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Increased Organohalogen Diversity after Disinfection of Water from a Prescribed Burned Watershed

Christopher I. Olivares, Habibullah Uzun, Cagri Utku Erdem, Wenbo Zhang, Carl Trettin, Yina Liu, Sarah D. Burton, Errol W. Robinson, Tanju Karanfil, and Alex T. Chow*

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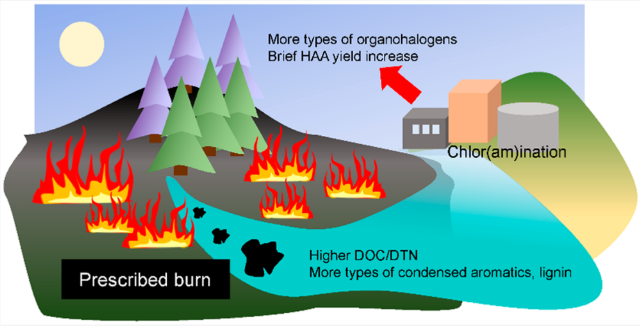

ABSTRACT: We evaluated impacts of prescribed burns on water quality by performing field sampling on adjacent first-order watersheds (Santee Experimental Forest, South Carolina), where one of the watersheds underwent a prescribed burn in 2016. We measured water quality parameters [dissolved organic carbon (DOC), nitrogen species, UV_{254} absorbance, and disinfection byproduct formation potential during chlorination and chloramination] before and after the burn. Using ultra-high-resolution mass spectrometry, we characterized dissolved organic matter features in raw water collected during the first postburn storm, as well as after chlorination and chloramination. After the burn, the median DOC to dissolved total nitrogen (DTN) ratio increased by 1.88 mg of DOC (mg of DTN)$^{-1}$ in the burned watershed. Likewise, the burned watershed showed a brief higher haloacetic acid yield after the burn [median of 95.6 μg (mg of DOC)$^{-1}$] compared to that of the unburned watershed. Despite similar molecular size distributions, more features were found (m/z 700−1000) for condensed aromatics and lignin-like features in the burned watershed. While chlorination yielded similar organohalogen diversity, chloramination yielded more halogenated molecular features in the burned watershed (m/z 300−600). The moderate impacts on DOC in this study suggest that prescribed fire likely poses a low risk to water quality.

KEYWORDS: *pyrogenic carbon, disinfection byproducts, ultra-high-resolution mass spectrometry, chemical fingerprint, dissolved organic matter, chloramination, fire*

INTRODUCTION

A larger quantity of dissolved organic matter (DOM) and changes in its chemical fingerprint[1] are expected as a consequence of wildfire or other frequent extreme weather events.[2] After a fire, the runoff from high-intensity storms mobilizes DOM, sediments, and nutrients into nearby water bodies.[3] Santín et al.[4] estimated that soil, freshwater, and coastal waters contain in total 300−500 Pg of pyrogenic carbon. Wildfires chemically transform organic matter, including the volatilization of organic compounds, the conversion of organic matter into black carbon, or mineralization.[5] As pyrogenic matter is formed, DOM increases its aromaticity and heterocyclic content.[6,7] Cawley et al.[8] observed higher chemodiversity of water extractable black carbon and black nitrogen features in sites previously impacted with wildfire and in lab burning at higher temperatures. Likewise, Thurman et al.[9] detected benzene polycarboyxlic acids and pyridine di- and tricarboxylic acids in thermally treated soils. Wagner et al.[7] identified series of pyrrole-containing compounds differing in the number of carboxylic acids.

Prescribed burns are low-temperature surface fires that decrease future wildfire severity, but they might also release fire-impacted DOM into the watershed. DOM changes pose public health risks because DOM forms unintentional toxic disinfection byproducts (DBPs) during water treatment disinfection. This is a water security issue because forested watersheds provide drinking water sources to two-thirds of the U.S. population,[10] impacting both rural and urban communities.[3]

Most studies connecting the effect of pyrogenic matter to DBPs focused on wildfires,[10−12] which have a wide range of fire severity, but as prescribed burns are used to mitigate larger impacts of wildfire, we need to understand the temporary changes that prescribed burns cause to the quantity and types of DBPs. In addition to trihalomethane (THM), haloacetic acid (HAA), *N*-nitroso dimethylamine (NDMA), and other known DBP yields, we also need to know changes to the

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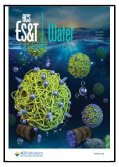

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chemodiversity of new unknown DBPs.[8,13,14] Postigo et al.[15] reported that most of the organic halogen content in chlorinated and chloraminated drinking water samples did not account for commonly measured DBPs and identified new DBP species, including highly unsaturated and polyphenolic compounds.[15]

Here, we evaluated two parallel first-order watersheds in a coastal forest in South Carolina, where one watershed was under prescribed burn management. The objectives of this study were (1) to identify prescribed burn effects in DOM quantity and chemical composition and (2) to characterize DBP formation potential in DOM after a prescribed burn.

