

Chapter 16

Prescribed Fire Alters Dissolved Organic Matter and Disinfection By-Product Precursor in Forested Watersheds – Part II. A Controlled Field Study

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Forest detritus material is one of the major terrestrial sources of dissolved organic matter (DOM) in source waters. There is a health concern on DOM because it reacts with disinfectants to form a variety of potentially carcinogenic disinfection by-products (DBPs) during drinking water treatments. Prescribed fire is a common forest management practice in Southeastern US to reduce the risks of wildfire and beetle infestation. However, this forest management practice alters the composition and quantity of detritus materials on forest floor, changing the DOM and DBP precursors exports from those forested watersheds. In this book chapter, we discussed a prescribed fire study conducted in three 20m x 20m experimental plots in Hobcaw Barony, Georgetown, South Carolina. Litter and duff mixtures of field samples before and after prescribed fire were collected for water extraction experiments in the laboratory. In addition, water extracts were further exposed to sunlight for 15 days in order to understand the biogeochemical processes on the degradability of DOM and DBP precursors. The concentrations of water extractable organic carbon (WEOC) and water extractable total nitrogen (WETN) from unburned detritus (60.3 g-WEOC/m²

and 1.9 g-WETN/m²) were significantly greater than those from burned detritus (11.4 g-WEOC/m² and 0.5 g-WETN/m²). Importantly, the yield of DBP was significantly reduced from 3651 mg-THM/m² to 484 mg-THM/m² after fire. There was no change in specific DBP formation in both burn and unburned samples after sunlight exposure although significant decreases in ultraviolet absorbance and fluorescence intensity were observed. This field study showed that prescribed fire could significantly decrease the production of dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) per unit area in forest floor and potentially decrease the DBP formation in water supply.

Introduction

It is well known that natural organic matter (NOM) is the major precursor of disinfection by-products (DBPs) during the chlorination process in water treatment systems (1, 2). It is estimated that NOM constitutes 50-90% of dissolved organic carbon (DOC) in freshwater systems (3). Reducing the import of DOC into natural waters used as drinking water sources can potentially minimize the formation of DBP during the chlorination process. Water in forested watersheds is a critical source of drinking water. Approximately 180 million people in over 68,000 communities in the United States rely on forested lands to capture and filter their drinking water (4). Large scale of natural disturbance in forest could substantially influence water characteristics and consequently impact the treatability downstream.

Several studies have reported negative effects of wildfire on the water quality of forested watersheds (5-7). Prescribed fire treatment is usually implemented as a low-cost-effective tool to reduce hazardous fuels in the forest and risks of unwanted wildfires as well as recycling nutrients back to the soil. Richter and colleagues in their watershed scale study (8) indicated that periodic prescribed fire within the Francis Marion National Forest in South Carolina is not likely to have appreciable effects on the quality of stream rivers. Also, Arkle and Pilliod (9) found that prescribed fire had no effects on stream habitats in Payette National Forest, Idaho. Caldwell and colleagues (10) reported that carbon-nitrogen ratios did not differ between streams affected by prescribed fire treatment and reference streams within a grassland system on the Valles Caldera National Preserve, New Mexico. It is noted that nutrients were measured quantitatively in those researches to assess the effects of prescribed fire on the aquatic systems; however, little is known regarding the effects of prescribed fire on the quantity and quality of DOM exported from forest fuels.

Dead and down woody materials, litter, grasses, herbaceous plant materials, and short shrubs are not only forest fuels but are also parts of terrestrial sources of DOM in forested watersheds. According to Chow and colleagues (11), the DOC extracted from California oak woodland litter is an important precursor in

forming DBPs and the reactivity of litter and leaf leachate is dependent on types and decomposition stages of vegetation. When prescribed fire occurs, those forest litter materials could be chemically oxidized and transformed and consequently alter the quantity and quality of DOM exported from the forested watersheds.

In order to study effects of prescribed fire on water quality of forested watersheds, it is important to understand the characteristics of DOC leaching from burned litter and duff materials. Moreover, DOM in natural water may undergo various chemical, physical, and biological reactions during water conveyance in streams before entering water treatment facilities. Photochemical reactions of DOM such as solar irradiation may cause oxidative degradation of DOM and result in smaller and more labile organic carbon moieties (12, 13). In fact, exposure of DOM to natural sunlight could alter the characteristics of carbon exported from foliar litters and consequently affect DBP formation in water disinfection processes (14, 15). The objectives of this field study were to understand the influence of prescribed fire on DOM and DBP precursor productions using detritus mixture burned in the field instead of using single vegetation species burned in a temperature controlled oven, as in Part I of the study. In addition, the leachates extracted from burned and unburned detritus were further incubated under dark and light conditions for 15 days in order to determine the influences of biogeochemical processes on the characteristics of DOM and DBP precursors.

