



## Pilot Testing Project Report

# Reduction of Iron and Manganese Using Conventional Treatment and Greensand Filtration

Walkerton Clean Water Centre

October 29, 2018

## **Disclaimer**

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# Executive Summary

## Background

Iron and manganese are essential elements in human nutrition. In Ontario, no regulation limits have been set for these two elements. However, water may appear and taste unpalatable when iron concentrations exceed 0.3 mg/L (WHO, 2003) and manganese levels exceed 0.4 mg/L (WHO, 2003). At concentrations exceeding above levels, iron and manganese promote the growth of bacteria (including iron bacteria), stain plumbing fixtures and laundry (Health Canada, 1978; Health Canada, 1979). In consequence, the aesthetic objective for iron and manganese in drinking water are set as  $\leq 0.3$  mg/L and  $\leq 0.05$  mg/L, respectively (Ontario MOE, 2003).

A community located in South-Central Ontario has discovered elevated iron and manganese levels in their groundwater. Three pumphouses treat water from the community wells, which implement a series of treatment technologies including a chlorine injector, iron filter, water softener, cartridge filter and UV disinfection system.

The community has had several long-term do not drink water advisories issued and decided to design a new water treatment system; a modified conventional treatment system with flocculation, clarification/sedimentation, and filtration using potassium permanganate ( $\text{KMnO}_4$ ) oxidation and greensand in combination with granular activated carbon (GAC). The Walkerton Clean Water Centre was invited to investigate the performance of the proposed treatment system in pilot scale.

## Objectives

The overall objective of this pilot testing project is to reduce iron and manganese in the treated water.

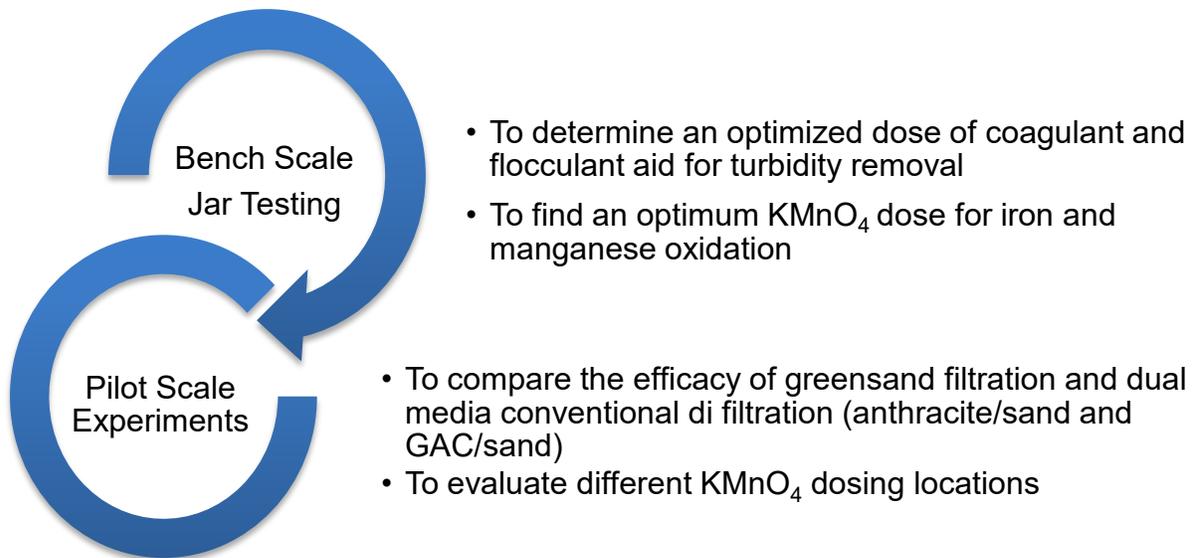
Specific objectives of pilot testing are:

- To reduce iron to less than 0.3 mg/L and manganese to less than 0.2 mg/L;

- To compare the performance of greensand filtration compared to conventional dual media filtration with anthracite/sand and GAC/sand filtration;
- To evaluate different  $\text{KMnO}_4$  dosing locations;
- To assess the reduction of organic matter, trihalomethanes (THMs) and haloacetic acids (HAAs).

## Approach

This project included bench scale jar tests and phases of pilot scale experiments. The objectives of bench and pilot scale tests are demonstrated in Figure ES-1. Raw water was collected from the community's well and hauled to the Centre for both bench and pilot scale testing.



**Figure ES - 1.** Objectives of bench scale testing and pilot scale experiments

**Bench Scale Jar Testing:** Jar Test 1 and 2 were conducted to determine the optimal dosage of coagulant (ClearPAC 180) and flocculant aid (ClearFloc 1065) for turbidity removal, respectively. Those optimized dosages were then used in Jar Test 3 to determine the optimal dose of  $\text{KMnO}_4$  for iron and manganese oxidation. Iron and manganese levels were monitored during the three jar tests. The optimized dosages of coagulant, flocculant aid and  $\text{KMnO}_4$  were applied to the subsequent pilot scale experiments.

**Pilot Scale Experiments:** Two phases of pilot testing were designed; 1) to investigate the efficacy of greensand filtration and conventional filtration and 2) to evaluate the impact of  $\text{KMnO}_4$  dosing location for iron and manganese reduction. Two conventional dual media filters were tested (anthracite/sand filter and GAC/sand filter).

**Phase 1 Pilot Testing:** Raw water was pumped through the pilot system and split into two trains. In both trains, water was dosed with coagulant (ClearPAC 180) at 20 mg/L, and then pumped through the rapid mixer, flocculator, and clarifier, simultaneously.

Afterwards, the flow from Train 1 clarifier was further split into two filtration trains:

- Filter 1 Train 1: anthracite/sand filter
- Filter 2 Train 1: GAC/sand filter

Effluent of Train 2 clarifier was pumped through the greensand filter.

**Phase 2 Pilot Testing:** Two replicated experiments were conducted to evaluate different  $\text{KMnO}_4$  dosing locations. Raw water was pumped through the pilot system and split into two trains, simultaneously. The setups of the two trains were kept the same except for the dosing locations of the oxidant. In both trains, water was dosed with 20 mg/L of coagulant (ClearPAC 180) in the rapid mixer, and then travelled through the flocculator and clarifier.  $\text{KMnO}_4$  was dosed at 0.3 mg/L in the lower port of the rapid mixer of Train 1 and dosed at 0.3 mg/L in the third flocculator cell in Train 2. Afterwards, clarifier effluent from each train was further split into two filtration trains:

- Filter 1, Trains 1/2: anthracite/sand filter
- Filter 2, Trains 1/2: GAC/sand filter

However, grab samples were only collected from the anthracite/sand filters from both trains.

## Key Findings

Through the bench scale tests, it was determined that:

- Bench Scale Test 1: The optimized coagulant (ClearPAC 180) dosage was found to be 20 mg/L.
- Bench Scale Test 2: The optimized flocculant aid (ClearFloc 1065) dosage was found to be 0.3 mg/L.
- Bench Scale Test 3: The optimized  $\text{KMnO}_4$  dosage was determined to be 0.3 mg/L for pilot testing as it yielded the best result for both iron and manganese oxidation.

The pilot plant experiments conducted at the Centre determined the following:

- Phase 1 Pilot Testing
  - Conventional treatment followed by anthracite/sand or GAC/sand filtration
    - Manganese was reduced from 43.5  $\mu\text{g/L}$  to less than 20  $\mu\text{g/L}$
    - Iron was reduced from 271  $\mu\text{g/L}$  to less than 5  $\mu\text{g/L}$
    - THMs were reduced from 67  $\mu\text{g/L}$  to 46  $\mu\text{g/L}$
    - $\text{HAA}_5\text{s}$  were reduced from 37  $\mu\text{g/L}$  to 20  $\mu\text{g/L}$
  - Conventional treatment followed by greensand filtration
    - Manganese increased after treatment
    - Iron was reduced from 271  $\mu\text{g/L}$  to less than 5  $\mu\text{g/L}$
    - THMs were reduced from 67  $\mu\text{g/L}$  to 44  $\mu\text{g/L}$
    - $\text{HAA}_5\text{s}$  were reduced from 37  $\mu\text{g/L}$  to 23  $\mu\text{g/L}$
- Phase 2 Pilot Testing
  - Dosing in the rapid mixer produced better water quality results compared to dosing in Flocculator Cell 3. Dosing  $\text{KMnO}_4$  was more effective when it had a longer detention and reaction time available.

# Table of Contents

Disclaimer .....	i
Executive Summary .....	ii
1. Introduction.....	1
2. Materials and Method .....	3
2.1 Jar Testing .....	3
2.2 Pilot Plant Experiments .....	5
2.3 Sampling and Methods of Water Quality Analysis .....	7
2.4 Simulated Distribution System for Disinfection By-Product Analysis.....	8
2.4.1. Simulated Distribution System Test for THMs and HAA <sub>5</sub> .....	8
2.5 Organic Nitrogen.....	9
3. Results and Discussion .....	9
3.1 Jar Test Results .....	9
3.1.1 Jar Test 1.....	9
3.1.2 Jar Test 2.....	10
3.1.3 Jar Test 3.....	11
3.2 Pilot Testing Results .....	14
3.2.1 Phase 1 Experiments.....	14
3.2.1.1 Manganese Reduction.....	14
3.2.1.2 Iron Reduction .....	16
3.2.1.3 Turbidity Reduction.....	17
3.2.1.4 Organics Reduction .....	18
3.2.1.5 General Water Quality .....	20
3.2.1.6 SDS-THMs and HAA <sub>5</sub> Tests.....	21
3.2.1.7 Organic Nitrogen .....	23
3.2.2 Phase 2 Experiments.....	24
3.2.2.1 Manganese Reduction.....	24
3.2.2.2 Iron Reduction .....	25
3.2.2.3 Turbidity Reduction.....	26
4. Conclusions .....	28
References.....	29

## List of Tables

Table 1. Methods of Water Quality Analysis.....	8
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## List of Figures

Figure 1. Jar test objectives .....	3
Figure 2. Jar test conditions .....	4
Figure 3. Schematics for Experiments 1 & 2 .....	6
Figure 4. Schematics for Experiments 3 & 4 .....	7
Table 1. Methods of Water Quality Analysis.....	8
Figure 5. Effect of coagulant dosage on A) turbidity, B) DOC, C) pH and D) UV <sub>254</sub> absorbance in Jar Test 1 .....	10
Figure 3. Effect of Coagulant Dosage on (A) Turbidity, (B) Dissolved Organic Carbon, (C) pH and (D) UV Absorbance in Jar Test 1.....	10
Figure 6. Effect of flocculant aid dosage on A) turbidity, B) DOC, C) pH and D) UV <sub>254</sub> absorbance in Jar Test 2.....	11
Figure 4. Effect of Flocculant Aid (coagulant dose-20 mg/L) Dosage on (A) Turbidity, (B) Dissolved Organic Carbon, (C) pH and (D) UV Absorbance in Jar Test 2. ....	11
Figure 7. Effect of KMNO <sub>4</sub> (coagulant dose-20 mg/L, Flocculant Aid -0.3 mg/L) on A) Turbidity, B) DOC, C) pH, D) UV Absorbance, E) Manganese and F) Iron in Jar Test 3...	13
Figure 8. Phase 1 (Experiments 1 & 2) results - average particulate and dissolved manganese (mg/L ± max/min).....	15
Figure 9. Phase 1 (Experiment 1 & 2) results – average particulate and dissolved iron (mg/L ± max/min) .....	17
Figure 10. Phase 1 (Experiments 1 & 2) results – average turbidity (NTU ± max/min) .....	18
Figure 11. Phase 1 (Experiment 1 & 2) results – average DOC (mg/L ± max/min).....	19
Figure 12. Phase 1 (Experiment 1 & 2) results – average UV <sub>254</sub> Absorbance.....	20

(cm <sup>-1</sup> ± max/min) .....	20
Figure 13. Phase 1 (Experiment 1 & 2) results – average THMs .....	21
(Chlorine contact time of 5 days).....	21
Figure 14. Phase 1 (Experiment 1 & 2) results – average HAAs.....	22
(Chlorine contact time of 5 days).....	22
Figure 15. Phase 1 (Experiment 1 & 2) results – average organic nitrogen concentrations .....	23
Figure 16. Phase 2 results – average particulate and dissolved manganese concentrations (mg/L ± max/min) .....	25
Figure 17. Phase 2 results – average particulate and dissolved iron concentrations .....	26
(mg/L ± max/min) .....	26
Figure 18. Phase 2 (Experiment 3 & 4) results – average turbidity levels (NTU ± max/min) .....	27

# 1. Introduction

Iron and manganese occur naturally in groundwater. In water, iron is most likely present as Fe(II) or Fe(III). Fe(III)-containing salts are generally found in surface water when pH is above 7 (Health Canada, 1978). Most of those salts are unstable and are precipitated as insoluble Fe(III) hydroxide, which can settle out as a rust-colored silt (WHO, 2003). Manganese most often exists as the dioxide, carbonate or silicate. It may be present in oxidation states ranging from -3 to +7, whereas the manganous ( $Mn^{+2}$ ) and manganic ( $Mn^{+4}$ ) oxidation states are the most important for aquatic systems (Health Canada, 1979).

