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**Final Report**

# Chlorine Demand/Decay and Simulated Distribution System Disinfection By-Product Testing for a Large Municipal Residential System in Ontario

Walkerton Clean Water Centre

Research & Technology Department

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## Disclaimer



## Acknowledgements

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# Executive Summary

## Background

The Water Treatment Plant (WTP) for a municipality in Ontario has reached the end of its original constructed service life. The municipality, along with hired consultants and the community, is currently conducting the Water Servicing Class Environmental Assessment (Schedule C) under the Environmental Assessment Act. The goal of this study is to identify and evaluate the alternatives and upgrades required to meet and exceed current and future water demands for the system.

Currently, the WTP utilizes a conventional treatment process, with the addition of polyaluminum chloride (PAX XL6) for coagulation, flocculation, and sedimentation. Chlorine is injected in the effluent of the pretreatment tanks, prior to the filters, and at the point of entry to the distribution system for disinfection and to prevent bacterial growth in the distribution system. The system also adds fluoride to the water to aid in preventing tooth decay.

A treatability study is currently being conducted by the municipality to evaluate the feasibility of membrane filtration. The Centre was contacted for assistance in conducting chlorine demand and decay testing, as well as simulated distribution system disinfection by-product (SDS-DBP) tests on membrane permeate water.

## Objectives

The objectives of the bench-scale study are:

1) to determine the chlorine demand and decay of the source water; and
2) to conduct SDS-DBP testing to quantify formation potential of trihalomethanes (THMs) and haloacetic acids (HAA5s).

## Approach

Membrane permeate water collected from the WTP was shipped to the Centre. Two sets of chlorine demand and decay tests and SDS-DBP tests were conducted. One set was completed using water sampled in the spring and the other used water collected in the summer to encompass a range of water quality conditions that fluctuate seasonally.

## Key Findings

The following conclusions were drawn from the bench-scale testing:

- The optimum dose of chlorine for membrane permeate water during spring conditions was determined to be 2.0 mg/L to meet the criteria for residuals outlined in the treatability study.
- Chlorine demand in the spring water sample was low.
- When the spring water sample was dosed with 2.0 mg/L chlorine and held for the seven-day detention time, results for THMs and HAA5s were both below the maximum acceptable concentration (MAC).
- The optimum dose of chlorine for membrane permeate water during summer conditions was determined to be 1.8 mg/L.
- Chlorine demand in the summer water sample was low.
- When the summer water sample was dosed with 1.8 mg/L chlorine and held for the seven-day detention time, it resulted in THMs and HAA5s both below the MAC.

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# 1. Introduction

A municipality located in Ontario has a water treatment plant (WTP) that currently provides water to more than 10,000 people in the area. The WTP intakes raw water from a surface water source (a river). Polyaluminum chloride (PAX XL6) is used as the coagulant in the conventional treatment process. Chlorine is injected in the effluent of the pretreatment tanks, which is prior to the filters, and at the point-of-entry to prevent bacterial growth in the distribution system. Fluoride is also added to the water to help prevent tooth decay.

One drawback of free chlorine disinfection is the formation of disinfection byproducts (DBPs). The common chlorinated DBPs are trihalomethanes (THMs) and the sum of five haloacetic acids (HAA5s). THMs and HAA5s are regulated at 100 µg/L and 80 µg/L maximum acceptable concentration (MAC), respectively, and are expressed as a running annual average (RAA) measured quarterly. The compounds that comprise THMs are chloroform, bromodichlormethane, dibromochloromethane, and bromoform. The compounds that comprise HAA5s include monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid. These DBPs are formed by the reaction of chlorine with natural organic matter (NOM) in the source water. NOM is usually detected by measuring total organic carbon (TOC) and dissolved organic carbon (DOC). Ultraviolet absorbance at 254 nm (UV254) is also a useful parameter to detect the NOM present in the water. Generally, one of the most effective methods to reduce DBPs is by reducing the NOM concentration in the source water.

The treatability testing study is part of an ongoing WTP membrane pilot study. The chlorine demand/decay and simulated distribution system (SDS) testing will be used to mimic the effects of chlorine disinfection on membrane permeate water, evaluating the potential of DBP formation under conditions which closely match the full-scale process.

