Ozone and Chloramines: A Proven Combination at Conventional and Lime Softening Plants

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High levels of natural organic matter (NOM), hardness, and bromide present unique challenges for drinking water plants to meet more stringent disinfection and disinfection byproduct (DBP) regulations, as well as aesthetic goals. Tastes and odors (T&O) and contaminants of emerging concerns (CECs) further complicate treatment. Additionally, an increased public awareness of lead corrosion places a greater emphasis on maintaining the water quality that is going to customer taps. As such, water producers across the United States have optimized ozone and chloramine processes to address source water supplies that are challenged. Ozone (with and without biologic filtration) and chloramines have proven to be an effective combination for disinfection, T&O control, DBP control, and stability of water in distribution systems with respect to microbial regrowth and corrosion control.

Optimizing Ozone and Chloramines

The evaluation and development of treatment alternatives and the optimization of ozone,

chlorine, and ammonia application begin with the following activities:

- *Establishing Treatment Goals*: Water quality and operational goals are based on utility and customer expectations, existing and anticipated future regulations, and other drivers. Goals should also address resiliency and redundancy issues, such as production reliability requirements, daily and seasonal variability in water quality, and long-term changes to sources of supply due to development, climate change, or other influences.
- *Evaluating Source Water Quality*: Source water quality will impact the application points, doses, and contact times for ozone, chlorine, ammonia, and other treatment chemicals. Important water quality characteristics include—but are not limited to—NOM, bromide, pH, turbidity, temperature, alkalinity, and hardness.
- *Identifying Plant Constraints*: Available area, plant hydraulics, soils/geologic hazards, power, safety, security, and other site limitations may affect the viability of the ozone and chlorine-chloramine improvements.

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- *Assessing Capital and Operating Costs*: Permitting, design, construction, operations, and maintenance and equipment replacement costs should be factored into process selection and optimization.

Figure 1 presents a process flow diagram for a conventional treatment plant. The flow diagram depicts many of the process options available for ozone and chloramines to be added or optimized into the overall process. For example, process decisions and design criteria must be developed to optimize the treatment process with respect to:
- Ozone application shown with both the raw water and/or settled water
- Filtration options include granular media (conventional or biologic), pressure membranes, and submerged membranes
- Postfiltration granular activated carbon (GAC) adsorption and final disinfection with ultraviolet light (UV), chlorine, or chloramines (or any combination of these unit processes)
- Multiple chemical application points for pH adjustment, oxidation, coagulation, stability and corrosion control, and other treatment techniques

Similarly, Figure 2 presents a process flow diagram for a lime softening/clarification plant. The diagram highlights the options for applying ozone to the raw and softened/settled waters and the major process decisions and design criteria that must be developed to optimize the overall treatment process.

Raw water quality data from two conventional plants and two lime softening plants are summarized in Table 1.

Ozone process optimization rankings typically place the highest priority on primary disinfection, followed by control of DBPs, removal
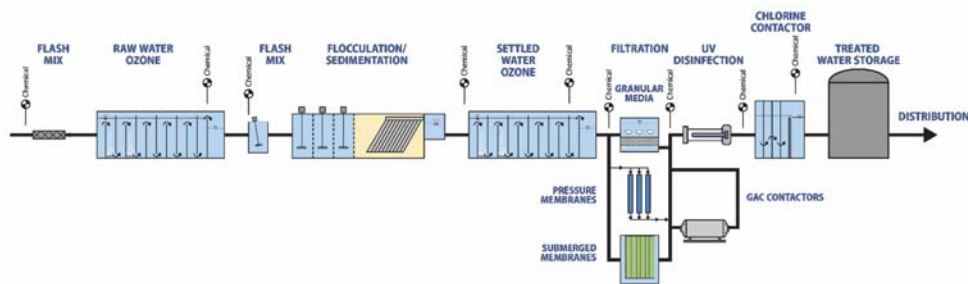

Figure 1. Conventional treatment process with options for raw and settled water ozone.
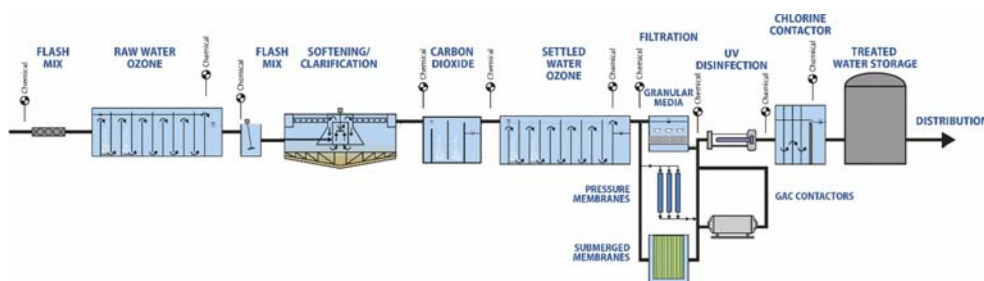
Figure 2. Lime softening/clarification process with options for raw and settled water ozone.

of T&O and CECs, microbial regrowth potential, final (residual) disinfection, and corrosion. Depending on the specific treatment goals for each project, the priorities for addressing these (and potentially other) water quality objectives may change. The following paragraphs present data from the plants that explain how ozone and chloramines can be optimized to address disinfection, DBPs, T&O and CECs, microbial regrowth, residual disinfection, and corrosion.

