

Effectiveness of chlorine dioxide in meeting the enhanced surface water treatment and disinfection by-products rules

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ABSTRACT

Bench-scale *Cryptosporidium* inactivation, pilot-scale disinfection by-product (DBP) formation and bench-scale inorganic DBP control experiments were conducted to evaluate the effectiveness of chlorine dioxide in meeting the current and future enhanced surface water treatment and disinfectant/disinfection by-product rules. A new chlorine dioxide generation process in which dilute, humidified chlorine gas is in contact with solid sodium chlorite was employed for this study. Chlorine dioxide was found to be effective in achieving CT values (pH=8 and temperature=20°C) of approximately 50 and 100 mg · min/l for 1-log and 2-log *Cryptosporidium* inactivation, respectively. Chlorine dioxide did not form significant amounts of trihalomethanes or haloacetic acids. Water spiked with high bromide concentrations resulted in insignificant amounts of organic DBPs after reaction with chlorine dioxide. Reaction of chlorine dioxide with water constituents resulted in the formation of chlorite and chlorate ions. Addition of ferrous ion is an effective treatment strategy for chlorite ion control.

Key words | chlorine dioxide, costs, *Cryptosporidium*, disinfection by-products, inactivation

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INTRODUCTION

Disinfection of potable water is required to guard against microbial contaminants, however, it produces unwanted DBPs, some with potential adverse health effects. Water utilities have to evaluate different disinfectants which are effective against a variety of microbes while still meeting DBP regulations. Chlorine, the traditional potable water disinfectant, is ineffective against *Cryptosporidium*, and also produces halogenated DBPs. Two sets of these halogenated DBPs, trihalomethanes (THMs) and haloacetic acids (five from a possible nine) will be regulated as part of the Stage I DBP Rule (Federal Register 1994, 1997, 1998). Chlorine dioxide and ozone are the two chemical disinfectants which are most effective for *Cryptosporidium* inactivation (Finch *et al.* 1997). Recent studies have shown that ultraviolet (UV) technology is also capable of inactivating *Giardia* and *Cryptosporidium* (Bukhari *et al.* 1999; Clancy *et al.* 2000; Shin *et al.* 2000), however, its cost effectiveness, compared with other feasible technologies,

has not been studied on long-term full-scale trials. The selection between available disinfectants at a water treatment facility may depend on site specific conditions, such as raw water bromide level, oxidant demand, on-site availability of chlorine gas and project cost.

Chlorine dioxide is a strong oxidant and, therefore, can also be used for control of iron, manganese, and taste and odor causing compounds. Because the pathways for disinfection and formation of by-products with chlorine dioxide are different when compared with chlorine, it does not produce significant levels of trihalomethanes and haloacetic acids. It has been used as a secondary disinfectant in many European countries. However, chlorine dioxide forms inorganic by-products (chlorite and chlorate ions) upon its reaction with water constituents, and a water utility may need to provide additional treatment depending on the level of these inorganic by-products and their regulatory requirements (Gordon & Bubnis 1995).

Regulations associated with chlorine dioxide use

The maximum residual disinfectant level goal and maximum residual disinfectant level for chlorine dioxide in the DBP rule (Federal Register 1998) is 0.8 mg/l measured as ClO_2 . A water utility using chlorine dioxide in pretreatment will have to monitor for finished water chlorine dioxide residual daily prior to the entry of water into the distribution system. The maximum contaminant level goal (MCLG) and maximum contaminant level (MCL) for chlorite ion is 0.8 (from 0.08 mg/l in the proposed rule) and 1 mg/l, respectively. Regulation of chlorate is waiting for results of ongoing toxicology studies. The compliance of chlorite will be based on the average of three monthly samples taken at the specified locations: one before the first customer, one at the middle of the distribution system and one at the maximum detention time of water in the system. Depending on their levels, a water utility may have to provide treatment for these ions prior to the point of entry to the distribution system. Alternatives for chlorite control include reaction with sulfite or ferrous ions, or adsorption (or chemisorption) onto activated carbon. Formation of chlorate can be minimized by controlling the chlorine dioxide production reaction and avoiding exposure of the treated water to sunlight (Gordon & Bubnis 1995).

Inactivation of protozoa

Chlorine dioxide is an effective disinfectant for control of *Giardia lamblia*, and the required CT values for 1-log inactivation range from 5 mg · min/l at 20°C to 21 mg · min/l at 0.5°C (USEPA 1989). The 3-log inactivation CT values range from 19 mg · min/l at 15°C to 63 mg · min/l at 0.5°C. These values are 3 to 14 times less than those required for free chlorine, but approximately 20 times more than those required for ozone.

Peeters *et al.* (1989) reported 1.5 and 1.2-log of *Cryptosporidium* inactivation, using an animal infectivity method, for CT values (calculated based on an average of initial and final concentrations) of 3 and 9.8 mg · min/l, respectively. Korich *et al.* (1990) reported a CT value of 78 mg · min/l (based on an initial concentration of 1.3 mg/l and a contact time of 60 min) for a 90% (1-log)

inactivation of *Cryptosporidium* based on mouse infectivity. Based on an average of the initial and final concentrations, the CT for 1-log inactivation was calculated to be 51 mg · min/l. Finch *et al.* (1995) recalculated the Korich data using a dose-response model developed for CD-1 mice and estimated a 99% (or 2-log) inactivation level. Ransome *et al.* (1993), employing the *in vitro* excystation viability method, reported *Cryptosporidium* inactivation ranging from 0.14 to 1.4-log for average CT values ranging from 6.5 to 67.5 mg · min/l, respectively. Based on results from 12 experiments (animal infectivity), Finch *et al.* (1997) reported *Cryptosporidium* inactivation ranging from 0 to greater than 3.2-log for average CT values ranging from 12.5 to 212 mg · min/l. In these experiments, a large drop in chlorine dioxide concentration beyond contact times of 30 min was observed, and this observation could result in low CT values. Average CT values of 30 and 105 mg · min/l were observed for 1 and 2-log *Cryptosporidium* inactivation. Using chlorine dioxide and a modified *in vitro* excystation method, Ruffle *et al.* (1998) observed inactivation of *Cryptosporidium* with chlorine dioxide as a function of pH and reported 2-log *Cryptosporidium* disinfection values of 120, 75 and 60 mg · min/l at pH values of 6, 8 and 10, respectively. In a later publication, Ruffle *et al.* (2000) reanalyzed their data using a method proposed by Rennecker *et al.* (1999) and reported similar CT values at pH of 6 and 8, even though CT values at a pH of 10 were approximately 20 to 30% lower than those at a pH of 8.

Formation of disinfection by-products

Since chlorine dioxide does not react with the unsaturated bonds of organic precursors, it does not produce significant amounts of halogenated organic DBPs (Gordon & Bubnis 1995). However, inorganic by-products such as chlorite and chlorate are formed either during production of chlorine dioxide or through its reaction with compounds in the water.

Griese *et al.* (1992) reported results of ferrous ion reduction of chlorine dioxide and chlorite in pilot-scale experiments and compared two chlorine dioxide production methods at Evansville, IN, USA. Ferrous chloride

treatment (doses ranging from 20 to 50 mg/l) resulted in complete removal of chlorine dioxide and chlorite within a reaction time of 30 min. Knocke & Iatrou (1993) confirmed the stoichiometric reaction between chlorite and ferrous ion for different pH values ranging from 5.0 to 7.0. The reaction kinetics were very rapid with over 90% chlorite reduction within 90 sec. The reaction also did not produce any chlorate but formed chloride as a by-product. Hurst & Knocke (1997) recommended a ferrous ion dose 10 to 20% higher than the stoichiometric value of 3.3 for chlorite ion control for alkaline waters (pH 8 to 10). The additional ferrous dose was required because of its faster reaction kinetics with aqueous oxygen in alkaline waters. Further, removal of chlorite ion by ferrous ion was affected by the presence of dissolved organic content (1.4 to 13.6 mg/l) and aqueous oxygen (>5 mg/l) in tested waters with a pH greater than 9.0.