# 2. Objectives

The objectives of the bench-scale study are:

1) to determine the chlorine demand and decay of the source water; and
2) to conduct SDS-DBP testing to quantify formation potential of trihalomethanes (THMs) and haloacetic acids (HAA5s).

# 3. Materials and Methods

## 3.1 Sample Water Collection and Analysis

The project was conducted in two separate sampling periods to capture the effects of seasonal raw water quality variation, the first in the spring and the second in the summer. Samples of membrane permeate water were collected on-site at the WTP in 10L plastic containers, and immediately upon collection tested for water temperature, pH, and turbidity, as outlined in Table 1. Samples were then sent to the Centre, where they were refrigerated at approximately 4°C until bench scale studies commenced.

**Table 1:** On-Site Sample Water Collection

| Sampling Period | Sample | Volume Sampled (L) | Data Recorded Upon Sample Collection |
|---|---|---|---|
| Spring | Membrane Permeate | 20L | Water temperature, pH, turbidity |
| Summer | | | |

Prior to commencing bench-scale testing, additional general water quality parameters were analyzed at the Centre to further understand the quality of the membrane permeate collected and to ensure samples had not deteriorated during storage. Parameters that were measured and monitored throughout the study, including their respective methods of analysis, are identified in Table 2.

**Table 2:** General Water Quality Parameters and Methods of Analysis

| Parameter | Preparation | Method | Range |
|---|---|---|---|
| Turbidity | N/A | USEPA Method 180.1 | 0 to 1000 NTU |
| pH | N/A | Hach Method 8156 | 0 to 14 |
| Temperature | N/A | Hach Method 8156 | N/A |
| UV254 | Filter sample using 0.45 µm, PES filter | Real Tech UV254 Method | 0 to 2 abs/cm |
| DOC | Filter sample using 0.45 µm, PES filter | Standard Method 5310C UV/persulfate oxidation with conductometric detection | 4 ppb to 50 ppm |
| Alkalinity | N/A | Hach Method 10244 Titration | 10 to 4,000 mg/L as CaCO3 |
| Free chlorine | N/A | Hach Method 8021 | 0.02 to 2.00 mg/L Cl2 |
| Total chlorine | N/A | Hach Method 8021 | 0.02 to 2.00 mg/L Cl2 |

## 3.2 Bench-Scale Testing

### 3.2.1 Chlorine Demand and Decay

An initial trial-and-error chlorine dosing test, utilizing three different doses, was conducted to determine the amount of sodium hypochlorite stock solution needed to satisfy the treatability study's target residuals. Chlorine demand free amber glass bottles (250mL) were filled with either deionized (DI) water or membrane permeate sample. Bottles were dosed with varying amounts of chlorine stock solution, held at room temperature, and chlorine residuals were measured at each of the specified detention times. Conditions of the treatability study can be seen below in Table 3.

A chlorine demand and decay test with a more refined sodium hypochlorite dose was completed for both the spring sample and the summer sample. The chlorine demand was calculated for each dose at each of the specified detention times, and the dose best meeting the treatability study's objectives from the chlorine demand and decay test was selected for SDS-DBP testing.

Each time a sample of membrane permeate water was dosed with chlorine, DI water was also dosed with chlorine, as a control to ensure the chlorine dosage was accurate and the chlorine did not decay over 7 days.

**Table 3:** SDS-DBP Test Conditions

| **SDS-DBP Sampling Guide** | | |
|---|---|---|
| **Sample** | **Spring** | **Summer** |
| Chlorine (free and total) | Chlorine Contactor Time:<br>0, 15, 30mins<br>Distribution System:<br>1, 3, 5, 7 days | Chlorine Contactor Time:<br>0, 15, 30mins<br>Distribution System:<br>1, 3, 5, 7 days |
| DBP (THMs and HAA5s) | Chlorine Contactor Time:<br>30mins<br>Distribution System:<br>3, 5, 7 days | Chlorine Contactor Time:<br>30mins<br>Distribution System:<br>3, 5, 7 days |
| **SDS-DBP Test Conditions** | | |
| Temperature | 0.5 | 23 |
| **Chlorine Contactor** | | |
| Target Free Chlorine Residual at Contactor Time 15 mins (mg/L) | 1.5 | 1.5 |
| Target Free Chlorine Residual at Distribution System Time 7 days (mg/L) | 0.2 | 0.2 |

