

Spatiotemporal controls on the delivery of dissolved organic matter to streams following a wildfire

Jesse Alan Roebuck¹, Kevin D Bladon², David Donahue³, Emily B Graham¹, Samantha Grieger⁴, Karl Morgenstern³, Matthew J Norwood⁴, Katherine A Wampler², Lisa Erkert³, Lupita Renteria¹, Robert E. Danczak⁴, Susan Fricke³, and Allison Myers-Pigg¹

¹Pacific Northwest National Laboratory (DOE)

²Oregon State University

³Eugene Water and Electric Board

⁴Pacific Northwest National Laboratory

November 23, 2022

Abstract

Warmer and drier climate has contributed to increased occurrence of large, high severity wildfires in the Pacific Northwest, drawing concerns for water quality and ecosystem recovery. While nutrient fluxes generally increase post-fire, the composition of organic matter (OM) transported to streams immediately following a fire is poorly constrained, yet can play an integral role in downstream water quality and biogeochemistry. Here, we quantified spatiotemporal patterns of dissolved OM (DOM) chemistry for five streams burned by wildfires in Oregon, USA in 2020. We sampled over a 24-hour storm event one month after the fire, revealing variable temporal behavior in DOM dynamics. DOM chemistry was directly related with burn severity spatially. Specifically, nitrogen and aromatic character of DOM increased in streams burned at greater severity. Our results suggest a spatial overprinting of DOM dynamics immediately following fire activity and highlight a key gap in our knowledge of post-fire DOM transport to streams.

Hosted file

essoar.10511361.1.docx available at <https://authorea.com/users/546670/articles/602498-spatiotemporal-controls-on-the-delivery-of-dissolved-organic-matter-to-streams-following-a-wildfire>

Hosted file

roebuck et al_2022_gr1_supporting information.docx available at <https://authorea.com/users/546670/articles/602498-spatiotemporal-controls-on-the-delivery-of-dissolved-organic-matter-to-streams-following-a-wildfire>

Jesse Alan Roebuck, Jr.¹, Kevin D. Bladon², David Donahue³, Emily Graham⁴, Samantha Grieger¹, Karl Morgenstern³, Matthew J. Norwood¹, Katie A. Wampler², Lisa Erkert³, Lupita Renteria⁴, Robert Danczak⁴, Susan Fricke³ and Allison N. Myers-Pigg^{1,5*}

¹Marine and Coastal Research Laboratory, Pacific Northwest National Laboratory, Sequim, WA

²Department of Forest Engineering, Resources, and Management, Oregon State University, Corvallis, OR, USA

³Eugene Water & Electric Board, Eugene, OR, USA

⁴Pacific Northwest National Laboratory, Richland, WA

⁵Department of Environmental Sciences, University of Toledo, Toledo, OH, USA

*Corresponding author: Allison Myers-Pigg (allison.myers-pigg@pnnl.gov)

Key Points:

Dissolved organic carbon concentrations in stream water were driven by local hydrology during the first post-fire storm event.

Burn severity was a primary control on dissolved organic matter composition delivered to streams.

Spatial variation in dissolved organic matter composition in streams overprinted hydrological controls.

Abstract

Warmer and drier climate has contributed to increased occurrence of large, high severity wildfires in the Pacific Northwest, drawing concerns for water quality and ecosystem recovery. While nutrient fluxes generally increase post-fire, the composition of organic matter (OM) transported to streams immediately following a fire is poorly constrained, yet can play an integral role in downstream water quality and biogeochemistry. Here, we quantified the spatiotemporal patterns of dissolved OM (DOM) chemistry for five streams burned by wildfires in Oregon, USA in 2020. We sampled over a 24-hour storm event one month after the fire, revealing variable temporal behavior in DOM dynamics. DOM chemistry was directly related with burn severity spatially. Specifically, nitrogen and aromatic character of DOM increased in streams burned at greater severity. Our results suggest a spatial overprinting of DOM dynamics immediately following fire activity and highlight a key gap in our knowledge of post-fire DOM transport to streams.

Plain Language Summary

Wildfires are increasing in frequency and intensity in the Pacific Northwest. Following a wildfire, rain events can mobilize large amounts of charred material from the ground and transport to local water bodies, thus leaving major concerns for how changes in wildfires will impact local water quality. Our study

aimed to understand how the water quality of small streams that have been impacted by varying degrees of burn severity responds to major storm events immediately following a wildfire. To achieve this objective, we collected water samples throughout a storm event for 24 hours in 1-hour intervals from 5 streams impacted by the 2020 Holiday Farm Fire in Oregon, USA. We found differences in the dissolved materials that were delivered to the streams that was directly related to how severe the fire burned. These results will help improve our understanding of how streams respond to wildfire activity and be able to predict how more frequent and intense fires impact local water quality.

1 Introduction

Fire regimes in the western U.S. are changing, with patterns in burn area and burn severity becoming disconnected from historical fire regimes (Haugo et al., 2019). These shifting fire patterns are of increasing concern for watershed biogeochemical processes when considering the known impacts of wildfire on water quality and aquatic ecosystem health, which can persist for years post-fire (Bladon et al., 2014; Emelko et al., 2016; Niemeyer et al., 2020). The intermediate- and long-term influences of wildfires on water quality are diverse across affected watersheds (Rhoades et al., 2019; Santos et al., 2019; Sherson et al., 2015). Post-fire stream water chemistry, for example, is thought to result from an interplay between biogeochemical and hydrologic processes impacted by fire, such as water availability and soil water repellency (Niemeyer et al., 2020). In fact, the environmental fate of fire-impacted materials—also termed pyrogenic organic matter (PyOM)—is thought to be determined by its first interactions in water post-fire (Masiello & Berhe, 2020). The short-term hydrological response to fires is also regionally dependent. For example, high hydrological connectivity between hillslopes and streams in highland regions of the western U.S. accelerates the delivery of water to streams post-fire (Hallema et al., 2017). This immediate hydrologic response is dependent on a complexity of factors that alter the chemical and physical properties of the watershed soils, including burn severity (Moody et al., 2016).

Shifts in the hydrological response of watersheds post-fire is often accompanied by an immediate increase in the delivery of materials to aquatic systems, seen through increasing in-stream turbidity and elevated nutrient inputs (Dahm et al., 2015). The increased mobilization of materials post-fire is most notable during storm events (Murphy et al., 2012). However, little is known of how storm events alter the mobilization of organic matter to streams post-fire as few studies exist that identify such controls. For example, dissolved organic matter (DOM) exports following a prescribed fire in South Carolina, USA were greatest during the first post-fire storm events, returning to pre-fire concentrations by the fourth storm (Olivares et al., 2019). In unburned watersheds, storm events can also mobilize greater amounts of DOM of varying composition (Fellman et al., 2009; Raymond et al., 2016) due to increased surface runoff and altered hydrologic flow paths (Inamdar et al., 2011), both of which are influenced by wildfires.

