

Seminole County Markham Regional Water Treatment Plant: Regulatory Compliance Considerations, Treatment Challenges, and Solutions

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Hydrogen sulfide (H₂S), is now regulated by the Florida Department of Environmental Protection (FDEP), and can lead to taste and odor complaints in the distribution system. Ozone (O₃) oxidation was selected by Seminole County as the preferred treatment process to oxidize H₂S from the groundwater supply wells. The H₂S reduction will reduce the amount of applied chlorine, which will reduce trihalomethane (THM) formation. The THM reduction will have the

added benefit of potentially mitigating Stage II disinfection byproducts (DBP) requirements.

Pilot-scale testing of a hybrid side stream ozone application to oxidize H₂S, thereby resulting in reduced chlorine dosage and disinfection byproducts, was performed at the 17-mgd Markham Regional Water Treatment Plant in Seminole County. The objective of the pilot study was to develop ozone design criteria for a hybrid side stream ozone injection system to be designed and constructed.

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Table 1. Florida Department of Environmental Protection Chapter 62-555.320 Total Sulfide Treatment Recommendations

Potential for Impacts without Total Sulfide Removal	Source Water Sulfide Level	Potential Water Treatment Technique
Low	Total Sulfide (TS) < 0.3 mg/L; or Dissolved Iron (DI) < 0.1 mg/L ¹	Direct chlorination ²
Moderate	0.3 mg/L ≤ TS ≤ 0.6 mg/L @ pH ≤ 7.2	Conventional aeration ³ (maximum removal efficiency ≈ 40% to 50%)
	0.3 mg/L ≤ TS ≤ 0.6 mg/L @ pH > 7.2	Conventional aeration with pH adjustment (maximum removal efficiency ≈ 40% to 50%)
Significant	0.6 mg/L ≤ TS ≤ 3.0 mg/L @ pH ≤ 7.2	Forced Draft Aeration ³ (maximum removal efficiency ≈ 90%)
	0.6 mg/L ≤ TS ≤ 3.0 mg/L @ pH > 7.2	Forced Draft Aeration with pH adjustment ^{4, 5} (maximum removal efficiency ≈ 90%)
Very Significant	TS > 3.0 mg/L	Packed Tower Aeration with pH adjustment ^{4, 5} (maximum removal efficiency ≈ 90%)

Note: These recommendations are to be used as guidance and not as a requirement.

- High iron content raises concern if chlorination alone is used and significant dissolved oxygen exists in the source water. Filtration may be required to remove particulate iron prior to water distribution.
- Direct chlorination of sulfide in water in the pH range normally found in potable sources produces S₀(s) and increased turbidity. Finished-water turbidity should not be more than two nephelometric turbidity units (NTU) greater than raw-water turbidity.
- Increased dissolved oxygen entrained during aeration may increase corrosivity.
- Reduction of alkalinity during pH adjustment and high dissolved oxygen entrained during aeration may increase corrosivity. Corrosion control treatment such as pH adjustment, alkalinity recovery, or use of inhibitors may be required.
- High alkalinity will make pH adjustment more costly, and use of other treatment may be in order. Treatment that preserves the natural alkalinity of the source water may enhance the stability of finished water.

Ozone demonstration testing was conducted for three individual wells and three well blend combinations. Testing was performed at low and high ozone dosages. The goals of the O₃ testing were to provide design constraints and demonstrate whether the water quality compliance requirements to reduce sulfide and control disinfection byproducts (DBPs) can be achieved. The following tasks were performed:

- Designed and constructed a mobile side stream O₃ injection system with a 10-min O₃ dissipation contact vessel.
- Verified O₃ dosage.
- Confirmed O₃ dissipation rates.
- Evaluated THM formation potential (THMFP) and bromate formation potential.
- Evaluated chlorine demand and decay of ozonated water.
- Determined viability of using oxidation-reduction potential (ORP) in a feedback control loop to control O₃ feed rates for a hybrid side stream O₃ injection system.
- Recommended whether total organic carbon (TOC) removal is necessary for disinfection byproduct (DBP) control.

On-site demonstration testing of a hybrid side stream O₃ application to oxidize (H₂S) was performed on the Seminole County Markham Regional Water Treatment Plant wellfield. The purpose of ozone is to oxidize hydrogen sulfide (H₂S), thereby resulting in reduced disinfection by-product (DBP) formation resulting from a low chlorine dosage. The goal of the demonstration unit was to provide design constraints and demonstrate regulatory compliance.

Background

The County owns and operates the Markham plant. The plant is a 10.368-mgd groundwater treatment plant, which is currently being expanded to serve as the regional plant for the Northwest Service Area (NWSA). The Heathrow Water Treatment Plant will be retired once its wellfield is diverted to the Markham plant for treatment.

Both treatment plants have seven potable water production wells and currently treat groundwater with cascade tray aeration for H₂S removal and disinfect with free chlorine using liquid bleach. Total sulfide in the groundwater wells has been ranging from 1.2 to 1.6 mg/L for the Markham plant and 1.3 to 1.8 mg/L for the Heathrow plant. Currently, both plants employ cascade tray aeration, which is the treatment recommended by FDEP for H₂S concentrations below 0.6 mg/L.

