J Water SRT — Aqua Vol. 48, No. 3, pp. 92–105, 1999

Disinfection/disinfectant by-product optimisation with ozone, biological filtration and chloramines

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ABSTRACT: The upcoming Disinfection/Disinfectant By-product and Enhanced Surface Water Treatment Rules will require utilities in the USA to increase their current level of disinfection and, at the same time, reduce the concentration of disinfection by-products formed during the disinfection process. To address these complex issues, the Jefferson Parish Water Department conducted a detailed pilot column evaluation on clarified lower Mississippi River water using ozone, biological filtration and chloramines, which achieved calculated removals of 5.5 logs for *Giardia* and 8 logs for virus, while limiting annual average disinfection by-product formation to less than 10 μg/L for trihalomethanes and haloacetic acids. While elevated concentrations of biologically degradable organic carbon (BDOC) and aldehydes were produced by ozonation, biological filtration with empty bed contact times of 5 and 9 min was effective in preventing any significant increase in BDOC or total aldehyde concentrations above those normally produced by chloramine disinfection. Total organic carbon removal as required by enhanced coagulation under the proposed Disinfection/Disinfectant By-product Rule were also achieved by ozonation and biological filtration.

INTRODUCTION

With the advent of the proposed Disinfectants and Disinfection By-products Rule (D/DBPR) and Enhanced Surface Water Treatment Rule (ESWTR), utilities will be required to provide increased levels of disinfection to achieve adequate protection from pathogens, while simultaneously reducing the concentrations of chlorinated disinfection by-products (DBPs) formed. Enhanced coagulation or granular activated carbon (GAC) filtration, combined with chlorine as the primary residual disinfectant has been proposed as the best available technology for meeting the proposed reduction in chlorinated DBPs. However, utilities having source waters with a high buffering capacity and high concentrations of DBP precursors, which are impractical to remove by enhanced coagulation, may consider the use of alternative disinfectants such as ozone and chloramine in order to increase the level of disinfection achieved while avoiding the high cost of implementing GAC filtration. While previous studies [1,2] have indicated that the use of ozone combined with sand filtration and chloramine as the residual disinfectant can result in annual average DBP concentrations as low as 12 μg/L, concern has developed regarding the concentration of ozone by-products produced and their potential to increase biological regrowth in the distribution system. This study was designed to examine the effects of ozone on clarified lower Mississippi River water to evaluate: the extent of ozone by-product formation at an ozone dosage required to achieve 3 logs of *Giardia* removal [3], the use of biological filtration with various media as a viable method of removing ozone by-products, the requirements for secondary disinfection following ozonation and subsequent biological filtration and the potential of the ozonation process to enhanced biological regrowth in the distribution system. Virus inactivation across the ozone contact system was also evaluated using MS2 coliphage.

EXPERIMENTAL DESIGN AND METHODOLOGY

Pilot column system

Study objectives were evaluated using a pilot column system (Fig. 1) constructed of stainless steel, glass and Teflon components which included three basic process types: ozone disinfection followed by biological filtration and subsequent chloramine disinfection, ozone disinfection followed by chloramine disinfection and subsequent anthracite/sand filtration, and chloramine disinfection followed by anthracite/sand filtration. The biological filtration process was further subdivided to evaluate three different media types: sand, anthracite/sand and GAC/sand. To evaluate the use of GAC as a long-term adsorptive nonregenerable biological media, the pilot column system was operated for over 12 months prior to the start of the operational period. Prior operation of the pilot column system was conducted to assure an initially stable microbiological population on all filter media and to achieve a 'steady-state' or equilibrium condition for the GAC media relative to typical influent organic carbon levels. The influent to the pilot column system was taken from the effluent of full-scale up-flow sludge blanket contact clarifiers, which received an annual average treatment of 4.2 mg/L diallydimethylammonium chloride

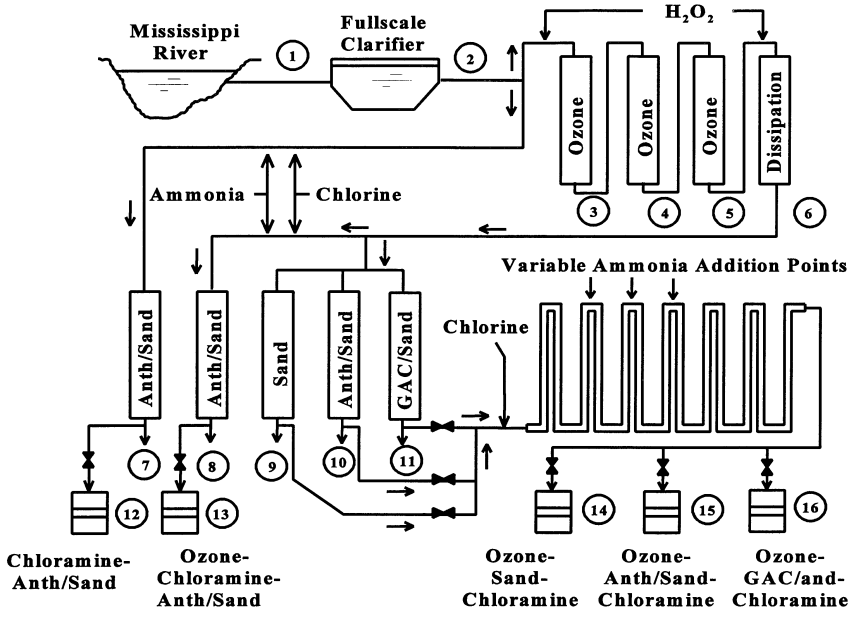

Fig. 1 Pilot column configuration and sample point locations.

