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# Wildfires Alter Forest Watersheds and Threaten Drinking Water Quality

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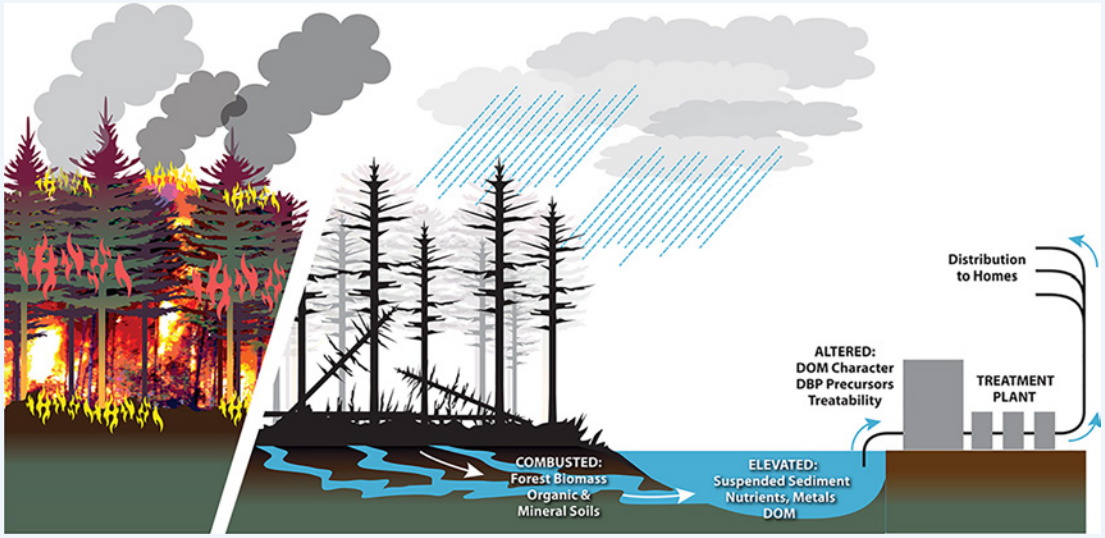


**CONSPECTUS:** Wildfires are a natural part of most forest ecosystems, but due to changing climatic and environmental conditions, they have become larger, more severe, and potentially more damaging. Forested watersheds vulnerable to wildfire serve as drinking water supplies for many urban and rural communities. The highly variable nature of wildfire behavior combined with spatially complex patterns in vegetation, landscape, and hydrologic factors create uncertainty surrounding the postfire effects on water supplies. Wildfires often cause dramatic changes in forest vegetation structure and soil conditions, and alter the watershed processes that control streamflow, soil erosion, nutrient export, and downstream water chemistry. The authors' work centers on field and laboratory studies to advance knowledge of postfire changes in soil and water chemical composition that influence drinking water treatment. High intensity postfire rainstorms typically increase runoff that erodes ash and soil from burned landscapes and dramatically elevates turbidity, nutrient, and dissolved organic carbon (DOC) levels in surface waters, which can cause short-term challenges for water providers. There is also growing evidence that water quality impacts can persist after high severity fires due to slow vegetative recovery, and nitrogen and DOC have remained elevated for 15 years following high severity fire. Low-moderate temperatures during wildfire may also influence water quality. Research by the authors showed that the solubility of organic matter, and C and N released from soils increased following soil heating at temperatures $\leq$ 350 °C. Further, the water extracted organic matter from soils heated at 225−350 °C included higher proportions of condensed aromatic structures, such as black carbon and black nitrogen. Short-term postfire water quality degradation following high intensity rainstorms can force water treatment plants to shut down or can significantly challenge treatment process performance. Extreme turbidity and high DOC in poststorm water, coupled with compositional organic matter changes, reduced the coagulation efficiency of postfire water supplies. Field and lab-based studies documented the formation of small, aromatic soluble compounds during wildfire that contribute to inefficient DOC removal from postfire stormwater. Due to increased postfire DOC concentrations, and poor treatability of poststorm runoff, toxic disinfection

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byproduct (DBP) formation increased during water treatment. Exceedance of drinking water standards for the carbonaceous DBPs, trihalomethanes and haloacetic acids, may present a critical management concern for water providers following wildfires. Further, postfire formation of nitrogen compounds and increased nitrogenous DBP precursors for haloacetonitriles and chloropicrin were discovered. N-DBPs pose a public health concern due to their toxicity, and water providers should be aware of potential increases in N-DBP formation following fire. Evidence from the authors' studies demonstrates that even partially burned watersheds and wildfires burning at moderate temperature can have significant, lasting effects on C and N exports, source water quality, drinking water treatability, and DBP formation. Both short- and long-term postfire water quality impacts can create challenges for drinking water providers as they confront variability in supply and treatability. Communities, forest managers, and potable water providers will need to adapt to more frequent, destructive wildfires and anticipate greater variability in water quality.

## INTRODUCTION

Wildfires are a natural part of most forest ecosystems, but due to changing climatic and environmental conditions, wildfires pose a greater threat to forest watersheds across the United States and globally. Higher temperatures and prolonged droughts have extended fire season lengths worldwide during recent decades and generated larger, more severe wildfires.[1,2] A century of wildfire suppression has increased tree densities[3] and unprecedented levels of tree mortality during recent bark beetle outbreaks[4] have elevated dead fuel loads in many western North American forests. These conditions are aggravated by reduced forest management and growing residential and recreational development within the wildland-urban interface.[5] Furthermore, projected increases in warming and drying are predicted to increase wildfire potential in the United States, South America, Australia, and parts of Asia, Europe, and Africa.[6−8] Recently, wildfires have claimed human lives, destroyed property and infrastructure, and devastated communities in the United States, Europe, and Australia.[9−11] These aggregate changes have prompted a growing awareness of the need for communities, forest managers, and potable water providers to adapt to more destructive wildfires.[12,13]

Forested watersheds vulnerable to wildfire commonly function as drinking water supplies for downstream communities in both rural and urban settings. Wildfires can drastically impact the vegetation, soils and watersheds that regulate significant sources of water supplies for municipal and other uses.[14] Combustion and loss of forest vegetation and organic soil cover during severe wildfires expose soils to short-term (e.g., months) sediment, nutrient, metal and organic matter losses, significantly altering the biogeochemical processes which control water quality.[15−18] Wildfires can also influence water quality over longer time frames (e.g., >10 years) by reducing plant nutrient demand and increasing soil nutrient availability.[19−21] Water quality consequences vary with wildfire behavior (e.g., severity, extent, location) and the physical and hydrologic components of a watershed. Wildfire behavior is a complex response to weather (i.e., wind, temperature, relative humidity), fuel (i.e., amount, spatial arrangement, moisture content) and landscape (i.e., slope gradient and aspect) conditions. These factors influence the combustion temperature, oxygen level and duration, fire rate of spread, degree of canopy and surface fuel consumption, and production of pyrogenic material that all affect how watersheds respond following wildfire. The highly variable nature of wildfire behavior combined with spatially complex patterns in vegetation, landscape, hydrologic, and other factors contribute to large uncertainty surrounding the postfire effects on surface water composition and drinking water treatment.

The wide range of short- and long-term postfire water quality changes can lead to significant challenges for downstream water treatment plants that will have to confront variability in supply and treatability. An assortment of potential postfire water treatment implications may occur and vary in timing and magnitude for individual fires and water systems. Extreme postfire erosion can damage infrastructure, accumulate in reservoirs, and challenge coagulation, filtration, and solids handling processes.[22,23] Elevated nutrients combined with greater light exposure and stream temperatures may lead to postfire algal blooms in reservoirs, which can adversely affect aquatic life, release harmful toxins, and strain water treatment operations.[22,24] Postfire increases in metal concentrations have been documented,[25,26] and may create taste and odor issues, or toxicity concerns. Changes in the quantity and composition of dissolved organic matter (DOM) exported from burned watersheds can influence treatment process performance and the formation of disinfection byproducts (DBPs). DBPs include probable human carcinogens such as trihalomethanes and haloacetic acids, that are regulated by the U.S. Environmental Protection Agency (EPA) in finished water,[27] and currently unregulated nitrogen based DBPs (N-DBPs; e.g., haloacetonitriles). Though general understanding of wildfire effects is advancing, drinking water providers require greater clarity regarding expected magnitude and duration of postfire changes in the chemical composition of source waters to anticipate the consequences of future wildfires. The objective of this paper is to synthesize recent work completed by the authors and other research teams that examines the links between wildfire behavior and postfire soil and water changes that influence water treatment processes and drinking water quality.

