



Pilot Testing Project Report

Optimizing Regeneration Process of Greensand Filtration to Reduce Disinfection By-Products

Walkerton Clean Water Centre

May 18, 2021

Disclaimer

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Acknowledgements

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List of Acronyms

AO	Aesthetic objective
DBPs	Disinfection by-products
DI	Deionized water
DOC	Dissolved organic carbon
DWS	Drinking water system
EBCT	Empty bed contact time
HAAs	Haloacetic acids
MAC	Maximum acceptance concentration
NOM	Natural organic matter
NTU	Nephelometric turbidity units
ORP	Oxidation reduction potential
RAA	Running annual average
SDS	Simulated distribution system
TDS	Total dissolved solids
THMs	Trihalomethanes
UVA	Ultraviolet absorbance

Executive Summary

Background

A community located on Lake Simcoe has been experiencing increasing levels of disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs). The THMs and HAAs both exceeded Ontario's maximum acceptable concentration (MAC) of 100 µg/L and 80 µg/L, as a running annual average (RAA), respectively (MECP, 2020).

DBPs can form in chlorinated waters with organic precursors. High chlorine doses can contribute to higher DBP concentrations. High levels of naturally occurring ammonia have been detected in the community's wells, which significantly increases chlorine demand. This results in a very high chlorine dose prior to greensand filtration. The pilot testing project is designed to assess the impact of potassium permanganate (KMnO₄), as an alternative oxidant upstream the greensand filter, to ultimately reduce the overall chlorine dose and thus reduce the formation of DBPs.

Objective

The objective of this pilot testing project is to compare the performance of chlorine and KMnO₄ on greensand regeneration and their impact on formation of THMs and HAAs.

Approach

The pilot testing experiments were conducted using a dual-train greensand system. Raw water from the community's Well #3 was dosed with sodium hypochlorite at 15 mg/L and KMnO₄ at 1.4 mg/L in Train 1 and Train 2, respectively. Afterwards, the water dosed with oxidant in each train was either pumped directly through a greensand filter or pumped through a contact tank followed by a greensand filter. Prior to the pilot test experiments, a chlorine demand test and a KMnO₄ trial run were conducted to determine the optimal dose of chlorine and KMnO₄, respectively. By running the pilot system with or without the contact tank, two contact times (30 seconds and 10 minutes) were tested for each oxidant. For each pilot test run, samples were collected before and after the greensand filter to evaluate the

performance of each oxidant on greensand regeneration. In addition, a simulated distribution system (SDS) test was conducted on the greensand effluent of each pilot test run to investigate the impact of the selected oxidant on the formation of THMs and HAAs. Two contact times (1 day and 5 days) were selected for the SDS test based on the detention time of the community's distribution system.

Key Findings

The results of the pilot testing project are summarized below:

- A high chlorine dose (15 mg/L) was required to satisfy the chlorine demand, which was mainly attributed to the elevated levels of naturally occurring ammonia (1.20 – 1.64 mg/L) in the community's well water. The high chlorine dose can contribute to the formation of DBPs, such as THMs and HAAs.
- The optimal dose of KMnO_4 was determined as 1.4 mg/L. At this dose, KMnO_4 can effectively regenerate the greensand media, resulting in high removal of iron and manganese. Meanwhile, no KMnO_4 residual was detected in the filter effluent, ensuring that pink discolouration of the water did not occur.
- When comparing the performance of the selected oxidant (chlorine and KMnO_4) at two contact times (30 seconds and 10 minutes):
 - The greensand oxidation/filtration process achieved high removal of iron and manganese (84% - 88% of iron removal and 66% - 81% of manganese removal), regardless of oxidant type and contact time.
 - Among all test runs, the KMnO_4 run with 10 minutes of contact time provided the lowest effluent turbidity (0.17 ± 0.02 NTU).
 - Chlorine removed nearly all ammonia from the raw water to satisfy the chlorine demand (approximately 14 mg/L) and generated a free chlorine residual to regenerate greensand media. Therefore, relatively low chlorine doses were used for chlorination disinfection in the chlorine train (Train 1).
 - KMnO_4 had limited impact on the ammonia levels in the raw water. The greensand filter effluents of the KMnO_4 train had about 14 mg/L of chlorine

demand due to the elevated levels of ammonia. A high chlorine dose was selected for chlorination disinfection in the KMnO_4 train (Train 2).

- The THM levels of both trains were either close to or higher than the MAC, regardless of the oxidant contact time of pilot tests and detention time of the SDS tests. Yet, the KMnO_4 train had slightly lower THM levels in both trains. Increasing the SDS detention time from 1 day to 5 days significantly increased the formation of THMs.
- All the HAA results of the chlorine train (Train 1 of each run, 80 – 139 $\mu\text{g/L}$ of HAAs) exceeded the MAC, regardless of the oxidant contact time in the pilot tests and SDS detention time. The KMnO_4 train had HAA levels below the MAC after 1 day of SDS detention time (60.3 – 65.3 $\mu\text{g/L}$), regardless of oxidant contact time. But the HAA levels increased beyond the MAC after 5 days of detention time (87.3 – 95.1 $\mu\text{g/L}$). Increasing the SDS detention time from 1 day to 5 days increased the formation of HAAs for both oxidants. The KMnO_4 formed approximately 25% - 29% less HAAs than the chlorine train.

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1. Introduction

A community's drinking water system (DWS) serves a population of 1,836 people, supplying a maximum raw water taking of 957 m³/day with a rated capacity of 2,622 m³/day. The DWS relies on three drilled wells at the same location as the pump house. The drinking water system blends all three wells together and is followed by chlorination. The chlorinated water enters one of the two alternating greensand filters and the filter effluent gets collected in a reservoir. The treated water is then chlorinated again before it enters the distribution system. Currently, the community's water is supplied by Well #3, while Well #1 and Well #2 are not in operation. The community's drinking water contains elevated levels of trihalomethanes (THMs) and haloacetic acids (HAAs), with values approaching the maximum acceptable concentration (MAC) of 100 µg/L and 80 µg/L of THMs and HAAs, respectively as a running annual average (RAA) (MECP, 2020).

The greensand filtration treatment is in place to remove iron and manganese. Iron and manganese are commonly found in groundwater and are not considered a health concern. Ontario has established aesthetic objectives (AO) for iron and manganese as 0.3 mg/L and 0.05 mg/L, respectively (MECP, 2006). Iron and manganese can be removed by adsorption/oxidation or by oxidation/filtration (Tobiason et al., 2008). The DWS involves greensand filtration, which follows the adsorption/oxidation method. This method uses a greensand filter media, which is chemically treated grain sand coated with manganese oxide, to adsorb both iron and manganese. The media is then oxidized with sodium hypochlorite to precipitate iron and manganese out into an insoluble form. The insoluble iron and manganese are then removed by backwashing. The greensand filter typically contains three layers from top to bottom: anthracite, manganese dioxide coated greensand, and gravel. The greensand filter can be regenerated by continuous or intermittent regeneration (Tobiason et al., 2011). Continuous regeneration involves continuous oxidation with either chlorine or potassium permanganate (KMnO₄) prior to the greensand filter (Tobiason et al., 2011). Intermittent regeneration involves raw water passing through the greensand filter for a specified volume of water and then down-flow passage of oxidant through the media to regenerate the adsorption capacity (Tobiason et al., 2011).

The community's greensand filters use continuous regeneration and were originally designed to reduce iron and manganese to < 0.02 mg/L and 0.025 mg/L, respectively. Since January 2019, the average iron and manganese concentrations found in Well #3 raw water are 0.237 mg/L and 0.078 mg/L, respectively, and the average iron and manganese levels found after the greensand filter are 0.05 mg/L and 0.014 mg/L, respectively. Chlorination prior to greensand filtration is in place to oxidize the iron and manganese and continuously regenerate the greensand media. According to the greensand filter operational manual, the pre-feed chlorine dose should be sufficient to satisfy the 12 mg/L of chlorine demand and maintain a residual of 1.5 mg/L in filtered water. The DWS uses sodium hypochlorite, which is a weaker oxidant compared to KMnO_4 , and does not readily oxidize manganese prior to the filters. Therefore, manganese remains in a soluble form when it contacts with the greensand filters. Manganese is then removed by greensand media by adsorption (Tobiason et al., 2008). However, the continuous pre-filter chlorination can cause an increase in levels of disinfection by-products (DBPs) due to the higher exposure of chlorine with natural organic matter (NOM), compared to intermittent regeneration (Tobiason et al., 2008). Some utilities have investigated intermittent regeneration instead of continuous regeneration to reduce DBP levels; however, this should be done in caution and for specific water characteristics, such as little or no iron levels (Tobiason et al., 2008).

It was anticipated that the current greensand filtration media had reached the end of its lifecycle (approximately 10 years); therefore, in 2020 the community replaced the existing greensand filter media with virgin media.

The community requested pilot testing services from the Walkerton Clean Water Centre (Centre) to initially test the impact of virgin and aged greensand filter media with two different chlorine doses on the formation of THMs and HAAs. Once the greensand filter media was replaced at the wells and THMs and HAAs continued to remain high in the community, the Centre and the community agreed to shift the focus of the pilot testing project to assess the effect of different oxidation chemicals on the greensand filter operations and the impact of THMs and HAAs.

The objective of this project is to compare the effect of oxidation chemicals including chlorine and KMnO_4 , on the formation of THMs and HAAs, using the raw water from Well #3.

2. Materials and Method

2.1. Raw Water Quality

Raw water samples were collected from each of the three wells in August 2020 and then transported to the Centre for water quality analysis. Understanding the raw water quality of each well would provide insight on major precursors for DBP formation. NOM is considered the predominant precursor to DBP formation and is usually quantified by the measurement of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm of wavelength (UVA₂₅₄). The specific ultraviolet absorbance (SUVA) indicates the characteristics of NOM and is calculated by Equation 1 (Edzwald and Tobiason, 1999; USEPA, 1999).

$$\text{SUVA} = \frac{\text{UV}_{254} (\text{cm}^{-1})}{\text{DOC} \left(\frac{\text{mg}}{\text{L}}\right)} \times \frac{100 \text{ cm}}{1 \text{ m}} \dots\dots\dots \text{Equation 1}$$

SUVA values greater than 4 L/mg-m indicate that the organics are highly hydrophobic with high molecular weights and highly aromatic structures (Edzwald and Tobiason, 1999; USEPA, 1999). Highly aromatic organic carbons (SUVA greater than 4 L/mg-m) are a major group of precursors for the formation of THMs and HAAs (Hua et al., 2015). The raw water samples from Well #1 and Well #2 have SUVA values above 4 L/mg-m, which indicates that NOM in those two wells is highly aromatic (Table 1). Well #3's SUVA value falls in a range of 2 – 4 L/mg-m, indicating that NOM in the Well #3 is a mixture of hydrophobic and hydrophilic organics (Edzwald and Tobiason, 1999; USEPA, 1999) (Table 1). Hydrophobic NOM has low molecular weights and few aromatic structures, which is less likely to form DBPs.

Table 1. Summary of raw water quality

Parameter	Average Values ± SD ¹ (n) ²			
	Collected on August 28 2020 (Chlorine Demand Tests)			Collected on Feb 24 – 25 2021 (Pilot-scale Tests)
	Well 1	Well 2	Well 3	Well 3
Alkalinity (mg/L as CaCO ₃)	164	178	201	N/A
Total Ammonia (mg/L)	1.20	1.64	1.36	1.43 ± 0.53

Conductivity ($\mu\text{S}/\text{cm}$)	320	330	363	N/A
DOC (mg/L)	3.455	2.906	2.132	2.16 ± 0.07
Total Hardness (mg/L as CaCO_3)	114	137	168	N/A
Total Iron (mg/L) (measured at the Centre)	0.50	0.41	0.24	N/A
Total Iron (mg/L) (measured immediately after collection)	0.50	0.44	0.25	0.25 ± 0.00
Total Manganese (mg/L)	0.061	0.088	0.105	0.100 ± 0.007
pH	8.01	8.12	8.03	7.86 ± 0.06
Temperature ($^{\circ}\text{C}$)	18.0	10.1	9.6	11.9 ± 1.0
Total Dissolved Solids or TDS (mg/L)	83.9	86.5	95.2	N/A
Turbidity (NTU)	1.00	0.92	0.59	0.33 ± 0.12
UV ₂₅₄ absorbance (cm^{-1})	0.183	0.149	0.082	0.090 ± 0.002
SUVA (L/mg-m)	5.30	5.13	3.85	4.04 ± 0.21

It is also noted that the ammonia concentrations are high in all wells (1.20 – 1.64 mg/L $\text{NH}_3\text{-N}$) (Table 1). Ammonia is a major contributor to chlorine demand, which increases the chlorine dose required for the chlorination process. A high chlorine dose can result in forming high levels of DBPs.

2.2. Water Quality Analysis

Water quality analysis was completed using the methods described in Table 2.

