Water quality following extensive beetle-induced tree mortality: Interplay of aromatic carbon loading, disinfection byproducts, and hydrologic drivers

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Keywords

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Abstract

The recent bark beetle epidemic across western North America may impact water quality as a result of elevated organic carbon release and hydrologic shifts associated with extensive tree dieback. Analysis of quarterly municipal monitoring data from 2004-2014 with discretization of six water treatment facilities in the Rocky Mountains by extent of beetle impact revealed a significant increasing trend in total organic carbon (TOC) and total trihalomethane (TTHM) production within high (~>50% areal infestation) beetle-impacted watersheds while no or insignificant trends were found in watersheds with lower impact levels. Alarming, the TTHM concentration trend in the high impact sites exceeded regulatory maximum contaminant levels during the most recent two years of analysis (2013-14). To evaluate seasonal differences, explore the interplay of water quality and hydrologic processes, and eliminate variability associated with municipal reporting, these treatment facilities were targeted for more detailed surface water sampling and characterization. Surface water samples collected from high impact watersheds exhibited significantly higher TOC, aromatic signatures, and disinfection byproduct (DBP) formation potential than watersheds with lower infestation levels. Spectroscopic analyses of surface water samples indicated that these heightened DBP precursor levels are a function of both elevated TOC loading and increased aromatic character. This association was heightened during precipitation and runoff events in high impact sites, supporting the hypothesis that altered hydrologic flow paths resulting from tree mortality mobilize organic carbon and elevate DBP formation potential for several months after runoff ceases. The trends found here likely underestimate the full extent of TTHM shifts due to monitoring biases with the extended seasonal release of DBP precursors increasing the potential for human exposure. Collectively, our analysis suggests that while water quality impacts continue to rise nearly one decade after infestation, significant increases in TOC mobilization and DBP precursors are limited to watersheds that experience extensive tree mortality.

1. Introduction

Recent drought and warmer temperatures associated with climate change have increased the magnitude and scale of forest mortality (Williams et al., 2010), with continued widespread conifer loss predicted in the coming decades (McDowell et al., 2015). These land cover disturbances can impact watershed hydrologic and biogeochemical cycles, as well as alter water quality and quantity making source waters more difficult to treat (*Agriculture, Hydrology and Water Quality*, 2002; Mikkelsen et al., 2013a; Smith et al., 2011; Tong and Chen, 2002). Additionally, these events may create the need for municipalities to more actively manage source waters or expand technologies used in drinking water treatment facilities to handle changes in influent water quality. For instance, forest fires and flood events are natural disturbances that rapidly alter surface waters, leading to an increase in nutrient content, suspended solids, and sediment loading in adjacent streams and storage reservoirs (Burke et al., 2013; Smith et al., 2011; Whitworth et al., 2012). Alternatively, anthropogenic disturbances such as timber harvesting can also impact organic carbon, major ions, and nitrate concentrations in proximal waters (Kalbitz et al., 2004; Likens et al., 1970; Vitousek et al., 1979). Studying shifts in vegetation response and biogeochemical cycling after forest disturbances can help predict and address water quality in analogously impacted systems.

Here, we focus on water quality effects associated with extensive tree mortality caused by the bark beetle epidemic in the Rocky Mountain region of North America (Raffa et al., 2008). Although indigenous, bark beetles have impacted millions of hectares of evergreen forest across the western United States and Canada over the last two decades due to warming temperatures and drought conditions (Park Williams et al., 2012; Raffa et al., 2008; Williams et al., 2010). Analogous infestations are also occurring in coniferous regions of Europe (Štursová et al., 2014) and Asia (Tokuchi et al., 2004) as well as deciduous portions of North America (Hermes and McCullough, 2014). As these infested forests die, shifts in aqueous carbon cycling have been shown to alter water quality (Mikkelsen et al., 2013b). The unique nature and delayed timeframe

of beetle-induced forest mortality makes this natural disturbance anomalous from more traditional studies of forest disturbance such as wildfire or timber harvesting (Adams et al., 2012; Mikkelsen et al., 2013a). Initially within the first year of infestation, tree death occurs and production of root exudates ceases causing a decline in organic carbon inputs into the soil (Moore et al., 2013; Štursová et al., 2014). After the tree stops transpiring, needles turn red and fall to the ground in a comparatively rapid pulse (1 to 3 years post-infestation). Eventually roots decompose and the tree falls to the forest floor (Mikkelsen et al., 2013a). Deposits of needles and other tree components after forest die-off contain high molecular weight compounds such as lignin and cellulose that are recalcitrant in character (Štursová et al., 2014; Weintraub et al., 2007). Annual litterfall rates double for several years after infestation (Kaňa et al., 2013) leading to elevated organic pools in upper soil horizons beneath impacted trees (Huber et al., 2004; Kaňa et al., 2013) which may change the composition of surface and ground water sources.

These waters can experience increases in disinfection byproduct (DBP) formation during drinking water treatment as added chlorine comes into contact with humic and fulvic fractions of natural organic matter. Resultant DBPs including trihalomethanes (THMs) and haloacetic acids (HAAs) (Grünwald et al., 2002; Jung and Son, 2008; Nikolaou and Lekkas, 2001) are regulated by the Environmental Protection Agency's (EPA) Stage 1 and 2 Disinfection Byproduct Rules and are known carcinogens (*Comprehensive Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2): Quick Reference Guide*, 2010; Richardson and Postigo, 2011). A recent investigation revealed elevated total organic carbon (TOC) levels in beetle-impacted municipal water sources compared to control municipalities, while median effluent DPB concentrations were tenfold higher in beetle-impacted municipalities compared to control municipalities (Mikkelsen et al., 2013b).