Materials and Methods

Prescribed Burn in a Managed Forest

The controlled field study was conducted at Hobcaw Barony, a 71-km² wildlife refuges near Georgetown, South Carolina. The field site represents a typical coastal plain forest with loblolly pine (*Pinus taeda* L.) and longleaf pine (*Pinus palustris* P.). Within a mixed hardwood-pine stand that was scheduled to undergo a growing season prescribed fire, three adjacent 20×20m experimental plots (latitude 33°21'14 dpm, longitude 79°12'19") were established for the study. A field investigation on vegetation and fuel was conducted a month prior to the prescribed burn. Down woody materials were evaluated using Brown's Planar Intersect Method (16, 17) to obtain average litter and duff depths for each plot. Nine measurements were conducted in each plot. In addition, prior to the execution of the growing season prescribed fire, a representative sample containing detritus material from each 20m x 20m plot was collected in 17"x9" quadrants with care as to avoid as much mineral soil collection as possible. Samples were placed into labeled brown paper bags that were oven-dried and stored for later analysis. On May 29, 2014, a prescribed fire classified as a periodic growing season burn was conducted using a drip torch and a backing fire technique. Characteristics of the prescribed fire were visually observed and recorded according to the National Park Service Fire Monitoring Handbook (18). The fire was naturally extinguished after approximately 3 hours.

Characterization of DOM and DBP Precursors

An hour prior to ignition and immediately after fire extinction, destructive surface detritus materials samples including the mixture of litter and decomposed duff without mineral soil were randomly collected from each plot (one composite sample from 3 subsamples per plot). Sealed plastic bags were used to transport the samples to the lab where they were weighted and placed into a drying oven at 50°C. After 72h samples were re-weighted and moisture content calculated.

Dried unburned and burned forest detritus were grounded and sieved through a 2 mm screen and fraction < 2 mm was used for analysis. To simulate rainwater flush on forest detritus and to collect the leachate extracted, 20 g of sieved material was mixed with 200 ml Milli-Q water in a 250 ml Erlenmeyer flask and placed on an orbital shaker operated at 250 rpm for 2h. Milli-Q water was used because it generally extracts a greater amount of DOC comparing with other water solutions containing salt (18), and also minimize any contamination of carbon source. Extracts were filtered using 0.45 μm polyethersulfone membrane filters (Supor-450, Pall Gelman Science) previously flushed three times with Milli-Q water. Ultraviolet absorbance at 254 nm (UVA_{254}), fluorescence, water extractable organic carbon (WEOC) and water extractable total nitrogen (WETN) were measured in the filtered extracts. The ultraviolet absorbance scanning from 200 to 700 nm was measured using a Shimadzu UV-1800 in room temperature. WEOC and WETN were measured using a Shimadzu TOC-VCSH/CSN analyzer. Specific ultraviolet absorbance at 254 nm (SUVA_{254}) was defined as carbon normalized UVA_{254} ($\text{SUVA}_{254} = \text{UVA}_{254}/\text{WEOC}$). Fluorescence scans were conducted using a Shimadzu spectrofluorescence RF5301 with a 5-nm slit in excitation and a 5-nm slit in emission. In excitation-emission matrix (EEM) fluorescence spectroscopy, the matrixes were delineated and operationally defined into five regions using consistent excitation (ex) and emission (em) wavelength boundaries based on fluorescence of freshwaters (19): Region I, aromatic protein I (ex: 200-250 nm; em: 280-330 nm); Region II, aromatic protein II (ex: 200-250 nm; em: 330-380 nm); Region III, fulvic acid-like (ex: 200-250 nm; em: 380-550 nm); Region IV, soluble microbial by-product-like (250 nm < ex < 400 nm; em: 280-380 nm); and Region V, humic acid-like (250 nm < ex < 400 nm; em: 380-550 nm).

