Low water treatability efficiency of wildfire-induced dissolved organic matter and disinfection by-product precursors

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ABSTRACT

Wildfire could alter both the quantity and composition of terrestrial organic matter exported into source water, and water treatability of fire-impacted dissolved organic matter (DOM) could be different from its unburned counterpart. Currently, there is no standard protocol to treat wildfire-impacted source water. To identify the best treatment practices in handling post-fire runoffs, we conducted a systematic controlled study using leachates of unburned white fir (*Abies concolor*) and Ponderosa pine (*Pinus ponderosa*) and black and white ashes (collected immediately and one year after the 2013 Rim Fire, California) to evaluate coagulation and oxidation strategies for controlling disinfection byproducts (DBPs) formation. Results showed that the efficiency (%) of alum coagulation in removing dissolved organic carbon and nitrogen followed the order of litter > ash immediately after the fire > ash one year after the fire. Alum coagulation was less effectiveness in removing DOM and DBP precursors in ash leachates, compared to litter leachates. This may be attributed to the loss of side chains and the decrease of DOM molecular weight during the wildfire, thus inducing lower removal efficiency of the DOM and DBP precursors during the alum coagulation. Considering use of brominated flame retardants by firefighters, the addition of bromide (Br^-) (100 μg/L) greatly increased the formation of haloacetonitriles by chlorine, and this increase was relatively lower in ash leachates. The influence of reaction time and pH on DOM reactivity was similar among the leachates of litter and ash samples. Our results show that alum coagulation followed by chloramination at alkaline pH is an effective strategy for reducing post-fire DBP formation in drinking water.

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1. Introduction

Water from forested lands has been widely used for drinking water production due to its high quality and lower treatment costs (Brown et al., 2008; Cunha et al., 2016; Elias et al., 2013; Murphy et al., 2015). However, carcinogenic disinfection byproducts (DBPs) can form throughout drinking water facilities via the reaction of oxidants/disinfectants with dissolved organic matter (DOM) present in the source waters. Because of warmer weather conditions, forest wildfires, especially in western North America, have increased in frequency and severity (Miller et al., 2009; Schoennagel et al., 2017; Westerling et al., 2006). Wildfires increase

the exports of sediments and nutrients to surface water (Oliver et al., 2012), resulting in devastating effects on downstream water quantity and quality (Bladon et al., 2014; Khan et al., 2015; Smith et al., 2011). Compared to reference watersheds, higher turbidity, dissolved organic carbon (DOC), and dissolved organic nitrogen (DON) were reported in streams draining from burned watersheds after the 2003 Lost Creek Wildfire, Canada, based on a four-year monitoring study by Emelko et al. (2011). Also, DBP formation in wildfire-induced DOM differs from that in DOM from unburned detritus. Writer et al. (2014) documented an increase in not only DOC concentrations and DBP formation but also DBP yields (μg/mg-DOC) in the Poudre River after less than 10% of the watershed was burned by the 2012 High Park Wildfire, Colorado. Our previous study (Wang et al., 2015) documented changes in terrestrial DOM characteristics and reactivity following the 2013 Rim Fire in California: while the DOM reactivity (μg/mg-DOC) in forming carbonaceous DBPs (C-DBPs; i.e., trihalomethanes [THMs] and haloacetic

acids [HAAs]) decreased, the reactivity (μg/mg-DOC) in forming carcinogenic nitrogenous DBPs (N-DPBs; i.e., haloacetonitriles [HANs] and *N*-nitrosodimethylamine [NDMA]) and brominated DBPs (e.g., dichlorobromomethane [DCBM]) increased. Therefore, further investigation of the water treatability of wildfire-induced DOM along with DBP precursors will help us develop mitigation strategies for water facilities to ensure drinking water safety (Bladon et al., 2014).

To minimize the occurrence of DBP in drinking water, the removal of DBP precursors prior to disinfection is considered the most effective approach (Kristiana et al., 2011). Coagulation and flocculation followed by sedimentation/flotation and filtration is one of the most common and economically feasible treatments (Matilainen et al., 2010; Sillanpaa et al., 2018). Besides DOM content (i.e., DOC and dissolved organic nitrogen [DON] concentrations) and chemical composition, the formed DBPs are greatly affected by disinfection conditions (i.e., oxidant type, oxidant dose, reaction time, water pH) and the presence of bromide ion (Br^-) (Fang et al., 2010; Hong et al., 2013; Yang et al., 2007). The operational conditions/parameters (i.e., reaction time and water pH) during disinfection are generally optimized to reduce DBP formation. To reduce the regulated carbonaceous DBPs such as THMs and HAAs, drinking water facilities have been increasingly shifting from chlorination to chloramination in the US, potentially increasing the formation of N-DBPs, which have greater health risks as compared to the regulated DBPs (Bond et al., 2011; Zhu et al., 2015). Bromide (Br^-) is oxidized by chlorine/chloramine to bromine species ($HOBr/OBr^-$), resulting in the shift of chlorinated DBPs to brominated ones with significantly higher health risks (Hansen et al., 2012; Hua and Reckhow, 2012; Sharma et al., 2014). The increase in Br^- level was reported in laboratory studies using water extracts of wildfire ash (Wang et al., 2015) and field studies using water intakes from the burned watershed (Uzun et al., 2020). Such increases could be caused by a widespread use of brominated flame retardants by firefighters (Zhang et al., 2016), whereas atmospheric deposition/seawater intrusion could be another reason for their presence in coastal forest ecosystems with close proximity to ocean (Chow et al., 2007). However, the influence of the presence of Br^- coupled with wildfire-induced DOM on source water safety has not been thoroughly studied and emphasized. Overall, limited studies have evaluated the influence of wildfire-induced DOM on the water treatment process (Emelko et al., 2011; Writer et al., 2014). An investigation on the influence of operational conditions on removing fire-derived DOM and DBP precursors will benefit water treatment professionals during post-fire periods.

Systematic studies examining the removal of wildfire impacted DOM and DBP precursors via alum coagulation and subsequent DBP formation under typical distribution conditions with different oxidation strategies (i.e., chlorination vs. chloramination, oxidant contact time, and water pH) are limited in the literature. Currently there are no standard protocols for treating wildfire-impacted source water. To identify the best treatment practices in handling post-fire runoffs, we conducted a systematic investigation by using leachates of unburned and burned samples from the 2013 Rim Fire, immediately and one year after the wildfire event. The objectives of this study were to (1) compare the effectiveness of alum coagulation in the removal of DOM and DBP precursors from leachates of litters versus wildfire ashes; (2) determine the effect of Br^- presence on DBP speciation and formation in fire-impacted treated waters; and (3) examine the effects of different operational factors (i.e., oxidant type [chlorination vs. chloramination], reaction time [12, 24, and 72 h], and water pH [6.5, 7.5, and 8.5]) on the formation of DBPs in fire-impacted treated waters. The results will provide further guidance to engineers during the treatment of water sources in fire-impacted watersheds.