Iron and manganese are essential elements in human nutrition. Iron has no evidence of dietary toxicity in the general population (Health Canada, 1978), whereas manganese is regarded as one of the least toxic elements, with acceptable daily intake from water of 0.005 mg (Health Canada, 1979). Therefore, in Ontario, no regulation limits have been set for iron and manganese. However, water may taste and appear unpalatable, when iron concentration exceeds 0.3 mg/L (WHO, 2003) and when manganese levels exceed 0.4 mg/L (WHO, 2003). At concentrations exceeding these levels, iron and manganese promote the growth of bacteria (including iron bacteria), stain plumbing fixtures and laundry and gradually clog distribution pipelines (Health Canada, 1978; Health Canada, 1979). In consequence, the aesthetic objective for iron and manganese in drinking water in Ontario are set as  $\leq 0.3$  mg/L and  $\leq 0.05$  mg/L, respectively (Ontario MOE, 2003).

A community located in South-Central Ontario has discovered elevated iron and manganese levels from their groundwater wells. This community provides drinking water to 236 people using a blend of private and community well sources. The existing water source is classified as groundwater under the direct influence of surface water (GUDI). Three existing pumphouses treat water from the community wells which implement a series of treatment technologies including a chlorine injector, iron filter, water softener, cartridge filter and UV disinfection system.

The community has had several long-term do not drink water advisories and hired a consulting company to conduct a feasibility study followed by the design of new source

community wells, a new water treatment plant, upgrades to the existing pumphouses and new watermains.

During the preliminary design of the new water treatment plant, the consultant conducted various bench-scale studies and suggested to upgrade the treatment process to a modified conventional treatment system with coagulation, flocculation, clarification/sedimentation, and filtration using potassium permanganate ( $\text{KMnO}_4$ ) oxidation and greensand for the removal of iron and manganese in combination with GAC filtration for organics removal.

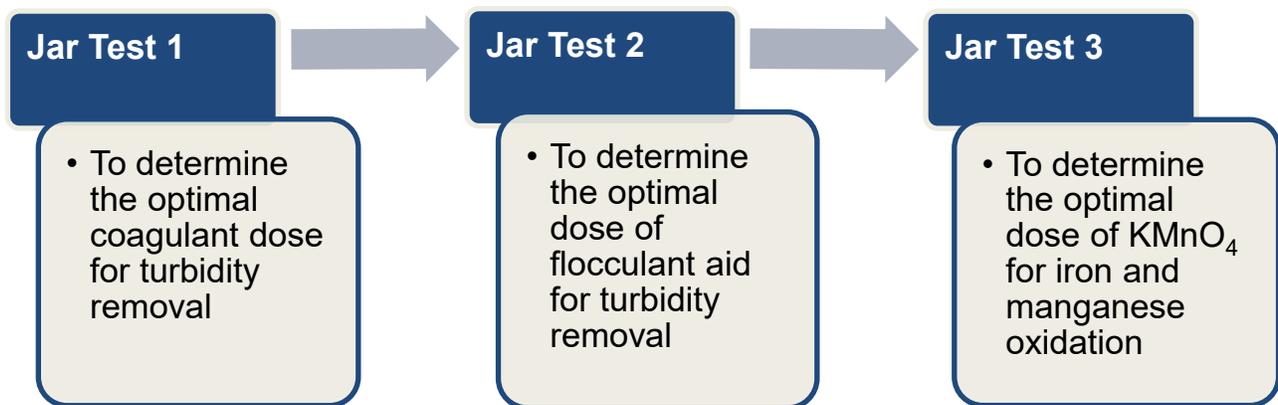
The Walkerton Clean Water Centre (Centre) was involved to investigate the performance of the proposed treatment system in pilot-scale. The overall objective of this pilot testing project was to reduce iron and manganese in the treated water. Specific objectives of the pilot testing experiments were:

- To reduce iron to less than 0.3 mg/L and manganese to less than 20  $\mu\text{g/L}$ ;
- To compare the performance of greensand filtration compared to conventional filtration with anthracite and sand dual media;
- To evaluate different  $\text{KMnO}_4$  dosing locations;
- To assess the reductions of organic matter, trihalomethanes (THMs) and haloacetic acids (HAAs).

## 2. Materials and Method

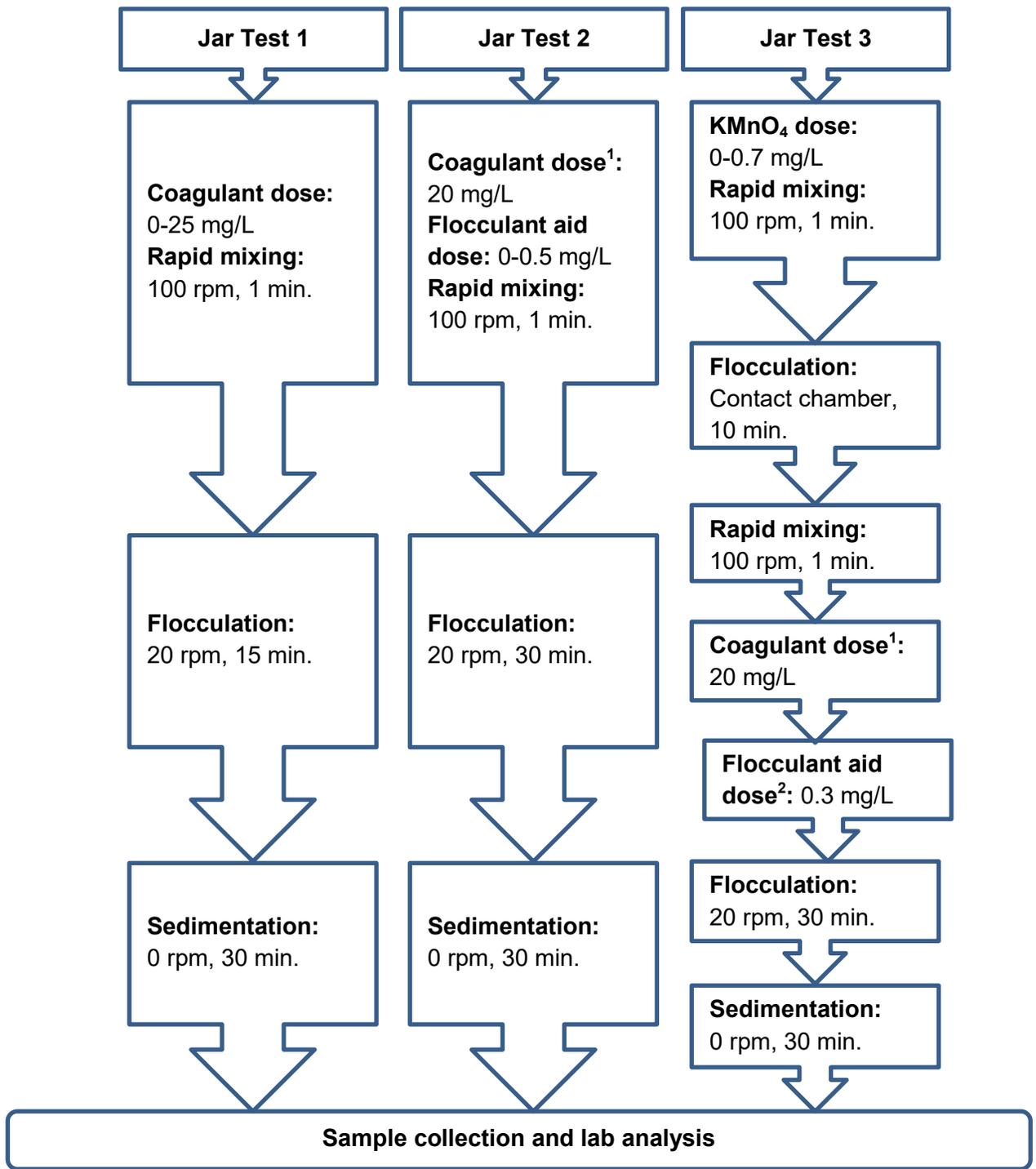
### 2.1 Jar Testing

The primary purpose of conducting jar tests was to determine the optimal dosage for coagulant (CleanPAC 180), flocculant aid (ClearFloc 1065) and  $\text{KMnO}_4$ . Water samples for jar testing were collected by the Centre's staff from the community's well. Three jar tests were conducted at the Centre. The objectives of those jar tests are shown in Figure 1 and test conditions are summarized in Figure 2.



**Figure 1.** Jar test objectives

After jar testing, samples were collected from each jar and analyzed for parameters including turbidity, dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm ( $\text{UV}_{254}$ ), iron, manganese, apparent colour and true colour. Jar testing was completed prior to pilot testing. Results obtained from the jar tests were applied for the pilot testing experiments.



<sup>1</sup> Optimal coagulant dose determined in Jar Test 1

<sup>2</sup> Optimal dose of flocculant aid determined in Jar Test 2

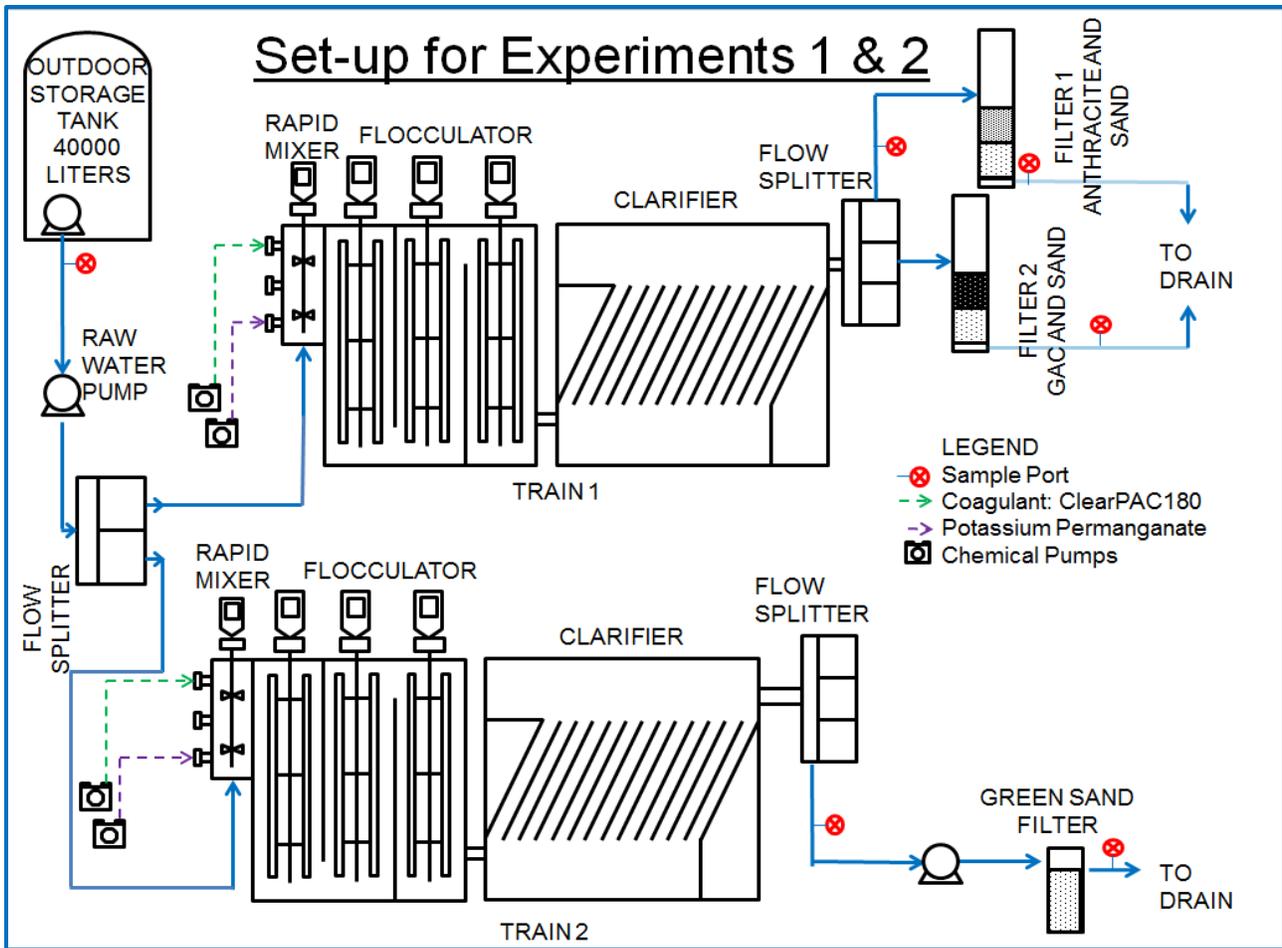
**Figure 2.** Jar test conditions

## 2.2 Pilot Plant Experiments

Raw water collected from the well was hauled to the Centre and stored in the outdoor storage tank (capacity of 40,000 L). The truck tank was intentionally overfilled to prevent air from entering and oxidizing the iron and manganese. The recirculation pump of the outdoor storage tank (at the Centre's Technology Demonstration Facility) was not operated to prevent further oxidation of iron and manganese. Raw water was pumped into the pilot plants located in the Technology Demonstration Facility. The data previously obtained from the jar tests were utilized to run the pilot plants. All experiments were conducted for 15 hours to achieve steady state conditions within the pilot plant prior to water sampling. Prior to the experiments, water from the flocculator cells and clarifiers was drained to avoid contamination from other source water.