## WILDFIRE TRANSFORMATIONS ON THE LANDSCAPE

Wildfire extent and severity, the relative amount of vegetation and organic matter combusted, influence the magnitude and duration of water quality responses. In North American forests, high-severity wildfires combust most vegetation and soil organic layers,[28] and the dramatic changes in forest vegetation structure and soil conditions alter the watershed processes that control streamflow, soil erosion, nutrient export, and downstream water chemistry.[29−31] In contrast, low-severity fire kills few overstory trees and has minimal effect on belowground plant structures, organic soil layers (e.g., litter and duff), and watershed conditions. The vegetation and organic soil[32,33] remaining after less severe wildfires typically limit postfire changes in water quality and facilitate watershed recovery.[34]

Soil heating during wildfires causes physical and chemical changes in soil layers that determine wildfire effects on the



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surrounding ecosystem. For instance, wildfires create a water repellent layer of hydrophobic compounds[35,36] that increase surface runoff.[37] While wildfires may consume organic soil layers, carbon-rich input from charred vegetation can be incorporated into the soil profile.[38] Following fires, ash is the particulate residue composed of mineral and charred organic materials that have been chemically and physically altered during combustion.[39] Ash is readily entrained and mobilized by overland runoff and transported downslope and downstream, impacting water quality.

The authors quantified the relationship between combustion temperature, atmospheric carbon losses, and compositional changes that influence DOM export from organic (O horizon) and mineral (A horizon) soil layers across a range of temperatures (150−550 °C). Soil layers were heated for 2 h under oxic conditions intended to simulate wildfire conditions[40] and to systematically evaluate the effect of temperature on soil properties. In addition to temperature, oxygen availability and duration of heating also vary during wildfires and were considered in work by others.[41] Combustion of C and N increased with heating temperature, and the residual amount in the solid phase decreased (Figure 1). C and N losses from the O horizon occurred at temperatures as low as 150 °C and complete gaseous losses occurred between 450 and 550 °C for both organic and mineral soils. Though soils can exceed 550 °C during wildfires, above this temperature DOM export to surface waters would be minimal.

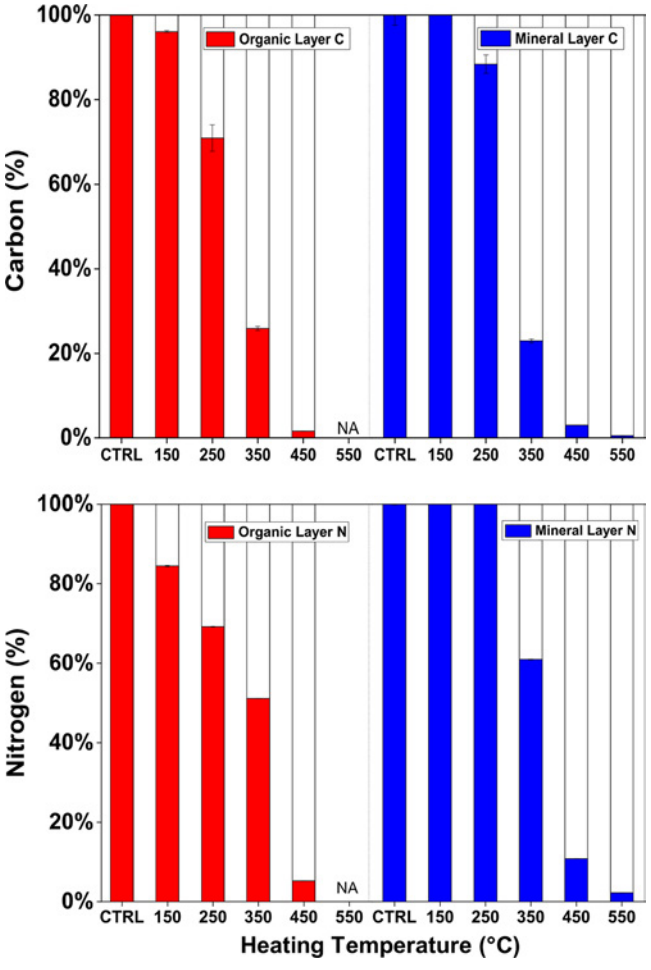


**Figure 1.** Carbon (top panel) and nitrogen (bottom panel) remaining in organic and mineral soil horizons after heating. Soil samples were collected from a watershed west of Boulder, Colorado, USA. CTRL = control.

Of particular interest is the observation that the apparent solubility of the soil organic matter (SOM) increased at low-moderate temperatures (≤350 °C).[42] Water extractable organic C and organic N (i.e., WEOC = DOC/total soil C and WEON = dissolved organic nitrogen (DON)/total soil N, respectively) in mineral soil layers peaked between 250 and 350 °C (Figure 2). Another study performed by Santos et al. observed similar trends where the amount of DOC leached from soils peaked at 250 °C.[43] In the current study, for the organic soil layers, WEOC and WEON decreased dramatically above 150 °C, indicating that in this soil layer water-soluble C and N forms are more susceptible to combustion losses at low temperatures. Overall, these findings suggest that low-moderate temperature heating during wildfires may increase the amount of C and N leached from soils, despite losses to the atmosphere. The increased transport of organic carbon and nitrogen via overland and subsurface flow paths significantly alters downstream water chemistry.

The increased solubility of SOM at low-moderate temperatures could be the aggregate effect of physical changes in soil structure and chemical changes that influence SOM composition. A study by Jian et al.[44] showed that increasing temperature disrupts soil aggregates due to rapid vaporization of pore water, thus exposing physically protected SOM to leaching. However, results from the current study suggest that changes in SOM chemistry are also responsible for enhanced release of DOC and DON from soils after heating.[42] Work by Cawley and co-workers[42] indicates that, after heating soils at 225−350 °C, the water extracted organic matter included higher proportions of condensed aromatic structures, such as black carbon and black nitrogen (Figure 3). Black carbon can form during high temperature biomass combustion and is characterized by a highly condensed aromatic structure.[45] Black carbon exports to surface waters have been observed after wildfires.[46] Black nitrogen is characterized by small, dense, heteroaromatic N compounds that form during the heating and transformation of peptides,[47] and is important to the chemical composition of postfire char.[48] Changes in chemical composition and overall export of DOM from wildfire impacted watersheds can influence water treatment and the reactivity to form DBPs. Although there is still lack of clarity on chemical and physical mechanisms which explain the aforementioned discussion, the variability and range of wildfire impacts on water quality are evidenced by postfire monitoring studies.

## ■ POSTFIRE VARIABILITY IN WATER QUALITY

The landscape, vegetation, and soil changes that determine postfire water quality reflect fire extent, severity, and watershed specific factors. The authors studied the short-term changes in source water quality the first year after the 2012 High Park Fire which burned the Cache la Poudre (CLP) watershed in northern Colorado.[23] The CLP River provides drinking water to over 300 000 municipal consumers and serves as a significant water supply for regional agricultural users. Comparison of streamwater from an unburned, upstream reference site and a municipal water intake within the burned area revealed significant changes following the fire (Figure 4). Turbidity, total phosphorus (TP), and total nitrogen (TN) increased by an order of magnitude the first year following the


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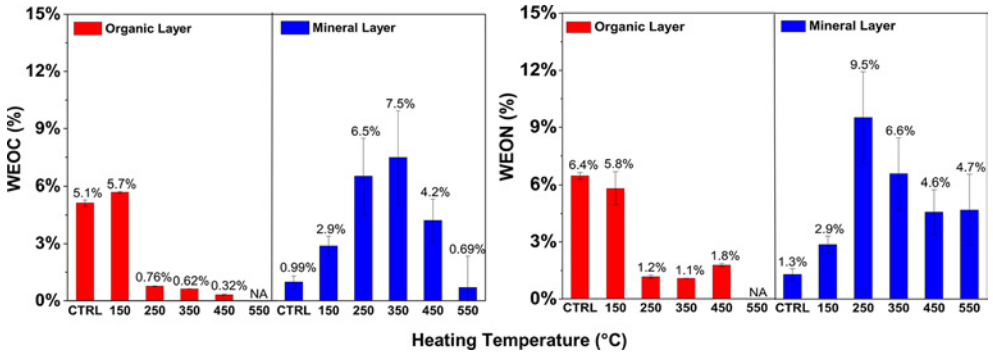


**Figure 2.** Water extractable organic carbon (WEOC, left) and nitrogen (WEON, right) for both organic and mineral soil horizons. The water extractable fraction is calculated from the dissolved organic carbon (DOC) or dissolved organic nitrogen (DON) leached per unit total soil C and N, respectively, remaining after heating. CTRL = control.