2. Materials and methods

2.1. Sample collections

Rim Fire (August 17 − September 6, 2013), one of the largest fires in California history, consumed about 1050 km^2 of forest consisting primarily of mixed conifers (i.e., incense cedar [*Calocedrus decurrens*], ponderosa pine [*Pinus ponderosa*], and white fir [*Abies concolor*]). The details on the fire incidence can be found in Wang et al. (2015) and Wang et al. (2016). To test the effect of high intensity burning on the reactivity of DOM and precursors of DBPs, we collected the composite samples of black ash (B1) and white ash (W1) (visually determined) from burned areas (site #1 in Fig. S1) and fir and pine from adjacent unburned areas on October 2, 2013 (no rainfall was recorded between fire incidence and the sample collection date). Another set of black ash (B2) and white ash (W2) samples was collected at the same burned sites (site #1 in Fig. S1) on August 5, 2014, after cumulative precipitation of ~617 mm (http://www.cnrfc.noaa.gov/arc_search.php). We observed the total mortality of vegetation and total O horizon consumption at site #1 and estimated the burn severity of 3% high severity and 97% moderate severity at this site based on white vs. black ash distribution. The ash depth was generally 5 cm thick, with the white ash samples somewhat thicker than the black ash samples (Wang et al., 2015). We used a stainless-steel hand shovel to separate and collect the surficial ash from the underlying soil. Considering the spatial variability, the composite sample consisted of three subsamples collected within a 10 m radius. Detritus from unburned sites (dominated by ponderosa pine or white fir) were collected from a forest located about 2 km north of the northern-most burned-area sampling site (site #1 in Fig. S1) near Cherry Lake (see Supporting Information). The black and white ash samples were visually identified in the field and were considered as two end-members recognizing that the landscape-level ash layer displayed great short-range spatial variability in both horizontal and vertical dimensions (Bodi et al., 2014). White ash is usually generated at higher burning temperature with more aromatic compounds, compared to black ash (Bodí et al., 2014; Ku et al., 2018; Pereira et al., 2012), and total ash content consisted of ~90% and ~10% black and white ashes after the Rim fire, respectively. To eliminate moisture and microbial survival, the composite samples were air-dried immediately after collection at room temperature (22 ± 1 °C) until constant weight was reached. Samples were then ground and passed through a 2-mm screen and stored in sealed jars under a ventilated and dry indoor environment.

2.2. Leachate and treatability

Around 120-L of rainwater was collected at Anderson, South Carolina in glass containers between March and May 2017, filtered with 0.45 μm pre-washed filters (Supor Polyethersulfone membrane) immediately, and stored at 4 °C before the leaching tests. After the preliminary experiments, we soaked 5.06, 5.06, 57, 31, 545, and 1212 g of sieved fir, pine, B1, W1, B2, and W2 in 23-L collected rainwater, respectively, by shaking at 30 rpm for 24 h and filtered via 0.7 μm glass microfiber filters (Whatman 934-AH). The DOC concentrations in the raw leachates were diluted to 8.60 ± 1.16 mg/L for the alum coagulation (9.03, 8.86, 7.57, 7.8, 10.6, and 7.72 mg/L for fir, pine, B1, W1, B2, and W2, respectively). To determine the optimum alum dose (mg/L), the preliminary treatability tests were conducted on the raw leachates using four alum [$Al_2(SO_4)_3 \bullet 18H_2O$] doses (50, 60, 70, and 80 mg/L for litter/ash leachates) at pH = 6 ± 0.1 (10 mM carbonate buffer, NaOH and HCl). The optimum alum doses of 50−70 mg/L were determined for the litter/ash leachates according to their DOC removal trends (Fig. S1).

After the optimum alum coagulation, the DOC concentrations in the treated leachates of fir, pine, B1, W1, B2, and W2 were 5.12, 5.09, 5.05, 5.32, 8.46 and 6.61 mg/L, respectively.

2.3. Chemical analyses

All the filtered water samples were analyzed by a Shimadzu TOC-V$_{CHS}$ analyzer to determine the concentrations of DOC and dissolved total nitrogen (DTN). The levels of nitrate ($NO_3^- $-N), nitrite ($NO_2^-$-N), and Br^- were determined by Dionex ICS 2100 (Thermo Fisher Scientific, MA) following the US Environmental Protection Agency (EPA) Method 300, while phosphate (PO_4^{3-}) and ammonia (NH_4^+-N) concentrations were detected by HACH Test Kit using US EPA PhosVer® 3 (asorbic acid) Method and Salicylate Method, respectively (Uzun, 2016) (Table S1). The DON concentration was calculated by DON = DTN - ($[NO_3^-$-N] + $[NO_2^-$-N] + $[NH_4^+$-N]) (Lee and Westerhoff, 2005). Specific ultraviolet (UV) absorbance at 254 nm (SUVA$_{254}$; L/mg-C/m) was calculated by normalizing the UV absorbance measured at 254 nm (UV-1800, Shimadzu, Japan) with DOC concentration (Wang et al., 2015), and the E$_2$/E$_3$ ratio was obtained by dividing the UV absorbance at 254 nm with absorbance at 365 nm (Peuravuori and Pihlaja, 1997). After analysis by 3D spectrofluorometry (RF5301, Shimadzu, Japan) for the fluorescence emission−excitation matrix (EEM), we divided the peak area under the emission wavelengths (Em) of 435−480 nm by the peak area under Em = 300−345 nm at the excitation wavelength (Ex) = 254 nm to calculate the humification index (HIX) (Ohno, 2002). The fluorescence index (FI), as a ratio of fluorescence intensity at Em 470 nm−520 nm at Ex = 370 nm, was used to differentiate the DOM origins (i.e., terrestrial [~1.2] or microbial origins [~1.8]) (Cory and McKnight, 2005). Using fluorescence regional integration based on Simpson's rule, EEM was operationally divided into five regions: (I) tyrosine-like proteins, (II) tryptophan-like proteins, (III) fulvic acid-like organics, (IV) soluble microbial byproducts, and (V) humic acid-like organics (Chen et al., 2003; Zhou et al., 2013). The fluorescence response in region i (P$_{i,n}$; %) was obtained by dividing the area-normalized volume in region i with that in all five regions.

The DBP formation potential (FP) test was carried at pH = 7.5 and 22 ± 1 °C for 72 h using excess amounts of chlorine (Cl$_2$) (3 × DOC + 7.6 × NH_4^+ + 10) (Krasner et al., 2004) or pre-formed monochloramine (NH$_2$Cl) (100 mg/L and Cl$_2$:N = 4) on the leachates of fir, pine, B1, W1, B2, and W2 before and after alum coagulation. Removal of FPs was calculated by using the following formula: [(C$_{raw}$-C$_{treated}$)/C$_{raw}$*100] where C$_{raw}$ and C$_{treated}$ were the formed DBP concentrations before and after the alum coagulation. To mimic the DBP formation under typical US water distribution conditions, the uniform formation conditions (UFC) test was performed at 22 ± 1 °C using a relatively lower amount of oxidants (Uzun et al., 2019), which were determined by preliminary tests for keeping certain amounts of residual oxidants (~1.5 ± 0.25 mg/L Cl$_2$ or ~ 2.5 ± 0.5 mg/L NH$_2$Cl) in each sample after 72 h of incubation time. The UFC tests were conducted on treated leachates of fir, pine, B1, and W1 after alum coagulation under the conditions of (1) regular UFC test: reaction time = 24 h at pH 7.5; (2) formation kinetic tests: reaction time = 12, 24, and 72 h at pH 7.5; and (3) pH effect tests: reaction time = 24 h at pH 6.5, 7.5, and 8.5. The DOC concentrations in the treated leachates of B2 and W2 were diluted to 4.92 and 5.02 mg/L using the rainwater for the UFC tests. In addition, we ran replicate samples (without and with the addition of Br^-) in the FP and UFC tests to determine the changes in the levels of formed DBPs by increasing bromide (Br^-) by 100 μg/L.