Disinfection

Ozone demand and decay are critical to primary disinfection as measured by CT products where "C" is the disinfectant concentration and "T" is the contact time for 10 percent of the flow to pass through the contactor or basin. Ozone concentration for a given water can be expressed by the following equation:

$$C = (C_o - C_i)e^{-Kt}$$

where:

C = ozone concentration in milligrams per - liter (mg/L) at time "t"
C_o = applied ozone dose in mg/L
C_i = instantaneous ozone demand in mg/L
K = ozone decay rate in minutes^{-1}
t = time (after ozone application) in minutes

At conventional plants, higher ozone doses are typically required to meet disinfection requirements in the raw water as compared to the settled water because of the following two main factors resulting from coagulation:

♦ *Removing Constituents Reduces Oxidant Demand.* Coagulation removes portions of NOM, metals, turbidity, and other constituents that create demands for ozone or other oxidants. This typically results in lower instantaneous demands and lower decay rates.

♦ *Reducing pH Produces More Persistent Ozone Residuals.* Ozone residuals in water persist longer as pH is reduced. Coagulation will remove some of the demand-causing constituents listed previously and lower the pH (typically to 6.5 to 7.5 units) due to the acidic characteristics of most metal salts (e.g., alum, ferric chloride, ferric sulfate, etc.). The water quality change from raw to settled water will result in lower decay rates.

The impacts of pH on ozone doses demand/decay in raw water and softened/settled water are illustrated in Figures 3 and 4, respectively. Ozone doses of 2 mg/L were applied to waters at the ambient pH in the raw water (approximately 8 units) and the softened/settled water (approximately 9.4 units after lime addition and carbon dioxide stabilization). Additional ozone demand/decay tests were conducted with sulfuric acid added to the high-alkalinity raw water and carbon dioxide added to the low-alkalinity softened/settled water. Reducing pH in both the raw and softened/settled waters produced higher, more-persistent ozone residuals, which allows plants to meet primary disinfection requirements at lower ozone doses.

At lime softening plants, determining the optimal application point(s) for ozone is more complicated and less predictable than at conventional plants. This is because of competing processes and the following factors:

Table 1. Summaries of raw water quality at conventional and softening plants with ozone.

| Raw Water Characteristic	Units	Plant No. 1 Conventional, Raw O₃, Microfiltration	Plant No. 2 Conventional, Settled O₃, GAC/Sand	Plant No. 3 Softening, Raw O₃, Anthracite	Plant No. 4 Softening, Raw O₃, GAC/Sand
Total Organic Carbon	mg/L	1.7 to 18	2.3 to 8.3	3.2 to 6.4	3.2 to 6.1
Bromide	mg/L	0.03 to 0.60	0.05 to 0.26	0.03 to 0.21	ND to 0.10
pH	pH units	6.5 to 8.7	6.5 to 8.7	6.7 to 8.8	7.5 to 9.0
Turbidity	NTU	2 to 89	0.8 to 118	5 to 1,650	0.8 to 23
Temperature	°C	5 to 25	9 to 25	2 to 32	2 to 32
Alkalinity as CaCO₃	mg/L	25 to 100	38 to 122	61 to 181	124 to 180
Hardness as CaCO₃	mg/L	40 to 110	38 to 145	93 to 220	261 to 382
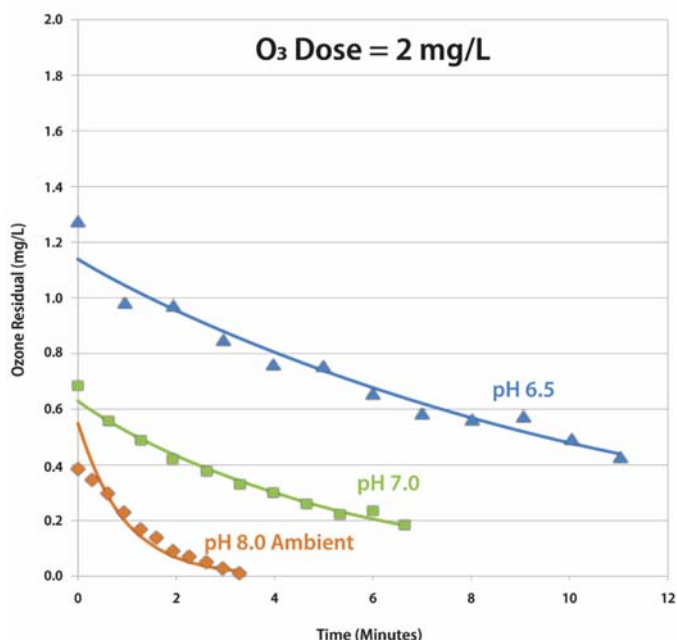
Figure 3. Impact of pH on raw water ozone demand/decay.water ozone.
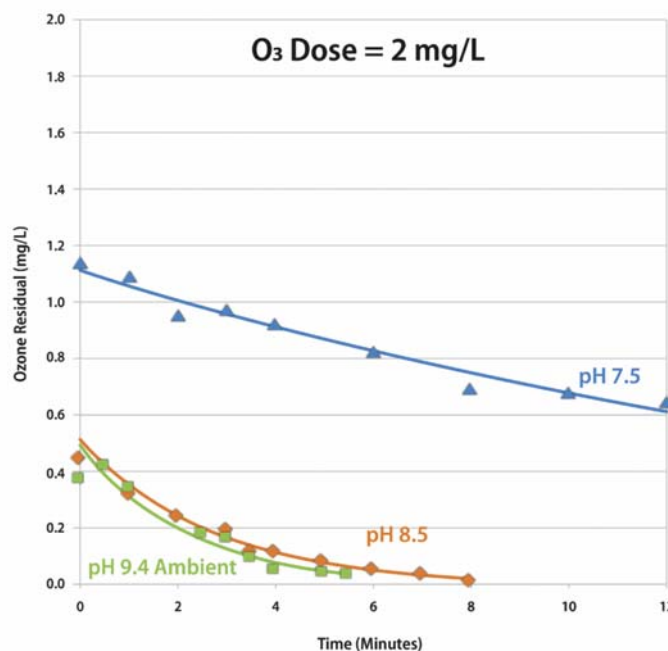
Figure 4. Impact of pH on softened/settled water ozone demand/decay.