Although prior work has demonstrated that altered carbon cycling in infested forests increased TOC and subsequent DBP formation for municipalities reliant on source waters from beetle-impacted watersheds (Mikkelsen et al., 2013b), questions still exist regarding shifts in

organic carbon character and aromaticity following beetle infestation as well as the timeframe associated with these shifts. Furthermore, extensive forest mortality alters hydrologic processes that may impact water quality. Trees no longer transpire within one growing season following infestation, decreasing vegetative water uptake from the subsoil (Hubbard et al., 2013). The resulting loss of needles and canopy cover also decreases interception, changing soil moisture and snowmelt patterns (Biederman et al., 2012; Mikkelsen et al., 2013a). These alterations to the hydrologic cycle have been found to increase groundwater contributions to streams in the summer and fall months, change hydrologic flow paths, and create a lag in timing between annual peaks in TOC and DBP precursors that typically occur during spring runoff (Bearup et al., 2014; Mikkelsen et al., 2013b; Penn et al., 2016). Previous historical analysis was limited to quarterly TOC and DBP data collected by treatment facilities for regulatory compliance (*Comprehensive Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2): Quick Reference Guide*, 2010; Mikkelsen et al., 2013b). This constraint obscures questions relating to seasonal timing and hydrologic drivers of water quality, differences in treatment operation, confounding variability in the blending of surface and groundwater, delineation of groundwater capture zones (Bakker and Strack, 1996), and groundwater residence times that can mitigate water quality impacts associated with land cover change (Baker et al., 2000; McGuire et al., 2005). These limitations inhibit the kind of predictive understanding necessary to inform long-term management and technological evolution following forest disturbance.

Further investigation into water quality impacts following tree mortality can elucidate the timing and degree of organic matter loading in impacted watersheds along with changes in its structure. Noting the above limitations, our study analyzed additional historical water quality data coupled to a surface water sampling campaign conducted from 2013-2014 that was designed to improve the resolution and interpretation of water quality impacts with further delineation of degree and timeframe of beetle impact. The objective of this work was to evaluate differences in organic carbon loading, character, and DBP precursors derived from montane catchments with

varying degrees of beetle impact while delineating seasonal hydrologic shifts and drivers of these water quality parameters. The data presented here provides an example of how land cover change can alter biogeochemical cycling of carbon and associated shifts in seasonal water quality, which may be of interest to water providers and stakeholders experiencing beetle mortality or analogous watershed disturbances.

2. Materials and Methods

2.1 Watershed Classification

Beetle-impacted and control watersheds utilized by municipalities for drinking water in the Rocky Mountain region of Colorado were considered for analysis in this study. Historical water properties, water treatment practices, and soil characteristics are detailed in prior work (Mikkelsen et al., 2013b). Municipal sources that utilized surface water were further considered for water quality analysis (Table SI-1). After removing one municipality that obtained surface water from irregular sources (a reservoir and a spring fed stream), six municipalities were selected for historical analysis and the expanded sampling campaign (Figure 1).

Temporal quantification of beetle infestation was quantified within each delineated watershed using ArcGIS software and United States Forest Service (USFS) Aerial Detection Survey data from 1994-2013. This provides shapefiles of tree mortality with the associated damage causal agent. Only USFS shapefiles with bark beetles or disease complexes associated with beetle impact (5 needle pine decline, subalpine fir mortality, true fir pest complex, and pinyon pine mortality) listed as their damage causal agent were included in the analysis (*Areas with tree mortality from bark beetles*, 2014). The 2001 and 2011 National Land Cover Datasets (NLCD) were also used to determine the various land cover types in each watershed. The infestation shapefiles were then clipped by the evergreen and mixed forest land cover types found through the NLCD to ensure infestation areal accuracy.

After the infestation analysis, watersheds were labeled as either high, moderate, or low impact as of 2013 (Figure 1) to allow historical and averaged seasonal trends to be easily depicted and characterized. Watersheds with less than 20% infestation area were considered low impact and were used as healthy controls (Aspen and Carbondale), watersheds with 20-40% infested area were considered moderate impact (Gypsum and Glenwood Springs), and watersheds with greater than 40% infested area were considered high impact (Granby and Steamboat).

Figure 1. Map of beetle infestation and the 6 sample locations analyzed in the study with diamonds denoting high beetle impact, squares denoting moderate impact, and triangles representing low impact watersheds. The inset depicts beetle infestation temporal trends from 2000-2013 for the analyzed

watersheds delineated into the three infestation bins. The percent of forested area within each watershed impacted by bark beetles as of 2013 (as opposed to total area) is provided to the right of inset legend.

2.2 Long-Term Trends

Historical trend analysis of TOC and DBP concentrations was conducted beginning in 2004 with the introduction of expanded EPA regulatory monitoring requirements through 2014 to allow characterization prior to and following beetle infestation and build upon previous published historical analyses (Mikkelsen et al., 2013b). Historical water quality data were collected primarily from the Colorado Department of Public Health and Environment. Any missing data were collected directly from water-treatment facility archives. Data were quality checked and boundaries were established as follows: (1) TOC concentrations that were 250% greater than the average monthly value were removed (limited to Granby in October, 2004) to correct for sample bias or extreme weather events and (2) recorded TOC and DBP concentrations below detection levels were reassigned to analytical detection thresholds of 0.5 mg/L for TOC and 1 ug/L for DBPs.

