Pilot Testing Project Report:

A study to investigate alternative secondary disinfection methods and disinfection by-product formation in the community's drinking water supply

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Walkerton Clean Water Centre

Research & Technology Institute

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Acknowledgments

This project report was prepared by:

Jeff Avedesian, BSc, MSc, Scientist,

Geoff Graham, BES (Hons), Technician,

Geordie Gauld, BEng ENVE, Technician,

Lindsay Ariss, BSc, Technician,

Souleymane Ndiongue, PhD, PEng, Manager,

Executive Summary

Background and Rationale

The First Nation community in Northwestern Ontario, located about 170 km north east of Thunder Bay, has a water treatment plant process which includes pre-ozonation, a granular activated carbon and gravel roughing filter, followed by slow sand filtration, UV irradiation for primary disinfection, and chlorine dioxide for secondary disinfection (J.R. Cousin, 2006). The detention time was estimated at approximately 6 to 8 days in the distribution system. The community was interested in discontinuing chlorine dioxide as a secondary disinfectant and would like to trial alternative secondary disinfection methods. They are favoring chlorination as an economical, safe, and practical secondary disinfectant option if it does not produce disinfection by-products (DBPs) above the regulated levels.

DBPs are formed when certain natural organic matter (NOM) compounds are present in water and contact chemical disinfectants, such as chlorine (MECP, 2006). The common by-products that are formed are trihalomethanes (THMs), haloacetic acids (HAAs), and are regulated at a maximum acceptable concentration (MAC) of 100 µg/L, 80 µg/L, respectively, due to their presumed carcinogenic effects (Health Canada, 2017). N-nitrosodimethylamine (NDMA) is another DBP often associated with chloramination disinfection and regulated at 0.009 µg/L because it is a semi-volatile organic chemical and potent carcinogen (USEPA, 2014). This study tested the effects of chlorination and chloramination doses on DBP formation using a conservative approach and detention time that represented the distribution system.

Objectives

The objective of this project was to monitor the concentration of DBPs, specifically THMs, HAAs, and NDMA that would be potentially produced in the treated drinking water supply using chlorine and chloramine disinfection strategies over a one-year period.

Approach

The Centre conducted general water quality analysis of the raw, roughing filter and treated water; and conducted preliminary bench scale chlorination and chloramination demand tests. After preliminary testing, samples were tested for DOC, UVa, chlorine demand, and DBP formation.

Key Findings

The bench test results determined:

- Chloramination produced THMs and HAAs above the respective MACs
- NDMA was below the detection limit
- Chlorination produced THMs and HAAs above the respective MACs

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1. Introduction

The First Nation community in Northwestern Ontario, located about 170 km north east of Thunder Bay, has a water treatment plant process which includes pre-ozonation, a granular activated carbon and gravel roughing filter, followed by slow sand filtration, UV irradiation for primary disinfection, and chlorine dioxide for secondary disinfection (J.R. Cousin, 2006). The detention time in the distribution system was estimated at approximately 8 days.

The community was interested in discontinuing chlorine dioxide as a secondary disinfectant and wanted to trial alternative disinfection methods. They prioritized chlorination as their preferred secondary disinfectant option if it did not produce disinfection by-products (DBPs) above the regulated levels. Chloramination was included as a contingency option in case chlorination did not produce satisfactory results.

2. Rationale

DBPs are formed when certain natural organic matter (NOM) is present in water and reacts with chemical disinfectants, such as chlorine (MECP, 2006). NOM is a general term to describe complex organic compounds that vary between the geographic region and the source water (Health Canada, 2019). Although NOM does not cause adverse health effects directly, it is a challenge for many drinking water utilities due to its effects on other health-based standards such as DBP formation and water quality characteristics such as colour, taste and odour. Additionally, NOM is highly variable and source water specific when it comes to treatment efficacy, DBP formation potential and limitations in monitoring technologies. NOM compounds can differ in molecular size, shape, charge, biodegradable half-life, reactivity, and hydrophobic or hydrophilic properties (Health Canada, 2019) and all respond differently to available treatment strategies.