polymer, 0.7 mg/L dimethylamine polymer (winter treatment), 2.1 mg/L powdered activated carbon (continually added for chemical spill protection), and 2.6 mg/L fluosilicic acid (25%). Influent pH was not adjusted and remained at ambient river water concentrations (7.1–7.9). Ozone was applied to satisfy the requirements of the Surface Water Treatment Rule for a 3-log *Giardia* removal [3] which is based upon: the average ozone residual across the contact chamber (C), the detention time at which 90% of the water passing through the contact chamber is retained within the chamber (T_{10}), and water temperature at a pH range of 6–9. Disinfection CT_{10} was derived from the sum of the products of the average of the influent and effluent ozone concentrations across the second and third contact chambers with their respective fluoride tracer T_{10} times. While some disinfection did occur across the first ozone contact chamber, it could not be quantified because no ozone was present in the influent water. To achieve a 3-log *Giardia* removal, the required values of CT_{10} range from 1.9 mg/L.min at 5 °C to 0.48 mg/L.min at 25 °C and above. For one week each month, hydrogen peroxide was added alternately to the influent of either the dissipation chamber or ozone contactor no. 1 at a molar ratio of 0.5 H_2O_2/O_3, to evaluate its effect on DBP formation. Each of the process streams was dosed with chlorine and ammonia at a 4:1 Cl_2:NH_3 ratio (w/w) prepared from reagent grade sodium hypochlorite and ammonium hydroxide to achieve a chloramine residual of 3.0 mg/L in the final product water. Chloramines were formed *in situ* with no measurable free chlorine contact time for the chloramine–anthracite/sand and ozone–chloramine–anthracite/sand process streams. A chloramination pipe loop was used to add chlorine and ammonia solutions to the effluent of the three biological filters. The pipe loop was constructed of schedule 80 PVC pipe which was conditioned for over 12 months with process water. Variable ammonia addition and sampling points in the chloramination pipe loop were used to assess free chlorine contact requirements for HPC reductions following biological filtration. Nonchlorinated effluent from the biological ozone–anthracite/sand column was typically used to backwash all pilot filters.

The effects of residence time on water quality in a chloraminated distribution system was evaluated via insulated 133 L stainless steel storage tanks (sampling points 12–16). Short-term water storage (three days) and subsequent three-day recirculation through a biologically active sand (bio-sand) filter (Fig. 2) was used to assess distribution system regrowth potential as biodegradable organic carbon (BDOC) following transmission through the distribution system and subsequent residual dissipation at the ends of the distribution system. The recirculating bioreactor was designed by following the BDOC recirculating reactor method described by Mogren *et al.* [4], except that the sand-to-sample ratio (v/v) was increased to 0.6 and the incubation time was reduced to three days.

To initially stabilise the indigenous source water organisms on the bio-sand media, nondisinfected sand filtered water was passed through the bio-sand columns for a period of over 12 months. To maintain the native biota on the bio-sand filter media during the operational period, the five biological filters were seeded each week with approximately 1.9 L/min of non-disinfected sand-filtered water at ambient river water temperature for four days prior to the three-day recirculation period of process stream water. Approximately 133 L of water from each of the five process streams with an initial chloramine residual of 3 mg/L were dosed with 1 mg/L of zinc sodium hexametaphosphate corrosion inhibitor and stored for three days at ambient river water temperature. The remaining chloramine residual was then stoichiometrically reduced with sodium thiosulphate and 57 L of the initial 133 L of stored process

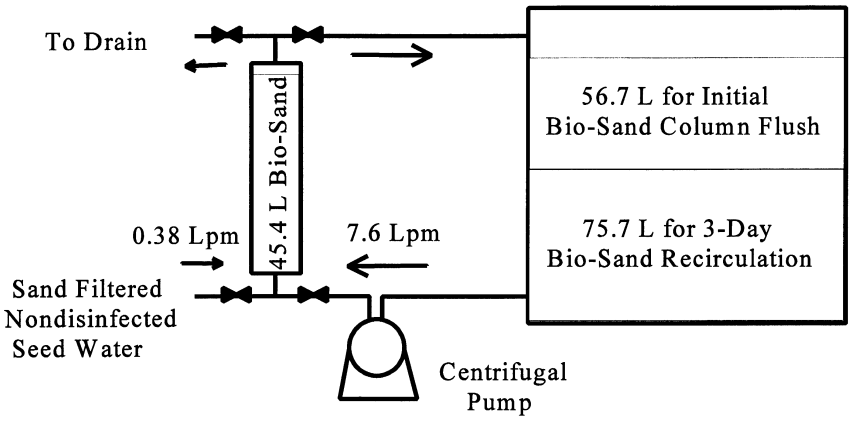

Fig. 2 Tank storage and biological recirculation system.

water was used to flush the bio-sand column of the nondisinfected 'seed' water that was initially contained within the column. The remaining 76 L of the process water was recirculated through the bio-sand filter at 7.6 L/min for three days at ambient river water temperature. The quality of the stored water was assessed at the beginning, as well as after the three-day storage with a chloramine residual, and at the end of the three-day biorecirculation period.