- *Removing Constituents Reduces Oxidant Demand*. While combined clarification/softening can effectively remove calcium (hardness), metals, and turbidity, it can also be less efficient for removing NOM due to the higher pH (typically 10 to 11 units). If relatively high concentrations of NOM remain, only small reductions in instantaneous demand and decay rates may be realized.

- *High pH Increases Ozone Decay Rates*. Lime softening typically increases the pH of the settled water to a range of approximately 10 to 11 pH units and the addition of carbon dioxide (recarbonation) may only lower the settled water pH to 8.5 to 9.5 units. The resulting ozone decay rates between raw and softened waters may vary by order of magnitude. High ozone doses may be required to meet CT goals in high pH waters to compensate for the rapid decay of residuals and corresponding short contact times.

Disinfection Byproduct Control

Ozone as the primary disinfectant, coupled with chloramines as the residual disinfectant, can provide greater levels of disinfection and reduce chlorinated DBPs as compared to disinfection with free chlorine. Mechanisms for reducing chlorinated DBPs include:

- Removal of NOM (DBP precursors) through oxidation and improved coagulation
- Further reduction of NOM through biologic filtration
- Reduction or elimination of free chlorine contact time

Trihalomethanes and Haloacetic Acids

Figures 5 and 6 present trihalomethane (THM) and haloacetic acid (HAA) concentrations, respectively, for two disinfection strategies evaluated at a treatment plant. These strategies assume that the treatment plant practices combined clarification/softening, followed by recarbonation and filtration through biologically active carbon/sand filters:

- *Chlorine-Ammonia*: Primary disinfection for *Giardia* and viruses in the biological activated carbon (BAC)/sand-filtered water with free chlorine at contact times ranging from 15 to 120 minutes. followed by ammonia addition to form monochloramine.
- *Ozone-Chlorine-Ammonia*: Primary disinfection for *Giardia* in the settled/recarbonated water with ozone, followed by primary disinfection for viruses in the BAC/sand filtered water with free chlorine for viruses at a contract time of five minutes, and then followed by ammonia addition to form monochloramine.

Compared to disinfection with free chlorine followed by ammonia, the optimized ozone-chlorine-chloramine process reduced THMs by approximately 75 to 87 percent, and HAAs by approximately 25 to 60 percent.
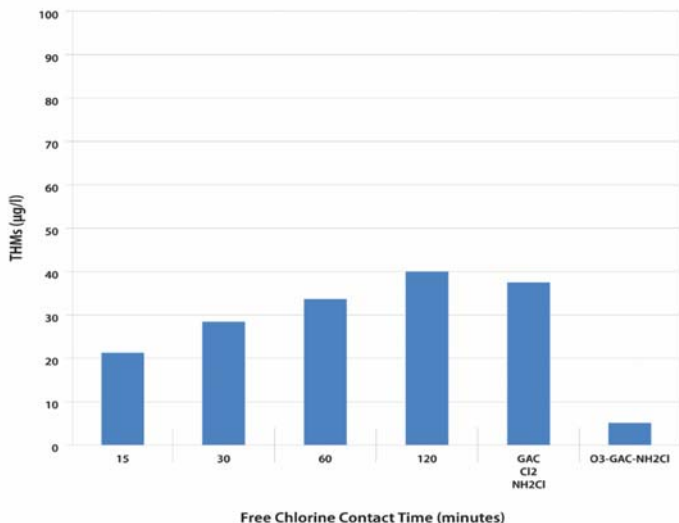

