 1 and is an average across the two days. Results on

photo-bleaching are also presented as averages. Photo-bleaching experiments for AJ25 and AJ400 were conducted on Day 2; and HM25 and HM400 were conducted on Day 3.

Modeling Photo-bleaching/Photochemical Activity

A three-component energy-based model comprising of a fast photo-bleaching wDOM component ($wDOM_f$), a slow photo-bleaching wDOM component ($wDOM_s$) and a photo-bleaching resistant component ($wDOM_{res}$) adequately described the $wDOM_r$ - E_{UVA-V} photochemical activity relationship. The equation for the model was:

$$wDOM_r = wDOM_{f,0}e^{-\phi_f \cdot E_{UVA-V}} + wDOM_{s,0}e^{-\phi_s \cdot E_{UVA-V}} + wDOM_{res} \quad (1)$$

where, $wDOM_{f,0}$ and $wDOM_{s,0}$ are the initial fraction of wDOM present as fast and slow photo-bleaching wDOM, respectively; ϕ_f and ϕ_s are the respective energy flux constants ($\text{m}^2 \text{MJ}^{-1}$) for $wDOM_f$ and $wDOM_s$; and $wDOM_{res}$ is the fraction of fluorophoric wDOM that was not photo-bleached up to the maximum E_{UVA-V} of 2.21 MJ m^{-2} . The non-linear regression analysis tool of Graphpad Prism (version 8) was used to write and fit the model using least squares minimization. The relationship between the proportion of wDOM components (i.e., $wDOM_f$, $wDOM_s$ and $wDOM_{res}$), respective photoenergetics parameters ($E_{photo,f}$ and $E_{photo,s}$) and NMR-derived chemistry of wDOM (functional group, structural carbon and lattice parameters) were assessed using the non-parametric Spearman correlation analysis in Graphpad Prism.

Results and Discussion

Structural Information on wDOM from Solid-state ^{13}C NMR Spectroscopy

Solid-state ^{13}C NMR spectra for freeze-dried EC-, SG-, AJ-, and HM-derived wDOM and calculated, dimensions of structural domains are presented in Figure B.2. and

Table B.1.^{30,31} The variability of chemical composition/structure of aromatic and aliphatic domains within the wDOM were of particular interest in this study. Aromatic carbon number in clusters ranged from 6 to 9 (average = 7.0 ± 1.0) for wDOM extracted from both uncharred and charred biomass—indicative of a preponderance of single-ringed aromatic to benzopyran domains (Figure 3.1). Benzopyran domains were favored in charcoal-derived wDOM as well as in HM- versus SG-, AJ- or EC-derived uncharred samples. However, there was no evidence for increase in wDOM aromatic domains under the charring conditions used. This was qualitatively consistent with a recent study by Bostick et al.²³ showing relatively constant size/condensation in aromatic domains of wDOM extracted from oak charcoals, produced at temperatures between 250 and 650 °C. The size suggested by Bostick et al.²³ for aromatic domains in their charcoal-derived wDOM were on the order of 3–4 rings. As noted in the Material and Methods, wDOM extracted from our samples using the same method as Bostick et al.²³ and that from microwave-assisted extraction had the same chemistry. Hence the difference in the size of aromatic domains in the two studies could not be plausibly related to extraction approaches. Instead, it is most likely related to differences in material chemistry and/or pyrolysis conditions. For example, Bostick et al.²³ used a longer heat treatment duration (3 hours) and a N₂-atmosphere—which would favor higher charring intensities³³ and plausibly larger size aromatic domains at comparable HTT to our samples (at 1 hour heat treatment duration and O₂-limited atmosphere).

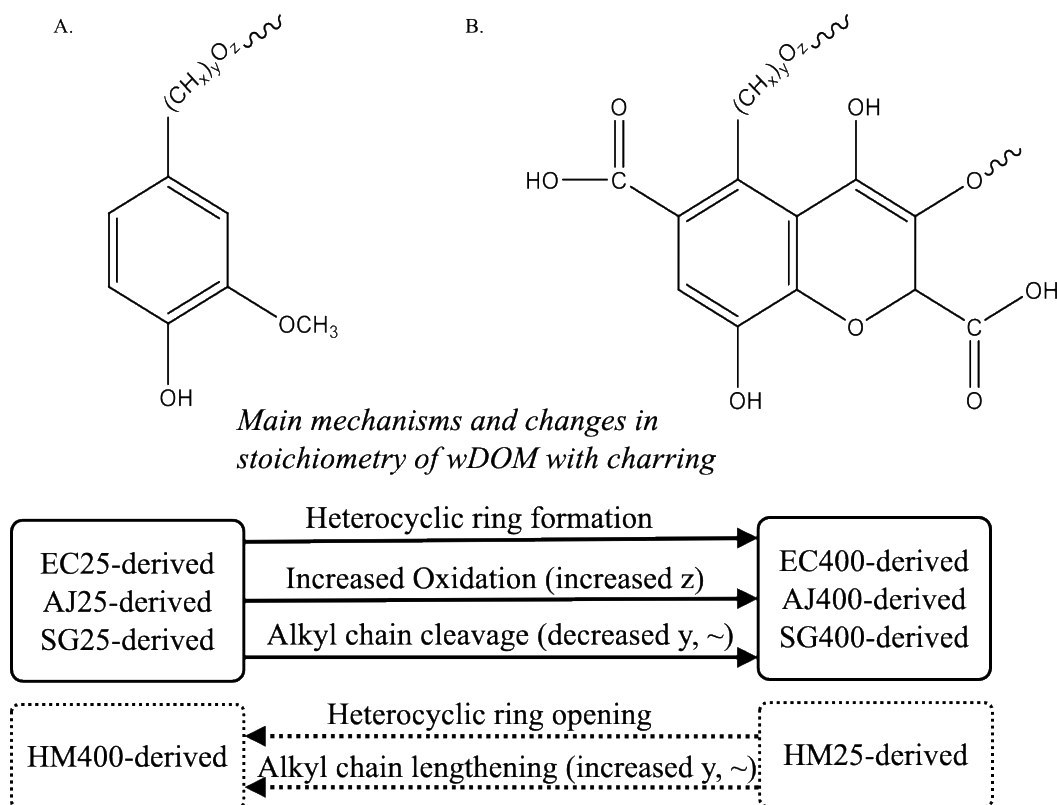


Figure 3.1. Basic chemical structures determined from ^{13}C -NMR based on the average dimensions and elemental stoichiometry of the aromatic domains in wDOM derived from (A) uncharred switch grass (SG25), eastern red cedar (EC25), ashe juniper (AJ25), charred honey mesquite (HM400); and (B) charred switch grass (SG400), eastern red cedar (EC400), ashe juniper (AJ400) and uncharred honey mesquite (HM25). Charring of samples was at 400 °C.

In EC25-, AJ25-, SG25- and HM25-derived wDOM, the aliphatic: aromatic C ratios were 2:1, 2:1, 3:1 and 0.6:1, respectively while in the EC400-, SG400- and HM400-derived wDOMs this ratio was 0.5:1, 0.5:1 and 1.5:1, respectively. The variations pointed to aliphatic (rather than the single-ringed aromatic) domains as 1) being the primary source of molecular diversity across the wDOMs and 2) generally having lower complexity in the charcoal- versus non-charcoal-derived wDOMs. A shortening (by a factor of 2–9) in the length of alkyl groups attached to the aromatic backbone in SG400-, EC400- and AJ400-derived wDOM (compared to their respective

uncharred counterparts) was congruent with charring-induced side chain cleavage being an important driver of variation in the aliphatic domain and the overall chemical heterogeneity in these samples. A 2–3 times higher number of oxygenated attachments in SG400- and EC400-derived wDOM (compared to their SG25- and EC25-derived counterparts) also pointed to contributions from oxidation and heterocyclic ring formation in these samples.^{8,25} While charring-induced oxidation could not be ruled out in the HM-derived wDOM, a higher carbon number in alkyl attachments from HM400-derived wDOM (4 times that of HM25-derived wDOM) was more consistent with charring-induced heterocyclic ring opening (rather than ring formation). The charring-induced, heterocyclic ring-opening mechanism in the HM-derived wDOM versus the ring-forming mechanism in the other samples points to the fate of wDOM in fire-impacted systems to have at least some level of dependence on biomass type (i.e., hardwood structures) for the different wDOMs as well as mechanisms accounting for charring-induced shifts in stoichiometry of key structural components and molecular diversity in the wDOMs.

To our knowledge, the apparent heterocyclic ring opening mechanism reflected in HM400-derived (versus HM25-derived) wDOM (or its impact on reactivity) has never been reported in previous wDOM studies. However, there is precedence from charcoal studies that point to very different behaviors for leguminous/nitrogen-rich feedstocks (like HM) compared to their non-leguminous/nitrogen-deficient counterparts.^{34,35} For instance, Knicker et al.³⁵ found that while charcoals from non-leguminous/nitrogen-deficient feedstocks tended towards increased aromatic condensation, higher alkyl C contents are typical of charcoals from leguminous/nitrogen-rich feedstocks. Knicker et al.

³⁵ further noted that this higher alkyl C content in charcoals from leguminous/nitrogen-rich feedstocks would render them more susceptible to biological or chemical oxidation and subsequently dissolution than would be commonly assumed. Harvey et al. ³⁴ found that while the diversity in R-groups attached to carboxyl decreased in grass charcoals between 350 °C and 650 °C; that in HM charcoals increased over the same HTT range. The difference in the trajectory of R-group diversity with charring was attributed to HTT-promoted condensation of the soft tissue-dominated grass feedstock compared to HTT-promoted disintegration of the more thermally resistant, nitrogen-rich HM feedstock. It is a similar contrasting feedstock-driven response to charring and its expression in the water-soluble fraction of the charcoal that is being reflected in the different chemical trajectories observed in HM-, compared to the SG-, EC- and AJ-derived wDOM. The consequence and impact of these differences on photo-bleaching/photo-oxidation is discussed later.

Solar Energy Input and Photochemical Activity of wDOM

Total E_{solar} measured during the experiment was 18.2 MJ m⁻² on days 1 and 2, 22.2 MJ m⁻² on day 3 and 11.5 MJ m⁻² on day 4 (see Figure B.3 for solar spectrum of Day 1). These values are consistent with expectations for a typical spring and summer day—based on long term average solar irradiance—in the Southwest US.³⁶ Of the measured E_{solar} only energy from the UVA ($\lambda = 320\text{--}400$ nm) and violet-blue ($\lambda = 400\text{--}450$ nm) regions of the solar spectrum were shown to be absorbable by (or induced significant fluorescence in) the wDOM (Figure B.3). For instance, on day 1 and solar exposure times of 1, 4 and 8 h this wDOM-absorbable portion of solar energy, herein referred to as E_{UVA-v} , accounted for 6.4, 9.5 and 10.4 % of the measured E_{solar} , respectively (Figure B.3).

Thereby, indicating that a maximum E_{UVA-V} of between 0.07 and 1.89 MJ m⁻² was available on days 1 and 2 for photochemical transformation of the fluorophoric wDOM. For Days 3 and 4, the maximum E_{UVA-V} was 2.21 and 1.09 MJ m⁻², respectively.

Fluorescence emission maps and/or spectra of initial and solar-exposed samples, at the monitoring excitation wavelength of 405 nm, indicated that fluorophores in charcoal-derived wDOMs were generally blue-shifted (focused around lower visible emission wavelengths) relative to those from uncharred materials (Figure 3.2). Blue shifts are often attributed to aggregation,³⁷ organo-metal complexation,³⁸ decrease in molecular weight³⁹ and loss of conjugated bonds in a chain structure.⁴⁰ A decrease in molecular weight and/or loss of conjugated bonds in wDOM components, arising from pyrolysis-induced cleavage of lignocellulose,³⁵ are plausible explanations for the observed blue shifts in fluorescence behavior of charcoal-derived wDOM. This was consistent with ¹³C NMR derived structural parameters (Table B.1), which indicated much lower numbers of C in alkyl attachments in wDOM from EC400 (C₈) and SG400 (C₄) compared to that from EC25 (C₁₆) and SG25 (C₃₁).

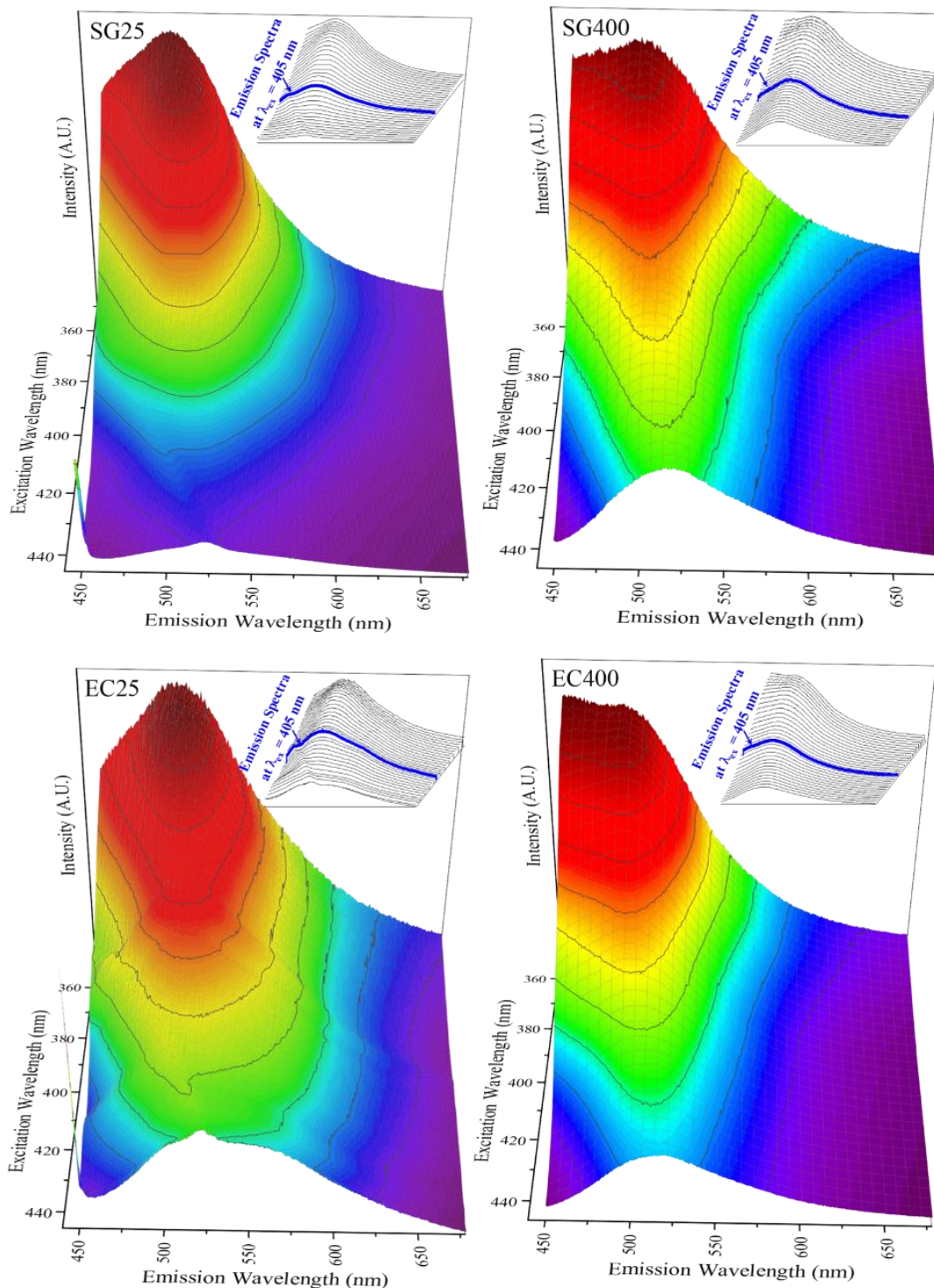


Figure 3.2. Excitation-Emission characteristics of wDOM derived from (A) uncharred switch grass (SG25), (B) switch grass charred at 400 °C (SG400), (C) uncharred eastern red cedar (EC25) and (D) eastern red cedar charred at 400 °C (EC400). Insets show the emission spectra at the excitation wavelength (highlighted in blue) used for tracking photoactivity of fluorophoric wDOM when exposed to natural sunlight

