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Drinking water treatment response following a Colorado wildfire

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ABSTRACT

Wildfires can greatly alter the vegetation, soils, and hydrologic processes of watersheds serving as drinking water supplies, which may negatively influence source water quality and treatment. To address wildfire impacts on treatment, a drinking water intake below a burned watershed and an upstream, unburned reference site were monitored following the High Park wildfire (2012) in the Cache la Poudre watershed of northern Colorado, USA. Turbidity, nutrients, dissolved organic matter (DOM) character, coagulation treatability, and disinfection byproduct formation were evaluated and compared to pre-fire data. Post-fire paired spatial differences between the treatment plant intake and reference site for turbidity, nitrogen, and phosphorus increased by an order of magnitude compared to pre-fire differences. Fluorescence index (FI) values were significantly higher at the intake compared to the reference site ($\Delta = 0.04$), and higher than pre-fire years, suggesting the wildfire altered the DOM character of the river. Total trihalomethane (TTHM) and haloacetonitrile (HAN4) formation at the intake were 10.1 μg L^{-1} and 0.91 μg L^{-1} higher than the reference site. Post-fire water was amenable to conventional treatment at a 10 mg L^{-1} higher average alum dose than reference samples. The intake was also monitored following rainstorms. Post-rainstorm samples showed the maximum observed FI values (1.52), HAN4 (3.4 μg mg_C^{-1}) and chloropicrin formation yields (3.6 μg mg_C^{-1}), whereas TTHM and haloacetic acid yields were not elevated. Several post-rainstorm samples presented treatment challenges, and even at high alum doses (65 mg L^{-1}), showed minimal dissolved organic carbon removal (<10%). The degraded water quality of the post-rainstorm samples is likely attributed to the combined effects of runoff from precipitation and greater erosion following wildfire. Wildfire impacts cannot be separated from rainfall effects due to the lack of post-rainstorm samples from the reference site. Results suggest for this study region, wildfire may have consequences for influent water quality, coagulant dosing, and DBP speciation.

1. Introduction

Wildfires are dramatic disturbances that drastically alter forests in a relatively short time frame, and can severely impact the ecological integrity of watersheds, including surface water quality. Forested watersheds supply nearly two-thirds of potable water sources in the United States, and billions of consumers world-wide (National Research Council, 2008). The sustainability of forested water supplies is at risk as the frequency, size, and severity of wildfires have increased in recent decades (Flannigan et al., 2013, 2009; McKenzie et al., 2004; Westerling, 2006). Wildfire activity is expected to continue increasing, largely attributed to climate change and increased fuel loads (Flannigan et al., 2009; McKenzie et al., 2004; Westerling, 2006), and may present challenges to drinking water providers who will need to address post-fire changes in supply, quality, and treatability. As a result, the potential impact of wildfire on water supplies is drawing increased attention (Bladon et al., 2014; Sham et al., 2013), particularly among water providers relying on fire-prone watersheds. An understanding of wildfire effects on drinking water quality and treatability is needed to develop management strategies for communities susceptible to wildfire.

Water quality responses to wildfire are influenced by many confounding seasonal and inter-annually varying factors, including hydrology and precipitation patterns, as well as wildfire specific factors, such as burn severity, forest type, location and extent within a watershed (Neary et al., 2005; Smith et al., 2011). Increased erosion following wildfire can result in higher total suspended

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solids (TSS) (Lane et al., 2006; Malmon et al., 2007; Mast and Clow, 2008; Sheridan et al., 2007; Wilkinson et al., 2006) and turbidity levels (Emelko et al., 2011; Murphy et al., 2012; Oliver et al., 2011; Rhoades et al., 2011; Writer et al., 2014) in surface waters. For water providers, high particulate levels can cause considerable infrastructure and treatment challenges, yet few studies have evaluated post-fire changes to water treatment processes (Emelko et al., 2011; Writer et al., 2014). Elevated nutrient (phosphorus, nitrogen, nitrate) concentrations in streams following wildfire are often observed (Bladon et al., 2008; Emelko et al., 2011; Hauer and Spencer, 1998; Lane et al., 2008; Mast and Clow, 2008; Rhoades et al., 2011; Son et al., 2015; Writer et al., 2012); however, responses vary widely and are influenced by forest catchment environments and hydrologic regimes (Hauer and Spencer, 1998; Smith et al., 2011).

Post-fire increases in dissolved organic matter (DOM), quantified as dissolved organic carbon ($\text{DOC} - \text{mg}_\text{C}\ \text{L}^{-1}$), have also been observed (Revchuk and Suffet, 2014; Emelko et al., 2011; McEachern et al., 2000; Minshall et al., 2001), which presents a concern for potable water systems, as DOM can react with disinfectants upon water treatment to form disinfection byproducts (DBPs) (Christman et al., 1983; Rook, 1977; Stevens et al., 1976). DBPs pose a concern to public health as they have been linked to cancer risks and reproductive developmental effects (Muellner et al., 2007; Plewa et al., 2008, 2004; Richardson et al., 2007; Villanueva et al., 2006). Carbonaceous DBPs (C-DBPs) include trihalomethanes (THM) and haloacetic acids (HAA), which are regulated by the USEPA and commonly studied (USEPA, 2006). Nitrogenous disinfection byproducts (N-DBPs), such as haloacetonitriles (HAN), halonitromethanes (e.g., chloropicrin), and nitrosamines, are also of interest as they have been shown to be more of a health concern than C-DBPs, even at lower concentrations (Muellner et al., 2007; Plewa et al., 2008, 2004).

Following wildfire changes in DBP formation and speciation upon water treatment may result as excess nutrients can influence the DOM character in surface waters. Post-fire increases in stream water organic nitrogen (Bladon et al., 2008; Carignan et al., 2000; Emelko et al., 2011) may enrich N-DBP formation (Krasner et al., 2008; Mitch et al., 2009) and di-halogenated acetic acid formation (Westerhoff and Mash, 2002). Increased particulate levels and DOC concentrations will likely create challenges during coagulation processes, with implications for treatment operations and costs (Emelko et al., 2011), and finished water DBP concentrations. Wildfire alterations to DOM character may result from drastic changes to watershed vegetation and soils (Knicker, 2007), which could negatively impact DOM removal by coagulation, increase DBP formation (Revchuk and Suffet, 2014), or cause a shift in DBP speciation upon chlorination (Wang et al., 2015a).

While previous studies address post-wildfire water quality, they primarily speculate regarding impacts to drinking water, lacking a direct evaluation of the treatability following wildfire. The goal of this work was to assess the impact of a wildfire on drinking water quality and treatability in a watershed serving as a direct drinking water supply for several communities. The High Park wildfire (2012) burned a northern Colorado, USA watershed. A water treatment intake within the burned area and a site upstream of the burned area were monitored during the first snowmelt season (2013) and rainstorm events (water intake only) following the fire. Monitoring was also conducted in 2012 immediately following the fire (Writer et al., 2014) and is expanded upon in this study. Four years of pre-fire water quality data from the intake and reference site were used for comparison to post-fire monitoring results. Turbidity and nutrients (total phosphorus (TP), total nitrogen (TN), total organic carbon (TOC)) were measured to address wildfire effects at the water intake. The objective of this study was to couple post-wildfire influent water quality with changes in DOM optical properties, DBP precursors (THM, HAA, HAN, and chloropicrin) and the efficacy of conventional treatment by coagulation. Together, these studies represent the first comparison of pre- and post-fire source water DOM character and DBP reactivity (Writer et al., 2014).

2. Site description

The Upper Cache la Poudre (CLP) River located in northern Colorado, USA serves as a drinking water source for the City of Fort Collins, and two smaller communities, directly providing water to over 300,000 consumers before eventually joining the South Platte River. The CLP watershed is a snowmelt-dominated system, with the highest flows in the spring during the peak of snowmelt (Fig. S8). The region experiences intense localized rain events in the summer months due to convective storms. These precipitation events, along with small contributions from groundwater, also influence the hydrology of the CLP River. An emerging contaminant monitoring study showed anthropogenic wastewater inputs are minimal within the watershed upstream of Fort Collins (Oropeza and Heath, 2013).

