Disinfection Byproduct Formation Potential Reduction and Hydrogen Sulfide Treatment Using Ozone

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The Orlando Utilities Commission (OUC) is performing an upgrade and replacement program for the ozone treatment systems at all seven OUC water treatment plants (WTPs). The plants utilize liquid oxygen (LOX) as the feed gas for the ozone generation equipment. In order to standardize equipment and increase ozone generation and dissolution efficiencies, OUC and CDM Smith are performing a design and implementation plan for the treatment system upgrades at each of the WTPs.

The purpose of this testing is to outline the procedure and interpret the results from the full-scale ozone system testing at three of OUC's plants and the effects on the sizing of the ozone generation and dissolution systems. The goals from this testing effort are to:

- Determine the base ozone demand for hydrogen sulfide (H_2S) oxidation.
- Measure and trend the ozone decay rate in the raw water at various ozone-applied doses.
- Ascertain possible effects and correlations of the ozone-applied dose to the disinfection byproduct (DBP) formation potential of the raw water.
- Establish ozone-to-sulfide dose ratio that will be applied to each facility for the design of the system improvements.

The three facilities used for the testing are the Conway, Navy, and Pine Hills WTPs. These facilities were chosen because they represent a wide range of flows and water quality constituent concentrations with regards to all seven WTPs and will be used to represent the other facilities. The Pine Hills WTP has the lowest H_2S and lowest average total organic carbon (TOC) concentrations, the Conway WTP has midrange concentrations of H_2S and TOC in the raw well water, and the Navy WTP has a higher concentration of H_2S in its two wells.

Process Testing Protocol

The three facilities have the same basic flow scheme and attributes: raw water wells, ozone generation with liquid oxygen as the feed gas and fine-bubble diffusion dissolution system, ozone residual sampling and monitoring, chlorination, and storage and pumping. The overall protocol for testing involves:

- Locating the sample lines for ozone residual monitoring.
- Operating at a constant well flow through one ozone contactor, with the same wells operating continuously throughout the testing.
- Setting the ozone-applied dose to a constant level for selected wells for steady state flow.
- Sampling the selected wells for water quality data, such as H_2S concentration, pH, temperature, oxidation reduction potential (ORP), and dissolved oxygen (DO).
- Transferring the ozone residual monitoring device from the nonoperating contactor to the second sample point location on the operating contactor.
- Calibrating the ozone residual devices.
- Performing ozone demand and decay tests.
- Gathering samples for DBP formation potential tests and for other water quality parameters.

The testing started with the base-applied ozone dose, or "base dose," resulting in an approximate ozone residual of 0.1 mg/L, which represents the dose required to achieve complete oxidation of hydrogen sulfide in the raw well water. Subsequent ozone-applied doses of 0.5, 1.0, 1.5, and 2.0 mg/L *above* the base dose were also used for testing. For each applied ozone dose, ozone decay tests were performed, along with trihalomethane formation potential (THMFP) tests.

Conway Water Treatment Plant

Setup and Methodology

The reporting sample point for ozone residual at this facility is sample point No. 2 (SP 2). The on-line ozone analyzer is mounted to the side of the contactor and gathers its samples from a sample line feeding into cell No. 2 of Contactor No. 1. There is a sample pump that helps draw the water out of the contactor and through the analyzer header, which assists with lowering the sample line residual time. For this testing procedure, a bypass line was opened to increase the flow through the sample lines drawn for sample

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point 1 and sample point 2, reducing the residence time in the sample piping. The flow through the sample lines was measured using a graduated beaker and a stopwatch. Each flow test was performed three times for the bypass line and analyzer flows. The flow through the bypass line, which was measured to be approximately 4.23 gal per minute (gpm), is the total for SP 1 and SP 2. The flow through the analyzers was measured to be approximately 0.39 gpm. This corresponds to a flow of 2.5 gpm from SP 2, with a lag time of 15 seconds.

Calibration

The calibration of the ozone analyzers was performed by placing the two ozone analyzer units in series. For 10 minutes, the readings from the analyzers were recorded at 15-second intervals. Concurrently, every 2 minutes a grab sample was taken and analyzed for ozone concentration using a spectrophotometer, and all results were recorded. After the calibration cycle was completed, the recorded measurements from both analyzers and the grab samples were plotted against time. If the grab samples are close to the analyzer readings and are within ±1 standard deviation from the average analyzer reading, the analyzers are considered calibrated. The analyzers at Conway were not adjusted after the calibration testing.

Results

Raw Water Well Testing

During the ozone process testing, OUC staff performed raw water well tests on the wells that were in operation during the testing. The tests for the raw water wells included: H_2S concentration, temperature, pH, ORP, and DO. Table 1 shows the results from the raw water well testing.

The H_2S concentrations are used to help define the "base ozone dose" for hydrogen sulfide oxidation and confirm the applied ozone doses utilized during testing.