We quantified volatile DBPs including four THMs, six HANs, and chloral hydrate (CHD; C$_2$H$_3$Cl$_3$O$_2$) and non-volatile DBPs including nine HAAs, following US EPA Methods 551.1 (i.e., THMs, HANs, CHD) and 552.2 (i.e., HAAs), respectively. The detailed DBP species included (1) tribromo- (TBM; CHBr$_3$), dibromochloro- (DBCM; CHBr$_2$Cl), DCBM (CHBrCl$_2$), and trichloro- (TCM; CHCl$_3$) methanes in the category of THMs; (2) tribromoacetic (TBAA; C$_2$HBr$_3$O$_2$), dibromochloroacetic (DBCAA; C$_2$HBr$_2$ClO$_2$), dibromoacetic (DBAA; C$_2$H$_2$Br$_2$O$_2$), bromodichloroacetic (BDCAA; C$_2$HBrCl$_2$O$_2$), bromochloroacetic (BCAA; C$_2$H$_2$BrClO$_2$), monobromoacetic (BAA; C$_2$H$_3$BrO$_2$), monochloroacetic (CAA; C$_2$H$_3$ClO$_2$), dichloroacetic (DCAA; C$_2$H$_2$Cl$_2$O$_2$), and trichloroacetic (TCAA; C$_2$HCl$_3$O$_2$) acids in the category of HAAs; and (3) dibromo- (DBAN; C$_2$HBr$_2$N), bromochloro- (BCAN; C$_2$HBrClN), bromo- (BAN; C$_2$H$_2$BrN), chloro- (CAN; C$_2$H$_2$ClN), dichloro- (DCAN; C$_2$HCl$_2$N), and trichloro- (TCAN; C$_2$Cl$_3$N) acetonitriles in the category of HANs.

3. Results and discussion

3.1. Fire reduced dissolved organic matter treatability by alum coagulation

We measured the general water quality before and after the fire and found that the yields (mg/g-material) of PO_4^{3-}, NH_4^+-N, and DTN followed the order of litter > ash immediately after the fire > ash one year after the fire (Table S2). Specifically, we observed that the Br^- yields in the leachates of ash were higher than in the leachates of litter, which were consistent with the findings of our previous study (Wang et al., 2015). The yields (mg/g-material) and removal percentages of DOC and DON followed the order of litter > ash immediately after the fire > ash one year after the fire (Table 1). The wildfire reduced the amount of exported DOC per gram of materials through the combustion of organic-rich soil horizons and vegetation mass (Wang et al., 2015). Increases in the amounts of sediments, DOC, and DON in source water from burned watersheds were commonly observed in previous studies (Emelko et al., 2011; Writer et al., 2014). This result can be explained by the fact that forest biomass/soil (especially O-horizon), which can filter DOM from water (Ramos et al., 2018) and act as a sink for organic compounds (Khan et al., 2015), is combusted almost completely during wildfires (Chow et al., 2019), resulting in the export of a large amount of sediments and DOM to downstream waters (Emelko et al., 2011). The DOC exported from ash was further reduced one year after the fires, possibly due to soil leaching and surface runoff during the post-fire rainfall events (Wang et al., 2016). Our recent study (Uzun et al., 2020) on the 2015 Wragg Fire found significant decreases in DOC concentrations in stream water from the burned watershed during the second post-fire rain season relative to the initial flashes. We concluded that more mobile DOC generated by fire through consumption of a large amount of litter/vegetation is quickly flushed (<1 year) from a burned watershed during the post-fire rainy season. The positively-charged Al species are efficient when DOM is dominated by negatively-charged functional groups because organic compounds with negatively-charged functional groups (e.g., phenolic and carboxylic) can be neutralized by the hydrolysis products of alum (i.e., Al(OH)$_2^+$ and Al(OH)$_2^{4+}$), resulting in the decrease of their solubility and the promotion of their precipitation (Sillanpaa et al., 2018). During the fire, those functional groups as the side chains were sheared with the enrichment of (poly)aromatic structures (Alexis et al., 2010; Gonzalez-Perez et al., 2004; Kaal and Rumpel, 2009). Therefore, the lower removal percentages in the ash leachates immediately after the fire, compared to litter leachates, possibly resulted from the loss of negatively-charged side chains during the fire. The DOC/DON ratios before alum coagulation with the order of litters > ash immediately after the fire > ash one year after the fire indicates that fire resulted in the relative accumulation of organic nitrogen in DOM, which was further enhanced one year after the fire. The lower DOC/DON ratio

Table 1
Water quality parameters for leachates before and after alum coagulation.

Treatments	Fir	Pine	B1	W1	B2	W2
DOC (mg/g-material)						
Raw	41.1	40.3	3.05	5.79	0.45	0.15
Treated	23.3	23.1	2.04	3.95	0.36	0.13
Removal (%) [a]	43.3	42.6	33.3	31.8	20.0	14.4
DON (mg/g-material)						
Raw	1.18	0.98	0.25	0.47	0.26	0.18
Treated	0.35	0.50	0.17	0.36	0.25	0.17
Removal (%)	70.6	49.2	31.5	23.5	1.83	1.91
DOC/DON						
Raw	34.7	41.3	12.1	12.2	1.75	0.83
Treated	66.8	46.7	11.8	10.9	1.42	0.72
Removal (%)	−92.5	−13.1	2.63	10.9	18.6	12.7
SUVA$_{254}$ (L/mg-m)						
Raw	3.61	3.28	3.73	4.36	5.24	3.48
Treated	1.28	1.33	2.89	3.45	4.39	2.99
Removal (%)	64.5	59.6	22.5	20.8	16.2	14.2
HIX						
Raw	6.67	8.79	9.22	11.3	8.38	5.41
Treated	1.88	1.27	13.47	4.99	8.47	5.90
Removal (%)	71.8	85.6	−46.1	55.7	−1.07	−9.06
E$_2$/E$_3$						
Raw	5.25	4.67	5.14	5.72	5.44	7.28
Treated	6.55	7.10	6.57	7.04	5.40	7.62
Removal (%)	−24.8	−52.0	−27.8	−23.1	0.74	−4.67
FI						
Raw	1.42	1.40	1.77	1.73	1.84	2.08
Treated	1.59	1.72	1.85	1.86	1.85	2.04
Removal (%)	−12.0	−22.9	−4.52	−7.51	−0.54	1.92
P$_{I,n}$ (%)						
Raw	8.70	7.03	0.76	1.78	1.77	2.35
Treated	12.8	16.4	2.64	1.91	1.76	1.77
Removal (%)	−47.4	−133	−247	−7.30	0.56	24.7
P$_{II,n}$ (%)						
Raw	13.9	13.2	14.1	16.6	15.9	20.9
Treated	17.8	17.4	16.2	19.6	15.6	19.8
Removal (%)	−28.0	−31.9	−15.2	−18.1	2.26	5.26
P$_{III,n}$ (%)						
Raw	27.1	28.4	26.7	25.4	27.9	27.0
Treated	18.4	15.2	24.3	22.4	26.9	25.7
Removal (%)	31.9	46.4	9.17	12.0	3.62	4.71
P$_{IV,n}$ (%)						
Raw	18.3	17.9	24.4	25.4	23.2	24.1
Treated	28.2	31.6	27.0	29.6	24.2	25.9
Removal (%)	−53.8	−76.6	−10.9	−16.8	−4.13	−7.68
P$_{V,n}$ (%)						
Raw	32.0	33.4	34.0	30.8	31.2	25.7
Treated	22.7	19.3	29.8	26.5	31.6	26.8
Removal (%)	28.9	42.3	12.4	14.1	−1.35	−4.24

[a] Removal (%) = (raw - treated)/raw × 100%.

from ash leachates is consistent with the findings of previous laboratory (Wang et al., 2015) and field (Hohner et al., 2016; Uzun et al., 2020) studies.

