Reconsidering Ozone as an Oxidant in Manganese Treatment

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OUTLINE

Fe and Mn Chemistry

Mn Treatment Theory

2 Case Studies

Conclusions

Thoughts and Observations

CHEMISTRY

Iron and Manganese are generally found in groundwater as Fe^{+2} and Mn^{+2}; both species generally form soluble complexes.

Untreated Fe and Mn become problematic when oxidized into species that form insoluble complexes.

CHEMISTRY

Iron oxidizes quite easily from Fe^{+2} to Fe^{+3}.

$$2Fe^{+2} + 1/2O_2 + 5H_2O \rightarrow 2Fe(OH)_{3(s)} + 4H^+$$

Fe oxidation forms common rust.

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CHEMISTRY

Manganese oxidation is thermodynamically favored but kinetically slow, unless in the presence of a catalyst, such as MnO_2.

$$Mn^{+2} + 1/2O_2 + H_2O \rightarrow MnO_{2(s)} + 2H^+ \text{ (Slow)}$$

$$Mn^{+2} + 1/2O_2 + H_2O \xrightarrow{MnO_2} MnO_2(s) + 2H^+ \text{ (Fast)}$$

MnO_2 is a black precipitate.

Mn TREATMENT

Fe and Mn treatment by oxidation/filtration involves oxidizing to form the insoluble species and capturing those insoluble species on filter media.

Since Mn oxidation requires catalysis, filtration media with a MnO_2 surface is used.

- Greensand
- Greensand Plus®
- Birm®
- MTM®
- Pyrolusite

Mn TREATMENT - OXIDATION

Oxidant	Half Reaction	E^o, Volts
Ozone	$1/2\ O_{3(aq)} + H^+ + e^- \rightarrow 1/2\ O_{2(aq)} + 1/2\ H_2O$	2.04
Hydrogen Peroxide	$1/2\ H_2O_2 + H^+ + e^- \rightarrow H_2O$	1.78
Permanganate	$1/3\ MnO_4^- + 4/3\ H^+ + e^- \rightarrow 1/3\ MnO_2 + 2/3\ H_2O$	1.68
Hypochlorous Acid	$1/2\ HOCl + 1/2\ H^+ + e^- \rightarrow 1/2\ Cl^- + 1/2\ H_2O$	1.49
Oxygen	$1/4\ O_{2(aq)} + H^+ + e^- \rightarrow 1/2\ H_2O$	1.27

Relative Oxidant Strength

$$\mathbf{O_3} > \mathbf{H_2O_2} > MnO_4^- > HOCl > O_2$$

Ozone is stronger than the other commonly used oxidants.

