



Pilot Testing Project Report

Effect of Chlorine Detention Times on Disinfection By-Products

Walkerton Clean Water Centre

Research and Technology

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Disclaimer

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Executive Summary

Background

The Drinking Water System (DWS) has been experiencing increased trihalomethanes (THMs) over the past few years. The THMs are approaching the maximum acceptable concentration (MAC) of 100 µg/L as a running annual average (MECP 2020).

Disinfection by-products (DBPs), such as THMs and haloacetic acids (HAAs) can form in chlorinated waters with organic precursors. However, the majority of the THMs are brominated THMs, suggesting that bromide contributes to the DBP formation.

The reservoir can have a detention time up to 10 days. This increased detention time can contribute to higher THMs as well.

Objective

The objective of this project is to complete a simulated distribution system (SDS) test for THMs and HAAs after three different detention times through bench-scale testing.

Approach

Samples were collected at the DWS and sent to the Centre. An SDS test was conducted to test various chlorine dosages and contact times.

Key Findings

Through bench-scale testing it was determined that:

- For Well #1, the majority of the THMs were brominated THMs. THMs were above the MAC of 100 µg/L only after 2 days of detention time when dosed with 7 mg/L of chlorine. THMs increased with increasing detention time.
- For Well #2, the majority of the THMs were chlorinated. THMs were consistently below the MAC of 100 µg/L when samples were dosed with 4.5 mg/L of chlorine.

THMs remained below the MAC even though the THMs increased with increasing detention time.

- For Well #3, the majority of the THMs were brominated. THMs were above the MAC of 100 µg/L only after 2 days of detention time when samples were dosed with 6 mg/L of chlorine. THMs increased with increasing detention time.
- For blended Well #1 and #2, THMs were below the MAC of 100 µg/L when samples were dosed with 6 mg/L of chlorine after 2 days of detention time. After 10 days of detention time, the THMs exceeded the MAC of 100 µg/L.
- All HAAs were below the MAC of 80 µg/L, regardless of well source and detention time.

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1. Introduction

The Drinking Water System (DWS) is in Central Ontario and services a population of 510 and relies on three drilled wells. Well #1 and #2 are fed and blended into the reservoir. However, majority of the town's water is provided by Well #3. The DWS has been experiencing increased trihalomethanes (THMs) in the past few years. The THMs values are approaching the maximum acceptable concentration (MAC) of 100 µg/L as a running annual average (RAA) (MECP 2020). Although the community does not have high haloacetic acids (HAAs), this report includes HAAs to ensure that HAAs trends are also tracked in the project.

Disinfection by-products (DBPs), such as THMs and HAAs, can form in chlorinated waters with organic precursors. Although the total organic carbon is generally low in the community's source water (1.6 mg/L Well #1, 0.8 mg/L Well #2, 1.5 mg/L Well #3), the bromide levels can contribute to brominated DBP formation (0.4 mg/L Well #1, <0.05 mg/L Well #2, 0.34 mg/L Well #3). Therefore, controlling bromide can ultimately reduce the formation of brominated THMs (e.g. bromoform, dibromochloromethane and bromodichloromethane) (Soyluoglu *et al.* 2020). Methane has also been detected in the Town's raw water. Membrane filtration (e.g. reverse osmosis or nanofiltration) and sorption processes (e.g. granular activated carbon or ion exchange resins) are common bromide removal treatment technologies (Soyluoglu *et al.* 2020).

Contact time is another major factor in DBP formation. The reservoir can have a detention time up to 10 days. Therefore, it is important to assess the THMs formation at different detention times.

The Walkerton Clean Water Centre (Centre) tested the impact of detention times and DBPs precursors, such as bromide, to ultimately control THMs and HAAs.

Using the individual groundwater sources from the DWS, the objective is to conduct a simulated distribution system (SDS) test for THMs and HAAs after three different detention times through bench-scale testing.

2. Materials and Method

2.1 Raw Water Quality

Raw water samples were collected from each well source, shipped to the Centre and analyzed at the Centre. Some water samples were also sent to an accredited laboratory to test water quality parameters.

Samples were collected to test methane on-site at the same time and location that the raw water was collected. Methane was also tested once WCWC staff received the shipped sample bottles (Table 1). The methane was drastically reduced in samples taken from the shipped carboys, compared to samples taken on-site. It is suspected that a lot of methane was released in the transportation process. Some headspace was noted in the carboys upon arrival, which would have contributed to the loss of methane.