■ MATERIALS AND METHODS

Study Site and Sample Collection. The first-order watersheds paired in this study are in the Santee Experimental Forest, Cordesville, South Carolina (Figure 1). One watershed (155 ha) has been managed with prescribed burns since the 1960s (hereafter termed the "burned watershed"), and the reference watershed (160 ha) has not been managed in the past 50 years (hereafter termed the "unburned watershed").[16] Because of this adjacent watershed system with similar catchment areas, this location is uniquely suited to compare the impacts of prescribed burns on DOM. In late April 2016, the U.S. Forest Service carried out a prescribed burn in the burned watershed through aerial ignition. On the basis of soil disturbance,[17] the burned watershed exhibited 77% moderate-severity and 22% low-severity burn effects.[18] After the prescribed burn, a dry period stopped stream gauge flow until the first postburn storm (June 7−11, 2016). We sampled intensely at this time because most fire-related organic matter transport occurs during the first high-intensity storms following fires.[19,20] We used prerinsed amber bottles for duplicate grab water samples at each watershed sampling gauge from January to April [before the prescribed burn (n = 6)] and in June [postburn storm (n = 10)] (Figure S1). We kept samples at 4 °C before analysis to minimize DOM changes.

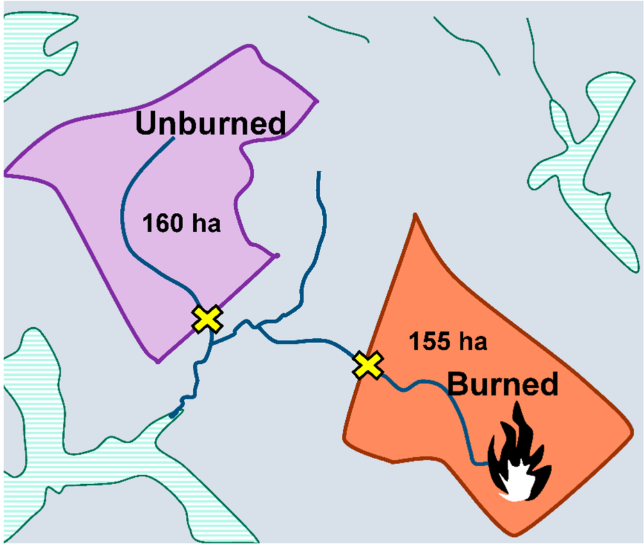

Figure 1. Burned and unburned first-order watersheds at the Santee Experimental Forest in coastal South Carolina. The yellow crosses indicate the location of sampling gauges.

Water Quality Analyses. Samples were filtered with a 0.45 m Supor PES membrane (Pall Corp.) for water quality analyses. DOC and dissolved total nitrogen (DTN) were measured in a Shimadzu (Kyoto, Japan) TOC-VCHS carbon analyzer following Standard Method 5310B. Concentrations of inorganic nitrogen species were quantified by ion chromatography (ICS-2100, Dionex Corp.) for nitrate (NO_3^-) and nitrite (NO_2^-). NH_4^+-N was measured with the salicylate method using a portable Hach (Loveland, CO) colorimeter at 610 nm. Dissolved organic nitrogen (DON) values were calculated by using the formula DON = DTN − (NO_2^--N + NO_3^--N + NH_3/NH_4^+-N). Ultraviolet−visible (UV−vis) spectra (200−700 nm) were recorded to calculate the specific absorbance at 254 nm normalized to DOC (SUVA). We compared the distribution of water quality parameters between the burned and unburned watersheds during both periods (before and after the prescribed burn) using Wilcoxon rank sum tests (α = 0.05) in R.

Disinfection Byproduct Formation Potential Tests. DBP formation potential tests during two common disinfection procedures, chlorination and chloramination, were performed in raw water samples as described by Yang et al.[21] Briefly, 125 mL of each sample was exposed to free chlorine (pH 8, 10 mM phosphate buffer) for 5 days in the dark at room temperature. Excess chlorine was supplemented on the basis of the predicted requirement by mass, 3 × DOC + 8 × NH_3-N + 10.[22] At the end of the incubation, samples were quenched with a stoichiometric amount of ascorbic acid and extracted into methyl *tert*-butyl ether for analysis with gas chromatography coupled to an electron capture detector.[21] The THMs monitored comprised trichloro-, dichlorobromo-, dibromochloro-, and tribromo-methanes (THM_4). The HAAs measured included chloro-, bromo-, dichloro-, bromochloro-, trichloro-, dibromo-, bromodichloro-, dibromochloro-, and tribromo-acetic acids (HAA_9). Total absorbable organohalogens (TOX) for excess chlorination were measured by pyrolysis followed by offline ion-exchange chromatography.[23] NDMA formation potential tests were conducted by spiking 1 L of sample with 100 mg/L monochloramine (Cl_2/N ratio of 4/1)[24] at pH 7.8, and the reaction was quenched after contact time (5 days) with $Na_2S_2O_3$. Samples were then extracted and analyzed by GC-MS/MS.[25] Minimum reporting levels of measured DBPs and TOX were presented elsewhere.[23,26]

Collection of Ultra-High-Resolution Mass Spectra, Formula Assignment, and Analysis. DOM extracts were collected from raw water, as well as chlorinated and chloraminated samples (∼60 mL) for ultra-high-resolution mass spectrometry. Acidified samples (pH ∼2) were sorbed into Bond Elut PPL cartridges (Agilent Technologies, Santa Clara, CA) and rinsed twice with distilled deionized water before elution with 100% methanol.[27] The DOM extracts were then infused into a Bruker 12T Tesla Bruker SolariX Fourier-Transform Ion Cyclotron Mass Spectrometer (FTICRMS) equipped with an electrospray ionization (ESI) source and operated in negative mode (Bruker Daltonics Inc., Billerica, MA). The samples were infused at a flow rate of 3.0 μL/min through an Agilent 1200 series pump (Agilent Technologies). The ESI source was equipped with a fused silica tube (30 μm inside diameter). The FTICRMS conditions used to run the samples were as follows: needle voltage, 4.4 kV; Q1 set to m/z 50; and heated resistively coated glass capillary operated at 180 °C. Spectra were collected at 400000 resolving power ($m/\Delta m$50% at m/z 400) and averaged over 200 individual scans.