Two phases of pilot testing experiments were conducted for iron and manganese reduction. Phase 1 experiments were designed to compare the performance of greensand filtration with conventional filtration, anthracite/sand and GAC/sand filtration, whereas Phase 2 experiments were conducted to evaluate different  $\text{KMnO}_4$  dosing locations. Two replicated experiments were included in each phase to verify experimental results.

In Phase 1 (Experiments 1 and 2, Figure 3), water was pumped through the pilot system and equally split into two trains (Figure 3).  $\text{KMnO}_4$  and coagulant (ClearPAC 180) were then dosed identically in both trains.  $\text{KMnO}_4$  was dosed at 0.3 mg/L in the first (bottom) port of the rapid mixer of Train 1 and Train 2. Coagulant (ClearPAC 180) was dosed at 20 mg/L in the third (top) port of the rapid mixer of both trains. Afterwards, water was pumped through the flocculator followed by clarifier in both trains. Then, the settled water from Train 1 clarifier was split evenly to go through an anthracite/sand filter (Filter 1, Train 1) and a GAC/sand filter (Filter 2, Train 1), whereas the settled water from Train 2 clarifier travelled through a greensand filter.



**Figure 3.** Schematics for Experiments 1 & 2

Phase 2 (Experiments 3 and 4, Figure 4) was aimed to evaluate different  $\text{KMnO}_4$  dosing locations. Therefore,  $\text{KMnO}_4$  was dosed at 0.3 mg/L in the first (bottom) port of the rapid mixer of Train 1 and dosed at 0.3 mg/L in the third flocculator cell in Train 2. Coagulant (ClearPAC 180) was dosed at 20 mg/L in the third port of the rapid mixer on both trains. In both trains, the settled water from the clarifier was split evenly to an anthracite/sand filter (Filter 1, Train 1) and a GAC/sand filter (Filter 2, Train 1); however, grab samples were only collected from the anthracite/sand filters from both trains.

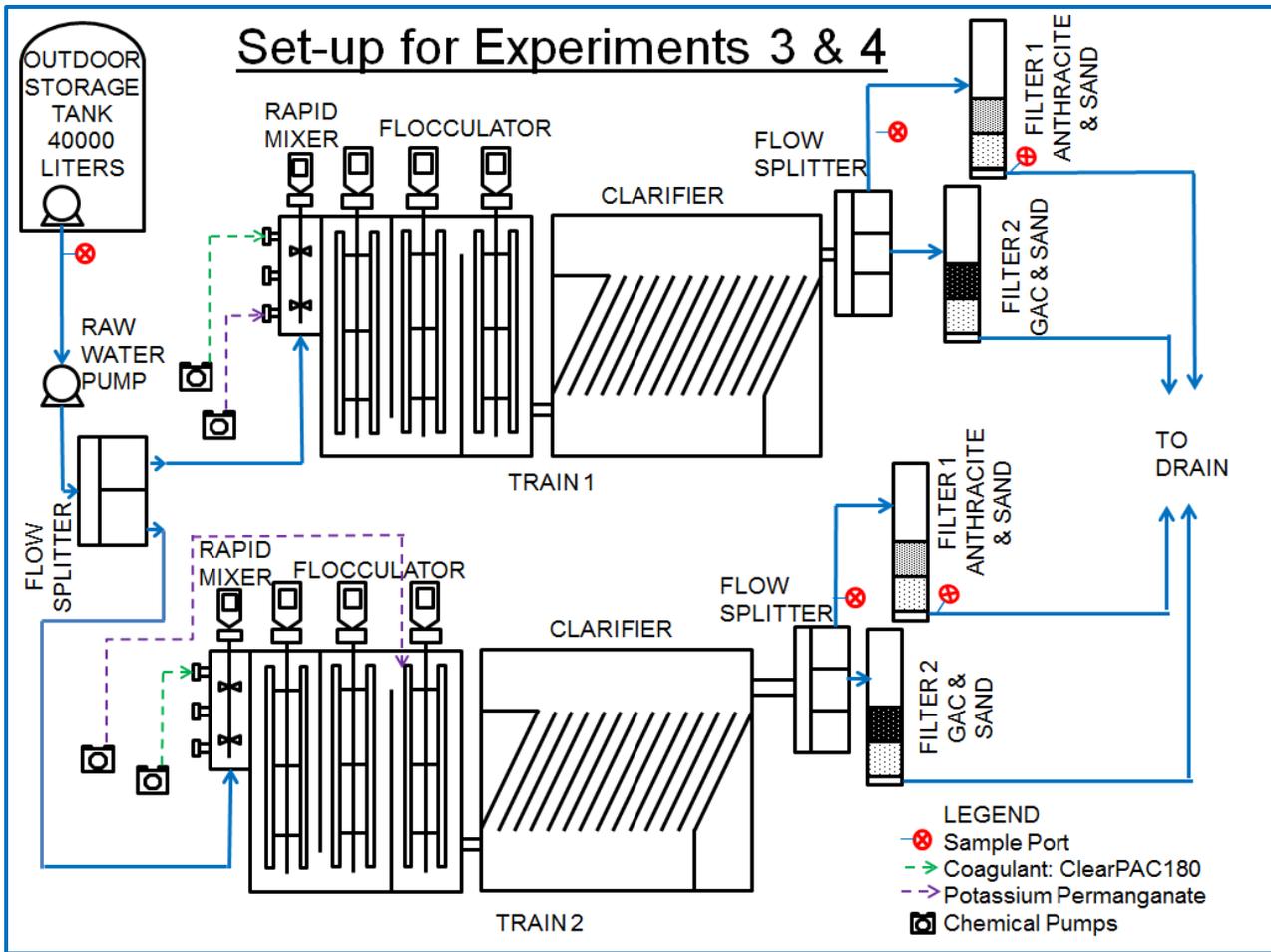


Figure 4. Schematics for Experiments 3 & 4

### 2.3 Sampling and Methods of Water Quality Analysis

As is shown in Figure 3, samples were collected from the following locations for each experimental run: raw water, after clarifier both trains, after conventional filter (anthracite/sand, Train 1) and green sand filter (Train 2) for Phase 1 (Experiments 1 and 2). The sampling for Phase 2 (Experiments 3 and 4) was collected at the ports similar to the primary experiments, except that the filtered samples were collected from the conventional filter (anthracite/sand, Train 1 and Train 2) instead of the greensand filter (Figure 4).

Throughout jar testing and pilot testing experiments, water quality parameters were analyzed at the Centre. Samples were analyzed for turbidity, pH, alkalinity, apparent colour, total iron and total manganese. Samples were also filtered using 0.45 µm

polyethersulfone (PES) filter paper and analyzed for DOC, UV<sub>254</sub> absorbance, dissolved iron, dissolved manganese and true colour. Details of the methods of analysis for water quality parameters are outlined in Table 1.

**Table 1.** Methods of Water Quality Analysis

Parameter	Method	Range
Total and dissolved iron (Fe)	Hach Method 8147 FerroZine Method	0.009 to 1.400 mg/L Fe
Total and dissolved manganese (Mn)	Hach Method 8149 1-(2-Pyridylazo)-2-Naphthol PAN Method	0.006 to 0.700 mg/L Mn
DOC	Standard Method 5310C UV/persulfate oxidation with conductometric detection	4 ppb to 50 ppm
Alkalinity	Hach Method 10244 Phenolphthalein and Total Alkalinity	10 to 4000 mg/L CaCO <sub>3</sub>
True and apparent colour	Hach Method 8025 Platinum-Cobalt Standard Method	15 to 500 colour units
UV <sub>254</sub> absorbance	Real Tech UV254 Method	0 to 2 cm <sup>-1</sup>

## 2.4 Simulated Distribution System for Disinfection By-Product Analysis

After Experiments 1 and 2 were completed, grab samples were collected to be tested for disinfection by-products (DBPs, i.e. total THMs and HAA<sub>5</sub>). A simulated distribution system (SDS) test was completed on the grab samples prior to the analysis of total THMs and HAA<sub>5</sub>.

### 2.4.1. Simulated Distribution System Test for THMs and HAA<sub>5</sub>

Simulated distribution system testing was conducted on the raw water, clarifier effluents and filter effluents (anthracite/sand, GAC/sand and greensand) collected from

Experiments 1 and 2. Samples were transferred into 500 mL chlorine demand free, amber glass containers. To prepare the 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.

Each sample was dosed with 6 mg/L of chlorine to account for (approximately) 0.5 mg/L ammonia in the raw water and the bottles were stored at room temperature for a 5-day contact time. The contact time was determined based on the community's average detention time reported in their distribution system. After 5 days, samples were transferred to sample bottles with sodium thiosulfate and ammonium chloride preservatives for THMs and HAA<sub>5</sub> analysis, respectively. Samples were tested at an accredited laboratory.

## **2.5 Organic Nitrogen**

Grab samples from Experiments 1 and 2 were collected and transferred to sample bottles with sulfuric acid preservative. Samples were then sent to an accredited laboratory for organic nitrogen analysis. Organic nitrogen was calculated and reported as the difference between total Kjeldahl nitrogen and the sum of ammonia and ammonium.

