Lasting Effects of Wildfire on Disinfection By-Product Formation in Forest Catchments

Alex T. Chow,* Kuo-Pei Tsai, Timothy S. Fegel, Derek N. Pierson, and Charles C. Rhoades

Abstract

Severe wildfires often have dramatic short-term effects on water quality, although there is increasing evidence that in some catchments their effects can persist for many years. Forest recovery after the 2002 Hayman Fire burned catchments that supply drinking water to over a half million users in Denver, CO, has been extremely slow and has caused persistent water quality concerns. To evaluate whether postfire water quality changes increase the potential to form undesirable by-products of water disinfection, we compared stream water from eight burned catchments within the Hayman Fire and five adjacent unburned catchments. We tested dissolved organic carbon (DOC) concentrations and the formation of disinfection by-products (trihalomethanes [THMs], haloacetonitriles [HANs], chloral hydrate [CHD, and haloketones [HKTs]) in stream water monthly during 2014 and 2015. Stream DOC, THMs, and CHD and specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) were elevated in catchments with a moderate extent of high-severity wildfire (8–46% of catchment area) relative to catchments that were unburned and those that burned more extensively (>74% of catchment area) 14 yr after the fire. In contrast, formation of highly toxic but unregulated nitrogenous HANs increased linearly with wildfire extent. Although these findings should not raise concern regarding drinking water safety, they highlight the long-term influences of high severity wildfire on source water C content, composition, and treatability.

Core Ideas

- Wildfire impacts on source water quality could last over a decade.
- Formation of highly toxic nitrogenous DBP precursors increased linearly with wildfire extent.
- DBP formation was highest in streams draining moderately burned catchments.

FOREST CATCHMENTS supply drinking water to millions of people in the United States. Severe wildfires can generate extreme postfire erosion and biogeochemical and abiotic changes that have consequences for aquatic ecosystems, stream water quality, and water treatment (Wang et al., 2015b; Abney et al., 2019). Ash and sediment losses are typically greatest during the first postfire rainstorm (Pannkuk and Robichaud, 2003; Badía et al., 2008). Stream temperature and solute concentration often increase immediately after wildfires and remain elevated for months (Minshall et al., 2004). While postfire sediment and ash losses are often relatively short-lived, growing evidence indicates that water quality responses to severe wildfire can persist for 5 yr to more than a decade (Rhoades et al., 2011, 2018; Rust et al., 2018). Drinking water utilities respond to short-term, postfire increases in ash and suspended sediment by altering coagulation and filtration procedures or by shifting to alternate water sources (Hohner et al., 2016). The increased size and frequency of severe wildfires observed during recent decades (Westerling et al., 2006; Westerling, 2016) has elevated concern regarding long-term treatment options and source water protection in wildfire-prone forest catchments (Emelko et al., 2011; Bladon et al., 2014; Martin, 2016).

Combustion of vegetation and surface organic material (e.g., litter and duff in soil O horizons) during wildfires alters the amount and composition of dissolved organic C (DOC) exported from burned catchments. Wildfires transform lignin and polysaccharide-rich and relatively degradable C into polycyclic and aromatic, recalcitrant black C (Santín et al., 2016). Formation of USEPA-regulated polycyclic aromatic hydrocarbons and loss of soil organic matter in burned catchments have been observed and reported (Chen et al., 2018; Abney et al., 2019). The lasting effects of wildfires on plant composition, soil conditions, and catchment hydrology (Francos et al., 2016; Hallema et al., 2016; Zhang and Biswas, 2017) also alter the chemical characteristics of C inputs to streams and the biogeochemical processing and release of DOC. Combusted forest detritus creates challenges for drinking water treatment (Wang

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et al., 2015a; Tsai and Chow, 2016; Hohner et al., 2017), specifically via downstream delivery of disinfection by-product (DBP) precursors that can form hazardous compounds during water treatment chlorination (Wang et al., 2015b; Hohner et al., 2016). It is likely that the export of DBP precursors varies with severity and extent of a wildfire and subsequent catchment recovery due to spatial complexity in fuels and wildfire behavior, although such responses remain uncertain.

High-severity wildfires kill most vegetation and combust surface soil organic horizons (Keeley, 2009), and the exposed soils and reduced plant nutrient uptake lead to high postfire nutrient losses. As a result, most water quality constituents increase with wildfire severity and extent (Riggan et al., 1994; Kershner et al., 2003). Changes are typically less pronounced after smaller, less-severe wildfires since residual unburned vegetation and soil organic layers (O horizon) mitigate the sediment and nutrient losses from burned patches. Unlike typical sediment and nutrient responses, however, there is evidence that postfire changes in DOC are greatest at low to moderate combustion temperature (Santos et al., 2016; Hohner et al., 2017). For example, soil organic layers combusted at moderate temperature (250°C) in controlled laboratory experiments released more DOC and DBP precursors than that burned at higher temperature (>400°C) (Wang et al., 2015a; Cawley et al., 2017). Catchment-scale observations may agree with laboratory findings if the chemical alteration that occurs during organic matter combustion combines with physical stabilization of charred material and residual unburned organic matter. The combined inputs of organic compounds from burned vegetation and organic matter would elevate DOC and DBP precursor export from catchments burned to moderate extent. Conversely, combustion of vegetation and organic soil layers by high-severity wildfire and subsequent erosion will reduce ecosystem C inventory and lower DOC production and export.

The 2002 Hayman Fire was the largest fire (558 km^2) in recent Colorado history (Graham, 2003). It burned catchments of the Upper South Platte River, a primary drinking water supply for the Denver, CO, metropolitan area. A century of fire suppression has increased fuel loads in these and many Colorado forests, and a severe drought in 2002 created conditions that resulted in high-severity wildfire across large areas of the burn. Postfire forest recovery has been extremely slow (Chambers et al., 2016; Malone et al., 2018; Rhoades et al., 2018), and given projected warmer and drier climatic conditions, the long-term revegetation trajectory remains uncertain (Wang and Zhang, 2017). In this study, we compared stream water DOC composition and DBP formation and precursor export from 13 catchments burned to varying extent (0–91%) by high-severity wildfire. Given projections of increased frequency, intensity, and size of North American wildfires, our results will help inform land managers and water utilities about the links between wildfire behavior, postfire water quality, and water treatability.