Variations in total fluorescence (i.e., $wDOM_r$), indicated progressive photo-bleaching in $wDOM$ s with increasing E_{UVA-V} —reflecting increased photochemical alteration of $wDOM$ with solar exposure (Figure 3.3). Initial fitting of equation 1 to this data indicated that despite being conducted on different days and in different geographic locations the photo-bleaching behavior of EC- and AJ-derived $wDOM$ s within the same heat treatment group (uncharred/charred) were not different and was sufficiently described by the same model and model parameters across E_{UVA-V} ; i.e., one model could be used to capture E_{UVA-V} -photo-bleaching behavior of EC25- and AJ25-derived $wDOM$ and another model captured photo-bleaching behavior of both EC400- and AJ400-derived $wDOM$. To this end, photo-bleaching behavior and model parameters for EC- and AJ-derived $wDOM$ are presented and discussed collectively as Con25 and Con400, indicative of $wDOM$ derived from uncharred and charred conifer plant materials, respectively. For $wDOM$ derived from uncharred plant materials the order of total loss in fluorescence and consequently degree of photo-bleaching over the course of the experiment was for the maximum E_{UVA-V} (2.21 MJ m^{-2}) recorded over the course of the study was Con25 (94%) > SG25 (46%) $\geq$ HM25 (41%), reflecting a strong control of plant biomass type on the proportion of photochemically-alterable (and by extension, photochemically-resistant) fluorophores. That is, $wDOM$ derived from uncharred conifer materials contained a much higher relative proportion of photo-bleachable (conversely, much lower photo-bleaching-resistant) fluorophores that emit in the visible range, than does $wDOM$ derived from uncharred grass or hardwood. This could be most plausibly linked to the higher oleoresins (e.g., diterpenes) content typical of conifers versus non-conifer plant materials.⁴¹ For $wDOM$ derived from the charcoals, the degree of photo-

bleaching after exposure to E_{UVA-V} of 2.21 MJ m^{-2} followed the order Con400 (76%) > HM400 (55%) > SG400 (44%) further confirming plant biomass control on photo-bleaching but also pointing to an important role for materials processing (here charring) and mechanism on the quantity of photo-bleachable wDOM. For example, here the charring-induced alkyl chain cleavage, heterocyclic ring formation and oxidation indicated by ^{13}C NMR in Con400- and SG400-derived wDOM is shown to result in a decrease in photo-bleachable wDOM compared to their uncharred counterparts. While the charring-induced heterocyclic ring opening and associated increase in alkyl chain length in HM400-derived wDOM increased the total quantity of photo-bleachable wDOM compared to HM25-derived wDOM. It is also worth noting that the higher degree of photo-bleaching observed in the Con400-derived wDOM (compared to their SG- and HM-derived counterparts) suggested that the more thermally-stable oleoresins survived the charring conditions used in the study—congruent with the low charring intensities expected for natural vegetation fires. Also, it is the higher molecular unsaturation (preponderance of C-H moieties) in oleoresins that would make them particularly susceptible to cleavage, volatilization and as our results suggest, photo-bleaching compared to lignocellulose (or the lignin phenols produced during charring).⁴¹⁻⁴³

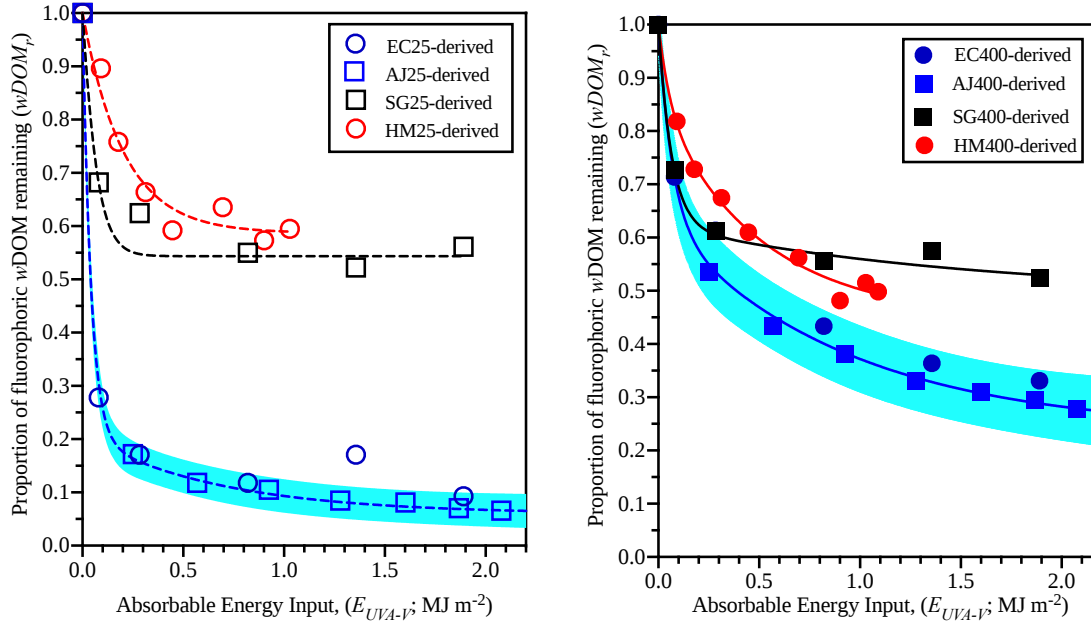


Figure 3.3 Proportion of fluorophoric water-extracted dissolved organic matter remaining ($wDOM_f$; points) and model fits (lines) for switchgrass (SG)- and eastern red cedar (EC), ashe juniper (AJ) and honey mesquite (HM)-derived water-extracted dissolved organic matter exposed to up to 22.2 MJ m^{-2} of solar energy from natural sunlight of which absorbable solar energy input (E_{UVA-V}) was up to 2.2 MJ m^{-2} . Samples labeled with the numbers 25 and 400 indicate uncharred feedstock and feedstock charred at 400°C , respectively.

Despite differences in the proportions of photo-bleaching across $wDOM$ sources, $wDOM_f$ - E_{UVA-V} relationships were all characterized by a sharp initial decline in $wDOM_f$ followed by a more gradual decline with increasing E_{UVA-V} (Figure 3.3). This was consistent with a progressively higher unit quantity of E_{UVA-V} being required to initiate the photochemical alteration of the next persisting fluorophores. Model fits indicated that the fastest photo-bleachable ($wDOM_f$) component accounted for approximately 27–100% of the total photo-bleached $wDOM$ (i.e., $\frac{100 \times wDOM_{f,0}}{wDOM_{f,0} + wDOM_{s,0}}$) in the study; and was generally higher in uncharred compared to charred $wDOM$ from the same plant material (Table 3.1). This component was also completely bleached at $E_{UVA-V} < 1.0 \text{ MJ m}^{-2}$ and mean

energy flux ($E_{mean,f} = 1/\phi_f$) of 42–204 kJ m⁻² (Figure 3.4 and Table 3.1). By comparison, the slow photo-bleaching ($wDOM_s$) component was more persistent throughout the experiment and required 3–110 times higher mean energy flux ($E_{mean,s} = 1/\phi_s = 168$ –1540 kJ m⁻²; Table 3.1) for phototransformation than the $wDOM_f$ component.

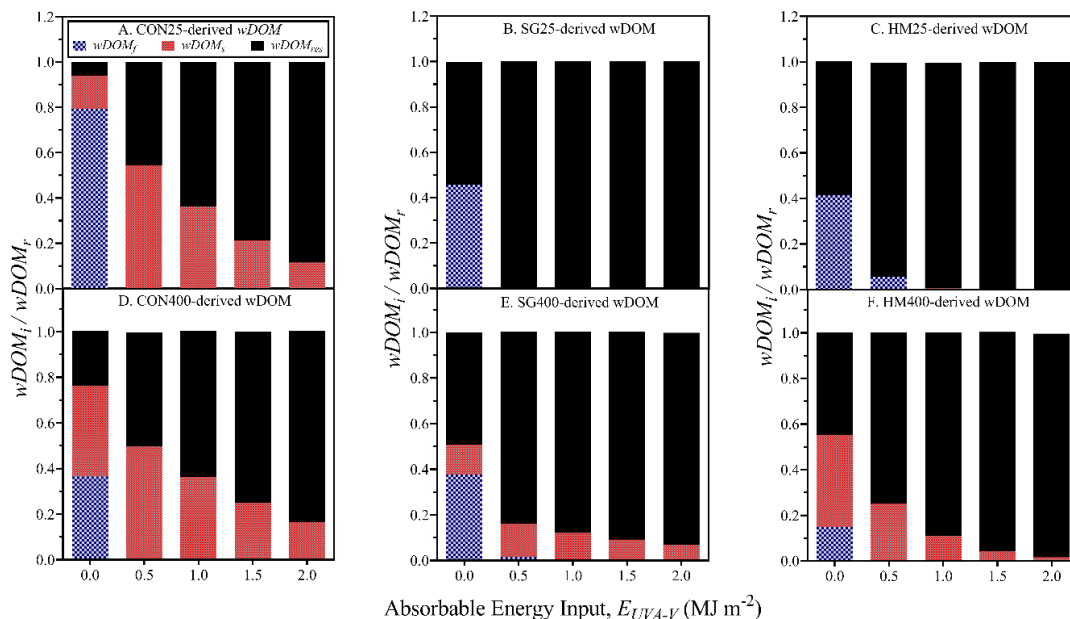


Figure 3.4. Solar energy-induced shifts in proportions of fast ($wDOM_f$), slow ($wDOM_s$) and resistant ($wDOM_{res}$) water-extracted dissolved organic matter from uncharred (SG25, HM25 and Con25) and charred (SG400 HM400 and Con400) switchgrass (SG), honey mesquite (HM) or eastern red cedar (EC) plant materials and then exposed to a maximum of 22.2 MJ m⁻² of solar energy from natural sunlight. Only energy from the UVA and violet-blue region of the solar spectrum were shown to induce fluorophoric response in $wDOM$. This resulted in absorbable solar energy input (E_{UVA-V}) of up to 2.2 MJ m⁻².

In addition to highlighting some new links between chemical structure of $wDOM$ and photolability, the trends in the distribution of $wDOM$ components and the associated photo-bleaching energetics was congruent with some recurring structure-photochemical associations. Firstly, while the $wDOM_{res}$ fluorophores were predominant in the lignocellulose-dominated SG- and HM-derived $wDOM$ across all E_{UVA-V} (accounting for

45–100% of fluorescence emission at E_{UVA-V} up to 2.21 MJ m^{-2}); in Con-derived extracts, $wDOM_{res}$ was only dominant after the systematic processing/removal of the likely more innately photolabile oleoresin/alkyl-dominated $wDOM_f$ component via charring or photo-bleaching. Secondly, while $wDOM$ source is the main driver of total photo-bleachable $wDOM$ content, the quality/overall innate photolability of $wDOM$ (given by the mean and specific energy fluxes in Table 3.1) was controlled in large part by material processing (in our case, charring) and transformation mechanisms. For instance, the mean and specific energy fluxes in Table 3.1 suggest that in Con- and SG-derived $wDOM$, the charring-induced alkyl chain cleavage, heterocyclic ring formation and oxidation increase the energy barrier of photo-bleaching (decrease innate photolability) in the $wDOM_f$ component. Conversely, the charring-induced heterocyclic ring opening and associated increase in alkyl chain length in HM-derived $wDOM$ decrease the energy barrier to photo-bleaching (increased innate photolability) of the same fraction; i.e., loss of alkyl character in fresh $wDOM$ increase the energy barrier to photo-bleaching and decrease the propensity to undergo photo-induced transformation.

Table 3.1. Fitted model and derived energy parameters obtained for 3-component modeling of variations in fluorescence emission for conifer (Con)-, switchgrass, (SG)- and eastern cedar (EC)-derived water-extracted dissolved organic matter exposed to up to 22.2 MJ m⁻² of natural sunlight of which absorbable solar energy input (E_{UVA-V}) was up to 2.21 MJ m⁻². Model form and definitions for model parameters are provided within the table.

	Water-extracted DOM, wDOM					
	Con25- derived	Con400- derived	SG25- derived	SG400- derived	HM25- derived	HM400- derived
Fitted Model Parameters¹						
Fraction of initial wDOM as fast photo-quenched wDOM ($wDOM_{f,0}$)	0.79	0.37	0.46	0.38	0.41	0.15
Fraction of initial wDOM as slow photo-quenched wDOM ($wDOM_{s,0}$)	0.15	0.40	0	0.13	0	0.40
Fraction of initial wDOM as photo-quenching resistant wDOM ($wDOM_{res}$)	0.06	0.24	0.54	0.49	0.57	0.45
Energy Flux constant for $wDOM_f$ (ϕ_f ; m ² MJ ⁻¹)	24.1	14.8	23.9	15.3	4.9	17.2
Energy Flux constant for $wDOM_s$ (ϕ_s ; m ² MJ ⁻¹)	1.48	1.08		0.65		1.97
Derived Energy Parameters						
Mean energy flux for $wDOM_f$ photoquenching ($E_{mean,f}$; kJ m ⁻²)	42	68	42	65	204	58
Mean energy flux for $wDOM_s$ photoquenching ($E_{mean,s}$; kJ m ⁻²)	677	926		1540		168
Specific energy flux for photoquenching of $wDOM_f$ ($\Delta E_{photo,f}$; kJ m ⁻² % ⁻¹)	0.5	1.9	0.9	1.7	5.0	3.9
Specific energy flux for photoquenching of $wDOM_s$ ($\Delta E_{photo,s}$; kJ m ⁻² % ⁻¹)	456	23		118		13

$$^1 wDOM_r = wDOM_{f,0} e^{-\phi_L \cdot E_{UVA-V}} + wDOM_{s,0} e^{-\phi_H \cdot E_{UVA-V}} + wDOM_{res}$$

A third observation from Table 3.1 and Figure 3.4 was that, compared to $wDOM_f$, the $wDOM_s$ fraction was more variable in its occurrence and overall energy requirements for photo-bleaching, across the materials. While $wDOM_f$ was present in all extracts, no $wDOM_s$ was apparent in SG25 and HM25 extracts despite accounting for 15–40% in all other extracts. This pointed to both a native and charring origin for the slow photo-bleaching, $wDOM_s$ component in all other extracts but a purely charring-induced origin for this component in SG and HM extracts—as depicted by its presence in charred but not uncharred extracts (Figure 3.4). A common link across all the materials is that charring was associated with increased oxidation suggesting that the $wDOM_s$ component would be more oxidized than the $wDOM_f$ component. For extracts containing an initial $wDOM_s$ component, the mean energy flux required for photo-bleaching ($E_{photo,s}$) was 3–23 times higher than that for the $wDOM_f$ component indicating that the difference in chemistry between these fractions confers significantly higher “photo-persistence” to $wDOM$ with increasing $wDOM_s$ content. This is reasonably in line with observed decrease in photolability observed in water-soluble extracts of lab chars with increasing pyrolysis temperature.¹⁶

Structure-Energy-Photochemical Activity Relationships of wDOM

Although correlation, does not definitively imply causation, the non-parametric correlation analysis (Spearman r ; r_s) employed in this study pointed to; 1) the distinctive chemical characteristics of the three resolved $wDOM$ components ($wDOM_f$, $wDOM_s$ and $wDOM_{res}$) and 2) a systematic component-specific response of these $wDOM$ components when exposed to natural sunlight. The correlation matrix is presented in Figure 3.5. The strongest positive correlation between $wDOM_f$ content and ^{13}C NMR-derived $wDOM$

chemistry was with protonated aromatic C content, di-*O*-alkyl content and carbon number (C_n) of alkyl attachments consistent with the chemical structure of the fast photo-bleaching $wDOM_f$ component being dominated by protonated aromatic structures with di-*O*-alkyl attachments of varying C_n . The strongest negative correlation of $wDOM_f$ was with total aromatic and olefinic C content, aromatic bridgehead C content and carboxyl functionalities, pointing to this fraction lacking significant aromatic clustering, and the associated di-*O*-alkyl attachments being ethers. For $wDOM_s$ content, the strongest positive correlations were with phenolic/ aromatic ether, tertiary alkyl and oxygen attachments per cluster while the strongest negative correlations were with *O*-alkyl groups and was consistent with the slow photo-bleaching ($wDOM_s$) component comprising primarily of a non-protonated aryl ether (O-Ar) backbone with phenolic and tertiary alkyl side groups. In contrast, the residual ($wDOM_{res}$) component was comprised of more condensed aromatic clusters as indicated by the strongest correlation between $wDOM_{res}$, and the aromatic bridgehead content.