### 3.2.2. Simulated Distribution System DBP Formation

The Centre conducted SDS tests to assess the DBP formation potential of the membrane permeate water. The procedure of the SDS test is adapted from *Standard Methods for the Examination of Water and Wastewater.* Chlorine residuals (free and total), temperature, and pH were measured at contact times of 0, 15, and 30 minutes, as well at detention times of 1, 3, 5, and 7 days. THMs and HAAs were measured at chlorine contact times of 30 minutes and at detention times of 3, 5, and 7 days. Samples for THMs and HAA5s analysis were collected in vials with the preservative sodium thiosulphate and ammonium chloride, respectively. THMs and HAA5s were sent to an external laboratory for analysis.

# 4. Results and Discussion

## 4.1 Sample Water Collection and Analysis

General water quality analysis was performed to ensure water quality remained representative of site-specific conditions prior to starting each test. DOC and UV254 readings were used as the primary indicator of sample deterioration. DOC and UV254 are commonly used surrogates for organics in drinking water, which effect chlorine demand and contribute to DBP formation. Overall, water quality did not deteriorate during shipment to the Centre and storage at 4°C. The general water quality of both spring and summer samples can be seen below in Table 4.

**Table 4:** Water Quality Analysis of Raw and Sample Water

| Sample Period | Sample Type | Sample Date | Volume Sampled | Analysis Date | Temp. (°C) | pH | Alkalinity (mg/L $CaCO_3$) | Turbidity (NTU) | UV254 ($cm^{-1}$) | DOC (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| **Spring** | Raw Water | 31-May-21 | - | 31-May-21 | - | 7.72 | - | 3.56 | - | 1.7 |
| | Membrane Permeate | 31-May-21 | 20L | 31-May-21 | 12.2 | 8.22 | - | - | - | - |
| | | | | 3-June-21 | 19.0 | 7.99 | 80.4 | - | 0.013 | 1.611 |
| | | | | 25-June-21 | 17.9 | 7.81 | 85.0 | - | 0.013 | 1.578 |
| **Summer** | Raw Water | 10-Aug-21 | - | - | - | - | - | - | - | - |
| | Membrane Permeate | 10-Aug-21 | 20L | 10-Aug-21 | 23.7 | 7.40 | - | - | - | - |
| | | | | 13-Aug-21 | 24.6 | 7.72 | 112 | 0.08 | 0.010 | 1.561 |
| | | | | 27-Aug-21 | 20.0 | 7.59 | 133 | - | 0.011 | 1.536 |

## 4.2 Bench-Scale Testing

### 4.2.1. Chlorine Demand and Decay

The results of the trial-and-error chlorine dosing tests on the membrane permeate water can be seen below in Table 5.

The initial trial-and-error chlorine demand and decay test resulted in residuals that were higher than outlined in the conditions set out in the treatability study requirements (Table 3). Therefore, the chlorine dose was lowered and the chlorine demand and decay test on spring water was repeated, as seen in Table 6.

Overall, the spring water sample was dosed at six different concentrations of chlorine to satisfy the specific chlorine demand prior to the SDS tests. The results indicated that the chlorine demand of the spring water was low. At a chlorine dose of 1.6 mg/L, the free chlorine residual was around 0.12 mg/L after 7 days of contact time. As expected, at chlorine doses of 1.8 and 2.0 mg/L, the chlorine residuals were much higher. Following review of the results obtained and the treatability study's target free chlorine residual at 7 days (0.2 mg/L), the chlorine dose of 2.0 mg/L was chosen for the SDS testing as it was a conservative dose that would ensure no SDS-DBP samples dropped below the target residual values.

A third chlorine demand and decay test was conducted on summer sample water. Results can be seen below in Table 7.