Elemental formulas were assigned on the basis of exact masses using Formularity,[28] a software based on the automated Compound Identification Algorithm.[29] Formulas were classified into the following operational compound classes on the basis of atomic ratios:[30,31] lipid, $O/C \geq 0$, $O/C \leq 0.2$, $H/C \geq 1.5$, $H/C \leq 2.3$, $N/C \leq 0.04$, $P/C \leq 0.03$; protein, $O/C \geq 0.2$, $O/C \leq 0.52$, $H/C \geq 1.5$, $H/C \leq 2.2$, $N/C \geq 0.178$, $N/C \leq 0.44$, $P/C \leq 0.06$; amino sugar, $O/C \geq 0.52$, $O/C \leq 0.7$, $H/C \geq 1.5$, $H/C \leq 2.2$, $N/C > 0.07$, $N/C \leq 0.182$, $P/C < 0.167$; carbohydrate, $O/C \geq 0.7$, $O/C \leq 1.1$, $H/C \geq 1.5$, $H/C \leq 2.4$, $N = 0$, $P = 0$; condensed aromatic, $O/C \geq 0$, $O/C \leq 0.25$, $H/C \geq 0.5$, $H/C \leq 1.25$; lignin, $O/C \geq 0.25$, $O/C \leq 0.67$, $H/C \geq 0.75$, $H/C \leq 1.5$; tannin, $O/C \geq 0.67$, $O/C \leq 0.97$, $H/C \geq 0.53$, $H/C \leq 1.5$. The Shymanski identification confidence level for features with assigned formulas was level 4, and features without a formula were level 5.[32] Because feature intensities observed with FTICRMS cannot be directly equated to absolute concentrations,[33] we based our analyses on the presence or absence of molecular features. We calculated the mean of molecular feature counts of three samples (June 7, 8, and 9) during the postburn storm and performed unpaired *t* tests ($\alpha = 0.05$) to evaluate the statistical significance of differences between watersheds.

DOM Reactivity and Simulated Chlorine and Bromine Substitution Reactions. We defined reactive DOM as the number of molecular features detected in the raw water samples but not present in the chlorinated and chloraminated samples. This definition of reactive DOM captures chemical transformation with chlorine-containing oxidants, primarily oxidation and, to a lesser extent, halogenation.[34] Within the chlorinated and chloraminated samples, potential chlorinated features were determined by the presence of the ^{37}Cl isotope [M + 1.99705] and its relative abundance (20−40% of the ^{35}Cl candidate feature), and brominated features were determined by the presence of the ^{81}Br isotope [M + 1.99795] and its abundance (40−60% of the ^{79}Br feature).[35] Halogenated candidates were screened against the neutral masses to ensure Cl or Br was not the adduct (tolerance of 0.1 ppm) or had previously assigned molecular formulas. To identify plausible precursors to organohalogens from raw water, we performed computer simulations of chlorine and bromine substitution reactions. We simulated H−Cl [M + 33.9610] and H−Br [M + 77.9105] substitution reactions to each molecular ion in the raw water samples and checked for the presence of the corresponding halogenated product ([M − H + Cl] or [M − H + Br]) in the chlorinated feature list. We understand that the dynamic range in FTICRMS might not yield the same isotopic ratio and depends on the degree of halogenation, but the same conditions are applied on both unburned and burned watersheds even if the halogenated species are overestimated.

RESULTS AND DISCUSSION

Dissolved Organic Carbon and Nitrogen Changes after Prescribed Fire. DOC released in the burned watershed during the postburn storm was masked by accumulated DOC during the dry period (late April to May), which resulted in the release of a large amount of DOC in both unburned and burned watersheds (Figure 2A). Before the prescribed burn, there were significant differences between the DOC concentration distribution in the burned and unburned watersheds (Wilcoxon rank sum test; $p = 0.0086$), but after the prescribed burn, both watersheds had a 16 mg L^{-1} median increase in DOC and had similar DOC medians ($p = 0.4359$).