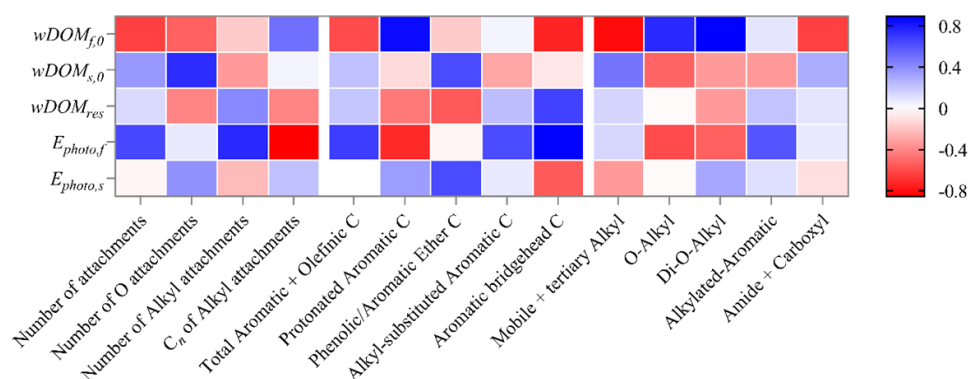


Figure 3.5. Correlation between proportions of fast ($wDOM_f$), slow ($wDOM_s$) and resistant ($wDOM_{res}$) water-extracted dissolved organic matter from uncharred (SG25, HM25 and EC25) and charred (SG400, HM400 and EC400) Switchgrass (SG), honey mesquite (HM), or Eastern red cedar (EC) plant material, their respective mean energy flux for photo-bleaching ($E_{photo,f}$ and $E_{photo,s}$) and ^{13}C NMR-derived chemical structure.

The suggested variations in chemical structure across wDOM fractions point to photo-bleaching being linked to carbon oxidation state and being less favored in the more oxidized fractions. For example, being less favored in the more oxidized wDOM_s versus the alkyl-dominated wDOM_f fraction. This was further supported by strong negative correlations between $E_{photo,f}$ and O-alkyl/di-O-alkyl and ketone/aldehyde content—indicative of increasing higher energy flux required for photo-bleaching as the proportion of -C-O-CH_n in wDOM decreases (Figure 3.4). Strong positive correlation for $E_{photo,f}$ with the aromatic bridgehead carbon, total aromatic C, alkyl substituted aromatic C, number of attachments as well as $E_{photo,s}$ with phenolic/aromatic ether content was further consistent with decreased innate photolability in fresh wDOM being plausibly linked to alkyl chain cleavage /shortening, increased heterocyclic character and oxidation of wDOM components.

Environmental Significance

The experimental results of this study suggest that the photodegradative fate of fresh plant-derived wDOM is inextricably tied to source material chemistry, the response of chemical components to alteration, the processes/mechanisms involved, the energy barrier to transformation and the available energy/energy flux. More specifically, the experimental results were consistent with wDOM photochemical activity occurring within a structure-energy-reactivity paradigm with component-specific photoresponse coming from distinct components. The modeling aspects of the study suggests that through the combination of systematically acquired data with a component-specific, energy-based model the photodegradative trajectory and fate of wDOM and its components can be reasonably predicted. For example, by systematically studying the

photo-bleaching behavior of fresh wDOM across common variations in plant material (grass, softwood and hardwood), material processing congruent with natural systems (uncharred versus low charring intensity charcoals), and varying natural photoenergy input we were able to determine that fresh wDOM under the experimental conditions; 1) was comprised of three chemically distinct components with different innate but quantifiable differences in photo-reactivity; 2) the proportion of each component determines wDOM fate via their control on the required energy barrier to transformation and; 3) the proportion of each component, and hence energy barrier to photodegradation, in wDOM is ultimately dictated by the initial material and mechanisms involved in processing. Here, we found that for wDOM derived from uncharred or via low intensity charring of plant biomass, the chemical diversity and subsequent photoreactivity is not controlled by the level of aromaticity but, in large part, by the nature and properties (e.g., redox status) of side chains attached to the single-ring aromatic/benzopyran domain in each wDOM component.

Given the anticipated increases in the size of vegetation fires, plus the dearth of information on how the associated carbon may influence and/or be influenced by abiotic/biotic processes, the results from this study have significant value in obtaining insights into estimating spatiotemporal variation in photodegradative wDOM cycling. By combining the energy-based model in equation 1 with georeferenced solar irradiation (adjusted to E_{UVA-V}) and vegetation cover type; spatiotemporal trends in photodegradative cycling of wDOM under different scenarios can be obtained. Figure 3.6 shows the results of doing so with long-term daily average direct solar irradiation across the State of Texas,³² for the vegetation type we used in our experiments and assuming a fire versus

non-fire scenario (similar to that used in our experiments). More specific details on how this was executed are provided in Appendix B. The results pointed to a quick photodegradative turnover of wDOM (half-life of hours to a day) across the State with significant vegetation controls on the absolute magnitude of potential photodegradative cycling of the wDOM. Under fire or non-fire scenarios, and despite receiving the lowest natural UV energy input, the potential for photodegradative cycling of wDOM in the conifer-dominated regions in the eastern part of the State is estimated to be about twice that of the grass- or hardwood shrub-dominated central and western regions, respectively. The conifer-dominated areas are also where most of the State's lakes and rivers are located. Consequently, without significant engineering or natural protection against photo-bleaching, it can be reasonably expected that (after a day) the wDOM in the photic zone of these aquatic systems would be highly photo-oxidized (compared to the initial wDOM) and dominated by benzene derivatives. Although the effects of salinity and trace metals on photobleaching of wDOM were not considered in this study, the same could be expected for the allochthonous wDOM entering brackish and marine ecosystems from terrestrial sources.

Comparison of predicted photodegradative cycling of wDOM by shifting from a non-fire to fire-impacted scenario suggested that vegetation fires would; 1) decrease photodegradative cycling of fresh wDOM in conifer-dominated areas of the east by a factor of ~ 1.3 , 2) have little to no impact on photodegradative cycling of this carbon pool in the centrally-located grass-dominated areas but 3) increase the photodegradative cycling potential of wDOM by a factor of ~ 1.3 in the hardwood shrub-dominated west. Further studies expanding to a larger number of plant species, times and geographic

locations—nationally and globally—and the incorporation of field sampling to validate the model at strategic locations would represent the next step in improving our understanding of the link between wDOM chemical structure, photoenergy input and photodegradative outcomes paradigm for wDOM.

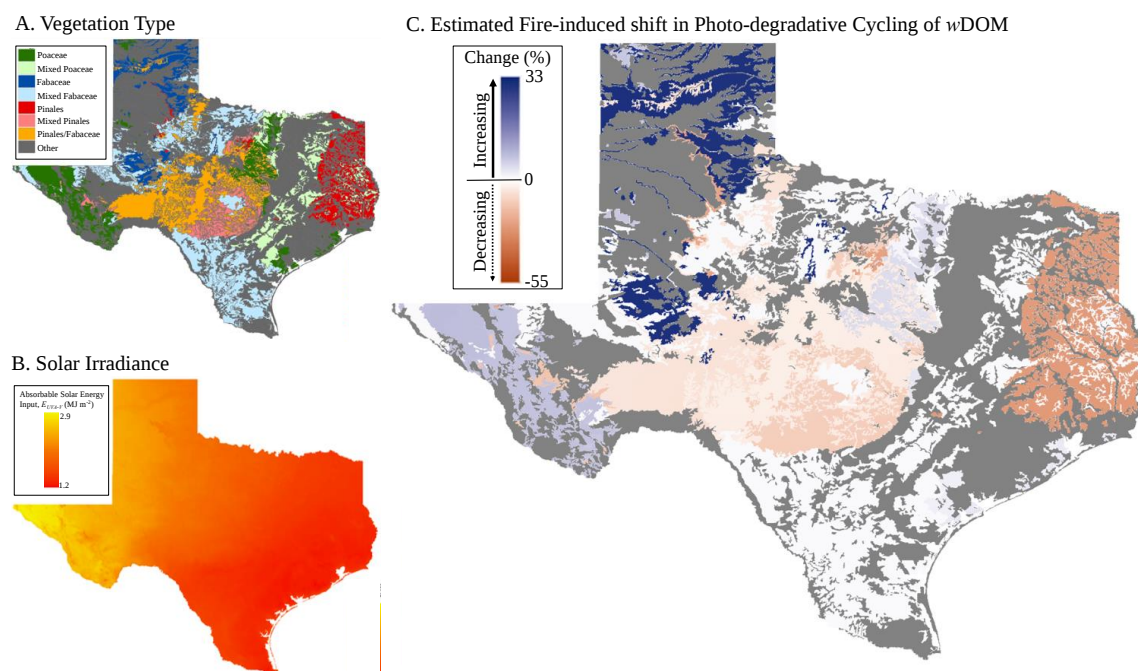


Figure 3.6. Predicted change in photodegradative cycling of vegetation-derived wDOM when shifting from fire-free to a 400 °C vegetation fire scenario across Texas, United States. Values for change in photodegradative cycling were obtained by combining georeferenced (A) vegetation cover and (B) daily absorbable solar irradiance (E_{UVA-V}) with equation 1 and model fit parameters from Table 3.1 for honey mesquite, switchgrass, conifer (eastern red cedar and ashe juniper). Vegetation cover was classified at the family level for honey mesquite (Fabaceae) and switchgrass (Poaceae), and at the order level for eastern red cedar and ashe juniper (Pinales). In areas with mixed vegetation cover, model outputs were weighted based on percent cover, which was between 33 and 50% for a given vegetation type in a mixture.

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CHAPTER FOUR

Component-Specific Photobleaching Controls Mineral Preservation of Pyrogenic Dissolved Organic Matter

This chapter is in preparation for submission to *Environmental Science & Technology*.

Abstract

Variation in the chemical properties of dissolved organic matter (DOM) are expected to exhibit strong controls on its aqueous transformation and association with minerals. However, how these unravel, and the trajectories involved are still being resolved. Here, we report on the interplay between chemical properties of water-extracted DOM (wDOM) across plant-material sources, processing (uncharred vs. charred), solar exposure and its sorptive preservation onto nano-crystalline boehmite. Three fluorophoric wDOM components (*C1*, *C2*, and *C3*) with fluorescence lifetimes (τ) of 0.08-0.37 ns; 0.96-2.93 ns, and 5.6-10.4 ns, respectively were identified. Charring increased τ for a given wDOM component while solar exposure decreased τ . The ^{13}C NMR spectroscopy and correlation analysis pointed to *C1* having the most condensed wDOM structures and lacked evidence for alkyl side chains; *C2* had multiple alkyl attachments; and *C3* was the least oxidized and dominated by alkyl structures. Flow adsorption microcalorimetric studies showed that wDOM sorption to nano-crystalline boehmite was a net exothermic process—irrespective of source, processing or solar exposure. The total energy released during sorption was highest in wDOM with larger numbers and/or shorter alkyl attachments to aromatic domains. Thus, suggesting that sorptive preservation of wDOM by minerals is enhanced where multidentate and inner-sphere complexation are favored.

Introduction

Black carbon produced from vegetation fires accounts for 15% of soil organic carbon globally and is critical to long-term C sequestration because of its chemical recalcitrance in the environment.^{1,2} Contrarily, the dissolved component is chemically reactive and makes up 10% of the 250 Tg of carbon transported by rivers to the oceans annually.³⁻⁵ Photodegradation of dissolved organic matter (DOM) and its sorption to metal oxides have been shown to be the primary controls on DOM processing in sunlit^{6,7} and sediment-rich waters,⁸ respectively. Dissolved organic matter components are deprotonated in acidic to neutral pH environments and have a high affinity for positively charged surfaces such as iron- and aluminum oxyhydroxides. This leads to mineral-associated DOM that is enriched in larger/aromatic compounds with carboxylic and hydroxyl/phenolic substituents and, the enrichment of the surrounding solution with smaller/saturated compounds,^{9,10} Hence, sorption of DOM by metal oxides can alter the mineral surface charge, its sorption efficiency and the chemistry of the dissolved and particulate carbon pool.¹¹ Photodegradation is a critical, indirect control on microbial DOM uptake and has been shown to increase bioavailability of organic carbon by breaking down larger more complex aromatic structures into smaller more labile compounds that can be utilized by aquatic microbiota.¹² In Arctic lakes and rivers, the rate of photodegradation is 3-19 times the rate of dark respiration by bacteria and accounts for up to 95% of carbon processed during the summer months.⁶ Unlike microbial degradation, the aromaticity of dissolved black carbon increases its photoreactivity.¹³ However, the influence of chemical structure on photodegradation of DOM and its sorption to metal oxides remains questionable.

The effect of photoirradiation on the sorption of DOM onto mineral surfaces is important where a combination of these processes might occur such as estuarine systems,¹⁴ or at the confluence of a DOM-rich river with a high-sediment river.⁸ Moreover, despite studies identifying aromatics and condensed aromatics as being more vulnerable to photodegradation,^{15,16} recent evidence has indicated that fluorophoric wDOM fractions with a higher oxidation state and a more condensed aromatic structure are more photo-resistant than alkyl-dominated fractions.¹⁷ Pullin et al.¹⁸ investigated the effect of photoirradiation on the sorption behavior of stream DOM onto goethite and reported a 60% decrease in equilibrium adsorption concentrations after 48 h of exposure that was attributable to the complete loss or photodecarboxylation of DOM. The combined effects of photodegradation and adsorption also resulted in a significant decrease in aromaticity of DOM that was greater than either process alone. However, photodegradation is not a major direct process of organic carbon mineralization but rather produces a suite of smaller more oxidized photoproducts.^{12,16} Furthermore, on shorter time scales (< 24 h) photodegradation may result in the initial production of carboxylic groups as DOM becomes more oxidized.¹⁹

In this study, we examined the photochemical alteration of wDOM from a component-specific perspective using fluorescence lifetime spectroscopy and compared the sorption dynamics onto nano-crystalline boehmite (NCB) before and after sunlight exposure using flow adsorption microcalorimetry. The wDOM extracted from ashe juniper and honey mesquite plant biomass and their respective chars were exposed to natural sunlight to determine photochemically induced changes in fluorescence lifetime and ¹³C NMR spectra. We chose wDOM from plant biomass because of its comparable

aromatic character^{17,20} which was useful for investigating the importance of substituents on photochemical activity of wDOM and its sorption energetics to NCB. We expected that changes in component lifetimes of wDOM from (un)charred plant biomass would reflect exposure to sunlight and that NMR spectra could provide information on the photoreactivity of particular functional groups. These methods provide qualitative descriptions of wDOM chemistry at the molecular level that may be used with calorimetric measurements of wDOM sorption onto NCB to interpret the effects of photochemical reactions on sorption energetics. The sorption of photo-irradiated wDOM onto NCB is expected to be significantly less energetic than non-irradiated samples because photodegradation primarily leads to a loss of properties needed for sorption.

