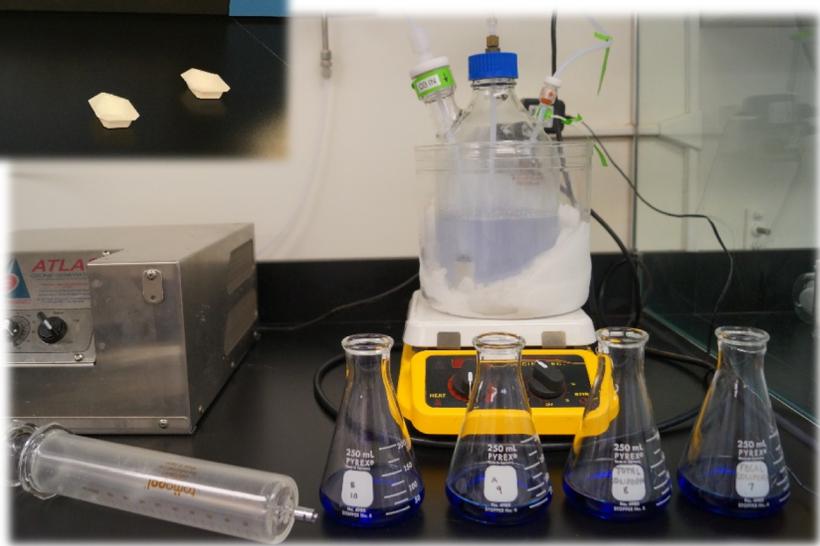
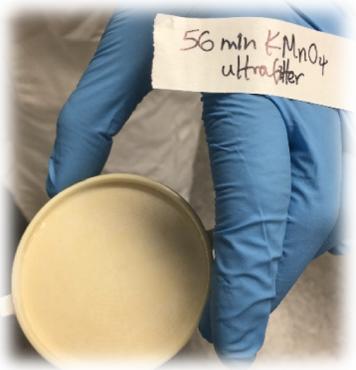


ALL SPIKED WITH 0.1 mg/L Mn^{2+}
 C/S WATER AFTER STANDARD JAR TEST
 (Spike $Mn^{2+} \rightarrow KMnO_4 \rightarrow C/S$)

	56 min rxn $KMnO_4$	5 min rxn $KMnO_4$	concurrent addition coagulant, then $KMnO_4$
20.5 mg/L alum			
20.5 mg/L PAC			



MANGANESE REMOVAL BENCH-TEST RESULTS

Stanislaus Regional Water Authority Water
 Supply Project

November 2018



TECHNICAL MEMORANDUM

Stanislaus Regional Water Authority Water Supply Project Manganese Removal Bench Test Results

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Subject: **Seasonal Manganese Removal Bench Test Results**

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EXECUTIVE SUMMARY

The Stanislaus Regional Water Authority (SRWA), a joint powers authority between the Cities of Turlock and Ceres, is pursuing a new water supply project to provide treated water from the Tuolumne River as a supplement to their existing groundwater supply. Candidate treatment options for the project were evaluated by Trussell Technologies (Trussell Tech) through a year-long bench-scale testing program (November 2016 – October 2017), which included (1) enhanced coagulation for turbidity and total organic carbon (TOC) removal using three alternative coagulants, (2) monthly ozone demand of both the raw water and coagulated water, and (3) quarterly manganese removal. Results from these quarterly manganese removal bench tests are presented in this technical memorandum.

A review of both historical and more recent source water manganese concentrations indicated that total manganese concentrations can be elevated—certainly above the finished water treatment goal for manganese (i.e., 0.015 mg/L)—and dissolved manganese concentrations were generally below or close to the treatment goal. If the dissolved manganese is in the +2 oxidation state (Mn^{2+}), removal through conventional treatment with ozone in the treatment train can be challenging. Based on the 2006-2008 source water sampling campaign, the manganese concentrations and speciation do not indicate problematic manganese levels for the SRWA water treatment plant. However, even low levels of manganese in the distribution system can cause colored water complaints and associated aesthetic or health issues. Experience in water treatment design indicates it will be prudent to plan for future unknowns and consider the optimum treatment approach for manganese removal particularly since ozone will be used for primary disinfection and must be included in the treatment train.

The preferred treatment train selected for this new WTP includes coagulation, ozonation, filtration and final disinfection with free chlorine. Therefore, one of the primary objectives of these seasonal manganese removal tests was to identify the preferred location for ozonation (i.e., pre-ozonation of the raw water or intermediate ozonation of the coagulated water) and the most effective approach for total manganese removal.

Key conclusions from these quarterly bench tests are the following:

- Ambient manganese was removed below the treatment limit (≤ 0.015 mg/L) with ozone in conjunction with coagulation for both pre-ozonation and intermediate ozonation.
- Ferric chloride coagulant adds reduced manganese (Mn^{2+}) to the raw water because this coagulant commonly contains a small percentage Mn^{2+} as a contaminant.
- Intermediate ozonation was clearly superior to pre-ozonation for manganese removal. Pre-ozonation with coagulation did not remove the sub-colloidal fraction (i.e., smaller than 30,000 Daltons), which would be able to pass through granular media filtration.
- If reduced manganese is present in the WTP influent, the preferred treatment approach to reduce both the colloidal and sub-colloidal manganese fractions to



concentrations below the finished water limit (≤ 0.015 mg/L) is permanganate → coagulation → intermediate ozonation → filtration.

- Conventional clarification appeared to more effectively remove manganese than sand-ballasted clarification due to less effective settling of particulate manganese in the SBC tests. For both conventional and SBC clarification, the combined colloidal and sub-colloidal fractions were below the total manganese limit of 0.015 mg/L when the permanganate reaction time was at least five minutes with alum as the coagulant. These comparative results should be viewed with caution, though, since coagulant dose optimization was not performed for the SBC jar test procedure.
- Based on these quarterly test results, recommendations for the SRWA WTP design are:
 - Require a finished water total manganese limit of 0.015 mg/L
 - Require intermediate ozonation as opposed to pre-ozonation for primary disinfection
 - Do not allow ferric chloride for coagulation during startup and acceptance testing since manganese is a common contaminant of iron-based coagulants. However, the chemical storage and feed system should be designed to accommodate (i.e., chemical compatibility and dose) either an aluminum or ferric based coagulant in case SRWA prefers to switch primary coagulants at some time in the future.
 - Include the ability to add permanganate ahead of coagulant addition, with a minimum permanganate reaction time of 2 minutes before coagulant addition.



1 Introduction

The Stanislaus Regional Water Authority (SRWA), a joint powers authority between the Cities of Turlock and Ceres, is pursuing a new water supply project to provide treated water from the Tuolumne River as a supplement to their existing groundwater supply. Candidate treatment options for the project were evaluated by Trussell Technologies (Trussell Tech) through a year-long bench-scale testing program (November 2016 – October 2017), using water samples collected monthly from the Tuolumne River. Bench testing addressed (1) enhanced coagulation for turbidity and total organic carbon (TOC) removal using three alternative coagulants, (2) monthly ozone demand of both the raw water and coagulated water, and (3) quarterly manganese removal. The purpose for these tests was to select the preferred treatment train to meet SRWA's treatment goals and to set chemical doses and design criteria for the new water treatment plant (WTP). The first year of test results were discussed in an October 2017 Technical Memorandum (TM) (Trussell Technologies, October 18, 2017). The seasonal ozone demand results were discussed in an August 2018 TM (Trussell Technologies, August 27, 2018). This TM presents the results of the seasonal manganese removal test results.

A review of both historical and more recent source water manganese concentrations indicated that total manganese concentrations can be elevated—certainly above the finished water treatment goal for manganese (i.e., 0.015 mg/L)—and dissolved manganese concentrations were generally below or close to the treatment goal. Even low levels of manganese in the distribution system can cause colored water complaints and associated aesthetic or health issues. Thus, one of the treatment objectives for this new WTP is a finished water total manganese concentration less than 0.015 mg/L. This treatment recommendation of a finished water total manganese limit of 0.015 mg/L is consistent with literature recommendations (Brandhuber, 2013; Kohl and Medlar, 2006; Tobiasson, 2018).

Experience in water treatment has shown that even if an initial source water characterization indicates low risk, manganese can become a treatment issue in the future as a result of changes in the watershed, drought, introduction of new (or temporary) source waters, reservoir stratification, etc. For SRWA, other unknowns that could introduce reduced manganese (Mn^{2+}) into the WTP are (a) unknowns about the behavior of the currently untested infiltration gallery intake system, (b) use of a coagulant such as ferric that has manganese as a low-level contaminant, and (c) recycle flows from dewatering.

The preferred treatment train selected for this new WTP includes coagulation, ozonation, filtration and final disinfection with free chlorine. Manganese removal with ozonation in the treatment train can be particularly challenging since ozone oxidation of Mn^{2+} is known to form colloidal and sub-colloidal sized manganese dioxide (MnO_2) that can pass through granular media filters without effective particle destabilization (Wilczak, et. al., 1993; Brandhuber, et al., 2013). Therefore, one of the primary objectives of these seasonal manganese removal tests was to identify the preferred location for ozonation (i.e., pre-ozonation of the raw water or intermediate ozonation of the coagulated water) and the most effective approach for manganese removal.



2 Overview of Manganese Chemistry

Manganese chemistry is quite complex because, in water, manganese can exist in several oxidation states: 0, II, III, IV, V, VI, and VII. The oxidation states generally considered important in water treatment are II (Mn^{2+} , or manganous ion), IV ($MnO_2(s)$, or manganese dioxide—a solid), and VII (MnO_4^- , or permanganate ion). With strong oxidants such as permanganate and ozone, oxidation rates are fast but rates are also influenced by pH with faster rates occurring at higher pH. Manganese is known to form complex oxide particles (MnO_x) in addition to $MnO_2(s)$. Strong oxidants can oxidize Mn^{2+} to particulate and/or colloidal sized particles, and these particles can pass through granular media filters and may require particle destabilization for effective removal. Overdosing with a strong oxidant such as ozone can lead to pink water due to the formation of permanganate ion. Three excellent references that discuss manganese chemistry and treatment are Brandhuber, et al. (2013), Tobiason, et al. (2007), and Kohl and Miller (2006).

In this study, manganese concentrations were determined in three phase classifications: (1) total manganese, (2) passing through a 0.45 μm filter, and (3) passing through a 30k Dalton filter. The analytical results from these three phases yield four size-based manganese fractions, as identified in Table 2-1, that will be used in this report to characterize treatment impacts. Manganese that passes through the 30 kDa filter is assumed to be truly dissolved manganese (e.g., Mn^{2+}). This definition is consistent with Brandhuber, et al. (2013).

Table 2-1. Definition of manganese fractions used in bench tests

Total Mn	Total Mn in unfiltered sample
Particulate Mn	Mn retained by 0.45 μm filter
Colloidal Mn	Mn passing through 0.45 μm filter, but retained by 30 kDa ultrafilter
Sub-Colloidal Mn	Mn passing through 30k Dalton ultrafilter

The laboratory definition of “dissolved” is what passes through a 0.45 μm filter. However, because $MnO_2(s)$ can exist in sizes smaller than 0.45 μm , these particles can pass through 0.45 μm filters and be classified as dissolved. Generally, in natural waters with sufficiently high dissolved oxygen, a high percentage of the total manganese is measured as particulate (> 0.45 μm) and easily removed through clarification and filtration. Problems occur when the source water contains reduced manganese (Mn^{2+}), which can pass through a water treatment facility unchanged (Mn^{2+}) or can be oxidized to form particulate or colloidal MnO_2 that can pass through the treatment facility if the particles are not destabilized and removed through granular media filtration.

In this study, bench testing was used to simulate the impact of individual treatment steps on manganese removal, including ozonation, permanganate oxidation, and clarification (i.e., coagulant addition, flocculation, and settling); granular media filtration was not tested because this process cannot be effectively simulated at the bench-scale. In analyzing the resultant manganese removal data, it is assumed the sub-colloidal



fraction is truly dissolved and will pass through a granular media filter (GMF). However, it cannot be assumed that all particulate MnO_2 formed during ozonation will be effectively removed through full-scale GMFs. If these MnO_2 particles are stable, even though they were retained by the 0.45 μm laboratory filter, all or some portion may pass through the granular media filters, and particle destabilization with a coagulant or polymer (e.g., filter aid) may be required at the full-scale. Therefore, to a large degree, conclusions about Mn^{2+} removal in this TM are conservatively based on the sub-colloidal fraction and the colloidal fraction (also assumed to pass through a GMF).

3 Bench Study Objectives

These seasonal bench tests were conducted to evaluate removal of dissolved manganese through coagulation and settling and to determine the speciation of particulate, colloidal, and dissolved manganese through the process train when ozone is included as a treatment step. Tests were conducted quarterly—in December 2016, March, June and October 2017.

Initially, the intent was to evaluate manganese removal in relation to varying seasonal raw water quality and raw water manganese concentrations. However, because raw water dissolved manganese concentrations (i.e., passing through the 0.45 μm lab filter) were consistently near the analytical detection limit and too low for quantitative bench testing, the test water had to be spiked with Mn^{2+} for effective testing and the objectives changed to address the impact of ozone location (i.e., pre- or intermediate ozone) and identification of an optimized treatment approach. Specific questions that these bench tests were designed to answer are the following:

- **Removal of ambient manganese:** Is the ambient manganese in the Tuolumne River water readily removed through clarification with and without ozone? Does the location of ozonation affect ambient manganese removal? Will ozonation of ambient manganese result in soluble permanganate (VII oxidation state) causing “pink” water?
- **Location of ozonation:** If reduced manganese (Mn^{2+}) is present in the source water, will pre-ozonation or intermediate ozonation provide better treatment for minimizing colloidal MnO_2 formation and overall manganese removal?
- **Ozone dose:** If reduced manganese (Mn^{2+}) is present in the raw water, will the ozone dose needed for disinfection cause a change in oxidation state from Mn^{2+} (II oxidation state) to permanganate (VII oxidation state) resulting in “pink” water? Does ozone dose affect colloidal MnO_2 formation?
- **Effectiveness of permanganate pre-oxidation and required reaction time:** If permanganate is added prior to ozonation to improve manganous ion removal (Wilczak, et al., 1997), how much reaction time is needed for effective oxidation of Mn^{2+} by the permanganate? Where should the permanganate feed point be located?
- **Coagulant Performance for Manganese Removal:** How do the three conventional coagulants—ferric, alum, and polyaluminum chloride (PACl)—compare for removing manganese?



- **Type of clarification system:** Is a conventional flocc/sed system similarly effective to a sand ballasted clarification system for removing colloidal manganese (i.e., the form that is difficult to filter), or is one system superior?

A summary of the simulated treatment train and test conditions for each of the quarterly tests is provided in Table 3-1.



Table 3-1. Overview of Manganese Removal Bench Tests and Associated Test Conditions

Test Quarter	Test No. ¹	Mn ²⁺ Spike Conc. (mg/L)	Ozone Location	Simulated Treatment Train ²	Test Conditions
Round 1 (Dec 2016)	1.1	0.3	None	Pre-Oxidation only	
	1.2	0.3	None	Mn ²⁺ Spike → KMnO ₄ → C/S	<ul style="list-style-type: none"> 1- and 5-minute KMnO₄ contact times; Equivalent alum and ferric doses
	1.3	0.3	Pre-O ₃	Mn ²⁺ Spike → O ₃ → C/S	<ul style="list-style-type: none"> Two O₃:TOC ratios (0.25, 0.6); Two ferric doses and one alum dose
	1.4	0.3	Interm-O ₃	Mn ²⁺ Spike → KMnO ₄ → C/S → O ₃	<ul style="list-style-type: none"> 5-minute KMnO₄ contact time; One alum dose and one ferric dose; Three O₃:TOC ratios (0.4, 0.6, 0.8)
Round 2 (March 2017)	2.2	0.1	--	Pre-Oxidation only	
	2.3	0.1	Pre-Ozone	Mn ²⁺ Spike → O ₃ → C/S	<ul style="list-style-type: none"> O₃:TOC ratios (0.25, 0.6, 1.0) Equivalent alum and PACl doses
	2.4	0.1	Intermediate-Ozone	Mn ²⁺ Spike → KMnO ₄ → C/S → O ₃	<ul style="list-style-type: none"> 56-minute KMnO₄ contact time Equivalent alum doses O₃:TOC ratios (0.25, 0.6, 1.0)
	2.5	0.1	Intermediate-Ozone	Mn ²⁺ Spike → KMnO ₄ → C/S → O ₃	<ul style="list-style-type: none"> 20-minute KMnO₄ contact time Equivalent PACl doses O₃:TOC ratios (0.25, 0.6, 1.0)
Round 3 (June 2017)	3.2	(Ambient)	Pre-Ozone	O ₃ → C/S	<ul style="list-style-type: none"> O₃:TOC ratios (0.25, 0.5, 1.0) Equivalent alum doses
	3.3	0.1	Pre-Ozone	Mn ²⁺ Spike → O ₃ → C/S	<ul style="list-style-type: none"> O₃:TOC ratios (0.25, 0.5, 1.0) Equivalent alum doses
	3.4	0.1	Pre-Ozone	Mn ²⁺ Spike → O ₃ → KMnO ₄ → C/S	<ul style="list-style-type: none"> O₃:TOC ratios (0.25, 0.5, 1.0) 5-minute KMnO₄ contact time Equivalent alum doses
	3.5	0.1	Pre-Ozone	Mn ²⁺ Spike → KMnO ₄ → O ₃ → C/S	<ul style="list-style-type: none"> 60-minute KMnO₄ contact time O₃:TOC ratios (0.25, 0.5, 1.0, 2.0) Equivalent alum doses



	3.6	0.1	Pre-Ozone	Mn ²⁺ Spike → O ₃ → KMnO ₄ → C/S	<ul style="list-style-type: none"> • O₃:TOC ratio (1.0) • 0- and 5-minute KMnO₄ contact time • Equivalent alum doses
	3.7	(Ambient)	Intermediate-Ozone	C/S → O ₃	<ul style="list-style-type: none"> • Equivalent alum and PACl doses • O₃:TOC ratios (0.5, 1.0)
Round 4 (Oct 2017)	4.3	0.1	Intermediate-Ozone	Mn ²⁺ Spike → KMnO ₄ → Actiflo C/S → O ₃	<ul style="list-style-type: none"> • 0-, 1-, 5-, and 56-minute KMnO₄ contact time • Equivalent alum + anionic polymer doses • O₃:TOC ratios (0.6)
	4.4	0.1	Intermediate-Ozone	Mn ²⁺ Spike → KMnO ₄ → Actiflo C/S → O ₃	<ul style="list-style-type: none"> • 0-, 1-, 5-, and 56-minute KMnO₄ contact time • Equivalent PACl + anionic polymer doses • O₃:TOC ratios (0.6)
	4.5	0.1	Intermediate-Ozone	Mn ²⁺ Spike → KMnO ₄ → C/S → O ₃	<ul style="list-style-type: none"> • 0-, 1-, 5-, and 56-minute KMnO₄ contact time • Equivalent alum and PACl doses • Equivalent anionic poly dose • O₃:TOC ratios (0.6)

¹ Except for Round 1, the first test of each Round was to prepare C/S water for seasonal ozone demand tests. Those test conditions are not included in this table since they were not related to manganese removal.