The efficacy of a single treatment is not universal for NOM and may change seasonally due to natural events like temperature changes, snow melt and precipitation. Consequently, a utility should monitor NOM if possible; and may need to adopt multiple treatment strategies to adapt to the changing water conditions (Health Canada, 2019). NOM is typically monitored using total organic carbon (TOC), which measures the suspended and dissolved portions of organic carbon;

dissolved organic carbon (DOC), which measures only the dissolved portion of organic carbon; and/or ultraviolet absorbance (UVa) that measures a relative portion of organic carbon that absorbs UV light at a 254nm wavelength.

The specific ultraviolet absorbance (SUVA) is a relationship between the measurement of DOC and UVa, and acts as an operational indicator of the organic composition (Edzwald and Tobiason 1999). It is typically used operationally for estimating the removal of DOC using the coagulant aluminum sulphate (alum) but can also be used to gauge the proportion of DOC that absorbs UV light and understand more about the composition of the organics.

Table 2.1. Guidelines for Organic Composition

SUVA	Composition
≥ 4	Mostly aquatic humic, hydrophobic, high molecular weight
2 – 4	Mixture of humics and non- humics
≤ 2	Mostly non-humics, hydrophilic, low molecular weight

(Edzwald and Tobiason 1999)

The SUVA value obtained from the water estimates the organic composition, or DOC. If the SUVA value is ≥ 4, the organics are mostly high in molecular weight (MW), humic compounds, and are hydrophobic in nature. A larger proportion of the organics will absorb UV light, meaning a higher UVa per milligram (mg) of DOC. Conversely, as the SUVA value decreases, so does the molecular weight. The humic compounds and the proportion of DOC that absorbs UV light also decreases with the SUVA value.

In this water treatment system, ozone is used to oxidize high MW organic compounds into lower MW compounds, making them available for biological filtration in the slow sand filter. If the UVa value consistently represents a higher portion of the DOC (SUVA $\geq$4), then UVa monitoring may be a good strategy to monitor DOC. In this context, the change in SUVA and/or UVa throughout treatment may be useful as an operational indicator for the performance of the pre-ozonation system. Additionally, the change in raw water SUVA may also be an indicator of seasonal changes to water quality due to the natural degradation of organics throughout the year.

When NOM reacts with chlorinated disinfection chemicals, the commonly formed DBPs are Trihalomethanes (THMs) and Haloacetic Acids (HAAs). They are regulated at a maximum acceptable concentration (MAC) 100 µg/L and 80 µg/L for THMs and HAAs, respectively, due to their presumed carcinogenic effects (Health Canada, 2017). Chloramination and chlorine dioxide systems typically produce lower levels of THMs and HAAs. N-nitrosodimethylamine (NDMA) is another potential DBP often associated with chloramination disinfection and regulated at 0.009 µg/L because it is a semi-volatile organic chemical and potent carcinogen (USEPA, 2014). Generally, the preferred approach to reduce DBPs is by reducing the concentration of NOM in the treated water. Reducing NOM in the treated water will also improve the taste, odour, and colour, while decreasing the chlorine demand and biological regrowth in the distribution system (Matilainen et al. 2006).

To reduce NOM in the treated water, each treatment component in the water treatment plant should be evaluated for TOC, DOC, and/or UVa reduction. Conventional slow sand filters have been reported to remove up to 15-30% of DOC and up to 20-35% of THM precursors (Amy et al. 2006). The addition of pre-ozonation has reportedly improved DOC and THM precursor removal up to 55% and 64%, respectively (Graham, 1999). However, the performance of the downstream treatment is dependent on the previous step to cumulatively provide DOC removal efficacy. For example, pre-ozonation has commonly been used to oxidize complex NOM into a biodegradable or useable food source for microbes in the slow sand filter (SSF) (Matilainen et al. 2006). The roughing filter (RF) is typically made up of various sized gravel with a layer of granular activated carbon, capable of quenching the residual ozone to protect the microbe viability in the SSF.

NOM will react with secondary disinfectants such as chlorine, chloramine or chlorine dioxide. Higher amounts of NOM increase the amount of chemical dose required to maintain a residual to ensure safe drinking water. Conversely, a lower amount of NOM in the treated water results in a lower amount of disinfection by-products, and a more desirable aesthetic water quality.