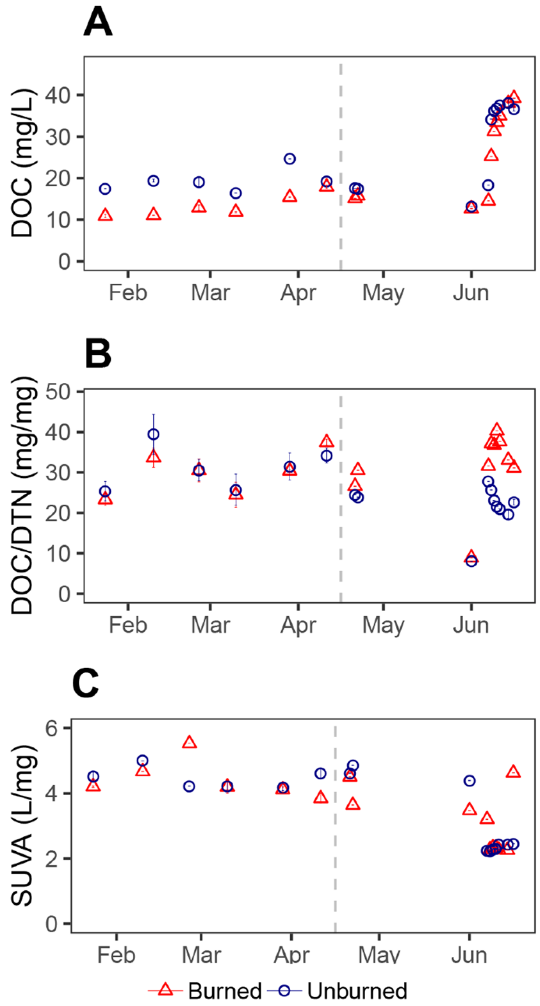

Figure 2. (A) Dissolved organic carbon (DOC), (B) DOC/dissolved total nitrogen ratio, and (C) specific UV$_{254}$ absorbance (SUVA) in water collected at the burned (red triangles) and unburned (blue circles) watersheds before the prescribed burn [January to mid-April ($n = 6$)] and after the prescribed burn in the burned watershed [late April to June ($n = 10$)]. The dotted gray line shows the prescribed burn date (April 16). Error bars are shown for duplicate samples at each sampling time point.

Despite no observable differences in DOC concentrations from the prescribed burn, the median DOC/DTN ratio increased by 1.88 mg of DOC (mg of DTN)$^{-1}$ during the postburn storm compared to prefire conditions (Figure 2B). Unlike the burned watershed, the median DOC/DTN ratio decreased by 8.18 mg of DOC (mg of DTN)$^{-1}$. During the postburn storm, dissolved organic nitrogen (DON) comprised >80% of the DTN present in both watersheds (Figure S2). However, the burned watershed continued to have a DON/DTN ratio of >80% throughout the storm, while the DON contribution to dissolved nitrogen in the unburned watershed decreased to 56% of DTN. The median SUVA (Figure 2C) decreased in both watersheds during the postburn storm compared to preburn values (burned, 1.88 L mg^{-1}; unburned, 1.92 L mg^{-1}), and similar to DOC concentrations, there were no differences between watersheds after the prescribed burn (Wilcoxon rank sum test; preburn $p = 0.6991$; postburn $p = 0.7394$).

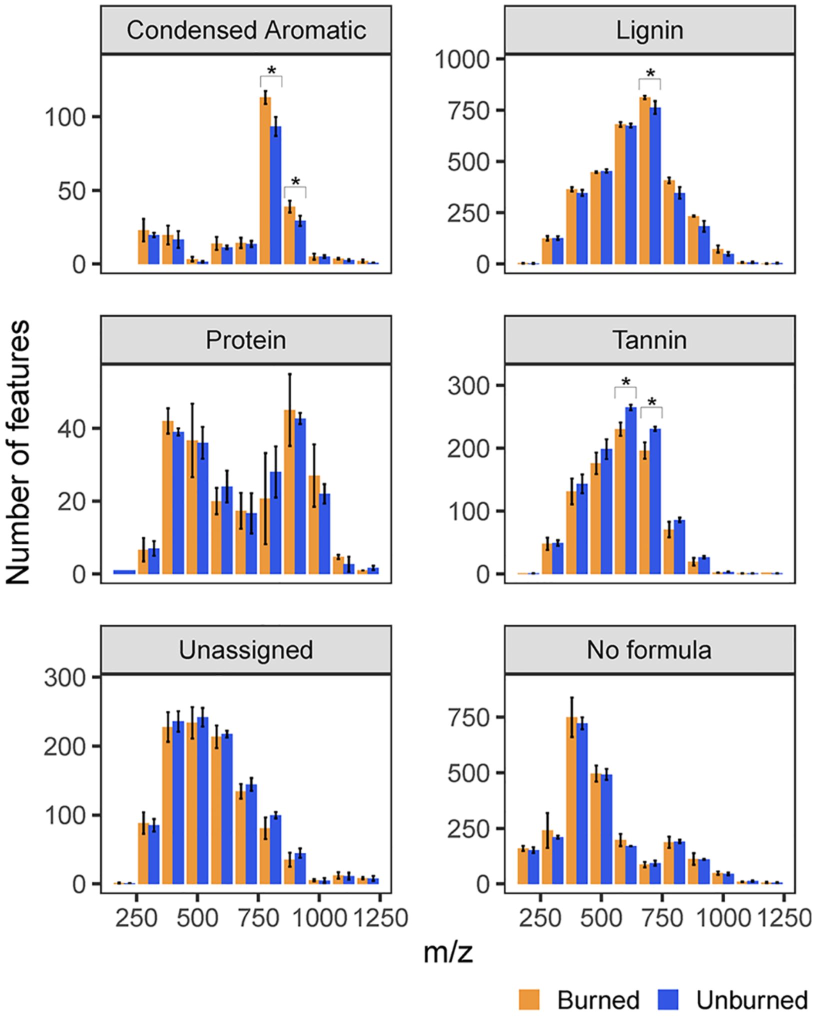

Figure 3. DOM-detected molecular features in burned and unburned watersheds during the first postburn storm. Each histogram (bin width of *m*/*z* 100) shows the number of features detected on the basis of compound classes: Condensed Aromatic, Lignin, Protein, and Tannin. The heading Unassigned indicates features that were assigned a formula but did not fall into a compound class, and the heading No formula indicates molecular features without a successful formula assignment. Bars show the standard deviation of three samples (June 7, 8, and 9) for each watershed during the postburn storm. Asterisks denote comparisons between the burned and unburned watershed with significant differences (unpaired *t* test; $p \leq 0.05$).