2.3 Influent Water Collection

Aqueous samples were collected at municipal surface water intakes or sampling nozzles prior to the application of water treatment processes within 8 hours of one another for all six water treatment facilities during each sampling date. Samples were collected in amber glass bottles approximately monthly at each municipality during the snow-free window of May 2013 through December 2013 and more frequently during runoff events for improved water quality resolution. Four additional samples were taken from each municipality in the snow-free portion of 2014 as additional time points prior to, during, and after runoff. During winter months, samples were not collected as water characteristics were stable and because of weather-related access issues. Once collected, samples were shipped overnight on ice for laboratory analyses.

2.4 Water Quality Analyses

Influent water samples were tested for TOC, total nitrogen (TN), DBP formation potential, UV, and fluorescence. TOC and TN were analyzed using a Shimadzu TOC-V_{CSH} with a TNM-1 unit after acidification using 0.1 M HCL. The DBP formation potential test was performed using Standard Method 5710. Samples were chlorinated at various concentrations using a sodium hypochlorite dosing solution, buffered to a pH of 7 with phosphate (10 mM final concentration), and left at room temperature (approximately 21°C). After seven days, free chlorine was measured and samples with a concentration closest to 3-5 mg/L (optimal for analysis by ensuring complete DBP formation) were then quenched. Chloroform, bromoform, bromodichloromethane, and dibromochloromethane were measured using a purge and trap gas chromatography-mass spectrometer system, which were summed and reported as total trihalomethanes (TTHM) (U.S. EPA Method 524.2). Concentrations of monobromoacetic acid, dibromoacetic acid, monochloroacetic acid, dichloroacetic acid, and trichloroacetic acid were analyzed using liquid-liquid extraction followed by a gas chromatography-electron capture detector system (U.S. EPA Method 552.2), and were summed and reported as five haloacetic acids (HAA5). DBP concentrations were measured prior to the addition of chlorine during the early sampling events and concentrations were found to be below detection limits.

UV spectroscopy was conducted using a PerkinElmer Lambda 45 UV/VIS spectrometer. Total specific UV absorbance (TSUVA) or the carbon-normalized aromaticity was calculated by dividing UV absorbance at 254 nm by TOC concentration which can indicate the degree of disinfection byproduct formation potential of a water sample (Kitis et al., 2001). Excitation emission matrices (EEM) were also collected using a scanning fluorometer (PTI QM4) for excitation wavelengths from 240 to 470 nm in 2.5 nm steps and emission wavelengths from 280 to 580 nm in 1 nm steps. UV correction was conducted by running DI water blanks in conjunction with each sample to remove Raman scattering. The resulting EEMs were then carbon normalized

and used to provide additional information on organic matter character. Specific peak intensities in the A and C regions were calculated. These peaks are associated with humic-like fluorescence with Peak C correlating with hydrophobicity, aromaticity, and THM formation potential (Bieroza et al., 2009; Coble, 1996; Kalbitz et al., 1999). Fluorescence index (FI) was calculated from the ratio of intensities at emission wavelengths 470 and 520 nm (both at an excitation wavelength of 370 nm), which has been used to distinguish sources of aquatic fulvic acids (McKnight et al., 2001). Fluorescence regional integration (FRI) of 5 regions within the EEMs was also conducted to further quantify carbon character signatures (Chen et al., 2003). Additional information regarding carbon character analysis can be found in the supplementary information.

2.5 Hydrologic Data

Stream discharge data were collected during the ice-free season for 3 watersheds that contained USGS gauges (Aspen, Granby, and Steamboat). The gauge for Steamboat was located at the water quality sampling point while the other two gauges were located either upstream or downstream of the sampling location. Monthly precipitation rates and monthly average temperatures from 2004-2014 and 30-year normals were collected from the National Climatic Data Center. Gauges closest to the watershed sampling points were selected for analysis. While a gauge collecting 30-year normals for Carbondale was not identified, climatic data for Glenwood Springs and Aspen likely reflects general trends in Carbondale due to their proximal nature (within 30 km).

2.6 Statistical Analyses

Linear regression was utilized to determine historical trends in TOC, DBPs, and climate data from 2004-2014 in accordance with prior approaches (Mikkelsen et al., 2013b). All historical water quality and climate data utilized to investigate long-term trends were decomposed using

moving averages to smooth seasonal differences. The Mann-Kendall test was then utilized to determine if decomposed trends were significantly different from zero (R Core Team, 2015). Friedman Tests were used to determine significant differences between high, moderate, and low impact sites for each water quality parameter investigated during the sampling campaign. A post-hoc Wilcoxon test was then used to evaluate significant differences between two bins and compared high to moderate, high to low, and moderate to low impacted sites for all collected samples. Mann-Whitney tests were utilized to determine significance between 2013-2014 climate data and 30-year normals. Pearson correlations were used to determine correlations between UV₂₅₄, TSUVA, and DBP formation potential. P-values ≤ 0.05 were considered significant throughout the study.

3. Results and Discussion

3.1 Decade-Long Trend Toward Impaired Water Quality

Quarterly regulatory monitoring data collected by water treatment facilities from 2004 through 2014 were used to better understand temporal impacts of large-scale beetle-induced forest mortality on water quality (Figure 2). Initially identified in a prior study that contrasted impacted versus control regions (Mikkelsen et al., 2013b), watersheds were further discretized into 3 impact level bins. In conjunction with temporal evolutions of beetle impact, this provides the ability to query associations between potential thresholds of infestation, water quality shifts, and watershed hysteresis. This analysis also included 3 additional years of data from 2012-2014 as well as filled gaps in missing TOC concentration data for all watersheds from 2006-2008. Both high impact watersheds reached at least 41% areal infestation by bark beetles between 2004 and 2007 with areal infestation in each watershed reaching approximately 50% or higher by 2008 (Figure 1). This corresponds to enhanced needle drop between 2006 and 2009 (three years post infestation) allowing trends to be analyzed prior to and following infestation. Moderate impacted

sites contained between 26-29% areal infestation with low impact sites containing <13% infestation.