3. Objectives

The objective of this project was to monitor concentrations of DBPs, specifically THMs, HAAs, and NDMA that may be produced in a drinking water supply when using chlorinated disinfection strategies. This project obtained grab samples over the course of one year to capture seasonal changes to water quality and the effects on the formation of disinfection by-products.

4. Methods

A sample of raw (untreated), roughing filter (RF), and treated sample (UV disinfected, with no chlorine dioxide) was analyzed by WCWC staff at the beginning of the experiment to determine the water quality using the parameters, instruments and methods listed in Table 4.1.

Table 4.1. Bench Scale Sampling and Laboratory Analysis

Parameters	Method	Instruments	Treatment
Turbidity	Nephelometric	Hach 2100P	
UV absorbance	Method 10054	Real UV$_{254}$	0.45 µm Filter
DOC	Persulphate- UV oxidation	Sievers 5310C Laboratory TOC	0.45 µm Filter
pH	Method 8156	Hach HQ40D/ PHC201	
SUVA	Calculation		
Cl$_2$ demand	Method 8021	Hach DR 3900	
[1]Alkalinity	Method 8203	Hach Digital Titrator 16900	
[1]Aluminum	Method 8326	Hach DR 3900	
[1]Ammonia	Method 8155	Hach DR 3900	
[1]Hardness, Total	Method 8213	Hach Digital Titrator 16900	
[1]Iron	Method 8008	Hach DR 3900	
Manganese	Method 8149	Hach DR 3900	
[1]Apparent Colour	Method 8025	Hach DR 3900	
True Colour	Method 8025	Hach DR 3900	0.45 µm Filter
[1]TDS		Hach HQ40D/ CDC40101	
[1]Fluoride		Hach HQ40D/ ISEF121	
[1]Sodium		Hach HQ40D/ ISENA381	

[1]Raw water only

Water samples were taken from the water treatment plant as raw, roughing filters 1 and 2, slow sand filters 1 and 2, and the treated from both trains. In the treated sample, a simulated distribution system (SDS) DBP test, adapted from *Standard Methods for the Examination of Water and Wastewater* (APHA, 2017), was completed to show how chlorination and chloramination doses would impact the formation of DBPs for this drinking water supply at the time of sampling. The treated water from the plant was dosed with the selected disinfectants based on the residual and demand after 6 or 8 days of detention. A large distribution leak that altered the distribution detention time from 8 days to 6 days was present during most of this study and was factored into applicable samples. Samples were collected in amber glass bottles that were pretreated to be chlorine demand free. All glassware used in the SDS-DBP experiments was treated to be chlorine demand free. The water samples were dosed with a range of concentrations and immediately measured for free and total chlorine; then stored at room temperature and kept in darkness with no headspace. After the designated detention time, the samples were measured for free and total chlorine. The dose that yielded a residual closest to 1.0 mg/L was transferred into the respective DBP vial and shipped to an external lab for DBP analysis. Chlorination doses were measured for THMs and HAAs; and chloramination doses were measured for THMs, HAAs, and NDMA.

5. Results and Discussion

5.1. Chloramination

The chloramination strategy for secondary disinfection was tested on three grab samples from October 2019 to March 2020. An example of the chloramination strategy shows a dose of 0.42 mg/L of ammonia and multiple doses of chlorine for the chlorine breakpoint curve from the October sample (Figure 5.1.1). It was determined that a target of 0.42 mg/L of ammonia and 2 mg/L of chlorine would yield a combined chlorine residual of 0.30 mg/L after 6 days, above the minimum of 0.25 mg/L. This was used as a reference to guide the doses for the next chloramination SDS-DBP tests.

The THMs and HAAs were below the MAC in December but were both above the MAC in March. The Centre and the community agreed to discontinue chloramination as a strategy due to the undesired DBP results and other factors related to system dosing and on-site storage