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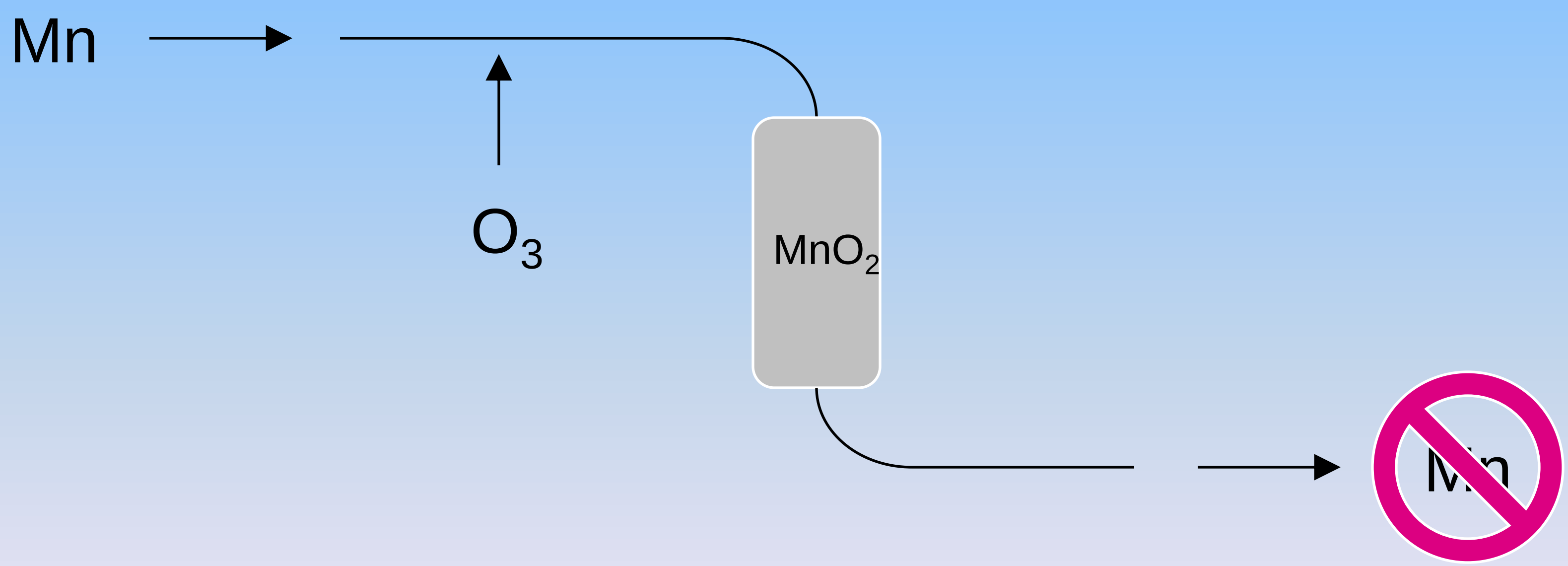
Mn TREATMENT

Theoretically, coupling ozone with a catalytic media should provide good manganese removal.



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CASE STUDY 1 - BACKGROUND

City of Snoqualmie

Existing iron and manganese treatment facility (Ozone/Birm®)

Served by three wells

1,100 gpm

Startup in 1997

Planned expansion to 1,650 gpm

City wanted to revisit technology due to maintenance and taste and odor issues.

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RAW WATER QUALITY

Water Quality Parameter	Average Value	MCL	Range of Values
Manganese	0.143 mg/L	0.05 mg/L	0.117 – 0.191 mg/L
Ammonia	0.19 mg/L	NA	NA
Iron	0.128 mg/L	0.3 mg/L	0.069 –0.199 mg/L
Arsenic	0.013 mg/L	0.010 mg/L	0.011 – 0.015 mg/L