Table 1. Numbers of Molecular Features in the Burned and Unburned Watershed for Each Compound Class and Percentages of Features That Reacted upon Chlorination or Chloramination Formation Potential Tests[a]

	raw water (no. of features)		chlorinated (% reacted)		chloraminated (% reacted)	
	burned	unburned	burned	unburned	burned	unburned
condensed aromatic	237 ± 7	194 ± 5	50.6 ± 3.8	43.9 ± 4.2	26.3 ± 4.6	23.3 ± 5.4
lignin	3159 ± 13	2961 ± 138	36.9 ± 0.5	33.6 ± 3.3	16.9 ± 1.1	12.7 ± 1.7
protein	221 ± 14	220 ± 3	73.2 ± 6.8	70.0 ± 6.8	40.8 ± 7.3	38.0 ± 5.2
tannin	876 ± 86	1006 ± 46	25.2 ± 5.7	30.4 ± 3.03	13.9 ± 4.1	19.1 ± 1.8
unassigned class	1040 ± 95	1094 ± 56	54.8 ± 6.2	56.7 ± 3.5	45.9 ± 6.5	48.4 ± 2.5
no formula	2293 ± 123	2205 ± 49	56.9 ± 6.2	62.5 ± 3.2	46.6 ± 6.8	52.3 ± 4.2

[a] Mean and standard deviation of the three samples collected during the first storm after the prescribed burn.

Increased Chemodiversity and Smaller Molecular Size after a Prescribed Burn. The burned watershed had slightly more molecular features detected (mean of 7825 ± 207) compared to the unburned watershed (mean of 7679 ± 211), but the differences in molecular feature distribution were not statistically significant (unpaired *t* test; $p = 0.44$). Of the detected features, 62.6% were successfully assigned a formula in the burned watershed, compared to 65.1% in the unburned watershed. The largest gap in formula annotation was in features below *m*/*z* 600 (Figure S3). Despite similar distributions of detected molecular features, the burned watershed had more condensed aromatic (*m*/*z* 800−1000; unpaired *t* test, $p \leq 0.05$) and lignin-like (*m*/*z* 800−900; unpaired *t* test, $p \leq 0.05$) features (Figure 3 and Table 1). Conversely, the unburned watershed had more tannin-like features (*m*/*z* 600−800; unpaired *t* test, $p \leq 0.05$) (Figure 3).

