# Evaluating Options for Bromodichloromethane Reduction Through Bench-Scale and Pilot Testing for a Wastewater Treatment Facility

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Table 1. List of All Disinfection Alternatives Considered

| Alternative | | Disinfection Options: UV | NaOCl | Ozone | Peracetic Acid | Ferrate | UVT Improvers or DBP Preventers: Peracetic Acid | PAC/GAC | Ozone | Ferrate | Process | MIEX | UV | Peroxide | Coagulation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **FULL TREATMENT OPTIONS** | | | | | | | | | | | | | | | |
| FT | 1 | X | | | | | X | | | | | | | | |
| FT | 2 | X | | | | | | | X | | | | | | |
| FT | 2A | | X | | | | | | X | | | | | | |
| FT | 3 | X | | | | | | | | X | | | | | |
| FT | 4 | X | | | | | | | | | X | | | | |
| FT | 4A | X | | | | | Methanol to A2O Process | | | | | | | | |
| FT | 5 | X | | | | | | | | | | | | | X |
| FT | 6 | | X | | | | | | | | | | | | X |
| FT | 7 | | | | | X | | | | | | | | | |
| FT | 8 | X | | | | | | | | | | | X | | |
| FT | 9 | X | | | | | | | | | | X | | | |
| FT | 10 | | X | | | | | | | X | | | | | |
| FT | 11 | | | X | | | | | | | | | | | |
| FT | 12 | | X | | | | | | | | | X | | | |
| FT | 13 | | X | | | | | X – Downstream of chlorination to remove BDCM | | | | | | | |
| FT | 14 | X | | | | | | | X – Upstream of Filters | | | | | | |
| FT | 15 | X | | | | | | | X – At Headworks | | | | | | |
| FT | 16 | | X | | | | Use air to strip BDCM | | | | | | | | |
| FT | 17 | X | | | | | | | | | | | | X | |
| FT | 18 | | | | X | | None | | | | | | | | |
| **SPLIT TREATMENT OPTIONS – SIDESTREAM DISINFECTION** | | | | | | | | | | | | | | | |
| ST | 1 | X | | | | | X | | | | | | | | |
| ST | 2 | | X | | | | | X – Downstream of chlorination to remove BDCM | | | | | | | |
| ST | 3 | X | | | | | | | X | | | | | | |
| ST | 4 | X | | | | | | | | X | | | | | |
| ST | 5 | | | X | | | | | | | | | | | |
| ST | 6 | | | | | X | | | | | | | | | |
| ST | 7 | X | | | | | | | | | | | X | | |
| ST | 8 | X | | | | | | | | | | X | | | |
| ST | 9 | | X | | | | | | | | | X | | | |
| ST | 10 | X | | | | | | | | | | | | X | |
| ST | 11 | X | | | | | None | | | | | | | | |
| ST | 12 | | | | X | | | | | | | | | | |
| ST | 13 | X | | | | | Design for 48 percent UVT | | | | | | | | |

The City of Largo (City) owns and operates the Largo Advanced Wastewater Reclamation Facility (AWWRF), which has a permitted annual average daily capacity of 18.0 mil gal per day (mgd). The current annual average flow is approximately 12 mgd and is expected to increase to approximately 14.5 mgd within 20 years. The AWWRF wastewater treatment process consists of primary treatment, an activated sludge system with biological nutrient removal (BNR), denitrifying filtration, disinfection using gaseous chlorine, dechlorination using sulfur dioxide, and surface water discharge/reuse of the effluent. With the use of chlorine for wastewater disinfection, whether liquid (sodium hypochlorite) or gaseous, there is a potential for formation of disinfection byproducts (DBPs). Trihalomethanes (THMs) are one family of DBPs that may result from the use of chlorine. The state of Florida imposes numeric limits on certain DBPs that are set as maximums in many permits.

Through a consent order, and at the time these studies were performed, the Florida Department of Environmental Protection (FDEP) required that the City comply with the regulatory limit of 22 μg/L of bromodichloromethane (BDCM) in the final effluent before it is discharged to surface waters. Until the new disinfection system is in place, however, an interim limit has been set at 30 μg/L. The BDCM is one of the THMs formed by the reaction of chlorine with organic compounds present in the wastewater. Currently, with the chlorination system in place, the annual average BDCM level ranges from about 26 to 30 μg/L.