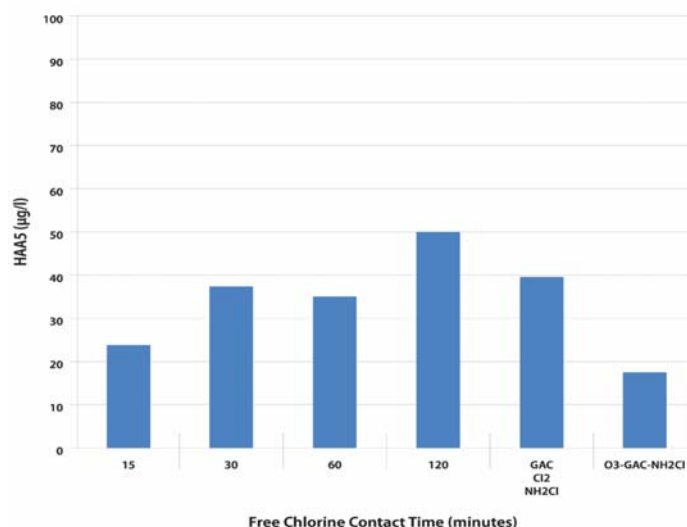Figure 5. Trihalomethane formation with chlorine-ammonia and ozone-chlorine-ammonia.

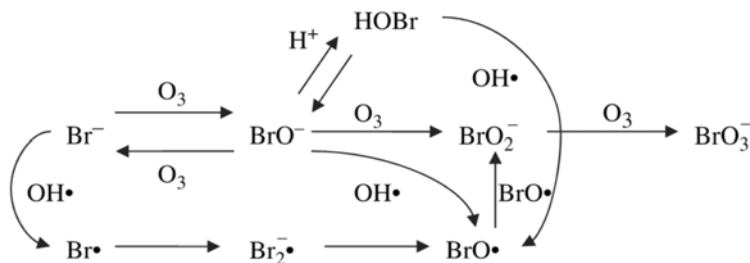Figure 6. Haloacetic acid formation with chlorine-ammonia and ozone-chlorine-ammonia.

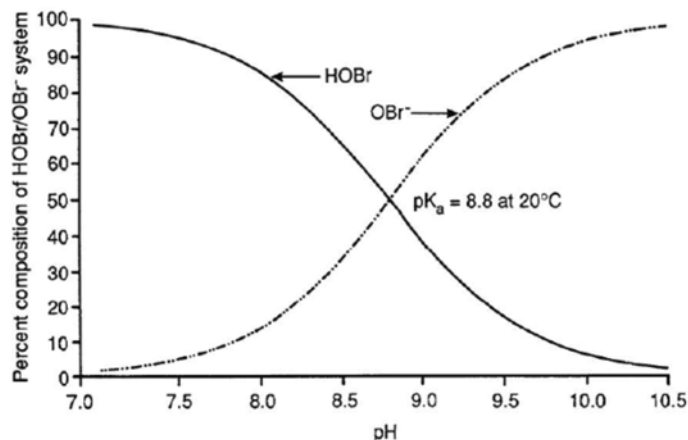Figure 7. Haloacetic acid formation with chlorine-ammonia and ozone-chlorine-ammonia.

Figure 8. HOBr/OBr⁻ Equilibrium Distribution in Aqueous Solution as a Function of pH *(Canada, 2016)*.

Bromate

The oxidation of bromide (Br⁻) to bromate (BrO₃⁻) during ozonation occurs through a complex chemical process. Bromate is formed through two complex chemical pathways, as shown in Figure 7. The first pathway is through direct oxidation. Ozone reacts with bromide to form hypobromite (BrO⁻), which is then further oxidized by ozone to form bromate. The second pathway results from interaction of ozone with water to form hydroxyl radical (OH•), which has a higher oxidation potential than ozone. The hydroxyl radical reacts with Br− to form the bromide radical (Br•), which is then converted to bromate through further reactions with OH• or ozone (Jarvis, 2007).

