SECTION 4.0 – PILOT TESTING PLAN

This section presents the detailed pilot testing plan developed in advance of the pilot testing activities.

4.1 PILOT EQUIPMENT SETUP

The pilot plant was installed at the Del Valle WTP in Livermore and operated from May to October 2008. The pilot plant consisted of two parallel trains: a conventional ozone contactor and a pipeline Peroxone contactor. The conventional ozone train was designed to mimic the type of standard over-under baffled contactors used by SCVWD and ACWD. At a flow rate of 6.5 gpm, the hydraulic residence time (HRT) through this contactor was 10 minutes. The pipeline contactor was designed to mimic a pipeline in which ozone and hydrogen peroxide are added in-line. At a flow rate of 3.5 gpm, the pipeline contactor had an HRT of 2.6 minutes. Figures 4.1 and 4.2 are schematic drawings of the two trains in the pilot plant. There was a holding tank upstream of the two parallel contactors; downstream of the tank, the flow split into the two separate contactors.

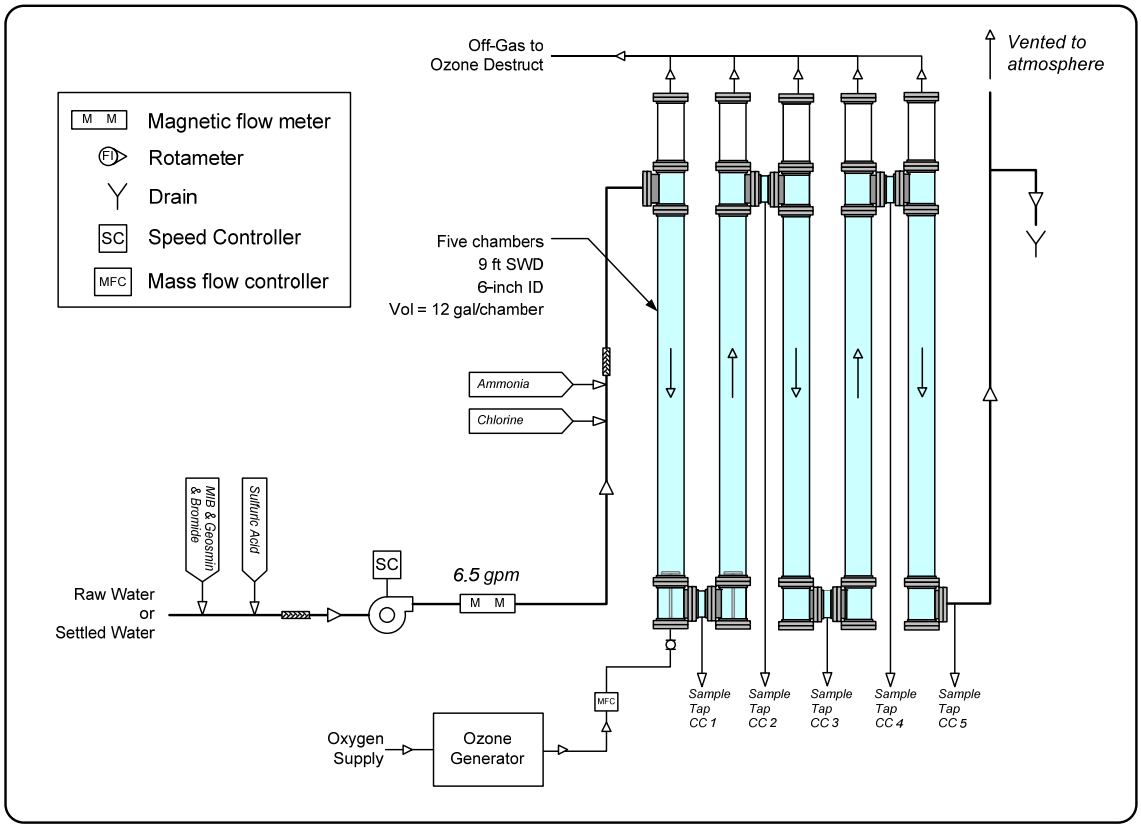

Figure 4.1 – Schematic of Conventional Contactor Showing Chemical Injection Points and Sampling Locations

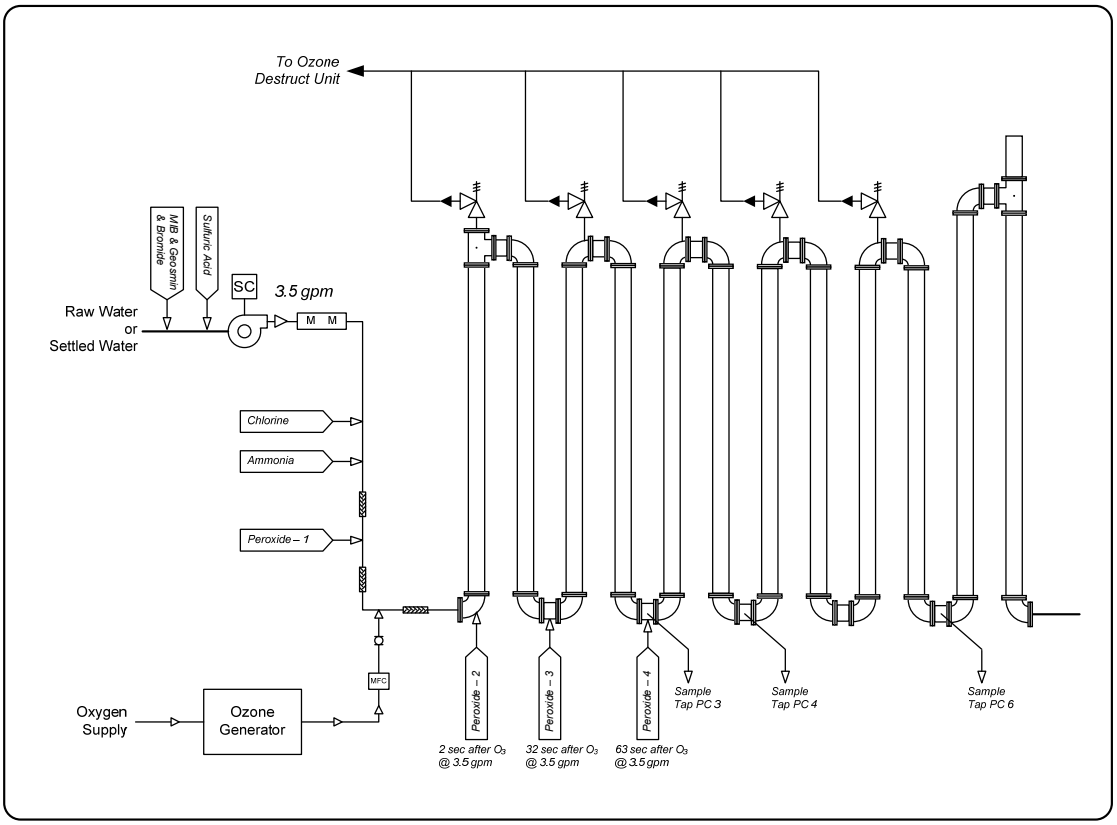

Figure 4.2 – Schematic of Pipeline Contactor Showing Chemical Injection Points and Sampling Locations

4.2 PILOT TESTING PROGRAM

The ozone or Peroxone process could be inserted at the raw, settled, or filtered water locations at the Del Valle WTP, or at the raw or filtered water locations at the Patterson Pass WTP. In order to determine the best application point, several questions had to be answered (these apply to each potential injection location):

1. *What ozone (alone) dose is necessary for T&O control?*
2. *What ozone (alone) contact time is necessary for T&O control?*
3. *How much less ozone is used with Peroxone (vs. ozone alone) for T&O control?*
4. *How does Peroxone affect the contact time (vs. ozone alone) for T&O control?*
5. *What is the optimum ratio of ozone:hydrogen peroxide for T&O control?*
6. *What levels of chlorinated byproducts can be expected when using ozone or Peroxone for T&O control followed by free-chlorine for disinfection?*
7. *What levels of bromate can be expected when using ozone or Peroxone for T&O control?*
8. *Do high bromide levels affect the efficiency of T&O control methods?*

9. Do high TOC levels affect the efficiency of T&O control methods?

10. What is the impact of bromate-control technologies on T&O control performance?

11. What are the impacts on the downstream chlorination processes?

Based on a review of work done by others (see Section 3 – Literature Review) it was assumed that the performance of ozone and Peroxone in settled water would be very similar to that of filtered water. Therefore, only the raw and settled waters were tested during this study, not filtered water. All findings related to settled water performance (ozone dose, contact time, etc.) will be assumed to be the same for a filtered-water application.

In addition to gathering information about T&O control, one of the objectives of the pilot study was to gather information on the stability of the Peroxone process in SBA water. The variability of the pH and temperature in this water has been discussed in this Report, and is highly important to monitor and assess during this testing. Figure 4.3 includes data from ACWD's ozone plant showing the measured raw water pH and temperature over a four-day period in the summer. This type of diurnal variability is also observed at the Del Valle WTP (the variability is not as pronounced at the PPWTP because of the raw water reservoir). Figure 4.4 includes data from ACWD for the same four-day period showing the measured variation in ozone residual. During this time, the ozone dose was constant. The stability of the ozone residual in water is highly dependent on both temperature and pH. As the pH and temperature rise, the rate at which the ozone residual decays increases. Therefore, for a constant ozone dose, the ozone residual measured at a fixed sampling point will vary.

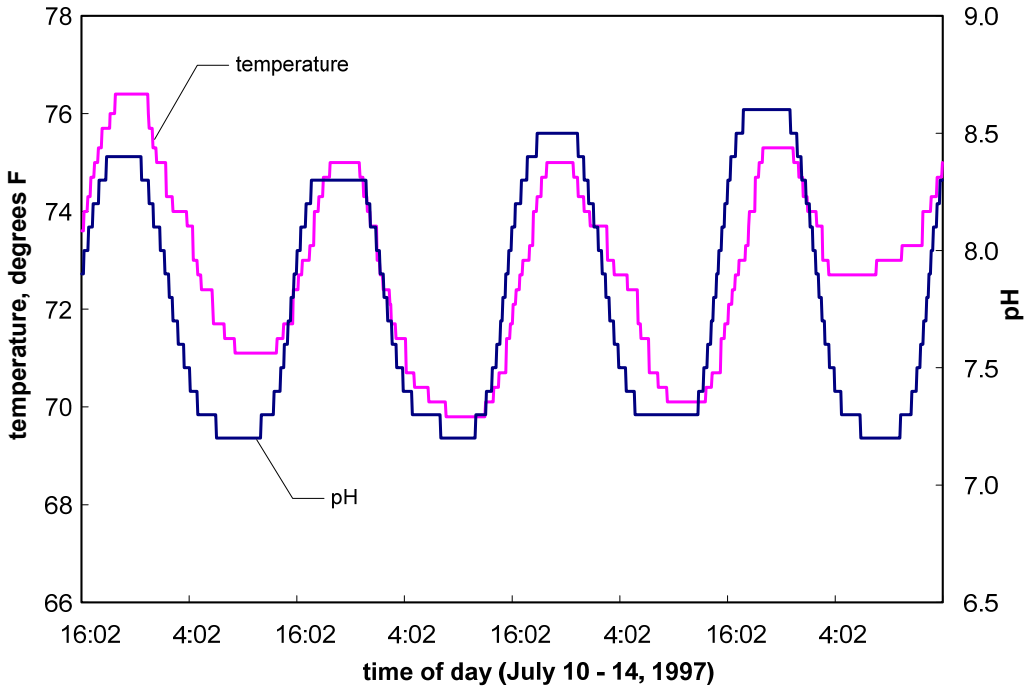

Figure 4.3 – Raw Water pH and Temperature Variability in SBA Water (ACWD 1997)

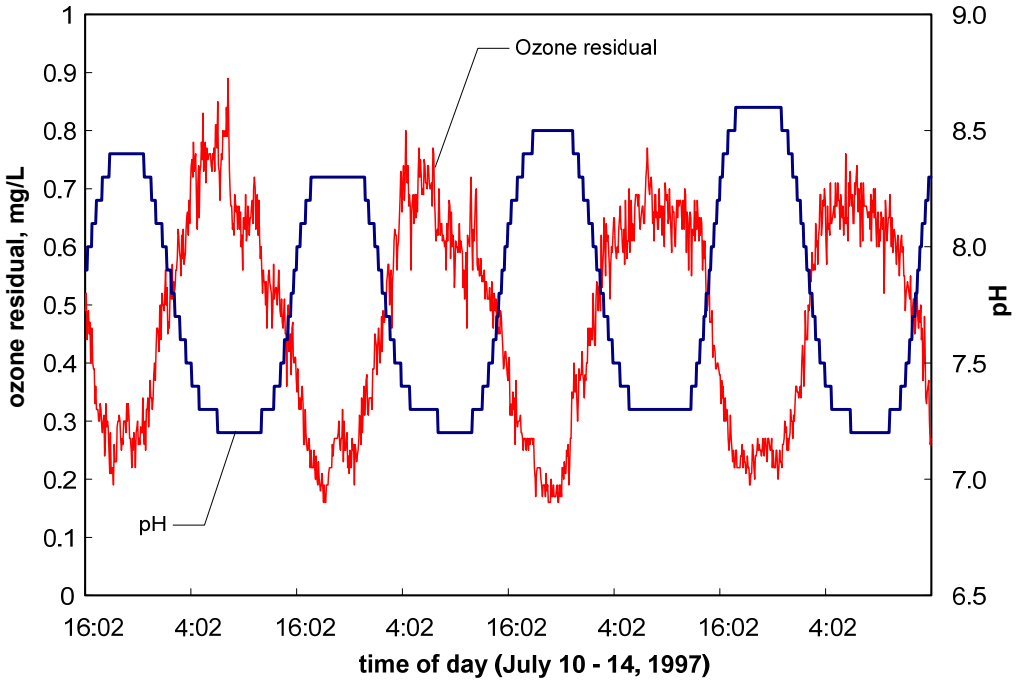

Figure 4.4 – Sample of Ozone Residual Variability in SBA Water (ACWD 1997)

This degree of variability in the ozone residual may make controlling a Peroxone system challenging. Several options for process control may be used, such as pacing the peroxide feed off the measured ozone residual, or adjusting the pH ahead of the ozone process in order to stabilize the ozone residual. It is not known if this type of variability will be observed when hydrogen peroxide is added ahead of the ozone, nor whether chloramine addition (a potential bromate control technique) will impact the results. Further, since this is a T&O control application and not a disinfection process, this type of variability may not be important. It may, however, have implications for the downstream processes (e.g. chlorine demand) and bromate formation. Finally, it is important to characterize the remaining ozone residual at various times to ensure that the design of the contactor does not allow for the presence of any unacceptable levels of ozone in the water leaving the contactor.

The pilot testing was conducted during the period of May through October of 2008 (a total of six (6) months of testing). Based on historical data, a T&O event was most likely to occur during this time. The pilot-testing program will include two phases. During Phase I, the pilot plant equipment will be set up and calibrated, and the various components will be checked to ensure that they are performing properly. During Phase II, testing will be conducted to evaluate and optimize the processes. The following sections describe the activities that were planned during each phase of testing.

4.2.1 Phase I – Startup and Unit Calibration

The first phase included system startup, which included completing the hydraulic and electrical connections to the pilot, preparing initial chemical feed solutions, refinement of analytical techniques, and initial quality control procedures. The following activities were conducted during system startup:

- Verify the accuracy of flow measurements
- Verify the accuracy of the chemical injections
- Calibration of online analyzers (pH, ozone residuals)
- Verify performance of automated control loops
- Refine sample collection and analytical techniques

4.2.2 Phase II – Process Performance Evaluations

Two types of information were gathered during this study:

- *Operational data* – such as flow rates, chemical dosages, contact times, etc.
- *Water quality data* – these included water quality analyses conducted on-site by WQTS (such as ozone residuals, pH, temperature), and analyses conducted by Zone 7's laboratory such as bromate, MIB, geosmin, TOC, THMs, etc.

All operational data were gathered by WQTS staff using the datasheets developed for this purpose and the automated data-logging capabilities of the pilot plant. All analyses that required laboratory support were handled by Zone 7's water quality laboratory. WQTS staff collected the samples in accordance with the experimental matrix and delivered the water samples to the Zone 7 laboratory. Zone 7 staff conducted the analyses (or sent them to a contracted laboratory) and reported the experimental and standard QC results to WQTS.

Testing during Phase II assessed the performance of ozone and Peroxone under various operating conditions that had been identified as a result of the data and literature review. These operating conditions are described herein. In developing the experimental matrix to answer the questions listed above, certain assumptions were made that influenced the decisions regarding the specific tests to be conducted. These assumptions were as follows:

1. *Adding ozone to raw SBA water without a bromate control strategy is not feasible due to the formation of bromate above the MCL of 10 µg/L. Therefore, when testing raw water ozonation, one or more bromate control technique(s) would always be used. A baseline bromate sample would be collected during each group of tests as a positive control, but this condition would not be fully evaluated.*

2. *The two strategies for bromate control that would be tested are pH suppression and chlorine/ammonia addition upstream of the ozone contactor.*

3. *Settled water pH is typically less than 7, and further pH suppression for bromate control would not likely be needed. Therefore, elevated pH values for the settled water would not be tested.*

4. *The chemical reactions associated with Peroxone were expected to be quite fast. Therefore, it was not necessary to test Peroxone under the long contact times associated with a conventional ozone contactor, since the oxidation of MIB and geosmin was likely to occur in the first few minutes.*

The quality of the water in the South Bay Aqueduct varies seasonally. During this 6-month pilot study, the temperature, turbidity, pH, alkalinity, and the nature and concentration of the natural

organic matter in the water were expected to change significantly. In order to gather sufficient data for the full-scale application, the challenge testing matrix was repeated three times (June, August, and October). The matrix took approximately two weeks to complete. In between challenge testing, the pilot plant was run under steady-state conditions in order to gather continuous operational stability information. Table 4.1 includes the matrix of experimental conditions used during the three rounds of testing.

Table 4.1 – Summary of Experimental Variables during 2008 Matrix Testing

Parameter	Round 1 June 16 - 27	Round 2 August 18 - 29	Round 3 October 13 - 24
Raw water ozone doses, mg/L	2, 3, 4	1, 2, 3	1, 2, 3
Raw water pH	amb[2], 7, 6.5	amb[2], 7.5, 6.5	amb[2], 7.5, 6.5
Contact times, min	1, 3, 6,10	1, 3, 10	3, 10
Chloramine doses, mg/L	0, 0.75	0, 0.75	0, 0.75
Settled water ozone dose, mg/L	0.5, 1, 1.5	0.5, 1.5, 3	0.5, 1, 2.5
Settled water pH	amb[2], 6.0	amb[2], 6.0	amb[2], 6.0
Peroxone ratio[1]	0, 0.2, 0.8	0, 0.5, 1	0, 0.5, 1
Peroxide injection point[3]	1	3	1, 2, 3, 4
Total number of separate tests	54	61	63
Number of MIB/geosmin and bromate samples	162	160	99

[1] Peroxone ratio is equal to the H_2O_2 dose, expressed in mg/L, divided by the ozone dose, also expressed in mg/L
[2] "amb" refers to ambient pH (no acid added), which ranged from 7.7 to 9.0 for the raw water and from 6.5 to 6.8 for the settled water
[3] Peroxide injection points shown on Figure 6.

Throughout the study, sampling of the raw water for analyses conducted by the laboratory was done once per week. These data were used primarily to characterize the changes in raw water quality, and Table 4.2 includes the parameters measured. These parameters were routinely analyzed by Zone 7's laboratory (or by their contracted laboratory).

Table 4.2 – Parameters to be Measured in the Raw Water

Alkalinity	Dissolved Organic Carbon (DOC)
Bromide	TOC
Hardness	Turbidity
Conductivity	Ultraviolet Absorbance at 254nm (UV254)
Iron	pH
MIB	geosmin
Manganese	Temperature

Four primary tasks were accomplished during the pilot study as detailed in the following paragraphs. Tasks 1, 2, and 3 pertained to the experimental matrix (challenge testing with spiked MIB, geosmin, bromate and TOC) while Task 4 pertained to the operational stability testing.

Task 1 – Evaluate the Impact of Ozone Dose and Contact Time on MIB and geosmin Destruction with Ozone Alone

This task focused on identifying the ozone doses and contact times needed to destroy MIB and geosmin when present at a concentration of up to 30 ng/L. Based on prior work by others, the following conditions were evaluated:

- Raw water ozone doses of 2 and 4 mg/L
- Settled water ozone doses of 0.5 and 2 mg/L
- Contact times of 6 and 10 minutes in the conventional contactor
- Contact times of 1 and 2 minutes in the pipeline contactor
- pH values in raw water from ambient to 6.5
- pH values in settled water from ambient to 6.0
- Chloramine doses of 0 and 0.75 mg/L
- Peroxone ratios (H_2O_2:O_3) between 0.2 and 1

During each test, ozone residual measurements were collected along the length of each contactor.

Since MIB and geosmin are both biodegradable and highly volatile, fresh working solutions were prepared during each day of challenge testing. MIB and geosmin were spiked into the pilot plant up to a concentration of 30 ng/L for these tests. This spiking was only conducted during the three challenge testing periods. For each test condition, samples were collected from the contactor effluents for the constituents shown in Table 4.3.

Table 4.3 – Parameters to Be Measured for Each Test Condition in Experimental Matrix

By Zone 7 Lab	By WQTS Staff
bromate	ozone residuals
MIB and geosmin	pH
	temperature
	free chlorine*
	combined chlorine*
	peroxide residual*

* *only when chlorine or peroxide is added as part of testing*

Task 2 – Evaluate MIB Destruction with Peroxone

Task 2 focused on evaluating the impact of peroxide addition on the effectiveness of MIB and geosmin destruction. The range of tests included in the ozone-only portion of the matrix (various ozone doses and contact times) were repeated, but with peroxide added ahead of the contactors for each test condition. Hydrogen peroxide-to-ozone ratios –commonly referred to as the Peroxone Ratio– of 0.2, 0.4 and 0.8 by weight were used. For each test, ozone residual measurements were made along the length of the contactors and if possible, hydrogen peroxide residuals was measured.

