


Trihalomethane precursor reactivity changes in drinking water treatment unit processes during a storm event

Chelsea W. Neil, Yingying Zhao, Amy Zhao, Jill Neal, Maria Meyer and Y. Jeffrey Yang 

ABSTRACT

Source water quality can significantly impact the efficacy of water treatment unit processes and the formation of chlorinated and brominated trihalomethanes (THMs). Current water treatment plant performance models may not accurately capture how source water quality variations, such as organic matter variability, can impact treatment unit processes. To investigate these impacts, a field study was conducted wherein water samples were collected along the treatment train for 72 hours during a storm event. Systematic sampling and detailed analyses of water quality parameters, including non-purgeable organic carbon (NPOC), UV absorbance, and THM concentrations, as well as chlorine spiking experiments, reveal how the THM formation potential changes in response to treatment unit processes. Results show that the NPOC remaining after treatment has an increased reactivity towards forming THMs, and that brominated THMs form more readily than chlorinated counterparts in a competitive reaction. Thus both the reactivity and quantity of THM precursors must be considered to maintain compliance with drinking water standards, a finding that should be incorporated into the development of model-assisted treatment operation and optimization. Advanced granular activated carbon (GAC) treatment beyond conventional coagulation–flocculation–sedimentation processes may also be necessary to remove the surge loading of THM-formation precursors during a storm event.

Key words | chlorination, climate variability, disinfection byproducts, trihalomethanes, turbidity, water treatment

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ABBREVIATIONS

THM	Trihalomethane
TTHM	Total trihalomethane
GAC	Granular activated carbon
FAC	Free available chlorine
GCWW	Greater Cincinnati Water Works
DBP	Disinfection by-product
NPOC	Non-purgeable organic carbon
RAW	Raw water samples
LMEF	Lamella effluent samples
SETT	Settling reservoir samples

FLIN	Sand filter influent samples
GACI	GAC influent samples
CW1I	Clear well #1 influent samples

INTRODUCTION

Hydrological perturbations from intense precipitation events or prolonged drought can impact the quality of surface water and thus, downstream drinking water treatment (Li *et al.*

2014; Khan *et al.* 2015). These long-term or temporary source water quality changes make it necessary for water treatment plants to adjust their treatment unit design and operation to ensure that treated water continues to meet drinking water quality standards. For treatment adaptation, it is essential to understand and quantify the impacts of these source water changes on treatment performance (Levine *et al.* 2016).

The formation of trihalomethanes (THMs) as disinfection byproducts during water treatment is concerning due to their carcinogenic effects (Hildesheim *et al.* 1998). Four chlorinated and brominated THMs (chloroform, bromoform, bromodichloromethane, and dibromochloromethane) are regulated by the US Environmental Protection Agency (EPA), which has set a limit on the total concentration, referred to as the total trihalomethanes (TTHMs), of 80 ppb in the finished production water (Yue & Economy 2005). THMs form from reactions between organic matter and chlorine, which is added to disinfect the water, and/or bromine, which can be naturally present (Westerhoff *et al.* 2004). Some THMs are volatile, but many persist from treatment through distribution to consumers. THM exposure routes include inhalation while showering, consumption of water containing THMs, and dermal absorption while bathing or swimming in chlorinated pools (Xu *et al.* 2002).

The degree of bromide incorporation in THMs is important because brominated THMs are generally more cytotoxic and genotoxic (Richardson *et al.* 2007). During water treatment, bromine present in the source water can be rapidly oxidized into highly reactive hypobromous acid (HOBr) species. HOBr is a more potent halogenating species than HOCl; therefore, increases in the ratio of bromine to organic matter and the ratio of bromine to free available chlorine (FAC) will result in a kinetic shift toward more bromo-substituted species (Symons *et al.* 1993).