Results indicate a statistically significant increasing trend of $0.04 \text{ mg TOC L}^{-1} \text{ yr}^{-1}$ for the high impact watersheds while a similar trend in the moderate and low impact sites was not found. High impact sites also displayed a significant increase of $2.37 \text{ ug TTHM L}^{-1} \text{ yr}^{-1}$ while an increasing trend in watersheds with less beetle infestation was not observed. Alarming, the slope for TTHMs has gotten steeper with time since 2008 while the extended analysis through 2014 reveals that the increasing TTHM trend in the high impact sites has continued for nearly a decade after initial peak tree mortality. This observation highlights the long-term effects associated with recalcitrant needle and woody debris degradation and water quality shifts associated with this form of forest disturbance. The long-term extent and timeframe of water quality shifts with beetle infestation is still unknown; therefore, continuing water quality monitoring as depicted here is important in elucidating how long these effects will last. HAA5 analysis was also conducted but results were inconclusive due to unavailable data (Gypsum, Carbondale, Glenwood Springs) during portions of the analysis period or sample error (4 quarterly samples were below or near the detection limit of 1 ug/L for Granby while the majority of samples contained at least 15 ug/L).

Analysis of the three infestation bins, while limited in number, alludes to the interpretation that water quality impacts may not be altered until a high level of tree mortality occurs ($\sim > 50\%$ areal infestation), with possible mitigating factors keeping water quality stable in lower impact watersheds. If water quality continues to exceed regulatory levels, alternative water sources or enhanced treatment techniques may need to be adopted to decrease DBP precursor levels and formation. Collectively, results demonstrate continuing increases in organic carbon loading and DBP precursor levels associated with beetle-induced forest mortality well after maximal infestation and suggest a heightened TTHM response in the heavily impacted watersheds beyond that observed in a prior 2004-2011 analysis (Mikkelsen et al., 2013b).

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318 **Figure 2.** Analysis of compiled water quality data obtained from six water treatment facilities reveals an
 319 increasing trend in high impact watersheds compared to lower impacted facilities. Panels depict water
 320 quality data from 2004-2014 where **a-c.** display binned TOC concentrations and **d-f.** portray binned TTHM
 321 concentrations in high (red diamonds), moderate (orange squares), and low impact (green triangles)
 322 watersheds with a regulatory TTHM maximum contaminant level (MCL) of 80ppb (*Comprehensive*
 323 *Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2): Quick Reference Guide*, 2010). P-
 324 values were found through the Mann-Kendall test after decomposition with significance demonstrating a
 325 departure from a slope of zero. Trends for individual watersheds revealed similar results and can be found
 326 in Table SI-2.

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328 Importantly, during the most recent two years (2013-14) the trend analysis for the high
 329 impact sites exceeded the maximum contaminant level (MCL) of 80 ug TTHM L⁻¹ (Figure 2d).
 330 Discreet analysis of each of these impact sites reveals that Steamboat Springs exceeded TTHM
 331 and HAA5 MCLs during 3 quarters while Granby exceeded the TTHM MCL during one quarter
 332 between 2011-2014 (Table SI-3). This increasing trend is particularly alarming as water
 333 municipalities are only required to sample for DBPs once each quarter and can select a sampling
 334 date within this window; hence municipal reporting contains an inherent bias that may not

accurately capture seasonal fluctuations in water quality. For example, the average quarter 2 and quarter 3 sampling dates for all municipalities in this study from 2004 to 2013 was May 14th and August 17th. When evaluating the high impact sites only, the average second quarter sampling date shifted almost two weeks earlier to May 3rd. The water quality data collected in the following portion of this study showed TOC and DBP formation potential peaked with runoff in early to mid-June in both years analyzed (Figure 3). Therefore, by collecting quarterly water quality data prior to and after runoff, municipalities are not capturing maximal peaks in TOC and DBP formation in their water treatment systems. Hence, trends obtained from municipal data may underestimate the increase in water quality impacts from beetle infestation or other analogous shifts in land cover, demonstrating the importance of more frequent monitoring.

Although this data mining approach provides long-term data allowing TOC and TTHM shifts with beetle infestation to be investigated, several caveats exist that limit interpretation. As with many large datasets collected from multiple participants, not all data during the analysis period was available for all watersheds. Granby, Steamboat, and Aspen had complete quarterly datasets for DBPs; however, Gypsum, Glenwood Springs, and Carbondale moved to a reduced monitoring schedule in the later half of the analysis period, only recording values once a year. This prevented the calculation of a TTHM p-value for the moderate impact sites. Besides missing data, Carbondale and Gypsum TOC concentrations were typically below detection limits. These municipalities rely primarily on groundwater sources that are occasionally blended with surface waters, which lower TOC concentrations and DBP precursor levels as seen here. Groundwater may also mitigate detection of water quality shifts due to longer residence times and unclear delineation of supply capture zones. Elevated aromatic carbon character may also increase DBP production, but data evaluating carbon structure are not typically analyzed by these treatment facilities and were unavailable.

3.2 Carbon Loading and Aromatic Character

Due to these limitations with the water provider data, an independent sampling campaign was conducted in the six identified watersheds from 2013-2014 to increase the resolution of TOC and DBP data. The goal was to better understand TOC properties and potential for DBP formation as well as to allow a more refined temporal analysis so that hydrologic drivers of water quality could be investigated. Only surface waters were analyzed and carbon character analyses were conducted to determine if differences in aromatic structure exist in watersheds with variable beetle-induced tree mortality. The additional sampling campaign also alleviates inherent uncertainties in the historical analysis associated with variable water treatment operation, ground versus surface water sources, sample timing, and other collection biases.