The pH of water during the ozonation of bromide affects the formation of bromate. As pH increases, the production of bromate also increases, as shown in Figure 8. This can be partly attributed to the increased formation of OH• radicals at high pH, due to the increased concentration of hydroxyl ions (OH⁻). Additionally, the HOBr/OBr⁻ equilibrium (pKa = 8.8) plays a key role in the formation of bromate during ozonation. With an acid dissociation constant (pKa) of 8.8 at 20°C, above pH 8.8 OBr⁻ is predominant and below pH 8.8 HOBr is predominant (Canada, 2016).

In the direct pathway, ozone oxidizes OBr⁻ to bromite (BrO₂⁻), then bromate. Increased pH favors BrO⁻, the more unstable and reactive compound, in the HOBr/OBr⁻ equilibrium (Pinkernell and Von Gunten, 2001). Additionally, at lower pH, ozone residuals are more stable; therefore, the ozone dose required to achieve disinfection credit is lower. Consequently, fewer hydroxyl radical reactions, and more direct and molecular ozone reactions, take place.

For bromate control at ozone plants, several processes have been evaluated and implemented. Notable implementations include pH reduction, ammonia addition, and chloramine addition. Reducing pH to between 6 and 7 units has been effective at plants with low bromide levels (e.g., less than 0.1 mg/L) to suppress bromate formation below the primary drinking water standard of 10 µg/L; however, as bromide levels increase, pH adjustment alone may not comply with the bromate standard. This is particularly true for source waters that require high ozone doses to meet disinfection and aesthetic goals. The addition of ammonia or chloramines prior to ozone inhibits bromate production by forming bromamine and other compounds, and this prevents ozone from oxidizing the bromide (in its natural state) to bromate. Dosing chloramine at 0.5 to 1 mg/L has generally proven more effective than ammonia alone in suppressing bromate formation, potentially offering cost savings, operational advantages, and water quality benefits.

Figures 9 and 10 present bromate formation data for ozone applied to raw water, and to softened/settled water, respectively. The data illustrate that applying 0.5 to 1 mg/L of chloramines before ozone application is more effective than pH suppression or adding ammonia alone.

Contaminants of Emerging Concerns

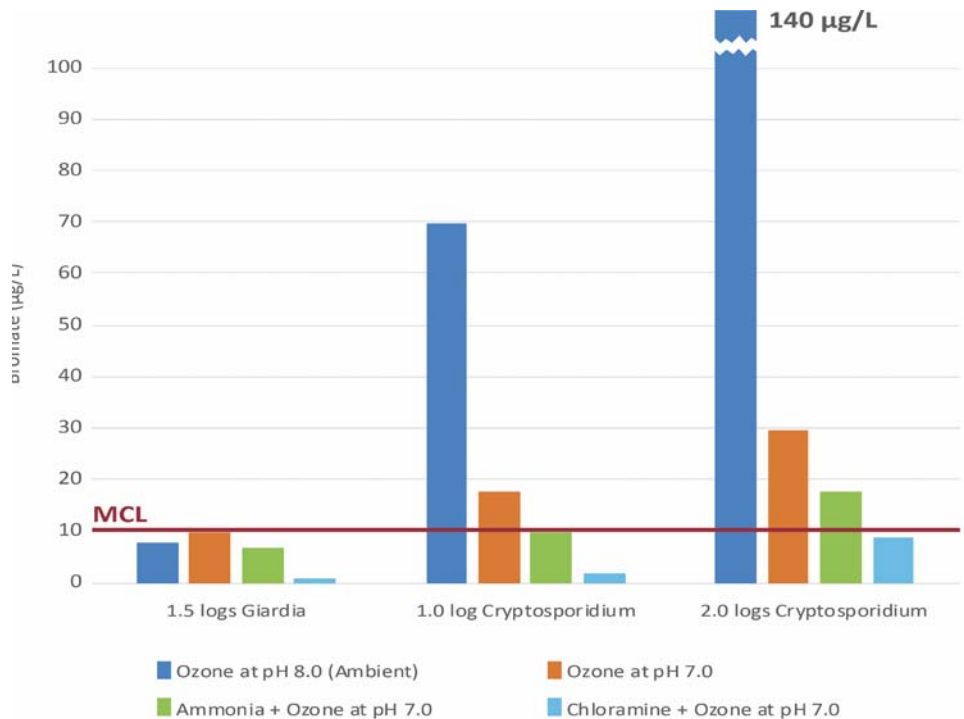For decades, removal of algal-based T&O has been a primary benefit of ozone. In recent

Figure 9. Bromate formation and control in raw water.