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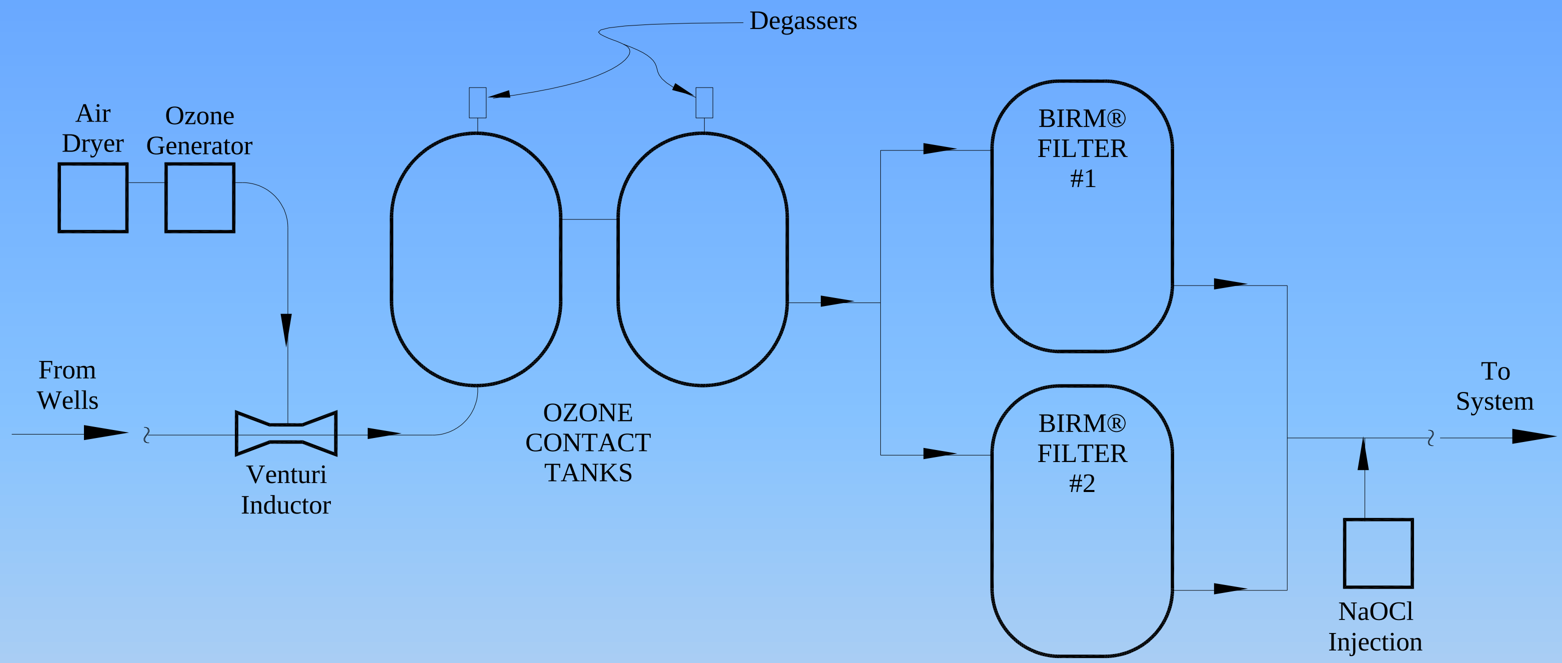
EXISTING PLANT



Parameter	Value
Ozone Dose	0.65 mg/L
Ozone Contact Tanks per Train	2
Total Ozone Contact Time	6.5 minutes
Filter Media	Birm®
Number of Filter Tanks per Train	2
Filter Loading Rate	3.5 gpm/square foot

EXISTING PLANT

Ozone Contact Tanks

Filter Units

TASTE AND ODOR ISSUES

Customer complaints & survey - Unsatisfactory taste and smell over 50% of the Time

Dirty	Earthy	Algae-like
Sour	Chlorinous	

Staff noted musty backwash odor and biofilm in ozone contact tanks and filters.

Lab analysis confirmed presence.

- Iron Bacteria (*Gallionella ferruginea*)
- Sulfur Bacteria (*Thiodendron mucosum*)
- Protozoa
- Larval Crustaceans
- Nematodes

BIOFILM GROWTH

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INITIAL INVESTIGATION

Initial investigation focused on ozone performance.

Ozone nameplate capacity – 0.65 mg/L

Post injector ozone concentration – 0.1 mg/L

Post ozone contactor concentration – 0 mg/L

Hypothesis: Insufficient ozone dose in ozone contact tanks allowed biogrowth to occur.

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FULL-SCALE OZONE INVESTIGATION

Bench-scale tests indicated 1.1 mg/L dose required.

Additional ozone equipment rented

- Ozone dose – 1.1 mg/L (0.65 mg/L Pre-test)
- Post injector ozone concentration – 0.4 mg/L (0.1 mg/L)
- Post ozone contactor concentration – 0.1 mg/L (0 mg/L)