Understanding the raw water quality of each well source will provide insight on major precursors for THMs formations. Natural organic matter (NOM) is the predominant precursor to DBP formation. Although the dissolved organic carbon (DOC) is low for each well source, the specific ultraviolet absorbance (SUVA) was calculated using filtered UV absorbance and DOC (Equation 1) (Edzwald and Tobiason 1999, EPA 1999).

$$SUVA = \frac{UV_{254} (cm^{-1})}{DOC (\frac{mg}{L})} \times \frac{100 cm}{1 m}$$

Equation 1. SUVA Calculation

Raw water SUVA values can characterize the NOM and predict the formation potential of DBPs (Hua *et al.* 2015). SUVA values greater than 4 indicate that the organics are highly hydrophobic with high molecular weights and highly aromatic structures (Edzwald and Tobiason 1999, EPA 1999). SUVA values between 2 – 4 indicate that the organics are a mixture of hydrophobic and hydrophilic organics and a mixture of molecular weights (Edzwald and Tobiason 1999, EPA 1999). SUVA values less than 2 indicate that the

organics have low hydrophobicity with low molecular weights and few aromatic structures (Edzwald and Tobiason 1999, EPA 1999). Highly aromatic organic carbons (SUVA greater than 4) are considered to be the major precursor for THMs and HAAs (Hua *et al.* 2015). Well #1 and Well #3 are slightly above 2 and Well #2 was below 2, which indicate that the organic matter is not highly aromatic. Studies have shown that when the SUVA values are lower (e.g. low humic content), it tends to be a weaker indicator of reactivity of DOC (Hua *et al.* 2015).

It is also noted that bromide concentrations are high in Well #1 and Well #3. The bromide in the water can increase the reactivity of the DBP formation with chlorination and NOM. Additional detail of this reaction is outlined in Section 3.2. Simulated Distribution System.

Table 1. Raw Water Quality

	Parameter	Well #1	Well #2	Well #3
Samples collected on-site	Methane (L/m ³) ¹	8.2	0.03	14
	Bromide (mg/L) ¹	0.45	<0.05	0.39
	Total Organic Carbon (mg/L) ^{1,2}	2	<1	2
	Dissolved Organic Carbon (mg/L) ^{1,2}	2	1	2
Samples collected at WCWC from received samples	Turbidity (NTU)	1.13	3.36	0.097
	pH	8.35	7.65	8.26
	Methane (L/m ³) ¹	1.9	<0.02	1.6
	UV ₂₅₄ absorbance (unfiltered) (cm ⁻¹)	0.053	0.052	0.042
	UV ₂₅₄ absorbance (filtered) (cm ⁻¹)	0.047	0.016	0.042
	Alkalinity (mg/L as CaCO ₃)	126	198	184
	Iron (mg/L)	0.09	0.63	0.6
	Manganese (mg/L)	0.01	0.074	0.004
	Ammonia (mg/L)	0.27	0.22	0.25
	SUVA (L/mg•m)	2.35	1.60	2.10

¹Note. These parameters were measured by an accredited laboratory.

²Note. Well #2 had <1 mg/L of Total Organic Carbon (TOC) but had 1 mg/L for Dissolved Organic Carbon (DOC), implying that DOC was higher than TOC. Since TOC is the sum of DOC and particulate organic carbon, TOC should always be greater than or equal to DOC. The discrepancy could be because the values are close to the laboratory's method limit of detection of 1 mg/L for DOC and TOC.

2.2 Water Quality Analysis

Water quality analysis was completed throughout the project using the methods described below (Table 2).

Table 2. Methods of Water Quality Analysis

Parameter	Preparation	Method	Range
In-House Analysis			
Turbidity	N/A	USEPA Method 180.1	0 – 1000 NTU
pH	N/A	Hach Method 8156	0 – 14
UV ₂₅₄ absorbance (UV transmittance)	0.45 µm filtered	Real Tech UV ₂₅₄ Method	0 – 2 Abs/cm
Alkalinity	N/A	Hach Method 8203	10 – 4000 mg/L as CaCO ₃
Chlorine (free and total)	N/A	USEPA DPD Method	0.02 – 2.00 mg/L
Iron	N/A	Hach Method 8008	0 – 3.00 mg/L
Manganese	N/A	Hach Method 8149	0.006 – 0.700 mg/L
Ammonia	N/A	Hach Method 8155	0.01 – 0.50 NH ₃ -N
Parameter	Preparation	Method	Method Detection Limit
Analyzed at a Licensed Laboratory			
Bromide	N/A	Ion Chromatography EPA300	0.05 mg/L
Methane	N/A	Lab Specific Method	0.02 L/m ³
Total Organic Carbon (TOC)	N/A	Standard Methods 5310	1 mg/L
Dissolved Organic Carbon (DOC)	0.45 µm filtered	Standard Methods 5310	1 mg/L
Total trihalomethanes	Chlorine dosage varied on well source and stored for three different contact times.	EPA 5030B/8260C	0.5 µg/L
Haloacetic acids	Chlorine dosage varied on well source and stored for three different contact times.	EPA 552.3	5.3 µg/L