SUVA$_{254}$ decreased after alum coagulation, indicating the decrease in DOM aromaticity (Karanfil et al., 2002). In general, high SUVA$_{254}$ value (>4 L/mg-C/m) indicates the relative high faction of hydrophobic DOM, whereas low SUVA$_{254}$ value (<2−3 L/mg-C/m) suggests the high fraction of hydrophilic DOM. The removal percentage of SUVA$_{254}$ by alum coagulation followed the order of litter > ash immediately after the fire > ash one year after the fire (Table 1). This result suggests that the fire-produced ash materials contain more hydrophobic DOM with lower removal performance during alum coagulation due to the loss of side chains (Writer et al., 2014). The changes of SUVA$_{254}$ before and immediately after a fire could be related to fire severity. Relative to the reference, the SUVA$_{254}$ in water intakes in the first rainy reason from the burned watershed was not significant in the Rocky Fire but 31 ± 17% higher in the Wragg Fire with relatively high severity (estimated to be medium severity) (Uzun et al., 2020). Wang et al. (2015) found the

SUVA$_{254}$ in water extracts followed the order of white ash (high burn severity) > unburned detritus > black ash (low burn severity), due to the less soluble aromatic fraction in black ash after the loss of −OH and/or −COOH groups. The HIX, positively correlated with the humification degree (higher HIX, more humified materials) (Fellman et al., 2010; Lavonen et al., 2015), decreased for fir, pine, and W1 but increased for B1, B2, and W2 after alum coagulation. Alum coagulation was effective in removing the humified fraction (indicated by HIX) in litter other than ash leachates. The E$_2$/E$_3$ ratio, inversely correlated to DOM molecular weight (MW) (Wang et al., 2009), was higher in raw ash leachates, relative to raw litter leachates, indicating DOM after the fire with lower MW (Hohner et al., 2016). This ratio increased (except B2) after alum coagulation, suggesting that compounds with high molecular weight (HMW) were preferred as the alum targets (Writer et al., 2014). With a slight variety [(−22.9)−1.92%] on removal percentage by alum coagulation, FI increased with the order of litter (1.40−1.42) < ash immediately after the fire (1.73−1.77) < ash one year after the fire (1.84−2.08), indicating the increasing ratio of microbial-to terrestrial- originated compounds in DOM. We observed the increase of tyrosine-like proteins [region I; (−133)−(-47.4)%], tryptophan-like proteins [region II; (−31.9)−(−28.0)%], soluble microbial byproducts [region IV; (−76.6)−(−53.8)%] and the decrease of fulvic acid-like (region III; 31.9−46.4%) and humic acid-like (region V; 28.9−42.3%) organics in litter leachates after alum coagulation, suggesting the preferable removal of fulvic/humic acid-like organics by alum coagulation (Sanchez et al., 2013; Yang et al., 2015). Differently, the results showed relatively small changes in the five fluorescence components of ash leachates [(-18.1%)−14.1% except tyrosine-like proteins (region I) in B1 (−247%) and W2 (24.7%)] during alum coagulation, mainly due to the alternation of chemical structures by high-intensity fire.

3.2. Fire reduced the removal of DBP precursors during alum coagulation

The DBP precursor yields (µg/g-material) in the leachates of ash immediately after the fire were one order of magnitude lower than those in the litter leachates but higher than those in the leachates of ash one year after the fire for all the studied DBP categories, except CHD, using chloramine (no CHD formed in pine, B1, or W1) (Fig. 1 and Table S3). For example, the THM yield (µg/g-material) using chlorine was 4,135, 3,614, 227, 408, 27, and 9 in fir, pine, B1, W1, B2, and W2, respectively. This result indicates that DBP precursors in the litter were eliminated by the high-intensity fire, which were further reduced via the biogeochemical processes such as soil erosion during the one year after the fire. The consumption of organic matter through the burning in wildland fires (Wang et al., 2015) contributed significantly to the reduction of DBP FPs. The yields (µg/g-material) of all the studied DBP categories were positively related to both DOC (mg/g-material) and DON (mg/g-material) (Table S4), indicating DOC and DON as the simple and rapid surrogates for the DBP levels in samples related to fire (Xue et al., 2014). Our previous study (Wang et al., 2016) also found a decrease in DOC and DBP FPs in water extracts of wildfire ash with an increase in the amount of sequential leaching. Additionally, the DBP precursor yields using chlorine were higher for THMs, HAAs, and CHD but lower for HAN, compared to those using chloramine. This result is consistent with the traditional view that chlorine produces more C- and O-DBPs but fewer N-DBPs, compared to chloramine (Chuang et al., 2013; Zhang et al., 2020).

Compared to litter leachates, the alum coagulation was less effective for ash leachates in reducing both DBP-FPs (µg/g-material; except for HAA-FPs by chloramine) and specific DBP-FPs (SDBP-FP; µg/mg-DOC; except for HAN by chloramine and HAA). For example,
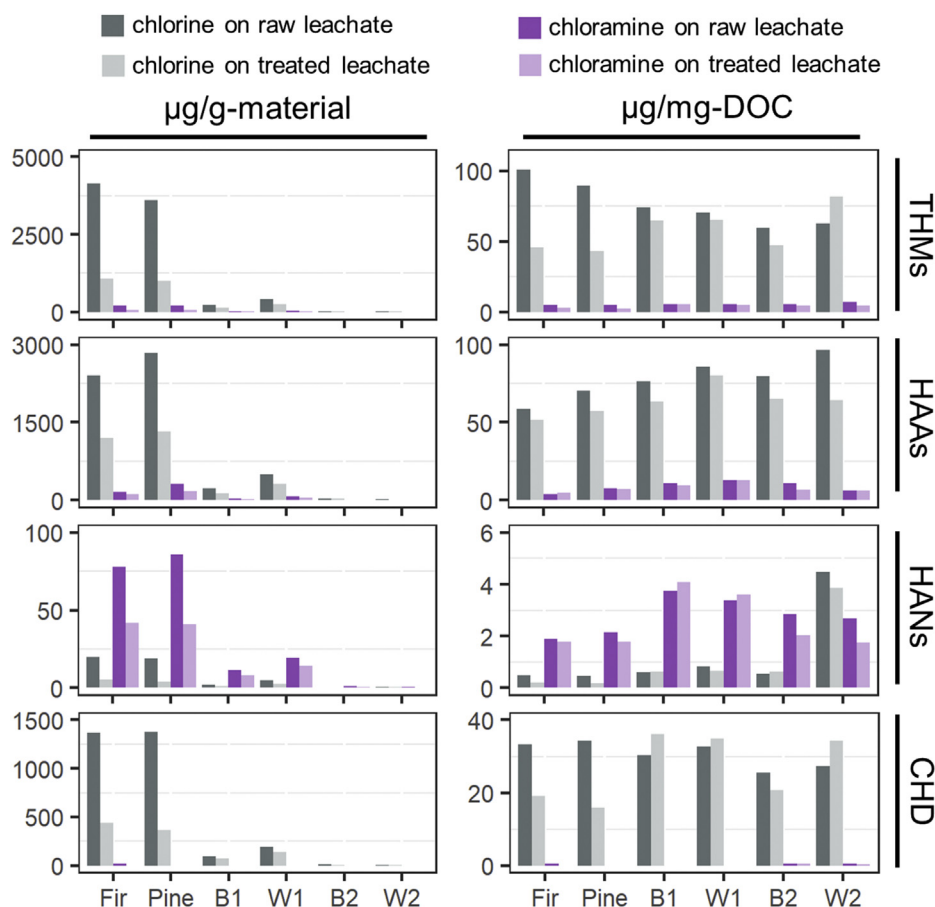
Fig. 1. Disinfection byproduct (DBP) formation potentials (DBP-FPs; μg/g-material) and specific FPs (SDBP-FP; μg/mg-DOC) in fir, pine, black ash, and white ash leachates. Leachates before (raw) and after (treated) alum coagulation were reacted with chlorine (Cl₂) and chloramine (NH₂Cl) for 72 h under pH 7.5.