Task 3 – Evaluate impact of bromate control strategies

The purpose of this Task was to evaluate the impact of different bromate control strategies on the performance of the ozone and Peroxone in reducing MIB and geosmin. Two bromate control strategies were evaluated:

- pH suppression in the raw water to 7.0 and 6.5 (settled water pH may not need adjustment)
- Chloramine addition ahead of ozonation for both raw and settled water

The same set of conditions listed in Tasks 1 and 2 (ozone doses, contact times, and Peroxone ratios) were tested, each with a bromate control technique applied. For each set of conditions, a baseline bromate sample was collected before the bromate control technology was started. For example, if pH suppression were to be tested, the pilot plant was configured appropriately, the ozone doses and contact times adjusted, and immediately before the acid feed was turned on, a sample was collected for bromate (not MIB/geosmin). This served as a positive control.

Task 4 – Evaluate the stability of the ozone and peroxone processes

The purpose of this Task was to assess the impact of varying raw water quality on the ozone and peroxone processes. The pilot plant was run nearly continuously during this portion of the study, and data were gathered by the online instruments as well as by collection of grab samples. Some of the issues evaluated included the following:

1. *How much does the ozone residual vary between day and night?*
2. *What is the impact of this variation on the peroxone process?*
3. *Does adjusting the pH help stabilize the ozone residual?*
4. *What is the maximum ozone dose that can be added such that there is no measurable ozone residual leaving the contactor?*
5. *What is the decay rate of the ozone residual, and how does it vary over time?*
6. *When adding peroxide, how fast does the ozone residual degrade in the contactor?*
7. *How sensitive is the ozone residual to the peroxide dose? In other words, if the peroxide dose is not correct, or if the peroxide feed is lost, what happens to the ozone residual?*
8. *What is the impact of residual peroxide on the subsequent chlorine demand?*

The Operational Stability testing was conducted in between the three rounds of challenge testing.

4.2.3 Additional Data Collected

During the Operational Stability testing, frequent samples were collected from the contactor effluent for Simulated Distribution System (SDS) DBP formation testing. To match full-scale plant conditions, the chlorine dose (as sodium hypochlorite) used by the plant operators was added to the sample bottles at the start of a 1-hour free chlorine contact period. After one hour, ammonia was added at a 4.5-to-1 ratio by weight, matching the full-scale plant conditions. This

bottle was gently mixed by manual swirling, capped, and stored in the dark at room temperature (20 ± 2°C) for 24 hr. After this contact period, samples were collected for THMs, HAAs, and total chlorine. Additionally, weekly samples of carboxylic acid were collected from the raw water and the effluent of each contactor in service.

In addition to the MIB, geosmin, and bromate samples collected during the challenge testing periods, periodic samples (up to four per week) for these parameters were collected during the operational stability testing period.

One of the key questions to be answered is whether or not biological filtration should be installed downstream of a Peroxone process. Biofiltration downstream of a traditional ozone processes is commonly practiced in order to remove the increased amount of biodegradable organic matter (BOM) formed by ozone. As part of the pilot testing, the level of BOM formed by either the ozone or Peroxone process was measured using Assimilable Organic Carbon (AOC) as a surrogate parameter. However, the literature is not clear in the interpretation of how significantly BOM levels must increase to negatively impact distribution system regrowth and/or nitrification. One possible approach was to ensure that BOM levels following T&O control (or, eventually leaving the water treatment plant) were not greater than the BOM levels following the current, existing treatment processes. However, that may be too highly conservative and a less strict solution could be determined.

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SECTION 5.0 – PILOT TESTING RESULTS

This section presents the results of the pilot testing program. The first subsection presents the general quality of the water received by the DVWTP during the pilot testing period. The second subsection presents the results of the three rounds of matrix testing that identified the ozone doses required to meet the T&O destruction goals and the resulting bromate formation. The third subsection focuses on various design and operational parameters relevant to the application of the ozone or Peroxone process.

5.1 GENERAL WATER QUALITY

During the course of the study, Zone 7's water quality staff collected raw water quality samples and analyzed them for various parameters. Some parameters were collected weekly, while others were collected monthly. The average, minimum, and maximum values of the parameters analyzed are presented in Table 5.1.

Table 5.1 – General Raw Water Quality during Pilot Testing

Parameter	Unit	Number of Samples	Average	Min.	Max.
TOC	mg/L	28	4.1	2.7	7.6
UV-254	cm^{-1}	28	0.125	0.081	0.203
Turbidity	NTU	28	6	2	22
Bromide	µg/L	6	203	80	390
Alkalinity	mg/L $CaCO_3$	28	76	61	102
Conductivity	µs/cm	7	481	317	642
Tot. Hardness	mg/L $CaCO_3$	6	106	80	131
Iron	µg/L	3	440	220	600
Manganese	µg/L	6	16	5	23

Of significance to the use of ozone or Peroxone are the organic content of the water (i.e., TOC and UV-254 absorbance levels) and the bromide concentration. While the bromide levels varied from 80 to 390 µg/L, the water entering the pilot plant was spiked with bromide as needed during the testing program to simulate high-bromide levels and assess their impact on bromate formation. However, the organic content of the water during the three rounds of testing is of significance because it greatly impacts the ozone demand of the water. It could also impact the ozone dose required to meet specific T&O destruction goals.

Figure 5.1 shows a timeline of the raw water TOC, filtered water TOC, raw water UV-254 absorbance, and raw water Specific UV absorbance (SUVA) measured by Zone 7 water quality laboratory during the study. The periods of Round 1, 2, and 3 are also shown on Figure 7. Round 1 was conducted between June 16 and 27, 2008. Figure 5.1 shows that the organic content of the water during that period was much higher than those during the other rounds of testing. Specifically, the TOC concentration during Round 1 was as high as 7.6 mg/L, while that

during Round 2 was approximately 3.5 mg/L, and that during Round 3 was approximately 3.2 mg/L. During the study period, the plant achieved a consistent 50% removal of TOC, the filtered water from the plant was consistently half that in the raw water. The majority of the TOC is removed with coagulation and clarification compared to filtration. Therefore, it is expected that the filtered-water TOC profile shown in Figure 5.1 closely represents that of the settled water treated at the pilot plant during the study. The bottom portion of Figure 7 shows the SUVA levels. SUVA is calculated as the ratio between the UV-254 absorbance (in m^{-1}) and the TOC of the water (in mg/L). An increase in the SUVA value typically suggests an increase in the concentration of highly-reactive organic matter, while a decrease in SUVA values suggests a decrease in the concentration of reactive organics. While the TOC concentration during Round 1 was more than double that during Rounds 2 and 3, the SUVA value was virtually identical, if not slightly lower. This suggests that the increase in TOC was mostly due to nonreactive organic matter that should not greatly impact the ozone demand of the water.

In order to assess the impact of TOC on the ozone demand of the water, the results collected from the conventional ozone contactor during Rounds 1, 2, and 3 were compared. The comparison is shown in Figure 5.2 for the raw water and settled water. The plot contains the ozone residual measured in the outlet of the 1st chamber of the contactor as a function of the transferred ozone dose. The comparison shows that there was little to no difference in the ozone demand profile of the raw water between Rounds 1, 2, and 3, which confirms the SUVA observation discussed above. The same observation is made with settled water where there was no difference in the demand profile of the water between Rounds 1 and 2 in spite of the significant difference in the TOC concentration in the water between the two rounds of testing. Figure 5.2 also shows that there was little to no effect of water pH between 6.5 and 7.5 on the demand profile of the raw water.

The lack of impact of the higher TOC concentration on the ozone demand of the water during Round 1 does not necessarily mean that it would also have no impact on the performance of the ozone or Peroxone process for T&O destruction. As discussed later in this section, it is our suspicion that the change in the organic content of the water during Round 1 greatly impacted the performance of the Peroxone process when hydrogen peroxide was added upstream of ozone injection.

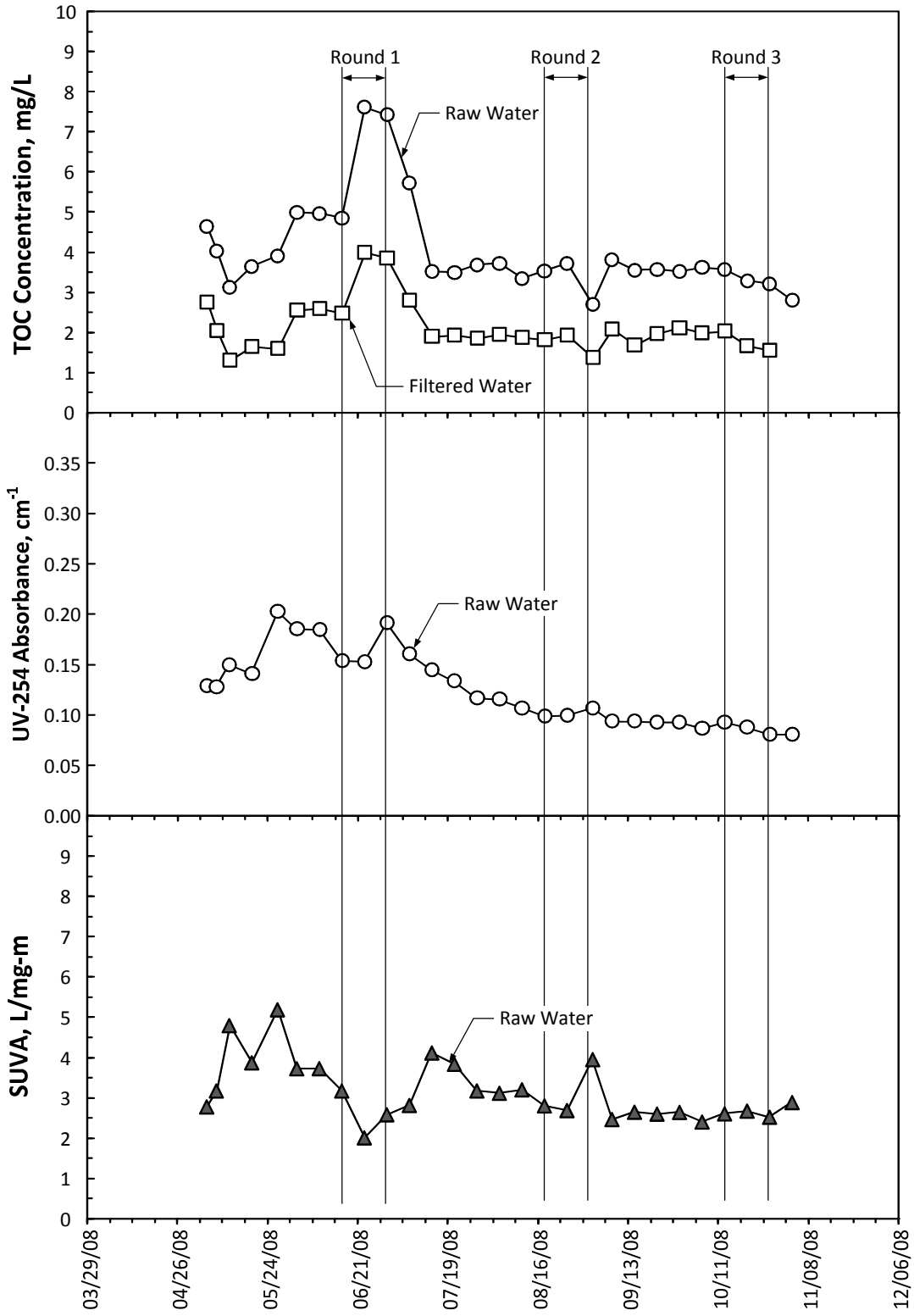


Figure 5.1 – Profile of TOC and UV-254 Levels in DVWTP Raw Water during Pilot Testing

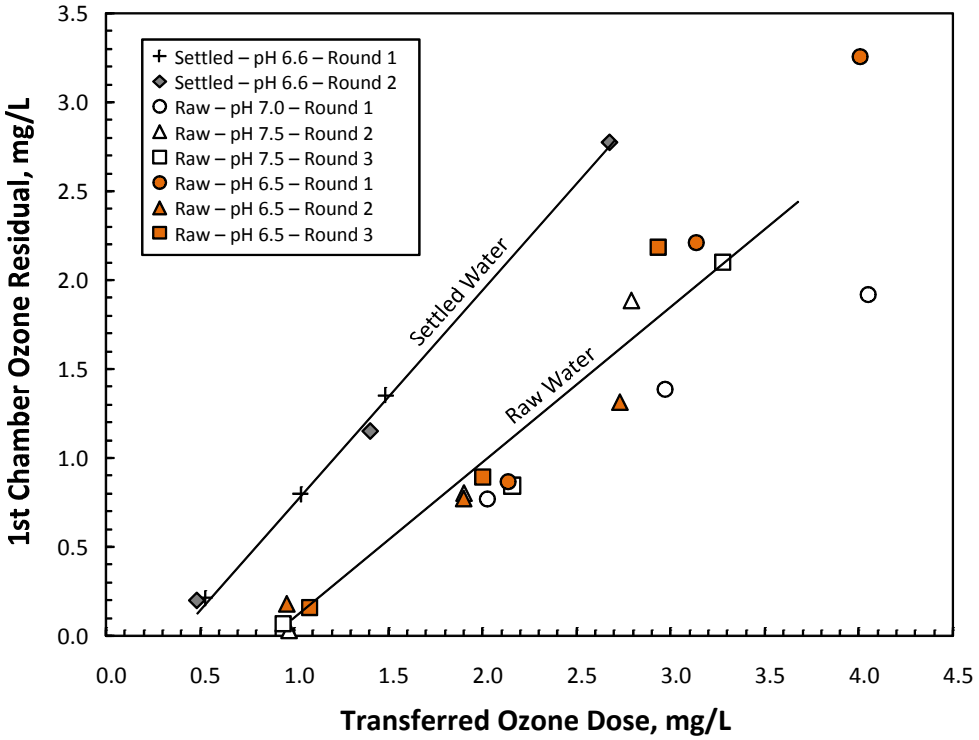


Figure 5.2 – Ozone Demand of Raw & Settled Water through the 1st Chamber of the Conventional Ozone Contactor

5.2 MATRIX TESTING RESULTS

Three matrix testing events were conducted over the six month pilot testing effort. Each matrix consisted of a large number of tests conducted over a two-week period. During each matrix test, the Peroxone process was compared side-by-side with the conventional ozone process treating either raw water or settled water. In the following subsections, results from all three rounds of testing of the conventional ozonation process are presented. For the Peroxone results, only the data obtained in Rounds 2 and 3 are presented and discussed. The Round 1 Peroxone results are not included in this analysis because the location of hydrogen peroxide addition was significantly different in Round 1 compared to Rounds 2 and 3. The effect of the peroxide addition point is discussed under section 3.3.

5.2.1 Raw Water Testing Results

A total of 54 tests were conducted on raw water during Round 1, 61 tests during Round 2 and 63 tests during Round 3. The conditions varied during these tests included pH, prechloramine addition for bromate control, Peroxone ratio (for the AOP process), and ozone dose. The raw water entering the pilot plant was spiked with 40 to 60 ng/L of both geosmin and MIB, as well as bromide during Rounds 1 and 2 (ambient bromide was high during Round 3). Appendix B includes the complete data from all three rounds of testing, as well as detailed graphs for most of the testing conditions.

In analyzing the results, the minimum ozone dose required to meet both the MIB destruction goal of >71% and the geosmin destruction goal of >73% was identified for each round and for each set of pH and prechloramine conditions. In all cases, the dose need to achieve MIB destruction was the higher of the two. One of the difficulties encountered in analyzing the results is that the performance of both processes varied significantly between the three rounds of testing. While such variability is expected with a natural water source, especially SBA water, it ultimately presents a challenge to the selection of the appropriate design criteria.

The raw water results summarized in Tables 5.2-A and 5.2-B, and in Figures 5.3 through 5.5. Note that the Peroxone results presented in this section focus on the H_2O_2:O_3 ratio (i.e., Peroxone ratio) of 0.5:1. The impact of various Peroxone ratios on the performance of the process is discussed later in this Section. Where only one value is shown (e.g. pH 6.5 with Peroxone) this condition was tested in only one round; therefore a range is not available.

Table 5.2-A – Conditions that Meet the MIB & Geosmin Destruction Goals in Raw Water <u>without</u> Prechloramine Addition

Type	pH	Ozone Dose to MIB & Geosmin Goals, mg/L	Bromate, µg/L	Effluent Ozone Residual, mg/L
Conventional Ozone	Ambient	--	--	--
	7.5	1.9 – 2.5	22 – 32	<0.05 – 0.4
	6.5	1.8 – 2.5	13 – 18	0.10 – 0.35
Pipeline Peroxone (0.5:1)	Ambient	--	--	--
	7.5	1.2 – 1.4	22 – 31	<0.05 – 0.1
	6.5	1.3 – 1.9 (est)[1]	24	<0.05 – ??

[1]This value is estimated from other tests with similar conditions.

Table 5.2-B – Conditions that Meet the MIB & Geosmin Destruction Goals in Raw Water <u>with</u> Prechloramine Addition

Type	pH	Ozone Dose to MIB & Geosmin Goals, mg/L	Bromate, µg/L	Effluent Ozone Residual, mg/L
Conventional Ozone	Ambient	1.3 – 2.4	14	<0.1 – 0.3
	7.5	1.4 – 2.8	7 – 11	<0.05 – 0.5
	6.5	--	--	--
Pipeline Peroxone (0.5:1)	Ambient	1.2 – 2.2	4 – 11	<0.05 – 0.15
	7.5	1.3 – 2.7 (est)[1]	4 – 11 (est)[1]	<0.1
	6.5	--	--	--

[1]This value is estimated from other tests with similar conditions.

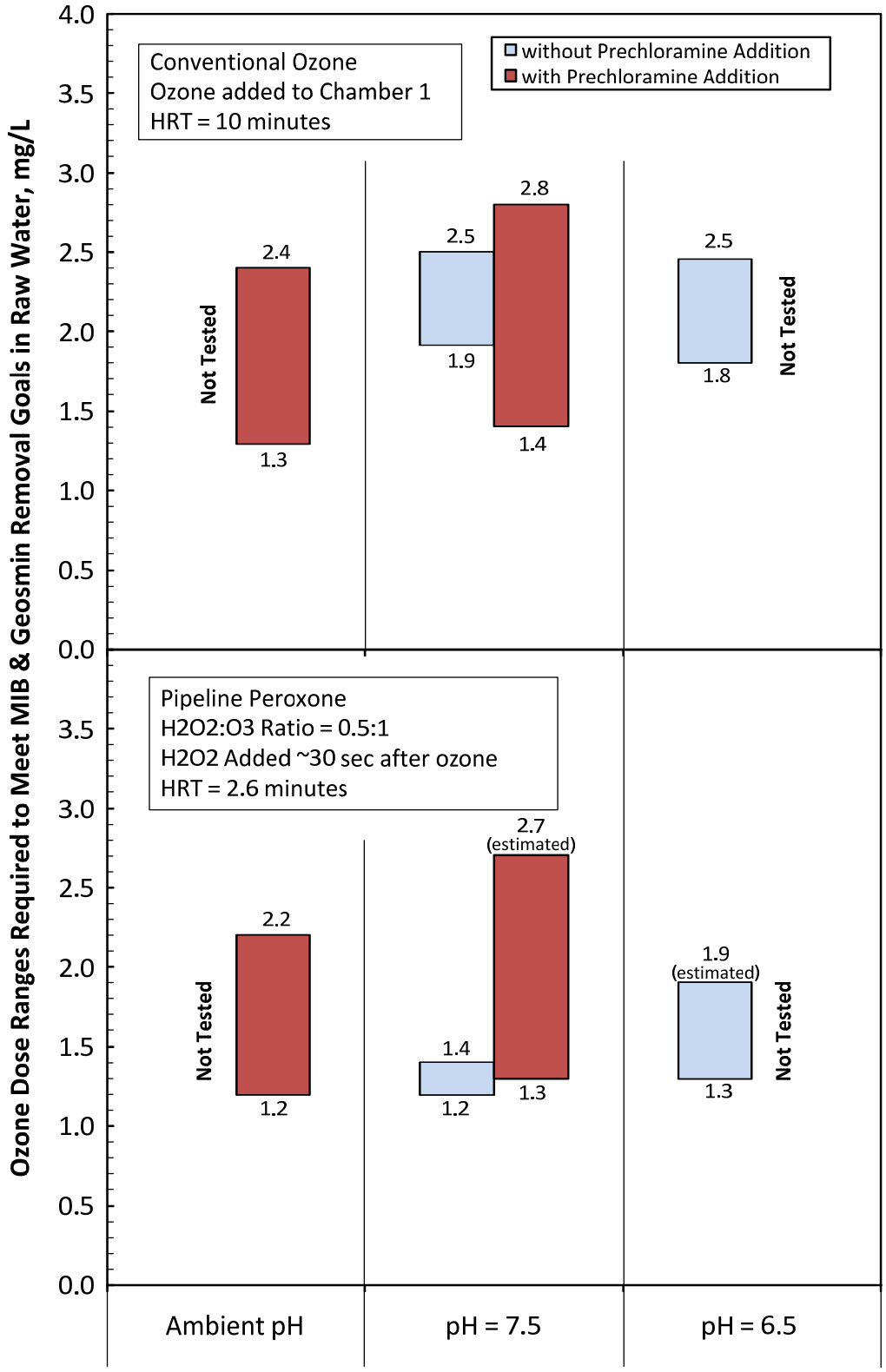


Figure 5.3 – Summary of Results for Raw Water – Range of Ozone Doses Required to meet the MIB & Geosmin Destruction Goals

Table 5.2-A summarizes the results obtained without prechloramine addition for bromate control, while Table 5.2-B summarizes the results obtained with prechloramine addition. Figure 5.3 shows a plot of the ozone dose ranges that were required to meet the MIB and geosmin destruction goals of 71% and 73%, respectively, in raw water during the testing period. The limits of each dose range are the doses obtained from the testing. In analyzing the information presented in Figure 5.3, the following observations are made:

1. Peroxide addition lowers the necessary ozone dose. Without chloramine addition (Table 5-A), the ozone dose required by the Peroxone process to meet the MIB and geosmin destruction goals in raw water is lower than the ozone dose required by the conventional ozone process. The advantage is most pronounced at pH 7.5 where the difference in ozone dose may be approximately 1.0 mg/L, while it is less significant at pH 6.5 where the difference may be only 0.5 mg/L.
2. However, the addition of chloramine adversely affects T&O destruction and lessens the effect of the peroxide (Table 5.2-B). The results suggest that when chloramine is added for bromate control, the two processes (i.e., Peroxone or ozone) may require the nearly same ozone dose to meet the MIB and geosmin destruction goals. It is speculated that the chloramine present in the water reacts with the hydroxyl radicals formed by the Peroxone process, thus reducing their ability to oxidize MIB and geosmin.

