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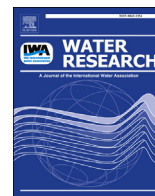
Publication Date

2016-08-01

DOI

10.1016/j.watres.2016.04.030

Peer reviewed



Temporal variations of disinfection byproduct precursors in wildfire detritus



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ARTICLE INFO

Article history:

Received 8 January 2016

Received in revised form

8 April 2016

Accepted 13 April 2016

Keywords:

Dissolved organic matter

Forest fires

Water quality

Source water treatment

Trihalomethanes

ABSTRACT

The Rim Fire ignited on August 17, 2013 and became the third largest wildfire in California history. The fire consumed 104,131 ha of forested watersheds that were the drinking water source for 2.6 million residents in the San Francisco Bay area. To understand temporal variations in dissolved organic matter (DOM) after the wildfire and its potential impacts on disinfection byproduct (DBP) formation in source water supply, we collected the 0–5 cm ash/soil layer with surface deposits of white ash (high burn severity) and black ash (moderate burn severity) within the Rim Fire perimeter in Oct 2013 (pre-rainfall) for five sequential extractions, and in Dec 2013 (~87 mm cumulative precipitation) and Aug 2014 (~617 mm cumulative precipitation) for a single water extraction. Water-extractable DOM was characterized by absorption and fluorescence spectroscopy and DBP formation tests. Both increasing cumulative precipitation in the field or number of extractions in the lab resulted in a significant decrease in specific conductivity, dissolved organic carbon, and DBP formation potential, but an increase in DOM aromaticity (reflected by specific UV absorbance). However, the lab sequential leaching failed to capture the increase of the NO_3^- -N/ NH_4^+ -N ratio and the decrease in pH and dissolved organic carbon/nitrogen ratio of ash/soil extracts from Oct 2013 to Aug 2014. Increasing cumulative precipitation, inferring an increase in leaching after fire, led to an increase in DOM reactivity to form trihalomethanes, haloacetic acids, and chloral hydrate, but not for halo ketones, haloacetonitrile, or *N*-nitrosodimethylamine, which were more related to the original burn severity. This study highlights that fire-affected DBP precursors for different DBP species have distinct temporal variation possibly due to their various sensitivity to biogeochemical alterations.

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1. Introduction

Wildfire is one of the strongest disturbances to forests in western North America and is likely to have more frequent and severe impacts on forest health and water supply as a result of global climate change and increasing human activities (Jolly et al., 2015; van Mantgem et al., 2013; Westerling et al., 2006). As more than 120 million people depend on water supplied from national forests in the USA (United States Forest Service, 2007), understanding how wildfires affect drinking water quality is critical for effective management of drinking water supply (Bladon et al.,

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2014). Studies across a spectrum of geographical locations have collectively recognized that wildfires have the potential to cause water quality deterioration in terms of increased loads of sediment, nutrients, metals, and persistent organic pollutants (Bladon et al., 2008, 2014; Smith et al., 2011). As demonstrated by previous post-fire water quality studies of the 2002 Hayman Fire (55,893 ha), Colorado (Rhoades et al., 2011) and 2003 Lost Creek Wildfire (21,000 ha) in Alberta, Canada (Emelko et al., 2011), wildfires are likely to have persistent effects on water quality (e.g., sediments and nutrients) ranging from a few years to more than a decade.

Compared to these relatively known water quality effects, less information is available on how wildfires can potentially affect dissolved organic matter (DOM) quantity and chemistry and disinfection byproduct (DBP) precursors in burned forest watersheds (Bladon et al., 2014). DBPs are a group of potentially harmful

chemicals formed during drinking water treatment where the oxidants (e.g., chlorine, chloramine, and ozone) react with DBP precursors like natural organic matter and inorganic constituents in source waters (Karanfil et al., 2008; Xie, 2004). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the carbonaceous DBPs regulated by the US-EPA with maximum contamination levels of 80 µg/L and 60 µg/L, respectively (Richardson et al., 2007). The highly toxic nitrogenous DBPs such as haloacetonitriles (HANs) and *N*-nitrosodimethylamine (NDMA) (Plewa and Wagner, 2009), although unregulated, are often detected in chlorinated and chloraminated drinking waters, respectively (Lee et al., 2007; Shah and Mitch, 2012). Previous studies have clearly shown that different DOM chemical compositions have a wide range of reactivity with oxidants to form DBPs (Dotson et al., 2009; Lee and Hur, 2014; Wang et al., 2012, 2014). Wildfires cause major transformations in DOM quantity and chemical composition depending on fire temperature and oxygen availability (Bladon et al., 2014; Santin et al., 2015; Wang et al., 2015a,b). Thus, understanding the load and reactivity of DOM following wildfires is critical for assessing the potential effects of wildfire on DBP formation in water supplies.

Following wildfires, a significant fraction of terrestrial DOM can enter surface waters via surface runoff and soil leaching contributing to increased DBP precursor concentrations in water supplies (Chow et al., 2009; Revchuk and Suffet, 2014). In a study of the 2013 Rim Fire in California (104,131 ha), Wang et al. (2015a) found distinct changes in the chemistry of water extractable DOM with burn severity being an important variable affecting the chemical characteristics of the DOM and its reactivity to form DBPs. With higher burn severity, the reactivity of DOM from surface ash/soil extracts to form THMs and HAAs was decreased; however, the formation of the more toxic brominated THMs, HANs, and NDMA was increased. After the High Park Fire in Colorado (35,323 ha), Writer et al. (2014) studied the temporal variation of stream water quality and the associated DBP formation potential in burned and unburned sites using monthly sampling. They found that the first storm event caused high concentrations of dissolved organic carbon (DOC; up to 13.7 mg/L) and DBP precursors (>250 µg/L THMs; >400 µg/L HAAs; 32.1 µg/L HANs) in burned watersheds. The reactivity of fire-affected DOM showed higher reactivity to form HANs, but comparable reactivity to form THMs and HAAs relative to the unburned site. Revchuk and Suffet (2014) found that the average DOC in source water was elevated by the 2007 Zaca Fire in California (97,208 ha) from 2.8 mg/L pre-fire to ~4.8 mg/L one year post-fire (~70% increase), and the THM formation potential was increased to ~200–290 µg/L (~49% increase).