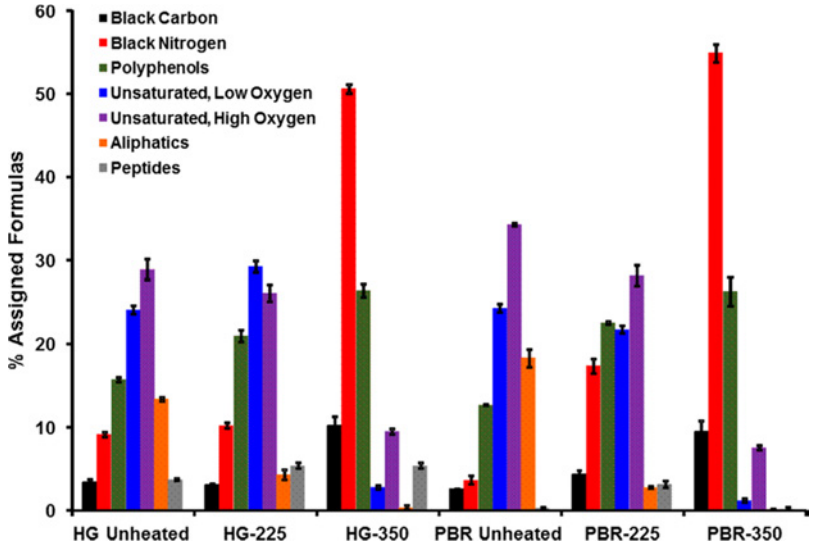


**Figure 3.** High resolution mass spectroscopy results showing the percent assigned formulas for unheated, low (225 °C) and moderate (350 °C) temperature soil leachates. HG soils were collected from the 2012 Hewlett Gulch Fire burn area in the Cache la Poudre watershed in northern Colorado. PBR soils were collected from an unburned soil site from the same watershed. Reproduced with permission from ref 42. Copyright 2016 American Chemical Society.

fire. Total organic carbon (TOC) concentrations also increased and were much more variable after the fire. Turbidity, TP, TN, and TOC all reached extremely high levels following postfire rainstorms.[23]

The magnitude of water quality responses often increase with the proportion of a watershed exposed to high severity wildfire. For example, two research watersheds at the San Dimas Experimental Forest in southern California that were burned at high severity released 7-times more nitrate than watersheds burned at lower severity.[49] Similarly, during the first 5 years after Colorado's Hayman Fire, individual watersheds that sustained high severity wildfire on >45% of their area had nitrate and turbidity roughly 3-fold the levels measured in basins with ≤10% burned under such conditions.[50] Plant nutrient demand remained low due to slow vegetation recovery in areas burned at high severity, so stream total dissolved nitrogen (TDN) levels have remained elevated for 15 years after the Hayman Fire (Figure 5),[51] though postfire total suspended sediment (TSS) levels have abated. In contrast, the unburned and partially charred organic material retained on the forest floor following less severe wildfires represent sustained inputs of carbon to streams resulting in higher DOC concentrations, compared to catchments burned at high severity (Figure 5). Notably, DOC remained elevated for 15 years[51] compared to the sediment erosion responses that largely subsided within the first 5 postfire years.[50] These patterns create substantial variability in postfire water chemistry that generate short and long-term challenges for water treatment systems.

## ■ POSTFIRE VARIABILITY IN WATER TREATMENT

Severe wildfires cause extremely high fluctuations in source water quality that can challenge water treatment operations, process selection, and long-term planning. High intensity, postfire rainstorms are the greatest concern for drinking water treatment plants, specifically small, single source systems without the ability to bypass highly turbid water. When intense storms fall on recently burned landscapes they dramatically increase surface runoff that erodes ash and soil and degrades water quality.[53,54] Turbidity and DOM are the key variables that drive treatment operations, and abrupt and extreme postfire spikes in these parameters may necessitate additional treatment, or cause a plant to shut down.[55] Smaller and sustained seasonal increases in turbidity or DOM may require greater coagulant dosing, and result in shorter filter run times


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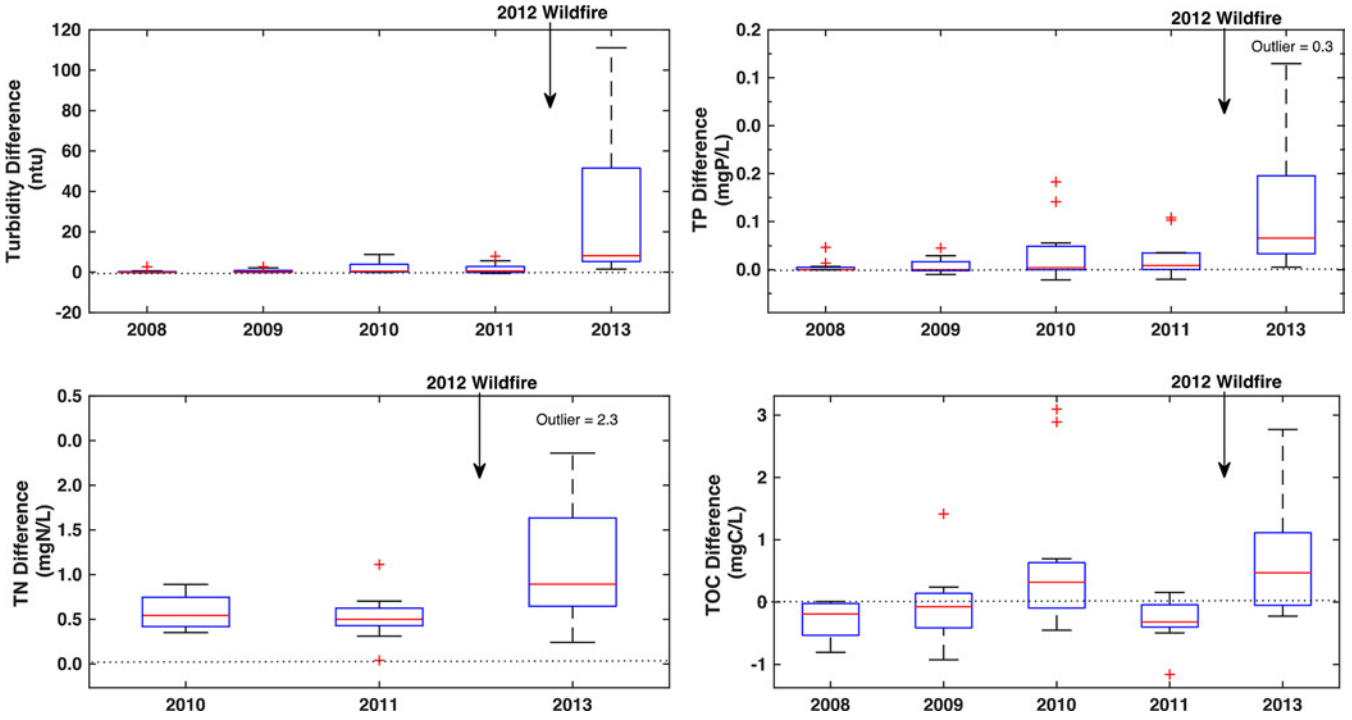


**Figure 4.** Paired differences in streamwater concentrations at an unburned, upstream reference site and near a municipal water intake within the High Park Fire (2012) burn area before and the first year after the fire. Samples were collected biweekly or monthly from May to October; $n$ = 10–11 per year, per site. The dashed line indicates a difference of zero between the burned site and reference site. Reproduced with permission from ref 23. Copyright 2016 Elsevier.

and increased solids processing, but the effects are less severe than postfire rainstorms.

