Water-quality impacts from climate-induced forest die-off

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Increased ecosystem susceptibility to pests and other stressors has been attributed to climate change¹, resulting in unprecedented tree mortality from insect infestations². In turn, large-scale tree die-off alters physical and biogeochemical processes, such as organic matter decay and hydrologic flow paths, that could enhance leaching of natural organic matter to soil and surface waters and increase potential formation of harmful drinking water disinfection by-products^{3,4} (DBPs). Whereas previous studies have investigated water-quantity alterations due to climate-induced, forest die-off^{5,6}, impacts on water quality are unclear. Here, water-quality data sets from water-treatment facilities in Colorado were analysed to determine whether the municipal water supply has been perturbed by tree mortality. Results demonstrate higher total organic carbon concentrations along with significantly more DBPs at water-treatment facilities using mountain-pinebeetle-infested source waters when contrasted with those using water from control watersheds. In addition to this differentiation between watersheds, DBP concentrations demonstrated an increase within mountain pine beetle watersheds related to the degree of infestation. Disproportionate DBP increases and seasonal decoupling of peak DBP and total organic carbon concentrations further suggest that the total organic carbon composition is being altered in these systems.

The mountain pine beetle (MPB, Dendroctonus ponderosae) infestation has reached epidemic proportions and is generating growing concern for regional water resources with little known about potential impacts. In the Rocky Mountains, warmer winter minimum temperatures and persistent drought conditions have contributed to an ongoing MPB epidemic⁷ that has affected more than 4 million acres of lodgepole pine forests in Colorado and Wyoming (Fig. 1). Changes in hydrology following barkbeetle infestation such as decreased interception, increased erosion and particulate transport8, increased soil moisture and increased radiation to the forest floor⁵ can lead to altered degradation and transport of soil organic matter in both particulate and dissolved forms⁹. Total organic carbon (TOC, which comprises particulate and dissolved organic carbon) increases have been observed across large areas of the Northern Hemisphere, and although there is no scientific consensus on the driving mechanisms of increased TOC a number of different factors have been proposed including changes in acid deposition¹⁰, variability in climate¹¹ and land-use changes¹². We propose that the recent bark-beetle epidemic is another mechanism that may alter TOC loading and composition in surface and groundwaters.

Changes in TOC characteristics and increased loading can lead to human health concerns as humic and fulvic fractions of natural organic matter (NOM) have been correlated with the formation of DBPs, such as trihalomethanes (THMs, known carcinogens), during chlorination^{3,13,14}. Hence, the potential for exceedance of regulatory limits, human health impacts and increased treatment costs are potential concerns for water-treatment facilities associated with bark-beetle-infested watersheds. The objective of this study was to collect and analyse archived, publicly available water-quality data from water-treatment facilities located in the Rocky Mountain region of Colorado. Water-quality data were compared between MPB-infested watersheds and regionally analogous facilities located in watersheds that did not experience the same degree of MPB infestation (control watersheds).

Archived water-quality data were collected from nine different treatment plants in Colorado, which included four control (Aspen, Carbondale, Glenwood Springs and Gypsum) and five MPBimpacted facilities (Kremmling, Steamboat Springs, Winter Park, Dillon and Granby). The average level of infestation at the control sites was about a quarter $(0.8 \pm 0.2 \text{ trees killed per hectare})$ that of the MPB-impacted sites $(3.0 \pm 0.8 \text{ trees killed per hectare})$ and sites were as geographically similar as the available data would allow (Supplementary Fig. S4). Most treatment facilities collect their water from surface-water sources; however, Winter Park and Dillon primarily use a groundwater supply whereas Carbondale, Aspen and Steamboat Springs use both groundwater and surface-water supplies (Supplementary Table S2). Waterquality samples were collected and analysed by the treatment facilities in quarterly intervals in compliance with Environmental Protection Agency (EPA) standardized procedures¹⁵ and span the years of 2004-2011, during which the impacted lodgepole pine forests experienced heavy MPB infestation (Fig. 1). Although facilities were analysed individually (Supplementary Table S3), trends were more significant owing to larger sample sizes when analysed as a group (that is, MPB or control) and thus aggregated results will be presented.