Ozone Demand Characteristics

The average H_2S concentration from the three Conway WTP operating wells was 2.53 mg/L. For test scenario B1, the raw water was treated with an applied ozone dose of 10 mg/L (~0.1 mg/L ozone residual at SP 2), which represents an ozone-to-sulfide ratio of approximately 4:1. Table 2 shows the scenarios performed, the corresponding ozone dose, well flow, and ozone production for each scenario. The testing was performed in the order of B4, B3, B1, B2, and B6.

Scenario B2 and B5 were performed under the same conditions. With multiple people running various tests, the nomenclature for the operating scenarios were slightly miscommunicated the first day. The applied ozone doses were the overriding factor for the testing scenarios and were used to correlate the different naming conventions. The DBP testing for scenario B2, with an applied ozone dose of 11.5 mg/L, was repeated the second day, and given the name of B5. The testing for Conway occurred over two calendar days and allowed fine-tuning of the testing procedures, coordination, and result reporting.

Ozone Decay Characteristics

Before the decay tests were performed, the plant was operated at a steady applied ozone dose (depending on trial run) and a flow of 16.5 mil gal per day (mgd) for a minimum of 30 minutes to obtain a steady ozone residual and dose for the raw water. For each scenario, the decay test was performed twice. Figure 1 shows the decay test results for the first test performed for each scenario

The data show a logarithmic decay of the ozone residual in the water. The natural log of the ratio of measured ozone concentration to initial ozone concentration data were then plotted against time in order to get the decay coefficients at the various ozone-applied doses. The slope of the trend line of each of these scenarios is the decay coefficient for the ozone decay at each applied dose. Table 3 presents the average decay coefficients. The decay data show the ozone decay rate that will be utilized when designing the ozone system to prevent any possible ozone residual carry-over from the contactors to the ground storage tanks.

Trihalomethane Formation Potential

After each decay test was performed, and before changing the applied ozone dose for the next scenario, samples of the treated water were taken

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Table 1. Conway Water Treatment Plant – Raw Water Well Test Results

Well No.	Date	pH	ORP (mV)	Temp (°C)	DO (mg/L)	H_2S (mg/L)
1	1/11/2010	7.77	-119.4	24.32	1.69	2.67
3	1/11/2010	7.81	-78.4	24.31	6.11	2.48
5	1/11/2010	7.80	-126.3	24.58	1.56	2.45

Table 2. Conway Water Treatment Plant Ozone Testing Scenarios

Scenario	Applied Ozone Dose (mg/L)	Additional Applied Dose (mg/L)	Ozone Production (lb/day)	Well Flow (mgd)
B1	10.0	Base Dose	1,370	16.5
B6	10.5	+ 0.5	1,443	16.5
B3	11.0	+ 1.0	1,515	16.5
B2/B5	11.5	+ 1.5	1,580	16.5
B4	12.0	+ 2.0	1,650	16.5

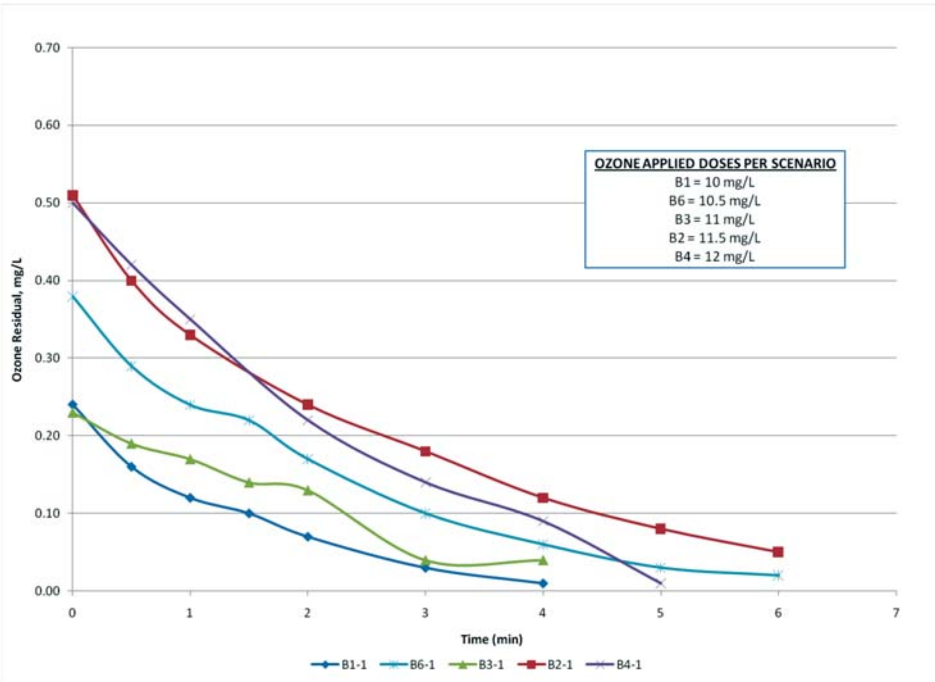

Figure 1. Conway Water Treatment Plant Ozone Decay Results (First Test)

Table 3. Conway Water Treatment Plant Average Ozone Decay Coefficients

Scenario	Applied Ozone Dose (mg/L)	Additional Applied Dose (mg/L)	Ozone Decay Coefficient (k, min^{-1})
B1	10.0	Base Dose	- 0.74
B6	10.5	+ 0.5	- 0.53
B3	11.0	+ 1.0	- 0.53
B2/B5	11.5	+ 1.5	- 0.39
B4	12.0	+ 2.0	- 0.62

Notes:
1)Decay coefficients based upon C=Coekt, where C is the time dependent ozone residual in the treated water, Co is the initial ozone residual, and t is the time from the initial residual measurement.