2.3 Simulated Distribution System

The water collected from each source was transferred into 250 mL chlorine demand free, amber glass containers and tested using the (SDS) test (APHA 2017). To achieve chlorine demand free containers, the glassware was treated with 10 mg/L of chlorine solution for a minimum of 3 hours, rinsed with deionized water and left to air dry.

Prior to the SDS test, the chlorine demand of each groundwater source was determined. A blended groundwater source was created by mixing 53% of Well #1 and 47% of Well #2. This ratio was selected to represent the rate of blending of the two sources at the DWS. To achieve a chlorine residual of 1 mg/L after 10 days, it was determined that the appropriate chlorine dosages were different for each well source (Table 3).

Table 3. Chlorine Dosage determined after chlorine demand test.

Detail	Well #1	Well #2	Well #3	Well #1 + Well #2 Blended
Target Chlorine Dosage	7 mg/L	4.5 mg/L	6 mg/L	6 mg/L
Chlorine Demand	5.82 mg/L	3.37 mg/L	4.56 mg/L	4.51 mg/L
Chlorine Residual after 10-day contact time	1.04 mg/L	1.13 mg/L	1.14 mg/L	1.19 mg/L

The bottles were stored at room temperature and samples were collected and sent for THMs and HAAs analysis after 2 days, 4 days and 10 days of contact time. After each contact time, samples were transferred to sample bottles with sodium thiosulphate and ammonium chloride preservatives for THMs and HAAs tests, respectively. The samples were sent to an accredited laboratory. Total THMs (TTHMs) results reflect the sum of bromodichloromethane, bromoform, chloroform and dibromochloromethane concentrations. The five HAAs will include bromoacetic acid, chloroacetic acid, dichloroacetic acid, dibromoacetic acid and trichloroacetic acid.

3. Results and Discussions

3.1 Chlorine Demand

Each well was dosed differently to satisfy specific demand that was identified prior to the (SDS) test. The goal was to have a chlorine residual of close to 1 mg/L after 10-day detention time for each well source. At Day 0, the samples were dosed with chlorine and the residual was measured immediately after; however, the chlorine residual was reduced by approximately 50% due to immediate demand (Figure 1). Despite the different dosages of chlorine for each well, the chlorine residual from each well was similar after 2 days of contact time and resulted in a residual of close to 1 mg/L after 10 days of contact time (Figure 1). The biggest reduction in chlorine residual was found after 2 days and the residual only slightly decreased after 4 and 10 days of contact time (Figure 1).

The deionized water (DI) was dosed with 7 mg/L, 6 mg/L and 4.5 mg/L as a control to ensure the chlorine dosage was accurate and the chlorine did not decay over 10 days (Figure 1). The chlorine residual in the DI samples remained stable throughout the 10 days of contact time.