**Table 5:** Trial-and-Error Chlorine Dosing

| Sample Period | Temperature (°C) | Chlorine Dose (mg/L) | Sample Type | Chlorine Residual | Day 0 – 0 min | Day 0 – 15min | Day 7 | Chlorine Demand (mg/L) |
|---|---|---|---|---|---|---|---|---|
| **Spring (04-June-21)** | 12.2 | 5 | DI | Free (mg/L) | 4.55 | 4.55 | 4.45 | 0min: 0.25<br>15min: 0.30<br>7-day: 1.90 |
| | | | | Total (mg/L) | **4.85** | 4.75 | 4.55 | |
| | | | Membrane Permeate | Free (mg/L) | **4.60** | **4.55** | **2.95** | |
| | | | | Total (mg/L) | 4.90 | 4.75 | 3.20 | |
| | | 6 | DI | Free (mg/L) | 5.71 | 5.70 | 5.40 | 0min: 0.12<br>15min: 0.36<br>7-day: 2.28 |
| | | | | Total (mg/L) | **5.88** | 6.12 | 5.60 | |
| | | | Membrane Permeate | Free (mg/L) | **5.76** | **5.52** | **3.60** | |
| | | | | Total (mg/L) | 5.94 | 5.82 | 4.00 | |
| | | 7 | DI | Free (mg/L) | **7.50** | 7.20 | 6.40 | 0min: 0.43<br>15min: 0.50<br>7-day: 2.80 |
| | | | | Total (mg/L) | 7.40 | 7.30 | 6.45 | |
| | | | Membrane Permeate | Free (mg/L) | **7.07** | **7.00** | **4.70** | |
| | | | | Total (mg/L) | 7.21 | 7.00 | 4.85 | |

**Table 6:** Spring Chlorine Demand and Decay Testing

| Sample Period | Temperature (°C) | Chlorine Dose (mg/L) | Sample Type | Chlorine Residual | Day 0 – 0 min | Day 0 – 15min | Day 7 | Chlorine Demand (mg/L) |
|---|---|---|---|---|---|---|---|---|
| **Spring (04-June-21)** | Room Temperature | 1.6 | DI | Free (mg/L) | 1.56 | 1.57 | 1.44 | 0min: 0.05<br>15min: 0.06<br>7-day: 1.46 |
| | | | | Total (mg/L) | **1.58** | 1.59 | 1.53 | |
| | | | Membrane Permeate | Free (mg/L) | **1.53** | **1.52** | **0.12** | |
| | | | | Total (mg/L) | 1.60 | 1.59 | 0.23 | |
| | | 1.8 | DI | Free (mg/L) | 1.74 | 1.72 | 1.65 | 0min: 0.11<br>15min: 0.12<br>7-day: 1.33 |
| | | | | Total (mg/L) | **1.80** | 1.79 | 1.71 | |
| | | | Membrane Permeate | Free (mg/L) | **1.69** | **1.68** | **0.47** | |
| | | | | Total (mg/L) | 1.79 | 1.76 | 0.63 | |
| | | 2.0 | DI | Free (mg/L) | 1.98 | 1.96 | 1.80 | 0min: 0.06<br>15min: 0.16<br>7-day: 1.13 |
| | | | | Total (mg/L) | **2.00** | 2.00 | 1.89 | |
| | | | Membrane Permeate | Free (mg/L) | **1.94** | **1.84** | **0.87** | |
| | | | | Total (mg/L) | 2.07 | 1.96 | 0.97 | |

