

Impact of the High Park wildfire on water quality

Prepared by:

Amanda K. Hohner, Kaelin M. Cawley and Fernando L. Rosario-Ortiz

Department of Civil, Environmental and Architectural Engineering
University of Colorado, Boulder

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Executive Summary

Background

The Cache la Poudre (CLP) watershed was impacted by the High Park wildfire that burned approximately 87,284 acres from June 9 to July 1, 2012. The CLP River and its heavily forested watershed serve as the source water for three major water districts in northern Colorado, including the City of Fort Collins, serving more than 350,000 customers. The immediate and future impacts of this fire on the water quality of this watershed were a concern for the local water districts.

The main objective of this study was to evaluate the impact that the High Park wildfire had on the water quality in the CLP watershed, specifically evaluating the potential changes in DBP formation (following uniform formation conditions), treatability (using alum coagulation) and using fluorescence spectroscopy (e.g. fluorescence index) as an indicator of DOM character and reactivity.

Methods

The team collected samples from three sites within the watershed: PBR, which represented a control site located outside of the burned area, and PNF and PSF, which were categorized as fire-impacted. Samples were collected bi-weekly during spring snowmelt and summer (April through August, 2013), monthly for the fall of 2013 and during select storm events (PNF only). Samples were analyzed for general water quality parameters and DOM character, including fluorescence and size exclusion chromatography. Samples were chlorinated at the bench-scale following uniform formation conditions and analyzed for TTHMs, HAA5s, and HANs. Additionally, samples from PNF and PBR were coagulated with alum and analyzed for DOC and DBP precursor removal. Optical properties, such as UV-visible absorbance and fluorescence spectroscopy, were also used to determine significant relationships that may be useful as surrogates for quantity and reactivity of organic matter.

Results

The overall results showed minimal differences in DOC concentrations and SUVA values between the control (PBR) and impacted sites (PNF, PSF), suggesting that the system was dominated by baseline DOC and the impact of the fire was not significant in terms of altering the DOC. Although DOC levels and SUVA values for storm event samples were considerably greater than baseline or spring snowmelt levels, it is unclear what impact the wildfire had on the storm event samples, as these concentrations are highly dependent on the mobilization of organic material from hydrologic changes. Another measure of DOM composition, obtained from fluorescence, is the FI, which varied a small bit between burned and unburned sites. However, the variability due to seasonal changes was greater than the variability among fire impacted samples and samples from the control site. Another metric evaluated was the molecular size distribution for the samples, which showed little difference between samples from a given sampling date, but showed clear seasonal trends with the average molecular weight increasing at the onset of spring snowmelt (indicated by a shift to shorter retention times) and then decreasing as the spring progressed).

Total dissolved nitrogen (TDN) values and nitrate + nitrite concentrations overall were fairly similar between sites, but the early season samples showed some variation, compared to

DOC, indicating that the impacts of the fire were more notable in nutrients. This suggests there was mobilization of nutrients at the onset of the spring runoff, and these affects were felt more strongly from the wildfire. Nutrient mobilization was further supported by the notable differences in TDP concentrations that were observed between impacted and control sites. Overall DBP formation for all three DBP groups (TTHM, HAA5, HAN) showed little differences between wildfire impacted and control sites. Given the limited differences in DOC concentrations discussed previously, these results are not surprising. As to be expected, DBP formation for all groups was highest during spring snowmelt when the greatest amount of DOM and DBP precursor material is being flushed into the Poudre River.

Differences in DBP species between fire-impacted and control sites were not evident. For TTHMs, chloroform was by far the dominant species for all three sites (average = 95%). Bromide was always below detection limit for all samples and brominated DBP formation was very limited. HAA formation was mostly dichloroacetic acid (DCAA) (average = 41%) and trichloroacetic acid (TCAA) (average = 57%) for all samples. Lastly, HAN formation was dominated by dichloroacetonitile (DCAN) (89%).

In addition to DBP concentrations, DBP yields were used to evaluate the reactivity of the DOM. DBP yields represent the concentration normalized to the DOC for a water sample ($\mu\text{g DBP}/\text{mg}_C$). Again, notable differences between impacted and control sites were not observed. Even though storm event samples showed extreme TTHM and HAA5 concentrations, when normalized to carbon the yields for these samples were in the same range as spring snowmelt and baseline sample yields. Alternatively, HAN yields for about half of the storm event samples were the highest compared to spring snowmelt and base-flow conditions.

In general PNF water samples were effectively treated, jar test effluent DOC concentrations were consistently below $3\text{ mg}_C/\text{L}$ even during spring snowmelt. All PBR samples except for two spring snowmelt samples were treated to DOC effluent concentrations below $2.0\text{ mg}_C/\text{L}$. PNF on average required a higher alum dose ($43.8\text{ mg}/\text{L}$) for DOC removal than PBR ($34.2\text{ mg}/\text{L}$), suggesting that the fire impacted site was more difficult to treat. Generally post-coagulation SUVA values were around $2\text{ L}/\text{mg}\cdot\text{m}$. These results support the overall findings from this study that the fire impacted water were relatively susceptible to alum coagulation for both DOC and SUVA removal. In addition, several of the storm samples were effectively treated with effluent DOC concentrations below $3.0\text{ mg}_C/\text{L}$. However, two of the storm event samples were very difficult to treat, most likely due to an extremely high level of particulates in both samples which could not be overcome even at high alum doses.

For all coagulated PNF and PBR samples (excluding storm events) TTHM formation was below the regulated MCL ($80\text{ }\mu\text{g}/\text{L}$) with the exception of one sampling date, and all samples were treated below the HAA5 MCL ($60\text{ }\mu\text{g}/\text{L}$). HAN precursors were not as well removed as the C-DBP precursors, as to be expected. DBP removal was also more challenging for several of the storm samples. Five of the samples were still above the MCL for TTHMs following coagulation. Four of the six storm samples exceeded the HAA5 MCL, the two exceptions being early season and late season storm events. HAN precursor removal for the storm samples was comparable to the PNF non-storm event samples.

Optical properties are likely to be a useful surrogate for organic matter quantity and reactivity. Absorbance of water samples at 254 nm was significantly correlated to DOC

concentration ($r^2 = 0.9352$, $p < 0.0001$) and may be the best proxy for DOC concentration in the CLP watershed. A 6 component PARAFAC model was validated for the samples analyzed in this study. The relative abundance of the PARAFAC components and fluorescence metrics were correlated to TTHM, HAA5, and HAN yields. SUVA was well correlated to both TTHM ($r^2 = 0.7346$, $p < 0.0001$) and HAA5 ($r^2 = 0.7458$, $p < 0.0001$) yields, but not HAN yield ($r^2 = -0.5171$, $p = 0.0139$). Thus, the aromaticity of DOM may influence its reactivity towards DBP formation. C1 had the strongest correlation among the PARAFAC components to both TTHM ($r^2 = 0.8416$, $p < 0.0001$) and HAA5 ($r^2 = 0.7844$, $p < 0.0001$) yields. No significant correlations were found between the protein-like PARAFAC components and TTHM, HAA5, or HAN yields. Unlike the other classes of DBPs, HAN yields were well correlated only to C3, the blue-shifted humic-like PARAFAC component ($r^2 = 0.7194$, $p = 0.0001$). Based on these correlations, different DOM characteristics drive the formation of TTHMs and HAA5s compared to HANs.

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Acronyms

BCAN: Bromo-chloroacetonitrile

CLP: Cache la Poudre

CU-Boulder: University of Colorado, Boulder

DBAN: Di-bromoacetonitrile

DBP: Disinfection byproducts

DCAA: dichloroacetic acid

DCAN: Di-chloroacetonitrile

DOC: Dissolved organic carbon

DOM: Dissolved organic matter

DPD: N,N-diethyl-pphenylenediamine

EEM: Excitation emission matrix

FI: Fluorescence index

GC-MS/MS: Gas-chromatography tandem mass spectrometry

HAA: Haloacetic acids

HAA5: Five regulated HAAs

HAN: Haloacetonitriles

IC: Ion chromatography

MCL: Maximum contaminant level

PARAFAC: Parallel factor analysis

PBR: Poudre below Rustic

PNF: Poudre below North Fork

PSF: Poudre below South Fork

SEC: Size exclusion chromatography

SUVA: Specific UV absorbance at 254 nm

TCAA: Trichloroacetic acid

TCAN: Tri-chloroacetonitrile

TDN: Total dissolved nitrogen

THM: Trihalomethanes

TOC: Total organic carbon

TP: Total phosphorous

TTHM: Total THMs

UFC: Uniform formation conditions

UV₂₅₄: UV-Visible absorbance at 254 nm

Introduction

The Cache la Poudre (CLP) watershed was impacted by the High Park wildfire that burned approximately 87,284 acres from June 9 to July 1, 2012. The CLP River and its heavily forested watershed serve as the source water for three major water districts in northern Colorado, including the City of Fort Collins, serving more than 350,000 customers. The immediate and future impacts of this fire on the water quality of this watershed were a concern for the local water districts.

One of the concerns with regards to the impact of the High Park Fire on water quality is with regards to the formation of disinfection byproducts (DBPs), including both carbon based (i.e., THM and HAA) as well as nitrogenous DBPs (i.e. haloacetonitriles and nitrosamines). In addition, understanding how effective coagulation is for treating fire impacted water and removing DOM and DBP precursors also presents another significant concern to drinking water utilities

The main objective of this study was to evaluate the impact that the High Park wildfire had on the water quality in the CLP watershed, specifically evaluating the potential changes in DBP formation (following uniform formation test), treatability (using alum coagulation) and using fluorescence spectroscopy (e.g. fluorescence index) as an indicator of DOM character and reactivity.

Materials and Methods

Sample Collection and Transport

Samples were collected from the CLP River and transported to the lab at the University of Colorado, Boulder (CU-Boulder). Samples were collected bi-weekly from April 1st- July 29th, 2013 and monthly until the end of October. Three sampling sites were selected based on discussions with the City of Fort Collins drinking water staff. Two of these sites were within the High Park Fire burn area and denoted as impacted (Figure 1). Poudre below North Fork (PNF) represents the City of Fort Collins drinking water intake on the Poudre River. Poudre below South Fork (PSF) is also located in the burn area and is located just downstream of the confluence of the main stem and the South Fork. Lastly, Poudre below Rustic (PBR) was selected as the control site due to its location upstream and outside of the burn area.

In addition to the routine monitoring samples previously discussed, storm event samples were collected from PNF when the City of Fort Collins deemed appropriate based on spikes of in-stream turbidity data. An auto-sampler was installed at their drinking water intake and was used for storm event sampling. Unfortunately, control samples were not collected during storm events due to the localized nature of intense rain events in the region, as well as the risk associated with collecting samples during extreme weather events. Lastly, at CU-Boulder, samples were filtered through 0.7 μm GF/F filters and stored at 4 °C. The methods used for analysis are described below.

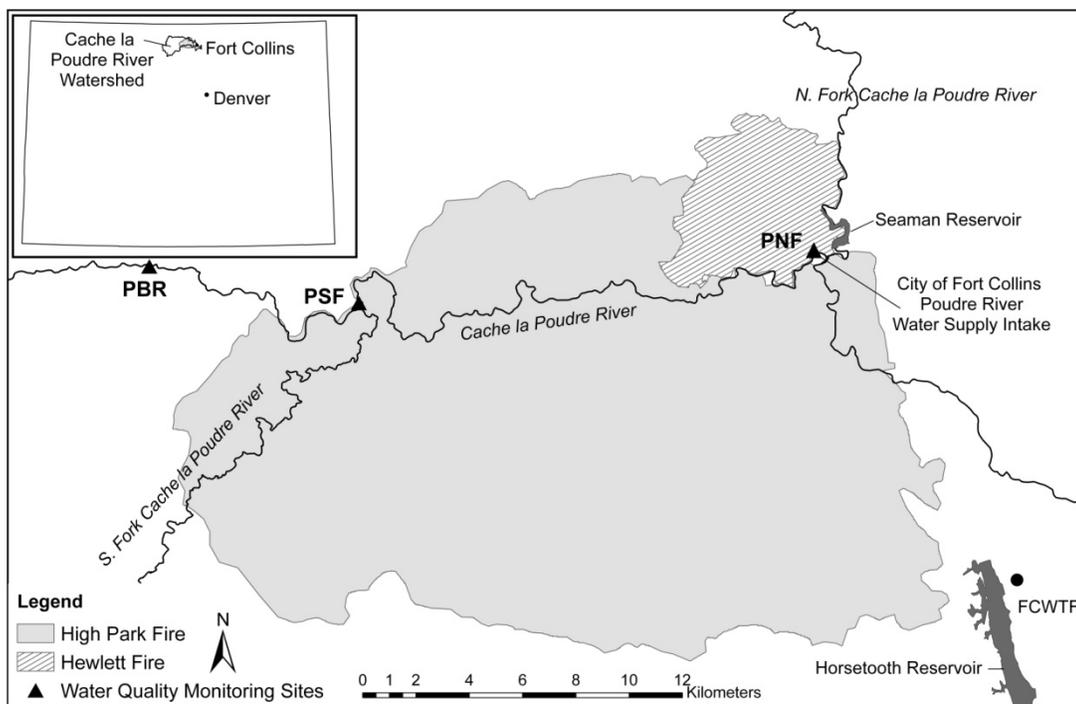


Figure 1. The sampling sites within the burned area include the City of Fort Collins drinking water intake (PNF) and just above the confluence of the South Fork and the Poudre main stem (PSF). The control site was located upstream and outside of the burn area (PBR).

Water Quality

TOC, DOC, and total dissolved nitrogen (TDN) measurements were performed 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). Ammonium was measured using a BioTek Synergy 2 Microplate Reader. Total phosphorous (TP) was measured with a Lachat QuikChem 8500 spectrophotometric flow injection. Bromide was analyzed using a Metrohm 761 Compact IC. UV₂₅₄ was measured using a UV-Vis spectrophotometer (Cary 100, Agilent Technologies) with a 1-cm path length quartz cuvette. Specific ultraviolet absorption (SUVA) was determined by dividing UV₂₅₄ absorbance by the DOC concentration (Weishaar et al. 2003).

Chlorination methods followed uniform formation conditions (UFC) (Summers et al. 1996). Samples were chlorinated at room temperature with a pH 8, buffered hypochlorite solution. Water samples were also buffered with a pH 8 borate buffer and incubated in the dark for 24 hours (± 1 hour) at room temperature ($20 \pm 1.0^\circ\text{C}$). Doses were determined in order to obtain a chlorine residual of 1.0 mg/L (± 0.4 mg/L). Chlorine residuals were measured with the DPD (N,N-diethyl-p-phenylenediamine) colorimetric method (SM4500-Cl G) and quenched with ammonium chloride.

DBP analysis was completed within two weeks of chlorination. EPA Method 551.1 (1995) was used for the analysis of trihalomethanes (TTHM) and haloacetonitriles (HAN).

Species included in HAN analysis are: 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.

Chloramination and Nitrosamines (subset of samples)

Two samples (PNF 5/14 and PBR 5/14) were chloraminated and analyzed for nitrosamines using automated solid phase extraction and GC-MS/MS. A preformed chloramine solution was generated by mixing ammonium hydroxide with sodium hypochlorite using a chlorine:ammonia ratio of ~ 3:1 by weight (2.81:1). Samples were dosed at 45 mgCl₂/mgC, buffered with a 10 mM phosphate buffer (pH = 6.79) and incubated for 10 days at room temperature in 1 L amber bottles. Total chlorine residuals after 10 days were measured following the DPD colorimetric method (SM 4500-Cl-G).