To fully understand the risk of THM formation in water treatment, we must quantify THM precursors and examine additional factors which impact formation kinetics and reaction extents. It is widely known that THM formation depends on source water chemistry as well as specific treatment plant processes (Sadiq & Rodriguez 2004; Chen *et al.* 2007; Hua & Reckhow 2007). Thus, a detailed investigation of the treatment efficiency of each unit process under changing source water conditions can provide insights into the quantitative relationships between design parameters for model

development, allowing for the development of adaptation strategies for treatment plants with similar unit operations.

The goals of this study are twofold. The first goal is to characterize which treatment unit processes are most effective at removing THM precursors during a storm event. These units will serve as a safeguard against anticipated future source water quality variation. The second goal is to closely examine how each unit process impacts the reactivity of THM precursors. The results will form the basis for improved models of THM formation during water treatment and further our understanding of how source water constituents impact the THM formation potential.

METHODS

In this study, we examined water treatment plant performance at the Greater Cincinnati Water Works (GCWW) Miller treatment plant, which supplies drinking water to more than 1.1 million people in the Cincinnati metropolitan region in the US Midwest. The Miller treatment plant takes surface water from the adjacent Ohio River and treats using conventional coagulation–flocculation–sedimentation/filtration processes followed by advanced granular activated carbon (GAC) treatment (Metz *et al.* 2004). This two-step approach is referred to throughout this paper as a multi-barrier treatment strategy. The extra GAC treatment step allows for the use of substantially less chlorine for disinfection and better control of THM and other disinfection by-product (DBP) formation in the finished water.

Field sampling procedure

To characterize the effects of hydrological perturbations on treatment, water quality of the source water from the plant intake and along the treatment chain was characterized using *in situ* measurements and *ex situ* analytical instrumentation on grab samples collected hourly for 72 hours during a storm event that increased the river flow. Source water quality was impacted by the storm event over the entire sampling period, as evidenced by the continually increasing turbidity in RAW samples (Figure S1 in the Supporting Information (SI), available with the online version of this paper). Duplicate samples were collected at 18, 36, 54, and 72 hours.

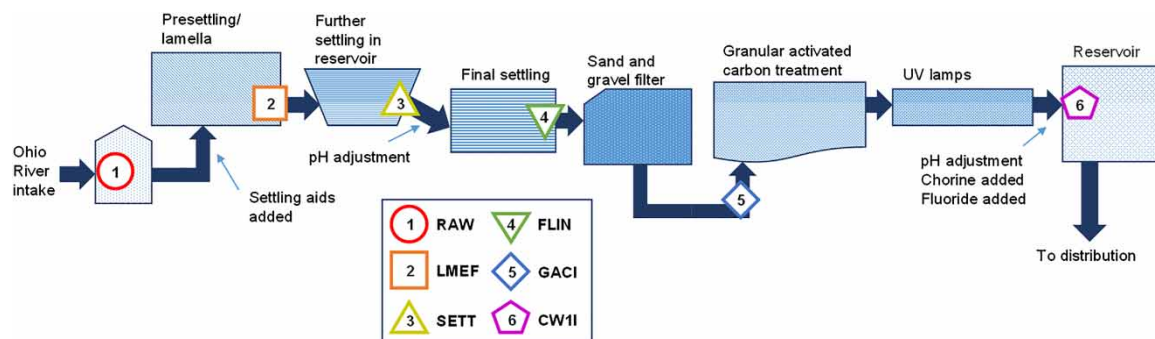


Figure 1 | Diagram of the GCWW Richard Miller Treatment Plant. Sampling locations are labelled with sampling site abbreviations.

Samples were taken along the treatment train starting with the raw source water (RAW), and then at the subsequent unit treatment processes in the order of their application: the lamella effluent (LMEF), settling reservoirs (SETT), sand filter influent (FLIN), GAC influent (GACI), and clear well #1 influent (CW1I) (Figure 1). These locations were chosen to quantify the performance of water treatment unit processes including coagulation, flocculation, sedimentation, filtration, GAC adsorption, and chlorine disinfection.