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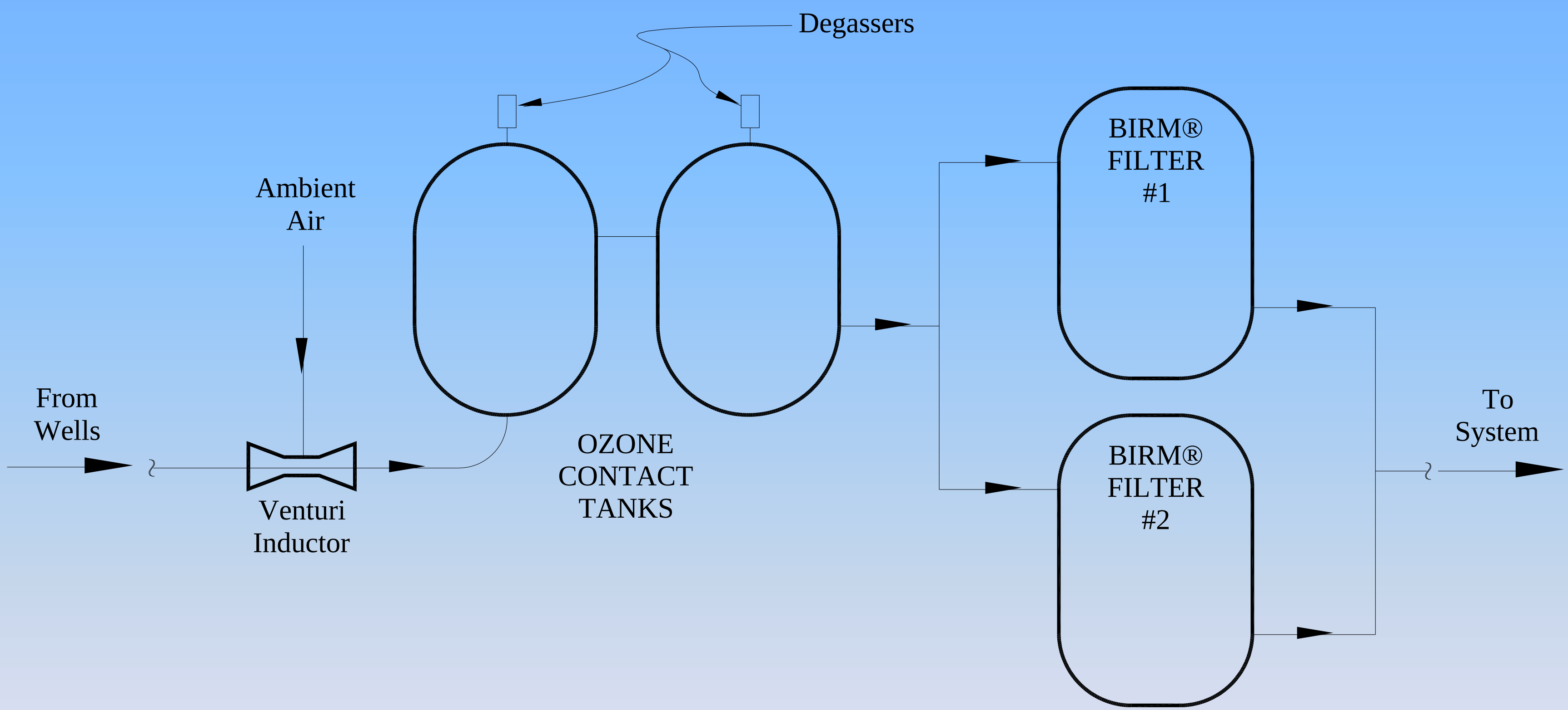
FULL-SCALE OZONE INVESTIGATION

Increased ozone improved water quality

- Fewer customer complaints – Not totally eliminated
- No biofilm present
- Staff noted backwash musty odor diminished

But we wanted to know what would happen if…..

… ambient air injected at venturi instead of ozone?



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EXISTING PLANT

Venturi Inductor for Ambient Air

ADDITIONAL FULL-SCALE INVESTIGATION

Results of ambient air injection test

Customer complaints decreased compared with ozone.

Biofilm present but no musty odor.

Iron and manganese removal <u>same</u> as with ozone.