Each week the pilot column system was operated under different conditions consisting of variations in filter hydraulic loading (Table 1) and H_2O_2 addition. After changing the conditions, the pilot columns were equilibrated for 7 days before sampling and subsequent adjustment for the next week's conditions. Conditions for week one consisted of H_2O_2 addition at a hydraulic loading of 4.9 m/h. H_2O_2 was introduced at the influent to ozone contactor no. 1, or to the influent to the dissipation column on alternating months. During week two, the pilot column filters were operated without H_2O_2 at a hydraulic loading of 8.6 m/h, except for the ozone–sand filter (Location 9) which was operated at the original rate of 4.9 m/h. Week three conditions were identical to week one but without the addition of H_2O_2. Week four was dedicated to MS2 coliphage spiking of the pilot column system. This four-week schedule was continually repeated to evaluate each process stream under all seasonal water quality conditions.

Table 1 Pilot column system design parameters

Ozone contact columns	
No. of stages	3
Size	5.2 cm diam. × 3.0 m
Water flow, L/min	6.0 & 9.3
O_3 gas flow (each stage), L/min	1.2
T_{10} contact, min	6.0 & 4.0
Ozone dissipation column	
Size	5.2 cm diam. × 3.0 m
Water flow, L/min	5.9 & 9.3
Air flow, L/min	1.2
H_2O_2/O_3 ratio	0.5 molar
Process filters	
Size	5.2 cm diam. × 3.0 m
Water flow, L/min	1.5 & 2.6*
Hydraulic loading, m/h	4.9 & 8.6*
Effective media size, min	
—sand	0.48
—anthracite	0.99
—GAC	0.85
Media depth, em	
—sand	76
—anthracite/sand	51/25
—GAC/sand	51/25
Media EBCT, min	9.2 & 5.2
GAC EBCT, min	6.1 & 3.5
Biological recirculating filters	
Size	15.2 cm diam. × 0.78 m
Effective sand size, mm	0.48
Sand depth, cm	62
Seed water flow, L/min	1.9
Recirculating water flow, L/min	7.6

* Higher flow for mixed media filters only.

Analytical methodology

Surrogate organic parameters included dissolved organic carbon (DOC) and total organic halide (TOX) analyses. DOC analyses were performed using EPA Method 415.2 with river and clarified water samples centrifuged at 2000 ***g*** for 30 min prior to analysis, while TOX analyses were measured via EPA Method 450.1. The disinfection by-products monitored included the trihalomethanes (THMs), haloacetic acids (HAA), haloacetoniltiles (HAN), aldehydes, haloketones, chloral hydrate, and cyanogen chloride (CNCl). THMs were analysed via EPA Method 502.2. CNCl was measured by salted liquid extraction as described by Sclimenti *et al.* [5]. Separate CNCl samples were collected and preserved with 100 mg/L ascorbic acid, with subsequent analysis of 35 mL aliquots on the same day of sample collection. The minimum detection limit for CNCl analysis was 0.05 μg/L. Stock standards of CNCl were prepared according to the procedure of Flesch &

Fair [6]. HAA and HAN analyses were performed via EPA Methods 552 and 551, respectively. EPA Method 551 was also used to measure chloropicrin, haloketones and chloral hydrate. A preservation study comparing ammonium chloride and ascorbic acid preservatives for chloral hydrate, as described in the method, indicated no significant difference between the two preservatives for this source water. Therefore HAN and chloral hydrate analyses were performed simultaneously on the same sample aliquot. Aldehydes were analysed by the *o*–(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) derivatisation method described in Standard Methods [7] 6252 B with detection limits ranging from 0.04 μg/L for acetaldehyde to 0.87 μg/L for formaldehyde.