Nitrosamines (nitrosodimethylamine, nitrosodibutylamine, nitrosodiethylamine, nitrosodiphenylamine, nitrosodipropylamine, nitrosomethylethylam, nitrosomorpholine, nitrosopiperidine, nitrosopyrrolidine) were analyzed at the Southern Nevada Water Authority using previously described methods (Holady et al. 2012). Briefly, isotopically labeled internal standards were applied to water samples and analytes were concentrated by automated solid-phase extraction (SPE, AutoTrace workstation, Dionex, Sunnyvale, CA). Analytes were eluted from the SPE cartridges with dichloromethane and concentrated to a final volume of 500 µL. Extracts were analyzed by gas-chromatography tandem mass spectrometry (GC-MS/MS).

Alum Coagulation

Jar tests were performed using a 6-jar programmable jar tester (Phipps & Bird model 7790-901) with 2 liter B-KER² jars. Alum (Aluminum Sulfate, Mallinckrodt Chemicals, 3208-04) was used as a coagulant. Mixing conditions included a rapid mix phase (1 minute, 290 rpm), two flocculation phases (10 minutes at 55rpm and 10 minutes at 20 rpm) and a 30-minute sedimentation period. Dose response curves (alum dose vs. DOC concentration) were developed based on doses ranging from 20-120 mg/L. From this the optimum alum dose for DOC removal was selected and a final jar test was conducted. The supernatants from jar tests were filtered through Whatman GF/F filters to isolate the dissolved fraction for DOC, UV₂₅₄, chlorination, and DBP analyses (TTHM, HAA5, HAN).

Size Exclusion Chromatography (SEC)

Size distribution of the molecules in solution was determined using a high pressure liquid chromatograph equipped with a protein-pak column (waters), UV detector (280 nm), and polystyrene sulfonate standards (210, 1000, 4300, 6800, and 17000 Da). A phosphate buffer solution (pH = 6.8) was used as the mobile phase at a flow rate of 0.7 mL/minute. Larger molecular weight compounds travel through the column more quickly than smaller molecular weight compounds due to their exclusion from small pores within the column. Therefore, retention time is negatively related to the log of the molecular weight of molecules in solution.

Fluorescence

Fluorescence excitation emission matrix (EEM) were recorded using a John Yvon Horiba FluoroMax-4 spectrofluorometer over excitation wavelengths of 240 nm to 450 nm in 10 nm increments, and fluorescence intensity was measured at emission wavelengths from 300nm to 600 nm in 2 nm increments. Slit widths of 5 nm and integration times of 0.25s were used for both excitation and emission wavelengths. The signal was collected in S_v/R_c mode to incorporate instrument-specific correction factors. EEMs were corrected for primary and secondary inner filter effects using the corresponding UV-Vis absorbance spectrum EEMs were blank subtracted and Raman normalized based on the Raman peak area for 18.2 MΩ MilliQ water collected at an excitation wavelength of 350 nm. Corrected EEMs are presented in Raman Units (RU). Lamp scans and cuvette contamination checks were performed daily. EEMs were corrected and analyzed using MATLAB.

Figure 1 and Table 1 show a generic EEM for a DOM sample showing the different observable peaks in an EEM and their corresponding classification based on components of the DOM. The fluorescence index (FI) is also shown. This is defined as the ratio of the emission at 470 nm to that at 520 nm with an excitation at 370 nm. The expected range for the FI lies between 1.2-1.9. Low values are associated with DOM from terrestrial origin, high values are associated with DOM from microbial sources. The FI can also be used to follow the impact of different processes, including coagulation and releases of algae derived organic matter. For example, during a coagulation process, it is expected that the FI should increase as the process will preferentially remove more aromatic material.

A parallel factor analysis (PARAFAC) model was built using 101 EEMs from dissolved and extracted particulate material collected in the CLP watershed and the N-way Matlab toolbox (Stedmon and Bro 2008). Model components were split-half validated (Figure 1). Model fit was considered suitable if the signal in the residual EEM (modeled EEM subtracted from measured EEM) was less than 10 % of the measured EEM. Statistical analyses, including pairwise comparisons were performed in JMP Pro 11.0 software.

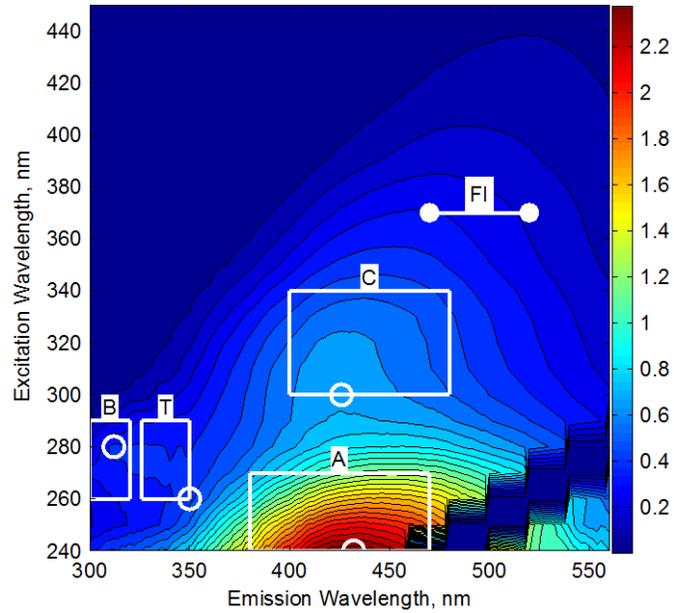


Figure 1. Fluorescence EEM for a generic DOM sample. Intensity is presented in Raman units (RU). Boxes outline the four peak regions (A, B, C and T) with labels above. Hollow circles indicate the location of the peak intensity in each region.

Table 1. Defined peak regions based on the values in literature.

Peak	Range	Type
A	Ex: 240-270 nm Em: 380-470 nm	Humic-like
B	Ex: 260-290 nm Em: 300-320 nm	Tyrosine-like
C	Ex: 300-340 nm Em: 400-480 nm	Humic-like
T	Ex: 260-290 nm Em: 326-350 nm	Tryptophan-like

Results and Discussion

Cache la Poudre Watershed geology and geography

The Cache la Poudre River is located west of the City of Fort Collins and the watershed extends into southern Wyoming. The Poudre River drains 4895 km². The dominant vegetation in the CLP watershed is a combination of ponderosa, lodgepole, mixed conifer, shrubs and grasses. This is a common sub-alpine, Front Range Colorado vegetation community. The average annual temperature is between 48°F and 51°F. Winds tend to be stronger during the day

than at night and average about 9 to 10 miles per hour annually. The geology of the watershed is heterogeneous and comprised of 26 identified formations. The hydrology of the river is snowmelt dominated with summer monsoonal thunderstorms also increasing the transport of terrestrial material into the stream.

Water Quality Data

Table 2 and Figures 2-7 present the water quality data obtained during the project. On average the DOC was 96% of the TOC. In many cases, the differences between DOC and TOC were not statistically significant based on instrument variability (Shimadzu TOC-V analyzer). The DOC values for the samples collected are shown in Figure 2, plotted temporally. The baseline DOC was around 2 mg_C/L, and increased to approximately 8 mg_C/L during the peak of the spring runoff and snowmelt, which occurred in mid May of 2013. There was little difference observed in DOC concentrations between the control (PBR) and impacted sites (PNF, PSF). This result suggests that the system was dominated by baseline DOC and the impact of the fire was not significant in terms of altering the DOC. Storm samples were collected periodically from PNF throughout the summer when the City of Fort Collins observed intense rainfalls. DOC values for storm samples are also shown in Figure 2 and were typically significantly greater than baseline or spring snowmelt values. A storm event sample collected on September 6th, shortly before the September floods, had a DOC concentration of 18.2 mg_C/L. However, it is unclear what impact the wildfire had on the elevated DOC concentrations for storm events as these concentrations are highly dependent on the mobilization of organic material from significant hydrologic changes. Unfortunately the research team was unable to collect storm event samples from the control site due to safety concerns (the PNF site has an auto-sampler installed). Also, storm events in the region are often localized and may not be occurring at both locations at the same time.

Table 2 Water quality results for all samples collected April-October, 2013. PNF= Fort Collins drinking water intake; PSF= Poudre below South Fork; PBR= Poudre below Rustic (control site).

Date	Site	TOC	DOC	TDP	TDN	NO3+NO2	NH4	DON	Bromide	TSS	UV254	SUVA ₂₅₄	FI
		mg-C/L	mg-C/L	mg-P/L	mg-N/L	mg-N/L	mg-N/L	mg-N/L	mg/L	mg/L	cm ⁻¹	L/mg-m	-
4/1/2013	PNF	2.5	2.4	0.013	0.19	0.074	0.023	0.092	<0.0031	-	0.067	2.8	1.44
	PSF	2.5	2.4	0.009	0.13	0.043	<0.007	0.100	<0.0031	-	0.064	2.7	1.40
	PBR	2.6	2.5	0.001	0.09	0.003	<0.007	0.081	<0.0031	-	0.065	2.6	1.36
4/20/2013	PNF	1.9	1.8	0.008	0.31	0.239	0.010	0.086	<0.0031	12.4	0.045	2.5	1.43
	PSF	1.7	1.5	0.005	0.18	0.128	0.009	0.053	<0.0031	12.7	0.039	2.7	1.41
	PBR	1.6	1.4	<0.0011	0.08	0.005	<0.007	0.049	<0.0031	2.2	0.031	2.2	1.38
5/4/2013	PNF	6.8	5.9	0.033	2.09	1.841	0.016	0.286	<0.0031	238.5	0.185	3.1	1.44
	PSF	5.3	5.2	0.008	0.86	0.655	<0.007	0.204	<0.0031	30.6	0.154	3.0	1.40
	PBR	4.6	4.0	0.004	0.14	<0.001	<0.007	0.110	<0.0031	1.7	0.125	3.1	1.35
5/14/2013	PNF	7.1	7.4	0.032	0.71	0.425	0.017	0.272	<0.0031	482.5	0.258	3.5	1.41
	PSF	6.4	7.0	0.013	0.27	0.062	<0.007	0.206	<0.0031	179.4	0.253	3.6	1.38
	PBR	7.9	7.6	0.011	0.23	0.009	<0.007	0.406	<0.0031	25.3	0.269	3.5	1.37
6/1/2013	PNF	6.7	6.3	0.010	0.26	0.076	<0.007	0.181	<0.0031	27.4	0.260	4.1	1.35
	PSF	6.4	6.0	0.011	0.21	0.040	<0.007	0.166	<0.0031	8.9	0.259	4.3	1.35
	PBR	6.7	5.9	0.015	0.24	0.033	<0.007	0.202	<0.0031	4.8	0.252	4.3	1.35
6/14/2013	PNF	5.4	4.9	0.007	0.25	0.095	<0.007	0.153	<0.0031	26.8	0.220	4.5	1.35
	PSF	5.4	5.1	0.002	0.27	0.080	<0.007	0.185	<0.0031	10.6	0.219	4.3	1.34
	PBR	5.3	5.0	0.001	0.24	0.090	<0.007	0.144	<0.0031	9.6	0.216	4.3	1.34
6/29/2013	PNF	2.9	2.9	0.004	0.17	0.044	<0.007	0.118	<0.0031	15.1	0.113	4.0	1.36
	PSF	2.7	2.8	0.011	0.20	0.115	<0.007	0.078	<0.0031	3.4	0.113	4.0	1.37
	PBR	2.9	2.7	0.004	0.20	0.078	0.011	0.109	<0.0031	2.3	0.111	4.2	1.36
7/14/2013	PNF	3.0	3.0	0.047	0.39	0.270	<0.007	0.116	<0.0031	120.5	0.072	2.4	1.40
	PSF	2.5	2.6	0.004	0.13	0.025	0.010	0.099	<0.0031	16.5	0.063	2.4	1.38
	PBR	2.4	2.5	0.024	0.21	0.110	0.010	0.090	<0.0031	3.0	0.059	2.4	1.37

7/29/2013	PNF	2.7	2.9	0.032	0.25	0.067	<0.007	0.171	<0.0031	336.7	0.070	2.4	1.43
	PSF	2.5	2.3	0.021	0.14	0.015	<0.007	0.120	<0.0031	26.4	0.058	2.6	1.37
	PBR	2.2	2.2	0.010	0.12	0.027	0.011	0.082	<0.0031	15.9	0.054	2.5	1.38
8/24/2013	PNF	2.9	2.7	0.013	0.17	0.045	0.017	0.104	<0.0031	62.7	0.097	3.6	1.40
	PSF	2.5	2.5	0.004	0.16	0.046	0.019	0.095	<0.0031	4.0	0.081	3.3	1.37
	PBR	2.6	2.5	0.006	0.14	0.046	0.008	0.088	<0.0031	2.3	0.084	3.3	1.37
9/29/2013	PNF	6.4	5.9	0.015	0.42	0.237	<0.007	0.173	<0.0031	12.5	0.197	3.4	1.43
	PSF	4.9	5.2	0.006	0.22	0.070	<0.007	0.143	<0.0031	4.0	0.186	3.6	1.38
	PBR	4.6	4.4	<0.0011	0.15	0.026	<0.007	0.115	<0.0031	1.5	0.162	3.7	1.39
10/24/2013	PNF	3.9	3.7	0.013	0.19	0.101	0.039	0.049	<0.0031	-	0.131	3.6	1.44
	PSF	3.5	3.5	0.014	0.11	0.035	0.027	0.048	<0.0031	-	0.122	3.5	1.40
	PBR	3.4	3.4	0.018	0.19	0.067	0.016	0.103	<0.0031	-	0.123	3.7	1.38
Storm Samples													
5/9/2014	PNF	-	7.3	0.036	1.37	1.052	0.019	0.304	<0.0031	-	0.241	3.3	1.44
7/2/2013	PNF	-	15.7	0.631	2.44	1.242	0.269	0.934	<0.0031	-	0.686	4.4	1.44
7/12/2013	PNF	-	15.8	1.039	2.59	0.786	0.600	1.204	<0.0031	-	0.894	5.7	1.52
8/23/2013	PNF	-	4.1	0.080	0.38	0.175	0.010	0.196	<0.0031	-	0.216	5.3	1.40
9/6/2013	PNF	-	18.2	0.443	2.03	0.415	0.454	1.162	<0.0031	-	0.848	4.7	1.50
9/18/2013	PNF	-	9.5	0.034	0.83	0.592	<0.007	0.230	<0.0031	-	0.374	3.9	1.43

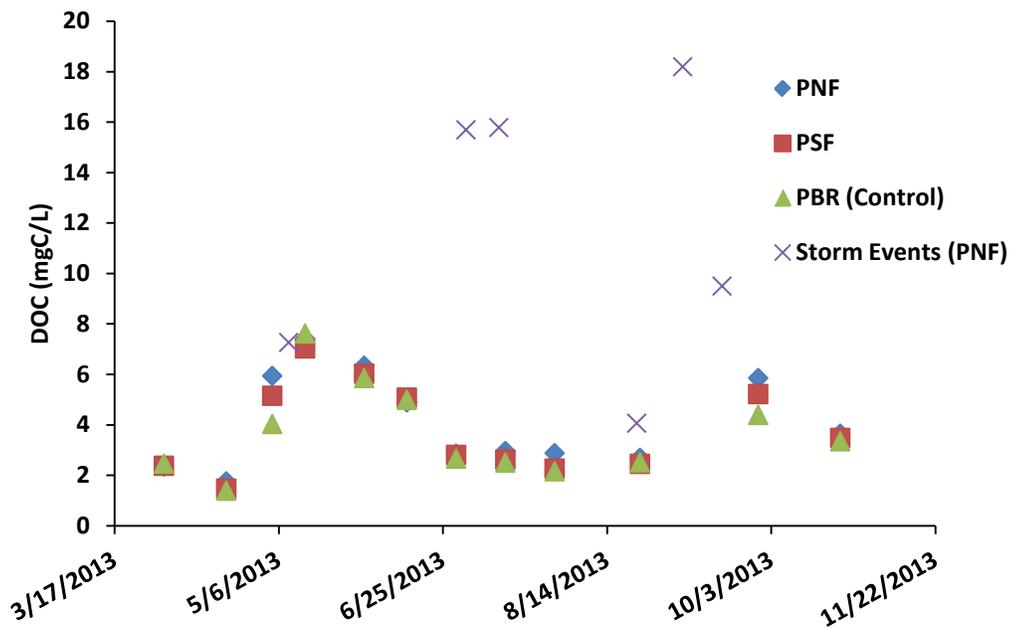


Figure 2. DOC values for all samples collected April-October, 2013.