McGuire *et al.* (1989) applied chlorine dioxide as a pre-disinfectant in a research study to evaluate the feasibility of the granular activated carbon process for removal of precursors and control of disinfection by-products. For applied source water chlorine dioxide doses ranging from 0.3 to 1.0 mg/l, a removal capacity of 14.6 mg chlorite/g GAC was found for empty bed contact times (EBCT) of 7.5 and 15 min. These values were much lower than those (80 to 90 mg chlorite/g of GAC) reported by Voudrias *et al.* (1983). The differences in chlorite uptake on GAC were attributed to the presence of natural organic matter in the water and the fouling of the GAC surface.

To remove chlorite and chlorate from water treated with chlorine dioxide, Vel Leiter *et al.* (1996) employed ozonation, UV light and GAC processes. Reaction of chlorite (1.9 mg/l in tap water) with ozone (2.0 to 2.5 mg/l) resulted in complete removal of chlorine dioxide (an intermediate reaction product) and chlorite, however, the reaction also resulted in the formation of chlorate (1 mole chlorate/mole of chlorite). UV irradiation at 254 nm converted chlorite into chloride and chlorate. Treatment with GAC (bituminous coal, EBCT of 4 min) removed 128 mg of chlorite per gram of GAC when chlorite concentration in the feed tap water was 1 mg/l. The reported capacity is much higher than that reported by either McGuire *et al.* (1989) or Voudrias *et al.* (1983). Since the natural organic matter levels in the tap water were not

provided, their impact on the GAC capacity could not be assessed.

Gordon & Bubnis (1994a) evaluated removal of chlorite in distilled water with sulfite ion, and reported that the reaction was influenced by pH and oxygen content. Gordon & Bubnis (1994b) also conducted experiments on the removal of chlorite with sulfite using three source waters from Pennsylvania. For each source water, removal of spiked chlorite (0.9 mg/l) at the ambient water pH values (7.9 to 8.3) at a sulfite dose of 100 mg/l was inversely dependent on pH (13 to 22% at 15 min of contact time) and increased with contact time (22% at 15 min to 63% at 48 min).

Objectives of the study

The specific objectives of the study were to:

- evaluate inactivation of *Cryptosporidium* with chlorine dioxide;
- evaluate formation of disinfection by-products at the chlorine dioxide doses required for *Cryptosporidium* inactivation;
- evaluate treatment strategies for control of chlorite and chlorate ion; and
- compare the implementation costs for chlorine dioxide with those of ozone.

MATERIALS AND METHODS

Chlorine dioxide must be generated on site as it is shock sensitive (danger of explosion) in liquified form for transportation purposes. A laboratory-scale unit (CDG Technology, Inc., NY, USA) based on a new process (Gordon & Bubnis 1995) in which dilute, humidified chlorine gas is in contact with solid sodium chlorite to produce chlorine dioxide gas was used for this study. Fresh chlorine dioxide stock solutions (500 ml for disinfection experiments and 18.9 litres for pilot experiments) were prepared on the day of experiments.

Cryptosporidium oocysts were recovered from the feces of naturally infected calves (LeChevallier *et al.* 1996). Immediately prior to each disinfection trial, solutions

were adjusted to 101% of the target concentration (0.51 mg/l to 1.52 mg/l of ClO_2) at the appropriate pH. Disinfectant solutions were adjusted to the appropriate temperatures (10°C or 20°C) and 99 ml of disinfectant was introduced into a stirred beaker. Two controls were used for each trial: one beaker in which no disinfectant was added to identify any loss of oocyst infectivity due to experimental conditions, and a second beaker which contained the same amount of disinfectant but no oocysts to identify any loss of disinfectant due to experimental conditions. One ml aliquots of purified *Cryptosporidium* were introduced into the reaction beaker. Samples (2 ml) were withdrawn at 10-minute intervals over a total of 60 min from each beaker. Chlorine dioxide was promptly quenched using an equal volume of 0.1% (wt/vol) sodium thiosulfate. Aliquots were also withdrawn from the *Cryptosporidium* and disinfectant control beakers at 10-minute intervals up to a total of 60 min. Beakers (100 ml) were covered with parafilm during the entire period to minimize any loss due to volatilization of chlorine dioxide. *Cryptosporidium* oocysts exposed to chlorine dioxide were subjected to an in vitro excystation assay (Campbell *et al.* 1992; Robertson *et al.* 1993) and a cell culture infectivity method (LeChevallier *et al.* 1996). Chlorine dioxide losses of 0.29 mg/l and 0.12 mg/l were observed for experiments conducted at initial concentrations of 1.5 and 0.5 mg/l, respectively, after a total contact time of 60 min.

To evaluate formation and control of DBPs, a conventional pilot unit (Reliant Unit, Roberts Filter, Inc., PA, USA), capable of treating water up to 37.9 litres per minute (lpm), was used. The pilot unit (1.2 m × 2.1 m × 1.8 m) was divided in three sections: a flocculation basin with a paddle mixer, a sedimentation basin fitted with tube settlers, and a dual media filter. In addition, the pilot plant consisted of three chemical metering pumps and injection points, an in-line mixer and a backwash pump. The pilot study was conducted at the Swimming River water treatment plant (SRTP) of the New Jersey-American Water Company. The raw water for SRTP is obtained from the Swimming River Reservoir and is conventionally treated in circular clarifiers and dual media filters. The plant uses polyaluminum chloride (PACl, Westchlor 700S, Westwood Chemical Corpor-

ation) as a coagulant, chlorine and chlorine dioxide for pre-oxidation and primary disinfection, and chlorine as a secondary disinfectant. The raw water for the pilot unit was supplied by a submersible pump (rated capacity 190 lpm) and a flexible hose. The pilot unit was housed in a building approximately 50 m from the intake, and backwash water was obtained from a nearby fire hydrant using a flexible hose. The backwash flowrate and pressure (up to 160 lpm at 210 kPa) were adjusted using a series of valves and pressure gauges. Prior to applying chlorine dioxide to the pilot unit, the oxidant demand of the source water was determined to be 1 mg/l. The demand occurred in the first minute of chlorine dioxide application. Chlorine dioxide for the pilot study was produced in batches using the same laboratory unit as used for the disinfection experiments. The concentrated solution, to achieve an applied dose of approximately 2.5 mg/l, was fed into the pilot plant using a peristaltic metering pump (Masterflex, Cole Palmer, IL, USA). Chlorine for the pilot experiments was prepared by diluting 5% commercial chlorine and was dosed at the full-scale applied doses.