The construction of production Well #4 in 2009 at the Markham plant has triggered a regulatory need to address H₂S removal. Additionally, future regulatory compliance with the Stage 2 Disinfection Byproduct Rule (DBPR) has further driven the County to select treatment enhancements for the Markham plant. The FDEP Chapter 62-555.315 (5) (F.A.C., 2010), shown in Table 1, recommends removal of total sulfide to less than 0.3 mg/L prior to disinfection for groundwater wells constructed after August 2003. In 2006, the County selected O₃ to treat H₂S, which will result in reduction of the amount of chlorine applied to reduce DBPs.

In 2006, elevated total dissolved solids (TDS) concentrations in production Wells #2 and #3 were experienced. Elevated TDS re-

sulted in an increase in bromide concentrations, which created regulatory compliance challenges associated with control of brominated DBP and THM species, and potential for bromate formation once ozone is employed for H₂S treatment.

In 2009, the County conducted a production well modification and rehabilitation program to reduce TDS concentrations in Well #2 and #3. The wells were modified by back-plugging to match the depth of Well #1 and #4 and rehabilitated by acidification to increase lateral transmissivity. Initially the modifications were successful; however, TDS and resultant bromide concentration have returned to previous conditions.

Materials and Methods

Chemicals

All chemicals were obtained from Fisher Scientific, except as noted.

Ozone Pilot Test Unit Set-Up and Procedure

On-site ozone pilot test unit is as shown in Photo 1. Figure 1 presents the process flow diagram of the hybrid ozone unit. The ozone unit comprises of three components:

- 1) *Ozone generation system.* Pacific Ozone Model RHC21002M Horizon O₃ System equipped with ORP control kit.
- 2) *Ozone contact chamber.* 6-in. schedule 80 polyvinyl chloride (PVC) pipe constructed on-site. The chamber is sized to provide 5 min of contact time for the ozone residual to dissipate at a flow rate of 15 gallons per minute (gpm). Sample taps were inserted on the contact chamber to collect ozone dissipation residuals.
- 3) *Chlorine disinfection system.* The chlorine disinfection system is comprised of the following components: a chlorine storage tank and containment system and a 5-gal chemical feed bucket placed into a 20-gal contain-

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Photo 1. Pilot-Scale Ozone Unit

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ment box. On-site 12.5 percent liquid chlorine was diluted and used to refill supply when needed, a chemical feed pump (0.2 – 0.3 gph peristaltic chlorine feed pump) was used to provide 1 to 20 mg/L to treat 5 to 30 gpm of ozone treated water, and a static mixer (2-in. static mixer) was installed downstream of chlorine injection. A sample tap was installed after the static mixer to collect chlorine residual and THMFP samples.

Raw water was sent through the ozone contact chamber, followed by chlorine dosing. Testing was conducted for three individual wells (#1, #2, and #3) as well as blend combinations of the wells (#1/#2, #1/#3, and #2/#3). For each raw water source, ozone testing was conducted for two scenarios as well as a baseline condition:

- 1) *Low ozone dose* – Slightly overdose O₃ for H₂S oxidation to a O₃ residual of 0.5 mg/L.
- 2) *High ozone dose* – Overdose O₃ for H₂S oxidation to a O₃ residual of 1.5 mg/L.

- 3) *Baseline conditions* - Chlorination only to compare the effects of existing chlorine treatment to ozone treatment for H₂S reduction.

Raw water sample was passed through the unit after the well was flushed with three well volumes. Ozone-treated samples were collected no earlier than 12 min from well flushing startup to allow raw water to pass through the ozone contact chamber in the pilot unit.

Raw water quality, using pH, temperature, dissolved oxygen, turbidity and conductivity, H₂S, total organic carbon (TOC) and bromide, was measured. Treated water was filled into individual 500-mL glass amber bottles with Teflon caps and stored at room temperature (approximately 75°F). Samples were collected from the bottles at prescribed water ages and measured for THM, bromate, ozone, and chlorine residual.

Water Quality Data Analysis

Table 2 presents the water quality parameters measured along with the associated standard method.

Results and Discussion

Ozone Dosing Conditions and Associated Ozone Dissipation

Table 3 presents the ozone dosing conditions to achieve a target ozone residual of 0.5 mg/L and 1.5 mg/L for the individual wells and well combinations. The ozone dose to meet the target ozone residual of 0.5 mg/L averaged 5.2 mg/L, with a transfer efficiency of 87 percent. Well #3 and well combinations with Well #3 requires a 30 percent higher ozone dose (increase from 5 mg/L to 7 mg/L).

Ozone dosing is affected by H₂S, iron, manganese, and bromide concentration in the raw water. Theoretical O₃:H₂S demand ratio is 3:1 (Rakness 2005). The Markham plant production wells have moderately high levels of H₂S and bromide and low levels of iron. Previous bench-scale testing in 2006 indicated an O₃:H₂S ranging from 3.9:1 to 4.4:1. The O₃:H₂S demand ratio for low dose, as determined by the pilot study, averages 3.9:1, ranging from 3.3:1 to 4.7:1. Well #3 and well combinations with Well #3 tended to have a higher O₃:H₂S demand ratio.