Materials and Methods

Description of Study Site

The 2002 Hayman Fire, the largest wildfire in Colorado's recorded history, burned ponderosa pine (*Pinus ponderosa* Dougl. ex Laws) and Douglas-fir [*Pseudotsuga menziesii*

(Mirb.) Franco] forests of the lower montane elevation zone (1980–2750 m). The majority of the area burned is underlain by the Pikes Peak batholith, a coarse-grained biotite and hornblende-biotite granite (Bryant et al., 1981). Soils are weakly developed (Typic Ustorthents), excessively drained, coarse sandy loams (Cipra et al., 2003). Depth to bedrock ranges from 25 to 50 cm, and coarse fragments represent 25 to 50% of the soil volume.

Sample Collection

We sampled 13 first- and second-order catchments that span from 5 to 530 km^2 in contributing area (Fig. 1, Table 1; see Rhoades et al. [2011, 2018] for additional details on sampling location and descriptions of the catchments). We sampled five unburned catchments, six that burned to a moderate extent (<50% of catchment area with <25% at high severity) and two that burned extensively (75–95% of catchment area with 50–60% at high severity). Monthly stream water grab samples were collected between October 2014 and September 2016, representing the 12th and 13th postfire water years. Samples were collected in precombusted (3 h at 500°C) amber, borosilicate bottles and then filtered through 0.7-μm nominal pore size mesh glass fiber prefilters (Millipore Corporation). This study complements earlier research of the effects of the Hayman Fire on stream nutrients, sediment, and temperature (Rhoades et al., 2011, 2018), and the current assessment is our first evaluation of stream C composition and DBP formation.

Measurement of Water Quality

Water Chemistry

Analyses of DOC and dissolved total nitrogen (DTN) were conducted using high-temperature combustion catalytic oxidation on Shimadzu TOC-V$_{CPN}$ total organic carbon/nitrogen analyzer (Shimadzu Corporation). Minimum detection limits for DOC and DTN were 0.2 and 0.02 mg L^{-1}, respectively. For optical characterization and DBP formation tests, samples were further filtered through prewashed Millipore 0.45-μm polyvinylidene difluoride membrane filters to remove particulate organic matter. Filtered water samples were scanned from 200 to 700 nm wavelengths using ultraviolet and visible (UV/VIS) spectroscopy (Shimadzu UV-1800, Shimadzu Corporation) and were calculated for specific UV absorbance at 254 nm and E2/E3 ratio (the ratio of absorption at 254 nm to absorption at 365 nm). Specific UV absorbance at 254 nm (SUVA$_{254}$, L mg^{-1} C m^{-1}) was calculated by normalizing UV absorbance to DOC concentration. The SUVA$_{254}$ measurement provides an average absorptivity for all DOC molecules and is an index of DOC aromaticity that is well correlated to aromatic C determined by ^{13}C nuclear magnetic resonance (Weishaar et al., 2003). Absorbance spectra tend to change with average molecular weight (Helms et al., 2008), and the E2/E3 ratio is negatively correlated to the molecular weight of DOC (Ågren et al., 2008). General cations and anions of water samples were determined and reported in previous publications (Rhoades et al., 2011, 2018). In particular, bromide was also determined in all water samples using ion chromatography but every sample was below the detection limit of 0.01 ppm.
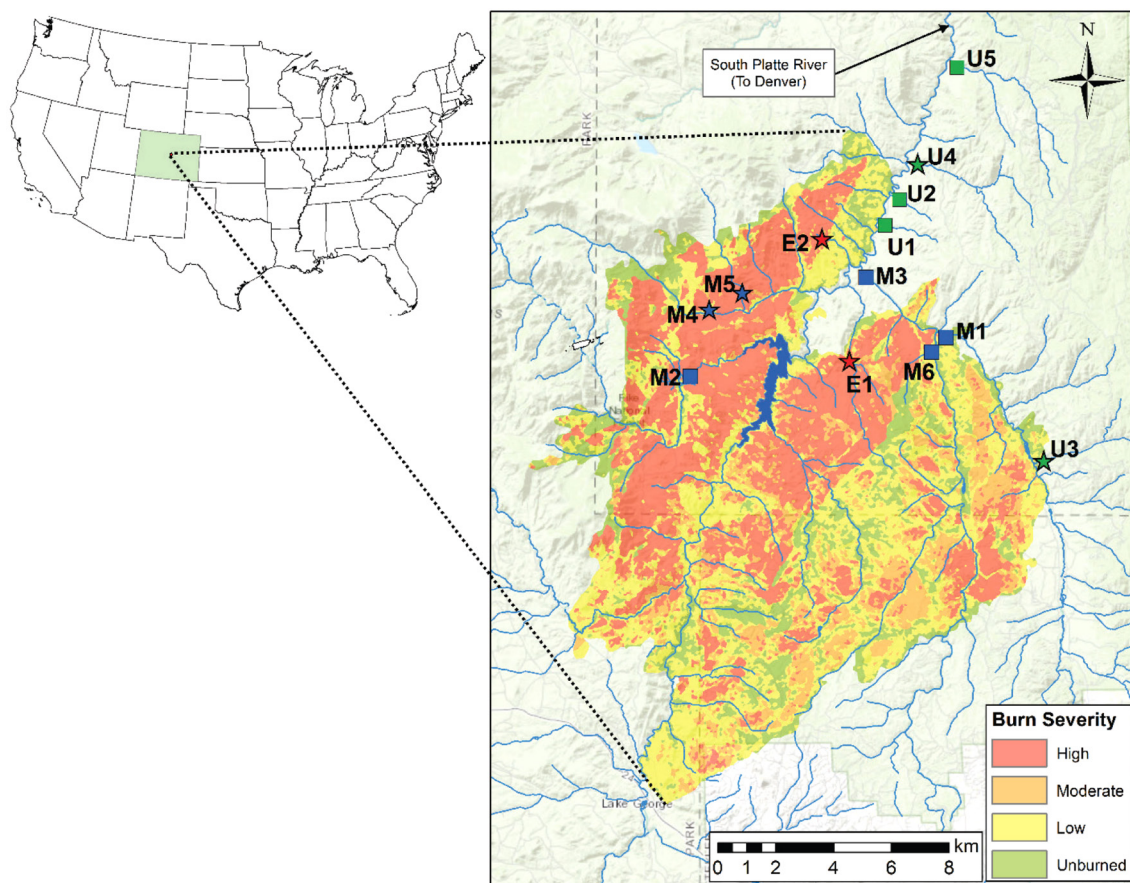
Fig. 1. The 2002 Hayman Fire with sampling locations in 13 subcatchments. U1–U5 labeled with green legends represent unburned catchments; M1–M6 labeled with blue legends represent moderately burned catchments; E1–E2 labeled with red legends represent extensively burned catchments. Sites labeled with stars (i.e., U3, U4, M4, M5, E1, and E2) had similar catchment areas and were used to illustrate the trends of dissolved organic carbon and disinfection by-product parameters as shown in Fig. 4 and 5.