The analysis of DBPs formation was based on uniform formation condition (UFC) with sodium hypochlorite solution (Sigma-Aldrich) as a chlorination reagent as described in Part I. UFC was selected because its reaction condition is more closely related to conventional water treatment practice and the DBP formation in the UFC test is similar to those in finished water. DBPs including four trihalomethanes (THMs) (trichloromethane, dichlorobromomethane, dibromochloromethane, tribromomethane), four haloacetonitriles (HANs) (trichloro-acetonitrile, dichloro-acetonitrile, bromochloro-acetonitrile, dibromo-acetonitrile), and chloral hydrate (CHD) were measured according to USEPA method 551.1 using a gas chromatograph with a ^{63}Ni electron capture detector (Agilent 7890). The specific DBPs formation (i.e. specific THM formation, specific HAN formation, and specific CHD formation) were calculated by normalizing THM, HAN, and CHD concentrations with WEOC concentration

of water extracts. The measurement of specific DBP formation represents the reactivity of carbon in forming DBP during chlorination.

Potential changes in organic matter chemical composition due to fire effects were assessed using a pyrolyzer (CDS5500) connected to a GC–MS system Agilent 7890 equipped with a fused silica capillary column HP5MS (30 m×250 μm×0.25 μm inner diameter). Approximately 2 mg of unburned and burned samples were placed in tiny platinum capsules and pyrolysis was set to 700°C. Pyrolysis products were identified according to GC retention times, mass spectra with reference to the Wiley/NIST libraries and published mass spectra of pyrolysis products (20). Major identified compounds were classified as: aromatic (Ar), lignin (Lg), lipid (Lp), polycyclid aromatic hydrocarbon (PAH), phenolic (Ph), polysaccharide (Ps), and nitrogen compounds (N). Individual identified organic compounds are included in the list shown in Part I of this Chapter.

Dark and Light Incubations

To simulate effects of biogeochemical processes on DOM and DBP precursors during water conveyance from watershed to treatment facilities, 120 ml of diluted water extracts from burned and unburned samples were placed into 200 ml custom-made quartz tubes and exposed to sunlight. For each sample were used 2 quartz tubes, wrapping one with aluminum foil for a dark incubation and using the other one for sunlight incubation. All quartz tubes were placed in a wide-open area in the Baruch Institute (about 1 km from the burned experimental plots), for 15 days (October 7th to October 22^{ed}, 2014). According to the National Estuarine Research Reserve System sampling station from North Inlet Winyah Bay, SC (21), daily maximum photosynthetically active radiation (PAR) values ranged from 1200 to 1600 mmol/m²/15 min (except for 400 mmol/m²/15 min on October 12th) and temperature ranged from 12 to 30 °C during the entire experiment. After 15 days incubation, samples were characterized for DOC, DTN, UVA, fluorescence EEM, and DBP formation as described above.

Statistical Analysis

A paired t-test was used to determine differences in characteristics between water extracts from unburned and burned samples. The level of significance was set to $P < 0.05$. All data were analyzed using SPSS.

Results and Discussion

Controlled Field Burns

A field investigation on vegetation and fuel was conducted a month prior to the prescribed burn. The depth of litter and duff layers prior to fire in the experimental plots was 3.6 ± 2.3 cm and 1.1 ± 0.2 cm, respectively. Fuel moisture content was $11.6 \pm 5.7\%$ and top soil moisture content was $20.4 \pm 13.1\%$. At the start of the prescribed fire, cloud cover was 30% and the wind speed was 8 km/h out of the north as reported on the National Weather Service's website (22).

Precipitation was zero and the air temperature was 30°C with 63.5% of relative humidity as obtained from the HOBO U30-Wi-Fi station at the Baruch Institute (latitude 33°21'39, longitude 79°13'31). Approximately, the average flame height ranged from 30 to 60 cm, and flame length and depth ranged from 15 to 30 cm. The area after the prescribed burn had a mosaic burn pattern and was categorized at light burn severity (23) with the percent burned area of the three plots visually determined as $35 \pm 5\%$. Mass of detritus before burn was $3.5 \pm 0.7 \text{ kg/m}^2$, being reduced to $1.1 \pm 0.4 \text{ kg/m}^2$ after fire. Images of detritus material prior to, during, and following the prescribed fire are shown in Figure 1.