Figure 5.4 shows the bromate levels formed from the ozone dose range required to meet the MIB and geosmin destruction goals in raw water. It is important to emphasize that the bromide levels during the testing were as high quite high (generally >400 ppb). With this in mind, the following observations are made from Figure 5.4:

1. Without prechloramine addition ahead of the ozone or Peroxone process, and with the addition of sufficient ozone to achieve MIB and geosmin destruction, the bromate levels formed in the effluents of both processes were higher than the MCL of 10 µg/L by a significant margin. This was true even at the reduced pH of 6.5.
2. With the addition of 0.75 mg/L chloramine ahead of the conventional ozone process and the pipeline Peroxone process, bromate formation was significantly reduced.
3. With the addition of 0.75 mg/L chloramine ahead of both processes, the Peroxone process produced slightly lower levels of bromate compared to the conventional ozone process.

Figure 5.5 shows the range of ozone residuals measured in the effluent of each of the two contactors at the ozone doses required for sufficient MIB and geosmin destruction. While the ozone residual is neither a water-quality goal nor a regulatory limit, it is a safety and air-quality concern. If the ozone residual in the water leaving the contactor is above a certain level (typically 0.1 mg/L), off-gassing of the ozone will take place in the subsequent basins that would expose the operators to unhealthful levels of ozone in the air. Therefore, if elevated ozone residuals are present in the effluent of an ozone contactor, either the ozone dose must be reduced to reduce the effluent ozone to an acceptably low level, or an ozone-quenching chemical must be added and allowed to react with the residual ozone before the water exits the contactor. These chemicals include sodium thiosulfate or calcium thiosulfate. A third option is to increase the size of the contactor, thus allowing more time for the ozone residual to decay. In this application, since the ozone dose is selected based on the target MIB and geosmin destruction goals, the first remedy is not available, which means that the use of an ozone-quenching chemical or a larger contactor would be the only viable options. To reduce cost and operational complexity, it would be highly desirable that an ozone or Peroxone system is selected such that an ozone-quenching chemical would not be needed.

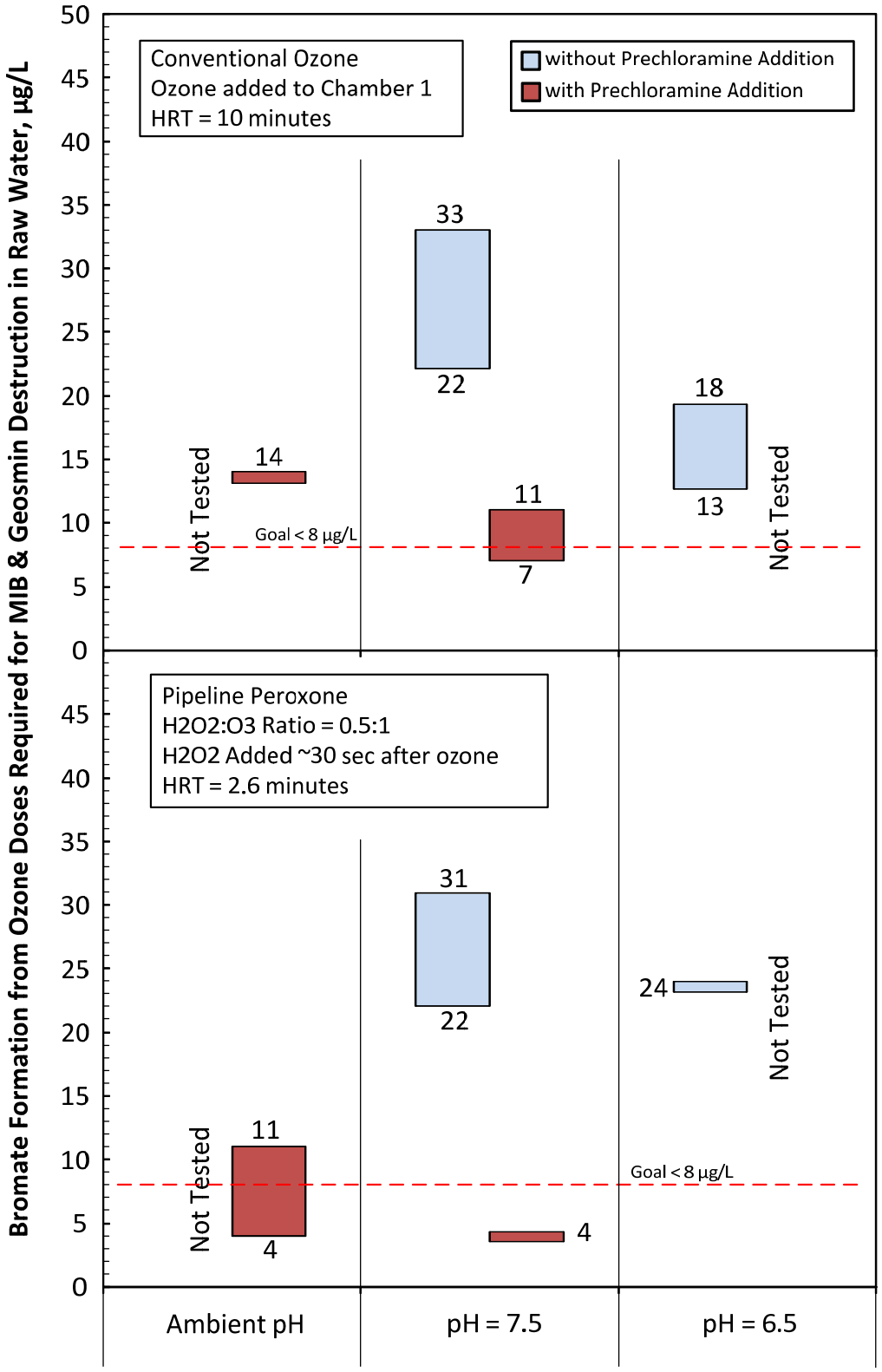


Figure 5.4 – Summary of Results for Raw Water – Bromate Formation under the Ozone Doses Required to meet the MIB & Geosmin Destruction Goals

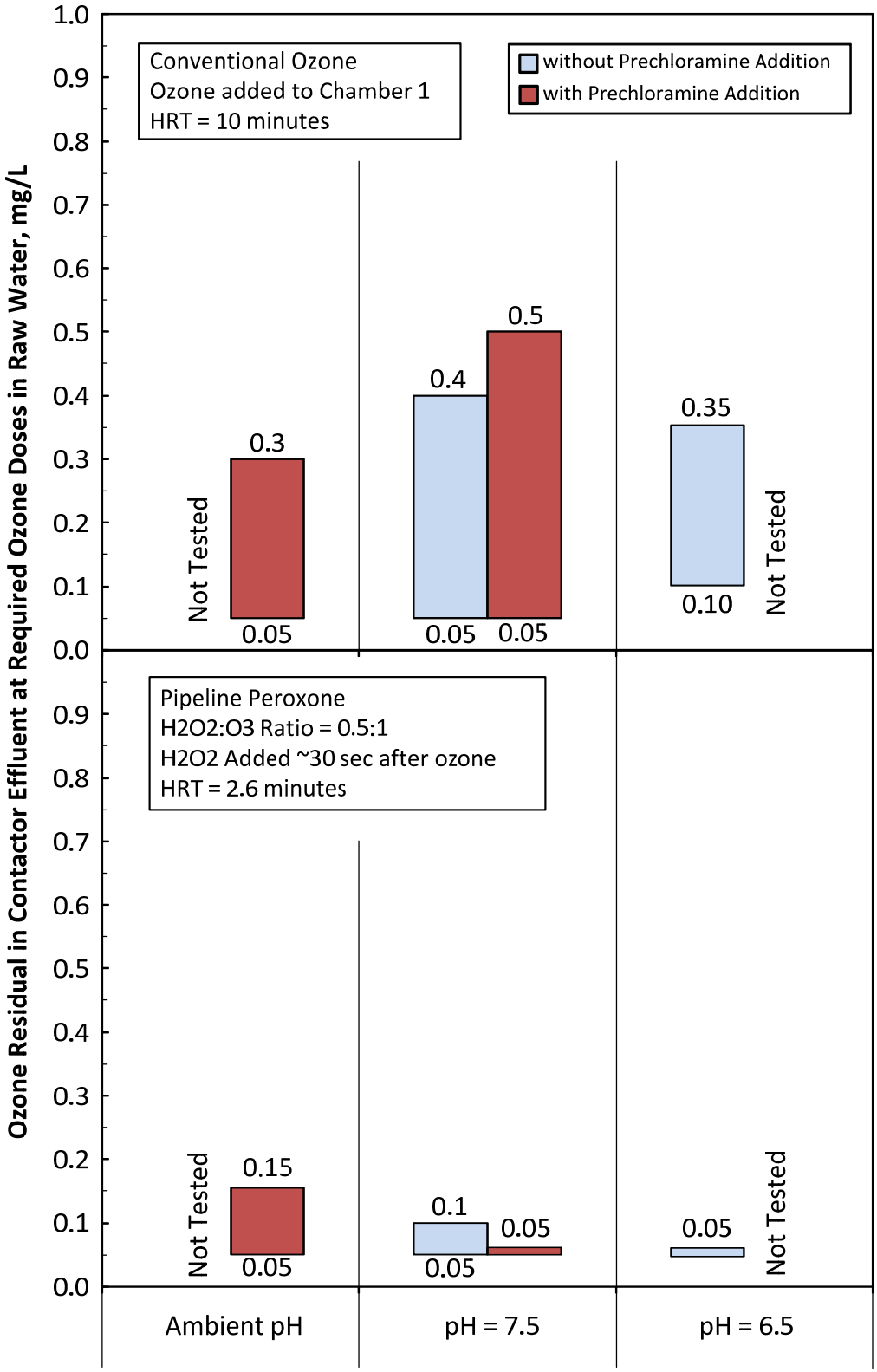


Figure 5.5 – Summary of Results for Raw Water – Ozone Residual Levels in Contactor Effluent Under the Ozone Dose Range Required to meet the MIB & Geosmin Destruction Goals

With the preceding discussion in mind, the following observations are made from Figure 5.5:

1. Under all conditions tested with the conventional ozone contactor, and under the ozone doses required for MIB and geosmin destruction, the ozone residual concentration in the effluent of the 10-minute contactor ranged from non-detectable (0.05 mg/L) to 0.5 mg/L. Some of these levels are well above the commonly acceptable level of 0.1 mg/L, which would require the addition of an ozone-quenching chemical or the use of a larger contactor.
2. However, with the ozone doses required in the 2.6-minute pipeline Peroxone process, the ozone residual under all but one condition tested were at or below the threshold level of 0.1 mg/L. This suggests that a pipeline Peroxone process may be operated to treat raw SBA water without the need for an ozone quenching chemical.

In summary, the raw water testing results obtained suggest that the use of a 2.6-minute Peroxone process could be more economical and more practical than the use of a 10-minute conventional ozone process, especially if the raw water pH is adjusted to approximately 7.5. The condition required the lowest ozone dose and had consistently low ozone residuals. However, during periods of elevated bromide levels, the addition of chloramine ahead of the Peroxone process would be necessary in order to control bromate formation, and this will reduce the economic benefit of the Peroxone process over the conventional ozone process.

5.2.2 Settled Water Testing Results

The settled water entering the pilot plant was pumped directly from the effluent of Superpulsator #4, upstream of the plant's chlorine addition point. As was done with the raw water testing, the settled water was also spiked with 40 to 60 ng/L of geosmin and MIB, as well as with bromide during Rounds 1 and 2 (the ambient bromide was sufficiently high during Round 3). The detailed graphs for each set of conditions are presented in Appendix A. In analyzing the results, the ozone dose ranges required to meet both the MIB destruction goal of >71% and geosmin destruction goal of >73% were identified for each set of pH and prechloramine conditions. As was the case with the raw water results, the dose required for MIB destruction was always higher than that required for geosmin destruction.

The summary of the results for the application of ozone or Peroxone to the settled water is presented in Tables 5.3-A and 5.3-B, and in Figures 5.6 through 5.8. Similar to the raw water results, the Peroxone results presented in this section focus on the H_2O_2:O_3 ratio (i.e., Peroxone ratio) of 0.5:1. The impact of the Peroxone ratio on the performance of the Peroxone process is discussed later in this Section.

Table 5.3-A – Conditions that Meet the MIB & Geosmin Destruction Goals in Settled Water without Prechloramine Addition

Type	pH	Ozone Dose to MIB & Geosmin Goals, mg/L	Bromate, µg/L	Effluent Ozone Residual, mg/L
Conventional Ozone	Ambient (6.5-6.7)	2.9 – 4.5 (est)[1]	37 - >70	1.0 - >2.0
	6.0	>4.5	>40	>2.0
Pipeline Peroxone (0.5:1)	Ambient (6.5-6.7)	1.1 – 1.2	21 – 23	0.25 – 0.5
	6.0	2.1	18 – 30	0.8 – 1.9

[1]This value is estimated; highest ozone dose applied was not able to meet goal

Table 5.3-B – Conditions that Meet the MIB & Geosmin Destruction Goals in Settled Water with Prechloramine Addition

Type	pH	Ozone Dose to MIB & Geosmin Goals, mg/L	Bromate, µg/L	Effluent Ozone Residual, mg/L
Conventional Ozone	Ambient (6.6)	>3.5 - >5 (est)[1]	ND - ??	>2.0
	6.0	--	--	--
Pipeline Peroxone (0.5:1)	Ambient (6.6)	1.3 – 1.7	9 – 10	0.3 – 0.9
	6.0	--	--	--

[1]This value is estimated; highest ozone dose applied was not able to meet goal

Table 5.3-A summarizes the results obtained without prechloramine addition for bromate control, while Table 5.3-B summarizes the results obtained with prechloramine addition. Figure 5.6 shows a plot of the ozone dose ranges required to meet the MIB and geosmin destruction goals of 71% and 73%, respectively, in settled water. The following observations are made from Figure 5.6:

1. The ozone dose needed for MIB destruction using conventional ozonation was very high. Under both the ambient settled water pH or an adjusted pH of 6.0, the conventional ozone process could not meet the MIB and geosmin destruction goals even with a projected ozone dose of up to 4.5 mg/L.
2. Peroxide addition significantly improved MIB destruction. Without the addition of chloramine for bromate control, an ozone dose of approximately 1.2 mg/L added to the 2.6-minute Peroxone contactor was sufficient to meet the MIB and geosmin destruction goals at ambient pH. This dose increased to 2.1 mg/L after adjusting the pH to 6.0.
3. With the addition of 0.75 mg/L prechloramine, the ozone dose required to meet the MIB and geosmin destruction goals in the Peroxone contactor increased to a range of 1.3 to 1.7 mg/L. Similar to the raw water results, prechloramine addition adversely affected the efficacy of the Peroxone process for T&O destruction.

Figure 5.7 shows a plot of the bromate levels formed from the ozone doses required to meet the MIB and geosmin destruction goals in settled water. It is important to emphasize that the bromide levels in the raw water during the two rounds of testing were high, ranging from 346 µg/L to 531 µg/L. With this in mind, the following observations are made from Figure 5.7:

1. Bromate formation in the conventional ozone process applied to the settled water cannot be quantified since the doses required to meet the MIB and geosmin goals were higher than the highest dose tested (>3.5 mg/L). Nevertheless, without prechloramine addition, the bromate level formed at the highest transferred ozone dose of 2.7 mg/L was as high as 70 µg/L at the ambient pH of 6.6, and 30 µg/L at an adjusted pH of 6.0.
2. Without prechloramine addition, the bromate level formed in the Peroxone process ranged from 21 to 23 µg/L at the ambient settled-water pH of 6.6. With the addition of prechloramine, the amount of bromate formed at the same pH decreased to 9 µg/L.
3. With a reduced settled water pH to 6.0, the addition of 2.1 mg/L ozone dose to the Peroxone process still resulted in the formation of approximately 18 to 30 µg/L of bromate. While reducing the pH to 6.0 would be expected to reduce bromate formation, the need for the higher ozone dose to meet the T&O destruction goals, eliminated the advantage of the lower pH value.

Figure 5.8 shows the range of ozone residuals measured in the effluent of each of the two contactors at the ozone dose ranges required for sufficient MIB and geosmin destruction. The following observations are made from Figure 5.8:

1. The anticipated ozone residual in the effluent of the conventional contactor could not be quantified since the doses required to meet the MIB and geosmin goals could not be determined. Nevertheless, based on the results collected, the residual ozone concentration is projected to be >2 mg/L. This is a very high residual value, and would certainly require the addition of an ozone-quenching agent before the water exits the contactor.
2. Even with the Peroxone process, the residual ozone concentration in the contactor effluent at the ozone doses required for MIB and geosmin destruction was still higher than the desired maximum of 0.1 mg/L. At the ambient settled water pH of 6.6, the ozone residual in the effluent of the 2.6-minute Peroxone process ranged from 0.25 to 0.5 mg/L without prechloramine addition, and from 0.4 to 0.75 mg/L with prechloramine addition.
3. At the adjusted pH of 6.0, the residual increases to a range of 0.8 to 1.9 mg/L without prechloramine addition. These levels are also quite high, and would require the addition of an ozone-quenching agent before the water exits the contactor.
4. The addition of a quenching agent is not trivial. Additional contact time would be required for the quenching chemical to destroy the ozone residual left in the water. The magnitude of this contact time required was not evaluated in the study. Further, the chemical may exert a chlorine demand, possibly affecting the downstream chlorination process.

In summary, the settled water testing results suggest that the application of conventional ozone to meet the MIB and geosmin destruction goals in the settled water at a pH of 6.6 or 6.0 requires an ozone dose that is likely to exceed 3.5 mg/L. However, an ozone dose of 1.7 mg/L applied to a 2.6-minute Peroxone process is sufficient to meet these goals at the ambient settled-water pH of 6.6. The dose increases to about 2.1 mg/L with a reduced pH of 6.0. However, the addition of an ozone-quenching chemical would be required to destroy the ozone residual before the water exits the contactor. Finally, during periods of elevated bromide levels, the addition of chloramine ahead of the AOP process would be required to control bromate formation.

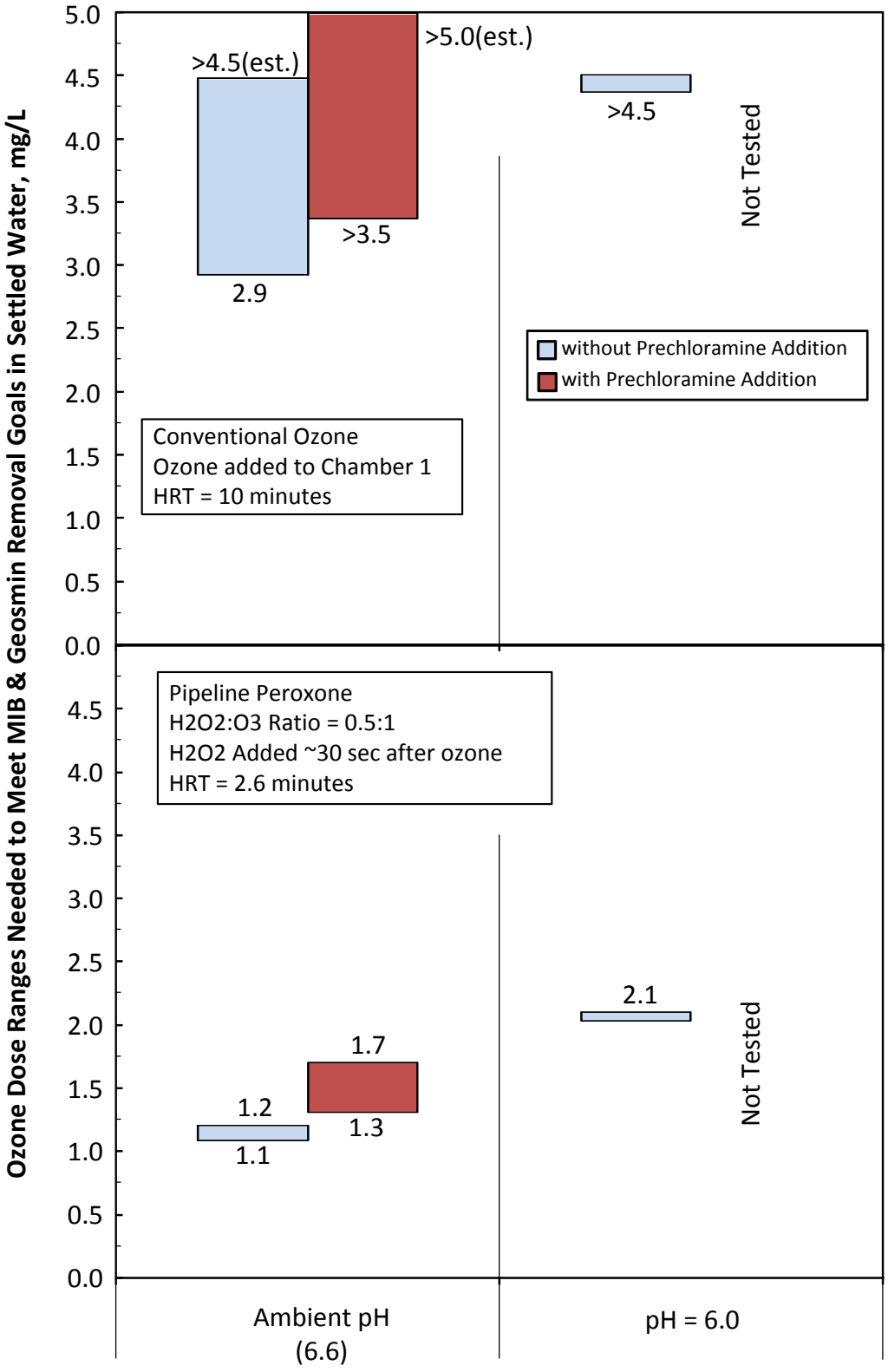


Figure 5.6 – Summary of Results for Settled Water – Range of Ozone Doses Required to meet the MIB & Geosmin Destruction Goals