Two wildfires burned the CLP watershed in 2012: (1) the Hewlett Gulch fire burned from May 14th–May 22nd and (2) the High Park fire began on June 9th due to a lightning strike and was contained on July 2nd (Fig. 1). The High Park fire was the third largest wildfire in Colorado history, combined the fires burned ~384 contiguous km^2. The proximity of the two fires to the Fort Collins drinking water intake presented a high concern to the City's water supply (Fig. 1). The fires burned forested land comprised of lodgepole and ponderosa pines at lower elevations and mixed conifers at higher elevations. Both fires burned at mixed severities, as shown in Fig. 1 (Hewlett Gulch: 20% high severity, 8% moderate, 71% low, and 1% unburned; High Park: 7% high severity, 40% moderate, 37% low, and 16% unburned) (BAER, 2012). The impacts of the two fires on CLP River water quality cannot be completely separated due to overlapping burn perimeters, and the combined effects will be referred to as from the High Park fire for simplicity.

Significant portions of the CLP watershed were impacted by the mountain pine beetle (MPB) epidemic, which began in this region in the late 1990s and peaked around 2008 (USDA, 2015), possibly contributing to the size and severity of the wildfires (Oropeza and Heath, 2013). Following the High Park fire, from October 2012 through October 2013, mulch was applied as follows: 11.7 km^2 of wheat straw and 4.5 km^2 of wood mulch to private land, and an additional 19 km^2 of agricultural straw and 3.6 km^2 of wood shred were applied to U.S. Forest Service lands. The wood shred mulch was applied at a rate of 785–919 Mg per km^2, with a targeted coverage of 70%. Percent ground coverage was verified by field surveys. The application of mulch to severely burnt areas potentially mitigated the erosion of soil materials from the landscape to the watershed, decreasing the post-fire response on water quality. However, cumulatively mulching covered approximately 11% of the total area burned and the effects on the results presented here are expected to be minimal.

3. Materials and methods

3.1. Study design and sample collection

River samples were collected immediately following the wildfire (2012) and precipitation events in the burned area. The response of the Fort Collins Water Treatment Facility and initial post-fire data collected in 2012 were published previously (Writer et al., 2014). The study presented here expands upon previous work, with sampling of the CLP River from April 1st, 2013 through

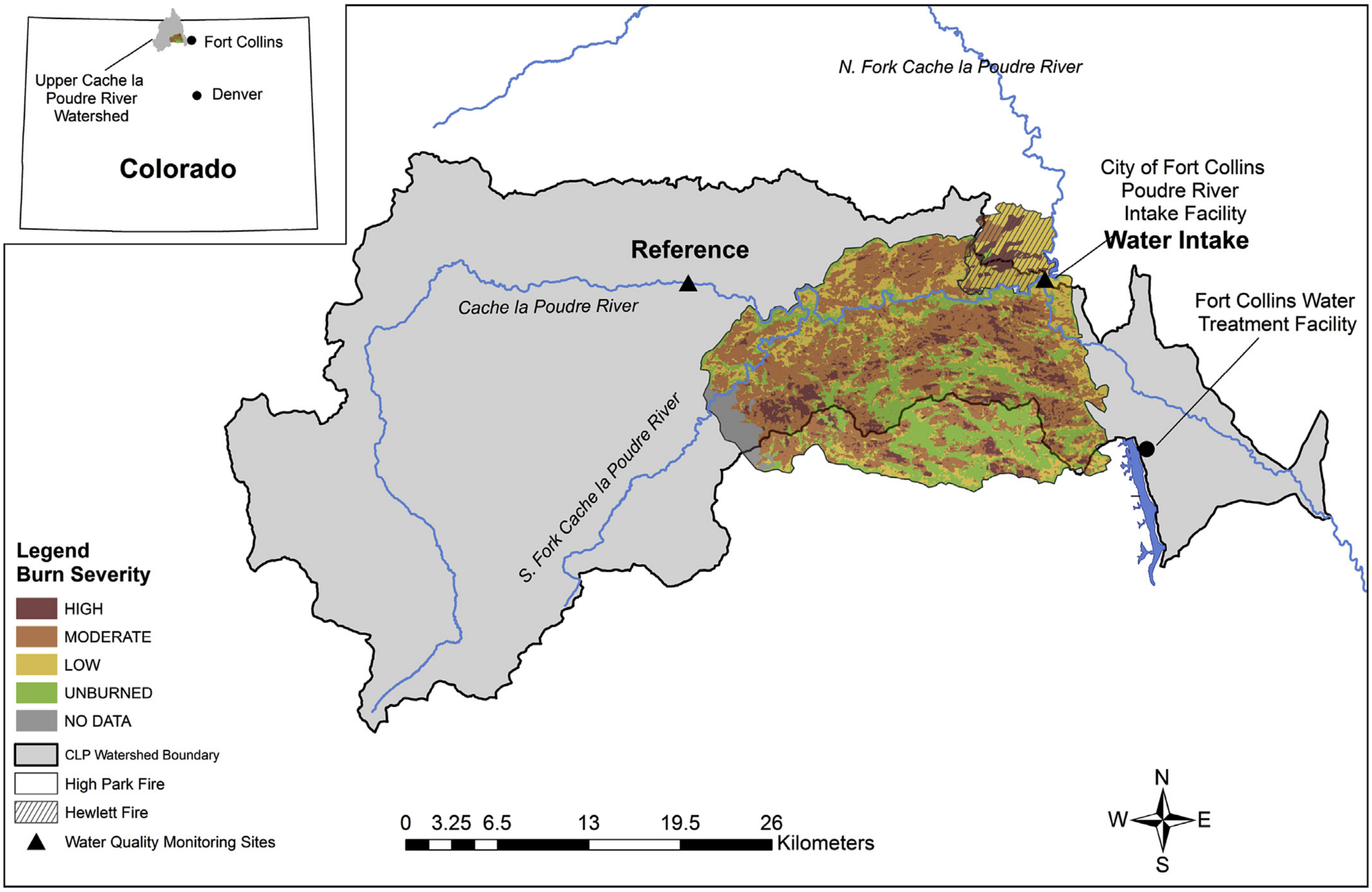

Fig. 1. Cache la Poudre (CLP) River sampling sites include the City of Fort Collins drinking water intake within the High Park fire burn area and the reference site, upstream and outside of the burned area. The watershed boundary shown includes drainages upstream of the confluence with the North Fork of the CLP River.

the end of October 2013, including three overlapping sample dates from Writer et al., 2014 (4/1, 5/4, 6/1/13). Samples were collected in glass amber bottles (heated in a furnace at 550 °C for 3 h) and/or pre-cleaned plastic carboys, and transported to the laboratory at the University of Colorado, Boulder. Bi-weekly samples were collected through late July 2013 followed by monthly sampling. Spring snowmelt (2013) began in mid-May and lasted until late June (mean flow = 28.6 $m^3\ s^{-1}$; Fig. S8). The flows before and after spring snowmelt will be referred to as baseflow (mean flow = 7.4 $m^3\ s^{-1}$).

The City of Fort Collins drinking water intake is located along the mainstem of the CLP River, just upstream of the confluence with the North Fork, and represents the influent water quality for the treatment facility. The wildfire burned areas encompassing the riverbank near the water intake, and upstream areas draining to the intake (Fig. 1). The hill slopes immediately surrounding the water intake were primarily vegetated by grasses and shrubs, and burned at low severity (BAER, 2012). Wildfire effects on water quality were predicted to be most evident at this location due to the cumulative influence of the numerous sub-drainages burned in both the High Park and Hewlett Gulch fires, including the South Fork of the CLP River. The reference site is located upstream and outside of the burn area, approximately 40 km from the water intake. The location of the reference site was chosen because of its catchment similarities to the water intake including geology, soils, hydrology, and vegetative cover. Although drainage area and elevation of the intake and reference site differ (Table S7), importantly, the water quality of the two sites prior to the wildfire were similar, established from an analysis of pre-fire data, discussed in further detail in section 4.1.