Table 2. Methods of water quality analysis

Parameter	Preparation	Method	Range
In-House Analysis			
Alkalinity	N/A	Hach Method 8203	10 – 4000 mg/L as CaCO_3
Total Ammonia	N/A	Hach Method 8155	0.01 – 0.50 $\text{NH}_3\text{-N}$
Free and Total Chlorine	N/A	USEPA DPD Method	0.02 – 2.00 mg/L
Total Chlorine	N/A	Hach Method 8167	0.02 – 2.00 mg/L
Conductivity/ TDS	N/A	Direct Measurement Method (Hach Method 8160)	0.01 $\mu\text{S}/\text{cm}$ – 200 mS/cm

Parameter	Preparation	Method	Range
DOC	0.45 µm filtered	Standard Method 5310C UV/persulfate oxidation with conductometric detection	0 – 10 mg/L
Total Hardness	N/A	Hach Method 8213	10 – 4000 mg/L
Total Iron	N/A	Hach Method 8008	0 – 3.00 mg/L
Dissolved Iron	0.45 µm filtered	Hach Method 8008	0 – 3.00 mg/L
Total Manganese	N/A	Hach Method 8149	0.006 – 0.700 mg/L
Dissolved Manganese	0.45 µm filtered	Hach Method 8149	0.006 – 0.700 mg/L
ORP	N/A	Hach Method 10228	-2000 – 2000 mV
pH	N/A	Hach Method 8156	0 – 14
KMnO ₄	0.22 µm filtered	WCWC SOP #37 KMnO ₄ DPD Analysis	0.07 – 2.00 mg/L
Turbidity	N/A	USEPA Method 180.1	0 – 1000 NTU
UV ₂₅₄	0.45 µm filtered	Real Tech UV ₂₅₄ Method	0 – 2 Abs/cm
Parameter	Preparation	Method	Detection Limit
Analyzed at a Licensed Laboratory			
HAAs	Chlorine doses and contact times vary for chlorine demand	EPA 552.3	5.3 µg/L
THMs	tests and pilot tests.	EPA 5030B/8260C	0.5 µg/L

2.3. Chlorine Demand Tests

Prior to the pilot-scale tests, chlorine demand tests were conducted at the Centre. The raw water was collected from each well, shipped to the Centre and dosed with chlorine at 6 mg/L, 8 mg/L, 10 mg/L, 14 mg/L, 16 mg/L and 18 mg/L. The samples were then stored in the dark at room temperature. The chlorine residual was measured after 5 minutes (Day 0), 1 day and 5 days of contact time. A sample of deionized water (DI) was also dosed at 6 mg/L, 8 mg/L, 10 mg/L, 14 mg/L, 16 mg/L and 18 mg/L as a control to ensure the chlorine dose was accurate and the chlorine did not decay during the 5 days of contact time. All glassware used in the chlorine demand test was pretreated to be chlorine demand free.

2.4. Pilot-scale Tests

2.4.1. Pilot Plant Schematic

The pilot plant was installed and commissioned at the community's DWS. Before commissioning, the pressure tanks were loaded with 0.25 ft³ of gravel, 0.5 ft³ of Greensand Plus media and 0.25 ft³ of anthracite, providing a total volume of 1 ft³ of all media altogether, which represents that same ratio as in greensand filters. The greensand media was backwashed until fines were removed from the bed surface before loading anthracite, as recommended by the manufacturer. The media was conditioned with 3 g/L of KMnO₄ and soaked overnight. Then, the media was backwashed and rinsed to remove any remaining KMnO₄ before the pilot plant was installed on-site.

The pilot plant consisted of two greensand filtration trains with two different oxidants (Figure 1). The pilot tests were conducted on February 24 – 25, 2021. Train 1 was dosed with sodium hypochlorite and Train 2 was dosed with KMnO₄ (Figure 1, Table 3). Each train ran at 11 L/min and each greensand filter had an empty bed contact time (EBCT) of 2.57 minutes. Run 1 and Run 3 bypassed the contact tank to demonstrate the effect of a short oxidant contact time (30 seconds) on the greensand filtration performance (Figure 1, Table 3). Run 2 and Run 4 included a 30-gallon contact tank to provide longer oxidant contact time (10 minutes) prior to the greensand filtration (Figure 1, Table 3). Preceding the construction of the pilot plant, a sodium chloride tracer study was conducted at the Centre for the 30-gallon contact tank, which determined the tank's effective time (T_{10}) as 2.1 minutes despite the hydraulic detention time (10 minutes). For each run, additional contact time was provided by including a 30 ft long, 1 inch internal diameter coiled line as well as the freeboard above the greensand media in the pressure vessel.

Table 3. Design of pilot plant test

Run	Train	Oxidant Dose	Contact Time with Oxidant (before greensand filter)	Contact Tank
1	Train 1: Chlorine	15 mg/L	30 seconds	No
	Train 2: KMnO ₄	1.4 mg/L	30 seconds	No
2	Train 1: Chlorine	15 mg/L	10 minutes	Yes
	Train 2: KMnO ₄	1.4 mg/L	10 minutes	Yes
3 (repeat of Run 1)	Train 1: Chlorine	15 mg/L	30 seconds	No
	Train 2: KMnO ₄	1.4 mg/L	30 seconds	No
4 (repeat of Run 2)	Train 1: Chlorine	15 mg/L	10 minutes	Yes
	Train 2: KMnO ₄	1.4 mg/L	10 minutes	Yes

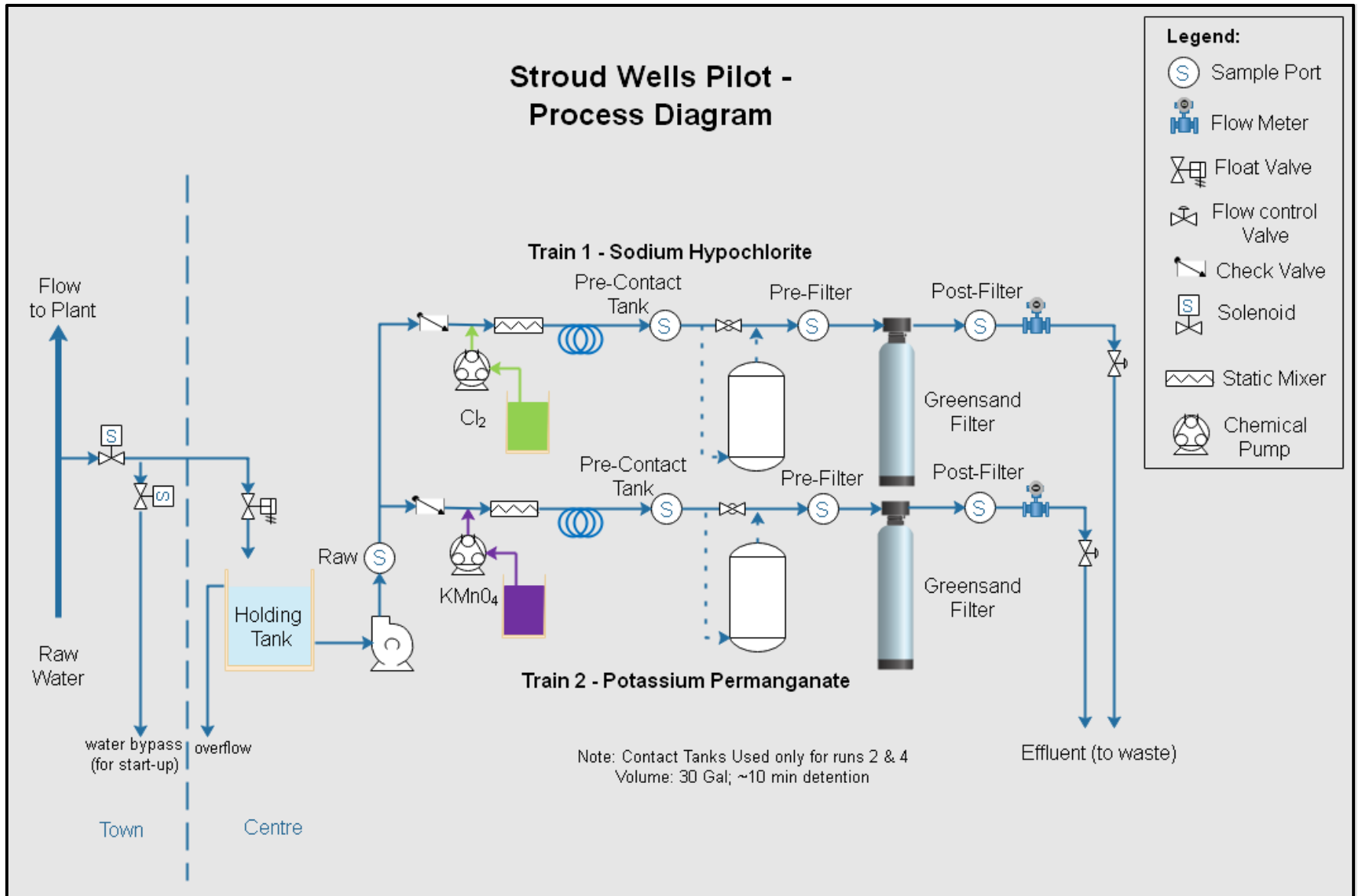


Figure 1. Pilot plant schematic

2.4.2. Water Quality Analysis – Pilot-Scale Tests

During pilot testing, the pilot plant was operated at a steady-state for four hydraulic detention times, which was approximately 20 minutes for the runs without the contact tanks (Run 1 and Run 3) and 60 minutes with the contact tanks (Run 2 and Run 4). Grab samples were then collected at each sampling port and tested on-site for 12 parameters, including turbidity, pH, temperature, ORP, total iron, dissolved iron, free chlorine residual, total chlorine residual, KMnO_4 residual, total manganese, dissolved manganese and total ammonia. Samples were then transported to the Centre for UVA_{254} and DOC analysis.

2.4.3. Simulated Distribution System Tests

After each run, grab samples of the treated water of each train were also collected to complete a simulated distribution system (SDS) test. The SDS test was performed to determine the impact of oxidant type and oxidant contact time on the formation of DBPs, particularly THMs and HAAs.

The greensand effluent samples collected from the chlorine train (Train 1) had high levels of free chlorine residuals and were dosed an additional 1 mg/L and 2 mg/L of sodium hypochlorite. The greensand effluent samples collected from the KMnO_4 train (Train 2) were dosed with 16 mg/L of sodium hypochlorite. As expected, those samples of Train 2 contained no KMnO_4 residual. After dosing with chlorine, the samples were stored at room temperature and sent to an accredited lab for THM and HAA analysis after 1 day and 5 days of contact time. The THM results reflect the sum of bromodichloromethane, bromoform, chloroform and dibromochloromethane concentrations. The HAA results indicate the sum of the levels of bromoacetic acid, chloroacetic acid, dichloroacetic acid, dibromoacetic acid and trichloroacetic acid.

However, the 5-day combined chlorine residuals of the KMnO_4 train (0.4 – 1.9 mg/L) indicated the chlorine doses selected for this train did not satisfy the chlorine demand of ammonia in water and a higher chlorine dose was demanded.

In addition, combined chlorine residual was calculated by subtracting free chlorine residual from total chlorine residual. Free chlorine residual was measured using Hach's DPD (N,N-

diethyl-p-phenylenediamine) method, which is highly interfered with by monochloramine. As indicated by the pilot results, KMnO_4 did not remove ammonia from the raw water. Ammonia reacts with chlorine and forms monochloramine before free chlorine residual is formed. When chlorine was underdosed in the SDS test, the presence of monochloramine resulted to false positive readings of free chlorine residuals. Therefore, the combined chlorine residuals of the KMnO_4 train could have been higher than the readings obtained.

To determine the proper chlorine dose for the KMnO_4 train, the KMnO_4 pilot tests were repeated on March 31, 2021 to collect greensand effluents and a chlorine demand test was then conducted at the Centre using the collected greensand effluents from the pilot test. Water quality parameters were measured during the pilot test to ensure the pilot system was running under a similar condition as the previous pilot tests conducted on February 24 – 25, 2021.

Based on the results of the chlorine demand test, 16 mg/L was selected as the chlorine dose for the 5-day SDS of the KMnO_4 train.

3. Results and Discussions

3.1. Chlorine Demand Test Results

3.1.1. Chlorine Demand

The community's DWS uses chlorination for primary and secondary disinfection processes. Sufficient chlorination is required to achieve and maintain a certain level of free chlorine residual in the treated water for a certain period of time (usually equal to or longer than the detention time of the distribution system). To achieve sufficient levels of free chlorine residuals, chlorine dose is required to be high enough to overcome chlorine demand in the water. The community's well waters have elevated levels of naturally occurring ammonia, which is considered as one of the main contributors of chlorine demand.

The chlorine demand was monitored for each well by measuring the total chlorine residual at an increasing chlorine dose and at three contact times (0, 1 and 5 days). For each well, the chlorine demand was determined as approximately 14 mg/L, regardless of contact times (Figure 2). Free chlorine residual started to present when chlorine dose was beyond 14 mg/L. Therefore, to achieve and maintain sufficient free chlorine residuals for primary disinfection, a high chlorine dose (over 14 mg/L) was required to satisfy the chlorine demand in the wells.

As shown in Figure 2, in DI water, the total chlorine residual consistently increased with the chlorine doses and the total chlorine residual remained stable with increased contact times (0, 1 and 5 days). Therefore, the chlorine solution was stable at a dose of 6 – 18 mg/L and did not self-decay during a detention time of up to 5 days.