² Abbreviations: C/S = Coagulated/Settled; O₃ = Ozonation



4 Test Procedures

Jar test procedures and solution ozone test (SOT) procedures are described in detail in Appendix A (Experimental Methods and Materials). To address the low levels of dissolved manganese in the source water, manganous ions (Mn^{2+}) were added to the raw water during select tests at the desired initial concentration. Spiking the source water with Mn^{2+} allowed for assessment of manganese removal at levels above the method reporting limit. Potassium permanganate was added to the raw water for some tests to assist particulate formation. Reaction kinetics for permanganate oxidation were evaluated by varying the reaction times ahead of coagulant addition, ranging from concurrent addition to 56 minutes .

In general, samples were collected after each bench testing treatment step, filtered (where appropriate), and bottled for analysis by Eurofins Eaton Analytical laboratory in sets of three – 1) unfiltered, 2) filtered through a 0.45 μm filter, and 3) filtered through a 30 kDa ultrafilter.

5 Source Water Manganese Concentrations

As discussed in a previously prepared source water quality assessment report (Trussell Technologies, Sept. 2016), the Tuolumne River was sampled at the infiltration gallery location between 2006 and 2008. A probability plot of these historical total manganese measurements is presented in Figure 5-1. One unusually high total manganese concentration of 0.850 mg/L was considered an outlier and excluded since a duplicate sample taken the same day measured 0.130 mg/L. This historical sampling program measured only total manganese concentrations; this dataset did not include dissolved manganese measurements—making it difficult to assess manganese treatment for this new SRWA WTP.

Subsequently, as part of this SRWA project, a year-long intensive source water monitoring program was conducted between October 2016 and November 2017. Appendix B summarizes the raw water quality characteristics of the samples used for manganese removal bench tests. Both total and dissolved manganese concentrations were measured. These 2016-2017 data are summarized and compared with the historical concentrations in Table 5-1 and plotted over time in Figure 5-2.

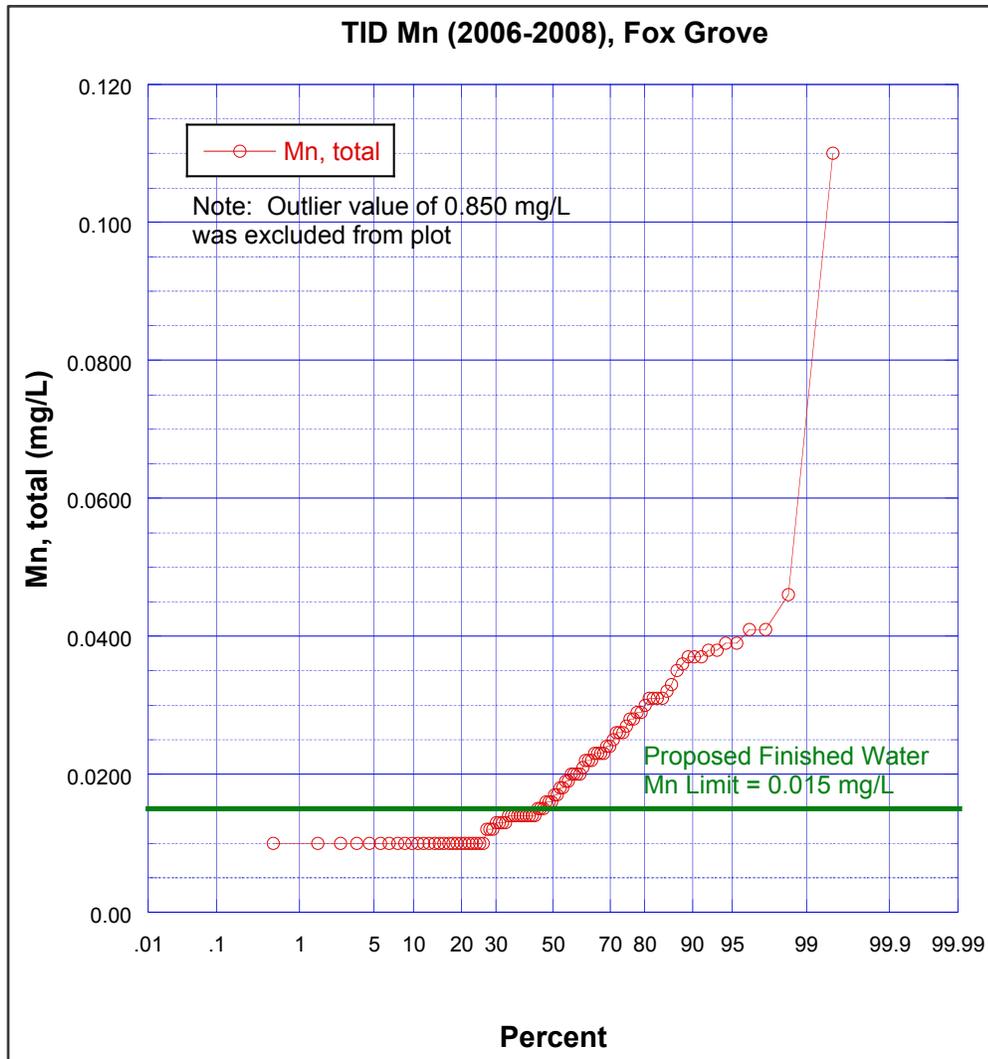


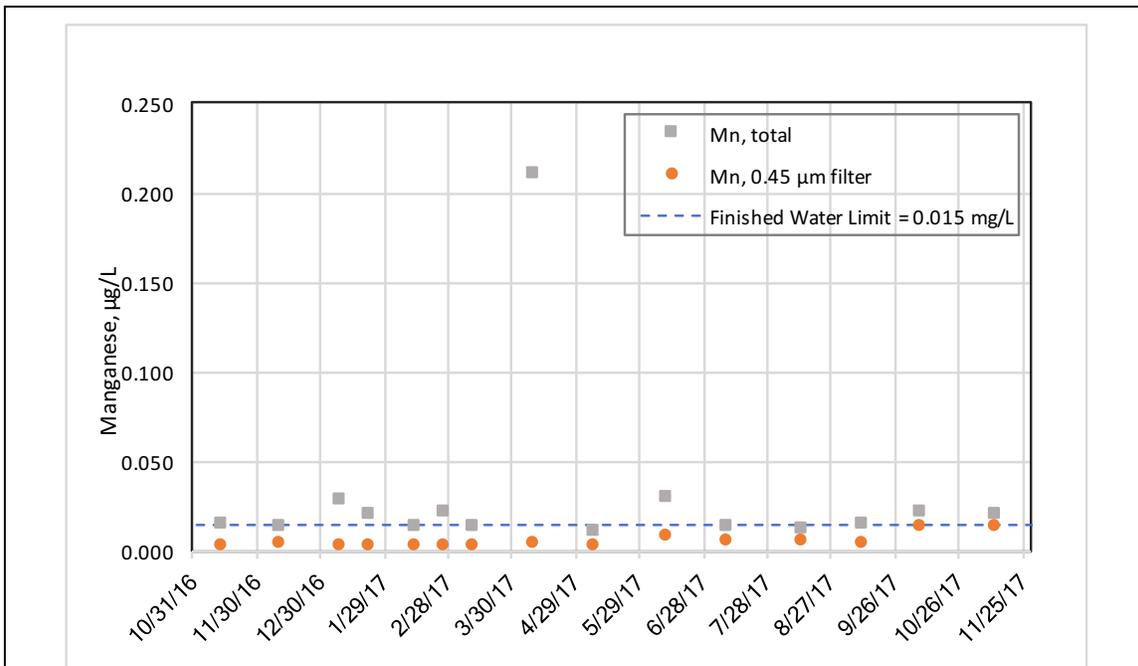
Figure 5-1. Probability of raw water total manganese concentration exceeding the proposed finished water total manganese limit, using historical data collected by Turlock Irrigation District (TID)



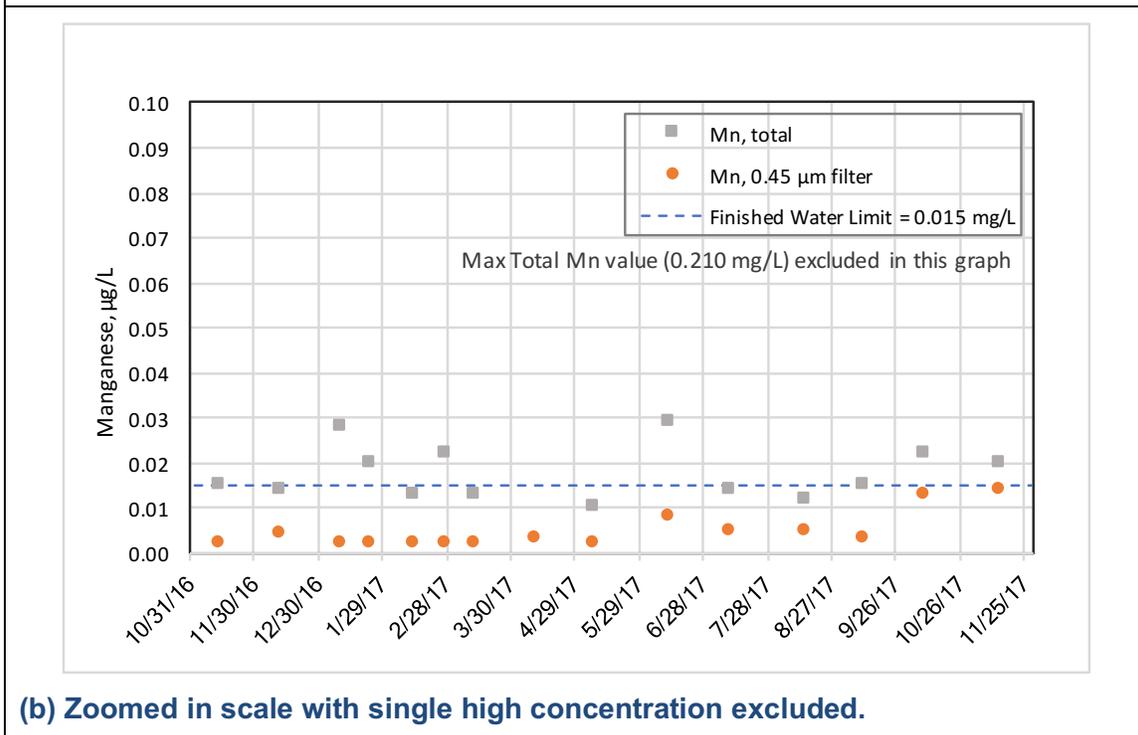
Table 5-1. Summary of Source Water Manganese Concentrations

Parameter	Statistic ²	Historic Data ¹ (May 2006 – Oct 2008)		SRWA Monitoring Program (Oct 2016 – Nov 2017)
		Near Basso Bridge	Infiltration Galley Location	Infiltration Gallery Location
Manganese, Total (mg/L)	Min	<0.010	<0.010	0.010
	Max	0.018	0.850	0.210
	Average	<0.010	0.017	0.030
	Median	<0.010	0.029	0.015
	Count	48	95	15
Manganese, Diss. (mg/L) (passing 0.45 µm filter) ³	Min	--	--	<0.002
	Max	--	--	0.013
	Average	--	--	0.004
	Median	--	--	<0.002
	Count	--	--	15

¹ Data source was Turlock Irrigation District's (TID) Watershed Sanitary Survey of the Lower Tuolumne River and Turlock Lake plus additional monitoring data supplied by TID.
² When calculating the statistics, values reported as non-detect (ND) were replaced with the method reporting limit (MRL).
³ The laboratory definition of "dissolved" is the portion that passes through a 0.45 µm filter.



(a) Zoomed out scale to accommodate a single high concentration.



(b) Zoomed in scale with single high concentration excluded.

Figure 5-2. Temporal distribution of total and dissolved manganese concentrations measured at the infiltration gallery location during the 2016-2017 source water monitoring program: (a) scale including all data and (b) higher resolution with the maximum concentration excluded



As part of assessing treatment options for manganese removal, the source water collected for the bench tests was analyzed in three fractions (total, passing through 0.45 μm filter, and passing through a 30k Dalton ultrafilter) to determine the speciation of the manganese present in the raw water, as shown in Table 5-2.

Table 5-2. Raw water manganese speciation measurements from samples collected for manganese removal testing

Raw Water Manganese	Round 1 (Dec 2016)	Round 2 (Mar 2017)	Round 3 (Jun 2017)	Round 4 (Oct 2017)
Lab Results:				
Manganese, total (mg/L)	0.014	0.013	0.020	0.021
Manganese, passes 0.45 μm filter (mg/L)	0.0054	<0.002	0.012	0.0036
Manganese, passes 30k Dalton filter (mg/L)	0.0052	0.0022	0.010	0.0043
Calculated Speciation:				
Particulate Manganese (mg/L)	0.0086	0.0110	0.0080	0.0174
Colloidal Manganese (mg/L)	0.0002	0.0000	0.0020	0.0000
Sub-Colloidal Manganese (mg/L)	0.0052	0.0022	0.010	0.0043

The source water manganese concentrations presented in Figure 5-2 and Tables 5-1 and 5-2 did not indicate problematic dissolved manganese levels. Considering the target finished water total manganese concentration of 0.015 mg/L, 9 of the 15 samples collected between October 2016 and October 2017 were at or below the target prior to treatment. The dissolved manganese concentrations in October and November 2017 were at the finished water limit. As discussed previously, uncertainties about the effect of the infiltration gallery on water quality and future changes in source water quality make it prudent to assess manganese removal when selecting the location for ozonation.

6 Manganese Removal Test Results and Discussion

While reviewing these results, the following should be considered:

- Round 1 tests considered ferric, alum, and PACl as coagulants. These results were summarized in the Bench Test Results TM #1 (Trussell Tech, October 2017).
- Although ferric chloride was initially identified as a preferred coagulant for turbidity and TOC removal, it was later rejected as the preferred coagulant because it was found to contain 0.4% manganese. Because ozone is known to form colloidal MnO_2 when oxidizing Mn^{2+} , it is preferable for the ozone influent to have the lowest reduced manganese concentration possible. Therefore, the decision was made to use only alum and/or PACl (i.e., aluminum-based

- coagulants) for all manganese removal test following the November (Round 1) tests.
- As discussed previously in this TM, because GMF performance cannot be tested at the bench-scale, it is assumed that that colloidal and sub-colloidal (i.e., dissolved) fractions are able to pass through full-scale filters. Because testing of GMFs could not be done, it cannot be stated with complete assurance that GMFs will be able to remove the particulate MnO₂ (i.e., retained on the 0.45 µm filter). It is likely the filters may be able to remove particulate MnO₂, but addition of a filter aid polymer may be required. To be conservative, conclusions about Mn²⁺ removal in this TM are based largely on the sub-colloidal and the colloidal fractions (i.e., both assumed to pass through a GMF) in the final test water.
 - Multiple ozone doses were tested, and these doses were a function of the water's TOC concentration. Ozone doses are referred to as the ozone:TOC (O3:TOC) ratio, and all figures are labeled accordingly. For example, if the coagulated water TOC concentration was 1.0 mg/L, and an O3:TOC ratio of 0.5 was used for the ozone dose, then the ozone dose would have been 0.5 mg/L (1.0 mg/L TOC x 0.5 O3:TOC = 0.5 mg/L ozone)
 - For these bench tests, the term “finished” water is used to represent the water collected after the final step of the simulated treatment train. For example, when referring to the pre-ozonation treatment train (i.e., ozonation → coagulation), “finished” water refers to the settled water after the coagulation jar test. When referring to the intermediate ozonation train (i.e., coagulation → ozonation), “finished” water refers to the ozonated water after the ozone residual has decayed to below detection.
 - Except for a few tests evaluating removal of ambient manganese, Mn²⁺ was spiked into the water in order to have a high enough starting concentration to observe measurable treatment results.

Test results are presented and discussed in the following subsections addressing each of the objectives and questions presented in Section 3. Data from all of the manganese removal bench tests are provided in Appendix C of this TM.

6.1 Removal of Ambient Manganese with Ozone

Despite low ambient manganese levels measured in the source water, understanding the impact of ozonation on the removal of ambient manganese was of interest. Two tests were completed during Round 3, to assess the impact of pre-ozonation (Test 3.2) and intermediate ozonation (Test 3.7) on ambient manganese removal. Both alum and PACl were used for coagulation. The raw water total manganese concentration from the Round 3 sample was 0.020 mg/L and was comprised of 40% particulate manganese, 10% colloidal manganese, and 50% sub-colloidal manganese.

The ability of clarification alone to remove ambient manganese is shown in Figure 6-1. Approximately 100% of the particulate and colloidal Mn fractions were removed during clarification with both alum and PACl—prior to ozonation. Only the sub-colloidal fraction remained after clarification, and clarification alone reduced this fraction by approximately 50%.

