UNIVERSITY OF CALIFORNIA SAN DIEGO

Life After a Fiery Death: The Role of Fire and Browning on Dissolved Organic Carbon Dynamics in Experimental Freshwater Ponds

A Thesis submitted in partial satisfaction of the requirements
for the degree Master of Science

in

Marine Biology

by

Cody J. Spiegel

Committee in charge:

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Professor Andrew Barton, Co-Chair
Professor Jeff Bowman

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The Thesis of Cody J. Spiegel is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2022

DEDICATION

Maya, my love,

your boundless patience, support, and gracious feedback form the keystone of this great accomplishment.

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ABSTRACT OF THE THESIS

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Master of Science in Marine Biology

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Drier and hotter conditions linked with anthropogenic climate change increase wildfire activity which can influence terrestrial and aquatic carbon cycles at broad spatial and temporal scales. Other aspects of environmental change such as climate warming enhance soil decomposition leading to accelerated rates of sedimentation and leaching from soils into aquatic systems, a phenomenon known as "browning." Large-scale ecological disturbances like wildfire can increase the occurrence of browning from post-fire erosion. I tested the effects of fire-treatment (burned vs. unburned plant material) and its interaction with terrestrial loading on dissolved organic carbon (DOC) composition, concentration, and degradation (biological vs.

photochemical) in freshwater mesocosms. DOC concentration increased nonlinearly with added plant material in both burning treatments and degraded most rapidly at intermediate concentrations, indicating that decomposition at intermediate concentrations removes DOC at a faster rate than at higher concentrations. Excitation-Emission Matrix (EEM) fluorescence spectroscopy showed that the effect of fire and browning changed chemical signatures apparent in the EEMs, and that both mainly affected the humification index and the specific ultraviolet absorbance at 254 nm over time. Incubations showed that biodegradation contributed more to DOC decomposition than photodegradation, and that DOC decomposition was most rapid at intermediate loading levels likely because anoxia at high terrestrial input inhibited microbial activity. My thesis shows that fire and browning elicit non-linear responses in the dynamics and composition of DOC in aquatic systems, and that fire alters the chemistry of organic detritus in ways that impact its processing and role in aquatic environments.

INTRODUCTION

Each year wildfires are responsible for roughly 5 to 10 percent of global CO_2 emissions (after accounting for offsets from forest regeneration in burned areas), making fires a notable part of the Earth's carbon (C) balance (Bowman et al., 2009; van der Werf et al., 2017). Wildfire frequency depends on geography, antecedent weather conditions, plant demography and composition, and sufficiently dry fuels (Bond & Keane, 2017). The relative significance of these factors for driving trends in fire activity, including the variability among fire-climate relationships, differs greatly across global ecoregions (Bowman et al., 2009; Davis et al., 2019; Keeley & Syphard, 2019; McKenzie et al., 2004). Nonetheless, it is clear that drier and hotter regional conditions linked with anthropogenic climate change increase wildfire frequency and intensity that influence terrestrial C cycles at broad spatial and temporal scales (Abatzoglou & Williams, 2016; Barbero et al., 2015; Holden et al., 2018; Jones et al., 2019; Lasslop et al., 2019; Westerling, 2016; Williams et al., 2019).

Wildfires cause considerable financial damage, accidental deaths, and ecological destruction (Bowman et al., 2009; Keeley et al., 2011; Keeley & Syphard, 2019). For instance, greater wildfire extent and intensity can trigger landscape shifts such as the replacement of woody vegetation or shrublands with more flammable grasslands (Davis et al., 2019; Keeley & Fotheringham, 2001; J. Keeley & Syphard, 2016). Recent work has demonstrated that repeated burning depletes C and nitrogen in watersheds and the tissues of plant species (Granath et al., 2021; Pellegrini et al., 2015) and alters the chemical properties of organic matter (Ward et al., 2017) with fire causing rapid C release through combustion (Cornelissen et al., 2017; Cornwell et al., 2009; Wozniak et al., 2020). Fires also destabilize soil structure leading to debris flows that mobilize burned organic materials (collectively, pyrogenic carbon (PyC)) into aquatic

ecosystems like lakes and streams (Bird et al., 2015; DeLuca et al., 2020; Forbes et al., 2006; Rust et al., 2018). The exchange of burned C particulates between ecosystem pools raise environmental and biological concerns due to the persistence within ecosystems and bioaccumulation potential (Burton et al., 2022; Campos & Abrantes, 2021).

Aquatic ecosystem metabolism is regulated by organic and inorganic material from either internal (autochthonous) production as well as terrestrial (allochthonous) inputs that directly influence trophic dynamics and nutrient cycling (Bixby et al., 2015; Cole et al., 2007; Mulholland & Elwood, 1982; Solomon et al., 2015). For example, as dissolved organic matter (DOM) and carbon (DOC) concentrations in lakes increase with terrestrial loading, community respiration tends to exceed internal primary productivity (Hanson et al., 2003), suggesting that allochthonous material serves as a primary regulator on aquatic ecosystem function (Berggren et al., 2022; Fonseca et al., 2022; Symons et al., 2019). Despite covering a small fraction of the Earth's surface, biogeochemical activity within lakes and rivers are a critical component of the global C cycle (Cole et al., 2007). The fate of organic C may either be transported to the ocean via fluvial networks, emitted as respired CO_2, or stored in sediments, or (Cole et al., 2007; Sutula et al., 2021). The amount of C buried annually in lake sediments is comparable to that stored in the ocean via the C pump (Ward et al., 2017). However, aspects of environmental change such as climate warming increases the rate of terrestrial organic matter loading into aquatic systems by accelerating decomposition and leaching from soils, a phenomenon known as “browning” (Kritzberg et al., 2020). The occurrence of browning may be accelerated by other large-scale ecological disturbances like wildfire leading to additive or even interactive effects on aquatic ecosystem function.

Wildfires can directly impact C dynamics in aquatic systems. As downstream recipients, lakes are vulnerable to post-fire erosion and sedimentation (Cooper et al., 2015; Forbes et al., 2006; McCullough et al., 2019; Rhoades et al., 2019; Rust et al., 2018). Organic materials like burned plant litter can significantly influence lake metabolism through alternations to its quality and quantity (Bixby et al., 2015; Pereira et al., 2011; Santos et al., 2019). Regular monitoring or sampling in response to fire show increases in post-fire lake DOC in addition to reduced water quality (Bowring et al., 2022; Earl & Blinn, 2003; McEachern et al., 2000; Rhoades et al., 2019; Wagner et al., 2018). Ash and C particulates may thus cause extensive fire-mediated biogeochemical changes within lakes (Dempsey et al., 2020). For example, Allen et al. (2003) surveyed water chemistry in two-year post-fire lakes on Alberta's Boreal Plain and found that mean DOC concentrations in lake water from burned watersheds was 1.4-fold higher compared to reference watersheds. In contrast, other studies show that post-fire increases in DOC were confounded by autochthonous DOC production (McEachern et al., 2000; Moody & Worrall, 2017). The large variation in the chemical composition of DOC due to the heterogeneity in the vegetation of burned watersheds and *in situ* production makes it difficult to distinguish how the sources of most organic C inputs and critical nutrients control aquatic production. Associated changes to the molecular composition of DOC with increased concentrations remain unclear as monitoring often includes limited measures of DOC quality. Identifying changes in post-fire DOC chemistry is therefore of great importance as it will provide insight into DOC persistence, fate, and reactivity.

Photochemical and microbial degradation are the dominant controls on the biogeochemical cycling of C in lakes (Berggren et al., 2022; Chen et al., 2022; Dempsey et al., 2020; Larson et al., 2007). The extent of DOC assimilation and degradation depends on the rate

at which DOC reacts and the time over which that reaction occurs (Moody & Worrall, 2017). For example, light absorbing chromophoric DOC (CDOM) compounds contribute to the large variation in photo- and biodegradation rates between lakes with different allochthonous inputs from watersheds (Cory et al., 2007; Helms et al., 2013; Laurion & Mladenov, 2013); debris flows containing aromatic PyC have also been found to strongly influence the structure of microbial communities (Chen et al., 2022). The various degradation pathways and subsequent chemical attributes of DOC due to the heterogeneity of terrestrial ecosystems in the context of increasing wildfire may in turn affect microbial metabolism in aquatic ecosystems (Lennon & Pfaff, 2005). I therefore hypothesize that the effects of fire and browning weaken the photodegradation and microbial decomposition of DOC from the combination of increased light attenuation due to shading and greater aromaticity from burning (Adair et al., 2017; Chen et al., 2022).