Postfire changes in DOM composition influence coagulation efficiency[22,23] and DBP precursor reactivity and speciation.[56,57] The authors studied the relations between DOM alterations and drinking water treatability for the first year following the 2012 High Park Fire.[23] The efficacy of conventional treatment (i.e., coagulation/flocculation/sedimentation/filtration) with aluminum sulfate (alum) for DOM removal, and carbonaceous and nitrogenous DBP formation upon chlorination were evaluated. Postfire rainstorms created turbidity (>4000 ntu) and DOC spikes (>18 $mg_C/L$) and significant treatment challenges that resulted in closure of the water intake.[23,58] Higher alum doses (e.g., 65 mg/L) were applied to the rainstorm samples to optimize treatment, yet in spite of that, DOC removal was limited to nearly half of that removed from the nonstorm samples (i.e., 34% vs 60% removal) (Figure 6). Substantial aromatic DOM (i.e., high specific ultraviolet absorbance at 254 nm: $SUVA_{254}$) remained in the treated stormwater.[59] Consequently, due to the high residual DOC and high aromatic content, formation of the C-based DBPs total trihalomethanes (TTHMs) and five regulated haloacetic acids (HAA5s) exceeded maximum contaminant levels for nearly all post rainstorm treated water samples.[23]

Greater abundance of lower molecular weight compounds may contribute to inefficient DOC removal from postfire stormwater due to the hydrophilic nature of the DOM composition compared to higher molecular weight, hydrophobic humic substances.[60,61] The DOM sampled in postfire rainstorms had a higher fluorescence index (FI) (Figure 7), correlated with a lower molecular weight DOM composition,[62] which is more challenging to remove by coagulation.[60,63] Further, the FI values of samples collected from the burned area (water intake) were statistically higher than the reference site (+ 0.038), and higher than prefire data.[23] In a different study, the authors also observed an increase in FI and blue-shifted emission spectra for leachates of soils heated at a moderate temperature (350 °C).[42] Similarly, Wang et al. (2015) reported higher FI for burned detritus extracts from the Rim Fire compared to unburned detritus,[56] providing additional evidence for post-fire changes in DOM chemistry.

There is also parallel evidence for an increase in hydrophobic, aromatic compounds that are preferentially removed by coagulation. For example, a higher $SUVA_{254}$ (4.5 ± 0.9 L/mg·m), consistent with more aromatic DOM,[59] was observed for postfire storm samples. The higher raw water $SUVA_{254}$ should favor DOC removal.[63−66] However, $SUVA_{254}$ primarily captures DOM chromophores that absorb light at 254 nm, while this work shows that smaller, aromatic, soluble compounds that evade coagulation are likely also formed during wildfire. The level of DOM aromaticity appears to be regulated by combustion temperature, with more aromatic DOM released from ash formed at high temperature.[56] Coagulation efficiency was reduced by high turbidity and DOC, combined with DOM compositional changes (i.e., shift in molecular weight, changes in polarity), in stormwater after the High Park Fire.[23]

To complement previous work, and further investigate the effects of forest floor heating on changes in DOM character and coagulation treatment, organic and mineral soil layers were heated in the laboratory at 225 °C to simulate wildfire.[67,68] Field and laboratory studies have shown low-temperature heating may have greater consequences for DOC transport to source waters than higher temperatures when more organic matter is combusted. Unheated (control) and heated soil layers were leached and treated with aluminum sulfate


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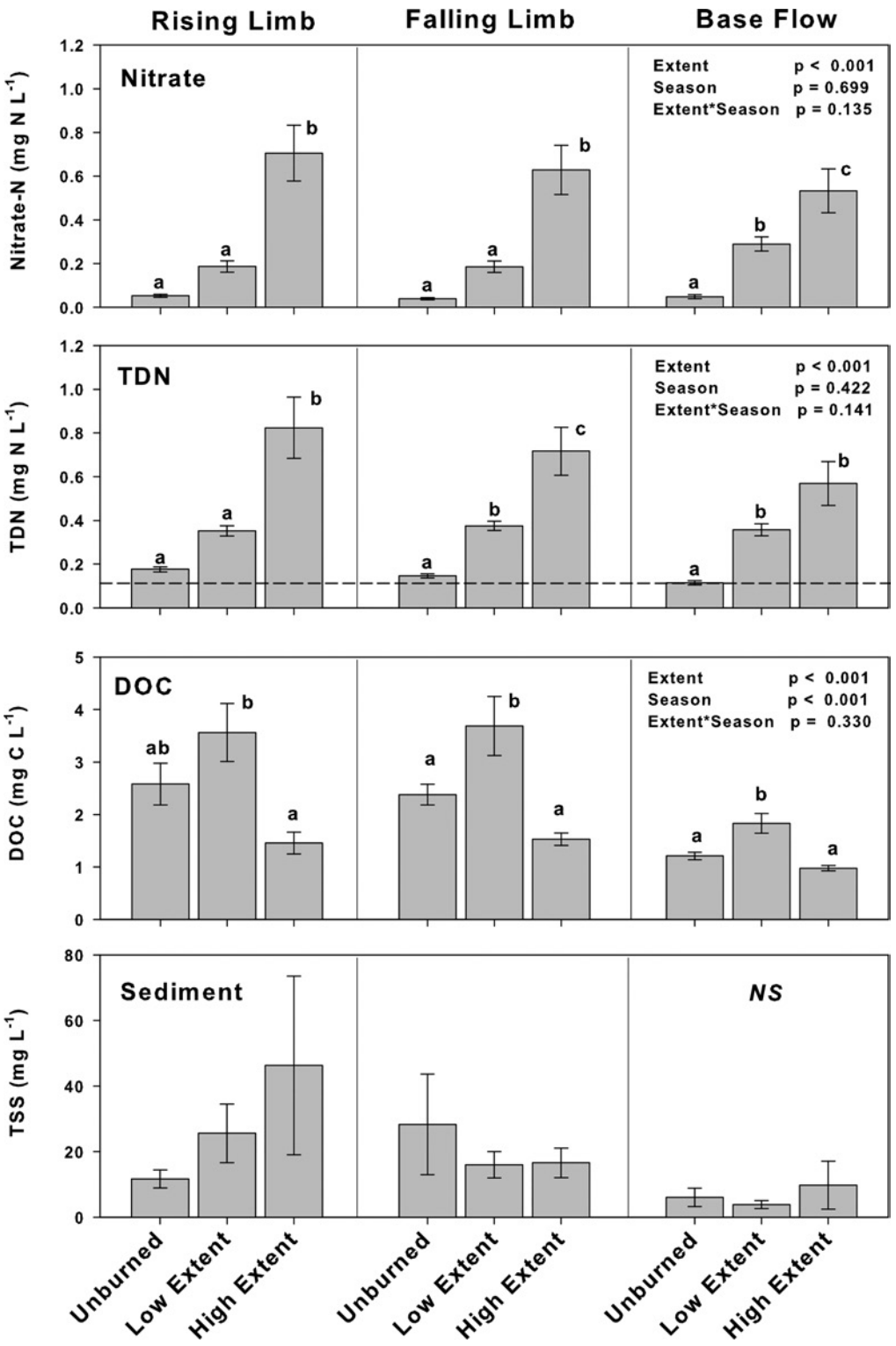


**Figure 5.** Seasonal mean nitrate, total dissolved nitrogen (TDN), dissolved organic carbon (DOC), and total suspended sediment (TSS) concentrations from four catchments burned by the 2002 Colorado Hayman Fire and two nearby, unburned catchments. Burn Extent classes as follows: High Extent: >60% burned, Low Extent: 30−60% burned, and unburned. Means were derived from 2015 and 2016 monthly samples for two catchments per Burn Extent class ($n$ = 12 for each season). The dashed line on the TDN panel denotes the proposed TN threshold concentrations for least-impaired reference streams in the Western Forest Region.[52] Reproduced with permission from ref 51. Copyright 2018 Springer Nature.

coagulation. The leachates had similar raw water turbidity and DOC concentrations, but the heat-altered DOM was less amenable to coagulation, and even at optimal alum dosing only 24 ± 4.8% DOC removal was achieved compared to 55 ± 6.7% removal for the control samples (Figure 8). That is, 0.03 and 0.09 mg of DOC removed/mg of alum for the heated and control samples, respectively. It is evident that low temperature heating imparted clear changes in DOM composition that


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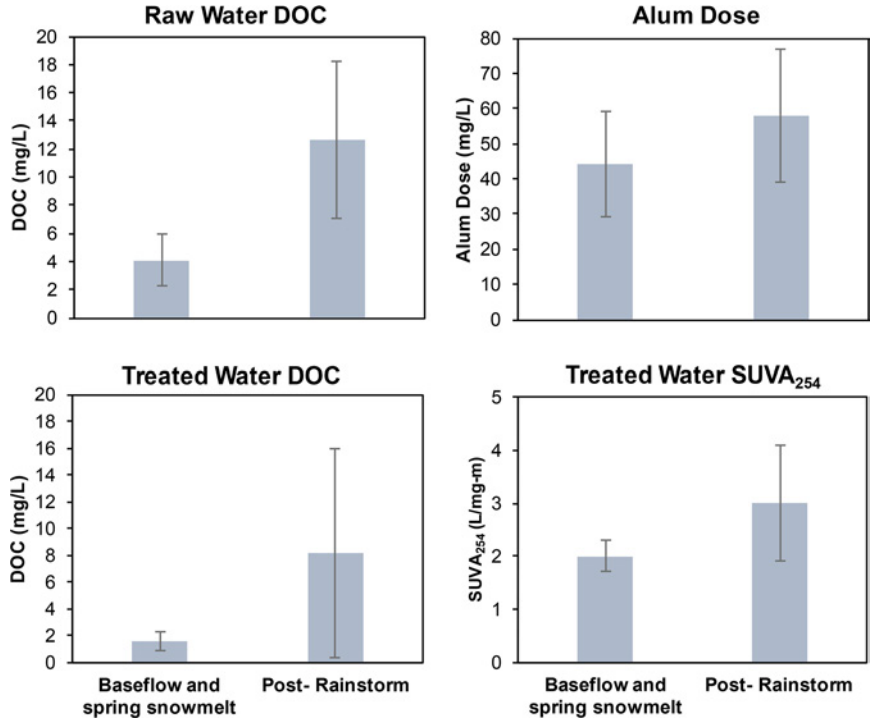