COMPARISON OF TREATMENT TECHNOLOGIES

Process	Manganese Removal
0.65 mg/L Ozone and Birm® (Historical)	82%
1.1 mg/L Ozone and Birm® (Full Scale Pilot)	93%
Ambient Air and Birm® (Full Scale Pilot)	93%

The City operated the plant for several months with only ambient air until the technology was replaced with hypochlorite and pyrolusite.

CASE STUDY 2 - BACKGROUND

North Beach Water District

Small SW Washington System with 2 Wellfields

North Wellfield – 8 Wells (Study Focus)

South Wellfield – 2 Wells

Fe, Mn, and some As

Ozone, Polymer, and MTM® Filtration

Bromate is a concern, as are operations and maintenance costs.

CASE STUDY 2 – RAW WATER QUALITY

Well	Iron, mg/L	Manganese, mg/L	Arsenic, mg/L	Bromide, mg/L
North 1	0.15	0.069	0.010	ND
North 2	0.97	0.090	0.010	0.166
North 3	2.09	0.25	NA	0.195
North 4	0.25	0.058	0.015	0.177
North 5	0.20	0.085	0.014	0.174
North 6	0.84	0.022	0.008	0.166
North 7	0.40	0.073	0.009	ND
North 8	0.36	0.070	NA	0.163
MCL	**0.30**	**0.05**	**0.01**	**NA**

CASE STUDY 2 - BACKGROUND

Airsep Oxygen Generator

5 Ozonation Stations

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CASE STUDY 2 - BACKGROUND

4 Treatment Trains

(1 Contact Tank, 3 Parallel Filters each)

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CASE STUDY 2 – HISTORICAL Fe PERFORMANCE
May – October 2011

Treatment Train	Wells Treated	Raw Water Iron, mg/L	Finished Water Iron, mg/L	Removal
1	7	0.40	0.018	96%
2	3	2.1	0.029	99%
2	4	0.25	0.019	93%
3	6	0.84	0.043	95%
3	8	0.36	0.050	86%
3	6 & 8	0.59	0.057	90%
4	1 & 2	1.4	0.045	97%
4	2	0.97	0.029	97%

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CASE STUDY 2 – HISTORICAL Mn PERFORMANCE
May – October 2011

Treatment Train	Wells Treated	Raw Water Manganese, mg/L	Finished Water Manganese, mg/L	Removal
1	7	0.072	0.0079	89%
2	3	0.27	0.044	84%
2	4	0.058	0.027	53%
3	6	0.22	0.036	83%
3	8	0.074	0.010	86%
3	6 & 8	0.14	0.034	76%
4	1 & 2	0.058	0.025	58%
4	2	0.091	0.028	70%

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CASE STUDY 2 – HISTORICAL OZONATOR PERFORMANCE – DECEMBER 2011

Well	Ozone Station	Nominal O_3 Dose, mg/L	Measured O_3 after Injector, mg/L	Measured O_3 after Contact Tank, mg/L	Measured O_3 after Filters, mg/L	Raw Water Iron, mg/L	Finished Water Iron, mg/L
3	3	2.7	0.10	0.05	0	2.39	0.1
4	2	1.6	0.71	0.64	0.01	0.29	0.02
5	2	1.6	0.59	0.04	0	0.10	0
6	4	1.8	0.78	0.75	0	0.85	0.04
7	1	1.4	0	0	0	NA	0
8	4	2.0	0.97	0.9	0.15	0.22	0.01

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PILOT STUDY – INITIAL PHASE

Goal – Investigate the effectiveness of each treatment step

- Oxidant
  - Ozone
  - Oxygen (Air prep on/ozonator off)
  - Ambient Air
- Polymer on/off
- Filtration

Started on two well schemes

- Well 3 (Highest Fe & Mn)
- Wells 6 & 8 (Highest Combined Flow)

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CASE STUDY 2 – INITIAL PILOT WORK