In this study, I address the influence of fire and browning on the concentration, composition, and decomposition of DOC in a controlled experimental design. I consider both the effects of fire-treatment and the quantity of plant biomass on DOC cycling in freshwater mesocosms. Using an array of 30 (400 L) tanks with a gradient design that incorporates gradually increasing plant biomass, I ask the following: (1) How does the quality (either burned or unburned plant material) and quantity of terrestrial loading affect DOC concentration? (2) Does the fire-treated plant material result in a change in mesocosm DOC chemical composition as indicated by Excitation-Emission Matrix (EEM) fluorescence spectroscopy? (3) How do microbial activity and photodegradation contribute to DOC decomposition among varying supply rates between burned and unburned sources? DOC degradation is source-dependent, so I predict an increase in DOC concentrations from initial C leaching, but reduced DOC

concentrations in the burned ponds due to C depletion from combustion; I also predict that photo- and microbial degradation will be impaired because of greater aromaticity and shading effects due to burning and detrital loading. My study aims to advance knowledge of aquatic DOC dynamics by using a gradient experimental design to detect nonlinearities and critical thresholds in response to browning and fire.

MATERIALS AND METHODS

2.1 Mesocosm experimental design

Thirty mesocosms (400 L plastic Rubbermaid cattle tanks) filled with freshwater were assembled at the University of California, San Diego Biological Field Station in October of 2021. A plankton mixture collected from Lake Murray and Lake Miramar in San Diego, CA using a vertical tow (64 μm mesh net; 7.6 m depth) was used in equal aliquots (~ 433 mL) to stock mesocosms with resident plankton communities. Tanks were regularly filled with fresh water to replace losses to evaporation. In the gradient design each tank received incremental increases of plant biomass ranging from 0 g to 400 g with a total of fifteen tanks per plant treatment type (burned vs. unburned). This design allowed me to test nonlinear relationships with the response variables. Tanks were filled on 1 November 2021, the plant material was added on 5 November, 2021, and the experiment ended on 16 March, 2021.

2.2 Plant material

I selected two California native plants species *Salvia leucophylla* (hereafter, sage) and *Salix lasiolepis* (hereafter, willow) to simulate the effects of terrestrial loading. Sage grows on

arid, sandy, and rocky soils, and is common throughout western North America at elevations from 762 to 3000 m (Keeley & Fotheringham, 2001). Sage was chosen due to its wide distribution and availability to grown in pots. Willow was also used because it is a deciduous species found in riparian zones (Schulze & Walker, 1997). Both species occur in fire-prone scrub and woodland ecosystems in California. Twenty-three individual sage plants were purchased from a nursery on June 9th, 2021 and transplanted into pots with a sand-vermiculite mixture and grown for 60 days. I harvested willow from the University of California Dawson Los Monos Reserve in San Diego, CA. Cut stems (~ 1 cm diameter) and leaves from sage and willow branches were placed inside a greenhouse to air dry for 24 hours. The plant material was then placed in a drying oven at a constant temperature (24 h at 45°C) until dry.

To simulate the effects of wildfire on the plant material, I defined two burn categories: low and high severity. A portion of sage and willow was charred in a 75 L aluminum container using a blow torch. To ensure material was not completely combusted, I used the container's lid to regulate oxygen flow and smother plant material as needed. Through visual assessment, the plants were divided into the two severity groups (low vs. high) and combined. All leaves, sticks, and stems were then gathered and pooled according to treatment (burned vs. unburned). All burned and unburned plant material was packed into separate 25 x 15 cm nylon bags of 250 μm mesh size. Leaf little bags aided in sinking once added to the mesocosms while also allowing for water flow and grazing of microorganisms and other small invertebrates. In total, each tank received a 1:1 mass ratio of sage and willow to reach the cumulative target mass. After weighing, the nylon bags with plant material were set in a drying oven (24 h at 45°C) before being placed in their assigned tanks. At the end of the experiment all litter bags were removed and oven-dried

(7 d at 45°C) and re-weighed. The initial and final masses of sage and willow were used to measure overall leaf-litter decomposition.

2.3 DOC concentration analysis

DOC concentration was measured at 5 discrete intervals over the course of the experiment: before plant addition (Day 0), and 10, 31, 59, and 96 days thereafter. To prepare for concentration analysis, samples were filtered through pre-combusted (2 h at 550°C) glass-fiber filters (0.7 μm GF/F; Whatman, Maidstone, UK) into muffled (5 h at 550°C) borosilicate amber vials (60 mL), and then acidified with 37% HCl to a pH of 3. DOC concentration analysis was conducted using a high temperature combustion method (Shimadzu TOC-L Total Organic Carbon Analyzer) in The Water Innovative and Reuse Lab (WIRLab) at San Diego State University (SDSU). Samples were calibrated with potassium hydrogen phthalate standards (ranging from 1 to 50 mg C/L) and analyzed according to WIRLab standard protocols with ~ 10% of samples in duplicate. For all duplicated samples, standard deviations were within 10% of mean values; sample results falling outside of this range were either re-analyzed or not included.

2.4 Mesocosm in-situ incubations

To test the roles of photo- and biodegradation on DOC decomposition, I conducted three incubation experiments (November 2021 (Day 10), December 2021 (Day 31), and January 2022 (Day 59). The last two experiments were excluded because I observed positive net changes in DOC due to potential contamination or methodological issues. The first experiment on Day 10 is presented and showed the greatest changes in DOC.

A combination of clear and opaque Sterile Whirl-pak© bags were used to construct UV treatments that transmitted the entire solar spectrum or completely excluded light exposure. 100 mL of water from each tank was collected and filtered (F) through pre-combusted 0.7 μm GF/Fs to limit but not fully exclude microbial activity; other bags were filled with unfiltered water (UF) that included microbes resident in the tanks. This resulted in four treatment conditions in a 2 x 2 factorial design: UV transmissible-unfiltered [UV-UF]; UV transmissible-filtered [UV-F]; Non-UV transmissible-unfiltered [NoUV-UF]; and Non-UV transmissible-filtered [NoUV-F]. All bags (four per tank x 30 tanks, n = 120) were then secured to 8.8 x 25.4 x 7.6 cm plastic trays and suspended ca. 15 cm below the surface. At the end of the incubation period (7 d; see Dempsey et al., 2020), all bags were removed, filtered through pre-combusted 0.7 μm GF/Fs into muffled borosilicate amber vials, and transported on ice to the WIRLab at SDSU.

Filtration is an essential step for measuring DOC concentration with studies recommending a 0.45 or 0.2 μm pore size to remove microbiota from samples (Dahm et al., 2015; Dempsey et al., 2020; Magyan & Dempsey, 2021; Bistarelli et al., 2021; Wilske et al., 2020). Many 0.45 and 0.2 μm filters, however, are composed of organic material such as cellulose acetate, which can induce contamination problems, leading some researchers to recommend 0.7 μm GF/F filters (Denis et al., 2017; Khan & Subramania-Pillai, 2006). Though the efficiency of filtration to remove bacteria and regrowth over the course of the experiment or during storage was not verified during this study I concluded that the 0.7 μm filters were sufficient to remove most large microorganisms since filtering reduced DOC decomposition at many plant treatment levels (see Results).

These conditions were used to distinguish between effects of photodegradation vs. microbial decomposition on DOC loss. The percent change in DOC concentration between the

four whirl-pak bag treatments and ambient tank conditions yielded effects for individual degradation pathways: 1) photodegradation, 2) microbial degradation, and 3) the combined effect of both photo- and microbial degradation. That is, the percent change in DOC concentration over the seven-day incubation was determined for each bag in each tank. The photodegradation effect was indicated by the difference in percent change in DOC composition between the UV-UF and NoUV-UF, the microbe effect was the difference in percent change in DOC between the UV-UF and UV-F, and total decomposition was the difference between the UV-UF and NoUV-F.

2.5 EEM spectral analysis

The excitation and emission wavelengths at which fluorescence occurs are characteristic of specific molecular structures (Coble, 1996; Fellman et al., 2010). I used EEM spectral analysis to characterize the chemistry of the compounds that made up the DOC in the ponds. I collected and individually filtered water from every tank (n = 30) through a 64 μm mesh into 100 mL acid-washed (10% HCl) polypropylene containers. The filter mesh was rinsed with ddH_2O between collections to prevent cross-tank contamination. Samples were filtered into muffled borosilicate amber vials using 0.7 μm GF/Fs, refrigerated (< 24 h) and then transported on ice to the WIRLab for analysis.