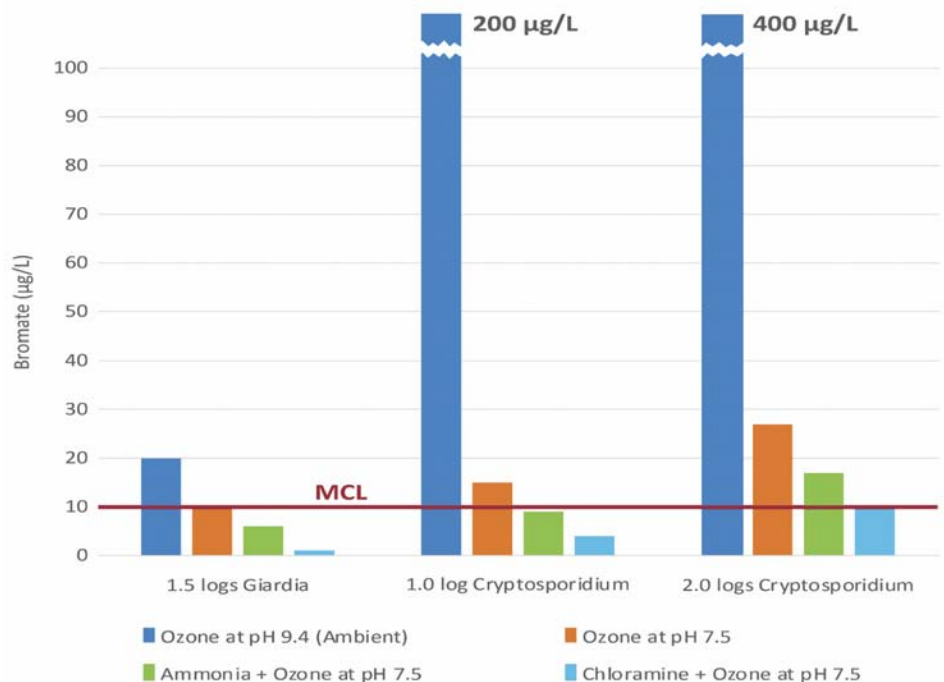Figure 10. Bromate formation and control in raw water.

years, health advocates, water suppliers, researchers, regulators, and other water industry professionals have increased focus on the removal of a wide variety of the trace contaminants found in some drinking water supplies. The contaminants include, but are not limited to, pesticides, herbicides, pharmaceuticals, personal care products, perchlorate, per- and polyfluoroalkyl compounds, and other CECs.

Ozone alone, and when combined with hydrogen peroxide, has proven effective for oxidizing many organic T&O compounds and CECs. Removal of T&O compounds and some CECs can often be enhanced when biologic filtration follows the ozone or advanced oxidation process. Figures 11 and 12 illustrate geosmin and 2-methylisoborneol (MIB) removal for a conventional treatment process, with ozone applied in raw and settled water, respectively. The data are from pilot studies that spiked geosmin and MIB at concentrations of approximately 100 parts per trillion (ppt), or nanograms per liter (ng/L), into the raw water and then evaluated raw and set-

tled water ozone in parallel treatment trains. Both pilot trains included biologic filters configured with anthracite/sand and GAC/sand media configurations.

For the raw water ozone process (Figure 11), ozone was applied at a dose of 3 mg/L alone and with hydrogen peroxide (H_2O_2). Three $O_3:H_2O_2$ ratios (by weight) were tested: 1:1, 2:1, and 10:1. The pH of the raw water ranged from 7.4 to 7.7 units, and the ozone dose of 3 mg/L was selected to meet a primary disinfection goal of at least 1.5-logs of *Giardia* inactivation. Only data for the anthracite/sand filters are shown. The data indicate that raw water ozone, followed by biologic filtration, removed approximately 76 percent of the MIB and 84 percent of the geosmin. Advanced oxidation increased MIB and geosmin removals to greater than 90 percent at all the $O_3:H_2O_2$ ratios tested.

For the settled water ozone process (Figure 12), ozone was applied at a dose of 1.6 mg/L with no H_2O_2. The pH of the settled water after coagulation ranged from 6.5 to 6.8 units, and the ozone dose of 1.6 mg/L was selected to meet a

primary disinfection goal of at least 1.5-logs of *Giardia* inactivation.

Data are shown for both anthracite/sand and GAC/sand filters operated in biologic mode. The data show approximate removals of 47 percent and 73 percent for the MIB and geosmin through the anthracite/sand filter, and approximate removals of 81 percent and 94 percent for the MIB and geosmin through the GAC/sand filter. The GAC was approximately six months old, so improved removal of the T&O compounds through the GAC/sand filter may be attributed to adsorption.

When comparing the effectiveness of ozone applied to the raw water versus the settled water, the data indicate that the combination of higher pH and a higher ozone dose at the raw water provided better removal of MIB and geosmin than the lower pH and lower ozone dose at the settled water. This trend has been observed during several treatment studies and at several plants.