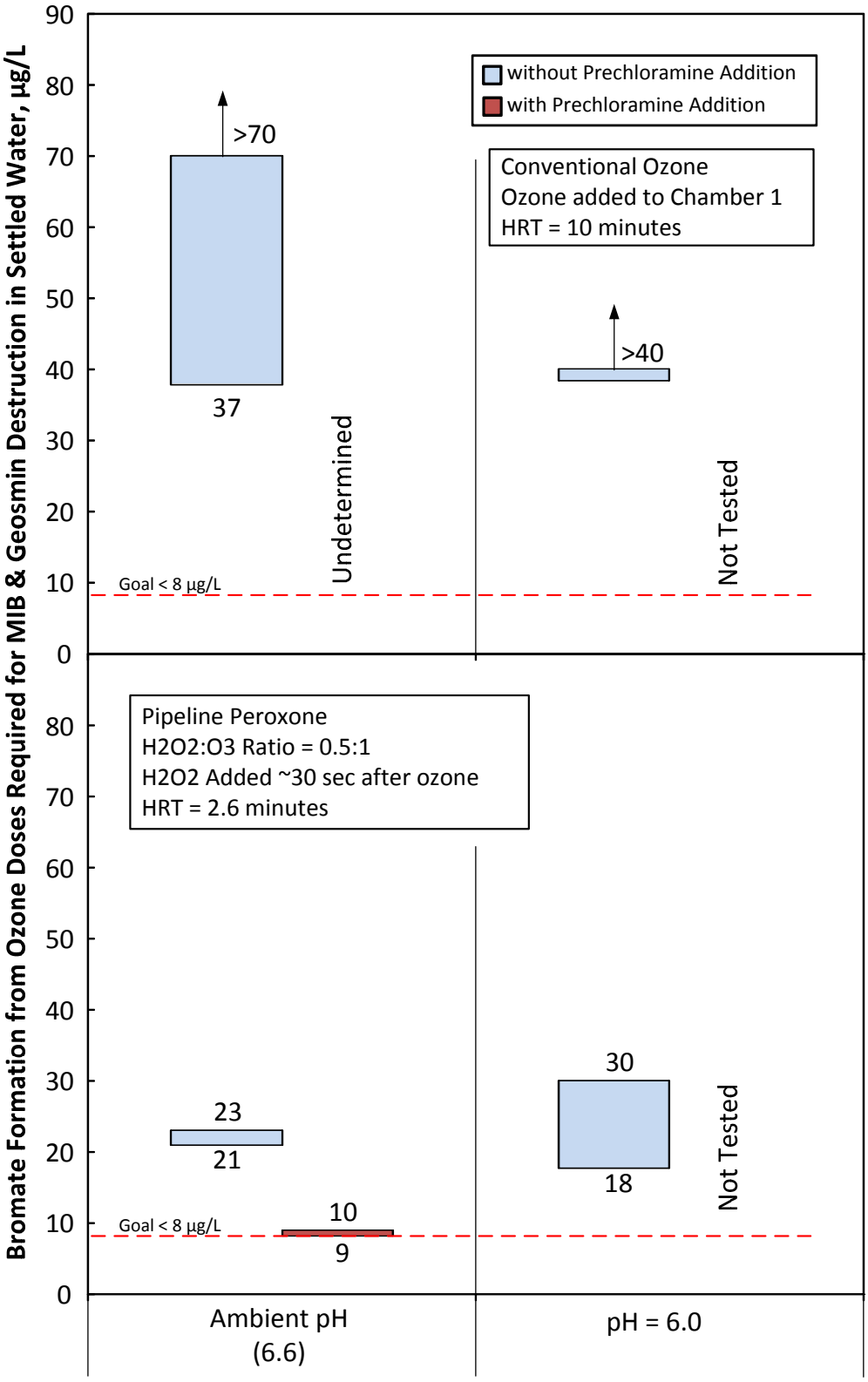


Figure 5.7 – Summary of Results for Settled Water – Bromate Levels Formed Under the Ozone Doses Required to meet the MIB & Geosmin Destruction Goals

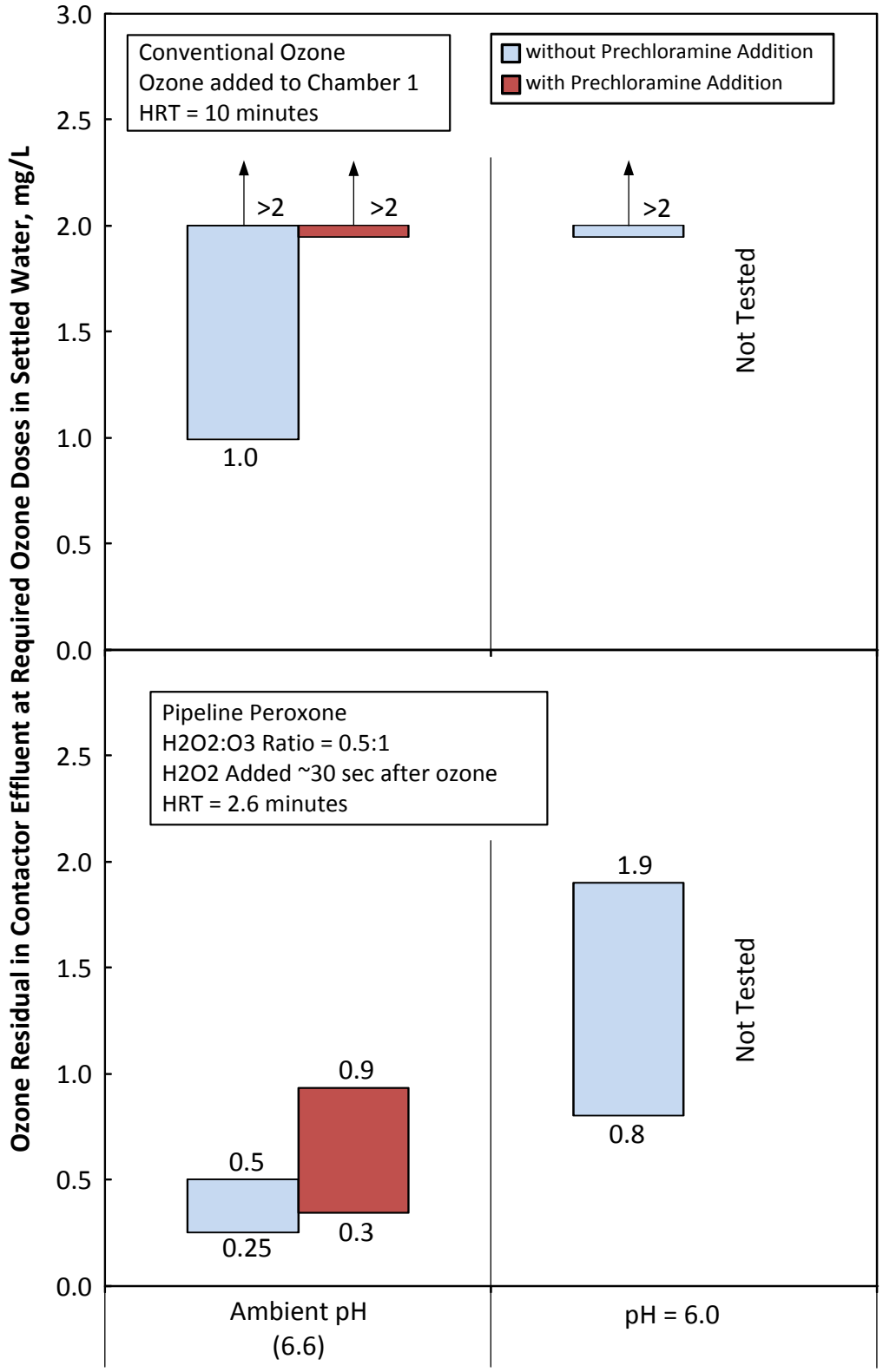


Figure 5.8 – Summary of Results for Settled Water – Ozone Residual Levels in Contactor Effluent Under the Ozone Dose Ranges Required to meet the T&O Destruction Goals

5.3 OTHER TESTING RESULTS

The previous section focused on identifying the ozone dose range required to meet the MIB and geosmin destruction goals in raw or settled water using a conventional ozone contactor or a pipeline Peroxone contactor. The previous section also evaluated the use of prechloramine for bromate control under elevated bromide levels in the raw and settled water. This section addresses some of the other design and operational questions related to the application of conventional ozone or Peroxone. Specifically, the following questions are addressed in this section:

1. How will the diurnal variations in the pH and temperature of SBA water affect the design and operation of the Peroxone process?
2. What is the impact, if any, of the location of the hydrogen peroxide injection point and the H_2O_2:O_3 ratio on the performance of the Peroxone process?
3. What are the by-products of the Peroxone process and how do they compare to those of the ozone process?

Each of the subsequent sections addresses one of the above questions.

5.3.1 Impacts of Diurnal Fluctuations in SBA Water Quality

One of the concerns with the use of ozone to treat SBA water is the wide diurnal fluctuations in the pH of and temperature in the water. Figure 5.9 shows a plot of these diurnal variations recorded by ACWD at WTP2. The plot shows that the water pH fluctuated between 7.3 in the morning to 8.7 in the evening. This is accompanied by a parallel fluctuation in temperature from 22 °C in the morning to 25 °C in the evening.[5] Similar fluctuations are recorded regularly at the Del Valle WTP during the summer and fall seasons. The lower portion of Figure 5.9 shows the impact of these fluctuations on the decay of ozone in the water. With a constant ozone dose of about 3.2 mg/L, the ozone residual measured at the effluent of the first chamber ranged from a high of about 0.8 mg/L when treating low-pH & low-temperature water, to a low of 0.15 mg/L when treating high-pH & high-temperature water. In 2001, ACWD installed a CO_2 feed system designed to maintain a stable pH in the water entering the ozone contactor by varying the CO_2 dose as the raw water pH varies during the day. This helps maintain a stable ozone system operation.

During the pilot testing effort, the impact of the diurnal fluctuations in raw water pH on the operation and performance of the Peroxone process was investigated because of its potential impact on the design of the system. This evaluation was conducted by operating the ozone and Peroxone processes in two modes: “constant residual” mode and “constant dose” mode. During the “constant residual” mode, the PLC was set to automatically adjust the ozone dose in order to maintain a constant ozone residual as measured by the online ozone analyzer. During “constant dose” mode, the ozone dose was fixed, regardless of the value of the ozone residual. The two pilot contactors were then operated in parallel for several 24-hour cycles.

[5] Data gathered in July 1997.

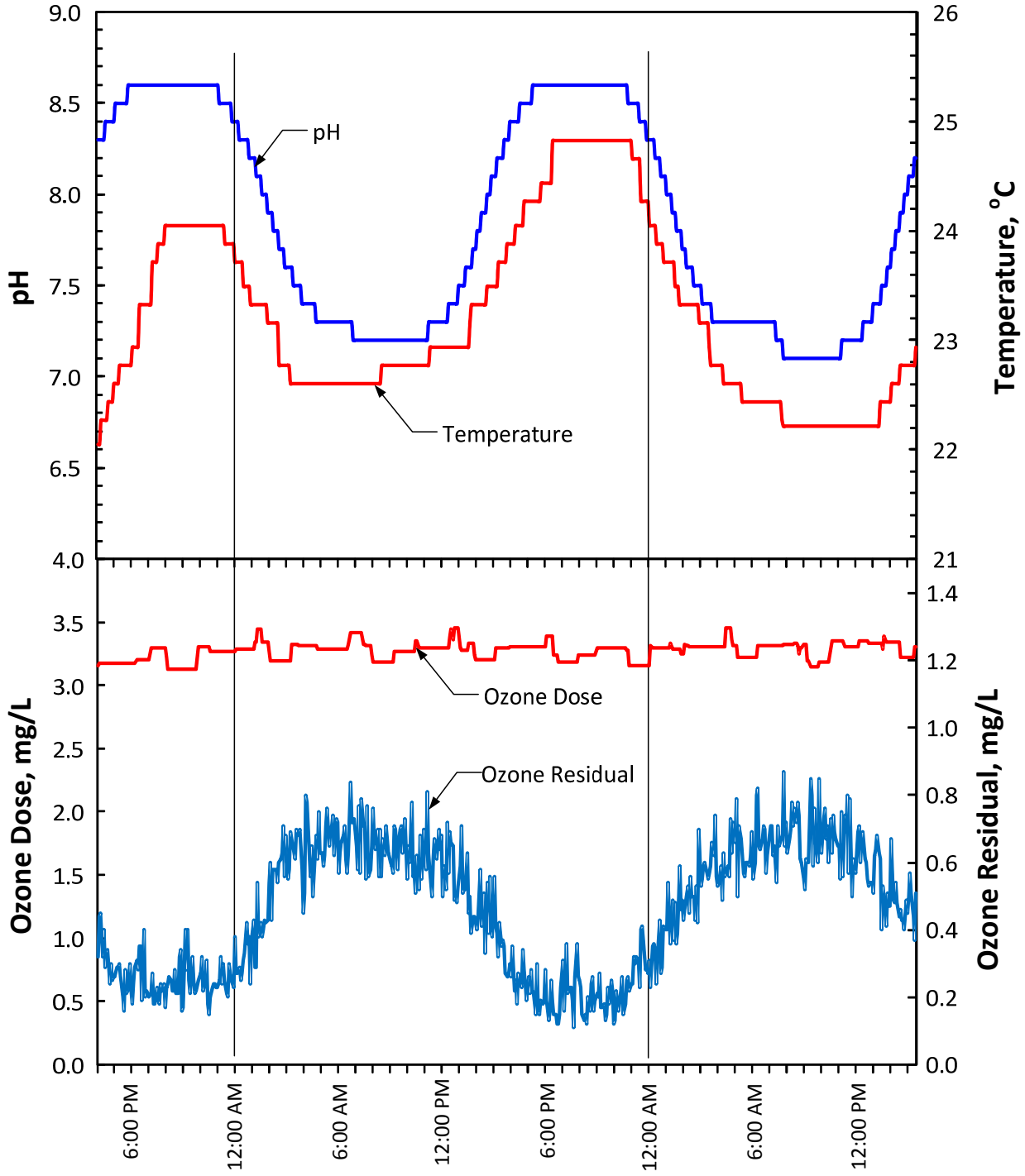


Figure 5.9 – Diurnal Fluctuations in SBA Water pH & Temperature, and their Impacts on the Decay of Ozone Applied to SBA Water (ACWD data)

5.3.1.1 Constant Residual Mode Test Results

Figures 5.10 and 5.11 show plots of the varying pH in the raw water, and the corresponding ozone residuals and ozone doses for the two contactors when they were operated in "constant residual" mode without pH adjustment. For the conventional ozone contactor, the analyzer was supplied by water drawn from the effluent of the 1st chamber. This method of operation is typical for conventional ozone contactors operating to achieve disinfection goals. For the pipeline Peroxone contactor, different analyzer locations were investigated. For the results shown in Figure 5.10, the ozone analyzer on the Peroxone process was supplied by water from the mid-point of the 2.6-minute contactor, approximately 60 seconds downstream of ozone injection. During these tests, the pH of the raw water varied significantly, decreasing from a high of approximately 8.6 to a low of approximately 7.6.

The top half of Figure 5.10 shows the ozone dose that was needed for the conventional ozone contactor in order to maintain the target ozone residual of 0.4 mg/L at the effluent of the 1st chamber. During the high pH period, the ozone dose was approximately 2.1 mg/L. As the pH decreased below 8.0, the required ozone dose decreased to approximately 1.2 mg/L. This translates into a dose difference of 0.9 mg/L, which is significant. The bottom half of Figure 5.10 shows the ozone dose that was needed for the Peroxone contactor in order to maintain the target ozone residual of 0.4 mg/L at the effluent of the 2.6-minute contactor during the same period of time. The results show that the impact of the change in water pH on the Peroxone process was far more significant than that on the conventional ozone process. As shown in the lower half of Figure 5.10, when the pH of the water was 8.3, the ozone dose required to maintain the target ozone residual was as high as 6.7 mg/L. As the pH decreased to less than 8.0, the ozone dose decreased to approximately 2.7 mg/L. This is a very large difference of 4.0 mg/L, and it is attributed to the fact that the system was trying to maintain a stable and measurable ozone residual one minute downstream of the ozone addition point. The rate of decay of the ozone residual in the presence of hydrogen peroxide at an elevated pH is very fast, therefore in order to maintain an ozone residual of 0.4 mg/L after a minute of reaction time, the required dose was very high.

A second test was conducted in which the ozone residual control point was moved upstream to a location only 30 seconds downstream of the ozone addition point, which is also the location of hydrogen peroxide addition. The two contactors were then operated in a "constant residual" mode, and the results are shown in Figure 5.11. Figure 5.11 is similar to Figure 5.10 in that it shows a plot of the varying pH values and corresponding ozone doses and ozone residuals when operated in "constant residual" mode with the relocated sample tap for the Peroxone contactor. The lower portion of Figure 5.11 shows that with the relocated sample point, the required ozone dose to maintain the target ozone residual was less variable (1.7 mg/L to 4.0 mg/L) compared to that reported in Figure 5.10 (2.0 mg/L to 6.7 mg/L). This variability in the ozone dose with the relocated control point is still quite variable (a difference of 2.3 mg/L), but it is closer to that needed for the conventional contactor shown in the upper portion of Figure 5.11.

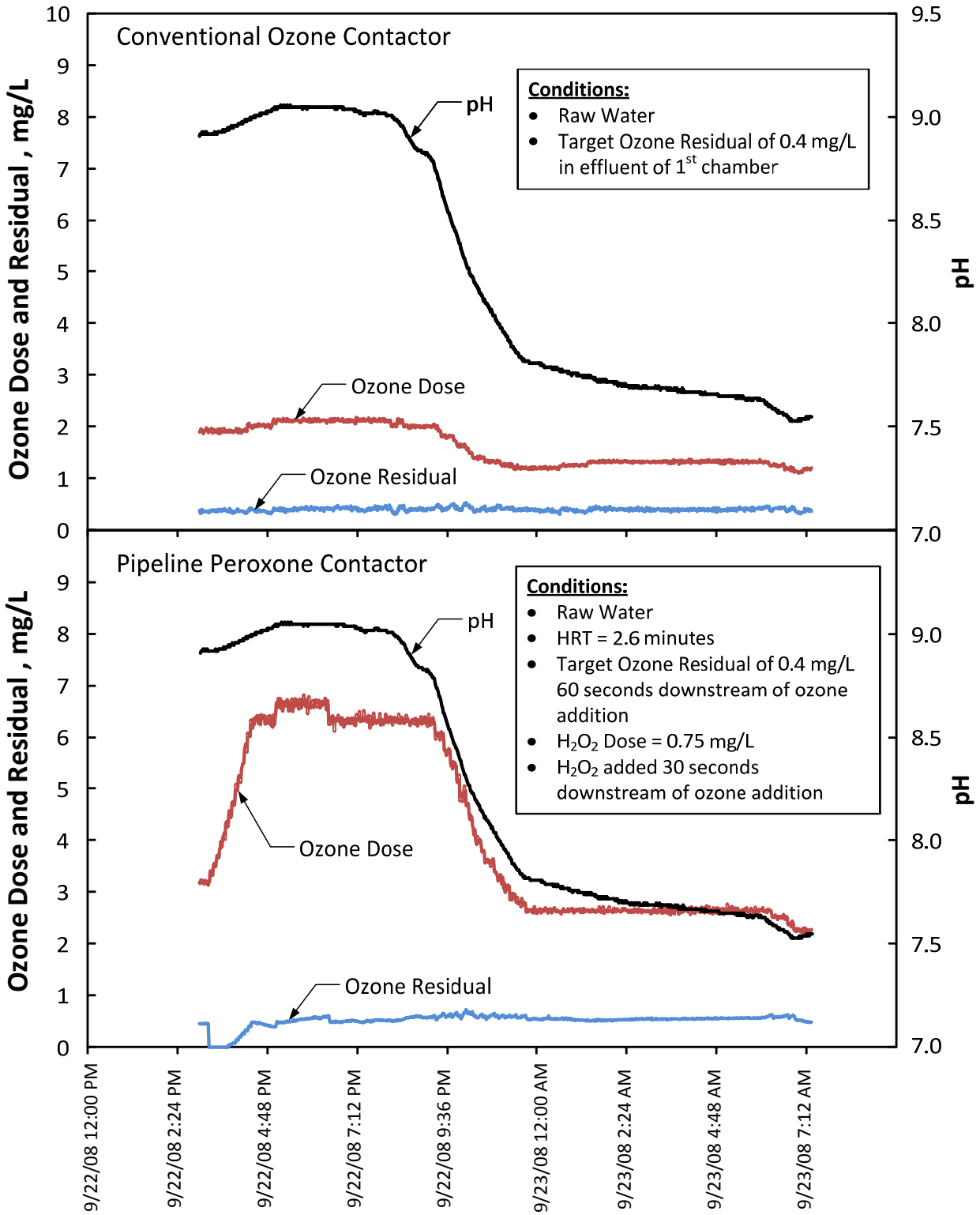


Figure 5.10 – Impact of Diurnal pH Changes on the Ozone Demand of the Raw Water Treated by a Conventional Ozone Contactor or a Pipeline Peroxone Contactor
[Control point located 60 seconds downstream of ozone injection]