Materials And Methods

Nano-crystalline Boehmite (NCB) and wDOM Preparation

The NCB was prepared at room temperature via the dropwise addition of 1M NaOH to 200 mL of a 0.1M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution, under constant stirring, until the suspension pH reached 7.5. The suspension was then repeatedly centrifuged and washed until the supernatant's EC was $<80\mu\text{S cm}^{-1}$. The residue, which represents the NCB paste, was then dried at 80 °C to constant weight, crushed, sieved (125-250 microns) and stored at room temperature for use in subsequent experiments. Details on plant material preparation, char production and wDOM extraction and composition have been published previously.¹⁷ In brief, chars were produced by pyrolyzing above ground portions of honey mesquite (*Prosopis glandulosa*) and ashe juniper (*Juniperus ashei*) plant biomass under oxygen-limited conditions in a furnace at 400 °C for 1 h. This temperature was within the

range of that for a sub-tropical scrub fire²¹ and was chosen to capture the thermal degradation point of cellulose (315-400 °C) which is characterized by changes to the alkyl character of wDOM without significant alteration to aromaticity.^{20,22} Chars were subsequently ground, sieved to < 250 microns, and stored in airtight glass jars for extraction. For microwave-assisted extraction of wDOM, 25 g of plant material/char was added to 1000 mL of nanopure water then vacuum-filtered through 0.7-micron glass fiber filters. The filtrate was stored in the freezer for use in photobleaching experiments. The wDOM from uncharred ashe juniper and honey mesquite are named AJ25 and HM25, respectively, whereas that from chars are AJ400 and HM400.

Photobleaching Experiments

The solutions for photobleaching experiments were prepared by adjusting the pH of previously frozen extracts to 5 ± 0.1 then adding 100 mL of solution to custom built-quartz tubes capped at the end with rubber stoppers.¹⁷ For each light-exposed treatment, a dark control was produced by wrapping quartz tubes in aluminum foil. Both dark controls, and light-exposed treatments were placed in direct sunlight for 5 h. After exposure to sunlight, subsamples of light-exposed and dark controls were freeze-dried for fluorescence and NMR analysis. The extent of photo mineralization was examined by measuring the change in DOC using a Shimadzu TOC analyzer. The CO₂ was sparged from all samples using nitrogen gas flow for one minute prior to TOC measurement. Photomineralization was calculated as the difference of TOC in light-exposed and dark control samples. The standard deviation of 2 replicate injections was <1%.

Flow Adsorption Microcalorimetry Experiments

The design, operation, and conditions of the flow adsorption microcalorimetry experiments closely followed that of Leonce et al.¹⁷ The sorption experiments were carried out at a pH of 5; and a solution flow rate of 0.50 mL min⁻¹. Prior to experiments, 50 mg of NCB was hydrated in 50 mM NaNO₃, packed into the column and flushed with 50 mM NaNO₃ until a stable baseline was obtained which was indicative of thermal equilibrium and complete NaNO₃ saturation of NCB. The freeze-dried wDOM from light-exposed and dark control samples was dissolved in a 50mM background NaNO₃ solution and adjusted to an absorbance of 0.15 ± 0.05 at 365 nm. Sorption of wDOM onto NO₃-saturated NCB was initiated by switching the pump valve from NaNO₃ solution to the wDOM solution. The evolution or absorption of heat in the sensing unit and the absorbance of the effluent at 365 nm were used to monitor the transfer of sorbate to NCB until thermal equilibrium (signal returned to baseline) was achieved and no further change in effluent concentration was recorded. The cumulative energy (heat of sorption; E_{total}) for the duration of the experiment was calculated as the integral of the thermogram converted to energy units per mass of sorbent (J g⁻¹) using a calibration curve (Figure C.1).

Fluorescence Measurements and Solid-state ¹³C NMR Characterization

The fluorescence excitation emission matrix (EEM) spectra were measured using a Duetta spectrofluorometer (Horiba) and a 1cm x 1cm quartz fluorescence cuvette. The EEMs were collected by scanning excitation wavelengths from 210-525 nm at 5 nm intervals and detecting the fluorescence emission between 250 and 600 nm at 0.5 nm intervals. The data integration time was 1s. Raman scattering effects were corrected using

the fluorescence emission spectrum for water.²³ The average loss in fluorescence intensity because of photobleaching at excitation wavelength (λ_{exc}) 275 nm (f_{photo}) was quantified using the area under the Raman-corrected emission spectra of light-exposed treatments normalized to the area of the respective dark control. The normalized area was quantified for emission wavelength (λ_{em}) values between 295 and 600 nm.

The Fluorescence lifetime was measured on a FluoTime 300 fluorometer (PicoQuant, GmbH) using a 375 nm diode laser for excitation set at a repetition rate of 10MHz. The fluorometer was equipped with an R3809U-50 ultrafast microchannel plate photomultiplier detector (MCP-PMT; Hamamatsu, Inc.) with emission observation made at λ_{em} 480 nm. This region was chosen as it is commonly associated with simpler fluorophores of humic substances from terrestrial sources.²² The FluoTime 300 used a PicoHarp Module (PicoQuant, GmbH) for Time Correlated Single Photon Counting (TCSPC) with a 4ps/bin resolution. Fluorescence lifetimes were measured in the magic angle (54.7°) condition and data analyzed in FluoFit4 (PicoQuant, GmbH) using a multi-exponential fitting model in the form of Equation (1):

$$I(t) = \int_{-\infty}^t IRF(t') \sum_i \alpha_i e^{-(t-t')/\tau_i} \quad (1)$$

Where, $I(t)$ is the intensity of fluorescence, $IRF(t')$ is the Instrumental Response Function at time $t = t'$, and α_i is the amplitude of the i^{th} components' decay at time t and τ_i is the lifetime of the i^{th} element. The Instrument Response Function (IRF) was collected for the 375nm laser excitation with a Ludox sample (scatter) in a 1 cm x 1 cm quartz cuvette. In addition to the component-specific amplitude and lifetime, an intensity-weighted average lifetime (τ_{avg}) was determined for each sample using Equation (2).

$$\tau_{avg} = \sum_i f_i \tau_i \quad \text{where,} \quad f_i = \frac{\alpha_i \tau_i}{\sum_i \alpha_i \tau_i} \quad (2)$$

The NMR analyses closely followed the methods described in Leonce et al.¹⁸ Both light and dark controls were freeze-dried prior to ¹³C NMR analyses. For the current study, we simplified the chemical information into six spectral regions representing carbon compound classes typical of DOM: i) Alkyl C (0-45 ppm) consisted of methyl and methylene groups, ii) N-alkyl + Methoxy C (45-60 ppm), iii) O-alkyl C (60-110 ppm) corresponded to O-alkyl and di-O-alkyl groups, iv) Aryl C (110-145 ppm), v) O-aryl C (145-165 ppm) and vi) Carbonyl C (165-219 ppm) corresponding to amide + carboxyl C and ketone (Table C.1). The algorithms developed by Solum et al.^{24,25} were used to calculate the average dimension and degree of substitution of aromatic structures in wDOM.

Non-parametric correlation analysis (Spearman r ; r_s) between lifetime fluorescence values (τ_{avg} , α_i), respective calorimetric parameters (E_{total}) and NMR-derived chemistry of wDOM was assessed using the nonparametric Spearman correlation analysis in Graphpad Prism. Only strong positive r_s values ($r_s \geq 0.80$) and strong negative r_s values ($r_s \leq -0.80$) were considered in our analysis.

Results and Discussion

Phototransformation of wDOM

The fluorescence spectrum of AJ25 and HM25 before exposure to sunlight displayed a peak maximum at the excitation/emission wavelength pair of 275/325 nm, whereas AJ400 and HM400 had a peak maximum at 275/375 nm (Figure 4.1 and Figure C.2). The narrow peak maximum at 275/325 nm indicated the presence of a tryptophan-like fraction commonly found in fresh DOM,^{26,27} whereas the peak maximum at 275/375

nm was more widely spread within the region associated with terrestrial humic-like fluorophoric DOM.²⁸ The fluorescence intensity of the tryptophan and terrestrial humic-like peak both decreased after exposure to sunlight (Figure 4.1). The average loss in fluorescence intensity at λ_{exc} 275 nm because of photobleaching (f_{photo}) followed the order HM25 (35%) < AJ25 (63%) < AJ400 (69%) < HM400 (73%). Higher losses in AJ25 versus HM25 and the fact that charring of ashe juniper did not significantly affect f_{photo} pointed to plant biomass as a significant driver of the proportion of photobleachable fluorophores in wDOM. Despite the extensive photobleaching of fluorophoric wDOM, the average TOC for all samples was less than 5% indicating that wDOM did not undergo significant photomineralization under the experimental conditions (Table C.1). Hence fluorescence loss was primarily because of photochemical transformation of wDOM molecular structure. This was in good agreement with results from a previous study on photo-oxidation of dissolved black carbon in arctic waters in which the authors reported that 10% of carbon was photomineralized to CO₂ after 17 hours of sunlight exposure, while up to 90% was partially photo-oxidized to compounds that remained in solution.⁷

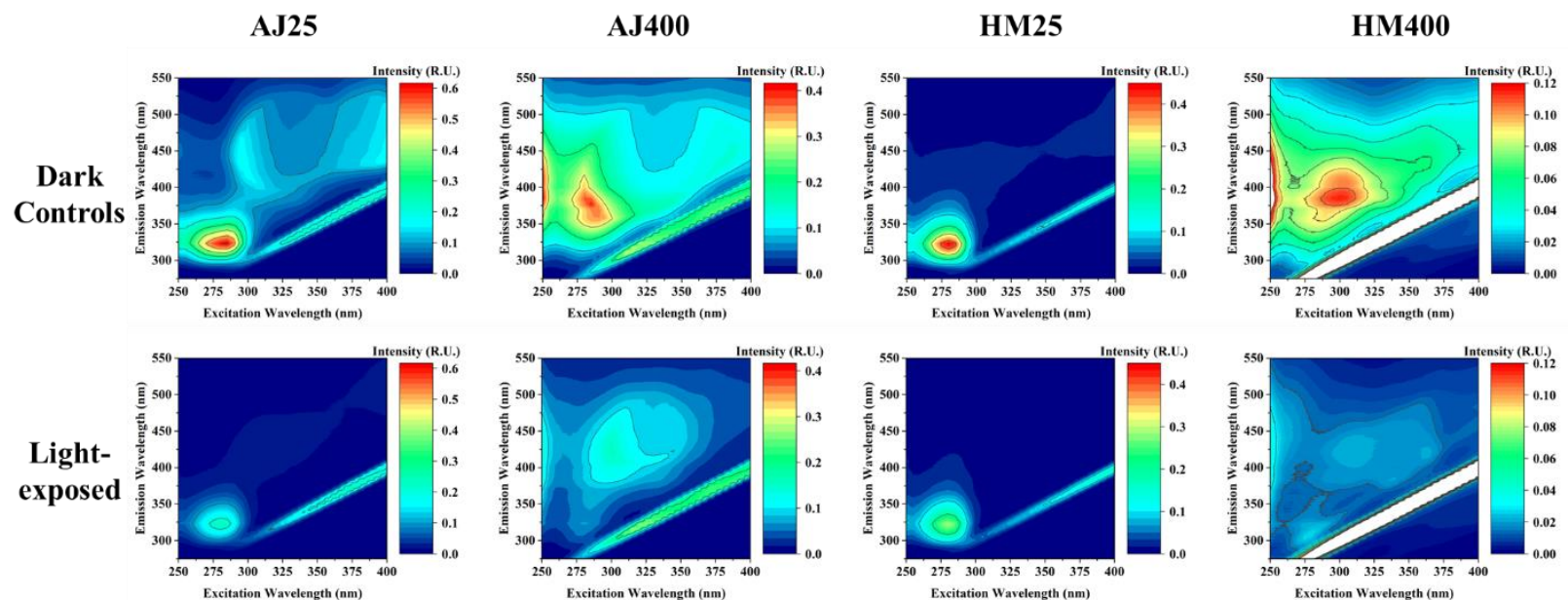


Figure 4.1. Steady-state fluorescence EEM spectra for dark controls and light-exposed wDOM from uncharred ash juniper (AJ25) and honey mesquite (HM25) and corresponding chars (AJ400 and HM400, respectively). Fluorescence intensities are in Raman units (R.U.).

Bulk Response of Fluorophoric wDOM to Photoirradiation

The average fluorescence lifetimes, (τ_{avg}) for the wDOM extracts at the λ_{ex} of 375 nm and λ_{em} 480 nm are shown in Figure 4.2A. Several trends were immediately observable from the values: (1) the τ_{avg} for wDOM from charred biomass was significantly higher than from their uncharred counterparts, (2) the τ_{avg} for AJ-derived wDOM was higher than HM-derived wDOM, (3) the τ_{avg} was lower in photoirradiated treatments than in dark controls, (4) the τ_{avg} of AJ25 was affected to the greatest degree by photoirradiation. The τ_{avg} of AJ25 increased by 13% from 1.87 ns to 2.15 ns after charring of plant biomass. The τ_{avg} for HM400 (2.1 ns) was five times higher than HM25 (0.4 ns) and was indicative of a more extensive alteration of water-extractable fluorophores by charring.

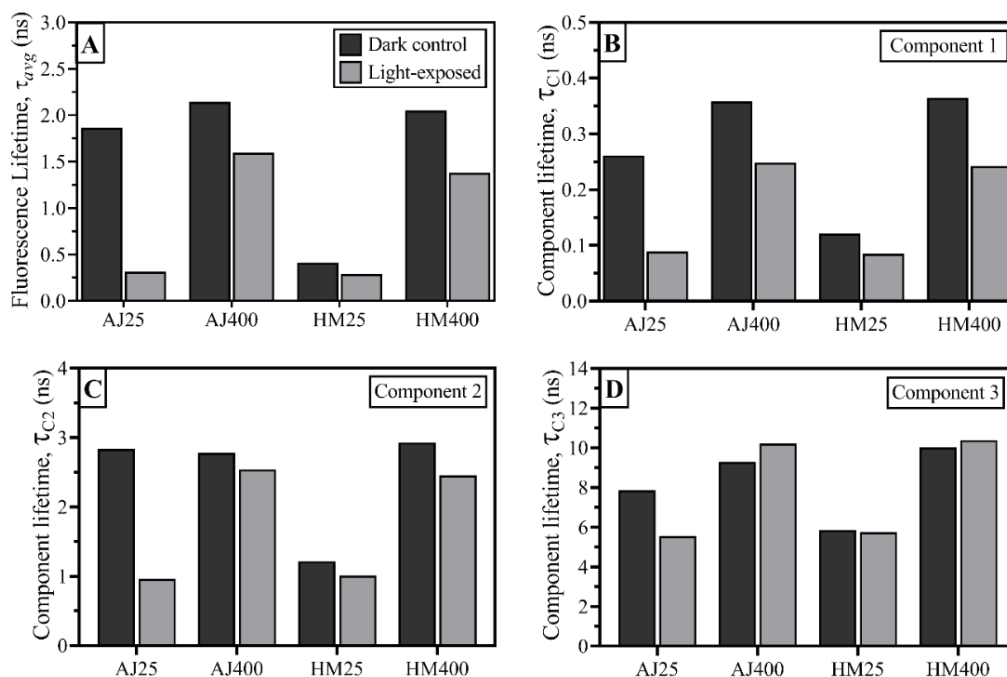


Figure 4.2. Solar energy-induced shifts in average fluorescence lifetimes (A) and component-specific fluorescence lifetime (B,C,D) of dark controls and light-exposed wDOMs from uncharred ashe juniper (AJ25) and honey mesquite (HM25) and corresponding chars (AJ400 and HM400, respectively).