In addition to bi-weekly monitoring, samples were collected during or immediately following rainstorm events at the water intake in 2012 (Writer et al., 2014) and 2013. Post-fire rainfall resulted in substantial debris flow and the mobilization of ash and sediment into the CLP River, causing clogging at the water intake pipeline, problems never encountered prior to the wildfire. Post-rainstorm samples were not collected from the reference site due to logistical and budgetary constraints, as well as safety concerns. The lack of post-rainstorm data from the reference site limits drawing strong conclusions related to wildfire specific effects, and rather the post-rainstorm samples reflect the compounding impacts of precipitation and the wildfire. Previous studies have shown the most extreme post-fire spikes in water quality often occur following rainstorms (Mast et al., 2016; Murphy et al., 2015; Smith et al., 2011), which may be of concern to water facilities if they do not have pre-sedimentation basins in place or alternate water supplies. Post-rainstorm samples are compared to water intake samples collected during baseflow and snowmelt, consistent with other study designs comparing river DOM following rainstorms (Wiegner et al., 2009).

3.2. Analytical methods

The City of Fort Collins Water Quality Laboratory measured turbidity, TP, TN, and TOC of the baseflow and spring snowmelt samples following methods outlined elsewhere (Oropeza and Heath, 2013). Post-rainstorm samples were analyzed for dissolved nutrients (total dissolved phosphorus (TDP), total dissolved nitrogen (TDN), and DOC) due to the high level of particulates. Samples were filtered through 0.7 μm GF/F filters (heated in a furnace at 550 °C for 3 h) and stored at 4 °C. DOC and TDN were analyzed at the Kiowa Laboratory, University of Colorado, with a Shimadzu TOC-V analyzer (Shimadzu Corp., Japan). Nitrate and nitrite were measured with an analytical flow solution IV spectrophotometric analyzer (OI Analytical, College Station, TX) and ammonium was analyzed using a BioTek Synergy 2 Microplate Reader. Dissolved organic nitrogen (DON) was calculated from the difference between TDN and dissolved inorganic nitrogen. For several samples the inorganic N concentration was high (>60% of TDN), and the DON calculation may be less accurate (Lee and Westerhoff, 2005). TDP was quantified with a Lachat QuikChem 8500 spectrophotometric flow injection. Bromide was analyzed using a Metrohm 761 Compact IC. Turbidity analysis was performed with a Hach 2100 N turbidimeter. UV_{254} was measured using a UV–Vis spectrophotometer (Cary 100, Agilent Technologies) and a 1-cm quartz cuvette. Specific ultraviolet absorption ($SUVA_{254}$) was calculated by normalizing UV_{254} absorbance by the DOC concentration and absorbance path length (Weishaar et al., 2003).

Fluorescence scans were collected using a Horiba Jobin Yvon Fluoromax-4 and a 1-cm quartz cuvette. The excitation and emission bandpass was set to 5 nm and scans were collected in signal/reference ratio mode with an integration time of 0.25 s. Scans were corrected for instrument optics within the Fluoromax-4 software prior to data export. Using Matlab software, corrections for inner-filter effects (Ohno, 2002), Raman normalization (Lawaetz and Stedmon, 2009) and blank subtraction with an 18 MΩ-cm lab-grade water blank were performed. The fluorescence index (FI), which describes DOM compositional differences (McKnight et al., 2001), was calculated as the ratio of the emission intensities at 470 nm and 520 nm at an excitation wavelength of 370 nm (Jaffé et al., 2008).

DBP analysis followed EPA Method 551.1 (1995) for: total trihalomethanes (TTHM), the regulated value representing the sum of four THM species, four haloacetonitriles (HAN4), and chloropicrin. HAN4 species included: di-chloroacetonitrile (DCAN), tri-chloroacetonitrile (TCAN), di-bromoacetonitrile (DBAN), and bromo-chloroacetonitrile (BCAN). EPA method 552.2 was used for analysis of haloacetic acids and reported as the five regulated HAAs (HAA5). An Agilent 6890 Gas Chromatography System with an electron capture detector was used. DBP analysis was completed within two weeks of chlorination.

3.3. Bench scale treatment methods

DBP formation was evaluated for all samples with bench scale chlorination following uniform formation conditions (UFC), representative of a typical water treatment plant (Summers et al., 1996). Samples were chlorinated with a buffered sodium hypochlorite dosing solution (pH 8) at 20 °C. A borate buffer was added to samples to maintain a pH of 8 (±0.3). Preliminary chlorine demand curves were used to determine doses required to yield a 24-h chlorine residual of 1.0 mg L^{-1} (±0.4 mg L^{-1}). Chlorine residuals were measured with the DPD (*N*,*N*-diethyl-p-phenylenediamine) colorimetric method (SM4500-Cl G) and quenched with ammonium chloride immediately following 24 h.

Jar tests were performed using a Phipps & Bird model 7790-400 jar tester with 2 L B-KER^2 jars. Aluminum sulfate (Mallinckrodt Chemicals, 3208-04) was used as the coagulant. Mixing conditions included a rapid mix phase (1 min, 290 rpm), two flocculation periods (10 min at 55 rpm and 10 min at 20 rpm) and a 30-min sedimentation period. Dose response curves (alum dose vs. settled water DOC concentration) were developed using doses ranging from 20 to 120 mg L^{-1}. The alum dose for optimal DOC removal was then selected for final coagulation tests. Coagulated samples were decanted and filtered (GF/F) to isolate the dissolved fraction for DOC, UV_{254}, chlorination, and subsequent DBP analyses.

3.4. Data analysis and statistical methods

The spatial differences between the water intake and reference site were assessed using pre-fire data (turbidity, TP, TN, TOC) to understand the inherent hydro-climatic watershed variability independent of the wildfire, including the contribution of the South Fork between the two sites. A paired statistical analysis of pre-fire data allows for an understanding of 1) any watershed differences between the sites prior to the wildfire and, 2) the magnitude of pre-fire differences for the respective water quality parameters. Paired data points for the two sites from the same sampling date were analyzed by taking the difference between the parameter values (water intake − reference site) to address seasonality. Post-rainstorm samples were not included in the calculation of paired differences. Data points below the detection limit were analyzed as the respective reporting limits, noted in Table 1 (footnote f). Non-parametric statistical tests were used (sign tests and Wilcoxon signed-rank tests) to determine if pre-fire spatial differences were significantly different from zero (Minitab 17® Statistical Software).

Pairwise data analysis was also used to address post-fire changes in source water quality for downstream drinking water plants. Pre-fire (2008–2011) daily spatial differences were compared to post-fire (2013) differences (Table 1) using Mann-Whitney tests (Minitab 17® Statistical Software). Data from 2012, the year of the wildfire, were not included due to potential skewing from splitting the data mid-season. When only post-fire data were available for both sampling sites pairwise differences were tested against zero using non-parametric tests. This approach allows for the contribution of the watershed to the water quality of the river to be assessed, and attempts to mitigate the influence of uncontrolled environmental factors (i.e., hydrology, average temperature) which vary temporally.

4. Results and discussion

4.1. Pre-fire spatial water quality analysis and potentially confounding factors

Pre-fire paired differences (Δ) in water quality concentrations between the water intake and reference site were evaluated and used to establish the upstream site as a reasonable reference for comparison to the intake. The spatial differences (or lack of) reflect the contribution of the flow from the South Fork of the river and other sub-drainages (Fig. 1) between the two sites, which could contribute inputs to, or dilute, the CLP River water quality. Continuous flow data for the South Fork were not available, however it was estimated using monthly point flow measurements from April through October (2008–2013) that the South Fork contributes approximately 13–34% of the flow at the water intake, varying seasonally.