The spatial heterogeneity of wildfire impacts within a landscape further complicates our understanding of post-fire hydrological and biogeochemical responses. Wildfires create a mosaic of burn severities upon watersheds, with extremely localized impacts on soil hydrologic properties (McGuire et al., 2018) and alterations in organic matter dynamics (Smithwick et al., 2005). This results in the post-fire transport of materials into streams (McGuire et al., 2021) related not only to burn severity, but also watershed characteristics (Santos et al., 2019). While large rivers generally act as an integrator of catchment-scale processes (Raymond et al., 2016), the redistribution of pyrogenic materials to river corridors is directly related with burn characteristics (Abney et al., 2019; Cotrufo et al., 2016; McGuire et al., 2021). As headwater streams are closely connected to their terrestrial landscapes (Pereira et al., 2014), such systems may experience varying impacts of a single wildfire event through space and time. The impact of wildfires on headwater streams is therefore likely a result of complex interactions between watershed characteristics, wildfire characteristics, and hydrologic responses.

Herein, we aimed to identify short-term spatial and temporal controls on DOM composition in headwater streams during early flushing events following a wildfire in Oregon, USA. We used high resolution sampling (1-hr intervals) across one of the first major storm events following a wildfire in five streams whose drainage areas were engulfed entirely within the burn perimeter. Our study focused on the short-term (storm event occurring post-fire) hydrological response of DOM delivery to streams post-fire, and how those responses varied spatially over gradients of burn severity and catchment characteristics.

2 Materials and Methods

2.1 Watershed and Wildfire Characterization

The McKenzie River Sub-basin (Oregon, USA) drains a land area of 1300 km² and is a primary tributary to the Willamette River within the larger Columbia River basin. Between September and October 2020, the Holiday Farm Fire burned approximately 700 km² of the McKenzie River watershed just east of Eugene, Oregon (Figure S1). Climate in the region is Mediterranean, with dry summers and wet winter seasons with around 150–230 cm of annual precipitation. Steep hillslopes within the burn perimeter averaged ~35° and the soils primarily consisted of weakly developed Inceptisols.

Vegetation data was obtained from the 2018 Oregon Statewide Habitat Map provided by the Oregon Spatial Data Library and credited to the Oregon Biodiversity Information Center, Portland State University (Kagan et al., 2019). Within the burn perimeter, vegetation was predominantly western hemlock (*Tsuga heterophylla*) with some mixed conifer and Douglas-fir (*Pseudotsuga menziesii*) (Table 1).

Table 1: Site characteristics for the five study catchments in the McKenzie River Sub-basin

Site Characteristic	Gate Creek	Bear Creek	Elk Creek	Marten Creek	Simmonds Creek
Area (km ²)	124.7	11.5	14.1	39.4	10.0
Slope (°)	88.0	88.5	88.5	88.2	88.6
Unburned (%)	1.2	0.5	0.03	0.4	0.3
Low Burn Severity (%)	17.5	13	9.7	7.8	10.4
Moderate Burn Severity (%)	65	73.8	70.5	74.5	55
High Burn Severity (%)	16.3	12.9	19.7	17.3	34.3
Young Growth Hemlock (%)	17	5	1	18	5
Medium Growth Hemlock (%)	42	30	16	35	34
Mature Growth Hemlock (%)	10	17	35	15	23
Old Growth Hemlock (%)	10	37	38	13	23
Other (Early Shrub/Conifer) (%)	15	7	3	13	5

Soil burn severity was obtained from the United States Forest Service as a part of the Holiday Farm Burn Area Emergency Response (BAER) assessment ("BAER Imagery Support Data Download," 2020) (Figure S1). Burn severity was designated along a spectrum ranging from light charring of the ground surface (low severity) to the complete consumption of pre-fire ground cover and surface organic matter with visible charring on large roots (high severity). Post fire watershed conditions suggested about 70% of the affected area was burned at moderate to high severity (Table 1).

2.2 Sample Collection and Processing

Five small tributaries to the McKenzie River whose drainage areas were completely engulfed within the burn area were sampled during the first major post-fire precipitation event (52 mm) on November 13, 2020. Yellow Springs Instruments (YSI) EXO2 water quality sondes were installed in stream sections generally representative of the overall flow to quantify turbidity at 10-minute intervals. We also collected stream water samples hourly over a 24-hour period with autosamplers (ISCO3700 or 6712 autosampler, Table S3) into HCl acid cleaned polypropylene bottles. The samples were then passed through a muffled (500 °C, 5 Hours) 0.7 µm Whatman GF/F filter followed by a 0.2 µm Pall Supor Membrane Filter. A small aliquot of filtrate was acidified with 20% phosphoric acid and analyzed for dissolved organic carbon (DOC) as non-purgeable organic carbon and total dissolved nitrogen (TDN) with a Shimadzu TOC-L Total Organic Carbon Analyzer equipped with a Total Nitrogen unit. We acidified 20 mL of the remaining filtrate to pH 2 with concentrated hydrochloric acid and concentrated via solid phase extraction (SPE) as described by Dittmar et al. (2008). Briefly, Bond Elut PPL cartridges were conditioned with methanol followed by pH 2 Milli-Q water. The samples were then loaded onto the cartridge followed by an additional rinse with pH 2 Milli-Q water to remove salts. Finally, the cartridges were vacuum dried followed by sample elution with methanol. Extracts were stored at -80°C until further analysis.

2.3 FTICR-MS Analysis

SPE extracts were analyzed on a 12 Tesla (12T) Bruker Solarix Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) (Bruker, Solarix, Billerica, MA) located at the Environmental Molecular Sciences Laboratory in Richland, WA. Analytical details are available in the Supporting Text S1. Molecular formulae were categorized into the following molecular compound groups as described Seidel et al. (2015) and in more detail in Table S1: (1) condensed aromatics with ≥ 15 C (including black carbon), (2) condensed aromatics with ≥ 15 C and heteroatoms (including black nitrogen), (3) high aromaticity index with <15 C, (4) polyphenol-like (including lignin and tannin-like compounds), (5) polyphenol-like with heteroatoms, (6) highly unsaturated compounds, (7) highly unsaturated compounds with heteroatoms (8) unsaturated aliphatics, (9) unsaturated aliphatics with heteroatoms (including peptide-like compounds), (10) highly saturated compounds with low O/C ratio (including lipid-like compounds), (11) highly saturated compounds with low O/C ratio and containing heteroatoms, (12), highly saturated compounds with high O/C ratio (including carbohydrate-like compounds), and (13), highly saturated compounds with high O/C ratio and heteroatoms (including aminosugars). Molecular formulae were also characterized for their elemental composition that included carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S).