Ozone dissipation rates were evaluated for the wells and well combinations to confirm the size of the ozone contact unit. Figure 2 presents contact unit ozone dissipation curves for target ozone residuals of 0.5 mg/L and 1.5 mg/L for individual wells and well combinations. Overall, low O₃ residual dissipated to less than 0.1 mg/L in 5 to 10 min.

Individual well dissipation rates were compared for varying low O₃ residuals (0.3 mg/L, 0.4 mg/L and 0.7 mg/L). An O₃ residual of 0.3 mg/L was able to dissipate to less than 0.1 mg/L

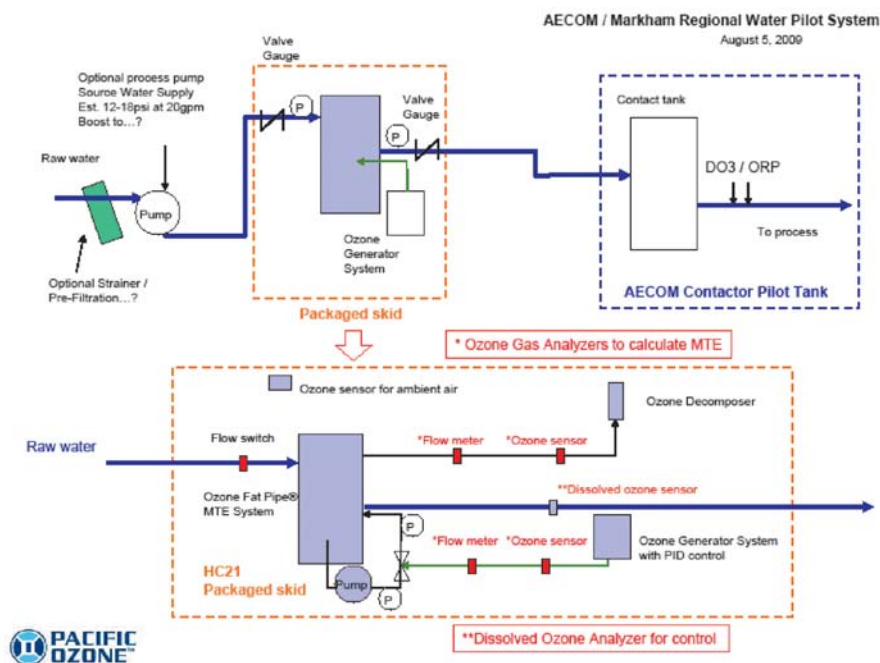


Figure 1. Hybrid In-Line O₃ Injection and Contact Chamber Controlled with Oxidation-Reduction Potential to Maintain Ozone Residual

Table 2. Water Quality Parameters

PARAMETER	Standard Method (Clesceri et al. 1998)	Range	Field/Lab
Ozone	4500-O ₃	0.01 to 1.5 mg/L	Field
H ₂ S	4500-S ₂ -F	0.1 to 20 mg/L	Field
Chlorine	4500-Cl G	0 to 9 mg/L	Field
Conductivity	field instrument		Field
pH	field instrument		Field
Temperature	field instrument		Field
Dissolved Oxygen	field instrument		Field
Turbidity	field instrument	0.01 to 1000 NTU	Field
ORP	field instrument	0 to 1000 mV	Field
THM	EPA524.2	0.1 to 200 ug/L	Lab
Bromide	EPA300.1	0.1 to 1 mg/L	Lab
Bromate	EPA 300.1	0.002 to 0.032 mg/L	Lab
TOC	5310 C	0.01 to 50 mg/L	Lab

Table 3. Ozone Dosing Conditions ^(a)

in 5 min. Well blend dissipation rates were compared at an O₃ residual of 0.5 mg/L. O₃ dissipated similarly, but required approximately 10 min to dissipate to less than 0.1 mg/L.

Bench-scale dissipation curves were developed to confirm contact unit ozone dissipation. Figure 3 presents bench-scale ozone dissipation curves. Low O₃ residual dissipated to less than 0.1 mg/L in 5 to 10 min, which was consistent with the pilot-scale test.

Instantaneous Chlorine Demand and Decay of Ozonated Water

Table 4 presents the instantaneous chlorine dosing conditions to achieve a target chlorine residual of 1.0 to 3.0 mg/L for the individual wells and well combinations. The chlorine dose range projected for ozonated water to achieve a target chlorine residual ranged from 5 to 7 mg/L, a 27 to 54 percent reduction in chlorine demand. Well #3 tended to have a higher chlorine demand compared to Well #1 and Well #2.

