

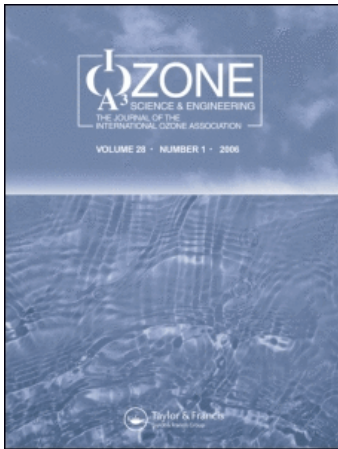
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Pilot-Scale Evaluation of Ozone vs. Peroxone for Trihalomethane Formation

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Both the direct ozone reaction and the indirect hydroxyl radical reaction are important in the ozonation of drinking water. This paper investigates the effectiveness of ozone versus ozone coupled with hydrogen peroxide (peroxone) with respect to trihalomethanes formation. The investigation was conducted on a pilot-scale at various H₂O₂:O₃ dose ratios of 0.1, 0.2, and 0.35 and change in peroxide addition point (pre- and post-ozonation). It was observed that the addition of peroxide, either before or after ozonation, increased trihalomethane concentrations and that increasing H₂O₂:O₃ increased trihalomethane concentrations. In comparing the addition point of peroxide, addition prior to ozonation better controlled trihalomethane formation than after ozonation.

Keywords Ozone, Peroxone, Trihalomethanes, Disinfection By-Products

INTRODUCTION

Trihalomethanes are a group of compounds that can form when the chlorine used to disinfect drinking water reacts with naturally occurring organic matter. Most drinking water treatment plants in Canada use some form of chlorine (i.e., chlorine, chloramines or chlorine dioxide) to disinfect drinking water, to treat the water directly in the treatment plant and/or to maintain a chlorine residual in the distribution system to prevent bacterial regrowth. The health risks from disinfection by-products, including trihalomethanes, are much less than the risks from consuming water that has not been disinfected. Water systems need to maintain low concentrations of disinfection by-products

without compromising disinfection (Health Canada, 2006). The trihalomethanes most commonly found in drinking water are chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (Health Canada, 2006).

Health Canada's guideline for the maximum acceptable concentration (MAC) for trihalomethanes (THMs) in drinking water is 0.100 mg/L (100 µg/L) based on a locational running annual average of a minimum of quarterly samples taken at the point in the distribution system with the highest potential THM levels (Health Canada, 2006).

The use of ozone for the treatment of drinking water is well established in Europe but relatively new in North America (Rakness, 2005). The first full-scale application of ozone in drinking water treatment occurred in 1893 at Oudshoorn, Netherlands (Langlais et al., 1991). Ozonation plants grew rapidly throughout Europe with majority being located in France and many using it as a primary disinfectant. In the early 1900s, ozone was recognized to improve taste and odor, remove color, and oxidized iron and manganese in a water source. In the 1960s effects of ozone on coagulation were explored where ozone enhanced particle removal (Langlais et al., 1991). In the 1980s, ozone application was for disinfection by-product control (THMs) and biological stabilization (Langlais et al., 1991).

Ozone is a widely used disinfectant due to its ability to destroy resistant pathogens, such as *Cryptosporidium*, and its lower CT (concentration x contact time) value than conventional counterparts (USEPA, 1999). In addition to ozone's excellent disinfection capability it also has the added benefits of taste and odor removal, enhanced particulate removal, oxidation of iron and manganese, and reduction of trihalomethanes formation potential (Langlais et al., 1991; Jasim et al., 1998). Molecular ozone reactions with species in water tend to be highly selective, whereas reactions

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with the ozone decomposition by-product the hydroxyl radical ($\bullet\text{OH}$) are non-selective, resulting in faster reaction rates and degradation of compounds that are refractory to ozone (Glaze et al., 1992; Prado and Esplugas, 1999; Zwiener and Frimmel, 2000).

As a result more investigation is being conducted into the effectiveness and applicability of advanced oxidation processes (AOPs), which promote $\bullet\text{OH}$ production. The addition of hydrogen peroxide (H_2O_2) to ozone, known as peroxone, is a common AOP that greatly accelerates the ozone decomposition rate promoting $\bullet\text{OH}$ formation. Forni et al. (1982) found the half-life for ozone and ozone with hydrogen peroxide (water at a pH of 10.9) to be 1.9 sec and 0.047 sec, respectively.

Investigation of the AOP utilizing the peroxone system began in the late 1970's for wastewater treatment and in the late 1980s for drinking water treatment (Glaze et al., 1987). Duguet et al. (1985) showed the addition of peroxide enhanced the efficiency of oxidation of organic substances and THMs precursors, and increased ozone transfer rate. The addition of H_2O_2 can also reduce the formation of brominated organic species (Siddiqui and Amy, 1993). This has been attributed to the consumption of hypobromous acid, the main reactive species, by hydrogen peroxide.

When bromide is present in source water it may be oxidized by ozone to form hypobromite ion (OBr^-), which exists in equilibrium with HOBr , the speciation of which depends on the pH. Increased bromide levels can also increase the concentration of brominated organics formed during both ozonation and chlorination. Both chlorine and ozone are capable of oxidizing bromide to hypobromous acid (HOBr). The hypobromous acid can then react with NOM to produce brominated organics such as bromoform (in the case of ozone) and bromodichloromethane and dibromochloromethane (in the case of chlorine). Shukairy et al (1994) found that as bromide concentration increased so did the incorporation of bromine into the DBPs, and that ozone treated water (prior to chlorination) generally had greater bromine incorporation than water treated solely with chlorine.

Several water quality and operational conditions affect ozone treatment processes. A concept important in ozone and AOP systems is the R_{ct} value, which represents the ratio of $\bullet\text{OH}$ exposure to molecular O_3 exposure (i.e., $R_{\text{ct}} = [\bullet\text{OH}]/[\text{O}_3]$) (Elovitz and von Gunten, 1999). In ozone systems the hydroxyl radical concentration is low at approximately 10^{-12} M leading to a low R_{ct} , whereas in a peroxone system the R_{ct} is 3 times that of an ozone system alone (Acero and von Gunten, 2001).

Organic matter, depending on its type, can act as an initiator, promoter or inhibitor of ozone decomposition (Westerhoff et al., 1997). Elovitz et al. (2000) found, for a DOC range of 0.7–3.2 mg/L, that the R_{ct} increased by 80-fold with a 10-fold increase in $\bullet\text{OH}$ exposure and a 60-fold decrease in ozone exposure. However, in a

peroxone system DOC (1.1–2.2 mg/L) was found to not significantly affect R_{ct} , which demonstrates that the presence of H_2O_2 dominates the initiation of ozone decomposition, masking the effects of the DOC (Acero and von Gunten, 2001).