the removal percentages for THM-FPs by chlorine were 74.2%, 72.2%, 41.8%, 37.0%, 36.5%, and (−11.5)% in fir, pine, B1, W1, B2, and W2, respectively. The lower removal percentage for SDBP-FPs in ash leachates was because that the loss of side chains (Alexis et al., 2010; Sillanpaa et al., 2018) and the decrease of DOM MW (Hohner et al., 2016; Writer et al., 2014) by the high-intensity fire induced DBP precursors more recalcitrant during alum coagulation. Writer et al. (2014) reported the lower efficiency of alum coagulation in reducing organic matter with hill slope sediments and charred materials deposited in the river after the 2012 High Park Wildfire, Colorado, especially following the first post-fire flash thunderstorms. Hohner et al. (2019) found a poor performance of alum coagulation in removing turbidity and DOC from leachates of heated surface soil and litter samples by a laboratory furnace, even at high coagulation doses, possibly due to the reduction of DOM MW. Moreover, the increases of DOC, DON, and turbidity, especially during the first postfire year, were widely reported in water intakes from burned watersheds (Bladon et al., 2008; Hohner et al., 2016; Uzun et al., 2020), which increases the water utility challenges (Emelko et al., 2011). More efficient techniques or strategies in removing DOC and DON and DBP precursors will be needed in post-fire drinking water facilities. Interestingly, the removal percentages for specific HAN FPs (SHAN-FPs; μg/mg-DOC) by chloramine followed the order of ash one year after the fire > litter > ash immediately after the fire, indicating the increase of SHAN-FPs one year after the fire. In addition, before alum coagulation, the leachates of ash immediately and one year after the fire had lower DOC/DON ratio and higher DOM reactivity in forming HANs, compared

to litter leachates. Our previous study (Wang et al., 2015) also found the increase of SHAN-FPs (μg/mg-DOC) using chlorine with the order of water extracts from control (unburned), black ash, and white ash, due to the decrease of C/N ratio and the shift of organic nitrogen from amide/peptide to heteroaromatic forms.

3.3. Fire reduced the increase of HAN FP by the addition of 100 μg/L Br⁻

Compared to other DBP species, the level of HANs formed by chlorine increased greatly after the addition of 100 μg/L Br⁻. Because HANs had much higher cytotoxicity and genotoxicity than regulated THMs and HAAs (Muellner et al., 2007), the significant increase of HANs in drinking water will cause potential health risks. Adding 100 μg/L Br⁻ increased the concentration of HANs in both raw and treated leachates and a greater increase in treated leachates was observed, compared to raw leachates. Using chlorine on the leachates of fir, pine, B1, W1, B2, and W2, HAN-FPs (μM/g-material) increased from 0.17 to 0.72, 0.17 to 0.69, 0.02 to 0.09, 0.04 to 0.17, <0.01 to 0.01, and 0.01 to 0.01 in raw leachates and from 0.04 to 0.74, 0.03 to 0.65, 0.01 to 0.07, 0.02 to 0.12, <0.01 to 0.01, and <0.01 to 0.01 in treated leachates after the alum coagulation (Fig. 2 and Table S5). The increase in the levels of HANs by adding 100 μg/L Br⁻ was primarily due to the increase of BCAN. The relatively higher changes in treated leachates (50.0–1,833%), compared to raw leachates (47.4–452%), suggest DOM fractions in treated leachates as more active BCAN precursors in the presence of Br⁻.
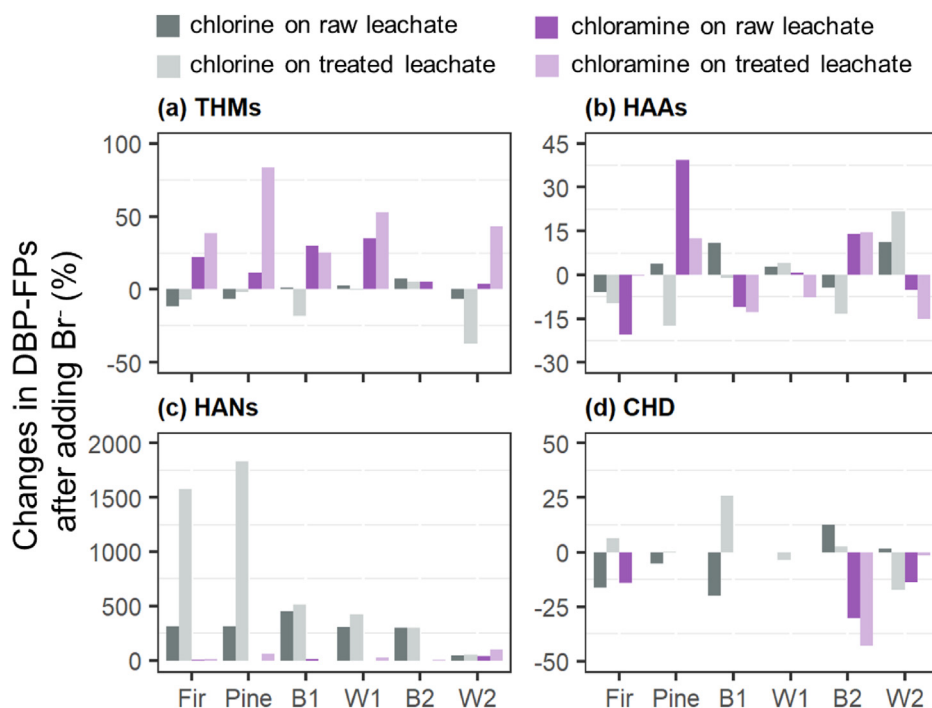
Fig. 2. Changes (%) in disinfection byproduct formation potentials (DBP-FPs; μM/g-material) after the increase by 100 μg/L Br^- in fir, pine, black ash, and white ash leachates. Leachates before (raw) and after (treated) alum coagulation were reacted with chlorine (Cl_2) and chloramine (NH_2Cl) for 72 h under pH 7.5. The DBP formation was evaluated using the formation potential test and the changes in % were calculated using ([DBP-FPs with adding 100 μg/L Br^-] − [DBP-FPs without adding 100 μg/L Br^-])/[DBP-FPs without adding100 μg/L Br^-] × 100%.