Results from two concurrent snow-free seasons (~1.5 years) of surface water sampling and characterization aided in the interpretation of surface water property shifts associated with beetle infestation. High impact watersheds exhibited the most elevated organic carbon loading with average TOC concentrations 3 to 5 times higher than the moderate and low impact sites (Figure 3a). Moderate impact watersheds displayed TOC concentrations that resided between those found in high and low impact sites. The smallest TOC concentrations were found in low impact watersheds with concentrations typically below 1 mg L^{-1} . Although nitrate concentrations are often significantly elevated after forest disturbances such as timber harvest (Burns and Murdoch, 2005; Feller and Kimmins, 1984), the total nitrogen concentrations in this study were often below the detection limit (0.2 mg-N/L). This supports findings of a minimal stream water nitrate response following beetle infestation in Colorado (Rhoades et al., 2013) and highlights the unique nature of this type of disruption when contrasted with timber harvest, windfall, fire or other abrupt forest disturbance (Adams et al., 2012).

Figure 3. Increases in organic carbon concentration, aromatic content, disinfection byproduct formation potential, and relationship to stream discharge are apparent when contrasting high, moderate, and low bark beetle-impacted watersheds (red diamonds, orange squares, and green triangles respectively). Panels display **a.** total organic carbon concentration **b.** total trihalomethane (TTHM) formation potential and **c.** discharge flow rates for two high impact watersheds (Granby, Steamboat) and one low impact watershed (Aspen). Water quality points represent the average value of the two watersheds in each infestation bin with error bars denoting sample values. Averaged total specific ultraviolet absorbance (TSUVA) and five haloacetic acid (HAA5) formation potential across the sampling period are shown to the right of panels **a**

and **b** with their corresponding standard deviations. Additional plots displaying water quality parameters for each individual watershed are shown in Figure SI-1.

In addition to increased organic carbon loading in impacted watersheds, the deposition of needle and tree material to the forest floor after beetle-induced forest mortality (Kaňa et al., 2013; Mikkelsen et al., 2013a) may change the structure and aromaticity of carbon transported to surface water sources used by municipalities (Beggs and Summers, 2011). After infestation, fallen needles and woody material continue to degrade which may increase leachate TSUVA, specific humic peak intensities, and lignin-associated carbon further elevating aromatic structure (Beggs and Summers, 2011; Kalbitz et al., 2006; Yavitt and Fahey, 1986). To investigate this phenomenon, TSUVA was calculated to provide a carbon-normalized value of UV absorbance to evaluate differences in aromatic structure. Averaged TSUVA values were 150% higher in the high impact sites compared to moderate and low impact watersheds, which tended to overlap throughout most of the study (Figure 3a, Figure SI-1b). The increased TSUVA in surface waters exhibited here at the catchment scale in high impacted watersheds supports prior findings of elevated soil digest TSUVA found below trees in beetle infested forest plots when contrasted with uninfested controls (Kaňa et al., 2015).

Analysis of EEM results further confirms that elevated aromatic character is found within beetle-impacted watersheds compared to healthy controls (Table 1). Averaged FI values were inversely proportional to impact, ranging from a high of 1.42 for Aspen to a low of 1.28 in Steamboat Springs. These results are consistent with terrestrially derived fulvic acids compared to microbially derived sources that typically have FI values around 1.9 (McKnight et al., 2001). The high impact watersheds also exhibited elevated carbon-normalized fluorescence in peak A and peak C specific intensities along with the humic and fulvic acid-like fluorescence regions. Averaged humic-like peak intensities were 18 to 54% and 22 to 45% higher in the peak A and C regions, respectively, for the high impact watersheds compared to the low impact watersheds.

Similarly, the averaged regional fluorescence in the high impact sites was elevated by 35-75% in the fulvic acid-like region and 17-47% in the humic acid-like region compared to the low impact watersheds. The moderately impacted watersheds displayed peak intensity and regional fluorescence values that were between the high and low impact watersheds.

Table 1. Fluorescence index (FI), carbon normalized specific peak intensity, and carbon normalized fluorescence regional integration (FRI) results. Units are RU L mg_c⁻¹ for peak intensities and FRI.

Treatment Facility	Impact Level	FI	Specific Peak Intensity		FRI	
			Humic-Like		Fulvic Acid-Like	Humic Acid-Like
			Peak A	Peak C	Region 3	Region 5
Steamboat Springs	High	1.28 ± 0.04	0.232 ± 0.080	0.073 ± 0.022	0.066 ± 0.021	0.020 ± 0.006
Granby		1.35 ± 0.05	0.292 ± 0.108	0.080 ± 0.025	0.085 ± 0.029	0.022 ± 0.007
Gypsum	Moderate	1.39 ± 0.06	0.216 ± 0.086	0.065 ± 0.021	0.062 ± 0.022	0.018 ± 0.006
Glenwood Springs		1.41 ± 0.04	0.217 ± 0.093	0.070 ± 0.022	0.063 ± 0.023	0.020 ± 0.006
Carbondale	Low	1.39 ± 0.04	0.189 ± 0.076	0.060 ± 0.019	0.052 ± 0.018	0.017 ± 0.005
Aspen		1.42 ± 0.04	0.196 ± 0.094	0.055 ± 0.020	0.053 ± 0.022	0.015 ± 0.006

3.3 Disinfection Byproduct Formation Potential

As most municipalities located in beetle-impacted regions of the Rocky Mountains use chlorine as a disinfectant during drinking water treatment, differences in DBP formation potential were also analyzed for the collected water samples. The uniform potential test was employed to evaluate the formation potential of THMs and HAAs as a more absolute measurement of water properties free from individual municipality management, sampling time, or water treatment biases (Figure 3b). Chlorinated species dominated this analysis (chloroform, dichloroacetic acid, trichloroacetic acid) with concentrations of brominated DBP species typically falling below detection limits. Waters from high impact sites produced both TTHM and HAA5 concentrations that were typically 3 to 6 times higher than the formation potentials found in the moderate and low impact watersheds. HAA5 formation potentials were typically higher than TTHM formation potentials during the sampling period but both DBPs displayed similar temporal trends for each infestation bin.