The herbicides measured included atrazine, cyanazine, simazine, metolachlor, alachlor, and acetochlor, which were analysed using EPA Method 505 with 8 g of sodium chloride applied to each sample which was subsequently extracted with a 1:1 hexane:methyl-t-butyl ether. Bacteriological parameters included heterotrophic plate count (HPC), total coliform (TC), MS2 coliphage and assimilable organic carbon (AOC). HPC and TC were measured via Standard Methods [7] 9215 D and 9222 B, respectively. AOC analyses were performed using the rapid method described by LeChevallier *et al*. [8] using two strains of heterotrophs, *Pseudomonas fluorescens* P17 and *Spirillium* NOX. MS2 coliphage and its host was obtained from the American Type Culture Collection, Rockville, Maryland. Coliphage propagation and plaque assay are described elsewhere [3,9,10]. Ozone and chlorine/chloramine residuals were measured using Standard Methods [7] 4500-O_3 B and 4500-Cl F, respectively. Chlorine demand was conducted by dosing 250 mL samples of deionised and clarified water with 3–4 mg/L free chlorine with incubation for 1 h at ambient water temperature and pH in accordance with Standard Methods [7] 2350 B. Reductions in disinfection by-product precursor concentrations were evaluated for ozone and ozone/hydrogen peroxide both before and after biological filtration. Sample aliquots were dosed with varying amounts of free chlorine, as determined by the relative demands of the actual samples, stored for five days at 30 °C and then quenched with the appropriate dechlorination agent according to the analytical method.

RESULTS AND DISCUSSION

Ozone was applied to achieve a 3-log reduction of *Giardia* in accordance with the guidance manual *CT* table [3] while conventional treatment achieved an additional 2.5 logs for a combined *Giardia* reduction of 5.5 logs. With an applied ozone dosage of 1.7–4.3 mg/L to the ozone contact system, ozone residuals in the effluents of contactors 1–3 averaged 0.01, 0.08 and 0.09 mg/L, respectively, at an average water temperature of 22 °C (6–32 °C). The average *CT* required was 0.69 mg/L.min while that achieved was 0.74 mg/L.min. Turbidity levels averaging 1.13 NTU in the effluent of the ozone dissipation column were reduced to 0.11 NTU in the effluent of all of the biological filters (ozone–sand, ozone–anthracite/sand and ozone–GAC/sand). Average turbidities for the ozone–chloramine–anthracite/sand and chloramine–anthracite/sand columns were slightly higher at 0.16 and 0.13 NTU, respectively. The backwash requirements for the pilot filters varied both with media type and pretreatment. The pilot filters were backwashed at 6 ft of headloss which resulted in an average filter run time of 3.5 days for the ozone–sand and ozone–GAC/sand filters, while the backwashing frequency for the ozone–anthracite/sand filter was every 11 days. The shorter filter runs observed from the ozone–GAC/sand filter were apparently the result of the build up of GAC fines at the surface of the filter. The chloramine–anthracite–sand filter had slightly longer filter runs, averaging 14 days, while the longest filter runs were observed for the ozone–chloramine–anthracite/sand filter at 28 days. Chloramine residuals averaged 3.0–3.1 mg/L in the effluent of the chloramine–anthracite/sand and ozone–chloramine–anthracite/sand filters, as did the chloramination pipe loop effluents for the three biological filters. No observed effects were indicated for the variations in hydraulic loading of 8.6–4.9 m/h or for the addition of hydrogen peroxide at 0.5 molar ratio to ozone residual.

Reduction in dissolved organic carbon (DOC)

Clarification of raw water via up-flow sludge blanket clarifiers with cationic polymers and a continuous feed of 2 mg/L powdered activated carbon produced an average DOC reduction of 11% (Fig. 3), from 3.59 to 3.20 mg/L. An additional reduction of 6% (0.22 mg/L) was removed by direct oxidation across the three-stage ozone contact system and the ozone dissipation chamber for a total average reduction of 17% with an average effluent concentration of 2.98 mg/L. Further DOC reductions were observed across the biological filters following ozonation. A cumulative reduction of 32% was achieved for the ozone/sand and ozone/anthracite/sand filters with average concentrations of 2.43 and 2.44 mg/L. The ozone/GAC/sand filter, which had reached a steady-state condition for DOC removal prior to the beginning of the operational period, produced the highest cumulative DOC removal of 37%, with an average concentration of 2.26 mg/L. Despite the relatively short empty bed contact time of the biological filters (5–9 min), the DOC reductions observed were adequate to meet the requirements of enhanced coagulation under the proposed Disinfectants and Disinfection By-product Rule [11] for TOC reduction of 30% at a source water TOC concentration of >2.0–4.0 mg/L and alkalinity of >60–120 mg/L. While reductions in DOC were adequate for meeting the requirements of the rule, reductions calculated from raw water TOC would be significantly greater based on the amount of particle-associated TOC present in the source water. One recent national study in which this utility participated evaluated enhanced coagulation compliance [12], and indicated that water obtained from the

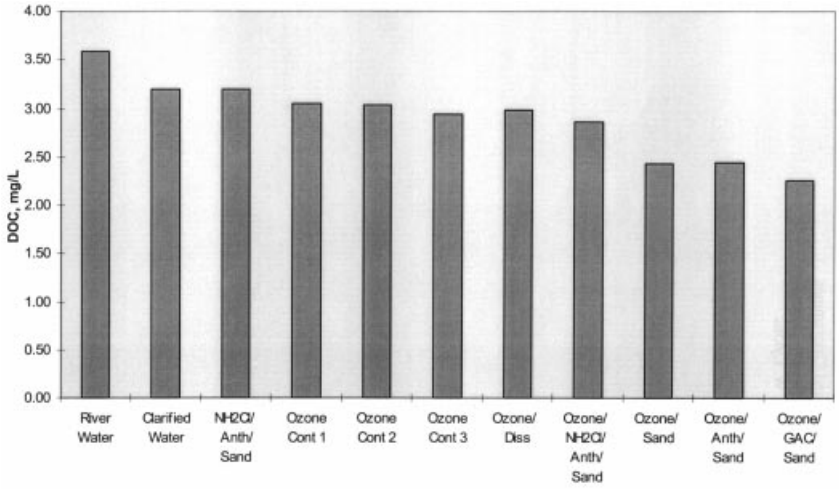

Fig. 3 Reductions in DOC by conventional treatment and ozonation with biological filtration.