Oxidant	Polymer	Raw, mg/L or SCU			Finished, mg/L or SCU			Ozone, mg/L		
		Fe	Mn	Color	Fe	Mn	Color	Injector	Post-Contact	Post-Filter
Well 3, Ozone Station 3, Filter Train 2										
Ozone	Yes	2.27	0.276	4	0	0.001	0	-	0	-
Ozone	No				0.040	0.007	0	0	-	0
O_2	Yes				0	0.011	0	-	-	-
O_2	No	2.35	0.278	0	0.010	0.010	0	-	-	-
Air	Yes	2.34	0.273	12	0	0.015	6	-	-	-
Air	No				0	0.009	8	-	-	-
Wells 6/8, Ozone Station 4, Filter Train 3										
Ozone	Yes	0.61	0.132	7	0.07	0.040	3.5	-	0.03	0.015
Ozone	No				0.21	0.066	14	0. 31	0.1	0.04
O_2	Yes				0.01	0.008	6	-	-	-
O_2	No	0.60	0.141	8	0.01	0.003	13	-	-	-
Air	Yes	0.63	0.140	15	0	0.01	14	-	-	-
Air	No				0	0	5	-	-	-

PILOT STUDY – INITIAL PILOT RESULTS

Well 3

Fe – Air and O_2 removed better than O_3.

Mn – O_3 removed better than air or O_2 but all showed good removal.

Wells 6 & 8

Fe & Mn – Air and O_2 removed better than O_3.

Polymer use slightly beneficial only with O_3 but not air or O_2.

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PILOT STUDY – SECOND PHASE

24 Hour Test for Each Well

Well No.	Iron, mg/L		
	Average Raw	Average Finished	% Removal
1	0.60	0.01	98%
2	1.12	0.01	99%
3	2.40	0.27	89%
4	0.27	0.03	89%
5	0.07	0.01	86%
7	0.23	0.02	91%
6&8	0.73	0.04	95%