# **3. Results and Discussions**

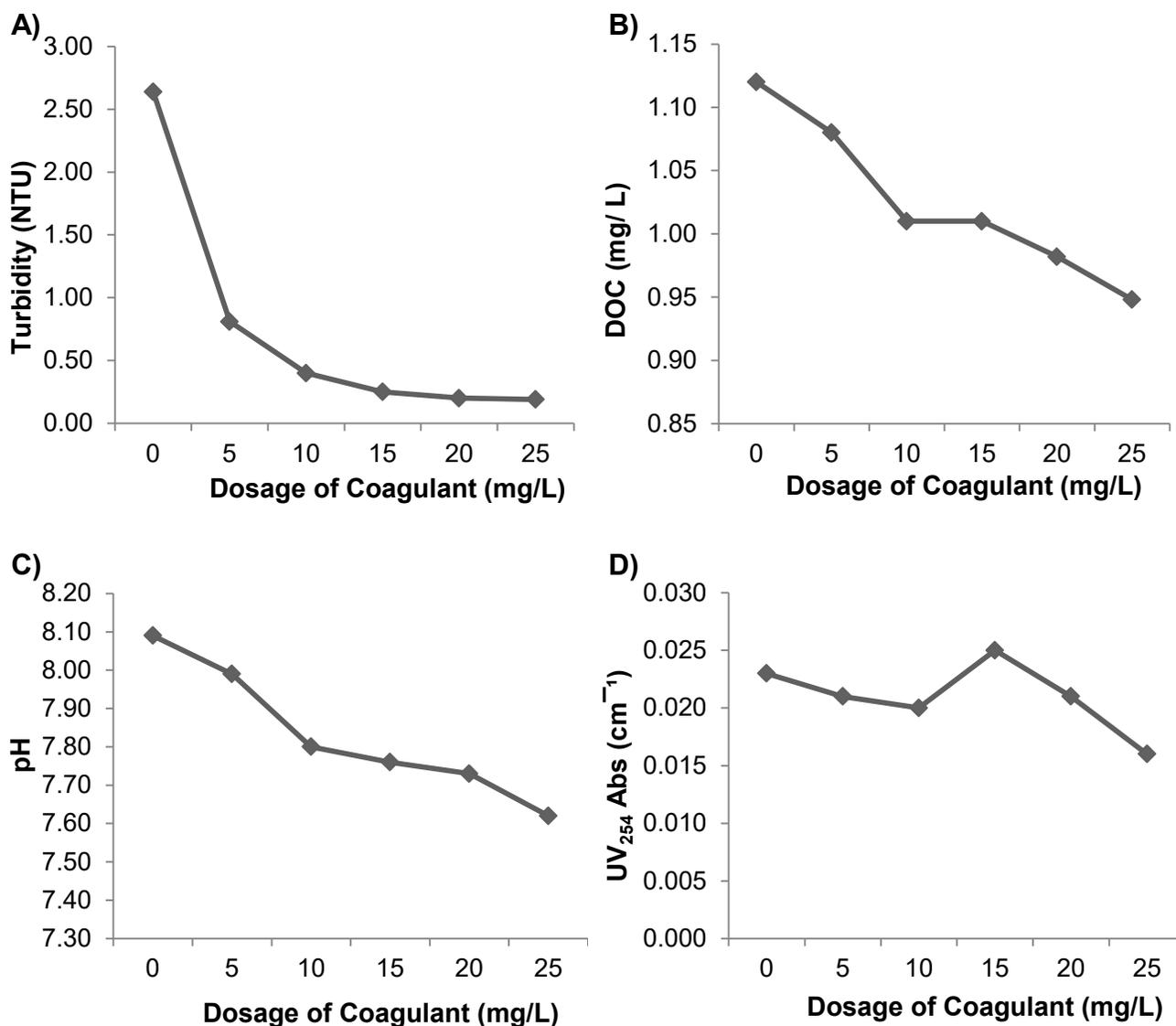
## **3.1 Jar Test Results**

### **3.1.1 Jar Test 1**

The objective of Jar Test 1 was to determine the optimal coagulant (ClearPAC 180) dose for turbidity removal. Results are presented in Figure 5.

The main purpose of using coagulant in this process is to settle oxidized iron and manganese particles and consequently reduce turbidity for Jar Test 1. Turbidity was reduced to 0.20 NTU with a coagulant dose of 20 mg/L. Although the minimum turbidity was 0.185 NTU using 25 mg/L coagulant dose, the optimal dose of coagulant was determined as 20 mg/L, because it is the point at which additional return is minimal. As expected, DOC and pH levels were reduced when additional coagulant was used.

However, the  $UV_{254}$  absorbance trend was not clear due to two outlier readings at 15 mg/L and 20 mg/L coagulant dose, possibly due to the low level of organics.

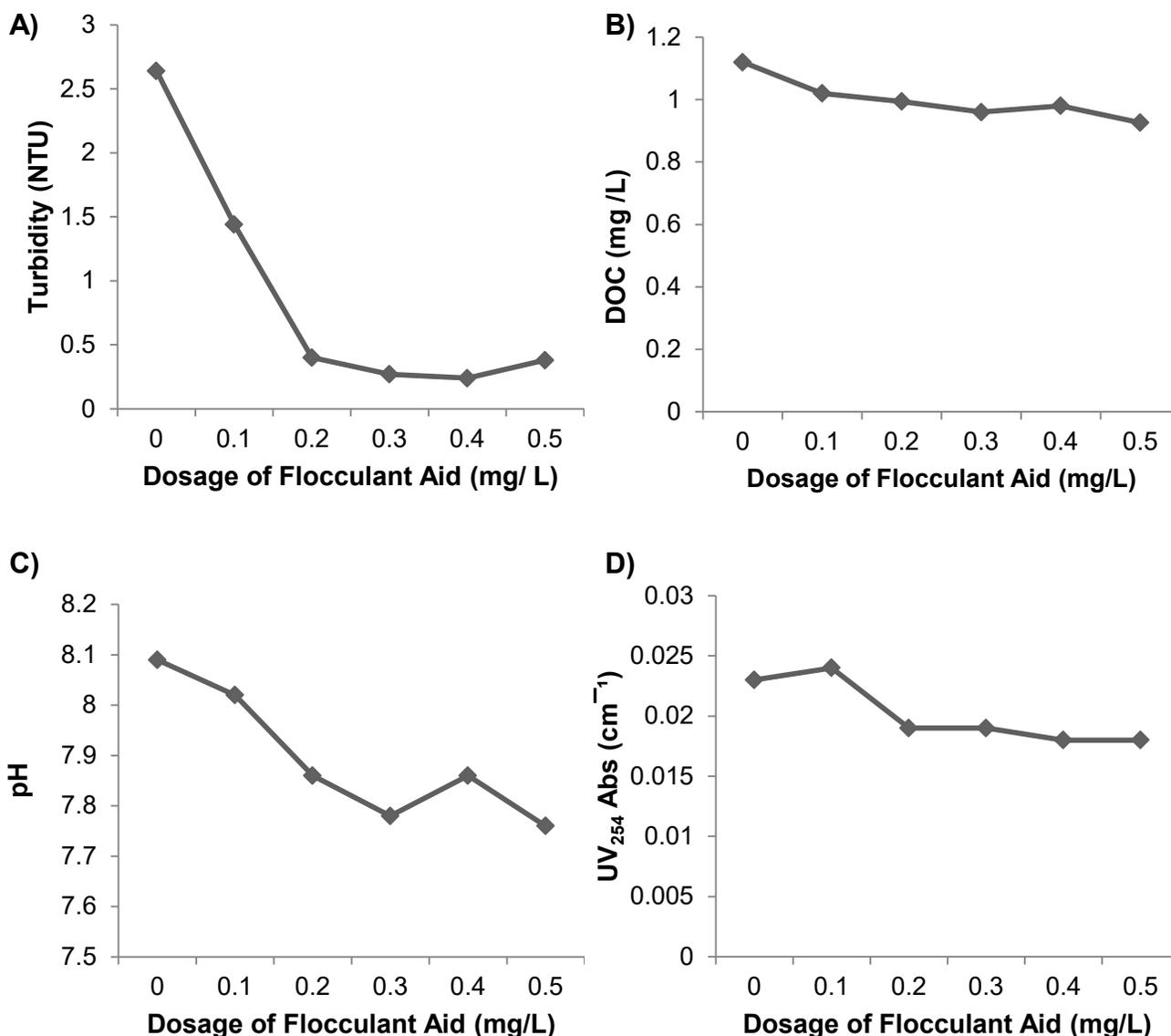


**Figure 5.** Effect of coagulant dosage on A) turbidity, B) DOC, C) pH and D)  $UV_{254}$  absorbance in Jar Test 1

### 3.1.2 Jar Test 2

The objective of Jar Test 2 was to determine the optimal dose of flocculant aid (ClearFloc 1065) for turbidity removal (Figure 6). The coagulant dose of 20 mg/L was used in all jars based on Jar Test 1 results. Based on Figure 6 (A), 0.3 mg/L was determined as the

diminishing return point, therefore this dose was selected as the optimal flocculant aid dose.



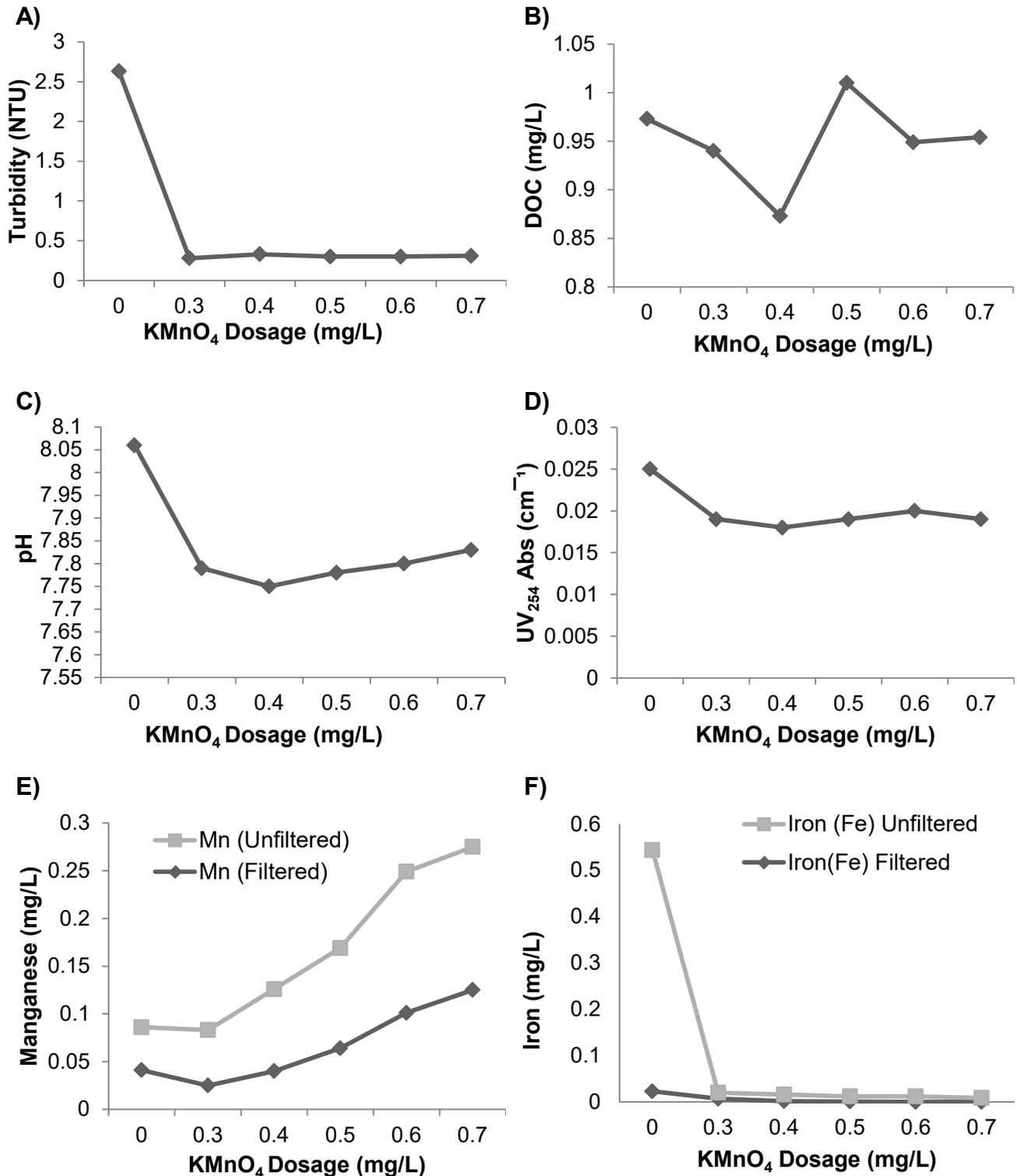
**Figure 6.** Effect of flocculant aid dosage on A) turbidity, B) DOC, C) pH and D) UV<sub>254</sub> absorbance in Jar Test 2

### 3.1.3 Jar Test 3

The objective of Jar Test 3 was to determine the optimal KMnO<sub>4</sub> dose using the optimized coagulant (20 mg/L) and flocculant aid (0.3 mg/L) dosages from Jar Tests 1 and 2, respectively. Raw water iron and manganese concentrations were analyzed after sampling raw water from the water treatment plant and found to be 0.47 and 0.023 mg/L,

respectively. It was estimated that 0.5 mg/L of total  $\text{KMnO}_4$  dose would be required for this specific water source, as 0.94 mg/L and 1.92 mg/L  $\text{KMnO}_4$  are required for every 1 mg/L iron and 1 mg/L manganese, respectively (Crittenden et al., 2005).

Figure 7 shows results of Jar Test 3. In raw water (Jar 1), iron and manganese concentrations were 0.521 and 0.045 mg/L, respectively. As more  $\text{KMnO}_4$  dose was added, manganese concentrations increased with increasing  $\text{KMnO}_4$  dosages. Dissolved (filtered) manganese also increased with elevated  $\text{KMnO}_4$  dose. This trend suggests that the increase in manganese was derived from the manganese reducing from dissociation of  $\text{KMnO}_4$  dosages in solution. On the other hand, iron concentrations were reduced significantly (97.5%) with 0.3 mg/L  $\text{KMnO}_4$  dose and decreased further with increased  $\text{KMnO}_4$  dose.  $\text{KMnO}_4$  dose of 0.3 mg/L was considered an optimum dose, as it achieved the lowest manganese concentration and significant iron removal. Although iron concentrations were reduced further with higher  $\text{KMnO}_4$  doses, the higher doses were not considered due to the increasing effects on manganese concentration. The optimized dose of 0.3 mg/L  $\text{KMnO}_4$  was also endorsed by the lowest turbidity level. DOC and  $\text{UV}_{254}$  absorbance did not show any clear trends in Jar Test 3.