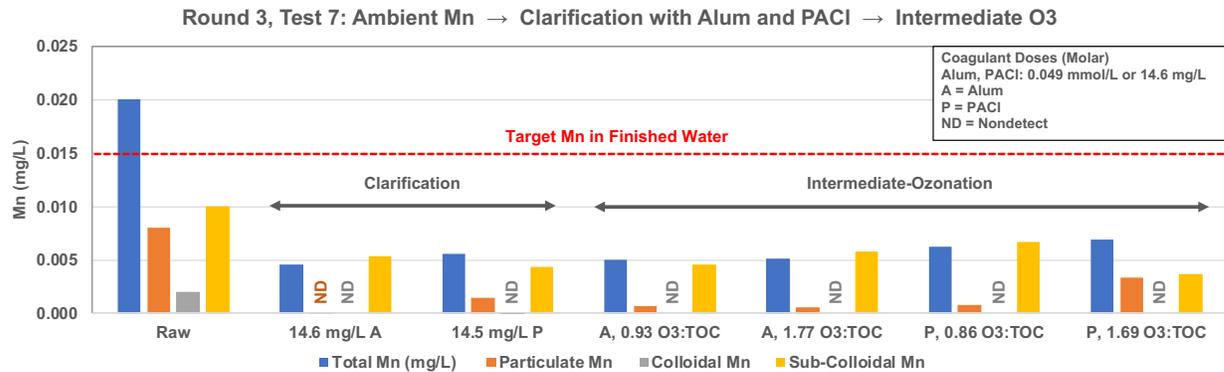


Figure 6-1. Removal of ambient manganese with clarification and intermediate ozone (Raw water: TOC = 2.29 mg/L and pH = 7.2; Clarified water with alum: TOC = 1.26 mg/L and pH = 6.5)

Figure 6-1 also shows that no additional manganese removal occurred as a result of intermediate ozonation (i.e., following coagulation). Two different ozone:TOC (O3:TOC) ratios were tested for each coagulant. For both coagulants at all O3:TOC ratios, both the coagulated/settled (C/S) water and ozonated water had total manganese concentrations below the finished water total manganese target of 0.015 mg/L.

Ambient manganese removal associated with pre-ozonation followed by coagulation is shown in Figure 6-2 for two O3:TOC ozone doses. Note that there was an issue with the samples collected for the total manganese measurements from the 0.25 and 0.50 O3:TOC doses, and no data was reported for these samples. Results showed that pre-ozonation did not reduce the sub-colloidal fraction or the particulate concentration of the ambient manganese, and ozone dose did not appear to affect the sub-colloidal concentration. Coagulation removed a large portion of the particulate manganese. Even without removing the sub-colloidal fraction during pre-ozonation, the finished water total manganese concentrations were all below the finished water target concentration of 0.015 mg/L.

Comparing pre-ozonation tests to intermediate ozonation tests, both the total and sub-colloidal manganese concentrations were substantially lower when intermediate ozonation was used instead of pre-ozonation. Intermediate ozone was the preferred location for ozonation for removal of ambient manganese.

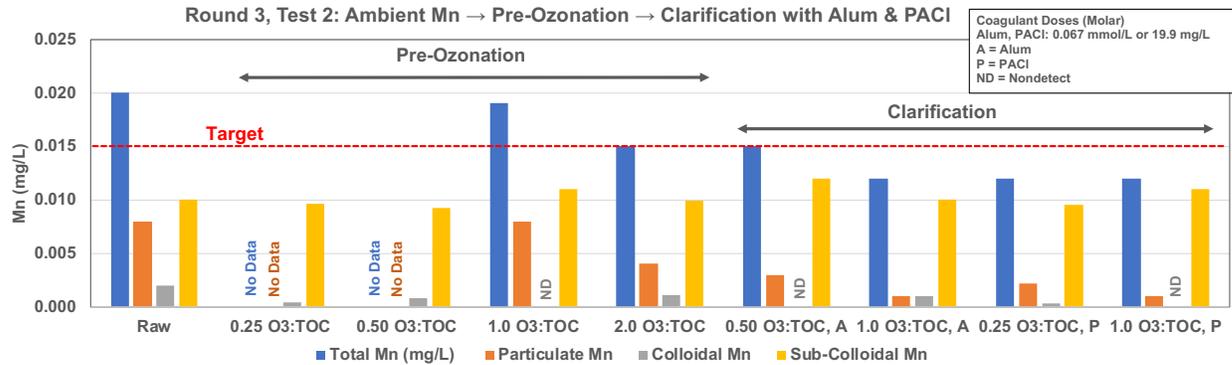


Figure 6-2. Removal of ambient manganese with pre-ozone and clarification (Raw water: TOC = 2.22 mg/L and pH = 7.1; Clarified water with alum: TOC = 1.3 mg/L and pH = 6.6)

Is the ambient manganese in the Tuolumne River raw water readily removed through clarification with and without ozone?

Yes, clarification alone (Figure 6-1) was found to remove both the particulate and colloidal fractions of manganese that were present in the raw water to levels below the finished water total manganese target. Intermediate ozone did not improve manganese removal. When preceded by pre-ozone, clarification (Figure 6-2) was effective for particulate removal but not for removing the sub-colloidal fraction. For ambient manganese removal, either approach resulted in finished water below the total manganese limit.

Does the location of ozonation affect ambient manganese removal?

Yes, intermediate ozonation (Figure 6-1) resulted in lower manganese concentrations in both C/S water and finished water compared to pre-ozonation (Figure 6-2).

Will ozonation of ambient sub-colloidal manganese result in soluble permanganate (VII oxidation state) causing “pink” water?

The oxidation state of the ambient sub-colloidal manganese before or after ozonation is not known. However, pink water associated with Mn (VII) was not observed in any of the tests with ambient manganese.

6.2 Preferred Location for Ozonation

For these tests, the source water was spiked with manganous ions (Mn²⁺) to achieve an initial Mn concentration high enough to be able to observe differences in treatment effectiveness. Test 2.3 assessed pre-ozonation followed by clarification (Figure 6-3), while Test 2.4 assessed clarification followed by intermediate ozonation with alum and PACI (Figures 6-4 and 6-5, respectively).

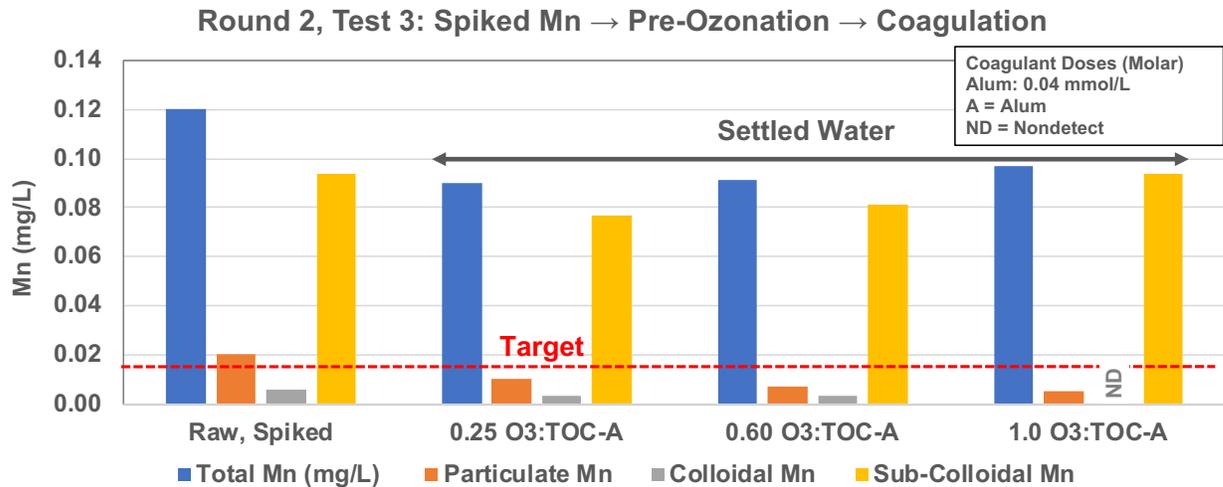


Figure 6-3. Removal of 0.1 mg/L spiked manganese with pre-ozone and clarification with alum (Raw water: TOC = 2.72 mg/L, pH = 7.3; Clarified water with 0.6 mg/L O3:TOC: TOC = 1.82 mg/L, pH = 6.87)

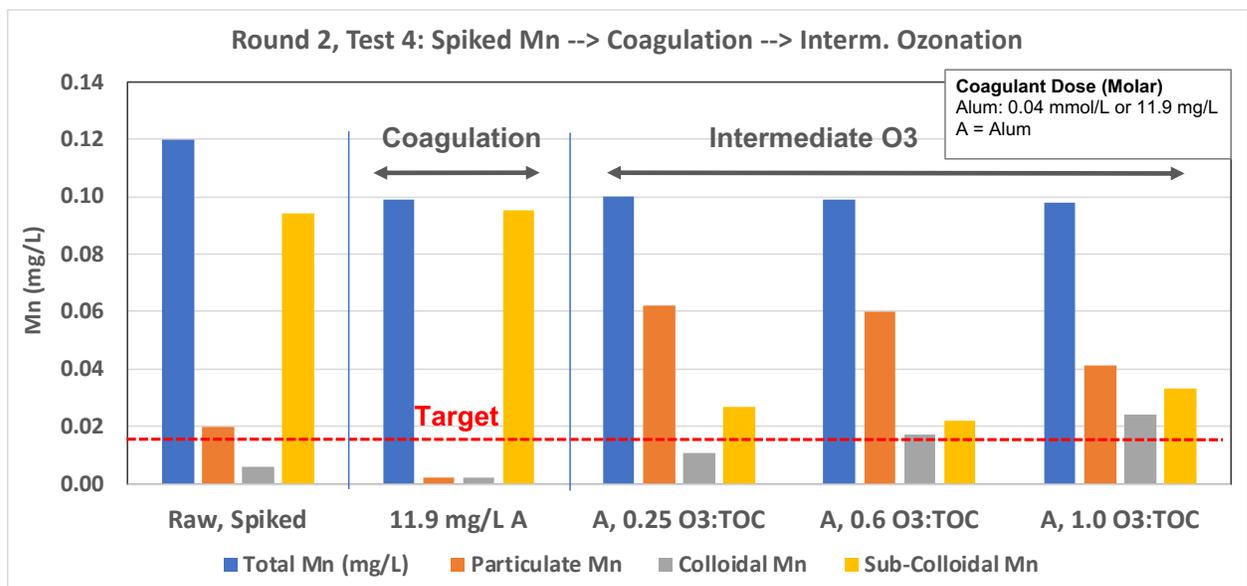


Figure 6-4. Removal of spiked manganese with clarification using alum and intermediate ozonation (Raw water: TOC = 2.72 mg/L, pH = 7.2; Clarified water: TOC = 1.74 mg/L, pH = 6.8)

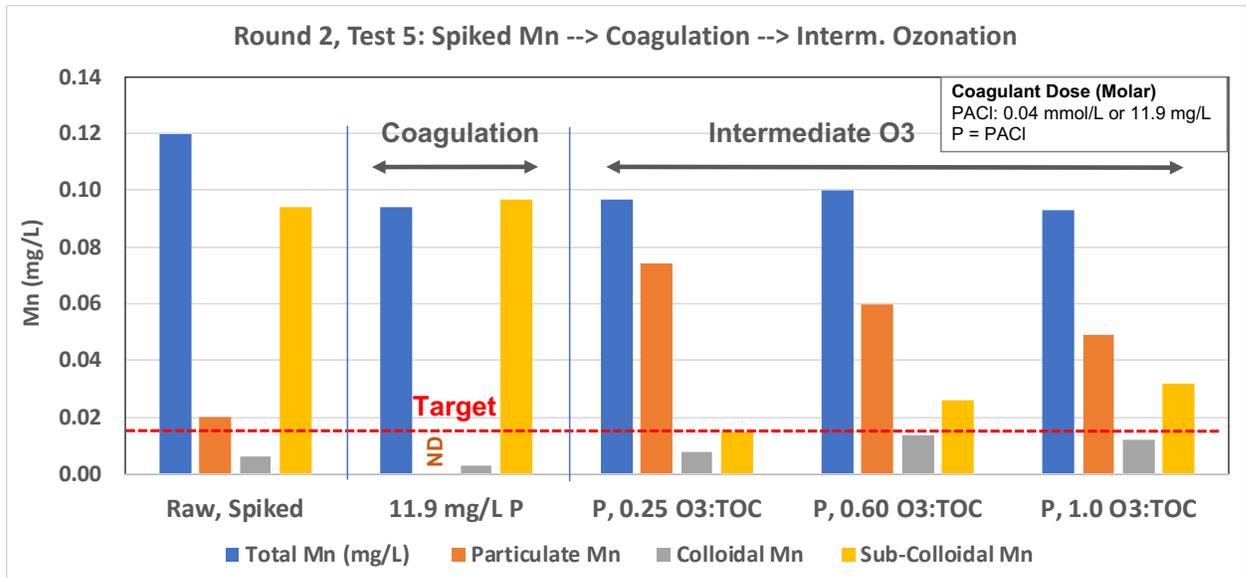


Figure 6-5. Removal of spiked manganese with clarification using PACl and intermediate ozonation (Raw water: TOC = 2.72 mg/L, pH = 7.2; Clarified water: TOC = 1.98 mg/L, pH = 7.2)

The total manganese concentration of the Mn^{2+} spiked raw water was slightly greater than the finished water following either pre-ozone or intermediate ozone treatment. Just as for the ambient manganese removal tests, pre-ozonation did not reduce the sub-colloidal fraction—known to be Mn^{2+} since it was spiked into the raw water—of the finished water (Figure 6-2). The sub-colloidal fraction of the finished water was more than three times greater with pre-ozone compared to intermediate ozone. The particulate fraction was substantially greater with intermediate ozone as compared with the pre-ozonation treatment train. As shown in Figures 6-4 and 6-5, the intermediate ozone oxidized sub-colloidal Mn^{2+} to particulate MnO_2 . Similar behavior was observed with the two different coagulants. Variation in ozone doses—ranging from an O3:TOC ratio of 0.25 to 1.0—resulted in only marginal differences in treatment.

Assuming that colloidal and sub-colloidal fractions will pass through GMFs, intermediate ozonation is preferred since it will result in a lower total manganese concentration in GMF filtered water. However, for a raw water Mn^{2+} concentration of 0.1 mg/L or greater, neither treatment approach is able to meet the finished water limit of 0.015 mg/L total manganese.

Which is the preferred location for ozone—pre or intermediate—for the purpose of manganese removal?

Intermediate ozonation performed better than pre-ozonation because it removes the sub-colloidal manganese fraction more effectively.

Is ozonation alone at the preferred location sufficient for meeting the treatment goal?

When the raw water was spiked with 0.1 mg/L Mn²⁺, neither of the treatment combinations with ozone and coagulation were sufficient to meet the treatment goal of <0.015 mg/L total manganese. The sub-colloidal manganese was closest to the target (Figure 6-5) following intermediate ozonation.

6.3 Effect of Ozone Dose on Manganese Removal

In full-scale treatment, ozone is being used for pathogen disinfection credit and the applied ozone dose needs to be high enough to meet the ozone demand of the water and meet the required CT (disinfectant residual x time) for *Giardia* and virus treatment (*Cryptosporidium* treatment will be achieved through filtration.). As a result, a series of tests were conducted to assess any associated impacts of ozone dose on manganese removal at and above the required doses for pathogen treatment.

Although dependent on the water’s TOC concentration, the seasonal ozone demand tests (Trussell Technologies, Inc., September 2018) indicated an average ozone dose of approximately 2 mg/L is needed to meet the demand of the water and achieve 1-log *Giardia* inactivation and 2-log virus inactivation with pre-ozonation; an ozone dose greater than 5.5 mg/L would be needed at the source water’s historical maximum measured TOC concentration. Multiple ozone doses were tested in parallel for pre-ozone (Test 3.3). Doses of 0.25, 0.5, 1.0, and 2.0 O₃:TOC (corresponding to 0.57, 1.14, 2.28, and 4.56 mg/L O₃) were applied to source water spiked with 0.10 mg/L Mn²⁺. Test results for manganese fractions following pre-ozonation and subsequent coagulation and settling are depicted for Test 3.3 in Figure 6-6.

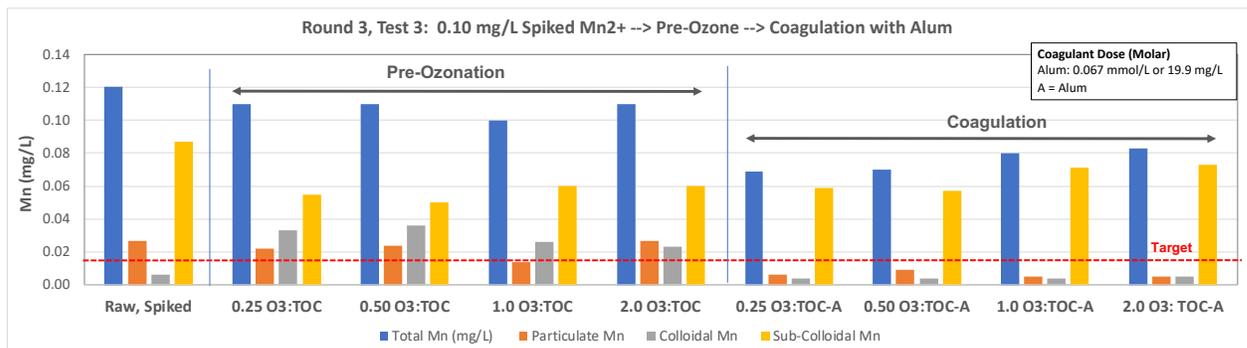


Figure 6-6. Removal of spiked manganese with pre-ozonation and clarification using alum (Raw water: TOC = 2.28 mg/L, pH = 7.2; Clarified water with 1.0 O₃:TOC: TOC = 1.37 mg/L, pH = 6.5)

Pre-ozonation formed colloidal manganese, which reduced the fraction of sub-colloidal manganese; the particulate manganese level following pre-ozonation remained approximately the same as in the raw water. Ozone dose did not seem to change the resultant colloidal and sub-colloidal fractions. Following subsequent coagulation, the particulate and colloidal manganese levels were reduced, but the sub-colloidal fraction

did not change compared to the pre-ozonated water. Increasing the ozone dose resulted in a slight increase in the sub-colloidal fraction.

