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Effect of magnetic ion exchange and ozonation on disinfection by-product formation

Ryan S. Kingsbury [a,*], Philip C. Singer [b]

[a] CDM Smith, 5400 Glenwood Ave., Ste. 300, Raleigh, NC 27612, USA
[b] University of North Carolina, Chapel Hill, NC, USA

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ABSTRACT

The purpose of this research was to investigate the performance of treatment with magnetic ion exchange (MIEX) resin followed by ozonation in achieving disinfection goals while controlling bromate and chlorinated disinfection by-product (DBP) formation. Three water samples were collected from raw water supplies impacted by the San Francisco Bay Delta to represent the varying levels of bromide and total organic carbon (TOC) that occur throughout the year. A fourth water was prepared by spiking bromide into a portion of one of the samples. Samples of each water were pre-treated with alum or virgin MIEX resin, and the raw and treated waters were subsequently ozonated under semi-batch conditions to assess the impact of treatment on ozone demand, ozone exposure for disinfection ("CT"), and bromate formation. Finally, aliquots of raw, coagulated, resin-treated, and ozonated waters were chlorinated in order to measure trihalomethane formation potential (THMFP). In the waters studied, MIEX resin removed 41–68% of raw water TOC, compared to 12–44% for alum. MIEX resin also reduced the bromide concentration by 20–50%. The removal of TOC by alum and MIEX resin significantly reduced the ozone demand of all waters studied, resulting in higher dissolved ozone concentrations and CT values for a given amount of ozone transferred into solution. For a given level of disinfection (CT), the amount of bromate produced by ozonation of MIEX-treated waters was similar to or slightly less than that of raw water and significantly less than that of alum-treated water. MIEX resin removed 39–85% of THMFP compared to 16–56% removal by alum. Ozonation reduced THMFP by 35–45% in all cases. This work indicates that in bromide-rich waters in which ozone disinfection is used, MIEX resin is a more appropriate treatment than alum for the removal of organic carbon, as it achieves superior TOC and THM precursor removal and decreases the production of bromate from ozone.

1. Introduction

The San Francisco Bay Delta is a major source of drinking water to communities throughout central and southern California. Due to its connectivity to the Pacific Ocean and two major rivers, water quality in the Delta varies seasonally, exhibiting a wide range of salinity (16–133 mg/L chloride) and total organic carbon (TOC) concentrations (2.5–10.5 mg/L; CALFED, 2007). Runoff from areas of intensive agricultural activity in the watershed elevates TOC levels in the Delta during rainy periods, while the increased freshwater flow lowers salinity. During drier periods, seawater from the San

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* Corresponding author.
E-mail address: ryanskingsbury@alumni.utexas.net (R.S. Kingsbury).

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Francisco Bay intrudes more readily into the Delta, increasing bromide and chloride levels while lowering TOC concentrations. This situation presents unique challenges for water treatment because both bromide and the natural organic material (NOM) comprising the TOC serve as disinfection by-product (DBP) precursors.

In response to these challenges, many utilities that draw water from the Delta employ ozone in order to control the formation of halogenated organic DBPs and because ozone is a more effective disinfectant against *Cryptosporidium* and other pathogens than free chlorine.

However, ozonation of bromide-containing waters can result in the formation of bromate, which is classified as a possible human carcinogen and is regulated in the US with a maximum contaminant level (MCL) of 10 μg/L (U.S. EPA, 2006b). Additionally, since ozone must often be used in combination with chlorine because it cannot provide a stable disinfectant residual in the distribution system, the presence of bromide in the water when chlorine is applied shifts the speciation of THMs and other halogenated by-products toward the more brominated forms which are thought to have a more detrimental public health impact than their chlorinated analogs (Richardson et al., 1999; Plewa et al., 2002).

In addition to serving as a DBP precursor, NOM can increase the ozone demand of a water, hampering the effectiveness of ozone for disinfection. Because higher amounts of ozone are needed to overcome the demand, the formation of oxidation by-products, such as aldehydes, is increased in waters with elevated NOM concentrations (Najm and Krasner, 1995; Johnson and Singer, 2004). These oxidation by-products, many of which are biodegradable, can cause biofilm problems in water distribution systems.

MIEX is a strong base anion exchange resin specifically designed to remove dissolved organic carbon (DOC) from water. It has been shown to remove DOC more effectively than enhanced coagulation (Singer and Bilyk, 2002; Fearing et al., 2004; Boyer and Singer, 2005; Humbert et al., 2005; Boyer and Singer, 2006) and to reduce the THM formation potential of water by up to 70% (Drikas et al., 2003; Mercer et al., 2004; Morran et al., 2004; Boyer and Singer, 2005). It is also able to remove bromide (Singer and Bilyk, 2002; Johnson and Singer, 2004; Humbert et al., 2005; Hsu and Singer, 2010). However, waters with high bromide concentrations also tend to have high concentrations of other dissolved salts, such as chloride, bicarbonate (alkalinity) and sulfate, which compete with bromide for exchange sites on the resin and therefore interfere with bromide removal (Singer and Bilyk, 2002; Johnson and Singer, 2004; Hsu and Singer, 2010). When used prior to ozonation, MIEX resin treatment has been shown to reduce the ozone demand and increase the level of *CT* (disinfection concentration, *C*, times contact time, *T*) achieved for a given amount of ozone transferred (Johnson and Singer, 2004; Wert et al., 2005).

Accordingly, this research was conducted to evaluate the combination of pre-treatment with MIEX resin followed by ozonation of Delta waters for achieving disinfection goals and controlling bromate and halogenated DBP formation. The research aims to confirm the above findings in an integrated set of experiments using several raw waters with different bromide and DOC concentrations, and to explore the implications of these findings for disinfection practice under challenging water quality conditions.

2. Experimental procedures

2.1. *General approach*

Water samples were collected from the North Bay Aqueduct (NBA), South Bay Aqueduct (SBA), and Lake Campbell (LC) in May, September, and December 2009, respectively, in order to capture some of the seasonal variability in TOC and salinity. A fourth water was prepared by spiking bromide into some of the Lake Campbell water. Upon receipt, the raw waters were analyzed for TOC, DOC, and ultraviolet (UV) absorbance at 254 nm. Portions of the raw water were used to conduct jar tests with MIEX resin and alum. Based on the effectiveness of the removal of organic material in these jar tests, a target dose of resin and alum were selected. Sixteen liters of the raw water were treated with the target MIEX resin or alum dose and subsequently ozonated in a semi-batch reactor to achieve a target dose of 1 mg O_3/mg TOC. The impact of each treatment on ozone demand, ozone exposure (CT), and bromate formation was evaluated. Finally, the raw, alum-treated, MIEX resin-treated, and ozonated waters were chlorinated under Uniform Formation Conditions (Summers et al., 1996) to determine their THM formation potential. The performance of MIEX resin in reducing ozone demand and DBP formation was compared to conventional alum coagulation and direct ozonation of the raw waters. Excitation–emission fluorescence spectroscopy was used to further characterize the NOM present in the raw, bulk-treated, and ozonated waters.