Despite the information gained from these previous studies, there remain significant knowledge gaps hindering our understanding of the chemical, hydrological, and biological mechanisms regulating the “black box” with wildfire as input and drinking water DBPs as output. A mechanistic understanding calls for systematic studies on variations in temporal terrestrial and aquatic DBP precursors and the effects of site-specific meteorology, topography, ecosystem types, hydrological conditions, and fire characteristics. Revchuk and Suffet (2014) proposed that precipitation leaching and biological consumption were the primary factors affecting DOC dynamics from wildfire ash. However, it remains unquantified how the leaching process affects the fire-affected terrestrial precursors for different types of DBPs. There are several important questions yet to be answered, such as how do terrestrial DOM chemistry and chlorine reactivity change with increasing time and increasing leaching after fire alteration of the forest floor detritus layer, i.e., the surface ash/soil (AS) layer? Do temporal variations in DOM leaching depend on sites and burn severity? Do carbonaceous and nitrogenous DBP precursors change synchronously with increasing time

after fire?

To explore these questions, we investigated the temporal variation in characteristics and chlorine reactivity of water extractable DOM in surface deposits with white ash (AS-W; indicator of high burn severity) and black ash (AS-B; indicator of moderate burn severity) from conifer and chaparral vegetation within the 2013 Rim Fire perimeter in California. This study used two approaches to evaluate the variation of DBP precursors with increased leaching in AS extracts: 1) temporal sampling of AS samples that were exposed to natural precipitation, biological activity, and other environmental factors for a one-year period; and 2) a laboratory sequential leaching of the AS (AS-W vs AS-B; conifer vs chaparral) collected before any precipitation events to examine whether the lab dissolution/leaching process was feasible for simulating the temporal variations in the field.

2. Materials and methods

2.1. Site information and ash/soil sampling

The Rim Fire was the largest wildfire on record in the Sierra Nevada Mountains and the third largest wildfire in California history. The effects of the Rim Fire on water quality raised considerable public concern as it occurred in watersheds supporting the drinking water supply for 2.6 million residents in the San Francisco Bay area. In the Rim Fire perimeter, one mixed conifer forest site (37°54'41.1"N, 119°57'56.8"W; 1020 m elevation; ~30% west-facing slope) and one chaparral site (37°50'50.5"N, 120° 0'1.9"W; 1080 m elevation; ~10% southwest-facing slope) in the Tuolumne River Watershed in the Stanislaus National Forest were selected (Fig. S1). The conifer forest site was dominated by ponderosa pine (*Pinus ponderosa*), incense cedar (*Calocedrus decurrens*), and white fir (*Abies concolor*), and the chaparral site by *Ceanothus* spp., manzanita (*Arctostaphylos* spp.), and chamise (*Adenostoma* spp.) as identified from the remaining portions of the burned trees and shrubs. The mean annual precipitation in the region was ~920 mm, and mean annual temperature ~15 °C (7 °C for January and 24 °C for July).

As black ash and white ash are commonly formed from burning with moderate and high burn severity, respectively (Cilimburg and Short, 2005), visual ash characteristics have been adopted as an indicator of burn severity (or fuel combustion completeness; Bodi et al., 2014). Ash/soil composite samples (0–5 cm) with surface deposits of white ash (AS-W) or black ash (AS-B) were collected from the conifer and chaparral sites, on October 2, 2013 (no rainfall), December 19, 2013 (~87 mm cumulative precipitation), and August 5, 2014 (~617 mm cumulative precipitation; http://www.cnrfc.noaa.gov/arc_search.php). Three AS-W and three AS-B composite samples were collected from each site, and each composite sample was a mixture of five randomly collected ash/soil cores (7.6 cm diameter × 5.0 cm depth). It should be noted that some of the AS-W samples may have contained some recognizable black ash at the interface with the mineral soil; however, the majority of the ash in the sampled materials was distinctly white with little mixing of black ash. The black ash samples contained no visual white ash materials. The thickness of ash layer in each soil core ranged from about 2.5 to 4 cm with an estimated mean thickness of 3 cm for the composite samples. The AS carbon and nitrogen concentrations were 3.6–7.1% and 0.1–0.8%, respectively (Table S1). Both sites were burned with relatively high burn severity as all surface detritus was consumed by the fire (Fig. S1), and there was complete vegetation mortality. The black and white ash coverage accounted for ~90% and ~10% respectively of the area at each site.

2.2. DOM preparation and characterization

Water-extractable DOM was obtained by mixing 40.0 g of the air-dried and sieved AS (<2 mm) with 200 mL Milli-Q water in a 250 mL Erlenmeyer flask at room temperature for 2 h at a rotary speed of 250 rpm. After filtration using a pre-rinsed 0.45 μm polyethersulfone filter, the filtrate was analyzed for pH and specific conductivity (SC) using an Accumet XL60 dual channel pH/Ion/Conductivity meter and the remaining filtrate was stored at 4 °C in an amber glass bottle for further analyses.

To simulate the effects of multiple rainfall events and dissolution/leaching processes on the DOM chemistry and quantity from the AS, we conducted five sequential leaching events (Chow et al., 2003) on the air-dried samples collected in October 2013. Each sample was extracted with water and filtered using the aforementioned method to obtain the filtrate, and before the extraction the total weight of flask (~140 g), sample (40.0 g), and water (200.0 mL) was recorded. The residual on the filter was carefully transferred back to the Erlenmeyer flask and less than 0.1 g solid sample was lost in each extraction. For each extraction, 175 ± 5 mL filtrate was obtained depending on the water holding capacity of the materials. The extracted AS residue was retained and stored at 4 °C for ~18 h. Then, the sample was warmed for 2 h to reach room temperature, Milli-Q water added to maintain a constant total weight (flask + sample + water), and shaken prior to extraction and filtration. Five sequential extracts were obtained for each AS sample. In addition, to investigate the temporal variation of field samples, the first extracts of AS samples collected in Oct 2013, Dec 2013, and Aug 2014 were compared. The temporal samples (Oct 2013 → Dec 2013 → Aug 2014) were noted as “TS” and the sequentially leached samples (from the first to fifth extractions of the Oct 2013 AS samples) were noted as “SLS”.