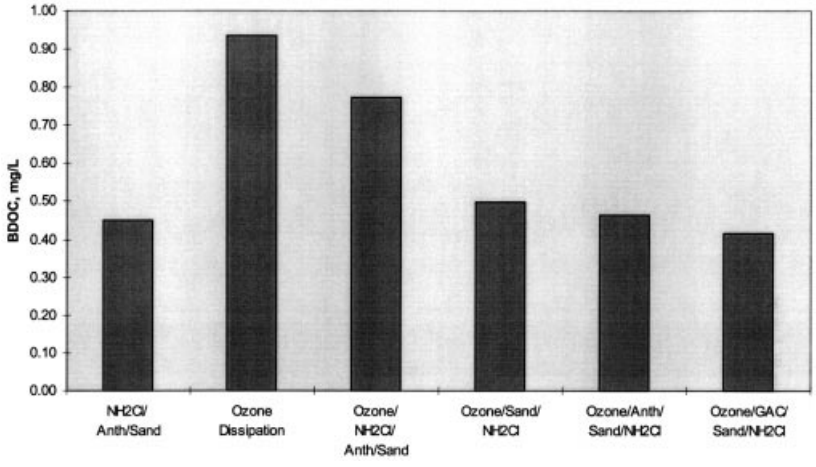

Fig. 4 Comparison of BDOC formed by conventional treatment and ozonation both with and without biological filtration.

lower Mississippi River required only settling without the addition of a coagulant to meet the TOC removal requirement. Subsequent investigation via weekly analysis over a nine month period has indicated that TOC removal by the normal treatment process described above was highly variable (0–48%) due to the variability of particle-associated TOC in the source water. The average TOC removal by the full-scale clarification process (described above) over this period was 20% at both treatment facilities, which are 6.3 river miles apart on opposite sides of the river.

Formation of biologically degradable organic carbon (BDOC)

BDOC was determined for the final finished water of each process stream by recirculation through biologically active sand (bio-sand) columns (Fig. 2) for three days at ambient water temperature. Prior to recirculation, each process stream was initially chloraminated to 3 mg/L and stored for three days to simulate the time to travel to the end of the distribution system. The remaining chloramine residual was then stoichiometrically reduced. The average BDOC of 0.93 mg/L indicated for the ozone dissipation column effluent (Fig. 4) was estimated by subtracting the average DOC remaining after three days of bio-sand recirculation of all the ozonated process streams from the average DOC of the ozone dissipation column. Ozonation followed by chloramine post-disinfection and subsequent anthracite/sand filtration produced a slight reduction in BDOC to an average of 0.77 mg/L. Ozonation followed by biological filtration resulted in average BDOC concentrations of 0.50, 0.47 and 0.42 mg/L for the sand, anthracite/sand and GAC/sand filters, respectively. These concentrations were only slightly higher or equivalent to the average of the chloramine/anthracite/sand process stream at 0.45 mg/L which simulated the current full-scale treatment process. The BDOC observed for the chloramine/anthracite/sand filter would appear to have been present as a background concentration in the influent clarified water as opposed to having been formed during the *in situ* formation of chloramine, as indicated by the AOC concentrations observed for these locations (Fig. 5). Thus, ozonation at a level required to achieve a 3-log *Giardia* removal essentially

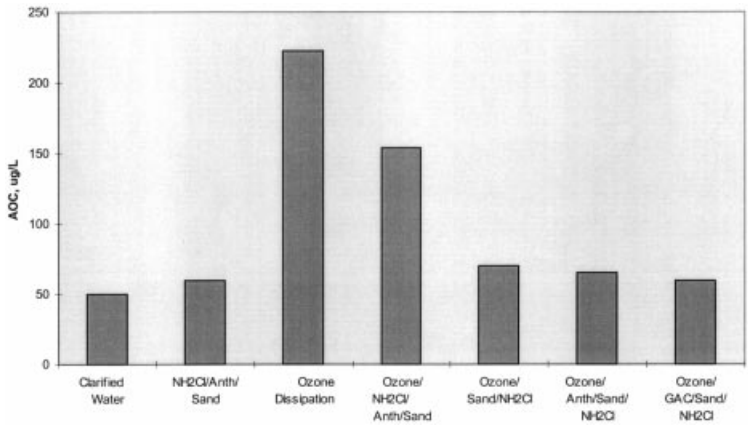

Fig. 5 AOC formation by ozonation and subsequent reduction by biological filtration.

doubled the background BDOC concentration in the clarified water with a subsequent reduction by biological filtration of 50% down to the original background concentration. These reductions in BDOC indicate that biological filtration is an effective means of removing BDOC, even at relatively short empty bed contact times (5–9 min) and in this case negated the effects of ozonation with regard to increased regrowth potential in the distribution system.