2.2. *Sample collection and handling*

All water samples were collected in a 208-L (55-gal) HDPE barrel by water treatment plant staff in California, shipped via freight carrier to the University of North Carolina, and placed in a refrigerator at 4 °C upon receipt. The waters were manually mixed for approximately 1 min before withdrawing aliquots for analysis or experimentation.

2.3. *Magnetic ion exchange resin*

Orica Watercare (Denver, CO) provided samples of virgin MIEX resin with both chloride and bicarbonate as the counterion. The resin was received in slurry form containing approximately 10% water by volume. Resin was stored in plastic containers at room temperature (20 °C), and deionized organic-free water (DOFW) was added, as needed, to each container to ensure that the resin remained in a wet slurry form during storage.

2.4. *Preliminary jar testing*

2.4.1. *MIEX resin treatment*

500 mL of raw water was measured into each of six glass beakers fitted with sampling ports approximately 2.5 cm from the bottom. MIEX resin doses of 0.5–2.0 mL/L were added to reflect operating conditions at full-scale MIEX plants

operating for TOC removal (Singer et al., 2009). Higher doses were also examined because bromide removal was a treatment objective and research has shown that higher resin doses are required to remove bromide (Johnson and Singer, 2004; Humbert et al., 2005; Hsu and Singer, 2010). The beakers were placed on a jar-testing apparatus (Phipps and Bird, Richmond, VA) and mixed at 100 rpm for 30 min. After 30 min of settling, approximately 200 mL of supernatant was decanted and subsequently analyzed for UV absorbance at 254 nm (UV254), TOC, and bromide (see Section 2.10). The results were plotted as a function of resin dose and used to select an appropriate dose for bulk treatment.

2.4.2. *Alum coagulation*

Alum jar tests were conducted on the same apparatus used for MIEX resin jar-testing. Selected doses of technical-grade aluminum sulfate (Fisher Scientific, Fair Lawn, NJ) in the range of 10–80 mg/L were added, and the paddle stirrer was set to 100 rpm for 1 min to provide dispersal of the coagulant. After the rapid-mixing period, the stirrer was slowed to 35 rpm and mixed for 30 min, after which the samples were allowed to settle for 30 min. Approximately 200 mL of supernatant was decanted and analyzed for UV254 absorbance, TOC, bromide, and turbidity (see Section 2.10). The results were plotted as a function of alum dose and used to select an appropriate dose for bulk treatment.

2.5. *Bulk treatment experiments*

Bulk coagulation and bulk MIEX treatment were performed in a 16-L glass carboy fitted with a variable-speed motor and an approximately 20-cm by 3 cm (8-in by 1.25-in) rectangular paddle (Dayton Electric Mfg. Co., Niles, IL). The desired dose of alum or MIEX resin as determined from the preliminary jar test results was added to the water, and the sample was rapidly mixed for 1 min at 80 rpm. The stirrer was then slowed to either 22 rpm (coagulation treatment) or 62 rpm (MIEX resin treatment). These speeds were initially calculated to replicate the velocity gradients in the containers used for jar testing. (The mixing intensity associated with bulk treatment was subsequently found to be significantly higher than that for jar testing.)

After mixing for 30 min, the electric motor and paddle were removed from the carboy and the sample was allowed to settle for 30 min. At the end of the settling period, a plastic tube was used to siphon 12 L of supernatant into pre-rinsed plastic containers. Care was taken not to disturb the settled alum floc or MIEX resin accumulated at the bottom of the carboy. Bulk-treated samples were immediately analyzed for temperature and pH, and later analyzed for TOC, DOC, UV254 absorbance, and bromide (see Section 2.10).

2.6. *Ozonation experiments*

Ozonation experiments were conducted at bench-scale in a semi-batch reactor. The ozonation apparatus consisted of an ultra-high purity oxygen tank (National Welders Supply Co., Durham, NC), a moisture trap (Alltech Associates, Deerfield IL) to control the humidity of the oxygen feed gas, a rotameter (Dwyer Instruments, Michigan City, IN) and stainless steel needle valve to control the gas flow rate, an ozone generator (Sander Model Certizon 200, Uetze-Eltze, Germany), and an 11.5-L cylindrical plexiglass reactor measuring 14 cm in diameter and 75 cm in height. The reactor was fitted with a sintered glass diffuser with a nominal pore size of 25–50 μm (Ace Glass Inc., Vineland, NJ). The reactor had a removable top affixed with eight stainless steel bolts and a PTFE gasket to keep the reactor air-tight and prevent leakage of ozone gas. Two liquid sampling ports were located 14 cm and 33 cm from the bottom. Connections between components were made using PTFE tubing and stainless steel fittings.

After cleaning the reactor and making it ozone demand-free, 9 L of the target water sample was poured into the reactor, and the top was sealed. The ozone generator was activated at the desired gas flow rate and vented to potassium iodide scrubbers. After the output reached steady-state, the ozone/oxygen mixture was directed into the reactor, beginning the experiment. Liquid- and gas-phase samples were withdrawn, respectively, from the reactor and the influent and effluent gas lines at various time intervals to track the dissolved ozone concentration and the amount of ozone transferred using the analytical methods described below. Additional liquid-phase samples were collected periodically into 40-mL glass vials and quenched with 1 drop of 100 mg/mL ethylenediamine (EDA) preservative solution for subsequent bromate analysis, as specified in EPA Method 300.1 (U.S. EPA, 1997).

The amount of ozone transferred into solution was calculated in real-time based on influent and effluent gas-phase ozone measurements. Ozonation was continued until a quantity of ozone corresponding to 1 mg O_3 per mg TOC had been transferred to the solution. Once this condition was achieved, ozonation was discontinued and any residual dissolved ozone was allowed to dissipate for approximately 1 h, after which the column was drained for storage and subsequent analysis of the ozonated water.

2.7. *Gas-phase ozone concentration*

During ozonation experiments, gas-phase ozone samples were collected in a 5-cm quartz cell fitted with two PTFE caps. A sampling tube from the inlet or outlet of the reactor was inserted into one of the openings, and the gas was flushed through the cell for 10 s. The opposite opening was capped, then the sampling tube was removed and the other opening was capped. The sample was immediately analyzed for absorbance at 253.7 nm using a UV spectrophotometer (Hitachi U-2000, Hitachi Instruments, Inc., Danbury, CT), zeroed using a 5-cm quartz cell containing ambient air. Absorbance measurements were converted into gas-phase ozone concentrations using Beer's Law and a molar absorptivity for ozone of 3000 L/cm-mol (IOA, 1998).

2.8. *Liquid-phase ozone concentration*

Dissolved ozone was measured according to the Indigo Method (Bader and Hoigne, 1981; Standard Method 4500-O_3 B, APHA et al., 1998). The indigo solutions were analyzed within 1 h of sample collection after filtering through a pre-rinsed 0.45 μm PVDF or PTFE syringe filter (Whatman, Inc., Piscataway, NJ and

Fisher Scientific, Fair Lawn, NJ, respectively) to minimize the effect of turbidity on absorbance readings. The absorbance of the sample was measured at 600 nm on a Hitachi U-2000 spectrophotometer (Hitachi Instruments, Inc., Danbury, CT). Absorbance of the blank was compared to the absorbance of an indigo-containing flask filled with DOFW to confirm that sample turbidity was not interfering with absorbance measurements.