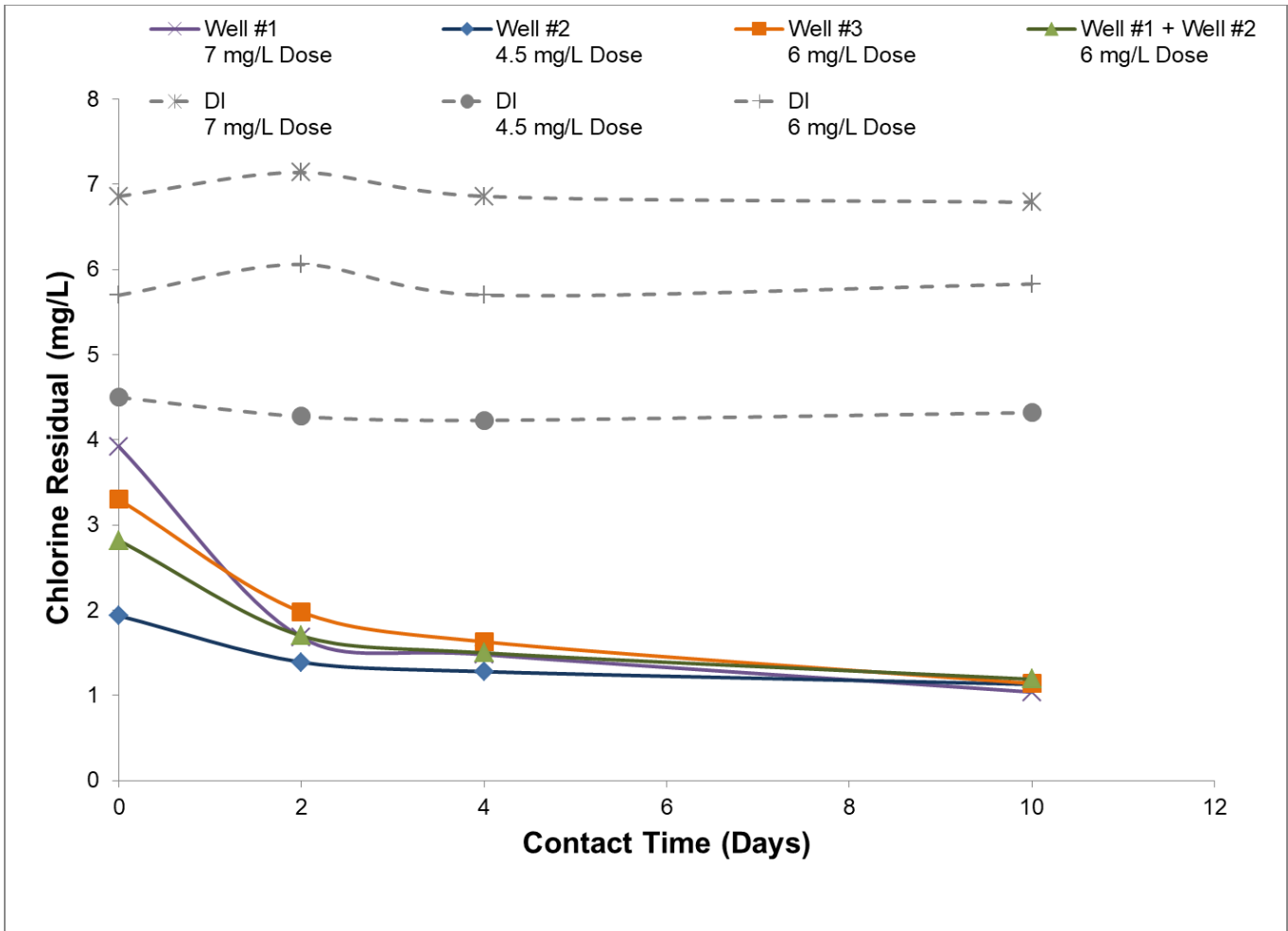


Figure 1. Chlorine Residual of Each Well Source and Deionized Water (DI) at Day 2, 4 and 10 Contact Time

3.2 Simulated Distribution System

The SDS test was performed to determine if there was an impact of detention time on the formation of DBPs, such as THMs and HAAs.

The THMs formation was dependent on the well source with specific chlorine dosage and increased with increasing contact time (Figure 2). Well #1 (7 mg/L chlorine dose) and Well #3 (6 mg/L chlorine dose) both contained THMs higher than the 100 µg/L MAC, regardless of the contact time (Figure 2). After 10 days of detention time, Well #1 and Well #3 contained 219 µg/L of total THMs with a chlorine residual of 1.04 mg/L and 1.14 mg/L, respectively.

The THMs were the lowest in Well #2 (4.5 mg/L chlorine dose) and remained below the MAC of 100 µg/L as a RAA (Figure 2). After 10 days of detention time, Well #2 contained 40 µg/L of total THMs with a chlorine residual of 1.13 mg/L.

The blended water (Well #1 and Well #2) (6 mg/L chlorine dose) contained THMs below the MAC after 2 days of contact time, but surpassed the 100 µg/L MAC after 4 days and 10 days of contact time (Figure 2). After 10 days of detention time, the blended water contained 131 µg/L with a chlorine residual of 1.19 mg/L.

When identifying the species of THMs, the majority of the THMs were attributed to brominated THMs (Dibromochloromethane, Bromoform and Bromodichloromethane) for Well #1, Well #3 and the blended Well #1 & #2.

An average of 93% and 94% of total THMs were from brominated THMs for Well #1 and Well #3, respectively (Figure 3). For Well #1 and Well #3, the increase in THMs levels over time was attributed to an increase in the brominated THMs (Figure 3). Detecting brominated THMs was expected, because bromide levels were 0.45 mg/L and 0.39 mg/L in Well #1 and Well #3, respectively (Table 1).