Paired spatial analysis of the pre-fire water quality data indicated TN and TOC levels were not statistically different ($p > 0.05$) for the two sampling sites before the fire (median Δ: < 0.01 mg_N L^{-1} and -0.12 mg_C L^{-1}, respectively). Spatial differences for turbidity and TP were statistically significant ($p < 0.05$). The mean and median TP concentrations for both sites were very close to the reporting limit (0.01 mg_P L^{-1}) and the median difference was <0.001 mg_P L^{-1}, therefore TP was assumed reasonably similar between the sites prior to the wildfire. Pre-fire paired spatial differences are presented in Table 1 (pre-fire p values not shown) and reveal the water quality concentrations of the sampling sites were similar before the wildfire. The main exception was the difference

Table 1
Analysis of pre- and post-fire water quality data collected from the water intake and reference sampling sites. Pre-fire analysis was used to assess paired spatial differences (Δ) between the sites. Statistical analysis comparing pre-fire spatial differences to post-fire differences was used to assess changes likely associated with the wildfire. Pre- and post-fire sampling seasons were from April–November, annually. Post-fire seasonal water quality data are presented in the supplementary material (Fig. S9).

Water quality parameter[f]		Pre-fire (2008–2011)[a]				Post-fire (2013)				p value[e]
		Concentration		$\Delta^{b,\,d}$ (intake − reference)	n	Concentration		$\Delta^{b,\,d}$ (intake − reference)	n	
		Water intake	Reference			Water intake	Reference			
Turbidity*, [c] (ntu)	Mean	3.6	2.2	1.3	42	35	4.4	30	12	<0.0001
	Median	1.4	1.1	*0.29		12	2.0	8.1		
	SD	(4.5)	(2.4)	(2.3)		(38)	(5.0)	(37)		
TP*, [c] (mg_P/L)	Mean	0.018	0.014	0.004	44	0.058	0.013	0.046	11	<0.001
	Median	0.013	0.012	0.000		0.023	0.011	0.013		
	SD	(0.014)	(0.007)	(0.008)		(0.077)	(0.004)	(0.077)		
TN (mg_N/L)	Mean	0.29	0.27	0.02	20	0.66	0.27	0.40	11	0.010
	Median	0.25	0.24	0.00		0.34	0.28	0.16		
	SD	(0.20)	(0.18)	(0.11)		(0.69)	(0.10)	(0.70)		
TOC (mg_C/L)	Mean	4.8	4.8	0.01	43	4.9	4.2	0.71	10	0.007
	Median	3.5	3.9	−0.12		4.6	4.2	0.47		
	SD	(2.8)	(2.7)	(0.80)		(1.9)	(1.9)	(0.91)		

[a] Pre-fire TN data are for 2010–2011.
[b] $\Delta_{Parameter} = Parameter_{Water\ intake} - Parameter_{Reference\ site}$.
[c] * Denotes the pre-fire difference (Δ) was statistically different from zero ($p < 0.05$).
[d] Post-rainstorm event data were not included in the calculation of Δ and p values.
[e] p values were determined by non-parametric Mann-Whitney test comparing pre- and post-fire spatial differences (Δ).
[f] The reporting limits are as follows: Turbidity = 0.01 ntu; TOC = 0.5 mg_C/L; TP = 0.01 mg_P/L; TN = 0.1 mg_N/L; Non-detect measurements analyzed as the respective limit values in the data analysis.

in turbidity which was higher at the intake (median $\Delta = +0.29$ ntu; $p = 0.02$). The upstream site was chosen as a reasonable reference location for comparison to the water intake due to the minimal differences in pre-fire water quality, which reflect the influence of basin characteristics (e.g., drainages, elevation) that could impact water quality.

By establishing pre-fire spatial differences between the two sites, downstream cumulative effects and other inherent watershed variability unrelated to the wildfire are considered in the analysis. Areas draining to both the water intake and reference site were impacted by the MPB beginning in the late 1990s (USDA, 2015) and the potential effects, such as elevated TOC (Mikkelson et al., 2013), would likely be observed in the pre-fire data (2008–2011) and at both sampling sites (Fig. S7). While tree die-off from the MPB could confound post-wildfire effects, wildfire constitutes an acute change in the watershed demonstrated by charring and combustion of soils and vegetation, compared to an incremental, gradual change as a result of the slow tree mortality from the MPB (Adams et al., 2011). The supplemental material includes a discussion of potential MPB effects on water quality.

A characterization of the South Fork contribution to the CLP River mainstem water quality was conducted to validate the study design and address potentially confounding effects. Data collected from two additional sites, including the South Fork upstream of the burned area (SFM), and just below the confluence of the South Fork with the mainstem of the CLP River (PSF), were analyzed for pre- (2008–2011) and post-fire (2013) years (Fig. S1). The water quality concentrations (turbidity, TP, TN, TOC) of the South Fork and PSF were not statistically different ($p > 0.05$) from the CLP River mainstem sites prior to the wildfire (Table S1; Fig. S2). However, pairwise analysis indicated post-wildfire differences between the water intake and South Fork were statistically significant ($p > 0.05$) compared to pre-fire differences for turbidity, TP, and TN (Table S2; Fig. S3), suggesting the burned areas downstream of the SFM site contributed increased inputs of these water quality parameters. During the fire (2012), and post-fire (2013), the South Fork drainage water quality upstream of burned areas was similar to the pre-fire South Fork and reference site water quality.

To further understand the CLP watershed water quality, two-way fixed effects regression models were developed using pre- and post-fire data for the mainstem and South Fork sampling sites (supplemental material). Site ID and sampling date were included as fixed effects to account for specific conditions for the site locations and sampling dates. The percentage of the drainage areas burned for the four respective sites (pre-fire data and unburned sites = 0% burned) was determined to be a significant ($p < 0.05$) independent variable for all water quality parameters (Table S5).

Additional historical (2000–2007) water quality data ($n = 100$ per site) for the CLP River mainstem and South Fork were also analyzed. The 2000–2007 pre-fire water quality of the South Fork and CLP River mainstem were not statistically different, and showed minimal variability between sites for TSS, TP, and TOC (Table S6; Fig. S6). Please refer to the supplemental material for more detail regarding the South Fork water quality before and after the wildfire, statistical comparisons to the CLP River mainstem sites, and justification of the study sampling design.

4.2. *Comparison of pre- and post-fire influent water quality*

Extensive post-fire water quality studies have previously been conducted in the hydrologic and watershed science communities. Although the observed responses vary depending on wildfire and watershed specific factors, research generally shows a post-fire increase in particle levels and nutrient concentrations as detailed in the introduction (section 1). For this study turbidity and nutrient concentrations were used as indicators of wildfire impacts. After first establishing a wildfire response at the water intake, drinking water treatment tests and analyses were evaluated. Sampling frequency and resolution were relatively low compared to other post-fire water quality studies due to the nature of the treatment tests performed, and may not have captured all post-fire peaks. Thus, a comprehensive analysis of post-fire water quality fluxes was outside the scope of this work. Water quality concentrations are reported, as water providers rely on these metrics for making treatment and operation decisions.