Chlorine demand is a function of oxidizing H₂S, TOC, iron, and manganese, or combining with ammonia in the raw water. In general, instantaneous chlorine demand ranged from 3.7 to 5.6 mg/L. Additional chlorine demand was suspected to be related to

PARAMETER	O ₃ Dose (mg/L)	O ₃ Residual (mg/L)	O ₃ Demand (mg/L) ^(b)	H ₂ S (mg/L)	O ₃ :H ₂ S Ratio ^(c)	O ₃ Generated (mg/L)	Transfer Efficiency ^(d)
Well #1							
Low O ₃ Residual	4.7	0.6	4.1	1.2	3.4	5.8	81%
High O ₃ Residual	6.1	1.6	4.5		3.7	6.8	90%
Well#2							
Low O ₃ Residual	4.8	0.3	4.5	1.3	3.5	5.2	92%
High O ₃ Residual	6.4	1.5	4.9		3.8	7.1	90%
Well #3							
Low O ₃ Residual	6.1	0.4	5.7	1.2	4.7	6.7	91%
High O ₃ Residual	7.5	1.4	6.0		5.0	8.4	89%
Blends							
Wells #1/#2	4.8	0.6	4.2	1.3	3.3	6.1	79%
Wells #2/#3	5.3	0.6	4.7	1.1	4.3	5.9	90%
Wells #1/#3	5.7	0.5	5.2	1.3	4.1	6.6	86%
Average 0.5 Target	5.2	0.5	4.7	1.2	3.9	6.0	87%
Average 1.5 Target	6.7	1.5	5.1	1.2	4.2	7.4	90%

a) Based on average values from data logger.

b) O₃ demand = O₃ dose - O₃ residual

c) O₃:H₂S Ratio = O₃ demand / H₂S

d) Transfer Efficiency = Applied O₃ dose / Generated O₃

ammonia in the raw water resulting in the need to reach breakpoint chlorination before a free residual was consistently achieved.

To reach breakpoint chlorination, a chlorine to ammonia dose ratio of 7.6:1 is stoi-

chiometrically needed. The average ammonia concentration of the wells is 0.4 mg/L as NH₄, which resulted in a chlorine demand of 3 mg/L before free chlorine disinfection began.

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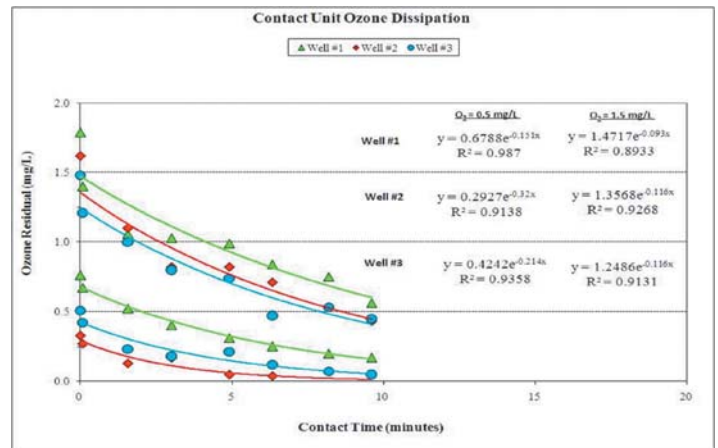
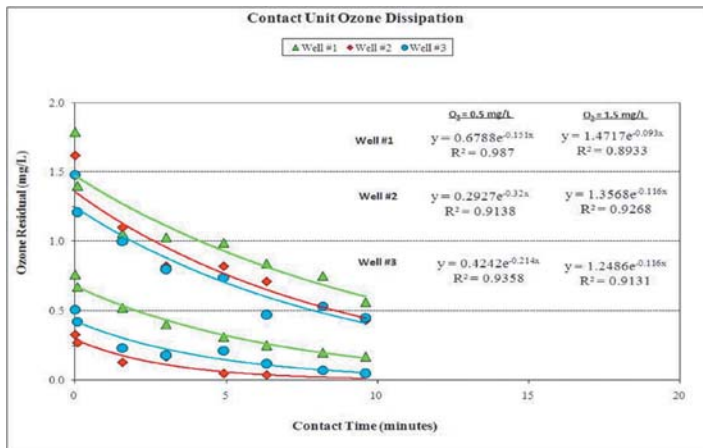


Figure 2. Contact Unit Ozone Dissipation Curves

Figure 3. Bench-Scale Ozone Dissipation Curves

Table 4. Instantaneous Chlorine Dosing Conditions

PARAMETER	O ₃ Residual (mg/L)	Cl ₂ Dose (mg/L)	Cl ₂ Residual (mg/L) ^(a)	Cl ₂ Demand (mg/L) ^(b)	Percent Reduction in Demand
Well #1					
Baseline	---	10.7	3.2	7.5	33%
Low O ₃ Residual	0.6	6.8	1.8	5.0	
High O ₃ Residual	1.6	6.8	1.8	5.0	
Well #2					
Baseline	---	10.7	3.2	7.5	44%
Low O ₃ Residual	0.3	6.8	2.9	3.9	
High O ₃ Residual	1.5	6.8	2.3	4.5	
Well #3					
Baseline	---	10.7	3.4	7.3	27%
Low O ₃ Residual	0.4	6.7	1.4	5.3	
High O ₃ Residual	1.4	6.7	1.4	5.3	
Well #1/#2 Blend					
Baseline	---	9.3	2.7	6.6	33%
Low O ₃ Residual	0.6	7.1	2.7	4.4	
Well #2/#3 Blend					
Baseline	---	10.2	1.7	8.5	54%
Low O ₃ Residual	0.6	5.3	1.4	3.9	
Well #1/#3 Blend					
Baseline	---	10.2	2.2	8.0	34%
Low O ₃ Residual	0.6	6.8	1.5	5.3	

a) Based on power chlorine decay curve.

b) Cl₂demand = Cl₂dose - Cl₂residual

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Figures 4, 5, and 6 present the chlorine decay curves for production Well #1, Well #2, and Well #3, respectively. Figures 7, 8, and 9 present the chlorine decay curves for well blend combinations #1/#2, #2/#3, and #1/#3, respectively. After initial chlorine demand was met, the bulk chlorine decayed at a rate ranging from 0.1 to 0.2 mg/L per day.