One of the most widely used metrics for DOM characterization is SUVA, which is correlated to the aromaticity of the material (Weishaar et al. 2003) and is also an indicator for the formation of regulated DBPs (White et al. 1997, Archer and Singer 2006, Bladon et al. 2008). Differences in SUVA values between impacted and control sites were also not significant, also suggesting that the fire did not greatly alter the DOM in the watershed (Figure 3). SUVA values were greater than values observed in previous work during spring snowmelt (2.9 L/mg-m) and baseflow (2.4 L/mg-m) (Beggs et al. 2013). SUVA values were greater than 4 L/mg-m during spring snowmelt and early summer, although these values were also observed at the control site, making it difficult to draw strong conclusions about the impact of the wildfire. Storm event samples consistently showed increased SUVA values compared to baseflow and spring snowmelt samples (Figure 3). There was a seasonal increase in SUVA values at all sites during spring snowmelt, likely due to the flushing of highly aromatic, terrestrially-derived DOM from the surrounding landscape into the CLP River (Figure 3). This indicates, as expected, that the increased flow had mobilized more aromatic DOM. It has also been reported that burned bog and upland soils release more soluble aromatic, higher SUVA DOM relative to unburned samples (Olefeldt et al. 2013). The lack of differences in SUVA between impacted and non-impacted sites were small, indicating that the mobilization of DOM was not dominated by DOM impacted by fire, but by DOM from within other parts of the watershed.

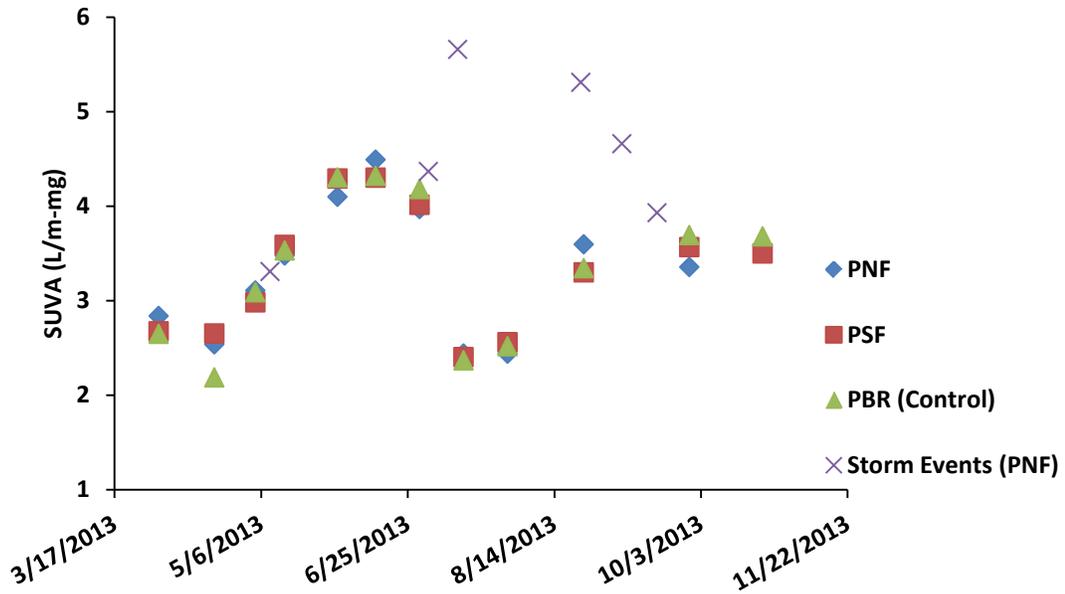


Figure 3. SUVA values for all samples collected April-October, 2013.

Total dissolved nitrogen (TDN) values were also fairly similar between impacted and control sites, although the early season, May samples showed some variation between sites, particularly the May 4th sample which had high values in general (Figure 4). Summer storm event TDN values were high compared to baseflow samples, and were comparable to the high May 4th value for the PNF site. These differences in TDN can be further understood by the concentrations of nitrate and nitrite (reported as total of both species) observed between PBR and the impacted sites (Figure 5). These differences were greatest for the April and May samples, where the PBR site had values below 0.010 mg_N/L, whereas values as high as 0.450 mg_N/L were observed for the impacted sites. A similar increase in export of inorganic N species was reported for a Rocky Mountain stream in Alberta, Canada following a wildfire in 2003 (Bladon et al. 2008). The differences in nitrate and nitrite values between impacted and control sites were minimal for samples later in the season following spring snowmelt, although slight variability in a handful of samples was observed. This suggests that there was mobilization of nutrients at the onset of the spring runoff. The organic fraction (DON) of the TDN appeared to be less impacted by the fire (Figure 6), with no clear differences between the sites, although storm samples did show elevated concentrations. Nutrient mobilization is further supported by the notable differences in TDP concentrations that were observed between impacted and control sites (Figure 7). In this case differences were still observed throughout the season, even after spring snowmelt occurred (July, August, and September samples). All storm event samples collected from PNF showed elevated TDP concentrations (Figure 7), as high as 1.04 mg_P/L.

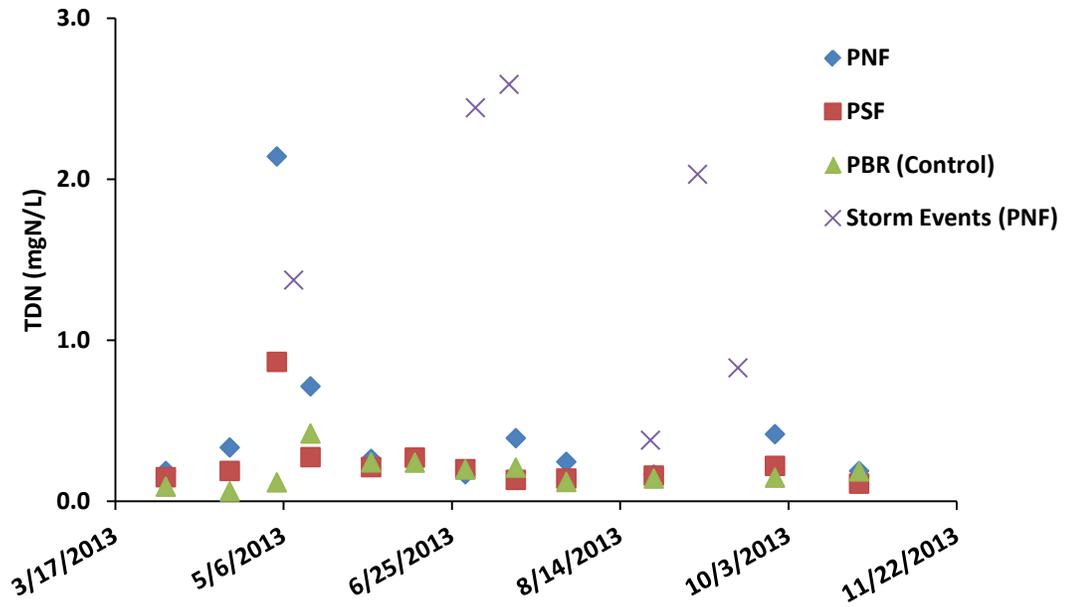


Figure 4. TDN values for all samples collected April-October, 2013.

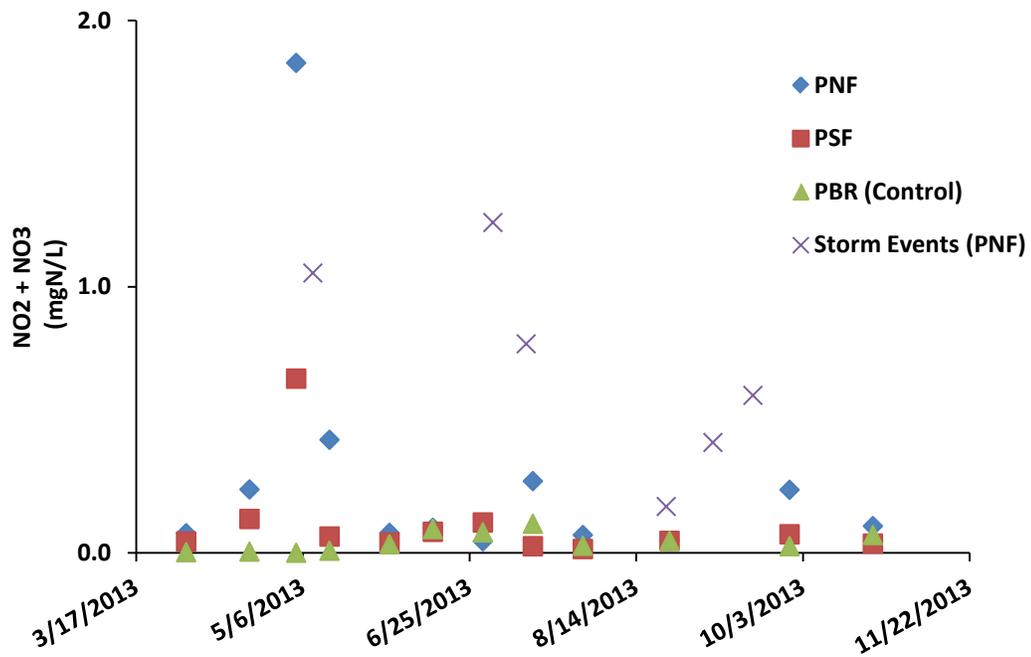


Figure 5. Sum of nitrate and nitrate for all samples collected April-October, 2013.

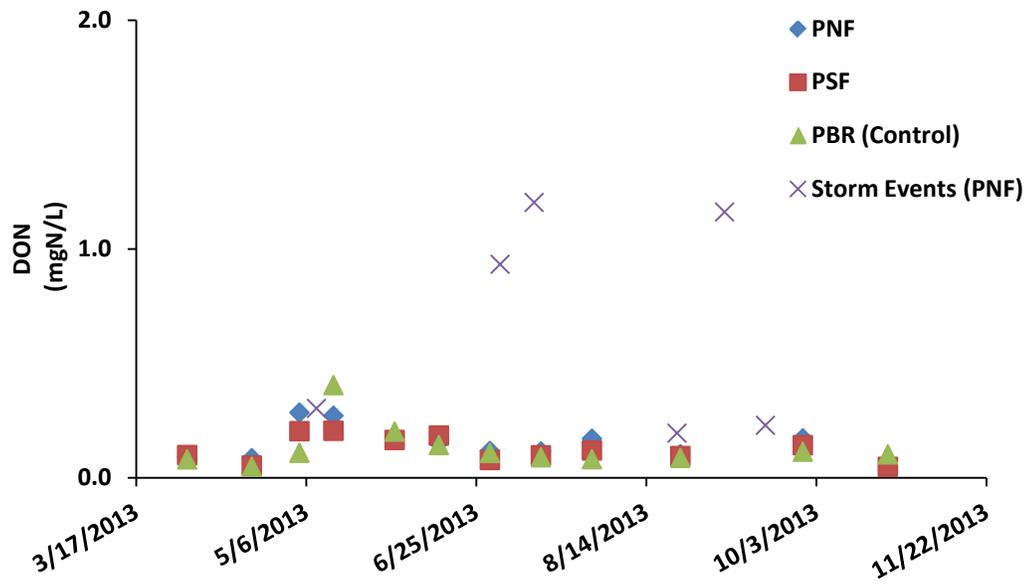


Figure 6. Dissolved organic nitrogen (DON) values for all samples collected April-October, 2013.

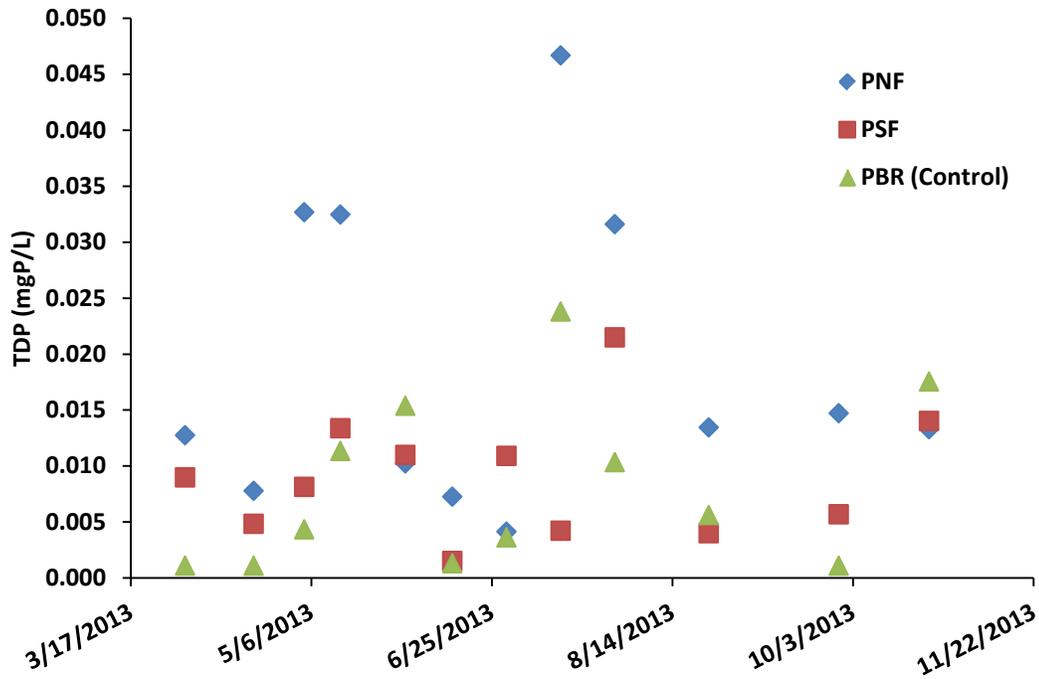


Figure 7. Total dissolved phosphorus (TDP) values for samples collected April-October, 2013. Storm event samples are not shown due to extreme values. See Table 2 for storm sample TDP concentrations.