The study used the $\text{H}_2\text{O}_2:\text{O}_3$ ratio in the range of 0.0, 0.1, 0.2, 0.35, (0.35 is the stoichiometric optimum), which is close to the range used in previous study for the removal of Taste and Odor, and to minimize DBPs formation in waters with comparable water quality (AWWARF, 1991). In that study, THMs production in water treated with peroxone followed by chlorine was higher than in water treated with ozone followed by chlorine. Hydrogen peroxide addition point can have a significant effect. Acero and von Gunten (2001) found that ozone exposure decreased and $\bullet\text{OH}$ exposure increased with an increasing $\text{H}_2\text{O}_2/\text{O}_3$ ratio. They also found that adding additional peroxide after a ratio of 0.19 did not further increase radical exposure.

The main purpose of this study was to evaluate the effects of ozone compared to ozone/hydrogen peroxide with respect to the production and speciation of trihalomethanes. Comparisons are made between pre- and post-ozonation addition as well as to conventional treatment.

EXPERIMENTAL

Material and Methods

A pilot plant located at the A. H. Weeks Water Treatment Plant in Windsor, Ontario, Canada was used for the conduction of the research. The raw water source used was the Detroit River, which connects Lake St. Clair and Lake Erie. The pilot plant is constructed of stainless steel, glass and inert fluorocarbons to eliminate organic contamination and corrosion by ozone. The plant is set up with two identical parallel process trains, Side 1 and Side 2, that include a rapid mixer for coagulant and coagulant aid addition, flocculation tanks, sedimentation basin, and dual media sand filter (Figure 1). The ozone is introduced to the water through a ceramic diffuser in which the injection of the gas flow (ozone) is counter-current to the liquid flow. The pilot plant is equipped with raw and treated water monitoring points, which include temperature, pH and turbidity meters.

Although ozonated water is able to be sent to both sides of the plant there are limitations and process changes are required, as illustrated in Table 1. For example, in order to run peroxone as a pre-ozonation peroxide addition process, it can only be run simultaneously with conventional treatment and not with ozone.

Ozone Generation

The ozone contactor in the pilot plant is a counter-current flow contactor in which ozone is injected in the lower base of the column, while water enters from the top. Ozone is generated using a PCI Ozone & Control

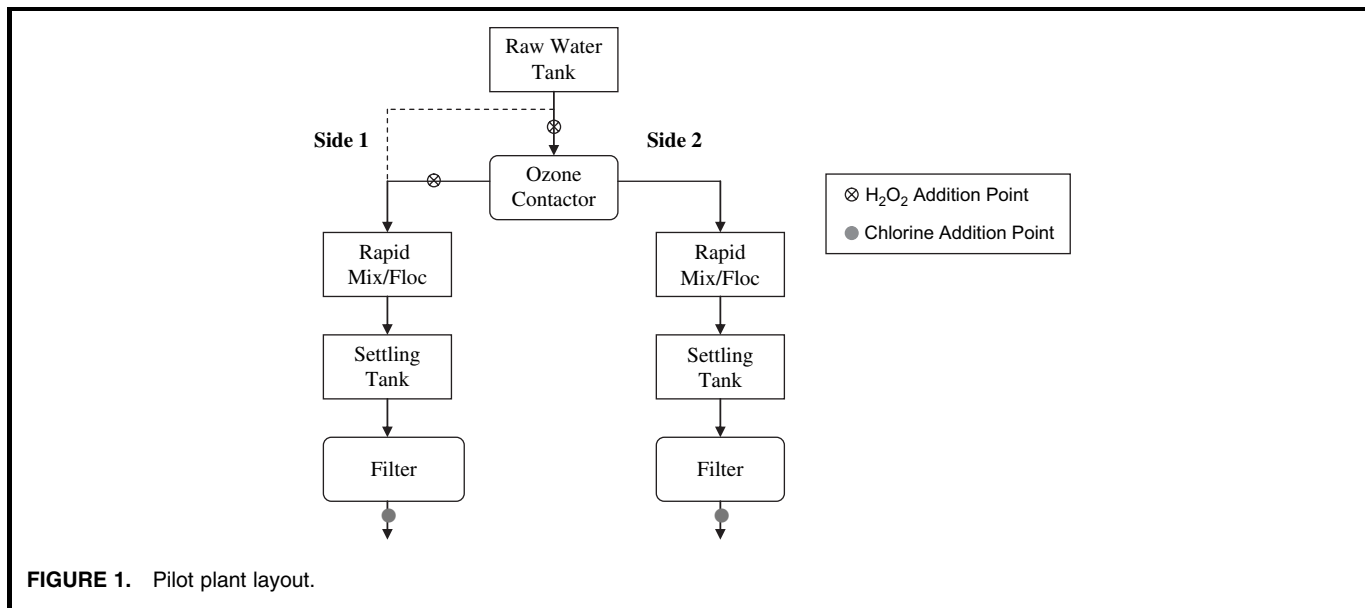


TABLE 1. Comparison of Process Changes for Operation of Ozone and AOP Experiments

Parameter		Pre-Ozonation H ₂ O ₂ Addition	Post-Ozonation H ₂ O ₂ Addition	No AOP
Treatment Process	<i>Side 1</i>	Conventional	Peroxone	Conventional
	<i>Side 2</i>	Peroxone	Ozone	Ozone
Ozone Contact Time*		13.2 min	6.6 min	13.2 min
Flow Rate Into Contactor		8.3 L/min	16.5 L/min	8.3 L/min
Flow Through Process Train	<i>Side 1</i>	8.3 L/min	8.3 L/min	8.3 L/min
	<i>Side 2</i>	8.3 L/min	8.3 L/min	8.3 L/min

*Based on flow rate and contactor volume, not used for disinfection calculations.

Systems, Inc (West Caldwell, NJ) GL-1 Laboratory Ozone Generator. The ozone generator output is measured using a PCI HC-12 ozone monitor. The ambient ozone concentrations are measured using a PCI LC-12 ozone monitor. The source of oxygen to the generator is an air production unit Peak Scientific Purifier Model AP-03. An Alnor Model 7200 (Alnor Instrument Co., distributed by Cole-Parmer Instrument Company, Niles, IL) is used to check the prepared air dew point. Any ozone off-gas from the contactor is destroyed using a PCI OD-2 ozone destruct unit equipped with a preheater before discharge.