Prior to the wildfire, turbidity, TP, and TN differences between the intake and reference site (Δ) were minimal. The median paired differences were generally near zero for all pre-fire years, whereas post-fire spatial differences were consistently higher and extreme (Fig. 2). When all pre-fire years are grouped (Table 1), the post-fire

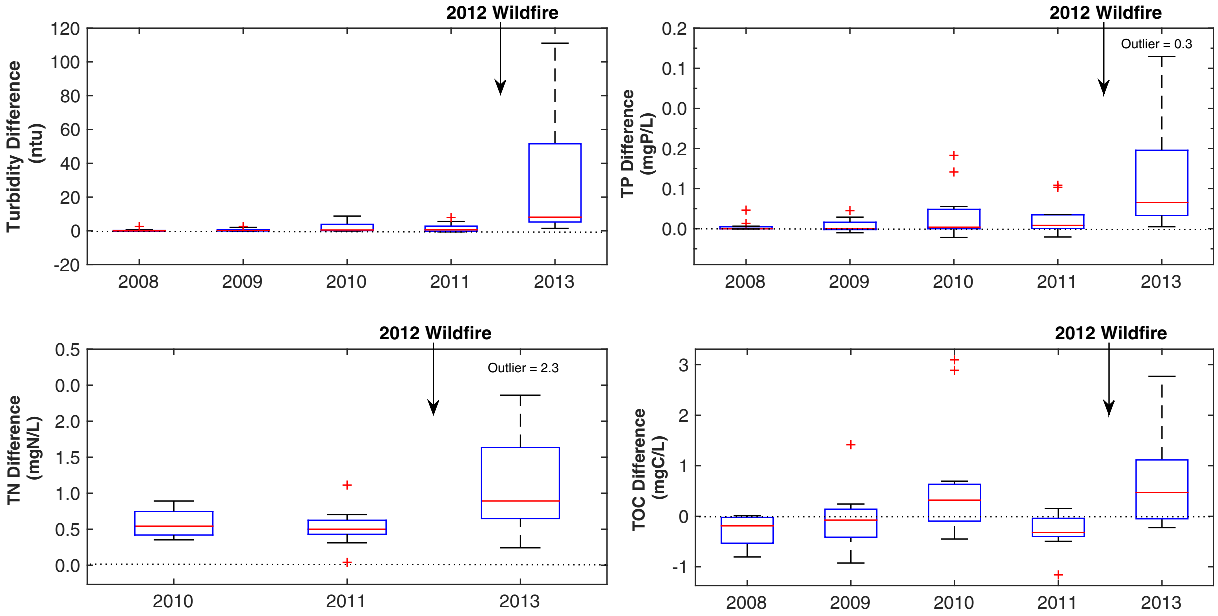

Fig. 2. Paired differences (water intake − reference) by date for pre- and post-fire water quality. Data from the year of the wildfire are not included. Red lines represent median values, blue boxes show 25th and 75th percentiles, the whiskers extend to the most extreme points excluding outliers, red crosses identify individual outliers. Rainstorm samples were not included in the calculation of paired differences. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

spatial differences for turbidity, TP, and TN were at least an order of magnitude greater than before the fire ($p < 0.01$). The elevated post-fire turbidity, TP, and TN likely reflect increased erosion and sediment transport to the stream channel (Hauer and Spencer, 1998).

TOC showed more spatial variability prior to the wildfire than the other parameters measured. In several pre-fire years TOC was higher at the reference site, and in 2010 the differences in TOC between sites varied substantially (max $\Delta = +3.1$ mg_C L^{-1}). Regardless, post-fire TOC spatial differences were significantly greater than before the fire (Table 1) and showed more variability than all pre-fire years (Fig. 2), likely indicating an increased watershed input of organic matter to the river after the wildfire. While the observed TOC increase is relatively small, only ~10% of the CLP watershed was burned and a greater response in TOC may be expected from a fire burning a larger drainage area. The post-fire DOC at the water intake was on average 95% of the TOC, similar to pre-fire conditions (Summers et al., 2013), indicating the contribution of particulate carbon to the TOC was minimal. Following precipitation events the particulate organic matter (POM) load to the river may be higher (Jeong et al., 2012; Wiegner et al., 2009), discussed in more detail in section 4.6.1. The DOM quantity of the CLP River was likely affected following the wildfire, although to a lesser extent than turbidity, TP, and TN. While small, an increase in TOC may impact coagulant dosing and DBP formation during treatment. Post-fire seasonal water quality trends, including biweekly and monthly concentrations, are presented in the supplementary material (Fig. S9).

4.3. DOM character and optical properties

Wildfire impacts on DOM were examined using optical indices (SUVA_{254} and FI), which can aid in understanding DOM properties (McKnight et al., 2001; Weishaar et al., 2003), treatability (Archer and Singer, 2006a; Edzwald, 1993; Liang and Singer, 2003; White et al., 1997), and DBP reactivity (Archer and Singer, 2006b; Beggs et al., 2009; Edzwald et al., 1985; Reckhow et al., 1990). After the fire, SUVA_{254} values at the water intake (mean = 3.3 ± 0.7 L mg^{-1} m^{-1}) were higher than pre-fire values (mean = 2.7 ± 0.5 L mg^{-1} m^{-1}; Table 2). Post-fire pairwise comparison of the water intake to the reference site indicated SUVA_{254} was not statistically different (Table 2), suggesting during baseflow and snowmelt conditions the aromaticity of the DOM was not significantly altered by the wildfire. The higher SUVA_{254} observed in 2013 may be attributed to temporal variability between years. Pre-fire SUVA_{254} and FI data were not available for the reference site, and therefore a pre-to post-fire spatial analysis was not possible. Elevated iron levels can interfere with both SUVA_{254} (Weishaar et al., 2003) and FI measurements (McKnight et al., 2001; Poulin et al., 2014), however interferences for baseflow and spring snowmelt samples are expected to be minimal, as estimated from available iron data (max = 0.27 mg_Fe L^{-1}; see supplementary material).

In general, pre- and post-fire FI values were all within a similar range (~1.4), implying primarily terrestrial derived DOM (McKnight et al., 2001). A higher FI value (e.g., 1.8) indicates a blue-shifted emission spectrum often associated with aquatic organic matter. A lower value (e.g., 1.2) indicates a more red-shifted emission spectrum with higher aromaticity, often associated with humic-rich material (McKnight et al., 2001). For both sites, FI values during snowmelt were similar (Fig. 3), suggesting the mobilization of terrestrial material by melting snow extending to all stream reaches (Miller et al., 2009). During baseflow the water intake exhibited higher FI values compared to snowmelt, and similarly FI for the reference site increased, but to a lesser extent. Watershed areas which contribute the majority of snowmelt to the CLP River are primarily located upstream of the wildfire-affected area, and snowmelt samples may not reflect wildfire impacts and likely dilute observed effects.

Temporal comparison showed post-fire mean and median FI values were higher than the pre-fire values (2008–2009) (Table 2), consistent with other work which observed increased FI from material leached from wildfire-impacted detritus (Wang et al., 2015a) and laboratory-burned detritus (Wang et al., 2015b). Spatial comparison indicated post-fire FI values were statistically higher at the water intake when compared to the reference site (median $\Delta = +0.038$; $p = 0.005$; Table 2). Elevated iron

Table 2
Pre- and post-fire DOM optical indices and DBP yields (μg mg_C^{-1}) for the water intake and reference site (post-fire only). Paired spatial differences (Δ) between the water intake and reference site are presented. Pre-fire data were only available for the water intake and a pre-to post-fire comparison of paired differences was not possible.

DOM parameter		Pre-fire (2008–2009)[a,b]		Post-fire (2013)				
		Water intake		Water intake	Reference	n	Δ[c] (intake − reference)	p value[d,e]
		Value	n	Value				
$SUVA_{254}$ (L mg^{-1} m^{-1})	Mean	2.7		3.3	3.3		0.005	
	Median	2.9	22	3.4	3.4	12	−0.018	1.0*
	SD	(0.5)		(0.7)	(0.8)		(0.21)	
FI	Mean	1.36		1.40	1.36		0.038	
	Median	1.36	21	1.42	1.37	12	0.038	0.005*
	SD	(0.05)		(0.03)	(0.02)		(0.029)	
TTHM yield (μg mg_C^{-1})	Mean	46.5		52.4	56.6		−4.3	
	Median	47.1	6	50.1	56.4	12	−5.7	0.388
	SD	(17.3)		(15.5)	(15.8)		(5.0)	
HAA5 yield (μg mg_C^{-1})	Mean	26.7		50.0	53.7		−3.7	
	Median	20.3	6	52.2	54.2	12	−1.1	0.388
	SD	(14.3)		(17.2)	(18.4)		(8.0)	
HAN4 yield (μg mg_C^{-1})	Mean			1.7	1.6		0.12	
	Median	NA		1.7	1.5	12	0.09	0.126*
	SD			(0.32)	(0.20)		(0.21)	
Chloropicrin yield (μg mg_C^{-1})	Mean			1.1	1.2		−0.09	
	Median	NA		1.1	1.1	12	−0.09	0.290*
	SD			(0.32)	(0.42)		(0.23)	

[a] Pre-fire data are from Summers et al. (2013) and Beggs (2010). Pre-fire TTHM and HAA5 data are from 2009 only; methods followed UFC chlorination conditions of raw water samples.
[b] Pre-fire HAN4 and chloropicrin data were not available.
[c] $\Delta_{Parameter} = Parameter_{Water\ intake} - Parameter_{Reference\ site}$.
[d] p values were determined by testing the spatial differences (Δ) against zero using the sign test. Parameters denoted with a * were tested using the Wilcoxon signed-rank test.
[e] Post-rainstorm event data were not included in the calculation of Δ and p values.