The water quality parameters and their analytical procedures for the pilot study are summarized in Table 1. Samples analyzed at the American Water Works Service Company's (AWWSC) Quality Control and Research Laboratory in Belleville, IL (Belleville Lab.) were shipped by overnight delivery. Distribution system THMs and HAA6 were estimated by conducting simulated distribution system (SDS) tests in which filtered samples were dosed with chlorine and chloramine at the ambient pH and stored for 2 days in the dark at a temperature of 20°C. The SDS samples were purged with sodium thiosulfate for THMs and ammonium chloride for HAA6 samples. The SDS samples were shipped overnight to the Belleville Lab. for analysis. Chlorite and chlorate samples were preserved with ethylene diamene (Gallagher *et al.* 1994) and were analyzed within 5 days of sample collection. For experiments evaluating control of chlorite and chlorate ions, jar tests were conducted with reagent grade sodium sulfite, ferrous sulfate and powdered activated carbon (PAC, Hydrodarco, Norit, Inc.). For each test, settled water samples from the pilot unit were collected and purged with nitrogen to remove any chlorine dioxide. Water samples were transferred to 2-l jars (Phipps & Bird,

Table 1 | Analytical methods for the water quality parameters

Analyzed parameters	Location	Method
Trihalomethanes	Belleville Lab	EPA 502.2
Haloacetic acids	Belleville Lab	SM 6251B
Dibromoacetic acid		
Dichloroacetic acid		
Monobromoacetic acid		
Monochloroacetic acid		
Trichloroacetic acid		
Bromochloroacetic acid		
Total organic carbon	Belleville Lab	SM 5310
Chlorite and chlorate	Belleville Lab	EPA 300
Chlorine dioxide: pilot plant	On-site	SM 4500-ClO ₂ C
Chlorine dioxide: inactivation studies	Belleville Lab	SM 4500-ClO ₂ D
Chlorine	On-site	SM 4500-Cl D
Alkalinity	On-site	SM 2320 B
Hardness	On-site	SM 2340 C
Turbidity	On-site	SM 2130 B
Bromide	Belleville Lab	EPA 300
UV-absorbance	On-site	SM 5910 B
Iron and manganese	Belleville Lab	EPA 300

Richmond, VA) and varying doses of either sulfite (sodium sulfite, Fisher Scientific, Pittsburgh) or ferrous ion (ferrous sulfate, Fisher Scientific, Pittsburgh) were added for a reaction time of 15 min. Where PAC was added to the jars, the water was mixed for 30 min. Samples were filtered through a 0.45 μm filter, and shipped to the Belleville Lab. for chlorite and chlorate analysis.

To evaluate removal of chlorite with the fixed-bed granular activated carbon (GAC) process, 35 gallons of

settled water were collected from the pilot plant. The water was passed through a 2.5 cm glass column filled with 10 g of Calgon's Filtrasorb (12 \times 40 mesh size) GAC. The flowrate through the column was 80 cm^3/min (4 gpm/ft^2) resulting in an empty bed contact time (EBCT) of 0.25 min. The EBCT was selected so that the experiment could be conducted in 1 day because a selected EBCT in the range of 5 to 15 min would have required several days of testing.

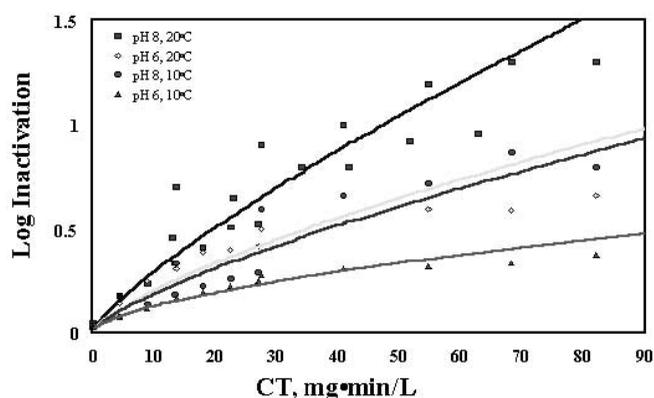


Figure 1 | Inactivation of *Cryptosporidium* using the excystation viability method.

RESULTS

Observed inactivation results

Inactivation of *Cryptosporidium* using chlorine dioxide was investigated using the excystation method at two temperatures (10 and 20°C), at two initial concentrations (1.5 and 0.5 mg/l) and at two pH values (6.0 and 8.0). Figure 1 displays the results plotted as log inactivation versus applied disinfection (measured as a product of concentration multiplied by time, CT). For each pH and temperature combination, data points for experiments conducted at different initial chlorine dioxide concentrations were combined. A logarithmic function rather than a linear relationship described the relationship

between log inactivation as a function of CT. Ruffle *et al.* (1998) also observed a similar leveling-off effect at higher CT values, and this may be attributed to loss of chlorine dioxide due to continued mixing at longer contact times. Inactivation of *Cryptosporidium* increased with an increase in temperature as well as pH. For 1-log inactivation (Table 2), CT values ranged from 48 mg · min/l at a pH of 8 and a temperature of 20°C to 310 mg · min/l at a pH of 6 and a temperature of 10°C. In contrast to inactivation of *Giardia* (USEPA 1989), Ridenour & Armbruster (1949) and Bernard *et al.* (1965) observed an increase in disinfection efficiency (for enteric bacteria such as salmonella and *E. coli*) of chlorine dioxide with an increase in pH. Ruffle *et al.* (1998) and Owens *et al.* (1999) have also reported inactivation of *Cryptosporidium* to be a function of pH. Since enhanced coagulation requirements are associated with low pH values (around 6.0), high CT values would be required to achieve inactivation of *Cryptosporidium*, if these processes were combined.

Figure 2 displays results from three separate experiments conducted at pH 8 and a temperature of 20°C. For a 1-log *Cryptosporidium* inactivation, CT values ranged from 41 to 55 mg · min/l. The variation in CT values indicates the degree of accuracy and precision associated with the experimental procedures, which may greatly affect the final result. In addition, variations in the results from different researchers using different viability procedures (Bukhari *et al.* 2000), and the impact of natural sample constituents on the oxidant demand and inactivation efficiency (Oppenheimer *et al.* 2000; Arora *et al.* 2001)

Table 2 | Estimated CT values[#] for *Cryptosporidium* inactivation

Model	2-Log inactivation pH/temperature (°C)				1-Log inactivation pH/temperature (°C)			
	8/20°C	8/10°C	6/20°C	6/10°C	8/20°C	8/10°C	6/20°C	6/10°C
Regression	115	257	246	1000	48	99	94	310
Cell culture	94	—	—	—	46	—	—	—
Combined correlation	101	—	—	—	44	—	—	—

Notes: [#]Values are expressed as mg · min/l and are calculated based on a 60 minute contact time.

—Data not available.

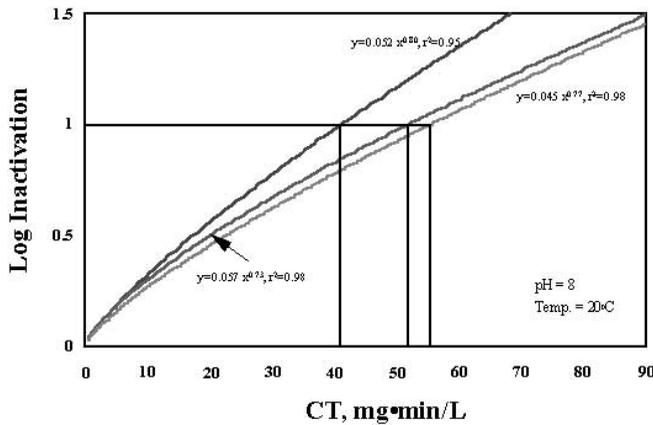


Figure 2 | Variation in inactivation results for experiments conducted under similar conditions.

should be considered in developing disinfection requirements for *Cryptosporidium* inactivation.

The *Cryptosporidium* inactivation results using the cell culture method are shown in Figure 3 and Table 2. In contrast to the excystation method, a linear relationship described the log inactivation as a function of applied disinfection (CT). For a 1-log inactivation, a CT value of 46 mg · min/l was obtained at a pH of 8 and a temperature of 20°C. Similarly, for a 2-log inactivation, a CT value of 94 mg · min/l would be required. The inactivation results for the cell culture method compared well with the excystation results (described above) from this study, and also with the results from most researchers using a variety of viability methods (Figure 4). Inactivation data from

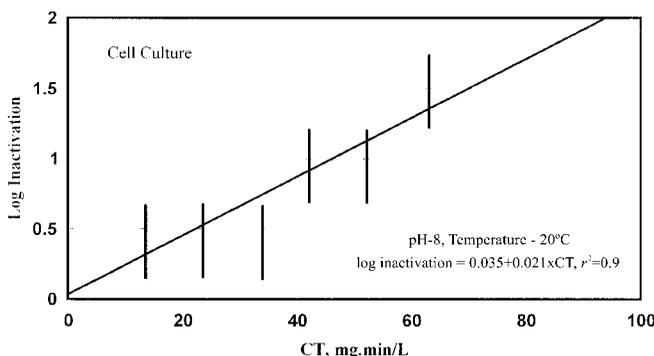


Figure 3 | Inactivation of *Cryptosporidium* using the cell culture viability method.