PILOT STUDY – SECOND PHASE

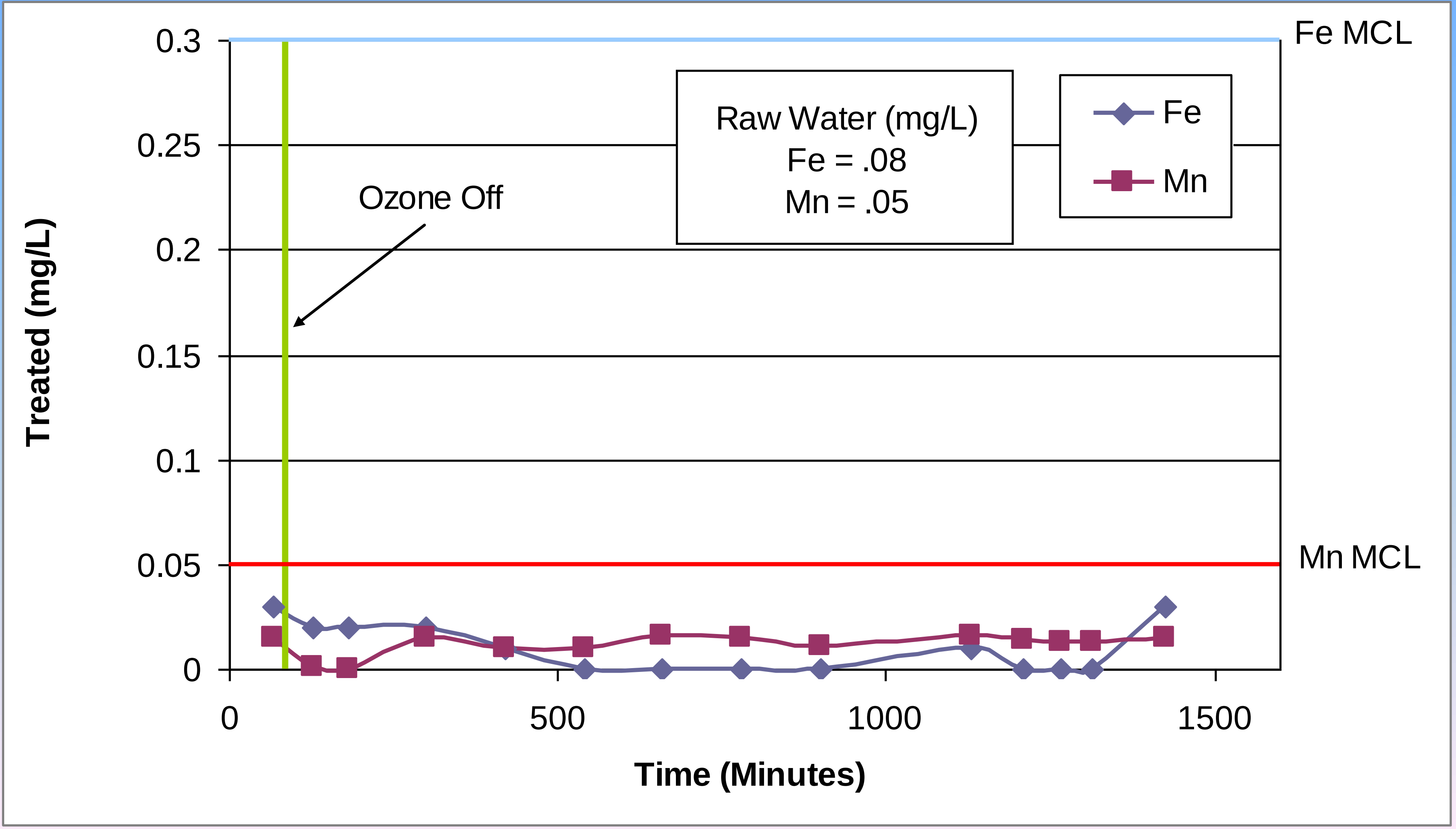
24 Hour Test for Each Well

Well No.	Manganese, mg/L		
	Average Raw	Average Finished	% Removal
1	0.018	0.002	89%
2	0.121	0.001	99%
3	0.285	0.155	46%
4	0.028	0.015	46%
5	0.058	0.012	79%
7	0.050	0.005	90%
6&8	0.140	0.000	100%

Generally good removal except for Well 3.