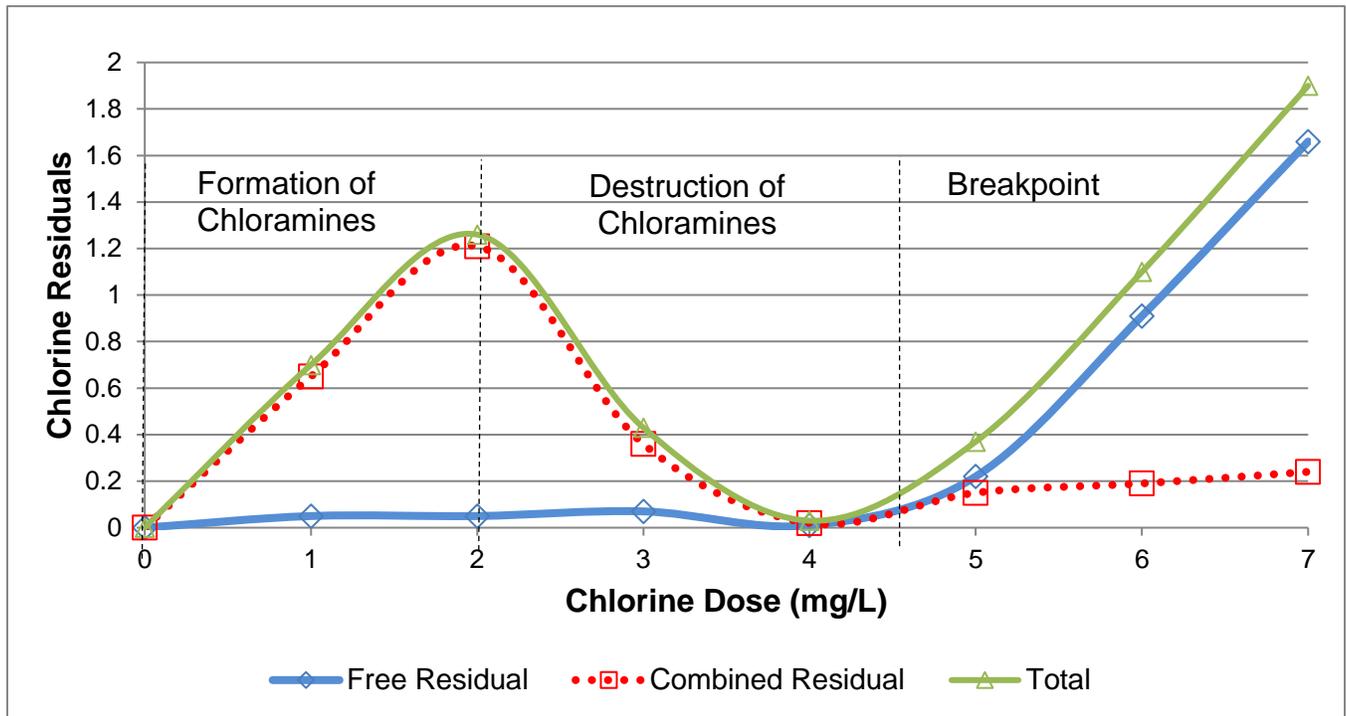requirements. NDMA was below the detection limit in December 2019 for the chloramination SDS-DBP tests.

Figure 5.1.1. Chlorination Breakpoint Curve on Treated Water after 18 h

5.2. Chlorination

Chlorination was the community's preferred approach and was tested throughout the year to determine if there would be seasonal variation in the results. Grab samples were taken about every two months from October 28th of 2019 until December 14th, 2020. On average, the SDS-DBP chlorine dose was 4.0 mg/L, the free chlorine demand was 3.3 mg/L, leaving a free chlorine residual around 0.66 mg/L after 6 or 8 days of detention. In all six of the SDS-DBP tests throughout the year, the THMs and HAAs were above the MAC with the only one exception for HAAs in December 2020 (Figure 5.2.1).

The water treatment plant replaced the granular activated carbon (GAC) in roughing filter 2 (RF2) towards the middle of November 2019. Immediately there was an improvement to the reduction in DOC in RF2 compared to RF1 (Figure 5.2.2), and this resulted in less DOC, THMs and HAAs in the treated water (Figure 5.2.1). This DOC performance improvement was temporary as

expected, because GAC media is used to quench ozone in the roughing filter, rather than treat for DOC.

The ozone system was upgraded in September 2020, identified in Figure 5.2.1. The water quality results following the upgrade suggested it may have had an impact on the treated water quality in October; but there wasn't enough data to make any conclusions. The DOC removal after the ozone upgrade in October of 2020 was 53% in the treated compared to 22% in October the year before. Conversely, the December 2020 DOC removal was only 7% with the new ozone system compared to 50% the previous year.