Moreover, after alum coagulation, the percentage changes achieved by adding 100 μg/L Br^- were greater in treated litter leachates of fir (from 0.04 to 0.74 μM/g-material; 1,579%) and pine (from 0.03 to 0.65 μM/g-material; 1,833%), compared to treated ash leachates of B1 (512%), W1 (424%), B2 (300%), and W2 (50.0%), possibly due to the differences in DOC/DON ratio and DOM optical properties. This result suggests that the increase of HAN levels by adding 100 μg/L Br^- on treated leachates was mitigated to some extents by the thermal burning in fire. The changes achieved by adding 100 μg/L Br^- were not great for HANs using chloramine and other DBP categories. Though studies (Liu et al., 2018; Sun et al., 2009) reported the increase of THM and HAA yields with the initial Br^- concentration during chlorination, our study observed relatively low changes in THMs [(-37.0)−7.26%] and HAAs [(-17.4)−21.7%] using chlorine, compared to those in HANs. Previous studies (Chu et al., 2011; Roccaro et al., 2013) reported that DHANs, including DCAN (C_2HCl_2N), BCAN ($C_2HBrClN$) and DBAN (C_2HBr_2N), were readily incorporated into bromine to form brominated DBPs. Obolensky and Singer (2005) used 160 sample records from five WTPs using free chlorine in the US and found that DHANs had relatively higher bromine incorporation compared to THMs and DHAAs (including DCAA, BCAA, and DBAA). Our previous study (Ersan et al., 2019) also found that bromine substitution factor (BSF) followed the order of DHANs > HAAs > THMs. The influence of the increase by 100 μg/L Br^- on CHD-FP was slight, with the changes of (−19.8)−25.9% using chlorine and no CHD formed in pine, B1, and W1 using chloramine. Notably, even though the changes in the levels of formed HANs achieved by adding 100 μg/L Br^- were great, their yields were still lower, compared to those of formed THMs. For example, by adding 100 μg/L Br^-, the yields (μg/g-material) from the raw leachate of fir, pine, B1, W1, B2, and W2 changed from 9.22−4,135 to 8.73−3,690 for THMs and from 0.25−19.8 to 0.97−83.7 for HANs when using chlorine (Table S6).

3.4. Adding 100 μg/L Br^- changed the speciation of THMs and HANs

Br^- could present in wildfire-affected forest ecosystems due to the widespread use of brominated flame retardants by firefighters (Zhang et al., 2016) and in coastal forest ecosystems due to close proximity to ocean and atmospheric deposition/seawater intrusion (Chow et al., 2007). The addition of 100 μg/L Br^- in either litter or ash leachates changed the speciation of THMs and HANs (Fig. 3), with increases in BSF (Fig. S2). The addition of Br^- shifted DBP categories to brominated species, due to the higher reactivity of bromine species (HOBr/OBr^-) compared to that of chlorine species. For THMs, TCM ($CHCl_3$) was dominated before adding Br^-, with the relative percentage of 76.0−100% using chlorine and 66.7−100% using chloramine (except W2). After adding Br^-, the percentages of DCMB ($CHBrCl_2$) increased from 0−19.2% to 2.96−31.2% using chlorine and from 0 to 9.00% (except W2) to 11.7−52.3% using chloramine, while DBCM ($CHBr_2Cl$) had a relatively high percentage of 12.2−26.3% using chloramine. For HANs, DCAN (C_2HCl_2N) was dominated before adding Br^-, with 63.3−94.3% using chlorine (except W2) and 68.6−100% using chloramine. After adding Br^-, BCAN ($C_2HBrClN$) with 59.1−94.0% was dominated using chlorine. Though DCAN, with 47.0−93.8%, was still the major species using chloramine, the percentages of BCAN ($C_2HBrClN$) increased from 0−28.1% to 4.71−51.5% after adding Br^-. DHANs were readily incorporated into bromine to form brominated DBPs (Chu et al., 2011; Roccaro et al., 2013) and their speciation shifted from DCAN to BCAN and then to DBAN with the increase of Br^- concentration (Bond et al., 2011). Interestingly, we observed the high percentage of 85.1% and 72.7% using chlorine and 27.0% and 28.1% using chloramine in formed BCAN in both raw and treated W2 leachates, possibly due to the high Br^- concentrations of 231 μg/L in the raw and treated W2 leachates before adding 100 μg/L Br^- (Table S2). Moreover, before adding 100 μg/L Br^-, relatively high
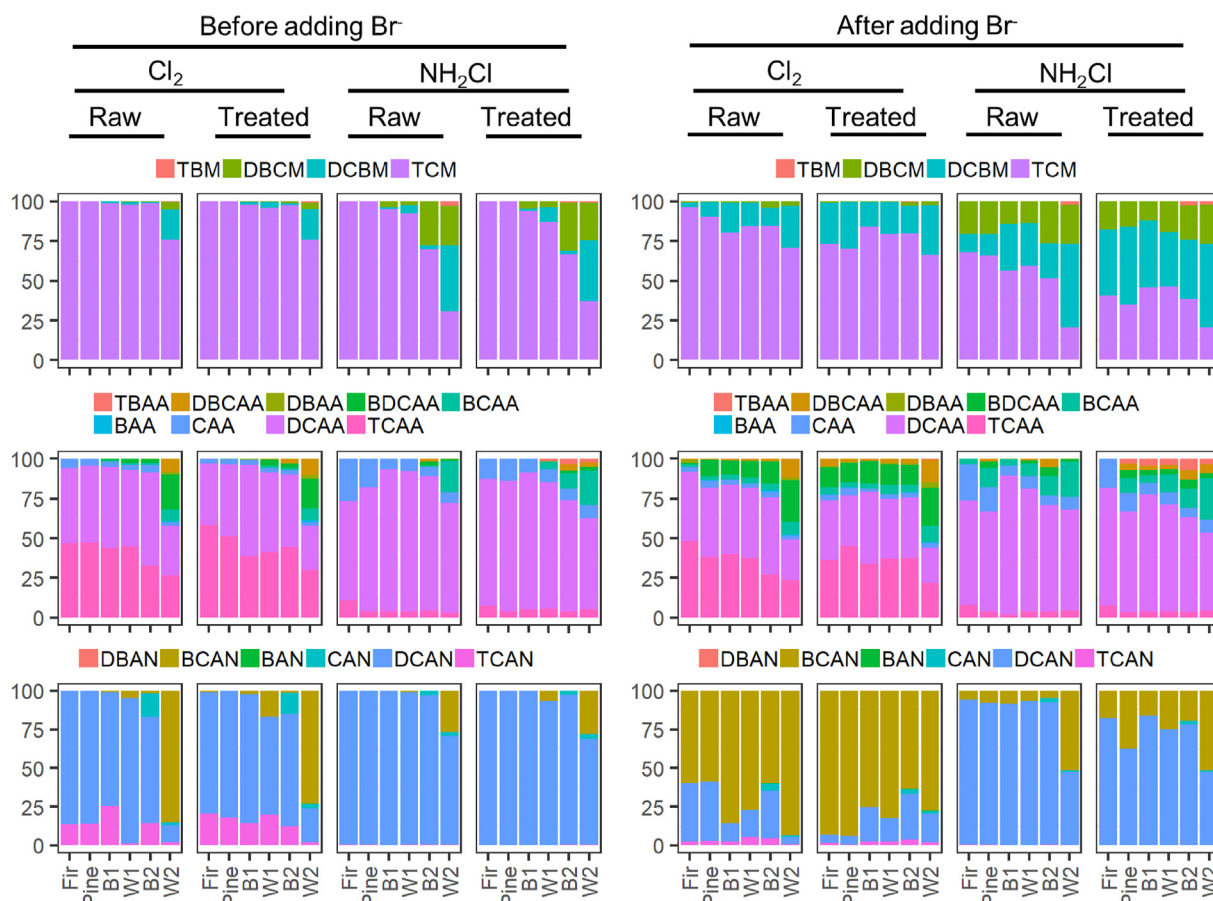
Fig. 3. Relative percentage of disinfection byproducts (DBPs) formed in fir, pine, black ash, and white ash leachates before and after the addition of 100 μg/L Br⁻. Leachates before (raw) and after (treated) alum coagulation were reacted with chlorine (Cl₂) and chloramine (NH₂Cl) for 72 h under pH 7.5. The DBP formation was evaluated using the formation potential (FP) test.