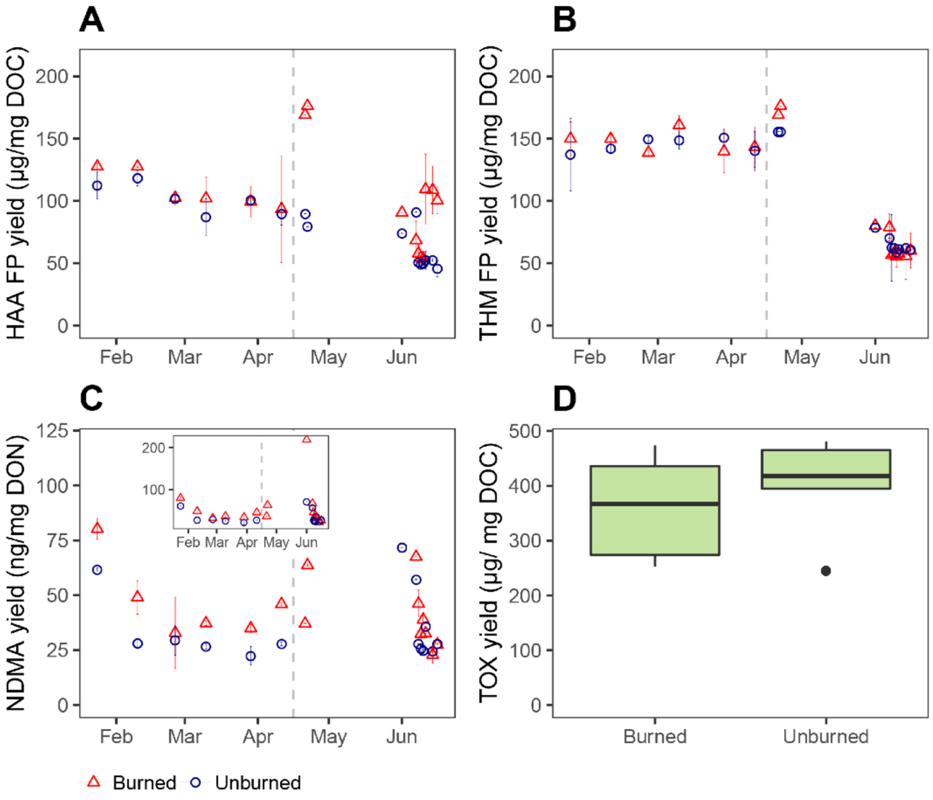

Figure 4. Disinfection byproduct formation potential tests in the burned and unburned watersheds before the prescribed burn [January to mid-April ($n = 6$)] and after the prescribed burn in the burned watershed [late April to June ($n = 10$)]. The dotted gray line indicates the prescribed burn date (April 16). (A) Haloacetic acid (HAA_9) and (B) trihalomethane (THM_4) yields after the chlorination formation potential test. (C) *N*-Nitrosodimethylamine (NDMA) yield after chloramination formation potential test. (D) Postburn total organohalogen yield during chlorination (TOX). No TOX yield data available from January to April and no NDMA yield available for unburned watershed April 21 and 22. Error bars are shown for duplicate samples at each sampling time point.

In agreement with our results, a study comparing a fire-impacted boreal forest to a long-unburned forest found more condensed aromatic and lignin-like features in the recently burned site.[36] The lignin-like features were attributed to burned plant residues in that study.

CHO-containing formulas comprised mostly lignin and tannin-like classes, whereas formulas with heteroatoms (N, P, and S) spanned primarily protein and condensed aromatic-like features (Figure S4B). Most of the condensed aromatic-like features contained nitrogen (Figure S5), which could be attributed to black nitrogen compounds previously reported in pyrogenic organic matter.[7−9]

Disinfection Byproduct Precursor Changes in Formation Potential Tests. Other factors common to both watersheds had a larger impact on carbonaceous DBP yield during chlorination compared to the impacts from the prescribed burn. Before the prescribed burn, both watersheds had similar HAA_9 [median burned, 102.3 μg of (mg of DOC)$^{-1}$; unburned, 101.4 μg (mg of DOC)$^{-1}$; Wilcoxon rank sum test, p = 0.3939] and THM_4 [median burned, 146.6 μg (mg of DOC)$^{-1}$; unburned, 145.4 μg (mg of DOC)$^{-1}$; p = 0.6991] yields compared to those after the burn (Figure 4A,B). After the prescribed burn, the HAA_9 yield was higher in the burned watershed [burned, 95.6 μg (mg of DOC)$^{-1}$; unburned, 52.5 μg (mg of DOC)$^{-1}$] and this difference was found to be significant (p = 0.0115). In both watersheds, the main HAA_9 species were trichloroacetic acid (64−71% of HAA_9) and dichloroacetic acid (29−31% of HAA_9). Bromochloroacetic acid was the main species [≤70 μg (mg of DOC)$^{-1}$ in both watersheds]. Unlike the HAA_9 yield, the THM_4 yield was similar after the prescribed burn [median burned, 59.2 μg (mg of DOC)$^{-1}$; unburned, 62.3 μg (mg of DOC)$^{-1}$; p = 0.3527]. The THM_4 composition was dominated by trichloromethane (>99% of THM_4) and had <0.15 μg (mg of DOC)$^{-1}$ of brominated THMs. Previously, lab burning showed an initial increase in the yield of THMs and HAAs at 225 °C but decreased yields of these DBPs have been reported at higher temperatures.[8]

While we observed an increased HAA_9 yield in the burned watershed (vs unburned) after the prescribed burn, the yields were lower than under preburn conditions. The moderate impacts on HAA_9 yields are indicative of the low severity of prescribed burns compared to wildfire and suggest that other factors common to both watersheds, such as the dry period during May (Figure S1), had a stronger impact on changes in THM4 and HAA_9 yield than the prescribed burn.

In chloramination formation potential tests before the prescribed burn, the NDMA yields were statistically significant before the prescribed burn [median burned, 41.6 ng (mg of DON)$^{-1}$; unburned, 27.9 ng (mg of DON)$^{-1}$; Wilcoxon rank sum test, p = 0.0411] (Figure 4C). After the fire, the difference in NDMA yield between watersheds was not significant [median burned, 32.6 ng (mg of DON)$^{-1}$; unburned, 26.7 ng (mg of DON)$^{-1}$; Wilcoxon rank sum test, p = 0.2743]. Despite the similarities, the outlier in the burned watershed [218 ng of NDMA (mg of DON)$^{-1}$ (insert of Figure 4C)] corresponded to the first sample of the postburn storm, which unlike all of the other samples had a very low DON/DTN ratio [0.11 mg