Microbial Regrowth and Corrosion Control

While ozone and chloramines are an effective combination to meet objectives for disinfection, DBPs, T&O, and other water quality objectives, these treatment techniques can also present potential challenges. Ozone, whether applied to the raw and/or settled water, can:

- Increase food sources for bacteria as measured by assimilable organic carbon (AOC) and biodegradable organic carbon (BDOC)
- Produce oxidation byproducts such as aldehydes and glyoxal acids
- Increase chlorine and/or chloramine demand

Although chloramines are more persistent as a final disinfectant in distribution systems as compared to free chlorine, chloramines can also present potential challenges, such as:

- Serving as a weak disinfectant for viruses and requiring longer contact time to inactivate bacteria
- Introducing ammonia, a potential food source for nitrifying bacteria, to the distribution system
- The potential for chlorinous odors if the chlorine to ammonia ratio is not optimized
- Changes in water chemistry can potentially affect corrosion control

The degrees to which these potential challenges are realized are highly site-specific and can depend on factors such as raw water and treated water characteristics; treatment processes and practices; and distribution system size, materials, and operations.
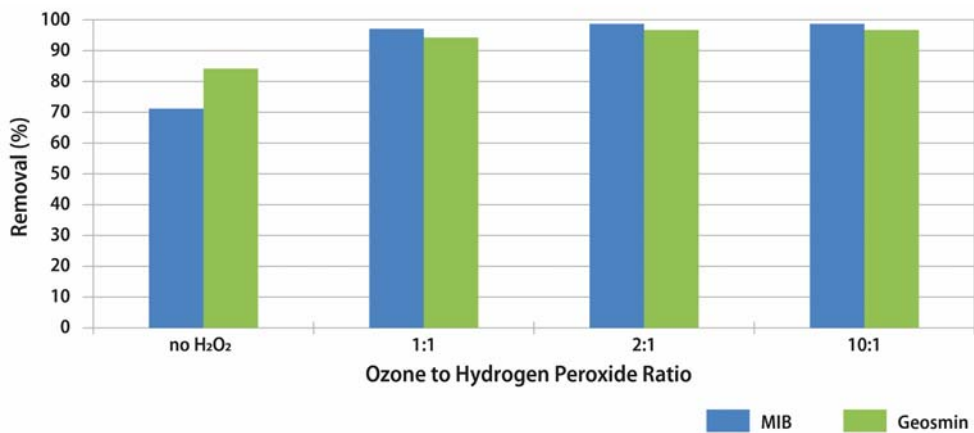

Figure 11. 2-methylisoborneol and geosmin removal with raw water ozone (3 mg/L) and hydrogen peroxide.
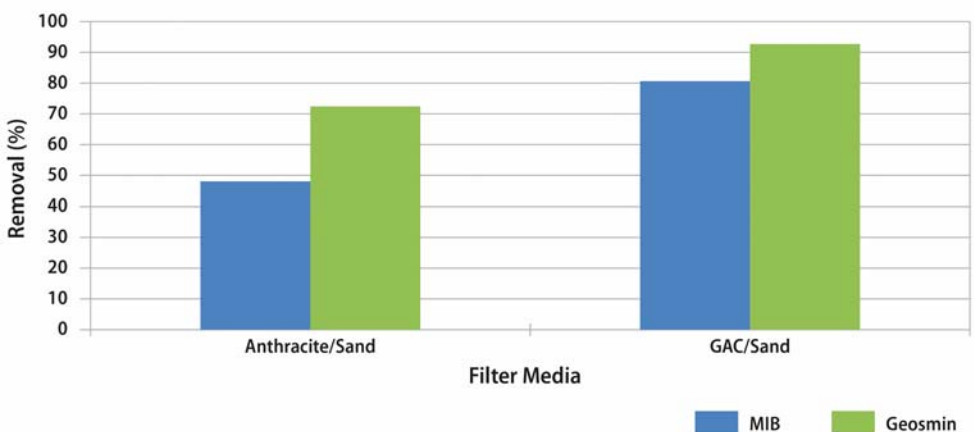

Figure 12. 2-methylisoborneol and geosmin removal with settled water ozone (1.6 mg/L).

Microbial Regrowth

Biologic filtration can provide multiple benefits with respect to enhancing water quality prior to final disinfection and distribution. These benefits include:

- Improved removal of TOC and NOM (DBP precursors)
- Reduced levels of AOC and BDOC
- Biodegradation of T&O compounds and other trace organics

A comparison of how microbial regrowth potential changes through the raw water and settled water ozone processes is presented in Figure 13. The AOC samples were collected from the raw water, after raw and settled water ozone, and after biologic filtration through anthracite/sand and GAC/sand filters. Raw water AOC levels ranged from approximately 100 to 400 µg/L as acetate-C. The averages of all the AOC samples collected at each location over three months of testing are presented.

Ozone doses ranged from 2.3 to 3.2 mg/L at the raw water and 0.9 to 1.2 mg/L at the settled water. In all cases, increases in AOC were observed after ozone was applied, and these increases in AOC were generally limited to less than an order of magnitude (i.e., less than a 10-fold increase). Similar trends in reductions in AOC were observed through the biologic filters where the final AOC levels returned to levels similar to, or in many cases, slightly less than the levels measured in the raw water.