**Figure 6.** Raw water (streamwater) DOC concentrations of samples collected from a water intake during baseflow and spring snowmelt conditions and following rainstorms in the High Park Fire burn area the first postfire year. Treated water aluminum sulfate (alum) coagulant doses, DOC, and $SUVA_{254}$ (specific ultraviolet absorbance at 254 nm) are shown. Data are means ($n$ = 6) with standard deviation. Data from ref 23.

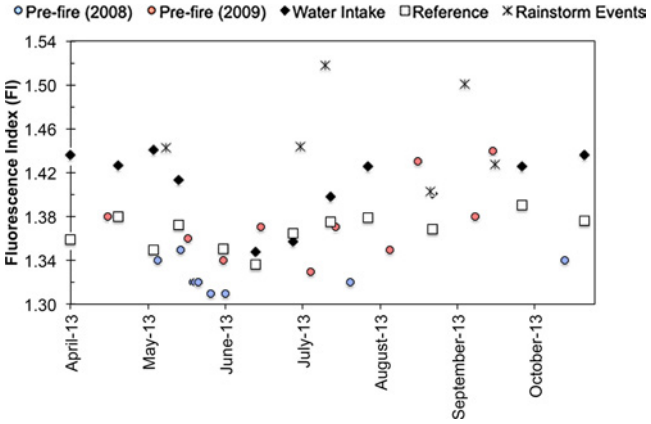


**Figure 7.** Seasonally varying fluorescence index (FI) values of pre- and postfire (2013) samples collected from a water intake within the High Park Fire burn area and an unburned, upstream reference site. Prefire FI data were collected for both sites in 2008 and 2009. Samples were also collected from the water intake following rainstorms in the burn area. Reproduced with permission from ref 23. Copyright 2016 Elsevier.

adversely affected the coagulation response. Although the heat-altered DOM was more aromatic (i.e., higher $SUVA_{254}$), size exclusion chromatography-UV analysis showed a clear shift toward lower molecular weight DOM.[67] Optical indices (E2/E3 and Sr) are inversely related to DOM size.[69,70] Work by the authors[67] and others[41] related increases in E2/E3 and Sr following heating to a smaller DOM composition. Wang et al. found that, in addition to combustion temperature, oxygen availability influenced DOM chemistry, with higher $SUVA_{254}$ released from DOM formed under oxic conditions compared to DOM released after anoxic combustion. The laboratory heating findings confirm the post rainstorm observations after the High Park Fire.[23] Wildfire changes to DOM chemistry should also be considered along with greater DOC and sediment loads drinking water treatment facilities may experience following fire.

## WILDFIRE EFFECTS ON DISINFECTION BYPRODUCT PRECURSOR REACTIVITY

A shift in DOM composition from wildfire heating may influence DBP formation and speciation during water treatment. Following the High Park Fire, post rainstorm samples had elevated haloacetonitrile (HAN) and chloropicrin precursor reactivity, whereas TTHM and HAA5 reactivity was similar to nonstorm samples.[23] To further explore postfire sources of DBP precursors, charred sediments that were eroded by rainstorms from the High Park Fire burn area and mobilized to the riverbank were collected.[57] The sediments were leached in source water and low carbon tap water (LCT) with minimal background organic matter (DOC < 0.3 $mg_C/L$). Sediment masses were added to leach between 2 and 5 $mg_C/L$ DOC. TTHM and HAA5 formation showed similar trends for the source waters with no sediments added (baseline waters) and sediment leachates (Figure 9), which indicates the wildfire did not significantly alter C-DBP precursor reactivity. However, N-DBP precursors were affected by the fire, and sediment leachates formed higher N-DBPs per unit carbon than baseline waters (Figure 9). The LCT leachates showed the highest overall N-DBP precursor reactivity. It appeared that DOM leached from wildfire affected sediments was more reactive for N-DBP formation when background organic matter was negligible. Competition from DBP precursors present in the source water may have restricted the reactivity of the DOM leached from the sediments. Another study by Wang et. al (2015) leached organic soil layers from the California


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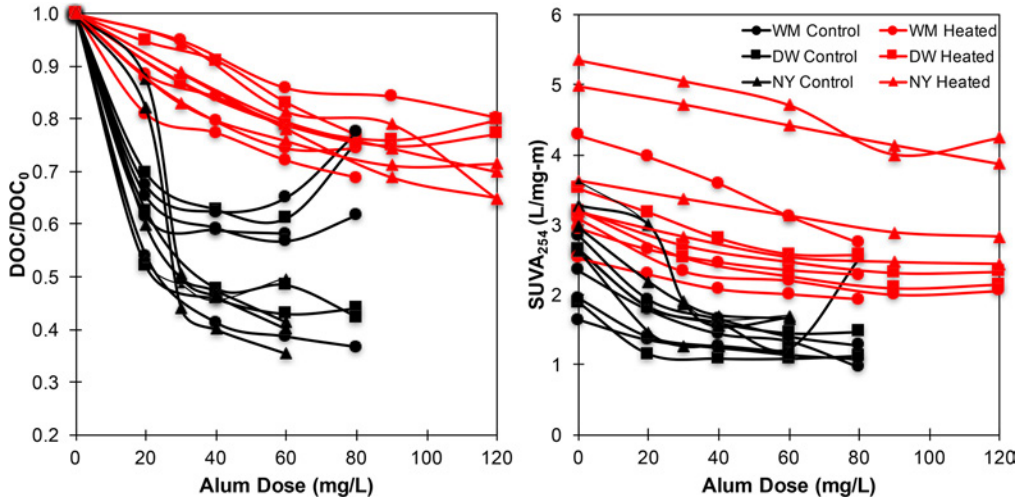


**Figure 8.** Decimal fraction of DOC remaining ($DOC/DOC_0$) and specific ultraviolet absorbance ($SUVA_{254}$) versus applied aluminum sulfate (alum) dose for control and heated samples from municipal watersheds in Colorado (Westminster, WM and Denver, DW) and New York (NY). Alum doses are reported as $Al_2(SO_4)_3 18H_2O$. Data from ref 67.