For all water extracts, we measured DOC and TDN using a Shimadzu TOC/TN analyzer, and ammonia/ammonium-N ($\text{NH}_4^+\text{-N}$) and nitrate/nitrite-N ($\text{NO}_3^-\text{-N}$) using a Systeaa® Easychem™ discrete analyzer (Chow et al., 2013). The UV-VIS absorption and fluorescence excitation-emission matrix (EEM) of the DOM was determined by a Shimadzu UV-1800 spectrophotometer (scan range: 200–700 nm) and Shimadzu spectrofluorometer RF5301 (emission, or Em: 200–550 nm; excitation, or Ex: 220–450 nm; slit width: 5 nm; Zhou et al., 2013). Based on the results, optical indices reflecting the DOM composition were calculated. Specific UV absorbance at 254 nm (SUVA_{254} in $\text{L mg}^{-1} \text{m}^{-1}$), an indicator for DOM aromaticity, was calculated by dividing the UV absorbance at 254 nm by DOC concentration (Karanfil et al., 2002). The E2/E3 ratio, an indicator of molecular size of DOM, was calculated as absorbance at 254 nm divided by absorbance at 365 nm (Peuravuori and Pihlaja, 1997). The raw EEM was corrected (Murphy et al., 2010) and the fluorescence regional integration based on Simpson's rule (Zhou et al., 2013) was used to divide the EEM into five operationally-defined regions: I, tyrosine-like; II, tryptophan-like; III, fulvic acid-like; IV, soluble microbial byproduct-like; and V, humic acid-like. The percent fluorescent response in each region i ($P_{i,n}$) was determined as the proportion of area-normalized volume in region i to the entire region.

Several fluorescence-based indices, including fluorescence index, freshness index, and humification index, were calculated following Fellman et al. (2010). Specifically, the fluorescence index (FI), a common index to differentiate microbial versus terrestrial origins of DOM (~1.8 for microbial origin and ~1.2 for terrestrial origin), was determined as the ratio of fluorescence signals at Em 470 and Em 520 nm, at Ex 370 nm (Cory and McKnight, 2005). The humification index (HIX), an index for the relative abundance of humic substances, was calculated as the area under the emission spectra 435–480 nm divided by the peak area 300–345 nm, at Ex

254 nm (Ohno, 2002). The freshness index (β/α), an index for the relative abundance of recently produced autochthonous DOM, was calculated as the ratio of the fluorescence signal at Em 380 nm divided by the maximum signal between Em 420 and 435 nm, at Ex 310 nm (Wilson and Xenopoulos, 2009).

2.3. Disinfection byproduct formation

The chlorine reactivity of the DOM was evaluated using the disinfection formation potential (FP) test (Krasner and Scilimenti, 1993). Specifically, all samples were diluted to a DOC concentration of ≤ 3 mg/L, buffered to pH 8.0 ($\text{H}_3\text{BO}_3/\text{NaOH}$), and chlorinated with freshly prepared $\text{NaOCl}/\text{H}_3\text{BO}_3$ solution (pH 8.0) at 25 °C in the dark for 24 h without headspace. The chlorine dose was based on the organic and inorganic chlorine demand calculated as $[\text{Cl}_2] = (3 \times [\text{DOC}]) + (7.6 \times [\text{NH}_3])$ based on mass concentration (Krasner and Scilimenti, 1993). After quenching the residual chlorine with 10% Na_2SO_3 solution, DBPs were liquid-liquid extracted with MTBE and quantified by GC-ECD (Agilent 7890) strictly following US-EPA method 551.1. All samples were quantified for four THMs (trichloro-, dichlorobromo-, dibromochloro-, and tribromo-methanes), four HANs (trichloro-, dichloro-, bromochloro-, and dibromo-acetonitriles), three halo ketones (HKS; 1,1-dichloro-2-, 1,1,1-trichloro-2-, 1,2,3-trichloro- propanones), and chloral hydrate (CHD). Five HAAs (chloro-, dichloro-, trichloro-, bromo-, and dibromo-acetic acids) were measured for one water extract of each AS type from the different sampling times based on US-EPA method 552.2 ($n = 12$). The minimum reporting levels (MRLs) for all DBP species were approximately 0.1–0.3 $\mu\text{g/L}$.

As a commonly found and toxic DBP species in drinking water disinfected with chloramine (Shah and Mitch, 2012), *N*-nitrosodimethylamine was measured for the first extracts for all AS samples after chloramination following US-EPA method 521 (Selbes et al., 2013). Specifically, AS extracts were diluted to ~3 mg/L DOC and then reacted with excessive chloramine (100 mg/L as Cl_2) at pH 7.8 (phosphate buffered) in the dark at 22 °C for 5 days. After quenching the residual chloramine, the samples were extracted using solid-phase extraction employing cartridges pre-packed with 2 g of coconut charcoal and eluted with dichloromethane. The extracts were analyzed using a Varian GC 3800-MS/MS 4000 equipped with a RTX-5MS column (Restek 30 m length, 0.25 mm id, 0.25 μm thickness) with a MRL of 3 ng/L.

The DOM reactivity to form DBPs was expressed as specific DBP formation potential (SDBP-FP; $\mu\text{g-DBP/mg-DOC}$), which was calculated as the ratio of the DBP concentration and initial DOC concentration. The DBP-FP per mass of AS (in $\mu\text{g-DBP/g-AS}$), was calculated as the SDBP-FP in $\mu\text{g/mg-DOC}$ multiplied by the water extracted DOC yield of the source material (mg-DOC/g-AS).