Well #2 contained an average of 62% of the total THMs as chloroform, which are not brominated THMs. For Well #2, the slight increase of total THMs levels over time was attributed to the increase in chlorinated THMs (e.g. chloroforms) (Figure 3). It was expected that there would be minimal brominated THMs in Well #2, because bromide in the Well #2 raw water was very low (<0.05 mg/L) (Table 1).

The blended water (Well #1 & Well #2) contained an average of 87% of the total THMs as brominated THMs (Figure 3). Brominated THMs increased over time more than the chlorinated THMs (Figure 3).

The reaction pathways of brominated THMs (e.g. bromoform, dibromochloromethane and bromodichloromethane) and chloroform vary and have different factors that influence their formations (Saidan *et al.* 2015). When bromide is present in drinking water and is exposed to hypochlorous acid (HOCl), the hypochlorous acid rapidly oxidizes bromide and forms hypobromous acid (HOBr) (Saidan *et al.* 2015, Watson 2012, Cooper *et al.* 1985). The HOBr can quickly react with NOM to form brominated THMs (Saidan *et al.* 2015, Watson 2012, Cooper *et al.* 1985). The reaction rate with HOBr and NOM is estimated to be 20 times more reactive than with HOCl and NOM, therefore the brominated THMs are formed first, and bromine fills the available sites on NOM (Saidan *et al.* 2015). With increasing reaction times, chlorinated THMs have been shown to shift to more brominated THMs (Saidan *et al.* 2015). It has also been shown in the literature that reaction time impacts brominated THMs more than chlorinated THMs (Saidan *et al.* 2015). The results in Figure 3 support the findings in the literature that the brominated THMs increase over time more than the chlorinated THMs, in the presence of bromide. Brominated THMs are more cytotoxic and genotoxic than chlorinated THMs (Soyluoglu *et al.* 2020, Saidan *et al.* 2015, Watson 2012).

The HAAs were consistently well below the MAC of 80 µg/L as a RAA, regardless of contact time or well source/chlorine dosage (Figure 4).