Table 1. Monthly average of dissolved organic C (DOC) and disinfection by-product (DBP) formation of 13 tributaries of the South Platte River.†

Site ID	Catchment area		DOC			DBP formation				
	Burned	Total	Concentration	SUVA$_{254}$	E2/E3	THM	HAN	CHD	HKT	BSF
	%	km²	mg L⁻¹	L m⁻¹ mg⁻¹		——————————— μg L⁻¹ ———————————				%
No name (U1)	0	3.8	0.9 ± 0.1	2.1 ± 0.3	7.5 ± 0.7	41 ± 5	3.6 ± 0.8	2.4 ± 0.2	6.4 ± 1.6	24.3 ± 2.4
Jenny (U2)	0	4.6	1.5 ± 0.2	2.4 ± 0.3	8.0 ± 0.7	64 ± 10	4.4 ± 1.0	3.4 ± 0.5	7.0 ± 2.1	13.9 ± 1.3
Fern (U3)	0	18.6	2.4 ± 0.4	3.5 ± 0.5	5.6 ± 0.2	186 ± 39	9.7 ± 2.0	8.6 ± 1.8	8.7 ± 2.4	8.5 ± 1.1
Sugar (U4)	0	34.3	1.8 ± 0.3	3.0 ± 0.2	5.3 ± 0.2	94 ± 17	5.1 ± 0.9	5.2 ± 0.9	8.0 ± 2.0	11.5 ± 1.0
Pine (U5)	0	35.2	2.5 ± 0.3	2.9 ± 0.3	5.6 ± 0.1	149 ± 22	8.6 ± 2.4	6.7 ± 1.0	7.2 ± 1.8	11.0 ± 1.0
Trout (M1)	8	325.9	3.9 ± 0.4	2.3 ± 0.1	6.1 ± 0.1	229 ± 25	10.6 ± 2.4	11.5 ± 2.2	8.5 ± 1.9	15.5 ± 1.5
Goose (M2)	10	215.3	3.6 ± 0.5	4.1 ± 0.4	4.8 ± 0.1	286 ± 46	9.5 ± 1.7	15.1 ± 2.3	9.9 ± 2.2	3.5 ± 0.6
Horse (M3)	22	529.8	2.9 ± 0.3	2.9 ± 0.2	5.4 ± 0.1	167 ± 21	8.4 ± 1.5	8.0 ± 1.4	7.6 ± 1.8	16.1 ± 1.7
Wigwam (M4)	35	43.3	2.2 ± 0.3	3.0 ± 0.1	5.6 ± 0.1	151 ± 24	6.1 ± 1.1	6.9 ± 1.1	8.9 ± 2.2	7.5 ± 0.9
Cabin (M5)	37	19.8	4.0 ± 0.6	4.2 ± 0.5	4.7 ± 0.1	308 ± 54	13.1 ± 3.8	17.6 ± 4.9	8.3 ± 2.0	6.6 ± 0.9
West (M6)	46	178.6	2.6 ± 0.3	3.4 ± 0.3	4.9 ± 0.2	155 ± 18	7.7 ± 1.1	7.8 ± 1.4	9.1 ± 2.1	11.7 ± 1.1
Fourmile (E1)	74	20.6	1.5 ± 0.1	3.0 ± 0.3	5.7 ± 0.2	79 ± 11	5.7 ± 1.1	4.0 ± 0.4	8.0 ± 2.1	13.3 ± 1.1
Brush (E2)	91	5.9	1.0 ± 0.1	1.6 ± 0.1	7.5 ± 0.6	41 ± 3	3.8 ± 0.7	2.5 ± 0.1	6.7 ± 1.9	17.8 ± 0.9
Unburned catchments avg. (U1-U5)			1.8 ± 0.2ᴬ‡	3.0 ± 0.2ᴬ	5.4 ± 0.1ᴬ	114 ± 17ᴬ	6.2 ± 0.9ᴬᴮ	5.8 ± 0.8ᴬ	8.1 ± 1.3ᴬ	14.5 ± 1.7ᴬ
Moderately burned catchments avg. (M1–M6)			2.9 ± 0.3ᴮ	3.4 ± 0.2ᴬ	5.2 ± 0.1ᴬ	203 ± 26ᴮ	8.6 ± 1.6ᴬ	10.6 ± 2.0ᴮ	8.9 ± 1.4ᴬ	8.1 ± 0.7ᴮ
Extensively burned catchments avg. (E1–E2)			1.3 ± 0.1ᴬ	2.3 ± 0.2ᴮ	6.5 ± 0.4ᴮ	60 ± 6ᴬ	4.7 ± 0.7ᴮ	3.2 ± 0.2ᴬ	7.3 ± 1.4ᴬ	15.5 ± 0.8ᴬ

† BSF, bromine substitution factor; CHD, chloral hydrate; E2/E3, ratio of absorption at 254 nm to absorption at 355 nm; HAN, haloacetonitrile; HKT, haloketone; SUVA$_{254}$, specific UV absorbance; THM, trihalomethane.