2.4. Statistical analyses

The effects of sampling time in TS (or leaching order for SLS) and AS type (AS-W vs AS-B; conifer vs chaparral) were evaluated for all water quality parameters using two-way ANOVA with Tukey's HSD test. In this study, we primarily focused on temporal variation of DOM as DBP precursors in AS. Correlations between the SDBP-FP and the optical indices of the AS DOM were evaluated using the two-tailed Pearson's method. All optical indices and SDBP-FP for AS DOM for TS were standardized and analyzed using principal component analysis (PCA). The SHAA-FP was not included in the PCA as we did not analyze HAA formation for all replicates, but it is expected that the SHAA-FP has a similar PCA loading to STHM-FP as it was highly correlated with STHM-FP ($r = 0.71$; $P < 0.001$).

3. Results and discussions

3.1. General extract quality

It has been widely reported that with higher soil burn severity, there will be lower organic matter remaining and higher soil pH due to the higher degree of mineralization and release of acid volatiles such as CO_2 (Certini, 2005; Wang et al., 2015a). For water extracts from October 2013 AS samples in this study, the chaparral AS-W extract had the lowest DOC (93.3 ± 19.6 mg/L) and DON (5.0 ± 2.6 mg/L) levels (Fig. 1) but the highest pH (11.8 ± 0.7), which collectively suggest the highest degree of detritus mineralization. There was little difference in extract quality between the conifer and chaparral AS-B samples, but large differences between the conifer and chaparral AS-W samples for most parameters (Table S2). The differences between AS-W samples are likely due to a higher soil surface temperature in the chaparral fire than in the coniferous forest fire (up to 700°C for chaparral and $200\text{--}400^\circ\text{C}$ for coniferous forest; Rundel, 1983). Comparing all sample types, the chaparral AS-W had the lowest potential to contribute DOM to water bodies.

From Oct 2013 to Aug 2014, all TS (temporal sample) extracts displayed decreasing pH, SC, DOC, and DOC/DON molar ratios with increasing post-fire leaching (Fig. S2 & Table S2). In this study, the decreases (mean \pm standard derivation) were $\Delta\text{pH} = 1.2 \pm 1.2$, $\Delta\text{SC} = 0.69 \pm 0.51$ mS/cm (equivalent to $62 \pm 26\%$ decrease), $\Delta\text{DOC} = 161 \pm 116$ mg/L ($74 \pm 17\%$), and $\Delta(\text{DOC}/\text{DON}) = 16 \pm 6$. The AS sample type commonly interacted with the sampling time to affect the general extract water quality (most $P < 0.01$; Table S4). The AS-W showed larger percentage loss in SC and DOC with increasing post-fire leaching compared to the AS-B (Fig. 1). For SLS (sequentially leached samples), pH and DOC/DON did not change significantly while the SC, DOC, TDN, DON, $\text{NH}_4^+\text{-N}$, and $\text{NO}_3^-\text{-N}$ consistently decreased with increasing leaching from the 1st to 5th

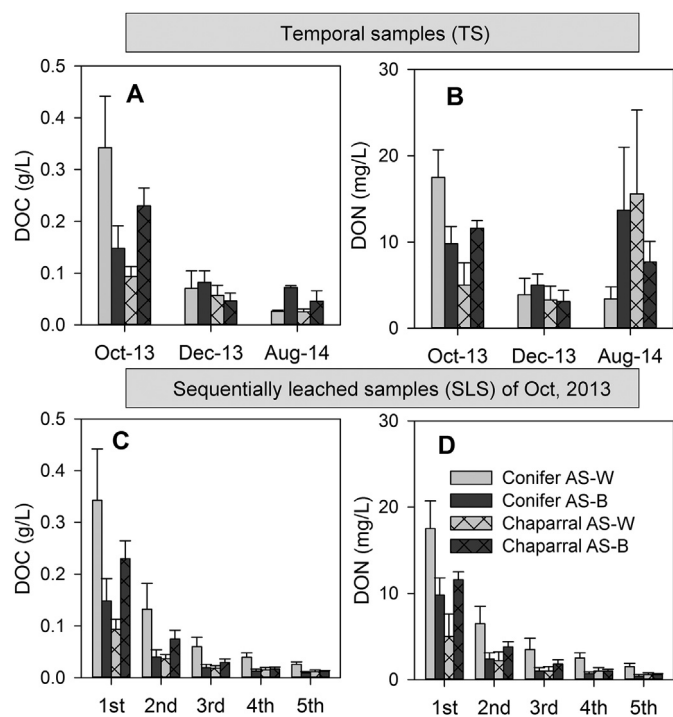


Fig. 1. Dissolved organic carbon (DOC) and nitrogen (DON) in ash extracts (40 g detritus: 200 mL water). Error bars refer to the standard deviation ($n = 3$). AS-W: ash/soil with white ash; AS-B: ash/soil with black ash.

extracts (Fig. 1 & Fig. S3; Table S3).

Both TS and SLS showed decreasing SC and DOC levels with increasing leaching (Figs. S2 and S3), suggesting that the dissolution/leaching process has contributed to the loss of soluble inorganic and organic materials from the AS to water bodies. The decrease in DOC agrees with Revchuk and Suffet (2014), which showed higher DOC in forest detritus 2 months after fire than detritus 2 years after fire, although the two samples were not from a same site. These observations can explain the highest stream inorganic and DOC concentrations in the first two storm events after fire relative to the later storm events in fire-affected watersheds (Audry et al., 2014; Writer et al., 2014). Most field studies observe elevated DOC concentrations in stream water following wild and prescribed fires (Gerla and Galloway, 1998; Mast and Clow, 2008; McEachern et al., 2000; Revchuk and Suffet, 2014; Writer et al., 2014), probably due to a higher degree of allochthonous contribution following fires (Shakesby, 2011).