2.4 Statistical Analyses

Multivariate statistical analyses were performed within the R statistical platform version 4.0.5 (R Core Team, 2015). Non-metric multi-dimensional scaling (NMDS) was used to identify relationships in DOM composition with environmental parameters across sites throughout the sampling campaign. The NMDS was performed with the Vegan package (Okansen et al., 2020) on Bray-Curtis distance matrices for presence-absence transformed FTICR-MS data. Significance was tested across sites at 10,000 permutations via permutation multivariate analysis of variance (PERMANOVA) with the pairwiseAdonis package (Pedro, 2017). Redundancy analysis (RDA) was also performed with the Vegan package (Okansen et al., 2020).

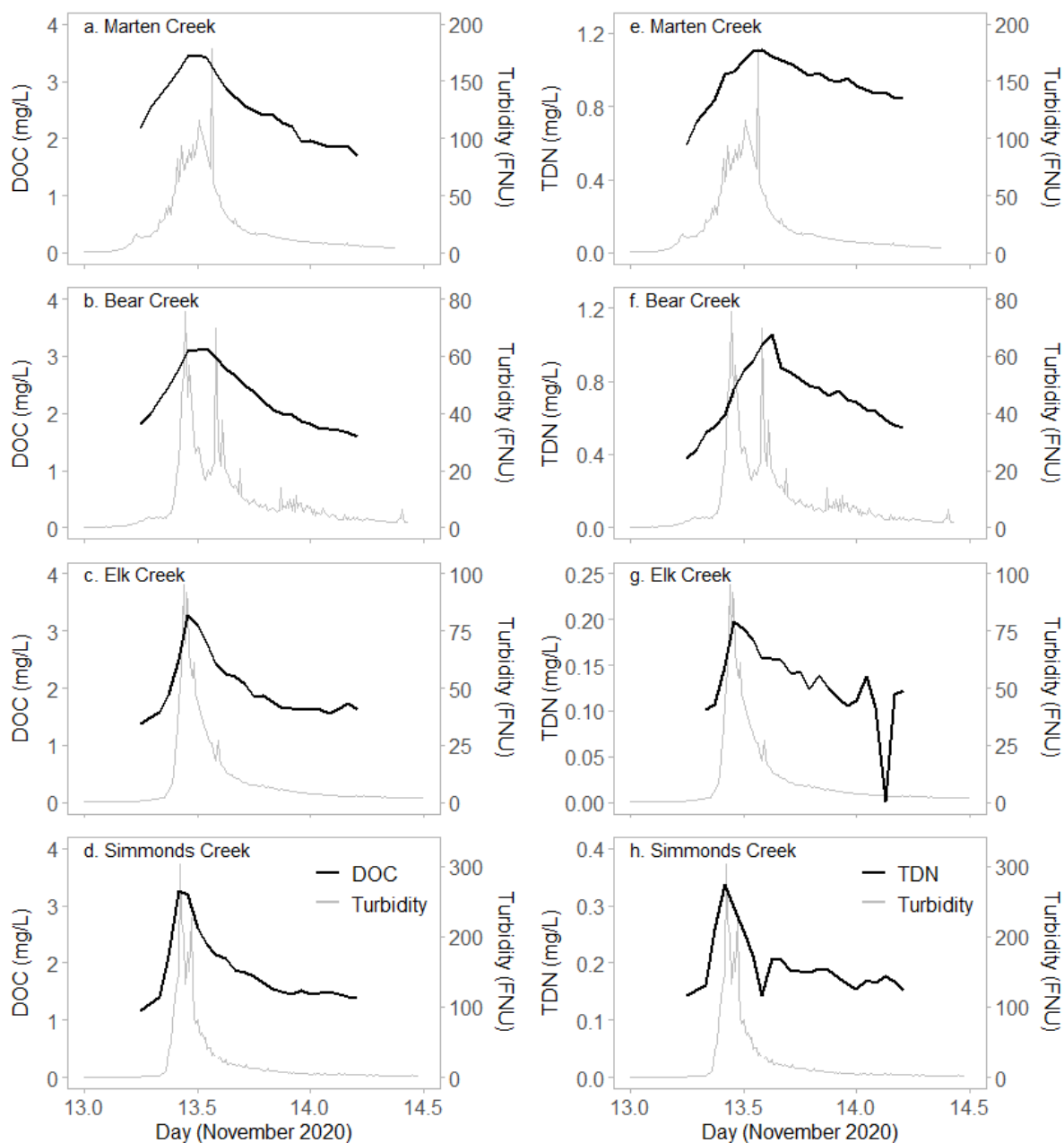
3 Results

Post-fire water quality in the McKenzie River tributaries was spatially reflective of catchment burn severity. Turbidity maximums ranged from 80–300 FNU across all tributaries. We measured the highest turbidity values in Simmonds Creek, which was the most severely burned sub-catchment (Table 1). At all sites, incoming precipitation led to elevated dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) responses. DOC increased from ~ 1.5 to ~ 3 mg C/L at all sites with no apparent differences in peak concentrations (Figure 1a–d). Peak concentrations in TDN, however, were more variable ranging from 0.25 mg N/L in the high burn severity catchments to 1.2 mg N/L in less severely burned catchments (Figure 1e–f). Tight coupling between DOC and turbidity was observed at all sites (Figure S2).

DOM composition, characterized by FTICR-MS, was largely decoupled from

trends in DOC and displayed more complex spatio-temporal heterogeneity. Elemental composition ranged from 55–85% for CHO, 10–35% for CHON, and less than 10% for CHOS and CHONS throughout the dataset (Table S3). Notable molecular compounds groups, such as polycondensed aromatics (group 1) and highly aromatic compounds (group 4) accounted for up to 2.5% and 12% of the identified molecular formulae respectively. Highly unsaturated compounds (group 6) and unsaturated aliphatics (group 9) represented up to 57% and 22.5%, respectively. The elemental composition and molecular compound group time series distributions were highly variable and displayed predominantly chemostatic trends throughout the storm at each of the sites (Figures S3 and S4).

Figure 1: Time series of DOC and turbidity (a-d) for Simmonds Creek, Elk Creek, Bear Creek, Marten Creek and TDN and turbidity (e-h) for those same sites, respectively.



Nonmetric multidimensional scaling (NMDS) derived from the total identified molecular formula across the dataset revealed an overprinting of spatial controls on DOM composition post-fire compared to temporal controls. Two distinct clusters among sites (Figure 2) were identified and generally included sites with elevated proportions of mature forest growth and more severe burn conditions

(Elk and Simmonds Creek). At these sites, the DOM composition generally had elevated proportions of aromatic compounds and N-containing functionality. This is compared to the second cluster, which was represented predominantly by sites with less severe burn conditions (Gate, Marten, and Bear Creek) that were elevated in less aromatic CHO and CHOS type compounds. The role of burn severity and hydrological parameters (e.g., turbidity) as explanatory variables for post-fire DOM composition was explored through constrained ordination (redundancy analysis, Table 2). Collectively, burn severity explained ~30% of DOM composition among the sampling locations while hydrological parameters were not significant ($p > 0.05$). The large proportion of unexplained variability highlights the complex spatio-temporal controls on DOM mobilization to streams immediately following fire activity.