Data Collection and Analysis

A SCADA system using Alan Bradley RS View 32 developed by Rockwell Automation (Windsor, ON) was used for data collection. Parameters monitored by the SCADA system were pH, temperature, flow rate, and ozone dose. Temperature was measured using an S-Products Model R88000 two-wire temperature transmitter with a Brian

Controls (Mississauga, ON) mineral insulated RTD Temperature Sensor. The pH was measured using a Rosemount Instruments Ltd. Model 1054A pH/ORP Microprocessor Analyzer (Mississauga, ON). Ozone residual samples were taken from the effluent of the contactor and were measured using the Indigo Colorimetric method of Standard Methods (APHA, 1999). Sample analysis for DOC and THM analysis was performed by EnviroTest (Waterloo, ON) based on Standard Methods 5310B and USEPA method SW846-8260, respectively.

Experimental Design

Experiments were carried out during the months of May, June and December 2004 and April 2005. For the months of May, June and December, hydrogen peroxide was added after the ozone contactor, whereas April was selected for addition prior to the contactor. In all trials the H₂O₂/O₃ ratio was varied (0.1, 0.2, and 0.35 mg/mg) while keeping applied ozone dose constant (2.0 mg/L). Carbon dioxide gas was also added to the raw water,

prior to ozonation, to lower the pH to approximately 6.8–7.0. The operational water flow rates and contact times are listed in Table 1. For the April trial, a direct peroxone (pre-ozonation) versus ozone comparison could not be made so a series of samples for peroxone versus conventional were taken and then a series of samples for ozone versus conventional.

The effluent from both filters was collected to which sodium hypochlorite was added. THM samples were taken from the filter effluent and treated as simulated distribution system (SDS THMs). The bottles were allowed to sit in the dark in a running water bath for a period of 24 hours to simulate a distribution system environment. From these bottles the samples for THM analysis were taken. The chlorine dose applied was such that the chlorine residual after a 20-minute retention time was between 1.1 and 1.2 mg/L.

RESULTS AND DISCUSSION

Discussed next are the results obtained for trihalomethanes based on simulated distribution systems THMs (SDS THMs). The results of the peroxone treatment are separated into sections for post-ozonation and pre-ozonation with a final section on the comparison of these two treatment systems.

Post-Ozonation Addition of Hydrogen Peroxide

The data presented in this section were a result of a series of SDS THMs samples taken during the months of June and December 2004. In previous studies some researchers found peroxone to lower concentrations of THMs while others found peroxone to increase their concentration (Wallace et al., 1988; MWDSC, 1991;

Sozanski and Walkowiak, 1999). The results obtained for this research, depicted in Figure 2, show the total THMs concentration is equal to or higher than that of ozone alone. Also, concentrations are higher in June than December due to warmer water temperatures (20 °C vs. 5 °C). The concentrations generated by the peroxone system were up to 47% higher (20% higher on average) than that of ozone. The MWDSC (1991) found that THMs concentrations were 25%–30% higher in a peroxone system (H₂O₂/O₃ ratio of 0.2) than ozone alone for a similar contact time (6 min) and ozone dose (2 mg/L) that coincide with this experiment.

Of importance is the impact of DOC levels and chlorine doses on the generation of THMs. For both the months of June and December, treated water DOC was lower, on average, for the peroxone samples than ozone only, yet the peroxone samples required a higher chlorine dose to attain the same 20-minute residual as the ozone samples. For the month of June, DOC and chlorine doses for peroxone vs. ozone were 0.97 mg/L vs. 1.2 mg/L and 2.4 mg/L vs. 1.7 mg/L, respectively. In December these values corresponded to 0.78 mg/L vs. 0.92 mg/L (DOC) and 1.4 mg/L vs. 1.2 mg/L (chlorine), respectively. The higher chlorine doses required for the peroxone samples may have resulted in the higher THM concentrations observed.

Hydrogen peroxide is used in the quenching of chlorinated water by reacting with HOCl (Krasner et al., 1993). Some residual hydrogen peroxide may have been present which created an additional chlorine demand, resulting in the peroxone samples requiring a higher chlorine dose to obtain the same residual as the ozone sample. Although the peroxone ratios were chosen at or below the optimal stoichiometric ratio for which no excess hydrogen peroxide

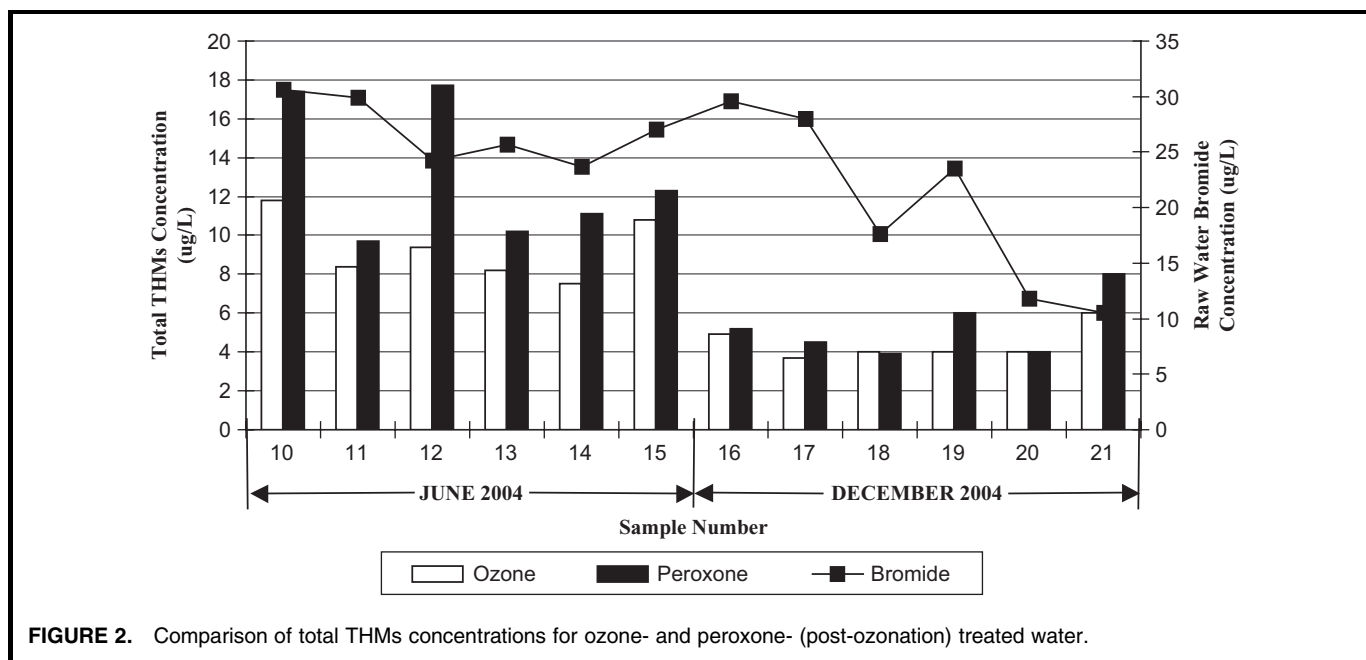


FIGURE 2. Comparison of total THMs concentrations for ozone- and peroxone- (post-ozonation) treated water.