Regarding other parameters, the SLS failed to capture the temporal trends of ash/soil acidification and organic matter decomposition/transformation associated with nitrogen leaching, DOC/DON ratio, and nitrogen speciation. First, the pH decreased in TS, but it was relatively stable for SLS (Figs. S2A & S3A). The acidic precipitation (Lajtha and Jones, 2013) over the winter season could be responsible for the temporal decrease in pH of the AS extracts; however, soil pH usually takes years to recover to pre-fire levels (Granged et al., 2011). Compared to non-burned sites in the same region (Wang et al., 2015a), our study suggests that within 1 year after fire the soil acidification had not yet recovered to pre-fire levels. The relatively stable pH for SLS in this study on ash or soil could not capture the temporal variation of field samples possibly because the short-term lab processes have excluded long-term biogeochemical processes. In addition, TS showed no distinct trends in dissolved nitrogen concentrations (TDN, DON, $\text{NH}_4^+\text{-N}$, and $\text{NO}_3^-\text{-N}$) but an increase of the $\text{NO}_3^-\text{-N}/\text{NH}_4^+\text{-N}$ ratio and a decrease of the DOC/DON ratio, whereas SLS showed decreases in all dissolved measures of nitrogen but no distinct trend for $\text{NO}_3^-\text{-N}/\text{NH}_4^+\text{-N}$ or DOC/DON ratios (Tables S2 and S3). Wan et al. (2001) conducted a meta-analysis on 87 fire studies and noted that soil $\text{NH}_4^+\text{-N}$ levels decreased but $\text{NO}_3^-\text{-N}$ levels increased within one year after fire. In this study, whereas a stable DOC/DON ratio in SLS indicates low microbial alteration, the lower DOC/DON ratio but higher $\text{NO}_3^-\text{-N}/\text{NH}_4^+\text{-N}$ ratio observed in Aug 2014 compared to Oct 2013 clearly reflect organic matter decomposition (organic carbon and nitrogen mineralization) and nitrification by microbes (Choromanska and DeLuca, 2002; Murphy et al., 2006; Wan et al., 2001). Overall, these contrasting results between TS and SLS indicate that field exposure of AS to natural processes (e.g., leaching, new input from plant recovery, microbial alternation, and sunlight irradiation) has an impact on AS DOM properties that is not manifested in the laboratory sequential leaching technique.

3.2. Optical characteristics of ash/soil extracts

Most optical parameters of TS extracts showed continuous changes with increasing leaching (Fig. S2H-L & Table S5). For example, the SUVA_{254} and HIX both increased with increasing post-fire leaching, from 1.81 to 3.92 to 2.93–4.55 L/mg-C/m and from 3.39 to 7.51 to 9.24–15.4, respectively. The E2/E3 decreased only for the AS-W extracts (from 9.47 to 11.2 to 6.01–6.29). Fluorescence regional integration (Fig. S4) showed decreased $P_{\text{II},n}$ (from 25.5–33.7% to 22.0–24.7%) and $P_{\text{IV},n}$ (from 11.5–12.4% to 10.1–12.1%) and increased $P_{\text{III},n}$ (from 37.0–41.6% to 42.7–45.9%) and $P_{\text{V},n}$ (from 11.8–14.1% to 17.6–18.7%) for all extracts. In contrast, $P_{\text{I},n}$ decreased only for AS-B extracts (from 8.18–10.8% to 2.86–5.05%). Although the FI decreased for the chaparral AS-W extract, there was no

consistent overall trend for FI or β/α across all extracts. Highly consistent with the TS, the SLS showed consistent trends for several optical parameters (Fig. S3 H–L & Table S6). Both SUVA₂₅₄ and HIX increased; E2/E3 decreased only for the AS-W extracts; $P_{II,n}$ and $P_{IV,n}$ decreased, $P_{III,n}$ and $P_{V,n}$ increased, and $P_{I,n}$ decreased for AS-B samples; FI decreased only for the chaparral AS-W extracts; and there was no significant change for FI or β/α across all samples. The AS sample type always interacted with the sampling time to affect the optical characteristics of extracts (all $P < 0.05$; Table S7).

As SUVA₂₅₄ is an index for aromaticity and HIX is an index for the degree of humification, the increases in these parameters for both TS and SLS suggest that the DOM from the early leachates after fire are less aromatic and humified than in the DOM from later leachates. Similarly, Revchuk and Suffet (2014) found an increase in SUVA₂₅₄ of detritus leachates two years after fire versus two months after fire in the Zaca and Jesuita fires (California) although they were not from exactly the same site. As the E2/E3 ratio is usually inversely correlated with the molecular size of DOM (Peuravuori and Pihlaja, 1997), the decreasing E2/E3 of AS-W extracts in both TS and SLS suggests that the molecular size of the DOM in AS-W extracts is lower in the early leachates compared to the later leachates.

Revchuk and Suffet (2014) found that fluorescence region I (tyrosine-like) was significantly lower in detritus leachates two years after fire versus two months after fire. This phenomenon was the case for the AS-B extracts from the Rim Fire which showed a sharp drop in $P_{I,n}$ from Oct 2013 to Dec 2013 in TS, and from the 1st to the 2nd sequential extracts in SLS. However, it was not the case in the AS-W extracts. Similar to the red shift in emission of fluorescence EEM in the present study (decreased $P_{II,n}$ and $P_{IV,n}$; increased $P_{III,n}$ and $P_{V,n}$), Revchuk and Suffet (2014; see their Fig. 8) observed a shift in the EEM of detritus leachates two years after fire versus two months after fire. As found in previous studies, the humic-like component of DOM from fire-affected ash/soil had a blue shift in emission, from “terrestrial humic-like” to “marine humic-like”, compared to DOM from non-burned detritus (Vergnoux et al., 2011; Wang et al., 2015a,b). The red shift in emission for the later leachates compared to the early leachates indicates a dissolution or degradation in DOM composition that transitions toward the composition of non-burned detritus over time (Revchuk and Suffet, 2014).