Figure 2: NMDS analysis, illustrating the spatial distribution of DOM quality throughout the McKenzie River catchments that were impacted by the Holiday Farm Fire. FTICR-MS groups are defined in more detail in section 2.3 and Table S1.

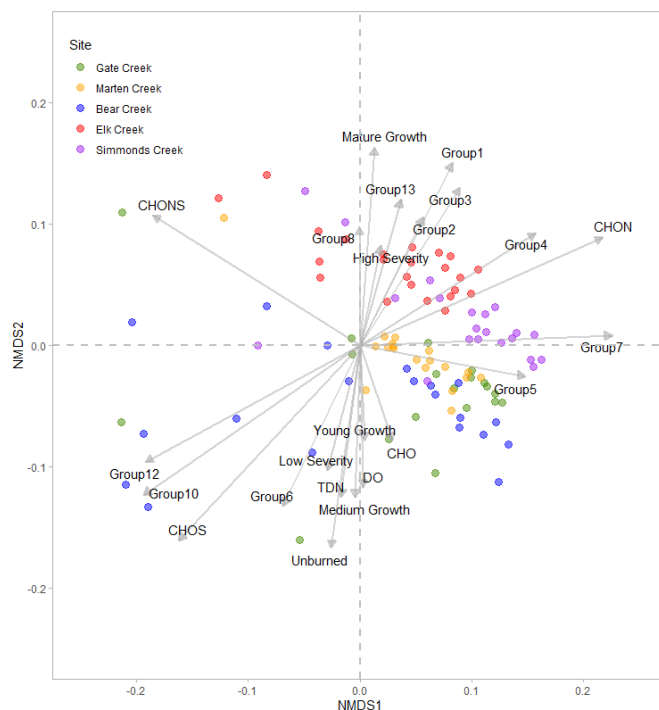


Table 2: Redundancy analysis results of FTICR-MS data for burn severity.

	Inertia	Proportion
Total	11.000	1.000
Constrained	3.277	0.298
Unconstrained	7.723	0.702

	Df	Variance	F	Pr (>F)
Unburned	1	0.154	2.054	0.094
Low Burn Severity	1	0.303	4.041	0.008
Moderate Burn Severity	1	2.496	33.285	0.001
High Burn Severity	1	0.324	4.316	0.005
Residual	103	7.724		

4 Discussion

4.1 Post-fire controls on stream water quality

Wildfires significantly impact water quality by altering water pathways and the transport of organic nutrients to streams. In the monitored McKenzie River sub-catchments, DOC concentrations peaked during the storm around ~3 mg/L. In contrast, peak TDN concentrations were more variable and related with burn severity. More severely burned catchments (Elk Creek and Simmonds Creek) peaked at ~0.3 mg/L whereas less severely burned catchments (Gate Creek, Marten Creek, and Bear Creek) peaked at ~1.1 mg/L. The DOC and TDN were each tightly coupled with turbidity (Figure S2). It is characteristic in the Western Cascades that with incoming precipitation, primary nutrient sources shift from deeper groundwater to subsurface pathways through organic rich surface horizons, which can lead to elevated nutrient concentrations (Hood et al., 2006; Tague et al., 2008). However, wildfires are destructive to surface organic layers and inhibit water infiltration into soils through pore clogging and increased surface hydrophobicity, leading to elevated surface runoff in streams in the short-term following fire activity (Cerdà & Robichaud, 2009). Thus, the tight coupling of DOC and TDN with turbidity at these sites suggest the elevated concentrations observed are most likely derived from mobilized surficial materials generated from post-fire runoff and erosion.

While DOC concentrations increased during the storm, concentrations were comparatively low with respect to regional observations for unburned forests in the region. For example, DOC concentrations typically exceed 6 mg/L at peak flow during autumn storms in neighboring WS10 within HJ Andrews (van Verveveld et al., 2009), located approximately 40 km from our burn sites. The lower observed DOC can be explained by the loss and transformation of surface soils to more refractory charred materials during the wildfire, which leaves a less soluble pool of OC available to streams post-fire (Bostick et al., 2018; Santín et al., 2016). While we recognize a directly comparable reference site is not available for this study, the lower DOC concentrations compared to historical records for the region are consistent with other studies that report lower stream DOC concentrations post-fire (Rodríguez-Cardona et al., 2020; Santos et al., 2019).

For TDN, the lower concentrations in the more severely burned catchments were unexpected. It is often reported that N concentrations peak following severe fire

activity, which is often attributed to increased nitrification and mineralization of soil organic N. However, these processes can take months after a fire before being significantly stimulated (Covington & Sackett, 1992) with nitrate, for example, often reported to peak around 1–2 years post-fire (Bladon et al., 2008; Santos et al., 2019). We note that our study was conducted roughly 1 month following the Holiday Farm Fire, and thus we suspected that our observations for TDN is again reflective of severe transformations in surface organic horizons that leave less nitrogen available for transport to the streams immediately post-fire (Boby et al., 2010). This hypothesis should be confirmed with future studies that more directly quantifies nutrient concentrations in streams post-fire in relation to availability in surface soils.

4.2 Post-fire controls on DOM composition

At each of the five streams sampled, DOM composition measured by FTICR-MS was largely decoupled from DOC concentration shifts. Contrary to the observed DOC concentrations, the proportion of CHO and CHON type compounds showed no clear temporal trends and were not correlated with turbidity at any of the sites (Figure S3). Similarly, when assigning FTICR-MS molecular formula into groups based on perceived DOM functionalities (See section 2.3), these groups also showed no clear hydrogeological trends at any of the sites (Figure S4). Admittedly, these trends were largely unexpected. DOM compositional trends are often well correlated with DOC across hydrological gradients as sources shift from DOC poor groundwater at baseflow to aromatic DOC rich sources mobilized from surficial pathways at peak flow (Stutter et al., 2012). Molecular scale trends in small streams identified by FTICR-MS further link the flushing of highly aromatic compounds from surficial pathways during storm events (Wagner et al., 2019). In fire impacted systems, the export of pyrogenic materials following a wildfire is also linked with hydrological processes (Myers-Pigg et al., 2017; Roebuck Jr. et al., 2018; Wagner et al., 2015). As observed in the present study, however, short-term impacts of fire within the catchment add significant complexity to the interpretation of DOM transport processes across hydrological gradients at each site. This is consistent with other studies, for example, that have also reported a decoupling of bulk DOC and fire-impacted DOC export (Myers-Pigg et al., 2017; Roebuck et al., 2018). Pyrogenic materials can easily be redistributed following a fire, and precipitation is a key driver in this process (Bellè et al., 2021; Masiello & Berhe, 2020; Moody & Martin, 2001). Our results strongly support through linkages with turbidity that DOC is made available for transport in this post-fire system through the dissolution and mobilization of particles via surface runoff, which has been observed in other systems where storm pulses contribute to increased DOC through dissolution of particles transported during rain events (Jung et al., 2014). As the storm in the current study represent the first major flush, occurring roughly one month following the Holiday Farm Fire, we suspect the heterogeneity of easily redistributed charred materials mobilized to the stream likely explain the significant degree of DOM compositional complexity and decoupling with bulk DOC concentration in this system.