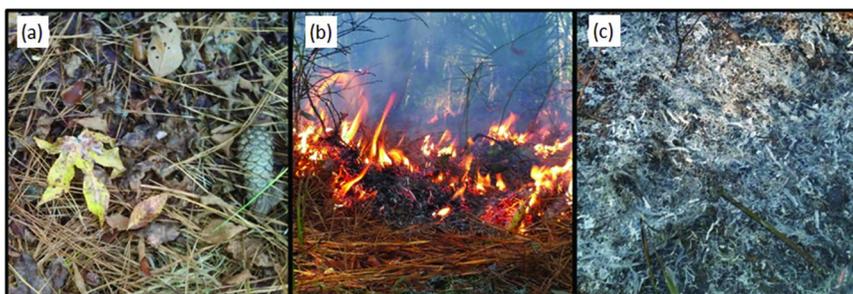


Figure 1. Images prior to (a), during (b), and following (c) the prescribed fire in Hobcaw Barony, SC.

Chemical Composition of Detritus Materials

Py-GCMS spectra from unburned and burned detritus materials are shown in Figure 2. A total of 53 and 46 peaks were identified in the unburned and burned sample respectively. Relative intensity of peaks usually decreased in burned detritus compared to original unburned detritus pointing to the loss of a high percentage of organic matter during burning. In addition, some of peaks such as trimethoxybenzene (38.8 min) and dimethoxyacetophenone (43.6 min) were missing in the burned samples (Figure 2). Meanwhile, an increase of peak intensity for compounds such as naphthalene (27.0 min) and biphenyl (36.0 min) were observed in burned samples, although those peaks were very small (Figure 2). Overall, Lg and Lp were decreased from 55 to 41% and 2 to < 1% respectively, whereas Ar, Ph, and PAH increased from 12 to 18%, 24 to 30%, and from 0.6 to 3%, respectively after fire. No obvious changes in N compounds and Ps were observed, staying at about 3 and 4% respectively. Importantly, the changes in relatively abundance of these fractions matched well with the controlled laboratory burns (Part I), suggesting mixed and individual species may not affect the results.

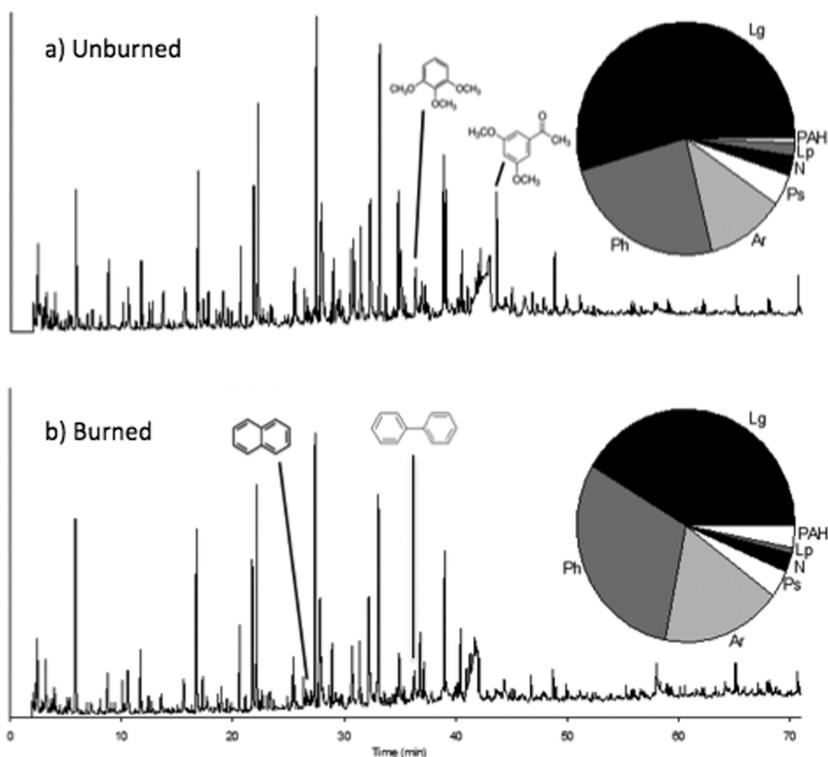


Figure 2. Py-GCMS Total Ion Chromatograms and relative abundance (pie charts; percentage) of different types of pyrogenic products from unburned and burned forest detritus material; aromatics (Ar); lignins (Lg); lipids (Lp); polysaccharides (Ps); nitrogens (N); polycyclic aromatic hydrocarbons (PAH); phenolics (Ph).