Formation of assimilable organic carbon (AOC)

Average AOC increased slightly during the chloramination process, from 50 μg/L in the clarified water to 60 μg/L following the addition of chlorine and ammonia (Fig. 5). Ozonation increased the AOC concentration dramatically to an average of 222 μg/L in the effluent of the ozone dissipation chamber. Biological filtration with 5–9 min of empty bed contact time and subsequent chloramination (with a 3-min free chlorine contact time) reduced these elevated concentrations by approximately 70% to 70, 66, and 60 μg/L, respectively, for the ozone/sand, anthracite/sand and GAC/sand filters. While a 30% reduction of AOC was observed across the ozone/chloramine/anthracite/sand filter, significant concentrations remained (averaging 154 μg/L) which may result in elevated bacterial regrowth at the extremities of the distribution system where little or no chloramine residual exists. After chloramination to 3 mg/L, storage for three days, stoichiometric residual quenching and three days of bio-sand column recirculation, residual AOC concentrations ranged from 32 to 40 μg/L for all storage tanks (ozone/sand, ozone/anthracite/sand, ozone/GAC/sand, ozone/chloramine/anthracite/sand, and chloramine/anthracite/sand). The significance of these residual concentrations is unclear.

The AOC concentrations in the chloraminated effluent of the biological filters, averaging 65 μg/L, were very similar to those observed in the normal chloraminated treatment plant discharge to the distribution system, which averaged 57 μg/L (biweekly analysis over 18 months). LeChavellier *et al.* [14] reported that AOC concentrations <100 μg/L resulted in very low coliform regrowth occurrence ($<1\%$) in the distribution system while concentrations >180 μg/L resulted in elevated coliform occurrence as high as 7.5%. A five-year history of Jefferson Parish East and West Bank distribution systems (from Oct 1992 to Sep 1997) indicated that both systems had positive coliform samples in 25 of the 60 months sampled (42%). The maximum percentage of monthly samples which were positive for total coliform during this period were 1.8% for the East Bank distribution system with a two-day maximum residence time, and 2.8% for the West Bank distribution system with a three-day maximum residence time. A significant increase in AOC concentration entering the distribution system, such as the 154 μg/L observed for the ozone/chloramine/anthracite/sand filter without biological filtration, would be expected to significantly increase coliform regrowth in the distribution system, possibly to the point of exceeding the MCL of the Total Coliform Rule (5% monthly positive samples). Thus, biological filtration following ozonation would be required to maintain an acceptable level of coliform regrowth in the distribution system.

A comparison of AOC and BDOC results (Figs 4 and 5) indicates that similar trends were observed with the concentration of biodegradable carbon increasing after ozonation followed by a reduction from biological filtration to concentrations typical of chloramination without ozonation. No significant difference in AOC/BDOC removals were observed at the different hydraulic loadings employed. While similar trends were observed, the AOC concentrations consumed during the three days of bio-sand recirculation were only 6–15% of the DOC concentrations consumed by indigenous bacteria. Additionally, relative comparisons of AOC concentrations were different from those of BDOC, with ratios of BDOC/AOC ranging from 4.2 to 7.5, primarily because of the difference in analytical methodology making any direct numerical comparison of these parameters extremely difficult. These comparisons suggest that while BDOC may be somewhat more difficult to measure analytically, it may provide a broader picture of the biological regrowth potential than AOC.

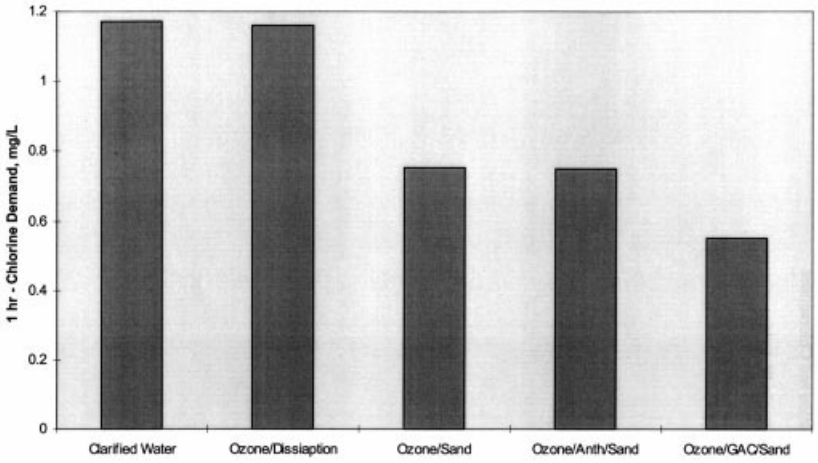

Fig. 6 Reduction in 1-h chlorine demand by ozonation with biological filtration.