**Figure 7.** Effect of KMNO<sub>4</sub> (coagulant dose-20 mg/L, flocculant aid-0.3 mg/L) on A) turbidity, B) DOC, C) pH, D) UV<sub>254</sub> absorbance, E) manganese and F) iron in Jar Test 3

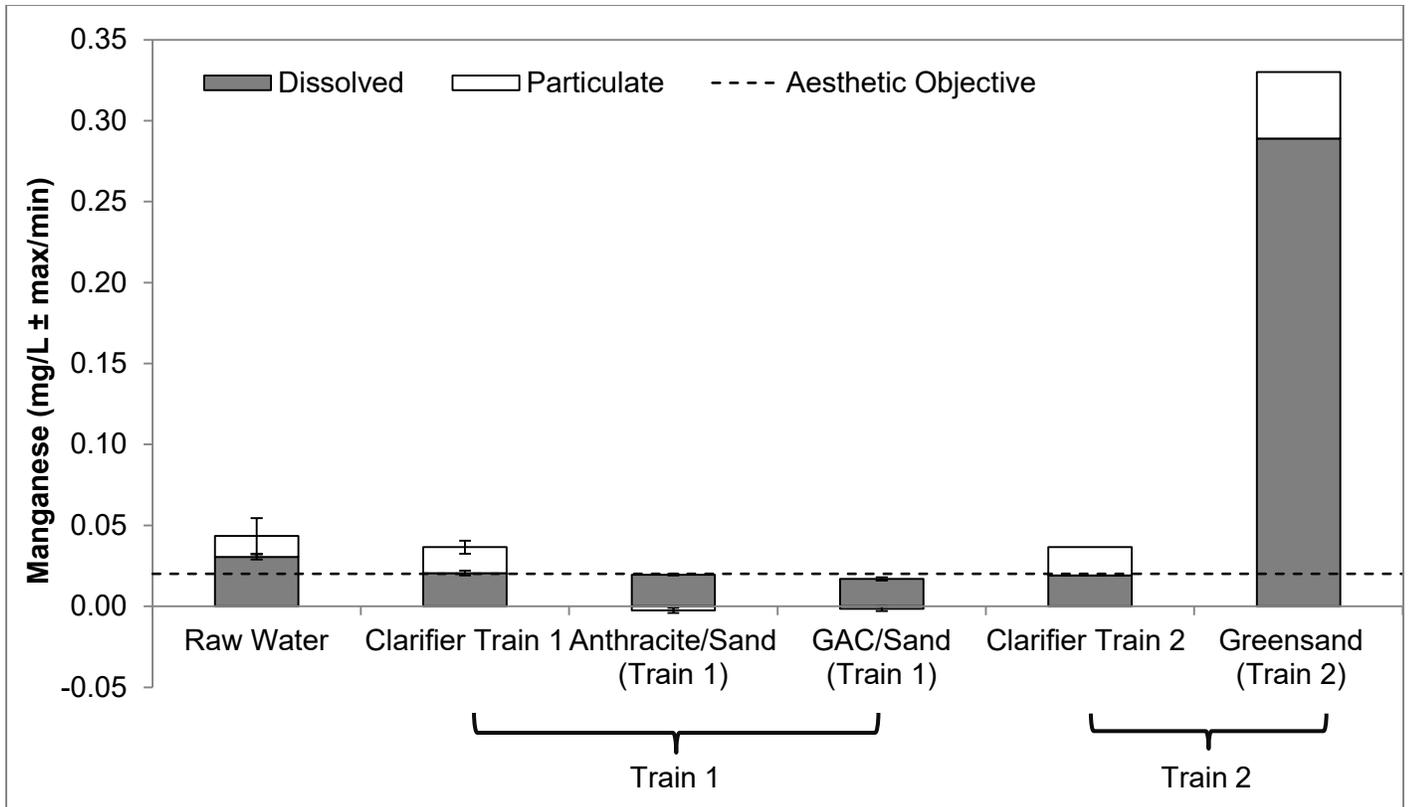
## 3.2 Pilot Testing Results

Dosing of flocculant aid (ClearFloc 1065) was discontinued in all pilot testing experiments, because the viscosity of solution was found to be too high for pumping and was not practically feasible for the pilot testing experiments. Iron and manganese results were compared on two bases: dissolved and particulate. Dissolved concentration was measured from the samples that were filtered through a 0.45 µm PES filter paper. Particulate concentration was calculated as the difference between the concentrations of unfiltered and filtered samples.

### 3.2.1 Phase 1 Experiments

#### 3.2.1.1 Manganese Reduction

Figure 8 shows total (unfiltered), particulate (unfiltered – filtered) and dissolved (filtered) manganese levels in Phase 1 experiments (Experiments 1 & 2). The aesthetic objective for manganese in drinking water systems in Ontario is currently 0.05 mg/L (Ontario MOE, 2006). However, Health Canada is proposing 0.02 mg/L of total manganese as an aesthetic objective (Health Canada, 2016). Therefore, the objective for this pilot plant study was based on achieving 0.02 mg/L of total manganese.



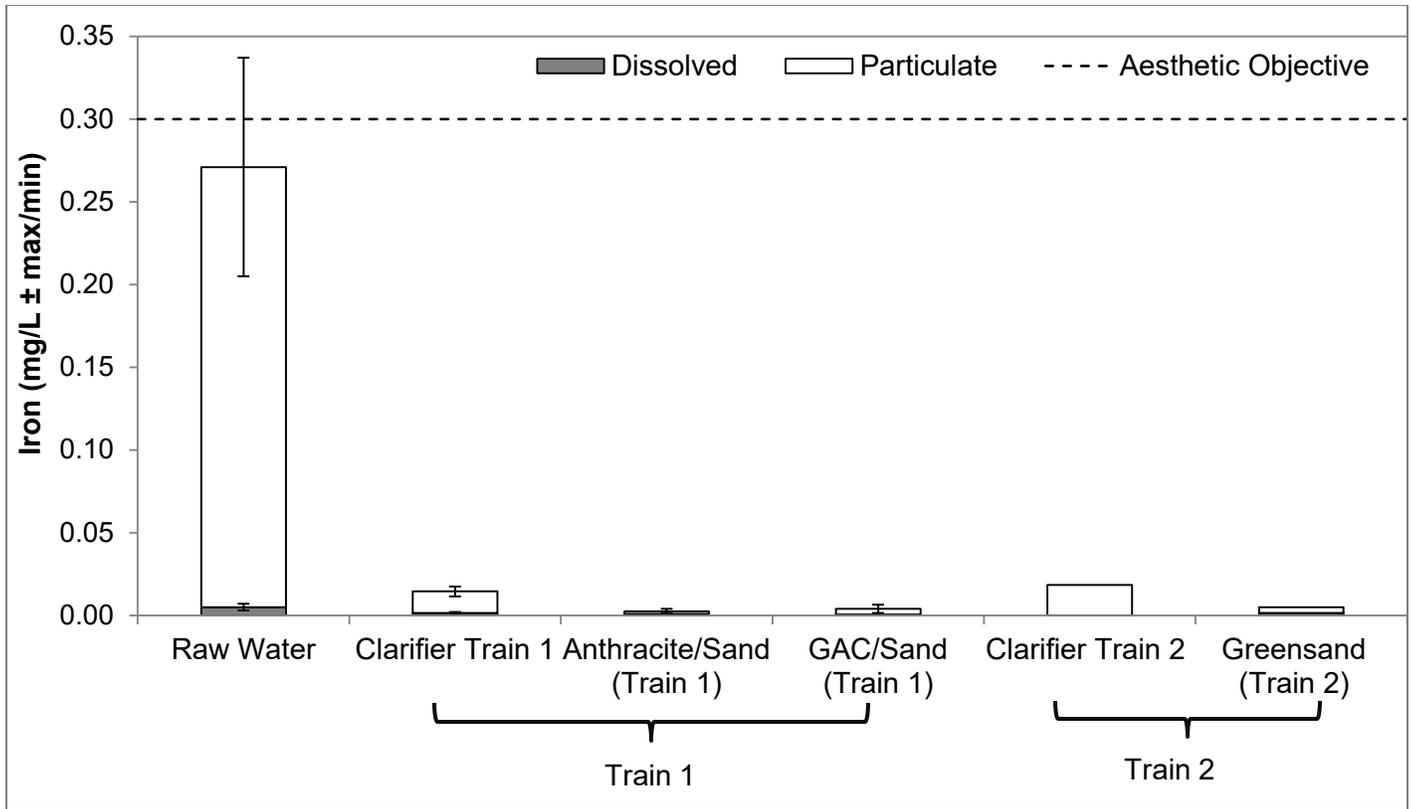
**Figure 8.** Phase 1 (Experiments 1 & 2) results - average particulate and dissolved manganese (mg/L  $\pm$  max/min)

In Phase 1 experiments, the clarifiers from Trains 1 and 2 achieved 16% removal of total manganese. The same concentration of manganese in both clarifiers endorses comparability of the two trains. Anthracite/sand and GAC/sand filters reduced the average manganese concentration by 53% and 58%, respectively in Train 1 compared to that of clarified water. Both filters (anthracite/sand and GAC/sand) removed the majority of the particulate manganese. However, the effluent from the greensand filter had an elevated manganese concentration by more than eight times. There are several possible explanations for this observation. Firstly, the greensand filter is not regularly used; therefore, manganese might have been leaching from the greensand media into the treated water. After further investigation, the greensand filter manufacturer recommended that the media may be exhausted. However, additional troubleshooting with an alternate water source was completed by the Centre and found that additional regeneration with  $\text{KMnO}_4$  seemed to restore the media and achieve reduced manganese levels. The second explanation is that, the  $\text{KMnO}_4$  dose might not have been high enough to satisfy the

demand and maintain an adequate oxidant residual prior to the greensand filter. It has shown that in the absence of pre-oxidation, the adsorption capacity of the greensand filter reached exhaustion as the surface adsorption sites were not regenerated (Knocke et al., 1991). This study also stated that continuous regeneration with  $\text{KMnO}_4$  and other strong oxidants should be applied with caution and may lead to elevated total manganese in the finished water, which was observed in this pilot testing study. Additionally, if greensand filters are out of service for an extended period of time, there is a potential to promote the reduction of manganese oxides to its soluble form and ultimately release dissolved manganese into the filter effluent (Knocke et al., 1991). The effluent from the greensand filter showed very high concentrations of dissolved manganese with somewhat of an increase in particulate manganese.

### ***3.2.1.2 Iron Reduction***

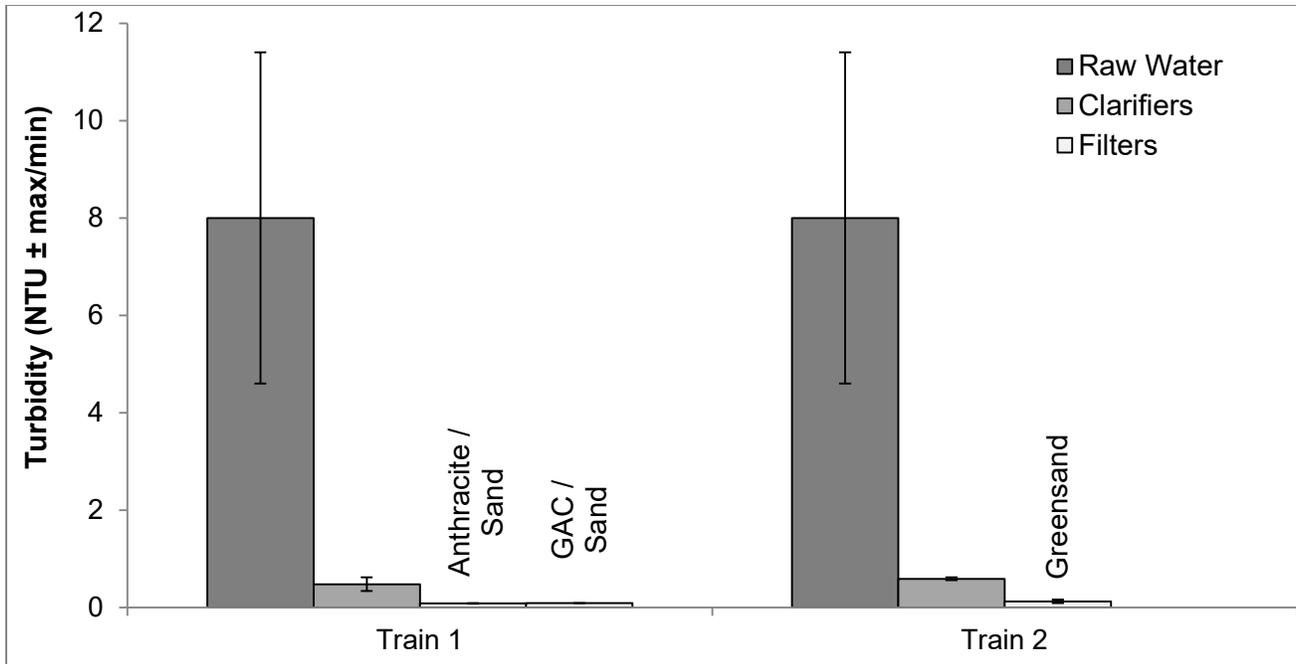
**Figure 9 shows** the changes of iron levels throughout Phase 1 experiments. The aesthetic objective for iron in drinking water systems in Ontario is 0.3 mg/L (Ontario MOE, 2006). As a precautionary measurement, it is better to reduce iron as much as possible to decrease consumer complaints and curb any potential operation and maintenance issues. Anthracite/sand, GAC/sand and the greensand filters showed 98-99% removal of total iron. Most of the iron was found oxidized and in particulate form, which is easier to remove compared to the dissolved portion.