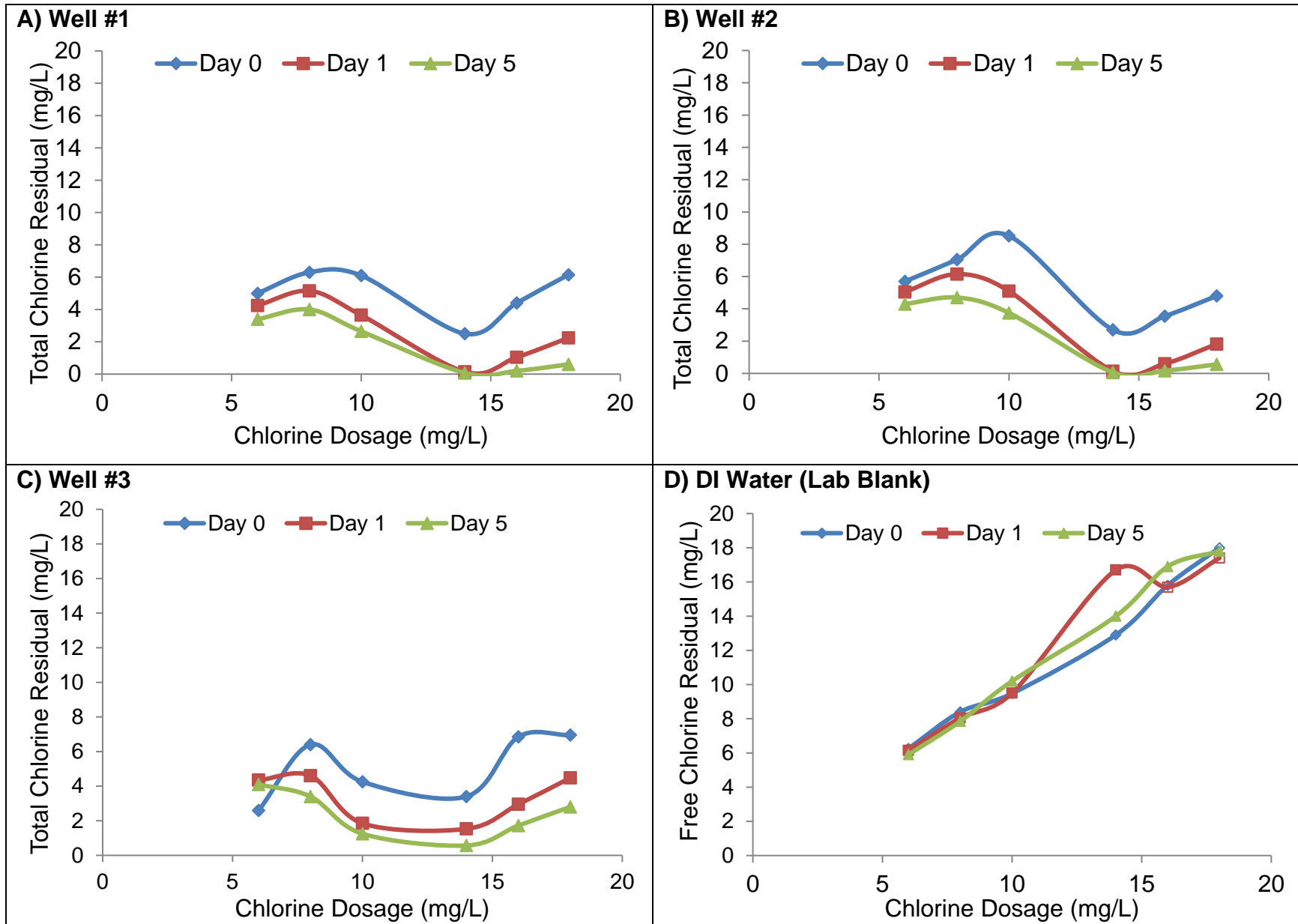


Figure 2. Chlorine breakpoint curves for Well #1, 2 and 3 at three contact times with lab blank

To determine the proper chlorine dose of the disinfection process for the KMnO₄ train, a chlorine demand test was conducted using the filter effluents of the KMnO₄ train. As indicated in Figure 3, the chlorine demand was determined as approximately 14 mg/L, regardless of chlorine detention time for disinfection and oxidant contact time for filter regeneration.

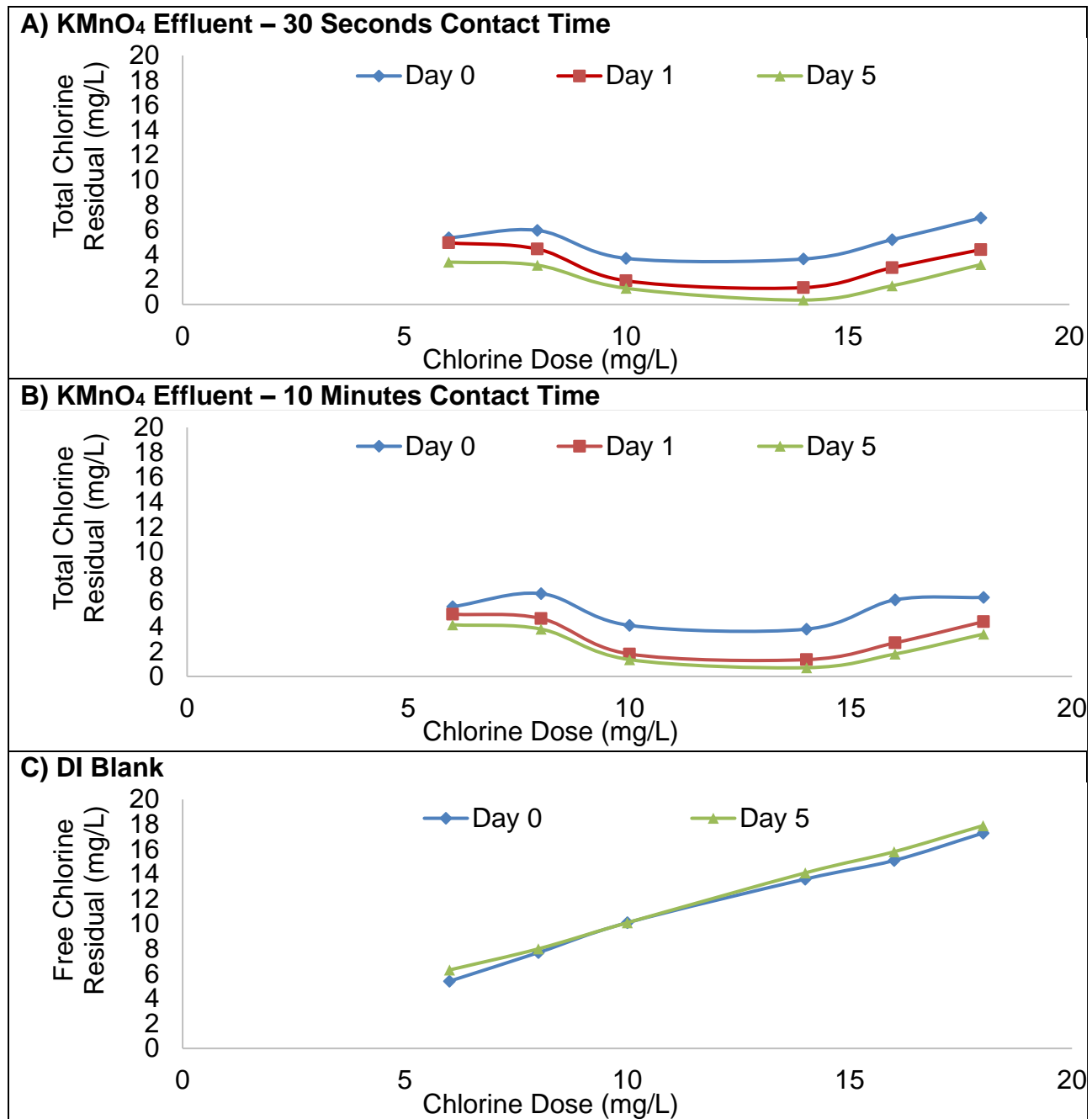


Figure 3. Chlorine breakpoint curves for KMnO₄ effluents at three contact times with lab blank

3.1.2. Free Chlorine Residual

Free chlorine residual was measured at an increasing chlorine dose and three contact times (0, 1 and 5 days) (Figure 4). At Day 0, the samples were dosed with sodium hypochlorite and free chlorine residual was measured approximately 5 minutes after dosing. Although the chlorine doses were as high as 18 mg/L, free chlorine residual was only detected as up to about 6.5 mg/L. The immediate demand of chlorine was noted and is suspected to be caused by the naturally occurring ammonia in the well water (1.20 – 1.64 mg/L NH₃-N). The samples that were dosed with 6 mg/L, 8 mg/L and 10 mg/L of chlorine resulted in a free chlorine residual less than 1 mg/L after 1 and 5 days of contact times, which suggests that these doses were not high enough to satisfy the demand in the water (Figure 4).

For Well #1 and Well #2, the samples that were dosed with 14 mg/L, 16 mg/L and 18 mg/L of chlorine also resulted in a free chlorine residuals of less than 1 mg/L after 5 days of contact time (Figure 4). The optimal chlorine dose for Well #1 and Well #2 may be higher than 18 mg/L; however, it should be noted that the community only uses Well #1 and Well #2 as 1 – 5% of the total average water takings.

For Well #3, the samples that were dosed with 14 mg/L of chlorine resulted in free chlorine residual of 1.3 mg/L and 0.43 mg/L after 1 day and 5 days of contact time, respectively (Figure 4). Whereas Well #3 samples dosed with 16 mg/L and 18 mg/L had chlorine residuals well above 1 mg/L after 5 days of contact time (Figure 4). The optimal chlorine dose for Well #3 was determined as 15 mg/L, which was used in the pilot testing experiments.

DI water, as a lab blank, was dosed with sodium hypochlorite at 6 – 18 mg/L and was stored in the dark for the same contact times as the samples. Free chlorine residuals were measured after 1 and 5 days of contact time. The free chlorine residuals after 1 day and 5 days of contact time remained consistently the same as the dose on day 0, which confirms that the chlorine solution was stable at the selected doses and did not self-decay for up to 5 days of contact time.

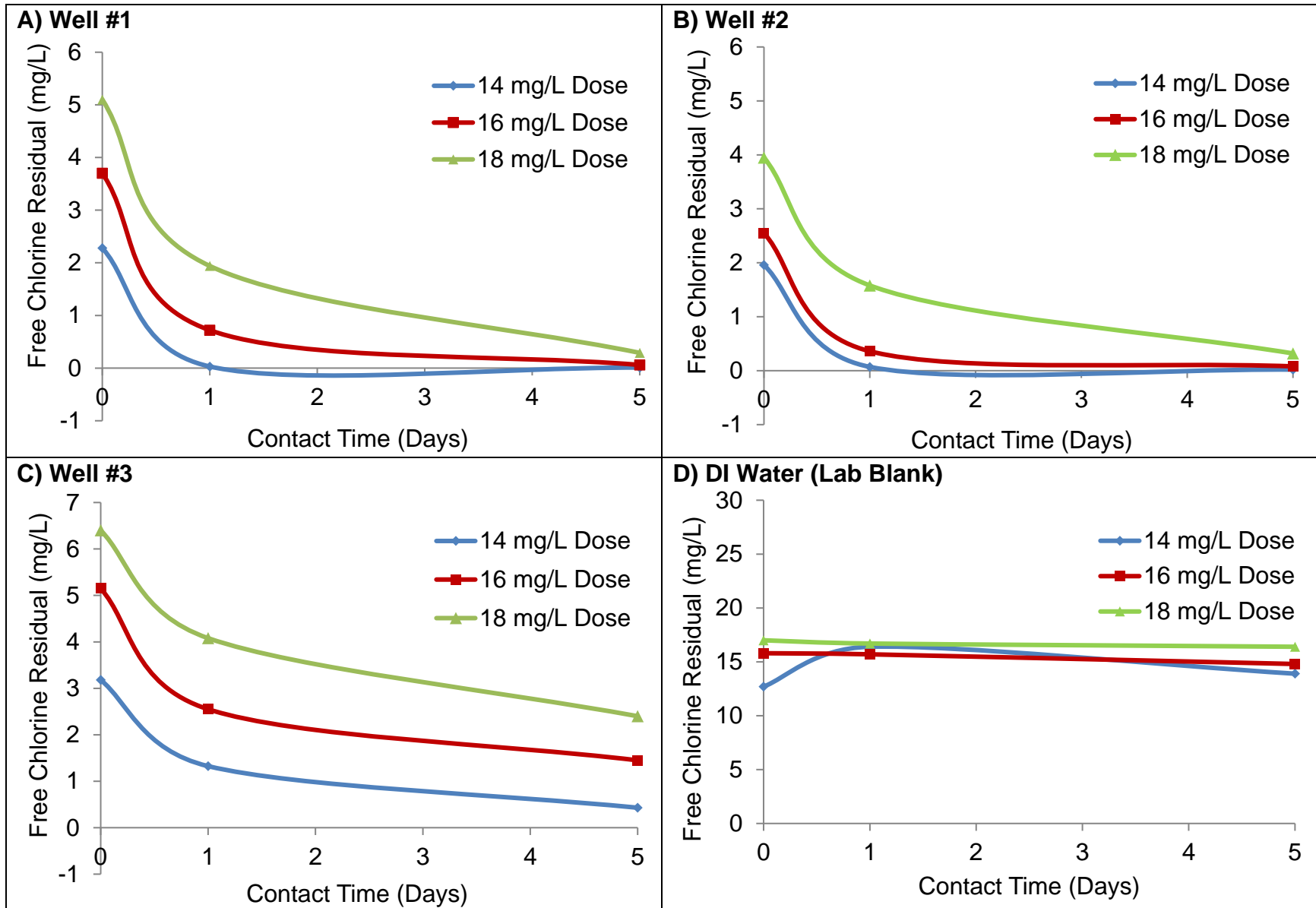


Figure 4. Free chlorine residual vs. contact time at six chlorine doses for Well #1, 2 and 3 with lab blank

To achieve effective disinfection for the KMnO₄ train, 16 mg/L was selected as the chlorine dose for the SDS test. At a chlorine dose of 16 mg/L and above, the treated water from the KMnO₄ train was able to maintain a free chlorine residual over 1 mg/L (Figure 5).