2.9. *Chlorine demand and uniform formation conditions*

Chlorine demand experiments were conducted to determine the dose that would give a 1.0 mg/L residual after 24 h of incubation at 20 °C at pH 8.0. THM formation potential of each water sample was then evaluated by chlorinating with that dose under these same Uniform Formation Conditions, after Summers et al. (1996). After 24 h, the chlorine residual was measured using the DPD titrimetric procedure (Standard Method 4500-Cl–F; APHA et al., 1998). THM samples were collected in 40-mL glass vials with PTFE-lined caps containing approximately 0.25 g of ACS-grade ammonium sulfate or sodium sulfite (Mallinckrodt Baker, Paris, KY) to quench the free chlorine residual and prevent further formation of THMs. Each THM sample was collected in duplicate vials and stored at 4 °C until extraction, which was performed within 2 weeks of chlorination.

2.10. *Analytical methods*

2.10.1. *Ultraviolet absorbance at 254 nm*

UV absorbance measurements were made on a Hitachi U-2000 spectrophotometer (Hitachi Instruments Inc., Danbury CT) using a 1-cm quartz cell zeroed with DOFW. Prior to analysis, all samples were filtered through a pre-rinsed 0.45 μm membrane filter (Pall Corporation, Ann Arbor, MI) or PVDF or PTFE syringe filters (Whatman, Inc., Piscataway, NJ and Fisher Scientific, Fair Lawn, NJ, respectively) as outlined above.

2.10.2. *Total and dissolved organic carbon*

TOC and DOC concentrations were measured on a Shimadzu TOC 5000 Analyzer (Shimadzu Corporation, Atlanta, GA). The instrument measures non-purgeable organic carbon according to the High Temperature Combustion Method (Standard Methods 5310 B, APHA et al., 1998).

2.10.3. *Bromide and bromate*

Bromide and bromate concentrations were analyzed by ion chromatography according to a method derived from EPA Method 300.1 (U.S. EPA, 1997). A Dionex (Sunnyvale, CA) ion chromatography system, equipped with analytical and guard columns (IonPac AS-19 and AG-19, respectively), was employed. The operating eluent was 15 mM NaOH. A Dionex ASRS chemical suppressor was used to mask the background conductivity of the eluent. All samples were filtered using pre-rinsed 0.45 μm PVDF or PTFE syringe filters (Whatman, Inc., Piscataway, NJ and Fisher Scientific, Fair Lawn, NJ, respectively) prior to analysis. A calibration mixture containing bromide, bromate, and chloride was prepared from granular ACS-grade reagents. Chloride and bromide were added in a 333:1 mass ratio to reflect their occurrence in natural waters (Stumm and Morgan, 1996; Magazinovic et al., 2004; Hsu and Singer, 2010). Typical retention times for bromate, bromide, and chloride were 6.5, 12, and 7.9 min, respectively.

2.10.4. *Total trihalomethanes (THM4)*

THM4 analysis was performed according to a liquid–liquid extraction procedure similar to that described in Standard Method 6232 (APHA et al., 1998). The extracting solvent was prepared on the day of extraction by adding 1,2 dibromopropane (the internal standard) to ACS-grade methyl tertiary-butyl ether (MtBE). Sample extracts were placed in amber glass GC vials capped with PTFE-faced caps, sealed with a crimping tool, and stored in the freezer until analysis. Analysis was performed on a Hewlett Packard Model 5890A Series II gas chromatograph (GC) with electron capture detection (Hewlett Packard Co., Cary, NC).

2.10.5. *Excitation–emission fluorescence spectroscopy*

Water samples were filtered through pre-rinsed 0.45 μm PVDF or PTFE syringe filters (Whatman, Inc., Piscataway, NJ and Fisher Scientific, Fair Lawn, NJ, respectively) prior to analysis, and placed in a 1-cm quartz cuvette. The absorbance spectrum of each sample over wavelengths from 200 nm to 700 nm (in increments of 2 nm) was measured using a Hewlett Packard Model 8452A diode array spectrophotometer (Hewlett Packard Co., Cary, NC). A Fluoromax-4 fluorometer (Horiba Jobin Yvon, Inc., Edison, NJ) equipped with a xenon lamp was used to generate excitation–emission fluorescence spectra (EEMs) using the parameters described in Cory et al. (2010). Water samples were excited across wavelengths of 240–450 nm in increments of 5 nm, and fluorescent emissions were measured at 320–500 nm in increments of 2 nm. The slit width for both excitation and emission was 5 nm. Post-processing of EEMs data was performed to remove potential interference due to strongly-absorbing carbon in the sample (Mobed et al., 1996), minimize Rayman and Rayleigh scattering peaks, and correct the EEMs for instrument-specific response using excitation correction factors generated with rhodamine (DeRose et al., 2007) and manufacturer-generated emissions correction factors. Post-processing was done in Matlab (v 7.7) following the procedures of Cory et al. (2010).

The fluorescence index (FI; described in McKnight et al., 2001) was calculated from each EEM as the ratio of the emission intensity at 470 nm to that at 520 nm at an excitation wavelength of 370 nm (Cory et al., 2010). Because of the different characteristics of fluorophores found in terrestrially- and microbially-derived fulvic acids, the FI offers insight into the nature and origin of the DOC in the water. Fluorescence index values less than 1.30 are indicative of terrestrial carbon, while values greater than 1.45 reflect microbially-derived carbon (Cory et al., 2010; McKnight et al., 2001).

3. Results and discussion

3.1. *Raw water characteristics*

The characteristics of the four waters studied are summarized in Table 1. The North Bay Aqueduct water had a moderate TOC concentration and a low bromide concentration. Water from

Table 1 – Summary of raw water characteristics.

Parameter	North Bay Aqueduct	South Bay Aqueduct	Lake Campbell	Lake Campbell (spiked)
Sample Date	05/28/09	09/10/09	12/15/09	12/15/09
TOC, mg/L	3.7	2.4[a]	8.7	8.7
DOC, mg/L	3.5	2.4	8.5	8.5
UV254, 1/cm	0.113	0.071	0.256	0.256
SUVA, L/mg-m	3.2	3.0	3.0	3.0
Fluorescence Index	1.39	1.43	1.43	1.43
pH	7.9	8.2	7.8	7.8
Bromide, μg/L	40	360	33	380

a Measured TOC was less than DOC, but within the margin of error of the instrument. TOC is assumed equal to DOC.

the South Bay Aqueduct was chosen for its high bromide concentration; this water contained low levels of TOC relative to the other samples. Finally, water from Lake Campbell was collected to represent the challenging water quality associated with the first rainfall events at the North Bay Regional Water Treatment Plant (WTP). This water had a very high TOC concentration but low bromide. In order to investigate the performance of MIEX resin in a water matrix containing both high TOC and high bromide concentrations, a portion of the Lake Campbell water was spiked with sodium bromide to achieve a final concentration of 380 μg/L bromide. This bromide level was chosen to correspond to the 75th percentile bromide concentration at Banks pumping station in the Delta (CALFED, 2007). Sodium chloride was also added to maintain a 333:1 mass ratio of Cl:Br, which is the ratio at which these anions occur in natural seawater (Stumm and Morgan, 1996; Magazinovic et al., 2004; Hsu and Singer, 2010). All four waters had similar specific ultraviolet absorbance (SUVA) values and fluorescence indices (FIs).