Each sample was aliquoted into a quartz cuvette that was then placed in a Horiba Aqualog-UV-800-C spectrofluorometer. Cuvettes were cleaned with ddH_2O water and ultra-pure rinsed (3x) before use. EEMs fluorescence was inner-filter corrected, blank-subtracted and Raman-normalized. Rayleigh scatter bands were excised (first order at each wavelength pair where excitation = emission ± bandwidth; second order at each wavelength pair where emission = 2 × excitation-environment ± (2 × bandwidth), see Laurion & Mladenov, 2013). Terrestrially-derived

humics reflect aromatics that account for the main light-absorbing compounds in the water column (Coble, 1996), while protein-like material such as tryptophan or tyrosine are often associated with microbial degradation (Coble, 1996; Gabor et al., 2014).

Six tanks at the highest biomass levels exceeded the Aqualog intensity limits resulting in EEMs oversaturation due to the pulse of DOC when the plant material was first added (see Results); here, representative tanks of low (5 g), intermediate (125 g), and high biomass (225 g) levels were used to illustrate the compositional shifts in DOC chemistry over the course of the experiment. The heights of major peaks in the EEMS corresponding to different molecular structures were identified using the wavelength ranges identified by (Coble, 1996, 2007): Peak A (λex=~250 nm; λem=380-460 nm), Peak C (λex=~405 nm; λem= 490-510 nm), Peak M (λex=~312 nm; λem=380-420 nm), and Peak B (λex=~275 nm; λem=~310-320 nm).

2.6 Indices generated by the UV-vis absorbance and fluorescence spectroscopy

I calculated three fluorescence indices: the humification index (HIX = ratio of areas under the emission curve at 435–480 nm and 300–345 nm plus 435–480 nm at an excitation wavelength 245 nm) that described the degree of humification (high HIX = more terrestrial humic-like material) (Zsolnay, 1999), the fluorescence index (FI = emission intensity at 470 nm divided with that of 520 nm at 370 nm excitation) which indicated source material (microbial-precursor FI value ≈ 1.8 or terrestrial-precursor FI ≈ 1.3) (McKnight et al., 2001; Wilske et al., 2020), and the freshness index (ß:α) was calculated as the ratio of emission intensity at 380 nm to the maximum emission intensity between 420 and 435 nm at excitation wavelength 310 nm (Parlanti et al., 2000).

Two UV absorabnce indices were calculated: the ratio of the slope (S_R) parameters ($S_{275-295}$:$S_{350-400}$) which has been used as a proxy for molecular weight (Helms et al., 2008) and the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) to indicate aromaticity (Stedmon & Bro, 2008; Weishaar et al., 2003).

Six data points at the highest loading levels were omitted due to the oversaturation from the EEM spectral analysis at Day 10.

2.7 Statistical analysis

I modeled treatment effects on these parameters using general additive models (GAMs) implemented in R's mgcv package (Wood, 2006). GAMs allowed for the covariate plant biomass to be replaced by the sum of a smooth non-parametric function. I estimated the effects of burning and browning using separate GAMs with a gaussian error distribution for all response variables. The use of flexible smoothers in a GAM framework was well suited to model the nonlinear responses given the nature of the experimental design.

I selected final models with the lowest generalized cross-validation (GCV) scores and greatest deviance explained (DE) using backward stepwise selection. Lower GCV scores typically correspond with higher DE indicating that a model minimizes the smoothed predictor terms while maximizing explanatory power (Marra & Wood, 2011; Wood, 2020). I also used the index available in mgcv to evaluate concurvity on a 0 to 1 scale with 0 indicating no concurvity and 1 indicating a total lack of identifiability (Wood, 2006); concurvity is much like collinearity but in a GAM framework which can complicate statistical inference (Pedersen et al., 2019).

I rejected models with concurvity values that exceeded 0.3 (see Johnston et al., 2019). For instance, to quantify the effects on DOC concentration I fitted coefficient models with

burning treatment (burned vs. unburned) as parametric categorical variable along biomass gradient. In total, five models were individually analyzed for each time point since results for a single full model introduced extreme concurvity (> 0.9). I therefore used this model selection procedure to identify whether browning affected the different DOC parameters, and whether the relationships were different between the burning treatments.

RESULTS

3.1 Mesocosm DOC concentration

DOC concentration showed a rapid nonlinear increase 10 days after plant addition and gradually declined in both burning treatments over time (Figure. 1A). The GAM explained 95%

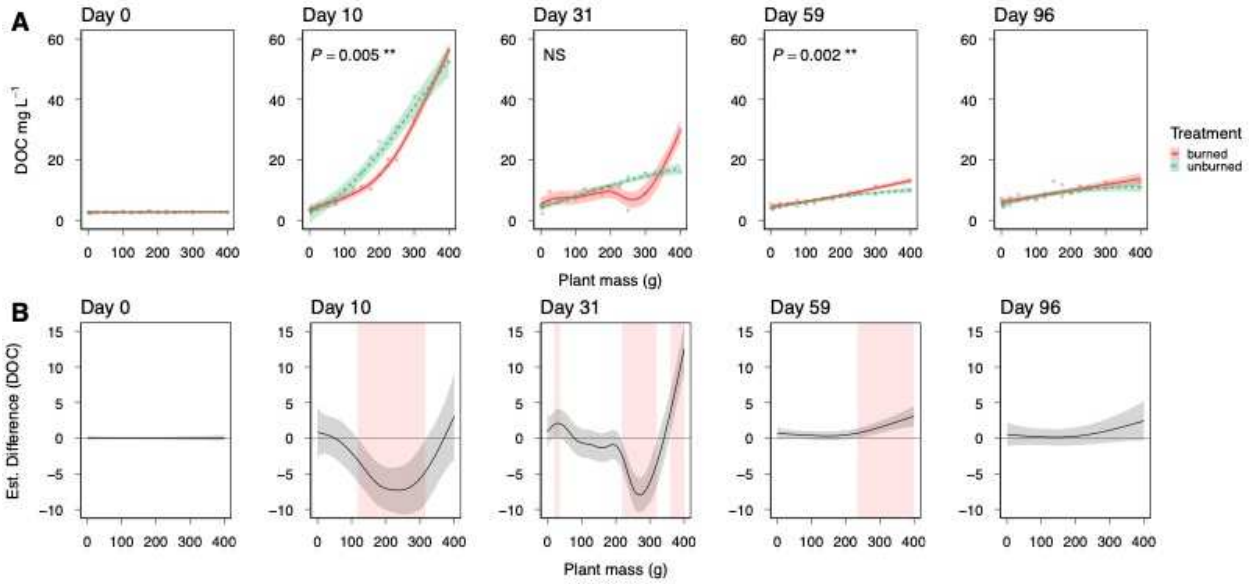

Figure. 1 Dissolved organic carbon (DOC) concentrations across plant biomass at five discrete intervals. **A:** 10 days after plant addition values ranged from 5.0 to 56.5 mg/L along the biomass gradient with a significant difference between the burning treatments ($P = 0.005$). The interaction of burning and browning on DOC was also significant at Day 59 ($P = 0.002$). By Day 96, DOC concentrations significantly declined in both burning treatments. **B:** Differences between fitted smooth functions between the burning treatments (difference in trends; solid lines) shown in red with approximate 95% confidence intervals. Intermediate loading levels in the burned treatment at Day 10 and 31 had lower DOC (mean difference of 8 and 9 mg/L, respectively), whereas high loading levels in the burned treatment at Day 56 had slightly greater DOC (mean difference of 4 mg/L).

of the deviance at Day 10 with values ranging from 5.0 to 56.5 mg/L along the biomass gradient with a significant difference between the burning treatments ($P = 0.005$). Intermediate loading levels for the burned treatment at 10 days showed about 1.2 times less DOC compared to the unburned treatment as evidenced by the differences between the fitted smooth functions (difference in trends; solid lines) shown in red with approximate 95% confidence intervals (Figure. 1B). For instance, averaged across all plant levels, the burned treatment had an average 8 mg/L less DOC than the unburned treatment. This indicated that the rate of DOC loss was dependent on concentration, and that decomposition was most rapid at intermediate loading levels. By Day 96, DOC concentrations in both burning treatments significantly declined with no significant effect of burning or browning.