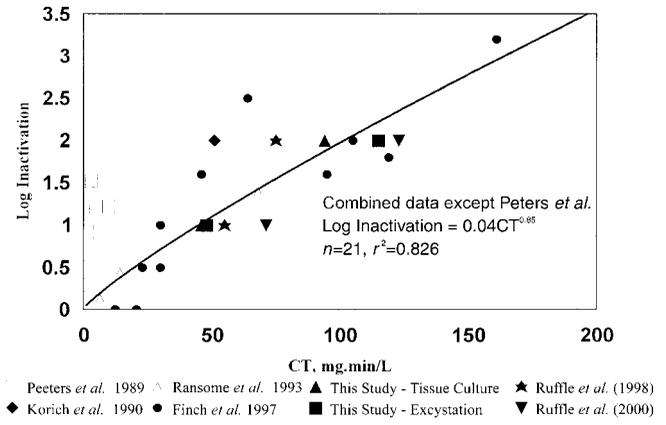


Figure 4 | Comparison of inactivation results from this study with other researchers.

Ransome *et al.* (1993) using the excystation viability method and that from Finch *et al.* (1997) using the animal infectivity method compared well with data from this study using the excystation and cell culture methods. Although the animal infectivity method was not employed in this study, other researchers (Chappel *et al.* 1999) have reported excellent comparisons between the cell culture method using the HCT-8 cells and the animal infectivity method. Figure 4 also shows a correlation for the combined data, which was used to estimate inactivation values (Table 2) from all studies except from Peeters *et al.* (1989).

The observed CT values (Table 2) associated with chlorine dioxide are much higher than those reported for ozone at 5 mg · min/l for 2-log inactivation at pH 8 and a temperature of 20°C (Finch *et al.* 1997; Rose *et al.* 1997). The estimated CT values for 2-log inactivation, especially at low pH and temperature levels, may be technically infeasible at a number of water treatment plants.

Formation and control of disinfection by-products

The observed source water quality during the pilot study is summarized in Table 3. The source water had moderate organic content, neutral pH, and low hardness and alkalinity.

The pilot plant operated at 30 lpm and employed full-scale chemical doses to simulate the full-scale filtered water samples in terms of UV-absorbance, alkalinity and

Table 3 | Summary of source water quality observed during the pilot testing

Water quality parameter	Range	Average
pH	6.9–7.3	7.1
Alkalinity, mg/l as CaCO ₃	25–27	26
Hardness, mg/l as CaCO ₃	54–56	55
Turbidity, NTU	3.3–4.7	3.7
Total organic carbon, mg/l	2.7–3.0	2.85
UV-absorbance at 254 nm (1/cm)	0.084–0.097	0.091
Temperature (°C)	12.8–14.0	13.6

hardness. Table 4 summarizes the five pilot runs including source water characteristics, coagulant type and dose, and formation of DBPs (THMs, HAA6, chlorite and chlorate) in the settled, filtered and simulated distribution system water samples. The first pilot run (Run #1) simulated the full-scale treatment using prechlorination. Similar to the full-scale plant dosages, PACl was fed at 7 mg/l (as product) and chlorine was added at 4.6 mg/l. Chlorite at 1 mg/l and chlorate at 0.26 mg/l were observed in the mixed sample (raw water after the application of chlorine), and were probably contributed from the commercial chlorine stock solution. Run #2 was conducted with the same treatment conditions as for Run #1 but with chlorine dioxide as the pre-disinfectant. A chlorine dioxide dose of 2.5 mg/l was chosen to account for the oxidant demand (approximately 1 mg/l), and to achieve more than 1-log of *Cryptosporidium* inactivation. The observed difference of chlorine dioxide levels in applied (2.5 mg/l) and mixed water (1.5 mg/l) confirmed the source water oxidant demand. A chlorite level of 0.9 mg/l in the mixed water sample indicated a 90% conversion of the oxidant demand into chlorite. This chlorite level of 0.9 mg/l in the mixed water sample increased to 1.5 and 1.7 mg/l in the settled and filtered water samples, respectively. Filtered water chlorite level was approximately 70% of the applied chlorine dioxide dose of 2.5 mg/l. Chlorate was observed at a typical level of less than 0.1 mg/l in the mixed, settled and filtered water samples.

To simulate the impact of pH on the formation of DBPs, Run #3 was conducted using chlorine dioxide as the pre-disinfectant and PACl as the coagulant at a settled water pH level of 7.9. Sodium hydroxide was added prior to the in-line static mixer to raise the water pH. In contrast to Run #2, TOC was not removed (raw to filtered) in Run #3, and this could be attributed to differences in the pH of coagulation. A chlorite level of 1 mg/l in the mixed water sample increased to 1.6 mg/l in the settled water sample and to 1.9 mg/l (approximately 75% yield with respect to applied chlorine dioxide dose) in the filtered water sample. Chlorate was observed at a slightly higher level (0.07 to 0.11 mg/l) than in Run #2 in the mixed, settled and filtered water samples.

Run #4 was conducted with chlorine as the pre-disinfectant and treatment conditions similar to Run #3. As observed for Run #3, TOC was not removed. As expected at high pH levels, formation of THMs was higher than levels observed for Run #1. However, formation of HAA6 was similar to the levels observed in Run #1. In contrast to Run #1, only chlorate was observed at 0.23 mg/l in the mixed and filtered water samples, probably due to a different batch of bleach.

Run #5 was conducted with ferric chloride as the coagulant at ambient water pH levels. Because ferric chloride consumes alkalinity in water, a drop of 0.5 pH units (raw versus settled) was observed for this run in contrast to pilot runs with PACl. Filtered water TOC was reduced by 17% (with respect to a raw water level of 2.7 mg/l), a value lower than that observed for Run #2 with PACl as coagulant. The observed chlorite level of 2.4 mg/l in the mixed water sample was unexplainably higher than the expected level, and could be attributed to either sample collection or analytical errors. Otherwise, chlorite yields in the settled and filtered water samples (both at 1.7 mg/l) were similar (65% yield) to other pilot runs with chlorine dioxide. Chlorate levels (approximately 0.1 mg/l) in the mixed to filtered water samples were also similar to other pilot runs with chlorine dioxide.