In sum, all the optical indices suggest that the dissolution/leaching process associated with long-term field exposure of AS preferentially removes the less aromatic, less humified, low-molecular-weight, and blue-shifted fluoro-active DOM components, and the remaining DOM in the AS is more aromatic and contains a higher humic-like fraction.

3.3. DBP precursors in water extracts from ash/soil

For the TS, DBP formation potential per unit mass of AS continuously decreased with increasing leaching from Oct 2013 to Aug 2014 (Fig. 2A–F) for all DBP species: THMs from 5.69 to 56.0 to 4.15–18.1 $\mu\text{g/g-AS}$ (14–89% decrease), HAAs from 14.1 to 81.9 to 4.61–17.1 $\mu\text{g/g-AS}$ (45–94%), HANs from 1.52 to 5.95 to 0.19–0.69 $\mu\text{g/g-AS}$ (58–94%), CHD from 1.63 to 4.70 to 0.40–1.39 $\mu\text{g/g-AS}$ (42–88%), and HKs from 0.11 to 0.78 to 0.03–0.13 $\mu\text{g/g-AS}$ (67–94%). There was a similar decreasing trend for NDMA from 7.04 to 21.4 to 1.62–7.75 ng/g-AS (48–90%) based on the chloramination test. For SLS, as the DOC level decreased with increased leaching (Fig. 1), the average DBP-FP decreased markedly for all DBP species (Fig. 2G–J).

For the TS, the SDBP-FP did not show a consistent temporal trend across all DBP species (Fig. 3A–F). The STHM-FP followed an increasing trend, from 11.9 to 33.0 to 32.1–55.4 $\mu\text{g/mg-DOC}$

($P < 0.001$; Table S8). The SHAA-FP and SCHD-FP were higher in Dec 2013 than Oct 2013, but there was no difference between Dec 2013 and Aug 2014 samples. The SHK-FP, SHAN-FP, and SNDMA-FP showed no statistical differences from Oct 2013 to Aug 2014. In contrast, for the SLS, the average SDBP-FP continuously increased for all DBP species (Fig. 3G–J). There was no statistical difference in SDBP-FP for either THMs or CHD between the 5th sequential extract and the Aug 2014 extract representing ~1 year of field exposure. In contrast, the SHAN-FP and SHK-FP of the 5th sequential extract were 3.3 and 2.5 times higher than the Aug 2014 AS extract, respectively. The large difference in SDBP-FP between the TS and SLS extracts suggested that the temporal changes in DOM reactivity to form DBP could not be explained by the simple laboratory dissolution/leaching processes.

Similar to the temporal patterns in TDN species (DON, $\text{NH}_4^+\text{-N}$, and $\text{NO}_x\text{-N}$) in AS extracts, the temporal variation in DOM reactivity to form HANs was not explained by dissolution/leaching processes alone. Relatively high SHAN-FP levels in DOM from AS extracts (particularly AS-W extracts) were previously observed in lab and field fire studies (Majidzadeh et al., 2015; Wang et al., 2015a,b). HAN concentrations were commonly $>2.5 \mu\text{g-HAN/mg-DOC}$ for field AS-W extracts and up to $17 \mu\text{g-HAN/mg-DOC}$ for lab burned litter. It suggests that there may be a potential concern for nitrogenous DBPs in managing drinking water supply following wildfires, especially during the first leaching events. In this study, the TS extracts did not show as high SHAN-FP as later extracts of SLS, suggesting that the reactive fire-produced HAN precursors in the AS were possibly photo-/bio-degraded/transformed, or rapidly diluted with less reactive precursors such as the recovered plant/soil-derived carbon-rich DOM (Wang et al., 2012) under field conditions. Thus, although HANs are an important concern as they are more potent carcinogens than common carbonaceous DBPs such as THMs or HAAs (Richardson et al., 2007) and high SHAN-FP has been found in lab-burned ashes ($>10 \mu\text{g-HAN/mg-DOC}$; Majidzadeh et al., 2015; Wang et al., 2015b), the extremely high reactivity of DOM to form HANs observed for the sequential AS extracts may not persist in field AS samples ($<5 \mu\text{g-HAN/mg-DOC}$ in Wang et al., 2015a) or source waters ($\leq 2.7 \mu\text{g-HAN/mg-DOC}$ in Writer et al. (2014)).

3.4. Correlations among SDBP-FP and optical properties

For SLS, most of the SDBP-FP and optical properties changed synchronously and thus there were remarkably high correlations among these parameters (Table S9). In contrast, TS displayed obvious disparities among the major carbonaceous DBPs (THMs, HAAs, and CHD) and nitrogenous DBPs (HANs and NDMA) resulting in low correlations of SDBP-FP among DBP species and correlations of SDBP-FP to different respective optical properties compared to those found for SLS extracts (Table S10). These results indicate that the DBP precursors for different DBP species changed differentially over time after fire and cannot be explained by laboratory dissolution/leaching processes alone.

The PCA of spectroscopic characteristics and chlorine/chloramine reactivity of DOM for the TS showed clear relations among different DOM properties (Fig. 4). While the STHM-FP, HIX, $P_{III,n}$, and $P_{V,n}$ showed high loading on the first principal component (PC1; 32.5% of total variance), the SHK-FP, SNDMA-FP, SUVA₂₅₄, E2/E3, FI, β/α , and $P_{I,n}$ showed high loading on the second principal component (PC2; 29.2% of total variance; Table S11). Whereas PC1 can be considered as the major effect of increased leaching, PC2 reflects the effect of soil burn severity. The PCA indicates that SDBP-FP for the major nitrogenous DBPs (HANs and NDMA) and a group of minor carbonaceous DBPs (HKs) are independent from the SDBP-FP for major carbonaceous DBPs (THMs, HAAs, and CHD) as they