**Figure 9.** Phase 1 (Experiments 1 & 2) results – average particulate and dissolved iron (mg/L ± max/min)

### 3.2.1.3 Turbidity Reduction

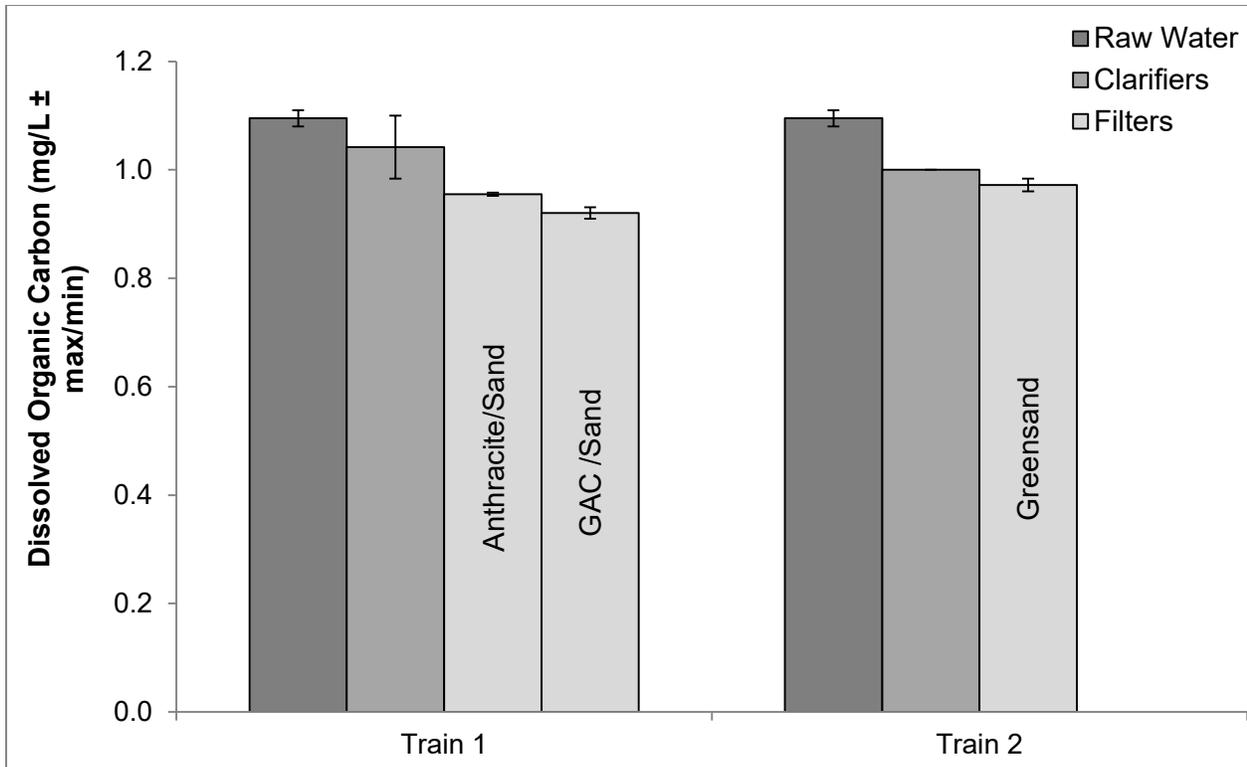
Figure 10 presents the average turbidity levels during primary experiments. Raw water turbidity was 8 NTU, which is comparatively high for a groundwater source. Coagulant (ClearPAC 180) effectively reduced turbidity to 0.48 and 0.59 NTU in clarifiers 1 and 2, respectively. In Train 1, anthracite/sand and GAC/sand effluents showed an average turbidity of 0.09 NTU. Effluent of the greensand filter showed an average turbidity level of 0.13 NTU.



**Figure 10.** Phase 1 (Experiments 1 & 2) results – average turbidity (NTU ± max/min)

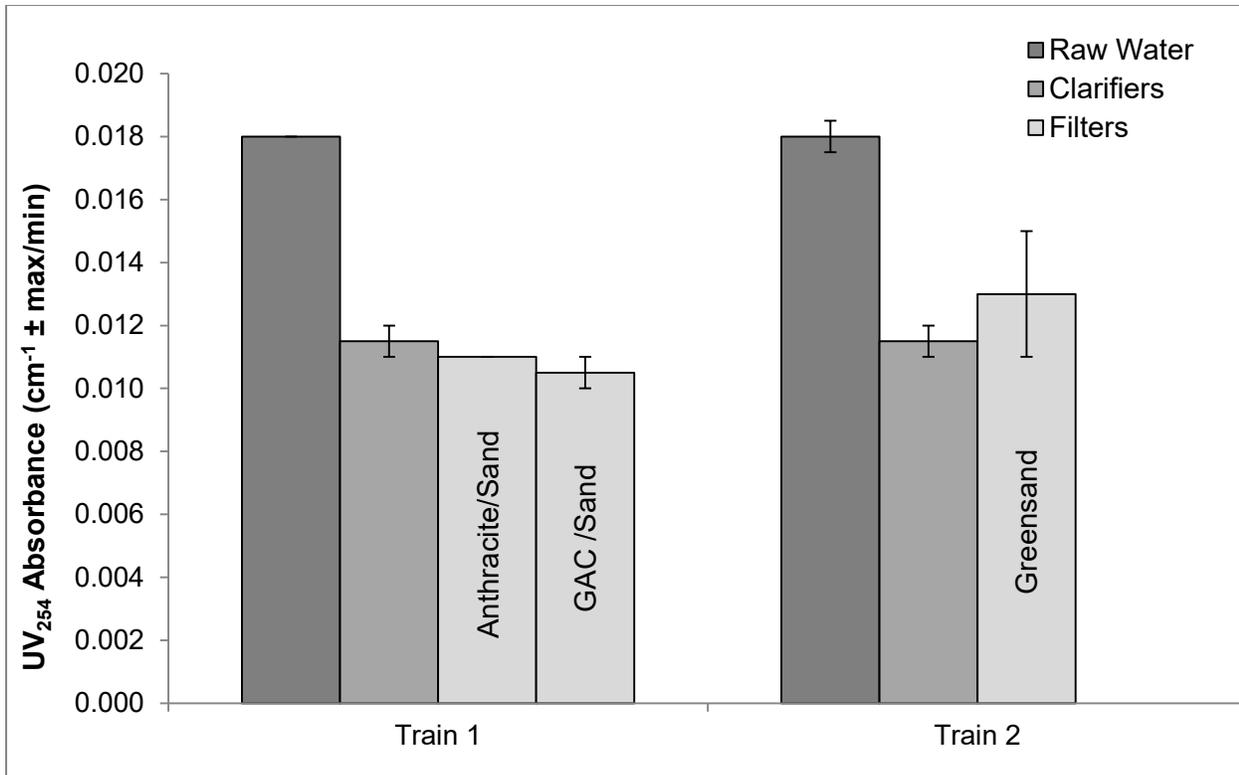
### 3.2.1.4 Organics Reduction

Although DOC has an aesthetic objective of 5 mg/L, high DOC concentrations in treated water may lead to high levels of DBPs, which are health-based regulated parameters (Ontario MOE, 2006). Figure 11 shows DOC levels during Phase 1 experiments. Clarifiers 1 and 2 showed 5.5% and 9.1% reduction of DOC, respectively. The DOC reductions were minimal, as the raw water’s SUVA (specific ultraviolet absorbance) values were 1.62-1.68 L/mg-m, which speculates that the raw water might have more fulvic acid type organics that are not amenable to be coagulated (Edzwald and Tobiason, 1999). The source of fulvic acid type organics may be derived from partial biodegradation of buried vegetation by soil microorganisms. DOC reductions were enhanced by filtration, which indicates that some small flocs that passed through the clarifier were removed by the filters.



**Figure 11.** Phase 1 (Experiment 1 & 2) results – average DOC (mg/L ± max/min)

UV<sub>254</sub> absorbance was also measured as an indicator of aromatic organics (Figure 12). After sedimentation, UV<sub>254</sub> absorbance was reduced by 36%, while additional removal by filters was minimal.



**Figure 12.** Phase 1 (Experiments 1 & 2) results – average UV<sub>254</sub> absorbance (cm<sup>-1</sup> ± max/min)

### 3.2.1.5 General Water Quality

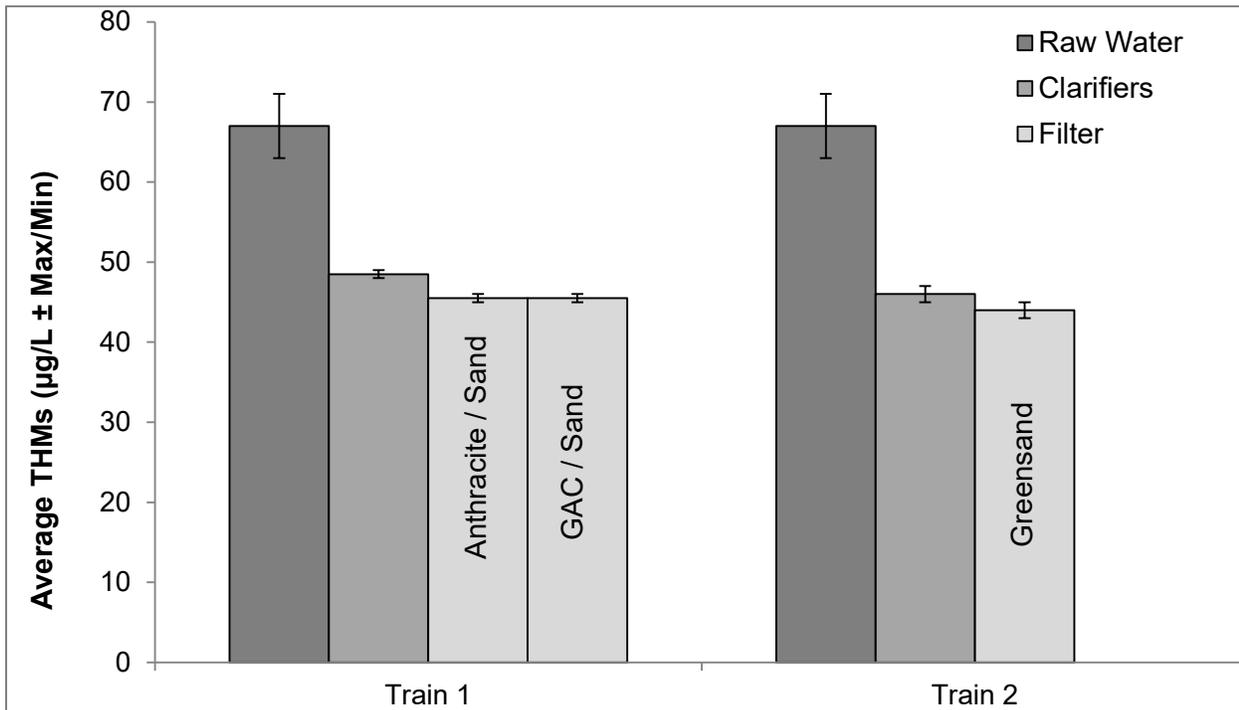
The raw water pH was 8. With the addition of coagulant, the pH was reduced by 0.2. The pH of the greensand filter effluent was 0.2 lower compared to that of the anthracite/sand filter effluent.