Samples for organic carbon measurement were collected in 40 mL amber bottles with preservative phosphoric acid (H_3PO_4) to maintain a pH below 2. UV-254 samples were collected in 250 mL amber glass bottles with Teflon-lined caps and zeta potential samples were stored in 60 mL sterile glass bottles. Separately, turbidity values were measured *in situ* at each sampling port (see Figure S1 in the SI). Temperature and pH values were collected on site using a lab-calibrated multi-parameter probe (Extech Instruments pH/mV/Temperature Meter) (Figure S2 in the SI, available online). In addition, samples for THM measurement were collected and stored headspace-free in 250 mL amber glass vials with Teflon-lined screw caps. They were collected at the first hour and after 18, 36, 54, and 72 hours from each of the six sample locations. For the CW1I THM samples, phosphate and sodium sulfate were added for sample preservation. All samples were stored at 5 °C prior to measurement.

The THM formation potential was further quantified by conducting chlorine spiking experiments on collected samples. To determine the THM formation potential, large-volume water samples simultaneously collected (at 1, 18, 36, 54, and 72 hours) were spiked with sodium hypochlorite,

yielding approximately 7.85% free available chlorine (FAC). At time 0 and after 36 hours, the free chlorine was measured and a 60 mL aliquot was drawn for THM analysis.

Instrumentation analysis

To characterize treatment efficiency, several water quality parameters were analyzed using *ex situ* laboratory instrumentation. Quantitative analyses included UV-vis absorption (Lambda 35 UV/VIS Spectrometer, PerkinElmer, Hebron, KY, USA), NPOC (non-purgeable organic carbon) measurement with a Shimadzu TOC-V CPH Total Organic Carbon Analyzer with ASI-V autosampler and regular sensitivity catalyst (Kyoto, Kyoto Prefecture, Japan, detection limit of 0.5 mg/L), bromide quantification by ion chromatography (IC) equipped with a conductivity detector (Dionex 500, Sunnyvale, CA, USA), zeta potential using a Malvern Zeta-sizer Nano ZS (Malvern, Worcestershire, UK), and THM measurement using a GC System with purge and trap (Agilent Technologies 7890A, Santa Clara, CA, USA). All instrumentation followed EPA standard analytical methods with approved quality assurance and quality control procedures. Details on instrumentation analysis and QA/QC outcomes can be found in the SI (available online).

RESULTS AND DISCUSSION

THM precursor concentrations

NPOC measurements showed a consistent decrease in concentration through treatment by each unit process