Although dependent on the clarified water’s TOC concentration, an average ozone dose of 1 mg/L is needed for 1-log *Giardia* inactivation and 2-log virus inactivation with intermediate ozonation. Tests 2.4 and 2.5 (Figure 6-4 and 6-5) compared the effect of intermediate ozone dose on manganese removal. Intermediate ozone doses of 0.25, 0.6, and 1.0 O₃:TOC (corresponding to 0.46, 1.11, and 1.85 mg/L O₃) were tested. Similar to the pre-ozonation results, slightly higher colloidal and sub-colloidal concentrations were observed with increasing ozone dose. However, comparing the sub-colloidal manganese in the finished waters, the concentrations were significantly lower after intermediate ozonation compared to treatment with pre-ozonation.

Does ozone dose affect colloidal MnO₂ formation?

The effects of ozone dose on colloidal MnO₂ formation appear to vary with the location of ozonation. Pre-ozonation did not significantly change either the colloidal or the sub-colloidal manganese concentration of the finished water. Intermediate ozonation indicated a slight increase in the colloidal fraction and little or no change in the sub-colloidal fraction in the finished water with increasing ozone dose.

Will ozonation cause a change in oxidation state from reduced manganese to soluble permanganate causing “pink” water?

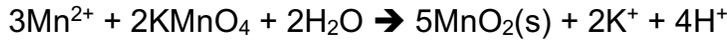
Ozone has the ability to oxidize Mn²⁺, with a valence state of II, to the permanganate MnO₄⁻, with a valence state of VII, resulting in “pink” water. Pink water was observed following pre-ozonation when high O₃:TOC dose ratios of 1.0 and 2.0 were applied (Test 3.4), as depicted in Figure 6-7. The color dissipated within approximately 20 minutes as the permanganate reacted with organic matter and inorganic constituents present in the water.



Figure 6-7. Pink water formed after pre-ozonation during Test 3.4. From left to right, jars were pre-ozonated with O₃:TOC doses of 0.25, 0.5, 1.0, 1.0, 1.0, 2.0.

6.4 Manganese Removal with Permanganate Pre-Oxidation in Conjunction with Ozonation

Permanganate oxidation was tested to determine the impact of a) addition location within the treatment train, b) reaction time, and c) dose relative to stoichiometry for oxidizing spiked manganese ion. Per the stoichiometric equation below, 1.92 mg of potassium permanganate is needed per mg of Mn (II) in the water.



6.4.1 Permanganate Pre-oxidation Alone, without Ozonation

Test 2.4 assessed permanganate oxidation when dosed at 1.0 times the stoichiometric amount needed to oxidize 0.1 mg/L Mn^{2+} plus the amount needed to address the permanganate demand of the water. A maximum reaction time of 56 minutes was used because it is representative of the reaction time possible if permanganate is dosed in the pipeline at the raw water pump station. Results are presented in Figure 6-8, compared to concentrations in the raw water spiked with Mn^{2+} and the calculated concentrations prior to oxidation reaction. Note that in Figure 6-8, the horizontal axis indicates the permanganate dose as “1.0 KMnO_4 ,” meaning permanganate was spiked at a dose of 1.0 times the stoichiometric amount needed for manganese oxidation above the raw water demand for permanganate.

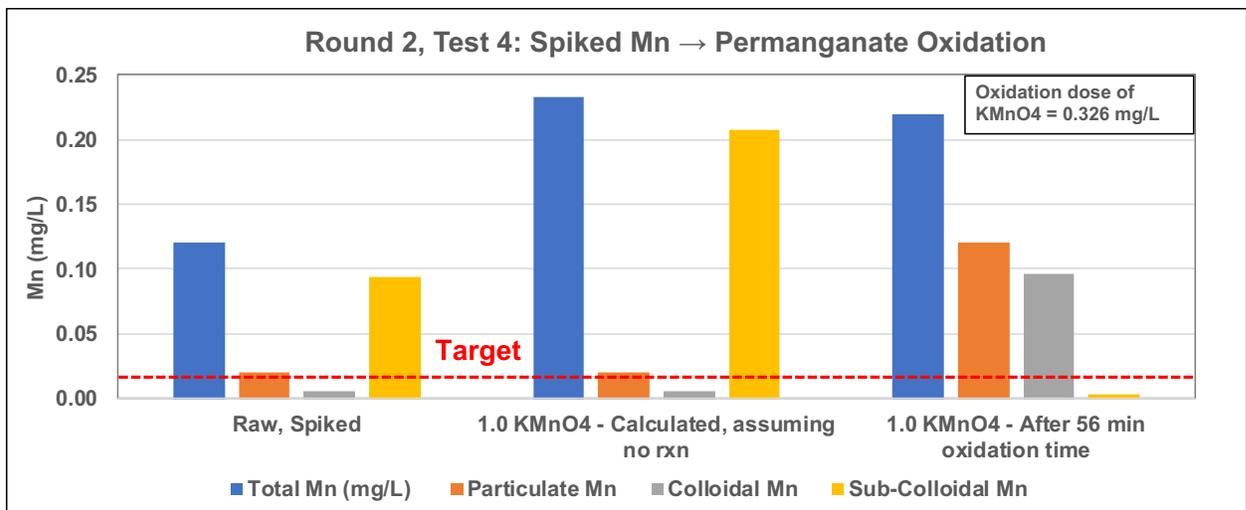


Figure 6-8. Removal of spiked manganese with permanganate oxidation; No clarification (Raw water: TOC = 2.72 mg/L, pH = 7.2)

These results show that permanganate oxidized the Mn^{2+} to colloidal and particulate MnO_2 . The sub-colloidal fraction in the finished water was very low. This particulate and colloidal MnO_2 is formed prior to clarification and should be easily removed through coagulation and granular media filtration.

The impact of permanganate pre-oxidation is further understood through comparison of C/S waters with and without prior permanganate oxidation (Figure 6-9). As indicated, without permanganate pre-oxidation, the sub-colloidal Mn^{2+} passed through coagulation. With permanganate pre-oxidation, the Mn^{2+} was oxidized to MnO_2 and a large percentage of the total was removed through coagulation. The particulate fraction should be effectively removed through coagulation—leaving only a sub-colloidal Mn^{2+} concentration that is well below the finished water target concentration.

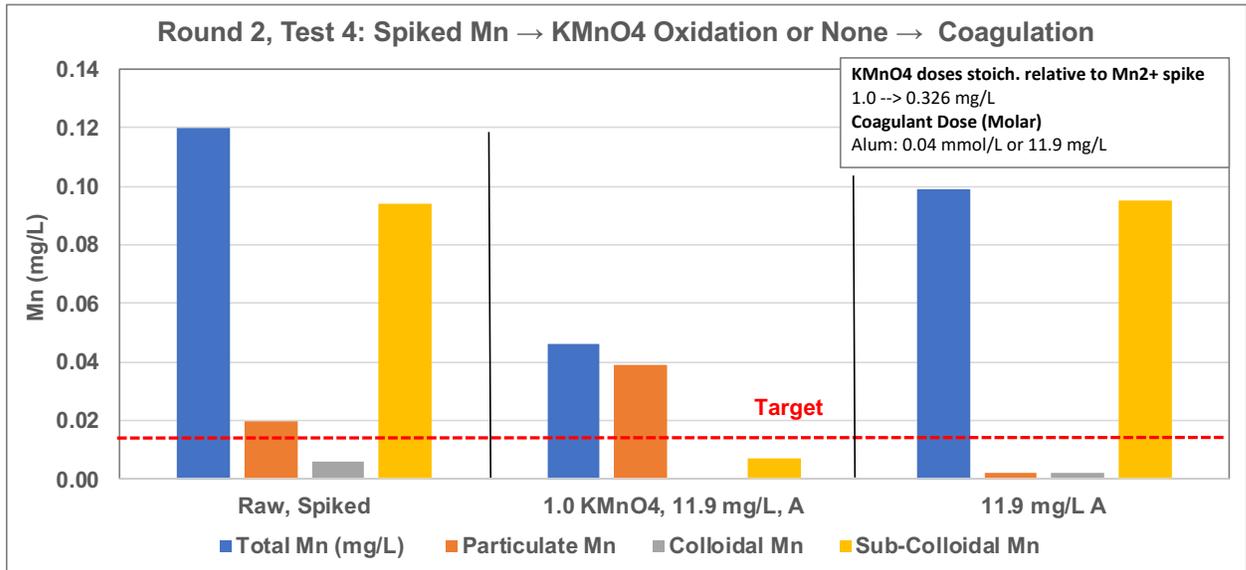


Figure 6-9. Removal of spiked manganese with (56 minutes of reaction time) and without permanganate oxidation, after coagulation (Raw water: TOC = 2.72 mg/L, pH = 7.2; Clarified water: TOC = 1.85 mg/L, pH = 6.8)

6.4.2 Permanganate Pre-Oxidation in Conjunction with Ozonation

Pre-ozone following permanganate pre-oxidation was evaluated in Test 3.5 (Figure 6-10) and can be compared with similar test conditions without permanganate pre-oxidation from Test 3.3 (Figure 6-11). When pre-ozone is added after permanganate oxidation (Figure 6-10), the manganese levels were not reduced compared with pre-ozonation without permanganate oxidation (Figure 6-11). Pre-oxidation with permanganate oxidized Mn^{2+} to colloidal $MnO_2(s)$. With subsequent pre-ozonation and coagulation, the colloidal MnO_2 was changed to sub-colloidal manganese, which was ineffectively removed through coagulation and therefore is assumed to pass through GMF and into the WTP’s finished water.

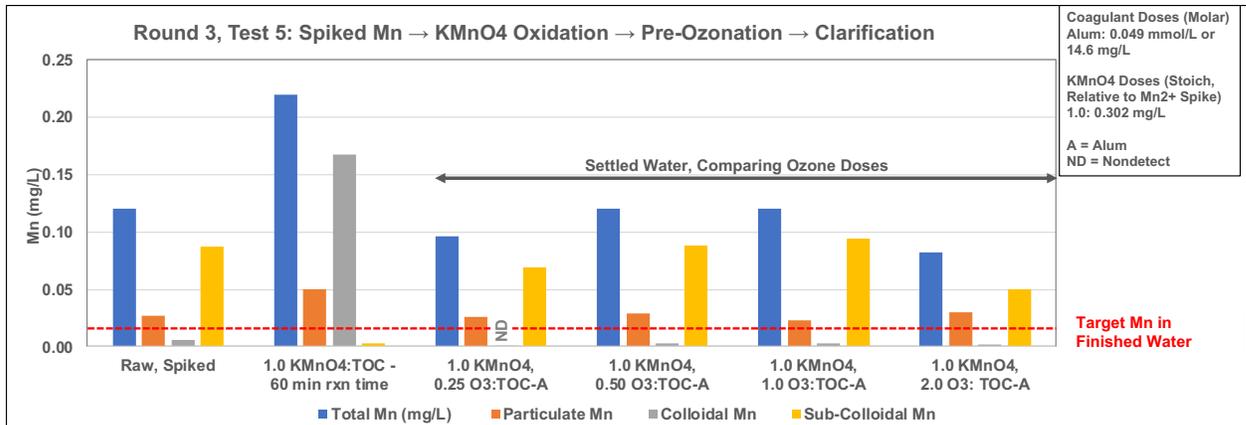


Figure 6-10. Removal of spiked manganese with permanganate oxidation (60 minutes reaction time), followed by pre-ozone and clarification using alum (Raw water: TOC = 2.30 mg/L, pH = 7.05; Clarified water with 1.0 O3:TOC: TOC = 1.19 mg/L, pH = 6.75)

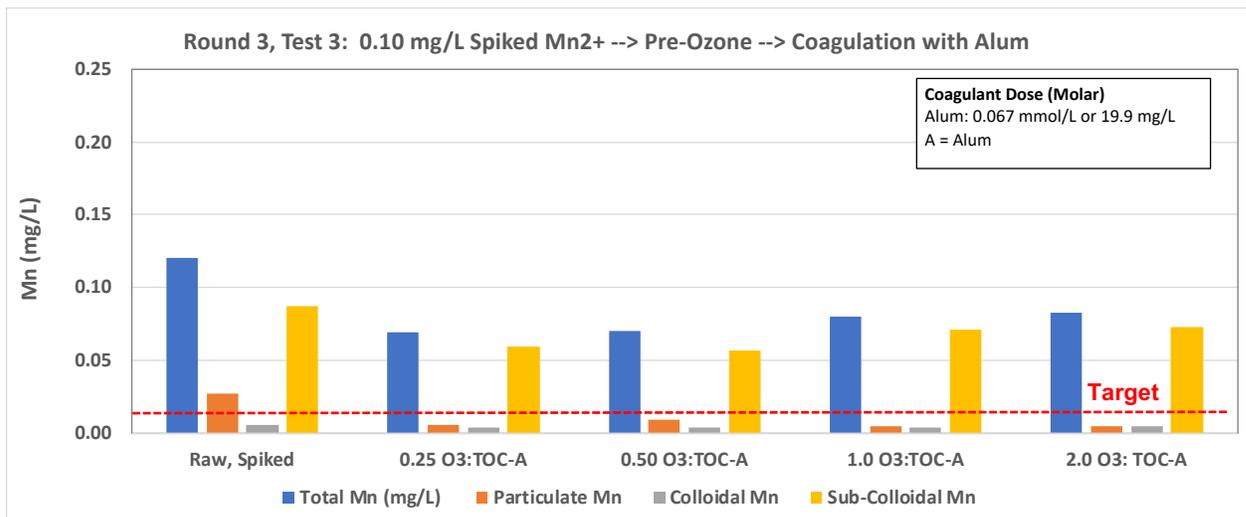


Figure 6-11. Removal of spiked manganese with pre-ozone and clarification using alum; no permanganate addition (Raw water: TOC = 2.28 mg/L, pH = 7.2; Clarified water with 1.0 O3:TOC: TOC = 1.37 mg/L, pH = 6.5)

Alternatively, the permanganate oxidation step was tested after pre-ozonation and before coagulation/settling in Tests 3.4 and 3.5. If the sub-colloidal manganese formed during pre-ozonation was in a reduced form and able to react with this subsequent oxidant, the permanganate would oxidize the sub-colloidal fraction to particulate manganese and be removed through subsequent coagulation. Results from Test 3.4, which included an extra-long permanganate reaction time of 2.5 hours, are presented in Figure 6-12. Shorter permanganate reaction times of 5 minutes and concurrent addition with coagulant (no reaction time) are also presented from Test 3.6 in Figure 6-13.

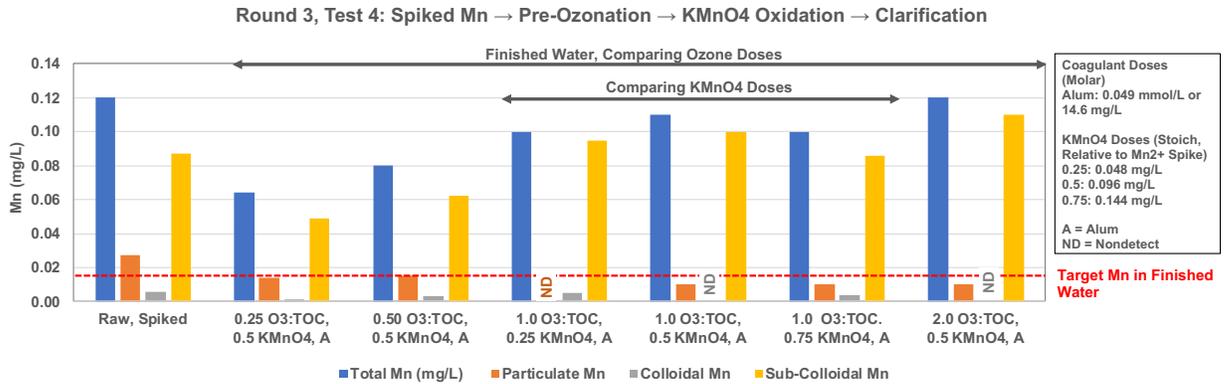


Figure 6-12. Removal of spiked manganese with pre-ozonation, KMnO₄ oxidation (2.5-hour reaction time), and clarification using alum (Raw water: TOC = 2.21 mg/L, pH = 7.11; Clarified water with 1.0 O₃:TOC and 0.75 KMnO₄: TOC = 1.28 mg/L, pH = 6.54)

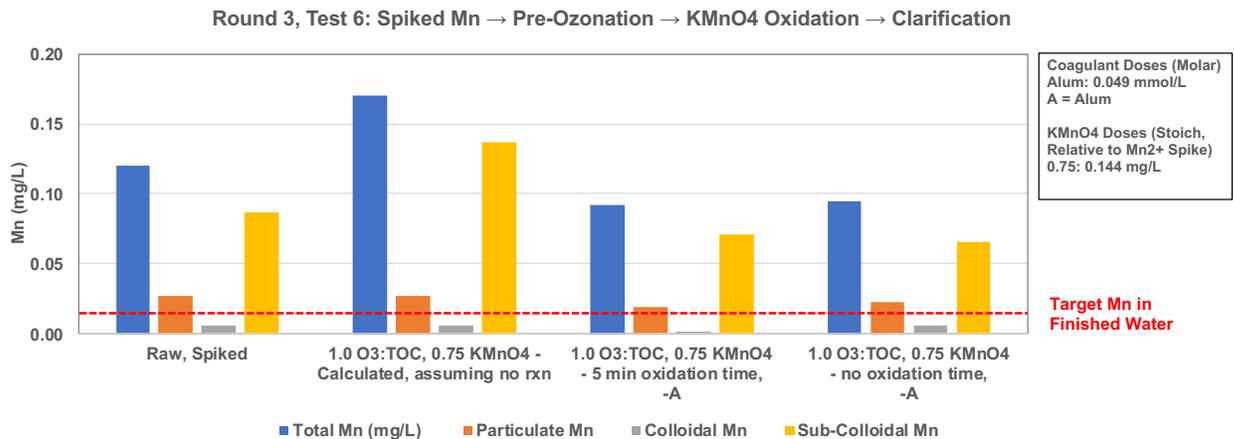


Figure 6-13. Removal of spiked manganese with pre-ozonation, KMnO₄ oxidation, and clarification using alum (Raw water: TOC = 2.31 mg/L, pH = 7.32; Clarified water with 5-minute reaction time: TOC = 1.18 mg/L, pH = 6.83)

Similar to permanganate oxidation followed by pre-ozonation (Figure 6-10), pre-ozonation followed by permanganate oxidation (Figures 6-12 and 6-13) was found to be ineffective for manganese removal. The sub-colloidal fraction was particularly high for all of these treatment conditions. Increasing the permanganate dose following pre-ozonation (Figure 6-12; 0.25, 0.5, and 0.75 KMnO₄) allowed for a marginal increase in oxidation of the sub-colloidal fraction, however the finished water sub-colloidal concentration was still well above the treatment target. These results show no improvement in manganese removal when permanganate was added after pre-ozonation.