Additional water quality results include bromide levels which were always below the detection limit (0.0031 mg/L) for all routine samples and storm samples collected during the sampling campaign (Table 2). TSS values were greatest for the impacted sites (PNF and PSF) compared to PBR (See Table 2). This was clearly visibly evident during filtering and handling of the samples. Differences in turbidity between the impacted and control sites were also evident (turbidity data provided by the City of Fort Collins and not presented here). Several storm event samples showed extreme turbidity levels (>2000 NTU). These observations are significant to drinking water utilities and treatment processes such as alum coagulation which will be discussed in more detail later.

Impact of the High Park Fire on DOM properties

The water quality section focused on the bulk parameters that are typically used to characterize water. In order to evaluate the composition and properties of the DOM in more detail we employed more advanced analytical techniques. The team evaluated other measures of DOM composition, including fluorescence spectroscopy. Figure 8 show fluorescence EEMs for the April 20th sample. The EEMs look similar with the PSF and PNF samples have higher fluorescence intensities, concomitant with higher DOC concentrations. The PBR sample showed a higher protein-like fluorescence region centered near excitation 270 nm and emission 340 nm relative to the intensity of the A and C peaks. PNF and PSF EEMs were dominated by fluorescence in the A and C peak regions.

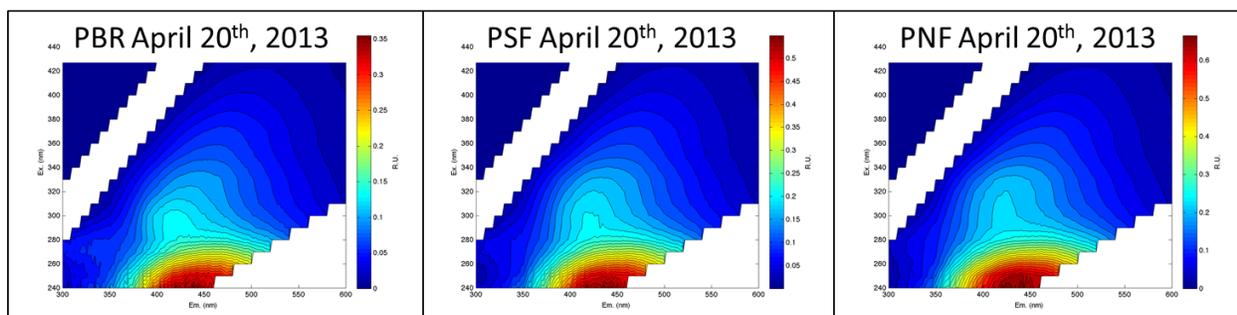


Figure 8. Excitation emission matrices (EEMs) of all fluorescence scans for all samples from April 20th, 2013.

Another measure of DOM composition obtained from fluorescence is the FI. As defined in the methods section, the FI is a ratio of emissions and has been used to trace different sources of the DOM. The expected range for the FI lies between 1.2-1.9. Low values are associated with DOM from terrestrial origin; high values are associated with DOM from microbial sources. It is not clear whether the FI is expected to increase or decrease for DOM impacted by fire. On one side, fire impacted DOM may be less mobile resulting in an increase in FI. The FI values for the samples are shown in Figure 9. FI varied a small bit in some samples, but the variability due to seasonal changes was greater than the variability among fire impacted samples and samples from the control site (Figure 9).

Another metric evaluated was the molecular size distribution for the samples. For this, SEC was used. The size distribution of DOM molecules determined by SEC showed little difference between samples from a given sampling date, but showed clear seasonal trends with the average molecular weight increasing at the onset of spring snowmelt (indicated by a shift to shorter retention times) and then decreasing as the spring progressed). The SEC results are shown in Figures 10 and 11.

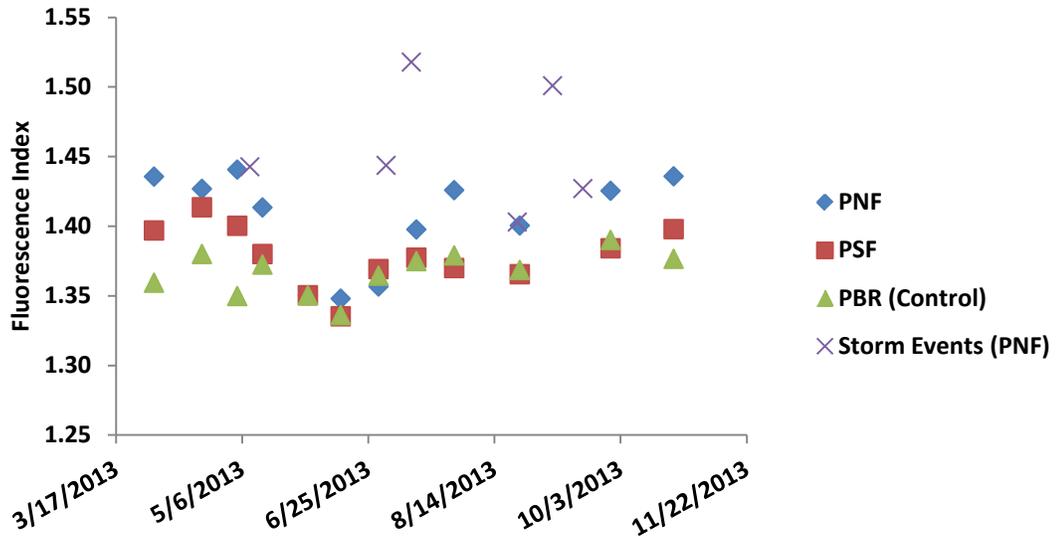


Figure 9. Fluorescence Index (FI) for all samples collected April-October, 2013.

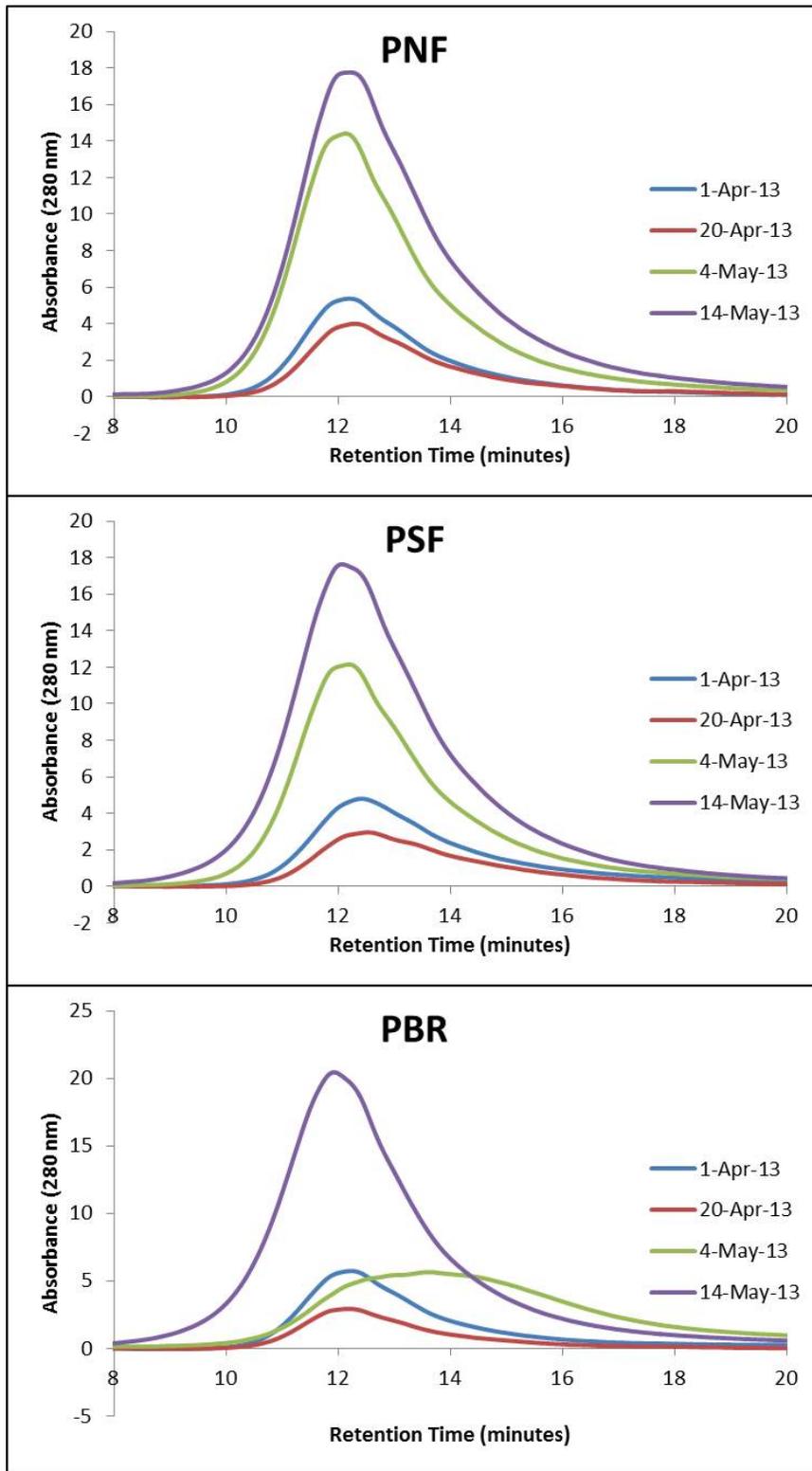


Figure 10. SEC chromatograms for spring samples for PNF, PSF, and PBR (control) sites

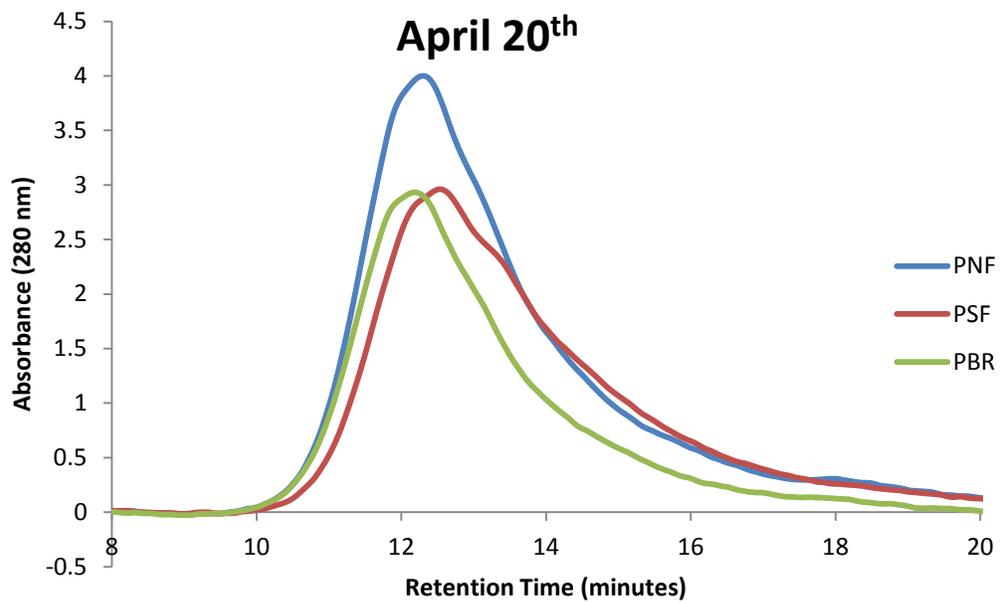


Figure 11. Comparison of SEC chromatograms for the April 20th samples for all three sites.

Impact on DBP formation and speciation

Filtered water samples were chlorinated at the bench-scale following uniform formation conditions in order to better understand the reactivity of the fire impacted DOM and inform utilities with useful information regarding the potential to form TTHMs, HAA5s, and HANs. These tests are conducted with the intent to understand the DOM and DBP precursor material better and at realistic chlorination conditions that a typical drinking water treatment plant would use.

Overall DBP formation for all three DBP groups showed little variation between wildfire impacted and control sites (Figures 12-14). Given the limited differences in DOC concentrations discussed previously, these results are not surprising. As to be expected, DBP formation for all groups was greatest in mid-late May during spring snowmelt when the greatest amount of DOM and DBP precursor material is being flushed into the Poudre River. The second peak in DBP formation in late September could be attributed to the mobilization of significant DOM and DBP precursor material during the September floods. Additionally, storm event samples, particularly during peak summer months, formed the highest levels of DBPs (Figures 12-14). Again, particularly high DOC levels were observed in storm samples, providing sufficient DBP precursor material. Storm event samples formed significant DBPs, some reaching very extreme values. For instance, the September 6th sample formed TTHM and HAA5s exceeding 1000 µg/L, and HANs exceeding 50 µg/L. Likewise, the July 12th sample formed HAA5s exceeding 1000 µg/L and HANs exceeding 50 µg/L. Under these chlorination conditions values in this range are extreme. If this water were to have entered the Fort Collins Water Treatment Facility (without being blended with Horsetooth Reservoir water) they would have faced significant treatment challenges and potential DBP exceedances would have been of high concern. To our knowledge, the Poudre intake was shut down during both of these events and 100% Horsetooth Reservoir water was being treated and distributed.

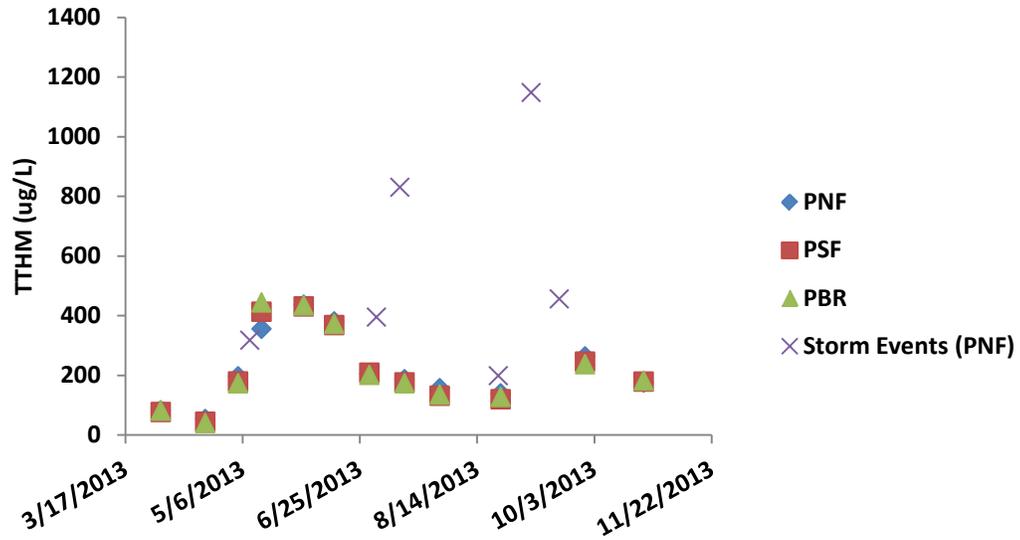


Figure 12. TTHM formation following UFC chlorination for all samples (prior to coagulation).