Comparison of similar chlorine residuals was performed on Well #1 and Well #3 ozonated samples, which resulted in a similar chlorine decay rate. Whereas, comparison of similar chlorine dosages was performed on Well #2 samples, which resulted in an increased chlorine demand for increased O₃ residuals. The 0.5 mg/L O₃ residual resulted in an additional chlorine demand of 0.5 mg/L as O₃ reacts with secondary oxidizers such as chlorine.

Trihalomethane Formation Potential

Figures 10, 11 and 12 present the THMFP curves for the Markham plant production Well #1, #2, and #3, respectively. The wells were dosed with high (1.5 mg/L O₃ residual) and low dosages (0.5 mg/L O₃ residual) of ozone,

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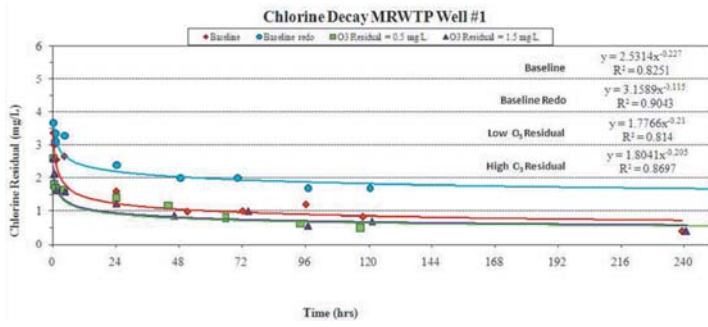