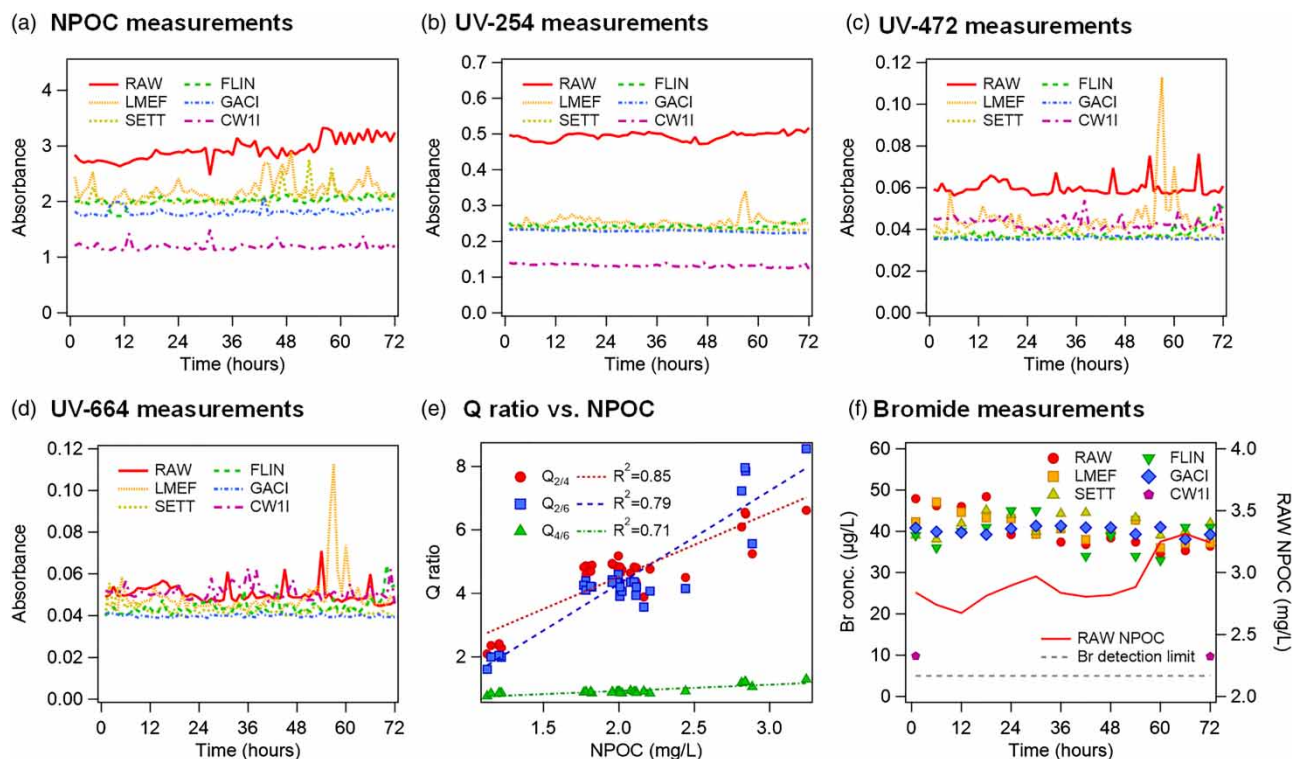


Figure 2 | (a) Temporal NPOC variation removed gradually through the unit processes. UV-vis absorption measurements at a wavelength of (b) 254 nm, (c) 472 nm, and (d) 664 nm indicating the presence of a different reactive fraction of organic matter. (e) Correlation between NPOC and UV-vis absorption ratios. (f) No bromide removal in unit processes prior to disinfection by chlorination.

(Figure 2(a)). The two most significant concentration decreases occurred between the RAW and LMEF samples, and between the GACI and CW1I samples. RAW NPOC measurements showed a gradual increase with time during the storm event, from 2.84 mg/L to 3.24 mg/L. The highest measured NPOC value of 3.24 mg/L was not extremely high relative to values observed historically in other drinking water sources. For example, organic carbon in the White River reached a maximum value of 11.90 mg/L during observation, while the average concentration was 3.86 ± 1.19 mg/L (Volk et al. 2005). Although our NPOC the increase was smaller, a significant concurrent increase in turbidity from 73.9 to 193.2 NTU was observed (Figure S1 in the SI), indicating that NPOC increased due to the storm event. The treatment process is thus being influenced by these storm-induced water chemistry changes.

Additionally, NPOC measurements had significant fluctuations for LMEF and SETT samples between 41 and 66 hours, consistent with the UV-vis observations of spikes in

LMEF samples around 57 hours (Figure 2(b)–2(d)). The UV-vis spikes were present at all absorbance wavelengths, but were especially prominent for absorbance at 472 and 664 nm. These temporal spikes in concentration were gradually removed by treatment units and totally disappeared after GAC treatment, indicating that the multi-barrier treatment strategy is effective.

Using NPOC data, the average percent reductions between treatment units were calculated (Table 1). Moving from the raw water to the lamella, the average reduction was $24.7 \pm 7.2\%$. Between the lamella and settling samples, the percent reduction was $5.4 \pm 7.8\%$, and it was only $2.2 \pm 5.5\%$ between settling and filter influent. After passing through the filter and before entering the GAC unit, the percent reduction was $10.1 \pm 6.1\%$. Finally, between the GACI unit and clear well, the percent reduction was the largest at $34.0 \pm 4.7\%$. In total, the pre-settling/lamella and GAC unit account for 77.3% of the total removal.