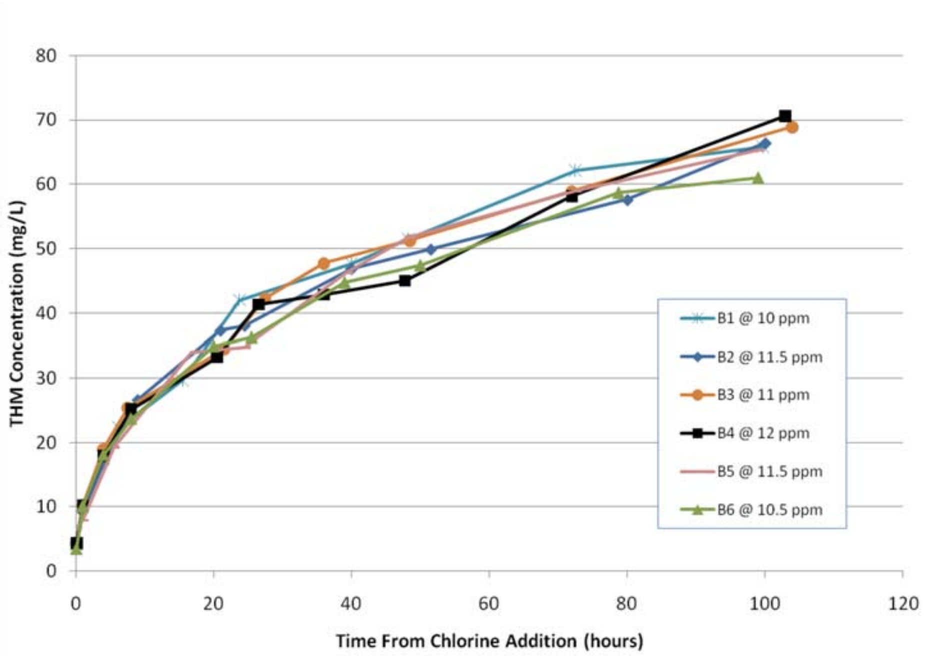

Figure 2. Conway Water Treatment Plant
Trihalomethane Formation Potential for Each Scenario

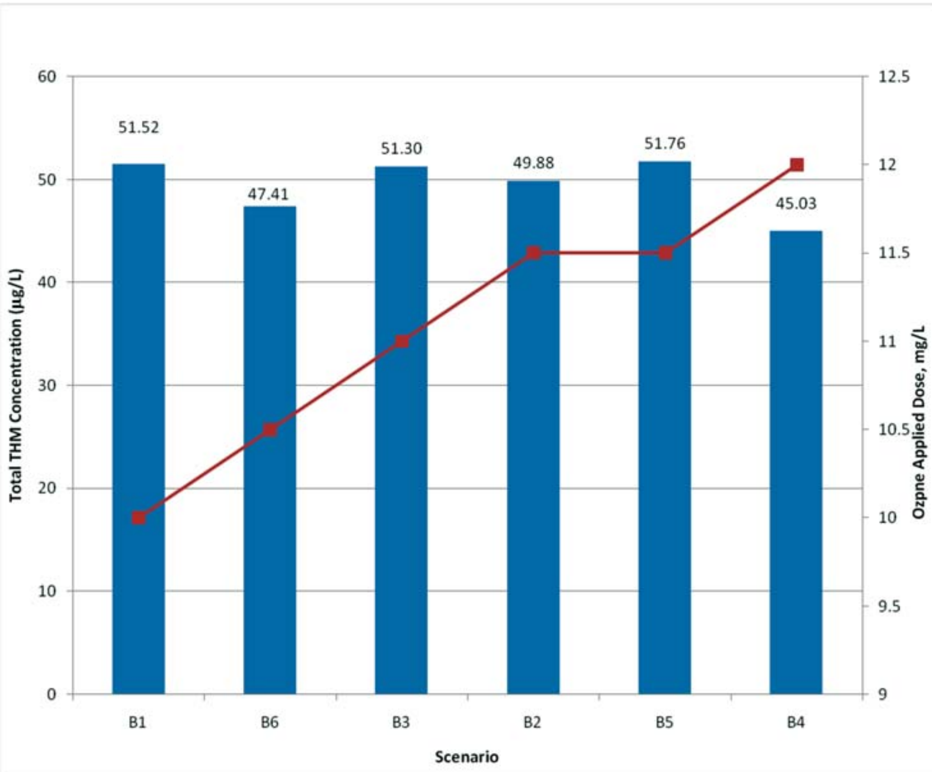

Figure 3, Conway Water Treatment Plant
48-Hour Trihalomethane Concentrations for Each Scenario