Table 5.2.1. Water Treatment Plant DOC Reduction Performance

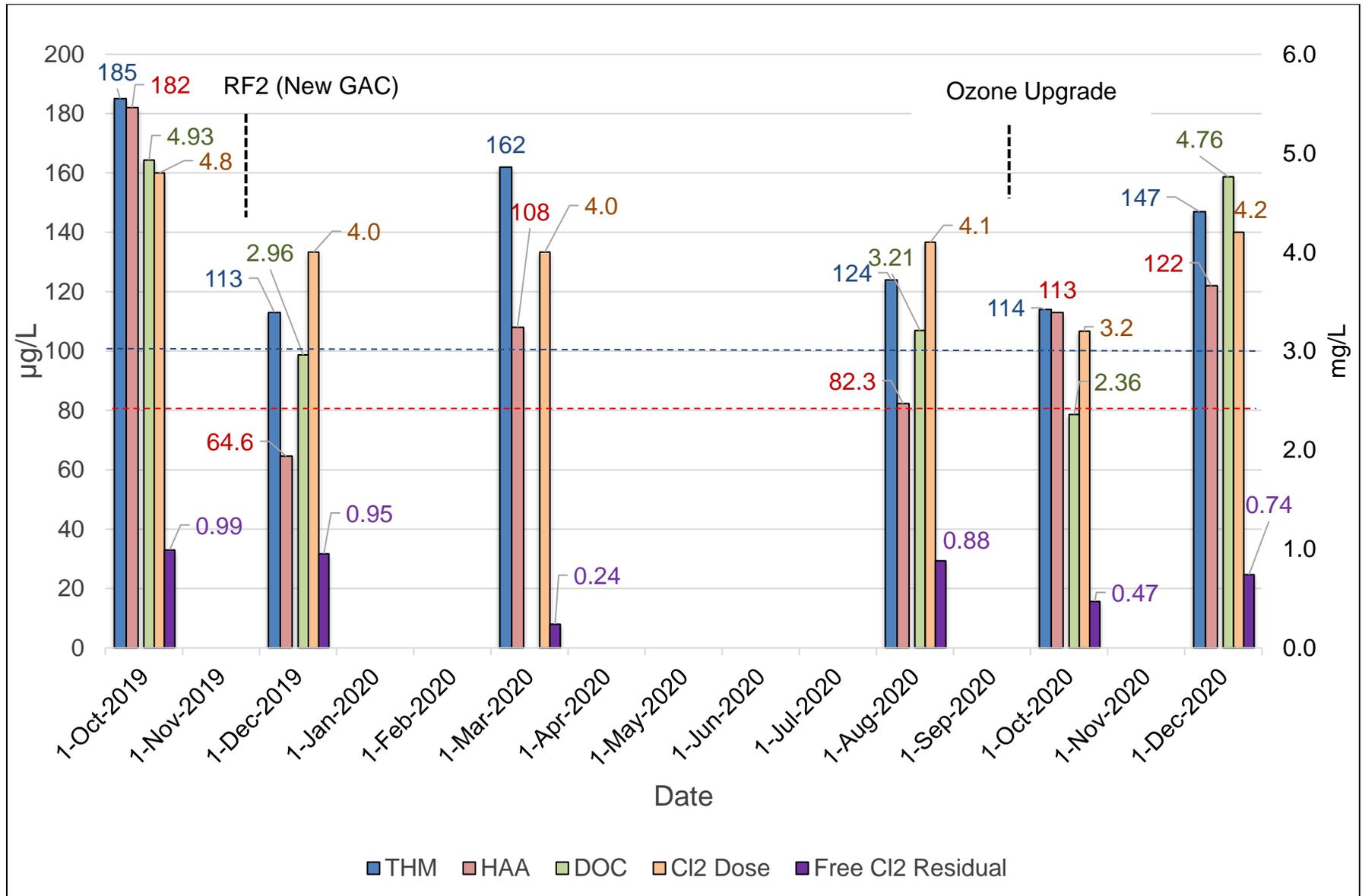| Grab Sample Date	RAW (mg/L)	Treated (mg/L)	Removal (%)
10/28/2019	6.3	4.93	22
12/9/2019	5.92	2.96	50
8/31/2020	5.31	3.21	40
10/20/2020	5	2.36	53
12/21/2020	5.1	4.76	7

Figure 5.2.1. Treated Water Quality Results for SDS- DBP, Chlorination, and DOC for 6 days of detention

Note: DOC data not available for March 2020, analyzer malfunctioned and reached end of life.