The alkalinity level of the raw water was 210-215 mg/L as CaCO<sub>3</sub>. As expected, alkalinity was reduced slightly after coagulation.

The raw water apparent colour showed variable readings from 30 to 70 Pt-Co units. However, the level of apparent colour went below the method's detection limit after treatment. Moreover, all true colour readings were below the method detection limit indicating that particulate matter was mainly responsible for the colour observed.

### 3.2.1.6 SDS-THMs and HAA<sub>5</sub> Tests

The SDS test for THMs and HAA<sub>5</sub> analysis were conducted on the samples collected from Experiments 1 & 2. More information about this procedure is presented in Section 2.4. Figure 13 demonstrates the results of THMs analysis.



**Figure 13.** Phase 1 (Experiments 1 & 2) results – average THMs (chlorine contact time of 5 days)

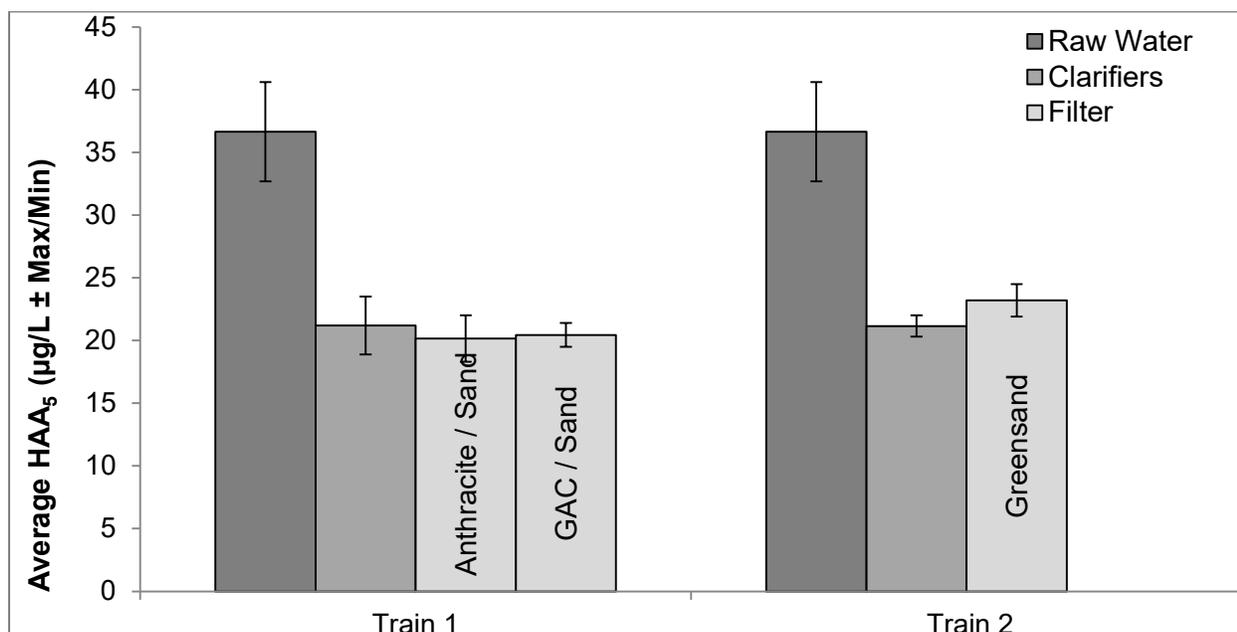
In spite of no treatment besides a 6 mg/L chlorine dose, the chlorinated raw water had THM levels of 67 µg/L, which is still less than the regulated running annual average (RAA) of 100 µg/L (Ontario MOE, 2006). This might be due to the low level of organics (1.1 mg/L) in the raw water.

Compared to the chlorinated raw water, conventional treatment reduced THMs by 27% and 31% for clarifiers Train 1 and 2, respectively. These reduction levels were similar to what was observed for organic matter (6% and 9% for Trains 1 and 2, respectively).

THMs were not significantly reduced by the filters in Phase 1 experiments (anthracite/sand, GAC/sand and greensand filters). Although the GAC filter provided an additional 3.7% removal of DOC compared to the anthracite/sand filter, THMs levels

stayed exactly the same. Ideally, the reduction of DOC should have resulted in the reduction of THMs. However, this was not observed in these results, which was likely due to low level of organics present in water. In Train 2, the greensand filter effluent showed 4% less THMs compared to the clarified water. Overall, the conventional treatment with anthracite/sand filtration or GAC/sand filtration (Train 1) and the conventional treatment with greensand filtration (Train 2) achieved 31% and 34% of THMs removal, respectively compared to that of the chlorinated raw water.

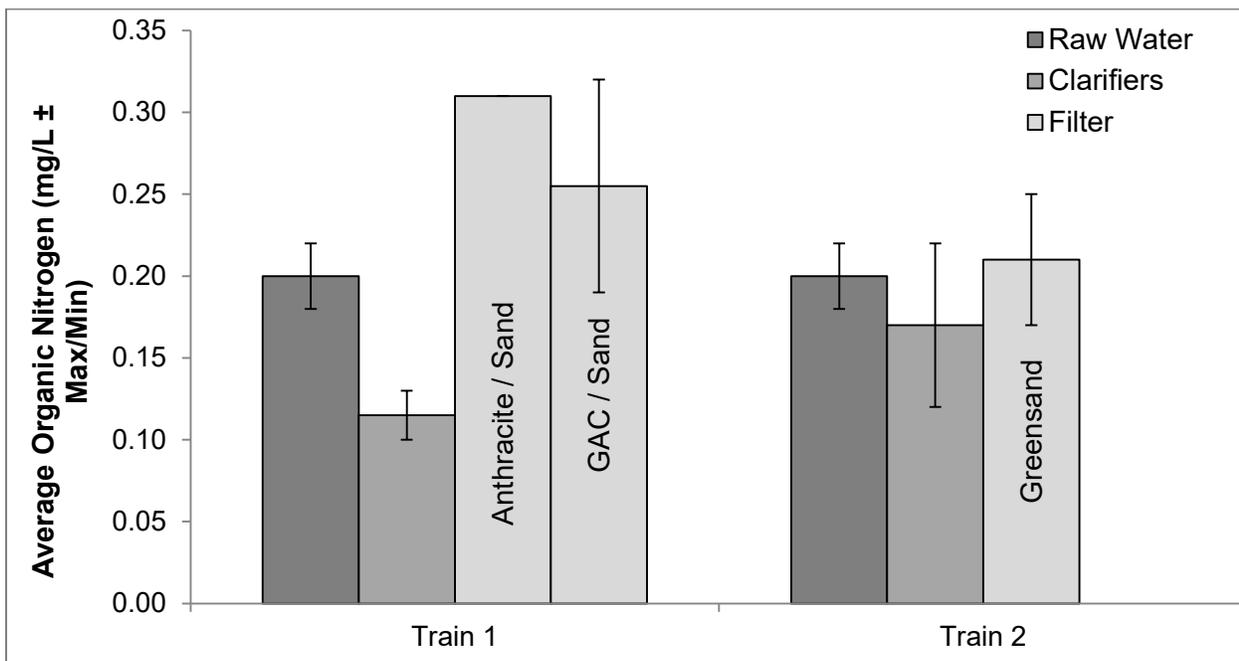
Figure 14 shows the average HAA<sub>5</sub> levels after 5 days of chlorine contact time. The average HAA<sub>5</sub> level of the chlorinated raw water was 37 µg/L, which is less than the reporting requirement of HAAs (RAA of 80 µg/L) (Ontario Regulatory Agency, 2015). As expected, clarifiers from both trains showed exactly the same HAA<sub>5</sub> level. Moreover, both anthracite/sand and GAC/sand filters exhibited the same level of HAA<sub>5</sub>, but slightly lower than that found in the clarifiers. However, the greensand filter effluent showed a 10% increase in HAA<sub>5</sub> levels, compared to that of the clarifier. Overall, the conventional treatment with anthracite/sand filtration and the conventional treatment with greensand filtration reduced HAA<sub>5</sub> by 43% and 38%, respectively compared to that of the chlorinated raw water.



**Figure 14.** Phase 1 (Experiments 1 & 2) results – average HAAs (chlorine contact time of 5 days)

### 3.2.1.7 Organic Nitrogen

The average organic nitrogen levels throughout the Phase 1 experiments are demonstrated in Figure 15. In Ontario, an operational guideline of 0.15 mg/L for organic nitrogen in the finished drinking water is specified by the Ontario MOE (2006). Organic nitrogen may cause taste and odour issues, reduce disinfection strength and may be a precursor of nitrogenous DBPs (Ontario MOE, 2006). The average raw water organic nitrogen level was 0.20 mg/L, which is above the operational guideline. Clarifiers of Train 1 and Train 2 were able to reduce the average organic nitrogen levels to 0.12 and 0.17 mg/L, respectively. However, it is difficult to identify why the two trains had a difference in organic nitrogen levels. As organic nitrogen is determined by calculating the difference of the total Kjeldahl nitrogen measurement and the ammonia + ammonium measurements, there may be some variability associated with calculations. It was expected that organic nitrogen levels should be further reduced by filtration process. However, all filter effluents (anthracite/sand and GAC/sand in Train 1 and greensand filter in Train 2) showed higher levels of organic nitrogen. Ideally, GAC is expected to have the ability to remove organic nitrogen. However, the experimental results do not support the last statement. Additional experiments may be needed to investigate this phenomenon.



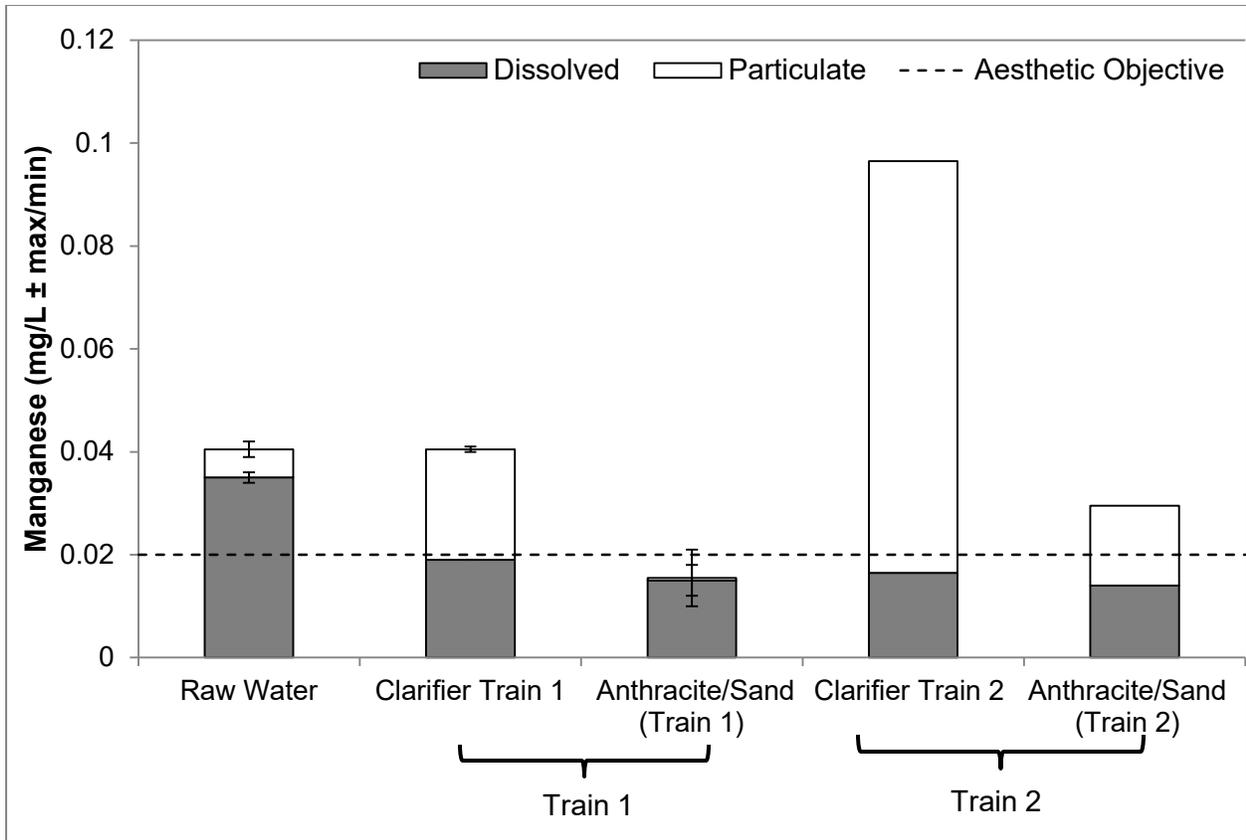
**Figure 15.** Phase 1 (Experiments 1 & 2) results – average organic nitrogen concentrations (mg/L ± max/min)

## 3.2.2 Phase 2 Experiments

Phase 2 experiments were conducted to find an ideal location for  $\text{KMnO}_4$  dosing.  $\text{KMnO}_4$  was dosed in the rapid mixer in Train 1, whereas  $\text{KMnO}_4$  was dosed in Flocculator Cell 3 in Train 2. All other water treatment conditions were kept the same for both trains.