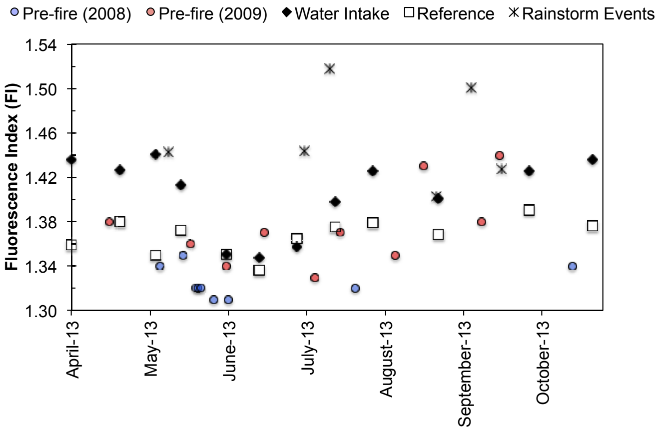

Fig. 3. Pre- and post-fire (2013) seasonal fluorescence index (FI) values at the water intake and reference site. Rainstorm event samples were collected at the water intake. Pre-fire data from 2008 and 2009 are for the water intake site only.

concentrations could possibly inflate the FI due to complexation with DOM (Poulin et al., 2014). However, the observed increase in FI cannot solely be attributed to iron interferences based on the maximum measured iron concentration (0.27 mg_{Fe} L^{-1}; see supplementary material). A decrease in the DOM molecular weight could be associated with an increase in the FI (Romera-Castillo et al., 2014). Low-molecular-weight structures of soil organic matter have been shown to form at low temperatures (200–300 °C) from amino acid pyrolysis (Sharma et al., 2003) and char materials (Norwood et al., 2013).

4.4. Disinfection byproduct formation

An analysis of DBP formation was conducted through bench scale chlorination (Summers et al., 1996) of raw water samples (GF/F filtered). TTHM formation was significantly higher at the water intake (median Δ = +10.1 μg L^{-1}; Table S8), likely associated with the higher TOC levels, as observed by others (Revchuk and Suffet, 2014). HAA5 formation at the intake was also higher than the reference site (median Δ = +3.8 μg L^{-1}), but was not statistically significant. Bromide was not detected in any of the water samples (detection limit = 0.003 mg L^{-1}), few brominated DBPs were formed, and bromine substitution factors (BSF) (Hua et al., 2006; Obolensky and Singer, 2005) were generally low. Post-fire BSF values were on average higher at the water intake compared to the reference site, but the differences were not significant (Table S8).

Carbon-normalized DBP formation yields (DBP concentration/DOC concentration) were used to represent the reactivity of DOM on a per unit carbon basis (μg mg_C^{-1}). Temporal analysis showed TTHM yields at the water intake were similar pre- and post-fire, whereas HAA5 yields were considerably higher in 2013 than 2009 (Table 2). At both sites post-fire TTHM and HAA5 yields followed similar seasonal trends (Fig. 4), peaking in mid-June and decreasing with the receding limb of snowmelt. The higher post-fire HAA5 reactivity was observed from July–September, whereas during spring snowmelt HAA5 yields were similar to pre-fire yields. Post-fire pairwise comparison indicated TTHM and HAA5 yields were not statistically different between the sites (Table 2), suggesting wildfire impacts on C-DBP reactivity per unit carbon were minimal for this watershed and wildfire, consistent with other work (Wang et al., 2015a). The higher HAA5 reactivity observed in 2013 at the water intake compared to 2009 may be attributed to temporal variability between years (i.e., hydrology, temperature, precipitation) resulting in a shift in the watershed HAA5 precursor material independent of the wildfire, such as increased primary productivity in the late summer, and would likely also be observed for the reference site. Pre-fire data were only available for the water intake, so a pairwise statistical analysis was not possible before the fire, limiting further conclusions.

Post-fire HAN4 formation at the water intake was significantly

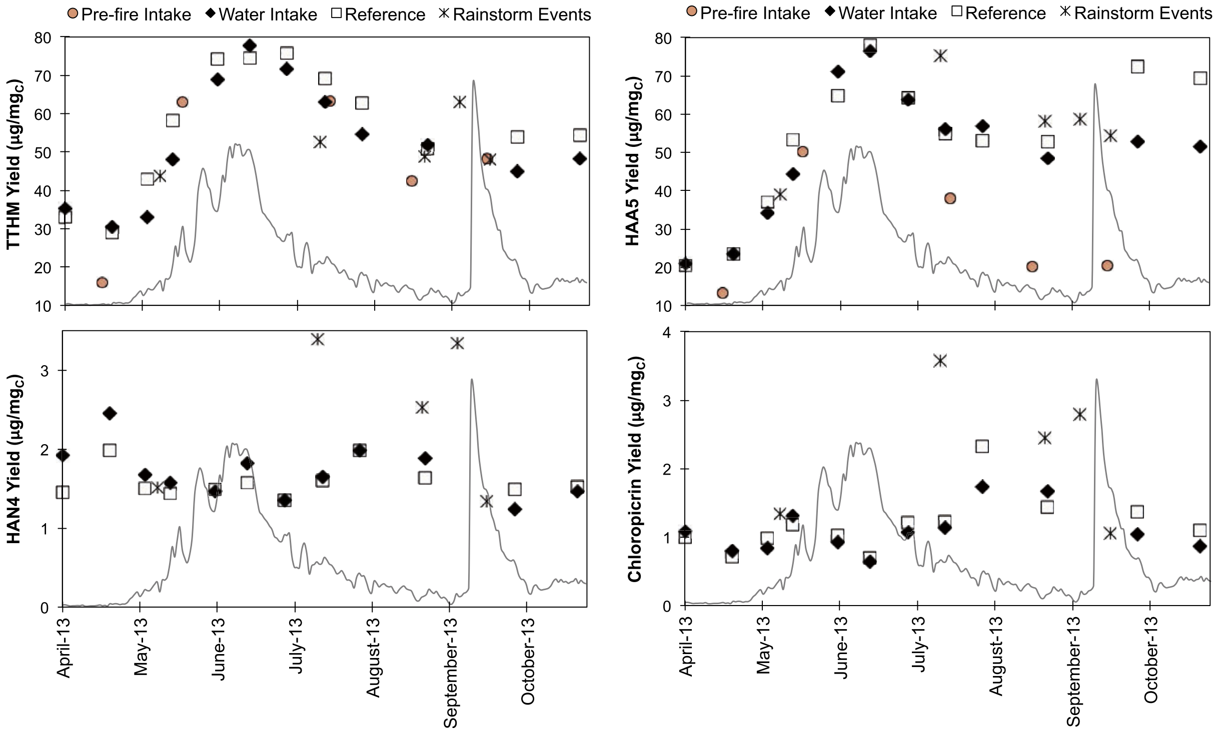

Fig. 4. Post-fire 2013 seasonal DBP yields for the water intake and reference site. Post-rainstorm samples (2013) were collected from the water intake only and are intended for comparison to baseflow and spring snowmelt water intake samples. Pre-fire TTHM and HAA5 yields are shown for the water intake site. The streamflow hydrograph is also plotted (gray line) and is available with scale in the supplementary material (Fig. S8). Post-rainstorm samples collected in 2012 are not shown (Writer et al., 2014).

higher than the reference site (median $\Delta = +0.91$ µg L^{-1}; $p = 0.003$; Table S8). Chloropicrin formation was also higher at the intake (median $\Delta = +0.07$ µg L^{-1}), but the difference was not statistically significant ($p > 0.05$). N-DBP formation yields (µg mg_C^{-1}) did not follow the same seasonal trend as TTHM and HAA5 yields (Fig. 4), showed less seasonal variability, and in some cases decreased when C-DBP yields increased, such as during snowmelt, possibly indicating N-DBP precursor mobilization is less driven by snowmelt compared to C-DBP precursors. Wang et al. (2016) observed different temporal trends for fire-affected C- and N-DBP precursors. The spatial differences for N-DBP formation yields were not statistically significant ($p > 0.05$) and pre-fire N-DBP data were not available.