Despite the high degree of temporal complexity observed at each of the five streams, when assessed holistically across the whole sample set, we found that DOM composition was most reflective of spatially distinct catchment features. NMDS analysis based on the DOM molecular formula revealed all samples collected throughout the storm were split into two clusters that represent a clear separation based on forest stand and burn severity within each catchment (Figure 2). Simmonds Creek and Elk Creek notably cluster together differentiating themselves as a region within the burn perimeter where the high proportion of mature forest stands was likely a catalyst for more severe fire activity. As such, these sites saw elevated proportions of highly aromatic and polycondensed aromatic molecular formula in addition to elevated proportions of N-containing compounds. These observations are in comparison to the remaining three sites (Gate Creek, Marten Creek, and Bear Creek) whose molecular make-up was elevated in less aromatic (e.g., unsaturated aliphatic) type compounds. It is important to note the contrast for this group where burn severity was relatively less severe in these catchments (Table 1). The observed spatial differences in DOM composition however are consistent with our expectations based on the known evolution of pyrogenic organic matter chemistries along temperature gradients, most specifically with the generation of polycyclic aromatic hydrocarbons at high temperatures in addition to the release of more soluble and bioavailable byproducts at lower temperatures (Bostick et al., 2021; Masiello, 2004; Norwood et al., 2013; Wagner et al., 2018). Previous studies have indicated, for example, that highly aromatic compounds account for up to 60% of the functionality in sediments impacted by high burn severities (Knicker et al., 2006; Mastrolonardo et al., 2015; Miesel et al., 2015; Nave et al., 2011). Furthermore, the increase in N-containing molecular formulae at higher temperatures can also be explained via this temperature evolution as amide-N can be directly converted into pyrogenic nitrogen. Coupled with the selective loss of unstable carbonaceous species (e.g., cellulose) at higher combustion temperatures, charred materials will often have a lower C:N ratio compared to their original source material (Knicker, 2010). This is further transcribed into the dissolved phase where elevated N-containing compounds have been observed in high temperature char leachates compared to the leachates of lower temperature chars (Wozniak et al., 2020).

Collectively, our results suggested that the spatial complexity in burn characteristics (e.g., burn severity) and catchment physiography masked the influence of hydrological gradients on the quality of DOM delivered to streams. For instance, redundancy analysis showed that burn severity alone explained ~30% of the variability in DOM composition. Comparatively, hydrologically related indices (e.g., turbidity) were not significantly related to DOM composition. The composition of eroded material from catchments burned at high severity are often preferentially enriched with pyrogenic carbon (Abney et al., 2019) and the heterogeneity of this pyrogenic material is likely a primary factor in the quality of DOM leached and transported in these streams during storm events. Catchment geomorphology, including soil type and slope steepness, as well as climatic variables (e.g., aridity) can further dictate the redistribution and trans-

port of pyrogenic material postfire (Abney et al., 2019; Bellè et al., 2021; Rust et al., 2019). We emphasize that the close proximity of our sampling locations allows us to study fire related controls on stream DOM quality outside of these typical geomorphological constraints. Thus, these results highlight that at localized scales absent of major geomorphological variations, burn severity is a major control on the quality of DOM available and delivered to streams post-fire.

5 Implications

The data presented suggest a complex interplay across spatial and temporal scales that govern the quality of organic materials delivered to streams immediately following a wildfire. The fate of pyrogenic materials is directly linked with its first interactions with the hydrological cycle (Masiello et al., 2020) and the ease of redistribution and composition of pyrogenic materials are directly related with burn characteristics following a fire (Abney et al., 2019; Cotrufo et al., 2016). Our results highlight this transferability into organic materials solubilized and delivered to streams post-fire. DOC concentrations were strongly linked with hydrological processes and the delivery of surface particles during the storm, yet the composition delivered was strongly governed spatially by burn severity among sampled catchments. As wildfires burn greater area and become more severe in the Western United States (Abatzoglou et al., 2021), concerns over the quality of DOM delivered to streams post-fire will continue to increase. For instance, the interactivity of highly aromatic compounds generated at high burn severity with heavy metals and pollutants can pose challenges for downstream water quality (McIntyre & Guéguen, 2013; Yamashita & Jaffé, 2008). Furthermore, the high variability in pyrogenic constituents generated across burn severities may have significant short- and long-term implications for aquatic hydrobiogeochemical processes. Highly aromatic compounds are strong light attenuators and can have significant implications for instream autotrophic activity (Cory et al., 2015; Creed et al., 2018; Zhang et al., 2007), whereas pyrogenic materials generated at low temperatures can be more directly utilized in microbial mediated processes in-stream (Myers-Pigg et al., 2015; Norwood et al., 2013). Finally, the incorporation of fire impacts in multiscale models to make predictive understanding of disturbances on terrestrial-aquatic hydrobiogeochemical processes requires short- and long-term analyses. Studies on the hydrological transport of DOM and dissolved PyOM in burned watersheds typically occur long after the first storm flush event (Myers-Pigg et al., 2017; Roebuck et al., 2018; Wagner et al., 2015) at which point pyrogenic materials have become more directly integrated in soil structures and export becomes disconnected from time since fire within the catchment (Ding et al., 2013). The high spatio-temporal variability in DOM composition observed following the Holiday Farm Fire highlights a significant short term-complexity in aquatic biogeochemical responses post-fire that likely evolves with ecosystem recovery and time since fire. Thus, to better represent disturbance impacts on aquatic biogeochemical cycles in multiscale models, future efforts should continue to address the immediate response of DOM chemistries in fire-impacted systems while also aiming to assess the evolution of these responses with ecosystem recovery.

Acknowledgments

This research was supported by the U.S. Department of Energy (DOE), Office of Biological and Environmental Research (BER), as part of BER’s Subsurface Biogeochemical Research Program’s Science Focus Area (SFA) at the Pacific Northwest National Laboratory (PNNL). A portion of this research was performed at the Environmental Molecular Science Laboratory (EMSL) User Facility. PNNL is operated for DOE by Battelle under Contract DE-AC06-76RLO 1830.

Open Research

All data used to support this manuscript is available in the Supporting Information. Individual sample IGSNs are provided in Table S3. A comprehensive data package is in preparation and will be made publicly available through ESS-DIVE prior to publication. A DOI for this data package will be provided with revisions.