The final treatment train tested with permanganate oxidation involved spiked Mn²⁺ followed by permanganate pre-oxidation, then clarification and intermediate ozonation. The particulate and colloidal MnO₂ formed with permanganate would be removed through coagulation before ozonation. This treatment combination was tested several

times. Water spiked with 0.1 mg/L Mn²⁺ was tested with permanganate pre-oxidation, followed by coagulation with both alum (Test 2.4, Figure 6-14) and PACI (Test 2.5, Figure 6-15) prior to intermediate ozonation. In addition, water spiked with 0.3 mg/L Mn²⁺ was tested with permanganate pre-oxidation, followed by coagulation with both alum (Test 1.4, Figure 6-16) and ferric (Test 1.4, Figure 6-17).

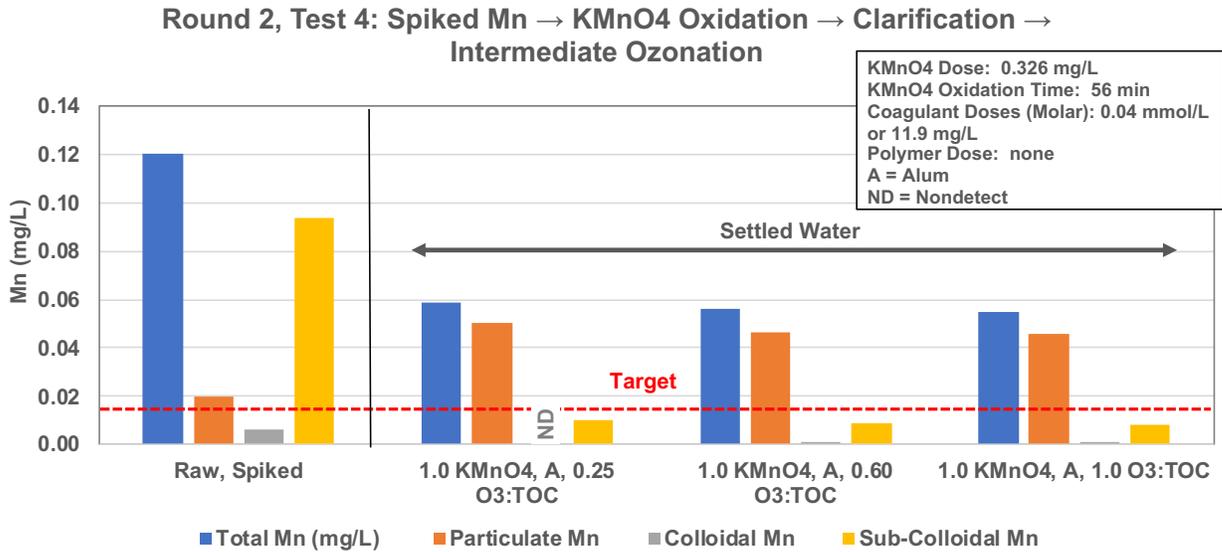


Figure 6-14. Removal of 0.1 mg/L spiked manganese with KMnO₄ oxidation (56 minutes reaction time), clarification using alum, and intermediate ozonation (Raw water: TOC = 2.72 mg/L, pH = 7.28; Clarified water: TOC = 1.85 mg/L, pH = 6.78)

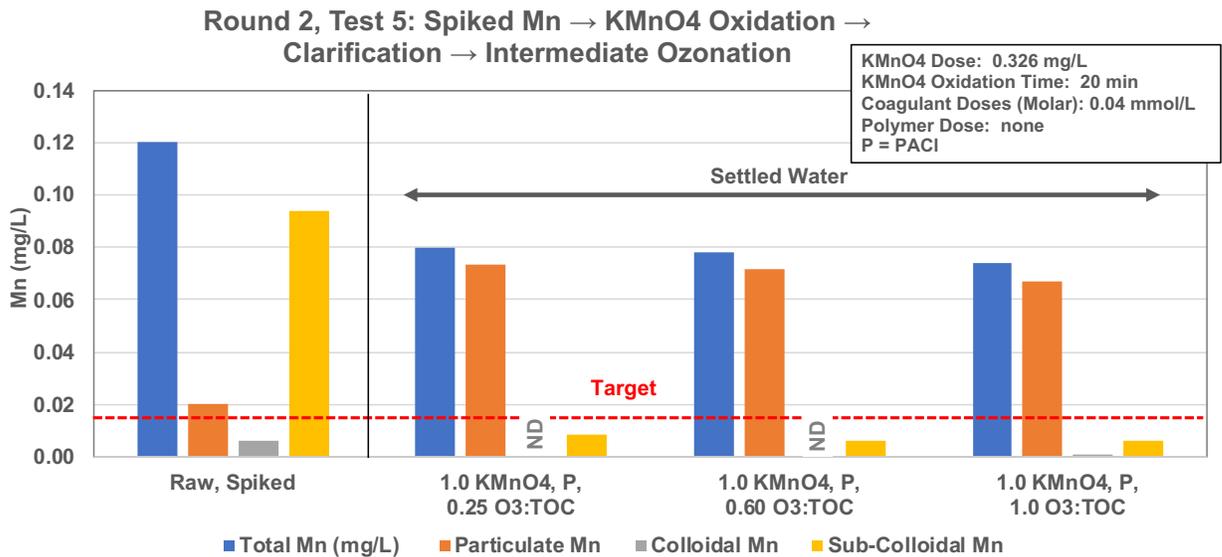


Figure 6-15. Removal of 0.1 mg/L spiked manganese with KMnO₄ oxidation (20 minutes reaction time), clarification using PACI, and intermediate ozonation (Raw water: TOC = 2.72 mg/L, pH = 7.28; Clarified water: TOC = 2.14 mg/L, pH = 7.11)

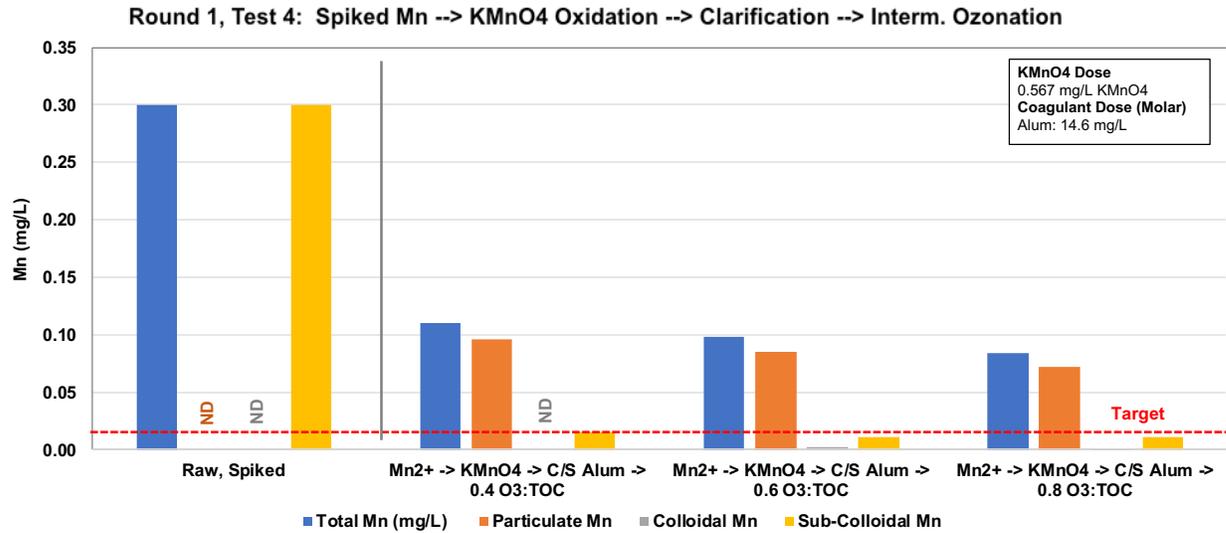


Figure 6-16. Removal of 0.3 mg/L spiked manganese with KMnO4 oxidation (5 minutes reaction time), clarification using alum, and intermediate ozonation (Raw water: TOC = 2.04 mg/L, pH = 7.45; Clarified water for 0.6 O3:TOC: TOC = 1.33 mg/L)

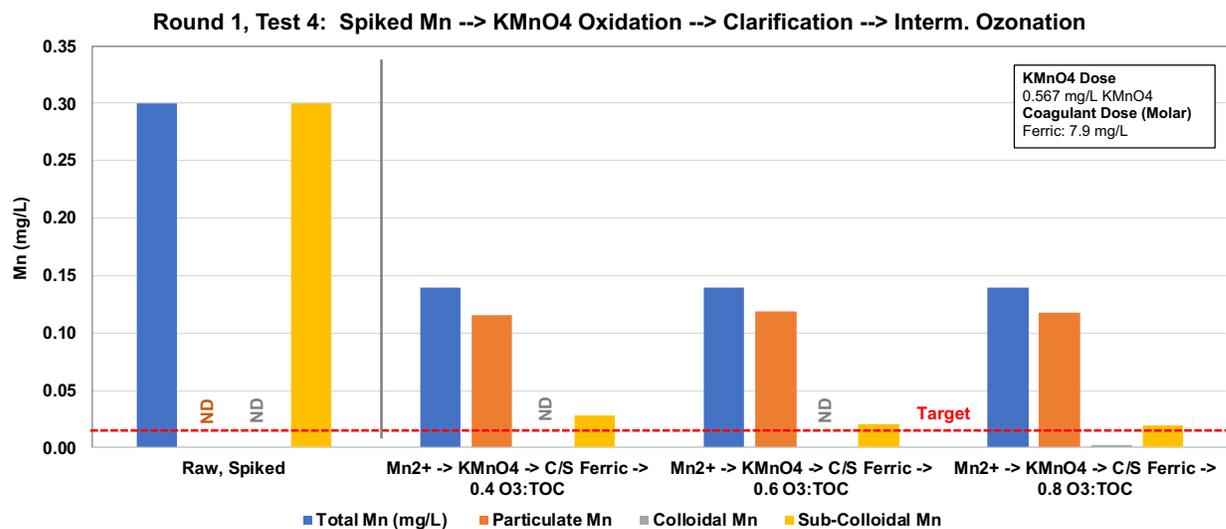


Figure 6-17. Removal of 0.3 mg/L spiked manganese with KMnO4 oxidation (5 minutes reaction time), clarification using ferric chloride, and intermediate ozonation (Raw water: TOC = 2.04 mg/L, pH = 7.45; Clarified water for 0.6 O3:TOC: TOC = 1.38 mg/L)

Colloidal and sub-colloidal fractions of manganese were particularly well removed through a treatment train of permanganate pre-oxidation, coagulation, and intermediate ozonation (Figures 6-14 and 6-15). The particulate manganese remained above the finished water manganese target but is assumed to be removed through subsequent GMF filtration, which may require the use of a filter aid polymer. When permanganate oxidation and clarification were included prior to intermediate ozonation, no real



difference was observed in manganese concentrations with increasing ozone dose. This occurred because permanganate oxidized the sub-colloidal manganese, allowing removal of a large fraction of manganese through clarification (Figure 6-9).

Comparing Figures 6-14 and 6-15 indicates that the particulate manganese formed through permanganate oxidation was better removed through coagulation with alum (Figure 6-14) than with PACl (Figure 6-15). The improved removal of manganese by alum (Figure 6-16) was also observed when compared with ferric chloride (Figure 6-17) after permanganate oxidation in Test 1.4. Improved manganese removal was also observed with increased ozone dose. The combined colloidal and sub-colloidal fractions of manganese were below the target for all three ozone doses, when preceded by permanganate pre-oxidation and clarification using alum. When ferric chloride was used for coagulation (Figure 6-17), it contributed additional Mn^{2+} since manganous ion is a common contaminant in ferric.

6.4.3 Permanganate Reaction Time

The final topic that was investigated with respect to permanganate oxidation was the impact of permanganate reaction time. This factor is best illustrated using results from Test 1.2 (Figure 6-18), comparing reaction times of 1 and 5 minutes, as well as Test 4.5 (Figure 6-19) comparing reaction times of 56 minutes, 5 minutes, and concurrent addition with coagulant.

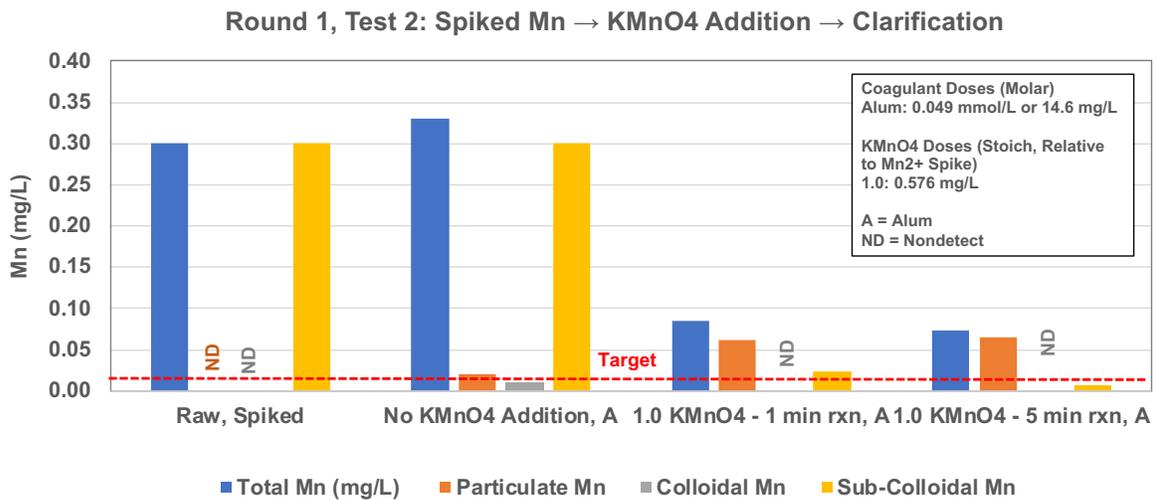


Figure 6-18. Removal of 0.3 mg/L spiked manganese without and with KMnO4 oxidation (1 and 5 minutes of reaction time), as well as clarification using alum (Raw water: TOC = 2.04 mg/L, pH = 7.45; Clarified water for 5-min contact time: TOC = 1.36 mg/L)

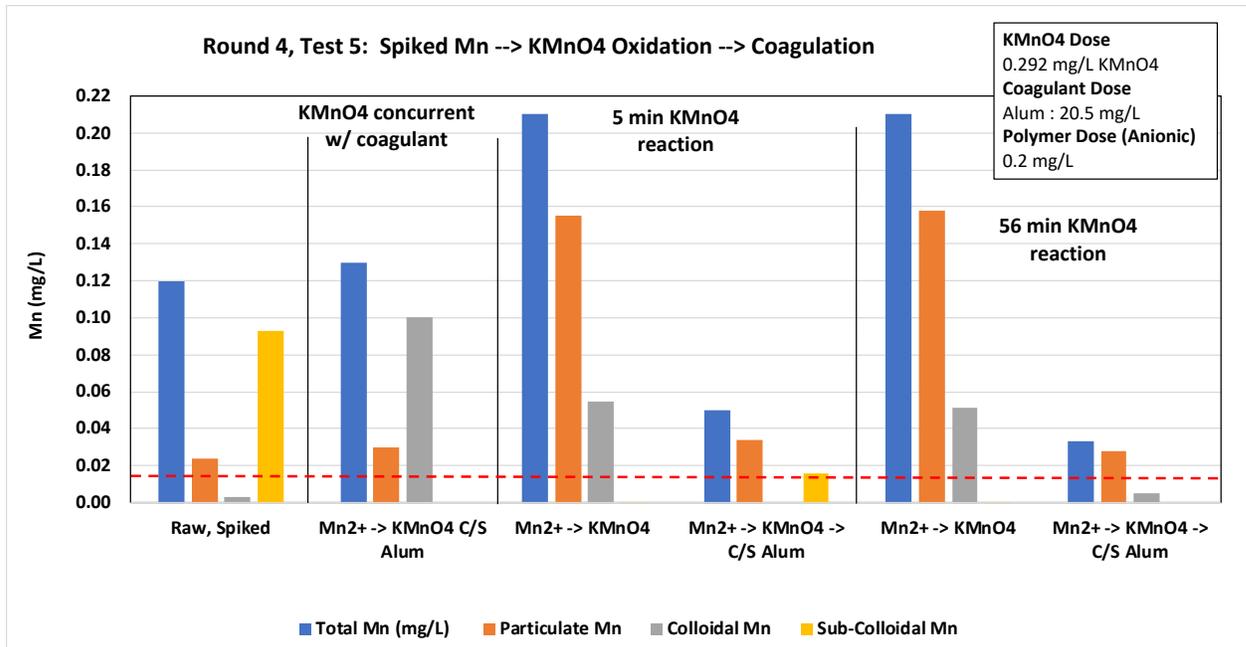


Figure 6-19. Removal of 0.1 mg/L spiked manganese with KMnO₄ oxidation (56, 5, and 0 minutes of reaction time), as well as clarification using alum (Raw water: TOC = 2.12 mg/L, pH = 7.10; Clarified water for 5-minute contact time: TOC = 1.28 mg/L, pH = 6.71)

Despite the higher spiked dose of 0.3 mg/L Mn²⁺, significant manganese removal was observed for the test conditions with both 1- and 5-minute permanganate reaction times (Figure 6-18). Colloidal manganese was below the detection limit, but the particulate fraction remained following coagulation with alum. The biggest differentiator was the sub-colloidal fraction, which was below the treatment target of 0.015 mg/L with 5 minutes of reaction time, but above the target with only 1 minute of reaction time with permanganate. Likewise, increased removal of the combined colloidal and sub-colloidal fractions of manganese was observed in Test 4.5 (Figure 6-19) with increasing reaction time with permanganate. The test condition with concurrent addition of permanganate and alum did not provide sufficient reaction time to remove the combined colloidal and sub-colloidal fractions of manganese to levels below the target.