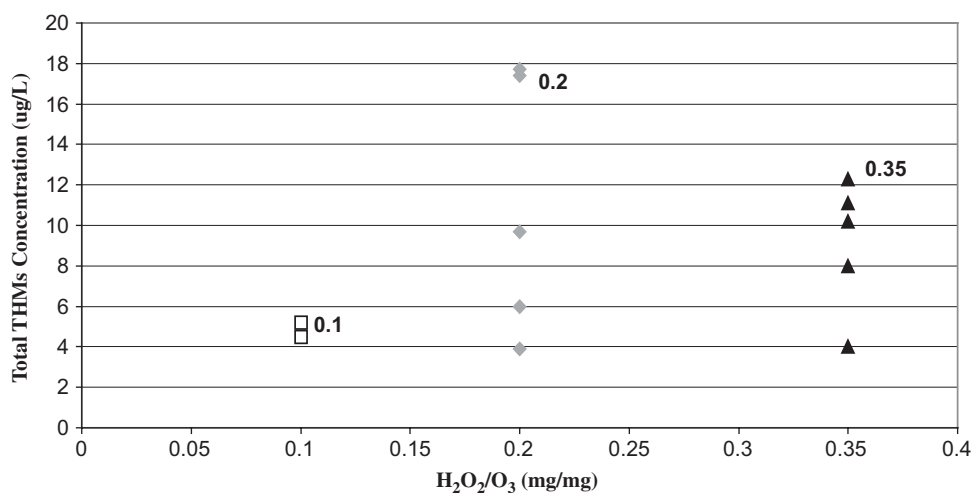


FIGURE 3. Effect of peroxone ratio on total THMs concentrations (post-ozonation).

would be present (0.35), natural waters have numerous compounds that inhibit and promote ozone decomposition, which can alter the optimal ratio (Langlais et al., 1991). As a result, not all the hydrogen peroxide may have been consumed and a residual remained.

When considering the effect of the peroxone ratio, it can be seen from Figure 3 that the smallest ratio of 0.1 generated the lowest THMs concentrations, while the 0.2 and 0.35 ratio generating higher concentrations. Increasing the hydrogen peroxide dose will generate greater concentrations of hydroxyl radicals. The study conducted by the AWWARF (1991), suggested that the hydroxyl radicals generated can react with organics such that it increases the active sites available for reaction with chlorine, thereby increasing THMs concentrations (the AWWARF study used the addition of hydrogen peroxide prior to ozone addition).

For the 0.1 ratio the sample with the highest TTHMs had a higher Cl₂ dose, higher treated water DOC, and higher treated water bromide concentration than the other sample for that ratio. For the ratio of 0.2 the two samples with the highest TTHMs concentrations had the highest treated water DOC and the highest Cl₂ dose, but lower treated water bromide concentrations relative to the other samples. For the final ratio of 0.35 the three highest TTHMs samples had the highest treated water DOC and Cl₂ doses, but lower treated water bromide concentrations compared to the lower two samples.

Effect of Treatment on Trihalomethanes Speciation (Post-Ozonation)

An important parameter that affects THMs speciation is bromide concentrations (Krasner et al., 1991; Shukairy et al., 1994). Research has found that as bromide to DOC ratio increases so does the incorporation of bromine into DBPs (Shukairy et al., 1994). Depicted in Figures 4 and 5

are the raw water bromide/DOC ratios and the corresponding speciation of THMs for ozone- and peroxone-treated water, respectively.

For ozone-treated water samples the variation in THMs species ranged from 27%–53% for chloroform, 14%–32% for dibromochloromethane, and 33%–42% for bromodichloromethane. For the peroxone system THM species ranged from 31%–58% for chloroform, 10%–28% for dibromochloromethane, and 32%–43% for bromodichloromethane. Bromoform concentrations in both the ozone and peroxone system were below the detection limit of 0.5 µg/L. The raw water bromide concentrations during the sampling period were relatively low, ranging from 10.5 µg/L – 30.6 µg/L. The lack of bromoform formation is most likely a result of the low raw water bromide concentrations.

Minear and Bird (1983) illustrated that bromoform was not detected until bromide levels reached almost 100 µg/L and did not become dominant until bromide levels reached above 1,000 µg/L. Shukairy et al. (1994) achieved a concentration of approximately 3 µg/L of bromoform at a bromide concentration of 60 µg/L. Also of note, is that the percent speciation of chloroform in each of the peroxone samples is higher than that of ozone, while the percent composition of bromine substituted species is higher in the ozone samples than the peroxone samples. As mentioned previously, chlorine doses for filter effluent samples were higher in the peroxone system and this may have resulted in the increased percentage of chloroform production. In general, in for both ozone and peroxone the chloroform composition tends to be slightly higher when higher chlorine doses were used.