Figure 4. Well #1 Cl₂ Decay

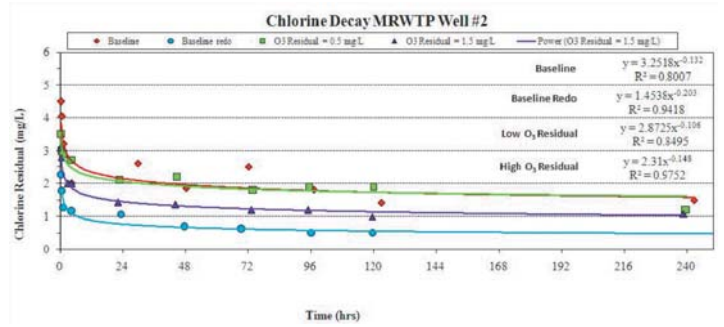


Figure 5. Well #2 Cl₂ Decay

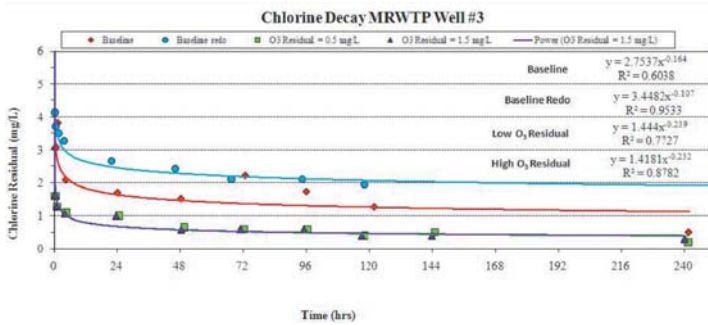


Figure 6. Well #3 Cl₂ Decay

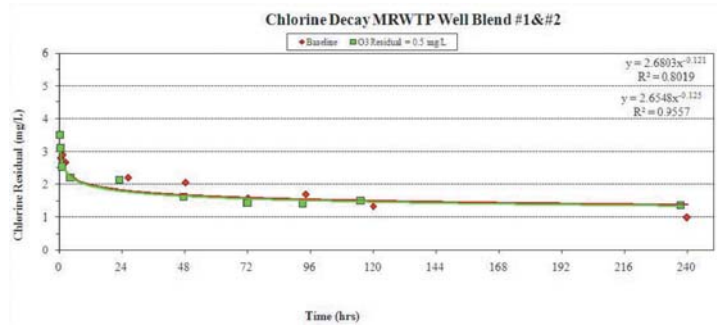


Figure 7. Well Blend #1/#2 Cl₂ Decay

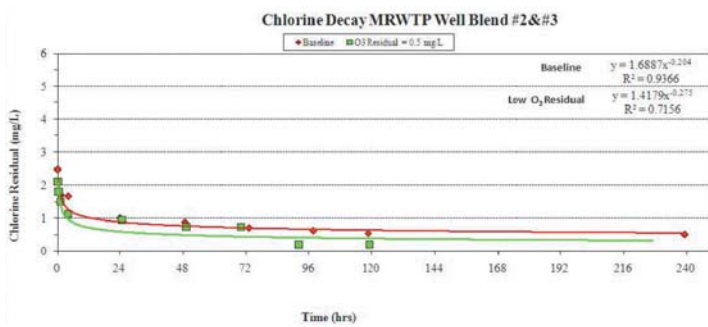


Figure 8. Well Blend #2/#3 Cl₂ Decay

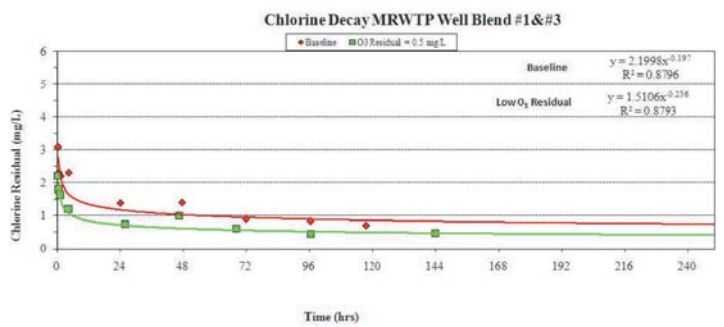


Figure 9. Well #1/#3 Cl₂ Decay

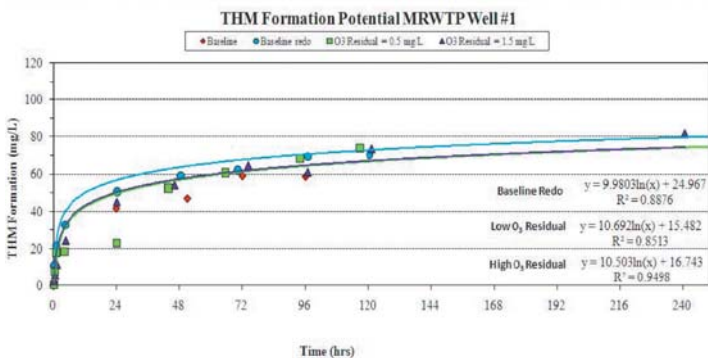


Figure 10. Well #1 Trihalomethane Formation Potential

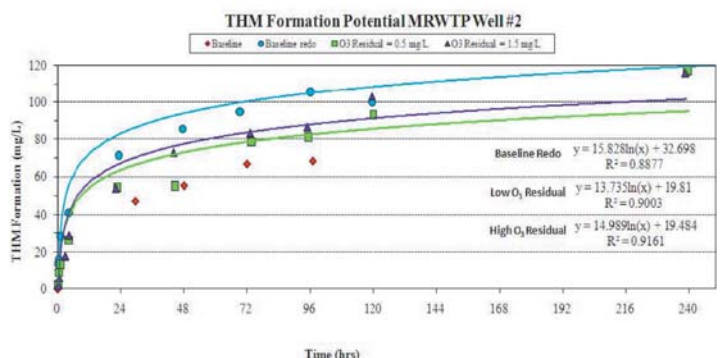


Figure 11. Well #2 Trihalomethane Formation Potential

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and then compared to the wells dosed with chlorine only. (Note, initial control of chlorine injection was suspect, therefore baseline dosing was repeated.)

The THM formation following ozone was reduced in Well #1 and Well #2 by approximately 10 µg/L and 13 µg/L. Hence, the use of ozone has the ability to reduce THMs for Well #1 and #2. However, ozonation of Well #3 did not show a change of THM formation, which is mainly attributed to brominated THM species that tend to have higher molecular weights (M.W.) associated with higher levels of bromide.

Table 5 presents THM speciation of the production wells. Well #1 was demonstrated to meet THM compliance beyond five days, with or without ozone. Well #2 was demonstrated to meet THM compliance for up to three days as a result of ozone application, whereas Well #3 tended to exceed THM compliance in approximately two days, with and without ozone.

Bromate Formation Potential

Table 6 presents bromate formation for the production wells after 20 min and 24 hours of reaction time for the target ozone residuals of 0.5 mg/L and 1.5 mg/L. Researchers (Song et al., 1997) have found that bromate ion formation is an important consideration for ozone application to source waters containing more than 100 µg/L (0.1 mg/L) bromide ion. The bromate compliance maximum containment level (MCL) is regulated to maintain bromate to less than 10 µg/L (0.01 mg/L) on an annual average basis from point-of-entry (POE), to distribution POE samples.

Bromate formation can be controlled by limiting O₃ residual and is relatively instantaneous with ozone (Rakness, 2005). Bromate compliance was met using Well #1 with a low (0.6 mg/L) O₃ residual. However, high O₃ residual of 1.6 mg/L resulted in challenges meeting bromate compliance. Well #2 and Well #3 have challenges meeting bromate compliance using either low or high O₃ residuals. Hence, a combination of well blending and tight control of low O₃ residuals is warranted to meet compliance.