Formation of DBPs

Chlorine dioxide is not only an effective oxidant and disinfectant, but it also does not produce significant levels

Table 4 | Summary of pilot runs conducted at the Swimming River Water Treatment Plant

Location	pH	Turbidity (NTU)	Alkalinity (mg/l CaCO ₃)	Hardness (mg/l CaCO ₃)	Temp (°C)	Pre-Cl ₂ (mg/l)	Pre-ClO ₂ (mg/l)	TOC (mg/l)	UV-254	THMs (µg/l)	HAA6 (µg/l)	Chlorite (mg/l)	Chlorate (mg/l)	Post-Cl ₂ (mg/l)	Post-NHCl (mg/l)	Res-Cl ₂ (mg/l)	Res-NHCl (mg/l)	
Run # 1	Coagulant: polyaluminum chloride, dose: 7 mg/L																	
Raw	7.3	4.27	26	55.0	13.8	NA	NA	2.87	0.094	ND	ND							
Mixed						4.6	NA				1.03	0.26						
Settled	6.9	NA	23	53.5	14.5	3.6	NA	2.83		32	20	NA	NA					
Filtered	6.9	0.04	22	54.0	14.8	1.2	NA	2.45	0.028	36	31	NA	NA					
Dis-Cl ₂										69	59			2.2	—	0.9	—	
Dis-NHCl										49	34			—	2.2	—	1.4	
Run # 2	Coagulant: polyaluminum chloride, dose: 7 mg/L																	
Raw	6.9	3.48	25	54.0	14	NA	NA	2.97	0.097	ND	ND							
Mixed							2.5					0.91	0.06					
Settled	6.7	1.92	23	55.0	14.5	NA	1.33	2.77	0.077	1	2	1.51	0.08					
Filtered	6.7	0.05	22	55.0	14.8	NA	0.57	2.22	0.046	1	3	1.70	0.06					
Dis-Cl ₂										17*	14*			2	—	0	—	
Dis-NHCl										9	9			—	2	1.1	—	
Run # 3	Coagulant: polyaluminum chloride, dose: 7 mg/L																	
Raw	7.1	3.3	26	54.0	13.8													
Mixed	8.2		36	63.0	14.2	NA	2.5	2.89	0.091	ND	ND	0.96	0.07					
Settled	7.9	2.6	34	64.0	14.5	NA	1.14	2.91	0.087	ND	5	1.60	0.11					
Filtered	7.2	0.07	33	65.0	14.6	NA	0.33	2.91	0.053	ND	7	1.90	0.10					
Dis-Cl ₂										39*	16*			2.1	—	0	—	
Dis-NHCl										19	17			—	2	—	0.9	

Continued

Table 4 | Continued

Location	pH	Turbidity (NTU)	Alkalinity (mg/l CaCO ₃)	Hardness (mg/l CaCO ₃)	Temp (°C)	Pre-Cl ₂ (mg/l)	Pre-ClO ₂ (mg/l)	TOC (mg/l)	UV-254	THMs (µg/l)	HAA6 (µg/l)	Chlorite (mg/l)	Chlorate (mg/l)	Post-Cl ₂ (mg/l)	Post-NHCl (mg/l)	Res-Cl ₂ (mg/l)	Res-NHCl (mg/l)	
Run # 4	Coagulant: polyaluminum chloride, dose: 7 mg/L																	
Raw	7.1	3.6	25	55.0	12.8													
Mixed	8.5		35	65.0	13.6	4.8	NA	2.82	0.089	ND	ND	0.25						
Settled	8.3	2.6	34	65.0	14.2	3.6	NA	3.04	0.071	36	23	NA						
Filtered	8.1	0.09	33	66.0	14.3	2.6	NA	3	0.05	48	28	ND	0.25					
Dis-Cl ₂										101	61			2		1.1		
Dis-NHCl										83	43				2.1			1
Run # 5	Coagulant: ferric chloride, dose: 6 mg/L																	
Raw	7.0	3.9	26.5	56.0	13.4	NA		2.71	0.084	ND	ND							
Mixed							NA	2.65				2.40	0.12					
Settled	6.5	4.9	16	56.0	14.2	NA	1.14	2.75	NA	ND	9	1.67	0.09					
Filtered	6.4	0.43	15	56.0	14.3	NA	0.38	2.23	0.032	ND	2	1.70	0.09					
Dis-Cl ₂										53*	27*			1.8		0		
Dis-NHCl										7	15				2.2			0.9

Notes:

Temp: Temperature in °C.

Pre, Post, Res-Cl₂: Preinfection (applied dose), postinfection (applied dose) and residual chlorine.

Post, Res-NHCl: Postinfection and residual chloramine.

Pre-ClO₂: Preinfection with chlorine dioxide, applied dose.Dis-Cl₂: 2-day simulated distribution system DBPs with post chlorination.

Dis-NHCl: 2-day simulated distribution system DBPs with post chloramination.

NA: Not available.

ND: Not detected.

*Chlorine residual was not detected in the SDS samples after two days of detention time.

of trihalomethanes and haloacetic acids in potable water treatment. For the three pilot tests employing chlorine dioxide as the disinfectant, the observed formation of THMs in the filtered water samples (a contact time of 45 min) ranged from non-detectable to 1 $\mu\text{g}/\text{l}$. The corresponding filtered water THM levels with chlorine as the pre-disinfectant ranged from 36 $\mu\text{g}/\text{l}$ at a pH of 7.0 to 48 $\mu\text{g}/\text{l}$ at a pH of 8.1. HAA6 levels in water treated with chlorine dioxide as the pre-disinfectant ranged from 2 to 9 $\mu\text{g}/\text{l}$ in the settled or filtered water samples from three pilot runs. These levels were significantly lower than the 28 $\mu\text{g}/\text{l}$ at a pH of 8.1 and 31 $\mu\text{g}/\text{l}$ at a pH of 6.9 in the filtered water samples of pilot runs employing chlorine as the pre-disinfectant.

For the SDS tests with chlorine and chloramine, formation of THMs and HAA6 in the chlorine dioxide treated water was dependent on water pH and/or removal of precursors. Formation of SDS-THMs and SDS-HAA6 with chlorine and chloramine was higher at a pH of 7.9 (Run #3) compared to a pH of 6.7 (Run #2). Formation of SDS-THMs and SDS-HAA6 with chlorine dioxide was higher with lower precursor removal (17% in Run #5 with ferric chloride) compared to higher precursor removal (25% in Run #2 with PACl). Formation of SDS-THMs and SDS-HAA6 with chlorine and chloramine as post-disinfectants was 2 to 12 times higher in pilot runs with chlorine as the pre-disinfectant than in pilot runs when chlorine dioxide was the pre-disinfectant.

Impact of bromide in source waters

The SRTP raw water during the pilot testing contained 0.05 mg/l of bromide. To evaluate potential source water bromide reactions with chlorine dioxide, reagent grade potassium bromide was added to a 10 gallon sample of raw water and treated with chlorine dioxide (bromide level of 1.36 mg/l). The collected water was mixed in a covered jar (to avoid sunlight) for 45 min, and samples were collected for DBP analysis. THMs were below the detection limit, while HAA6 were detected at 4 $\mu\text{g}/\text{l}$. The detected HAA species included monobromoacetic acid at 3 $\mu\text{g}/\text{l}$ and dibromoacetic acid at 1 $\mu\text{g}/\text{l}$. Formation of brominated HAA species in this experiment can be attributed to the

presence of high bromide levels as the brominated species in the settled, filtered and SDS samples from the three pilot runs (low bromide SRTP water) with chlorine dioxide were all below their detection limits. Formation of bromate, which may also be influenced by presence of light, was not analyzed.

Control of inorganic by-products

Use of chlorine dioxide in water results in the formation of chlorite and chlorate. The proposed Stage I MCL for chlorite is 1 mg/l, and toxicology data are being collected for regulation of chlorate. Available methods for control of chlorite include reduction with sulfite or ferrous ion and adsorption (or chemical reaction) on activated carbon.

Sulfite ion treatment reduction

Figure 5 displays the chlorite removal results using sulfite ion for three sets of experiments for water collected from pilot Runs #2, #3, and #5. Overall, removal of chlorite was better at lower pH levels with addition of sulfite ion, but doses higher than 50 mg/l were required for approximately 50% removal. A sulfite dose of 5 mg/l resulted in an increase of chlorate ion, and this yield increased with an increase in pH level. Sulfite ion is a potential treatment technique for chlorite ion removal, but has slow reaction kinetics.