3.2 DOC composition as indicated by EEM spectral analysis

3.2.1 Day 10

The peak intensities of the A and C regions in both burning treatments reflected more humic-like substances (Figure. 2I, Figure 2II), while the peak intensities of M and B indicated microbial degradation by-products, and the presence of protein-like substances. At intermediate loading levels, the intensities of region A and C suggested greater terrestrially-derived materials which corresponded to the increase in DOC at 10 days after the plant material was added. The highest loading levels showed a high peak M fluorescence intensity (> 14) suggesting material produced *in situ* by microbial processes (Coble, 2007; Helms et al., 2013) (Figure. 2VI). All peak intensities increased with increasing biomass, especially at intermediate levels (Figure. 2).

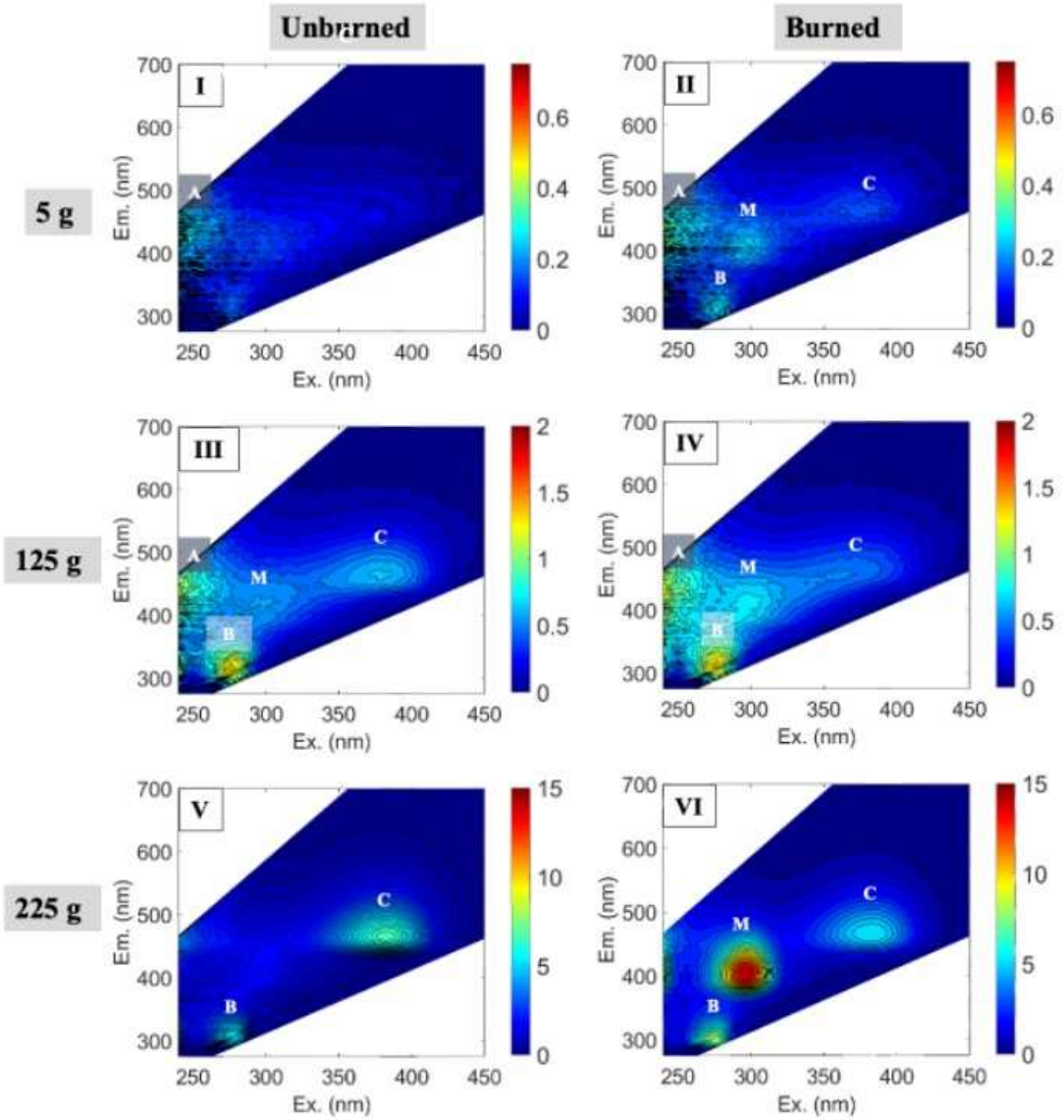

Figure. 2 Six Excitation-Emission Matrices (EEMs) showing fluorescence of dissolved organic carbon (DOC) at Day 10: Panel A = 5g, unburned; Panel B = 5g, burned; Panel C = 125g, unburned; Panel D = 125g, burned; Panel E = 225g, unburned; Panel F = 225g, burned. Note, the presence or absence of fluorescence peaks, intensity of fluorescence response, and shifts in peak maxima have all been shown to provide information about DOC chemistry and origin: Peak A (humic-like, λex=~250 nm; λem=380-460 nm), Peak C (humic-like, λex=~405 nm; λem= 490-510 nm), Peak M (protein-like, λex=~312 nm; λem=380-420 nm), and Peak B (protein-like, λex=~275 nm; λem=~310-320 nm).

3.2.2 Day 96

The effects of browning and burning exhibited the strongest observable changes in DOC chemistry at Day 96 (Figure. 3). For instance, peak A was the most intense region at low and intermediate loading levels, especially in the intermediate burned treatment with a maximum intensity of 1.5 (Figure. 3II, Figure. 3IV). This change in intensity suggested an increase in