To reach a potential compliance strategy, a cursory review of well blending combinations was developed to determine potential well operating scenarios for using combinations of Markham plant wells with Heathrow plant wells. Potential well blending combinations are provided in Table 7. Blending combination mass balance scenarios⁽¹⁾ were developed to result in bromate formations less than 10 µg/L. In general:

- Well #2 and Well #3 should not be operated simultaneously, except for emergency situations.

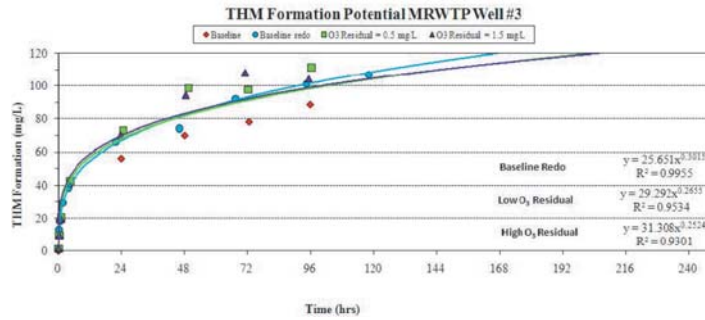


Figure 12. Well #3 Trihalomethane Formation Potential

Table 5. Trihalomethane Speciation Formation

PARAMETER	Well #1			Well #2			Well #3		
	Base line	Low O ₃	High O ₃	Base line	Low O ₃	High O ₃	Base line	Low O ₃	High O ₃
Bromide (µg/L)		71			169			188	
Bromate (ug/L)	2	8	13	2	21	44	2	26	44
TOC (mg/L)		1.7			1.4			1.7	
THM – 1 day (µg/L)	51	38	45	71	54	54	66	73	70
CHCl ₃ (M.W. 119)	23	14	18	5	6	5	13	4	3
CHBrCl ₂ (M.W. 164)	17	13	16	14	15	13	21	14	13
CHClBr ₂ (M.W. 208)	10	10	11	31	25	26	26	35	33
CHBr ₃ (M.W. 253)	1	1	1	21	9	10	6	20	21

CHCl₃ = Chloroform
 CHBrCl₃ = Bromodichloromethane
 CHClBr₂ = Dibromochloromethane
 CHBr₃ = Bromoform

Table 6. Bromate Formation

Parameter	Bromide (µg/L)	Cl ₂ Residual (mg/L)	O ₃ Residual (mg/L)	Bromate Formation	
				20 min	24-hr
Well #1					
Baseline		2.4	---	2	2
Low O ₃ Residual	71	1.6	0.6	8	8
High O ₃ Residual		1.7	1.6	13	14
Well #2					
Baseline		1.3	---	2	2
Low O ₃ Residual	169	2.8	0.3	20	22
High O ₃ Residual		2.0	1.5	44	43
Well #3					
Baseline		3.2	---	2	2
Low O ₃ Residual	188	1.2	0.4	25	26
High O ₃ Residual		1.1	1.4	44	44

- Simultaneous operation of Well #1 and Well #2 need to blend with Well #4, plus two Heathrow wells, providing at least 2,420 gpm from low bromide wells to result in bromate formation < 10 µg/L.
- Simultaneous operation of Well #1 and Well #3 need to blend with Well #4, plus four

Heathrow wells, providing at least 5,470 gpm from low bromide wells to result in bromate formation < 10 µg/L.

⁽¹⁾ Mass balance blending scenarios were developed based on the following assumptions:

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Table 7. Potential Well Operating Scenarios for Blending to Control Bromate with Ozone Process

PARAMETER	Bromide (ug/L)	Bromate (ug/L)	Br : BrO ₃	Pump Capacity (gpm)	Operating Scenarios (on/off)			
					MAR		MAR + HEA	
					#1/#2	#1/#3	#1/#2	#1/#3
Markham Regional WTP Wellfield								
MAR-1	71	8	8.9	2,400	ON	ON	ON	ON
MAR-2	169	21	8.0	2,400	ON	OFF	ON	OFF
MAR-3	188	26	7.2	2,400	OFF	ON	OFF	ON
MAR-4 (a)(b)	71	8	8.9	2,400	ON	ON	ON	ON
Heathrow WTP Wellfield (c)								
HEA-2	40	5	8.9	1,250	OFF	OFF	ON	ON
HEA-5	45	5	8.9	1,250	OFF	OFF	OFF	ON
HEA-6	50	6	8.9	1,800	OFF	OFF	OFF	ON
HEA-4 (stdby)	49	6	8.9	1,170	OFF	OFF	ON	ON
Bromate Blend (ug/L)					12	14	10	10
Pump Rate (gpm)					7,200	7,200	9,620	12,670

- a) Bromide in MAR-4 assumed to be same as MAR-1
- b) Bromate formation assumed to be same as MAR-1
- c) Bromate formation estimates based on Bromide

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- a) Future conditions of the Markham plant wellfield bromide levels were not considered.
- b) Newly constructed Well #4 bromide is similar to Well #1, because TDS is similar in both wells.
- c) Well #4 bromate formation is similar to Well #1.
- d) Heathrow wells are similar to Well #1 bromides, as well as resultant bromate.