References

- Abatzoglou, J. T., Juang, C. S., Williams, A. P., Kolden, C. A., & West-
erling, A. L. (2021). Increasing Synchronous Fire Danger in Forests of the
Western United States. *Geophysical Research Letters*, 48(2), e2020GL091377.
<https://doi.org/10.1029/2020GL091377>
- Abney, R. B., Kuhn, T. J., Chow, A., Hockaday, W., Fogel, M. L., & Berhe,
A. A. (2019). Pyrogenic carbon erosion after the Rim Fire, Yosemite National
Park: The Role of Burn Severity and Slope. *Journal of Geophysical Research:
Biogeosciences*, 124(2), 432-449. <https://doi.org/10.1029/2018JG004787>
- BAER Imagery Support Data Download. (2020). Retrieved from
<https://burnseverity.cr.usgs.gov/baer/baer-imagery-support-data-download>
(Last Accessed: 2022-05-06)
- Bellè, S. L., Berhe, A. A., Hagedorn, F., Santin, C., Schiedung, M., van
Meerveld, I., & Abiven, S. (2021). Key drivers of pyrogenic carbon redistri-
bution during a simulated rainfall event. *Biogeosciences*, 18(3), 1105-1126.
<https://doi.org/10.5194/bg-18-1105-2021>
- Bladon, K. D., Emelko, M. B., Silins, U., & Stone, M. (2014). Wildfire and the
Future of Water Supply. *Environmental Science & Technology*, 48(16), 8936-
8943. <https://doi.org/10.1021/es500130g>
- Bladon, K. D., Silins, U., Wagner, M. J., Stone, M., Emelko, M. B., Mendoza,
C. A., et al. (2008). Wildfire impacts on nitrogen concentration and production
from headwater streams in southern Alberta’s Rocky Mountains. *Canadian
Journal of Forest Research*, 38(9), 2359-2371. <https://doi.org/10.1139/x08-071>
- Boby, L. A., Schuur, E. A. G., Mack, M. C., Verbyla, D., & Johnstone,
J. F. (2010). Quantifying fire severity, carbon, and nitrogen emis-

- sions in Alaska's boreal forest. *Ecological Applications*, 20(6), 1633-1647. <https://doi.org/10.1890/08-2295.1>
- Bostick, K. W., Zimmerman, A. R., Goranov, A. I., Mitra, S., Hatcher, P. G., & Wozniak, A. S. (2021). Biolability of Fresh and Photodegraded Pyrogenic Dissolved Organic Matter From Laboratory-Prepared Chars. *Journal of Geophysical Research: Biogeosciences*, 126(5), e2020JG005981. <https://doi.org/10.1029/2020JG005981>
- Bostick, K. W., Zimmerman, A. R., Wozniak, A. S., Mitra, S., & Hatcher, P. G. (2018). Production and Composition of Pyrogenic Dissolved Organic Matter From a Logical Series of Laboratory-Generated Chars. *Frontiers in Earth Science*, 6. Original Research. <https://doi.org/10.3389/feart.2018.00043>
- Cerdà, A., & Robichaud, P. R. (2009). Fire Effects on Soil Infiltration. In A. Cerdà & P. R. Robichaud (Eds.), *Fire Effects on Soils and Restoration Strategies* (pp. 81-103). Boca Raton, FL: Taylor & Francis Group.
- Cory, R. M., Harrold, K. H., Neilson, B. T., & Kling, G. W. (2015). Controls on dissolved organic matter (DOM) degradation in a headwater stream: the influence of photochemical and hydrological conditions in determining light-limitation or substrate-limitation of photo-degradation. *Biogeosciences*, 12(22), 6669-6685. <https://doi.org/10.5194/bg-12-6669-2015>
- Cotrufo, M. F., Boot, C. M., Kampf, S., Nelson, P. A., Brogan, D. J., Covino, T., et al. (2016). Redistribution of pyrogenic carbon from hillslopes to stream corridors following a large montane wildfire. *Global Biogeochemical Cycles*, 30(9), 1348-1355. <https://doi.org/10.1002/2016GB005467>
- Covington, W. W., & Sackett, S. S. (1992). Soil mineral nitrogen changes following prescribed burning in ponderosa pine. *Forest Ecology and Management*, 54(1), 175-191. [https://doi.org/10.1016/0378-1127\(92\)90011-W](https://doi.org/10.1016/0378-1127(92)90011-W)
- Creed, I. F., Bergström, A.-K., Trick, C. G., Grimm, N. B., Hessen, D. O., Karlsson, J., et al. (2018). Global change-driven effects on dissolved organic matter composition: Implications for food webs of northern lakes. *Global Change Biology*, 24(8), 3692-3714. <https://doi.org/10.1111/gcb.14129>
- Dahm, C. N., Candelaria-Ley, R. I., Reale, C. S., Reale, J. K., & Van Horn, D. J. (2015). Extreme water quality degradation following a catastrophic forest fire. *Freshwater Biology*, 60(12), 2584-2599. <https://doi.org/10.1111/fwb.12548>
- Ding, Y., Yamashita, Y., Dodds, W. K., & Jaffé, R. (2013). Dissolved black carbon in grassland streams: Is there an effect of recent fire history? *Chemosphere*, 90(10), 2557-2562. <https://doi.org/10.1016/j.chemosphere.2012.10.098>
- Dittmar, T., Koch, B., Hertkorn, N., & Kattner, G. (2008). A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnology and Oceanography: Methods*, 6(6), 230-235. <https://doi.org/10.4319/lom.2008.6.230>

Emelko, M. B., Stone, M., Silins, U., Allin, D., Collins, A. L., Williams, C. H. S., et al. (2016). Sediment-phosphorus dynamics can shift aquatic ecology and cause downstream legacy effects after wildfire in large river systems. *Global Change Biology*, 22(3), 1168-1184. <https://doi.org/10.1111/gcb.13073>

Fellman, J. B., Hood, E., Edwards, R. T., & D'Amore, D. V. (2009). Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. *Journal of Geophysical Research: Biogeosciences*, 114(G1). <https://doi.org/10.1029/2008JG000790>

Hallema, D. W., Sun, G., Bladon, K. D., Norman, S. P., Caldwell, P. V., Liu, Y., & McNulty, S. G. (2017). Regional patterns of postwildfire streamflow response in the Western United States: The importance of scale-specific connectivity. *Hydrological Processes*, 31(14), 2582-2598. <https://doi.org/10.1002/hyp.11208>

Haugo, R. D., Kellogg, B. S., Cansler, C. A., Kolden, C. A., Kemp, K. B., Robertson, J. C., et al. (2019). The missing fire: quantifying human exclusion of wildfire in Pacific Northwest forests, USA. *Ecosphere*, 10(4), e02702. <https://doi.org/10.1002/ecs2.2702>