For the ozone-treated samples chloroform levels were, on average, 27% lower for the samples with lower chlorine doses (~1.2 mg/L) compared to those with the higher doses (~1.7 mg/L). A similar result was observed in the

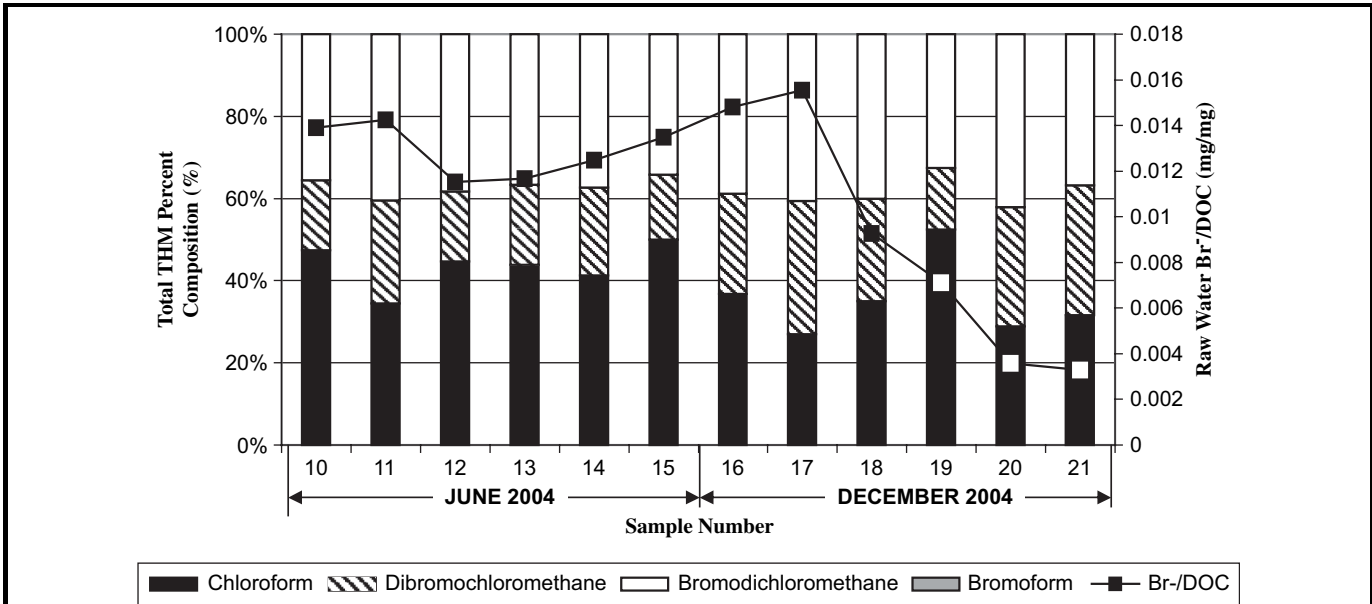


FIGURE 4. Speciation of total THMs as a function of bromide/DOC ratio for ozone-treated water samples.
Note: *Bromoform below detectible levels.

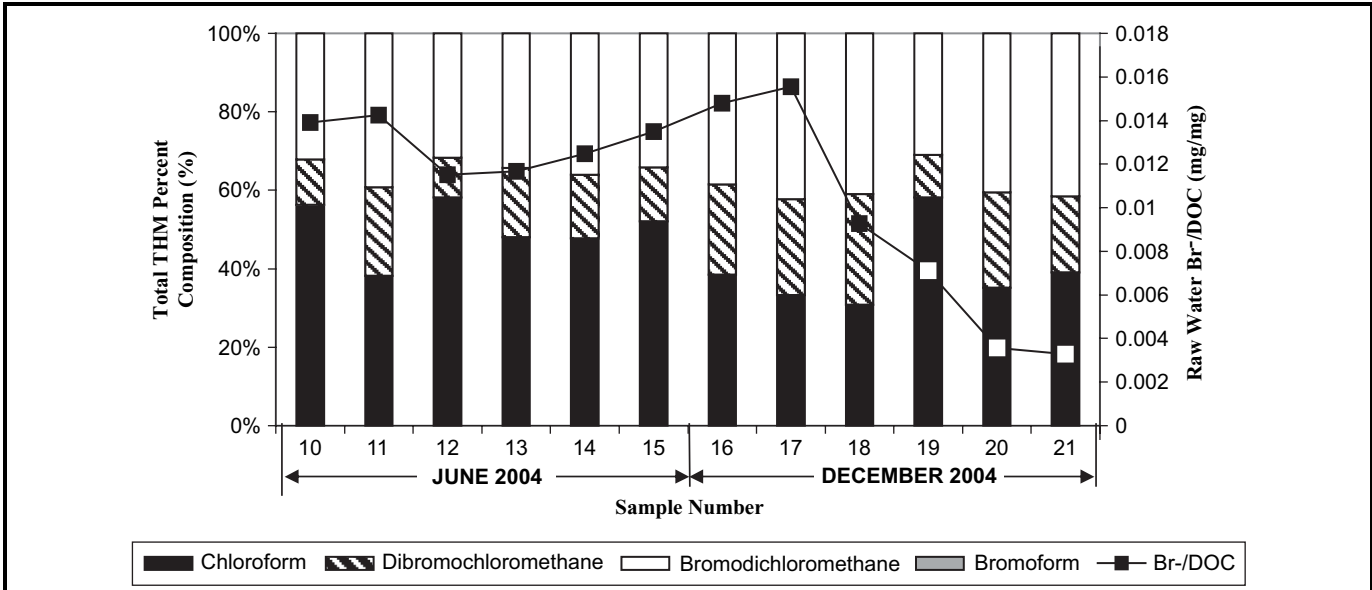


FIGURE 5. Speciation of total THMs as a function of bromide/DOC ratio for peroxone-treated water samples (post-ozoneation).
Note: *Bromoform below detectible levels.

peroxone system, with chloroform levels being, on average, 30% lower at lower chlorine doses (~1.4 mg/L) than those samples exposed to higher doses (~2.5 mg/L). Siddiqui and Amy (1993) have stated that hydrogen peroxide reacts with HOBr, depleting the concentration available to react with NOM, which may also account for the lower concentration of brominated species in the peroxone system.

Effect of Pre-Ozonation Hydrogen Peroxide Addition

In this section are the results of a series of ozone and peroxone samples that were taken in April 2005, with hydrogen peroxide added just prior to the ozone contactor. Because of the set up of the pilot plant the ozone and peroxone samples could not be directly compared to each other but to conventional treatment only. The results