Remarkably, despite HM25 having a 3-fold higher proportion of aryl carbons (45%) than all other samples ($14.4\% \pm 1.1$), the τ_{avg} was 4-5 times lower (Table C.1). This was surprising as the fluorescence properties of CDOM have been primarily attributable to its preponderance of conjugated π -electron systems which facilitate the excitation of electrons to higher energy levels whereas the absence of fluorescence is a consequence of aliphatic and sugar-like compounds that are primarily composed of low energy sigma bonds.²⁹ In DOM, concatenated and condensed aromatic ring systems have a more rigid structure which increases the freedom of π -electrons and contributes to their relatively longer lifetimes than compounds with a single benzene ring.³⁰ However, the ^{13}C NMR-derived functional group chemistry of wDOM extracted from plant biomass and their respective chars consisted of clusters of 6-9 aromatic carbons which was indicative of a preponderance of single-ring aromatic to benzopyran domains.¹⁷ In such a scenario, the freedom of π -electrons would also be dependent on the location of electron donor and withdrawing groups. Ortho- and para-directing groups tend to activate the benzene ring thereby increasing the freedom of π -electrons and increasing the time spent in the excited state. Contrastingly, meta-directing groups tend to withdraw π -electrons from the ring which reduces their freedom by increasing their localization.³¹ It is worth noting, that this interpretation is confounded by the fact that DOM molecules may be polysubstituted. Thus, the combined effect of electron-donating and electron-withdrawing groups on the benzene ring is obscure. Nor could we rule out the possibility of fluorescence mechanisms involving charge transfer interactions (although this phenomenon is still debatable)³²⁻³⁴ between lignin-type donor molecules (e.g., phenols and indoles) and acceptor molecules (e.g., quinones).³⁴ In spite of this, the alkyl:aromatic

C ratios for the wDOM prior to solar exposure were 0.7:1 (HM25), 1.7:1 (HM400), 1.9:1 (AJ25) and 2.5:1 (AJ400). Additionally, the τ_{avg} was positively correlated to alkyl C and alkyl:aryl ratio but was negatively correlated to the aryl C and O-alkyl groups (Figure C.3). These results pointed to alkyl attachments as the primary driver of fluorescence lifetime in wDOM. Over the course of the photodegradation experiment, τ_{avg} for AJ25 decreased by 83% (from 1.86 to 0.31 ns). By comparison, τ_{avg} for all other samples declined by $29.3\% \pm 2.9$. The decrease in τ_{avg} for all treatments after solar exposure was indicative of fluorescence quenching attributable to the photodegradation-induced alteration of fluorophores. The larger response in τ_{avg} for AJ25 compared to HM25, HM400 and AJ400 suggests a higher susceptibility to photobleaching that may be related to its higher oleoresin content.³⁵

Component-specific Response of Fluorophoric wDOM to Photoirradiation

Deconvolution of the multi-exponential fluorescence lifetime decay curve showed three fluorophoric wDOM components. That is, a short, medium, and long lifetime component, herein referred to as *C1*, *C2* and *C3* respectively (Table C.1). The lifetimes of these components (τ_{C1} , τ_{C2} and τ_{C3}) collectively contributed to the τ_{avg} of each wDOM shown in Figure 4.2. The τ_{C1} ranged from 0.08 to 0.36 ns; τ_{C2} was intermediate at 0.96 to 2.93 ns, and τ_{C3} was the longest at 5.6 to 10.4 ns. These findings aligned well with a previous study on riverine DOM composition that identified three components with lifetimes of <1 ns, ~2–3 ns, and ~6–9 ns.³⁶ Single aromatic ring compounds with oxygen, methyl and amino substituents have fluorescence lifetimes from 2 to 4 ns and may be present in fluorophores of component 2.³⁷

Trends in the lifetimes of $\tau C1$, $\tau C2$ and $\tau C3$ for treatments and dark controls were congruent with f_{photo} and τ_{avg} observations identifying biomass source and its chemical processing as key factors controlling the photobleaching of wDOM. With the exception of $\tau C2$ in AJ (which remained unchanged), the lifetimes of components increased upon charring to 400 °C with evidence of increased rigidity and/or an increase in π -domains (Figure 4.2). In contrast, solar exposure decreased the lifetime of all components across treatments except the $\tau C3$ of HM400 and AJ400. It is worthwhile noting that despite being least responsive to charring, $\tau C2$ of AJ25 was responsive to solar exposure highlighting the importance of phototransformation as a key driver in the chemical alteration of this component. The lack of response to solar exposure in $\tau C3$ of HM400 and AJ400 suggested a lower photolability of this component in pyrogenic wDOM.

Figure 4.3 shows the component-specific amplitude for C1 ($\alpha C1$), C2 ($\alpha C2$) and C3 ($\alpha C3$) in wDOM. These values give the relative proportion of excited molecules from each component contributing to the total fluorescence of the wDOM. Prior to solar exposure, contributions of components to the wDOM fluorescence followed the general order $\alpha C1 \gtrsim \alpha C2 > \alpha C3$. In HM25, solar exposure had no effect on contributions of $\alpha C1:\alpha C2:\alpha C3$ indicating that the lower τ_{avg} of treatments relative to dark controls was attributable to actual photo-induced decreases in $\tau C1$, $\tau C2$ and $\tau C3$ (Figure 4.2B,C,D). In AJ25, AJ400 and HM400, solar exposure increased $\alpha C1$ with a concomitant decrease in contribution from $\alpha C2$ and negligible shifts in contributions from $\alpha C3$ (Figure 4.3). This indicated that observed decreases in τ_{avg} of these samples with solar exposure were due to solar-induced changes in lifetimes and transformation of C2 to C1. It can be shown through correlation analysis between $\alpha C1$, $\alpha C2$, $\alpha C3$ and ^{13}C NMR functional groups that

1) *C1* fluorophores were comprised of condensed aromatic structures with limited alkyl attachments, 2) *C2* fluorophores most likely comprised of multiple alkyl attachments attached to an aromatic domain and 3) *C3* fluorophores lack significant aromatic clustering or oxygen containing functional groups. These findings are congruent with a recent study which showed that for environmental DOM and humic substances the shortest lifetime of the ultrafast component (on a picosecond time scale) was from high-molecular-weight, and aromatic rich sources whereas the low-molecular weight, aliphatic and oxygen rich fractions had longer lifetimes.³⁸

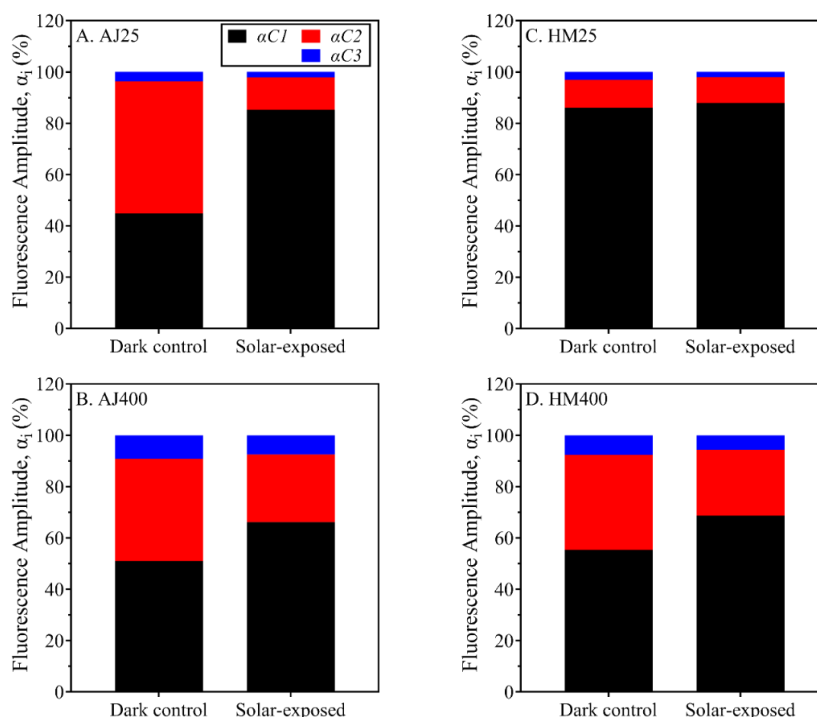


Figure 4.3. Solar energy-induced shifts in component-specific fluorescence amplitude (α_i) for low (*C1*), medium (*C2*) and long (*C3*) lifetime components in wDOM from uncharred ashe juniper (AJ25) and honey mesquite (HM25) and corresponding chars (AJ400 and HM400, respectively).

Consistent with our observations, Clark et al.³⁶ also found that artificial irradiation of riverine samples with UV-light had no effect on the long lifetime component but

decreased the lifetime of the short- and medium-lifetime components by a factor of ~ 4 (Table C.1). A mechanistic or molecular explanation was not given. Based on our current findings, we can now reasonably propose that the long lifetime *C3* fluorophores which comprises up to 10% of fluorophoric wDOM are highly aliphatic and the least photolabile of the three fluorophoric components. By comparison, *C2* fluorophores which makes up to 50% of wDOM fluorophores with its multiple alkyl chains attached to an aromatic domain is the most photolabile. Photo-induced transformation of *C2* fluorophores result in the cleavage of alkyl attachments to yield attachment-deficient, aromatic domains typical of *C1* fluorophores. The net effect is a proportional increase in fluorophoric contribution from the short lifetime *C1* fluorophores, and hence lower fluorescence lifetime of the wDOM, on the timescale of our solar exposure experiments. Also, that steady-state fluorescent measurements of wDOM for photolability assessments may be selectively focused on the less abundant, less photolabile, longer lifetime fluorophores while underestimating the importance of the more abundant, short lifetime fluorophores.

Calorimetric Insights into the Sorptive Preservation of Dark Control and Solar-Exposed wDOM by NCB

Thermograms from flow adsorption microcalorimetry experiments of dark wDOM controls sorbing to the NO₃-saturated NCB point to more complex sorption reactions than the simple ion exchange reactions observed with Cl⁻ on the same material (Figure 4.4 and Figure C.4). While Cl⁻ interacting with the NO₃-saturated oxide surface followed the classic expectation of being endothermic, unimodal and returning to baseline after approximately 15 minutes,^{39,40} interactions for wDOM were exothermic, multi-modal and returned to baseline after 30-70 minutes (Figure 4.4). Such multi-modal

and slower sorption, compared to that of Cl/NO₃, have also been observed for cinnamate and its hydroxylated derivatives (coumarate, ferulate and sinapate) sorbing onto ferrihydrite.⁴¹ The total amount of energy (E_{total}) involved in the sorption of dark wDOM controls to NCB ($E_{total} = 0.52$ to 3.06 J g^{-1}) were also comparable to that observed for cinnamates on ferrihydrite ($E_{total} = 1.12$ to 3.30 J g^{-1}) and interestingly, also encompassed that for Cl/NO₃ exchange ($E_{total} = 1.66 \text{ J g}^{-1} \pm 0.1$). Thereby, indicating the involvement of electrostatic interactions but also contributions from physisorption and other intermolecular interactions that are less or more energetic than Cl/NO₃.

Here we were not able to calculate molar heats of sorption for the different wDOMs on NCB, as was possible with the cinnamates on ferrihydrite, but ¹³C NMR-derived chemical structure provided some insight into the bonding mechanism involved. For instance, trends in the E_{total} for dark wDOM controls (Figure 4.4) followed the order HM25 (-3.06 J g^{-1}) > AJ400 (-1.73 J g^{-1}) > HM400 (-0.65 J g^{-1}) > AJ25 (-0.52 J g^{-1}) and was congruent with reported decrease in E_{total} associated with decreasing number of oxygenated substituents on the cinnamate backbone. Spearman Correlation analysis showed that E_{total} values for the different wDOM were positively correlated with the number of alkyl attachments but negatively correlated to the carbon number of alkyl attachments (Figure C.3). That is, there was more net energy release when sorption involved wDOM with higher numbers of, and/or shorter (lower C_n) alkyl attachments. Plausibly, more attachments would facilitate multidentate associations between wDOM and the mineral surface leading to higher net energy release compared to monodentate associations.⁴² Shorter attachments in wDOM would also favor shorter range, more inner-sphere surface associations known to release more energy.⁴³ It is worthwhile noting that

multidentate and/or more inner-sphere associations are generally stronger than their monodentate or outer-sphere counterparts and hence would enhance mineral preservation since higher energy investments would be needed to destroy/reverse the associations.⁴⁴ To this end, the observed trend in E_{total} for wDOM dark controls interacting with the NCB could plausibly reflect the potential for sorptive preservation of the wDOM. That is, the potential for sorptive preservation of wDOM by the oxide mineral followed the order HM25 > AJ400 > HM400 > AJ25.

Considerations of the involvement of a unique mix of mechanisms and associations arising from variations in the component-specific composition of wDOM is also worthwhile. For instance, the higher values of E_{total} observed for dark wDOM controls from HM25 and AJ400 could also be linked to the benzopyran domains - identified in these samples via ^{13}C NMR; as opposed to the benzene-type domains identified in HM400 and AJ25.¹⁷ Furthermore, the length of the wDOM sorption for HM25 and AJ400 which was at least twice as long as HM400 and AJ25 pointed to the involvement a broader diversity of reactions and/or steric restrictions in wDOM with the larger, more highly branched benzopyran domain (Figure 4.4 and Table C.1). A broader diversity of sorption reactions in dark wDOM controls from HM25 and AJ400 would also explain the higher complexity in sorption thermograms for these samples (Figure 4.4A, B). In addition to the electrostatic interactions and the physisorption mentioned prior, there is the potential for cation- π bonding involving the positively charged NCB (at pH 5) and delocalized pi-electron centers of oxygenated or aryl domains in the wDOM. Thereby, giving the heterocyclic benzopyran in dark wDOM controls from HM25 and AJ400 multiple additional modes of interaction with the mineral surface. The

involvement of cation- π bonding during sorption is also known to increase heats of sorption while being slower than pure electrostatic interactions.⁴⁵ Hence, in conjunction with physisorption and electrostatic interactions, a multimodal cation- π bonding mechanism could plausibly explain the more exothermic, more complex but slower sorption reactions of dark wDOM controls from HM25 and AJ400 compared to those HM400 and AJ25. With the exception of wDOM from HM400, prior exposure to sunlight, resulted in a reduction in the complexity and/or the E_{total} of wDOM sorption onto NCB (Figure 4.4). In the case of wDOM from AJ25, HM25 and AJ400 the decrease in E_{total} between dark control and solar exposed samples was from 0.52 J g⁻¹ to 0.19 J g⁻¹, 3.06 J g⁻¹ to 1.12 J g⁻¹ and 1.73 J g⁻¹ to 1.26 J g⁻¹ respectively. While it remains inconclusive in the case of HM400, the changes in sorption behavior of the dark versus solar-exposed wDOM from the other sources paralleled very well the solar-induced transformation in the samples. That is, the decrease in E_{total} and/or complexity in reactions observed in solar-exposed wDOM paralleled the photo-induced transformation of the alkyl attachment rich C2 fluorophores to yield attachment-deficient, C1 fluorophores. With such transformations it can be expected that the potential for the multidentate, inner-sphere and broader diversity for sorption mechanism would be significantly reduced in solar-exposed samples. It is therefore plausible to expect that solar-exposed wDOM will be less prone to being sorbed, sorbed strongly and hence preserved via sorptive preservation on metal oxide colloids.

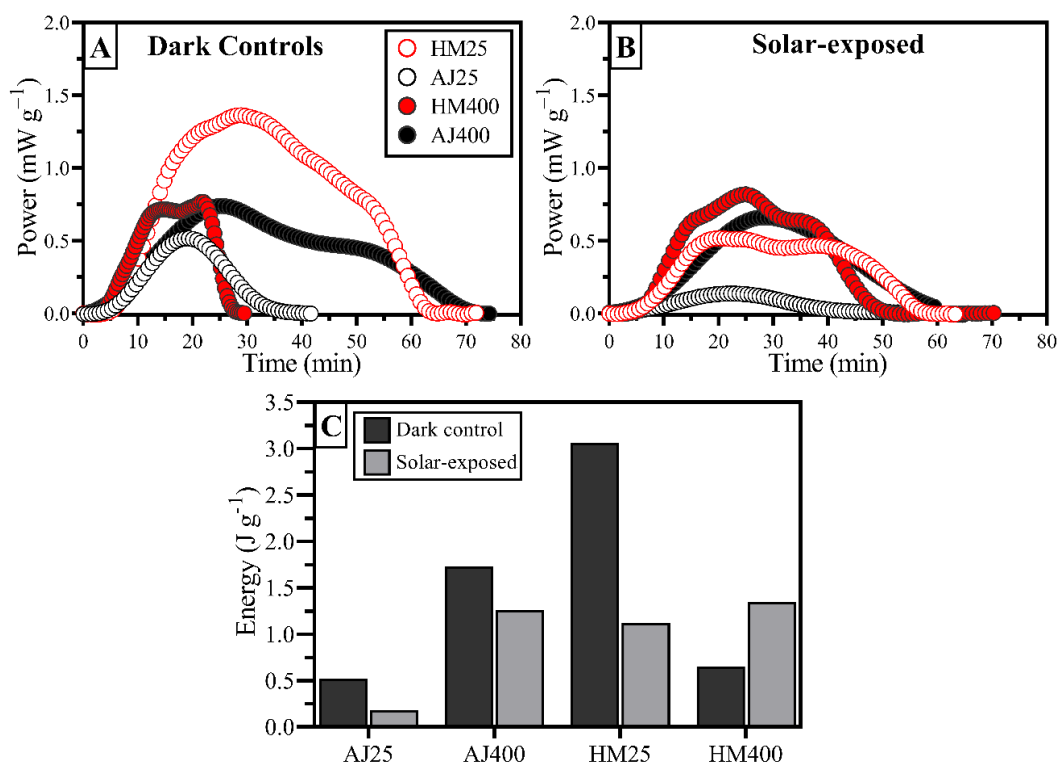


Figure 4.4 Mass-normalized energy (E_{total}) for sorption of dark control and light-exposed treatments of wDOM from uncharred ashe juniper and honey mesquite (AJ25 and HM25) and their charred counterparts (AJ400 and HM400).