In 2010, the City retained the team of Greeley and Hansen and CDM Smith to evaluate alternatives to the existing chlorine disinfection system and design a new disinfection system that reduces BDCM levels on an annual average basis. There are three basic options for reducing high BDCM concentrations:

- Replace chlorine with another disinfectant that eliminates or reduces the formation of BDCM.
- Remove the chemical precursors that promote the formation of BDCM and continue to use chlorine.
- Remove the BDCM after it is formed and prior to surface water discharge.

Bench- and pilot-scale testing was performed to assess the many alternatives that fit these three basic options. At many plants facing BDCM issues, ultraviolet (UV) disinfection has been used to replace chlorine. However, at Largo, the UV transmittance (UVT) was so low in wet weather that the use of UV disinfection for the effluent wastewater may be cost prohibitive. Most UV disinfection systems in Florida have been designed for UVTs of 60 percent or greater. The challenge in Largo is that the natural UVT drops to as low as approximately 38 percent in wet weather, likely due to the presence of specific dissolved organic carbons (DOCs). Thus, more than 30 alternatives have been considered, all falling within the three basic options.

The evaluation of these numerous disinfection alternatives using various technologies (ozone, peracetic acid (PAA), MIEX®, hydrogen peroxide, UV, ferrate, or activated carbon) in either a full flow or split flow configuration are detailed. What began as a list of more than 30 options was narrowed down to four viable alternatives for further consideration. After additional pilot testing and analyses, a final disinfection method was selected, in collaboration with the City staff, as the most appropriate alternative for implementation at the Largo AWWRF.

## Approach to Evaluation

### Objectives

The engineering team identified long-term solutions to reduce the concentration of BDCM. Solutions to the problem of high BDCM discharge to surface waters may be achieved by any combination of the three basic options described. In addition, full treatment and split treatment configurations were identified. In the full treatment configuration, the existing disinfection method, which treats all the flow, would be replaced by an alternative that also treats the full flow. In the split treatment configuration, chlorine (sodium hypochlorite) would be used for part of the flow and another chemical (or UV) would be applied to the remaining flow in such a way that the blended flow will have a BDCM concentration of less than a selected target of 15 μg/L. This target value was selected to be reasonably below 22 μg/L to assure compliance under all conditions. The objective of this evaluation is to determine the cost-effective, permittable solution that best fits the City's long-term objectives.

### Presentation of Alternatives

The team developed a list of alternatives from historical applications, literature reviews, experience, best available technologies, and suggestions from City personnel, as shown in Table 1. All alternatives fit into one of the three categories listed. Since the UVT is seasonally low, several means of raising the UVT were explored, ahead of using UV for disinfection. The alternatives are categorized into two major options in Table 1: the full treatment option and the split treatment option.

Potential alternatives originally listed were eliminated from further consideration due to results of laboratory analyses and other factors, such as not being practical for the Largo plant. The following section discusses the progression of the screening process.

### Selection Criteria

In order for a disinfection alternative to move forward in the screening process and remain on the table for further consideration, it needed to demonstrate BDCM reduction by means of any combination of the three options. In combination with the BDCM reduction strategies, the following items were taken into account when deciding to eliminate an alternative from further consideration or to keep it for additional investigation:

1. *City preference* – Does the City feel more comfortable with one alternative? Do the plant operators prefer certain alternatives over others? Has this technology demonstrated historical success in similar applications? Is the technology proprietary?
2. *Safety* – Historically, are there some alternatives that have been proven safer than others? What are the safety hazards and risks associated with each alternative? What types of training will be required before operators are allowed to work with a given chemical or technology?
3. *Cost* – What are the capital costs of each alternative? What are the operating, maintenance, and life cycle costs of each alternative?
4. *Complexity* – How much retrofitting of existing facilities (if any) will need to take place? What current buildings and structures (e.g., old chlorine contact chamber) can be reused for the new disinfection system? How much design of new facilities will need to be done? Does the AWWRF site have sufficient room to install a new disinfection facility? What are the treatment and storage requirements? What are the advantages and disadvantages of the split flow versus full flow configuration? What is the potential for each alternative to be permitted?
5. *Bench-scale/pilot-scale lab results* – Does bench- or pilot-scale testing show that the alternative is effective? Do the results show any unwanted consequences of the use of this approach?