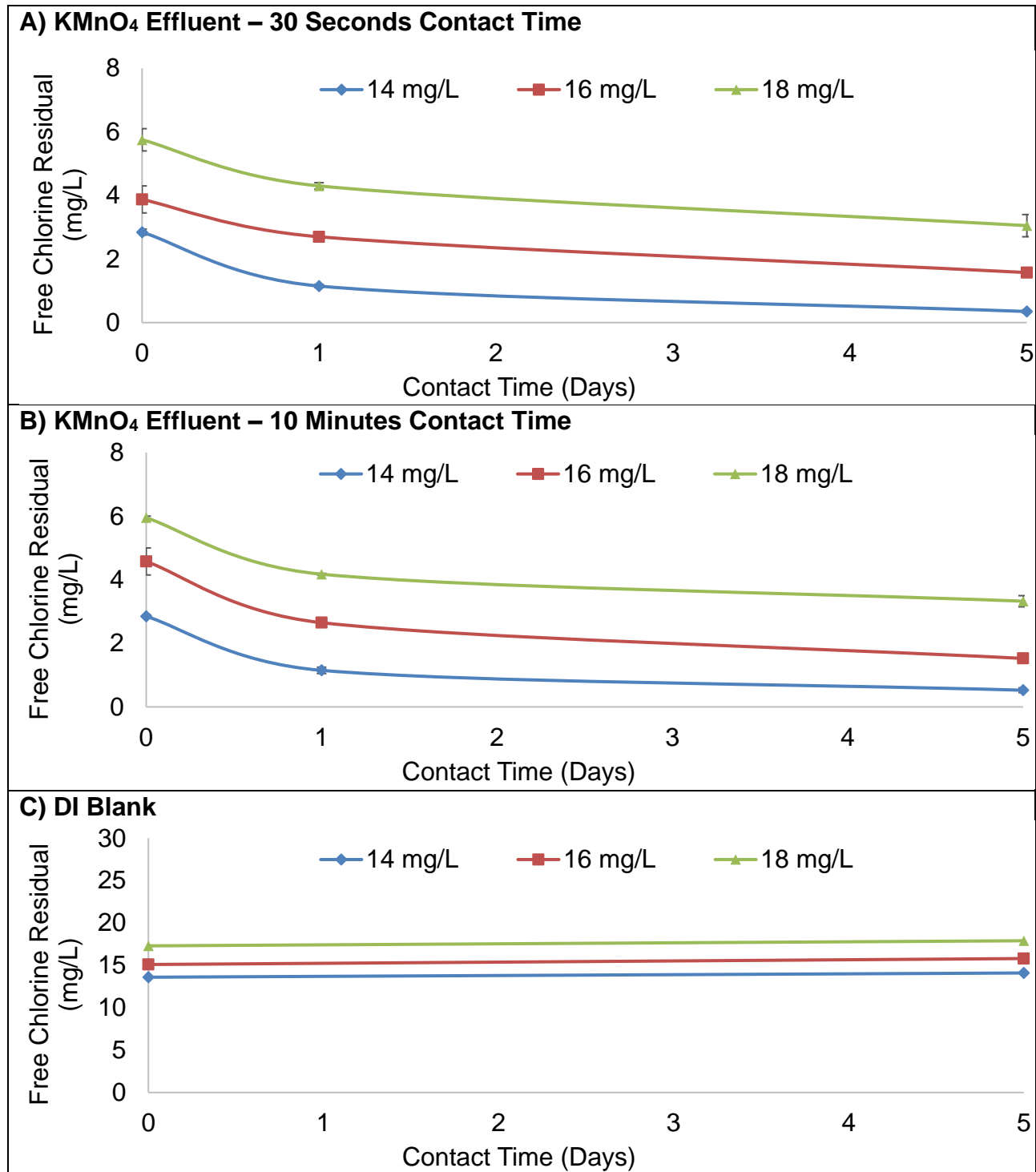


Figure 5. Free chlorine residual vs. contact time for KMnO₄ effluents at three contact times with lab blank

3.2. Pilot-scale Results

3.2.1. Oxidant Residuals

Train 1 was dosed with sodium hypochlorite (chlorine) and monitored for free and total residuals as well as ORP. Whereas Train 2 was dosed with KMnO_4 and monitored for KMnO_4 and ORP. The ORP is expressed in millivolts and indicates the oxidation of iron and manganese compounds and the oxidant's ability to successfully disinfect microbes (James et al., 2004).

To ensure continuous regeneration of the greensand filter, chlorine is required to be dosed prior to the greensand while maintaining free chlorine residuals. A chlorine dose of 15 mg/L was selected for the pilot testing experiment (Figure 6A & 6B). To ensure optimal filter performance, KMnO_4 dose is required to be high enough to oxidize manganese prior to the greensand filter and regenerate greensand media. Meanwhile, to prevent generating pink water, KMnO_4 needs to be underdosed having no residuals in the filter effluent. Theoretically, KMnO_4 dose can be calculated based on the iron and manganese concentrations in the raw water (Sommerfeld, 1999) (Equation 2). However, this equation does not consider the KMnO_4 demand derived from ammonia, NOM and other compounds.

$$\text{KMnO}_4 \text{ Dose } \left(\frac{\text{mg}}{\text{L}} \right) = 1 \times [\text{Fe Concentration}] + 2 \times [\text{Mn Concentration}] \dots \dots \text{Equation 2}$$

Based on the total iron (average = 0.25 mg/L) and total manganese (average = 0.10 mg/L) concentrations of the raw water in Well #3, the theoretical KMnO_4 dose was calculated as 0.45 mg/L. However, in practical applications a higher KMnO_4 dose was needed to satisfy the immediate KMnO_4 demand. The pilot project started with a trial experiment and the optimal KMnO_4 dose was determined as 1.4 mg/L. The optimal dose was determined by monitoring iron, manganese, and ORP while ensuring the greensand filter effluent didn't have excess KMnO_4 . KMnO_4 residual was monitored for Run 1 and 3, but it was noted that the KMnO_4 residual dissipated rapidly, particularly after 5 minutes of collection. Although KMnO_4 was dosed at 1.4 mg/L, the residual after 30 seconds (Run 1 and 3) and 10 minutes (Run 2 and 4) of contact time were 0.035 mg/L and 0.255 mg/L, respectively (Figure 6C & 6D). Samples collected from Run 1 and 3 were analyzed approximately 30 minutes after collection, which was attributed to the much lower readings and higher variability of the

KMnO₄ results (Figure 6C). For Runs 2 and 4, KMnO₄ residual was measured within 5 minutes of sample collection, which resulted in a higher reading with less variability (Figure 6D).

The ORP remained in a steady range for the chlorine train (Train 1) (668 – 713 mV), but the KMnO₄ train (Train 2) had more variable ORP readings (253 – 704 mV) throughout the pilot test runs (Figure 6). For the KMnO₄ train (Train 2), the samples collected from post-filter had no KMnO₄ residual, however the ORP remained in a high range (307 mV and 517 mV) (Figure 6C & 6D). The ORP probe required a long time to stabilize before a reading was obtained, which may have contributed to variable readings. Also, ORP is pH and temperature dependent and can vary in different water matrices. James et al. (2004) evaluated the impact of different oxidant types at varied concentrations on ORP readings. At pH of 8 at 23 °C, it was found that 3.2 mg/L of free chlorinated buffered water had a maximum ORP of 922 mV and 3.2 mg/L of KMnO₄ in buffered water had a maximum ORP of 795 mV (James et al., 2004). Similar ORP readings of chlorine and KMnO₄ were obtained in this project.

The KMnO₄ pilot tests were repeated on March 31, 2021. During the tests, KMnO₄ was dosed at 1.4 mg/L, resulting in a residual of 0.45 – 0.75 mg/L prior to the greensand filters regardless of KMnO₄ contact time (Figure 6E & 6F). Those residuals were higher than the readings obtained on February 25 – 26, 2021 (0.04 – 0.15 mg/L), although KMnO₄ dose was kept the same. This may be attributed to the analysis time of KMnO₄ samples, as KMnO₄ residual dissipated rapidly after collection and the residuals were measured within 3 minutes of collection. Similar to the previous tests (February 25 – 26), almost no KMnO₄ residuals were obtained in the greensand effluents, preventing the generation of pink water.

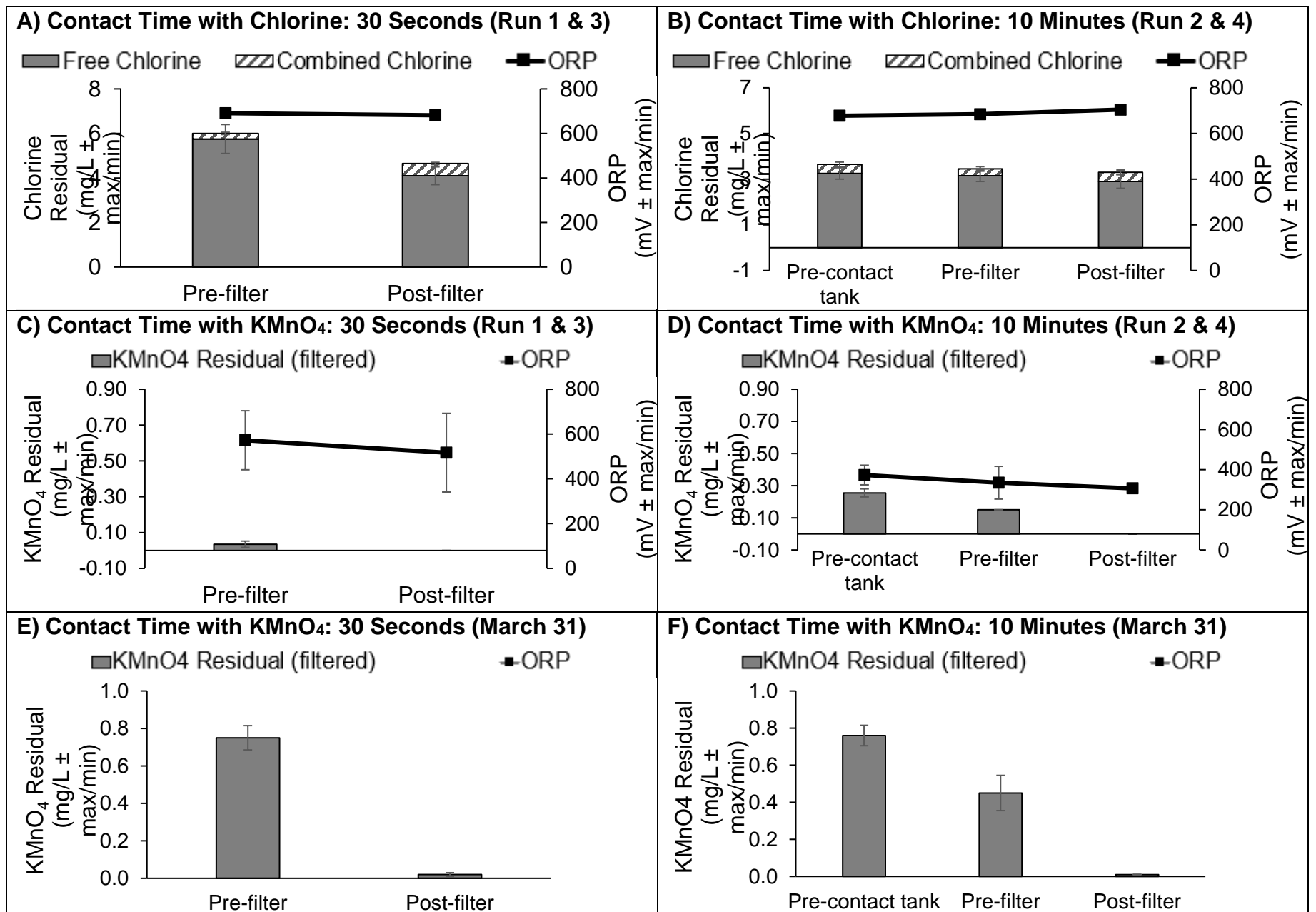


Figure 6. Oxidant residuals and ORP results of pilot tests

3.2.2. Turbidity

As shown in Figure 7, the turbidity of the raw water was 0.33 ± 0.12 NTU. With an oxidant contact time of 30 seconds (Run 1 and 3), the turbidity results of the greensand filter effluents in the chlorine train (Train 1) and the KMnO_4 train (Train 2) were 0.33 ± 0.02 NTU and 0.41 ± 0.10 NTU, respectively. By increasing the contact time of oxidant to 10 minutes (Run 2 and 4), the turbidity of the greensand effluents was reduced in the chlorine train (Train 1) and the KMnO_4 train (Train 2) as 0.21 ± 0.01 NTU and 0.17 ± 0.02 NTU, respectively.