‡ Means with different superscript letter in the same column within unburned, moderately burned, and extensively burned catchments indicate the difference is statistically significant (one-way ANOVA and post hoc Tukey test, $p \le 0.05$).

Formation of Disinfection By-Products

We quantified formation of a variety of DBPs to characterize the DBP precursors in postwildfire stream water. Disinfection by-product formation was analyzed using methods detailed in our previous publications (Wang et al., 2015a; Tsai et al., 2017). Briefly, water samples were buffered with a H_3BO_3/NaOH solution to pH 8.0 and chlorinated with freshly prepared NaOCl/H_3BO_3 solution (pH 8.0). Samples were incubated for 24 h in 64-mL tubes with no headspace at 25°C in the dark. Chlorine additions were calculated as follows: $[Cl_2] = (3 \times [DOC] + 7.6 \times [DTN])$, where the concentrations of Cl_2, DOC, and DTN are expressed in milligrams per liter. Residual chlorine was quenched with 0.2 mL of a 10% (w/w) Na_2SO_3 solution. We quantified the following DBP species by gas chromatography–electron capture detection (Agilent 7890): trihalomethanes (THMs; trichloro-, dichlorobromo-, dibromochloro-, tribromomethanes), haloacetonitriles (HANs; trichloro-, dichloro-, bromochloro-, dibromo-acetonitriles), haloketones (HKTs; 1,1-dichloro-2-, 1,1,1-trichloro-2-, 1,2,3-trichloro-propanones), and chloral hydrate (CHD) following USEPA method 551.1 (USEPA, 1995). Method reporting limits were approximately 0.1 to 0.3 $\mu g\ L^{-1}$. We calculated the bromine substitution factor (BSF) to characterize the yield of especially toxic brominated species in THM formation (Chow et al., 2007), as shown in Eq. [1]:

$$BSF = \frac{\sum_{n=0}^{3} n[CHCl_{(3-n)}\ Br_n]}{3\sum_{n=0}^{3} CHCl_{(3-n)}Br_n} \times 100\% \quad 0 \leq BSF \leq 100 \qquad [1]$$

where n = number of atom of Cl or Br in THMs. We also normalized DBP formation by the DOC concentration of the sample (e.g., specific DBP formation, $\mu g\ DBP\ mg^{-1}\ C$).

Typical of most watershed studies, filtered source water is directly chlorinated to identify the terrestrial sources of DBP precursors (Chow et al., 2007; Wang et al., 2015b). Excess chlorine is used to ensure all DBP reactive sites are reacted. Although this chlorination method does not reflect the actual DBP concentration in finished water, this approach provides useful information about the relative abundance of DBP precursors in different watershed sources. We recognize the characterization of DOC may change during water conveyance from headwater to water utility intake, and few studies have illustrated the biogeochemical changes in DBP formation potential through photochemical and microbial transformations. Importantly, the reactivity of DOC in forming a variety of DBPs including THM, HAN, and CHD are generally increased from 5 to >100% after biogeochemical transformations, depending on the DBP species (Chow et al., 2008, 2013). Therefore, DBP formation determined from source water may underestimate the reactivity of DOC entering water treatment facilities.

Dissolved Organic Carbon Export

Discharge was measured concurrently with stream water sampling using the velocity–area method and an OTT Hydromet MF Pro flowmeter (Hach Company); reported discharge was the sum of measurements recorded at 60% of the stream depth in 10- to 30-cm-wide intervals across each stream cross-section. Annual DOC yield (kg C km^{-2} yr^{-1}) was derived from instantaneous stream discharge and monthly DOC concentrations (Eq. [2]):

$$Annual\ DOC\ yield = \frac{1}{A} \sum_{i=Oct}^{Sept} Q_i \times D_i \times [DOC]_i \qquad [2]$$

where A is catchment area (ha), Q_i is the water discharge (L d^{-1}), D is the number of days in a month (d), and [DOC] is the concentration of DOC (mg C L^{-1}). The monthly load of individual DBP (g km^{-2}) in a catchment can be calculated by replacing the DOC concentration with the DBP formation (μg DBP L^{-1}) in Eq. [2].

Data Processing and Statistical Analysis

To detect differences in parameters among sites from each burn class, ANOVA and a post hoc Tukey's test were used. Linear regression and correlations were used to determine significant relationships between measured parameters with $p \leq 0.05$ level of significance. Furthermore, our study included a wide range of watershed areas, and we recognized the potential effects of watershed size on DOC and water chemistry (Larouche et al., 2015). To account for the environmental heterogeneity and fire mosaic, we selected two catchments with perennial streams from each burned class for more detailed analysis, including temporal trends and yields on DOC and DBP precursors, as discussed in section "Yields of Dissolved Organic Carbon and Disinfection By-Product Formation" below. Those watershed sites had similar areas, ranging from 5.9 to 43.3 km^2, and had continuous water flow in the 2-yr study periods (i.e., number of samples = 24). Our study used OrignPro Version 2016 (Northampton, MA) and RStudio Desktop version 1.0.44 (Boston, MA) for statistical analyses and data visualization.