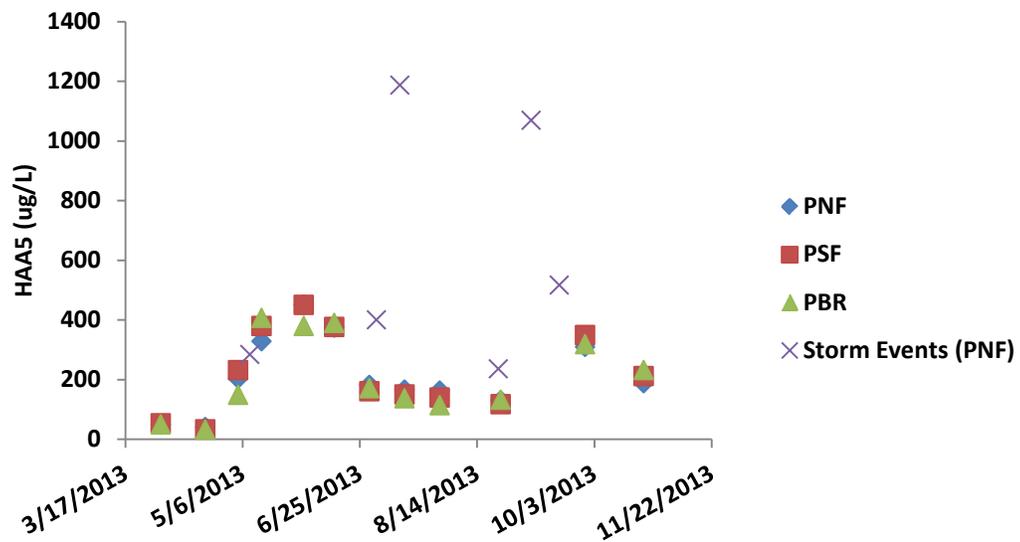


Figure 13. HAA5 formation following UFC chlorination for all samples (prior to coagulation).

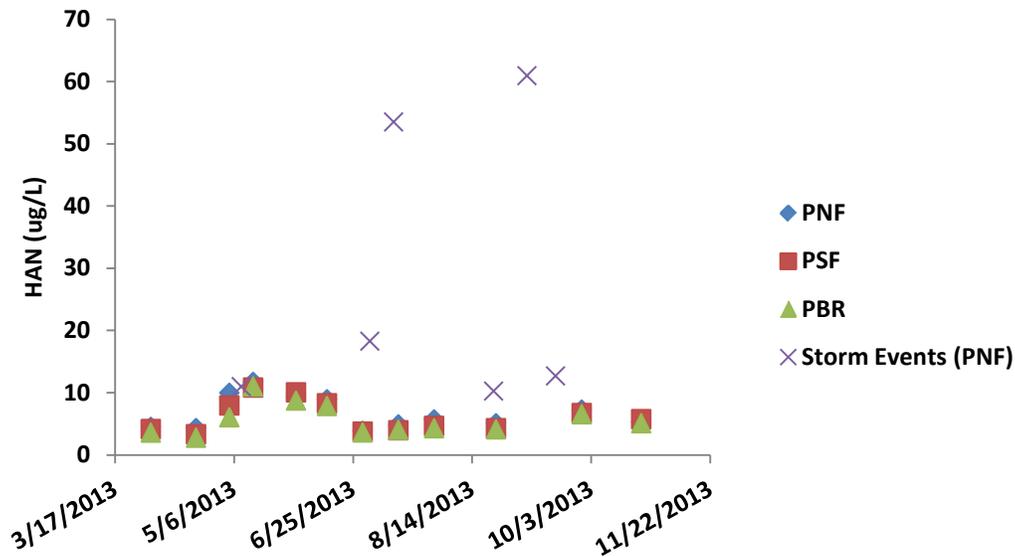


Figure 14. HAN formation following UFC chlorination for all samples (prior to coagulation).

DBP speciation values are shown in Figures 15-17 for all three DBP groups. For TTHMs, chloroform was by far the dominant species for all three sites. Differences between sites were not evident. On average, TTHMs were 95% chloroform for all samples. Bromide was always below detection limit (see Table 2), and so brominated DBP formation was very limited. Dichlorobromomethane (DCBM) was the second highest TTHM species formed. HAA formation was mostly dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) for all samples (Figure 16). The contribution of all other species was minimal. Notable differences between sites were not observed. On average for all samples DCAA formation was 41% of HAA5s and TCAA was 57%. Lastly, HAN formation was dominated by dichloroacetonitrile (DCAN), followed by trichloroacetonitrile (TCAN), as shown in Figure 17. Again, this is consistent with the water quality results which indicated limited to no bromide in the source water, leading to very minimal brominated DBP formation. Overall, on average DCAN formation was 89%, followed by TCAN formation which was 7%.

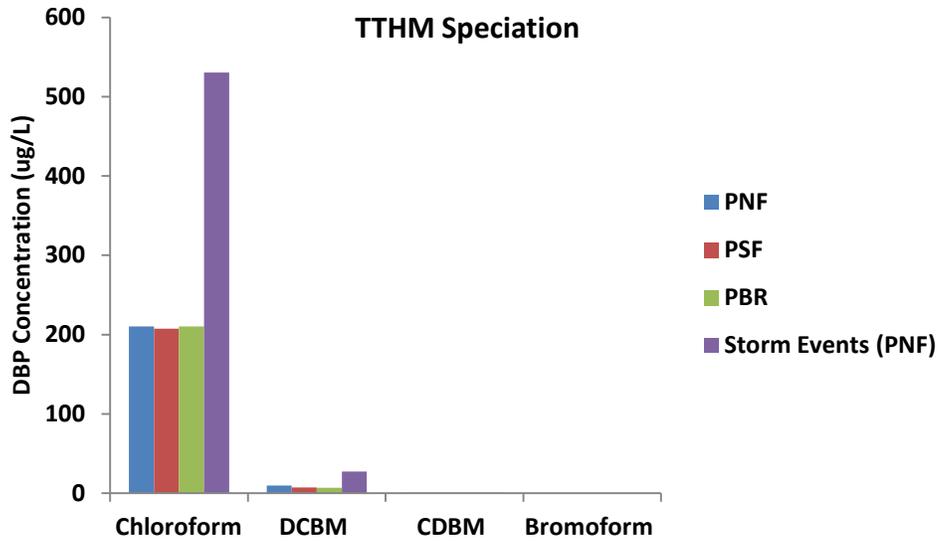


Figure 15. TTHM speciation for all samples prior to coagulation.

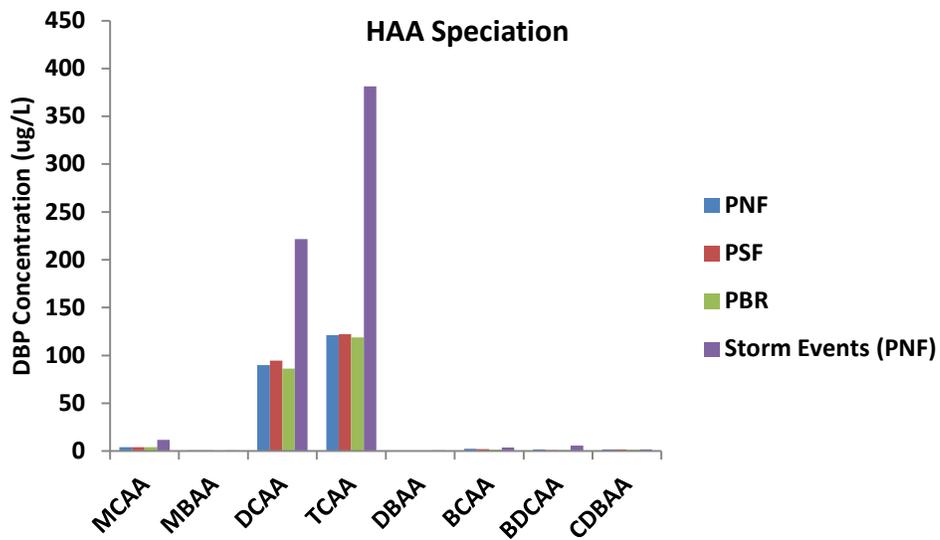


Figure 16. HAA speciation for all samples prior to coagulation.

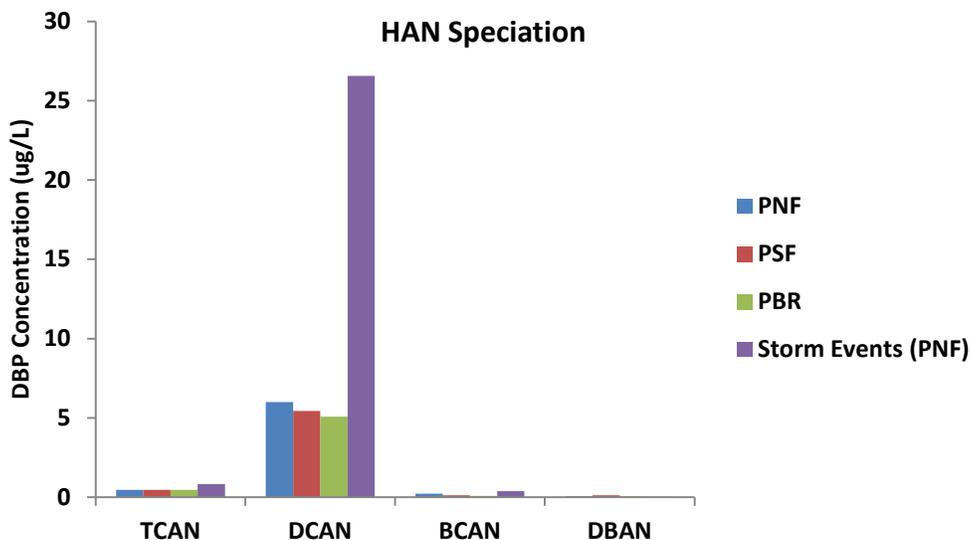


Figure 17. HAN speciation for all samples prior to coagulation.

DOM Reactivity and DBP Yields

In addition to DBP concentrations, DBP yields are useful for further evaluating the reactivity of the DOM and better understanding DBP precursor material. DBP yields represent the concentration normalized to the DOC for a water sample ($\mu\text{g DBP}/\text{mg}_C$). This allows for determining a specific water samples yield of a particular DBP per unit carbon, or essentially its reactivity. Figure 18 shows TTHM yields for all samples. Again, consistent with previous findings in this study, notable differences between impacted and control sites were not observed. However, some of the late season samples showed higher yields for PBR, followed by PSF and PNF. Also, it is important to note that although storm event samples showed extreme DBP concentrations, when they are normalized to carbon the TTHM yields for these samples were in the same range as spring snowmelt and baseline TTHM yields, and spring snowmelt samples actually showed higher TTHM yields than storm event samples. Similar trends were also observed for HAA5 yields. Alternatively, HAN yields for about half of the storm event samples were the highest compared to spring snowmelt and baseflow conditions. The May 9th, July 2nd, and September 18th samples yielded similar HANs to baseflow samples. The first spring samples collected showed minor differences in HAN yields. It is understood that HANs have different precursor material than THMs and HAAs, so these findings are not necessarily surprising, but are of interest to better understanding the impacts of the wildfire in this watershed.

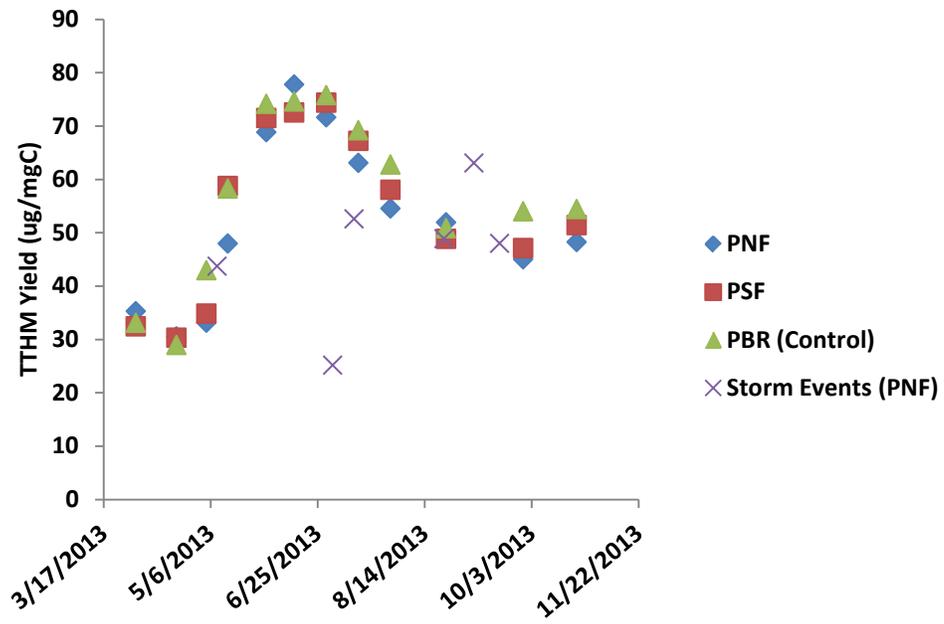


Figure 18. TTHM yields (DBP concentration normalized to DOC) for all samples.

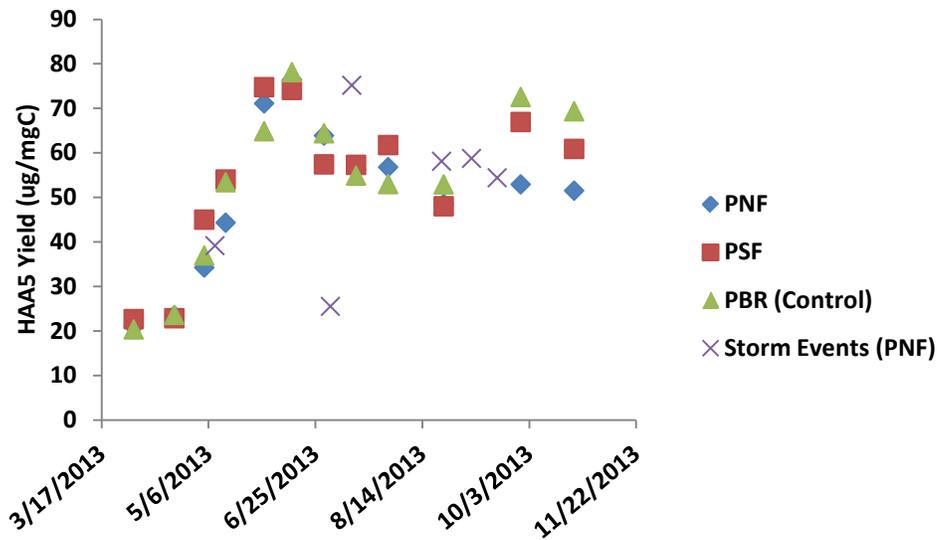


Figure 19. HAA5 yields (DBP concentration normalized to DOC) for all samples.