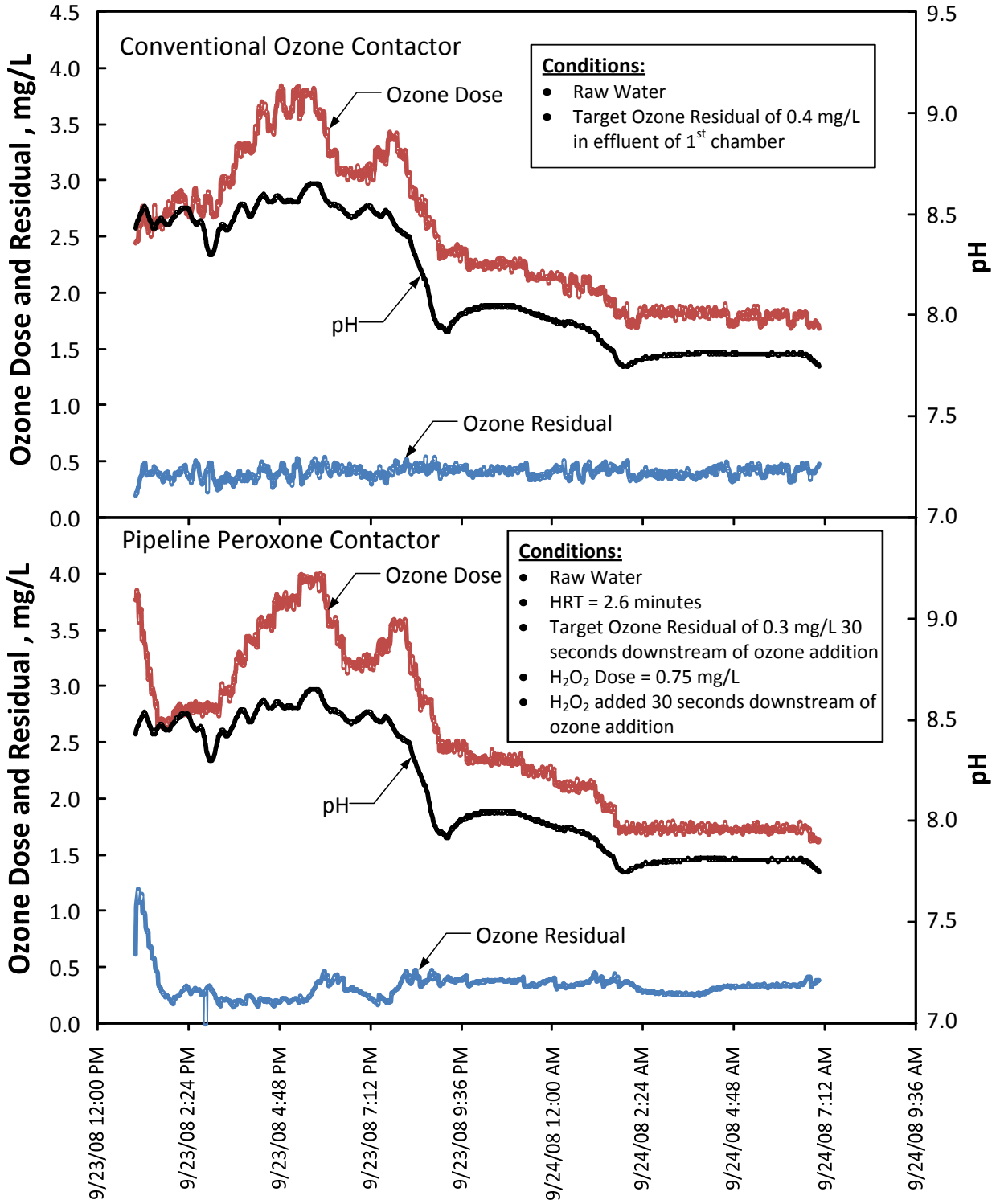


Figure 5.11 – Impact of Diurnal pH Changes on the Ozone Demand of the Raw Water Treated by a Conventional Ozone Contactor or a Pipeline Peroxone Contactor
[Control point located 30 seconds downstream of ozone injection]

The results presented in Figures 5.10 and 5.11 clearly demonstrate the strong impact of diurnal pH fluctuations on the ozone demand of the water for a conventional ozone contactor, as well as a pipeline Peroxone contactor. To eliminate this is effect, it is recommended to stabilize the pH upstream of the ozone or Peroxone process. This operational scenario was tested at the pilot plant. In this test, the ozone and Peroxone process were operated in a "constant residual" mode, but the pilot control system was set to maintain a constant pH in the influent water to both contactors. Sulfuric acid was added for pH adjustment. The pilot control system constantly adjusted the sulfuric acid dose to maintain the target pH as the raw water pH varied between night and day. The results of this 48-hr test are presented in Figure 5.12. During this test, the pH of the raw water varied between 9.4 and 7.7, and was adjusted at the pilot plant to a constant value of 7.3. The operating conditions were similar to those reported in Figure 5.11 in that the ozone dose to the conventional ozone contactor was varied to maintain a constant ozone residual of approximately 0.4 mg/L at the effluent of the 1st chamber. Since the pH of the water was stabilized at about 7.3, the ozone dose varied only between 1.4 and 1.9 mg/L. This is compared to a range of 1.5 to 3.8 mg/L shown in Figure 5.11. For the pipeline Peroxone contactor, the control system was also set up to vary the ozone dose so as to maintain a constant ozone residual of approximately 0.3 mg/L 30 seconds downstream of ozone injection (the same location as the hydrogen peroxide injection point). With the stable influent water pH at 7.3, the ozone dose varied only between 1.1 mg/L and 1.5 mg/L, compared to a range of 1.7 to 4.0 mg/L without pH adjustment (Figure 5.11).

The results reported in Figures 5.10, 5.11, and 5.12 clearly illustrate the following:

1. The varying pH of the SBA water has a profound impact on the ozone demand of the water, whether or not peroxide is used. Without pH adjustment, the required ozone dose to maintain a consistent ozone residual can vary by more than 2 mg/L between day and night.

2. When operating in "constant residual" mode, selection of the ozone residual control point for the Peroxone process is important. The control point should be very close to the ozone injection point in order to maintain a stable control system and to minimize the variations in the ozone dose required to maintain the target residual.

3. Stabilization of the pH greatly decreases the operational variability of both the ozone and Peroxone process, making the constant residual operating mode much more reliable.

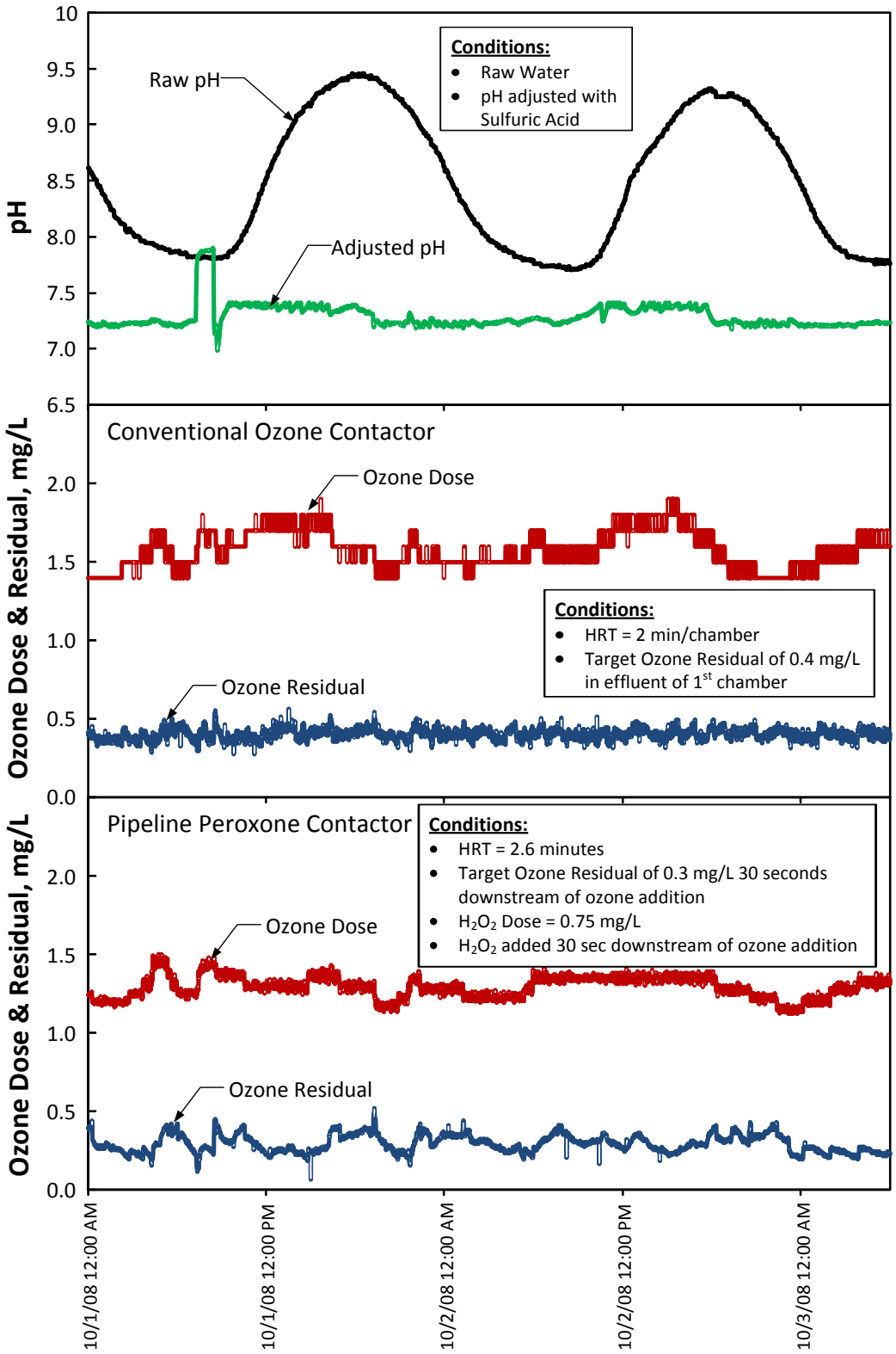


Figure 5.12 – Impact of pH Stabilization on the Ozone Demand of the Raw Water Treated by a Conventional Ozone Contactor or a Pipeline Peroxone Contactor

5.3.1.2 Constant Dose Mode Test Results

Tests were conducted using the "constant dose" mode. Consistent with the ACWD data shown in Figure 5.9, operation at a constant dose without adjusting the pH resulted in wide fluctuations in the ozone demand of the water, which translated into fluctuations in the ozone residual levels in the contactor. Figure 5.13 shows the results of the constant-dose tests conducted at the pilot plant in September. For the conventional contactor, the ozone dose was set at 2.5 mg/L. The top portion of Figure 5.13 shows that the decrease in pH from 8.7 in the afternoon to 7.4 in the morning of the following day resulted in an increase in the ozone residual from 0.6 mg/L (at pH 8.7) to 1.8 mg/L (at pH 7.4). For the pipeline Peroxone contactor, the ozone dose was set at 3.4 mg/L. The same shift in pH from 8.7 to 7.4 resulted in an increase in the ozone residual at the effluent of the ozone contactor (HRT = 2.6 minutes) from a low of non-detectable residual at pH 8.7 to a high of >2 mg/L at pH 7.4 (the online analyzer cannot measure values higher than 2 mg/L).

The results shown in Figure 5.13 illustrate the impact of pH changes in raw SBA water on the performance of an ozone-based process. This is important if a target ozone residual is to be maintained at all times (i.e., for disinfection CT calculation). However, if the plant is operated only for T&O oxidation and not for disinfection, then the measured ozone residual may not be as important. To investigate the need for maintaining an ozone residual, the pipeline Peroxone process was operated at a constant ozone dose for a period of seven (7) hours beginning at 10:30 AM and ending at 5:30 PM. The purpose of this test was to determine whether operating the Peroxone process under a constant ozone dose can still achieve the desired MIB and geosmin destruction goals, regardless of whether or not a residual ozone is maintained at some point in the contactor. During the seven-hour test period, the raw water entering the contactor was spiked with approximately 40 ng/L of each of MIB and geosmin. The Peroxone process was then monitored for influent and effluent MIB and geosmin levels every hour. During this period, the feed water pH was also monitored, along with the ozone residual concentrations at the middle and effluent of the Peroxone contactor. These locations are 60 seconds and 160 seconds from the point of ozone injection. The hydrogen peroxide was injected approximately 30 seconds downstream of the ozone injection point. The results are summarized in Figure 5.14. During the test period, the raw water pH increased from 8.1 at 10:30 AM to 8.9 at 5:30 PM. With the ozone dose maintained at 2.5 mg/L throughout the test, the ozone residual varied from a high of 0.15 mg/L to non-detectable levels at the mid-point of the contactor, and never exceeded 0.1 mg/L at the effluent of the contactor. The plot in the lower half of Figure 5.14 shows that the change in pH and lack of a measurable residual 30 seconds downstream of the hydrogen peroxide injection point had no effect on the destruction of MIB and geosmin. Throughout the seven-hour test, with the feed MIB and geosmin concentration held relatively constant between 40 and 45 ng/L each, the concentrations of MIB and geosmin in the effluent of the Peroxone process remained below 5 ng/L (approximately 90% destruction). These results suggest that maintaining a measurable residual for any appreciable amount of time downstream of hydrogen peroxide addition in a Peroxone process may not be necessary for satisfactory T&O destruction. It should be noted, however, that the need to control bromate formation remains to be a strong driver to reduce the pH of the water before ozonation.

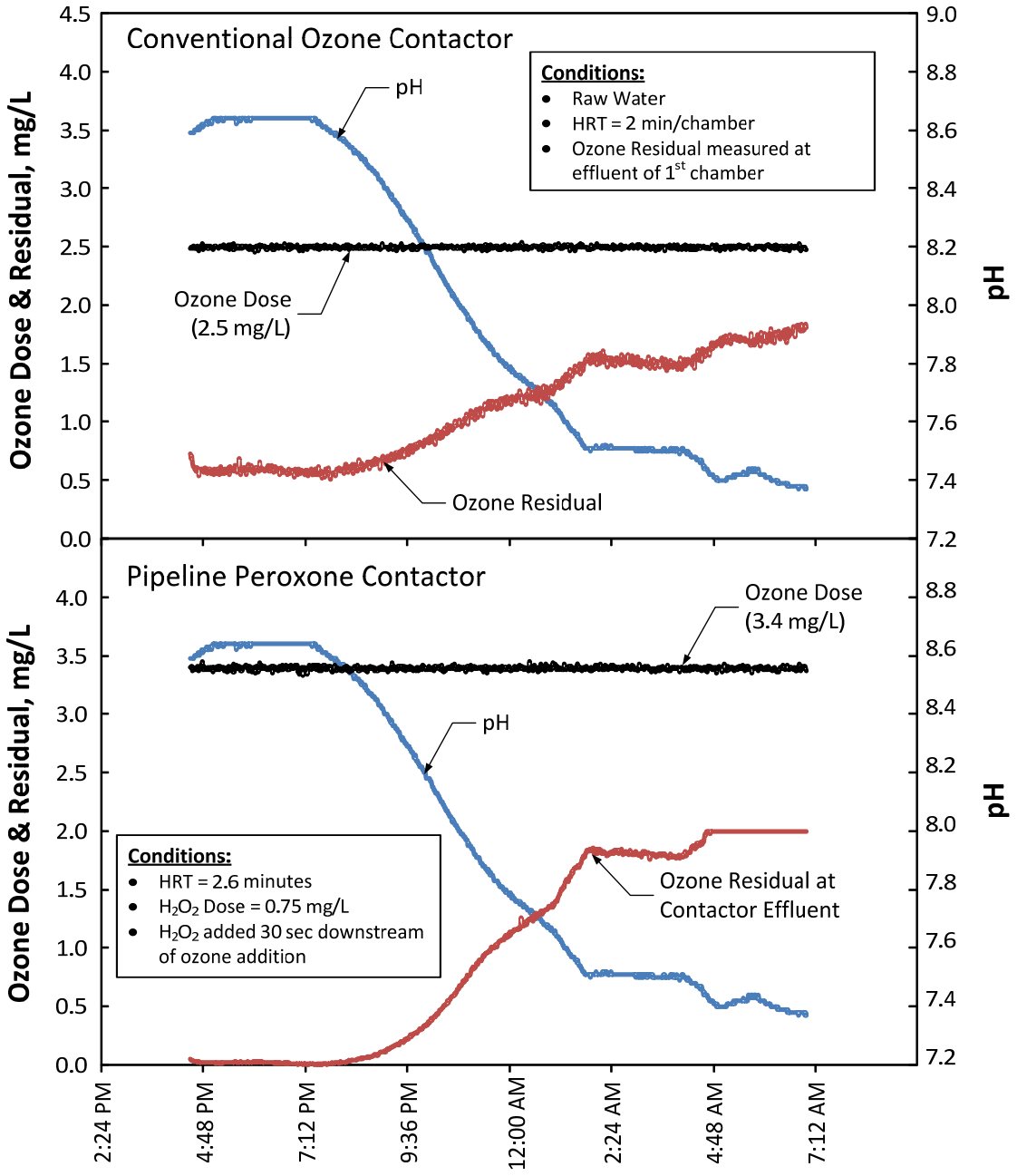


Figure 5.13 – Variability in Raw Water pH and its Impact on Ozone Residual in Both Contactors when Operated in Constant Dose Mode

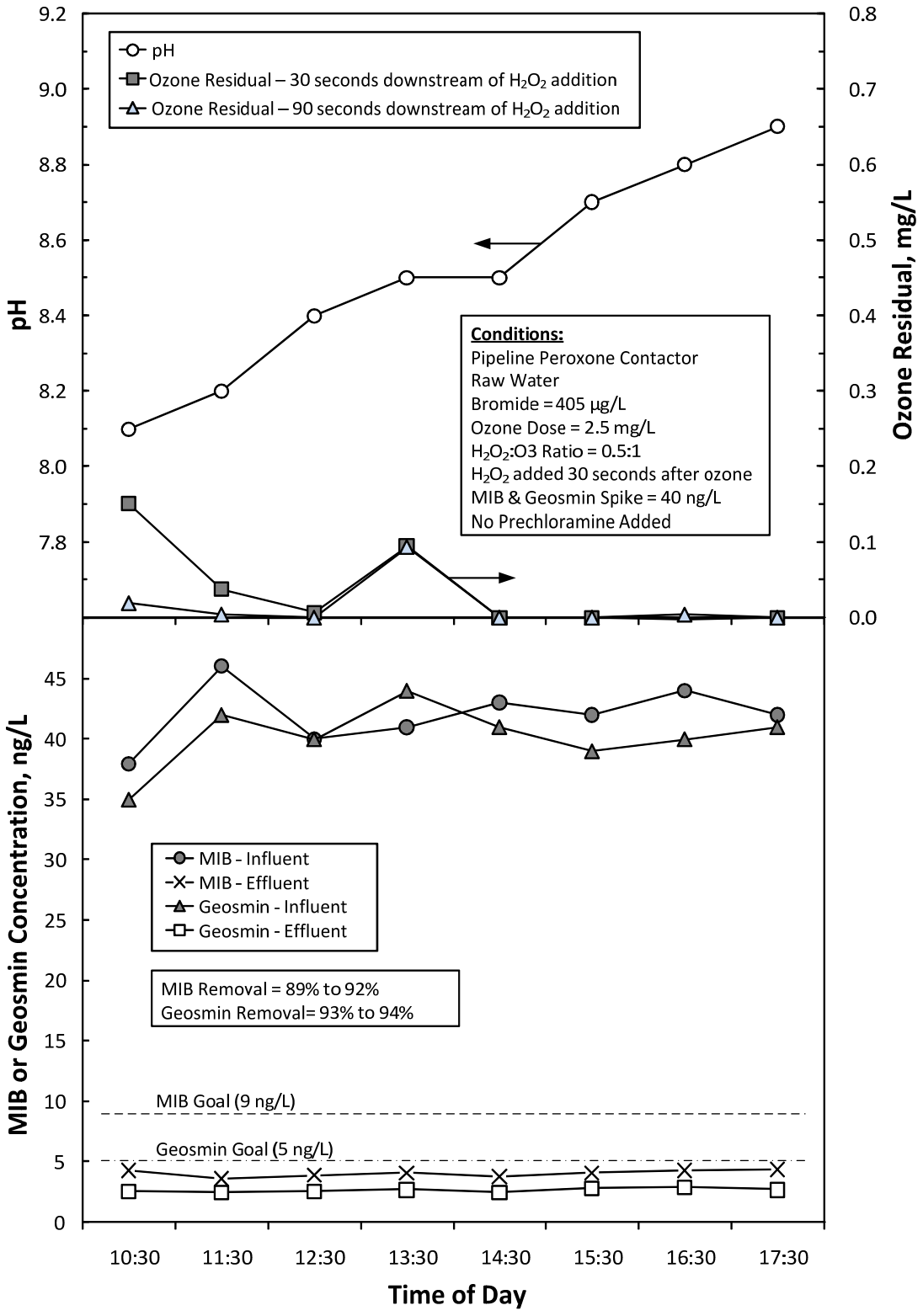


Figure 5.14 – Impact of Daily pH variation in the Raw Water on the Performance of the Pipeline Peroxone Process Operated at a Constant Ozone Dose

5.3.2 Impact of Peroxide Addition Point

One of the important questions to answer when designing a Peroxone process is "*where should the hydrogen peroxide be added?*" A Peroxone process is based on the principle that the combination of ozone and hydrogen peroxide generates hydroxyl radicals (OH•), which are stronger, less selective oxidants than molecular ozone, and should result in the same level of chemical destruction with lower ozone doses and shorter contact times. This principle suggests that the addition of hydrogen peroxide immediately upstream of ozone should result in the same level of OH• radical formation and the shortest process contact time, since the hydrogen peroxide will be immediately available to react with the ozone at the point of ozone addition.