## Analysis of Alternatives

Alternatives that passed the first round of screening were then tested in the Phase 1 bench-scale study.

### Phase 1 Bench-Scale Testing

The Phase 1 bench-scale study was performed through a series of jar tests to determine which of the non-chlorine oxidants and/or adsorbents could reduce DOC (and therefore, BDCM) or increase UVT. The doses were chosen based on a literature review, and a minimum of a 15-min detention time was used to simulate oxidation of the DOC. Ozone, PAA, hydrogen peroxide, powdered activated carbon (PAC), MIEX®, UV, and ferrate were all examined during Phase 1. Results of the Phase 1 testing showed that:

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- Ozone appeared to have a significant impact on the filter effluent UVT at doses corresponding to residuals of 3 mg/L and 4 mg/L of ozone in the sample. At these doses, there is significant reduction of background BDCM (before disinfection), suggesting that the use of ozone after chlorination may be a means of removing BDCM. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), and DOC concentrations remained largely unchanged. Some aldehyde byproducts were also present in the ozonated sample and decreased with an increase of the dissolved ozone concentration in the sample.
- Thirty-two percent PAA did not have any effect on the filter effluent UVT at doses ranging from 2 mg/L to 4 mg/L. (At this stage of the study, PAA was being tested as a means of increasing the UVT ahead of UV disinfection.)
- Hydrogen peroxide did not have any apparent effect on the filter effluent UVT at doses ranging from 2 mg/L to 4 mg/L. The DOC and BOD values remained unchanged.
- The PAC did not have any apparent effect on the filter effluent UVT or DOC concentrations at doses up to 30 mg/L. The BOD remained unchanged, although COD values declined with increasing concentration of PAC. There was also a slight reduction in BDCM concentration with the addition of PAC, and the trend indicates that higher doses of PAC may potentially have an even greater impact.
- The MIEX appeared to have similar impact on the filter effluent UVT as ozone at doses of 3 mg/L and 4 mg/L. It had no impact on BOD and COD values and little impact on BDCM. Higher concentrations of MIEX indicated some reduction in DOC.
- An advance oxidation process using UV and 50 mg/L peroxide exhibited a significant impact on the filter effluent UVT (UVT increased from 47 percent to 71 percent in the filter effluent) following 90 min of irradiation, based on information received from the UV manufacturer that ran the test. However, the duration of UV radiation is impractical for application at the City of Largo AWWRF.
- Ferrate was applied to the clarified effluent and not the filtered effluent, since the use at this location would allow the solids produced by ferrate application to be removed by the filters. Ferrate appeared to increase UVT of the clarified effluent at a dose of 3 mg/L, but required pH adjustment with an iron salt based on information received from the ferrate manufacturer that ran the test. The manufacturer also reported a reduction in DOC, total phosphorus, and fecal coliform. The reduction in fecal coliform, however, is ahead of the filters and would not be a credit toward disinfection.

Some alternatives did not present strong enough reasons to be eliminated from consideration and required additional bench- or pilot-scale testing to make a conclusive decision about their suitability for the Largo AWWRF.

Table 2. Viable and Non-Viable Alternatives
After Bench-Scale Testing and Pilot Results

| Flow | Alternative | Pilot Results |
|---|---|---|
| Full Flow Treatment | UV + Ozone (filter effluent) | Ozone is effective at improving the UVT to above 55 percent. |
| | NaOCl + Ozone (filter effluent) | Ozone was not effective in reducing the BDCM concentration through precursor removal. |
| | UV + Process Modification | N/A |
| | Ozone (filter effluent) | Limited testing showed lower than expected reduction in fecal coliform, but more testing may be required. |
| | UV + Ozone (clarified effluent) | Ozone improved the UVT of clarified effluent, but unacceptably increased the DO ahead of denite filters. |
| | PAA | A dose between 2 and 4 mg/L is likely to achieve full fecal kill.** |
| | Ozone (chlorinated effluent)* | Ozone was not effective in reducing the BDCM concentration after chlorination. |
| Split Flow Treatment | UV + Ozone (filter effluent) | Ozone is effective at improving the UVT to above 55 percent. |
| | Ozone (filter effluent) | Limited testing showed lower than expected reduction in fecal coliform, but more testing may be required.* |

* This alternative was developed during the pilot study.