DOC and UVa were plotted throughout the treatment steps and graphed using a column chart to better understand how NOM reacted to upgrades to the system and to the various stages of treatment (Figure 5.2.2). As ozone oxidation changes the composition of NOM, it doesn't affect the DOC as much as the UVa between the Raw and Splitter Box samples (Figure 5.2.2). The new GAC media adsorbed DOC temporarily, illustrated by the brief improvement to the RF2 DOC compared to RF1 after the new GAC. Since the UVa changes after oxidation with ozone, there is potential that UVa could be used as a surrogate to monitor the performance of ozone oxidation. More data is needed before UVa can be used to estimate the performance of downstream treatment.
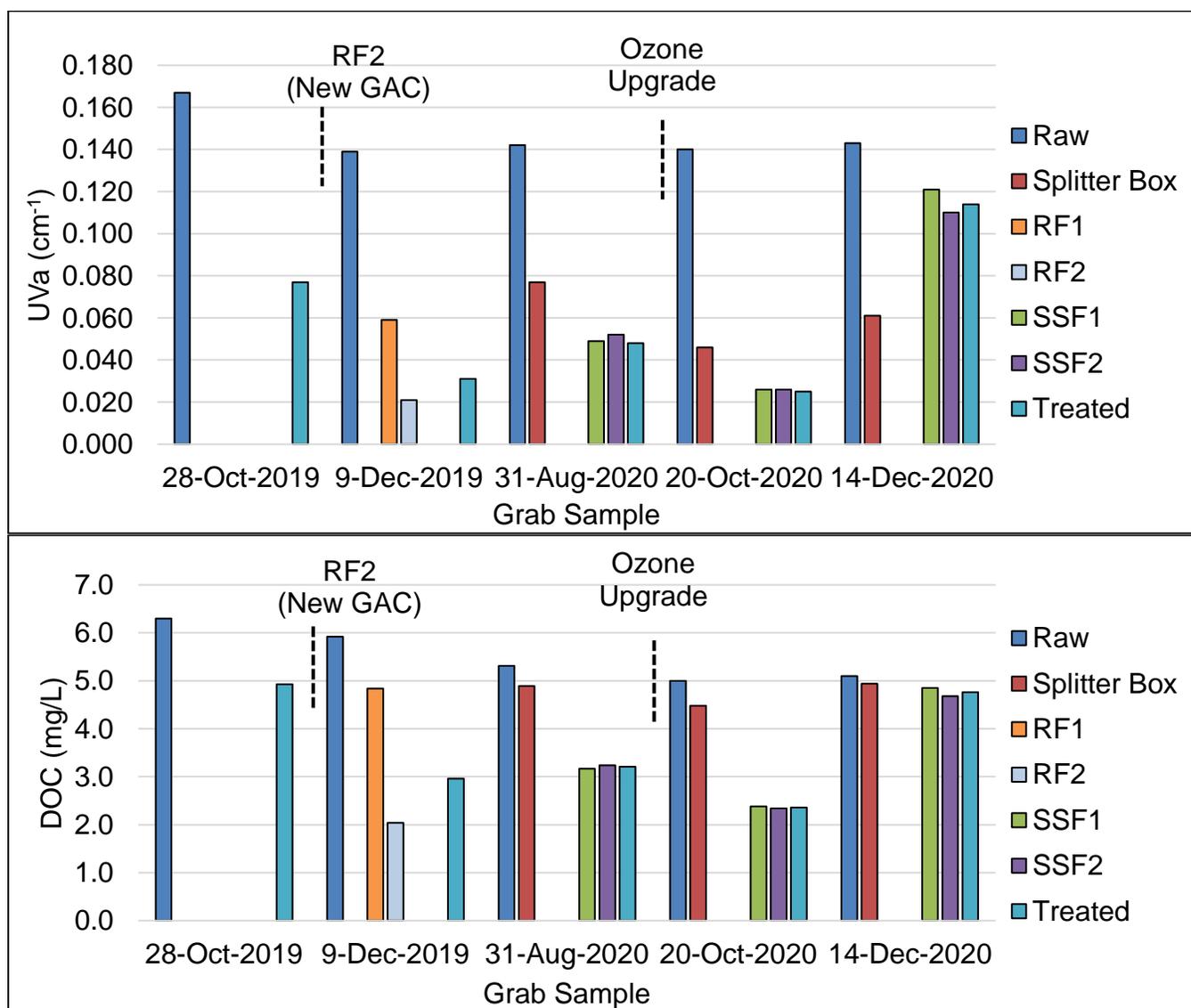
Figure 5.2.2. Change in UVa and DOC throughout Water Treatment Plant