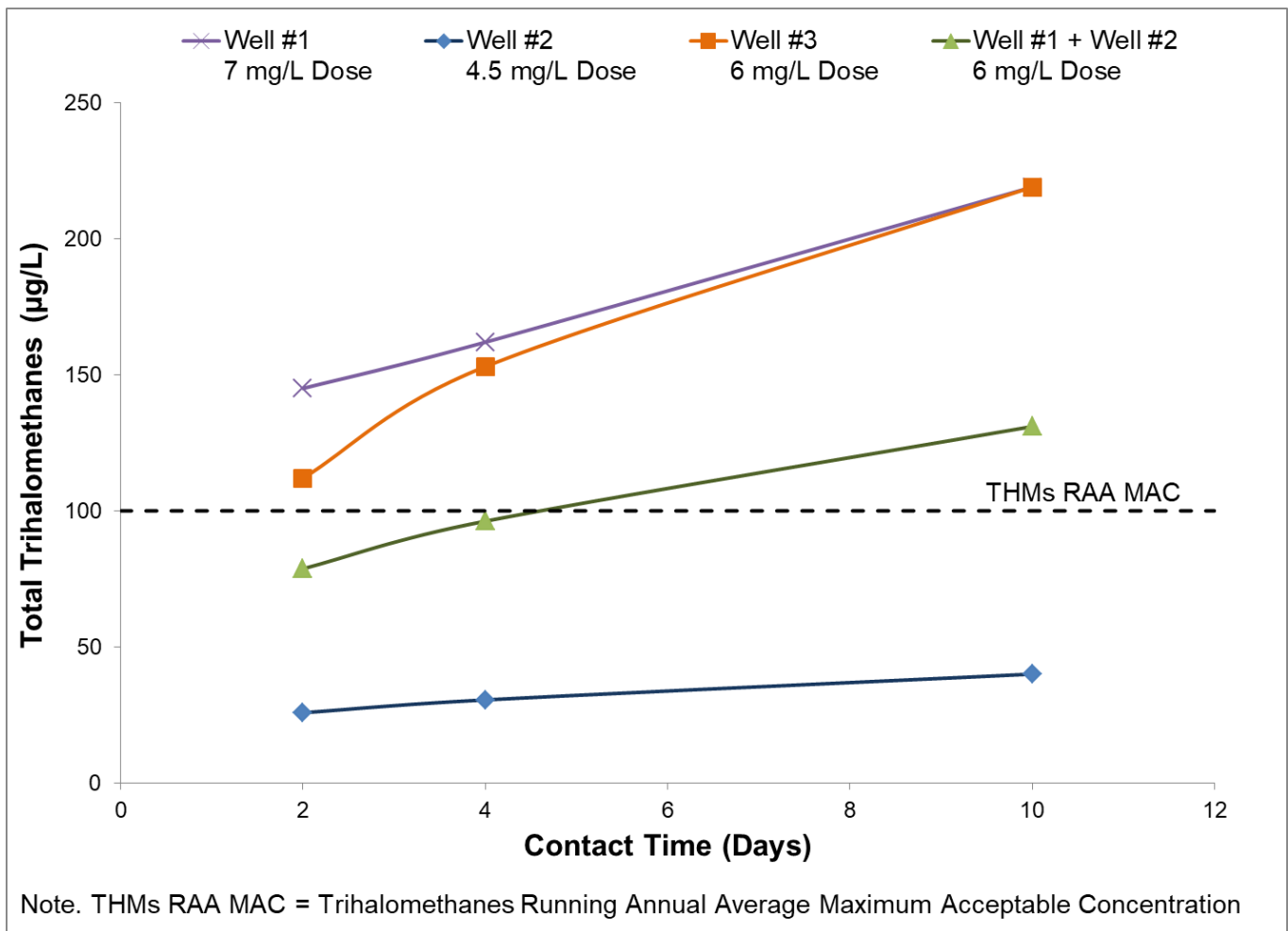
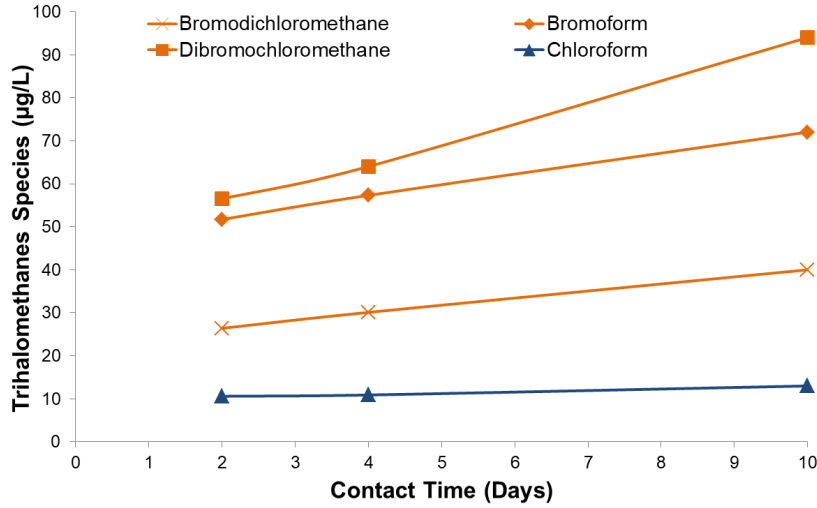
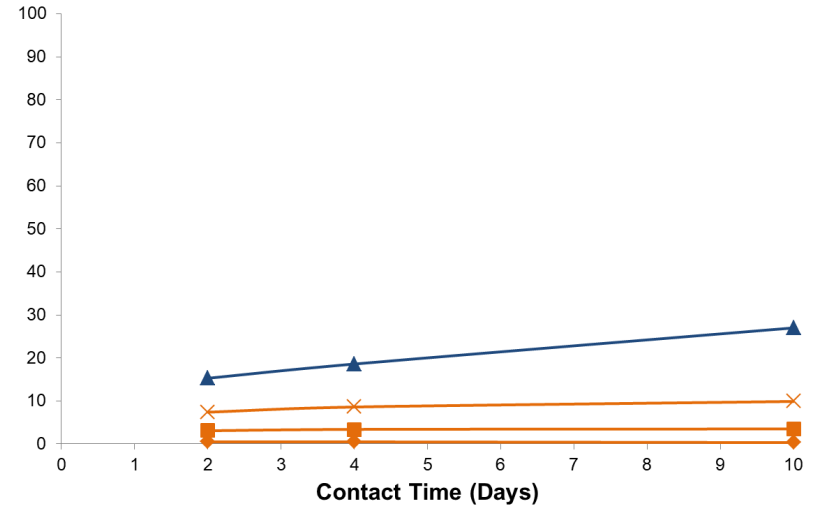