3.2. *TOC removal*

Jar testing of all waters with alum gave the following results: for NBA water, an alum dose of 35 mg/L reduced the TOC concentration by 27% and the UV absorbance by 50%; for SBA water, an alum dose of 25 mg/L reduced the TOC concentration by 31% and the UV absorbance by 48%; for Lake Campbell water, 80 mg/L alum reduced the TOC concentration by 40% and the UV absorbance by 56%. The doses indicated correspond to the “point of diminishing returns” as defined by the Stage 1 Disinfectants/Disinfection Byproducts (D/DBP) Rule (U.S. EPA, 2006b). The greater removal of UV-absorbing substances indicates that alum coagulation preferentially removed the hydrophobic fraction of the TOC, consistent with observations by others (White et al., 1997; Liang and Singer, 2003). SUVA decreased and the FI increased as a result of coagulation, as expected.

Illustrative results for the jar testing with MIEX resin are presented in Fig. 1 for Lake Campbell water. In general, for all four waters examined, modest differences in removal of TOC and UV-absorbing substances were observed between the chloride and bicarbonate forms of the resin, but no consistent trend was apparent. For NBA water, 2.0 mL/L of MIEX/Cl resin reduced the TOC concentration by 46% and the UV absorbance by 58%. For SBA water, 2.0 mL/L MIEX/Cl and MIEX/HCO_3 reduced the TOC concentration by 36% and 25% and the UV absorbance by 44% and 42%, respectively. These MIEX doses correspond to doses commonly used in practice.

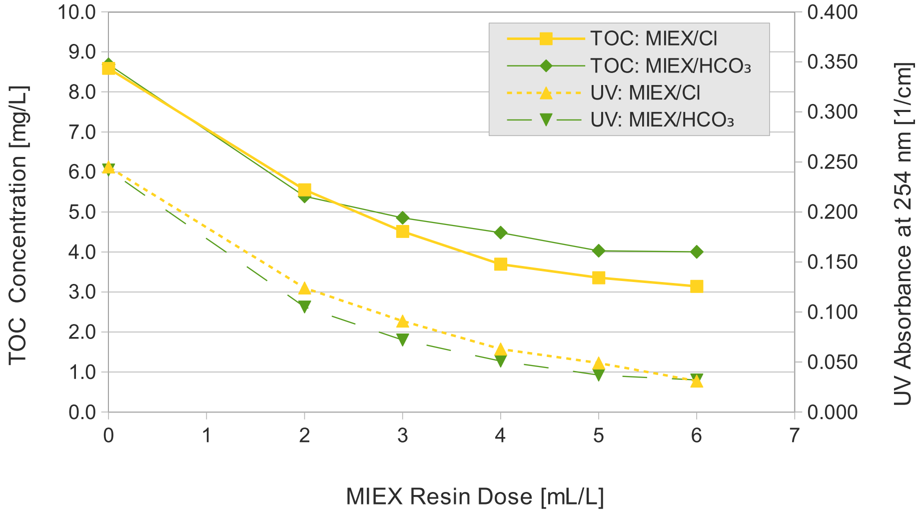

Fig. 1 – Effect of MIEX resin treatment on removal of TOC and UV-absorbing substances in spiked Lake Campbell water (380 μg/L bromide and 126.5 mg/L chloride).

Due to the high TOC concentration of the Lake Campbell water sample, MIEX resin doses of up to 6 mL/L were tested. 6.0 mL/L MIEX/Cl and MIEX/HCO_3 resin reduced the TOC concentration by 63% and 54%, respectively, and UV absorbance by 80%.

16-L samples of each of the four waters were treated in bulk with either alum or MIEX resin in both the chloride and bicarbonate forms. Only MIEX/HCO_3 was used for bulk treatment of Lake Campbell water. As noted above, alum doses for bulk treatment were chosen to approximate the point of diminishing returns for TOC removal, while the MIEX resin doses were selected to achieve a reasonable degree of TOC removal at a dose likely to be used in practice. Because bromide removal was of primary interest for the high-bromide waters, a higher MIEX dose was chosen than would have been selected on the basis of TOC removal alone.

The removal of TOC as a result of bulk treatment for all four waters is shown in Fig. 2; raw and treated water quality characteristics are summarized in Table 2.

The figure shows that in all cases, MIEX resin achieved significantly greater removal of TOC and UV-absorbing substances than alum. This is consistent with previous research (Singer and Bilyk, 2002; Boyer and Singer, 2005; Humbert et al., 2005; Boyer and Singer, 2006).

The relationship between the fluorescence index (FI) and SUVA before and after treatment is shown in Fig. 3. In all cases, treatment with alum or MIEX resin increased the FI, indicating that both treatments preferentially removed terrestrial or humic substances, and decreased the SUVA values, reflecting a greater removal of UV-absorbing substances compared to overall TOC removal. There is a clear correlation between lower SUVA values and a higher FI, indicating that the more hydrophilic components of DOC are microbially-derived. Moreover, the figure shows that water after MIEX resin treatment generally has a higher FI and lower SUVA than alum-coagulated or raw water. (The impact of ozonation on SUVA and FI is discussed below).

3.3. *Bromide removal*

Jar-testing with virgin MIEX resin was also performed to evaluate the removal of bromide. In the two low-bromide waters—NBA and Lake Campbell— neither alum nor MIEX resin reduced the bromide concentration to any significant degree. In contrast, MIEX resin removed 20–50% of the bromide in the two high bromide waters studied (SBA and spiked Lake Campbell water). Fig. 4 shows the results of jar testing of spiked Lake Campbell water, using MIEX/Cl and MIEX/HCO_3, respectively. Taken together, the results for all four waters (summarized in Table 2) indicate that bromide removal is primarily dependent on the initial bromide concentration and on resin dose. This is consistent with the competitive nature of ion exchange. Previous studies (Johnson and Singer, 2004; Hsu and Singer, 2010) have shown similar results.