Table 4. Navy Water Treatment Plant – Raw Water Well Test Results

Well No.	Date	pH	ORP (mV)	Temp (°C)	DO (mg/L)	H_2S (mg/L)
1	1/13/2010	7.84	-73	23.90	4.32	2.02

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from the last sample point at the back of the contactor. This sample was then taken to the OUC water laboratory and a simulated distribution system (SDS) test was performed to determine the THMFP of the treated water. As stated previously, Scenario B5 is a repeat sample of scenario B2 (11.5 mg/L applied dose). Figure 2 shows the SDS results and Figure 3 shows a 48-hour THM concentration for each scenario. The 48-hour time period was selected based upon the target design water age for the water distribution system.

These data indicate that there is not a significant impact of ozone dose on the THMFP of the treated water. The variability of ozone application and residuals could have impacted the consistency of DBP testing. If sidestream injection and/or a more consistent ozone dose and ozone residual can be achieved, DBP testing should be performed again.

Navy Water Treatment Plant

Setup and Methodology

The reporting sample point for ozone residual at this facility is sample point No. 1 (SP 1). The on-line ozone analyzer is mounted to the side of the contactor and gathers its samples from a sample line feeding into cell No. 2 of Contactor No. 1. After the ozone analyzers, the sample lines come to a common header where a sample pump helps draw the water out of the contactor, lowering the sample line residual time, and pumps it back to the top of the contactor for retreatment. A rotameter is used to measure flow through the sample line pumping system.

For this testing procedure, the pumped flow was measured using the rotameter, which was calibrated by the OUC water production operators. Flow through the on-line analyzers was measured using a graduated beaker and a stopwatch. Each test was performed three times for the analyzer flows. The flow through the sample pump was measured to be approximately 8 gpm (4 gpm from each sample point), and the flow through the analyzers was measured to be approximately 0.2 gpm. This represents a lag time for SP 1 of approximately 3 seconds.

Calibration

The calibration of the ozone analyzers was performed in the same manner as for the Conway WTP. After the calibration cycle, the SP 1 online analyzer was adjusted *down* 0.3 and the SP 2 analyzer was adjusted *down* 0.1.

Results

Raw Water Well Testing

During the ozone process testing, OUC

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Table 5. Navy Water Treatment Plant Ozone Testing Scenarios

Scenario	Applied Ozone Dose (mg/L)	Additional Applied Dose (mg/L)	Ozone Production (lb/day)	Well Flow (mgd)
B1	8.0	Base Dose	380	5.7
B2	8.5	+ 0.5	403	5.7
B3	9.0	+ 1.0	425	5.7
B4	9.5	+ 1.5	451	5.7
B5	10.0	+ 2.0	475	5.7

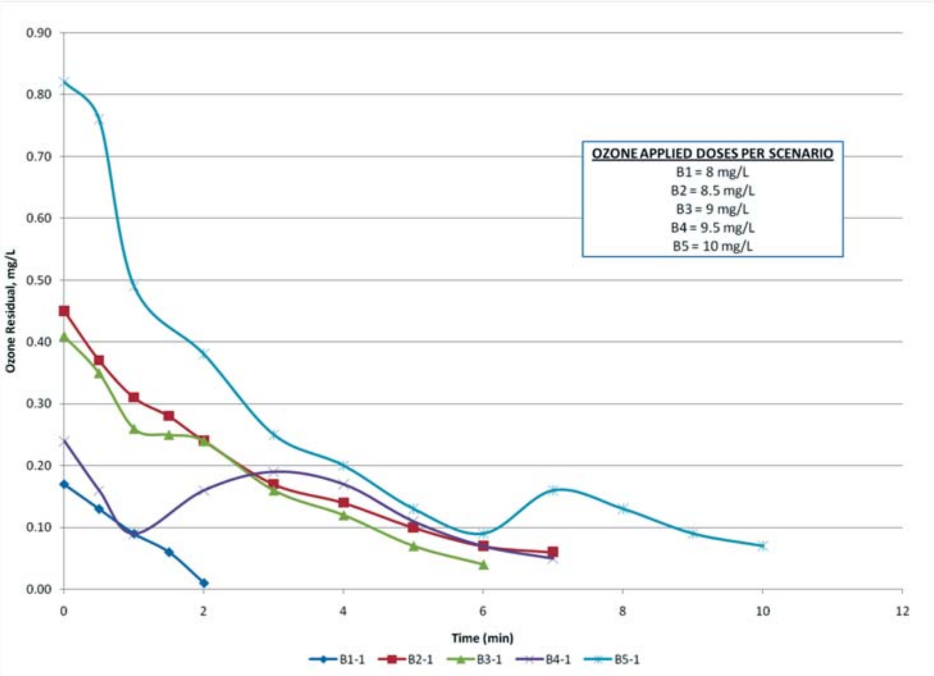

Figure 4 . Navy Water Treatment Plant Ozone Decay Tests (First Test)