Compared to raw water, the turbidity increased at the pre-contact tank and pre-filter sampling ports for both trains (Figure 7). This increase is likely due to the successful oxidation of iron and manganese, which converts dissolved iron and manganese into the particulate form leading to an increase in turbidity. The greensand filter reduced the turbidity, most likely due to the removal of particulate iron and manganese through the filtration process.

Similar turbidity results were obtained during the KMnO_4 pilot tests repeated on March 31, 2021 (Figure 7C).

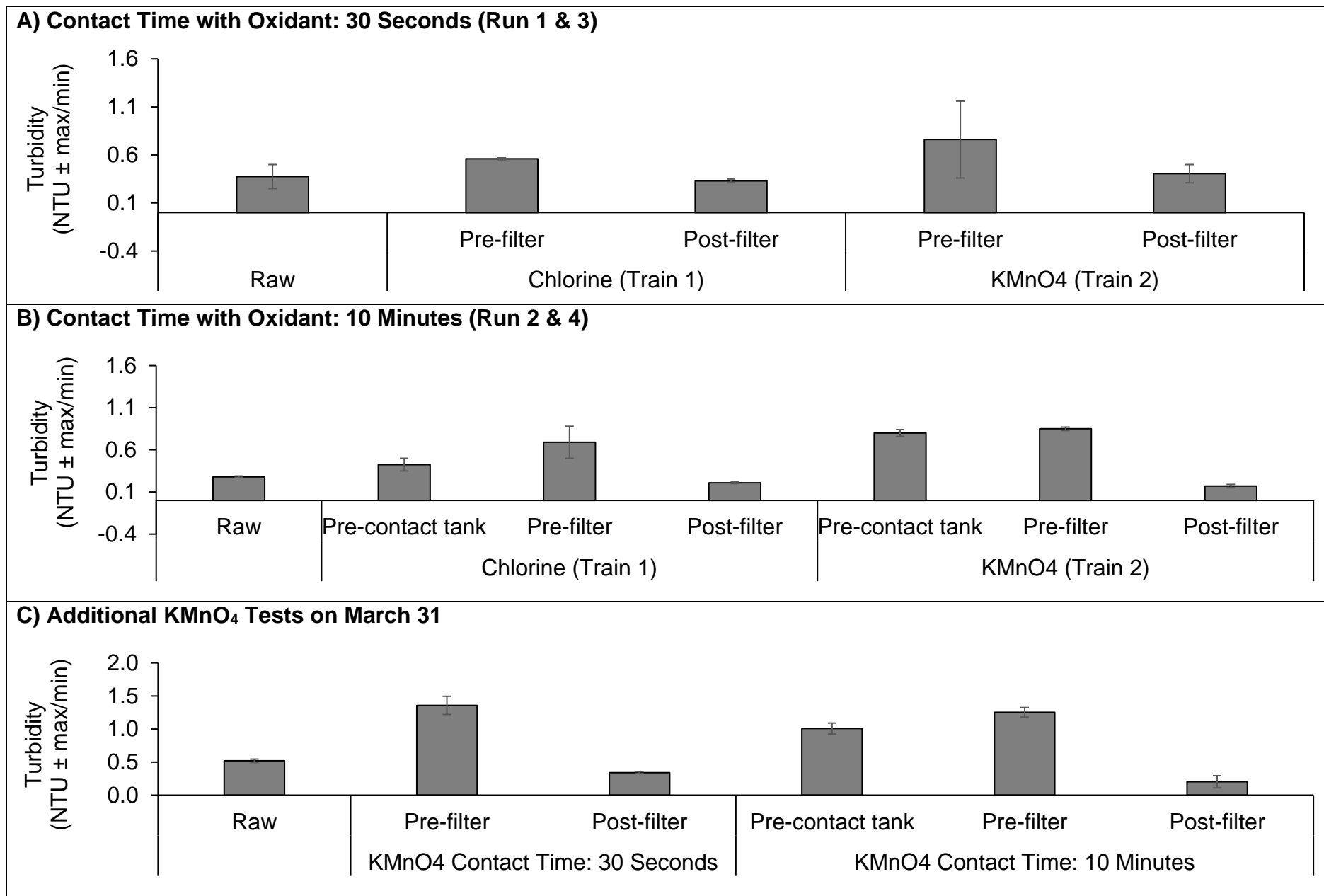


Figure 7. Turbidity results of pilot tests

3.2.3. DOC and UVA₂₅₄

NOM is considered one of the major groups of DBP precursors and can be quantified by DOC and UVA₂₅₄. As shown in Figure 8, the DOC of the raw water was 2.16 ± 0.07 mg/L. With an oxidant contact time of 30 seconds (Run 1 and 3), the greensand filters reduced 6.5% - 6.9% of DOC from the raw water, regardless of oxidant type. By increasing the contact time of oxidant to 10 minutes (Run 2 and 4), the greensand filters had a slightly higher DOC removal of 8.8% from the raw water for both oxidants.

Similar DOC results were obtained during the KMnO₄ pilot tests repeated on March 31, 2021 (Figure 8C).

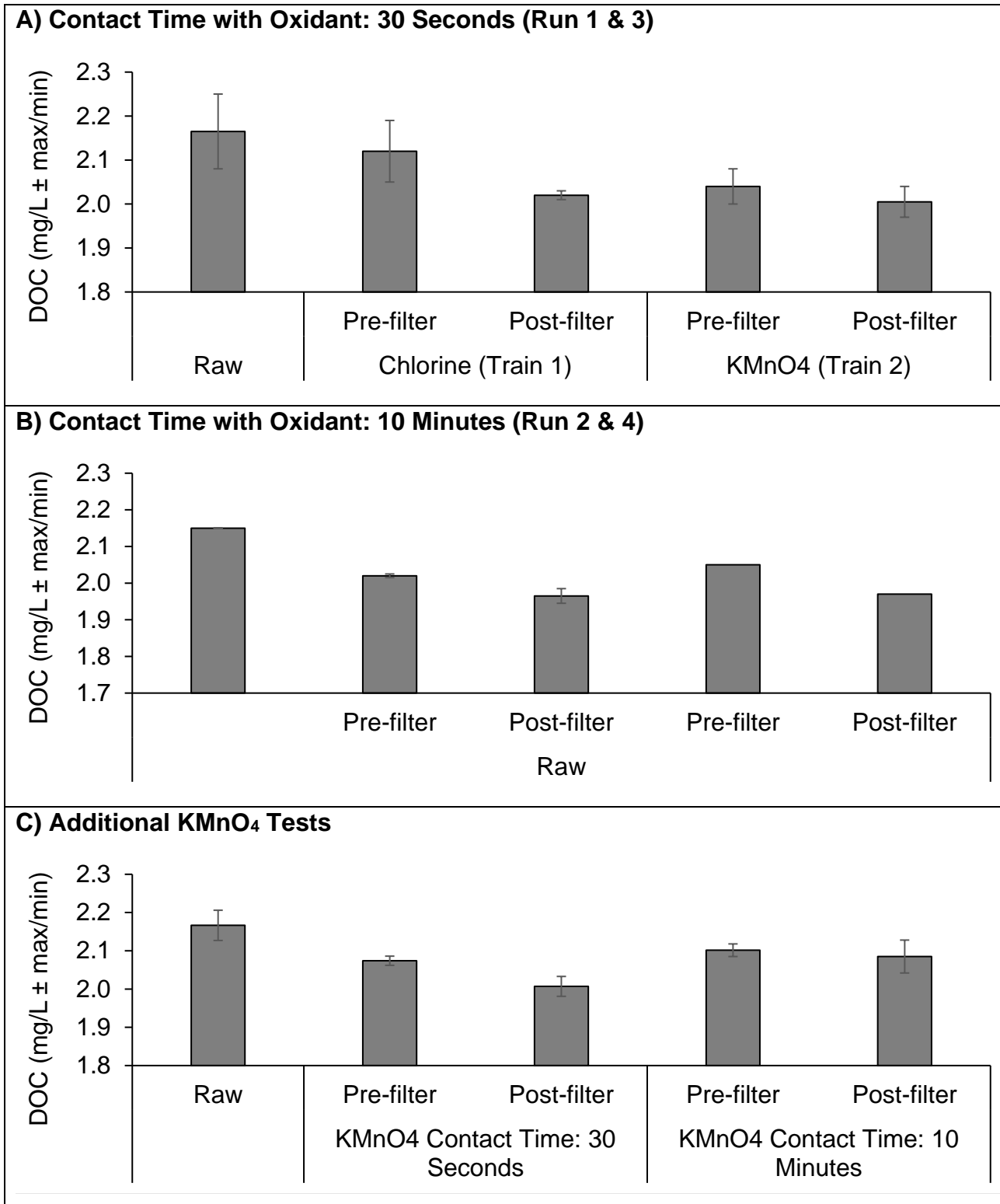


Figure 8. DOC results of pilot tests

Aromatic organics absorb ultraviolet light at a 254 nm wavelength in proportion to their concentration. Therefore, UVA_{254} is used as a surrogate of NOM (Edzwald and Tobiason, 1999; EPA, 1999). As shown in Figure 7, the UVA_{254} of the raw water was $0.090 \pm 0.002 \text{ cm}^{-1}$. With an oxidant contact time of 30 seconds (Run 1 and 3), the UVA_{254} of the greensand effluent of the chlorine train (Train 1) and the $KMnO_4$ train (Train 2) was measured as 0.043 cm^{-1} and $0.066 \pm 0.001 \text{ cm}^{-1}$, respectively. Increasing the contact time of oxidant from 30 seconds to 10 minutes has limited impact on the reduction of UVA_{254} , regardless of oxidant type. Compared to the raw water, both $KMnO_4$ and chlorine reduced the UVA_{254} , however chlorine provided a greater reduction than $KMnO_4$ (Figure 9).

Similar UVA_{254} results were obtained during the $KMnO_4$ pilot tests repeated on March 31, 2021 (Figure 9C).