To evaluate the importance of aromatic structure on the formation potential of DBPs, correlation plots were created between TSUVA and DBP formation potential for all samples collected (Figure SI-2). Positive correlations between DBP formation potential and TSUVA were found which is typical during aromatic analysis (Jung and Son, 2008) and confirms the validity of elevated DBP formation from increased aromaticity in our study watersheds ($R^2 = 0.58$, P -value ≤ 0.001). This correlation also indicates that elevated aromatic character seen in the high impact sites increases DBP precursors throughout the year. The matching trends between TOC and DBP formation potential (Figure 3) indicate that temporal variations in TOC loading in impacted watersheds drives the seasonal fluctuations seen in DBP precursor levels.

Statistical tests were also performed for the parameters analyzed during surface water sampling to determine if significant differences exist across infestation bins (Table 2). All water quality parameters were found to be significantly different when contrasting all bins using the Friedman test. When analyzing across two bins, significant differences between high-moderate and high-low were further revealed for TOC, UV_{254} , TSUVA, HAA5, and TTHM formation potential using a post-hoc Wilcoxon test. The post-hoc Wilcoxon test also found significant differences between the moderate and low bins for TOC and UV_{254} .

Table 2. Statistical differences between infestation bins for all water quality parameters analyzed were found through the Friedman and the post-hoc Wilcoxon tests with bold values indicating significant p-values.

Parameter Tested	Friedman Test		Post-hoc Wilcoxon Test p-values		
	p-value	chi-squared	High-Moderate	High-Low	Moderate-Low
TOC	< .001	44.087	< .001	< .001	< .001
UV 254	< .001	40.783	< .001	< .001	< .001
TSUVA	< .001	31.565	< .001	< .001	1.000
HAA5 FP	< .001	32.818	< .001	< .001	.300
TTHM FP	< .001	35.182	< .001	< .001	.130
FI	< .001	23.645	.001	< .001	1.000
Specific Peak A	.001	13.875	.620	.110	1.000
Specific Peak C	< .001	18.375	.900	.055	.543
FRI Region 3	< .001	19.625	.507	.055	.328
FRI Region 5	.007	9.875	1.000	.091	.507

Collectively, these results support the hypothesis that watersheds experiencing bark beetle-induced forest mortality produce an elevated concentration of organic carbon that also contains more aromaticity than unimpacted forests. The elevated TOC concentrations, increased aromatic signature, and TTHM formation potential in impacted watersheds supports historical data archived by municipalities presented both here and previously (Mikkelsen et al., 2013b), while bringing strong insights into unanswered questions about this trend. For instance, HAA5 formation potential in collected influent surface water was higher than TTHM formation potential and was significantly different between bins (Figure 3b, SI Figure 2 c-d). This contrasts with HAA5 concentrations reported by municipalities which were lower than TTHMs and were not found to increase significantly with beetle infestation (Mikkelsen et al., 2013b), which could be explained by the removal of humic-like HAA precursors (Hua and Reckhow, 2007) during water treatment prior to chlorination. Unlike the historical analysis of municipal data, the collected surface water samples were untreated waters. Therefore, the HAA5 formation potential in high impact sites is likely elevated compared to TTHM formation potential (Figure 3) due to the enhanced levels of humic-like substances as well as wood-derived lignin phenols which are more important precursors for HAA formation (Hua et al., 2014). Additionally, the differences in HAA formation between historical and sampled results could occur from bias in the formation potential test from high chlorine dosing, which may preferentially create reactions forming HAAs that would not otherwise occur from chlorine dosing at lower concentrations typical at water treatment facilities. This supports effective practitioner judgment at these municipalities and illustrates the importance of minimal dosing in decreasing DBP production.

3.4 Climatic and Vegetative Differences Between Watersheds

Several climatic factors such as precipitation and temperature along with differences in vegetation could contribute to the variations in historical and sampled water quality; however, these variables were analyzed and beetle-induced forest mortality is still the most probable cause. Trends in temperature and precipitation from 2004-2014 were typically insignificant (Table 3a). Any significant trends found were expected to limit shifts in water quality rather than induce them. Additionally, monthly temperatures and precipitation in each watershed during the 2013-2014 sampling campaign, which was when TTHM trends exceeded MCLs, were not found to be significantly different from their respective 30-year normals.

In headwater catchments similar to the watersheds analyzed here, organic matter primarily originates from terrestrial vegetative sources (Hood et al., 2005); therefore, ecological differences may play a role in water quality and were also investigated (Table 3b). Barren land cover was elevated in the low impact watersheds, comprising 26-44% of the total watershed area compared to the moderate and high impact sites, which contained less than 4% barren land. This may explain why TOC concentrations in the low impact control sites were consistently lower and displayed limited seasonal peaks than watersheds with more pronounced beetle infestation both when evaluating historical results and during the surface water sampling campaign. Although this vegetative difference between the healthy controls and more impacted sites confines interpretation, the vegetative area was similar between the high and moderate impact watersheds (89 to 99% vegetated: area without barren land, perennial snow/ice, or development) yet clear differences in historical and sampled TOC concentrations and DBP precursor levels were found. More detailed analysis of climatic and vegetative differences between watersheds is presented in the Supplemental Information.