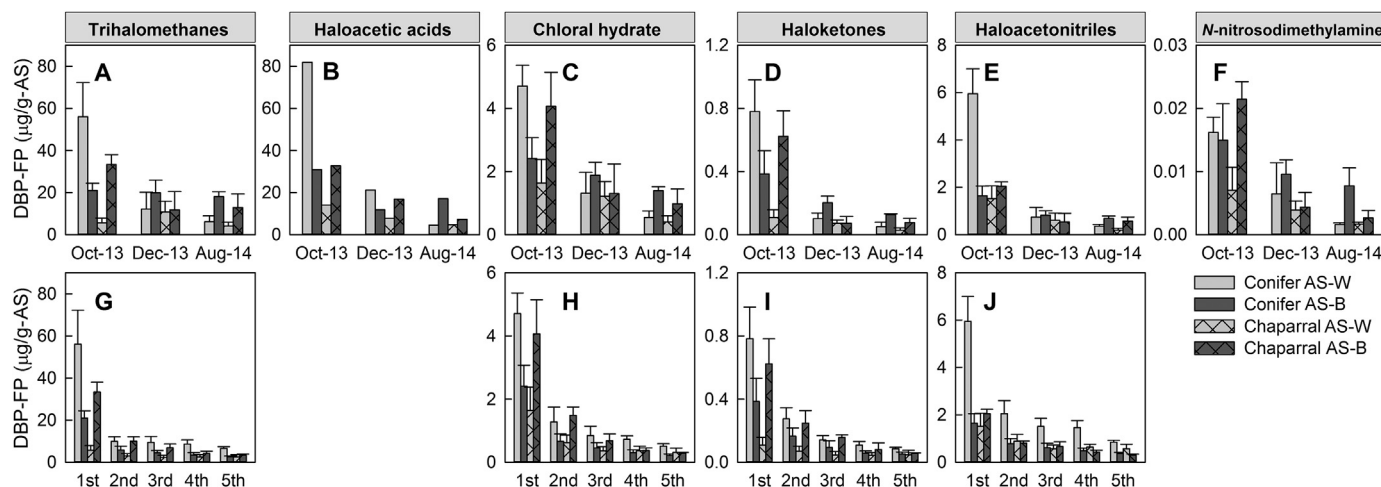


Fig. 2. Disinfection byproduct (DBP) formation potential (FP) per mass of ash. A–F: temporal sample (TS) extracts; G–J: sequentially leached sample (SLS) extracts for October 2013 ash/soil samples. Error bars refer to the standard deviation ($n = 3$). Haloacetic acids and *N*-nitrosodimethylamine were not measured for the sequentially leached sample extracts. AS-W: ash/soil with white ash; AS-B: ash/soil with black ash.

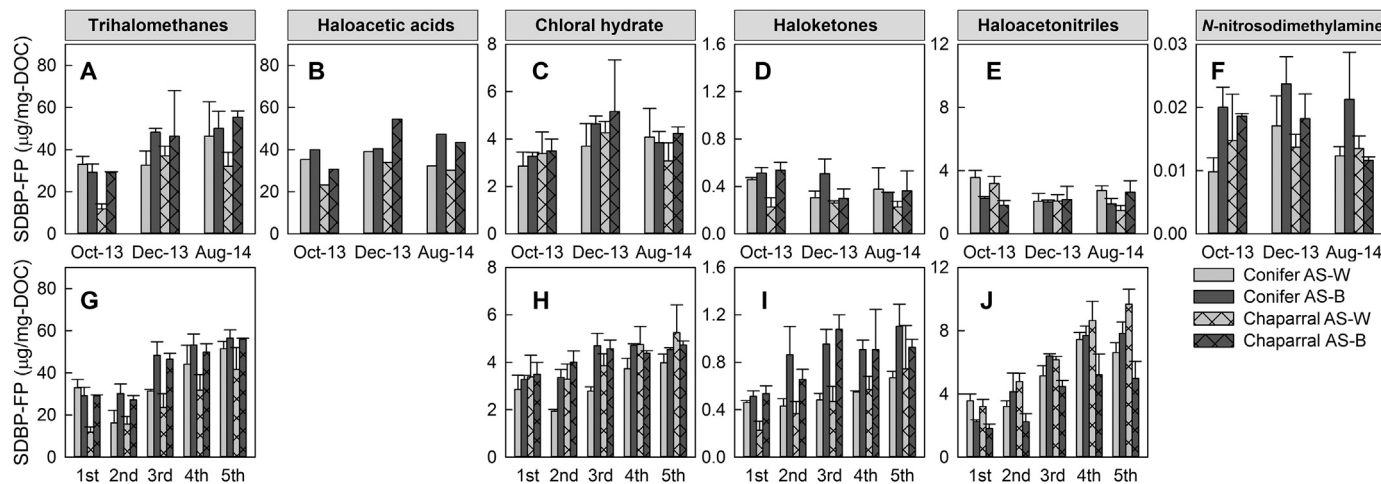


Fig. 3. Reactivity of dissolved organic matter from ash extracts to form disinfection byproducts (DBPs) as indicated by specific DBP formation potential (SDBP-FP). A–F: temporal sample (TS) extracts; G–J: sequentially leached sample (SLS) extracts for October 2013 ash/soil samples. Error bars refer to the standard deviation ($n = 3$). Haloacetic acids and *N*-nitrosodimethylamine were not measured for the sequentially leached sample extracts. AS-W: ash/soil with white ash; AS-B: ash/soil with black ash.

have considerably different loadings on the principal components (Fig. 4 & Table S11). This observation agrees with a recent study (Wang et al., 2015b) that showed THM and CHD precursors were more dependent on heating temperature, while HAN and HK precursors were highly dependent on oxygen availability. Based on the PCA results, the trends determined for the commonly monitored/regulated THM and HAA concentrations may not reflect the temporal trends for nitrogenous DBPs, such as HAN and NDMA concentrations.