Conclusions

The fluorescence lifetimes reported here for wDOM from (un)charred biomass correlate well with those previously measured for CDOM in an estuarine system³⁶ and were also consistent with that of hypothesized structural features of humic and fulvic substances isolated from environmental samples.⁴⁶ These findings suggest that fluorophoric wDOM from plant biomass share a common fluorophore with CDOM in soil and aquatic systems. Three structurally different fluorophoric components were identified. The most prevalent and photolabile component consisted of aromatic domains with multiple alkyl attachments whereas the least photolabile component was highly

aliphatic. The E_{total} measurements for sorption of wDOM from (un)charred biomass onto NCB were consistent with a multimodal sorption mechanism that included electrostatic, physisorption and cation pi-bonding interactions. The photo-induced cleavage of alkyl attachments and concomitant increase in attachment-deficient aromatic domains suggest that once terrestrial DOM is mobilized into aquatic environments, the oxidation state of carbon attachments influences its reactivity on short timescales, and the aromatic moieties may become more important on longer timescales.

Acknowledgments

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CHAPTER FIVE

Conclusions

Calorimetric measurements and molecular level chemistry were used to better understand the structure-reactivity mechanisms that govern sorption and photodegradation of organic carbon in aqueous environments. The primary objectives were to: i) elucidate the electro-steric effects of oxygen-containing side chains on sorption of lignin monomers, and ii) evaluate the influence of aromatic-alkyl character on the photochemical and sorption characteristics of wDOM.

The molar heat of sorption of lignin monomers (cinnamate, coumarate, ferulate and sinapate) was 1.17 kJ mol^{-1} and was consistent with an outer-sphere mechanism that comprised both electrostatic and physisorption interactions. Sorption was enhanced by multiple points of attachments between molecules and within the mineral pore structure. These results have profound implications for carbon cycling dynamics and highlight the susceptibility of this weakly adsorbed fraction of organic matter in response to changes in redox chemistry and microbial populations. Thermodynamic parameters derived from this study could also be used in models of the binding process to enhance the limited current knowledge on the fate and preservation of organic carbon in aquatic systems.

Photodegradation of organic matter extracts proceeded along an energy-dependent trajectory dictated by the nature of the attachments associated with single-ring aromatic domains. Specifically, photo-bleaching was lower in extracts where aliphatic attachments to the aromatic backbone had shorter alkyl chain lengths, was involved in heterocyclic

ring formation or was more oxidized. These findings challenge the previous view of photodegradation of DOM being dictated by the aromatic component. The photobleaching behavior was captured by a three-component, energy-based model. The photobleachable components required a UVA energy flux of 42-204 kJ m⁻² and 168-1540 kJ m⁻², respectively, whereas the third component was resistant to photobleaching under the experimental conditions. Modeled results for the photodegradative fate of DOM in Texas suggested that an increase in vegetation fires is likely to decrease photodegradative contributions to DOM cycling in the conifer-dominated east, have no effect in the grass-dominated central regions but increase contributions in the hardwood shrub-dominated west.

Three distinct fluorophoric components with varying degrees of photolability were identified in wDOM from plant biomass and their respective chars. The most photolabile component consisted of multiple alkyl attachments attached to an aromatic domain whereas the least photolabile component lacked significant aromatic clustering or oxygen-containing functional groups. Photolysis of the most photolabile component contributed to the proportion of condensed aromatics that make up the third remaining component. The photobleaching of DOM and the total energy of sorption to NCB was correlated to the preponderance of alkyl attachments thereby indicating that the oxidation state of carbon attachments influences its reactivity on short timescales, whereas the aromatic moieties may become more important on longer timescales.

APPENDICES

APPENDIX A

Supplemental for Leonce et. al., 2022

Section 1: Ferrihydrite Characterization

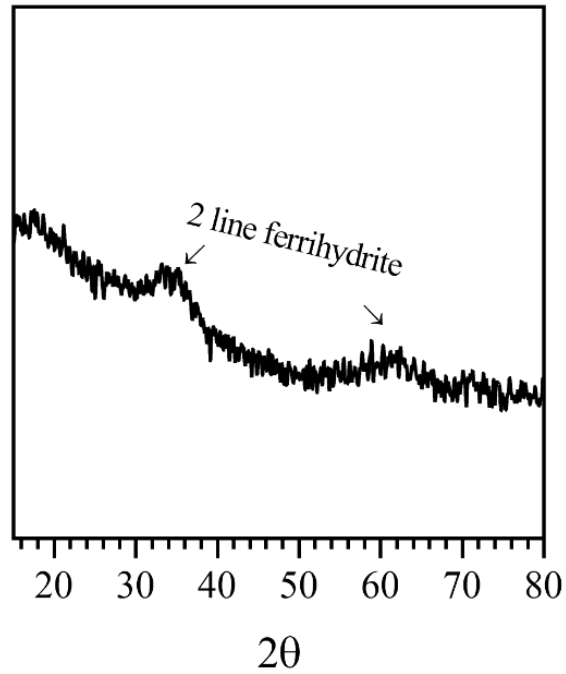


Figure A.1. Two peaks centered at 34° and 61° characteristic of 2-line ferrihydrite.

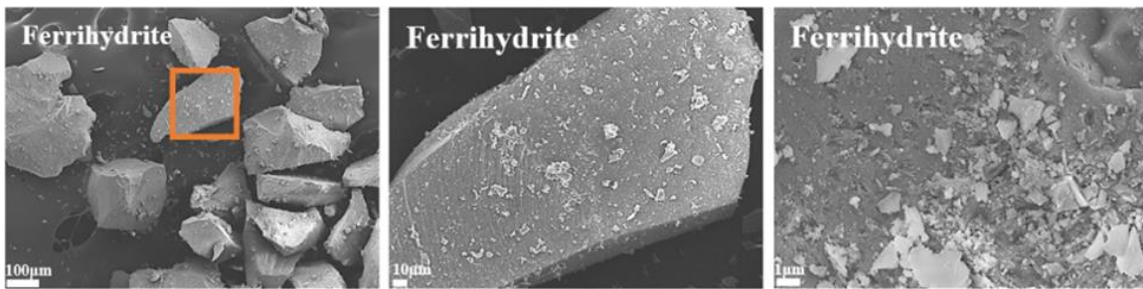


Figure A.2: Scanning electron microscope images of ferrihydrite grains. SEM images at different magnifications (scale) reflect a wide range (10s to 250 μm) of particle sizes.

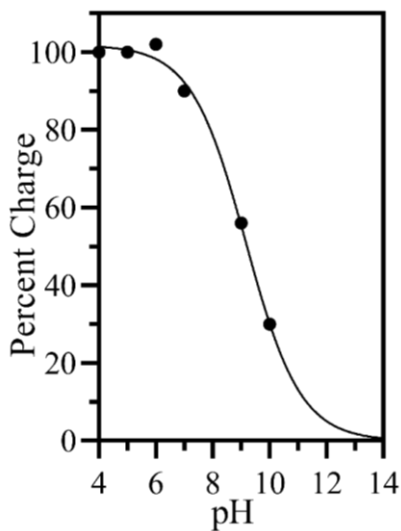


Figure A.3. Charge characteristics of ferrihydrite surface, modelled using simple ion exchange cycles and a modified Henderson-Hasselbalch model.¹

Section 2: Flow Adsorption Microcalorimeter

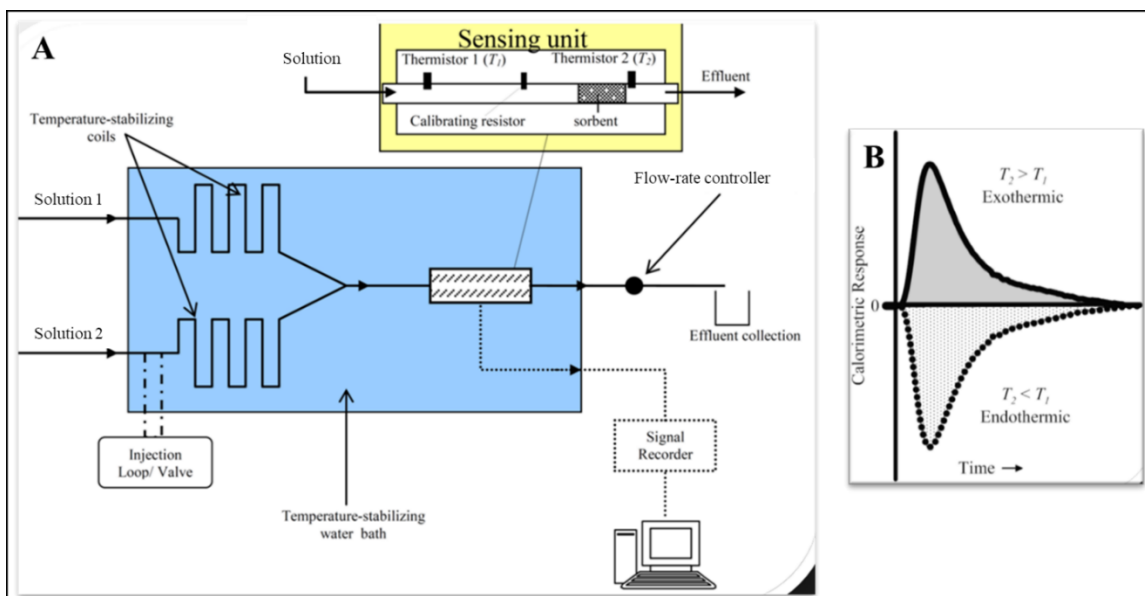


Figure A.4. Schematic diagram of flow-adsorption microcalorimetry experiments.

The reacting solutions were stored within glass containers (~150 mL volume) inside a stabilizing water bath. The solutions were pumped through temperature-stabilizing coils to the microcalorimeter sensing unit. The sensing unit is located within

an air-tight plastic container, immersed in 10 inches of water, inside the stabilizing water bath. This configuration keeps the sensing unit thermally isolated from ambient temperature changes during operation and reduces baseline drift. The sensing unit consists of two negative temperature coefficient thermistors (herein referred to as Thermistor 1 and Thermistor 2) on either side of a glass microcolumn and a calibrating resistor located upstream from the microcolumn. The temperature of the solution is captured by Thermistor 1 as it enters the sensing unit. After the solution interacts with the sorbent in the microcolumn, the temperature of the effluent is captured by Thermistor 2. Both thermistors are capable of measuring temperatures as low as 10^{-5} °C. The difference in temperature between Thermistor 1 and 2 is recorded every 5 seconds as a voltage difference. The lack of a voltage difference is interpreted as baseline conditions. The voltage difference recorded by the signal recorder is processed by a computer and the heat of reaction is presented as a plot of voltage difference (ordinate) versus time (abscissa). The calibrating resistor is used to calibrate the plot to known energy inputs (Figure A.4). Heat signals are reflective of the interactions between sorbate and the ferrihydrite surface. A positive heat signal represents an exotherm, whereas a negative heat signal represents an endotherm. A flat line before and after an exotherm or endotherm represents baseline conditions before and after a reaction, respectively.

The amount of (hydroxy)cinnamate sorbed to the surface was calculated using regression analysis of absorbance measurements of diluted stock solutions that was normalized to the mass of ferrihydrite (Q_s ; mmol g⁻¹). The area of each thermogram was obtained by integrating the calorimetric response in volts over time (V min) and multiplying each thermogram by the average flow rate (mL min⁻¹) to convert into an

averaged area-flow rate (i.e., V mL). The E_{total} is the cumulative energy for the duration of the experiment calculated using the calibration curve in Figure A.5 and normalized to the mass of ferrihydrite. The ΔH_{sorp} was in kJ mol^{-1} and calculated according to the equation:

$$\Delta H_{sorp} = E_{total}/Q_s$$

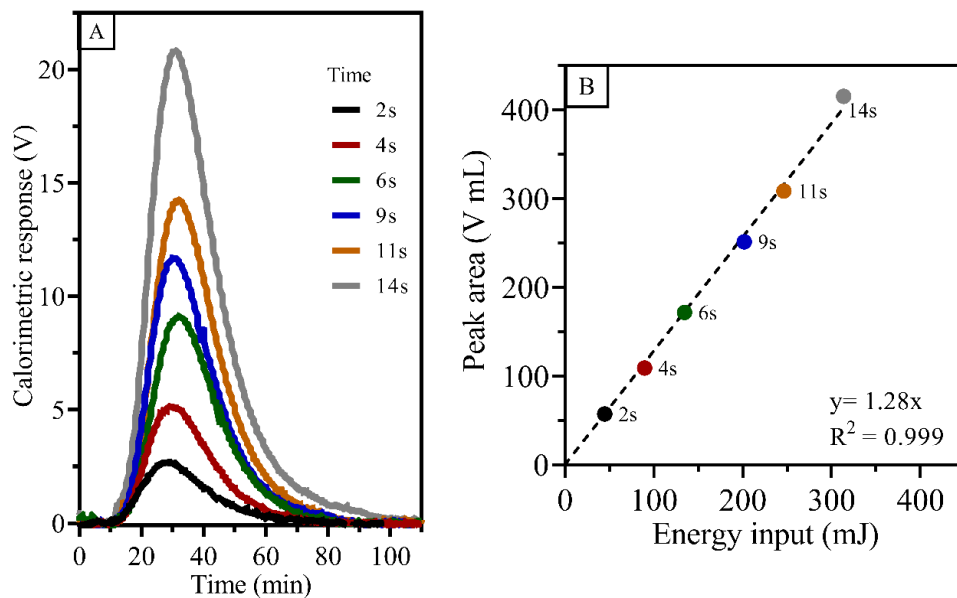


Figure A.5. Peaks obtained from timed heat pulses (A) and the associated calibration curve (B).

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APPENDIX B

Supplemental for Leonce et. al., 2020

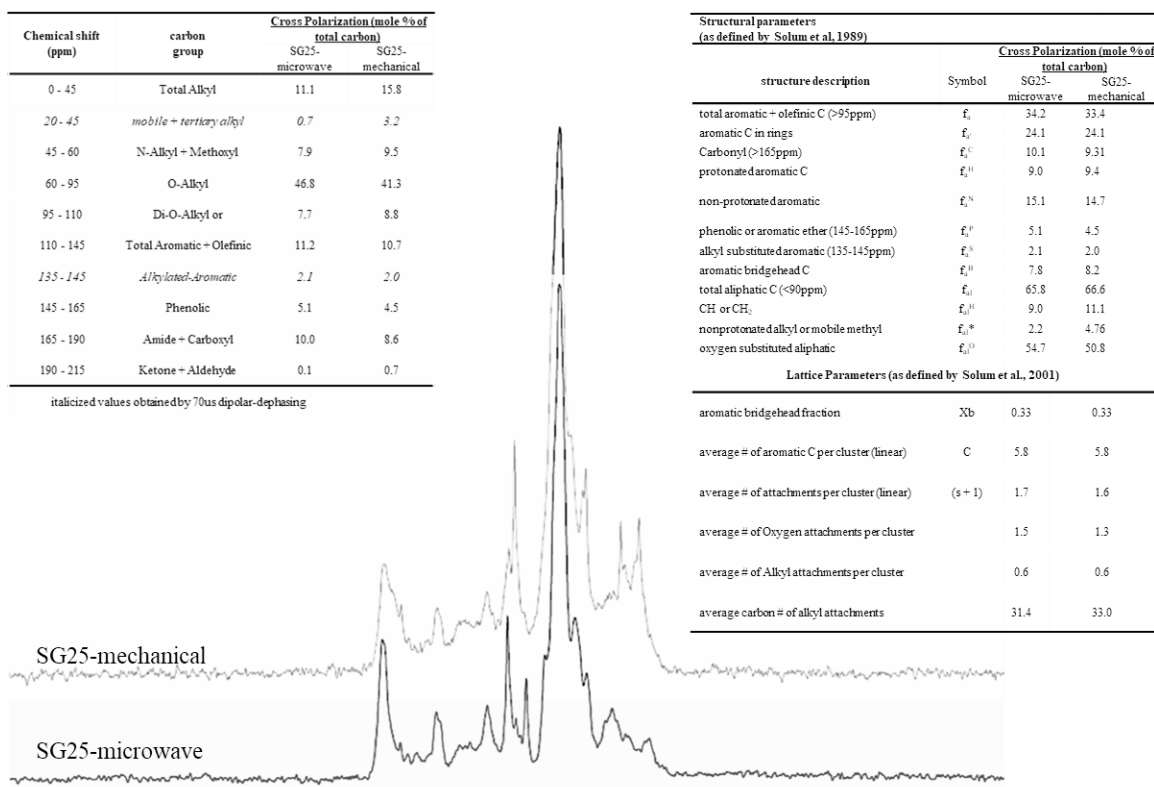


Figure B.1. Comparison of ^{13}C NMR spectra of wDOM extracted from uncharred switchgrass via mechanical shaking (top), and microwave-assisted extraction (bottom) and associated functional groups and structural parameters.