4.5. Post-fire source water treatability

All samples were coagulated with alum, followed by flocculation, sedimentation, filtration, and chlorination to evaluate the efficacy of conventional drinking water treatment (Table 3). Post-wildfire, the water intake samples required significantly higher alum doses than the reference site (median $\Delta = +7.5$ mg L^{-1}; $p = 0.025$) to achieve optimal DOC removal (Table S9), consistent with other work (Emelko et al., 2011). The water intake samples had higher initial turbidity than the reference site, exerting considerable demand on the coagulant, and resulting in elevated finished water DOC concentrations (median $\Delta = +0.2$ mg_C L^{-1}; $p = 0.039$; Table S9). Despite the higher alum demand, a similar mean percent DOC removal was achieved for the water intake and reference site (60% and 61%, respectively; Table 4)

$SUVA_{254}$ values of treated samples were similar for the water intake and reference site (median $\Delta = +0.03$ L mg^{-1} m^{-1}). DOC removal per mg-alum was also comparable for the water intake and reference site (0.06 and 0.07 mg_C per mg-alum, respectively), suggesting the post-fire DOM was of similar character for removal with alum (Table 3). Post-fire influent water was amenable to C-DBP precursor removal by coagulation. Treated water DBP formation yields (Table 3) and the percent decreases in DBP formation (Table 4) were similar for the water intake and reference site. At both sites a decrease in HAN4 and chloropicrin formation was observed following coagulation, although to a lesser extent than C-DBPs, and treated water N-DBP formation was more variable (Table 4).

4.6. Post-rainstorm event samples

4.6.1. Water quality and optical properties

Samples were collected from the CLP River during or immediately after rainstorms in 2012 (6/27, 7/6, 7/19, 7/25) (Writer et al., 2014) and 2013 (5/9, 7/2, 7/12, 8/23, 9/6, 9/18). Rainstorms are known to create hydrologic conditions that can be quantitatively important to POM, DOM, and organic nitrogen levels in streams (Inamdar et al., 2011; Inamdar and Mitchell, 2007; Jeong et al., 2012; Murphy et al., 2015; Wiegner et al., 2009). These high flux events may represent turbidity and TOC levels a water treatment plant could encounter, which might not be captured during baseflow and spring snowmelt monitoring. Post-rainstorm samples collected in 2012 and 2013 were highly turbid, had a smoky odor, and displayed dark, charred particulate material. Samples were analyzed for dissolved constituents (TDP, TDN and DOC) rather than total concentrations due to the extreme levels of particulates. Two September 2013 samples were collected during and after the heavy rains leading up to a flood event in the area which drastically increased the streamflow to greater than 70 m^3 s^{-1} (Fig. S8). As observed in Mast et al. (2016), the water quality response of the September samples may be largely attributed to the flood, rather than the wildfire.

Table 3
Post-fire treated water values for alum coagulated samples at the water intake and reference site. Raw water DOC concentrations and applied alum doses are also shown.

Sample type	Site		Alum dose[b] (mg/L)	Raw water DOC (mg_C L^{-1})	Treated water samples						
					DOC[b] (mg_C L^{-1})	DOC Removed/Alum dose (mg_C/mg-alum)	$SUVA_{254}$ (L mg^{-1} m^{-1})	TTHM yield (μg mg_C^{-1})	HAA5 yield (μg mg_C^{-1})	HAN4 yield (μg mg_C^{-1})	Chloropicrin yield (μg mg_C^{-1})
Baseflow and spring snowmelt	Reference	Mean	34	3.7	1.4	0.07	1.9	32.4	16.0	1.4	1.3
		Median	28	3.0	1.3	0.08	1.9	33.4	15.9	1.4	1.4
		SD	(15)	(1.8)	(0.5)	(0.03)	(0.1)	(11.1)	(2.5)	(0.7)	(0.5)
	Water intake	Mean	44	4.1	1.6	0.06	2.0	32.0	15.7	1.5	1.1
		Median	45	3.3	1.4	0.06	2.0	32.7	16.0	1.3	1.2
		SD	(15)	(1.8)	(0.7)	(0.03)	(0.3)	(7.1)	(3.0)	(0.8)	(0.7)
Rainstorm events[a]	Water intake	Mean	58	11.8	8.2	0.07	3.0	40.2	20.0	1.7	1.7
		Median	63	12.6	3.6	0.05	3.1	35.1	18.5	1.6	1.7
		SD	(19)	(5.6)	(7.8)	(0.11)	(1.1)	(17.4)	(8.5)	(1.0)	(0.5)

[a] Post-rainstorm event samples were collected at the water intake only.
[b] Alum dose and treated water DOC were statistically different for the water intake and reference samples using pairwise analysis ($p < 0.05$; Table S9).

All post-rainstorm samples showed elevated turbidity levels and several exhibited extreme turbidities in 2012 (>4200 ntu) and 2013 (>800 ntu; Fig. S9). In 2013 TDP concentrations (mean = 0.377 ± 0.407 mg_P L^{-1}) and TDN levels (mean = 1.61 ± 0.90 mg_N L^{-1}) following rainstorms were elevated compared to baseflow and snowmelt water intake samples. Post-rainstorm CLP River DOC concentrations were as high as 13.7 mg_C L^{-1} in 2012 and 18.2 mg_C L^{-1} in 2013 (2013 mean = 11.8 ± 5.6 mg_C L^{-1}), greater than any baseflow or spring snowmelt water intake concentrations. The high DOC concentrations are likely due to the increased mobilization of soil organic matter following the wildfire, which was greatly enhanced during the flood event in September 2013 (Fig. S9). In 2012 all post-rainstorm samples had $SUVA_{254}$ values > 3.0 L mg^{-1} m^{-1}. In 2013 post-rainstorm $SUVA_{254}$ values (data not shown) were higher than 2012, and were elevated (2013 mean = 4.5 ± 0.9 L mg^{-1} m^{-1}) compared to baseflow and snowmelt samples, which may be partially explained by iron concentrations (see supplementary material). Alternatively, increased aromatic material from wildfire-induced changes to soil organic matter structure (Almendros et al., 2003) may be mobilized to the river upon rainfall. Post-rainstorm samples revealed the highest FI values (mean = 1.46 ± 0.04; Fig. 3), potentially suggesting a lower molecular weight DOM leached from partially charred material (Wang et al., 2015b; Sharma et al., 2003) as discussed in section 4.3. Samples collected in 2012 were not analyzed for fluorescence.