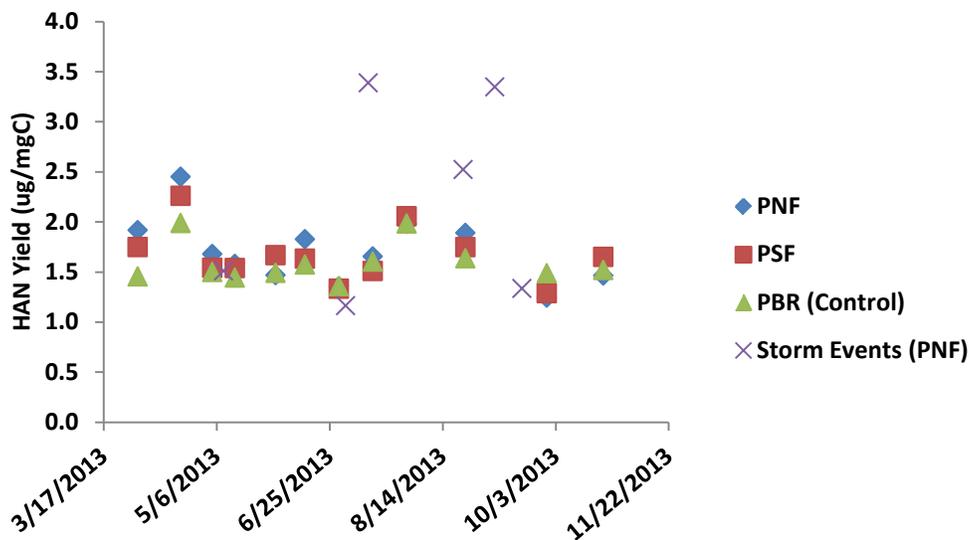


Figure 20. HAN yield (DBP concentration normalized to DOC) for all samples.

Chloraminated samples

PNF and PBR samples collected May 14th were chloraminated following the methods previously discussed. All nitrosamines were less than the MRL, with the exception of NDMA for the PNF 5/14 sample which was measured at 2.7 ng/L (MRL = 2.5 ng/L). Therefore the nitrosamine formation potential of these waters was negligible. Due to the little amount of wastewater influence in the area and limited organic nitrogen, this is as to be expected as a result of a lack of significant precursor material.

Efficacy of alum treatment

All samples collected from PNF and PBR (control) were coagulated with aluminum sulfate and measured for DOC, UV_{254} , and DBP formation upon bench-scale chlorination (UFC). The results are shown in Table 3 and Figures 21-28. Note that the team focused on DOC values since the coagulation procedure included filtration. In addition, most of the TOC was DOC. The team focused on regulated DBPs. As discussed above measures of unregulated DBPs (i.e., nitrosamines) showed no formation, with the exception of one compound which was very close to the detection limit. Prior to selecting a final dose, DOC alum dose response curves were developed for all jar test samples. These results showed differences between PNF and PBR sites for select sample dates. As shown in Figure 21, the May 4th PNF sample which was collected shortly before the peak TOC of the season, exhibited a different response than the May 4th PBR sample. This can be at least partially attributed to the initial difference in raw water DOC concentrations. In this case the optimal dose selected for PNF was 55 mg/L, whereas PBR (5/4) was dosed at 45 mg/L. On the other hand, the June 1st samples showed very similar responses to alum (Figure 22) and were both dosed at 30 mg/L. By June 1st sample collection all of the ash built up on the sides of the banks had been washed out by spring snowmelt, which may explain why differences were observed between PNF and PBR in early May, with minimal differences in dose response later in the season. A rain event also occurred on May 9th which could have contributed to more washing out of significant fire material prior to June.

In general PNF waters were effectively treated, with DOC removal averaging 60.4% and jar tests effluent DOC concentrations consistently below 3 mg_C/L even during spring snowmelt, with an average DOC of 1.6 mg_C/L for treated samples. PBR samples were also effectively treated, with an average DOC removal of 60.5%. All PBR samples except for two spring snowmelt samples were treated to DOC effluent concentrations of less than 2.0 mg_C/L, with an average jar test effluent of 1.4 mg_C/L. PNF on average required a higher alum dose (43.8 mg/L) for DOC removal than PBR (34.2 mg/L), suggesting that the fire impacted site was more difficult to treat (Table 3). SUVA values for raw waters and treated waters are also shown in Figures 24, 26, and 28. Overall SUVA decreased by 37.6% on average for PNF samples and 39.9% for PBR samples, generally with post-coagulation SUVA values around 2 L/mg-m. These results support the overall findings from this study that the fire impacted water were relatively susceptible to alum coagulation for both DOC and SUVA removal. DBP precursor removal will be discussed in more detail later.

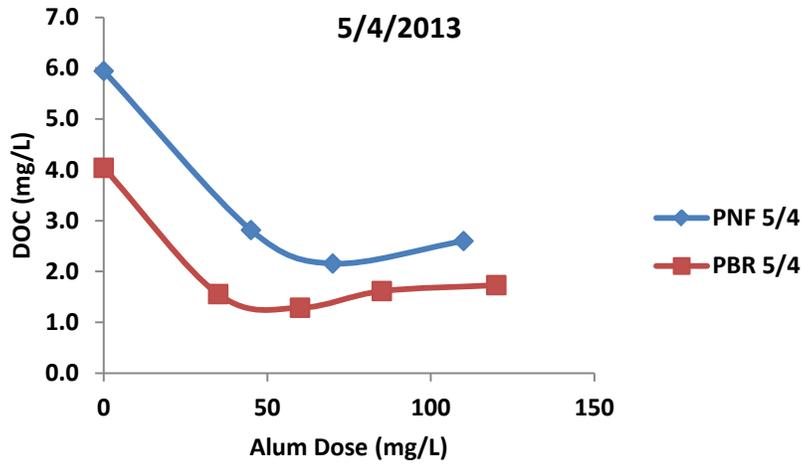


Figure 21. DOC dose response curve for PNF and PBR 5/4 samples.

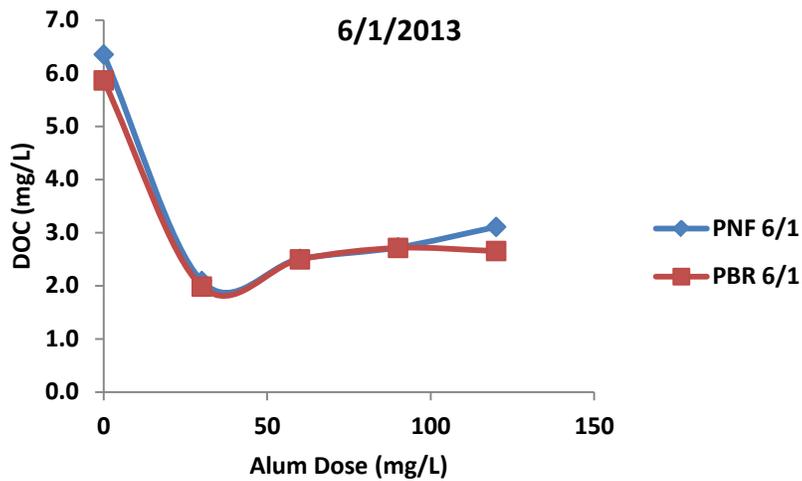


Figure 22. DOC dose response curve for PNF and PBR 6/1 samples.

Table 3. Jar test results following alum sulfate coagulation for all PNF, PBR, and storm event samples.

Date	Site	Alum Dose (mg/L)	pH	% Decrease DOC	% Decrease SUVA	% Decrease TTHM	% Decrease HAA5	% Decrease HAN
4/1/2013	PNF	50	6.3	56.4	26.9	71.5	71.6	47.1
4/1/2013	PBR	50	6.8	48.3	36.4	64.3	69.1	39.7
4/20/2013	PNF	65	7.5	51.8	35.2	61.0	71.5	36.0
4/20/2013	PBR	65	6.6	56.5	13.3	59.6	70.6	33.4
5/4/2013	PNF	55	6.8	55.4	37.2	70.7	85.5	45.8
5/4/2013	PBR	45	6.8	58.6	38.3	92.1	84.1	54.6
5/14/2013	PNF	70	5.8	65.6	45.7	81.3	91.4	63.4
5/14/2013	PBR	45	7.0	69.6	45.0	87.6	93.3	63.3
6/1/2013	PNF	30	6.3	63.5	49.3	83.1	95.1	53.0
6/1/2013	PBR	30	6.2	62.2	54.9	85.8	92.9	50.4
6/14/2013	PNF	35	6.2	66.3	40.1	81.1	90.9	80.8
6/14/2013	PBR	40	5.2	68.8	49.3	83.5	92.5	80.7
6/29/2013	PNF	20	6.4	62.6	48.2	82.6	91.7	85.3
6/29/2013	PBR	20	5.9	61.4	51.4	79.9	90.4	47.9
7/14/2013	PNF	30	6.4	64.6	7.3	81.2	89.5	79.9
7/14/2013	PBR	20	6.5	60.1	28.4	80.7	89.4	85.8
7/29/2013	PNF	30	6.4	55.4	21.6	74.3	85.5	82.1
7/29/2013	PBR	25	6.3	62.7	23.7	80.2	88.8	90.5
8/24/2013	PNF	40	6.0	66.8	35.3	73.0	87.4	78.0
8/24/2013	PBR	20	6.5	59.9	40.3	63.9	84.5	73.2
9/29/2013	PNF	50	6.7	59.7	47.2	66.7	88.2	58.8
9/29/2013	PBR	25	6.6	57.3	47.1	63.5	88.7	72.4
10/24/2013	PNF	50	6.2	56.6	57.5	68.8	84.8	1.4
10/24/2013	PBR	25	6.3	60.9	50.1	70.3	NA	18.4
Storm Event Samples								
5/9/2013	PNF	60	6.5	58.3	44.1	75.9	87.5	87.3

7/2/2013	PNF	50	6.9	85.3	30.5	68.0	84.2	76.1
7/12/2013	PNF	65	7.0	-21.8	22.2	17.2	62.7	-22.3
8/23/2013	PNF	25	6.6	13.8	27.0	-18.9	53.1	35.1
9/6/2013	PNF	65	6.9	5.5	32.0	64.7	77.6	62.7
9/18/2013	PNF	80	5.5	61.5	57.2	72.3	91.1	71.2

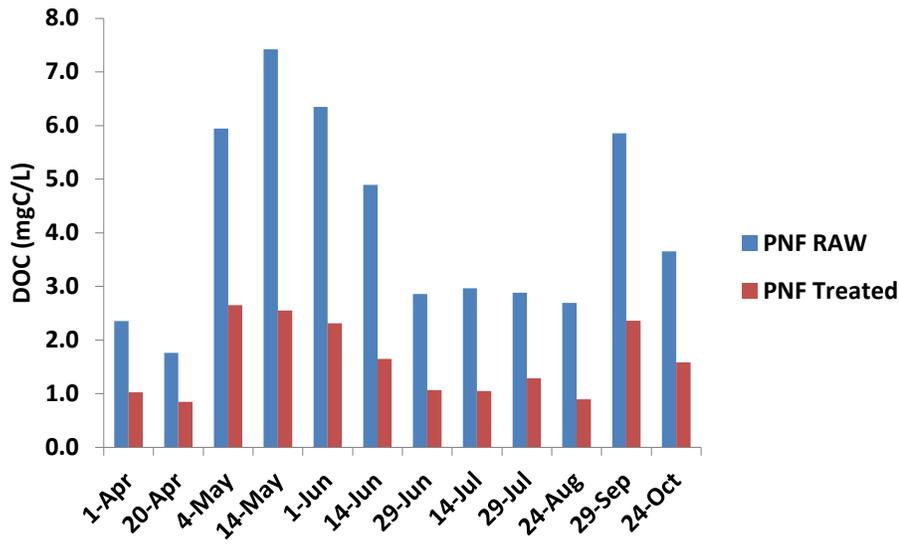


Figure 23. DOC concentrations before and after alum coagulation for all PNF samples.

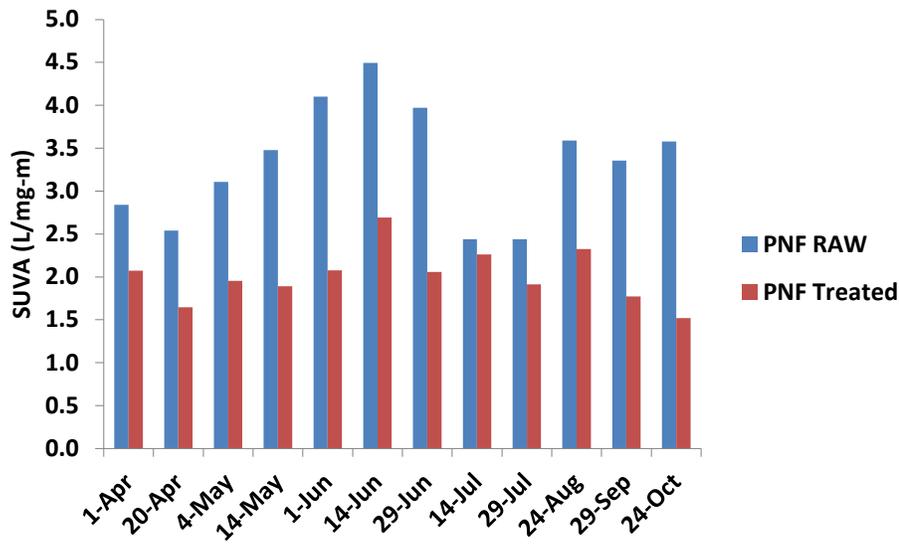


Figure 24. SUVA values before and after alum coagulation for all PNF samples.

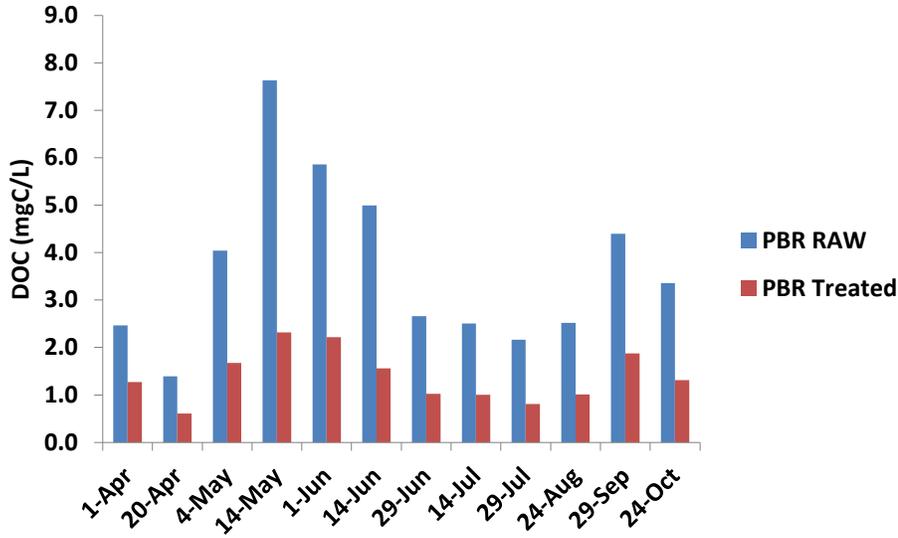


Figure 25. DOC concentrations before and after alum coagulation for all PBR (control) samples.