Is permanganate pre-oxidation alone effective for manganese removal if ozone were off-line or not part of the treatment train?

The use of permanganate oxidation with an extended reaction time of 56 minutes (Test 2.4, Figure 6-9) was sufficient to bring the sub-colloidal and colloidal fractions of manganese below the target without the use of ozone. The particulate manganese concentration remained above the target but is expected to be removed through subsequent granular media filtration. The granular media filtration step of the treatment train, however, was not tested since this treatment process does not lend itself to bench-scale testing. However, because ozone is included in the SRWA WTP treatment train for primary disinfection, this is relevant for the case where ozone is off-line.

Does permanganate addition in conjunction with pre-ozonation allow for meeting the treatment goal?

As depicted in Figure 6-10, the addition of permanganate prior to pre-ozonation hindered the removal of manganese compared with pre-ozonation alone (Figure 6-11).

Permanganate addition following pre-ozonation (Figures 6-12 and 6-13) was assumed to have over-oxidized the water – the manganous ions (Mn^{2+}) were oxidized to soluble permanganate ions (MnO_4^-) – and the manganese remained in a soluble form that would pass through treatment.

Does permanganate addition in conjunction with intermediate ozonation allow for meeting the treatment goal?

The treatment train including permanganate oxidation prior to clarification and intermediate ozonation (Figures 6-14, 6-15, 6-16, and 6-17) provided the best removal of colloidal and sub-colloidal manganese fractions, yielding combined colloidal and sub-colloidal manganese values below the target of ≤ 0.015 mg/L in the finished water (except when ferric chloride, which contained manganese impurities, was used as a coagulant). The particulate manganese, however, remained above the finished water total manganese limit.

What is the effect of reaction time on permanganate oxidation of Mn^{2+} ?

Permanganate oxidation was found to be most effective when added ahead of coagulation and intermediate ozonation. The clarified and settled water after permanganate oxidation was below the target for combined colloidal and sub-colloidal fractions of manganese when the reaction time with permanganate was 5 minutes or greater. Therefore, the full-scale WTP design should allow for permanganate addition with as long of a reaction time as the site can accommodate and a minimum reaction time of 2 minutes. Note that a 2-minute reaction time was not tested and is inferred from these test results. Brandhuber, et al. (2013) recommend a 2- to 4-minute reaction time. It should also be noted that the reaction rate is a function of pH with faster reaction rates at higher pH, so variations in pH may affect the necessary reaction time.

6.5 Coagulant Performance for Manganese Removal

How do the conventional coagulants compare for removing ambient manganese?

The removal of ambient manganese was tested with two different aluminum-based coagulants, alum and PACl. The performance of both coagulants seemed comparable in both the pre-ozonation (Figure 6-2) and intermediate ozonation (Figure 6-1) tests with ambient raw water manganese. However, as seen in ambient raw water manganese tests, intermediate ozonation resulted in lower settled water and finished water manganese levels, particularly for the colloidal and sub-colloidal manganese fractions.

Results from another jar test using equivalent doses of alum and PACl are presented in Figure 6-20. Manganese removals were similar with both coagulants (i.e., ambient manganese, no ozonation), with settled water manganese concentrations well below the treatment limit.

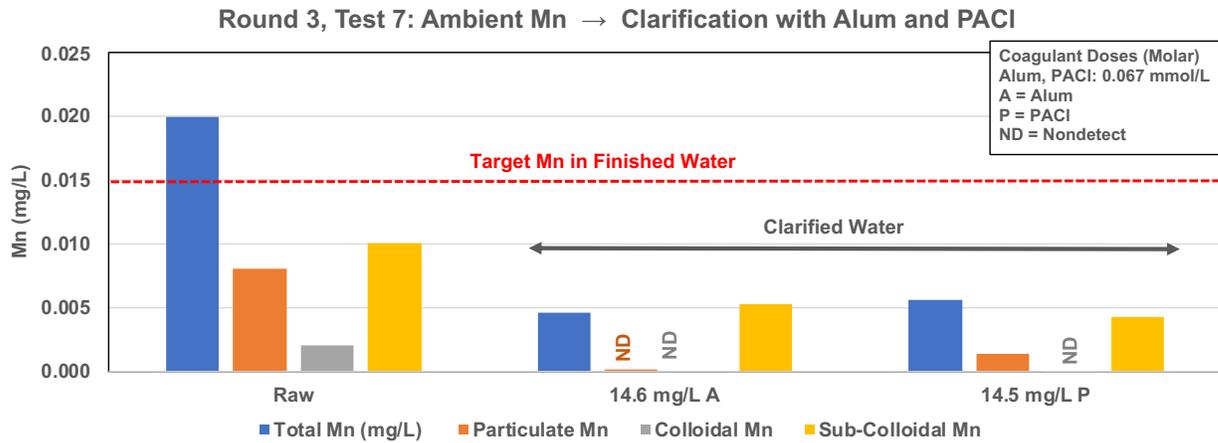


Figure 6-20. Comparison of clarification with alum and PACl for removal of ambient manganese. (Raw water: TOC = 2.29 mg/L, pH = 7.23; Clarified water with alum: TOC = 1.26 mg/L, pH = 6.53; Clarified water with PACl: TOC=1.34 mg/L, pH=6.89)

How do the three conventional coagulants compare for removing manganese when the source water was spiked with Mn²⁺?

The only manganese removal bench tests involving the use of ferric chloride were conducted during Round 1 using source water spiked with 0.3 mg/L Mn²⁺ to simulate worst-case raw water conditions. Because manganese is a common contaminant of ferric chloride, results of the Round 1 tests comparing alum (Figure 6-16) and ferric (Figure 6-17) showed better removal with alum.

As suggested previously, removal of manganese – particularly the combined colloidal and sub-colloidal fractions – was found to be similar when using alum and PACl for coagulation in combination with both pre-ozonation and intermediate ozonation.

6.6 Conventional Clarification Compared with Sand Ballasted Clarification for Manganese Removal

Sand ballasted coagulation (SBC) is incorporated in the proprietary Actiflo® treatment process and offers a high-rate alternative to the more conventional coagulation-flocculation-sedimentation with a more compact footprint. These two clarification methods were compared during Round 4 testing, using the standard jar test procedure for conventional treatment and the Actiflo® procedure as described in Appendix A Sections A.3 and A.4, respectively. Figures 6-21 and 6-22 compare permanganate oxidation with various reaction times (concurrent addition with coagulant, 5 minutes, and 56 minutes) combined with SBC and intermediate ozonation (0.6 O₃:TOC) to permanganate oxidation combined with conventional clarification (using alum and PACl, respectively) and intermediate ozonation (0.6 O₃:TOC).

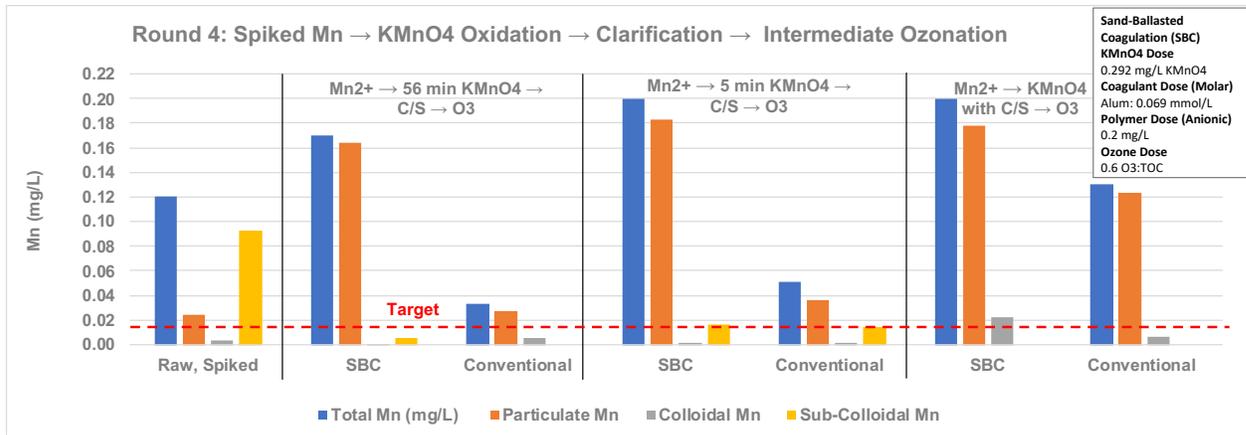


Figure 6-21. Removal of 0.1 mg/L spiked manganese with KMnO4 oxidation (56, 5, and 0 minutes of reaction time), as well as clarification with SBC and conventional jar tests using alum and anionic polymer, and intermediate ozonation (Raw water: TOC = 2.12 mg/L, pH = 7.10; Clarified water for 5-minute contact time with conventional: TOC = 1.28 mg/L, pH = 6.71)

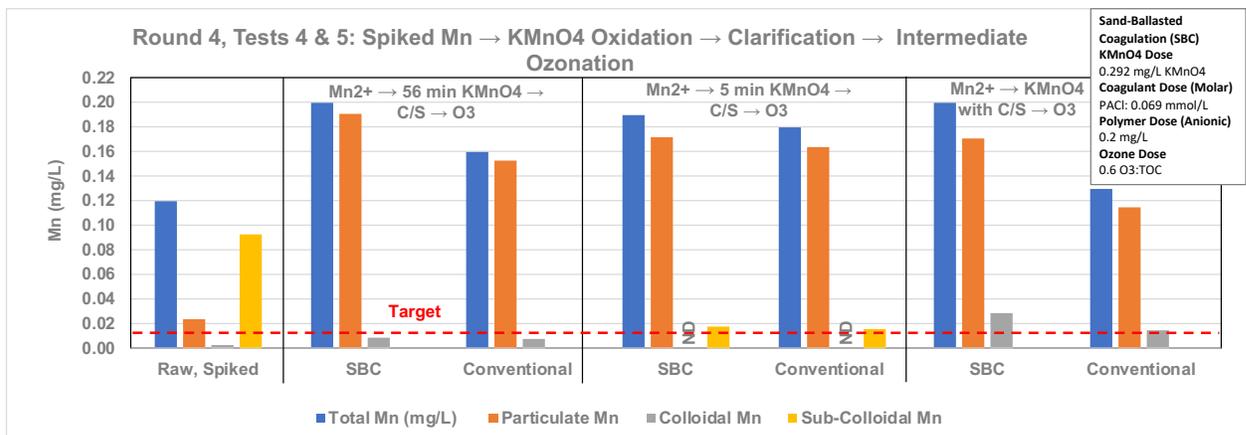


Figure 6-22. Removal of 0.1 mg/L spiked manganese with KMnO4 oxidation (56, 5, and 0 minutes of reaction time), as well as clarification with SBC and conventional jar tests using PACl and anionic polymer, and intermediate ozonation (Raw water: TOC = 2.12 mg/L, pH = 7.10; Clarified water for 5-minute contact time with conventional: TOC = 1.28 mg/L, pH = 6.71)

Is conventional clarification similarly effective to a sand ballasted clarification for removing manganese?

In all treatment conditions presented in Figures 6-21 and 6-22, manganese removal was better with conventional clarification than with SBC under equivalent treatment conditions. The biggest difference was that the particulate manganese did not settle well in the SBC tests. The colloidal and sub-colloidal fractions had similar behavior with both SBC and conventional clarification.



These comparative results should be interpreted with caution because coagulant doses had been optimized for enhanced coagulation (Round 1 of bench testing) with the conventional jar testing procedure, but no optimization was performed for the SBC procedure. In addition, Trussell Tech did not assess the representativeness of the SBC jar test procedure to full-scale SBC performance, while there is a long history of water treatment experience with the conventional jar test procedures.

What is the effect of reaction time on permanganate oxidation of Mn^{2+} ?

Longer permanganate oxidation reaction times resulted in lower concentrations of the combined colloidal and sub-colloidal manganese fractions (Figures 6-21 and 6-22), but the difference was not significant. The combined colloidal and sub-colloidal fractions were below the 0.015 mg/L target when the reaction time was at least five minutes when alum was used as a coagulant (Figure 6-21). The sub-colloidal manganese was slightly above the 0.015 mg/L target with a 5-minute reaction time when PACl was used for coagulation.

How do the two aluminum-based conventional coagulants compare for removing manganese when the source water was spiked with Mn^{2+} ?

Manganese removal, particularly with respect to the combined colloidal and sub-colloidal fractions, was marginally better when alum was used as a coagulant following permanganate oxidation and prior to intermediate ozonation (Figure 6-21 vs. 6-22). This enhanced removal was more pronounced with higher intermediate ozone doses.

7 Conclusions and Recommendations for Design

When drawing conclusions about these manganese removal tests and making recommendations for the SRWA WTP design, it is important to note that source water manganese concentrations and speciation do not indicate problematic manganese levels for treatment. Experience, however, indicates it would be prudent to plan for future unknowns and consider the optimum treatment approach for manganese removal particularly since ozone will be used for primary disinfection.

Key conclusions from these quarterly bench tests are the following:

- Ambient manganese was removed below the treatment limit (≤ 0.015 mg/L) with ozone in conjunction with coagulation for both pre-ozonation and intermediate ozonation.
- Ferric chloride coagulant adds manganous ions (Mn^{2+}) to the raw water because this coagulant commonly contains a small percentage Mn^{2+} as a contaminant.
- Intermediate ozonation was clearly superior to pre-ozonation based on both ambient manganese tests and spiked Mn^{2+} tests. Pre-ozonation with coagulation did not remove the sub-colloidal fraction, which would be able to pass through granular media filtration.



- Even with the preferred intermediate ozonation, it will be challenging to maintain finished water manganese concentrations below the manganese treatment goal (≤ 0.015 mg/L) with raw water Mn^{2+} levels as high as 0.1 mg/L, unless prior Mn^{2+} oxidation with another strong oxidant such as permanganate is implemented.
- Pink water related to Mn^{2+} being over-oxidized to permanganate ion (MnO_4^-) should not occur with intermediate ozonation at ozone doses needed for pathogen inactivation, even with Mn^{2+} levels as high as 0.1 mg/L.
- With Mn^{2+} levels as high as 0.1 mg/L, the preferred treatment approach to reduce both the colloidal and sub-colloidal manganese fractions to concentrations below the finished water limit is permanganate → coagulation → intermediate ozonation → filtration.
- Concurrent permanganate addition with coagulant did not provide sufficient reaction time for effective oxidation of Mn^{2+} to a particulate fraction. However, permanganate reaction times of 5 minutes or greater reduced the sub-colloidal and colloidal fractions to concentrations below the finished water manganese limit.
- Conventional clarification appeared to more effectively remove manganese than sand-ballasted clarification due to less effective settling of particulate manganese in the SBC bench tests. This conclusion should be viewed with caution, though, since coagulant optimization was never done for the SBC jar test procedure with this water.
- Based on these quarterly test results, recommendations for the SRWA WTP design are:
 - Require a finished water total manganese limit of 0.015 mg/L
 - Require intermediate ozonation as opposed to pre-ozonation for primary disinfection
 - Do not allow ferric chloride for coagulation during startup and acceptance testing since manganese is a common contaminant of iron-based coagulants. However, the chemical storage and feed system should be designed to accommodate (i.e., chemical compatibility and dose) either an aluminum or ferric based coagulant in case SRWA prefers to switch primary coagulants at some time in the future.
 - Include the ability to add permanganate ahead of coagulant addition, with a minimum permanganate reaction time of 2 minutes before coagulant addition.



8 References

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Appendix A - Experimental Methods and Materials

A.1 Source Water Collection

Samples of Tuolumne River water were collected by staff from FishBio concurrently with the source water monitoring samples near the infiltration gallery site indicated in Figure 8-1. A pole-mounted Kemmerer water sampler was used, pulling water from the middle of the water column at the time of sampling. The water samples were transferred into 5-gallon cubitainers and packed in coolers filled with ice packs. Field measurements made at the time of sample collection included: turbidity, pH, temperature, conductivity, and dissolved oxygen concentration. The filled coolers were shipped to the Trussell Technologies Laboratory (TT Lab) in Pasadena, CA via FedEx for next morning delivery. Upon receipt, the cubitainers of water were placed in the refrigerator until testing. Prior to each of the bench tests, the water was removed from the refrigerator and allowed to warm to the desired testing temperatures.