4.6.2. DBP formation and treatability

In 2012 TTHM and HAA5 formation following several rainstorms was higher than during baseflow conditions. Similarly, in 2013 post-rainstorm samples formed the highest concentrations of TTHMs and HAA5s, while C-DBP yields were comparable to baseflow and snowmelt intake samples (Fig. 4). The high $SUVA_{254}$ values suggest the C-DBP yields should be higher for the post-rainstorm samples, but iron levels may explain this disconnect. Post-rainstorm samples also displayed the overall highest HAN4 (2012 max = 32.1 μg L^{-1}; 2013 max = 53.5 μg L^{-1}) and chloropicrin formation (2013 max = 61.0 μg L^{-1}). Further, HAN4 yields (2012 max = 2.7 μg mg_C^{-1}; 2013 max = 3.4 μg mg_C^{-1}) and chloropicrin yields (2013 max = 3.6 μg mg_C^{-1}) were higher than during baseflow and snowmelt, demonstrating potentially increased mobilization of reactive nitrogenous precursors. In 2013, the post-rainstorm mean HAN4:TTHM ratio was 0.046 ± 0.13 compared to 0.037 ± 0.18 during baseflow and snowmelt at the intake. The chloropicrin:TTHM ratio (mean = 0.042 ± 0.016) was also higher than baseflow and snowmelt samples (mean = 0.022 ± 0.008), suggesting potential enrichment of N-DBP precursor material relative to C-DBP precursors following rainstorms in the wildfire-affected area. However, this may not be solely attributed to wildfire effects due to the lack of post-rainstorm reference site samples. Enhanced mobilization of DBP precursors following rain events has also been observed in unburned catchments (Jung et al., 2014; Nguyen et al., 2013).

CLP River samples collected following rainstorm events in the burned area were less responsive to coagulation, and required additional alum (2013 mean dose = 58 ± 19 mg L^{-1}) compared to the baseflow and snowmelt water intake samples (mean dose = 44 ± 15 mg L^{-1}; Table 3). Notably, several samples did not coagulate effectively, and even at high alum doses (>65 mg L^{-1}) minimal DOC removal was achieved (<10%). Similarly, a sample collected in July 2012 had extreme turbidity (>4200 ntu) and only 17% DOC removal was achieved (Writer et al., 2014). The mean DOC removed per mg-alum in 2012 and 2013 were 0.05 and 0.07 mg_C per mg-alum, respectively. Although DOC removal values were comparable to baseflow and snowmelt intake samples, considerable variability in the DOC response to alum was observed following rainstorms due to several poorly coagulated samples.

Table 4
Percent decrease in DOC and DBP concentrations following alum coagulation (post-fire samples only).

Sample type	Site		Percent decrease following coagulation treatment (%)				
			DOC	TTHM	HAA5	HAN4	Chloropicrin
Baseflow and spring snowmelt	Reference	Mean	61	76	86	59	57
		Median	60	80	89	59	56
		SD	(5.6)	(11)	(8.2)	(22)	(20)
	Water intake	Mean	60	75	86	59	61
		Median	61	74	88	61	61
		SD	(5.1)	(7.2)	(7.4)	(25)	(28)
Rainstorm events[a]	Water intake	Mean	34	47	76	52	50
		Median	36	66	81	67	59
		SD	(41)	(39)	(15)	(40)	(19)

[a] Post-rainstorm event samples were collected at the water intake only.

Following a July 2012 rainstorm $SUVA_{254}$ remained >4.0 L mg^{-1} m^{-1} after treatment, and the post-rainstorm treated water $SUVA_{254}$ values were also high in 2013 (mean = 3.0 ± 1.1 L mg^{-1} m^{-1}). Treated water DBP yields were higher and showed more variability for all DBP groups (Table 3) compared to the treated baseflow and snowmelt water intake samples. The percent decrease in C-DBP formation by coagulation was lower for the post-rainstorm samples, expected due to lower DOC removal (Table 4). Specifically, mean TTHM precursor removal was only 46% with high variability, likely associated with the poorly coagulated samples. Finished water HAN4 and chloropicrin concentrations following rainstorm events remained high on average with substantial variability (mean HAN4 = 17.4 ± 24.8 μg L^{-1} and chloropicrin = 14.0 ± 15.7 μg L^{-1}).

4.7. Discussion of post-wildfire impacts on water treatment processes and finished water quality

Although the post-fire increase in DOC at the water intake was minimal during baseflow and spring snowmelt, utilities should be aware of potential challenges meeting DBP maximum contaminant levels (MCLs), particularly during high DOC events following rainstorms. In 2012, two treated water post-rainstorm samples exceeded DBP MCLs and in 2013 five post-rainstorm samples exceeded DBP regulations. Post-fire N-DBP formation may also be a concern to water providers. HAN4 formation during baseflow and snowmelt at the water intake was elevated compared to the reference site. Further, the highest N-DBP concentrations and yields were observed following rainstorms. A lab-based study evaluating water extractable material of burned detritus from the Rim Fire revealed elevated HAN4 reactivity compared to unburned detritus (Wang et al., 2015a), which supports the increased N-DBP yields observed in the CLP River.

Following rainstorms in the wildfire-affected area samples were enriched in DON (2013 mean DOC:DON ratio = 21.9 ± 10.2 mg_C/mg_N) compared to baseflow and spring snowmelt intake samples (mean DOC:DON = 30.3 ± 15.1 mg_C/mg_N), which likely increased post-rainstorm N-DBP formation and reactivity. In unburned catchments rainstorms have been shown to transport DON to surface waters (Inamdar and Mitchell, 2007). Wildfire can enrich the organic nitrogen content of soil from partially charred sediments and vegetation (Fernández et al., 1997; Knicker, 2010; Knicker et al., 2005), which are more readily eroded and transported to surface waters following wildfire and rainfall. Black nitrogen has been shown to form during charring and contains altered components such as heteroaromatic N (Knicker, 2010; Knicker et al., 2005), which could potentially form N-DBPs during chlorination. The effects of wildfire changes to terrestrial sources of N-DBP precursors cannot be separated from the effects of rainstorms due to the lack of post-rainstorm samples from the reference site, however the findings are supported by other work (Wang et al., 2015a,b).

Overall, post-fire source water was amenable to conventional treatment during baseflow and snowmelt river conditions. Utilities will likely need to apply a higher coagulant dose than used prior to a wildfire to meet the desired DOC removal for their system, as a consequence of higher turbidity and DOC. Following several rainstorms in 2012 and 2013 extensive treatment challenges were encountered. High initial turbidities (276–4200 ntu) and DOC concentrations (13.7–18.2 mg_C L^{-1}) were observed for these samples, and the coagulant demand exerted by the particles and DOM combined could not be met. Ash and burned sediment may be difficult to remove and settle due to its fine particle size, low settling velocity, and higher organic content (Stone et al., 2011), and solids removal may cause extensive post-fire challenges for water utilities. Further, the observed post-fire increase in FI also suggests a lower molecular weight DOM structure, which is generally less amenable to removal by conventional coagulation processes (Archer and Singer, 2006b, 2006a; Liang and Singer, 2003; White et al., 1997) and may be enriched in N-DBP precursors (Bond et al., 2012). A post-fire increase in N-DBP precursor material may result in high concentrations in the distribution system due to poor removal of N-DBP precursors during conventional treatment attributed to lower molecular weight and low or absent anionic charge (Bond et al., 2012, 2009).

5. Conclusions

Wildfire effects on influent water quality for the treatment plant were demonstrated by statistically significant spatial differences between the water intake and reference site for turbidity, TP, TN, and TOC. Paired spatial differences were not detected or not as pronounced in the years prior to the fire, suggesting an increased contribution of sediments to the river. Results imply the DOM character of the river was altered following the wildfire, demonstrated by higher FI values, suggesting lower molecular weight DOM. Post-rainstorm HAN4 and chloropicrin yields at the water intake imply a potential link between wildfire, rainfall, and N-DBP precursor material. Further work is needed to separate wildfire impacts from precipitation effects due to the limitations of the study. In general post-fire source water remained treatable by conventional processes, although water utilities will likely need to apply a higher coagulant dose, which will raise operation costs. Several post-rainstorm samples did not respond to conventional treatment, and showed minimal DOC removal and high finished water DBP formation, exceeding DBP MCLs. Fortunately, the City of Fort Collins was able to rely solely on their alternate water supply during precipitation events, however many single source water utilities without this option may face greater challenges following wildfire.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.08.034.

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