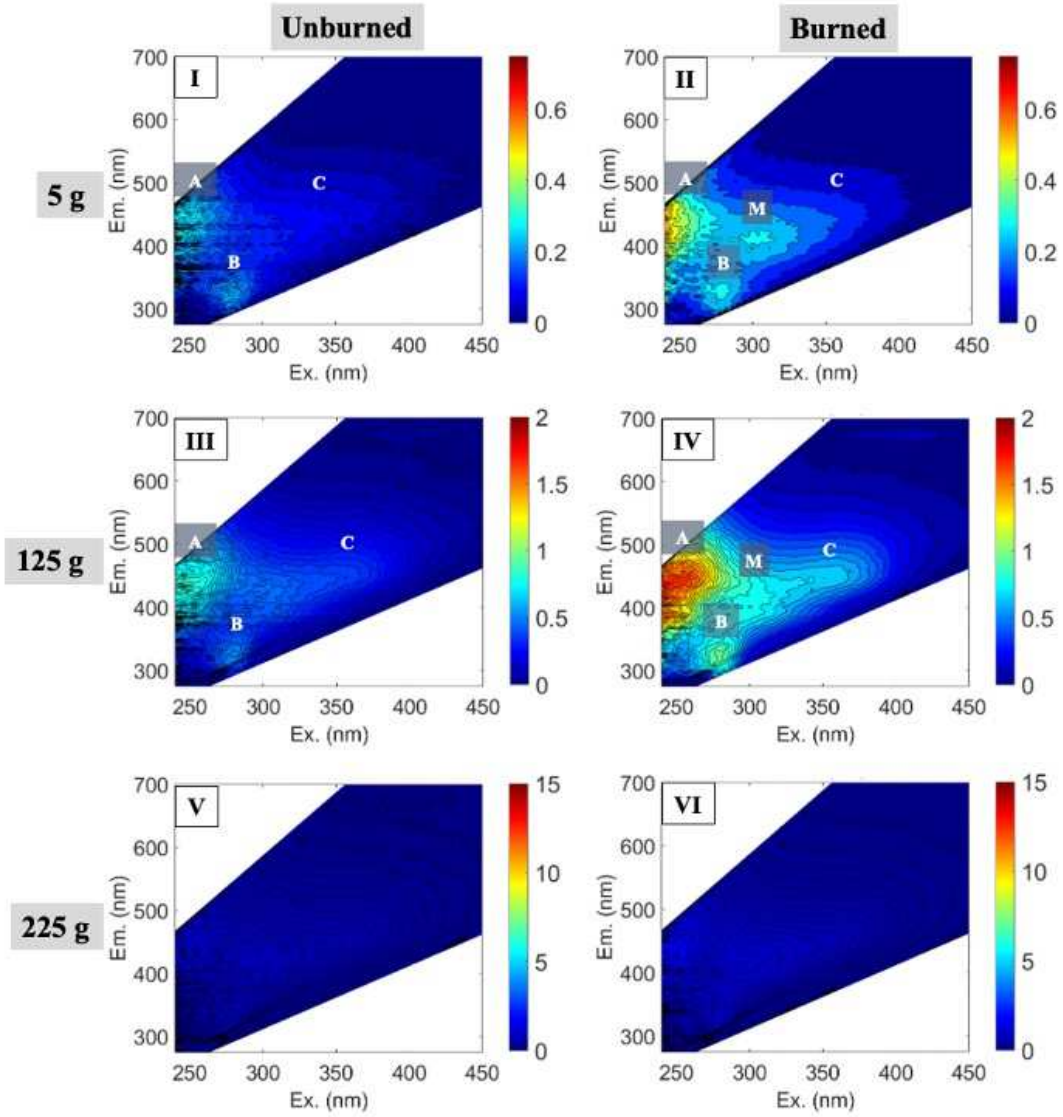

Figure. 3 Six Excitation-Emission Matrices (EEMs) showing fluorescence of dissolved organic carbon (DOC) at Day 96: Panel A = 5g, unburned; Panel B = 5g, burned; Panel C = 125g, unburned; Panel D = 125g, burned; Panel E = 225g, unburned; Panel F = 225g, burned. Note, the presence or absence of fluorescence peaks, intensity of fluorescence response, and shifts in peak maxima have all been shown to provide information about DOC character and origin. Peak A (humic-like, λex=~250 nm; λem=380-460 nm), Peak C (humic-like, λex=~405 nm; λem= 490-510 nm), Peak M (protein-like, λex=~312 nm; λem=380-420 nm), and Peak B (protein-like, λex=~275 nm; λem=~310-320 nm).

aromatic, high molecular weight (HMW) substances (Fellman et al., 2010; Helms et al., 2008; Huguet et al., 2009; Markechová et al., 2013). All of the initial fluorescence regions (Peaks A, C, M, and B) remained with time (see Figure. S1, Figure. S2), though the peak intensities may have fallen below the limit of detection at the highest loading levels (Figure. 3V, Figure. 3VI) by Day 96.

3.3 Fluorescence and absorbance indices

$SUVA_{254}$ showed a positive, nonlinear relationship with increasing biomass at Day 10, especially at intermediate loading levels (Figure. 4A). The increasing trend continued over time and was most apparent by Day 59 indicating greater aromaticity with significant differences between the burning treatments ($P < 0.0001$). Average across all plant levels, $SUVA_{254}$ increased by an average 12.4% by Day 96.

The S_R showed a negative relationship with plant biomass at Day 10, which remained consistent over time with no significant differences between the burning treatments (Figure. 4B). After Day 31, the S_R remained around an average value of 1.0 with no significance of burning treatment further indicating HMW compounds across all loading levels.

There was a strong negative trend in the HIX at Day 10 and 31 which indicated less humification with increasing biomass (Figure. 4C). By Day 59, the HIX showed a positive increase with a significant interaction between burning and browning ($P < 0.0001$). By Day 96, the HIX showed an average 39.2% increase across all plant levels with a significant difference between burning treatments as evidenced by the differential slopes ($P < 0.0001$).

There was a significant interaction between burning treatment and browning on the freshness index with more decomposed material in the unburned treatment at Day 10 ($P = 0.01$) (Figure. 4D). The trends in freshness remained over time as evidenced by the differential slopes.

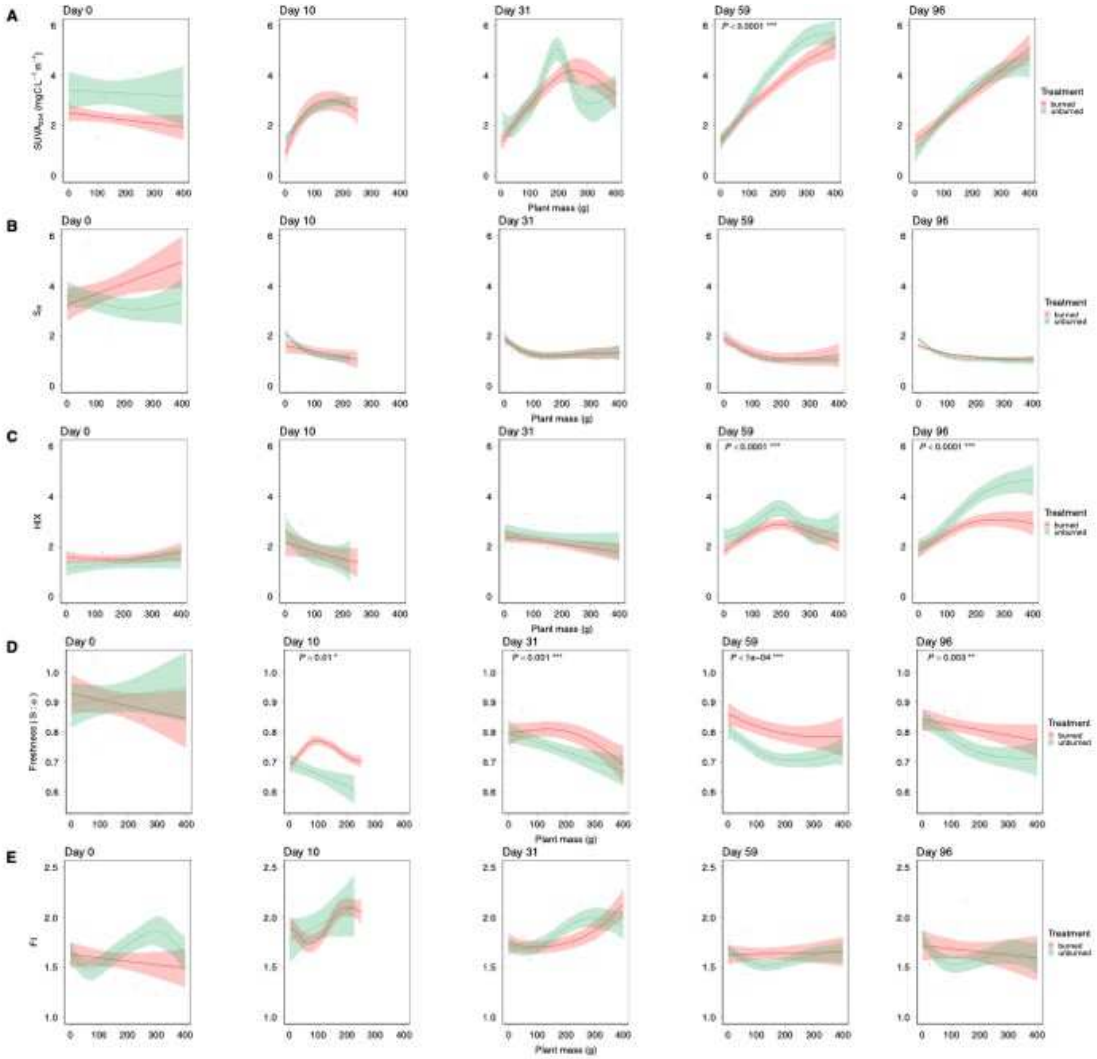

Figure. 4 Fluorescence and absorbance indices based on Excitation-Emission Matrix (EEM) spectroscopy. Six tanks at the highest biomass levels (> 250 g) are omitted from Day 10 due to oversaturated EEMs. **A:** $SUVA_{254}$ remained consistent with plant material added at Day 10 with slightly higher values at intermediate loading levels. There was a strong, positive trend by Day 59 indicating greater aromaticity with significant differences between the burning treatments ($P < 0.0001$). **B:** The S_R declined with plant material added at Day 10, then remained consistent with no significant differences between the burning treatments. **C:** There was a strong negative trend in the HIX at Day 10 and 31, but then significantly increased by Day 96 with an interaction between burning and browning ($P < 0.0001$). **D:** There was a significant interaction between burning treatment and browning on the freshness index with more decomposed material in the unburned treatment at Day 10 ($P = 0.01$). The trends in freshness remained over time as evidenced by the differential slopes. **E:** The FI showed a nonlinear positive trend at Day 10 and 31 that then decreased with no significant burning or browning effect.

The GAM explained 75.2 % of the deviance for the FI with plant material added at Day 10 (Figure. 4E). The positive, nonlinear trend along the gradient indicated greater microbial sources at intermediate loading levels. For instance, a maximum FI value (~ 2.0) was observed

for both burning treatments. The positive relationship continued into Day 31 with greater FI values at the highest biomass levels (> 250 g). By Day 96, however, the FI declined across all plant levels with no significant differences between the burning treatments indicating a mixture of both terrestrial and microbial sources in the ponds.