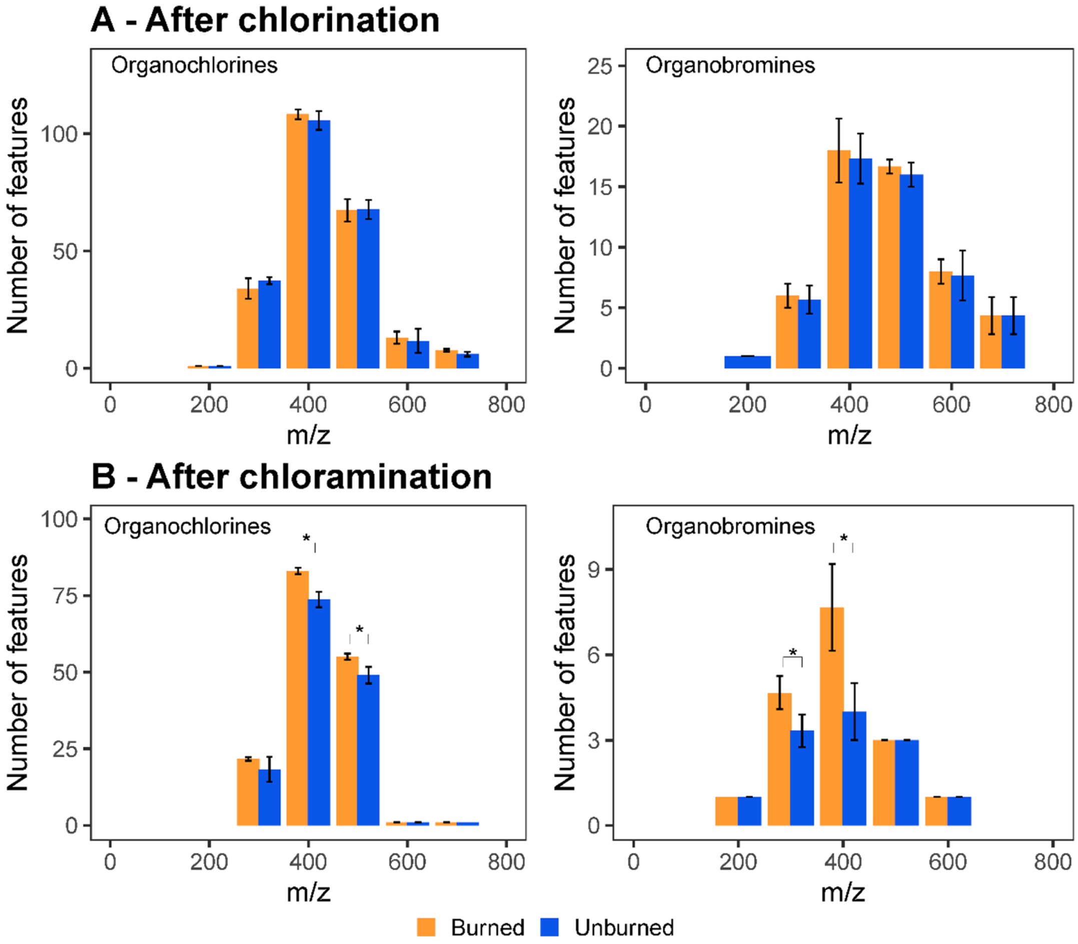

Figure 5. Tentative organohalogen features in the burned and unburned watershed samples during the first postburn storm (bin width of m/z 100). (A) Organohalogen features in chlorination formation potential samples. (B) Organohalogen features in chloramination samples. Bars show the standard deviation of three samples (June 7, 8, and 9) for each watershed during the postburn storm. Asterisks denote comparisons between burned and unburned watersheds with significant differences (unpaired t test, $p \leq 0.05$).

mg^{-1} (Figure S2)]. Our findings in this study contrast with increased NDMA yields observed in water extracts from organic matter in wildfire,[37] perhaps due to the low severity of the prescribed burn compared to wildfire.

Prescribed Burn Impacts on DOM Reactivity during Chlorination and Chloramination. The larger diversity in the chemical fingerprint of the burned watershed resulted in higher reactivity upon chlorination and chloramination. The burned watershed had a higher percentage of reactive condensed aromatic and lignin-like features compared to the unburned watershed (Table 1). Among compound classes, protein and condensed aromatic-like features had the highest proportion of reacted features (chlorination, 43.9−73.2%; chloramination, 23.3−40.8%) for both watersheds. The lower reactivity in chloraminated samples is consistent with observations on disinfection of chromophoric DOM.[38]

The difference in total organochlorine yield in both watersheds during the postburn storm was not significant (Wilcoxon rank sum test, p = 0.5887) (Figure 4D). In the chlorination formation potential tests, 20−25% was not captured by THMs and HAAs based on absorbable organic halides (Figure S6). Despite the similar TOX yield between watersheds, FTICRMS isotope analysis allowed us to determine plausible organohalogens. The distribution of chloraminated and chlorinated features was smaller (m/z <800) compared to the distribution of raw water features (Figure 5). This finding is consistent with a study of DBP formation during drinking water treatment in Sweden, which identified organohalogens in the range of m/z 240−570.[15] Moreover, chlorinated and chloraminated samples from both watersheds resulted in a more negative mass defect compared to raw water samples (Figure S7), which could be attributed to the introduction of oxygen and halogens, both expected reactions during chlorination of organic matter.[34] Chloramination of burned watershed samples yielded a larger number of organochlorine (m/z 400−600; unpaired t test, $p \leq 0.05$) and organobromine (m/z 300−500; unpaired t test, $p \leq 0.05$) features compared to the unburned watershed (Figure 5).