Table 6 . Navy Water Treatment Plant Average Ozone Decay Coefficients

Scenario	Applied Ozone Dose (mg/L)	Additional Applied Dose (mg/L)	Ozone Decay Coefficient (min^{-1})
B1	8.0	Base Dose	0.075
B2	8.5	+ 0.5	- 0.31
B3	9.0	+ 1.0	- 0.39
B4	9.5	+ 1.5	- 0.31
B5	10.0	+ 2.0	- 0.20

Notes:
1) Decay coefficients based upon C=Coekt, where C is the time dependent ozone residual in the treated water, Co is the initial ozone residual, and t is the time from the initial residual measurement.
2) For scenario B1, decay coefficient is based upon a linear relationship; units are mg/L-min.

Table 7. Pine Hills Water Treatment Plant – Raw Water Well Test Results

Well No.	Date	pH	ORP (mV)	Temp (°C)	DO (mg/L)	H_2S (mg/L)
1	1/14/2010	8.02	-76	23.08	1.04	0.51
5	1/14/2010	7.95	-106	22.87	0.87	0.76

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staff performed raw water well tests on Well number 1, the well that was in operation during the testing. The tests for the raw water well included: H_2S concentration, temperature, pH, ORP, and DO. Table 4 shows the results from the raw water well testing.

Ozone Demand Characteristics

The average H_2S concentration from the one operating Navy WTP well was 2.02 mg/L. For test scenario B1, the raw water was treated with an applied ozone dose of 8 mg/L (~0.1 mg/L ozone residual at SP 1). This represents an ozone-to-sulfide ratio of approximately 4:1. Table 5 shows the scenarios performed, the corresponding ozone dose, well flow, and ozone production for each scenario. The testing was performed in the order of B3, B5, B1, B4, and B2.

Ozone Decay Characteristics

Before the decay tests were performed, the plant was operated at a steady applied ozone dose (depending on trial run) and flow (5.7 mgd) for a minimum of 30 minutes to obtain a steady ozone residual and dose for the raw water. For each scenario, the decay test was performed twice. Figure 4 shows the decay test results for the first test performed for each scenario.

The data show a logarithmic decay of the ozone residual in the water for all but the B1 scenario. The natural log of the ratio of measured ozone concentration to initial ozone concentration data were then plotted against time in order to get the decay coefficients at the various ozone-applied doses. The slope of the trend line of each of these scenarios is the decay coefficient for the ozone decay at each applied dose. Table 6 presents the average decay coefficients. The decay data show the ozone decay rate that will be utilized when designing the ozone system to prevent any possible ozone residual carry-over from the contactors to the ground storage tanks.

Trihalomethane Formation Potential

After each decay test was performed, and before changing the applied ozone dose for the next scenario, samples of the treated water were taken from the last sample point at the back of the contactor. This sample was then taken to the OUC water laboratory and an SDS test was performed to determine the THMFP of the treated water. Figure 5 shows the SDS results and Figure 6 shows a 55-hour THM concentration for each scenario. The 55-hour samples have the closest water age to the OUC distribution system target water age, which is 48 hours. The applied chlorine dose for the B3 test was 0.5 mg/L less than the other samples. This lower chlorine dose caused the free chlorine residual to drop below 0.2 mg/L after the 41-hour sample was analyzed. The THMFP testing is to be stopped after the chlorine residual drops below 0.2 mg/L.

As a policy, OUC designs the distribution system for a maximum water age of 48 hours. At the 55-hour testing period, there does not appear to be an advantage to an increased ozone dose to reduce the THMFP of the treated water. There does seem to be a 10-12 mg/L drop in THMFP with the additional 1 mg/L of ozone added to the water; however, these tests should be repeated following construction of the ozone improvements at this WTP, and more data collected for a lesser number of time intervals to better establish this relationship.

Pine Hills Water Treatment Plant

Setup and Methodology

The reporting sample point for ozone residual at this facility is sample point No. 2 (SP 2). The on-line ozone analyzer is mounted to the side of the contactor and gathers its samples from a sample line feeding into cell No. 2 of Contactor No. 1. After the ozone analyzers, the sample lines come to a common header where a sample pump helps draw the water out of the contactor, lowering the sample line residual time, and pumps it back to the top of the contactor for re-treatment. There is not a rotameter on this header, so the flows were measured using a stopwatch and a graduated beaker.

Each test was performed three times for the analyzer flows. The flow through the sample pump was measured to be approximately 5.3 gpm (2.65 gpm from each sample point), and the flow through the analyzers was measured to be approximately 1.07 gpm. This represents a sample lag time for SP 2 of 1.2 seconds.

Calibration

The calibration of the ozone analyzers was performed following the same procedure as the Conway WTP. After the calibration cycle, the SP 2 online analyzer was adjusted *up* 0.1 to match the SP 1 analyzer and the grab samples.

Results

Raw Water Well Testing

During the ozone process testing, OUC staff performed raw water well tests on the wells that were in operation during the testing. The tests for the raw water well included: H_2S concentration, temperature, pH, ORP, and DO. Table 7 shows the results from the raw water well testing.