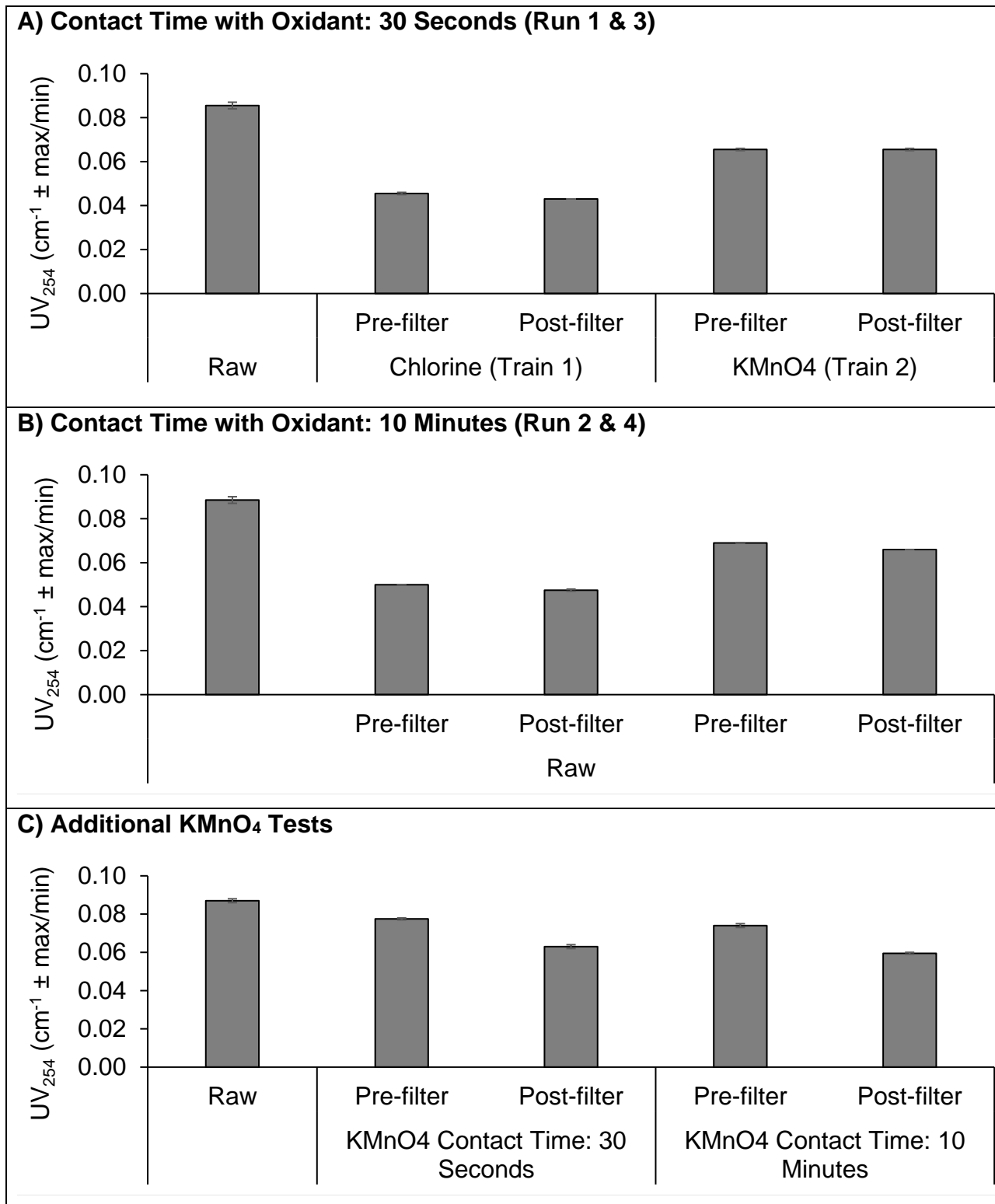


Figure 9. UVA₂₅₄ results of pilot tests

3.2.4. Total Ammonia

High levels of naturally occurring ammonia can be problematic in drinking water systems because it can create a high chlorine demand, increase the risk of nitrification, corrosion, and biofilm in the distribution system (AWWA, n.d.; Health Canada, 2013). To obtain free chlorine residuals, the chlorine dose must be high enough to satisfy the chlorine demand caused by the elevated levels of naturally occurring ammonia. In general, 1 mg/L of ammonia consumes 8 to 12 mg/L of chlorine (AWWA, n.d.; Health Canada, 2013). The high chlorine dose can consequently increase DBP levels.

As shown in Figure 10, the total ammonia of the raw water was measured as 1.43 ± 0.53 mg/L. In Run 1 and 3 (oxidant contact time of 30 seconds), the total ammonia concentration of the greensand effluent was measured as 0.01 mg/L and 1.25 mg/L for the chlorine train (Train 1) and KMnO_4 train (Train 2), respectively. In Run 2 and 4 (oxidant contact time of 10 minutes), the total ammonia levels of the greensand effluent for the chlorine train (Train 1) and KMnO_4 train (Train 2) were measured as 0.01 mg/L and 1.45 mg/L, respectively. KMnO_4 did not remove ammonia from the raw water, as the total ammonia levels of the KMnO_4 train (Train 2, 1.25 – 1.45 mg/L) was similar to that of the raw water (1.43 ± 0.53 mg/L). In addition, increasing the contact time of oxidant from 30 seconds to 10 minutes had limited impact on the levels of the total ammonia in the greensand effluent, regardless of the oxidant type. It is noted that the impact of oxidant dose on the removal of free ammonia was not evaluated in this study.

Similar ammonia results were obtained during the KMnO_4 pilot tests repeated on March 31, 2021 (Figure 10C).

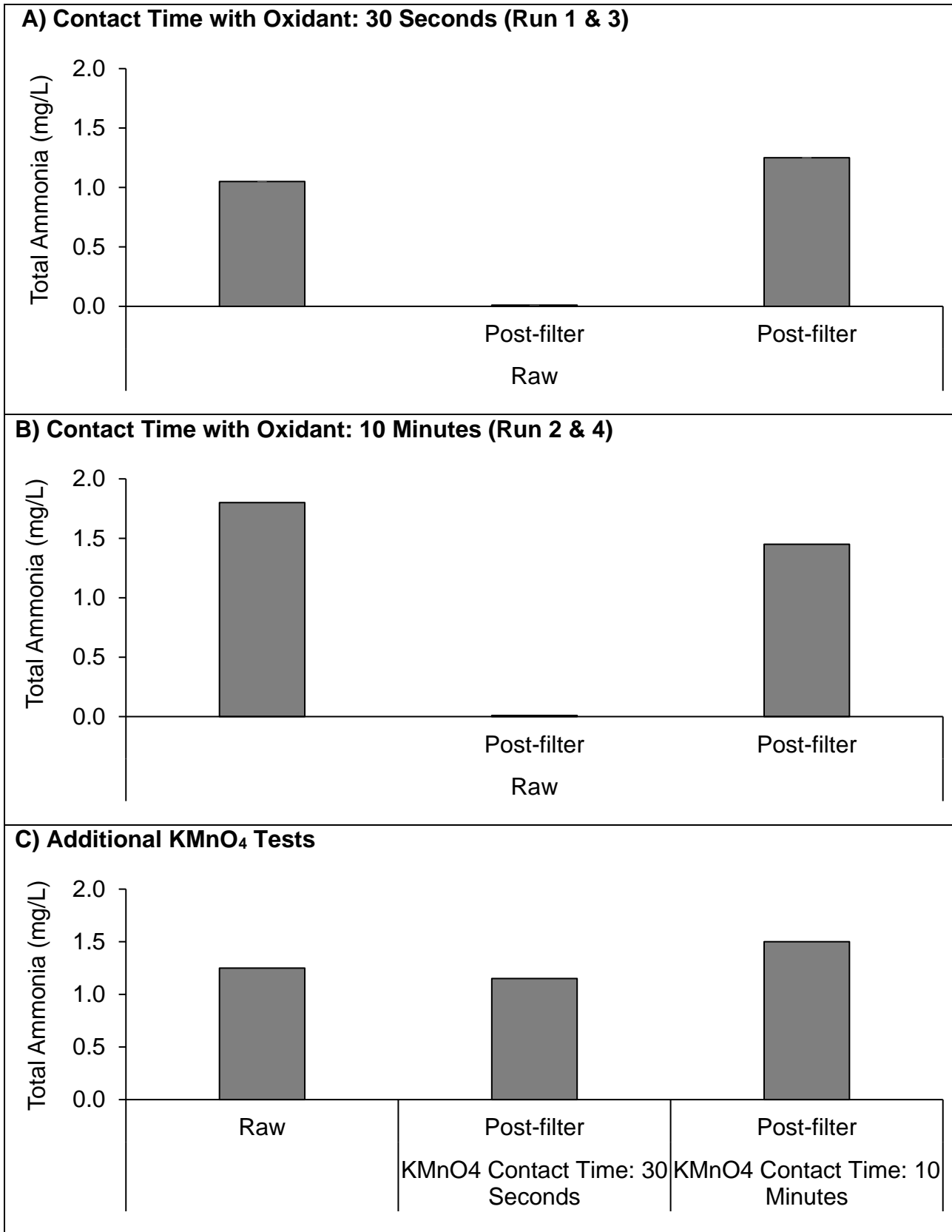


Figure 10. Total ammonia results of pilot tests

3.2.5. Iron

Iron can stain laundry and plumbing fixtures, cause colour and taste issues, and promote the growth of iron bacteria in the distribution system (MECP, 2006). In Ontario, the AO for iron is 0.3 mg/L in drinking water (MECP, 2006).

As shown in Figure 11, the total iron of the raw water was 0.25 mg/L. In Run 1 and 3 (oxidant contact time of 30 seconds), the total iron of the greensand effluent for the chlorine train (Train 1) and the KMnO_4 train (Train 2) were measured as 0.03 mg/L and 0.025 ± 0.005 mg/L, respectively. Whereas, in Run 2 and 4 (oxidant contact time of 10 minutes), the total iron was measured as 0.02 mg/L and 0.035 ± 0.005 mg/L in the greensand effluent for the chlorine train (Train 1) and the KMnO_4 train (Train 2), respectively. Overall, the oxidation and greensand filtration process reduced 84% - 88% of the total iron from the raw water, regardless of the oxidant type or contact (Figure 11).

A portion of each sample was filtered through a 0.45 μm filter and then tested for iron to determine the concentration of the dissolved iron. The difference between the concentrations of the total and dissolved iron was determined as the concentration of the particulate iron. It is expected that iron is oxidized by either chlorine or KMnO_4 into the particulate form. The greensand filter can then remove the particulate iron from water. During the pilot testing experiment, nearly all the particulate iron was removed from the raw water through the greensand oxidation/filtration process, regardless of oxidant type or contact time (Figure 11). The majority of the remaining iron in the greensand filter effluent was attributed to dissolved iron (Figure 11).

Similar iron results were obtained during the KMnO_4 pilot tests repeated on March 31, 2021 (Figure 11C).

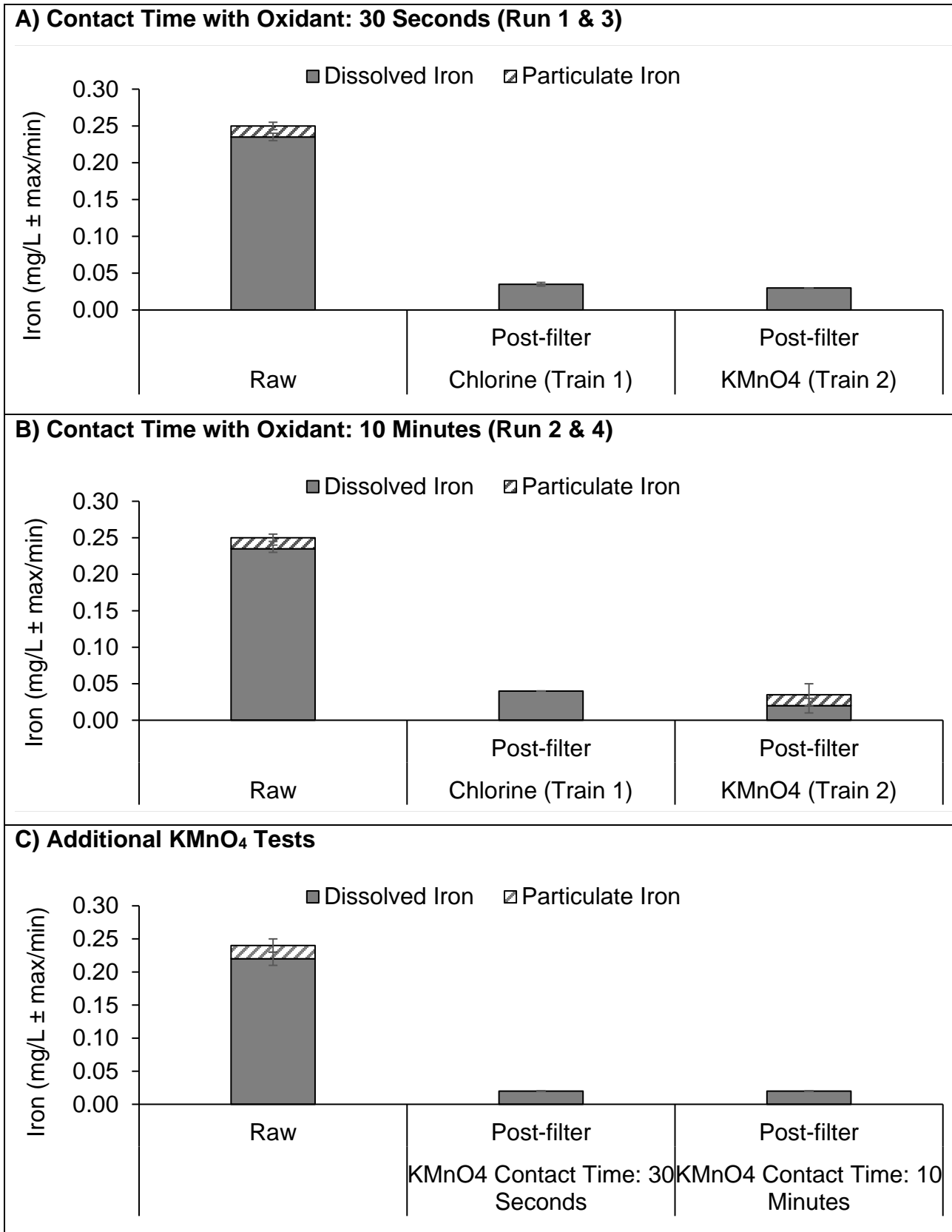


Figure 11. Iron results of pilot tests

3.2.6. Manganese

Manganese in drinking water can also stain laundry and plumbing fixtures and is typically more challenging to remove, compared to iron. In Ontario, the AO for total manganese in drinking water is 0.05 mg/L; however, Health Canada has lowered the AO to 0.02 mg/L for total manganese (MECP, 2006; Health Canada, 2019).