Table 3a. Precipitation and temperature trends from 2004-2014 and P-values comparing monthly precipitation and temperature data for 2013 and 2014 to 30-year normals

Watershed	Historical Climate Trends				Climate Differences Between Sample Year and 30-yr Normals			
	Precipitation Slope (mm yr ⁻¹) and P-value		Temperature Slope (mm yr ⁻¹) and P-value		2013 Precipitation P-value	2014 Precipitation P-value	2013 Temperature P-value	2014 Temperature P-value
Steamboat Springs	-1.42	<0.001	-0.01	0.418	0.126	0.889	0.952	0.976
Granby	-1.13	<0.001	N/A ¹	N/A ¹	0.667	0.873	N/A ¹	N/A ¹
Gypsum	-0.29	<0.001	0.04	0.169	0.889	N/A ¹	0.928	0.928
Glenwood Springs	0.04	0.066	N/A ¹	N/A ¹	0.509	0.126	N/A ¹	N/A ¹
Aspen	0.22	0.708	-0.07	<0.001	0.889	0.401	0.667	0.795

Climatic data were either unavailable or contained missing data¹

Historical P-values were calculated from the Mann-Kendall test following decomposition

2013 and 2014 P-values were calculated using the Mann-Whitney test

Table 3b. Land cover percentages for each watershed

Watershed	Evergreen Forest	Deciduous & Mixed Forest	Shrub, Herbaceous, & Pasture	Wetlands	Developed	Barren Land & Perennial Snow
Steamboat Springs	53.3	15.1	21.1	9.1	0.2	0.4
Granby	67.7	1.8	16.2	3.6	1.7	9.0
Gypsum	40.8	31.5	24.0	0.5	0.0	3.1
Glenwood Springs	35.8	17.9	43.6	2.3	0.0	0.2
Carbondale	27.6	19.6	9.2	0.0	0.0	43.6
Aspen	28.5	17.5	25.2	2.4	0.0	26.3

3.5 Hydrologic Connection to Organic Carbon Fluctuations

Carbon transport from its vegetative source to water municipality intakes is dependent on runoff and precipitation events (Dawson et al., 2008; Xu and Saiers, 2010). As such, we investigated the impact altered hydrologic processes have on water quality after tree dieback. Following beetle-induced tree mortality, transpiration ceases and canopy interception of precipitation declines as needles and branches fall to the forest floor (Mikkelsen et al., 2013a; Pugh and Gordon, 2013). This causes a decline in subsurface water demands and an increase in soil moisture (Adams et al., 2012), which have been found to increase late summer groundwater contributions in beetle-impacted watersheds and subsequently increase water table levels (Bearup et al., 2014; Penn et al., 2016). Natural organic matter concentrations are elevated in soil profiles closer to the ground surface and decline with depth and distance from their vegetative source (Mei et al., 2012; Michalzik and Matzner, 1999; Neff and Asner, 2001). Additionally, aromatic and hydrophobic organic carbon is generally less mobile and therefore concentrated in higher soil profiles (Jardine et al., 1990). These hydrophobic fractions tend to stay in the upper soil layers

during average soil moisture conditions and remobilize during precipitation events (Jardine et al., 1990). It follows that higher water table levels potentially mobilize pools of organic matter with higher aromatic content and decrease the degradation potential of mobile aqueous carbon due to shorter subsurface residence times (Mei et al., 2012).

This potential mechanism may partially explain the elevated TOC and aromaticity in surface waters associated with beetle-induced forest mortality (Graphical Abstract). Peaks in TOC and DBP formation potential at the impacted sites occurred during both seasonal runoff events captured in the study (Figure 3). During the first snowmelt-driven event, DBP formation potential peaked at the moderately impacted sites with runoff (early June 2013) and dropped down to a value similar to the low impact watersheds when discharge returned to baseflow conditions the following month. The DBP formation potential in high impact sites also peaked concurrently; however, DPB formation potential did not decline as rapidly and displayed a tailing effect, not reaching the lowest concentrations until the late summer and fall months. This tailing event may be indicative of increased mobilization resulting from elevated groundwater contributions and changing flow paths. TOC concentrations and DBP precursor levels reach an annual low point in the fall as colder temperatures decrease debris degradation (Davidson and Janssens, 2006), rainfall precipitation switches to snowfall, and water flow through the vadose zone declines.

The spike in DBP formation potential during mid-September 2013 in the high impact sites (Figure 3b, Figure SI-1) also revealed the importance of rainfall events in mobilizing organic carbon. This spike coincided with a historic precipitation and flooding event that occurred east of the analyzed watersheds in the front range of Colorado (Brennan and Aguilar, 2013). After comparing 30-year normal rainfall rates to their observed monthly totals, results indicated that all studied watersheds experienced rainfall rates that were approximately double the 30-year average during September 2013 (Table SI-5). USGS gauges also saw a rise in discharge during this time period. Importantly, even though all watersheds experienced a pulse of water during this large precipitation event, TOC and DBP formation potential spiked only within the high impact sites

indicating elevated mobilization of excess carbon in high impact watersheds. Although empirical (Bearup et al., 2014) and modeling (Penn et al., 2016) studies have demonstrated rising water tables following beetle infestation, future studies can target this hydrologic mechanism to further elucidate its effect on water quality while answering more detailed inquiries related to variable subsurface carbon pools, seasonal timing and degree of water table variation following beetle infestation, and quantification of water quality shifts related to elevated hydrologic flow paths.