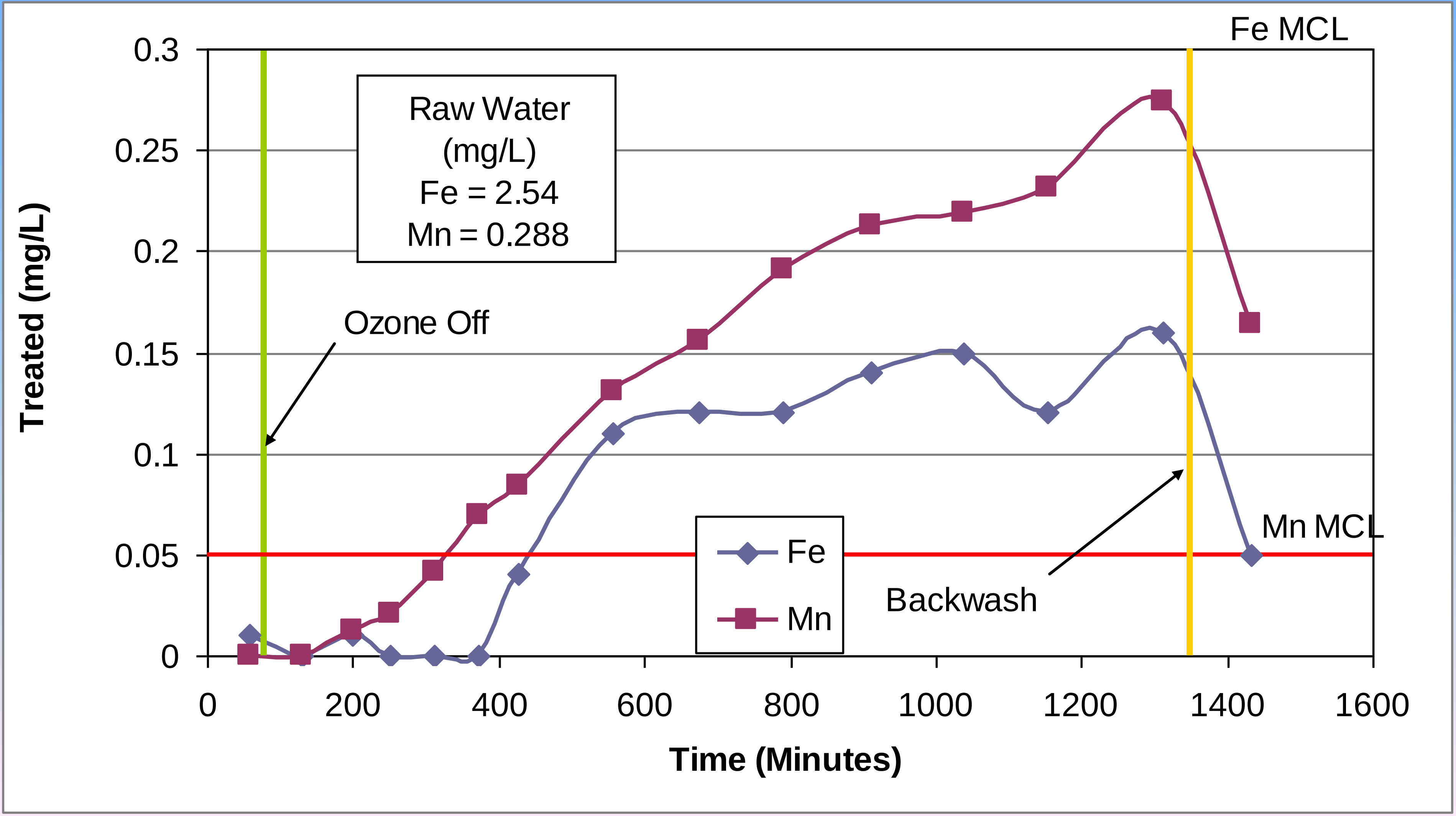
PILOT STUDY – SECOND PHASE

Well 5 results typical (except for Well 3).



PILOT STUDY – SECOND PHASE

Well 3 treatment degraded steadily over time.



PILOT STUDY – COMPARISON

Comparison of Historical Ozone Data and 24-Hour Ambient Air Test

Well No.	Historical Mn Removal with Ozone	24-Hour Test Mn Removal with Ambient Air
2	70%	99%
3	**84%**	**46%**
4	53%	46%
7	89%	90%
6&8	76%	100%

Generally, Mn removal is as good or better with ambient air compared to ozone, except for Well 3.

Iron results were generally similar for either oxidant.

Taste and odors and arsenic removal comparable with either oxidant.

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CONCLUSIONS

In many instances, ambient air injection can provide Mn (and Fe) removal as good or better than ozone.

The only significant exception in the case studies was Well 3 with much higher levels of raw water iron and manganese (2.09 mg/L and 0.25 mg/L, respectively).

Ambient air injection could provide an alternative oxidant in existing systems to ozone, providing lower maintenance and energy costs.

THOUGHTS AND OBERVATIONS

Since ozone is a strong oxidant, there are likely several competing reactions that influence ozone demand.

Most ozone-based oxidation/filtration systems have contact tanks, afterwhich there is little ozone residual remaining. Consequently, any oxidation of Mn by the catalytic media in the filter vessel does not use ozone as the oxidant.

Ozone can oxidize MnO_2 further to MnO_4^- affecting the catalytic surface.

QUESTIONS?

Thanks to:

City of Snoqualmie

North Beach Water District

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