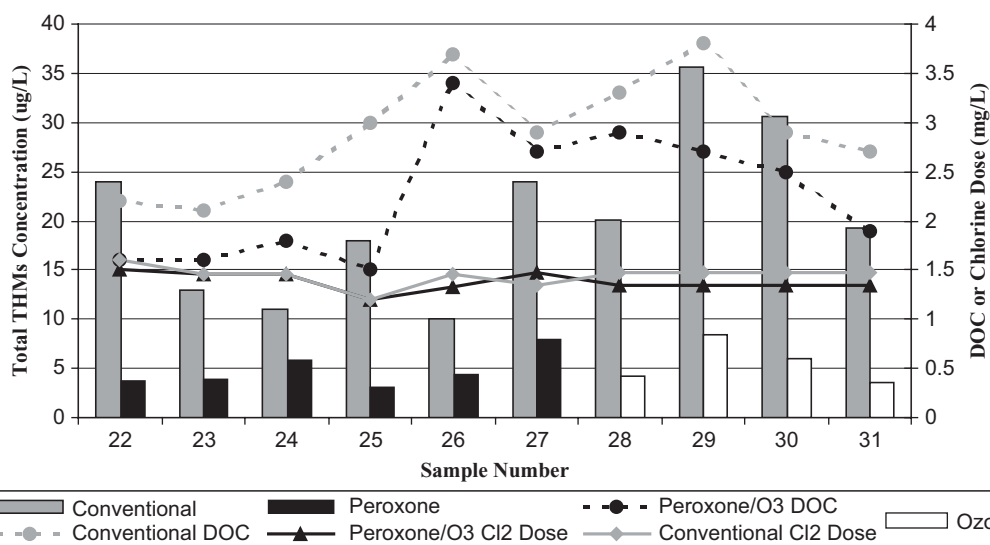


Figure 6. Comparison of Total THMs Relative to Treated Water DOC and Chlorine Dose for Ozone and Peroxone (Pre-Ozonation) Treated Water.

obtained for total THMs concentrations for peroxone, ozone and conventional treatment are shown in Figure 6. From the graph it can be seen that both the ozone and peroxone system were able to achieve lower concentrations of TTHMs than the conventional samples. The TTHMs concentrations from the peroxone samples were 47%–85% lower than conventional, while ozone TTHMs were 76%–81% lower than conventional. On average, compared to conventional treatment, peroxone achieved a 68% reduction and ozone achieved a 79% reduction in TTHMs. The lower concentrations observed in the non-conventional treatments is expected and consistent with other researchers' results (Wallace et al., 1988; Siddiqui et al., 1997; Galapate et al., 2001). Ozonating the water oxidizes organics, reducing the DOC concentration and chlorine dose required, thereby lowering the concentration of THMs produced.

The water treated by peroxone or ozone treatment had a lower treated water DOC concentration than the conventional treated water DOC. Peroxone and ozone treatment resulted in lower DOC concentrations of 8%–50% and 12%–30%, respectively. On average, the removal of DOC from raw water by the peroxone system was 45%, whereas the removal by ozone alone was 40%. This is in support of other researchers that claim peroxone systems better remove DOC due to the ability of hydroxyl radicals to react with a wide array of organic compounds that molecular ozone may not (Allemane et al., 1993; Glaze et al., 1987).

The chlorine doses required for the peroxone treated water were about equal to the conventionally treated water (sample numbers 22–27), whereas the chlorine dose for the ozonated water was lower than the conventional

(sample numbers 28–31). No quenching during ozonation was conducted, and so the presence of the highly reactive hydroxyl radicals during chlorination may have placed an added chlorine demand on the water (USEPA, 1999). The higher THMs observed in the conventional samples may be a result of the amount and type of organics present in the raw water. Galapate et al. (2001) discovered that ozone is able to transform hydrophobic organic matter to hydrophilic matter, which has a lower potential to form THMs, as well as to oxidize the reactive sites of DOC, thereby lowering TTHMs concentrations.

The effect of the peroxone ratio was examined and the results shown in Figure 7. The general trend seems to be that the higher the ratio the greater the production of THMs. On average the THMs concentrations for the ratios of 0.1, 0.2, and 0.35 were 3.8 $\mu\text{g/L}$, 4.4 $\mu\text{g/L}$, and 6.1 $\mu\text{g/L}$, respectively. As mentioned previously, the (AWWARF, 1991) study suggested that hydroxyl radicals react with organics such that it increases the active sites available for reaction with chlorine, thereby increasing THM concentrations. For the first ratio of 0.1, the two samples had similar parameters in that Cl_2 dose was the same (1.5 mg/L) and the DOC of the treated water was the same (1.6 mg/L). The one difference was that the peroxone treated water bromide concentration was 16.4 $\mu\text{g/L}$ for the sample with the higher TTHMs vs. 9.1 $\mu\text{g/L}$ for the other sample. For the ratio of 0.2, the sample with the higher TTHMs concentration had a higher Cl_2 dose (1.5 mg/L vs. 1.2 mg/L) and higher treated water DOC (1.8 mg/L vs. 1.5 mg/L), although the treated water bromide concentration was slightly lower (15.3 $\mu\text{g/L}$ vs. 17.5 $\mu\text{g/L}$). For the final ratio of 0.35, in comparing the two samples, the higher TTHMs concentration had a higher treated water bromide

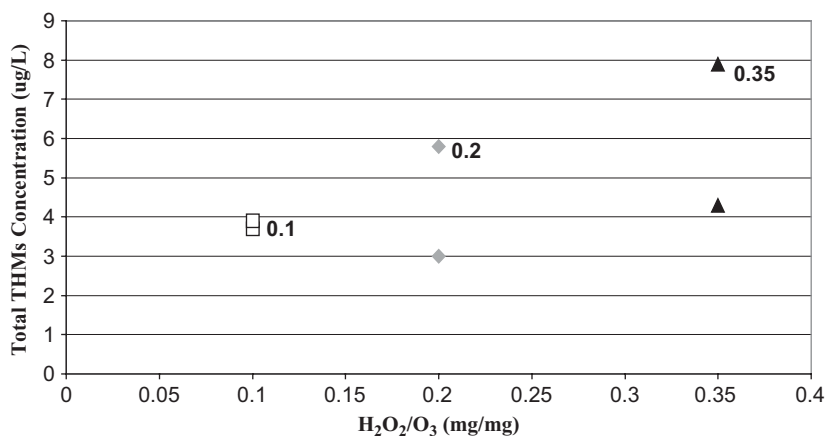


FIGURE 7. Effect of peroxone ratio on total THMs concentrations (Pre-Ozonation).

concentration (19.1 µg/L vs. 17.5 µg/L) and a higher Cl₂ dose (1.5 mg/L vs. 1.3 mg/L), but a lower treated water DOC value (2.7 mg/L vs. 3.4 mg/L).

Effect of Treatment on Trihalomethane Speciation (Pre-Ozonation)

It was indicated previously that Br⁻/DOC ratio is an important factor affecting the outcome of THMs speciation. It can help determine the relative amounts of brominated and non-brominated (i.e., chloroform) species that will be formed. Illustrated below in Figure 8 and Figure 9 is the composition of the total THMs relative to the raw water bromide/DOC ratio for the non-conventional and conventional treated waters, respectively.