Results and Discussion

Persistent Stream Dissolved Organic Carbon and Disinfection By-Product Formation Responses to Wildfire

The effects of the Hayman Fire on catchment-scale C export and composition persisted for 14 yr after the wildfire, and the influence of wildfire extent remained evident. Stream DOC concentration was lower in catchments that burned extensively (>74%) compared with those with moderate (<50%) wildfire extent (Table 1). An index of DOC aromaticity ($SUVA_{254}$) and specific THM formation decreased ($p = 0.06$ and $p < 0.01$, respectively) with increased wildfire extent (i.e., areas burned by severe wildfire) (Fig. 2a and 2c). Decreasing aromatic C and THM formation with wildfire fire extent likely relate to the sparse vegetation and residual organic materials in the extensively burned catchments (Fornwalt et al., 2016; Francos et al., 2016; Wang and Zhang, 2017). Conversely, DOC/DTN decreased with wildfire extent ($p < 0.01$) (Fig. 2b) due to higher N concentrations in streams draining extensively burned catchments (Rhoades et al., 2018). Importantly, DOC/DTN affects formation of THM and the nitrogenous DBP, HAN, in chlorinated water (Chow et al., 2011), and we found that HAN formation increased with wildfire extent ($p = 0.05$; Fig. 3b). Moderately burned catchments exported DOC that contained more THM precursors, whereas the DOC exported from extensively burned catchments had more HAN precursors.

In general, streams draining catchments with a moderate extent of wildfire had higher DOC concentration (2.9 ± 0.3 mg C L^{-1}) than either unburned catchments (1.8 ± 1.2 mg C L^{-1}) or those with extensive, high-severity combustion (1.3 ± 0.1 mg C L^{-1}). The index of DOC aromaticity ($SUVA_{254}$) was lowest and the index of DOC molecular weight (E2/E3 ratio) was highest on average in extensively burned catchments (Table 1). These patterns are the likely outcome of near-complete live vegetation and O-horizon combustion combined with postfire erosion and sparse vegetation recovery in those catchments (Wang and Zhang, 2017; Malone et al., 2018). In contrast, partial combustion in catchments that burned to a moderate extent created a mixture of live, dead, and charred organic matter sources, as well as residual live vegetation and organic soil layers that sustained C inputs.

Disinfection by-product formation generally increased with DOC concentration (Fig. 3) and was highest in catchments with moderate burn extent (Table 1). Overall, THMs had the highest concentrations of the analyzed DBPs, and THM formation in catchments with moderate burn extent was nearly double that of unburned catchments (203 ± 26 vs. 114 ± 17 µg L^{-1}). Conversely, THM formation in extensively burned catchments was about half that of unburned catchments. Formation of both HAN and CHD was higher in moderately burned catchments, although HKT formation did not differ between catchment types (Table 1). Unlike the THMs and CHD (Fig. 3a and 3c), HAN or HKT formation (Fig. 3b and 3d) was weakly related to stream DOC concentration. Specific THM formation, an index of the propensity for DOC to form THMs, was also highest, with an average of 62 ± 4 µg THM mg^{-1} C, in moderately burned catchments compared with 50 ± 3 and 43 ± 2 µg THM mg^{-1} C, in unburned and extensively burned catchments, respectively. The average THM yields from the unburned and extensively burned catchments were comparable to the THM yields of DOC collected immediately after a wildfire in California (Wang et al., 2015b). Among the four THM species, chloroform (CHCl$_3$) was the major species, followed by dichlorobromoform (CHCl$_2$Br), with the highest bromine substitution factor of 24% in an unburned watershed (U1). No bromoform was observed in any tested samples. Notably, the bromine substitution factor was lowest in moderately burned catchments (Table 1) indicating that increased THM production was associated with greater propensity of DOC to form THM rather than formation of brominated THM species.

Yields of Dissolved Organic Carbon and Disinfection By-Product Formation

The average annual water yield of unburned catchments was $5.0 \pm 0.9 \times 10^7$ L km^{-2} yr^{-1}, significantly lower ($p < 0.05$) than that of moderately ($8.7 \pm 0.8 \times 10^7$ L km^{-2} yr^{-1}) and extensively burned catchments ($9.8 \pm 1.4 \times 10^7$ L km^{-2} yr^{-1}). The greater
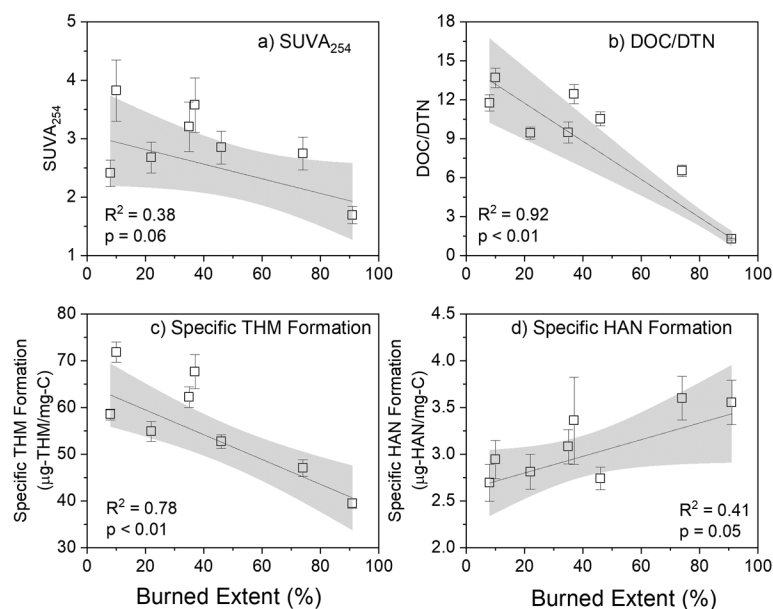