Effect of ozone on chlorine demand

The average 1 h-chlorine demand observed for the clarified water was 1.17 mg/L. The ozone which was applied to achieve a 3 log removal of *Giardia* resulted in no reduction of 1 h-chlorine demand following ozone dissipation (Fig. 6). A 36% reduction in 1 h-chlorine demand to 0.75 mg/L was observed following biological filtration for both sand and anthracite/sand media. The largest decrease (53%) in 1 h-chlorine demand was observed for the biological GAC/sand filter, with an average effluent 1 h-chlorine demand of 0.55 mg/L. Thus, at relatively low concentrations, ozone did not increase the 1 h-chlorine demand and, when combined with biological filtration, was effective in significantly reducing the 1 h-chlorine demand with relatively short empty bed contact times of 5–9 min at 8.6–4.9 m/h, respectively.

Total organic halide (TOX) formation

Ozone disinfection at 3-log *Giardia* removal reduced influent TOX from 39 μg/L to 23 μg/L, with a further reduction to 17 μg/L across the biofilters (Fig. 7). Chloramination of the clarified water, followed by anthracite filtration produced an average TOX of 155 μg/L. Ozonation exhibited the most dramatic reduction of TOX, at 31% for the ozone–chloramine–anthracite/sand filter with average concentrations of 107 μg/L. An additional 5–10% reduction was produced by biological filtration, with average concentrations of 94, 99 and 86 μg/L for the ozone–sand filter, the ozone–anthracite/sand filter, and the ozone–GAC/sand filter, respectively, following subsequent chloramination. A correlation of DOC reduction and TOX formation via chloramination indicated that TOX concentrations in the finished water were reduced at a rate of 80 μg/L per mg/L of DOC removed. After tank storage for three days at ambient water temperature with a 2.5-mg/L chloramine residual, minor TOX reductions were observed in some instances which may have been attributable to the presence of excess ammonia. An excess ammonia concentration of 0.8 mg/L was shown to produce a reduction in TOX of 10 μg/L in finished chloraminated water which had been stored for five days at 30 °C.

Minor TOX precursor reductions of 6% were observed

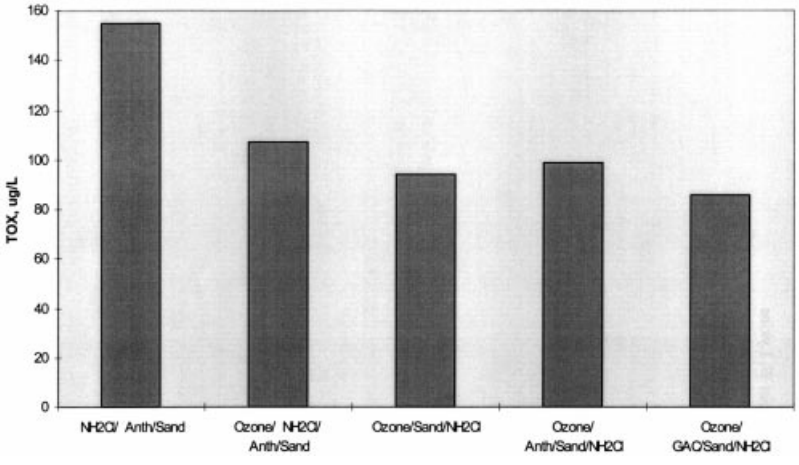

Fig. 7 Reduction in TOX by ozone and secondary chloramine disinfection.

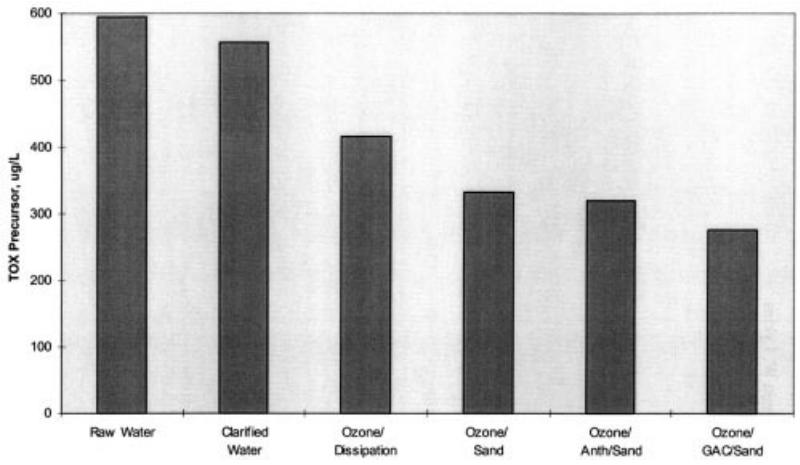

Fig. 8 Reduction of TOX precursors by ozonation and biological filtration.

across the clarification process, with average concentrations of 594 and 556 μg/L, respectively, for the raw and clarified water (Fig. 8). TOX precursor removal increased to 30% following ozonation, with an average of 417 μg/L for the ozone–chloramine–anthracite/sand filter. A further reduction to 44–46% occurred across the biological filters, with average concentrations of 333 and 320 μg/L for the ozone–sand and ozone–anthracite/sand filters. The greatest reduction for TOX precursors of 54% was observed for the spent GAC/sand filter following ozonation, with an average concentration of 276 μg/L. The reductions observed for TOX precursors paralleled those observed for finished water TOX relative to ozonation and ozonation, followed by biological filtration.