Yields of DOM and DBP Precursors

Results showed a significant reduction ($p = 0.01$) in WEOC after fire, decreasing from 1,703 to 925 mg/L. On a dried mass basis, WEOC was decreased from 17 to 9.3 mg-WEOC/g-detritus. In contrast, there was no significant changes in WETN, C:N ratio, and SUVA between unburned and burned extracts (Table 1).

Table 1. WEOC, WETN and DBPs Formation of Forest Detritus Samples before and after Burn; Average \pm Standard Deviation; n = 3

	<i>Before burn</i>	<i>After burn</i>	<i>P value</i>
Water Extractable Organic Matter (1:10 litter to water extraction)			
WEOC (mg/L)	1,703 \pm 271	925 \pm 373	0.01
WETN (mg/L)	55 \pm 15	43 \pm 17	0.29
C:N (mol: mol)	38 \pm 17	25 \pm 0	0.15
SUVA	2.03 \pm 0.16	1.98 \pm 0.47	0.44
Disinfection By-Product Formation			
THM (mmol/mol)	6.05 \pm 1.15	4.11 \pm 1.57	0.16
HAN (mmol/mol)	0.14 \pm 0.05	0.22 \pm 0.07	0.11
CHD (mmol/mol)	0.30 \pm 0.05	0.29 \pm 0.03	0.42

Fluorescence EEM of extracts of unburned and burned detritus materials with the same dilution factor are shown in Figure 3. The fluorescence intensities of the burned extracts were generally lower than that of unburned extracts, especially in fulvic acid-like (region III) and aromatic protein-like regions (regions I and II). However, the relative abundance of the five regions were no different when integrating with the fluorescence regional integration (FRI) method (data shown in Figure 5). Although changes in fluorescence regions were observed in Part I, the area after the prescribed burn had a mosaic burn pattern with the percent burned area of the three plots visually determined as $35 \pm 5\%$. In fact, significant portions of detritus materials, especially the lower layer of the detritus materials, were partially burned in this low intensity fire. DOM from this material may have influences on the overall characteristics of DOM in extracts.

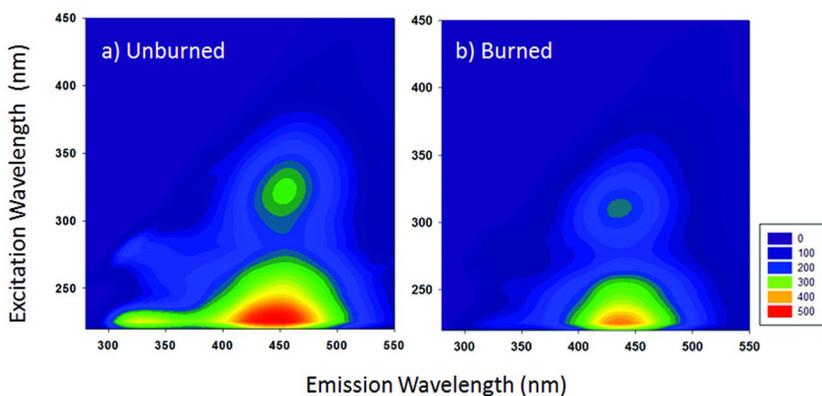


Figure 3. Fluorescence EEM of water extracts from (a) unburned and (b) burned detritus materials.

In terms of DBP formation, a lower reactivity in forming THM but a higher reactivity in forming HANs were observed after fire although those differences were statistically no significant. The reactivity of CHD was similar before and after burn. Therefore all the analyses showed that low intensity prescribed fire only reduced the quantity of WEOC but the chemistry, in terms of C:N ratio, optical properties including both UV/VIS and fluorescence measurements, and DBP formation, was no changed.

Biogeochemical Processes on DOM and DBP Precursors

Incubation experiment showed that quantity and quality of DOM in detritus leachate could be altered through biogeochemical process during water conveyance. Regardless of the fire effects, WEOC and WETN after both dark and sunlight incubations were lower than in the original samples (Figure 4), suggesting DOM in these extracts was highly degradable. These results were concomitant with the results showing that WEOC and WETN in burned detritus leachate were lower than in unburned detritus leachate (Figures 4a and 4b). Consider burned samples as an example, there were 76 and 59% decreases in WEOC and WETN respectively, in dark incubation, suggesting microbial processes possibly consumed these degradable organic matters. For the sunlight treatment, decreases of WEOC and WETN were even higher (78 and 72% respectively).