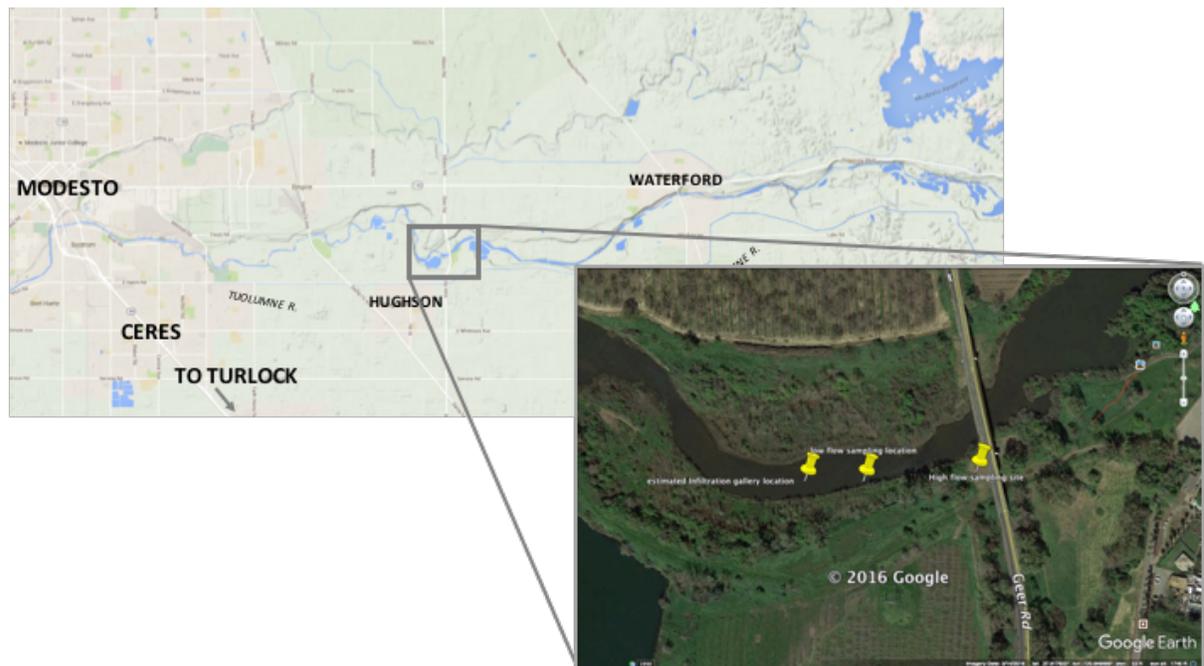


Figure 8-1. Tuolumne River source water monitoring locations (high and low flow conditions), east of Modesto, CA

The sample collection date and water volume collected by FishBio and shipped to the TT Lab for manganese removal bench testing rounds 1 through 4, are specified as follows:

- Round 1: December 12, 2016 – 30 gallons
- Round 2: March 13, 2016 – 20 gallons
- Round 3: June 12, 2017 – 20 gallons
- Round 4: October 9, 2017 – 30 gallons

A.2 Coagulants

Three different coagulants—alum, ferric, and PACl—were evaluated during the jar tests. Kemira Chemicals, Inc. provided samples of these three chemicals. A 0.05M stock solution of each coagulant was prepared for dosing the jars. Specifications of each coagulant along with the volume of each bulk chemical used to make the stock solutions are shown in Table 8-1. Samples of each stock solution, diluted to approximately 5 mg/L metal ion (e.g., 5 mg/L Fe³⁺), were sent to Eurofins Labs for aluminum or iron analysis to confirm the concentration of the stock solutions. Measured stock concentrations, shown in Table 8-1, confirmed the solutions were prepared correctly and were approximately equal to the desired concentrations. During the final round of manganese removal testing, sand ballasted coagulation (SBC) was tested and both sand (proprietary size, sample provided by Krüger) and anionic polymer were added to the jars. Kemira Chemicals provided their Superfloc 4818RS for these tests, an anionic polymer with very high viscosity and high anionic charge. The specific gravity of the Superfloc 4818RS was 1.077.

Table 8-1. Coagulant specifications.

Property	Ferric Chloride	Alum	Polyaluminum Chloride
Chemical Formula	FeCl ₃	Al ₂ (SO ₄) ₃ •14H ₂ O	PAX-18 Formula Unknown
Specific Gravity	1.452	1.332	1.373
% as Al ₂ O ₃	--	8.18	17.20
% as Alum	--	--	--
% as Ferric Chloride	41.31	--	--
mL of Bulk Chemical in 500-mL of Solution	6.76	11.70	5.40
Estimated Stock Concentration	0.05 mol Fe ³⁺ /L	0.05 mol Al ³⁺ /L	0.05 mol Al ³⁺ /L
Measured Stock Concentration	0.048 mol Fe ³⁺ /L	0.047 mol Al ³⁺ /L	0.047 mol Al ³⁺ /L

A.3 Jar Test Procedure – Conventional Coagulation and Settling

Prior to starting the jar tests, the water was taken out of the refrigerator and allowed to warm to approximately the same temperature as when collected. The raw water was analyzed for pH, temperature, turbidity, alkalinity, dissolved UV-254, TOC, dissolved organic carbon (DOC), total and dissolved manganese (Mn), as well as N-Nitrosodimethylamine (NDMA) in select rounds of testing. The concentration of NDMA,

a disinfection by-product, in the raw water was measured to document if there was a background concentration present in the Tuolumne River water.

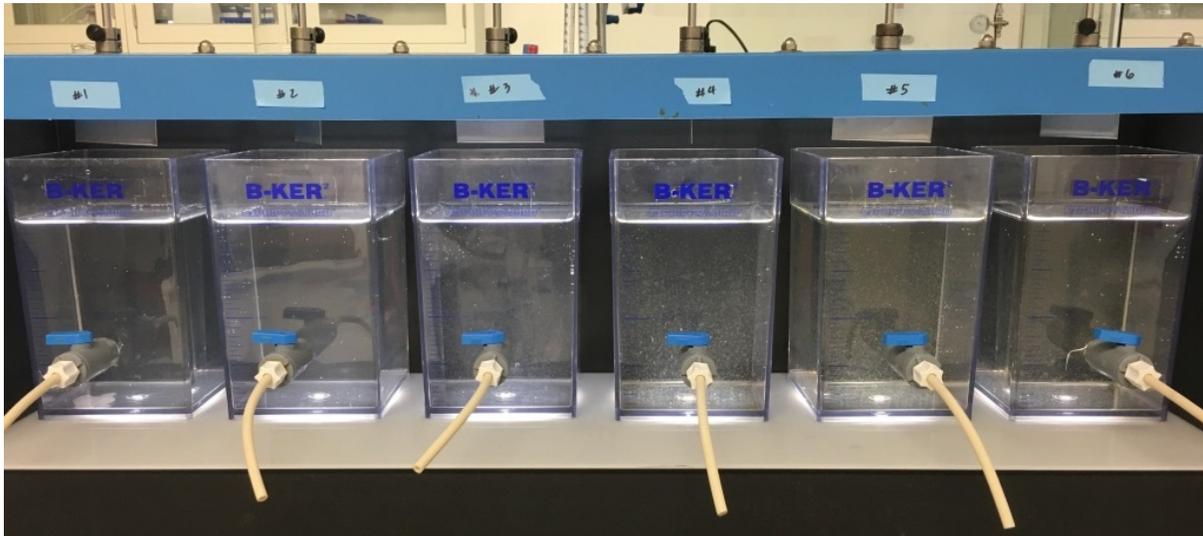
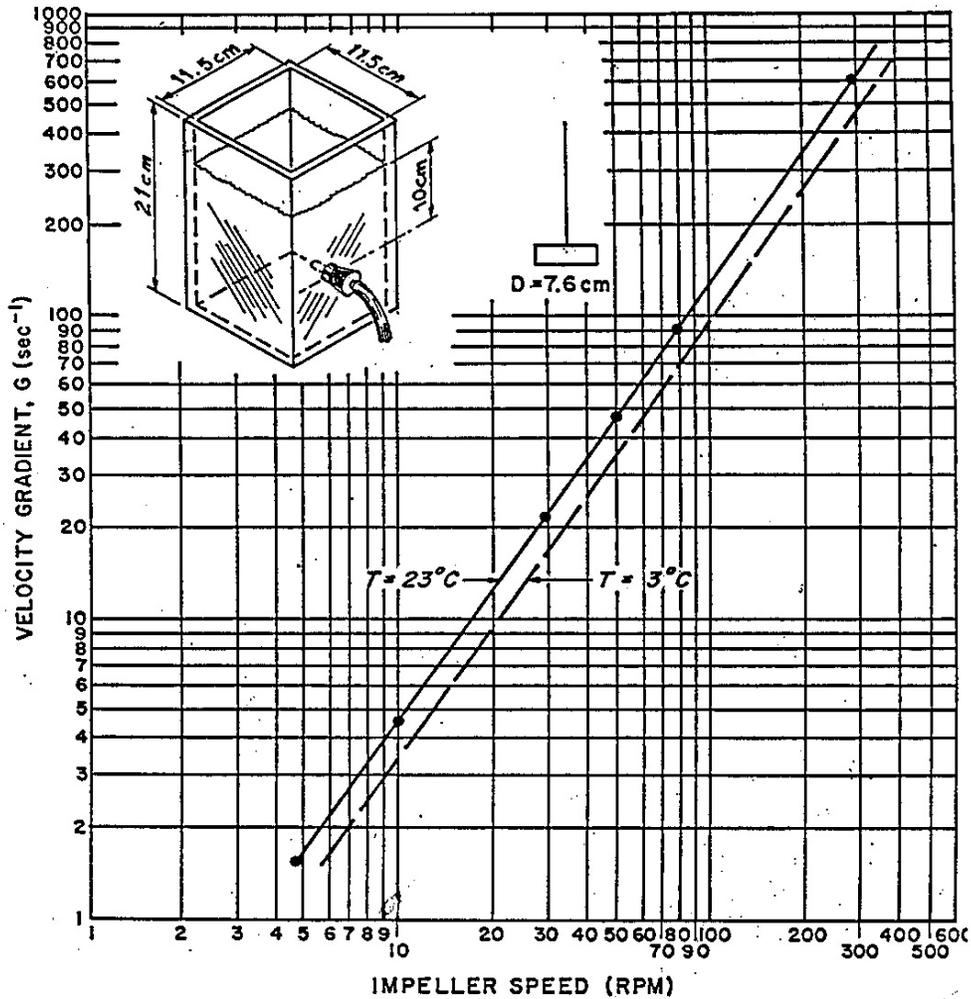


Figure 8-2. Phipps & Bird jar testing apparatus with B-KER² jars.

The procedures used for the jar tests followed generally accepted procedures as described in (Kawamura, 2000) and (AWWA, 2011), using square ‘gator’ jars—which Phipps & Bird calls the B-KER²—depicted in Figure 8-2. The mixing regime for all of the conventional coagulation and settling tests included rapid mix followed by four steps of tapered flocculation. The relationship between velocity gradient (G) and impeller speed for the Phipps & Bird mixer with B-KER² is shown in Figure 8-3. The maximum speed of the mixer was used for rapid mix for 1 minute. The velocity gradients used during tapered flocculation were 55, 40, 25, and 15 sec^{-1} , which correspond to mixing speeds of 55, 45, 33, and 22 rpm, respectively. Each step of tapered flocculation had a duration of 7.5 minutes for a total flocculation time of 30 minutes. Following coagulation, the water was allowed to settle for 30 minutes prior to sample collection. The sampling point was the same in all jars and was located 10 centimeters below the water surface.



LABORATORY G CURVES

Figure 8-3. G curves for Phipps & Bird 7.6-cm paddles and 2-liter B-KER² (AWWA, 2011)

A.4 Jar Test Procedure – Actiflo®

The final round of manganese removal testing incorporated the use of sand ballasted coagulation using Krüger’s Actiflo® Jar Test Procedure. Prior to the coagulation and settling stage (jar testing), the square ‘gator’ jars—which Phipps & Bird calls the B-KER²—depicted in Figure 8-2 were filled to the line (2000 mL) with the sample, and 5 grams of microsand provided by Krüger were added. The mixer was set to a maximum speed of 300 rpm for 2.0 minutes, and as the mixer was started the desired coagulant dose was simultaneously added. After 120 seconds, an anionic polymer (Section A.2) was added to one corner of the jars at a mixer speed of 300 rpm. At a time of 135 seconds, the mixer was reduced to 200 rpm for another 45 seconds, keeping the microsand in suspension. At a time of 180 seconds, the mixer was stopped and the floc was allowed to settle for 2.0 minutes prior to water quality sampling.

A.5 Solution Ozone Test

A modification of the solution ozone test (SOT) described by Rakness (2005) was used for bench scale ozone dosing and assessment of ozone demand. In brief, a stock ozone solution was prepared by bubbling ozone through deionized (DI) water. Oxygen was used as the feed gas for the ozone generator. Dry ice was packed around a custom-made ozone stock solution vessel to maintain a water temperature just below zero degrees Celsius for better gas transfer as ozone was bubbled in through a ceramic diffuser. The equipment setup for the SOT is shown in Figure 8-4. The resulting ozone stock solutions used for the SOT tests had very high ozone concentrations up to 90 mg/L of dissolved ozone. The SOT procedure delivers ozone in the form of an aqueous solution, rather than as a gas stream bubbled through the test sample. As a result, the applied ozone dose is the same as the transferred ozone dose, and ozone gas transfer efficiency is not a factor in determining ozone dose.

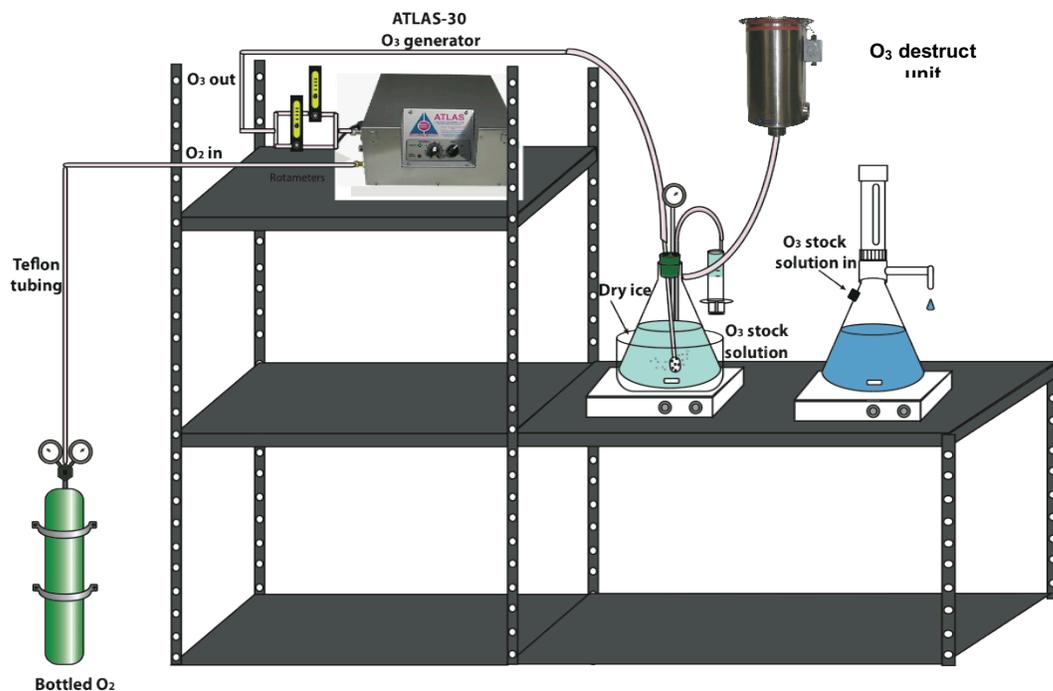


Figure 8-4. SOT apparatus

After bubbling ozone into the chilled DI water for at least 10 minutes to make the concentrated ozone solution, an aliquot of the ozone stock solution was removed using a glass syringe to measure the ozone concentration. The gravimetric indigo standard method (Rakness, 2005) was used for ozone analysis. The ozone stock solution was gradually added to a known volume (50 mL) of indigo solution using the syringe, and the



blue color of the indigo solution faded as it reacted with the ozone. Once the blue color was almost gone, the mass of the sample was measured for gravimetric determination of the ozonated solution volume dispensed into the indigo solution, and the residual indigo concentration was measured at 600 nanometers (nm) using the spectrophotometer. The ozone concentration of the stock solution was calculated from these measurements.

A.6 Ozone Decay

The ozone demand and decay coefficients of the water were determined using ozone decay curves. Once the concentration of the ozone stock solution was measured (Section 3.2), a known volume of the ozone stock solution was added to a known volume of sample, typically dosed as a ratio of ozone-to-TOC (e.g., 0.6 mg/L O₃ for each 1.0 mg/L TOC in the sample), and the sample was then stirred for about 10 seconds. The ozone residual was measured at the following time intervals (each in terms of time elapsed after the ozone dose was added): 30 seconds, then 1, 2, 3, 4, 5, and 6 minutes. The residual ozone was measured at each time interval by withdrawing an aliquot of the ozonated sample (using a dispenser system) into a small vial containing indigo solution and using the gravimetric indigo standard method described in Section A.4.

A.7 Analytical Methods

Eurofins Eaton Analytical Lab analyzed samples for TTHM, HAA₅, NDMA, total and dissolved manganese, iron, aluminum, bromide, and bromate. All other analyses were performed on-site at the TT Lab in Pasadena. The analytical methods implemented are shown in Table 8-2. Samples for DOC and UV-254 analysis were filtered through a 0.45-µm membrane filter prior to analysis.

Table 8-2. Analytical methods used during the jar tests.

Parameter	Method	Lab	Comments
pH	SM 4500-H+	TT	Hach IntelliCAL Standard pH probe
Temperature		TT	Digital thermometer
Turbidity	SM 2130	TT	HACH 2100AN
UV-254	SM 5910 B	TT	HACH DR5000. Samples were filtered using 0.45-µm filter before analysis.
Alkalinity	SM 2320	TT	Titration with 0.002N HCl



Parameter	Method	Lab	Comments
TOC	SM 5310C	TT	GE Sievers 5310C
DOC	SM 5310C	TT	GE Sievers 5310C. Sample filtered through a 0.45- μ m filter.
SDS DBP	SM 5710C	TT	Sample filtered through a 0.45- μ m Gelman Supor 450 (PES) membrane filter prior to setup for Round 4 only
TTHM	EPA 551.1	Eurofins	
HAA ₅	SM 6251B	Eurofins	
NDMA	EPA 521	Eurofins	
Free Chlorine	HACH 8021 (DPD Method)	TT	HACH DR900
Ammonia	EPA 350.1	TT	HACH DR900



Appendix B - Raw Water Quality Data Corresponding to Manganese Removal Bench-Tests

Table B-1 - Average¹ Raw Water Quality from Quarterly Tuolumne River Samples Collected for Seasonal Manganese Removal Tests

Parameter	Round 1 (Dec. 2016)	Round 2 (Mar. 2017)	Round 3 (Jun. 2017)	Round 4 (Oct. 2017)
Alkalinity (mg/L as CaCO ₃)	26	19	19	21
Turbidity (NTU)	1.24	8.80	1.09	1.30
pH	7.32	7.18	7.18	7.10
TOC (mg/L)	2.00	2.73	2.29	2.12
DOC (mg/L)	1.95	2.67	2.29	2.11
UV-254 (cm ⁻¹)	0.052	0.072	0.064	0.055
SUVA (L/mg•cm)	0.027	0.027	0.028	0.026
Total Mn (mg/L)	0.014	0.013	0.020	0.021
Mn, passes 0.45 µm filter (mg/L)	0.0054	<0.002	0.012	0.0036
Manganese, passes 30k Dalton filter (mg/L)	0.0052	0.0022	0.010	0.0043
Calculated Mn Speciation ² :				
Particulate Mn (mg/L)	0.0086	0.0110	0.0080	0.0174
Colloidal Mn (mg/L) ³	0.0002	0.0000	0.0020	0.0000
Sub-Colloidal Mn (mg/L)	0.0052	0.0022	0.010	0.0043

¹ Multiple (3 to 5) cubitainers of raw water were collected for each quarterly test. Averages were calculated for analyses made from each of the individual cubitainers.