3.4 DOC degradation

Proportional DOC loss increased with increasing detrital input at Day 10, as illustrated by both the incubation experiment (Figure. 5) and the change in the DOC concentration curve shown in Figure. 1. Photodegradation had minimal effects on DOC loss in both the burned and unburned treatments (a mean decrease of 3.2 and 2.1%, respectively) that was constant across all levels of plant addition.

The effect of microbes caused an average 1.4 % reduction at low DOC concentrations across both burning treatments, whereas DOC loss at high concentrations was 1.2 greater in the

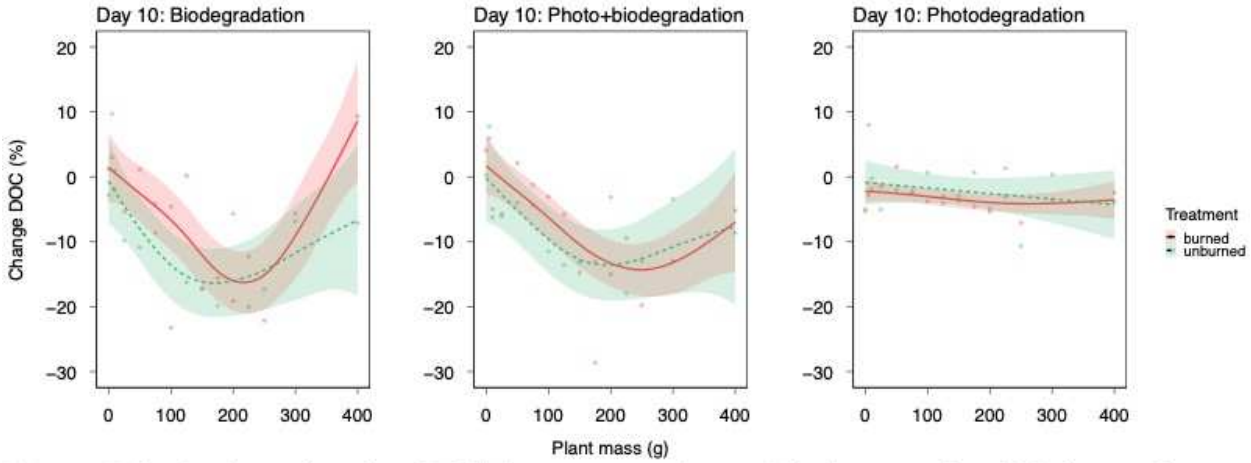

Figure. 5 Dissolved organic carbon (DOC) loss as percent change. Microbes caused a >20% decrease in DOC decomposition with no significant differences between the burning treatments, especially at intermediate concentrations. The effect of microbes caused an average 1.4 % reduction at low DOC concentrations, whereas DOC loss at high concentrations was 1.2 greater in the unburned treatment. Photodegradation had minimal effects on DOC loss in both burning treatments that was constant across all plant levels. Though there was no significant effect of burning on DOC change, the significant effect browning as evidence by the differential slopes of the two lines supported that detrital loading influenced the rate at which microbial decomposition occurred ($P < 0.004$).

unburned treatment though the minimal DOC change observed indicated that microbial decomposition was likely inhibited by anoxia at the highest loading levels (> 250 g) in both burning treatments. At intermediate concentrations, microbes caused a >20% decrease in DOC with no significant differences between the burning treatments. The microbial effect on DOC degradation therefore showed a unimodal relationship with the amount of browning. Thus, biodegradation had a greater effect on total DOC loss compared to photodegradation, and the effect of microbes was strongest at intermediate DOC concentrations. Though there was no significant effect of burning on DOC change, the significant effect of browning as evidence by the differential slopes of the two lines supported that detrital loading influenced the rate at which microbial decomposition occurred ($P < 0.004$).

3.5 Dry mass decomposition of sage and willow

I modeled dry mass decomposition of sage and willow as percent change for both burning treatments across plant specific mass (Figure. 6). Averaging mass loss for the burning treatments, sage decomposed about 1.3 times more than willow ($P < 0.003$). There were slight observable differences in sage mass loss at low plant specific mass levels but no significant effects of plant mass or burning treatment (Figure. 6A). Sage decomposition was constant across all plant specific mass levels. Willow mass loss did not differ between the burning treatments, and there

was no significant effect of plant specific mass levels on decomposition (Figure. 6B). This was supported by the large, overlapping 95% confidence intervals.

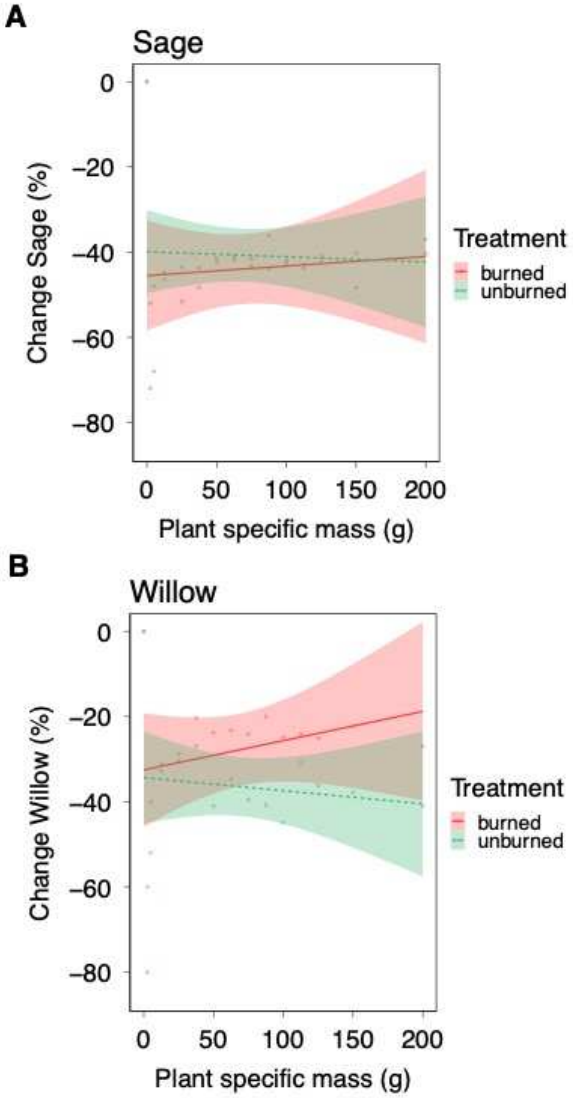

Figure. 6 Dry mass decomposition of sage and willow as percent change across plant specific mass. Averaging mass loss for both burning treatments, sage decomposed about 1.3 times more than willow ($P < 0.003$). **A:** There were slight differences in sage mass loss at low plant specific mass levels but no significant effects of plant mass or burning treatment. Sage decomposition was constant across all plant specific mass levels. **B:** Willow mass loss did not differ between the burning treatments, and there was no significant effect of plant specific mass levels on decomposition. This was supported by the large, overlapping 95% confidence intervals.

DISCUSSION

My thesis shows that the effects of fire and browning elicits nonlinear responses in the dynamics of DOC, and that both alter DOC chemical composition in ways that impact its processing and role in aquatic environments. The effects of burning and supply rate on DOC concentration were sometimes interactive. As predicted, DOC concentration increased rapidly with added plant material, and the GAM identified the strong, nonlinear relationship of increasing DOC concentrations with increasing biomass (Figure. 1). Past studies have found high DOC concentrations in lake and stream water from allochthonous inputs after wildfire (Allen et al., 2003; McEachern et al., 2000; Santos et al., 2019). However, the nonlinear relationship in DOC concentration indicated that decomposition at intermediate concentrations removes DOC at a faster rate than at higher concentrations. This difference was most apparent at intermediate loading levels which suggests that C stored in plant material is more sensitive to combustion as evidenced by the lower average DOC concentration in the burned treatment (Pellegrini et al., 2015, 2018).

I next asked how DOC chemical composition might change with fire-treated plant material as indicated by EEM spectral analysis. A fraction of chromophores in DOM are fluorescent compounds (Stedmon & Nelson, 2015), and certain regions present in the EEMs were used to characterize aspects of the chemical composition in the ponds. For instance, regions A and C which are thought to be most closely related to terrestrially-derived materials (Coble, 1996), occurred at a greater intensity in correspondence with the initial pulse of DOC at Day 10, especially at intermediate loading levels. Additionally, regions M and B both reflected protein-like substances associated with microbial activity (Coble, 1996; Stedmon & Nelson, 2015) which

was confirmed in the incubation experiment with the greatest loss of DOC occurring at intermediate concentrations (Figure. 5).