Fig. 4 shows that the MIEX/HCO_3 resin performed slightly better than the MIEX/Cl resin for bromide removal, particularly at the higher doses tested; 6.0 mL/L MIEX/HCO_3 reduced the bromide concentration by 57%, compared to 47% for MIEX/Cl. Although the affinity of MIEX for NOM is known to be greater than that for inorganic ions like bromide (Boyer and Singer, 2008; Hsu and Singer, 2010), competition by inorganic anions such as sulfate, bicarbonate and chloride has been shown to decrease the degree of bromide removal (Singer and Bilyk, 2002; Johnson and Singer, 2004; Boyer and Singer, 2005). Because the resin has a higher selectivity for chloride than for bicarbonate, it was expected that the MIEX/HCO_3 resin would allow bromide to compete somewhat more effectively for exchange sites. In SBA water, no significant differences between the two types of resin were observed; 2.0 mL/L of MIEX/Cl and MIEX/HCO_3 reduced the bromide concentration by 29% and 33%, respectively. Note that the results stated above apply to virgin MIEX resin; the bromide removal performance of the resin at pilot- or full-scale may be lower as a result of regeneration. Alum coagulation did not remove any bromide in either water.

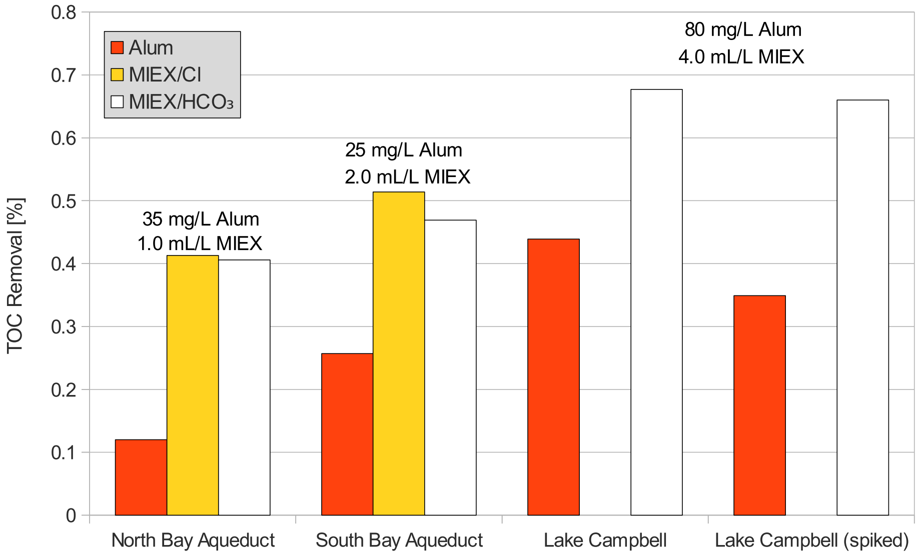

Fig. 2 – Summary of total organic carbon removal by alum and MIEX resin.

Table 2 – Removal of DBP precursors in bulk-treated waters by alum and MIEX resin.

	Type of treatment			
	Raw	Alum	MIEX/Cl	MIEX/HCO_3
North Bay Aqueduct				
Dose	–	35 mg/L	1.0 mL/L	1.0 mL/L
TOC, mg/L	3.7	3.2	2.2	2.2
UV254, 1/cm	0.113	0.073	0.058	0.053
SUVA, L/mg-m	3.2	2.4	2.7	2.4
Fluorescence Index	1.39	1.47	1.47	1.46
Bromide, μg/L	40	44	45	37
pH	7.9	7.7	8.2	8.2
South Bay Aqueduct				
Dose	–	25 mg/L	2.0 mL/L	2.0 mL/L
TOC, mg/L	2.4	1.7	1.1	1.2
UV254, 1/cm	0.071	0.040	0.024	0.021
SUVA, L/mg-m	3.0	2.5	2.3	1.9
Fluorescence Index	1.43	1.56	1.61	1.64
Bromide, μg/L	360	361	289	267
pH	8.2	7.6	8.1	8.2
Lake Campbell				
Dose	–	80 mg/L	–	4.0 mL/L
TOC, mg/L	8.7	4.9	–	2.8
UV254, 1/cm	0.256	0.117	–	0.033
SUVA, L/mg-m	3.0	2.4	–	1.1
Fluorescence Index	1.43	1.60	–	1.78
Bromide, μg/L	33	–	–	16
pH	8.2	7.7	–	8.0
Lake Campbell (Spiked)				
Dose	–	80 mg/L	–	4.0 mL/L
TOC, mg/L	8.7	5.7	–	3.0
UV254, 1/cm	0.256	0.126	–	0.034
SUVA, L/mg-m	3.0	2.3	–	1.2
Fluorescence Index	–	1.58	–	1.74
Bromide, μg/L	380	374	–	195
pH	8.2	7.7	–	8.3

3.4. *Ozone demand*

Each of the raw and bulk-treated waters was ozonated to achieve a transferred ozone dose of 1.0 mg O_3/mg TOC. Ozone dose, or ozone transferred, refers to the mass of ozone absorbed by the water at any given time. SUVA was observed to decrease as a result of ozonation for all four waters, but there was less of an effect on the FI, as illustrated in Fig. 3. All of the ozonated waters produced marked shifts in the FI-SUVA relationship compared to the raw, alum-treated, and MIEX-treated waters, reflecting chemical transformations in the structural composition of the DOC beyond those achieved by separation processes. Fig. 5 shows a typical relationship between dissolved ozone concentration and ozone transferred. Dissolved ozone concentration is a function both of the ozone absorbed by the solution (ozone transferred) and the presence of and reactions with ozone-demanding substances in the water, including NOM. Removal of DOC as a result of treatment with MIEX resin or alum resulted in a significantly higher dissolved ozone concentration for any given amount of ozone transferred. For example, at a transferred ozone dose of 1.0 mg/L, the dissolved ozone concentration in the MIEX resin-treated waters was 0.30–0.38 mg/L, while that in the raw water was only 0.03 mg/L.

Cumulative ozone exposure (CT) refers to the product of dissolved ozone concentration and contact time, and is the primary metric by which the efficacy of chemical disinfection is measured in water treatment. Note that a CT value of 1.0 mg-min/L corresponds to 0.5-log inactivation credit for *Cryptosporidium* at 20 °C (U.S. EPA, 2006a). The ozone exposure achieved at various transferred ozone doses is summarized in Table 3. Compared to the raw water, treatment with either alum or MIEX resin substantially increased the CT at any given ozone dose in the raw due to the higher dissolved ozone concentration arising from the removal of ozone-demanding organics.