² Particulate Mn = Total – Passes 0.45 µm filter
Colloidal Mn = Passes 0.45 µm filter – Passes 30kDa filter
Sub-Colloidal Mn = Passes 30kDa filter

³ Calculated negative values were replaced with 0.0000 and considered the result of acceptable analytical error.



Appendix C - Manganese Removal Testing Data

Round 1, Test 2 Results (Dec. 2016)

Mn²⁺ Spike → KMnO₄ → C/S

	1	2	3	4	5	6
Test Conditions						
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.300					
Initial Total Mn in raw water (mg/L)	0.014					
Initial TOC (mg/L)	2.04					
Oxidant – permanganate* (mg/L)	0.57				none	
Oxidant Contact Time (min)	5.00	1.00	5.00	1.00	5.00	5.00
Coagulant Type	Ferric	Ferric	Alum	Alum	Alum	Ferric
Coagulant Dose (mg/L)	7.90	7.90	14.60	14.60	14.60	7.90
Clarified Water TOC (mg/L)	1.47			1.36		
Results						
Clarified Water TOC (mg/L)	1.47	1.51	1.36	1.36	1.32	1.45
Final Total Mn (mg/L)	0.150	0.160	0.073	0.085	0.330	0.340
Passed 0.45 µm filter	0.017	0.018	0.007	0.023	0.310	0.320
Passed 30k Dalton filter	0.016	0.017	0.0075	0.023	0.300	0.310

*Permanganate added at 1 x stoichiometric amount required to oxidize Mn(II) to Mn (IV)

Round 1, Test 3 Results (Dec. 2016)

Mn²⁺ Spike → O₃ → C/S

	Preozonation Tests					
	1	2	3	4	5	6
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.3					
Initial Total Mn in raw water (mg/L)	0.014					
Initial TOC (mg/L)	2.04					
Target O3/TOC ratio	0.25			0.6		
Target O3 dose (mg/L)	0.51	0.51	0.51	1.22	1.22	1.22
Coagulant Type	Ferric	Ferric	Alum	Ferric	Ferric	Alum
Coagulant Dose (mg/L)	7.9	6.5	14.6	7.9	6.5	14.6
Results						
Final TOC (mg/L)	1.39	1.84	1.27	1.42	1.86	1.29
Final Total Mn (mg/L)	0.260	0.330	0.210	0.150	0.320	0.090
Passed 0.45 µm filter	0.230	0.230	0.190	0.080	0.090	0.034
Passed 30k Dalton filter	0.210	0.220	0.180	0.085	0.089	0.035

**Round 1, Test 4 Results (Dec. 2016)**Mn²⁺ Spike → KMnO₄ → C/S → O₃

Intermediate Ozonation Tests						
	1	2	3	4	5	6
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.3					
Initial Total Mn in raw water (mg/L)	0.014					
Oxidant - permanganate (mg/L); 5-min reaction time	0.567					
Coagulant Type	Ferric	Ferric	Ferric	Alum	Alum	Alum
Coagulant Dose (mg/L)	7.9	7.9	7.9	14.6	14.6	14.6
Clarified Water TOC (mg/L)	1.47	1.47	1.47	1.36	1.36	1.36
Target O ₃ /TOC ratio	0.4	0.6	0.8	0.4	0.6	0.8
Target O ₃ dose (mg/L)	0.588	0.88	1.18	0.54	0.82	1.09
Results						
Final Total Mn (mg/L)	0.140	0.140	0.140	0.110	0.098	0.084
Passed 0.45 µm filter	0.024	0.021	0.022	0.014	0.013	0.012
Passed 30k Dalton filter	0.028	0.021	0.020	0.015	0.011	0.011

Round 2, Test 3 (March 2017)Mn²⁺ Spike → O₃ → C/S

Test Conditions						
	1	2	3	4	5	6
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10					
Total Mn in raw water (mg/L)	0.12					
Mn in raw water passing through 0.45µm filter (mg/L)	0.10					
Mn in raw water passing through 30KDa filter (mg/L)	0.094					
Initial TOC (mg/L)	2.72	2.72	2.72	2.72	2.72	2.72
Target O ₃ /TOC ratio	0.25	0.6	1.0	0.25	0.6	1.0
Target O ₃ dose (mg/L)	0.68	1.632	2.72	0.68	1.632	2.72
Coagulant Type	Alum	Alum	Alum	PACl	PACl	PACl
Coagulant Dose (mg/L)	11.9	11.9	11.9	11.9	11.9	11.9
Results						
Final TOC (mg/L)	1.86	1.82	1.81	1.92	1.88	1.84
Final Total Mn (mg/L)	0.090	0.091	0.097	0.089	0.085	0.091
Passed 0.45 µm filter	0.080	0.084	0.092	0.080	0.082	0.093
Passed 30k Dalton filter	0.077	0.081	0.094	0.081	0.081	0.092



Round 2, Test 4 (March 2017)

Mn²⁺ Spike → KMnO₄ → C/S → O₃

Test Conditions						
	1	2	3	4	5	6
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10					
Total Mn in raw water (mg/L)	0.12					
Mn in raw water passing through 0.45um filter (mg/L)	0.10					
Mn in raw water passing through 30KDa filter (mg/L)	0.094					
Oxidant Dose as KMnO ₄ (mg/L)*	0.326	0.326	0.326	None		
Oxidant Contact Time (min)	56.0	56.0	56.0	None		
TOC of CS water (mg/L)	1.85	1.85	1.85	1.74	1.74	1.74
Target O ₃ /TOC ratio	0.25	0.6	1.0	0.25	0.6	1.0
Target O ₃ dose (mg/L)	0.46	1.11	1.85	0.44	1.04	1.74
Coagulant Type	Alum	Alum	Alum	Alum	Alum	Alum
Coagulant Dose (mg/L)	11.9	11.9	11.9	11.9	11.9	11.9
Results - Combined CS water (with KMnO ₄ and without KMnO ₄) into two containers						
Final Total Mn (mg/L)	0.059	0.056	0.055	0.100	0.099	0.098
Passed 0.45 µm filter	0.008	0.010	0.009	0.038	0.039	0.057
Passed 30k Dalton filter	0.010	0.009	0.008	0.027	0.022	0.033



Round 2, Test 5 (March 2017)

Mn²⁺ Spike → KMnO₄ → C/S → O₃

Test Conditions						
	1	2	3	4	5	6
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10					
Total Mn in raw water (mg/L)	0.12					
Mn in raw water passing through 0.45um filter (mg/L)	0.10					
Mn in raw water passing through 30KDa filter (mg/L)	0.094					
Oxidant Dose as KMnO ₄ (mg/L)*	0.326	0.326	0.326	None		
Oxidant Contact Time (min)	20.0	20.0	20.0	None		
TOC of CS water (mg/L)	2.14	2.14	2.14	1.98	1.98	1.98
Target O ₃ /TOC ratio	0.25	0.6	1.0	0.25	0.6	1.0
Target O ₃ dose (mg/L)	0.54	1.284	2.14	0.50	1.19	1.98
Coagulant Type	PACl	PACl	PACl	PACl	PACl	PACl
Coagulant Dose (mg/L)	11.9	11.9	11.9	11.9	11.9	11.9
Results - Combined CS water (with KMnO ₄ and without KMnO ₄) into two containers						
Final Total Mn (mg/L)	0.080	0.078	0.074	0.097	0.100	0.093
Passed 0.45 µm filter	0.007	0.006	0.007	0.023	0.040	0.044
Passed 30k Dalton filter	0.008	0.006	0.006	0.015	0.026	0.032

Round 3, Test 2 (Aug. 2017)

O₃ → C/S

Test Conditions				
	1	2	7	8
Total Mn in raw water (mg/L)	0.02			
Mn in raw water passing through 0.45um filter (mg/L)	0.012			
Mn in raw water passing through 30KDa filter (mg/L)	0.010			
Initial TOC (mg/L)	2.22	2.22	2.22	2.22
Target O ₃ /TOC ratio	0.25	0.5	1.0	2.0
Target O ₃ dose (mg/L)	0.555	1.11	2.22	4.44
Coagulant Type	Alum	Alum	PACl	PACl
Coagulant Dose (mg/L)	19.9	19.9	19.9	19.9
Results				
Final TOC (mg/L)	1.37	1.26	1.63	1.7
Final Total Mn (mg/L)	0.015	0.012	0.012	0.012
Passed 0.45 µm filter	0.012	0.011	0.0098	0.011
Passed 30k Dalton filter	0.012	0.010	0.0095	0.011

**Round 3, Test 3 (Aug. 2017)**Mn²⁺ Spike → O₃ → C/S

Test Conditions				
	1	2	3	4
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10			
Total Mn in raw water (mg/L)	0.12			
Mn in raw water passing through 0.45um filter (mg/L)	0.093			
Mn in raw water passing through 30KDa filter (mg/L)	0.087			
Initial TOC (mg/L)	2.28	2.28	2.28	2.28
Target O3/TOC ratio	0.25	0.5	1.0	2.0
Target O3 dose (mg/L)	0.57	1.14	2.28	4.56
Coagulant Type	Alum	Alum	Alum	Alum
Coagulant Dose (mg/L)	19.911	19.911	19.911	19.911
Results				
Final TOC (mg/L)	1.38	1.37	1.37	1.33
Final Total Mn (mg/L)	0.069	0.070	0.080	0.083
Passed 0.45 µm filter	0.063	0.061	0.075	0.078
Passed 30k Dalton filter	0.059	0.057	0.071	0.073

Round 3, Test 4 (Aug. 2017)Mn²⁺ Spike → O₃ → KMnO₄ → C/S

Test Conditions						
	1	2	3	4	5	6
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10					
Total Mn in raw water (mg/L)	0.12					
Mn in raw water passing through 0.45um filter (mg/L)	0.093					
Mn in raw water passing through 30KDa filter (mg/L)	0.087					
Initial TOC (mg/L)	2.21	2.21	2.21	2.21	2.21	2.21
Target O3/TOC ratio	0.25	0.5	1.0	1.0	1.0	2.0
Target O3 dose (mg/L)	0.553	1.105	2.21	2.21	2.21	4.42
Oxidant Dose (relative to stoichiometry)	0.5	0.5	0.5	0.25	0.75	0.5
Oxidant (KMnO ₄) /TOC dose (mg/L)	0.096	0.096	0.096	0.048	0.144	0.096
Coagulant Type	Alum	Alum	Alum	Alum	Alum	Alum
Coagulant Dose (mg/L)	14.6	14.6	14.6	14.6	14.6	14.6
Results						
Final TOC (mg/L)	1.33	1.34	1.30	1.36	1.28	1.18
Final Total Mn (mg/L)	0.064	0.08	0.110	0.100	0.100	0.12
Passed 0.45 µm filter	0.050	0.065	0.100	0.100	0.090	0.11
Passed 30k Dalton filter	0.049	0.062	0.100	0.095	0.086	0.11



Round 3, Test 5 (Aug. 2017)

Mn²⁺ Spike → KMnO₄ → O₃ → C/S

Test Conditions				
	1	2	3	4
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10			
Total Mn in raw water (mg/L)	0.12			
Mn in raw water passing through 0.45um filter (mg/L)	0.093			
Mn in raw water passing through 30KDa filter (mg/L)	0.087			
Initial TOC (mg/L)	2.30	2.30	2.30	2.30
Target O ₃ /TOC ratio	0.25	0.5	1.0	2.0
Target O ₃ dose (mg/L)	0.575	1.15	2.3	4.6
Coagulant Type	Alum	Alum	Alum	Alum
Coagulant Dose (mg/L)	14.6	14.6	14.6	14.6
Results				
Final TOC (mg/L)	1.21	1.22	1.19	1.14
Final Total Mn (mg/L)	0.096	0.12	0.120	0.082
Passed 0.45 µm filter	0.070	0.091	0.097	0.052
Passed 30k Dalton filter	0.069	0.088	0.094	0.05

Round 3, Test 6 (Aug. 2017)

Mn²⁺ Spike → O₃ → KMnO₄ → C/S

Test Conditions		
	1	2
Initial Total Mn - spiked with Mn ²⁺	0.10	
Total Mn in raw water (mg/L)	0.12	
Mn in raw water passing through 0.45um filter (mg/L)	0.093	
Mn in raw water passing through 30KDa filter (mg/L)	0.087	
Initial TOC (mg/L)	2.31	2.31
Target O ₃ /TOC ratio	1.0	1.0
Target O ₃ dose (mg/L)	2.31	2.31
Oxidant Dose (relative to stoichiometry)	0.75	0.75
Oxidant Dose as KMnO ₄ (mg/L as KMnO ₄)	0.144	0.144
Oxidant Dose as KMnO ₄ (mg/L as Mn)	0.050	0.050
Total Mn after KMnO ₄ addition (mg/L)	0.170	
Mn after KMnO ₄ passing through 0.45 µm filter	0.143	
Mn after KMnO ₄ passing through 30k Dalton filter	0.137	
Oxidant (KMnO ₄) Contact Time (min)	5.0	0.0
Coagulant Type	Alum	Alum
Coagulant Dose (mg/L)	14.6	14.6
Results		
Final TOC (mg/L)	1.18	1.17
Final Total Mn (mg/L)	0.092	0.095
Passed 0.45 µm filter	0.073	0.072
Passed 30k Dalton filter	0.071	0.066

**Round 3, Test 7 (Aug. 2017)**C/S → O₃

Test Conditions				
	1	2	3	4
Total Mn in raw water (mg/L)	0.02			
Mn in raw water passing through 0.45um filter (mg/L)	0.012			
Mn in raw water passing through 30KDa filter (mg/L)	0.010			
Initial TOC (mg/L)	2.29	2.29	2.29	2.29
Target O3/TOC ratio *	0.927	1.767	0.857	1.689
Target O3 dose (mg/L)	2.122	4.047	1.963	3.868
Coagulant Type	Alum	Alum	PACI	PACI
Coagulant Dose (mg/L)	14.6	14.6	14.5	14.5
Results				
Final TOC (mg/L)	1.23	1.29	1.33	1.35
Final Total Mn (mg/L)	0.005	0.0051	0.006	0.0069
Passed 0.45 µm filter	0.004	0.0046	0.005	0.0036
Passed 30k Dalton filter	0.005	0.0058	0.007	0.0037

*Adjusted O3:TOC dose ratio according to TOC of C/S water

Round 4, Test 3 (Oct. 2017)Mn²⁺ Spike → KMnO₄ → Actiflo C/S → O₃

Test Conditions				
	1	2	3	4
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10			
Total Mn in raw water (mg/L)	0.120			
Mn in raw water passing through 0.45um filter (mg/L)	0.096			
Mn in raw water passing through 30KDa filter (mg/L)	0.093			
Initial TOC (mg/L)	2.12			
Coagulant Type	Alum	Alum	Alum	Alum
Coagulant Dose (mg/L)	20.5	20.5	20.5	20.5
Target O3/TOC ratio	0.60	0.60	0.60	0.60
Target O3 dose (mg/L)	0.77	0.77	0.77	0.77
Results				
Final Total Mn (mg/L)	0.170	0.200	0.200	0.200
Passed 0.45 µm filter	0.006	0.017	0.027	0.022
Passed 30k Dalton filter	0.006	0.016	0.000	0.000



Round 4, Test 4 (Oct. 2017)

Mn²⁺ Spike → KMnO₄ → Actiflo C/S → O₃

Test Conditions				
	1	2	3	4
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10			
Total Mn in raw water (mg/L)	0.120			
Mn in raw water passing through 0.45um filter (mg/L)	0.096			
Mn in raw water passing through 30KDa filter (mg/L)	0.093			
Initial TOC (mg/L)	2.123			
KMnO ₄ Contact Time (min)	56	5	1	0
Coagulant Type	PACI	PACI	PACI	PACI
Coagulant Dose (mg/L)	20.5	20.5	20.5	20.5
Target O ₃ /TOC ratio	0.60	0.60	0.60	0.60
Target O ₃ dose (mg/L)	0.77	0.77	0.77	0.77
Results				
Final Total Mn (mg/L)	0.200	0.190	0.200	0.200
Passed 0.45 µm filter	0.009	0.018	0.039	0.029
Passed 30k Dalton filter	0.000	0.018	0.000	0.000

Round 4, Test 5 (Oct. 2017)

Mn²⁺ Spike → KMnO₄ → C/S → O₃

Test Conditions						
	1	2	3	4	5	6
Initial Total Mn - spiked with Mn ²⁺ (mg/L)	0.10					
Total Mn in raw water (mg/L)	0.100					
Mn in raw water passing through 0.45um filter (mg/L)	0.120					
Mn in raw water passing through 30KDa filter (mg/L)	0.096					
Initial TOC (mg/L)	0.093					
KMnO ₄ Contact Time (min)	56	5	0	56	5	0
Target O ₃ /TOC ratio	0.60	0.60	0.60	0.60	0.60	0.60
Target O ₃ dose (mg/L)	0.77	0.77	0.77	0.77	0.77	0.77
Coagulant Type	Alum	Alum	Alum	PACI	PACI	PACI
Coagulant Dose (mg/L)	20.5	20.5	20.5	20.5	20.5	20.5
Results						
Final Total Mn (mg/L)	0.033	0.051	0.130	0.160	0.180	0.130
Passed 0.45 µm filter	0.006	0.015	0.007	0.008	0.016	0.015
Passed 30k Dalton filter	0.000	0.014	0.000	0.000	0.016	0.000