** These are bench-scale results. The PAA pilot scale study identified a dose of 3.5 mg/L would likely achieve the full fecal kill.

### Phase 2 Bench-Scale Testing

Building on the results from Phase 1, the second phase of bench-scale testing aimed to identify the dose of reactants that would be required to achieve the objectives stated. Another purpose for Phase 2 testing was to determine the optimum location for chemical addition. This was achieved by using wastewater samples from various points in the treatment process: screened influent, clarifier effluent, filter effluent, and chlorinated effluent. The results of Phase 2 testing can be summarized as follows:

- Ozone addition to clarifier effluent significantly increased the dissolved oxygen (DO) concentration. This high concentration of DO would not allow the denitrifying microbes to thrive, since they need an anoxic environment in the denite filters.
- Ozone appeared to be quite effective in increasing the UVT of the filter effluent (in this test, from 60 percent to more than 80 percent).
- Ozone addition to the filter effluent did not appear to impact the DOC concentrations, confirming the findings from Phase 1.
- Granular activated carbon (GAC), in doses ranging from 50 mg/L to 150 mg/L, was not effective at increasing UVT or reducing DOC.
- The PAC increased the UVT of the filter effluent from 60 percent to approximately 70 percent at a dose of 100 mg/L (greater than Phase 1 testing). At doses of 50 mg/L and 150 mg/L, the UVT increased to approximately 64 percent and 74 percent, respectively.
- The PAC addition to the filter effluent lowered the DOC concentrations, as well as the BDCM concentrations.
- The MIEX appeared to reduce DOC by approximately 32 percent (from 10 mg/L to 6.8 mg/L) and increase UVT by approximately 20 percent (from 60 percent to 73 percent) at a feed dose of 3 mg/L. This follows similar results from Phase 1.
- Ozone and PAC appeared to be very effective in removing BDCM after it has formed following chlorination. The chlorinated effluent BDCM concentration of 26 μg/L was reduced to 8.7 μg/L with ozone use and to 5.5 μg/L with the use of 100 mg/L of PAC.

### Phase 3 Bench-Scale Testing

The PAA (a commercial solution of acetic acid, hydrogen peroxide, and water) has traditionally been used in hospitals and in the food processing industry. Only in the past several years has it been considered as a wastewater disinfectant. Testing was performed on filtered effluent samples using a 12 percent PAA solution from Solvay and a 15 percent PAA solution from FMC. Preliminary results indicated that:

- An application of about 3.5 mg/L of PAA would provide high-level disinfection for fecal coliform.
- The demand for PAA may not fully utilize the PAA in the disinfection tanks, leaving a residual that may need to be quenched.
- The UVT and the pH were virtually unchanged by application of PAA.

Based on the bench-scale results, PAA appeared to be a viable alternative disinfectant. A pilot study that simulates full-scale operational conditions was conducted to confirm these results.

## Pilot Testing

At the conclusion of the bench-scale tests, a number of alternatives still remained, as shown in Table 2.

Ozone appeared to be particularly viable, either as a way to improve UVT or as a stand-alone disinfectant. To verify conclusions drawn about ozone during bench-scale testing, a pilot test was conducted onsite at the Largo AWWRF under a simulation of full-scale operational conditions. The objectives of the pilot testing were to determine the optimum ozone dosage for:

1. Increasing the filtered effluent UVT to at least 55 percent.
2. Pre-treatment (for precursor removal), such that the BDCM formed subsequently following disinfection with chlorine will be less than 22 µg/L.
3. Passing the chronic toxicity test for surface water discharge, whether ozone is used as a disinfectant or for pretreatment.
4. Fecal coliform removal, if ozone is used as an alternative disinfectant.