Table 1 | Removal efficiencies of treatment unit processes for different water quality parameters

Unit process	NPOC percent removal	UV-254 percent removal	UV-472 percent removal	UV-664 percent removal	Zeta potential percent removal	Bromide percent removal
RAW → LMEF	24.7 ± 7.2%	48.6 ± 3.1%	24.3 ± 18.7%	2.0 ± 22.6%	36.4 ± 18.5%	-2.2 ± 7.3%
LMEF → SETT	5.4 ± 7.8%	7.2 ± 5.1%	15.5 ± 11.5%	10.8 ± 12.3%	11.9 ± 31.2%	-2.4 ± 9.5%
SETT → FLIN	2.2 ± 5.5%	-3.6 ± 3.0%	-2.8 ± 10.5%	-4.3 ± 11.6%	-10.7 ± 38.4%	5.7 ± 10.0%
FLIN → GACI	10.1 ± 6.1%	6.0 ± 2.8%	5.4 ± 7.5%	9.2 ± 7.3%	14.8 ± 28.1%	-3.6 ± 11.1%
GACI → CW11	34.0 ± 4.7%	42.1 ± 1.6%	-20.8 ± 8.9%	-27.9 ± 9.2%	61.3 ± 17.4%	-

The efficacy of each unit process in removing specific forms of organic matter was further characterized by analyzing changes in UV-vis absorption at specific wavelengths. The UV-254 spectrum is indicative of reactive organics (Figure 2(b)). UV absorbance in the 460–480 nm range (UV-472) is indicative of organic material at the beginning of humification (Figure 2(c)), and absorbance in the 600–670 nm range (UV-664) is indicative of less-reactive, strongly humified material (Figure 2(d)).

Results indicate that treatment is most effective in removing UV-254, particularly between the RAW and LMEF samples, where absorbance decreased by $48.6 \pm 3.1\%$. Additionally, temporal variance was not observed in RAW water samples, decoupling from turbidity and NPOC increases due to the storm event. For LMEF, SETT, FLIN, and GACI samples, absorbance varied slightly around 0.25. CW11 had the lowest absorbance of 0.132 ± 0.004 . This decrease of $42.1 \pm 1.6\%$ from the GACI samples indicates efficient removal of reactive organic matter during GAC adsorption.

For UV-472, there was much less absorbance compared with UV-254. Absorbance was highest in general for the RAW system, however, the decrease between RAW and other sampling points was less dramatic. For UV-664, measurements were similar for all sampling locations, indicating treatment does not effectively remove strongly humified organics. This observation may not be concerning because these organics are both less reactive and present at low concentrations.

The last water quality measurement conducted for characterizing organic THM precursors was zeta potential (Figure S3 in the SI, available with the online version of this paper). Zeta potential increased between the RAW and CW11 samples, from -15.6 ± 0.9 mV to -2.9 ± 1.3 mV.

LMEF, SETT, GACI, and FLIN samples had similar zeta potentials at -9.9 ± 2.7 , -9.1 ± 1.5 , -9.6 ± 2.0 , and -7.9 ± 1.8 mV, respectively. There was no temporal variance for zeta potential, similar to UV absorption, indicating that this measurement is less sensitive to variations in turbidity.

The negatively charged particles are expected to be organic matter. Thus, the overall trend matches that seen for NPOC and UV absorbance, further confirming that the initial pre-settling phase and GAC treatment are critical for removing organic THM precursors, and that multi-barrier treatment is effective even as turbidity increases due to the storm event.