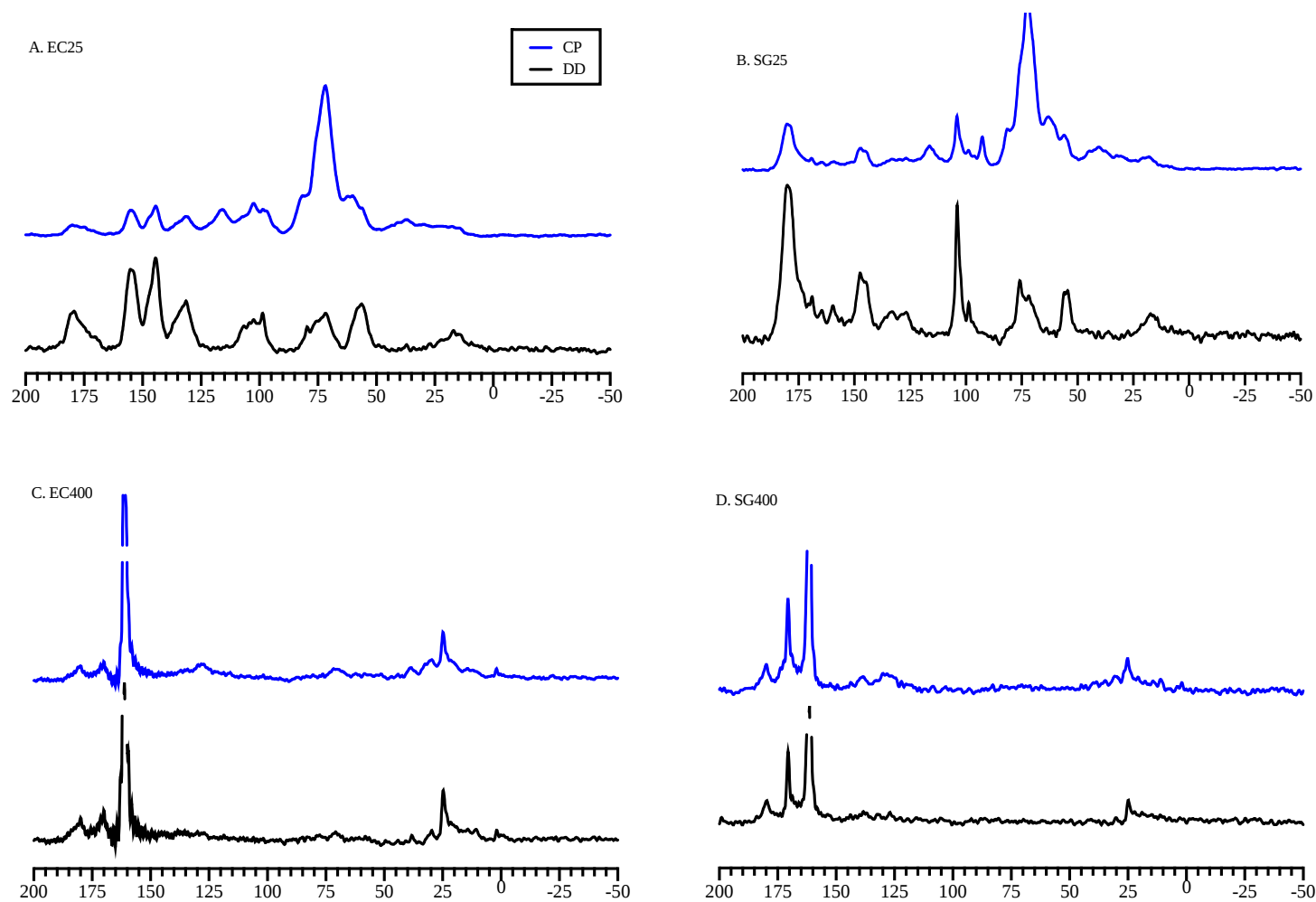


Figure B.2. Solid-state ^{13}C NMR spectra of water-extracted dissolved organic matter obtained from uncharred (SG25 and EC25) and charred (SG400 and EC400) switch grass (SG) or eastern red cedar (EC) plant materials.

Table B.1. Solid-state ^{13}C NMR-derived chemical properties of water-extracted dissolved organic matter obtained from uncharred (SG25 and EC25) and charred (SG400 and EC400) switch grass (SG), eastern red cedar (EC), or honey mesquite (HM) plant materials.

	SG25	SG400	EC25	EC400	HM25	HM400
<u>Functional Group</u>						
Total Alkyl (%)	11.1	16.5	9.3	22.9	10.5	30.9
<i>mobile + tertiary alkyl</i> (%)	0.7	3.9	0.8	5.6	1	11.5
N-Alkyl + Methoxyl (%)	7.9	2.3	6.5	2.2	3.6	2.8
O-Alkyl (%)	46.8	5.8	45.4	5.5	21.7	6.5
Di-O-Alkyl	7.7	2.2	9.6	1.8	6.9	2.5
Total Aromatic + Olefinic (%)	11.2	18.2	15.7	13.8	44.8	17.4
<i>Alkylated-Aromatic</i> (%)	2.1	7.1	3.9	3.86	14.5	3.9
Phenolic (%)	5.1	30.2	7.8	47.5	7.5	7
Amide + Carboxyl (%)	10	24	4.8	6.2	4.2	31.9
<i>Ketone + Aldehyde</i> (%)	0.1	0.8	0.8	0	0.9	1
<u>Structural Carbon</u>						
total aromatic + olefinic C (%)	34.2	75.4	38.7	69.4	64.2	59.8
aromatic C in rings (%)	24.1	50.5	33.1	63.2	59.1	26.9
Carbonyl C (%)	10.1	24.9	5.6	6.2	5.2	32.9
protonated aromatic C (%)	9	0.4	13.6	2.9	17	2.1
non-protonated aromatic C (%)	15.1	50.1	19.5	60.3	42.1	24.8
phenolic or aromatic ether C (%)	5.1	30.2	7.8	47.5	7.5	7
alkyl substituted aromatic C (%)	2.1	7.1	3.9	3.9	14.5	3.9
aromatic bridgehead C (%)	7.8	12.9	7.8	8.9	20.1	13.9
total aliphatic C (<90ppm) (%)	65.8	24.6	61.3	30.6	35.8	40.2
CH or CH ₂ (%)	9	8.2	7.2	12.9	8.9	14.6
nonprotonated alkyl or mobile methyl C (%)	2.2	8.4	2.1	10.1	1.5	16.3
oxygen substituted aliphatic C (%)	54.7	8.1	52	7.7	25.3	9.3
<u>Lattice Parameters</u>						
aromatic bridgehead fraction	0.33	0.25	0.24	0.14	0.34	0.52
average # of aromatic C per cluster (linear)	5.8	6.4	5.7	5.9	7.5	6.5
average # of aromatic C per cluster (annular)	7.1	7.9	7.1	7.2	9.4	8.1
average # of attachments per cluster (linear)	1.7	4.7	2	4.8	2.8	2.6
average # of attachments per cluster (annular)	2.1	5.8	2.5	5.9	3.5	3.3
average # of Oxygen attachments per cluster	1.5	4.7	1.7	5.4	1.2	2.1
average # of Alkyl attachments per cluster	0.6	1.1	0.8	0.4	2.3	1.2
average carbon # of alkyl attachments	31.4	3.5	15.8	7.9	2.5	10.2

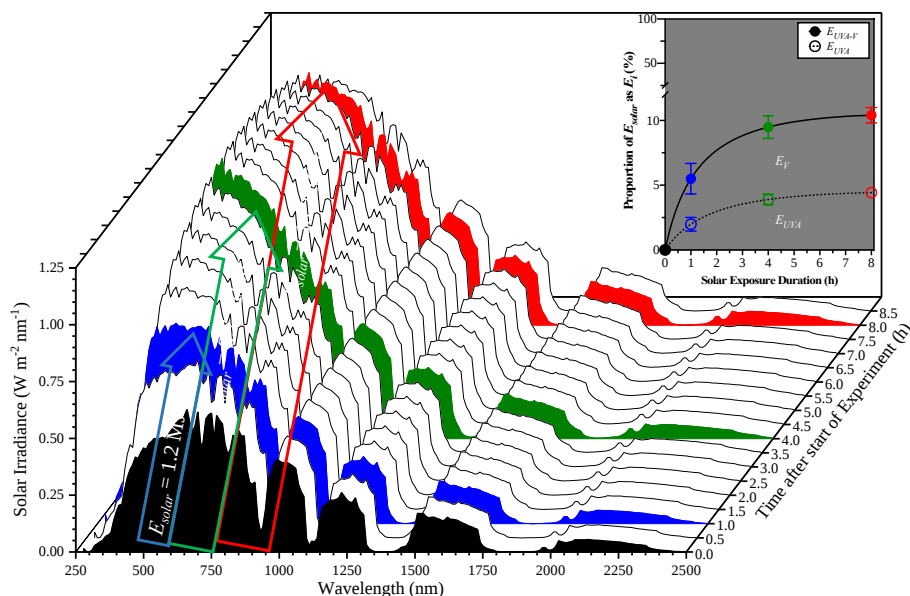


Figure B.3. Series of full solar spectrum, measured time-integrated solar energy input from the full spectrum (E_{solar} ; indicated in arrows) and proportion of E_{solar} available for wDOM transformation (E_{UVA-V} ; inset) at sampling times of 0, 1, 4 and 8h. Data for solar spectrum was obtained from <https://www2.pyllighthouse.com.au/calculators/> using study site specific inputs of location, date, time (in 30 minute intervals) and barometric pressure. The E_{solar} was measured directly at the study site using a solar irradiance meter. Proportion of E_{UVA-V} was obtained from the averaged time-integrated fraction of irradiance between wavelengths of 300-450 nm and times 0-1h, 0-4h and 0-8h for exposure times of 1, 4 and 8h respectively.

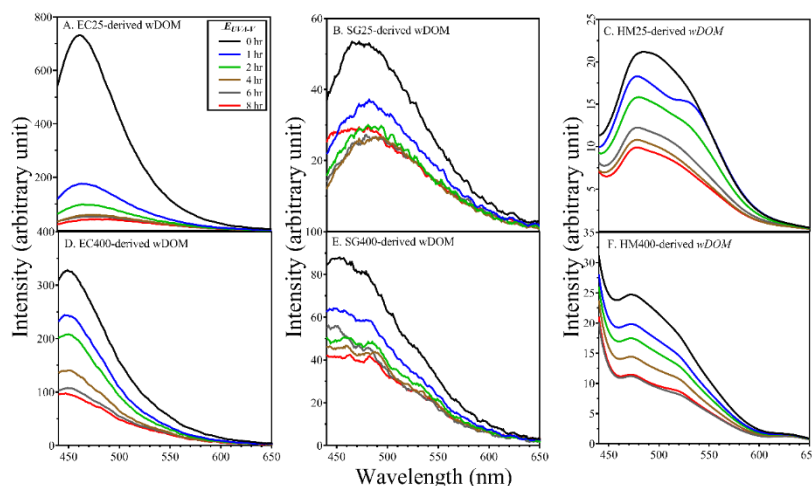


Figure B.4. Fluorescence emission spectra for water-extracted dissolved organic matter from charred (HM400, SG400 and EC400) and uncharred (HM25, SG25 and EC25) plant material after exposure of up to 2.21 MJ m⁻² of absorbable energy (E_{UVA-V}) from natural sunlight. Samples were excited at 405 nm and observed between 430 and 650 nm.

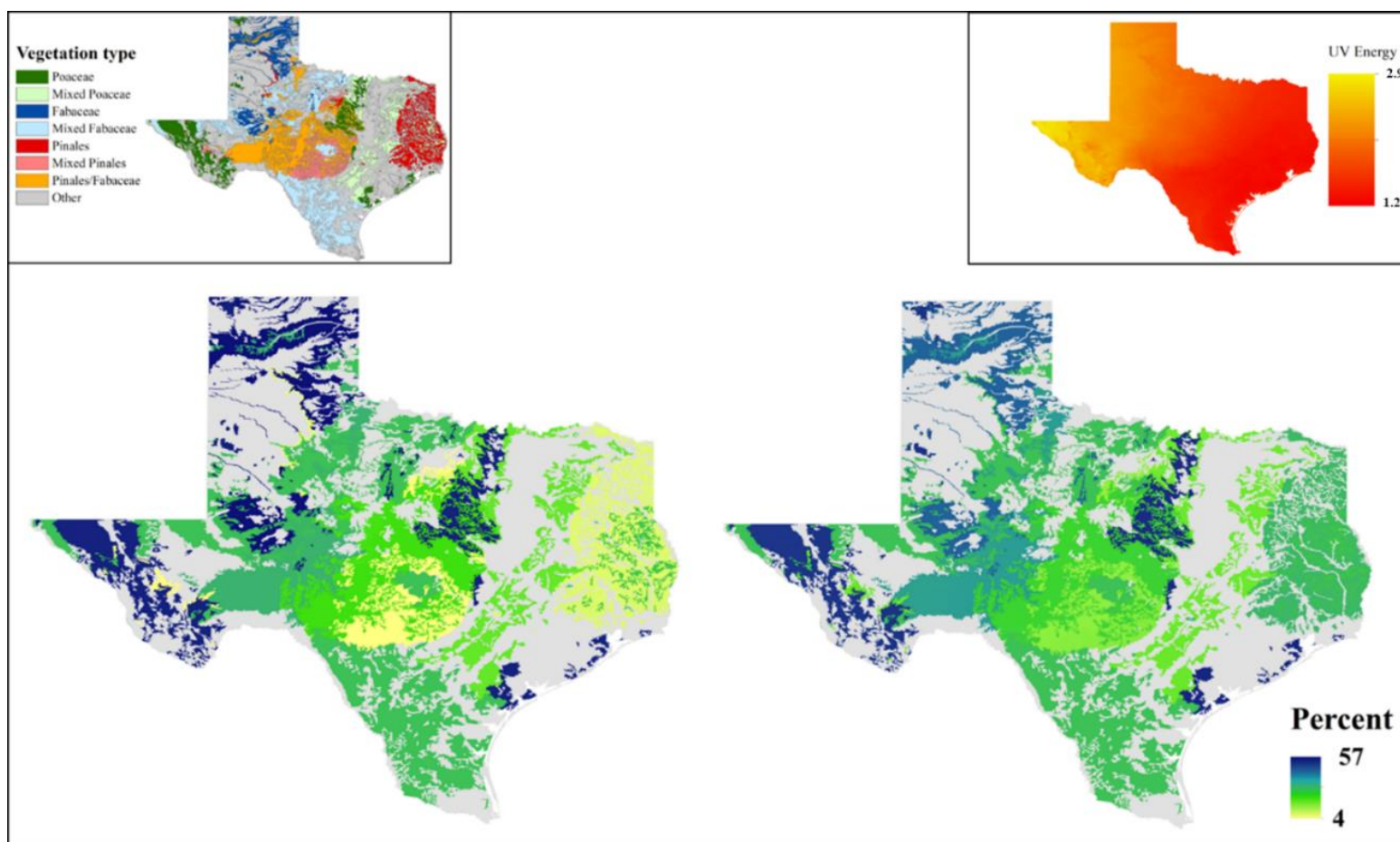


Figure B.5. Percent distribution of wDOM remaining ($wDOM_r$) for A) uncharred materials and B) charred materials after an average day of solar exposure. Values shown here are weighted to their georeferenced percent land cover at the family level for honey mesquite (Fabaceae), switchgrass (Poaceae) and the Order level for eastern cedar and ashe juniper (Pinales). Left inset shows the distribution of vegetation across Texas. Mixed vegetation is weighted to the georeferenced percent cover at that location and ranged from a minimum of 0.33:1 to a maximum of 1:1. Right inset shows average E_{UVA-V} across Texas.