Computer-simulated halogen substitution reactions (H−Cl and H−Br) allowed us to further investigate which of the watershed features in raw water samples underwent direct halogenation. Overall, direct halogen substitution precursors identified account for ~10% of total organohalides detected in Figure 5. The peak count range of these precursors is m/z 300−400 (Figure 6), whereas the peak considering all plausible organohalogens (Figure 5) is slightly higher (m/z 400−500). These observations suggest that the majority of halogenated features underwent other reactions, such as oxidation or hydrolysis, prior to halogenation. Lignin and tannin-like features comprised most of the precursors that underwent directly chlorine substitution reactions in both chlorination and chloramination (Figure 6). Lignin and tannin-like features

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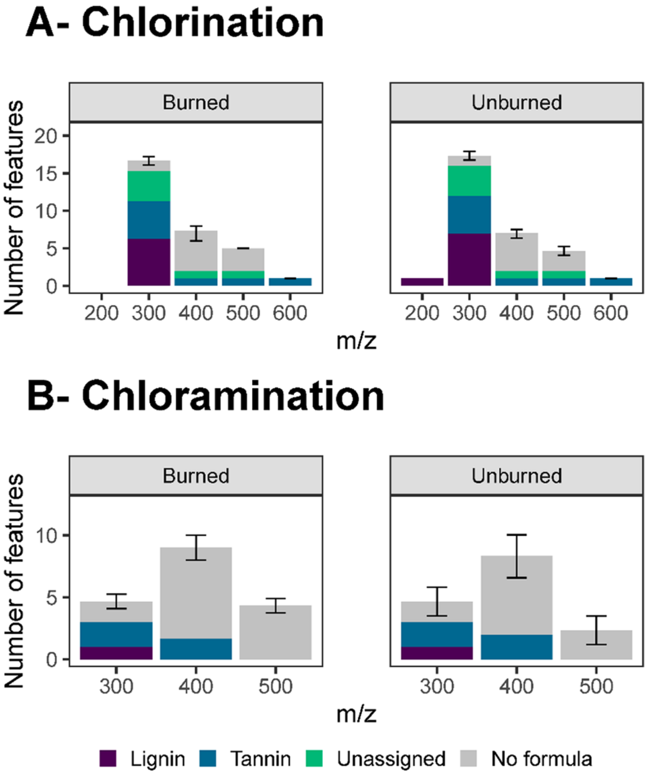

Figure 6. Precursors in raw water samples in burned and unburned watersheds that match computer-based substitution reactions for tentative halogenation features found in chlorination and chloramination. (A) H−Cl substitution precursors during chlorination and (B) H−Cl substitution precursors during chloramination. Fewer than five H−Br substitution precursors were found for chlorination, and none were identified for chloramination. Unassigned class indicates features that were assigned a formula but did not fall into a compound class, and No formula indicates molecular features without a successful formula assignment. Bars show the standard deviation of three samples (June 7, 8, and 9) for each watershed during the postburn storm.

include aromatic structures with medium to high O/C ratios that might be sources of BPCAs detected by Thurman et al.[9]

CONCLUSIONS

The moderate impacts on DOM in this study suggest that prescribed fire has a similar fingerprint and DOM concentrations compared to those of the unburned site, and that other environmental processes, like the dry period, wield a stronger influence on DOM dynamics. Prescribed fire did not show significant changes in DOC concentrations compared to the adjacent parallel watershed and resulted in only a brief HAA yield increase during the first postfire storm. However, the increased chemodiversity of condensed aromatics and lignin (*m*/*z* 700−1000) in the burned watershed and in chloraminated burned watershed water (*m*/*z* 300−600) should be further studied to identify if any of the detected features in this range pose a health risk. Taken together, our results suggest that prescribed burns likely pose low-water quality risks to drinking water sources.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00015.

Watershed flow and precipitation, DON/DTN ratios, *m*/*z* distribution of molecular futures detected, van Krevelen plots, N-containing polycondensed aromatic features, percentage of unknown organohalides, and mass defect plots(PDF)

AUTHOR INFORMATION

Corresponding Author

Alex T. Chow − *Department of Environmental Engineering and Earth Science, Clemson University, Clemson, South Carolina 29634, United States; Baruch Institute of Coastal Ecology and Forest Science, Clemson University, Georgetown, South Carolina 29440, United States;* orcid.org/0000-0001-7441-8934; Email: achow@clemson.edu

Authors

Christopher I. Olivares − *Department of Civil and Environmental Engineering, University of California, Berkeley, Berkeley, California 94720, United States; Department of Environmental Engineering and Earth Science, Clemson University, Clemson, South Carolina 29634, United States;* orcid.org/0000-0001-6213-7158

Habibullah Uzun − *Department of Environmental Engineering, Marmara University, 34722 Istanbul, Turkey*

Cagri Utku Erdem − *Department of Environmental Engineering and Earth Science, Clemson University, Clemson, South Carolina 29634, United States*

Wenbo Zhang − *Baruch Institute of Coastal Ecology and Forest Science, Clemson University, Georgetown, South Carolina 29440, United States*

Carl Trettin − *Center for Forested Wetland Research, USDA Forest Service, Cordesville, South Carolina 29434, United States*

Yina Liu − *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States; Department of Oceanography, Texas A&M University, College Station, Texas 77843, United States*

Sarah D. Burton − *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States;* orcid.org/0000-0003-3077-6304

Errol W. Robinson − *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States*

Tanju Karanfil − *Department of Environmental Engineering and Earth Science, Clemson University, Clemson, South Carolina 29634, United States;* orcid.org/0000-0003-0986-5628

Complete contact information is available at: https://pubs.acs.org/10.1021/acsestwater.1c00015

Notes

The authors declare no competing financial interest.

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