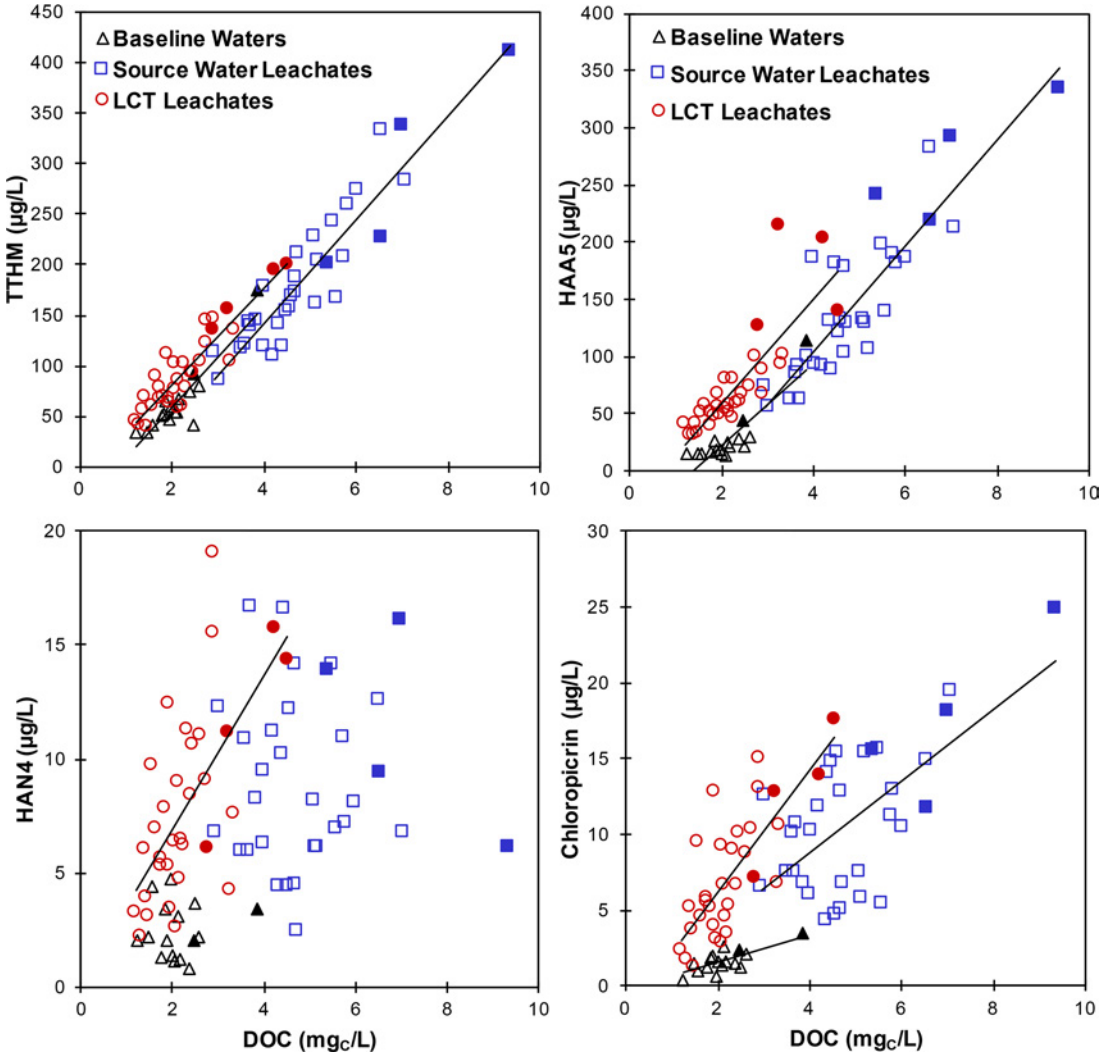


**Figure 9.** DBP formation vs DOC concentration for TTHM, HAA5, HAN4, and chloropicrin. Baseline waters were collected from source water supplies for two utilities. Wildfire-affected sediments were added to source waters (Source Water Leachates) and low carbon tap water (LCT Leachates). Solid symbols represent raw waters and open symbols indicate treated waters. Linear trend lines show when a significant ($p < 0.05$) correlation was observed. Reproduced with permission from ref 57. Copyright 2017 The Royal Society of Chemistry.



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Rim Fire and observed an increase in HAN and N-Nitrosodimethylamine (NDMA) reactivity for white (high severity) and black ash (moderate severity) extracts compared to unburned organic soil layers.[56]

The observed increase in N-DBP precursors may be explained by wildfire alterations to the landscape. Lower plant nutrient demand increases soil N that may release N-DBP precursors to surface waters, while partially charred soils and vegetative debris can be significant sources of organic nitrogen, depending on the level of combustion.[47,68,71] Following rainstorms in the High Park Fire burn area, samples were enriched in organic nitrogen, which suggests smaller, more hydrophilic organic moieties in the postfire runoff,[72] and likely reactive N-DBP precursors.[73] A shift in DBP speciation toward more nitrogenous precursors was consistently observed for the High Park Fire post rainstorm samples and sediment leachates, and for other fires.[56]

Laboratory studies demonstrate that heat-alterations to DOM may enhance N-DBP reactivity. The authors observed higher C- and N-DBP precursor reactivity for soils heated at 225 °C under oxic conditions, and enhanced haloacetonitrile (HAN) reactivity for soils heated at 350 °C.[42] Similarly, Wang et al. reported increased HAN reactivity following heating at 400 °C under oxic conditions, but observed a decrease in HAN reactivity for samples heated at the same temperature under anoxic conditions.[41] Wildfire formation of reactive nitrogen compounds is supported by an increase in black nitrogen from low-moderate temperature heating (Figure 3), however further research on black nitrogen and N-DBP precursors is warranted. N-DBPs are currently not regulated, but may be more of a health concern than regulated C-DBPs.[74,75] Evidence from these studies indicates that nitrogenous DBP formation in drinking water could be elevated following wildfire.

## FUTURE OUTLOOK

More extreme and frequent wildfires create a new set of unknowns about postfire conditions with significant consequences for water supply and treatability. There is need to design and conduct studies that explicitly couple spatial variability of wildfire behavior and fuel combustion with chemical changes in soil and water to evaluate laboratory and field-based observations across a range of conditions. In addition to characterizing wildfires, these approaches have utility for evaluating the biogeochemical consequences and effectiveness of postfire watershed rehabilitation treatments, prescribed fire, and forest fuel removal activities aimed at reducing threats to water supplies from severe wildfire. There is also the need to account for the added capital, operational, and monitoring costs of treating water from burned watersheds, and to evaluate how adjustments and investments in treatment processes may help communities adapt to higher frequency of severe wildfires. The short- and long-term risks water providers may experience, and the probability of such occurrences need to be understood to strengthen the resiliency of potable water supplies. Communities in fire-prone ecosystems confront the significant challenge of how to develop and operate efficient drinking water systems to treat higher sediment, nutrients, and DOM exported from burned watersheds, as well as unknown risks from changing fire behavior.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES


(1) Westerling, A. L. Increasing Western US Forest Wildfire Activity: Sensitivity to Changes in the Timing of Spring. *Philos. Trans. R. Soc., B* **2016**, *371*, 20150178.

(2) Sommerfeld, A.; Senf, C.; Buma, B.; D'Amato, A. W.; Després, T.; Díaz-Hormazábal, I.; Fraver, S.; Frelich, L. E.; Gutiérrez, Á. G.; Hart, S. J.; Harvey, B. J.; He, H. S.; Hlásny, T.; Holz, A.; Kitzberger, T.; Kulakowski, D.; Lindenmayer, D.; Mori, A. S.; Müller, J.; Paritsis, J.; Perry, G. L. W.; Stephens, S. L.; Svoboda, M.; Turner, M. G.; Veblen, T. T.; Seidl, R. Patterns and Drivers of Recent Disturbances Across the Temperate Forest Biome. *Nat. Commun.* **2018**, *9*, 2833.

(3) Dennison, P. E.; Brewer, S. C.; Arnold, J. D.; Moritz, M. A. Large Wildfire Trends in the Western United States, 1984−2011. *Geophys. Res. Lett.* **2014**, *41*, 2928−2933.

(4) Raffa, K. F.; Aukema, B. H.; Bentz, B. J.; Carroll, A. L.; Hicke, J. A.; Turner, M. G.; Romme, W. H. Cross-Scale Drivers of Natural