Ferrous ion treatment

Similar to sulfite ion treatment, varying doses of ferrous ion were added to settled water collected from pilot runs using chlorine dioxide and mixed for 15 min. Figure 6 displays the chlorite removal results using ferrous ion from three sets of experiments for water collected from pilot Runs #2, #3, and #5. For each experiment, chlorite levels ranging from 0.9 to 1.5 mg/l were reduced below its detection level with a ferrous ion dose of 5 mg/l. Chlorate ion levels remained unaffected with ferrous ion treatment. Because of the observed results, experiments were conducted to evaluate the stoichiometric and kinetic effects of

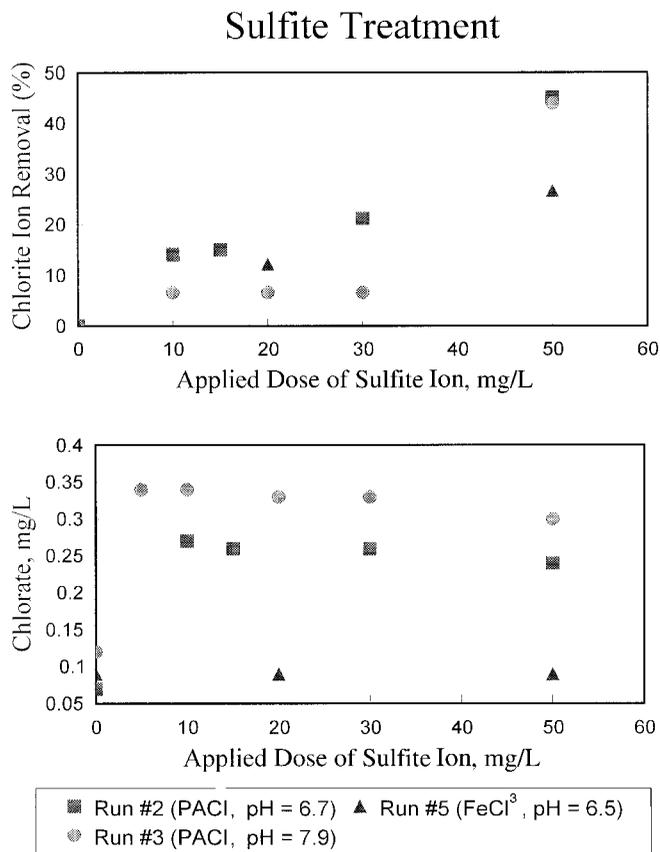


Figure 5 | Fate of chlorite and chlorate with sulfite ion treatment.

ferrous ion treatment for chlorite control. Sodium chlorite at 2 mg/l was added to the SRTP raw water. After transferring the water to jars, different doses of ferrous ion (1.5 to 7.5 mg/l) were added, and the water was mixed for 5 min before collection of samples. A ratio of mass of chlorite removed (mg) per mass of ferrous ion (mg) was calculated, and ranged between 2.4 to 3.0, with an average value of 2.7. Within the studied pH range, the observed ratio was similar to a ratio of 3.1 mg iron per mg chlorite reported by Knocke & Iatrou (1993). To determine the kinetics of the reaction, SRTP raw water spiked with chlorite (2 mg/l) was transferred to jars, and a ferrous ion dose of 6 mg/l was added. Samples were collected at 30, 60, 120 and 300 sec intervals and analyzed for chlorite ion. All of the collected samples were below the detection limit for chlorite, indicating that the reaction was complete in less than 30 sec. These results indicate that ferrous

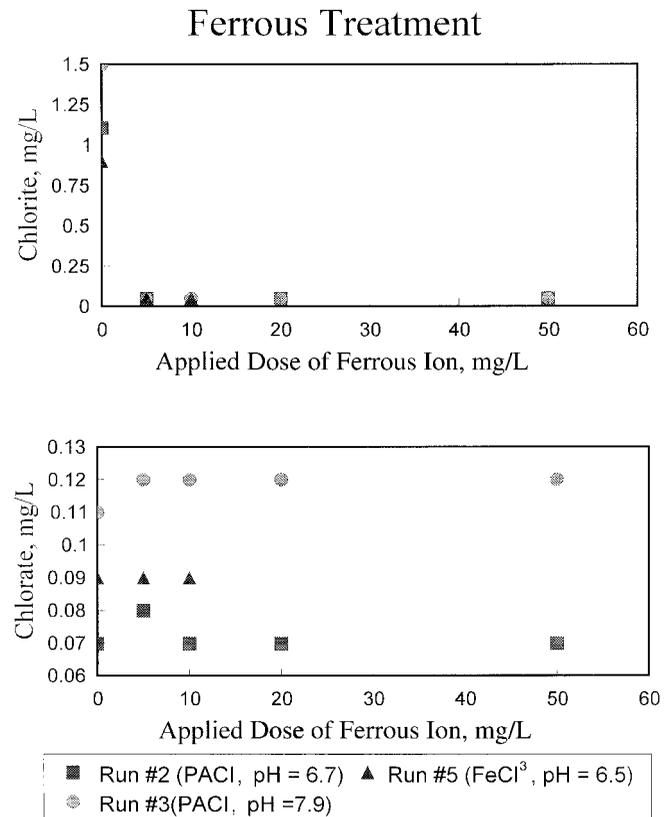


Figure 6 | Fate of chlorite and chlorate with ferrous ion treatment.

ion is an effective treatment strategy for chlorite ion control and the reaction is very rapid. The reaction forms a ferric floc which can be removed by conventional sedimentation or filtration.

Powdered activated carbon treatment

The SRTP employs powdered activated carbon for full-scale treatment, and therefore it was used for removal of chlorite in the jar tests. Similar to sulfite and ferrous ion treatments, settled water from pilot runs was collected and transferred to jars. A PAC stock solution was added to each jar and mixed with the water for a period of 30 min, which was then filtered through a 0.45 μm filter and samples were collected for chlorite and chlorate. As shown in Figure 7, PAC doses of up to 30 mg/l resulted in less than an 11% reduction in chlorite ion. Chlorate was

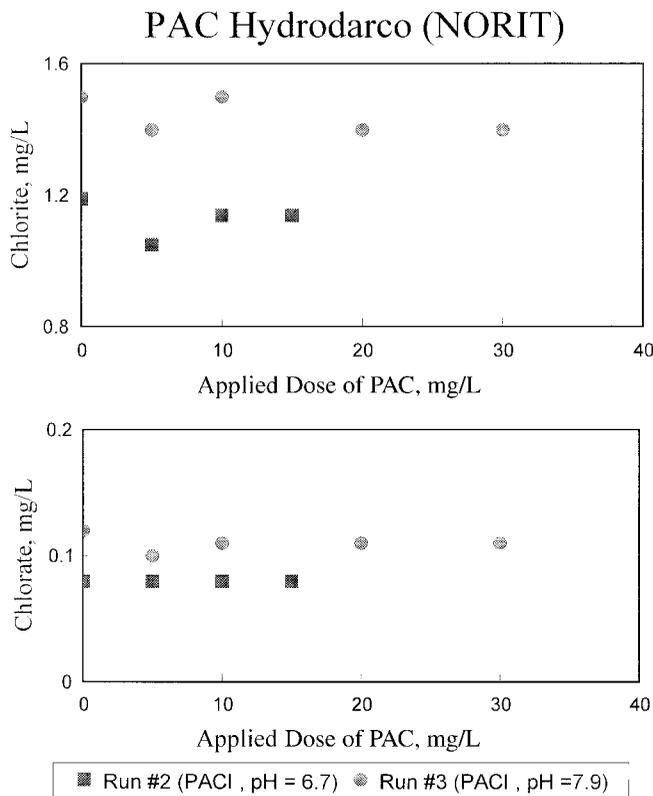


Figure 7 | Fate of chlorite and chlorate with powdered activated carbon treatment.

unaffected by PAC treatment. The observed results clearly indicate that PAC was ineffective for chlorite removal.