Ozone Demand Characteristics

The average H_2S concentration from the Pine Hills WTP operating wells was 0.64 mg/L.

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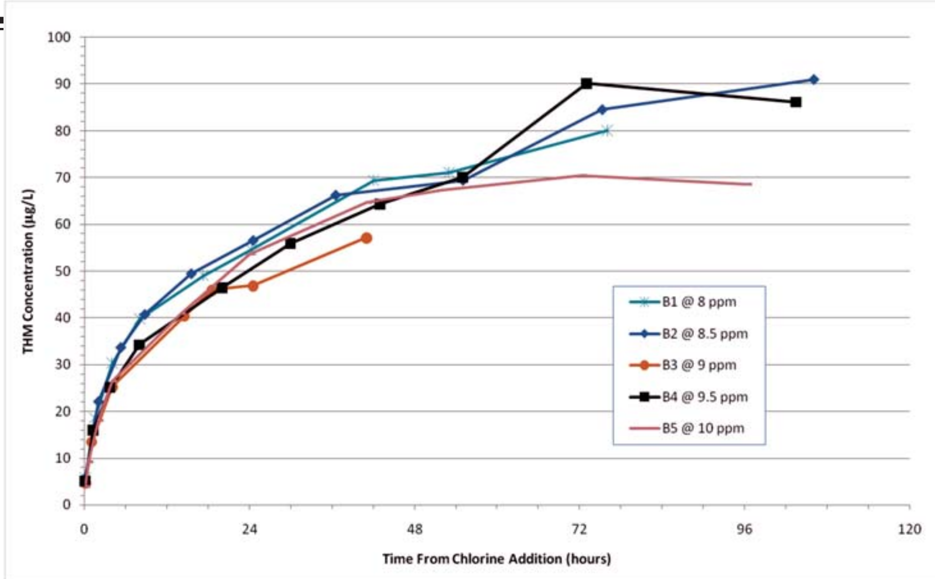

Figure 5 . Navy Water Treatment Plant Trihalomethane Formation Potential for Each Scenario

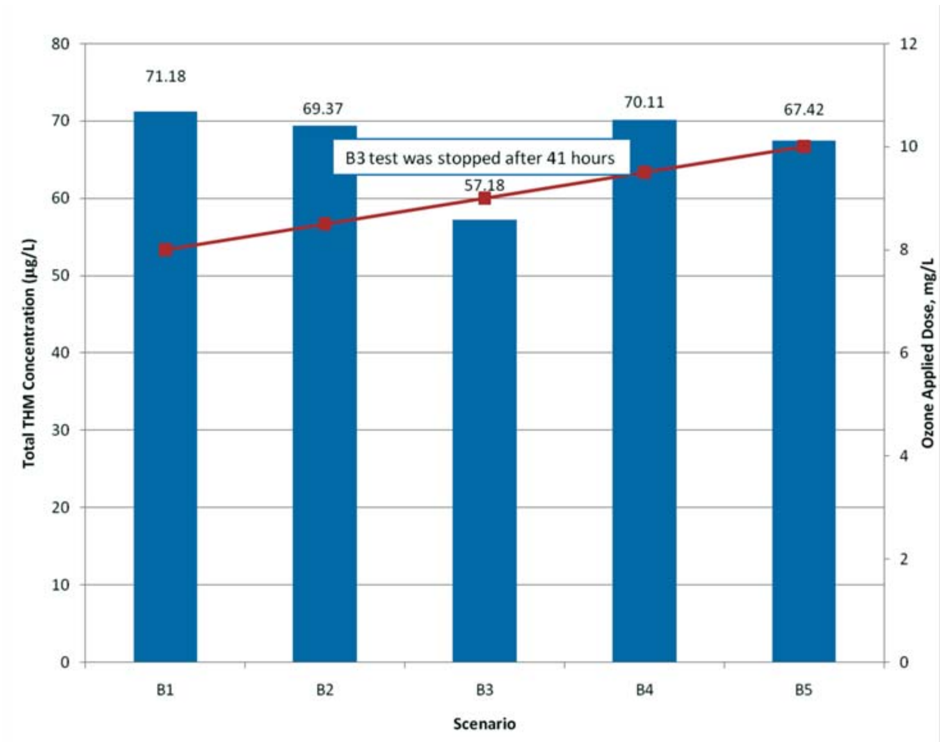

Figure 6. Navy Water Treatment Plant
55-Hour Trihalomethane Concentrations for Each Scenario

Table 8. Pine Hills Water Treatment Plant Ozone Testing Scenarios

Scenario	Applied Ozone Dose (mg/L)	Additional Applied Dose (mg/L)	Ozone Production (lb/day)	Well Flow (mgd)
B1	2.0	Base Dose	380	11.6
B2	2.5	+0.5	403	11.6
B3	3.0	+1.0	425	11.6
B4	3.5	+1.5	451	11.6
B5	4.0	+2.0	475	11.6

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For test scenario B1, the raw water was treated with an applied ozone dose of 2 mg/L (~0.1 mg/L ozone residual at SP 2). This represents an ozone-to-sulfide ratio of approximately 3.13:1. Table 8 shows the scenarios performed, the corresponding ozone dose, well flow, and ozone production for each scenario. The testing was performed in the order of B5, B1, B2, B3, and B4.