Quarterly TOC samples taken before water treatment were grouped for these distinct facilities (Fig. 2a). Our analysis demonstrates significantly more TOC in the MPB watersheds versus the control watersheds with respect to both mean and maximum concentrations (p < 0.0001 from Mann–Whitney test). As is typical in most watersheds, surface-water sources in impacted watersheds had significantly higher TOC concentrations than groundwater sources; however, this interpretation is limited as the only available TOC data from an impacted groundwater source was from the town

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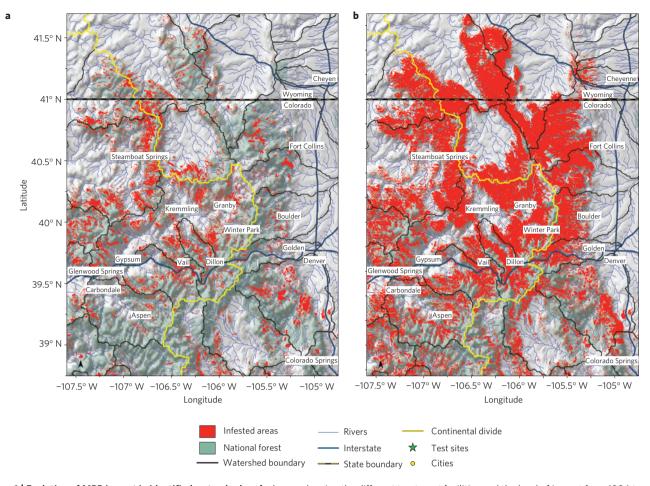


Figure 1 | Evolution of MPB impact in identified watersheds. a,b, A map showing the different treatment facilities and the level of impact from 1996 to 2002 (a) and 2011 (b).

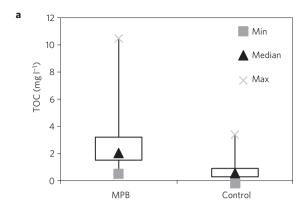
of Dillon (TOC data from Winter Park was not available). This result could provide evidence for the change in transpiration after infestation resulting in changes in the groundwater level¹⁶, possibly activating superficial flow through more TOC-rich soil layers close to the stream¹⁷. However, further analysis is needed to determine changes in flow paths after infestation.

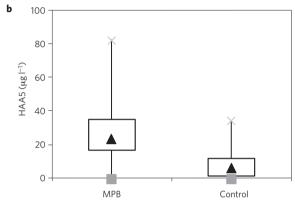
In parallel to increased TOC concentrations, higher DBP concentrations were observed in MPB-infested watersheds when contrasted with control watersheds (Fig. 2b,c) with a nearly tenfold difference between median concentrations. Means for both the sums of five haloacetic acids (HAA5) and total trihalomethanes (TTHM, four THMs) were significantly different between MPB watersheds and control watersheds (p < 0.0001). There were no significant differences in either of the DBPs when contrasting impacted groundwater and surface-water sources and treatment methods.

In light of the larger TOC concentrations and subsequent DBP formation in MPB-infested watersheds when compared with control watersheds, we conducted a temporal analysis of waterquality data to assess possible correlations during infestation progression. Although the significant differences between infested and control watersheds are interesting, and despite attempts to establish representative controls (Supplementary Table S2 and Fig. S4), there are possible site-specific factors incidental to barkbeetle infestation such as soil and hydrological flow paths that might also account for differences observed. For this reason, we chose to further investigate infested watersheds separately from the controls and found significant temporal trends within infested catchments that further support our hypothesis.

Quarterly averaged concentrations of TOC and TTHM (Fig. 3a,c respectively) are depicted for MPB-impacted and control facilities from 2004 to 2011. Using the Mann-Kendall test to include the seasonal fluctuations in TOC (ref. 18) and thus DBP concentrations, it was found that averaged quarterly TTHM concentrations have increased significantly since 2004 in MPB-infested watersheds whereas TOC concentrations have not (Fig. 3b,d and Supplementary Table S4). However, a positive trend was observed (Fig. 3 and Supplementary Table S4) where TOC seems to begin increasing after 2007, shortly after the main initial infestation, reaching an average of 3.5 mg l⁻¹ approximately four years later (a 40% increase from 2004 with an average increase of 0.04 mg l⁻¹ yr⁻¹). TTHM concentrations follow a more pronounced trend (an average increase of 2.05 μ g l⁻¹ yr⁻¹), reaching a mean value of around 70 μ g l⁻¹ (with individual facilities experiencing concentrations as high as $111 \,\mu g \, l^{-1}$ in the third quarter) followed by a slow decline. Recently, it has been found that modest increases in TOC can be equated to more pronounced shifts in NOM characteristics¹⁹, which may explain the observed trends.