**Table 7:** Summer Chlorine Demand and Decay Testing

| Sample Period | Temperature (°C) | Chlorine Dose (mg/L) | Sample Type | Chlorine Residual | Day 0 – 0 min | Day 0 – 15min | Day 7 | Chlorine Demand (mg/L) |
|---|---|---|---|---|---|---|---|---|
| **Summer (04-June-21)** | Room Temperature | 1.8 | DI | Free (mg/L) | 1.78 | 1.73 | 1.71 | 0min: 0.04<br>15min: 0.17<br>7-day: 1.14 |
| | | | | Total (mg/L) | **1.80** | 1.78 | 1.74 | |
| | | | Membrane Permeate | Free (mg/L) | **1.76** | **1.63** | **0.66** | |
| | | | | Total (mg/L) | 1.77 | 1.74 | 0.76 | |
| | | 2.0 | DI | Free (mg/L) | 1.93 | 1.89 | 1.89 | 0min: 0.01<br>15min: 0.08<br>7-day: 1.09 |
| | | | | Total (mg/L) | **1.93** | 1.94 | 1.89 | |
| | | | Membrane Permeate | Free (mg/L) | **1.92** | **1.85** | **0.84** | |
| | | | | Total (mg/L) | 1.95 | 1.89 | 0.93 | |
| | | 2.2 | DI | Free (mg/L) | **2.17** | 2.17 | 2.09 | 0min: 0.05<br>15min: 0.10<br>7-day: 1.18 |
| | | | | Total (mg/L) | 2.13 | 2.16 | 2.11 | |
| | | | Membrane Permeate | Free (mg/L) | **2.12** | **2.07** | **0.99** | |
| | | | | Total (mg/L) | 2.14 | 2.11 | 1.09 | |

Analysis of the summer chlorine demand and decay results indicated that the membrane permeate water had low chlorine demand. Further discussion with the municipality identified that pre-chlorination at the WTP began in May. Chlorine dosed at the intake would have satisfied the demand in the feed water to the membrane pilot plant, contributing to the low demand observed in the summer testing results. The optimum dose of sodium hypochlorite from the summer sampling period was identified as 1.8 mg/L, based on the ability to obtain residuals best matching the outlined treatability study requirements for 15 min and 7-day detention times.

Overall, both spring and summer sample water collected from the membrane permeate stream exhibited low chlorine demand and decay when dosed with various concentrations of sodium hypochlorite and held for specified detention times.

### 4.2.2. Simulated Distribution System DBP Formation

Results of the spring SDS-DBP test can be seen in Figures 1 and 2.