BSF values for THMs, HAAs, and HANs were observed in the W2 leachate, compared to other leachates.

3.5. Chloramination at alkaline pH as an option to control post-fire DBP formation

The FP test employs a high disinfectant dose and long reaction time to estimate the potency of water in forming DBPs, which maximizes DBP formation. The simulated distribution system (SDS) uses the site-specific conditions of the distribution system and can accurately represent DBP formation in a specific distribution system. However, the SDS test is greatly influenced by the conditions of a distribution system, such as detention time, pH, seasonal temperature, and limits the comparisons of performances among utilities in formation and speciation of DBPs (Summers et al., 1996). Based on a comprehensive survey, Summers et al. (1996) developed the UFC test, which represents the average distribution system conditions in the US. Thus, UFC test was selected and employed to examine DBP formation and speciation in this study.

An increase in pH (including 6.5, 7.5, and 8.5) resulted in a significant decrease in DOM reactivity (μg/mg-DOC) in forming THMs (by chloramine), HAAs, and HANs in both litter and ash leachates (Fig. 4 and Table S7). This tendency in DOM reactivity with pH was not significantly different among the leachates of litter and ash samples. Relative to pH 6.5, the levels of formed THMs using chloramine were 60.8−94.1% at pH 7.5 and 28.0−64.8% at pH 8.5. This decrease possibly resulted from the decreased hydrolysis rate

of chloramine to free chlorine (Doederer et al., 2014; Yang et al., 2007). The levels of formed HANs and HAAs also decreased with increasing pH from 6.5 to 8.5, with the pH 8.5/pH 6.5 percentages of 25.1−45.4% and 65.5−95.8% using chlorine and 28.9−51.6% and 43.8−92.3% using chloramine, respectively. Jia et al. (2016) reported the decrease of formed HANs with increasing pH from 6 to 9, due to the decrease in the yields of TCAN and DCAN. The decrease of HANs in our study was mainly due to the decrease of DCAN, which accounted for 82.2−100% in HANs (Fig. S4). Yang et al. (2007) indicated that DCAN undergoes the base-catalyzed decomposition, and its degradation rate was enhanced by increasing pH. Conversely, the formed THMs using chlorine had the pH 7.5/pH 6.5 and pH 8.5/pH 6.5 percentages of 131−175% and 166−230%, with the corresponding percentages of 60.8−94.1% and 28.0−64.9% using chloramine, respectively. Studies reported the increase of formed THMs with the pH value increasing from 6.5 to 8.5 (Ye et al., 2009) and from 6 to 8 (Hong et al., 2013), due to the alkaline condition favoring the hydrolysis reactions of intermediate DBPs to THMs. Additionally, there was no CHD formed by chloramine, and the level of formed CHD by chlorine increased to 106−145% at pH 7.5 and 136−171% at pH 8.5, compared to those at pH 6.5. Overall, using chloramine at alkaline pH facilitates the control of UFC DBP formation during drinking water disinfection for treating wildfire impacted source waters after alum coagulation.

The DOM reactivity of both litter and ash leachates in forming UFC DBPs greatly increased with reaction time (including 12, 24, and 72 h), except for HANs by chlorine (Fig. 4 and Table S7). We did
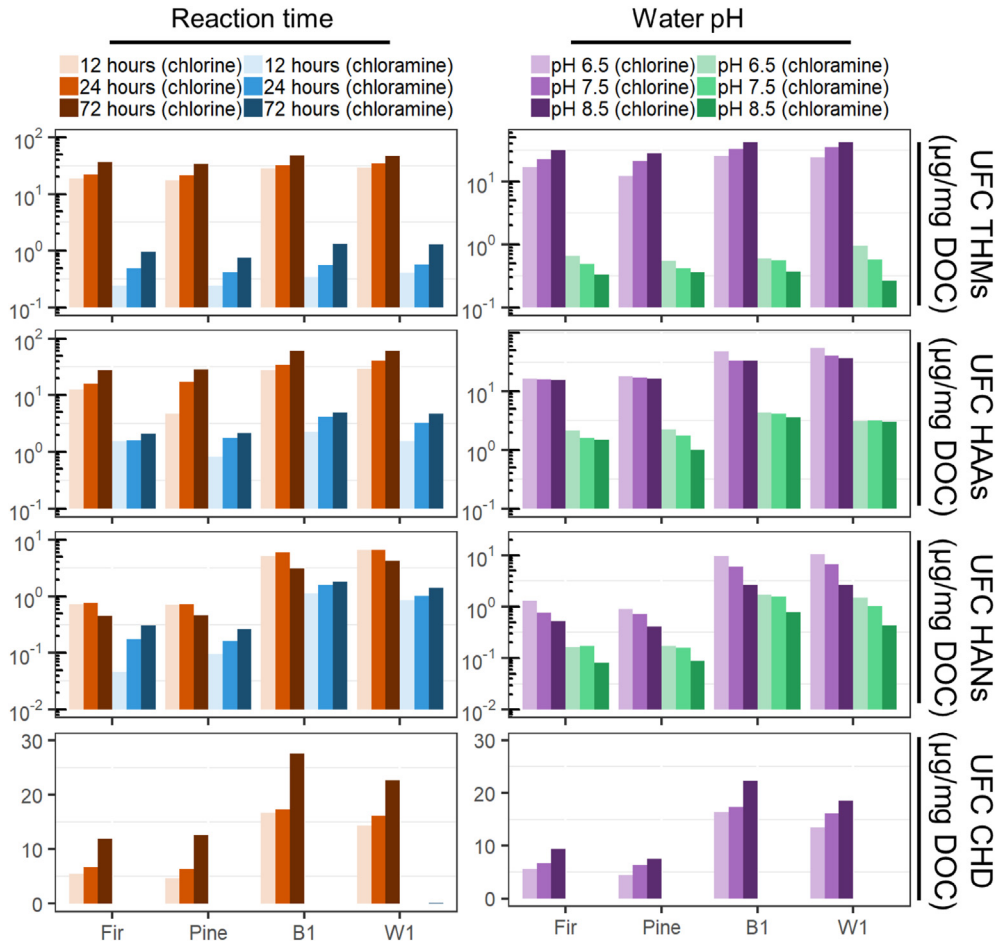
Fig. 4. Reactivity (μg/mg-DOC) of the fir, pine, black ash, and white ash leachates after alum coagulation in forming disinfection byproduct (DBP). Leachates were reacted with chlorine (Cl$_2$) and chloramine (NH$_2$Cl) under the (1) left column: the reaction time of 12, 24, and 72 h and pH of 7.5 and the (2) right column: the reaction time of 24 h and a pH of 6.5, 7.5, and 8.5. The DBP formation was evaluated using the uniform formation conditions (UFC) test.