Fig. 2. Linear regression between fire extent (percentage of total catchment area burned) and selected characteristics of dissolved organic C (DOC) in burned catchments. Shaded areas represent 95% confidence band. DTN, dissolved total N; HAN, haloacetonitrile; SUVA$_{254}$, specific UV absorbance; THM, trihalomethane.
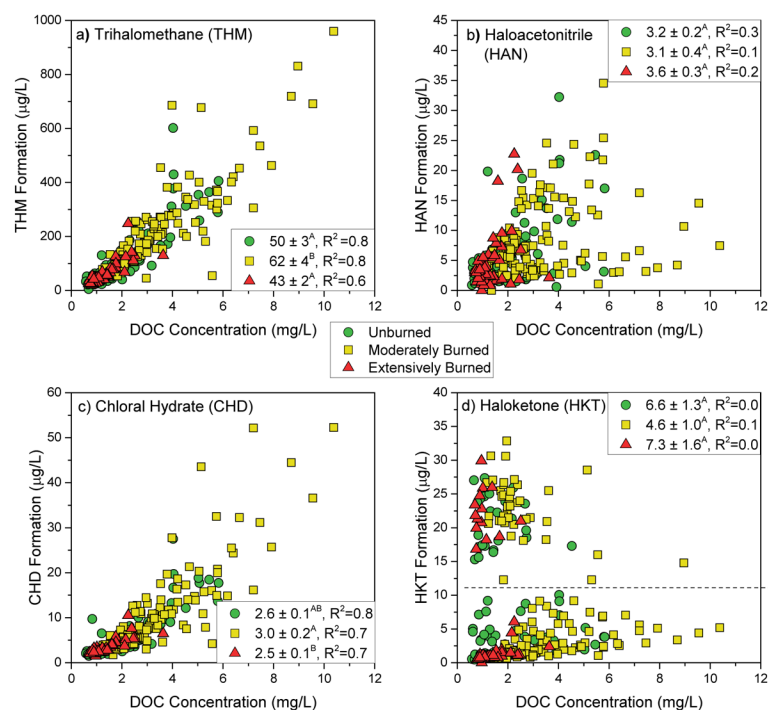

Fig. 3. Relationships of dissolved organic C (DOC) and disinfection by-product (DBP) formation among unburned, moderately burned, and extensively burned catchments. Values in the boxes are average specific DBP formation in µg DBP mg^{-1} C with standard error. Means with different superscript letter in the boxes indicate the difference is statistically significant (one-way ANOVA and post hoc Tukey test, $p \leq 0.05$). Seasonal differences in haloketone (HKT) formation were observed; the horizontal dashed line in (d) shows separation of HKT formation between the two sampling seasons, Jan.–May (upper) and June–Dec. (lower).

water yield from burned catchments has been reported elsewhere, mainly resulting from lower evapotranspiration following vegetation loss (Wang et al., 2018; Poon and Kinoshita, 2018). Importantly, yields of DOC and DBP formation from moderately burned catchments were significantly greater than

($p < 0.05$) those from unburned and extensively burned catchments (Table 2). Specifically, the yields of THMs in moderately burned catchments were 33.7 ± 7.2 kg km^{-2} yr^{-1}, 3.3 times that from unburned catchments. The change in CHD yield was the highest, with a 4.1-fold increase, from 491 ± 133 to 2019 ± 529 g km^{-2} yr^{-1}. The change in HANs was the lowest with only 1.8-fold increase, from 526 to 981 g km^{-2} yr^{-1}. The increase in HKT was 2.3-fold. Results demonstrated that long-term postfire processes may preferably increase the yield of carbonaceous DBP precursors in moderately burned watershed (i.e., THMs and CHD) compared with nitrogenous and oxygenated DBP precursors. The increase in carbonaceous DBP yields was attributed to both higher specific DBP formation and higher water yield in moderately burned catchments. On the other hand, there was no significant difference in DBP yields ($p > 0.05$) between unburned and extensively burned catchments. Notably, DOC in extensively burned catchments had less reactivity to form DBP, but the higher water yield generated similar DBP yields between unburned and extensively burned catchments.

Wildfire Long-term Influences on Seasonal Patterns of Dissolved Organic Carbon

Watershed size could be one of the factors affecting stream water chemistry (Larouche et al., 2015). Therefore, we selected two catchments with similar areas from each burned class (U3 and U4 from unburned, M4 and M5 from moderately burned, E1 and E2 from extensively burned) for more detailed comparisons and analyses. In addition to the changes in overall DOC quantity and chemical composition as described above, wildfires could have long-term influences on seasonal variability of DOC. We observed less seasonal variation in DOC concentration and DOC/DTN ratio in extensively burned catchments compared with unburned and moderately burned catchments for catchments of similar area (Fig. 4). The slow vegetation recovery and
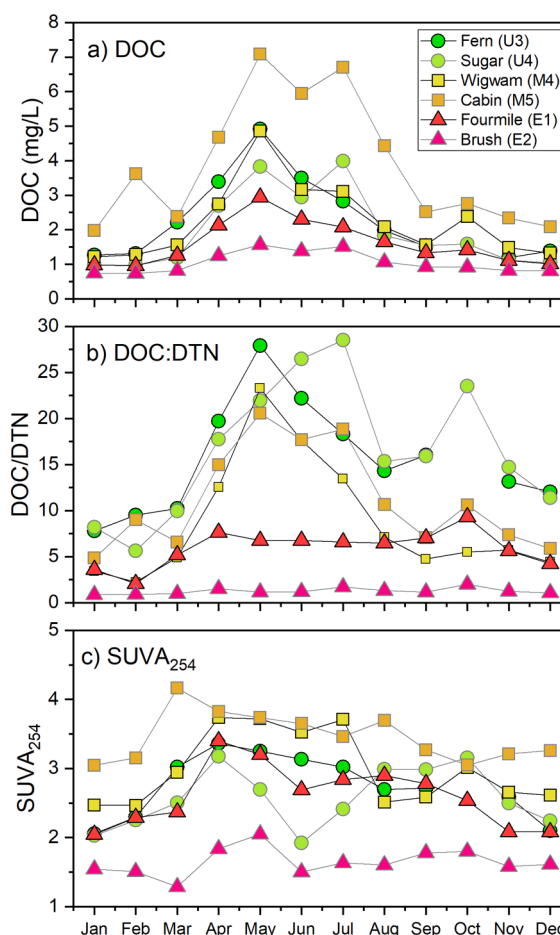