6. Conclusions

During the sampling period, the chlorinated water from the simulated distribution system resulted in THMs and HAAs from 113 µg/L to 185 µg/L and from 65 µg/L to 182 µg/L, respectively. For a detention time of 6 days and chlorine residuals between 0.24 mg/L and 0.99 mg/L, both THMs and HAAs exceeded the maximum acceptable concentration for the six SDS THMs HAAS tests.

The DOC of the raw and treated water ranged from 5.0 mg/L to 6.3 mg/L and 2.36 mg/L to 4.93 mg/L, respectively.

Considering the plant performance during the simulated distribution system tests, both chloramination and chlorination as a secondary disinfection would produce water that exceeds the maximum acceptable concentrations of THMs and HAAs.

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8. Appendix A

Table 8.1. Initial water characteristics (October 15th, 2019)

Parameters	Method	Instruments	Raw	Treated
Turbidity (NTU)	Nephelometric	Hach 2100P	0.74	0.22
UV abs (cm^{-1})	Method 10054	Real UV_{254}	0.148	0.062
DOC (mg/L)	Persulphate- UV oxidation	Sievers 5310C	5.88	4.48
pH	Method 8156	Hach HQ40D/ PHC201	7.93	7.33
SUVA	Calculation		2.5	1.38
Cl_2 demand (mg/L)	Method 8021	Hach DR 3900		3.5
[1]Alkalinity (mg/L)	Method 8203	Hach Digital Titrator 16900	75	
[1]Aluminum (mg/L)	Method 8326	Hach DR 3900	0.006	
[1]Ammonia (mg/L)	Method 8155	Hach DR 3900	0	
[1]Hardness, Total (mg/L)	Method 8213	Hach Digital Titrator 16900	66	
[1]Iron (mg/L)	Method 8008	Hach DR 3900	<0.02	
Manganese (mg/L)	Method 8149	Hach DR 3900	0.014	0.012
[1]Apparent Colour (PtCo)	Method 8025	Hach DR 3900	17	
True Colour (PtCo)	Method 8025	Hach DR 3900	13	13
[1]TDS (mg/L)		Hach HQ40D/ CDC40101	83.5	
[1]Fluoride (mg/L)		Hach HQ40D/ ISEF121	0.0551	
[1]Sodium (mg/L)		Hach HQ40D/ ISENA381	2.54	

[1]Raw water

9. Appendix B

Table 9.1. Grab Sample Raw Data for October 28th, 2019

Date	Parameters	Raw	RF (blended)	Treated
	DOC (mg/L)	6.30	6.12	4.93
	UV abs (cm^{-1})	0.167	0.095	0.077
	[1]SUVA	2.7	1.6	1.6
	TOC (mg/L)	6.44	6.22	5.08
	UV abs (cm^{-1})	0.173	0.114	0.095
	[1]SUVA	2.7	1.8	1.9
28-Oct-2019	pH	7.83	7.62	7.46
	(0 h) Cl$_2$ demand (mg/L)			0.60
	*6-day Cl$_2$ demand (mg/L)			3.20
	Cl$_2$ demand (mg/L)	Chlorination	Dose 4.8 mg/L chlorine, 6-day detention, (@ 20°C)	3.81
	THMs (µg/L)			185
	HAAs (µg/L)			182
	NDMA (µg/L)			<0.0008