The relationship between CT and ozone transferred for all alum- and MIEX resin-treated waters is summarized in Fig. 6. TOC concentrations are shown for each water. It is apparent

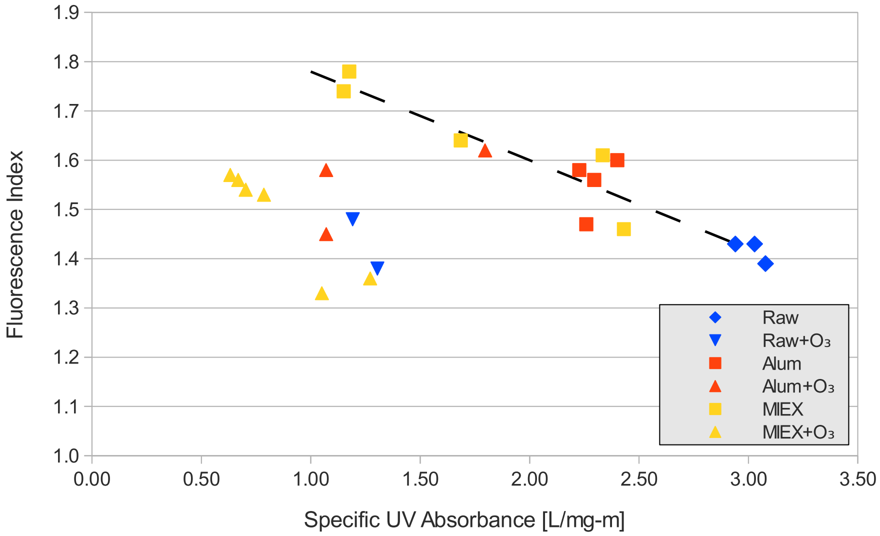

Fig. 3 – Relationship between fluorescence index and specific UV absorbance for all waters tested.

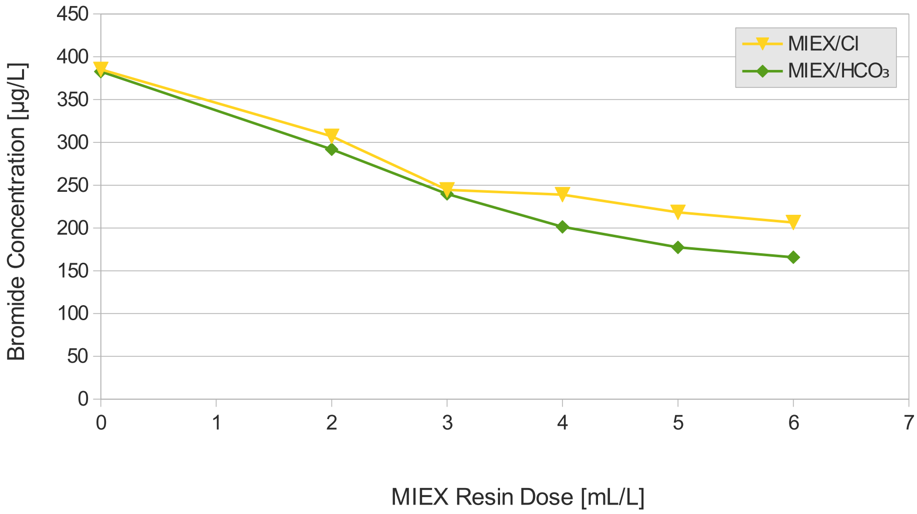

Fig. 4 – Comparison of bromide removal by MIEX resin with chloride and bicarbonate as the counterion in spiked Lake Campbell water (380 μg/L bromide and 126.5 mg/L chloride).

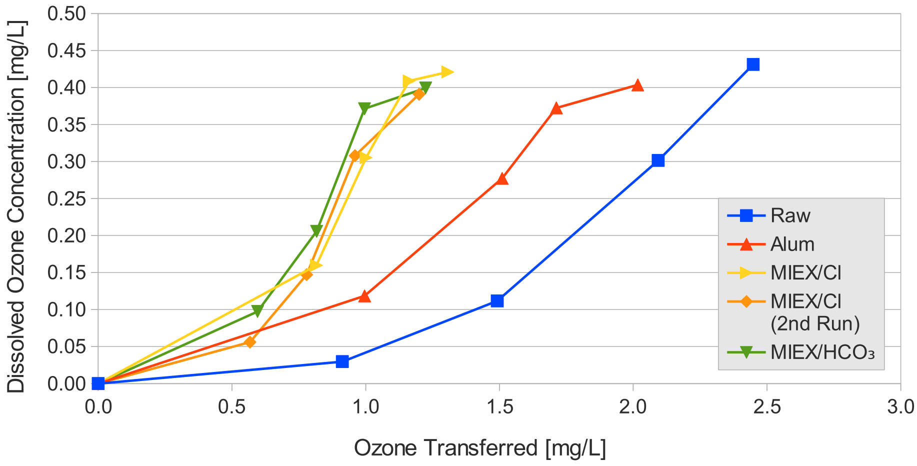

Fig. 5 – Relationship between dissolved ozone concentration and ozone transferred for South Bay Aqueduct water. Alum and MIEX doses used for treatment were 25 mg/L and 2.0 mL/L, respectively. The MIEX/Cl experiment was repeated to examine experimental reproducibility.

Table 3 – Ozone exposure (CT, mg-min/L) achieved at various transferred ozone doses.

Treatment	Alum or MIEX dose mg/L or mL/L	Source water	TOC	CT at transferred ozone dose:	
			mg/L	1 mg/L O_3	2 mg/L O_3
Raw	–	NBA	3.7	0	0.2
	–	SBA	2.4	0.2	1.5
	–	Spiked LC	8.7	ND[a]	ND[a]
Alum	35	NBA	3.2	0	0.5
	25	SBA	1.7	0.4	4
	80	Spiked LC	5.7	0	0
MIEX/HCO_3	1.0	NBA	2.2	0	0.6
	2.0	SBA	1.3	1	>>2
	4.0	Spiked LC	3.0	0	0.5

a Due to the high TOC concentration, raw water was not ozonated at the 1:1 O_3:DOC ratio, as this was deemed unrealistic in practice.

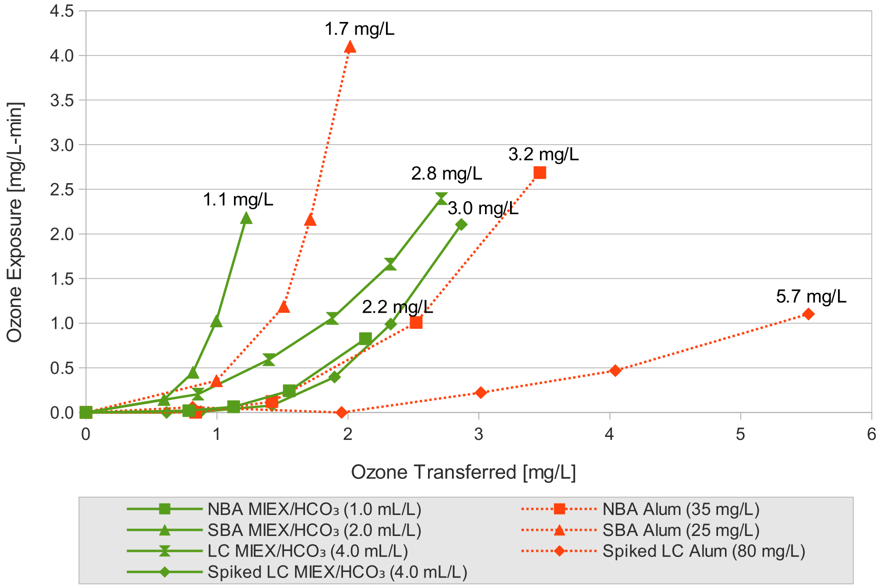

Fig. 6 – Relationship between TOC removal and ozone demand, as reflected by ozone exposure (CT). Type of treatment (alum or MIEX resin) is indicated by line type; source water is indicated by the shape of the marker. Numbers at the end of each curve represent the TOC concentration of the water.

that, in general, higher ozone exposure is achieved at lower ozone doses as the TOC concentration in the water is decreased. Because MIEX resin treatment removed TOC and reduced the ozone demand to a greater extent than alum coagulation, higher levels of ozone exposure were achieved at lower transferred ozone doses in the MIEX treated waters.