Hood, E., Gooseff, M. N., & Johnson, S. L. (2006). Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. *Journal of Geophysical Research: Biogeosciences*, 111(G1). <https://doi.org/10.1029/2005JG000082>

Inamdar, S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., et al. (2011). Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed. *Journal of Geophysical Research: Biogeosciences*, 116(G3). <https://doi.org/10.1029/2011JG001735>

Jung, B. J., Lee, J. K., Kim, H., & Park, J. H. (2014). Export, biodegradation, and disinfection byproduct formation of dissolved and particulate organic carbon in a forested headwater stream during extreme rainfall events. *Biogeosciences*, 11(21), 6119-6129. <https://doi.org/10.5194/bg-11-6119-2014>

Kagan, J., Zaret, K., Bernert, J., & Henderson, E. (Cartographer). (2019). Oregon Statewide Habitat Map - 2018. Retrieved from <https://spatialdata.oregonexplorer.info/geoportal/details;id> (Last Accessed: 2022-05-06)

Knicker, H. (2010). "Black nitrogen" – an important fraction in determining the recalcitrance of charcoal. *Organic Geochemistry*, 41(9), 947-950. <https://doi.org/10.1016/j.orggeochem.2010.04.007>

Knicker, H., Almendros, G., González-Vila, F. J., González-Pérez, J. A., & Polvillo, O. (2006). Characteristic alterations of quantity and quality of soil organic matter caused by forest fires in continental Mediterranean ecosystems: a solid-state ¹³C NMR study. *European Journal of Soil Science*, 57(4), 558-569. <https://doi.org/10.1111/j.1365-2389.2006.00814.x>

- Masiello, C. A. (2004). New directions in black carbon organic geochemistry. *Marine Chemistry*, 92(1), 201-213. <https://doi.org/10.1016/j.marchem.2004.06.043>
- Masiello, C. A., & Berhe, A. A. (2020). First interactions with the hydrologic cycle determine pyrogenic carbon's fate in the Earth system. *Earth Surface Processes and Landforms*, 45(10), 2394-2398. <https://doi.org/10.1002/esp.4925>
- Mastrolonardo, G., Rumpel, C., Forte, C., Doerr, S. H., & Certini, G. (2015). Abundance and composition of free and aggregate-occluded carbohydrates and lignin in two forest soils as affected by wildfires of different severity. *Geoderma*, 245-246, 40-51. <https://doi.org/10.1016/j.geoderma.2015.01.006>
- McGuire, L. A., Rasmussen, C., Youberg, A. M., Sanderman, J., & Fenerty, B. (2021). Controls on the Spatial Distribution of Near-Surface Pyrogenic Carbon on Hillslopes 1 Year Following Wildfire. *Journal of Geophysical Research: Earth Surface*, 126(6), e2020JF005996. <https://doi.org/10.1029/2020JF005996>
- McGuire, L. A., Rengers, F. K., Kean, J. W., Staley, D. M., & Mirus, B. B. (2018). Incorporating spatially heterogeneous infiltration capacity into hydrologic models with applications for simulating post-wildfire debris flow initiation. *Hydrological Processes*, 32(9), 1173-1187. <https://doi.org/10.1002/hyp.11458>
- McIntyre, A. M., & Guéguen, C. (2013). Binding interactions of algal-derived dissolved organic matter with metal ions. *Chemosphere*, 90(2), 620-626. <https://doi.org/10.1016/j.chemosphere.2012.08.057>
- Miesel, J. R., Hockaday, W. C., Kolka, R. K., & Townsend, P. A. (2015). Soil organic matter composition and quality across fire severity gradients in coniferous and deciduous forests of the southern boreal region. *Journal of Geophysical Research: Biogeosciences*, 120(6), 1124-1141. <https://doi.org/10.1002/2015JG002959>
- Moody, J. A., Ebel, B. A., Nyman, P., Martin, D. A., Stoof, C., & McKinley, R. (2016). Relations between soil hydraulic properties and burn severity. *International Journal of Wildland Fire*, 25(3), 279-293. <https://doi.org/10.1071/WF14062>
- Moody, J. A., & Martin, D. A. (2001). Initial hydrologic and geomorphic response following a wildfire in the Colorado Front Range. *Earth Surface Processes and Landforms*, 26(10), 1049-1070. <https://doi.org/10.1002/esp.253>
- Murphy, S. F., McCleskey, R. B., & Writer, J. H. (2012). Effects of flow regime on stream turbidity and suspended solids after wildfire, Colorado Front Range. In M. Stone, A. Collins, & M. Thoms (Eds.), *Wildfire and Water Quality: Processes, Impacts and Challenges* (Vol. 354, pp. 51-58). Wallingford, United Kingdom: International Association of Hydrological Science.
- Myers-Pigg, A. N., Louchouart, P., Amon, R. M. W., Prokushkin, A., Pierce, K., & Rubtsov, A. (2015). Labile pyrogenic dissolved organic carbon in major Siberian Arctic rivers: Implications for wildfire-

- stream metabolic linkages. *Geophysical Research Letters*, 42(2), 377-385. <https://doi.org/10.1002/2014GL062762>
- Myers-Pigg, A. N., Louchouart, P., & Teisserenc, R. (2017). Flux of Dissolved and Particulate Low-Temperature Pyrogenic Carbon from Two High-Latitude Rivers across the Spring Freshet Hydrograph. *Frontiers in Marine Science*, 4(38). Original Research. <https://doi.org/10.3389/fmars.2017.00038>
- Nave, L. E., Vance, E. D., Swanston, C. W., & Curtis, P. S. (2011). Fire effects on temperate forest soil C and N storage. *Ecological Applications*, 21(4), 1189-1201. <https://doi.org/10.1890/10-0660.1>
- Niemeyer, R. J., Bladon, K. D., & Woodsmith, R. D. (2020). Long-term hydrologic recovery after wildfire and post-fire forest management in the interior Pacific Northwest. *Hydrological Processes*, 34(5), 1182-1197. <https://doi.org/10.1002/hyp.13665>
- Norwood, M. J., Louchouart, P., Kuo, L.-J., & Harvey, O. R. (2013). Characterization and biodegradation of water-soluble biomarkers and organic carbon extracted from low temperature chars. *Organic Geochemistry*, 56, 111-119. <https://doi.org/10.1016/j.orggeochem.2012.12.008>
- Okansen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., et al. (2020). *Vegan: Community Ecology Package*. Retrieved from: <https://cran.r-project.org>
- Olivares, C. I., Zhang, W., Uzun, H., Erdem, C. U., Majidzadeh, H., Trettin, C., et al. (2019). Optical in-situ sensors capture dissolved organic carbon (DOC) dynamics after prescribed fire in high-DOC forest watersheds. *International Journal of Wildland Fire*, 28(10), 761-768. <https://doi.org/10.1071/WF18175>
- Pedro, M. A. (2017). *Pairwise Multilevel Comparison using Adonis*. Version 0.4. Retrieved from <https://github.com/pmartinezarbizu/pairwiseAdonis> (Last Accessed: 2022-05-06)
- Pereira, R., Isabella Bovolenta, C., Spencer, R. G. M., Hernes, P. J., Tipping, E., Vieth-Hillebrand, A., et al. (2014). Mobilization of optically invisible dissolved organic matter in response to rainstorm events in a tropical forest headwater river. *Geophysical Research Letters*, 41(4), 1202-1208. <https://doi.org/10.1002/2013GL058658>
- R. Core Team (2015). R: A Language and Environment for Statistical Computing. Retrieved from <https://cran.r-project.org/>
- Raymond, P. A., Saiers, J. E., & Sobczak, W. V. (2016). Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept. *Ecology*, 97(1), 5-16. <https://doi.org/10.1890/14-1684.1>
- Rhoades, C. C., Chow, A. T., Covino, T. P., Fegley, T. S., Pierson, D. N., & Rhea, A. E. (2019). The Legacy of a Severe Wildfire on Stream Nitrogen and Carbon in Headwater Catchments. *Ecosystems*, 22(3), 643-657.