### 3.2.2.1 Manganese Reduction

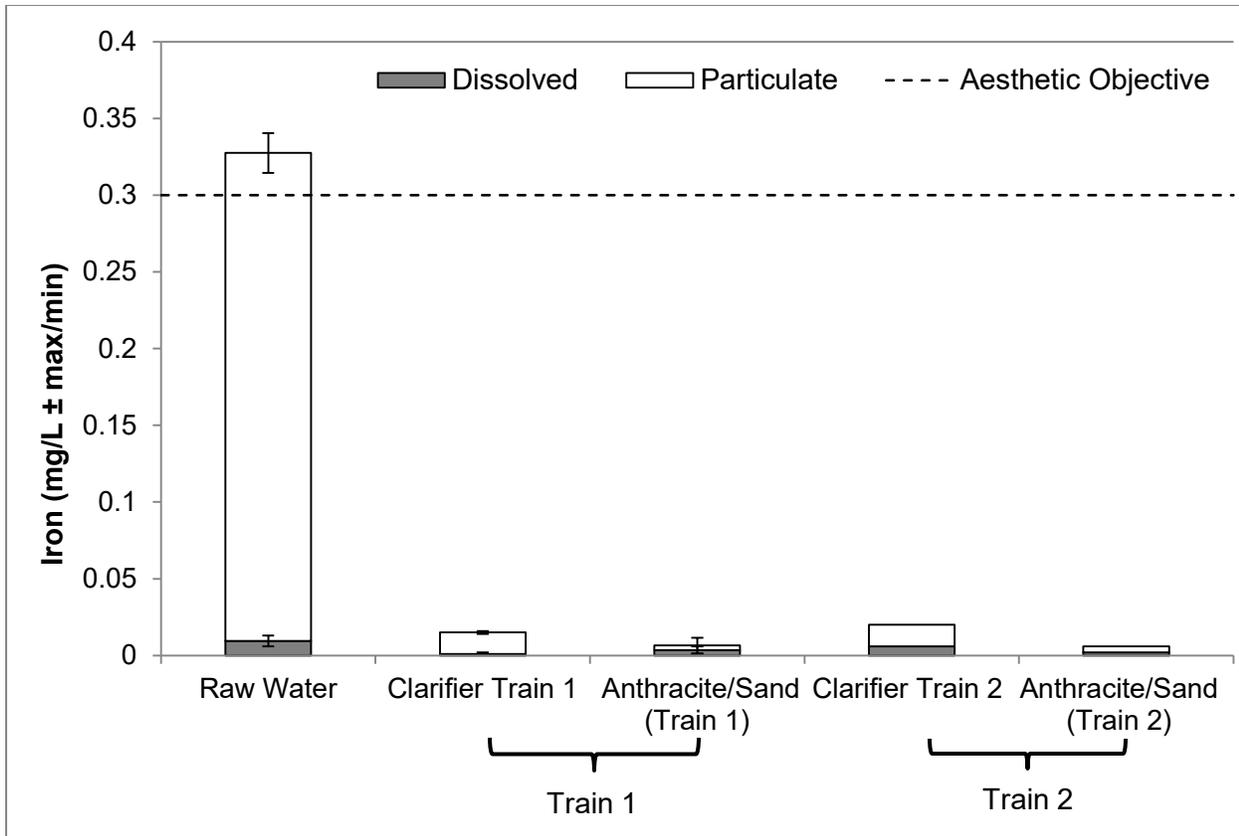
Figure 16 shows the average total, particulate and dissolved manganese levels in Phase 2 experiments (Experiments 3 & 4). Phase 1 experiments and Train 1 Phase 2 experiments had the same  $\text{KMnO}_4$  injection location; therefore, it was expected that the manganese trends would be similar. Train 1 clarifier showed the same average total (unfiltered) manganese concentration as that of raw water. However, the average total manganese concentrations, especially the particulate manganese levels, increased more than two times in the clarifier on Train 2 compared to that of the raw water. These increases were likely derived from the unused  $\text{KMnO}_4$ , which was being dosed in the third flocculator cell, resulting in less reaction time. Clarifier Train 1 has slightly higher (13%) dissolved manganese levels than the Clarifier Train 2. However, Clarifier Train 2 has more than 272% higher particulate concentration than the Clarifier Train 1, which indicates that the dosed  $\text{KMnO}_4$  was present in particulate form, possibly bound to flocs, in the clarified effluent. The average total manganese concentration of filtered water was 90% higher in the anthracite/sand filter on Train 2 compared to that of Train 1. The majority of the manganese that was higher in Train 2 anthracite/sand filter was present in particulate form, which is likely due to the additional particulate manganese load from the clarifier. Moreover, water above the filter (Train 2) visibly demonstrated darker black/brown coloured water when the filter was backwashed compared to that of the Train 1 filter. This also endorsed that the unused  $\text{KMnO}_4$  was in particulate form and was carried over from the clarifier and then captured by the Train 2 anthracite/sand filter. In short, it was found to be more effective to dose  $\text{KMnO}_4$  in the rapid mixer than Flocculator Cell 3 in terms of manganese removal.



**Figure 16.** Phase 2 results – average particulate and dissolved manganese concentrations (mg/L ± max/min)

### 3.2.2.2 Iron Reduction

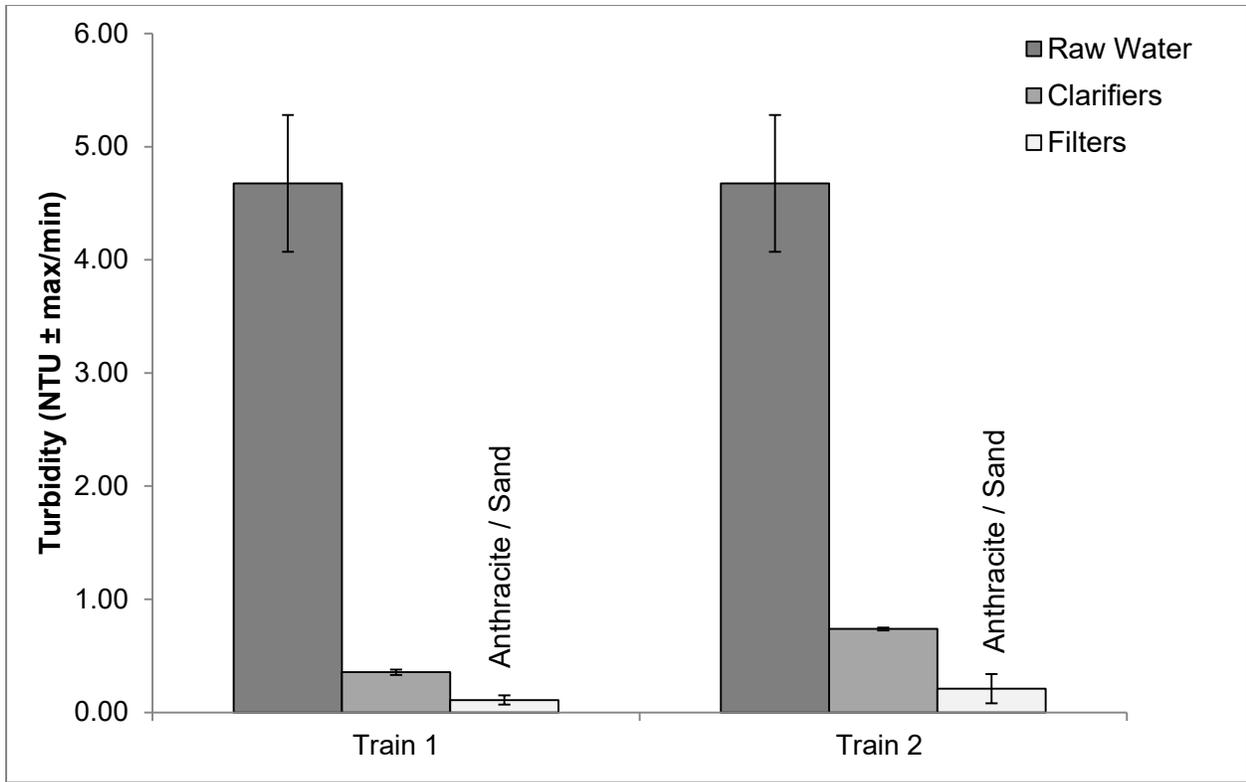
Figure 17 shows the total, particulate and dissolved iron levels in Phase 2 experiments. The average total iron concentration of raw water was 0.328 mg/L, which was slightly higher than the aesthetic objective of 0.3 mg/L (Ontario MOE, 2006). It was found that most of the iron in raw water was present in particulate form, which is easier to remove by the coagulation/flocculation/sedimentation process compared to the dissolved form. Both clarifiers and filters were able to remove iron by 94-95% and 98%, respectively, and hence the location of dosing  $\text{KMnO}_4$  did not have any effect on iron removal.



**Figure 17.** Phase 2 results – average particulate and dissolved iron concentrations (mg/L ± max/min)

### 3.2.2.3 Turbidity Reduction

Turbidity levels of Phase 2 experiments are presented in Figure 18. The raw water turbidity was 4.7 NTU, which is considered a high turbidity level for a groundwater source. The turbidity of Clarifier 2 was more than twice compared to that of Clarifier 1. This is likely due to the unused particulate  $\text{KMnO}_4$  that was dosed in Flocculator Cell 3. The same effect was also observed on the filters, which showed a 99% increase in turbidity in the anthracite/sand filter of Train 2 compared to that of Train 1. These results endorse that dosing  $\text{KMnO}_4$  in the rapid mixer had a more positive effect than dosing  $\text{KMnO}_4$  in Flocculator Cell 3.



**Figure 18.** Phase 2 (Experiments 3 & 4) results – average turbidity levels (NTU ± max/min)

## 4. Conclusions

Through the bench scale tests, it was determined that:

- Bench Scale Test 1: The optimized coagulant (ClearPAC 180) dosage was found as 20 mg/L.
- Bench Scale Test 2: The optimized flocculant aid (ClearFloc 1065) dosage was found as 0.3 mg/L.
- Bench Scale Test 3: The optimized  $\text{KMnO}_4$  dosage was determined as 0.3 mg/L for pilot testing as it yielded the best result for both iron and manganese reduction.

The pilot plant experiments conducted at the Centre determined that:

- Phase 1 Pilot Testing
  - Conventional treatment followed by anthracite/sand or GAC/sand filtration found that:
    - Manganese was reduced from 43.5  $\mu\text{g/L}$  to less than 20  $\mu\text{g/L}$
    - Iron was reduced from 271  $\mu\text{g/L}$  to less than 5  $\mu\text{g/L}$
    - THMs were reduced from 67  $\mu\text{g/L}$  to 46  $\mu\text{g/L}$
    - $\text{HAA}_5$  were reduced from 37  $\mu\text{g/L}$  to 20  $\mu\text{g/L}$
  - Conventional treatment followed by greensand filtration determined that:
    - Manganese increased after treatment
    - Iron was reduced from 271  $\mu\text{g/L}$  to less than 5  $\mu\text{g/L}$
    - THMs were reduced from 67  $\mu\text{g/L}$  to 44  $\mu\text{g/L}$
    - $\text{HAA}_5$  were reduced from 37  $\mu\text{g/L}$  to 23  $\mu\text{g/L}$
- Phase 2 Pilot Testing, comparing the location of dosing  $\text{KMnO}_4$ , determined that:
  - Dosing in the rapid mixer produced better water quality results compared to dosing in Flocculator Cell 3 due to it having a shorter detention and reaction time.

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