Oxidation-Reduction Potential Correlation to Ozone Residual

The relationship between ORP and ozone residual was evaluated to potentially serve as a basis of controlling ozone dosage. Figure 13 presents the relationship of ORP to O₃ residual for each production well. The ORP is very responsive to ozone residual as soon as a residual develops, then, as residual increases the ORP is less responsive. The ORP, as a simple analytic tool, shows promise given difficulties in measuring ozone residual continuously and reliably. The ORP was demonstrated to measure O₃ residual for system control from as low as 0.3 mg/L to as high as 1.5 mg/L.

The TOC and bromide removal is recommended ahead of the ozone process at the Markham plant, because of regulatory challenges regarding brominated DBP formation. Bromate formation was identified to be the primary regulatory driving factor because the potential to form bromate limits the use of Well #2 and Well #3.

Disinfection Byproduct Compliance Driving Factors

The THMs and bromate have been identified as the DBP compliance driving factors for ozonated Markham plant groundwater. Table 8 shows how the wells are driven on a regulatory basis.

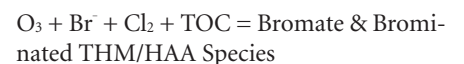
- Chlorine DBPFP is primarily related to TOC concentrations as follows:

$$TOC + Cl_2 = THM \& HAA$$

Solutions to control THMs and HAAs are as follows:

- Remove TOC ⇒ Ion Exchange or Granular Activated Carbon (TOC < 1 mg/L)
- Reduce Cl₂ Dosage ⇒ H₂S Removal
- Reduce TOC ⇒ Well Rotation (lowest cost)

- Ozone DBPFP is primarily related to bromide concentrations as follows:



Solutions to control bromate and brominated THM/HAA species are as follows:

Figure 13. Oxidation-Reduction Potential Correlation to O₃ Residual

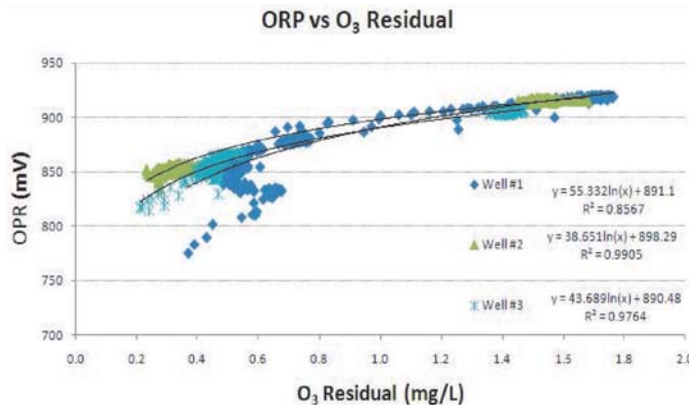


Table 8. Disinfection Compliance Driving Factors

PARAMETER	O ₃ Residual (mg/L)	Bromate (ug/L)	THMFP (ug/L @ 14 hrs) (a)	Hours to THM MCL
MAR-1 (Well #1)	0.5	8	43	226
MAR-2 (Well #2)	0.4	20	55	58
MAR-3 (Well #3)	0.3	25	60	28
New MAR-4 (Well #4)	---	8 (b)	43	226
Heathrow Wells	---	5	<38	226

- a) Represents 14 hrs of detention time at GST before entering distribution system.
- b) Assumes MAR-4 bromide is similar to MAR-1.

- Reduce O₃ Residual ⇒ Tighter O₃ dosage control to an O₃ residual < 0.5 mg/L
- Remove Br⁻ ⇒ IX or NF/RO (Br⁻ <100ug/L)
- Lower Br⁻ ⇒ Well Rotation (lowest cost)

Conclusions and Recommendations

The following conclusions and recommendations summarize the results of the on-site ozone demonstration testing:

1. Brominated THM formation and bromate formation were identified as the driving factors to meet regulatory compliance. To mitigate regulatory compliance, the County elected the following strategies:
 - a. Employ Well Rotation: Brominated THM species were prevalent as a result of source water bromide concentrations. Use Well #1 in combination with Well #2 or Well #3 and eliminate operation of Well #2 and Well #3 individually, or simultaneously, to mitigate THM formation. Also, continue to monitor source water bromide concentrations
 - b. Use ORP to Control a Low Ozone Residual: The ORP was successfully demonstrated to control ozone residual. Bromate formation increased with increasing bromide and ozone residuals. Establish a low O₃ residuals of less than 0.3 mg/L to mitigate bromate formation.
 - c. Remove TOC and Bromide from “Bad Actor” Wells: Ion-exchange demonstration testing is recommended to determine TOC and bromide removal efficiency to meet water quality regulatory compliance.
2. An average ozone dose of 5.2 mg/L is recommended to target an O₃ residual of less than 0.5 mg/L. Ozone dose is dependent on sulfide concentration. Demonstration testing O₃:H₂S ratio ranged from 3.9:1 to 4.4:1.
3. Design an ozone contact dissipation unit for 10 min of contact time. Low O₃ residuals (<0.5 mg/L) dissipated to less than 0.1 mg/L in 5 to 10 min; high O₃ residuals (>1.0 mg/L) dissipated to less than 0.1 mg/L in 15 to 20 min.

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