Spatial Modeling for Estimated Fire-induced Shift in Photo-degradative Cycling of wDOM

Spatial modeling for wDOM remaining ($wDOM_r$) was done by combining a georeferenced raster of long-term daily averaged solar exposure (as E_{UVA-V}) and the energy-based wDOM photobleaching model (and fitted model parameters) obtained from our experiments. The data for the georeferenced raster of E_{UVA-V} was obtained by converting a georeferenced raster of long-term (12-26 years) average daily direct normal irradiation (in kWh.m⁻²) to MJ m⁻² and then multiplying each raster cell value by 0.104 (the maximum absorbable proportion of solar irradiation after 8h in a clear sky scenario). The direct normal irradiation raster used was from <https://globalsolaratlas.info> and was processed using “raster” package² in R-GUI (version 3.6.3).¹ The resolution of the raster map was 0.0083 with 3,178,110 raster cells spread across the state of Texas. The direct normal irradiation raster was then converted to E_{UVA-V} .

To obtain the spatial distribution of total $wDOM_r$, the energy-based wDOM photobleaching model was applied to each raster cell. This model was of the form:

$$wDOM_r = [wDOM_{f,0} e^{-\phi_f E_{UVA-V}} + wDOM_{s,0} e^{-\phi_s E_{UVA-V}} + wDOM_{res}] \times 100,$$

with values of $wDOM_{f,0}$, ϕ_f , $wDOM_{s,0}$, ϕ_s and $wDOM_{res}$ for Con25-, Con400-, SG25-, SG400-, HM25-, and HM400-derived wDOM coming from Table 3.1. The resultant rasters were then converted from $wDOM_r$ to wDOM lost ($wDOM_l$) by subtracting each raster cell value from 100. This operation was also executed in R-Gui and the results of $wDOM_l$ for each material exported in spreadsheet format for graphing and mapping in ArcGIS Pro².

A shapefile of Texas vegetation landcover by type (including cropland) as delineated from Landsat Multispectral Scanner System satellite imagery and ground survey was obtained from the ArcGIS Online database.³ Shapefile was divided into

polygons according to vegetation type and coverage. Shapefile polygons containing a single vegetation type that was in the same family as switchgrass (Poaceae) and honey mesquite (Fabaceae) were reclassified as Poaceae and Fabaceae. Shapefiles polygons with a single vegetation type that was in the same Order as eastern red cedar were reclassified as Pinales. Polygons containing only one of the vegetation types and any other vegetation type not used to this study were classified as “Mixed”. For example, a polygon containing honey mesquite and oak would be classified as “Mixed Fabaceae.” Polygons labelled as Pinales/Fabaceae contained both vegetation types and another that was not of interest. Shapefile polygons that did not contain vegetation types from the Poaceae, Fabaceae and Pinales vegetation types were classified as “Other.”

To calculate the fire-induced shifts in photodegradative cycling, spreadsheets of $wDOM_l$ for Con 25, Con400, HM25, HM400, SG25 and SG400 were first converted to raster files in ArcGISro² for spatial analysis. An overlay of the categorically divided polygons from Texas vegetation shapefile were used to delineate corresponding $wDOM_l$ rasters. For example, SG25 and SG400 raster boundaries were delineated using Poaceae polygons. The HM- and Con- rasters were delineated using Fabaceae and Pinales polygons, respectively. To calculate the $wDOM_l$ for Mixed areas, individual rasters were weighted by coverage and added to produce a single raster. For example, for areas with a 50% coverage of Poaceae, each raster cell value was multiplied by 0.5. The fire-induced shifts in photodegradative cycling for each category were calculated as the percent difference between $wDOM_l$ rasters for char models (HM400, SG400 and Con400) minus that of its uncharred counterpart (HM25, SG25, Con25) as follows:

$$\frac{wDOM_{l,charred} - wDOM_{l,uncharred}}{wDOM_{l,charred}} \times 100$$

Categorically divided rasters were then merged to produce a single raster map of Texas.

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APPENDIX C

Supplemental for Chapter Four

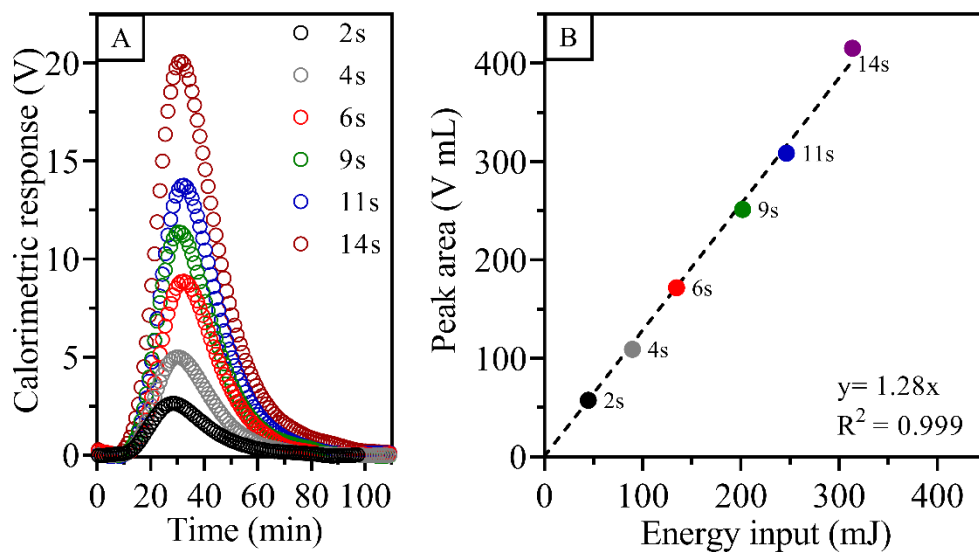


Figure C.1 Peaks obtained from timed heat pulses (A) and the associated calibration curve (B).

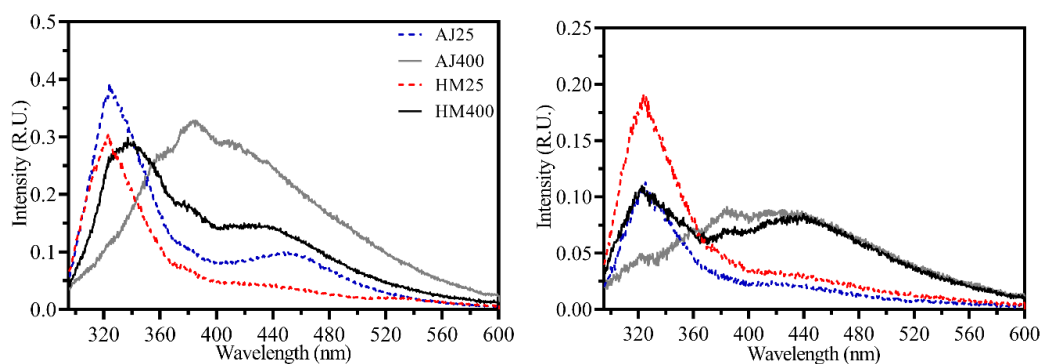


Figure C.2. Fluorescence emission spectra for water-extracted dissolved organic matter from uncharred (AJ25 and HM25) and charred (AJ25 and HM25) plant material after exposure to natural sunlight. Samples were excited at 275 nm and observed between 295 and 600 nm.

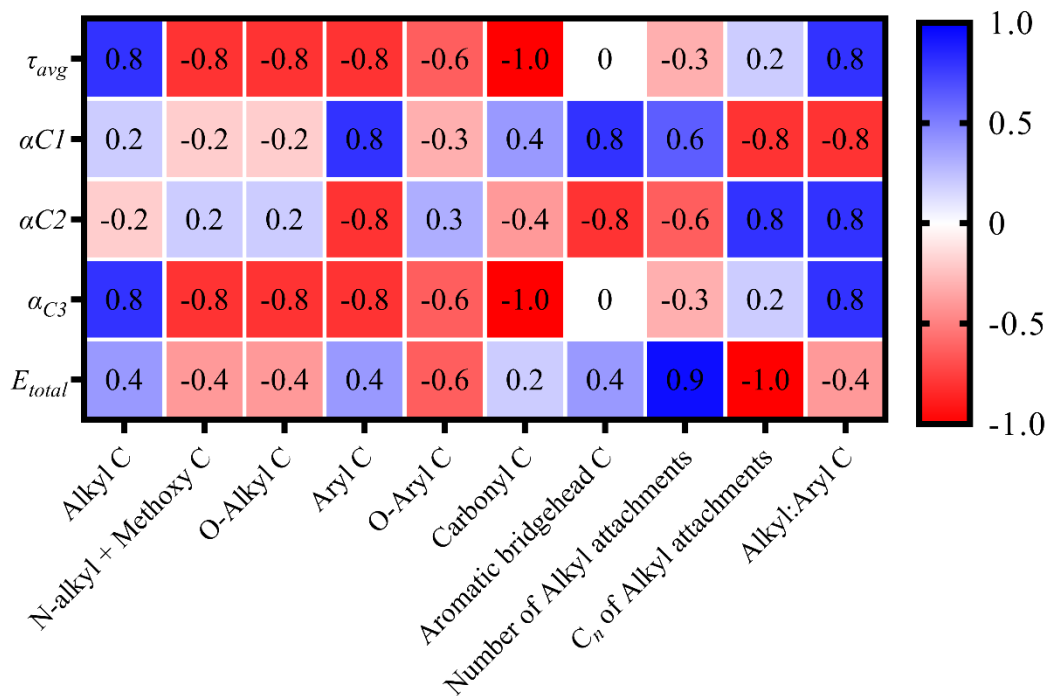


Figure C.3. Correlation between lifetime fluorescence values (τ_{avg} , α_i) and respective calorimetric parameters (heat of sorption; E_{total}) for AJ25, HM25, AJ400 and HM400.

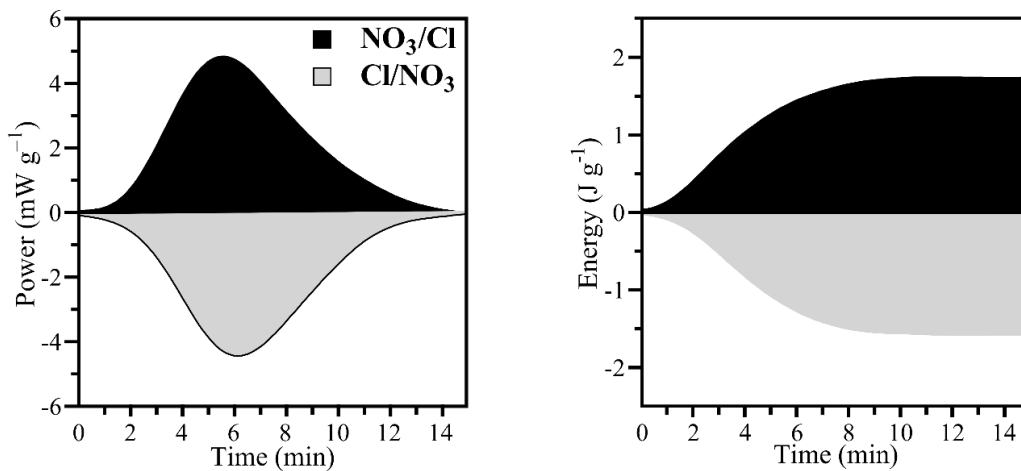


Figure C.4. Calorimetric thermograms of mass-normalized energy for chlorine replacing nitrate (Cl/NO₃) and vice versa (NO₃/Cl) and cumulative energy transfer (E_{total}) during the sorption reaction.

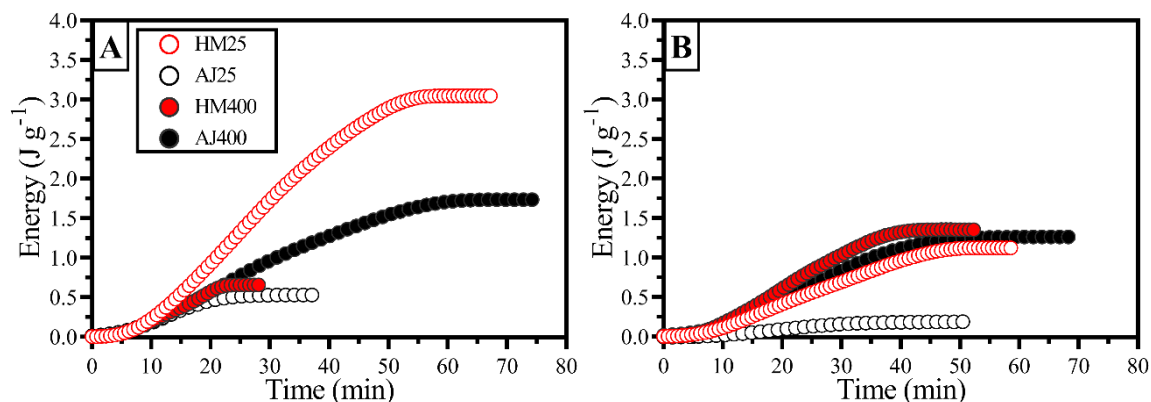


Figure C.5. Cumulative energy transfer (E_{total}) during the sorption of dark controls and light-exposed HM25, HM400, AJ25 and AJ400 onto nano-crystalline boehmite.

Table C.1. Sorption and photodegradation experiment measurements and derived parameters. Tau (τ) and alpha (α) values and ^{13}C -NMR functional group abundances are percent contributions.

	AJ25		HM25		AJ400		HM400	
	Dark control	Light-exposed	Dark control	Light-exposed	Dark control	Light-exposed	Dark control	Light-exposed
Total energy (J/g)	0.52	0.19	3.06	1.12	1.73	1.26	0.65	1.35
Reaction duration (min)	30	40	60	50	70	65	25	45
Peak Area (R.U.)	30.8	11.5	21.4	13.8	48.4	14.9	15.4	4.2
Average lifetime (ns)	1.87	0.31	0.41	0.29	2.15	1.60	2.05	1.38
$\tau C1$	0.26	0.09	0.12	0.08	0.36	0.25	0.36	0.24
$\tau C2$	2.84	0.96	1.22	1.01	2.78	2.54	2.93	2.45
$\tau C3$	7.85	5.56	5.85	5.75	9.29	10.2	10.0	10.4
$\alpha C1$	45	85	86	88	51	66	55	69
$\alpha C2$	51	13	11	10	40	26	37	26
$\alpha C3$	4	2	3	2	9	8	8	5
TOC (mg/L)	206	200	55	54	85	81	26	25
Carbon compound class								
Alkyl C	8.9	-	10.5	-	41.9	-	22.5	-
N-Alkyl+Methoxy	6.1	-	3.6	-	2.4	-	2.3	-
O-alkyl	55.1	-	28.6	-	6.1	-	7.2	-
Aryl C	15.7	-	44.8	-	13.1	-	14.4	-
O-aryl C	9.0	-	7.5	-	4.5	-	8.9	-
Carbonyl C	5.3	-	5.2	-	32.0	-	44.8	-

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