The total manganese of the raw water was 0.098 ± 0.007 mg/L. With a contact time of 30 seconds (Run 1 and 3), the greensand filter in the chlorine train (Train 1) and the KMnO_4 train (Train 2) reduced the total manganese levels to 0.020 mg/L and 0.035 ± 0.002 mg/L from raw water, respectively. By increasing the contact time to 10 minutes (Run 2 and 4), the levels of total manganese from the greensand effluent for the chlorine train (Train 1) and the KMnO_4 train (Train 2) were 0.021 ± 0.001 mg/L and 0.034 ± 0.005 mg/L, respectively. Overall, the greensand oxidation/filtration process reduced the total manganese from the raw water to somewhere below Ontario's AO (0.05 mg/L) (Figure 12). However, compared to KMnO_4 , chlorine further reduced the concentrations of total manganese, regardless of contact time. In this study, contact time has limited impact on the removal of total manganese.

To measure the levels of dissolved manganese, samples were filtered through a $0.45 \mu\text{m}$ filter prior to measurement. The difference between total manganese and dissolved manganese provided the concentration of particulate manganese. When chlorine is dosed prior to the greensand filter, it is expected that greensand media is continuously regenerated by chlorine and can remove dissolved manganese by an adsorption process. Whereas, when KMnO_4 is used, manganese is expected to be oxidized into the particulate form prior to the greensand filter and is then removed by the greensand filter mainly through a filtration process.

As shown in Figure 12, the majority of the manganese in the raw water presented in the dissolved form. With an oxidant contact time of 30 seconds (Run 1 and 3), the chlorine train (Train 1) and the KMnO_4 train (Train 2) had similar removal of dissolved manganese from the raw water as 83% and 78%, respectively. However, the chlorine train (Train 1) achieved 65% removal of particulate manganese, whereas the other train had limited removal. With

an oxidant contact time of 10 minutes, the chlorine train (Train 1) and the KMnO_4 train (Train 2) removed 84% and 67% of dissolved manganese from the raw water, respectively. However, the chlorine train (Train 1) had higher levels of particulate manganese than the raw water.

Similar manganese results were obtained during the KMnO_4 pilot tests repeated on March 31, 2021 (Figure 12C).

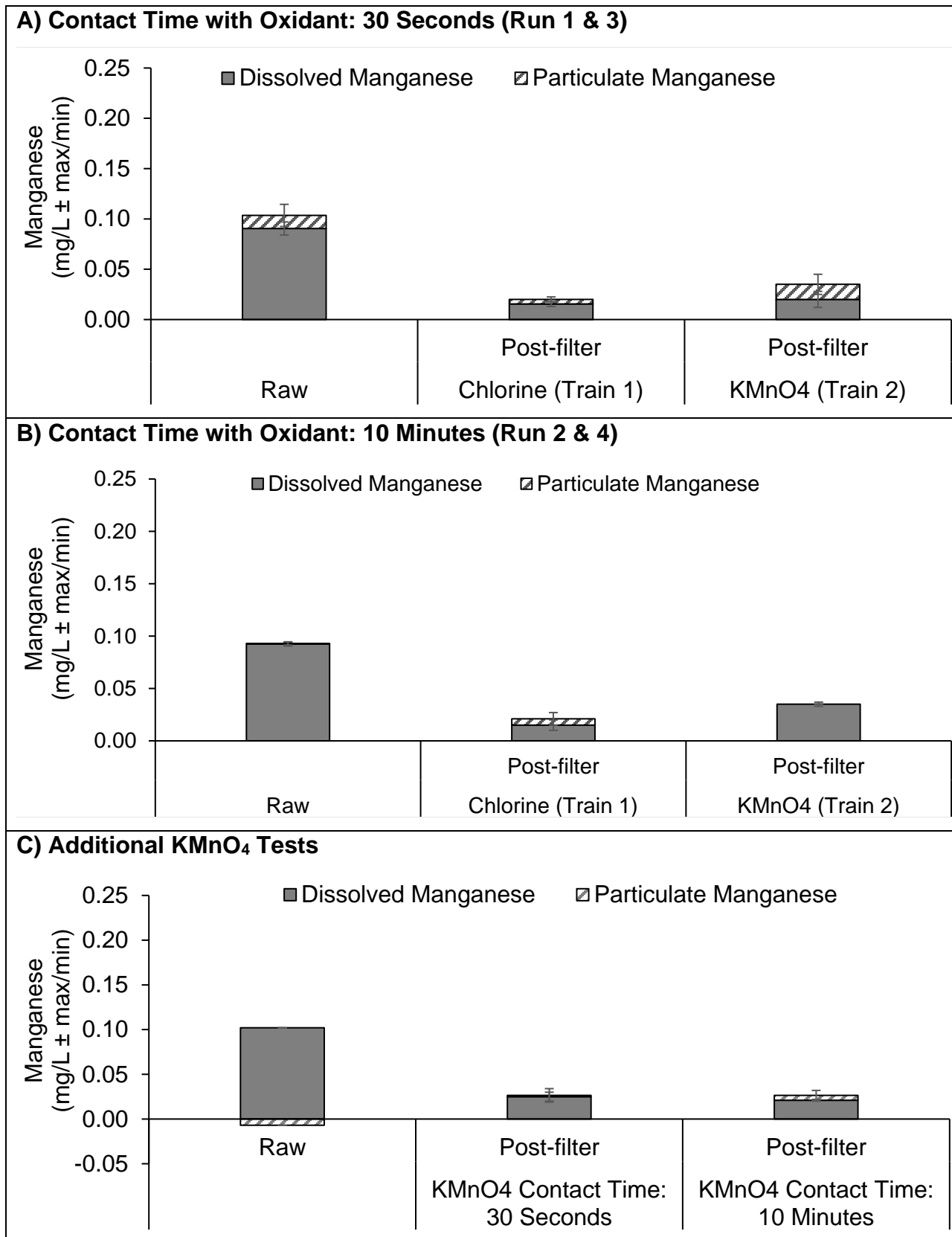


Figure 12. Manganese results of pilot tests

3.3. SDS Tests

All greensand effluent samples collected from the pilot testing experiment were further examined in the SDS tests. The SDS tests were performed to determine the impact of oxidant type and contact time on the formation of THMs and HAAs. During the SDS tests, chlorine was dosed in each sample at two doses. The selected chlorine dose was dependent on the oxidant type.

For the chlorine train (Train 1), chlorine was dosed at a high level prior to the greensand filter for media regeneration purposes and led to high chlorine residuals in the filter effluents. Therefore, chlorine doses of 1 mg/L and 2 mg/L were selected to be applied to all the samples collected from the chlorine train (Train 1).

However, in Train 2, KMnO_4 was used to oxidize manganese and regenerate greensand media. As a strong oxidant, KMnO_4 is expected to react with some reducing agents and consequently reduces chlorine demand from the raw water. But, KMnO_4 had limited impact on ammonia levels (Section 3.2.4.), which caused a high chlorine demand (14 mg/L discussed in Section 3.1.1). Also, to eliminate pink water issues, KMnO_4 was underdosed leaving no residuals in the filter effluents. Therefore, higher chlorine doses of 16 mg/L and 18 mg/L were selected for the samples collected from the KMnO_4 train. But only the samples dosed with 16 mg/L of chlorine were sent for THM and HAA analysis.

Free and total chlorine residuals were measured while taking THM and HAA samples (Figure 13). All selected chlorine doses for the SDS tests were able to maintain over 1 mg/L of free chlorine residual for up to 5 days of detention time. To reduce the formation of DBPs, chlorine dose could be further optimized for the primary disinfection process, but it is beyond the scope of this project.

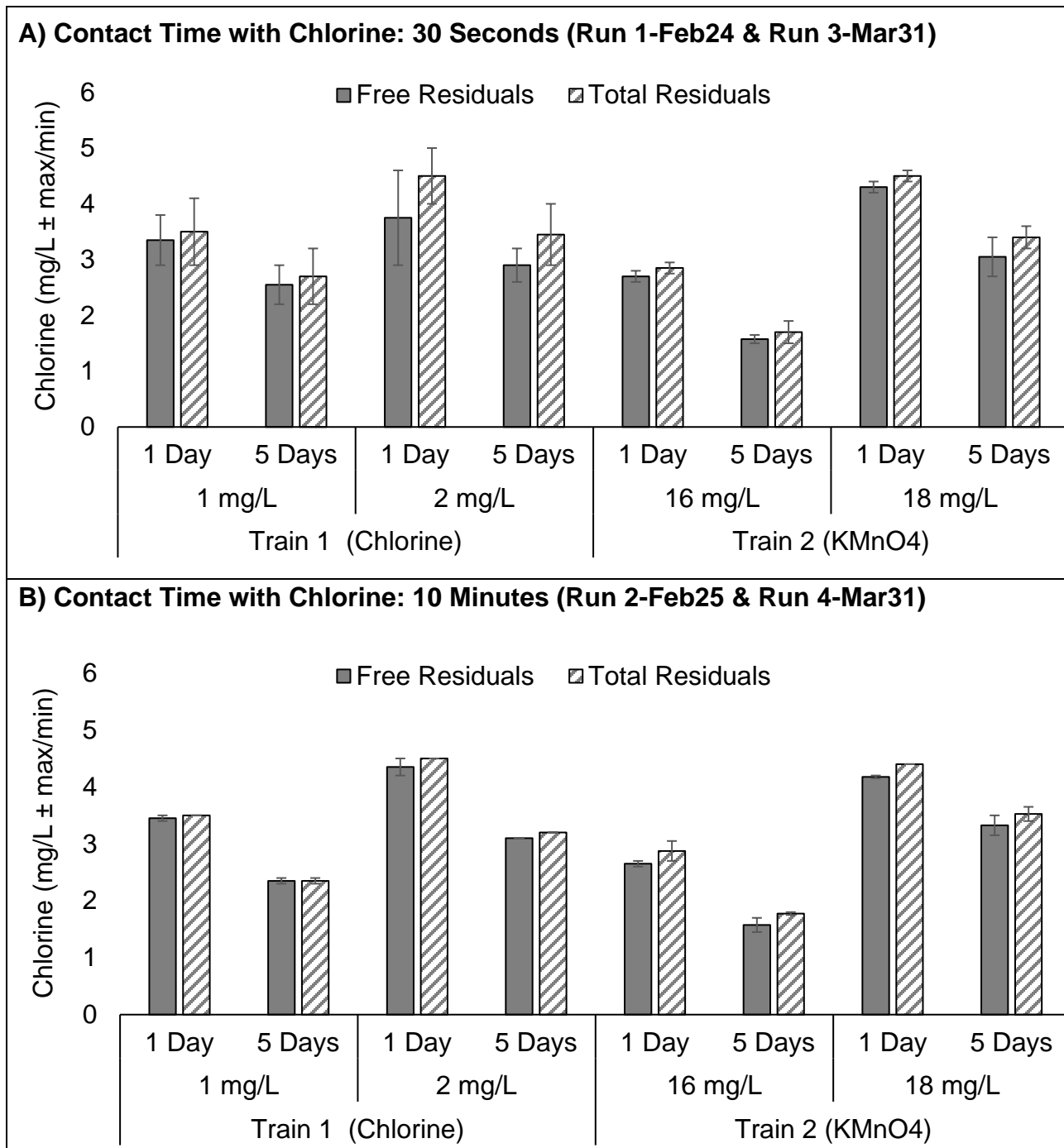


Figure 13. Free and total chlorine residuals of the SDS tests

3.2.1. THMs

The THM results of the SDS tests were demonstrated in Figure 14. In Ontario, the MAC for THMs in drinking water is 100 µg/L as a RAA (MECP, 2006; MECP, 2020). The THM levels of the chlorine train (Train 1 of each run, 89 – 149 µg/L of THMs) were either close to or

higher than the MAC, regardless of the oxidant contact time of pilot tests and detention time of the SDS tests (Figure 14). The KMnO_4 train had similar but slightly lower THM levels (92.8 – 130 $\mu\text{g/L}$).

The contact time between chlorine and THM precursors plays an important role for THM formation. As shown in Figure 14, with an oxidant contact time of 30 seconds in the pilot tests (Run 1 and 3), the THM levels for the chlorine train (Train 1) were measured as 89 – 99 $\mu\text{g/L}$ and 140 – 149 $\mu\text{g/L}$ for the 1-day and 5-day SDS detention time, respectively, regardless of the SDS chlorine dose. When using an oxidant contact time of 10 minutes in the pilot tests (Run 2 and 4), the chlorine train (Train 1) THM levels were detected as 106 – 112 $\mu\text{g/L}$ and 142 – 153 $\mu\text{g/L}$ after 1 day and 5 days of the SDS tests, respectively. Increasing the SDS detention time from 1 to 5 days statistically increased the formation of THMs with 95% confidence interval. However, increasing the chlorine contact time from 30 seconds to 10 minutes did not significantly increase the formation of THMs, regardless of the SDS detention time.

With an oxidant contact time of 30 seconds, the KMnO_4 train had THM levels of 93.6 – 95.6 $\mu\text{g/L}$ and 125.0 – 127.5 $\mu\text{g/L}$ for 1-day and 5-day SDS detention times, respectively. When the oxidant contact time increased to 10 minutes, the THMs were detected as 92.8 – 93.4 $\mu\text{g/L}$ and 126.5 – 130.0 $\mu\text{g/L}$ after 1 day and 5 days of the SDS tests, respectively. Increasing the SDS detention time from 1 to 5 days statistically increased the formation of THMs with 95% confidence interval. However, no significant increase of THM levels was found when the KMnO_4 contact time increased from 30 seconds to 10 minutes.