Increased TOC concentrations in watersheds can be associated with increased precipitation 20 , and increased temperatures have been associated with increased DBP formation potential 21 . However, annual precipitation and temperature do not exhibit increasing trends and thus do not explain the observed TOC trends (Supplementary Fig. S5). Importantly, an increasing trend was not observed in the TOC and TTHM values at control facilities (with an average decrease of $-0.05 \, \mathrm{mg} \, \mathrm{l}^{-1} \, \mathrm{yr}^{-1}$ and $-0.3 \, \mathrm{\mu g} \, \mathrm{l}^{-1} \, \mathrm{yr}^{-1}$ respectively; Fig. 3b,d) from 2004 to 2011, further highlighting the significance of the observed trends in impacted watersheds.





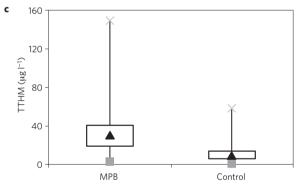


Figure 2 | Significantly higher TOC and DBP concentrations in MPB-impacted water-treatment facilities versus control facilities.

a, Comparison of TOC concentrations using a 50% confidence interval box and whisker plot. **b**, Comparison of HAA5 concentrations. **c**, Comparison of TTHM concentrations. In the legend, Min refers to the minimum concentration, Median to the median concentration, and Max to the maximum concentration recorded. The data were taken between 2004 and the third quarter of 2011.

We further analysed the TOC and TTHM data by quarters (Fig. 3a,c). Interestingly, in the MPB-impacted catchments, maximum TTHM concentrations were generally associated with the third quarter (July–September), whereas maximum TOC concentrations were generally reported in the second quarter (April–June). This seasonal trend differed from the control catchments where both TTHM and TOC concentrations were highest during the high streamflow months (second quarter), signifying that a factor other than temperature and precipitation was influencing TTHM and TOC concentrations.

Higher TTHM concentrations in the late summer rather than in the spring runoff (when TOC is at a maximum) for MPB-impacted watersheds could be explained by different hydrologic flow path dynamics during the low-flow season. THM and HAA formation is due to the chlorination of aromatic and aliphatic β -dicarbonyl moieties within NOM. The hydrophobic (humic and fulvic acids) fractions of NOM are dominated by 1,3-dihydroxyaromatic-type structures, which are known precursors of THMs (ref. 22), whereas aliphatic β -keto-acid-type structures residing in the hydrophilic fraction are known precursors of HAAs (ref. 23). Humic and fulvic acids have been shown to dominate the later stages of runoff in lodgepole pine forests^{24,25}, thus imparting higher TTHM concentrations despite lower TOC levels. As it has been shown that the hydrophobic proportions of TOC are higher in the lowflow season²⁶ (typically the third quarter in semi-arid regions of North America), it would be insightful to determine whether there is a resulting higher TTHM formation potential. This could be of particular concern as modelling⁵ and field results^{6,27} have demonstrated an increase in the duration of low flows in impacted watersheds.

With the main increase in TTHM occurring around 2008, we compared the yearly water-quality data before and after 2008, approximately 3–4 years after the MPB infestation began in most watersheds in Colorado. It has been shown that after a tree becomes infested with beetles it can take between 3 and 5 years for the needles to drop on the forest floor⁸. Hence, it stands to reason that a shift in the TOC concentrations in the water supply might occur around 2008–2009, corresponding to maximized forest floor litter, increased degradation of downed litter and the largest hydrologic changes.

Table 1 shows the range of TOC and TTHM values in MPB watersheds grouped before and after 2008. TOC concentrations are significantly larger (p=0.01) since 2008, whereas TOC concentrations in control watersheds are significantly smaller (p<0.04) since 2008. An analogous trend can be observed for TTHM concentrations when contrasting MPB-infested watersheds with control watersheds (p<0.04). In contrast, no significant difference in HAA5 concentrations in either MPB-impacted or control watersheds was observed.

Interestingly, although differences were observed between the impacted and control sites with respect to both DBPs (Fig. 2b,c), only TTHMs were observed to increase temporally in MPB watersheds. The cause for this difference is uncertain, and it is possible that NOM released as a result of MPB impact has a higher TTHM than HAA5 formation potential. Regardless of this uncertainty, our findings still reveal a significant temporal trend with regard to TTHM in impacted watersheds. According to ref. 25, after two months of degradation, pine litter leachate becomes significantly more aromatic and hydrophobic and it is possible that the transported TOC is in this stage of degradation. It has also been found that clear-cutting (an analogous process to bark-beetle mortality with some notable differences) results in the leaching of more aromatic organic matter⁹. It is possible that similar mechanistic and hydrologic changes occur in a bark-beetle infestation as do in clear-cutting forests; although not necessarily resulting in increased TOC flux, the characteristics of the TOC could be altered inducing higher TTHM levels.