* Estimated 6-day detention time due to distribution leak

Table 9.2. Grab Sample Raw Data for December 9th, 2019

Date	Parameter	Raw	RF 1	RF 2	Treated
	DOC (mg/L)	5.92	4.84	2.04	2.96
	UV abs (cm^{-1})	0.139	0.059	0.021	0.031
	SUVA	2.65	1.22	1.03	1.05
	(0 h) Cl$_2$ demand (mg/L)				0.52
	6-day Cl$_2$ demand (mg/L)				3.05
9-Dec-2019	Free Cl$_2$ residual (mg/L)	Chlorination	Dosed 4.0 mg/L chlorine, 6-day detention time (@ 20°C)		0.99
	THMs (µg/L)				113
	HAAs (µg/L)				64.6
	THMs (µg/L)		Dosed 0.42 mg/L ammonia,		24.4
	HAAs (µg/L)	Chloramination	Dosed 2.0 mg/L chlorine,		18.6
	NDMA (µg/L)		6-day detention (@ 20°C)		<0.0008

WTP replaced GAC in RF2 and wanted to monitor differences in treatment for each train going forward.

Table 9.3. Grab Sample Raw Data for March 9th, 2020

Date	Parameter	Raw	RF 1	RF2	SSF1	SSF2	Treated
	DOC (mg/L)	-	-	-	-	-	-
	UV abs (cm^{-1})	0.152	0.052	0.047	0.049	0.044	0.045
	pH	7.72	7.5	7.64	7.66	7.68	7.62
9-Mar-2020	(0 h) Cl$_2$ demand (mg/L)	Chlorination		Dosed 5.0 mg/L chlorine, 6-day detention time (@ 20ºC)			0.60
	6-day Cl$_2$ demand (mg/L)						3.76
	Free Cl$_2$ residual (mg/L)						1.24
	THMs (µg/L)						162
	HAAs (µg/L)						108
	THMs (µg/L)	Chloramination		Dosed 4 mg/L chlorine Dosed 0.64 mg/L ammonia (@20ºC) Combined chlorine residual 2 mg/L			113
	HAAs (µg/L)						106

No DOC data available, analyzer reached end of life; NDMA was below detection limit and discontinued in March.

Table 9.4. Grab Sample Raw Data for August 31st, 2020

Date	Parameter	Raw	Splitter	SSF1	SSF2	Treated
	DOC (mg/L)	5.308	4.893	3.17	3.24	3.21
	UV abs (cm^{-1})	0.142	0.077	0.049	0.052	0.048
	SUVA	2.7	1.6	1.5	1.6	1.5
31-Aug-2020	(0 h) free Cl$_2$ demand (mg/L)	Chlorination		Dosed 4.0 mg/L chlorine, 6-day detention time (@ 20ºC)		0.2
	6-day free Cl$_2$ demand (mg/L)					3.22
	THMs (µg/L)					124
	HAAs (µg/L)					82.3

Table 9.5. Grab Sample Raw Data for October 20th, 2020

Date	Parameter	Raw	Splitter	SSF1	SSF2	Treated
	DOC (mg/L)	5.00	4.48	2.38	2.34	2.36
	UV abs (cm^{-1})	0.14	0.046	0.026	0.026	0.025
	SUVA	2.8	1.0	1.1	1.1	1.1
20-Oct-2020	(0 h) free Cl_2 demand (mg/L)	Chlorination	Dosed 3.2 mg/L chlorine, 6-day detention time (@ 20ºC)			0.4
	6-day free Cl_2 demand (mg/L)					2.7
	THMs (μg/L)					114
	HAAs (μg/L)					113

The WTP installed a new ozone system in September.

Table 9.6. Grab Sample Raw Data for December 21st, 2020

Date	Parameter	Raw	Splitter	SSF1	SSF2	Treated
	DOC (mg/L)	5.10	4.94	4.85	4.68	4.76
	UV abs (cm^{-1})	0.143	0.061	0.121	0.11	0.114
	SUVA	2.8	1.2	2.5	2.4	2.4
21-Dec-2020	(0 h) free Cl_2 demand (mg/L)	Chlorination	Dosed 4.2 mg/L chlorine, 8-day detention time (@ 4ºC)			1.00
	8-day free Cl_2 demand (mg/L)					3.46
	THMs (μg/L)					147
	HAAs (μg/L)					122

Two sets of samples were stored at 20ºC and 4ºC. Only the highest dose and lowest temperature had a chlorine residual after 8 days.