Among the four regulated THM species, chloroform accounted for 87% - 92% of total THM readings, regardless of oxidant type, oxidant contact time and SDS detention time (Figure 14B & 14C). The elevated levels of chloroform are attributed to the high chlorine dose used for either greensand regeneration in the chlorine train or disinfection in the KMnO_4 train.

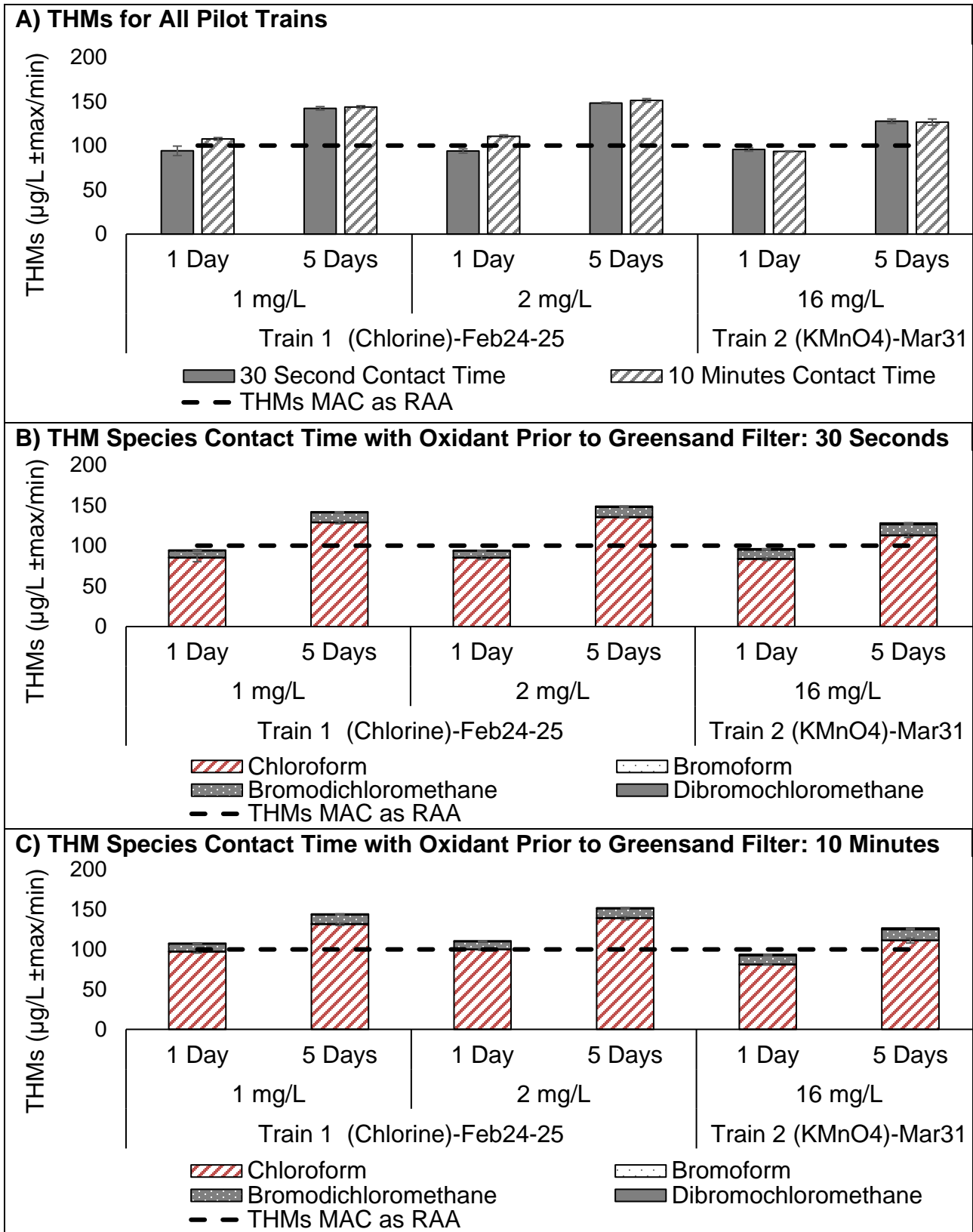


Figure 14. THMs results of the SDS test

3.2.2. HAAs

In Ontario, the MAC for HAAs in drinking water is 80 µg/L as a RAA (MECP, 2020). As shown in Figure 13, all the HAA levels of the chlorine train (Train 1 of each run, 80 – 139 µg/L of HAAs) exceeded the MAC, regardless of the oxidant contact time in the pilot tests and SDS detention time. The KMnO₄ train had slightly lower HAA levels (60.1 – 95.1 µg/L).

HAA formation is dependent on the contact time between chlorine and HAA precursors. Based on Figure 13, with a chlorine contact time of 30 seconds in the pilot tests (Train 1 in Run 1 and 3), the HAA levels for the 1-day and 5-day SDS detention times were measured as 92 – 102 µg/L and 126 – 139 µg/L, respectively. When the chlorine contact time was increased to 10 minutes in the pilot tests (Train 1 in Run 2 and 4), the HAA levels were measured as 80 – 92 µg/L and 112 – 125 µg/L, respectively. HAA formation statistically increased with the SDS detention time with 95% confidence interval. Similar to the THM results, when the chlorine contact time during the pilot tests increased from 30 seconds to 10 minutes, a statistical increase of HAA levels (with 95% confidence interval) was detected for the 1-day SDS detention time. However, this increase was not detected for the results obtained for the 5-day detention time.

With an oxidant contact time of 30 seconds, the KMnO₄ train had HAA levels of 64.5 – 64.9 µg/L and 95.1 – 92.2 µg/L for 1-day and 5-day SDS detention time, respectively. When the oxidant contact time increased to 10 minutes, the HAAs were detected as 60.1 – 60.3 µg/L and 91.2 – 95.1 µg/L after 1 day and 5 days of the SDS tests, respectively. Increasing the SDS detention time from 1 to 5 days statistically increased the formation of HAAs with 95% confidence interval. However, increasing the KMnO₄ contact time from 30 seconds to 10 minutes slightly reduced HAA formation after 1 day of SDS detention time. But this relationship was not detected after 5 days of SDS detention time.

Among the five regulated HAA species, dichloroacetic acids and trichloroacetic acids made up 34% - 50% and 50% - 66% of total HAAs, respectively, regardless of oxidant type, oxidant contact time and SDS detention time (Figure 15B & 15C). The elevated levels of dichloroacetic acids and trichloroacetic acids are closely related to the high chlorine dose

used for either greensand regeneration in the chlorine train or disinfection in the KMnO₄ train.

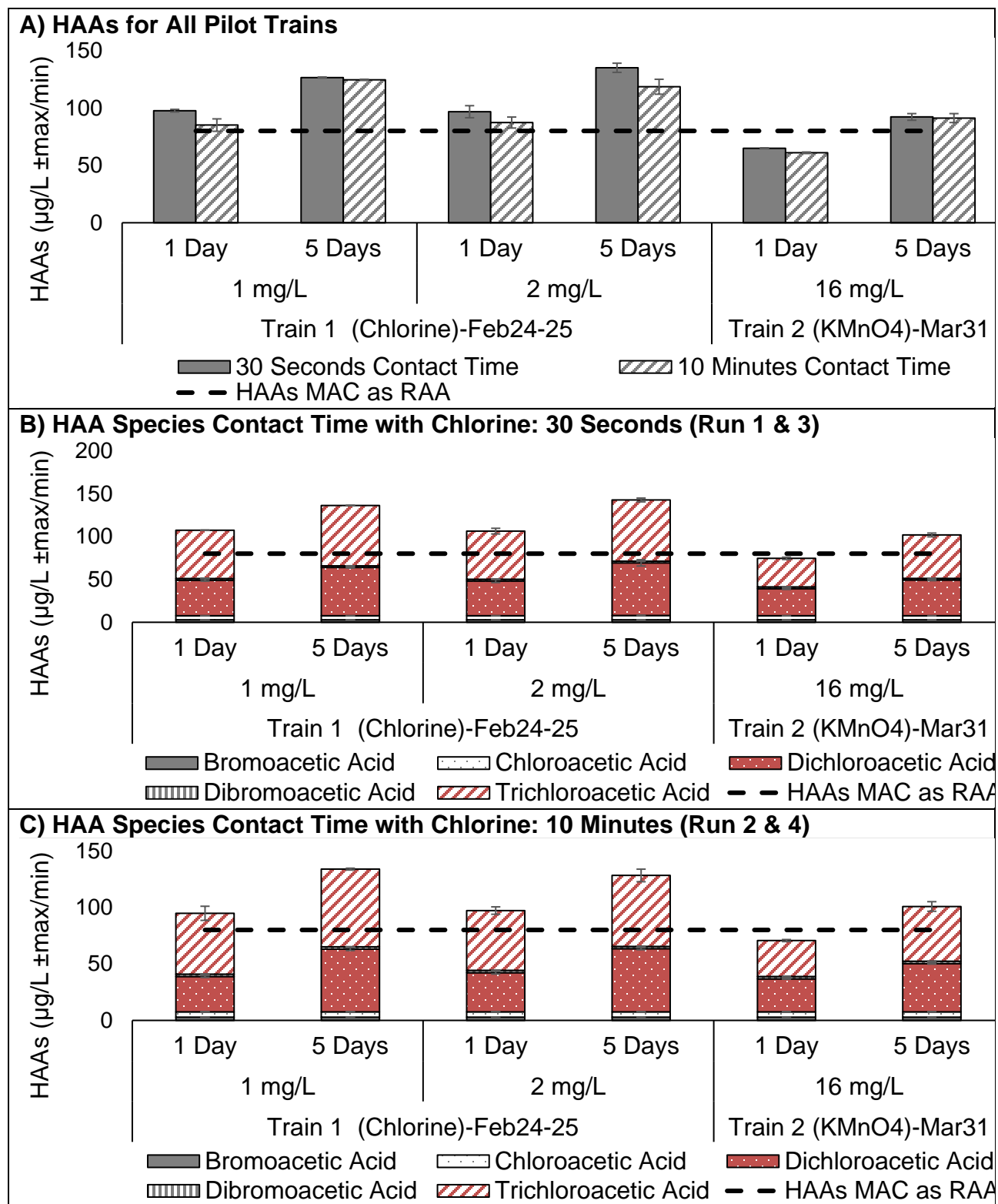


Figure 15. HAAs results of the SDS test

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 resulted from the materials found in the drinking water system were not considered in the SDS tests. For a conservative approach, the samples were stored at ambient room temperature; therefore, the rate of DBP formation is increased with higher temperatures.

5. Conclusions

The results of the pilot testing project are summarized below:

- A high chlorine dose (15 mg/L) was required to satisfy the chlorine demand, which was mainly attributed to the elevated levels of naturally occurring ammonia (1.20 – 1.64 mg/L) in the community's well water. The high chlorine dose can contribute to the formation of DBPs, such THMs and HAAs.
- The optimal dose of KMnO_4 was determined as 1.4 mg/L. At this dose, KMnO_4 can effectively regenerate the greensand media, resulting in high removal of iron and manganese. Meanwhile, no KMnO_4 residual was detected in the filter effluent, which prevented the generation of pink water.
- When comparing the performance of the selected oxidant (chlorine and KMnO_4) at two contact times (30 seconds and 10 minutes):
 - The greensand oxidation/filtration process achieved high removal of iron and manganese (84% - 88% of iron removal and 66% - 81% of manganese removal), regardless of oxidant type and contact time.
 - Among all test runs, KMnO_4 run with 10-minute contact time provided the lowest turbidity (0.17 ± 0.02 NTU).
 - Chlorine removed nearly all ammonia from the raw water to satisfy the chlorine demand (approximately 14 mg/L) and generate free chlorine residual to regenerate greensand media. Therefore, relatively low chlorine doses were used for chlorination disinfection in the chlorine train (Train 1).

- KMnO_4 had limited impact on the ammonia levels in the raw water. The greensand filter effluents of the KMnO_4 train had about 14 mg/L of chlorine demand due to the elevated levels of ammonia. A high chlorine dose was selected for chlorination disinfection in the KMnO_4 train (Train 2).
- The THM levels of both trains were either close to or higher than the MAC, regardless of the oxidant contact time of pilot tests and detention time of the SDS tests. Yet, the KMnO_4 train had slightly lower THM levels after 5 days of SDS detention time than the chlorine train. Increasing the SDS detention time from 1 day to 5 days significantly increased the formation of THMs.
- All the HAA results of the chlorine train (Train 1 of each run, 80 – 139 $\mu\text{g/L}$ of HAAs) exceeded the MAC, regardless of the oxidant contact time in the pilot tests and SDS detention time. The KMnO_4 train had HAA levels below the MAC after 1 day of SDS detention time (60.3 – 65.3 $\mu\text{g/L}$), regardless of oxidant contact time. But the HAA levels increased beyond the MAC after 5 days of detention time (87.3 – 95.1 $\mu\text{g/L}$). Increasing the SDS detention time from 1 day to 5 days increased the formation of HAAs for both oxidants. The KMnO_4 formed approximately 25% - 29% less HAAs than the chlorine train.

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