This study presents evidence of water-quality impacts from a climate-induced phenomenon in the Rocky Mountain region of North America. The data provide evidence for changing TOC concentrations and characteristics after large-scale forest die-off from beetle infestations. Most notably this was observed as a significant increase in THM formation, especially in late summer and early autumn months; however, at present a similar concern is not apparent for HAA formation. As the trees continue degrading and the hydrologic regime changes, it will be interesting to observe whether the leachate characteristics change, such that the organic material has a higher proportion of hydrophilic acids and thus HAA5 formation becomes more of a concern. Present EPA regulations stipulate that the yearly average of TTHM must be

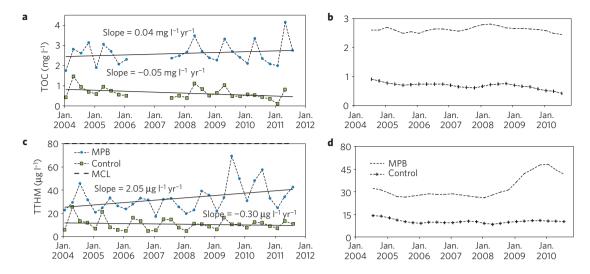


Figure 3 | **Seasonal shifts and trends in TOC and TTHM concentrations in analysed water-treatment facilities. a-d**, Quarterly averages from 2004 to 2011 in MPB-impacted and control facilities of TOC (**a**) and TTHM (**c**), and the change in variance after decomposition for the Mann-Kendall tests for TOC (**b**) and TTHMs (**d**). In **c**, a regulatory TTHM limit of 80 μ g l⁻¹ is shown for reference and a dashed line connects data points to depict seasonal trends. For clarity of presentation, additional statistical analysis associated with **a** and **c** can be found in Supplementary Table S5.

Table 1 | Comparison of TOC and DBP concentrations before and after 2008 between MPB-infested sites and control sites.

Analyte tested	MPB/ control	P value	Mean pre-2008	Mean post-2008	<i>n</i> ₁ , <i>n</i> ₂
HAA5	Control	0.84	6.7	6.6	104, 75
	MPB	0.22	28.8	26.3	106, 92
TTHM	Control	0.97	10.9	10.2	104, 75
	MPB	0.04	28.8	37.6	109, 92
TOC	Control	0.04	0.70	0.62	250, 191
	MPB	0.01	2.5	2.7	216, 227

The mean from pre-2008 spans the years 2004 to 2008 and the mean from post-2008 spans the years 2009 to the third quarter of 2011. The Mann–Whitney tests are at a 5% significance level ($\alpha = 0.05$); n_1 and n_2 give the number of samples before 2008 and after 2008, respectively.

below $80\,\mu g\,l^{-1}$ (ref. 28), and the present trend encroaches on this maximum contaminant level for two out of four quarters in the impacted watersheds, where TTHM levels are highest during the third quarter.

The present effects seem to be associated with a pulse of needle fall several years after the initial infestation, which is when hydrologic and biogeochemical changes may be maximal; however, the cumulative effect on water quality remains unknown as fractal residence times in watersheds could create tailing²⁹ that may minimize peak effects, but lead to a longer duration of water-quality impact. In the ensuing decade, skeletal trees will begin to fall and degrade and new vegetation will grow, and it is unclear what effect this sequence may have on overall water quality. With the changing climate altering ecosystem dynamics, and in the case of bark beetles, expanding their influence, it is important that we add water quality to the growing list of potentially adverse outcomes.

Methods

Source waters and data collection. Water-quality data were publicly available and collected from the Colorado Department of Public Health and Environment's records or directly from the water-treatment facilities. Data from nine different treatment plants were used, which included four control facilities (Aspen, Carbondale, Glenwood Springs and Gypsum). Although some of the control

watersheds have experienced small-scale infestation or are linked to areas of higher impact, the degree of impact is modest when contrasted with the five MPB-impacted facilities (Kremmling, Steamboat, Winter Park, Dillon and Granby; Fig. 1 and Supplementary Fig. S4). Bark-beetle infestation was determined using ArcGIS to calculate the average number of trees killed by beetles per acre within each watershed. Control watersheds were delineated by having approximately a quarter or less of the degree of impact as MPB-impacted watersheds. Watershed characteristics and the associated degree of impact were determined using ArcGIS and aerial survey data conducted by the USDA Forest Service. All areas are mid to high elevation (Supplementary Table S2) and are located in the mountainous regions of Colorado with similar soil and land-use characteristics (Supplementary Fig. S4).