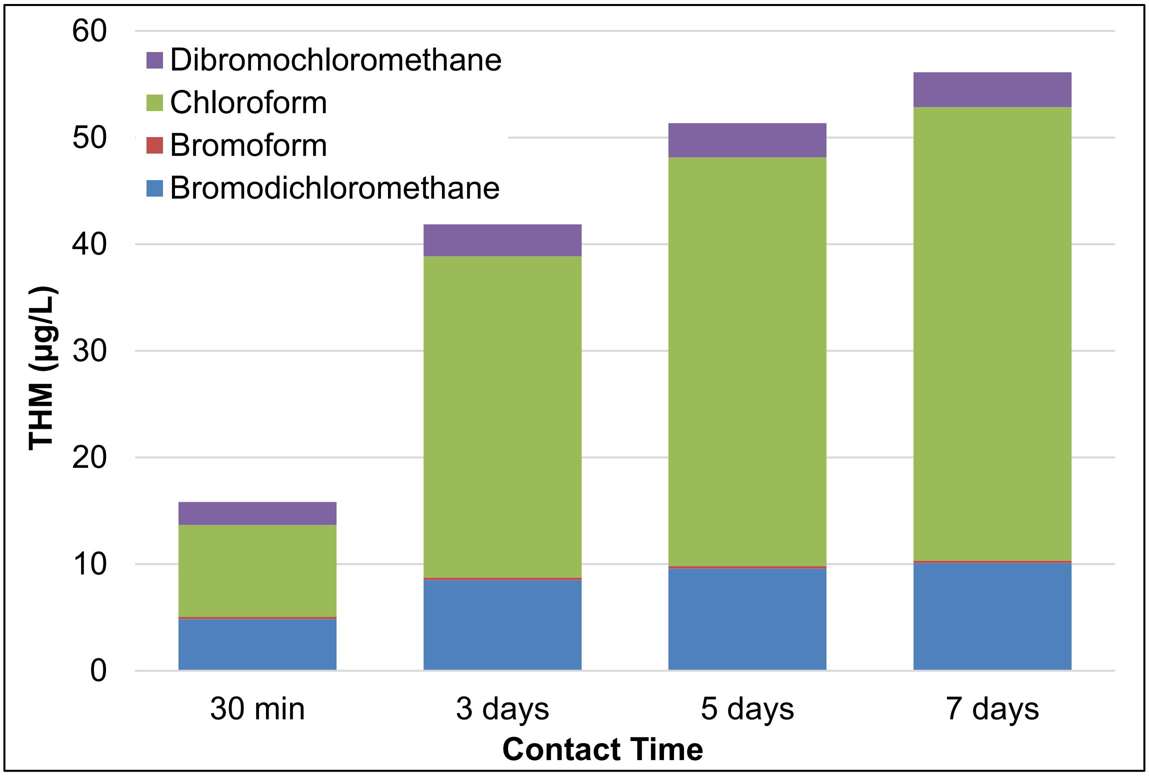


**Figure 1:** Spring SDS-DBP THM Formation (Data from Table 11)

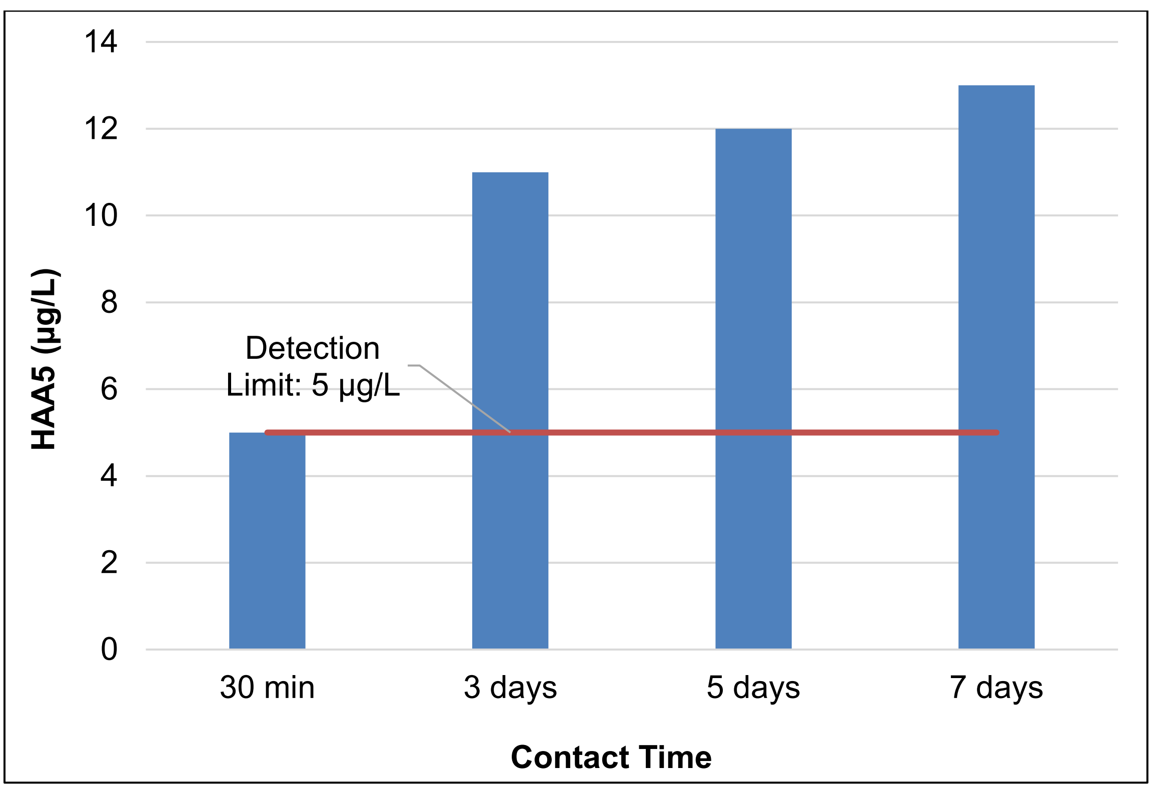


**Figure 2:** Spring SDS-DBP HAA5 Formation (Data from Table 11). Note: Only dichloroacetic acid measured above the minimum detection limit (MDL) in the HAA5 sample.