3.5. *Bromate formation*

The relationship between bromate formation and dissolved ozone concentration for SBA water is illustrated in Fig. 7. It is clear that, for any given dissolved ozone concentration, less bromate is produced in MIEX resin-treated waters than in either the raw or alum-coagulated waters. This result is most likely a consequence of bromide removal by the resin. Both forms of MIEX resin showed similar performance in reducing bromate formation, while alum coagulation increased the formation of bromate relative to the raw water to some degree. The reason for this finding is not clear, but it could be a consequence of the elevated Br:DOC ratio following alum treatment, which may make bromide relatively more accessible to oxidation by ozone.

Fig. 8 summarizes the relationship between bromate formation and ozone exposure for both waters in which bromate was detected. Both SBA and spiked Lake Campbell waters had appreciable bromide concentrations, whereas no significant bromate production took place in the unspiked Lake Campbell or NBA waters due to their low bromide

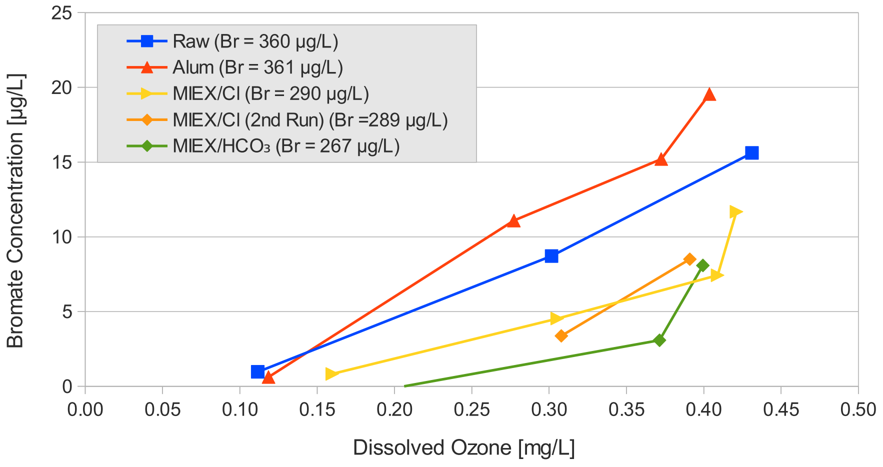

Fig. 7 – Relationship between dissolved ozone concentration and bromate formation in South Bay Aqueduct water. Alum and MIEX doses used for treatment were 25 mg/L and 2.0 mL/L, respectively. The MIEX/Cl experiment was repeated to examine experimental reproducibility.

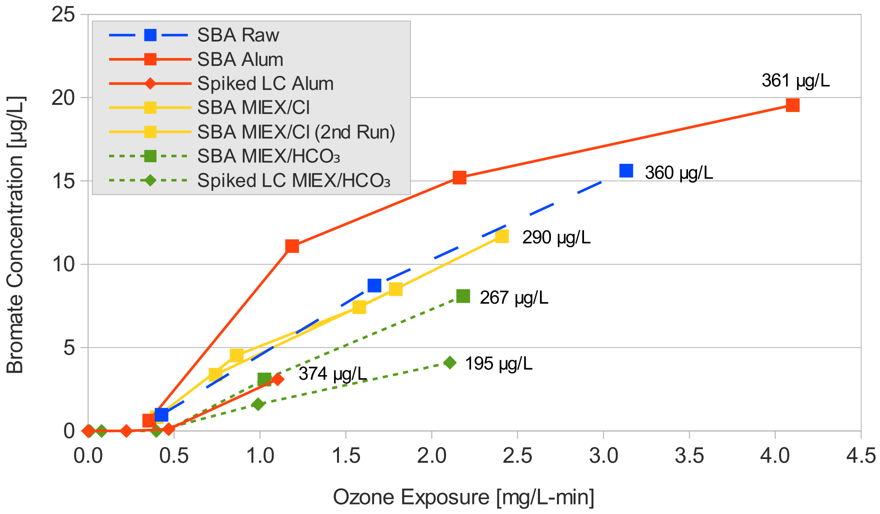

Fig. 8 – Summary of bromate production as a function of ozone exposure (CT) and bromide removal for high-bromide waters. Type of treatment is indicated by line type; source water is indicated by the shape of the marker. South Bay Aqueduct (SBA) and spiked Lake Campbell (LC) waters were treated with 2 mL/L and 4 mL/L MIEX and 25 mg/L and 80 mg/L alum, respectively. Values at the end of each curve indicate the bromide concentration in the water.

concentration (see Table 1). Fig. 8 shows that bromate formation tends to be driven primarily by the level of bromide in the water. Because MIEX/HCO_3 treatment provided the most effective bromide removal for both SBA and spiked Lake Campbell waters, these pre-treated waters produced the lowest amount of bromate. For any given level of ozone exposure, somewhat less bromate was formed in the MIEX/HCO_3-treated waters than in either the raw or MIEX/Cl-treated waters, which performed similarly in this regard. In both SBA and spiked Lake Campbell waters, alum-coagulated water formed more bromate than MIEX resin-treated water for any given level of CT. The apparent trend in bromate formation (alum > MIEX/Cl > MIEX/HCO_3) is consistent with the trend in Br:DOC ratio.

Table 4 summarizes these results in terms of the quantity of bromate produced at two different CT values. Ozonation of the spiked LC water produced little bromate in comparison with the SBA water, most likely because the elevated TOC concentration in LC water limited the formation of bromate.

Table 4 – Comparison of bromate production (in µg/L) associated with various CT values in South Bay Aqueduct and spiked Lake Campbell waters.

CT value (Ozone Exposure)	Type of treatment	Source water	
		SBA	Spiked LC
1.0 mg-min/L	Raw	5	–
	Alum	9	3
	MIEX/Cl	5	–
	MIEX/HCO_3	3	2
2.0 mg-min/L	Raw	10	–
	Alum	15	–
	MIEX/Cl	10	–
	MIEX/HCO_3	7	4

3.6. *THM formation*

Following ozonation and bulk coagulation or resin treatment, aliquots of each water were chlorinated under Uniform Formation Conditions to measure their THM formation potential (THMFP). Table 5 summarizes the impact of treatment with alum or MIEX resin and subsequent ozonation on chlorine demand and THMFP. As expected, alum and MIEX resin treatment lowered the chlorine demand by removing organic carbon.