We further analyzed NPOC removal using the Q -absorbance ratios for the wavelengths of UV-280, 472, and 664 ($Q_{2/4} = A_{280}/A_{472}$; $Q_{2/6} = A_{280}/A_{664}$; $Q_{4/6} = A_{472}/A_{664}$). These ratios have been used in the literature to assess the degree of humification of organic matter (Zbytniewski & Buszewski 2005). A low $Q_{2/6}$ or low $Q_{4/6}$ ratio indicates a larger fraction of strongly humified material; an increase in these ratios is characteristic of less humified compounds. The ratio of $Q_{2/4}$ indicates the point where organic matter begins humification. All three ratios showed a positive correlation with NPOC (Figure 2(e)) with the $Q_{2/4}$ ratio being strongest. Thus, $Q_{2/4}$ may be the best indicator to monitor for increases in reactive organics during a storm perturbation event.

In addition to organic matter, bromide is an important precursor for the formation of more toxic, bromo-substituted THMs. Figure 2(f) displays bromide concentrations along the treatment train. The only significant concentration decrease occurred between GACI and CW11, which were taken after chlorination. Historical measurements indicate that GAC treatment does not remove bromide (Table S2 in the SI, available online). Together these results indicate no

effective bromide removal during drinking water treatment. The decrease in bromide concentration during chlorination is thus partially attributable to the formation of brominated DPBs. A mass balance calculation indicates that the formation of brominated THMs only accounts for 8.1–11.6% of removal. Bromide incorporation into other DBPs such as haloacetic acids (HAAs) was not quantified in this study.

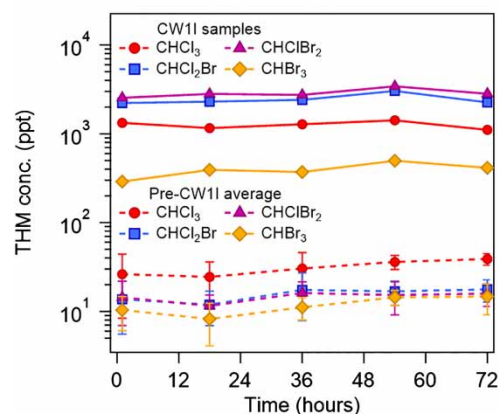
Table 1 presents the removal efficiencies of the water treatment unit processes for NPOC, UV absorbance, zeta potential, and bromide. Taken in unison, these different water quality parameters show a consensus on the importance of pre-settling/lamella treatment and GAC absorption for removing reactive organic THM precursors. These two processes accounted for the majority of NPOC, UV-254, and zeta potential decreases over the sampling period. Conversely, UV-472, UV-664, and bromide showed little decrease along the treatment train. To remove these constituents, more targeted treatment unit processes are needed.

THM species and concentration variations

Figure 3(a) presents the concentrations of the four THM species in *in situ* samples before and after chlorination. Low TTHM concentrations, ranging from 17.42 to 114.7 $\mu\text{g/L}$, were persistent for all treatment units prior to CW11, where concentrations increased to between 6,389 and 8,377 $\mu\text{g/L}$ due to chlorination. Before CW11, chloroform is the predominant THM species, which is consistent with field studies of THMs in the Ohio River (Rowe et al. 2004). After chlorination, dibromochloromethane, CHClBr_2 , has the highest concentration, followed by bromodichloromethane, CHCl_2Br . The high concentration of brominated THM species reflects that HOBr is a more potent halogenating agent than chlorine, particularly as CW11 samples were taken 20 to 30 minutes after chlorination. The molar proportion of Br-THMs may decrease over the longer timeframe of water distribution. One previous study by Tian et al. (2013) showed that the bromine incorporation factor – namely the bromine fraction in THMs – decreased with time after chlorination. The factor was 0.64, 0.47, and 0.39 at 30 minutes, 24 hours, and 72 hours, respectively.