For the peroxone samples, THMs species composition ranged from 30%–47% for chloroform, 16%–32% for dibromochloromethane, and 35%–39% for bromodichloromethane. In the ozonated samples the composition of the chloroform, dibromochloromethane and bromodichloromethane ranged from 28%–40%, 22%–34% and 38%, respectively. As with the post-ozonation hydrogen peroxide addition samples, bromoform was below the detection limit of 0.5 µg/L. From Figure 8 it can be seen that in general the chloroform composition was higher in the peroxone samples than the ozone-only samples and that the bromine substituted species were higher in the ozone-only system. On average, the chloroform comprised approximately 40% of the THMs in the peroxone

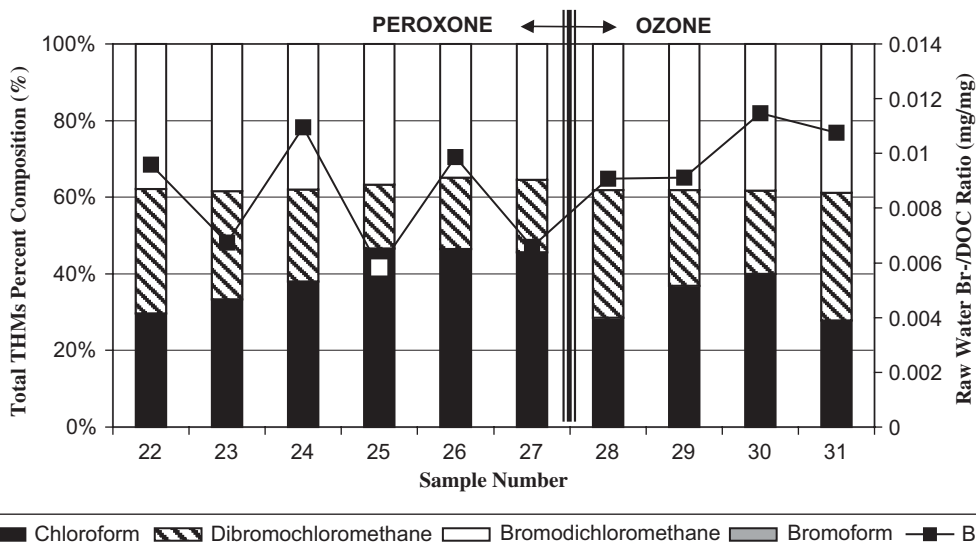


FIGURE 8. Speciation of total THMs as a function of bromide concentration for ozone and peroxone (pre-ozonation) treated water samples. Note: *Bromoform below detectible levels.

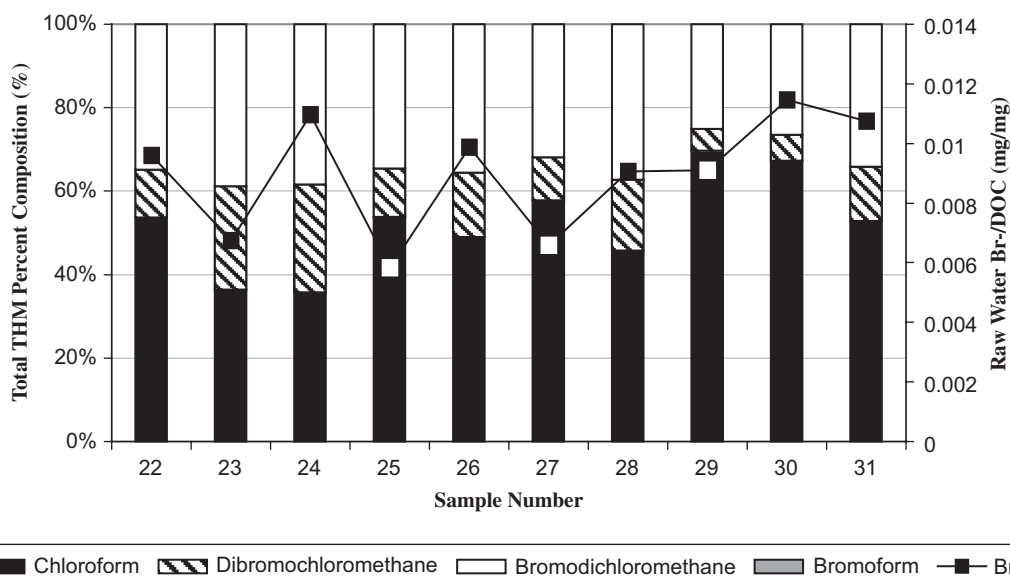


FIGURE 9. Speciation of total THMs as a function of bromide concentration for conventional treated water samples.
Note: *Bromoform below detectible levels.

samples, while in the ozone samples it made up approximately 33% of the total THMs.

This may be due to the fact that (i) the Br^-/DOC ratios were generally higher when the ozone samples were taken (ii) that in the peroxone samples the peroxide would react rapidly with the ozone lowering the amount of HOBr formed from the reaction of ozone with bromide (von Gunten et al., 1996) and (iii) any HOBr formed can be consumed by hydrogen peroxide, thereby lowering brominated DBP species. In addition, the concentration of peroxide and DOC present and available for reaction with ozone is much greater compared to bromide concentrations and much of the ozone would be consumed before reacting with bromide. In the conventionally treated samples (Figure 9) chloroform was more dominant ranging from 36%–70%, with an average of 52%, compared to the non-conventional samples with an average of 37%. Chloroform may be more dominant in the conventional samples since chlorine doses tended to be higher than the non-conventional treatment and due to the higher DOC concentration.

Comparison of Pre- and Post-Ozonation Hydrogen Peroxide Addition

Here, comparisons are made between the two peroxone systems (i.e., pre- and post-ozonation hydrogen peroxide addition) in terms of their effect on total THMs concentrations as well as speciation. Figure 10 illustrates the difference in TTHMs concentrations between the two processes. From the graph it can be seen that the pre-ozonation THMs samples have concentrations that are lower than the post-ozonation samples for June and

are comparable to December. The average concentrations for the months of June, December and April are 13.1 $\mu\text{g}/\text{L}$, 5.3 $\mu\text{g}/\text{L}$, and 4.8 $\mu\text{g}/\text{L}$. The relatively higher concentrations in the month of June can be attributed to the warmer temperatures, which averaged approximately 19.6 °C compared to the December and April averages of 5.2 °C and 7.3 °C, respectively. Comparing the months of April and December, the average raw water DOC concentrations were 3.9 mg/L and 2.6 mg/L respectively, yet in the system where peroxide was added prior to ozonation THMs concentrations were the same (or slightly lower). The post-ozonation addition of peroxide was also able to remove from the raw water, on average, 68% of the DOC in December, compared to 38% by the pre-ozonation system in April.