Granular activated carbon treatment

Figure 8 displays the breakthrough profiles of chlorite ion plotted as a function of bed volumes treated and litres of water treated per gram of GAC. The influent chlorite concentration ranged from 1.4 to 1.6 with an average value of 1.5 ($n = 4$). After the start of the test, the first effluent sample showed a chlorite concentration of 0.7 mg/l indicating instantaneous breakthrough. For a treatment objective of 1 mg/l chlorite ion, approximately 1,200 bed volumes of study water (or 0.5 litres of water per gram of GAC) could be treated. Based on an assumed bed with 10 min of empty bed contact time, the GAC would have to be replaced (or reactivated) in approximately

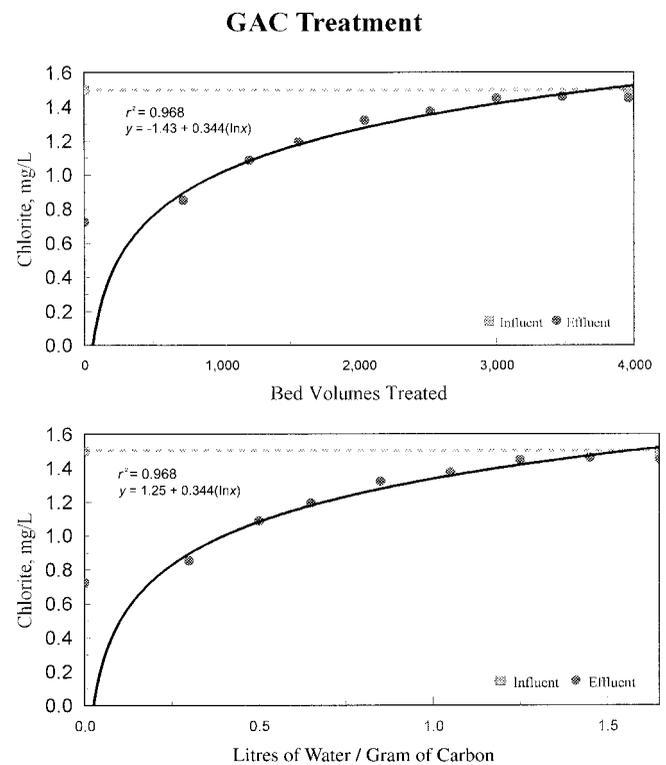


Figure 8 | Fate of chlorite ion with fixed-bed granular activated carbon treatment.

8 days. This very high GAC usage rate would be very expensive for chlorite removal.

The estimated chlorite removal capacity by GAC (4.1 mg chlorite per gram GAC) was much less than the 14.6 mg chlorite per gram of GAC reported by McGuire *et al.* (1989) to 128 mg chlorite per gram of GAC reported by Vel Leiter *et al.* (1996). The observed differences in capacity may be attributed to the short EBCT employed in this study and/or the differences in the organic content characteristics of studied waters (e.g. fouling of the GAC surface).

Chlorate was analyzed at 0.1 mg/l in the settled water fed to the GAC column, and its breakthrough profiles plotted as a function of bed volumes treated and litres of water treated per gram of GAC are shown in Figure 9. The GAC capacity for chlorate was exhausted after treating approximately 4,000 bed volumes. This would result in a GAC replacement frequency of approximately 27 days for a bed with an empty bed contact time of 10 min.

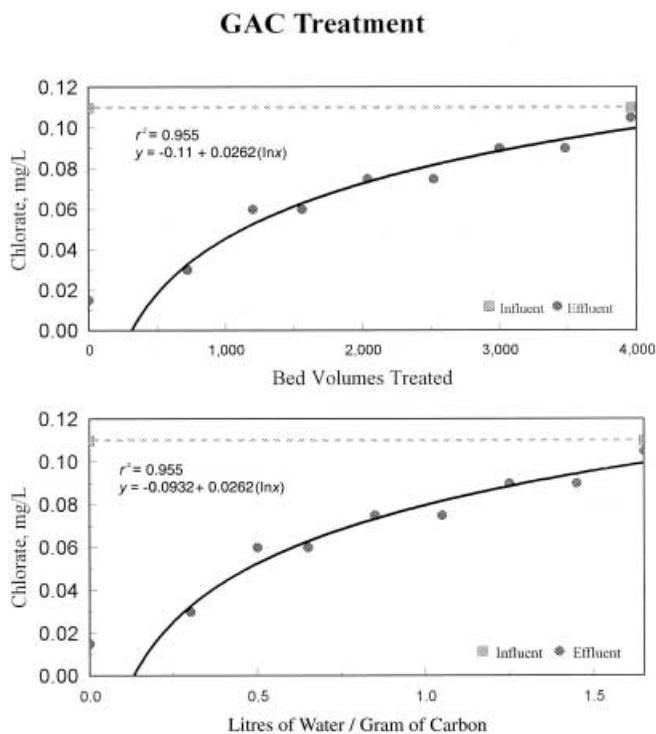


Figure 9 | Fate of chlorate ion with fixed-bed granular activated carbon treatment.

COMPARISON OF COSTS: CHLORINE DIOXIDE VERSUS OZONE

Chlorine dioxide, ozone and UV technology have the greatest potential to meet the anticipated disinfection requirements for *Cryptosporidium*. A technology may be technically feasible but its implementation in a WTP plant also depends on its financial feasibility. To compare the financial feasibility of chlorine dioxide with ozone, a preliminary cost comparison assuming a treatment plant with design and average day capacities of 4,730 and 3,150 m³/h, respectively, was conducted. UV technology was not included in the comparison because of a lack of operational and cost information at the time of the study. However, an AWWSC report (Hubel *et al.* 2000) estimated capital, and operation and maintenance costs for retrofitting UV technology at a plant with 30 mgd capacity to be \$3.7 million and \$197,000, respectively.

Design considerations

For a 2-log *Cryptosporidium* inactivation, ozone and chlorine dioxide CT values of 5 mg · min/l (Finch *et al.* 1997; Rose *et al.* 1997) and 115 mg · min/l at a pH of 8 and temperature of 20°C were used. It was assumed that an ozone dose of 2 mg/l would be sufficient to meet the oxidant demand of source water as well as inactivation of *Cryptosporidium*. A chlorine dioxide dose of 3 mg/l (including an oxidant demand of 1 mg/l) and sufficient contact time after intake and prior to filtration was assumed to provide a 2-log *Cryptosporidium* inactivation. It was assumed that the reaction of chlorine dioxide with the source water will produce 2 mg/l of chlorite ion (approximately two-thirds of the applied chlorine dioxide dose), and ferrous ion treatment would be used for chlorite control. As the reaction time for ferrous ion treatment of chlorite ion is rapid (less than 30 sec), ferrous ion can be added to pipes leading from clarifiers (or sedimentation basins) to filters. Water detention on top of the filters will provide additional contact time for chlorite reaction and the floc produced during the reaction would be filtered out.

Formation of chlorate can be minimized by limiting exposure of water to sunlight and by maintaining water pH greater than 5 (Fabian & Gordon 1992). To avoid sunlight, open tanks (such as clarifiers) may require covers, but these costs were not included in this analysis.