Water samples from filter, clarifier, and chlorinated effluents were exposed to various ozone concentrations in an attempt to achieve these objectives. Pilot testing of ozone considered dosing requirements for UVT improvement, bromate formation, and toxicity. It was concluded that an ozone dose of as much as 10 to 20 mg/L would be required to improve the UVT above 55 percent. Bromate formation did not appear to be excessive and all chronic toxicity testing with ozone doses up to 12 mg/L were negative. Subsequent testing demonstrated that a dose of 4 mg/L is sufficient for disinfection to non-detection limits for fecal coliform; thus, there would be no need to apply ozone at a higher dose for UVT improvement.

Pilot testing of PAA was completed with the engineering team and a supplier representative (from Peragreen Solutions LLC) of the PAA product (Proxitane® WW-12, a 12 percent PAA solution from Solvay). A full-scale flow scenario was created in an 18,000-gal baffled tank, with a metered PAA injection pump located upstream of the tank influent. Filtered effluent from the plant served as the pilot tank influent, and the tank effluent was returned to the plant's chlorine contact basin. Samples were taken at the clearwell (pilot influent) and the baffle tank effluent (post PAA treatment), and results were compiled and analyzed. Running a dye test on the tank determined actual residence times that were applied for analyzing the exposure time of PAA with the wastewater. PAA doses ranging from 1.0 mg/L to 4.0 mg/L were analyzed for exposure times ranging from 2 to 7 min.

For each sample point and each run, field measurements for pH, dissolved oxygen, conductivity, and PAA were taken, and samples were sent to the lab for BOD, COD, fecal coliform, and BDCM measurements.

## Final Alternatives

Testing with ozone has shown that, for this

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application, the quantity of ozone required for UVT improvement greater than 55 percent is much greater than that required for disinfection. Thus, ozone used on filtered effluent to improve UVT will have already disinfected the wastewater, making any downstream UV facility redundant for disinfection. For this reason, alternatives using ozone for UVT improvement were eliminated. Although unique in Florida, it was determined that designing for a UVT less than 55 percent may be acceptable. For the final alternatives to compare more rigorously, an alternative using UV equipment designed for a UVT of 48 percent (the 90th percentile value) was considered.

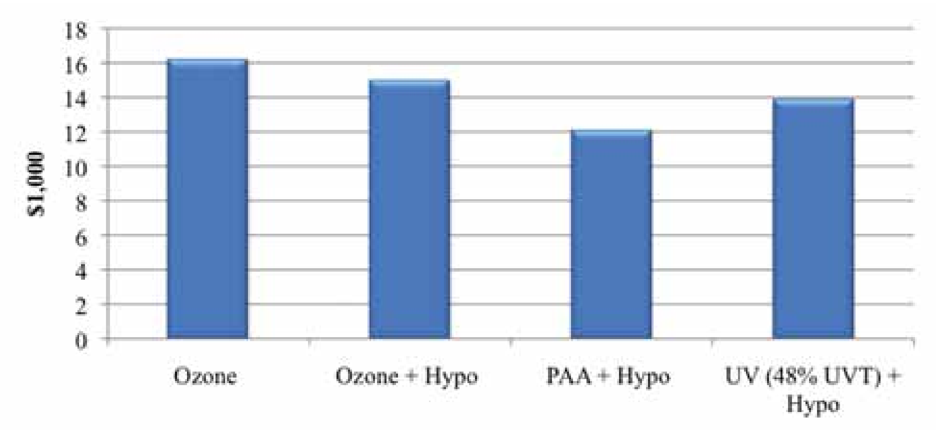
A life cycle cost analysis was performed based on the design parameters listed in Table 3. For split treatment, flows to the alternative (more expensive) disinfection option are to be kept relatively constant, while the diurnal variations are to be sent to the parallel chlorine contact tank using sodium hypochlorite.