Results from the spring SDS-DBP formation test show that when the water was dosed with 2.0 mg/L of chlorine and held for specified detention times as per Table 3, the amount of THMs and HAA5s formed in samples was low (Figures 1 and 2). At the 7-day detention time, a total of 56.12 µg/L of THMs were formed in the sample with the majority of THMs in the chloroform species. This is below the current maximum acceptable concentration (MAC) of 100 µg/L, measured as a running quarterly annual average, as set out in O. Reg. 169/03: Ontario Drinking Water Quality Standards. HAA5 analysis results from the spring membrane permeate water following the SDS-DBP test also showed low concentrations of HAA5s in samples collected. At the 7-day detention time, 13 µg/L of HAA5s were detected. This result is below the MAC of 80 µg/L, measured as a running quarterly annual average, as outlined in O. Reg. 169/03.

Results of the summer SDS-DBP testing can be seen below in Figures 3 and 4.

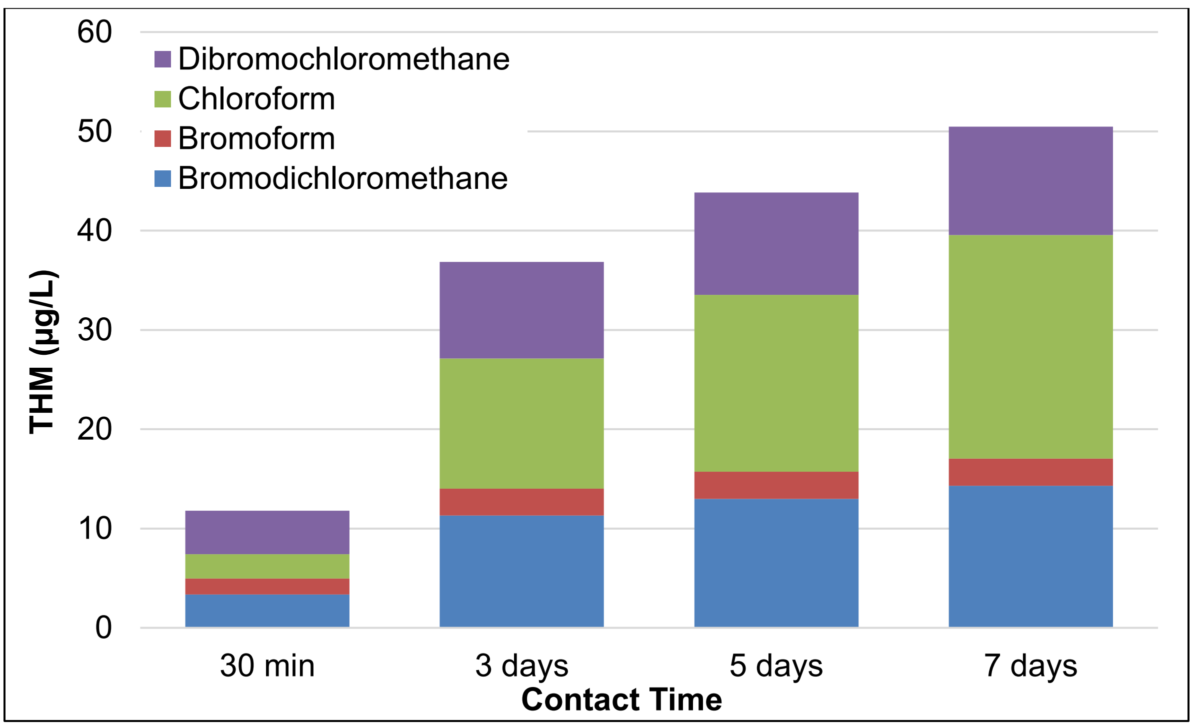


**Figure 3:** Summer SDS-DBP THM Formation (Data from Table 12)

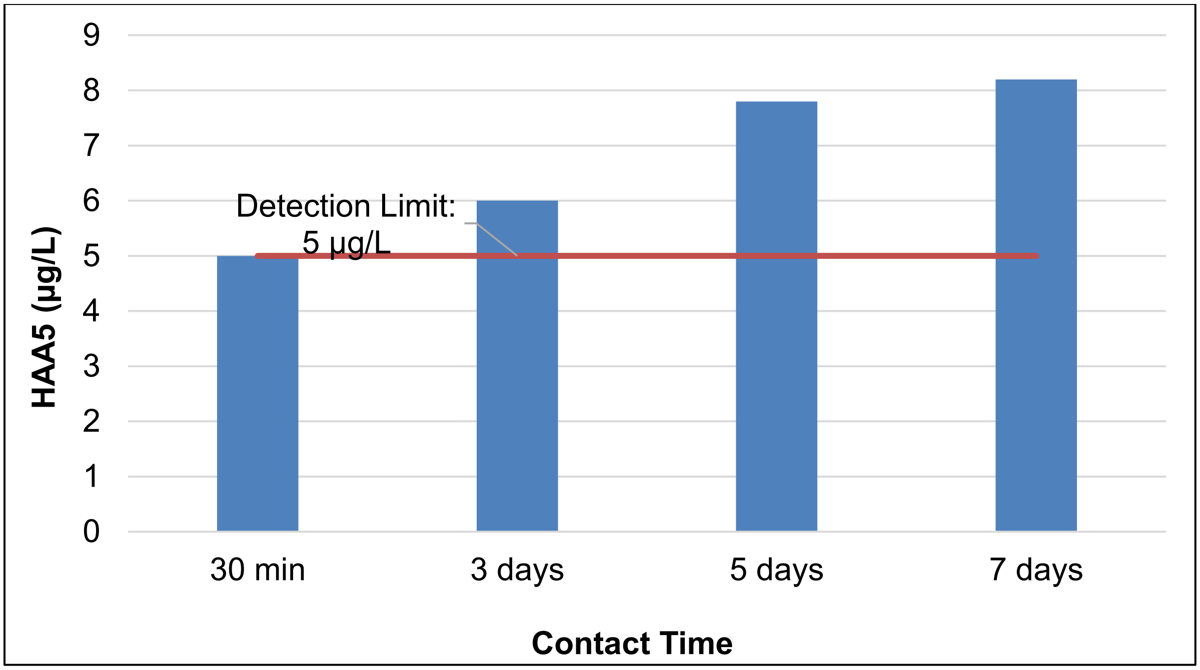


**Figure 4:** Summer SDS-DBP HAA5 Formation (Data from Table 12). Note: Only dichloroacetic acid was detected above the MDL in the HAA sample.

Results obtained from the summer SDS-DBP testing showed that when the membrane permeate water was dosed with 1.8 mg/L of chlorine and held for the specified detention times in Table 3, total THMs and HAA5s formed in the sample were low. THM speciation in the spring