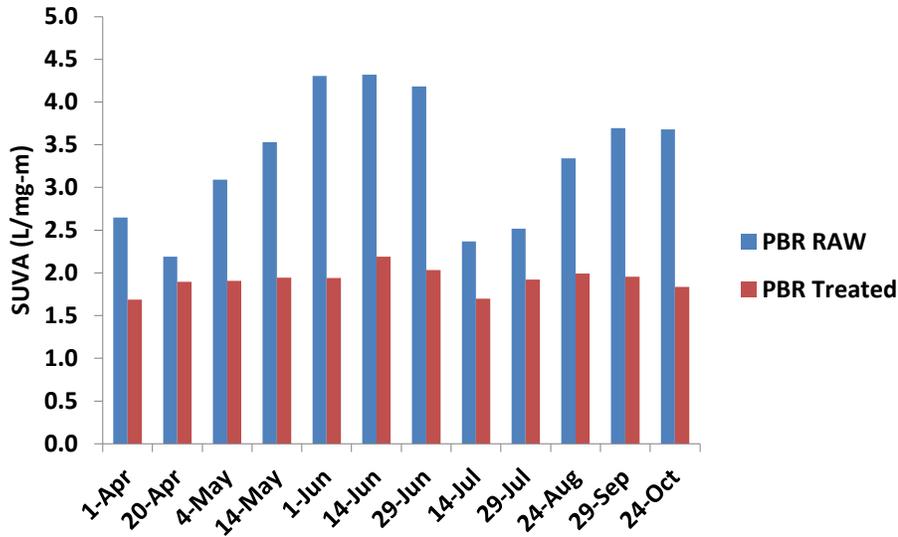


Figure 26. SUVA values before and after alum coagulation for all PBR (control) samples.

Storm event samples collected from PNF were also coagulated following the same methods and conditions as the baseflow and spring snowmelt samples discussed previously. Some of the samples were effectively treated (Figures 27 and 28), with effluent DOC concentrations below 3.0 mgC/L in some cases. This result again supports the overall finding that the fire impacted DOM was easily removed. However, two of the storm event samples (7/12 and 9/6) were very difficult to treat, most likely due to an extremely high level of particulates in both samples which could not be overcome by the alum even at high alum doses (turbidities >2000). Dose response tests for these two storm samples were conducted up to alum doses of 80 and 90 mg/L, with minimal removal observed. Although an increase in DOC was observed for the July 12th sample, the SUVA was observed to decrease from 5.7 to 4.2 L/mg-m. The 9/6

sample also was treated to a SUVA of 3.2 L/mg-m. Regardless, if the Fort Collins Water Treatment Facility were to treat 100% Poudre River water during one of these storm events they would have faced significant treatment challenges requiring extreme alum doses, with the possibility of still not achieving adequate DOM removal and implications for DBP formation. Average final alum dose for storm event samples only (n=6) was 57.5 mg/L, compared to an average alum dose of 43.8 mg/L for all other PNF samples. Also of concern, several of the treated storm samples still had significant visible color and some retained a smoky odor, although outside the scope of work of this project.

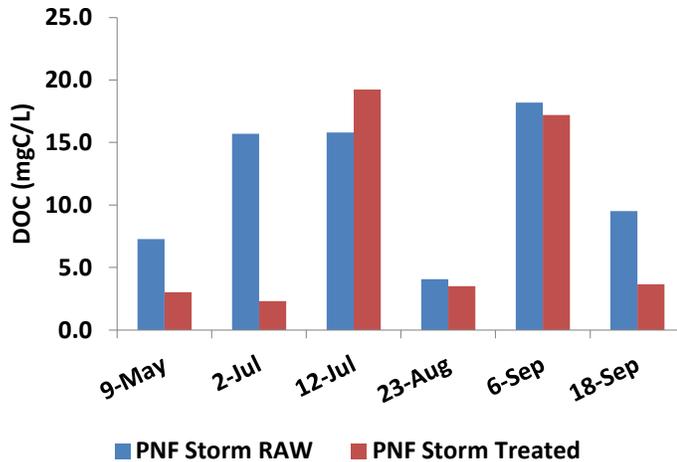


Figure 27. DOC concentrations before and after alum coagulation for all storm event samples.

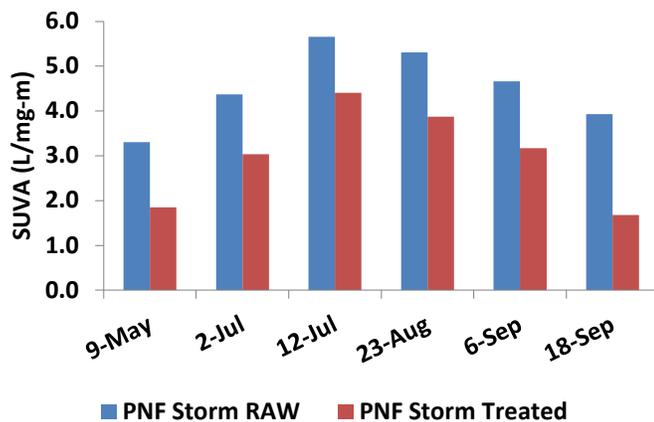
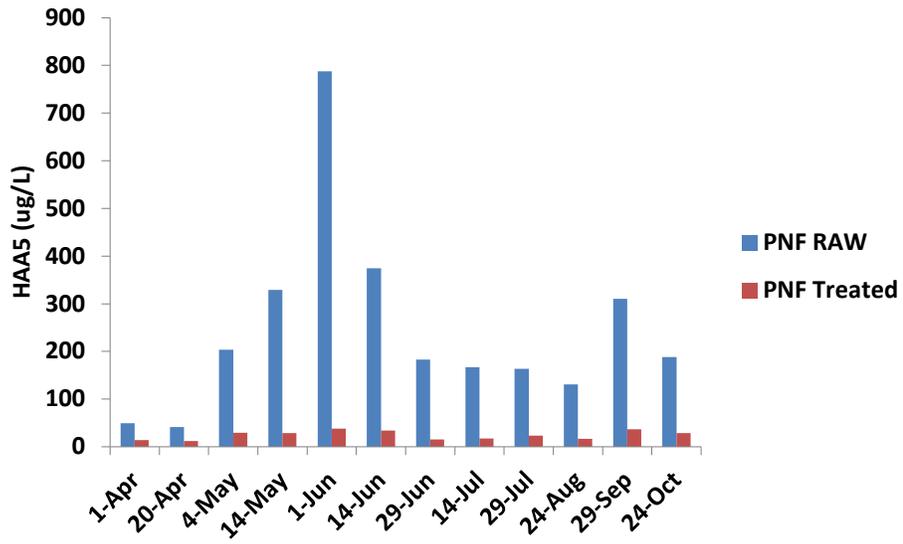
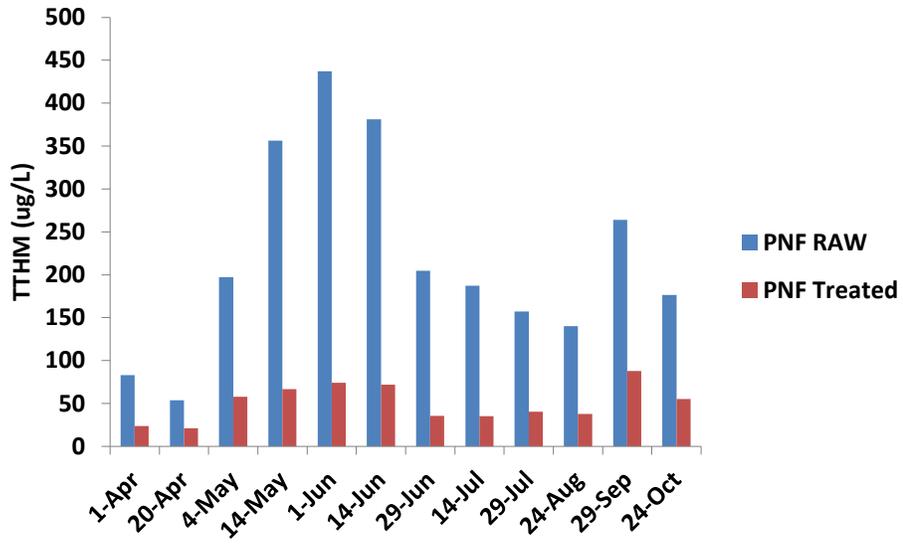


Figure 28. SUVA values before and after alum coagulation for all storm event samples.

Efficacy of alum coagulation for DBP precursor removal

All coagulated samples were also chlorinated following the same conditions as the raw samples discussed previously. Results comparing raw (prior to coagulation, filtered) and treated (coagulated, filtered) samples are shown in Figures 29-31 for PNF, PBR, and storm event

samples, respectively. TTHMs, HAA5s, and HANs formation values are shown for raw and treated samples. For PNF samples (excluding storm events) all samples were treated below the regulated TTHM MCL (80 µg/L) with the exception of PNF 9/29 (TTHM = 87.8 µg/L). The reason this sample was more difficult to treat could possibly be explained by the extreme storm event (September flooding) which flushed significant debris material from hill slopes into the Poudre River. Although the sample was collected several weeks after the flooding the impacts could have still been felt by the river. All PNF samples (excluding storm events) were treated below the HAA5 MCL (60 µg/L), including the 6/1 sample which had a raw water HAA5 formation of 787.2 µg/L (value above calibration curve). HAN precursors were not as well removed as the C-DBPs, with an average percent decrease of 59.3 for PNF samples. Average C-DBP removal was 74.6% and 86.1% for TTHMs and HAA5s, respectively. These results are to be expected since C-DBP precursors are typically more aromatic than N-DBP precursor material, and therefore more easily removed by coagulation.



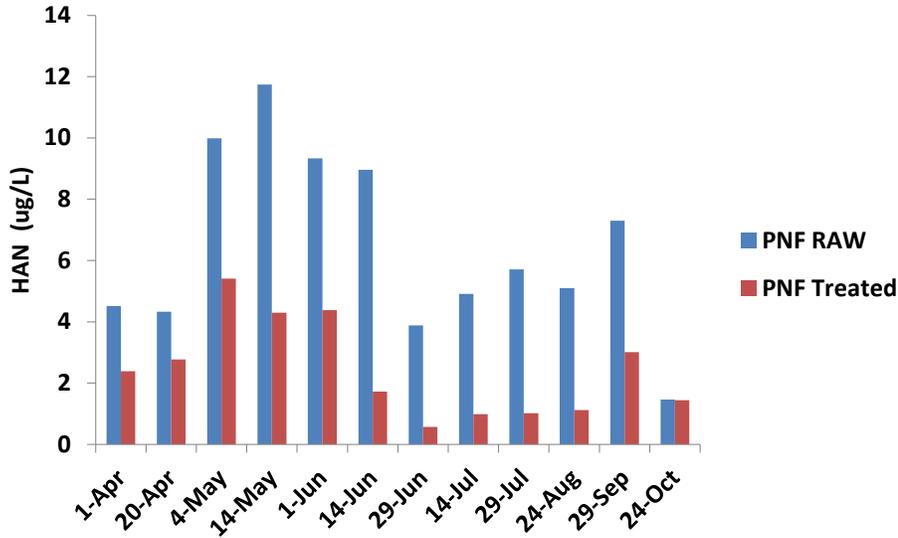
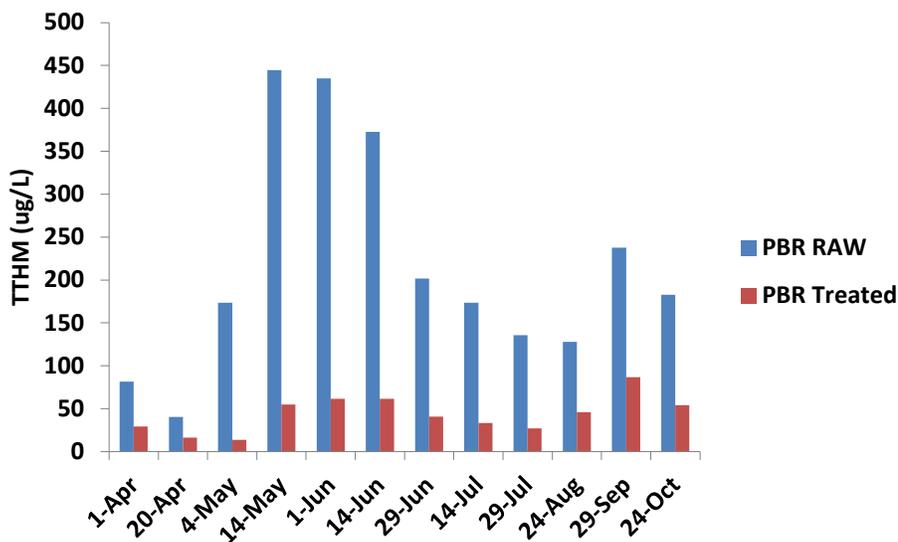


Figure 29. TTHM, HAA5, and HAN formation before and after alum coagulation for all PNF samples (excluding storm events).

PBR DBP precursor material was also well removed. As with the PNF 9/29 sample the PBR 9/29 sample was also still above the TTHM MCL even after coagulation (Figure 30). This finding suggests the DOM precursor material was not necessarily fire impacted or fire derived given that the control site showed very similar results to PNF, and was maybe strongly impacted by the extreme hydrologic changes of the September floods, but not necessarily related to fire impacted DOM. All PBR post-coagulation samples were treated to below the HAA5 MCL. Initial HAA5 concentrations (pre-coagulation) were not as great as the PNF extreme values. PBR HAN precursor removal was very similar to PNF, with an average percent decrease of 59.2. PBR average precursor removal for TTHMs and HAA5s was 76.0% and 85.8%, respectively, again very similar to the findings for PNF discussed earlier.