Based on the component scores for different time categories, the DOM from Oct 2013 to Aug 2014 increased along PC1, indicating an increased humic-like DOM fraction contributing to DOM reactivity to preferentially form THMs with increasing time after fire (Fig. 4A). It is not surprising as the humic-like DOM component has long been identified as a reactive DBP precursor (Singer, 1999). Regarding the difference in DOM between AS-W and AS-B, the DOM from AS-W showed higher PC2 scores than DOM from AS-B (Fig. 4B). These findings support the contention that the DOM from AS-W is more aromatic, smaller in molecular size, and less reactive in the formation of NDMA and HKs (Wang et al., 2015a,b).

The difference in the PC2 score between AS-W and AS-B became smaller from Oct 2013 to Aug 2014, suggesting that the differences in chemical properties between AS-W and AS-B decreased with increasing time after fire. These decreasing differences between AS-W and AS-B could be due to physical processes in the field, such as wind, precipitation, and erosion, which may mix white and black ash materials.

3.5. Limitation of lab sequential leaching to capture temporal variations

Dissolution/leaching appears to be a major process affecting the quantity and chemical composition of organic and inorganic DBP precursors in the AS materials, as supported by the high consistency between TS and SLS for DOC, SC, optical properties of DOM (Fig. 1, S2 & S3), and DBP-FP (Fig. 2). These variations in leachate chemistry suggest leaching of an initial pulse of fire ashes may cause significant DOM loss to surface water bodies (Revchuk and Suffet, 2014) and can partially explain the higher stream DOM levels in the first several storm events after fire (Audry et al., 2014;

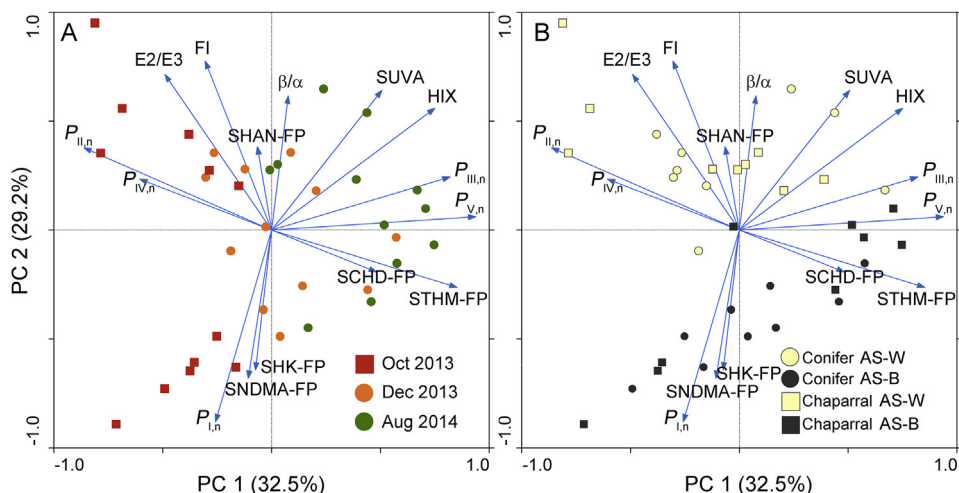


Fig. 4. Principal component analysis (PCA) for spectroscopic characteristics and chlorine/chloramine reactivity of DOM from ash/soil leachates. Panel A shows the component scores of different leaching stages after fire and panel B shows component scores of different sample types. Detailed PC loading for different DOM properties is available in Table S11. AS-W: ash/soil with white ash; AS-B: ash/soil with black ash.

Writer et al., 2014). Here, both TS and SLS suggest that AS DOM reactivity to form carbonaceous DBPs (THMs, HAAs, and CHD) can be elevated with increasing time or leaching after fire, as the DOM in early leachates is more hydrophilic, less aromatic, and less humified than that in later leachates. Thus, the lab dissolution/leaching process may partially capture the temporal dynamics of DBP precursor in burnt forest detritus. However, the lab dissolution/leaching processes alone failed to capture several temporal variations of ash/soil pH, DON concentration, DOC/DON ratio, nitrogen speciation (Tables S2 and S3), and DOM reactivity to form HANs (Fig. 3) in field incubated ash materials. One marked disadvantage of the lab dissolution/leaching process is that it cannot simulate several field biogeochemical processes, such as long-term microbial activity, plant recovery, photo-reaction, and other chemical reactions. Microbial processes are possibly important with increasing time after fire as reflected by the decreasing DOC/DON ratio, increasing $\text{NO}_x^-/\text{NH}_4^+$ ratio, and increasing humification degree (HIX) of DOM with increasing time and cumulative precipitation after fire.

4. Conclusions

This study investigated the temporal variations of spectroscopic characteristics and chlorine/chloramine reactivity for DOM from AS leachates after wildfire. Increasing cumulative precipitation after fire decreased SC and DOC concentrations in AS leachate, but increased DOM aromaticity, humic-like fraction, and reactivity to form THMs, HAAs, and CHD. The large losses of inorganic and organic constituents from AS samples for both TS and SLS clearly indicate that there was a large pulse of DOM released from the AS in the first year after the fire. The temporal variation was dependent on sample type with the AS-W (higher burn severity) having a greater percentage loss of SC and DOM when comparing to the AS-B (moderate burn severity). Temporal variations in TDN and the DOM reactivity in forming nitrogenous DBPs did not change significantly with increasing cumulative precipitation after fire, which could not be explained solely by dissolution/leaching loss. Also, DOM reactivity in forming nitrogenous DBPs was found to be more dependent on sample type (AS-W vs AS-B). In this study, we clearly demonstrated that fire-affected DBP precursors for different DBP species had distinct sensitivity to biogeochemical alterations with increasing cumulative precipitation after fire. Leaching effects only

partially explain the temporal variations of DBP precursors in wildfire detritus.

Acknowledgements

This work was funded by NSF RAPID grant (1361678) and partially supported by NIFA/USDA (SC1700489 and 2014-67019-21615) and the Joint Fire Science Program (14-1-06-19), as presented in technical contribution number 6425 of the Clemson University Experiment Station. J.W. appreciated the financial support from the China Scholarship Council (CSC[2011]3010).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.04.030>.

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