Changes in precursor reactivity along the treatment train were measured by using spiking experiments to calculate the THM formation potential of water samples collected

(a) THM *in situ* measurement



(b) THM spiking yields

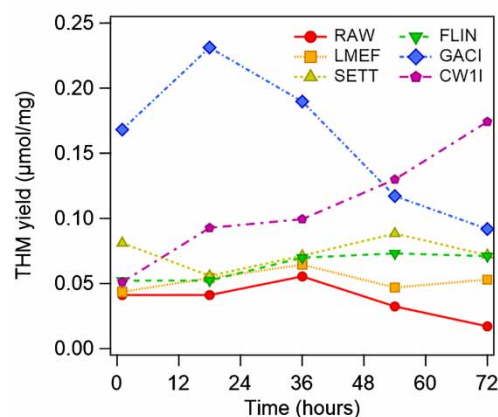


Figure 3 | (a) THM concentrations before and after chlorination showing large Br-THM formation after chlorination; (b) variations of TTHM yield potential with time and among the unit processes.

at 1, 18, 36, 54, and 72 hours. During spiking, the initial chlorine concentration was adjusted to ~ 1 mg/L, but quickly decreased to between 840 and 360 $\mu\text{g/L}$ by the time of initial free chlorine measurement. By 36 hours, all chlorine was depleted for samples other than CW11. Table S1 in the SI (available online) presents FAC measurement data and TTHMs used to calculate the THM yield. Compared with *in situ* measurements, TTHMs in the spiked samples were significantly higher, in the range 6–60 mg/L.

The THM yield potential, defined as the concentration ratio of TTHMs (in $\mu\text{mol/L}$) and NPOC (in mg/L), shows large variations across the unit process and to a lesser extent with time (Figure 3(b)). In the raw Ohio River water, the yield potential increased slightly to a maximum of 0.056 $\mu\text{mol/mg}$ at 36 hours, immediately

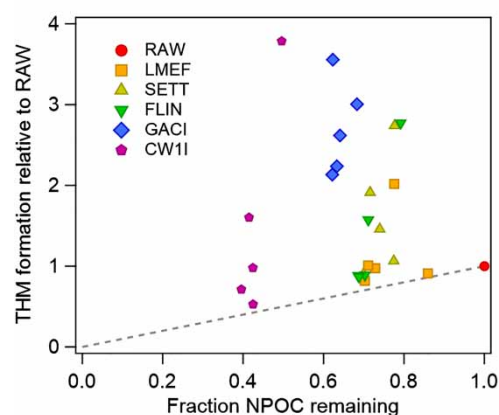
before the peak river flow, and subsequently decreased to $0.019 \mu\text{mol}/\text{mg}$. At early time-points, the highest THM yield potential was observed in GAC influent samples. However, a higher yield potential was observed in CW11 samples after 54 hours, corresponding to an increasing impact of the storm event on the source water according to turbidity measurements. There was no change in NPOC concentrations over this period (Figure 2(a)). Therefore, the reactivity of residual NPOC after treatment must be changing during the storm event.

Multi-barrier approach against storm perturbations

NPOC removal through the treatment train shows that a multi-barrier approach can manage the increased NPOC availability due to storm perturbations, preventing increased THM formation in the final production water (Table 1). The first barrier by coagulation and rapid mixing in the lamella (LMEF) removed a significant fraction of NPOC, while subsequent settling removed instances of concentration spikes, as shown in the difference between SET samples and the filter influent samples (FLIN) (Figure 2(a)–2(d)). The GAC process unit (GACI) is the most effective for NPOC removal, producing consistently low NPOC levels in the final water (CW11). Although not used universally in drinking water treatment, GAC treatment is an important barrier against NPOC increases associated with storm events.