Following the PAA pilot testing, further laboratory bench-scale testing was conducted to confirm the results in a more controlled environment and to hone in on the optimal PAA dose and contact time. PAA doses ranging from 2.0 mg/L to 4.0 mg/L were exposed to filtered effluent water for 15 or 25 min (more realistic contact times and similar to the plant's current chlorine disinfection setup). The final phase of bench-scale testing included a split filtered effluent sample; one part was exposed to a lower dose (2.0 to 3.0 mg/L) of PAA and the other part was exposed to sodium hypochlorite. After 15 min, the residual PAA or chlorine was measured, as well as the BDCM concentration. Next, the two samples were blended 50:50, and the residual PAA or chlorine was measured, as well as the BDCM concentration.

Table 3. Preliminary Basis of Design for Alternative Comparison Purposes

| Alternative | Annual Average Flow (mgd) | Peak Instantaneous Flow (mgd) | Dose (mg/L) | Storage Tanks | Electric Power Required (kwh/day) |
|---|---|---|---|---|---|
| FT-3:<br>Ozone | 14.5 | 37 | 4 | Two 11,000-gal tanks | 5,369 |
| ST-5:<br>Ozone + Hypo | Split Flow: 8<br>Main Flow: 6.5 | Split Flow: 10.5<br>Main Flow: 26.5 | Ozone: 4<br>Hypo: 12<br>Bisulfite: 4.04 | LOX: Two 3,500-gal tanks<br>Hypo: Two 9,000-gal tanks<br>Bisulfite: Two 2,000-gal tanks | 2,068 |
| ST-12:<br>PAA + Hypo | Split Flow: 8<br>Main Flow: 6.5 | Split Flow: 10.5<br>Main Flow: 26.5 | PAA: 3.5<br>Hypo: 12<br>Bisulfite: 7.8 | PAA: Two 3,000-gal tanks<br>Hypo: Two 9,000-gal tanks<br>Bisulfite: Two 1,000-gal tanks | Negligible |
| ST-13:<br>UV + Hypo | Split Flow: 8<br>Main Flow: 6.5 | Split Flow: 10.5<br>Main Flow: 26.5 | For 48 percent UVT<br>Hypo: 12 | Hypo: Two 9,000-gal tanks | 6,949 |

Figure 1. Present Worth of the Four Remaining Alternatives
($i$ = 5 percent; $n$ = 20 years)



Present worth costs are compared in Figure 1. Costs such as chemical storage tanks, chemical costs, electricity, construction materials and labor, and retrofitting existing structures were included in the present worth analysis for a 20-year lifespan.

Although the PAA alternative has the lowest present worth, other considerations must be taken into account before the final decision can be made. The following list of non-cost evaluation criteria were scored by the City and consultant staff. Individuals ranked and compared the following non-cost-related issues:

- Complexity
- Permitting (air and water)
- Space allocation
- Operation flexibility
- History of technology
- Construction sequencing
- Training requirements

The ranking of the PAA + Hypo alternative and the UV (48 percent UVT) + Hypo alternative were very close and were both lower than the alternatives using ozone.

## Conclusions and Considerations for the Future

Through a selective screening process, the alternatives that remained for consideration to replace gaseous chlorine for disinfection are for either a full treatment or split treatment approach. During each phase of the screening process, alternatives demonstrated their competitive advantages over the other alternatives. Through bench-scale testing, the effect of various disinfection technologies could be observed as applied to the Largo AWWRF wastewater specifically. As a result of this screening study, it can be summarized that a blended effluent of water disinfected by PAA, side-by-side with sodium hypochlorite, will be the most favorable disinfectant arrangement to replace the current chlorine disinfection at the Largo AWWRF in order to meet permitted BDCM concentrations. A split flow arrangement of PAA (3.5 mg/L for 15 min) and sodium hypochlorite would achieve non-detect levels of fecal coliform for high-level disinfection. Now that the final decision has been made on which disinfection alternative is most suitable for the City of Largo's AWWRF, the new disinfection system will be designed, constructed, and integrated into the current process.

## References

- Greeley and Hansen, CDM Smith. Disinfection Evaluation Report for the City of Largo, Florida. 2011.
- Metcalf & Eddy. Wastewater Engineering Treatment and Reuse. Fourth Edition. McGraw-Hill, New York. 2003.