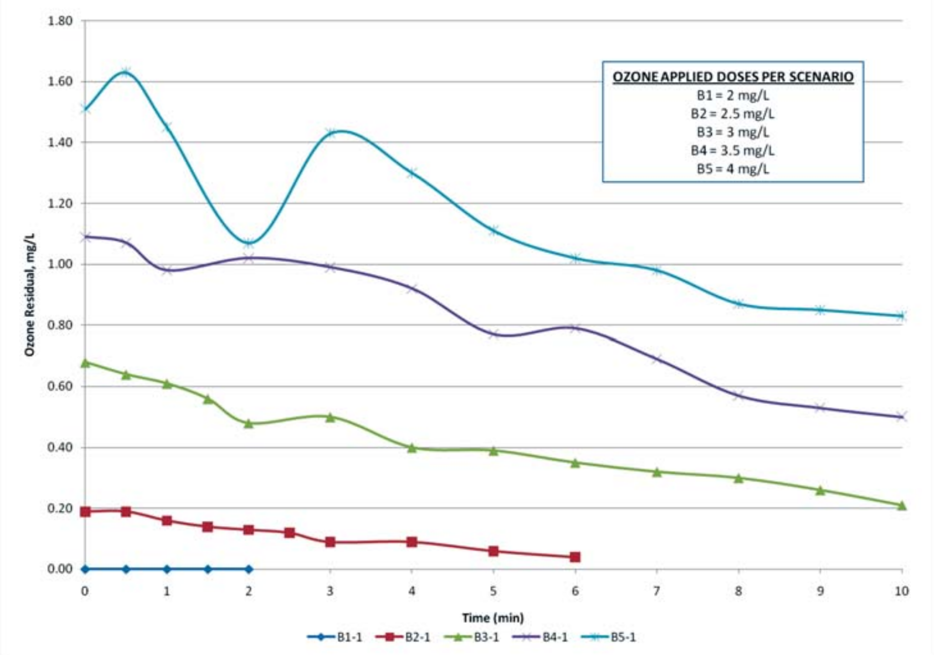

Figure 7. Pine Hills Water Treatment Plant Ozone Decay Tests (First Test)

Table 9. Pine Hills Water Treatment Plant Average Ozone Decay Coefficients

Scenario	Applied Ozone Dose (mg/L)	Additional Applied Dose (mg/L)	Ozone Decay Coefficient (min^{-1})
B1	2.0	Base Dose	N/A
B2	2.5	+ 0.5	- 0.18
B3	3.0	+ 1.0	- 0.10
B4	3.5	+ 1.5	- 0.07
B4	4.0	+ 2.0	- 0.03

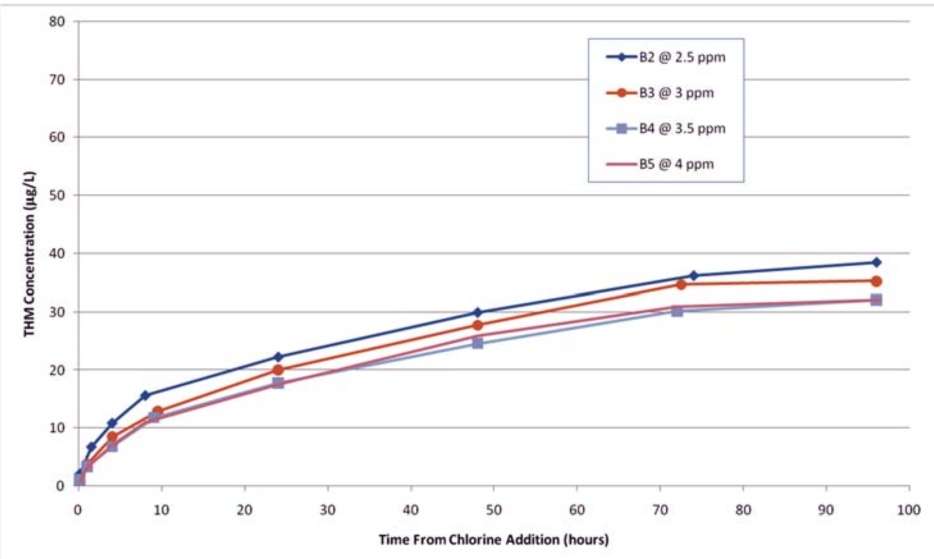

Figure 8 . Pine Hills Water Treatment Plant
Trihalomethane Formation Potential for Each Scenario

Ozone Decay Characteristics

Before the decay tests were performed, the plant was operated at a steady applied ozone dose (depending on trial run) and flow (11.6 mgd) for a minimum of 30 minutes to obtain a steady ozone residual and dose for the raw water. For each scenario, the decay test was performed twice. Figure 7 shows the decay test results for the first test performed for each scenario..