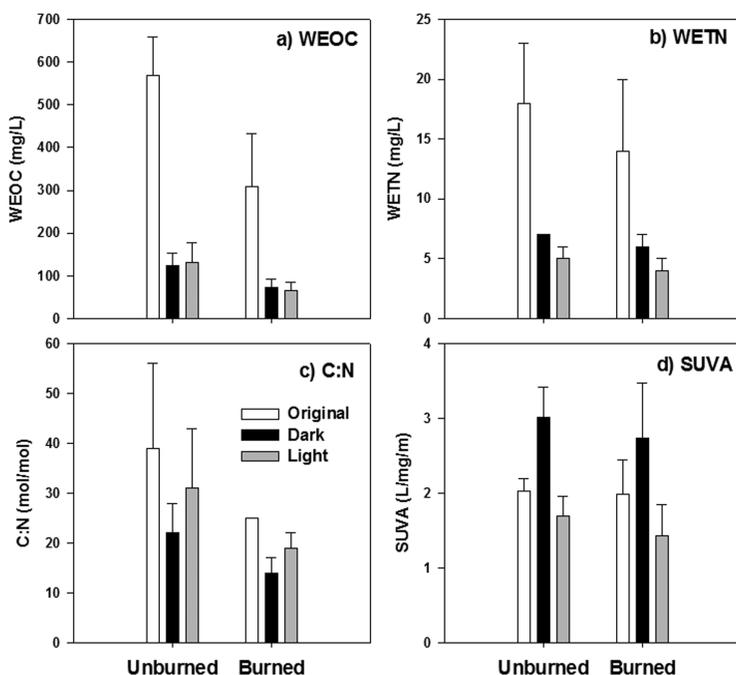


Figure 4. WEOC (a), WETN (b), C:N ratio (c), and SUVA (d) of the leachate extracted from unburned and burned detritus under 15-days dark and sunlight incubation; average \pm standard deviation; $n = 3$.

The C:N ratios of unburned and burned extracts after 15-days dark incubation were significantly lower than the values of original samples and sunlight incubation (Figure 4c), with an average of 22 and 14, respectively. On the other hands, the SUVA of dark incubation were highest among other treatments (Figure 4d). The SUVA values of unburn and burned extracts increased to 3.01 and 2.73 L/mg/m, respectively. Results might suggest microbial processes dominated in dark incubation and consumed degradable organic carbon, causing an increase in the proportion of relatively recalcitrant aromatic carbon in water. Lower C:N ratios and SUVA were observed after sunlight incubation when comparing to original samples (Figures 4c and 4d). In addition, an obvious decrease of humic acid-like fraction (Region V) in both unburned and burned extracts was observed after 15-day sunlight exposure (Figure 5). It has been demonstrated that sunlight could cause photobleaching of DOM is an important role in DOM characteristics in nature waters (24, 25).

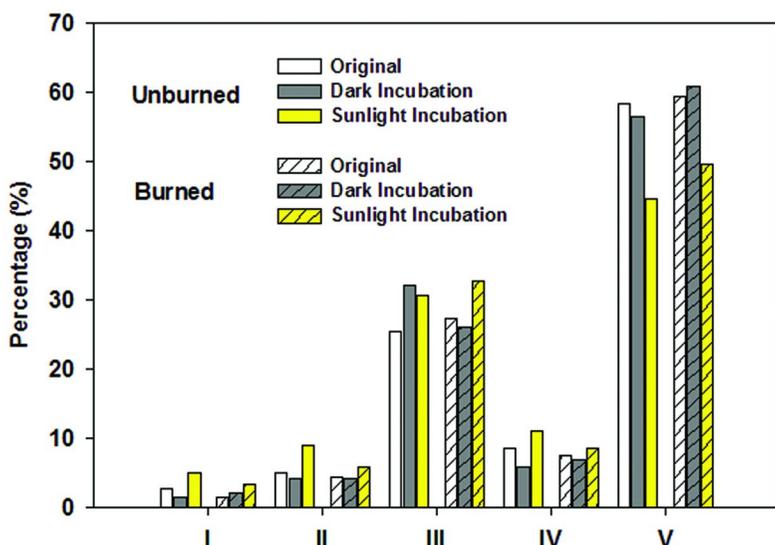


Figure 5. Percentage distributions of the five EEM regions of water extracts before and after prescribed fire and sunlight treatments. The five regions are: I (aromatic protein-like), II (aromatic protein-like II), III (Fulvic acid-like), IV (Microbial by-product-like), and V (Humic Acid-like).