Whereas Winter Park and Dillon primarily use a groundwater supply and Carbondale, Aspen and Steamboat use both groundwater and surface-water supplies, the remaining water-treatment facilities receive most of their water from surface-water sources (Supplementary Table S2). The treatment facilities use direct filtration (Carbondale, Gypsum, Kremmling and Dillon) or flocculation/sedimentation followed by filtration (Glenwood Springs, Aspen, Granby and Steamboat Springs), except for Winter Park, which only uses an ozonation system to treat its water, and hence, does report TOC levels. Flocculation/sedimentation can lead to higher TOC removal than just direct filtration; however, minimal TOC was removed from Aspen and Glenwood Springs treatment plants after flocculation and sedimentation (with an average loss of $0.07 \,\mathrm{mg}\,\mathrm{l}^{-1}$ for Aspen and $0.27 \,\mathrm{mg}\,\mathrm{l}^{-1}$ for Glenwood Springs). For the impacted sites using this treatment process, this is less of a concern as we still saw increases in THM levels despite flocculation/sedimentation. Ozonation can also result in lower DBP concentrations than other treatment trains; however, Winter Park is the only facility to use ozonation and is located in an infested watershed, which only increases the significance of the findings. Carbondale, Glenwood Springs, Kremmling and Aspen all use chlorination pre- and post-treatment, whereas the remaining five chlorinate only post-treatment (Supplementary Table S2).

Starting in 2004, water-treatment facilities in Colorado were required to submit quarterly reports as a result of EPA-instigated Stage 1 and Stage 2 Disinfectants and DBPs Rules for groundwater and small surface-water systems¹⁵. The sampling frequency of DBPs and TOC differs depending on the size of the population the treatment facility serves and whether the facility uses surface or groundwater. The quarterly reports from 2004 to Summer 2011 were used for the statistical analysis performed herein. Even though some of the forests experienced infestation before 2004, the absence of data creates a defining starting point for the data set. The water-quality data include TOC, TTHM (the mass concentration sum of bromodichloromethane, dibromochloromethane, bromoform and chloroform), with chloroform being the dominant THM in the data analysed, and five HAAs (HAA5; the mass concentration sum of monochloroacetic acid. dichloroacetic acid, trichloroacetic acid, monobromoacetic acid and dibromoacetic acid), where dichloroacetic acid and trichloroacetic acid are the dominant HAAs present in the analysed data. Samples are typically taken for TOC at the intake of the treatment plant. All of the facilities sample for DBPs at the maximum residence time distribution point as is required for most facilities according to EPA standards²⁸. There is a gap in all facilities' TOC data from April 2006 to June 2007 for unknown reasons.

Colorado average monthly precipitation and temperature data from 2004 to 2011 were evaluated for atypical years. None was found. An example area's climatic trends can be found in Supplementary Fig. S5.

Analysis of water-quality data. The quarterly reports from 2004 to Summer 2011 were used for statistical analyses. The Mann–Whitney non-parametric test was used to compare mean TOC, mean TTHM and mean HAA5 concentrations in MPB-infested watersheds versus control watersheds as the distributions were skewed left owing to sample values of zero. Data were delineated quarterly and analysed for seasonal differences by averaging each facility's quarterly data for every year (2004–2011) and comparing it with the yearly average. The standard EPA sampling quarters were used and are defined as follows: Q1, January–March; Q2, April–June; Q3, July–September; Q4, October–December.

The seasonal Mann–Kendal non-parametric test was used to analyse temporal trends associated with TOC and TTHM data for both control and MPB-infested data sets sets as it is typically used in trend analysis for hydrologic variables with a seasonal dependence³⁰. In the TOC quarterly data sets, the missing data were interpolated by averaging two measured values before and after the missing data point. The time series was then decomposed so that the trend and seasonality in the data could be extracted. The Mann–Kendall test was then run on the trend component of the time series to determine whether Kendall's tau was significantly different from zero, which would indicate a trend.

The Mann–Whitney non-parametric test was also used to assess mean TOC, TTHM and HAA5 values before and after impact of all individual water-treatment facilities and of binned control and MPB-infested facilities. A temporal comparison of before and after 2008 was conducted to determine how many years it took post infestation to see an increased TOC flux due to maximized forest floor litter. All pre-2008 data were averaged and compared with averaged post-2008 data. The year of 2008 was chosen as the delineation between high and low concentrations of TOC and TTHMs as the Mann–Kendall trend analysis showed an increasing trend in both analytes beginning around 2008 (Fig. 3b,d).

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Author contributions

K.M.M., E.R.V.D., J.O.S. and J.E.M. conceived the study, K.M.M collected and analysed the data, and K.M.M., E.R.V.D., J.O.S., J.E.M. and R.M.M. interpreted results and contributed to writing.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to K.M.M.

Competing financial interests

The authors declare no competing financial interests.

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