<https://doi.org/10.1007/s10021-018-0293-6>

Rodríguez-Cardona, B. M., Coble, A. A., Wymore, A. S., Kolosov, R., Podgorski, D. C., Zito, P., et al. (2020). Wildfires lead to decreased carbon and increased nitrogen concentrations in upland arctic streams. *Scientific Reports*, 10(1), 8722. <https://doi.org/10.1038/s41598-020-65520-0>

Roebuck Jr., J. A., Medeiros, P. M., Letourneau, M. L., & Jaffé, R. (2018). Hydrological Controls on the Seasonal Variability of Dissolved and Particulate Black Carbon in the Altamaha River, GA. *Journal of Geophysical Research: Biogeosciences*, 123(9), 3055-3071. <https://doi.org/10.1029/2018JG004406>

Rust, A. J., Saxe, S., McCray, J., Rhoades, C. C., & Hogue, T. S. (2019). Evaluating the factors responsible for post-fire water quality response in forests of the western USA. *International Journal of Wildland Fire*, 28(10), 769-784. <https://doi.org/10.1071/WF18191>

Santín, C., Doerr, S. H., Merino, A., Bryant, R., & Loader, N. J. (2016). Forest floor chemical transformations in a boreal forest fire and their correlations with temperature and heating duration. *Geoderma*, 264, 71-80. <https://doi.org/10.1016/j.geoderma.2015.09.021>

Santos, F., Wymore, A. S., Jackson, B. K., Sullivan, S. M. P., McDowell, W. H., & Berhe, A. A. (2019). Fire severity, time since fire, and site-level characteristics influence streamwater chemistry at baseflow conditions in catchments of the Sierra Nevada, California, USA. *Fire Ecology*, 15(1), 3. <https://doi.org/10.1186/s42408-018-0022-8>

Seidel, M., Yager, P. L., Ward, N. D., Carpenter, E. J., Gomes, H. R., Krusche, A. V., et al. (2015). Molecular-level changes of dissolved organic matter along the Amazon River-to-ocean continuum. *Marine Chemistry*, 177, 218-231. <https://doi.org/10.1016/j.marchem.2015.06.019>

Sherson, L. R., Van Horn, D. J., Gomez-Velez, J. D., Crossey, L. J., & Dahm, C. N. (2015). Nutrient dynamics in an alpine headwater stream: use of continuous water quality sensors to examine responses to wildfire and precipitation events. *Hydrological Processes*, 29(14), 3193-3207. <https://doi.org/10.1002/hyp.10426>

Smithwick, E. A. H., Mack, M. C., Turner, M. G., Chapin, F. S., Zhu, J., & Balser, T. C. (2005). Spatial Heterogeneity and Soil Nitrogen Dynamics in a Burned Black Spruce Forest Stand: Distinct Controls at Different Scales. *Biogeochemistry*, 76(3), 517-537. <https://doi.org/10.1007/s10533-005-0031-y>

Stutter, M. I., Dunn, S. M., & Lumsdon, D. G. (2012). Dissolved organic carbon dynamics in a UK podzolic moorland catchment: linking storm hydrochemistry, flow path analysis and sorption experiments. *Biogeochemistry*, 9(6), 2159-2175. <https://doi.org/10.5194/bg-9-2159-2012>

Tague, C., Grant, G., Farrell, M., Choate, J., & Jefferson, A. (2008). Deep groundwater mediates streamflow response to climate warming in the Oregon Cascades. *Climatic Change*, 86(1), 189-210. <https://doi.org/10.1007/s10584-007-9294-8>

- van Verseveld, W. J., McDonnell, J. J., & Lajtha, K. (2009). The role of hillslope hydrology in controlling nutrient loss. *Journal of Hydrology*, 367(3), 177-187. <https://doi.org/10.1016/j.jhydrol.2008.11.002>
- Wagner, S., Cawley, K. M., Rosario-Ortiz, F. L., & Jaffé, R. (2015). In-stream sources and links between particulate and dissolved black carbon following a wildfire. *Biogeochemistry*, 124(1), 145-161. <https://doi.org/10.1007/s10533-015-0088-1>
- Wagner, S., Fair, J. H., Matt, S., Hosen, J. D., Raymond, P., Saiers, J., et al. (2019). Molecular Hysteresis: Hydrologically Driven Changes in Riverine Dissolved Organic Matter Chemistry During a Storm Event. *Journal of Geophysical Research: Biogeosciences*, 124(4), 759-774. <https://doi.org/10.1029/2018JG004817>
- Wagner, S., Jaffé, R., & Stubbins, A. (2018). Dissolved black carbon in aquatic ecosystems. *Limnology and Oceanography Letters*, 3(3), 168-185. <https://doi.org/10.1002/lol2.10076>
- Wozniak, A. S., Goranov, A. I., Mitra, S., Bostick, K. W., Zimmerman, A. R., Schlesinger, D. R., et al. (2020). Molecular heterogeneity in pyrogenic dissolved organic matter from a thermal series of oak and grass chars. *Organic Geochemistry*, 148, 104065. <https://doi.org/10.1016/j.orggeochem.2020.104065>
- Yamashita, Y., & Jaffe., R. (2008) Characterizing the Interactions between Trace Metals and Dissolved Organic Matter Using Excitation-Emission Matrix and Parallel Factor Analysis. *Environmental Science & Technology*. 42(19), 7374-7379. Doi: <https://doi.org/10.102/es801357h>
- Zhang, Y. L., Zhang, E. L., Liu, M. L., Wang, X., & Qin, B. Q. (2007). Variation of chromophoric dissolved organic matter and possible attenuation depth of ultraviolet radiation in Yunnan Plateau lakes. *Limnology*, 8(3), 311-319. <https://doi.org/10.1007/s10201-007-0219-z>