Fig. 9 illustrates the removal of THMFP by bulk treatment with and without ozone for all waters studied. As shown, MIEX resin treatment lowered the THM formation potential of all waters by a greater amount than treatment with alum. This result is in agreement with the organic carbon removal noted above (see Fig. 2). The difference in performance between MIEX resin charged with chloride versus bicarbonate as the counterion was minimal with respect to THM formation. The figure also illustrates that ozone treatment generally reduced the THMFP by 35–45%, which comports with the observed decreases in UV absorbance after ozonation, shown in Table 5. By attacking conjugated structures, ozone reduced the UV absorbance and rendered the organic carbon less reactive with chlorine.

As noted above, treatment of bromide-containing waters with alum or MIEX resin increases the Br:DOC ratio because DOC is removed preferentially to bromide. Higher Br:DOC ratios result in a greater fraction of bromine-substituted THM species when the treated water is subsequently chlorinated (Krasner et al., 1989; Singer and Bilyk, 2002). The bromine incorporation fraction (BIF) is a value between 0 and 1, representing the molar fraction of brominated THM species relative to total THMs, and is defined as follows (after Obolensky and Singer, 2005), where the concentration of each species is in mol/L:

Table 5 – Impact of alum and MIEX resin treatment and ozone on THM formation potential.

	Type of treatment					
	Raw	Alum	MIEX	Raw + O_3	Alum + O_3	MIEX + O_3
North Bay Aqueduct						
Dose, mg/L or mL/L	–	35	1.0	–	35	1.0
THM Formation Potential, μg/L	247	196	144	151	117	68
Bromine Incorporation Factor	0.06	0.07	0.07	0.12	0.12	0.17
Cl_2 demand, mg/L	6.0	3.6	3.5	3.5	3.1	2.8
UV254, 1/cm	0.113	0.073	0.056	0.046	0.033	0.027
SUVA, L/mg-m[a]	3.2	2.4	2.6	1.30	1.1	1.2
South Bay Aqueduct						
Dose, mg/L or mL/L	–	25	2.0	–	25	2.0
THM Formation Potential, μg/L	199	167	98	138	96	61
Bromine Incorporation Factor	0.56	0.66	0.74	0.71	0.75	0.75
Cl_2 demand, mg/L	3.9	3.3	2.4	3.4	2.5	2.0
UV254, 1/cm	0.071	0.040	0.023	0.028	0.021	0.010
SUVA, L/mg-m[a]	3.0	2.5	2.2	1.2	1.1	0.8
Lake Campbell						
Dose, mg/L or mL/L	–	80	4.0	–	80	4.0
THM Formation Potential, μg/L	520	227	76	–	–	40
Bromine Incorporation Factor	0.02	0.03	0.04	–	–	0.04
Cl_2 demand, mg/L	11.0	5.6	2.9	–	–	2.5
UV254, 1/cm	0.256	0.117	0.033	–	–	0.016
SUVA, L/mg-m[a]	3.0	2.4	1.1	–	–	0.7
Lake Campbell (Spiked)						
Dose, mg/L or mL/L	–	80	4.0	–	80	4.0
THM Formation Potential, μg/L	–	375	156	–	239	83
Bromine Incorporation Factor	–	0.37	0.45	–	0.66	0.58
Cl_2 demand, mg/L	–	6.4	3.3	–	4.5	2.8
UV254, 1/cm	–	0.126	0.034	–	0.043	0.017
SUVA, L/mg-m[a]	–	2.3	1.2	–	1.0	0.70

[a] For ozonated waters, DOC was assumed to equal TOC for the purpose of calculating SUVA.

$$\mathrm{BIF} = \frac{\mathrm{BrCl_2CH} + 2 * \mathrm{Br_2ClCH} + 3 * \mathrm{Br_3CH}}{3 * (\mathrm{Cl_3CH} + \mathrm{BrCl_2CH} + \mathrm{Br_2ClCH} + \mathrm{Br_3CH})}$$

Because alum does not remove bromide, chlorination of bromide-containing water treated with alum is expected to result in a higher BIF than chlorination of the same raw water, even though the total DBP formation will be lower. Table 5 shows that the degree of bromine incorporation in the THMs increased as a result of treatment with alum, and increased to a greater degree as a result of treatment with MIEX resin. Even though MIEX resin removed some bromide, it removed proportionately more of the reactive DOC, so that the BIF

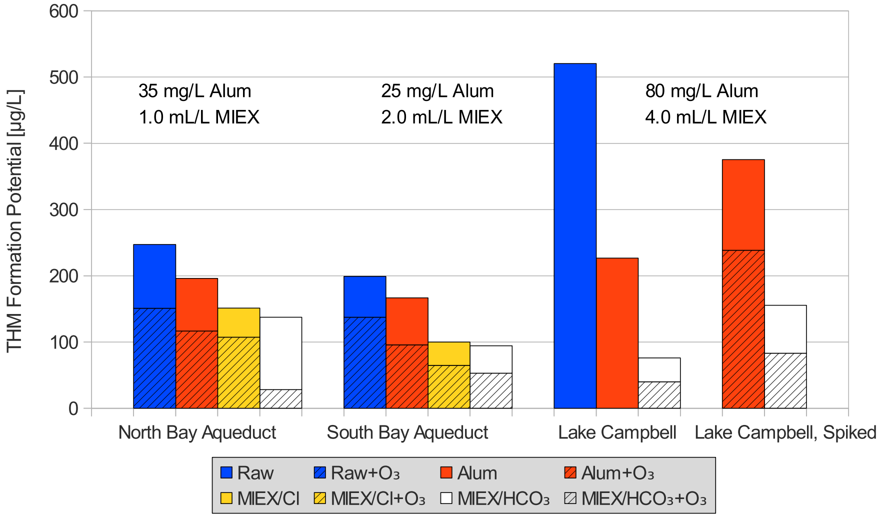

Fig. 9 – Reduction in THM formation potential as a result of treatment with alum, MIEX resin, and ozone. The clear bars represent THMFP after treatment with alum or MIEX resin alone, while the cross-hatched bars represent THMFP values after subsequent treatment with ozone.

increased after MIEX treatment. Ozonation increased the BIF of all waters slightly. This may be a consequence of destruction of aromatic structures of the organic carbon by ozone, which rendered the resultant DOC more hydrophilic. Hydrophilic carbon structures have been shown to be more reactive with respect to bromine (Liang and Singer, 2003). As expected, the high bromide waters exhibited much higher BIFs than the low bromide waters.

4. Conclusions

The use of MIEX resin prior to ozonation of drinking waters is an effective means of controlling bromate and halogenated organic DBP formation while achieving disinfection goals with ozone. Moreover, this process appears capable of accommodating the wide seasonal variability experienced in the San Francisco Bay Delta in California. This work indicates that in bromide-rich waters in which ozone disinfection is employed, MIEX resin is a more appropriate pre-treatment process than alum, as it achieves superior TOC and THM precursor removal and decreases the production of bromate.

5. Acknowledgments

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