The data show a logarithmic decay of the ozone residual in the water. The natural log of the ratio of measured ozone concentration to initial ozone concentration data were then plotted against time in order to get the decay coefficients at the various ozone-applied doses. The slope of the trend line of each of these scenarios is the decay coefficient for the ozone decay at each applied dose. Table 9 presents the average decay coefficients. The decay data show the ozone decay rate that will be utilized when designing the ozone system to prevent any possible ozone residual carry-over from the contactors to the ground storage tanks.

Trihalomethane Formation Potential

After each decay test was performed, and before changing the applied ozone dose for the next scenario, samples of the treated water were taken from the last sample point at the discharge of the contactor. This sample was then taken to the OUC water laboratory and an SDS test was performed to determine the THMFP of the treated water. Figure 8 shows the SDS results and Figure 9 shows a 48-hour THM concentration for each scenario. The data indicate that an additional 1.5-2.0 mg/L of applied ozone dose will yield a potential 5 μg/L reduction in THM formation. However, it is not efficient to apply this additional dose of ozone to the raw water for a marginal improvement to the THMFP when the water at this WTP has an already low THMFP.

Disinfection Byproduct Impacts

The Pine Hills WTP has the highest water quality (lowest H_2S, lowest TOC) out of all of the WTPs. Figures 8 and 9 show a minimal (5 μg/L) reduction of THMs, with an additional 1.5-2.0 mg/L applied ozone dose above the base dose.

At the Conway WTP, the data at the 48-hour time frame indicate that there is not an advantage to applying more ozone to the raw water to reduce the THMFP of the treated water. In addition, when looking over the complete 96-hour time period for the SDS testing, the data show no impacts as the lines continually cross each other, indicating no consistent reduction in the THMFP of the water.

At the Navy WTP, the 55-hour time frame data do show a 10-12 μg/L drop in THMFP with the additional 1 mg/L of ozone added to the water; however, this test was stopped after 41 hours and not allowed to proceed to 96 hours, like the other samples, due to the chlorine residual dissipating below 0.2 mg/L after 41 hours.

The THM formation data collected during the testing period do not suggest a definitive criterion for applying additional ozone to the water for DBP control. The addition of ozone above the doses required for H_2S oxidation does appear to have an impact on the THMFP of the raw water at the facilities. However, an accurate prediction of the impacts cannot be determined—only a possible trend that warrants further analysis. It is recommended to perform THMFP tests again at each plant after the systems have been upgraded to sidestream injection. The reduced ozone residual variability in the sampling system will improve operational control and more accurate testing results.

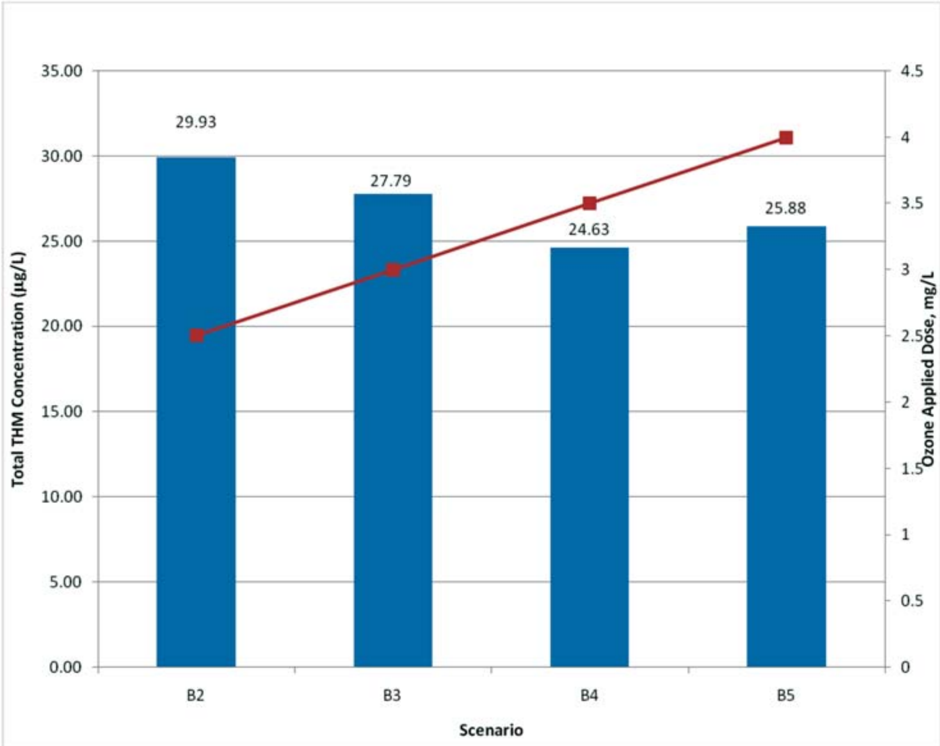

Figure 9. Pine Hills Water Treatment Plant
48-Hour Trihalomethane Concentrations for Each Scenario