Fig. 4. Temporal variations of dissolved organic C (DOC) characteristics in unburned (U3 and U4), moderately burned (M4 and M5), and extensively burned (E1 and E2) catchments of similar area (590–4340 ha). Values are average of monthly samples in 2014 and 2015 water years. DTN, dissolved total N; SUVA$_{254}$, specific UV absorbance.
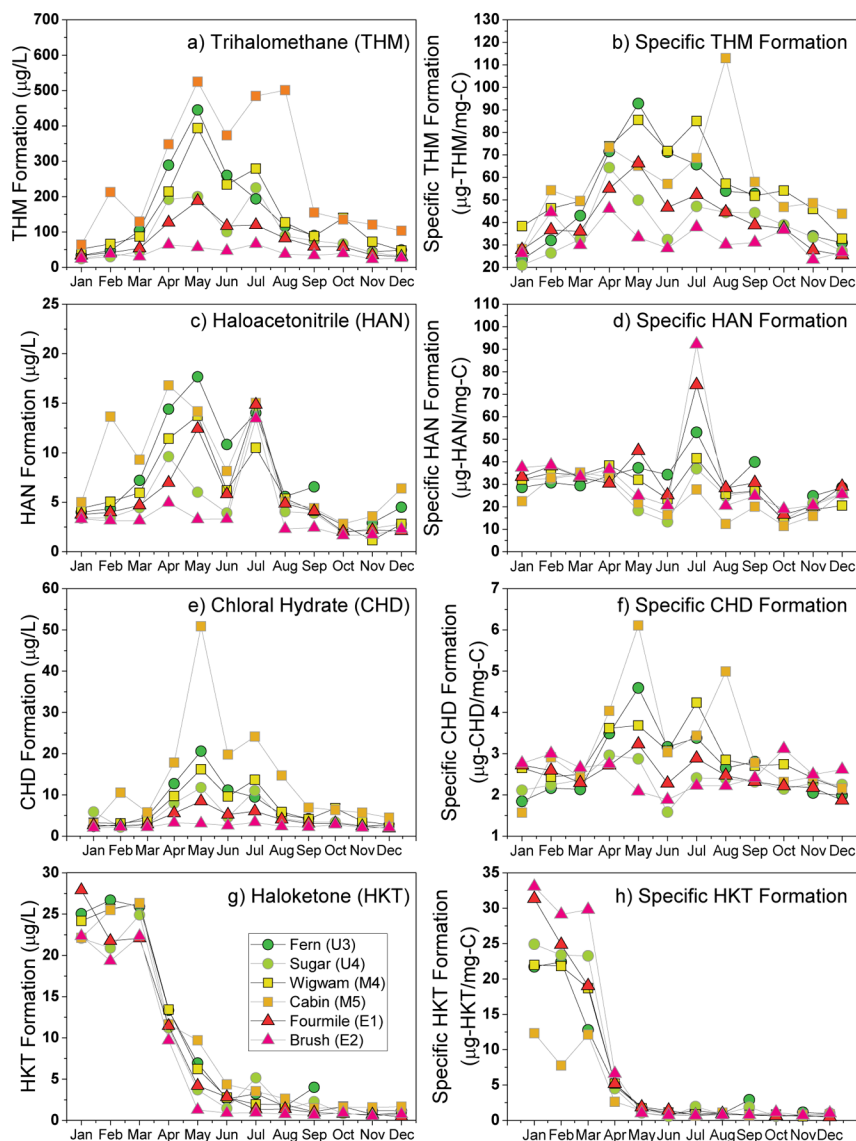
Table 2. Average of annual yields of water, dissolved organic C (DOC), and disinfection by-product formation of 13 tributaries of the South Platte River in water years 2014 and 2015.†

Site ID	Discharge	DOC	THM	HAN	CHD	HKT
	× 10^7 L km^{-2} yr^{-1}	kg km^{-2} yr^{-1}	kg km^{-2} yr^{-1}	g km^{-2} yr^{-1}	g km^{-2} yr^{-1}	g km^{-2} yr^{-1}
No name (U1)	2.4 ± 1.3	25 ± 9	1.2 ± 0.5	111 ± 0.8	63 ± 25	100 ± 78
Jenny (U2)	1.8 ± 0.1	41 ± 15	1.9 ± 0.8	109 ± 1.0	94 ± 42	54 ± 16
Fern (U3)	5.2 ± 0.9	198 ± 2	15.3 ± 4.5	646 ± 2.0	698 ± 197	348 ± 227
Sugar (U4)	6.8 ± 0.6	194 ± 59	10.4 ± 2.9	404 ± 0.9	570 ± 235	316 ± 37
Pine (U5)	9.0 ± 0.2	344 ± 59	22.7 ± 3.5	1362 ± 2.4	1028 ± 160	474 ± 220
Trout (M1)	5.1 ± 0.8	251 ± 89	16.8 ± 7.7	645 ± 2.4	1126 ± 693	291 ± 1
Goose (M2)	11.9 ± 1.7	691 ± 262	51.2 ± 22.9	1167 ± 1.7	2806 ± 1329	760 ± 189
Horse (M3)	6.3 ± 1.0	270 ± 118	15.1 ± 5.0	670 ± 1.5	885 ± 452	375 ± 18
Wigwam (M4)	16.7 ± 6.2	658 ± 388	47.2 ± 19.0	1270 ± 1.1	2059 ± 901	786 ± 38
Cabin (M5)	9.8 ± 1.7	634 ± 313	49.6 ± 27.8	1335 ± 3.8	3838 ± 2822	848 ± 140
West (M6)	9.4 ± 2.1	386 ± 171	22.3 ± 11.9	800 ± 1.1	1399 ± 921	541 ± 40
Fourmile (E1)	10.0 ± 0.6	226 ± 64	11.6 ± 0.3	728 ± 1.1	552 ± 45	424 ± 101
Brush (E2)	7.4 ± 0.4	94 ± 21	3.6 ± 0.5	335 ± 0.7	206 ± 32	209 ± 56
Unburned catchments avg. (U1–U5)	5.0 ± 0.9[A]‡	160 ± 41[A]	10.3 ± 2.9[A]	526 ± 169[A]	491 ± 133[A]	258 ± 72[A]
Moderately burned catchments avg. (M1–M6)	9.8 ± 1.4[B]	482 ± 93[B]	33.7 ± 7.2[B]	981 ± 115[B]	2019 ± 529[B]	600 ± 71[B]
Extensively burned catchments avg. (E1–E2)	8.7 ± 0.8[B]	160 ± 47[A]	7.6 ± 2.3[A]	531 ± 146[A]	379 ± 102[A]	317 ± 78[A]