Spectroscopic (absorbance and fluorescence) indices allowed me to further characterize the chemical composition of DOC in response to burning and browning. The indices generated by the EEMs data suggested greater microbial sources at intermediate loading levels as evidenced the higher FI (Figure. 4E) values ten days after plant addition. Here, the trends in the HIX and freshness index also shed light on the DOC composition in the ponds. For instance, humification occurs through the processing of organic material (Zsolnay et al., 1999). At Day 10, the negative trend in the HIX (Figure. 4C) suggests that the browning effect influenced the rate of processing based on the quantity of DOC present at the intermediate loading levels (i.e., the rate of humification, or processing of organic material, slowed at intermediate concentrations). Across time, however, the differences between the burning treatments were more apparent with the HIX and freshness indices showing greater humifaction and more decomposed materials, especially in the unburned treatment. My findings suggest that time is an important factor in the processing of DOC. For instance, these differential effects of burning and supply rate resulted in more humification and less microbial activity with time, especially in the unburned treatment suggesting that residence time might be a factor in controlling DOC cycling in aquatic systems (Stedmon & Nelson, 2015); future studies should measure DOC compositional changes using a similar experimental design with longer time intervals to better understand the physico-chemical effects that residence time may have on the DOM pool.

Though the interaction of browning and burning remained in the HIX and freshness indices, $SUVA_{254}$ indicated greater aromaticity with increasing biomass across time and no significant effect of burning. The greater intensification of the A region over time might suggest

that microbes preferentially degraded labile compounds over the aromatic compounds (Bostick et al., 2021). Additionally, Wickland et al. (2007) showed that microbial processing of DOM resulted in increases in $SUVA_{254}$ during a laboratory incubation of moss leachate, a finding supported by my results. And though the plant chemistry of sage and willow was not measured in my study, other findings have shown alterations to the chemical properties of organic matter from fire (Ward et al., 2017) which might explain the differences of the burning effect on the HIX and $SUVA_{254}$ along the gradient. Nonetheless, my findings show that the effects of burning, and loading across time resulted in composition changes such as greater humification and aromaticity and reduced microbial activity.

The incubation experiment allowed me to quantify the responses of DOC decomposition in response to fire and supply rate. I found that the degradability of DOC is more clearly linked by the quantity of terrestrial loading (or rate of browning) rather than burning as evidenced by the unimodal shape of the proportional rate of degradation as a function of supply (Figure. 5). Supply rate increased microbial activity, especially at intermediate loading levels as indicated by the low FI and greater peak intensity of regions B and M. The S_R values suggest that the molecular weight of the compounds at intermediate loading levels were possibly more susceptible to degradation by microbes (Lennon & Pfaff, 2005; Moran & Hodson, 1990). Moreover, previous studies have used first-order decay models to evaluate microbial decomposition on DOC (Chen et al., 2022; Wilske et al., 2020) and found that the rate of the reaction is proportional to the amount of that reactant. Here, the lower concentrations observed at Day 10 therefore explain why there was less change in DOC at the lowest loading levels. The incubations also confirmed that biodegradation contributed more to DOC decomposition than

photodegradation, and that decomposition was most rapid at intermediate loading levels, likely because anoxia at high terrestrial input also inhibited microbial activity.

My study differs in two important aspects from previous work (e.g., Bostick et al., 2021; Chen et al., 2022; Wilske et al., 2020). First, the GF/F pore size used in my study (0.7 μm) limited but did not completely remove microorganisms. While the disinfectant quality of UV radiation may have assisted in the complete removal of bacteria in the photodegradation experiment (Uzun et al., 2020; Yang et al., 2020), when compared to the microbe-present treatments, the effect of filtering on reducing DOC decomposition was noticeable. This suggests that removing microorganisms, even if incomplete, did impede decomposition.

Second, the incubation experiment showed that the effect of photodegradation on DOC was not significant between burning treatments or with supply rate. Previous work has shown that aromatic humic factions moderate bacterial activity due to photochemical transformations yielding labile compounds available as a primary bacterial substrate (Cory & Kling, 2018; Moran & Hodson, 1990). However, the compositional shifts as indicated by the indices and the incubation experiment suggests that the effects of microbes in response to burning and loading on DOC decomposition is stronger than photodegradation. While a successive photochemical-microbial degradation pathway may reduce DOC concentrations in aquatic systems (Bertilsson & Stefan, 1998; Bistarelli et al., 2021; Bostick et al., 2021; Bowring et al., 2022; Chen et al., 2022; Dempsey et al., 2020; Wilske et al., 2020; Zhang et al., 2013), further study should comparatively focus on the rate degradation and molecular change over a continuous temporal scale to disentangle the effects by photo- and microbial processes. The patterns in the concentrations of biologically and photochemically degradable DOC reported here allow for identifying DOC compounds and environmental factors linked to fire-effected aquatic systems.

Finally, I found a clear influence of fire treatment on the decomposition of willow and sage based on the relative change in biomass over time (Figure. 6). Previous studies have shown that woody structures decomposes more slowly than leaves (Cornelissen et al., 2017). However, fire can affect plant material by either reducing the availability of the substrate for microbial decomposition, or altering the chemical structure (e.g. by charring) which decreases its decomposability (Cornelissen et al., 2017; Hayer et al., 2022; Pellegrini et al., 2015). While the effect of fire or supply rate on sage and willow was not significant, willow showed less decomposition than sage suggesting an effect of its specific physiology such as its lignin-rich tissues or woody structure (Cornelissen et al., 2017). Thus, the traits of different species can greatly influence that rate at which it is decomposed. Past work has shown that plant community composition is important for fire regimes because the functional traits of different species impose strong effects on litter quality (Cornwell et al., 2009). As browning and wildfire are projected to increase (Barbero et al., 2015; Kritzberg et al., 2020) future work should consider the heterogeneity of the surrounding vegetation near a watershed with a framework that includes a greater variety of plant species. My findings suggest that decomposition of terrestrial material in aquatic systems may not necessarily depend on whether or not it is burned but rather on the plant-specific traits as evidenced by the greater decomposition of sage compared to willow.

4.1 Conclusions and Implications

The concentration and chemical composition of DOC along a gradient of increasing plant biomass provided evidence for greater microbial degradation as seen in the compositional shifts in the EEM spectral analyses, trends in the fluorescence and absorbance indices, and the incubation experiment. These results are important because many studies have shown that the

ability of microorganisms to uptake and respire DOM depends on its initial chemistry (e.g., Berggren et al., 2022; Cory et al., 2007; Cory & Kling, 2018; Moran & Hodson, 1990; Wilske et al., 2020). Therefore, my results imply that the browning of lakes may regulate the ability of microorganisms to mineralize DOC which can in turn affect how it is processed (stored in sediments or respired as CO_2) and exported to the ocean.

My study demonstrated that browning and fire elicits nonlinear responses in the dynamics and composition of DOC in aquatic systems with alternations to DOC chemistry. A nonlinear relationship was observed between the loading of terrestrial detritus and the concentration of DOC, indicating that decomposition at intermediate concentrations removes DOC at a faster rate than at higher concentrations. This inference was confirmed by the incubation experiment showing that removal of microbes by filtering reduced proportional DOC loss to the greatest degree at intermediate concentrations. The effects of fire and loading also changed chemical signatures apparent in the EEMs data, and that both mainly affected the HIX and $SUVA_{254}$ over time. These results suggest that browning and transformations due to burning affect the chemistry of DOC in surface waters and therefore its rate of degradation due to microbial respiration. The rate of browning, and alterations to the chemistry of DOC by fire may lead to extremely dystrophic systems where the threshold of adaptation is exceeded, and where recovery may no longer be possible. This may lead to changes in the structure and function of aquatic ecosystems that affects their capacity to store or process DOC, and their role in the global C cycle.