3.6 Water Quality Management and Environmental Implications

From a public health and regulatory perspective, municipal monitoring has revealed that DBP concentrations are now exceeding regulatory limits at high impact sites (Figure 1), and our analysis of this historical data in complement to our more rigorous surface water characterization suggests that biases in collection are likely underestimating the extent of this challenge. Watershed monitoring and management could be used to help municipalities understand and predict influent water quality properties to enhance water treatment efficacy, offer cost effective alternatives, and provide safer water for human consumption (Foran et al., 2000; Postel and Thompson, 2005). To be proactive in watershed protection, municipalities could conduct additional water quality sampling during runoff or precipitation events that mobilize contaminants of concern, particularly if their watershed is beetle-impacted. Implementing increased monitoring may also help better inform operators of the timing of contaminant loading within their watersheds, help predict when future contaminant spikes may occur, and aid in the selection of water treatment techniques that alleviate water quality impacts. For instance, the strong correlation in these watersheds indicates that monitoring UV_{254} could provide real time water quality characterization particularly during hydrologic events to aid in predicting DBP formation potential (Figure SI-2) or provide insight into when alternative disinfection processes could best be utilized.

It is possible that high impact water treatment facilities may need to consider alternative waters during high flow events or retrofit or expand existing treatment technologies if increases in DBP formation continue to surpass regulatory MCLs. Treatment technologies such as coagulation, filtration through granular activated carbon, or alternative disinfectant strategies such as chloramination can also lower TOC concentrations and DBP production (Singer, 1994). Municipalities may also mitigate the effects caused from watershed disturbances through source strategies such as blending surface and groundwater particularly during higher risk windows. Because groundwater contains lower levels of organic carbon in the Rocky Mountain Region (Bauch and Bails, 2004; Thurman, 1985) and can help protect against threats from land cover change or anthropogenic surface contamination (Custodio, n.d.; Metcalf and Robbins, 2013), municipalities that rely solely on surface water sources are more susceptible to water quality shifts toward MCL concentrations. Diversification to include a mix of surface and groundwater sources can provide safeguards against unanticipated water quality shifts as well as provide a low organic carbon groundwater source for blending or bypass during hydrologic events. Furthermore, groundwater can provide additional water during times of peak water demand which usually occurs in the summer months (Kenney et al., 2008) when TOC concentrations in surface waters are elevated.

The findings disseminated within our study reveal how shifts in biogeochemical cycling associated with ecological disturbances can have secondary effects on water resources altering TOC loading and DBP precursor levels. Although expanded tree fall will occur and increased TOC loading could continue with subsequent degradation of tree biomass, mitigating factors may begin to alleviate this concern. As regrowth of saplings and other vegetation occurs, increased transpiration may return groundwater contribution and water table depth to pre-infestation levels alleviating the changes associated with hydrologic flow paths (Bearup et al., 2014). Additionally, microbial communities have been found to shift in beetle-impacted forests (Mikkelsen et al., 2016) with a larger abundance of saprotrophic taxa that may increase the utilization and

degradation of woody material and decrease aromatic TOC loading into surface water sources (Štursová et al., 2014). Forest lands are an important source for safe and reliable drinking water globally; however, natural disturbances are predicted to create large changes in forested regions under a changing climate (Furniss, 2011; Williams et al., 2010). In extreme instances, extensive forest die-off can also have global consequences when forests switch from a carbon sink to a carbon source (Kurz et al., 2008; Schwalm et al., 2012). As such, understanding the shifts in biogeochemical cycling that occur following land disturbance is imperative in safeguarding these vital water sources while enabling more informed water resources management.

4. Conclusions

The water quality analyses presented here reveal that increased TOC loading and aromatic content from beetle-infested watersheds is reaching surface waters used by drinking water treatment facilities. This results in elevated DBP precursor levels particularly during rainfall and snowmelt events when organic carbon is mobilized. Additionally, while DBP precursors are typically elevated during runoff, concentrations in high impact sites may stay elevated for months afterward due to altered hydrologic flow paths and increased TOC mobilization. TTHM concentrations have continued to rise for nearly a decade after peak initial tree mortality demonstrating the long-term effects on water quality associated with this type of forest disturbance. Furthermore, this trend obtained from municipal data likely underestimates the full extent of water quality shifts due to collection biases. Alarming, TTHM concentrations have begun to exceed the regulatory MCL of 80 ug/L at sites hardest hit by bark beetle infestation. While clear differences in water quality were found between three infestation level bins (Figure 2 and 3), differences between the high versus moderate impact watersheds provide the most compelling contrast due to their ecological similarities and reveal a trend of heightened TOC mobilization following runoff and precipitation in the high impact sites. Our analysis also suggests that water quality is stable until a certain infestation threshold is exceeded (~>50%

watershed areal impact) enabling the identification of regions where water resources are most likely to be adversely affected. If these trends continue, high impact sites may need to adopt enhanced water quality monitoring, alternative treatment techniques, or utilize different water sources to reduce TOC levels and DBP production to protect human health.

Abbreviations

DBP	disinfection byproducts
EEM	excitation emission matrices
FI	fluorescence index
FP	formation potential
FRI	fluorescence regional integration
HAA5	five haloacetic acids
MCL	maximum contaminant level
TN	total nitrogen
TOC	total organic carbon
TSUVA	total specific ultraviolet absorbance
TTHM	total trihalomethane
UV ₂₅₄	ultraviolet absorbance spectroscopy at 254 nm

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