DOI: 10.1021/acs.accounts.8b00670
*Acc. Chem. Res.* 2019, 52, 1234−1244

Disturbances Prone to Anthropogenic Amplification: the Dynamics of Bark Beetle Eruptions. *BioScience* **2008**, *58*, 501−517.
(5) Radeloff, V. C.; Helmers, D. P.; Kramer, H. A.; Mockrin, M. H.; Alexandre, P. M.; Bar-Massada, A.; Butsic, V.; Hawbaker, T. J.; Martinuzzi, S.; Syphard, A. D.; Stewart, S. I. Rapid Growth of the US Wildland-Urban Interface Raises Wildfire Risk. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 3314−3319.
(6) Liu, Y.; Stanturf, J.; Goodrick, S. Trends in Global Wildfire Potential in a Changing Climate. *For. Ecol. Manage.* **2010**, *259*, 685−697.
(7) Hurteau, M. D.; Westerling, A. L.; Wiedinmyer, C.; Bryant, B. P. Projected Effects of Climate and Development on California Wildfire Emissions Through 2100. *Environ. Sci. Technol.* **2014**, *48*, 2298−2304.
(8) Jolly, W. M.; Cochrane, M. A.; Freeborn, P. H.; Holden, Z. A.; Brown, T. J.; Williamson, G. J.; Bowman, D. M. J. S. Climate-Induced Variations in Global Wildfire Danger From 1979 to 2013. *Nat. Commun.* **2015**, *6*, 7537.
(9) BBC. *Portugal Wildfires: Why Are They So Deadly?* www.bbc.com; June 1, 2017.
(10) Jergler, D. *Official Figure on Insured Losses for 2018 California Wildfires Reaches $9B*; www.insurancejournal.com.
(11) Blanchi, R.; Lucas, C.; Leonard, J.; Finkele, K. Meteorological Conditions and Wildfire-Related Houseloss in Australia. *Int. J. Wildland Fire* **2010**, *19*, 914.
(12) Schoennagel, T.; Balch, J. K.; Brenkert-Smith, H.; Dennison, P. E.; Harvey, B. J.; Krawchuk, M. A.; Mietkiewicz, N.; Morgan, P.; Moritz, M. A.; Rasker, R.; Turner, M. G.; Whitlock, C. Adapt to More Wildfire in Western North American Forests as Climate Changes. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 4582−4590.
(13) Higuera, P. E. Taking Time to Consider the Causes and Consequences of Large Wildfires. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 13137−13138.
(14) Bladon, K. D.; Emelko, M. B.; Silins, U.; Stone, M. Wildfire and the Future of Water Supply. *Environ. Sci. Technol.* **2014**, *48*, 8936−8943.
(15) Bormann, B. T.; Homann, P. S.; Darbyshire, R. L.; Morrissette, B. A. Intense Forest Wildfire Sharply Reduces Mineral Soil C and N: the First Direct Evidence. *Can. J. For. Res.* **2008**, *38*, 2771−2783.
(16) Homann, P. S.; Bormann, B. T.; Darbyshire, R. L.; Morrissette, B. A. Forest Soil Carbon and Nitrogen Losses Associated with Wildfire and Prescribed Fire. *Soil Science Society of America Journal* **2011**, *75*, 1926.
(17) Larsen, I. J.; MacDonald, L. H.; Brown, E.; Rough, D.; Welsh, M. J.; Pietraszek, J. H.; Libohova, Z.; de Dios Benavides-Solorio, J.; Schaffrath, K. Causes of Post-Fire Runoff and Erosion: Water Repellency, Cover, or Soil Sealing? *Soil Sci. Soc. Am. J.* **2009**, *73*, 1393.
(18) Pierson, D. N.; Robichaud, P. R.; Rhoades, C. C.; Brown, R. E. Carbon and Nitrogen Eroded From Burned Forests in the Western U.S. *Int. J. Wildland Fire* **2019**, DOI: 10.1071/WF18193.
(19) Wan, S. Q.; Hui, D. F.; Luo, Y. Q. Fire Effects on Nitrogen Pools and Dynamics in Terrestrial Ecosystems: a Meta-Analysis. *Ecological Applications* **2001**, *11*, 1349−1365.
(20) Certini, G. Effects of Fire on Properties of Forest Soils: a Review. *Oecologia* **2005**, *143*, 1−10.
(21) Turner, M. G.; Smithwick, E. A. H.; Metzger, K. L.; Tinker, D. B.; Romme, W. H. Inorganic Nitrogen Availability After Severe Stand-Replacing Fire in the Greater Yellowstone Ecosystem. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 4782−4789.
(22) Emelko, M. B.; Silins, U.; Bladon, K. D.; Stone, M. Implications of Land Disturbance on Drinking Water Treatability in a Changing Climate: Demonstrating the Need for "Source Water Supply and Protection" Strategies. *Water Res.* **2011**, *45*, 461−472.
(23) Hohner, A. K.; Cawley, K.; Oropeza, J.; Summers, R. S.; Rosario-Ortiz, F. L. Drinking Water Treatment Response Following a Colorado Wildfire. *Water Res.* **2016**, *105*, 187−198.
(24) Emelko, M. B.; Stone, M.; Silins, U.; Allin, D.; Collins, A. L.; Williams, C. H. S.; Martens, A. M.; Bladon, K. D. Sediment-Phosphorus Dynamics Can Shift Aquatic Ecology and Cause Downstream Legacy Effects After Wildfire in Large River Systems. *Global Change Biology* **2016**, *22*, 1168−1184.
(25) Rust, A. J.; Hogue, T. S.; Saxe, S.; McCray, J. Post-Fire Water-Quality Response in the Western United States. *Int. J. Wildland Fire* **2018**, *27*, 203.
(26) Smith, H. G.; Sheridan, G. J.; Lane, P. N. J.; Nyman, P.; Haydon, S. Wildfire Effects on Water Quality in Forest Catchments: a Review with Implications for Water Supply. *J. Hydrol.* **2011**, *396*, 170−192.
(27) United States Environmental Protection Agency. Office of Water. *Comprehensive Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2: Quick Reference Guide)*; 2010; EPA 816-F-10-080; pp 1−2; http://water.epa.gov/drink.
(28) Keeley, J. E. Fire Intensity, Fire Severity and Burn Severity: a Brief Review and Suggested Usage. *Int. J. Wildland Fire* **2009**, *18*, 116.
(29) Spencer, C. N.; Hauer, F. R. Phosphorus and Nitrogen Dynamics in Streams During a Wildfire. *Journal of the North American Benthological Society* **1991**, *10* (1), 24−30.
(30) Robichaud, P. R.; MacDonald, L. H.; Freeouf, J.; Neary, D.; Martin, D.; Ashmun, L. E. *Postfire Rehabilitation of the Hayman Fire*; USDA Forest Service Rocky Mountain Research Station General Technical Report, 14,; 2003; pp 1−22.
(31) Blake, W. H.; Theocharopoulos, S. P.; Skoulikidis, N.; Clark, P.; Tountas, P.; Hartley, R.; Amaxidis, Y. Wildfire Impacts on Hillslope Sediment and Phosphorus Yields. *J. Soils Sediments* **2010**, *10*, 671−682.
(32) Pannkuk, C. D.; Robichaud, P. R. Effectiveness of Needle Cast at Reducing Erosion After Forest Fires. *Water Resour. Res.* **2003**, *39*, 1515.
(33) Cerdà, A.; Doerr, S. H. The Effect of Ash and Needle Cover on Surface Runoff and Erosion in the Immediate Post-Fire Period. *Catena* **2008**, *74*, 256−263.
(34) Wagenbrenner, J. W.; MacDonald, L. H.; Rough, D. Effectiveness of Three Post-Fire Rehabilitation Treatments in the Colorado Front Range. *Hydrol. Processes* **2006**, *20*, 2989−3006.
(35) DeBano, L. F. The Role of Fire and Soil Heating on Water Repellency in Wildland Environments: a Review. *J. Hydrol.* **2000**, *231*, 195−206.
(36) DeBano, L. F. Water Repellency in Soils: a Historical Overview. *J. Hydrol.* **2000**, *231*, 4−32.
(37) Neary, D. G.; Ice, G. G.; Jackson, C. R. Linkages Between Forest Soils and Water Quality and Quantity. *For. Ecol. Manage.* **2009**, *258*, 2269−2281.
(38) Knicker, H.; González-Vila, F. J.; Polvillo, O.; Gonzalez, J.; Almendros, G. Fire-Induced Transformation of C- and N- Forms in Different Organic Soil Fractions From a Dystric Cambisol Under a Mediterranean Pine Forest (). *Soil Biol. Biochem.* **2005**, *37*, 701−718.
(39) Bodí, M. B.; Martin, D. A.; Balfour, V. N.; Santín, C.; Doerr, S. H.; Pereira, P.; Cerdà, A.; Mataix-Solera, J. Wildland Fire Ash: Production, Composition and Eco-Hydro-Geomorphic Effects. *Earth-Sci. Rev.* **2014**, *130*, 103−127.
(40) Retuta, A. M. Effect of Heating Temperature on Dissolvable Constituents From Soil and Litter Material in the Colorado Front Range. Masters Thesis, University of Colorado at Boulder, 2018; pp 1−111.
(41) Wang, J.-J.; Dahlgren, R. A.; Chow, A. T. Controlled Burning of Forest Detritus Altering Spectroscopic Characteristics and Chlorine Reactivity of Dissolved Organic Matter: Effects of Temperature and Oxygen Availability. *Environ. Sci. Technol.* **2015**, *49*, 14019−14027.
(42) Cawley, K. M.; Hohner, A. K.; Podgorski, D. C.; Cooper, W. T.; Korak, J. A.; Rosario-Ortiz, F. L. Molecular and Spectroscopic Characterization of Water Extractable Organic Matter From Thermally Altered Soils Reveal Insight Into Disinfection Byproduct Precursors. *Environ. Sci. Technol.* **2017**, *51*, 771−779.
(43) Santos, F.; Russell, D.; Berhe, A. A. Thermal Alteration of Water Extractable Organic Matter in Climosequence Soils From the Sierra Nevada, California. *J. Geophys. Res.: Biogeosci.* **2016**, *121*, 2877−2885.