It is also noted that NPOC reactivity changes across the treatment unit processes (Figure 4(a)). The dotted line in Figure 4(a) shows a 1:1 relationship between NPOC and THM formation relative to the RAW water. In subsequent unit processes, the THM formation potential increases along the steps of the conventional treatment with it being highest in the GAC influent and the last time-point in CW11. More frequent, intense storm events can increase turbidity and NPOC levels in river water and consequently increase loading to water treatment plants. As shown in this case study, conventional water treatment can remove a large fraction of the NPOC, but GAC treatment may be necessary to keep TTHMs below 80 ppb as water quality variability increases. A survey conducted by the US EPA found that GAC treatment was implemented in 17.8% of surface water treatment plants serving more than 500,000 people, and only 9.6% of all surface water treatment plants

(a) NPOC reactivity changes



(b) Chlorination changes with time

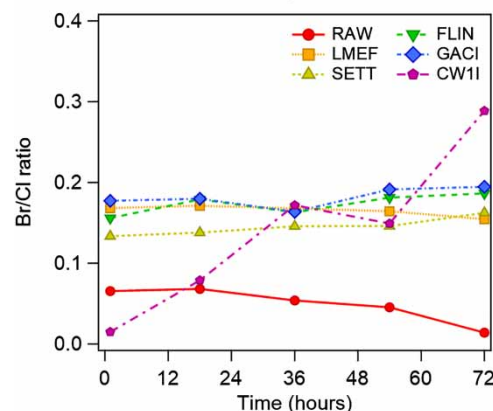


Figure 4 | (a) THM formation potential and fraction in progression of the unit treatment; (b) Br/Cl ratio changes in THM formed indicating relative reactivity variation with time.

(EPA 2009). More widespread use of GAC treatment as part of a multi-barrier strategy can thus be useful to combat future increases in THM precursor concentrations. In addition, NPOC which remained prior to GAC treatment (GACI) and in the clear well had elevated reactivity. Water treatment plant models should consider this phenomenon when planning operations.

Bromide and chlorine reactivity

Brominated and nitrogenous DPBs are gaining regulatory and research attention because of their carcinogenic effects in humans. In this study, bromine as a primary precursor was recalcitrant to both conventional and advanced GAC treatment (Figure 2(f)). High proportions of

brominated-THMs in the clear well before water distribution (Figure 3(a)) are likely a result of higher bromine reactivity than chlorine in competitive reactions. These reaction kinetics and practical consequences have also been reported in multiple recent studies (e.g., Sawade *et al.* 2016). The lack of bromine removal and resulting formation of hazardous Br-THMs needs attention despite TTHMs being below the US regulatory level.

Bromination trends yield insight into NPOC reactivity changes during treatment (Figure 4(b)). For the RAW system, the Br/Cl ratio in the formed THMs was less than 0.1 and increased to be between 0.1 and 0.2 for subsequent unit processes. Interestingly, in clear well samples, the Br/Cl ratio increased with time to approximately 0.3 at 72 hours. This trend correlates with observed increases in THM yield (Figure 3(b)). Because the concentration of bromine is nearly consistent along the treatment train (Figure 2(f)), the increasing bromination indicates the NPOC residual in treatment unit processes must have become more amenable to Br-halogenation. This reactivity change can also explain dominant Br-THMs in the *in situ* measurements.

CONCLUSIONS

The formation of THMs, particularly more toxic Br-THMs, during water treatment is a major health concern (Bull *et al.* 1995; Wang *et al.* 2007; Krasner 2009). The current study has undertaken a detailed analysis of water treatment system response to storm-induced source water variations. We observed that the multi-barrier strategy in the Miller treatment plant was effective at removing $59.1 \pm 3.8\%$ of NPOC, a measurement of organic THM precursors, regardless of increases in turbidity and organic matter concentration during the storm event. Despite their low concentrations, these residual precursors were more reactive, having THM yields up to four times that observed for NPOC in untreated source water samples. We also found that residual NPOC tended to form more hazardous Br-THMs, with a Br/Cl ratio of 0.29 in the final product water at 72 hours.

These findings have implications for water treatment adaptation to hydrological changes and for water treatment plant modeling. To better understand the observed trends, a more thorough investigation is needed into the chemical

characteristics of the organic matter responsible for the reactivity changes. By calling attention to the reactive NPOC which persists despite treatment, new treatment technologies may prove to be necessary for providing better management against source water perturbations.

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