Figure 2. Total Trihalomethanes

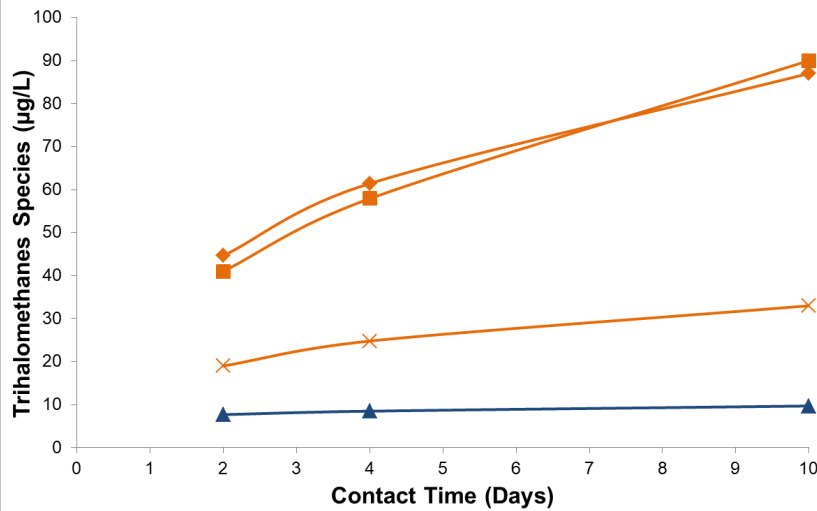
A) Well #1 (7 mg/L Chlorine Dose)



B) Well #2 (4.5 mg/L Chlorine Dose)



C) Well #3 (6 mg/L Chlorine Dose)



D) Well #1 & #2 (6 mg/L Chlorine Dose)

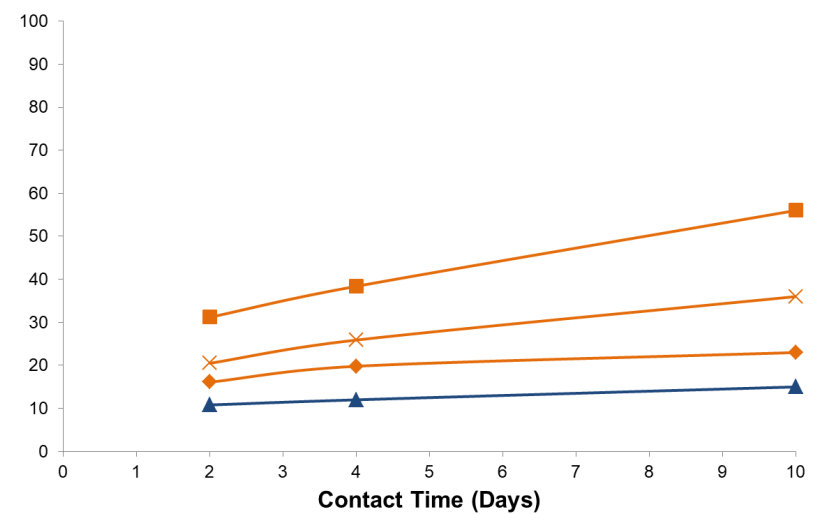


Figure 3. Trihalomethanes species from (A) Well #1, (B) Well #2, (C) Well #3 and (D) blended Well #1 & Well #2. The sum all four species equal total trihalomethanes.