Regardless of unburned and burned detritus leachate, results showed no significant changes on the THM formation after 15-day incubation (Figure 6a). SUVA₂₅₄ has been used as a measurement of DOC propensity to form THM and is generally proportional to specific THM formation (26, 27). However, this

study found that although sunlight exposure significantly decreased $SUVA_{254}$ values, the reactivity of DOC in forming THM was not significantly changed. Results also showed no significant changes on HAN formation after incubation, which suggested that the reactivity of DOC to form HAN was not sensitive to biogeochemical processes in such short time frame (Figure 6b). In contrast, an increase of CHD formation occurred after sunlight exposure as shown in Figure 6c, which is consistent with the previous studies (15).

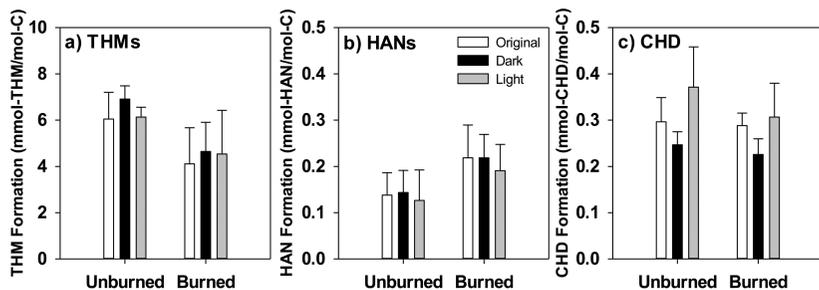


Figure 6. Specific formation potential of THMs (a), HANs (b), and CHD (c) of the leachate extracted from unburned and burned detritus under 15-days dark and sunlight incubation; average \pm standard deviation; $n = 3$.

Implications

Quantities of forest detritus, WEOC, WETN, and DBPs expressed per unit area in unburned and burned forest floor were summarized in Table 2. Prescribed fire consumed and oxidized detritus materials, reducing significantly ($p = 0.009$) the biomass per unit area ($\sim 65\%$ reduction). In addition, WEOC and WETN productions per unit biomass also reduced. Unburned detritus yielded 17 ± 2 g-WEOC/kg-detritus and 0.6 ± 0.2 g-WETN/kg-detritus, whereas burned detritus produced 9 ± 4 g-WEOC/kg-detritus and 0.4 ± 0.1 g-WETN/kg-detritus. Therefore there was a 81 and 74% reductions on WEOC and WETN per unit area, also resulting in a significant decrease in DBP yield per unit area. As summarized in Table 1, THM, HAN, and CHD yields were decreased in 87, 71, and 81%, respectively.

Table 2. Yields of Detritus, WEOC, WETN, and DBPs before and after Prescribed Burn in the Experimental Plots

	<i>Before burn</i>	<i>After burn</i>	<i>Reduction (%)</i>	<i>P value</i>
Detritus (kg/m ²)	3.5 ± 0.7	1.1 ± 0.4	65	0.009
WEOC (g/m ²)	60.3 ± 20.8	11.4 ± 8.5	81	0.01
WETN (g/m ²)	1.9 ± 0.6	0.5 ± 0.4	74	0.06
THM (mg/m ²)	3651 ± 682	484 ± 385	87	0.001
HAN (mg/m ²)	79 ± 6	23 ± 12	71	0.01
CHD (mg/m ²)	238 ± 56	46 ± 36	81	0.01

Both the controlled laboratory in Part I and controlled field studies in Part II (this chapter) demonstrated that prescribed forest fire could reduce DOM and DBP precursors in the detritus layers of forested watersheds in the southeastern US. Although our controlled laboratory study suggested DOM from burned materials could have a higher reactivity in forming N-DBPs during chlorination, significant loss in biomass and a reduction of extractability still result an overall reduction of DBP yield per unit area in a forested watershed. The results suggest that prescribed fire could be an effective watershed management controlling DBP precursors in source water.

Acknowledgments

Portions of this study were also supported by NIFA/USDA under project number SC1700489 and SCN-2013-02784, Joint Fire Science Program 14-1-06-19, and NSF Rapid grant 1264579 as presented in technical contribution number 6358 of the Clemson University Experiment Station.

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