With the above discussion in mind, the pilot testing was to be conducted with hydrogen peroxide addition immediately upstream of ozone injection, and the first round of matrix testing was conducted using this configuration. However, when the testing results were analyzed, it became apparent that the Peroxone process was not achieving the T&O destruction goals anticipated. Moreover, the results indicated that the addition of higher levels of peroxide had no effect on the destruction of MIB and geosmin with the Peroxone process, and the ozone residual in the effluent of the contactor was much higher than originally expected. An example of the unexpected outcome of the Round 1 tests is presented in Figure 5.15. The data plotted in Figure 5.15 were collected using raw water adjusted to pH 7.0. The "square" symbols represent MIB destruction as a function of the ozone dose applied to the Peroxone contactor with hydrogen peroxide added immediately upstream of the ozone injection point. The peroxone ratio was approximately 0.5:1. The contactor was operated at a flowrate resulting in a total hydraulic retention time of 2.3 minutes through the contactor. The "triangle" symbols represent the data points collected with the same Peroxone contactor, operated under the same conditions, but without the addition of any hydrogen peroxide. The "circle" symbols represent the MIB destruction measured across the conventional contactor with ozone added to the first chamber, and no hydrogen peroxide added to the water before or after ozone injection. Figure 5.15 clearly indicates that there was no discernable difference in the impact of ozone dose on MIB destruction through the pipeline Peroxone contactor or the conventional contactor, and, more importantly, that the addition of hydrogen peroxide at a ratio of 0.5:1 also had no noticeable effect on the ozone dose required for MIB destruction.

It is noted that Round 1 testing was conducted in June 2008. In light of the results obtained, tests were conducted in August 2008 to determine whether the lack of advantage of the Peroxone process over the conventional ozone process was due to the fact that the hydrogen peroxide was added upstream instead of downstream of the ozone injection point. The results, which are presented in Figure 5.16, clearly demonstrated that the peroxide addition point had a significant impact on the reaction between the ozone and hydrogen peroxide. In the test reported in Figure 5.16, the raw water flowrate was set at 2 gpm, which resulted in a 4-minute hydraulic retention time through the pipeline contactor. The ozone dose applied was 5 mg/L. With no hydrogen peroxide addition, the residual ozone at the outlet of the contactor was measured at 0.27 and 0.32 mg/L. With hydrogen peroxide addition upstream of the ozone injection point, the ozone residual at the outlet of the contactor was still measured at 0.24 mg/L at a H_2O_2:O_3 ratio of 1:1, and 0.23 mg/L at a H_2O_2:O_3 ratio of 2:1. However, when hydrogen peroxide was added 1 minute downstream of the ozone injection point, the ozone residual concentration in the effluent of the contactor was measured at 0.08 mg/L at a H_2O_2:O_3 ratio of 1:1, and ND at a H_2O_2:O_3 ratio of 2:1. Based on these findings, Rounds 2 and 3 tests were conducted with hydrogen peroxide addition downstream of ozone injection.

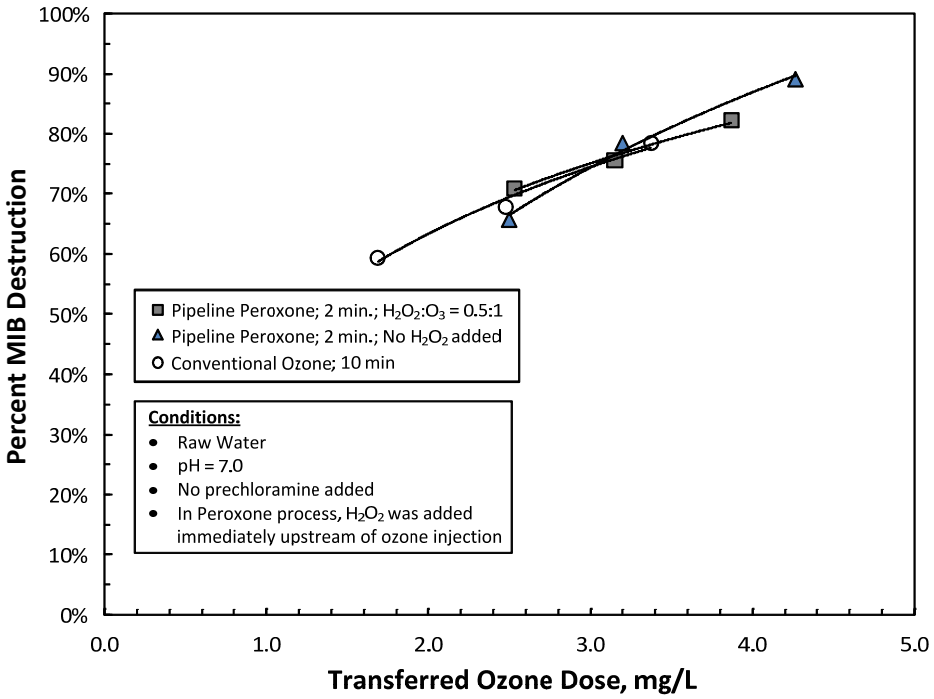


Figure 5.15 – Comparison in MIB Destruction between the Conventional Ozone Contactor and the Pipeline Peroxone Contactor with and without Hydrogen Peroxide Addition During Round 1 Testing

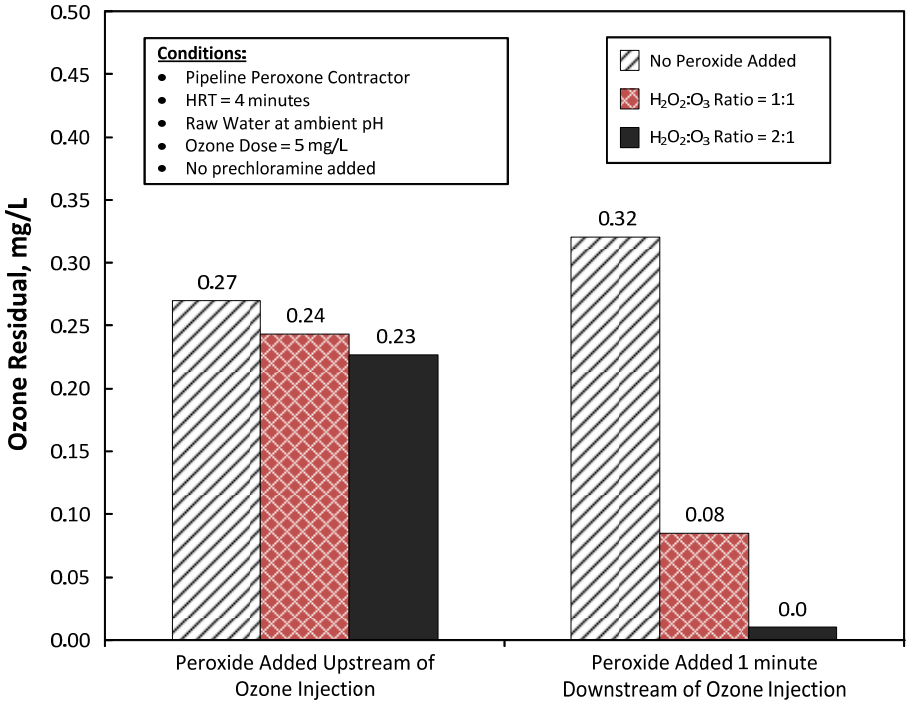


Figure 5.16 – Impact of Hydrogen Peroxide Addition Point on the Ozone Residual Measured at the Effluent of the Pipeline Peroxone Contactor (August 2008)

At the end of Round 3 testing conducted in October 2008, a test was conducted to determine whether the results of Round 1 and the follow up tests in August 2008 could be replicated. During this test, the hydrogen peroxide feed point was moved back upstream of the ozone injection point. The ozone residual concentrations in the Peroxone contactor effluent were then compared to those measured when the peroxide was added downstream of the ozone injection point, as well as to the levels measured when no peroxide was added. The results are shown in Figure 5.17. In this test, the addition of hydrogen peroxide upstream of ozone resulted in complete destruction of the ozone residual by the end of the contactor compared to the results with no peroxide addition. This is opposite from the results obtained during Round 1 and the subsequent testing conducted in August 2008 and reported in Figure 5.16 above. The results gathered with peroxide addition downstream of ozone injection were consistent with the previous results in that they too resulted in the destruction of the ozone residual to very low levels.

There is no clear explanation for why peroxide addition upstream of ozone performed so poorly during Round 1 and during the August testing, but then performed well during Round 3 in October. We speculate that the organic makeup of the water in July and August 2008 somehow affected the reactivity of hydrogen peroxide before the ozone was added, and that made it unavailable to react with the ozone in the Peroxone contactor to form hydroxyl radicals. This water quality characteristic then may have changed by October 2008 such that the addition of peroxide upstream of ozone performed as well as when it was added downstream of ozone. Unfortunately, we do not have the ability to prove or disprove this hypothesis. However, these findings suggest that adding hydrogen peroxide downstream of ozone injection is a more reliable approach to designing the Peroxone process for the DVWTP or PPWTP.

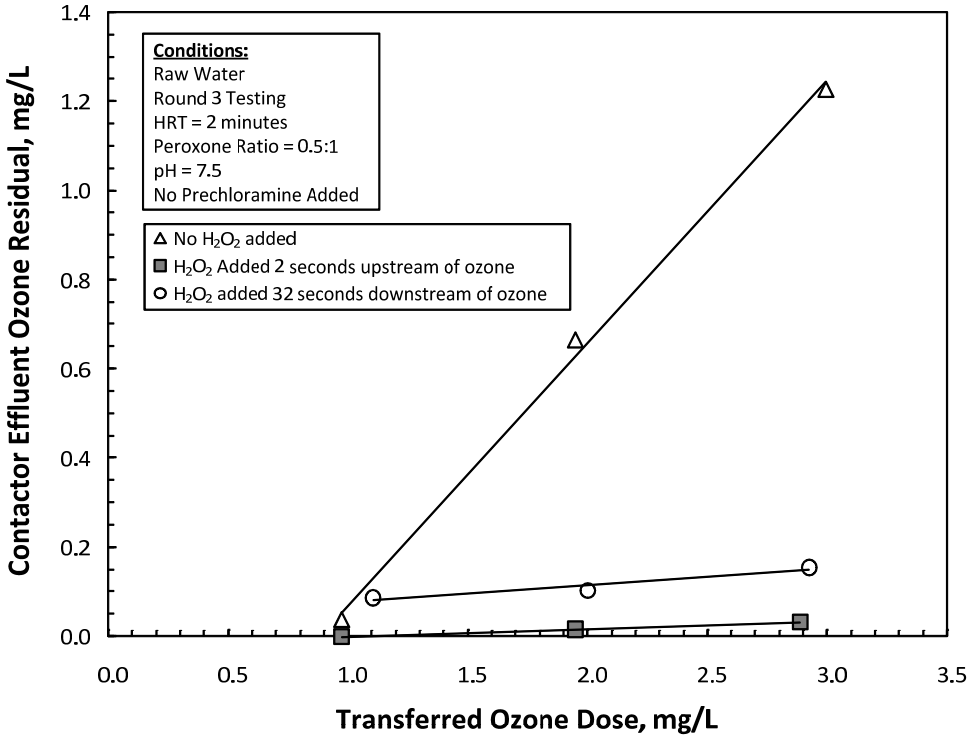


Figure 5.17 – Impact of Hydrogen Peroxide Addition Point on the Decay of Ozone through the Pipeline Peroxone Contactor During Round 3 Testing (October 2008)

The previous discussion focused on determining whether the peroxide should be added upstream or downstream of ozone. The conclusion is that adding hydrogen peroxide downstream of ozone resulted in more consistent performance. The only remaining question is whether the time between ozone addition and peroxide addition has an impact on the performance of the process. To answer this question, tests were conducted during Round 3 to evaluate and compare MIB and geosmin destruction through the Peroxone process when hydrogen peroxide is added immediately downstream of ozone, approximately 30 seconds downstream of ozone, and approximately 60 seconds downstream of ozone. The results are presented in Figure 5.18. These tests were conducted using raw water adjusted to pH 7.5 and spiked with 34 to 46 ng/L of MIB. The ambient bromide level in the water ranged from 343 and 381 µg/L during this test. The water was also dosed with 0.75 mg/L prechloramine upstream of the Peroxone process. The hydrogen peroxide dose was adjusted to result in a H_2O_2:O_3 ratio of 0.5:1.

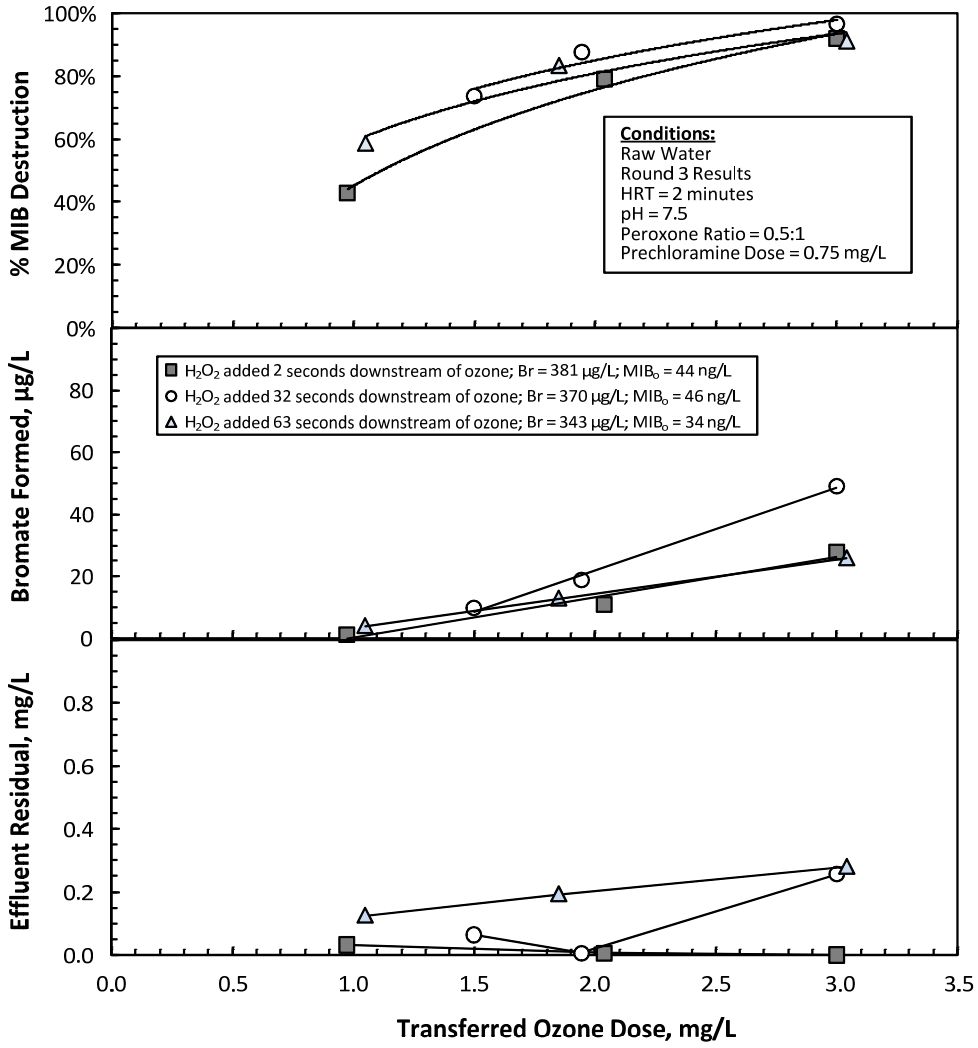


Figure 5.18 – Impact of Hydrogen Peroxide Addition Point on MIB Destruction, Bromate Formation, and Contactor Effluent Ozone Residual

The results reported in Figure 5.18 show that the lag time (2 to 60 seconds) between ozone and peroxide addition had no significant impact on the destruction of MIB or on bromate formation. It is interesting to note that the effluent residual from the 2.6-minute contactor was higher when the hydrogen peroxide was added 60 seconds after ozone injection. This is likely due to the fact that adding the hydrogen peroxide midway through the 2.6-minute contactor left only one minute from the peroxide injection point to the effluent of the contactor. The results suggest that this may be too short of a contact time for the reaction between ozone and peroxide to reach completion. For this reason, it would be desirable to add the hydrogen peroxide immediately downstream of the ozone addition point so as to provide adequate contact time for the peroxide to react with the ozone before the end of the contactor.

5.3.3 Impact of Peroxone Ratio

One of the important design factors for the Peroxone process is the H_2O_2:O_3 ratio (i.e., Peroxone ratio). The majority of the tests performed in this study were conducted with a ratio of 0.5:1. However, a number of tests were also conducted in Round 3 using a ratio of 1:1 and 2:1. The results were compared to determine the impact of the Peroxone ratio on the destruction of T&O chemicals, formation of bromate, and operation of the Peroxone process. The results presented in Figure 5.19. The top portion of Figure 5.19 shows that there was no discernable difference in MIB destruction between the three ratios tested. The middle portion of Figure 5.19 shows that the 1:1 and 2:1 ratios may produce slightly lower levels of bromate than the 0.5:1 ratio. However, it is important to emphasize that the results from the other tests conducted did not always show lower bromate formation with higher Peroxone ratio. In fact, some tests showed higher bromate formation with higher Peroxone ratios. Finally, the lower portion of Figure 5.19 shows that the ozone residual in the contactor effluent was low under all ratios. However, the higher Peroxone ratio of 2:1 resulted in completely non-detectable ozone residual levels in the contactor effluent.

Based on these results, while a Peroxone ratio of 0.5:1 is a reasonable target for the operation of the Peroxone process, it may be desirable to provide the flexibility of higher Peroxone ratios if needed by the operators to fully quench the ozone residual. A maximum ratio of 1:1 at the maximum ozone dose is a reasonable value for the design of the full-scale system.

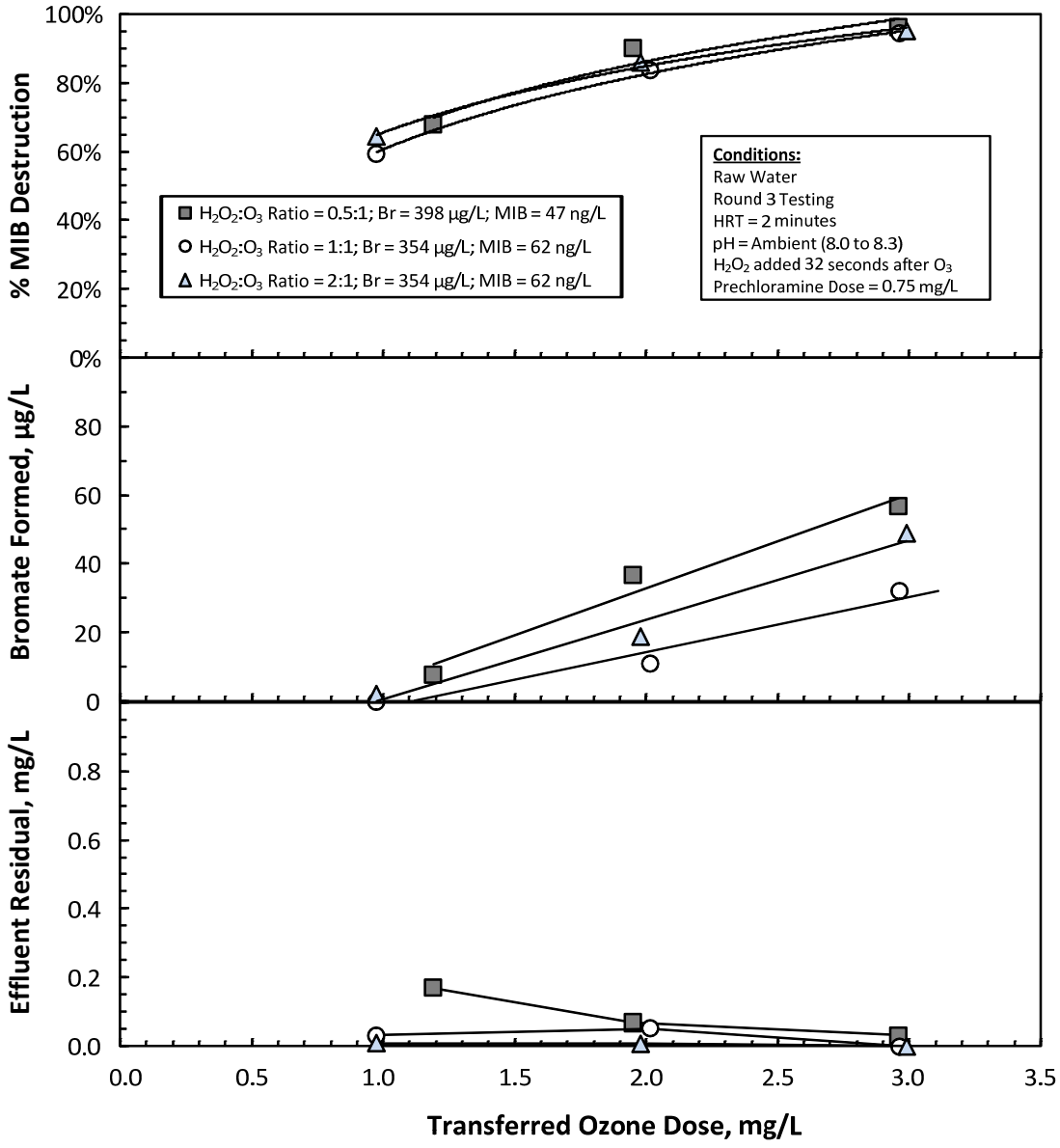


Figure 5.19 – Impact of Peroxone Ratio on MIB Destruction, Bromate Formation, and Contactor Effluent Ozone Residual Level

5.3.4 Evaluation of By-Product Formation

The results of the formation and control of bromate with ozone or Peroxone was thoroughly discussed earlier in this document. While bromate is the only regulated ozone by-product, the study also evaluated the impact of using ozone or Peroxone for the treatment of SBA water on three classes of by-products:

1. Assimilable Organic Carbon (AOC)
2. Chlorination by-products, primarily trihalomethanes (THMs) and haloacetic acids (HAAs)
3. Iodinated trihalomethanes (I-THMs) and halonitromethanes (HNMs)

This section presents the results of the investigation regarding the above DBPs.