Comparison of costs

The basis for cost comparison was 1997 (Table 5). Equipment costs (including structural, electrical and instrumentation costs) for the ozone process were based on the actual installed costs for a water treatment plant in New Jersey (AWWSC, 1993). The equipment costs for three 454 kg (a maximum dose of 8 mg/l of ozone with two generators at 4,730 m³/h) generators and reaction contactors were \$4 million after adjusting for inflation at 3% per year. Installation of the equipment was assumed to be 30% of the equipment costs. The annual equipment maintenance cost was assumed to be 2% of the equipment cost (Peters & Timmerhaus 1980). Electrical costs were estimated based on 9.9 kWh electricity per kg of ozone gas

Table 5 | Comparison of costs for ozone and chlorine dioxide**Ozone***Capital costs*

Ozone generation equipment (4,730 m ³ /h, 3–454 kg units)	\$4,000,000
Installation costs (30%) of equipment costs	1,200,000
Subtotal	<u>\$5,200,000</u>

Operation and maintenance costs

Annual electrical costs (3,150 m ³ /h, 9.95¢/kWh/kg O ₃ at a 2 mg/L dose)	\$ 27,400
Annual liquid oxygen costs (3,150 m ³ /h, 17 kg O ₂ /kg O ₃ at 8.8¢/kg O ₂)	82,800
Annual maintenance costs (2% of equipment costs)	80,000
Subtotal	<u>\$ 190,200</u>

Chlorine dioxide—CDG Technology, Inc*Capital costs*

Installation costs (included in costs of sodium chlorite)	\$ 0
Ferrous sulfate feed equipment	300,000
Subtotal	<u>\$ 300,000</u>

Operations and maintenance costs

Annual chlorine dioxide costs (dose of 3 mg/L, \$11/kg of ClO ₂ , $\eta=99\%$)	\$ 922,200
Annual chlorine costs (0.53 kg Cl ₂ /kg ClO ₂ , 55¢/kg Cl ₂)	12,600
Annual ferrous sulfate costs (6.6 mg/L, 28.6¢/kg)	261,200
Subtotal	<u>\$1,196,000</u>

Chlorine dioxide—International Dioxide, Inc.*Capital costs*

Installation costs (included in costs of sodium chlorite)	\$ 0
Ferrous sulfate feed equipment	300,000
Subtotal	<u>\$ 300,000</u>

Operations and maintenance costs

Annual sodium chlorite costs (11.9 kg/kgClO ₂ , \$1.1/kg NaClO ₂ , $\eta=95\%$)	\$ 519,000
Annual chlorine costs (0.53 kg Cl ₂ /kg ClO ₂ , 55¢/kg Cl ₂)	12,600
Annual ferrous sulfate costs (6.6 mg/L, 28.6¢/kg)	261,200
Subtotal	<u>\$ 792,800</u>

Continued

Table 5 | Continued**Analysis of costs**

Criteria: Capital costs \times 0.17 + Annual O&M costs = Revenue required

Ozone:

$$5,200,000 \times 0.17 + 192,000 = \$1,076,200$$

Chlorine dioxide (CDG Technology, Inc.)

$$300,000 \times 0.17 + 1,196,000 = \$1,247,000$$

Chlorine dioxide (International Dioxide, Inc.)

$$300,000 \times 0.17 + 792,800 = \$ 843,80$$

produced for an average day capacity of 3,150 m³/h. The annual costs for liquid oxygen, used for ozone production, were estimated based on 17 kg of oxygen consumed per kg of ozone gas produced, and a unit cost of 8.8 cents per kg of oxygen.

Chlorine dioxide costs were determined from two vendors: CDG Technology, Inc. (CDG), NY, USA, and International Dioxide, Inc. (IDI), RI, USA. In the CDG process, liquid chlorine gas is in contact with solid sodium chlorite, whereas, in the IDI process, chlorine gas is in contact with liquid sodium chlorite (typical chemical strength of 25%). Both these companies claim chlorine dioxide generation efficiency higher than a minimum of 95% as required by USEPA (Federal Register 1994, 1997). The capital cost of equipment and annual maintenance costs were included in the quoted price of either sodium chlorite (IDI) or consumption of chlorine dioxide gas at a location (CDG). For a water treatment plant with an average day production of 3,150 m³/h, annual costs for sodium chlorite for the IDI process were estimated at \$1.1 per kg of sodium chlorite (or \$5.95 per kg of chlorine dioxide gas). CDG costs were based on consumption of chlorine dioxide at \$11 per kg of gas, and the costs included replacement of spent sodium chlorite, generation equipment, its installation and regular maintenance, and training of operators.

It was assumed that ferrous ion treatment would be required for complete elimination of chlorite ion. For an assumed chlorite ion concentration of 2.0 mg/l, 6.6 mg/l

of ferrous ion (or 33 mg/l heptahydrate ferrous sulfate) will be required for the reaction. The costs for ferrous ion treatment were included for both chlorine dioxide production methods.

To compare the costs, the American Water Works Service Co., Inc.'s revenue requirement method for evaluating feasibility of capital projects was employed (Young 1997). In a simplified manner, for a capital project, the annual revenue requirement is calculated by adding the capital costs multiplied by a factor of 0.17 (equivalent to a six year return period) to the annual operational costs to compare different alternatives. For an investor-owned utility regulated by a public utility commission, this method is more applicable in comparing different feasible alternatives compared to a present worth analysis. For the examined conditions (pH = 8 and temperature = 20°C) and a comparison of the annual revenue requirements (Table 5), the chlorine dioxide (IDI) method was the cheapest alternative, followed by ozonation, and the chlorine dioxide (CDG) method was the most expensive alternative because of the high unit cost of special solid sodium chlorite.

CONCLUSIONS

Based on the observations of the study, the conclusions are summarized below:

1. Pure chlorine dioxide is effective in warm, high pH (pH = 8 and temperature = 20°C) water requiring CT values of approximately 50 and 100 mg · min/l for 1-log and 2-log *Cryptosporidium* inactivation, respectively.
2. Excystation and tissue culture viability methods yielded the same *Cryptosporidium* inactivation results.
3. Pure chlorine dioxide did not form any significant halogenated organic disinfection by-products of concern, as evidenced by the filtered water THM levels of less than 1 µg/l and HAA6 levels of less than 10 µg/l.
4. Pretreatment with chlorine dioxide resulted in reduced simulated distribution system DBPs (2-day detention time with chlorine and chloramine as postdisinfectants) by 2 to 12-fold when compared with chlorine as the pre-disinfectant.
5. Water spiked with high bromide resulted in insignificant amounts of organic DBPs after reaction with chlorine dioxide.
6. Reaction of chlorine dioxide with water constituents resulted in the formation of chlorite and chlorate ions. Sulfite ion treatment for chlorite ion has slow reaction kinetics. PAC under the studied conditions was ineffective for chlorite and chlorate removal. GAC treatment was effective for chlorite ion removal, but resulted in a high projected GAC usage rate. Chlorate ion can be removed by GAC. Ferrous ion is an effective treatment strategy for chlorite ion control and the reaction is very rapid.
7. A preliminary comparison of costs between application of ozone and chlorine dioxide (including chlorite ion reduction) for inactivation of *Cryptosporidium* at a water treatment plant resulted in lower estimated costs for the conventional chlorine dioxide production method (reaction of chlorine gas with sodium chlorite solution), followed by ozonation (using liquid oxygen for ozone generation) and the new chlorine dioxide production method (reaction of chlorine gas with solid sodium chlorite).

Selection of a final disinfectant to meet the *Cryptosporidium* inactivation requirements and compliance with the DBP regulations should be based on site-specific conditions. Under certain real world conditions, *Cryptosporidium* inactivation requirements may be very high (e.g. CT of 1,000 mg · min/l for a 2-log inactivation at pH 6 and temperature of 10°C, Table 3) and ozone or UV technology may be a cost-effective alternative for a variety of operating conditions. On the other hand, ozone may have limited use for source waters containing bromide because of the possibility of formation of bromate, which will be regulated at a relatively low level (10 µg/l). Another important consideration in selecting chlorine dioxide is the possible regulation of chlorate in the future, and the ineffectiveness of currently available technologies for its control.

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