not find obvious different tendencies in DOM reactivity among the leachates of litter and ash samples. Studies (Hong et al., 2013; Yang et al., 2007) reported the increase of formed DBPs with reaction time, though the increase rates become slow after a certain time, due to the decrease of disinfectants and reactive groups in DOM. Though the percentage on formed THMs in 72 h relative to 12 h was 161−196% by chlorine, much lower than 311−403% by chloramine, we still observed higher DOM reactivity of 34.1−47.8 μg/mg-DOC in forming UFC THMs by chlorine in 72 h, compared to 0.75−1.31 μg/mg-DOC by chloramine. Similarly, Sakai et al. (2016) found the 4-day/1-day percentage for THMs was 150% by chlorine and 420% by chloramine and DOM reactivity in forming THMs after 4 days by chloramine was lower compared to that by chlorine. Compared to 12 h, the percentage on formed HAAs in 72 h was 207−602% by chlorine and 134−303% by chloramine. There was no CHD formed by chloramine with reaction times of 12 and 24 h, and DOM reactivity in forming CHD by chlorine increased with reaction time, with the 24-h/12-h and 72-h/12-h percentages of 104−135% and 158−264%, respectively. Differently, the levels of formed HANs by chlorine increased when reaction time changed from 12 h to 24 h but decreased when reaction time increased from 24 h to 72 h. Compared to 12 h, the percentages of formed HANs in 24 h and 72 h were 124−372% and 60−66% by chlorine and 120−374% and 160−663% by chloramine. Tian et al. (2013) also observed that the concentrations of HANs decreased using Cl$_2$ but increased using NH$_2$Cl with reaction time (30 min, 24 h, and 72 h), possibly due to

the degradation and/or transformation of initially formed HANs in the late reaction with chlorine. The nitrile carbon in HANs could be attacked by hydroxide and hypochlorite to form haloacetamides and HAAs as primary intermediates and end products (Reckhow et al., 2001; Yu and Reckhow, 2015).

Similarly, with the increase of 100 μg/L Br$^−$, we observed the increase of BSF using the UFC tests (Figs. S5 and S6). For example, by the increase of 100 μg/L Br$^−$, the BSF values increased from 0−5.29% to 0−48.4% at pH 6.5−8.5 and 0−4.21% (except 19.2% in HANs from pine at 12 h using chloramine) to 0−48.2% at 12−72 h. After the increase of 100 μg/L Br$^−$, the BSF values decreased and increased with reaction time for UFC THMs using chlorine and chloramine, respectively. Compared to other conditions including disinfectants and reaction time, the BSF values for UFC THMs were relatively high at 24 and 72 h but low at 12 h when using chloramine (Fig. S5b), indicating chloramine with short reaction time as an option for controlling the UFC THMs. The BSF values generally decreased with pH for THMs and HANs (using chloramine) but increased with pH for HANs using chlorine and the lowest BSF values for both UFC THMs and HANs were observed under the condition of chloramine and pH 8.5 (Figs. S6b and f). Under both reaction time and water pH conditions (Figs. S5b, d, f and S6b, d, f), chlorine generated higher BSF values for both HAAs and HANs, compared to chloramine. In addition, the BSF values for HANs were lower in the treated leachates of B1 and W1, relative to fire and pine, indicating the less brominated HANs formed in the ash leachates. Overall, when Br$^−$ exists in the water distribution system,

	Litter/Ash	UFC THMs (72 h/12 h)	UFC THMs BSF [a] (NH₂Cl & 12 h)	UFC THMs (pH 8.5/pH 6.5)	UFC THMs BSF [a] (NH₂Cl & pH 8.5)
Litter	Fir	Cl₂: 196% NH₂Cl: 403%	9.31% (Max [b]: 21.8%)	Cl₂: 187% NH₂Cl: 50.2%	5.72% (Max [c]: 25.9%)
Litter	Pine	Cl₂: 194% NH₂Cl: 311%	8.99% (Max [b]: 20.2%)	Cl₂: 230% NH₂Cl: 64.8%	4.66 (Max [c]: 27.5%)
Ash immediate after fire	Black ash (B1)	Cl₂: 169% NH₂Cl: 386%	8.41% (Max [b]: 17.2%)	Cl₂: 166% NH₂Cl: 61.1%	4.43% (Max [c]: 23.5%)
Ash immediate after fire	White ash (W1)	Cl₂: 161% NH₂Cl: 317%	7.98% (Max [b]: 22.1%)	Cl₂: 175% NH₂Cl: 28.0%	5.17% (Max [c]: 22.4%)

Fig. 5. Chloramination at alkaline pH with short reaction time is an option for controlling disinfection byproduct (DBP) formation along with brominated DBP species in water sources from fire-impacted watersheds. THMs: trihalomethanes; UFC: uniform formation conditions test; BSF: bromine substitution factor. [a] after the increase by 100 μg/L Br⁻; [b] maximum BSF value under the condition of disinfectant (chlorine and chloramine) and reaction time (12, 24, and 72 h) (see Fig. S5b); [c] maximum BSF value under the condition of disinfectant (chlorine and chloramine) and water pH (6.5, 7.5, and 8.5) (see Fig. S6b).

chloramine at high pH could represent a viable strategy for controlling the formation of brominated DBP species, providing a means to treat wildfire impacted source waters after alum coagulation.

4. Conclusions

This study showed that removal percentages of DOC and DON by the alum coagulation followed the order of litter > ash immediately after the fire > ash one year after the fire. Alum coagulation was less effective in removing DOC and DON and reducing both DBP-FPs and DOM chlorine/chloramine reactivity in ash leachates, compared to litter leachates. This result was possibly due to the loss of side chains and the decrease of DOM MW during the wildfire, making the DOM and DBP precursors more recalcitrant during alum coagulation. Therefore, more efficient techniques or strategies in removing DOC and DON and DBP precursors will be needed when drinking water facilities using alum coagulation receive water from watersheds burned by wildfire. Elevated Br⁻ levels were frequently reported in water extracts of wildfire ash and downstream waters from burned watersheds, possibly due to the wide use of brominated flame retardants and/or atmospheric deposition/seawater intrusion into coastal forest ecosystems. An increase by 100 μg/L Br⁻ in both litter and ash leachates shifted the studied DBPs into more brominated species, as previously reported, and greatly increased the formation of HANs by chlorine. This increase was relatively lower in ash leachates. This result indicates that the increase of HANs formation (using chlorine) by increasing 100 μg/L Br⁻ in treated leachates was mitigated to some extents by wildfire burning. Using UFC tests, we observed that the DOM reactivity in forming the studied DBPs generally increased with reaction time and decreased with pH in both litter and ash leachates (Fig. 5), suggesting disinfection using chloramine at alkaline pH as an option for controlling the studied DBP in our work. The influence of reaction time and pH in DOM reactivity was similar among the leachates of litter and ash samples. Chloramination at alkaline pH produced relatively low brominated DBP species in the treated leachates of both litter (fir and pine) and ash (B1 and W1) after the increase of 100 μg/L Br⁻, as quantified by the BSF values (Fig. 5). Overall, chloramination at alkaline pH is an effective strategy and regulatory compliance for controlling the formation of the studied DBPs while treating wildfire-impacted water sources after alum coagulation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.116111.

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