5.3.4.1 AOC Formation

While naturally-occurring organic matter is not readily consumed by most bacteria, when it is exposed to ozone, the large non-biodegradable molecules are broken down to smaller, more biodegradable molecules. This translates into an increase in the concentration of biodegradable organic matter (BOM) in the water. The fact that some of the natural organic matter is more biodegradable after ozonation is of no health concern. However, the higher the concentration of "food" for natural bacteria in the water, the higher is the risk of bacterial growth in the distribution system, especially in zones where the chloramine residual is low. To help reduce this risk, biofiltration is typically practiced at the treatment plant downstream of ozone addition. Biofiltration simply employs attached micro-organisms on the filter media to consume some of the BOM before the water enters the distribution system, thereby reducing the "food" supply in the water. However, it should be emphasized that practicing biofiltration at the treatment plant does not guarantee a reduction in bacterial growth in the distribution system because bacterial growth is impacted by many water quality and operational factors that could be far more significant than the concentration of BOM in the water. Nevertheless, it is standard practice in the water industry to used biofiltration after ozonation to reduce the risk of bacterial growth in the distribution system.

This project did not evaluate biofiltration downstream of ozonation. However, sampling was conducted before and after ozone and Peroxone treatment and analyzed for the concentration of BOM in the water. The intent was to quantify the increase in the BOM concentration as a result of each process and compare them to the BOM levels in the current effluent of the DVWTP. There are numerous methods used to quantify BOM. The method used in this study is the Assimilable Organic Carbon (AOC) analysis, which is a Standard Method (SM-9217, approved 1997). In this method, a specific strain of bacteria is grown in a sample of water. The increase in the bacterial count over a specific period of time is translated into a concentration of AOC based on knowledge of the carbon demand of the specific bacteria used in the test. While this is not a direct measure of the BOM concentration, it is desirable because it is a Standard Method and is conducted by a number of commercial laboratories.

Figure 5.20 shows a plot of the AOC concentrations measured in the raw water treated with ozone and Peroxone. The samples were collected in June and July of 2008. The conditions under which the ozone and Peroxone systems were operated when these samples were collected are listed under the graph. Also shown in the graph are the AOC levels measured in the raw water and the DVWTP effluent on the same days. Figure 5.20 shows that the AOC concentration in the raw water ranged from 37 to 50 µg/L, while its concentration in the DVWTP effluent on the two days of sampling ranged from 126 µg/L to 151 µg/L. The addition of 1.8 mg/L ozone to a conventional ozone process or a Peroxone process, operated at a Peroxone ratio of 0.5:1 increased the AOC concentration to 418 µg/L. With an ozone dose of 2.5 mg/L, the AOC concentration in the ozonated water increased to 760 µg/L after conventional ozonation and to 381 µg/L after Peroxone treatment.

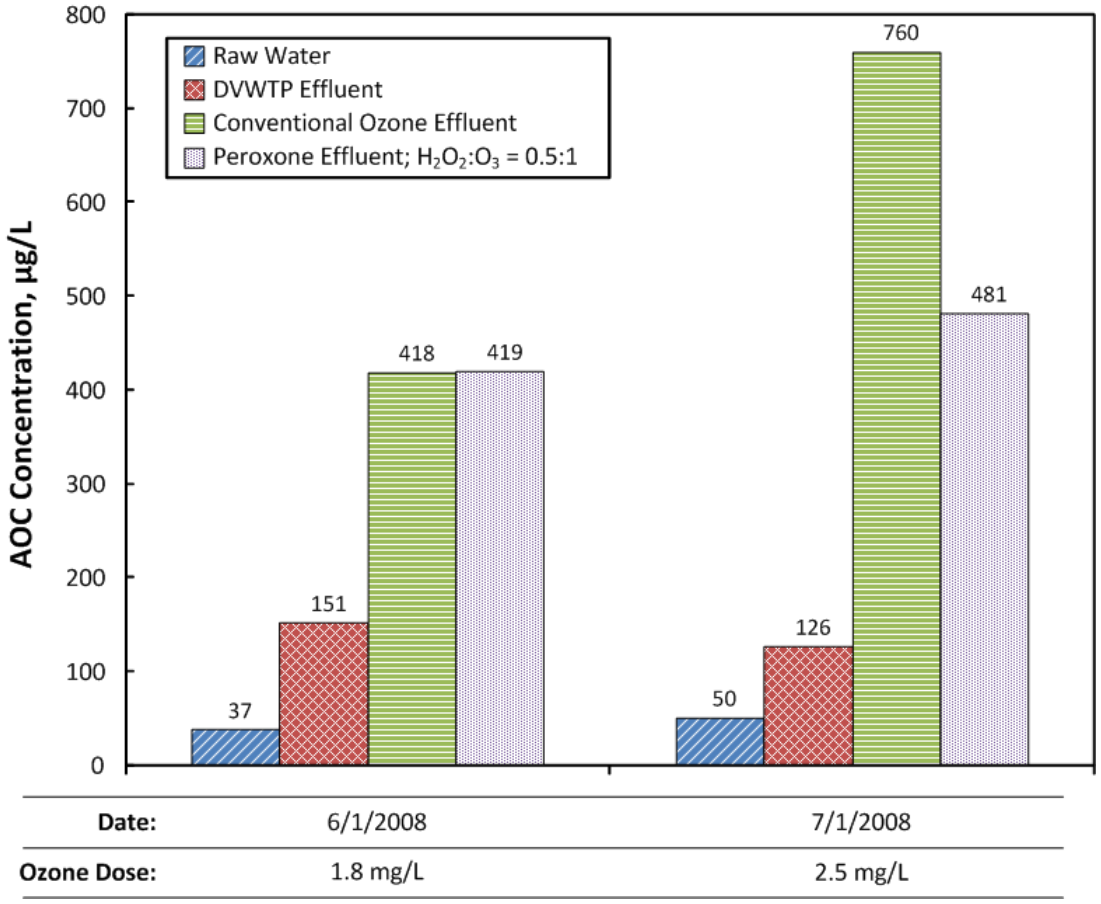
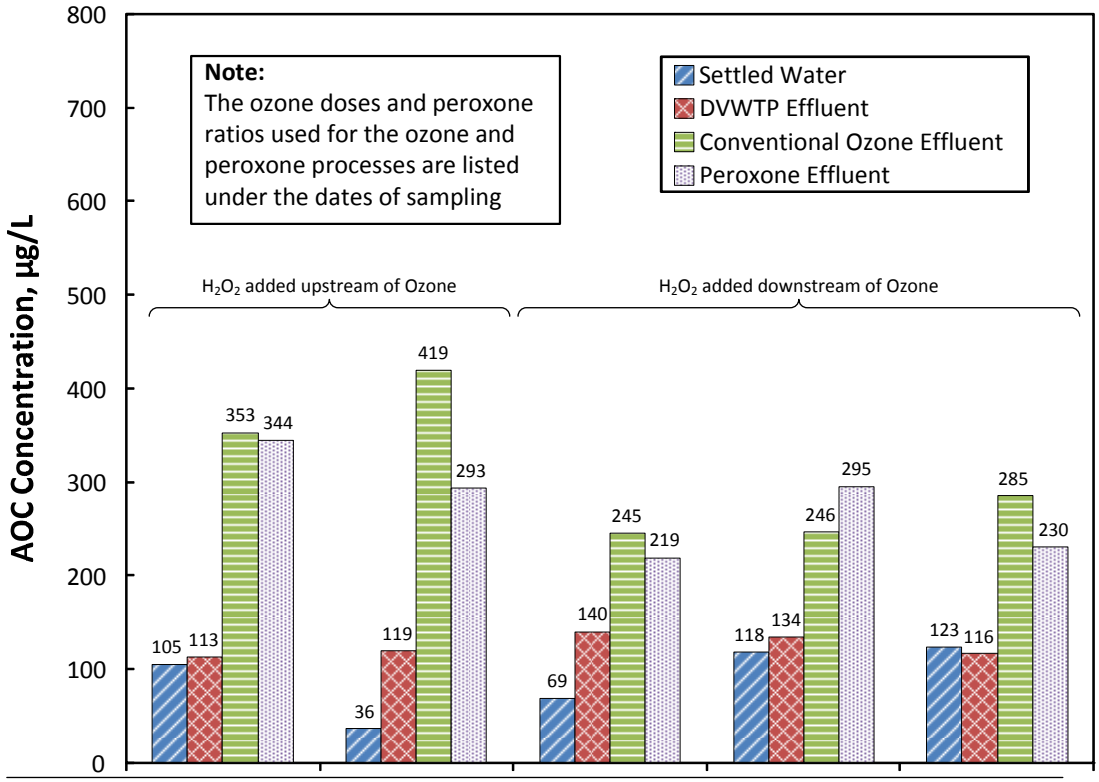


Figure 5.20 – AOC Formation in Raw Water

AOC samples were also collected from the effluent of the ozone and Peroxone processes on five different days when treating settled DVWTP water at the pilot plant. The results are plotted in Figure 5.21. Samples were also collected from the settled water and DVWTP effluent on the same days, and the AOC levels in those samples are also included in Figure 5.21. The operating conditions of the ozone and Peroxone processes at the time of sampling are listed under the graph. The results show that the AOC concentration in the settled water on these days ranged from a low of 36 µg/L to a high of 123 µg/L, while the concentration in the DVWTP effluent ranged from 113 µg/L to 140 µg/L. However, when the settled water was treated through conventional ozone or Peroxone, the AOC levels increased to a range of 219 µg/L to 419 µg/L.

Unfortunately, there is no criterion for determining whether a certain AOC concentration in a water sample is acceptable or too high for a normal distribution system. In fact, there are water treatment plants that use ozone but do not practice subsequent biological filtration. Ultimately, the decision whether to implement biological filtration after ozonation is a subjective decision made with several risk factors in mind. If one looks at the relative increase in AOC concentration from the current plant effluent to the expected ozonated water value, the AOC concentration will likely double or triple with the introduction of ozone to DVWTP and PPWTP. This may be sufficient for one to decide that this AOC level is too high and should be reduced with biological filtration. It is relevant to note that the current design for the Altamont WTP

includes a post-membrane GAC contactor for removal of BOM after ozonation. There is ample full-scale data to demonstrate the biological filtration is effective at removing AOC in this water source.



Date:	7/28/2008	8/11/2008	9/8/2008	9/22/2008	10/6/2008
Ozone Dose =	3 mg/L	1.5 mg/L	1 mg/L	1.5 mg/L	2 mg/L
pH =	6.6	6.8	6.9	6.6	6.7
H_2O_2:O_3 =	1.5:1	1:1	0.5:1	0.5:1	0.5:1

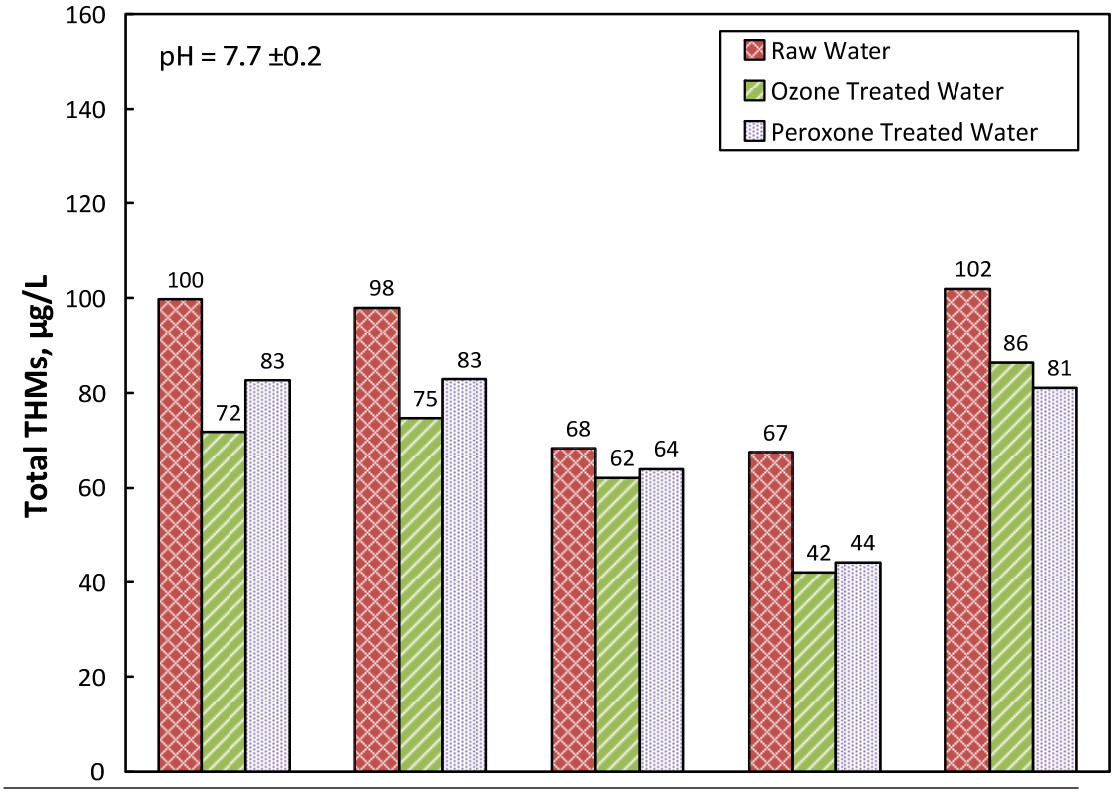
Figure 5.21 – AOC Formation in Settled Water

5.3.4.2 Impact on THM and HAA Formation

During the course of the pilot testing effort, a number of sampling events were conducted during which water samples were collected from the influent to the pilot plant, the effluent of the conventional ozone process, and the effluent of the Peroxone process, and utilized for Simulated Distribution System (SDS) DBP formation testing. This test is used to quantify the potential formation of THMs and HAAs in a distribution system after treatment with chlorine and chloramine. In this test, a sample of water was dosed with chlorine such that there was a chlorine residual of approximately 2.0 mg/L after 1 hour of contact time, and then the samples were dosed with ammonia to form chloramine. The water sample was then incubated in the

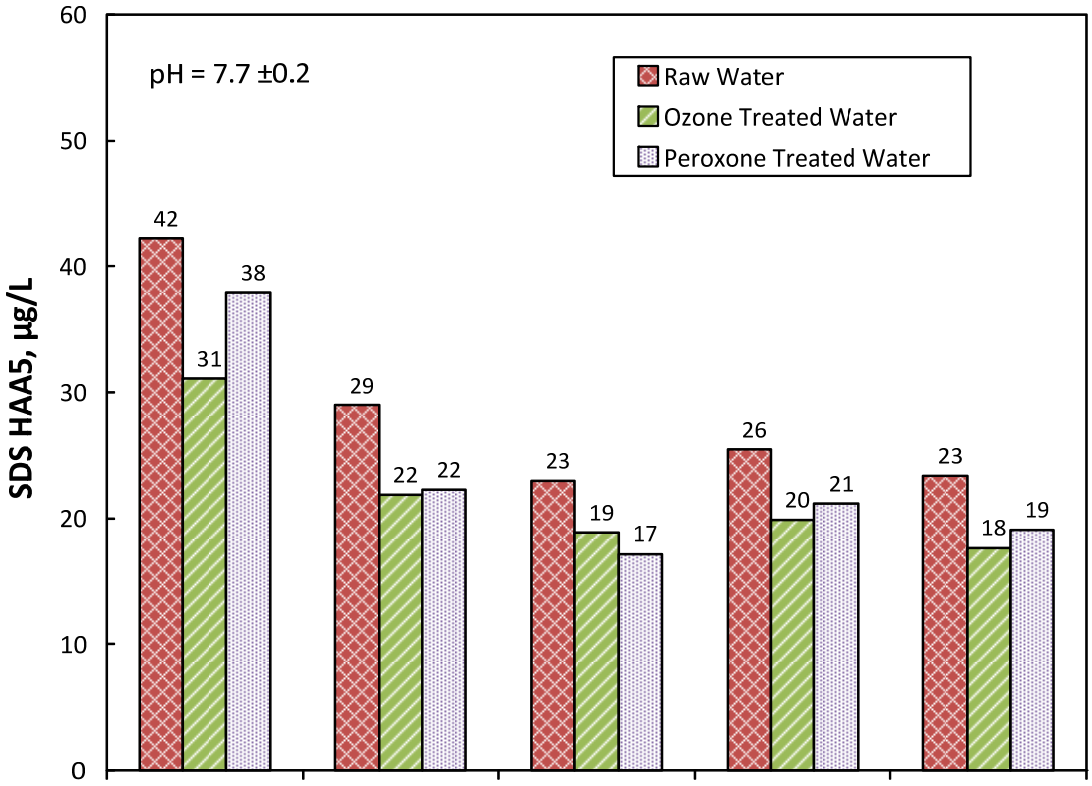
dark for 24 hours at room temperature. After incubation, the water was analyzed for THMs and HAA5 levels.

The results of the raw water tests are summarized in Figure 5.22 for THMs and Figure 5.23 for HAA5 levels. The SDS tests were conducted in June, July, and October of 2008. The THM level in the chloraminated raw water ranged from a low of 67 µg/L to a high of 102 µg/L, while the concentration of HAA5 ranged from a low of 23 µg/L to a high of 42 µg/L. It is interesting to note that the concentration of THMs and HAA5 formed in the chloraminated waters treated with ozone or Peroxone were consistently lower than those formed in the chloraminated raw water. In some cases, the reduction in THM or HAA levels formed was as high as 30%. These results suggest that the implementation of ozone or Peroxone at the DVWTP and PPWTP should help reduce the levels of THMs and HAA5 in Zone 7's water distribution system, even without any changes to the current free-chlorine disinfection practice. To that extent, it is also expected that biological filtration will further reduce the organic content of the water by about 5 to 15%, which should also contribution to THM and HAA5 reduction in the distribution system.



Date:	6/4/2008	6/10/2008	7/11/2008	7/22/2008	10/28/2008
Ozone Dose =	1.8 mg/L	4 mg/L	2.5 mg/L	2.5 mg/L	3 mg/L
H_2O_2:O_3 =	0.8:1	0.2:1	0.5:1	0.5:1	0.5:1
Cl_2 Dose =	5 mg/L	3.5 mg/L	2.4 mg/L	3.0 mg/L	3.5 mg/L

Figure 5.22 – SDS THM Formation in Raw Water



	6/4/2008	6/10/2008	7/11/2008	7/22/2008	10/28/2008
Date:	6/4/2008	6/10/2008	7/11/2008	7/22/2008	10/28/2008
Ozone Dose =	1.8 mg/L	4 mg/L	2.5 mg/L	2.5 mg/L	3 mg/L
H_2O_2:O_3 =	0.8:1	0.2:1	0.5:1	0.5:1	0.5:1
Cl_2 Dose =	5 mg/L	3.5 mg/L	2.4 mg/L	3.0 mg/L	3.5 mg/L

Figure 5.23 – SDS HAA Formation in Raw Water

5.3.4.3 Impact on I-THMs and HNM Formation

While bromate, THMs, and HAAs are regulated DBPs, there is ongoing research looking at new by-products of chlorination and chloramination of drinking water. In the interest of evaluating the impact of either ozone or Peroxone on the formation of these emerging DBPs, some samples were collected from the pilot plant and DVWTP and sent to Clemson University to be analyzed for two classes of by-products: iondinated trihalomethanes (I-THMs) and halonitromethanes (HNMs). The specific chemicals in each class of by-products are listed in Table 5.4 for reference. There are six individual I-THMs, and nine individual HNMs. While Clemson University analyzed all individual chemicals, the total concentration of each class is presented in this report.

Table 5.4 – Iodinated Trihalomethanes (I-THMs) and Halonitromethanes (HNMs) Analyzed

Iodinated THMs	
Name	**Formula**
Dichloroiodomethane	$CHCl_2I$
Bromochloroiodomethane	$CHBrClI$
Dibromoiodomethane	$CHBr_2I$
Chlorodiiodomethane	$CHClI_2$
Bromodiiodomethane	$CHBrI_2$
Triiodomethane	CHI_3

Halonitromethanes	
Name	**Formula**
Chloronitromethane	CH_2ClNO_2
Dichloronitromethane	$CHCl_2NO_2$
Trichloronitromethane	CCl_3NO_2
Bromonitromethane	CH_2BrNO_2
Bromochloronitromethane	$CHBrClNO_2$
Bromodichloronitromethane	$CBrCl_2NO_2$
Dibromonitromethane	$CHBr_2NO_2$
Dibromochloronitromethane	CBr_2ClNO_2
Tribromonitromethane	CBr_3NO_2

Since I-THMs and HNMs are believed to be by-products of chlorine and chloramine, and not ozone or Peroxone, the intent of the testing was to quantify the impact of implementing ozonation at DVWTP and PPWTP on the formation of these by-products with subsequent chloramination. The testing evaluated adding ozone and Peroxone to either the raw water or the settled water. It also evaluated the use of either prechloramine or pH depression for bromate control. To accomplish this goal, a testing protocol was developed and implemented similar to the SDS DBP test conducted for evaluating THM and HAA formation.

Using raw water as, two ozone treatment scenarios and two Peroxone treatment scenarios were simulated and analyzed. One ozone treatment scenario included prechloramine treatment at a dose of 0.75 mg/L for bromate control, followed by 2.0 mg/L ozone. The second ozone treatment scenario included pH suppression to 7.0 for bromate control, followed by 2.0 mg/L ozone. After ozone treatment, the two samples were then adjusted to pH 8.0 and dosed with 2.5 mg/L chlorine. After 10 minutes of free chlorine contact, the samples were dosed with 0.63 mg/L ammonia to form chloramine, and then incubated at room temperature for 24 hrs. The Peroxone scenarios were identical to the ozone scenarios with the addition of 1.0 mg/L hydrogen peroxide 30 seconds downstream of ozone injection (H_2O_2:O_3 Ratio of 0.5:1). Control samples were also analyzed for I-THMs and HNMs. These included a raw water sample that underwent no treatment, and more importantly, a sample of current DVWTP effluent.

The results of the tests conducted to simulate raw water ozone or Peroxone treatment are presented in Figure 5.24 along with the results of the two control samples. The results indicate that the current treatment train at DVWTP results in the formation of 1.3 µg/L I-THMs and 1.8 µg/L HNMs. For the simulated ozone treatment train, the I-THM and HNM levels formed were comparable at 2.3 µg/L and 1.1 µg/L, respectively. Unfortunately, due to a contamination problem, the ozone treatment sample with prechloramine for bromate control was invalidated because it had a very low pH of <3. The two Peroxone treatment scenarios resulted in the formation of slightly lower levels of I-THMs and HNMs compared to the current DVWTP effluent and the ozone treatment scenario. With prechloramine for bromate control, the I-THMs were non-detectable, while the HNMs were measured at 0.7 µg/L. With pH suppression for bromate control, 0.7 µg/L of I-THMs were formed along with 1.5 µg/L of HNMs. In general, the utilization of raw water ozone or Peroxone treatment is expected to form I-THM and HNM levels equal to or slightly lower than those formed by the current treatment train.