DOI: 10.1021/acs.accounts.8b00670
*Acc. Chem. Res.* 2019, 52, 1234−1244

(44) Jian, M.; Berli, M.; Ghezzehei, T. A. Soil Structural Degradation During Low-Severity Burns. *Geophys. Res. Lett.* **2018**, *45*, 5553−5561.
(45) Preston, C. M.; Schmidt, M. W. I. Black (Pyrogenic) Carbon: a Synthesis of Current Knowledge and Uncertainties with Special Consideration of Boreal Regions. *Biogeosciences* **2006**, *3*, 397−420.
(46) Wagner, S.; Cawley, K. M.; Rosario-Ortiz, F. L.; Jaffé, R. In-Stream Sources and Links Between Particulate and Dissolved Black Carbon Following a Wildfire. *Biogeochemistry* **2015**, *124*, 145−161.
(47) Almendros, G.; Knicker, H.; González-Vila, F. J. Rearrangement of Carbon and Nitrogen Forms in Peat After Progressive Thermal Oxidation as Determined by Solid-State 13C- and 15N-NMR Spectroscopy. *Org. Geochem.* **2003**, *34*, 1559−1568.
(48) Knicker, H. Black Nitrogen" − an Important Fraction in Determining the Recalcitrance of Charcoal. *Org. Geochem.* **2010**, *41*, 947−950.
(49) Riggan, P. J.; Lockwood, R. N.; Jacks, P. M.; Colver, C. G.; Weirich, F.; DeBano, L. F.; Brass, J. A. Effects of Fire Severity on Nitrate Mobilization in Watersheds Subject to Chronic Atmospheric Deposition. *Environ. Sci. Technol.* **1994**, *28*, 369−375.
(50) Rhoades, C. C.; Entwistle, D.; Butler, D. The Influence of Wildfire Extent and Severity on Streamwater Chemistry, Sediment and Temperature Following the Hayman Fire, Colorado. *Int. J. Wildland Fire* **2011**, *20*, 430.
(51) Rhoades, C. C.; Chow, A. T.; Covino, T. P.; Fegel, T. S.; Pierson, D. N.; Rhea, A. E. The Legacy of a Severe Wildfire on Stream Nitrogen and Carbon in Headwater Catchments. *Ecosystems* **2018**, 1−15.
(52) United States Environmental Protection Agency. *Nutrient Criteria Technical Guidance Manual Rivers and Streams*; Washington, DC, 2000; pp 1−253.
(53) Mast, M. A.; Murphy, S. F.; Clow, D. W.; Penn, C. A.; Sexstone, G. A. Water-Quality Response to a High-Elevation Wildfire in the Colorado Front Range. *Hydrol. Process.* **2016**, *30*, 1811−1823.
(54) Murphy, S. F.; Writer, J. H.; McCleskey, R. B.; Martin, D. A. The Role of Precipitation Type, Intensity, and Spatial Distribution in Source Water Quality After Wildfire. *Environ. Res. Lett.* **2015**, *10*, 1−13.
(55) Becker, W. C.; Hohner, A.; Rosario-Ortiz, F.; DeWolfe, J. Preparing for Wildfires and Extreme Weather: Plant Design and Operation Recommendations. *J. - Am. Water Works Assoc.* **2018**, *110*, 32−40.
(56) Wang, J.-J.; Dahlgren, R. A.; Erşan, M. S.; Karanfil, T.; Chow, A. T. Wildfire Altering Terrestrial Precursors of Disinfection Byproducts in Forest Detritus. *Environ. Sci. Technol.* **2015**, *49*, 5921−5929.
(57) Hohner, A. K.; Terry, L. G.; Townsend, E. B.; Summers, R. S.; Rosario-Ortiz, F. L. Water Treatment Process Evaluation of Wildfire-Affected Sediment Leachates. *Environmental Science: Water Research & Technology* **2017**, *3*, 352−365.
(58) Writer, J. H.; Hohner, A.; Oropeza, J.; Schmidt, A.; Cawley, K.; Rosario-Ortiz, F. L. Water Treatment Implications After the High Park Wildfire, Colorado. *J. - Am. Water Works Assoc.* **2014**, *106*, E189−E199.
(59) Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. *Environ. Sci. Technol.* **2003**, *37*, 4702−4708.
(60) Chow, C.; van Leeuwen, J. A.; Drikas, M.; Fabris, R.; Spark, K. M.; Page, D. W. The Impact of the Character of Natural Organic Matter in Conventional Treatment with Alum. *Water Sci. Technol.* **1999**, *40*, 97−104.
(61) Leenheer, J. A.; Croué, J.-P. Peer Reviewed: Characterizing Aquatic Dissolved Organic Matter. *Environ. Sci. Technol.* **2003**, *37*, 18A−26A.
(62) Romera-Castillo, C.; Chen, M.; Yamashita, Y.; Jaffé, R. Fluorescence Characteristics of Size-Fractionated Dissolved Organic Matter: Implications for a Molecular Assembly Based Structure? *Water Res.* **2014**, *55*, 40−51.
(63) Quang, V. L.; Choi, I.; Hur, J. Tracking the Behavior of Different Size Fractions of Dissolved Organic Matter in a Full-Scale Advanced Drinking Water Treatment Plant. *Environ. Sci. Pollut. Res.* **2015**, *22*, 18176−18184.
(64) Archer, A. D.; Singer, P. C. An Evaluation of the Relationship Between SUVA and NOM Coagulation Using the ICR Database. *J. - Am. Water Works Assoc.* **2006**, *98*, 110−123.
(65) White, M. C.; Thompson, J. D.; Harrington, G. W.; Singer, P. C. Evaluating Criteria for Enhanced Coagulation Compliance. *J. - Am. Water Works Assoc.* **1997**, *89* (5), 64−77.
(66) Liang, L.; Singer, P. C. Factors Influencing the Formation and Relative Distribution of Haloacetic Acids and Trihalomethanes in Drinking Water. *Environ. Sci. Technol.* **2003**, *37*, 2920−2928.
(67) Hohner, A. K.; Webster, J.; Cawley, K.; Rosario-Ortiz, F. L.; Becker, W. C. *Wildfire Impacts on Drinking Water Treatment Process Performance: Development of Evaluation Protocols and Management Practices*; Water Research Foundation, Ed.; Water Research Foundation: Denver, CO, 2018; pp 1−122.
(68) Fernández, I.; Cabaneiro, A.; Carballas, T. Organic Matter Changes Immediately After a Wildfire in an Atlantic Forest Soil and Comparison with Laboratory Soil Heating. *Soil Biol. Biochem.* **1997**, *29*, 1−11.
(69) Helms, J. R.; Stubbins, A.; Ritchie, J. D.; et al. Absorption Spectral Slopes and Slope Ratios as Indicators of Molecular Weight, Source, and Photobleaching of Chromophoric Dissolved Organic Matter. *Limnol. Oceanogr.* **2008**, *53*, 955−969.
(70) Peuravuori, J.; Pihlaja, K. Molecular Size Distribution and Spectroscopic Properties of Aquatic Humic Substances. *Anal. Chim. Acta* **1997**, *337*, 133−149.
(71) González-Pérez, J. A.; González-Vila, F. J.; Almendros, G.; Knicker, H. The Effect of Fire on Soil Organic Matter—a Review. *Environ. Int.* **2004**, *30*, 855−870.
(72) Westerhoff, P.; Mash, H. Dissolved Organic Nitrogen in Drinking Water Supplies: a Review. *Aqua* **2002**, *51*, 415−448.
(73) Hu, J.; Song, H.; Addison, J. W.; Karanfil, T. Halonitromethane Formation Potentials in Drinking Waters. *Water Res.* **2010**, *44*, 105−114.
(74) Plewa, M. J.; Wagner, E. D.; Jazwierska, P.; Richardson, S. D.; Chen, P. H.; McKague, A. B. Halonitromethane Drinking Water Disinfection Byproducts: Chemical Characterization and Mammalian Cell Cytotoxicity and Genotoxicity. *Environ. Sci. Technol.* **2004**, *38*, 62−68.
(75) Muellner, M. G.; Wagner, E. D.; McCalla, K.; Richardson, S. D.; Woo, Y.-T.; Plewa, M. J. Haloacetonitriles vs. Regulated Haloacetic Acids: Are Nitrogen-Containing DBPs More Toxic? *Environ. Sci. Technol.* **2007**, *41*, 645−651.


DOI: 10.1021/acs.accounts.8b00670
*Acc. Chem. Res.* 2019, 52, 1234−1244