As can be seen from Table 2, the THM compound compositions are virtually identical for the months of April and December. The average raw water bromide concentrations for April and December are 30.9 $\mu\text{g}/\text{L}$ and 20.2 $\mu\text{g}/\text{L}$, respectively. Numerically, the average concentrations of the brominated compounds for December are 3.2 $\mu\text{g}/\text{L}$ and 2.8 $\mu\text{g}/\text{L}$ for April.

Adding peroxide prior to ozonation allows the peroxide to react immediately with ozone before a significant amount of HOBr is formed (von Gunten et al., 1996). In the post-ozonation process, ozone has time to react with bromide first without the interference of hydrogen peroxide, generating greater amounts of HOBr, which can then produce brominated DBPs. In the post-ozonation system, hydrogen peroxide can react with the already formed HOBr at a relatively fast rate ($k = 2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$), degrading much of the HOBr formed during the

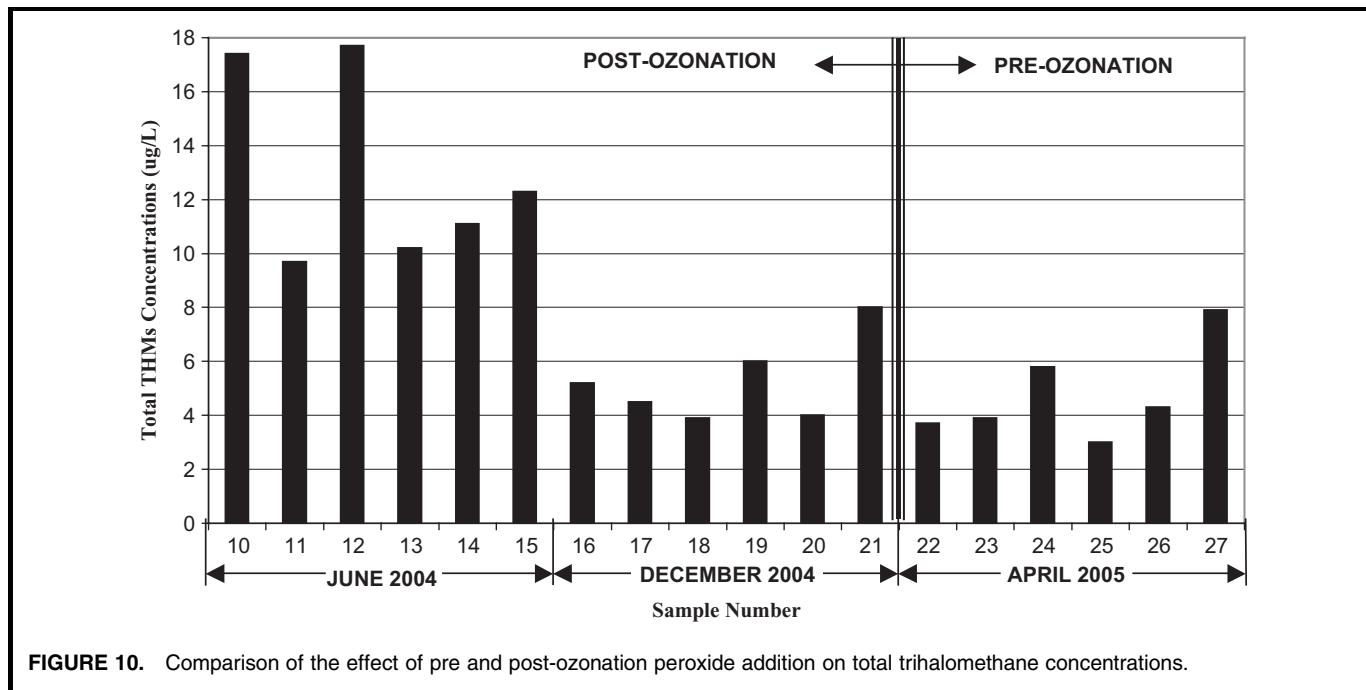


FIGURE 10. Comparison of the effect of pre and post-ozonation peroxide addition on total trihalomethane concentrations.

TABLE 2. Comparison of Average Speciation of Total THMs for Pre- and Post-Ozonation Peroxone Treated Water

Month	CHCl ₃	CHBr ₂ Cl	CHBrCl ₂	CHBr ₂ Cl + CHBrCl ₂
June 2004	50%	16%	34%	50%
December 2004	39%	22%	39%	61%
April 2005*	40%	22%	38%	60%

*Pre-ozonation.

ozonation period even though the reaction time is less than that of the ozonation period. This may explain the similar speciation of THMs in the pre and post-ozonation treatment systems. Although the month of April had factors more conducive to the formation of higher THM concentrations the resulting values were comparable to those of December. It may be that the use of a pre-ozonation peroxone system is more effective for the control of THM concentrations than a post-ozonation system.

CONCLUSIONS

This study was conducted on a pilot scale in Windsor, Ontario, Canada using the Detroit River as the source water. From this experiment the following conclusions were drawn:

1. The removal of DOC from raw water by the peroxone system was more effective than ozone alone, with the post-ozonation peroxone system achieving the greatest removal. The post-ozonation peroxone system removed 61% compared to 53% by ozone.

The pre-ozonation peroxone system removed 45% compared to 41% by ozone alone.

2. THMs concentrations were higher in the peroxone samples than ozone only for both pre- and post-ozonation peroxone systems. THMs concentrations were up to 47% higher in the post-ozonation peroxone system versus ozone. In the pre-ozonation peroxone trials, ozone alone achieved a greater reduction in total THMs concentrations (79%) than peroxone, and (68%) compared to conventional treatment.
3. In the post-ozonation peroxone system chloroform composition was 5% higher in the peroxone system versus ozone alone, and brominated compounds were 3% higher in the ozone system. In the pre-ozonation system chloroform was more dominant in conventional samples (52%) compared to ozone (33%) and peroxone (40%).
4. Pre-ozonation samples generated comparable results (April = 4.8 µg/L vs. December = 5.3 µg/L) in terms of total THMs concentration and speciation even though water quality during pre-ozonation

sampling was more conducive to increasing THMs concentrations (i.e. higher DOC and bromide concentrations).

5. The peroxone samples required a higher chlorine dose than ozone samples to attain the same 20-minute residual for both the pre- and post-ozonation peroxone systems.

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DISCLAIMER

The mention of commercial products does not constitute endorsement by the author or supporting agencies.

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