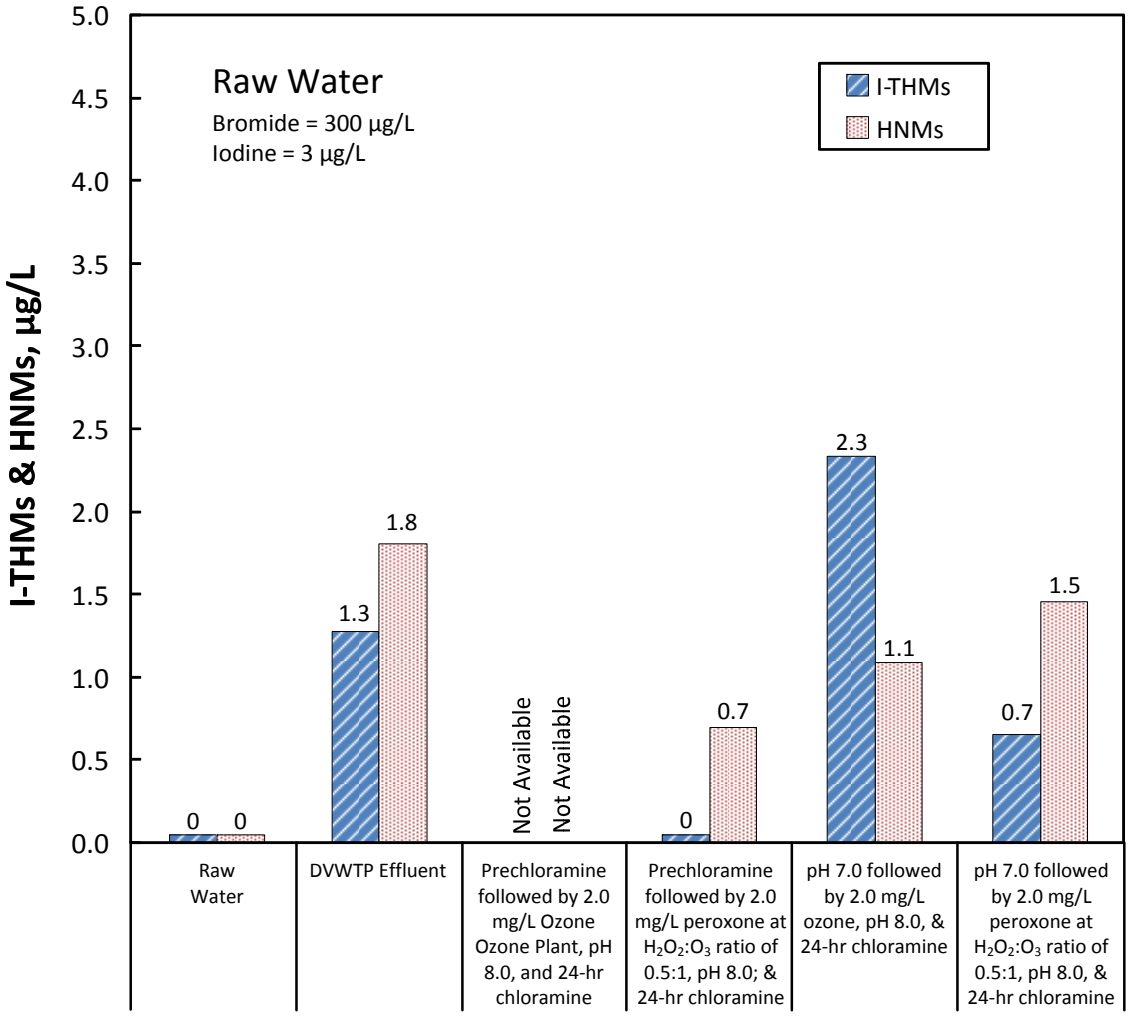


Figure 5.24 – Levels of I-THMs and HNMs Formed in Simulated Treatment of Raw Water with Ozone or Peroxone Compared to Current Treatment Train

The results of the tests conducted to simulate settled water ozone or Peroxone treatment are presented in Figure 5.25. Also shown in Figure 5.25 are the results of the DVWTP control sample as well as the results of a test conducted on settled water collected from DVWTP, adjusted to pH 8.0, dosed with 2.5 mg/L chlorine for 10 minutes, dosed with 0.63 mg/L ammonia to form chloramine, and then incubated at room temperature for 24 hrs. This test was conducted to compare the results of the simulated treatment protocol to those collected from the DVWTP.

The results indicate that the simulated chloramination of the settled water formed very similar levels of I-THMs and HNMs to those measured in DVWTP effluent. With the simulated settled-water ozone treatment train, the I-THM levels (1.2 µg/L) and HNM levels (1.9 µg/L). The simulated Peroxone treatment of the settled water with prechloramine for bromate control formed slightly lower levels of I-THM and HNMs compared to the other treatment scenarios.

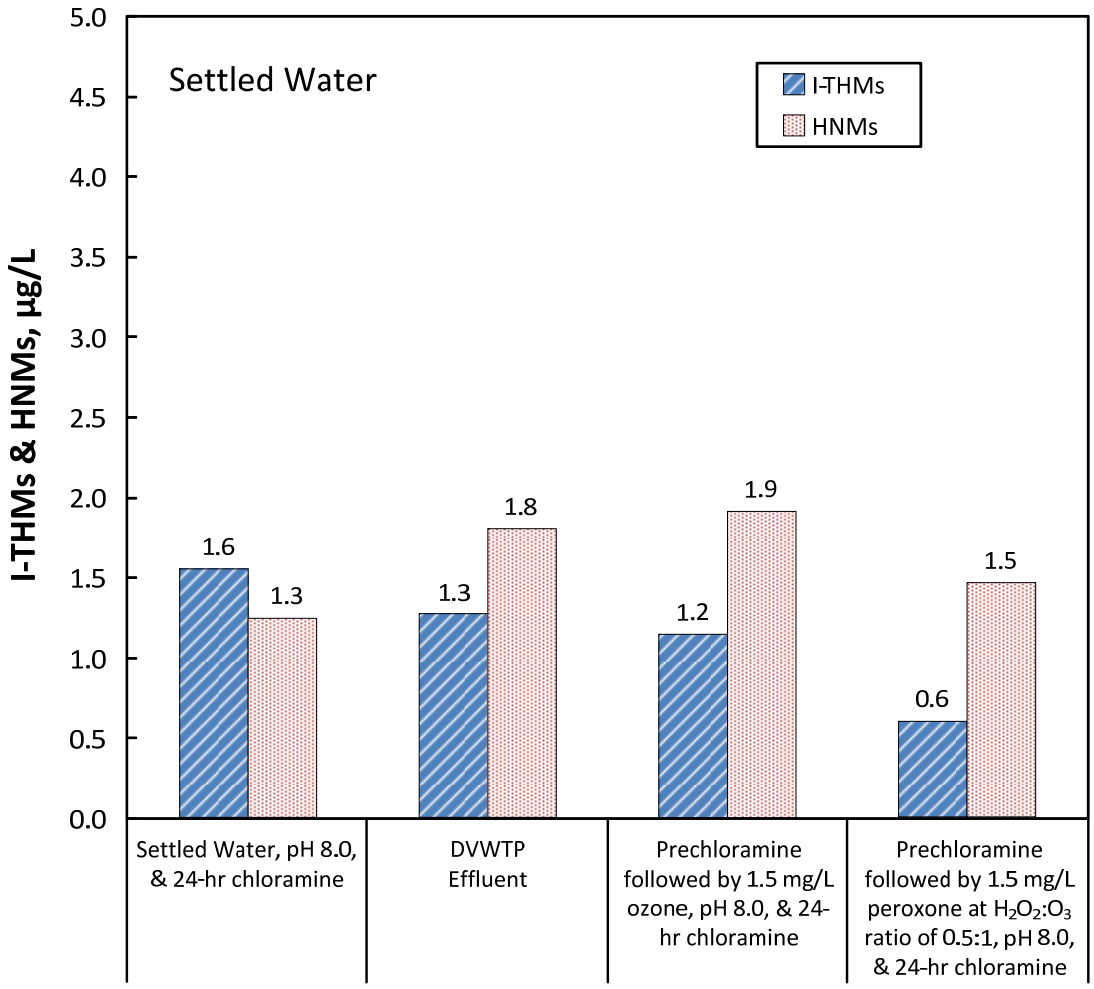


Figure 5.25 – Levels of I-THMs and HNMs Formed in Simulated Treatment of Settled Water with Ozone or Peroxone Compared to Current Treatment Train

Based on the results of the tests reported above, the utilization of ozone or Peroxone treatment at the raw water or settled water is expected to form I-THM and HNM levels equal to or slightly lower than those formed by the current treatment train.

5.4 ALTERNATIVES ANALYSIS & RECOMMENDATIONS

Section 5.3 presented and discussed the results of the pilot testing effort. In this section, the results are used to identify and evaluate the alternative ozonation scenarios for the DVWTP and the PPWTP. There are four combinations of alternatives for each treatment plant:

Alternative 1 – Raw water ozone
Alternative 2 – Raw water Peroxone
Alternative 3 – Settled water ozone
Alternative 4 – Settled water Peroxone

All four alternatives are viable for the DVWTP, but not for PPWTP. Due to the concern over the impact of ozone and/or peroxide residuals on the UF membranes, settled water ozone or Peroxone are not acceptable at this plant. During the July 2008 meeting of the Technical Advisory Committee (TRC), the option of adding either ozone or Peroxone to the filtered water in lieu of settled water at PPWTP was discussed as a viable option. The quality of the settled water in terms of ozone demand and MIB and geosmin destruction is expected to be quite similar to that of the filtered water such that the pilot results could be applied to either application point.

It is important to keep in mind that the selected process must work within the existing plants' process trains, and that all other water quality requirements must be met. The ozone or Peroxone process is intended to achieve the target destruction of T&O compounds, but the plants must continue meeting their particle removal and disinfection requirements. Any impact that the ozone or Peroxone process has on the existing plants' performance must be mitigated, and the costs for such mitigation must be included in the overall cost for the T&O control process.

5.4.1 Raw Water vs. Settled (or Filtered) Water Ozonation

Ozone systems have been implemented by many utilities to treat raw water, settled water, or filtered water. For example, raw water ozonation is practiced by ACWD at WTP2, the cities of Vacaville and Fairfield at the North Bay Regional Plant, and the city of Vallejo at the Fleming Hill WTP. Settled water ozonation is practiced by SCVWD at the Penitencia and Santa Teresa water treatment plants, and by CCWD at the Randall-Bold and Bollman water treatment plants. Filtered water ozonation is not as commonly practiced because of the desire to remove some of the BOM with biological filtration downstream of ozonation. Nevertheless, CCWD utilizes filtered-water ozonation at the Randall-Bold water treatment plant in addition to the settled water ozonation.

For all of the settled-water ozonation plants treating delta water, the systems were designed with disinfection as the primary treatment objective. Settled-water ozonation for disinfection is the clear choice from a cost point of view since it requires a significantly lower ozone dose to achieve the disinfection CT credit. Further, since the pH of settled water is typically lower than that of the raw water when alum or ferric chloride is used as a coagulant, additional pH suppression for bromate control may not be necessary. An examination of Figure 5.2 presented earlier in this report shows how the ozone demand of the settled water was approximately half that of the raw water. This means that the ozone dose required to achieve a particular 1st-chamber ozone residual in settled water is half that required to achieve the same 1st-chamber residual in raw water. For filtered-water application, the ozone demand is expected to be equal to or less than that of the settled-water.

While the above discussion favors settled-water application of ozone over raw water application, the following issues must be considered:

1. With T&O destruction as the primary goal, the pilot testing results showed that conventional ozonation of the settled water could not meet the minimum MIB and geosmin destruction goals of 71% and 73%, respectively, with a dose as high as 3.5 mg/L. This is a very high

dose for either raw or settled water ozonation. Therefore, only the Peroxone alternatives remain viable for settled-water or filtered-water ozonation.

2. When prechloramine is used for bromate control, the pilot testing results showed that the Peroxone dose required to meet the MIB and geosmin goals in settled water at its ambient pH of 6.6 is lower than that needed in raw water at pH 7.5 (1.7 mg/L in settled water vs. 2.7 mg/L in raw water).
3. However, in the absence of chloramine addition, the Peroxone dose required to meet the T&O goal in the settled water is similar to that needed in the raw water (1.2 mg/L in settled water vs. 1.4 mg/L in raw water). These results suggest that the use of chloramine for bromate control greatly affects the required ozone dose. Compliance with the bromate standard is calculated based on a rolling annual average of data collected each month. Since the T&O problem is seasonal, a Peroxone system could be operated seasonally. If the system were operated for only three months in one year, for example, the three bromate values measured would be averaged with nine months of no bromate formation, and Zone 7 could still be in compliance with the MCL as long as the average of the three bromate levels is less than 40 µg/L (i.e., four times the MCL). Chloramine addition would only be required under high raw water bromide conditions, and it is expected that the operating ozone dose would be significantly less than the design ozone dose.
4. For the settled water application, the ozone residuals in the effluent of the 2.6-minute Peroxone contactor were consistently too high. The contactor would either need to be much larger (e.g. 10 minutes), or a separate quenching chemical feed system would need to be constructed and utilized to destroy the ozone residual before the water exits the contactor. The utilization of the quenching agent itself would require a larger contactor since additional contact time would be required for the quenching chemical to react with the residual ozone.
5. It has been observed by a number of Delta water treatment plants that raw water ozonation greatly benefits the coagulation, flocculation, and clarification process, as well as produces lower filtered-water turbidity. With raw water ozone or Peroxone added for T&O control, improved performance of the downstream plant processes is expected.
6. Biofiltration is needed for reduction of BOM formed by both processes. This is most economically achieved by installing the process upstream of filtration and allowing the existing filters to run biologically. In the case of the filtered water application at the PPWTP, a new post-ozone biofiltration process would be needed. (It is understood that ozone or Peroxone application to the raw water at the PPWTP will only allow for biological filtration on the conventional train, but not on the membrane train. Therefore, only partial removal of the total BOM formed will be possible at the PPWTP with raw water ozonation.)
7. Biofiltration should also help with removal of most of the remaining residual peroxide in the effluent of the Peroxone process. Installing filtered-water Peroxone at PPWTP without biofiltration would be problematic because residual hydrogen peroxide will be present in the Peroxone contactor effluent. Hydrogen peroxide reacts rapidly with chlorine at a ratio of 2 mg/L chlorine for every 1 mg/L hydrogen peroxide present in the water. Any fluctuations in the concentration of hydrogen peroxide will result in fluctuations in the chlorine demand of the water. This will cause operational instability at a point where stability of the chlorine residual is necessary in order to meet the disinfection requirements. It is speculated that residual peroxide would be removed through the membrane train's clarification process, but this has not been confirmed.

For all the above reasons, WQTS recommends that only raw-water ozone or Peroxone be considered for the DVWTP and the PPWTP.

5.4.2 Peroxone vs. Conventional Ozone

A key question is whether a Peroxone process designed exclusively for T&O destruction provides significant financial advantages over conventional ozonation which is designed for both T&O control and disinfection. The results of the pilot testing effort have confirmed that a Peroxone process designed with a 3-minute contact time and operated intermittently is likely to require a lower average ozone dose than that required by a larger conventional ozone process to achieve the same T&O destruction goals. Therefore, the capital and O&M cost of a Peroxone process are likely to be substantially lower than those of a conventional ozone process. However, in selecting the appropriate process to implement, the following factors must also be considered:

1. If the Peroxone process is designed only for T&O control, then Zone 7 must continue to meet disinfection with chlorine. If biofiltration is to be implemented, the chlorine addition point must be moved to a location downstream of the filters. Currently, both DVWTP and PPWTP-conventional meet the disinfection requirement with free chlorine through the filters, and both plants rely on the low pH of the water to meet the *Giardia* disinfection requirements. If chlorination were to be delayed until after filtration, then either a dedicated chlorine contactor would need to be constructed downstream of the filters to meet the disinfection requirements, or modifications would need to be made to the clearwells such that disinfection could be achieved in these units. Ammonia and caustic addition would need to be moved further downstream, after disinfection is achieved. This will add to the cost of implementing the Peroxone alternative.
2. If the Peroxone process is designed for T&O destruction only, it is conceivable that it could be operated only during the T&O season, similar to the manner in which the current PAC systems are operated.
3. A Peroxone process designed solely for T&O control would likely decrease the degree of redundancy in equipment compared to an ozone process designed for disinfection.
4. The addition of Peroxone to the raw water will likely have an impact on the required coagulant dose; each time the system is turned on or off the coagulation/clarification process may need to be adjusted.
5. If the Peroxone process were to be operated only part of the year, then the bromate control strategy could be less stringent compared to that needed for a disinfection process that requires continuous operation. The reason is that periodic bromate levels above 10 µg/L during process operation would be averaged with zero bromate levels when the process is off-line.
6. The various systems associated with the Peroxone process (oxygen storage, ozone generation, peroxide storage and feed) would be off line for approximately nine months of the year, along with the analyzers, off-gas destruct system, etc. With most systems, an extended off-line period requires certain maintenance task to get everything up and running again. This may not be trivial as the type of equipment included with the Peroxone process is not expected to simply start up without any problems after being off line for nine months.

7. Even in the absence of MIB and geosmin, the addition of ozone or Peroxone could change the taste of the water. Many customer complaints about the taste of their water are due to changes in the water, and not necessarily due to the presence of a specific odorant. Turning the system on and off could result in an increase in such customer complaints.
8. An ozone process operated for both disinfection and T&O control would result in significantly lower levels of chlorinated DBPs such as THMs and HAAs compared to a free-chlorine based disinfection process.

5.4.3 Recommended Alternative

Tables 5.5 and 5.6 present summaries of the factors affecting the process selection for each water treatment plant based on the discussion presented earlier in this section. In Table 5.5, it is assumed that all four options include allowing the existing media filters at the DVWTP to become biologically active. For both tables, modifications are needed to allow for feeding both chlorine and ammonia upstream of the new ozone contactors.

Table 5.5 – Summary of Decision Factors for Del Valle Water Treatment Plant

Parameter	Raw Water Ozone	Raw Water Peroxone	Settled Water Ozone	Settled Water Peroxone
Design Ozone dose, mg/L	2.8	2.7	>3.5	1.7
HRT, min	10	3	12[1]	5[1]
pH adjustment?	Yes	No[2]	No	No
Peroxide storage and feed system	No	Yes	No	Yes
Quenching agent storage and feed	No	No	Yes	Yes
Disinfection	Ozone	Free chlorine[3]	Ozone	Free chlorine[3]
Improved downstream processes	Yes	Yes (intermittent)	No	No
THM and HAA5 levels	Very low	Somewhat lower (intermittent)	Very low	Somewhat lower (intermittent)
Residual peroxide	N/A	Should be removed through clarification and biofiltration	N/A	Should be removed through biofiltration

1. An additional two minutes is assumed to allow the quenching agent to destroy the ozone residual.
2. Although not needed for T&O destruction, might be necessary for bromate control
3. Either new chlorine contact chamber is needed or modifications to clearwells to allow for sufficient free chlorine contact time and relocation of ammonia and caustic feed points.

Table 5.6 – Summary of Decision Factors for Patterson Pass Water Treatment Plant

Parameter	Raw Water Ozone	Raw Water Peroxone	Filtered Water Ozone	Filtered Water Peroxone
Design Ozone dose, mg/L	2.8	2.7	>3.5	1.7
HRT, min	10	3	12[1]	5[1]
pH adjustment?	Yes	No[2]	No	No
Peroxide storage and feed system	No	Yes	No	Yes
Quenching agent storage and feed	No	No	Yes	Yes
Disinfection	Ozone	Free chlorine[3]	Ozone	Free chlorine[3]
Improved downstream processes	Yes	Yes (intermittent)	No	No
Biofiltration	Use existing conventional filters[4]	Use existing conventional filters[4]	New biofiltration contactors needed	New biofiltration contactors needed
THM and HAA5 levels	Very low	Somewhat lower (intermittent)	Very low	Somewhat lower (intermittent)
Residual peroxide	N/A	Should be removed through clarification and biofiltration	N/A	Should be removed through biofiltration

1. An additional two minutes is assumed to allow the quenching agent to destroy the ozone residual.
2. Although not needed for T&O destruction, might be necessary for bromate control
3. Either new chlorine contact chamber is needed or modifications to clearwells to allow for sufficient free chlorine contact time and relocation of ammonia and caustic feed points.
4. Since only a portion of the plant flow goes through the media filters, only a portion of the biodegradable organic material would be removed.

With all the factors discussed earlier, and those summarized in Tables 5.5 and 5.6, WQTS recommends that the ozone or Peroxone process be implemented on the raw water and not on the settled or filtered water. However, the choice between ozone and Peroxone is not yet clear based solely on the technical data gathered during the pilot study. As a result, it is WQTS' recommendation that the following two options be carried forward through cost estimation:

Option 1 – Conventional Ozone. This process will be applied to the raw water at each plant, and will utilize a conventional multi-chamber ozone contactor with standard average hydraulic residence time of 10 minutes. The process will be operated year-round and will satisfy two treatment goals: T&O control and disinfection. The chlorine addition point will be moved to a location immediately downstream of filtration. Ammonia will be added slightly downstream of chlorine addition to form chloramine.

Option 2 – Peroxone. This process will be applied to the raw water at each plant, and will utilize a smaller contactor with an average hydraulic residence time of three (3) minutes. Ozone and peroxide will be added only during T&O events. In order to permit biological activity in the media filters, the chlorine addition point will be moved to a location immediately downstream of filtration. Since disinfection is not achieved with the Peroxone process, a new chlorine contactor will be constructed downstream of filtration. Ammonia and caustic will be added to the effluent of the chlorine contactor.