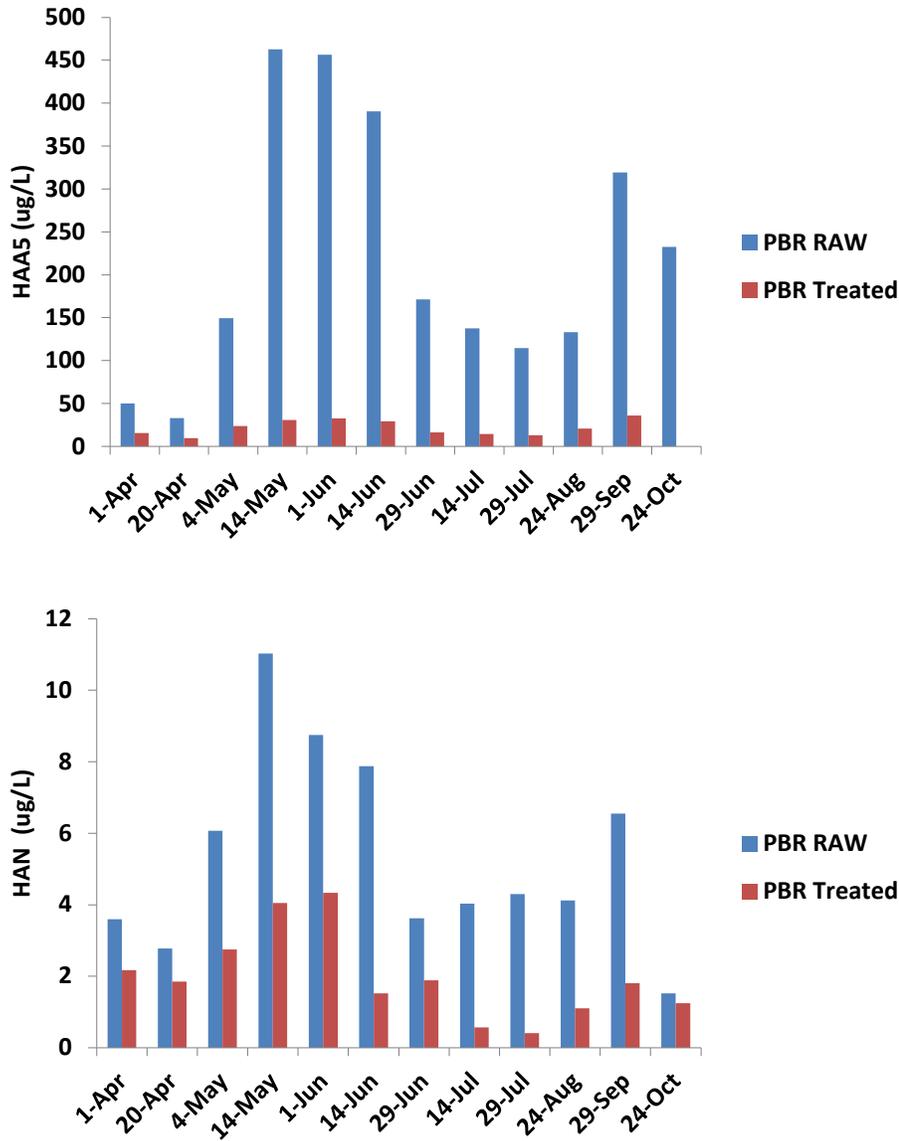
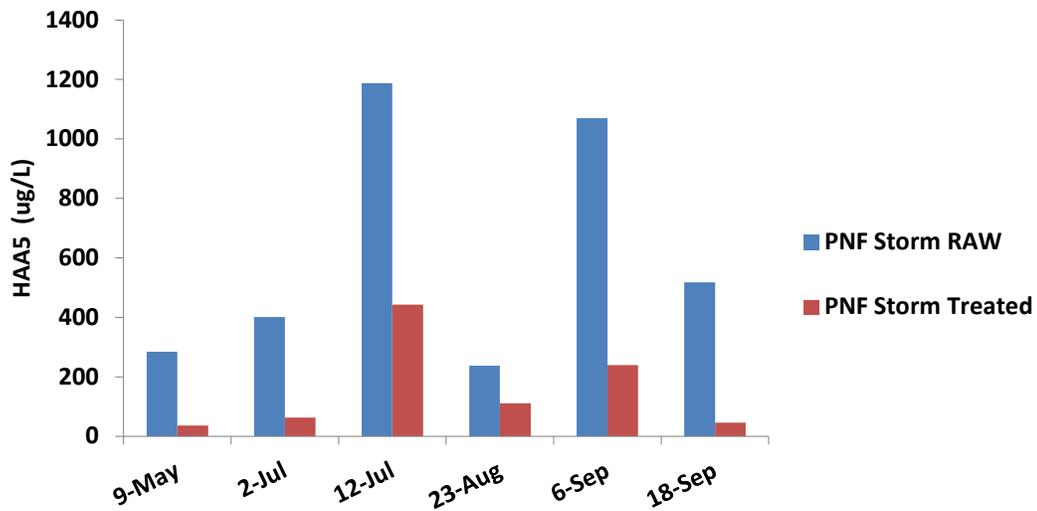
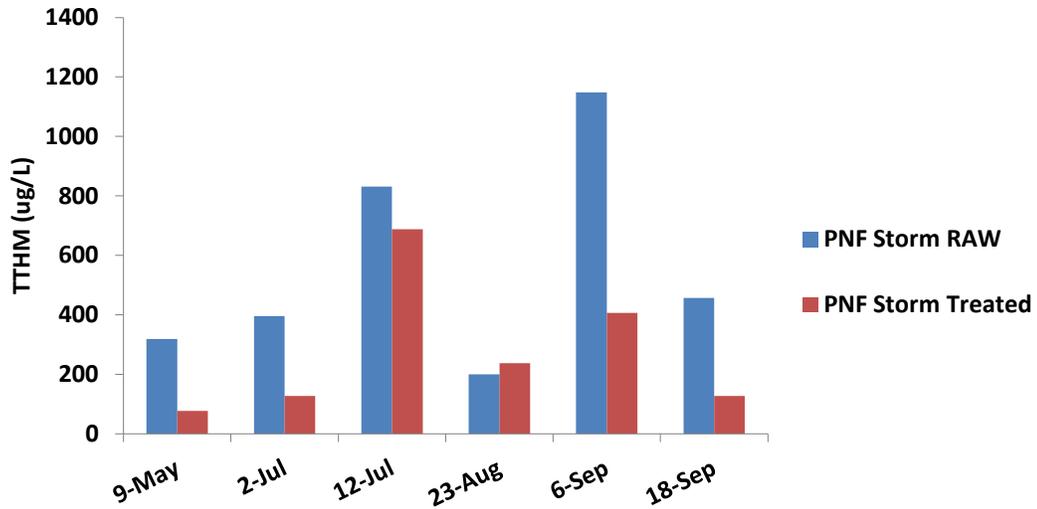


Figure 30. TTHM, HAA5, and HAN formation before and after alum coagulation for all PBR samples.

As with the DOC and SUVA post-coagulation results for the storm event samples, DBP removal was also more challenging for several of these samples. Five of the samples were still above the MCL for TTHMs following coagulation (Figure 31), the exception being the 5/9 sample which was an early season, milder storm. Average percent removal for TTHMs was 46.5 %, and one sample (8/23) showed an increase in TTHMs following coagulation, contributing to the low average removal. Four of the six storm samples exceeded the HAA5 MCL, the two exceptions being early season and late season storm events. Average HAA5 percent removal for storm events was 76.0 %, significantly higher than the TTHM precursor removal, most likely due to the overall good removal of HAA5 precursors for the 8/23 sample. This sample clearly

shows that TTHM and HAA5 precursors differ greatly in their characteristics and response to alum coagulation. HAN precursor removal for the storm samples was comparable to the PNF non-storm event samples, with an average percent removal of 51.7, even with an increase in HAN formation for the 7/12 storm sample. The results for the 7/12 sample, which did not coagulate well and resulted in an increase in DOC, are interesting given that TTHMs and HAA5s still decreased, but HAN formation increased. Again, it is important to note that N-DBP and C-DBP precursors are known to differ greatly, with C-DBP precursors being more easily removed by coagulation due to their hydrophobic and aromatic character.



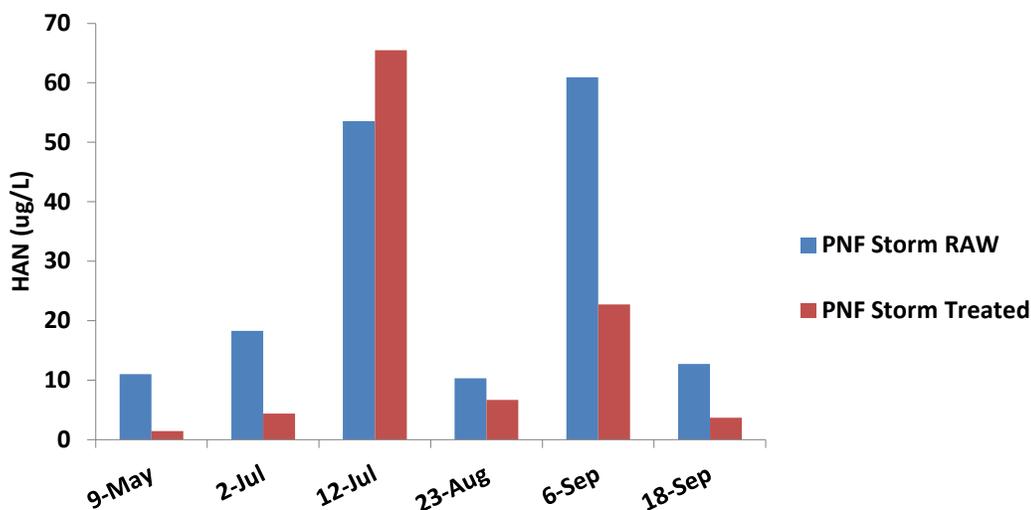


Figure 31. TTHM, HAA5, and HAN formation before and after coagulation for all storm event samples collected at PNF.

The DBP formation results following coagulation provide some of the most useful information for utilities dealing with fire impacted waters with extremely high particulates. The results clearly demonstrate that DBP formation and MCL exceedances are of high concern during intense storm events and mobilization of DOM and DBP precursors during spring snowmelt. The findings indicate that advanced treatment (PAC, GAC, etc.) may be necessary to reach MCLs. Fortunately the City of Fort Collins was able to rely on their alternate water supply which was not impacted by the High Park Fire.

Optical properties as surrogates for DOM quantity and quality

The PARAFAC model validated for this study contains 6 components. Component 1 (C1) has a spectral shape consistent with a ubiquitous humic-like fluorophore (Figure 32). Component 2 (C2) has a red-shifted (longer wavelength and lower energy) humic-like spectrum. Component 3 (C3) had a blue-shifted (shorted wavelength and higher energy) humic-like spectrum. Component 4 (C4) has a spectrum similar to terrestrially-derived humic-like material. Components 5 and 6 (C5 & C6) have spectra resembling protein-like fluorophores similar to tyrosine and tryptophan, respectively. The relative abundance of these components was used to determine if proxies for DOC concentration and reactivity (i.e., DBP yields) could be developed using fluorescence metrics only.

Pairwise correlations between DOC concentration and optical properties yielded some significant correlations ($p < 0.05$) indicating that optical properties may be useful for estimating DOC concentration in the CLP watershed. DOC was positively correlated to $SUVA_{254}$ ($r^2 = 0.5417$, $p = 0.0006$), which is generally an indicator of the aromaticity of DOM (Weishaar et al. 2003). DOC was positively correlated to the relative abundance of C1, C2, and C6 and was negatively correlated to C3, C4, and C5. Although the correlations the PARAFAC component relative abundances were significant ($p < 0.05$), they are not particularly strong predictors of DOC concentration since the r^2 values were all below 0.7. However, the absorbance of the

sample at 254 nm was significantly correlated to DOC ($r^2 = 0.9352$, $p < 0.0001$) and may be the best proxy for DOC concentration in the CLP watershed.

In order to investigate relationships between DOM quality and reactivity within the drinking water treatment process we calculated the well characterized FI value (McKnight et al. 2001), that does not require PARAFAC modeling, and we calculated two ratios based on PARAFAC results from this study. The first was the sum of the relative abundance of the protein-like fluorescence (%C5 + %C6) and the second was the ratio of terrestrial to ubiquitous humic-like PARAFAC components (C4/C1). The relative abundance of the PARAFAC components and fluorescence metrics were correlated to TTHM, HAA5, and HAN yields. SUVA was well correlated to both TTHM ($r^2 = 0.7346$, $p < 0.0001$) and HAA5 ($r^2 = 0.7458$, $p < 0.0001$) yields, but not HAN yield ($r^2 = -0.5171$, $p = 0.0139$). Thus, the aromaticity of DOM may influence its reactivity towards DBP formation. C1 had the strongest correlation among the PARAFAC components to both TTHM ($r^2 = 0.8416$, $p < 0.0001$) and HAA5 ($r^2 = 0.7844$, $p < 0.0001$) yields. No significant correlations were found between the protein-like PARAFAC components and TTHM, HAA5, or HAN yields. Unlike the other classes of DBPs, HAN yields were well correlated only to C3, the blue-shifted humic-like PARAFAC component ($r^2 = 0.7194$, $p = 0.0001$). Based on these correlations, different DOM characteristics drive the formation of TTHMs and HAA5s compared to HANs. These fluorescence and PARAFAC based metrics may be useful for predicting the likelihood of formation of various classes of DBPs irrespective of DOC concentration and could serve as the basis for online monitoring within watershed.

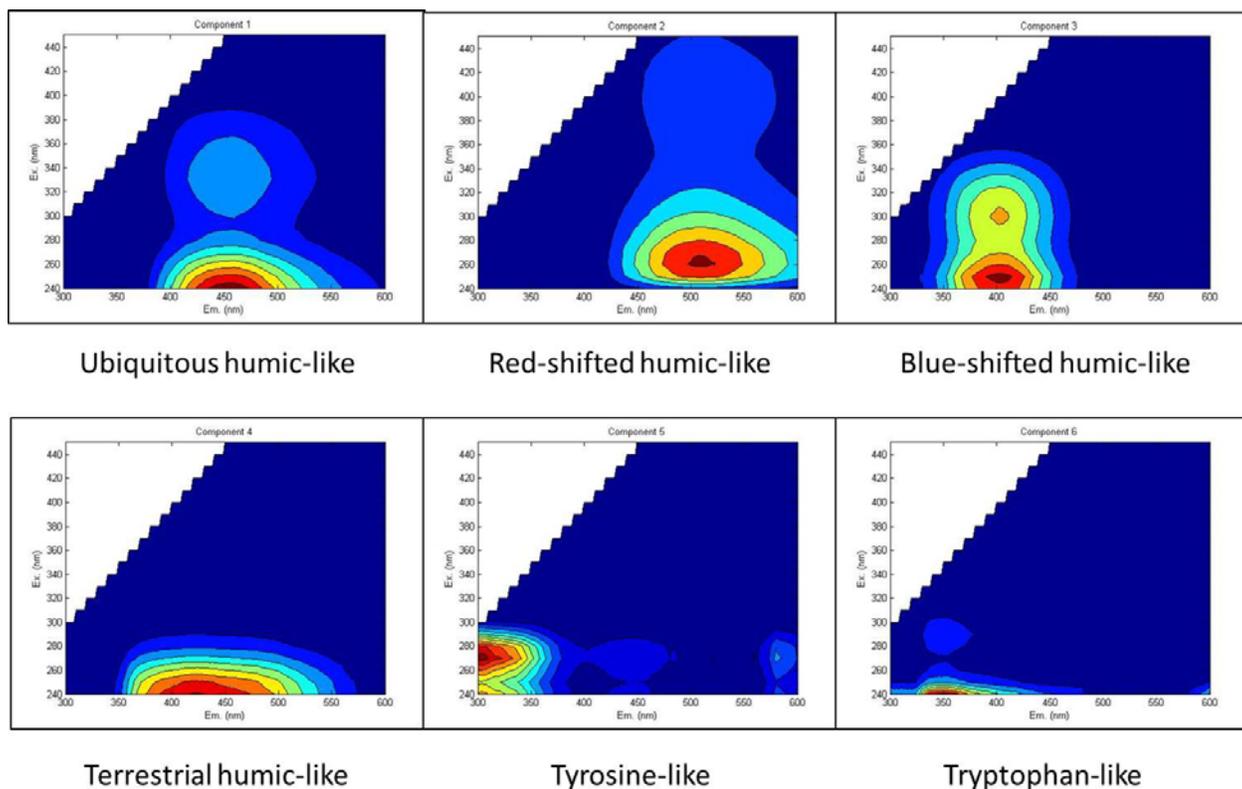


Figure 32. Spectra of the 6-component PARAFAC model developed for Poudre River samples. Emission wavelength is plotted on the x-axis and excitation wavelength is plotted on the y-axis. Identifications based on spectral characteristics are below each component.

Summary

This study evaluated the water quality, DOM properties and treatability of water samples collected from the CLP watershed after the High Park Fire. A total of 42 samples were collected, including bi-weekly samples and a series of storm events. The water quality results indicate that the main effect of the fire was the increased mobilization of nutrients, whereas the concentrations and properties of the DOM were similar between control and impacted sites, suggesting that the main source of the DOM is from upstream of the CLP watershed, from unburned areas. The formation of DBPs followed the DOC trends between sites and showed little variability, indicating again that the source of the DOM was mostly dominated by the upstream watershed. The use of fluorescence showed promise for following the impact of the wildfire on DOM properties and was more sensitive than other tools used. Further research with fluorescence analysis is needed in order to draw stronger conclusions.

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