† CHD, chloral hydrate; HAN, haloacetonitrile; HKT, haloketone; THM, trihalomethane.

‡ Means with different superscript letter in the same column within unburned, moderately burned, and extensively burned catchments indicate the difference is statistically significant (one-way ANOVA and post hoc Tukey test, $p \le 0.05$).

Fig. 5. Seasonal changes of disinfection by-product (DBP) formation and specific DBP formation in unburned (U3 and U4), moderately burned (M4 and M5), and extensively burned (E1 and E2) catchments of similar area (590–4340 ha). Values are average of monthly samples in 2014 and 2015 water years.

seasonal DOC fluctuations (Fig. 4a) with the least variation in extensively burned catchments. It is noteworthy that seasonal DOC and THM patterns were unrelated to $SUVA_{254}$ since it is considered an indicator of DBP precursors (Chow et al., 2008), and it seems likely that the observed fluctuations were associated with C inputs, such as algal biomass, that do not influence $SUVA_{254}$ (Strack et al., 2015; Lee and Lajtha, 2016). This may help explain the seasonal spike in specific HAN formation in July (Fig. 5c and 5d), when water temperature and radiation inputs were highest. In particular, specific HAN formation was higher in extensively burned sites, possibly due to higher N and algal biomass in burned streams (Rhoades et al., 2018; Tsai and Chow 2016). Unlike the other DBPs, HKT production was restricted to the winter months (Fig. 5g and 5h), and no differences were observed among the unburned, moderately burned, and extensively burned watersheds, suggesting that HKT precursor production was unrelated to wildfire occurrence or extent.

Implications for Water Treatability

This study demonstrates that even wildfires that burn a moderate extent of a catchment can have lasting effects on stream water chemistry and treatability. The elevated DOC concentration and propensity to form DBPs in moderately burned catchments do not result in immediate drinking water safety concerns but may have long-term consequences for water treatment. As is typical in streams draining forested catchments in western North America, DOC concentrations increased during spring and early summer in both burned and unburned catchments (Fig. 4). The average annual DOC concentration in our moderately burned catchments (2.9 ± 0.3 mg C L⁻¹ filtered) exceeded the USEPA's disinfectant and DBP criteria (2.0 mg L⁻¹ of total organic C in unfiltered water) (USEPA, 2015), and the elevated C supply may translate into increased coagulation and softening reagents and monitoring costs for water utilities (Jones et al., 2017; Price et al., 2017, 2018).

Increased N export from burned catchments (Rhoades et al., 2018) can promote algal blooms and supply dissolved organic N to water treatment intakes (Tsai and Chow, 2016; Tsai et al., 2017). Algal production has been associated with formation of nitrogenous DBPs such as unregulated, but highly toxic, HANs (Wert and Rosario-Ortiz, 2013; Cortés and Marcos, 2018). In contrast to THMs, the export of HAN precursors increased linearly with wildfire extent (Fig. 2d). It remains unclear whether standard treatment methods are effective at limiting HAN formation (Roccaro et al., 2014; Alansari et al., 2016). The potential for greater HAN formation that we observed in burned

relatively bare landscape of the extensively burned catchments (Chambers et al., 2016; Wang and Zhang, 2017; Malone et al., 2018; Rhoades et al., 2018) are the likely explanation for their uniformly low DOC concentrations. Increases in DOC concentration and DOC/DTN ratio in both unburned and moderately burned catchments could relate to the increases of ambient temperature and biological activities within the catchments (Rhoades et al., 2018). Unlike DOC and DOC/DTN, there were no obvious increases of $SUVA_{254}$ in summer, and they varied little seasonally in any of the catchments (Fig. 4c). Values of $SUVA_{254}$ could be source dependent (Chow et al., 2008). Stable $SUVA_{254}$ in source water suggested there were no significant changes in the composition of substrates and vegetation within the catchments across the water year. In other words, wildfire did not affect the seasonal variation of $SUVA_{254}$.

Surprisingly, seasonal fluctuation in both formation and specific formation of THM and CHD differs for seasonal $SUVA_{254}$ patterns (Fig. 4 and 5). The THM formation (Fig. 5a) tracked

catchments, coupled with projections for increased frequency of severe wildfires, justifies additional study of the terrestrial and aquatic sources and processes that supply these toxic nitrogenous compounds.

Numerous studies have demonstrated that wildfires can impair source water quality over the course of months to a few years, but our work demonstrates that severe wildfires can affect the quantity and composition of DOC exported downstream for well over a decade. We found that catchments with a moderate burn extent contribute a greater amount of DOC and DBP precursors to source water than either unburned or extensively burned catchments. On the other hand, formation of biologically harmful nitrogenous DBPs increases with burn extent. Although these findings should not raise immediate concern regarding drinking water safety, they highlight the long-term influences of high-severity wildfire on source water C content, composition, and treatability.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgments

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