samples consisted primarily of chloroform, whereas in the summer samples there was a shift in speciation to include chloroform, bromodichloromethane, and dibromochloromethane produced. Overall, the quantity of THMs produced in the summer sample set was slightly decreased from that of the spring sample, from 56.12 µg/L down to 50.40 µg/L. Both spring and summer THM results were below the MAC. HAA5s in the summer sample set also decreased from the spring results, from 13.00 µg/L to 8.20 µg/L. This result is also below the MAC, and just slightly above the MDL of 5 µg/L.

# 5. Conclusions

In conclusion, a total of three chlorine demand and decay tests and two SDS-DBP tests were performed on the membrane permeate water collected from the WTP. Results of the chlorine demand and decay testing showed low chlorine demand in the sample water for both the spring and summer sample periods. Water collected in the spring, dosed with 2.0mg/L, and held for the 7-day detention time for SDS-DBP analysis, resulted in a free chlorine residual of 0.35mg/L. This sample, when outsourced for THM and HAA5 analysis, produced results of 56.12 µg/L and 13.00 µg/L respectively.

For the summer sample water, when dosed with 1.8mg/L of chlorine, held for the 7-day detention time, and sampled for SDS-DBPs, produced THM and HAA5 results of 50.40 µg/L and 8.20 µg/L. Both membrane permeate samples, collected in the spring and summer, produced results below the MAC for THMs and HAA5s.

# 6. References

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