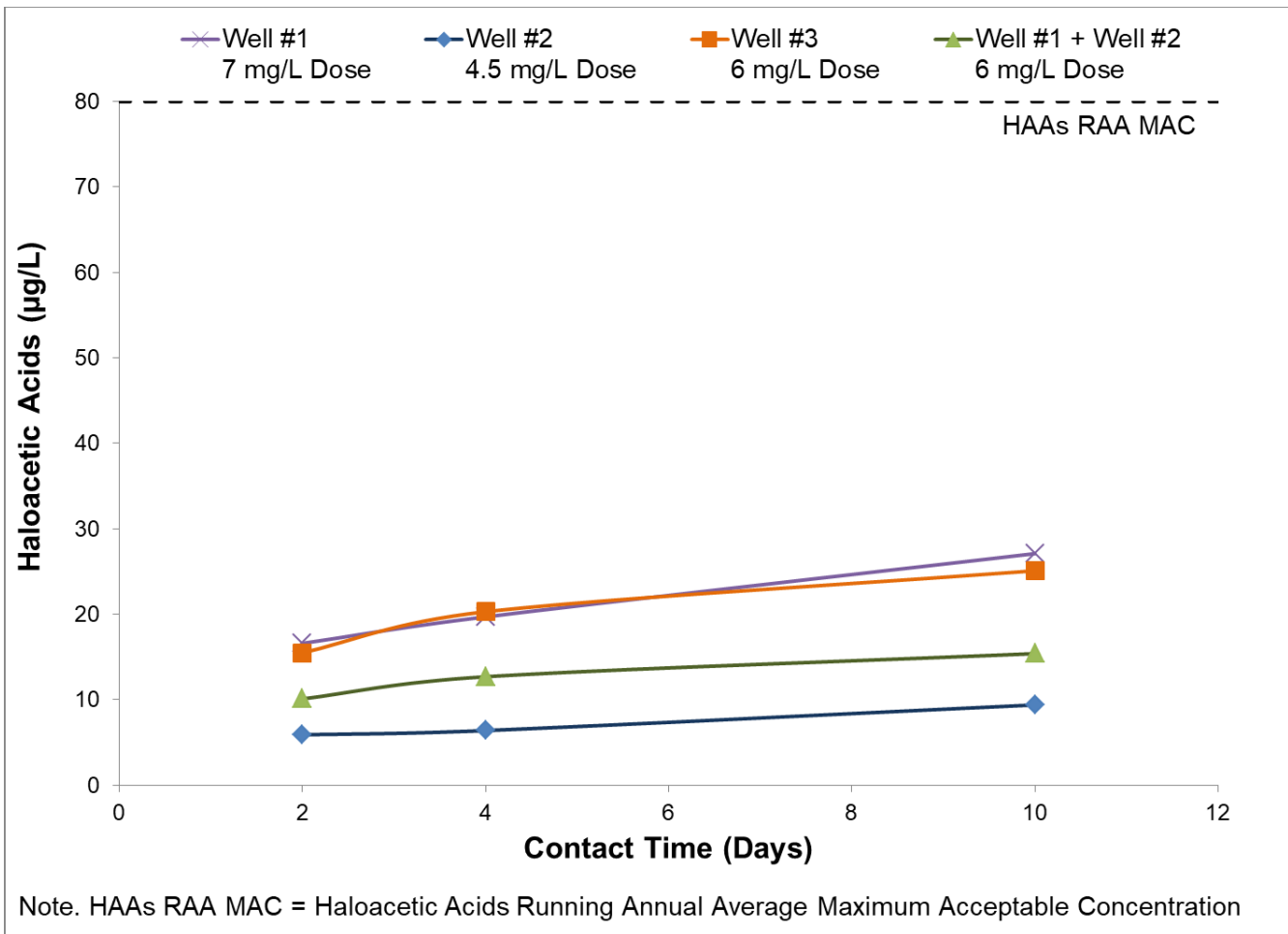


Figure 4. Haloacetic Acids

4. Limitations

The findings from this study do not consider the additional chlorine demand from the distribution system. All glassware was chlorine-demand free, so the demand from the materials was not considered in the simulated distribution system. For a conservative approach, the samples were stored at ambient room temperature; therefore, the rate of THMs formation is increased at higher temperatures. The temperature of the wells was recorded as 10.2 – 14.3 °C, therefore the rate of THMs formation in the full-scale DWS would be slower at these lower temperatures.

The simulated distribution system was designed to achieve the same chlorine residual of 1 mg/L after 10 days of contact time for each well source, which resulted in different initial chlorine dosages to satisfy demand specific to each well source. An increase of chlorine dosages can cause an increase in the formation of THMs.

Additionally, Well #1, #2 and #3 can blend together in the reservoir at the DWS. Well #3 is initially dosed with chlorine at the pump house and then can get exposed to additional chlorine at the reservoir. The tests done in this study did not include a second dose of chlorine.

5. Next Steps

To gain more insight on the removal strategies of THMs precursors to ultimately reduce THMs formation, additional work will be required to investigate the removal strategies of bromide through ion exchange and granular activated carbon pilot tests (Phase 2).

6. Conclusions

In conclusion, Well #1 and Well #3 both had high THMs above the 100 µg/L MAC, regardless of the detention time; whereas, Well #2 remained below the 100 µg/L MAC, regardless of the detention time. After 10 days of detention time, Well #1 and Well #3 contained 219 µg/L of total THMs with a chlorine residual of 1.04 mg/L and 1.14 mg/L, respectively. After 10 days of detention time, Well #2 contained 40 µg/L of total THMs with a chlorine residual of 1.13 mg/L. The blended water containing Well #1 and Well #2 had THMs trends that followed an approximate average between Well #1 and Well #2 on their own. After 10 days of detention time, the blended water contained 131 µg/L with a chlorine residual of 1.19 mg/L.

For Well #1 and #3, the majority of the total THMs were brominated THMs (Bromodichloromethane, Bromoform, Dibromochloromethane); whereas the majority of the total THMs in Well #2 were chlorinated THMs (Chloroform). The blended water of Well #1 and Well #2 contained an average of 87% of brominated THMs.

Although HAAs increased with increasing detention times, all HAAs were well below the 80 µg/L MAC and didn't exceed 30 µg/L.

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