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APPENDIX

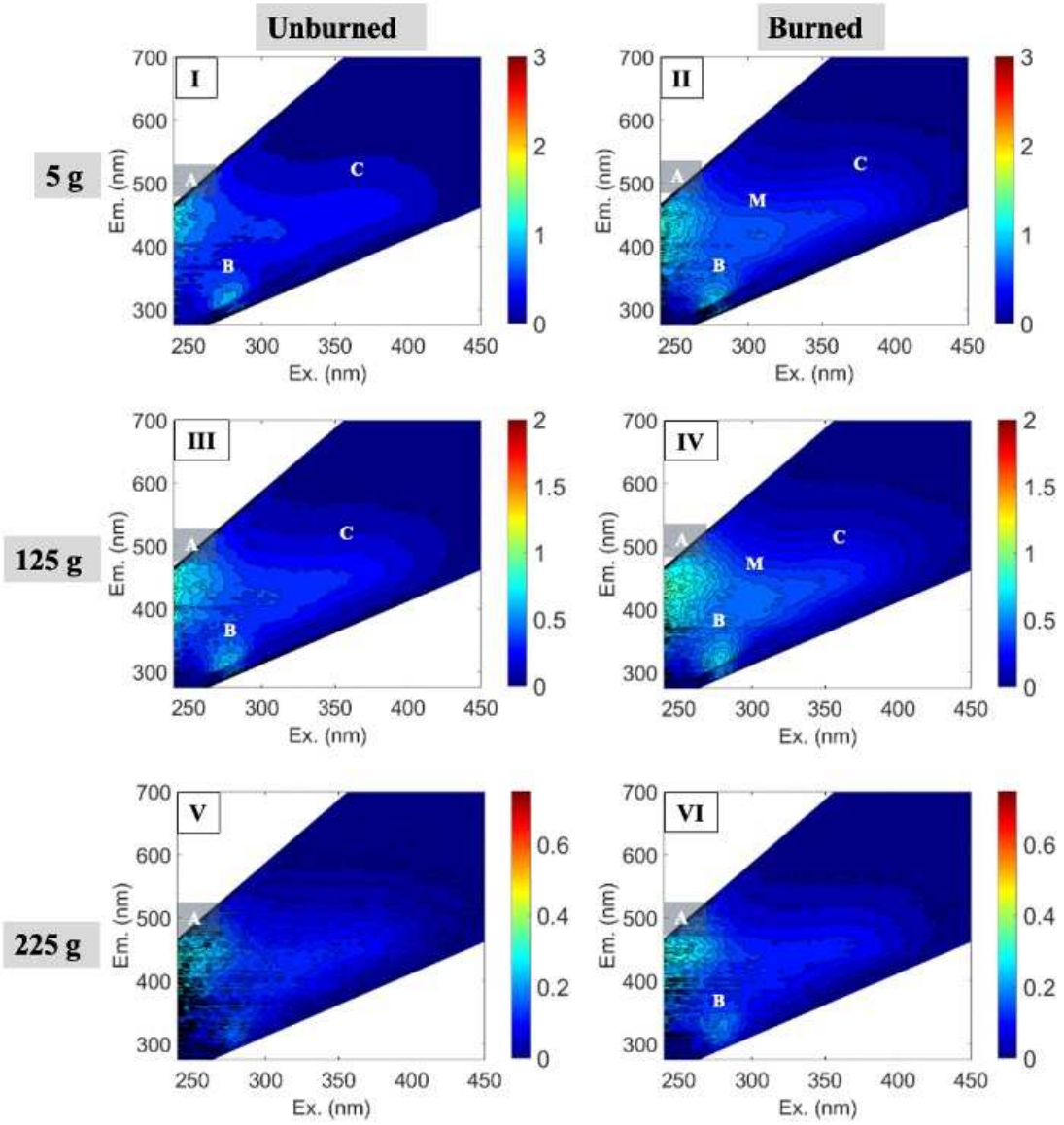

Figure. S1 Six Excitation-Emission Matrices (EEMs) showing fluorescence of dissolved organic carbon (DOC) at Day 31: Panel A = 5g, unburned; Panel B = 5g, burned; Panel C = 125g, unburned; Panel D = 125g, burned; Panel E = 225g, unburned; Panel F = 225g, burned. Note, the presence or absence of fluorescence peaks, intensity of fluorescence response, and shifts in peak maxima have all been shown to provide information about DOC character and origin. Peak A (λex=~250 nm; λem=380-460 nm), Peak C (λex=~405 nm; λem= 490-510 nm), Peak M (λex=~312 nm; λem=380-420 nm), and Peak B (λex=~275 nm; λem=~310-320 nm).

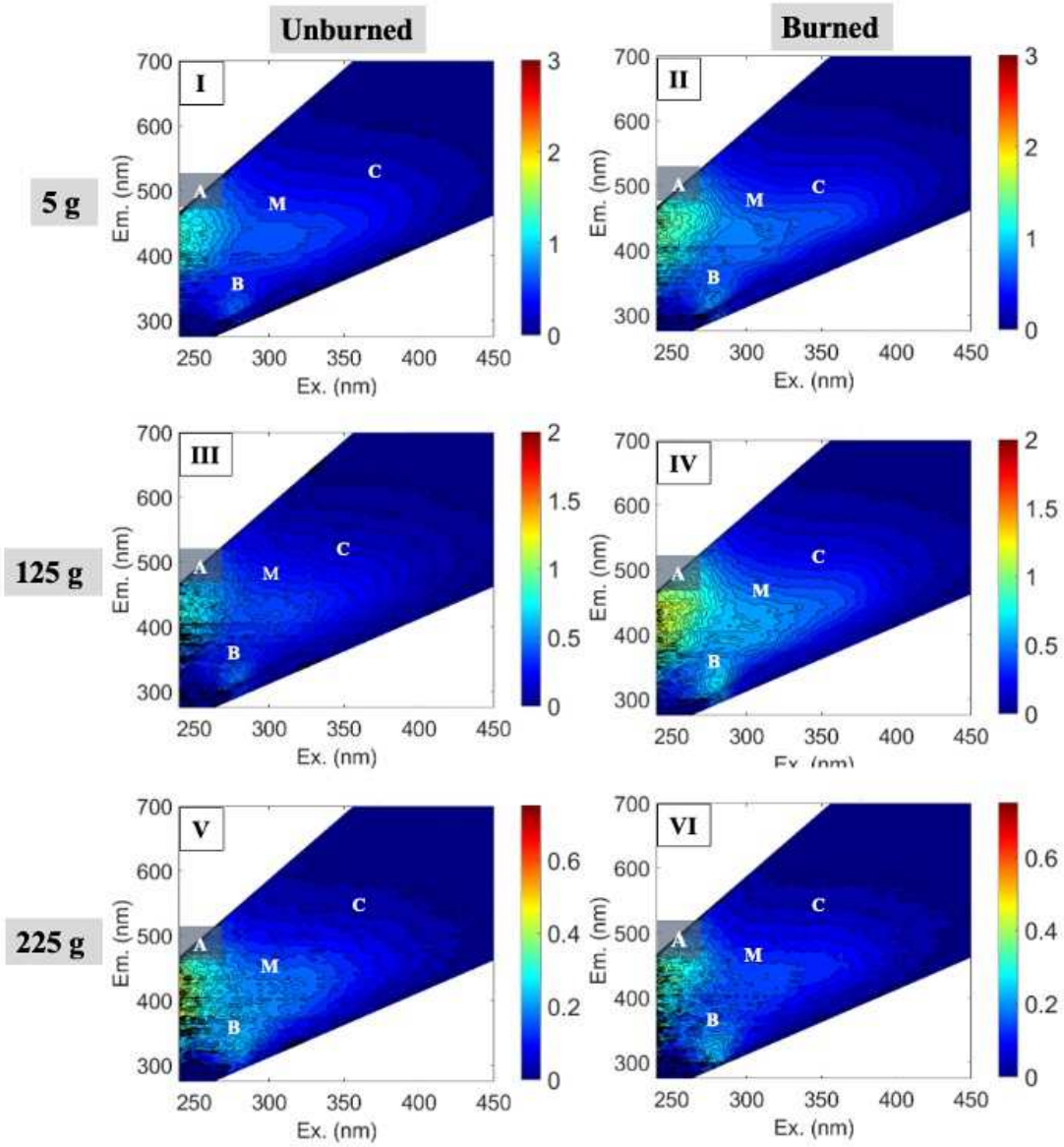

Figure. S2 Six Excitation-Emission Matrices (EEMs) showing fluorescence of dissolved organic carbon (DOC) at Day 59: Panel A = 5g, unburned; Panel B = 5g, burned; Panel C = 125g, unburned; Panel D = 125g, burned; Panel E = 225g, unburned; Panel F = 225g, burned. Note, the presence or absence of fluorescence peaks, intensity of fluorescence response, and shifts in peak maxima have all been shown to provide information about DOC character and origin. Peak A (λex=~250 nm; λem=380-460 nm), Peak C (λex=~405 nm; λem= 490-510 nm), Peak M (λex=~312 nm; λem=380-420 nm), and Peak B (λex=~275 nm; λem=~310-320 nm).

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