It's important to understand that not all drinking water systems that apply ozone and chloramines require biologic filtration. Ozone and chloramines without biologic filtration have been successfully implemented at unfiltered systems, conventional plants with membrane filtration, and lime softening plants with media filtration.

Corrosion Control

Because ozone residuals in water dissipate (or are quenched) within treatment plants, the direct impacts of ozone on corrosion control in distribution systems are small. With that said, the cumulative changes in pH, TOC, alkalinity, hardness, final disinfectant type and residual concentration, and other water quality characteristics can impact corrosion control. These variables must be understood, studied, and optimized to develop and implement effective corrosion control strategies if ozone is to be part of a new treatment plant or is to be incorporated into an existing plant.

Changing the residual disinfectant from free chlorine to chloramines presents additional variables that require evaluation and optimization to avoid unexpected conditions. The con-
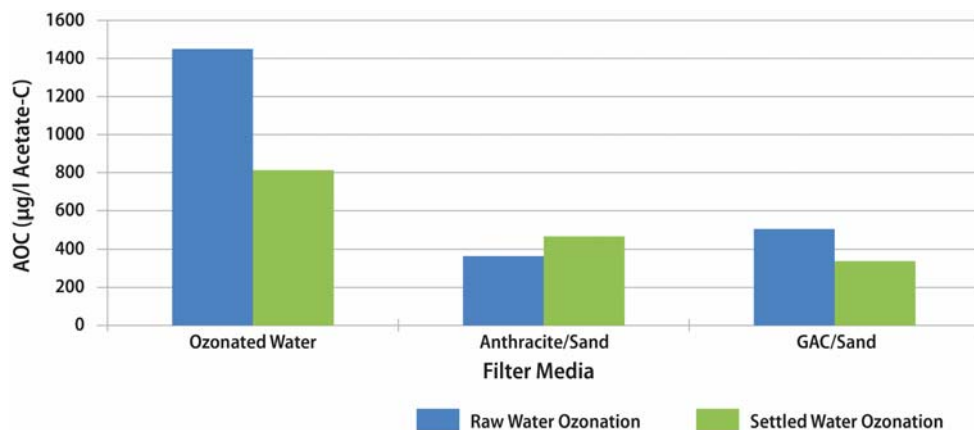

Figure 13. Assimilable organic carbon profiles for raw and settled water ozone.

sequences of not anticipating and addressing changes in distribution water quality can lead to:

- Formation or destruction of biofilms and protective scaling on pipe walls
- Losses of disinfectant residuals
- Microbial regrowth and/or microbial induced corrosion
- Changes in pH and speciation of DBPs
- Corrosion of piping and release of metals such as iron, manganese, lead, and copper
- Aesthetic problems such as turbidity and T&O

These and other consequences can be avoided through the development and implementation of an optimized corrosion control strategy.

Conclusion

Ozone and chloramines have proven to be an effective combination to meet objectives for disinfection, DBPs, T&O and CECs, microbial regrowth, and corrosion control. This is especially true for source waters with high levels of organic DBP precursors, high bromide, and elevated levels of pathogens that require increased disinfection.

Important lessons learned regarding ozone and chloramines include the following:

- NOM, pH, and temperature directly impact ozone demand/decay, and dose requirements for disinfection. Turbidity, metals and other constituents also affect ozone demand and decay, but to a lesser degree.
- Plant hydraulics, site constraints, operations and maintenance (O&M), and costs should be factored into the selection of the optimal ozone application point(s), along with the water quality considerations. There are trade-offs and these decisions are not always clear.

- Stabilizing raw water pH (with mineral acids or carbon dioxide) can lower ozone requirements for disinfection by producing more stable and persistent residuals.
- Ozone can improve coagulation by reducing coagulant doses and produce lower settled water turbidity when compared to no or other oxidants.
- Ozone can improve filtered water turbidity and particle removal, facilitate higher filter loading rates, reduce headloss accumulation, and increase run lengths between backwashes (compared to no or other oxidants).
- Biologic filtration can enhance water quality, but it's not always necessary if raw water quality is good and the distribution system does not have excessive water age, dead ends, high temperatures, or other adverse conditions.
- Comprehensive evaluation of both the apparent and subtle changes in water quality resulting from ozone, biologic filtration, or chloramines must be addressed to develop and implement an effective corrosion control strategy.

Water producers across the U.S. have optimized ozone and chloramine processes to address source water supplies that are challenged. High levels of NOM, hardness, and bromide present unique challenges for drinking water plants trying to meet more stringent disinfection and DBP regulations, as well as aesthetic goals. The T&O and CECs further complicate treatment. As such, implementing the optimal ozone and chloramine treatment techniques at conventional and lime softening plants requires a comprehensive approach in order to address water quality, constructability, O&M, and safety considerations. ⬦