Total trihalomethane (THM) formation

The trihalomethanes (THM) consisted primarily of chloroform (84%) followed by bromodichloromethane (15%) and dibromochloromethane (1%) as determined from raw water formation potential data. Bromoform was not detected in either instantaneous or formation potential samples. Low instantaneous concentrations resulted in only chloroform and dichlorobromomethane being detected. Because of the non-reactive nature of chloramines with the THM precursors, THM concentrations were minimal, with average THM concentrations ranging from 2 to 7 μg/L for all locations following chloramine addition. The THM precursor concentrations (or THM-formation potential) in the raw water averaged 140 μg/L and were reduced by 12% across the full-scale clarifiers (Fig. 9) and by a total of 19% after the application of ozone. A further reduction of 33–36% occurred after biological filtration through the ozone–sand and ozone–anthracite/sand filters with average precursor concentrations of 93 and 90 μg/L, respectively. The greatest reduction of THM precursors of 48% occurred in the effluent of the biological spent GAC/sand filter with an average effluent concentration of 72 μg/L.

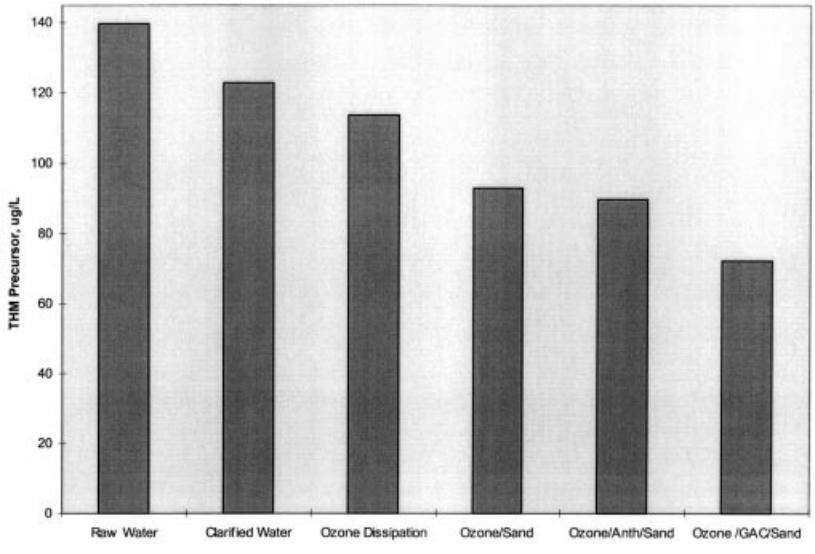

Fig. 9 Reduction of THM precursors by ozonation and biological filtration.

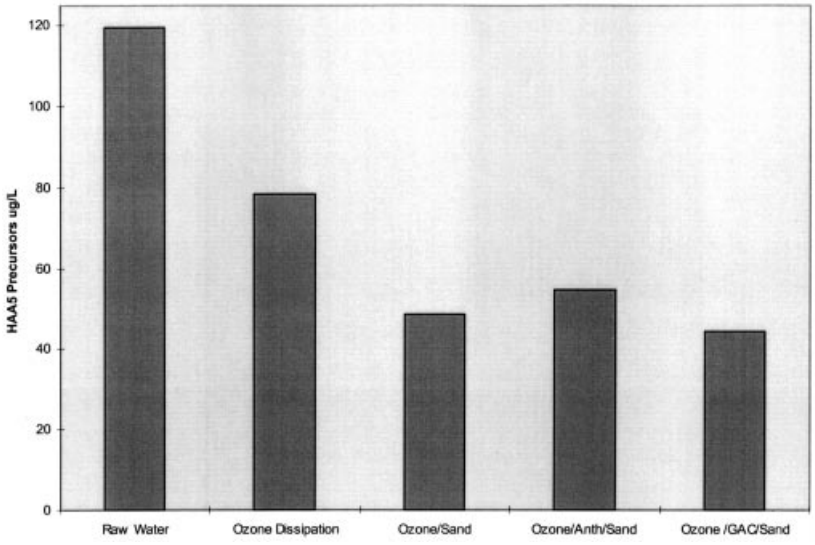

Fig. 10 Reduction of HAA5 precursors by ozonation and biological filtration.

Haloacetic acid (HAA) formation

As with the THMs, HAA formation was minimised by the use of chloramines. HAA5, consisting of those HAAs proposed for regulation (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid and dibromoacetic acid), occurred at average concentrations of 7–8 μg/L for all ozonated pilot filters following chloramination, either with or without prior biological filtration. The average effluent concentration of the chloramine–anthracite/sand filter was somewhat higher at 13 μg/L, suggesting a precursor reduction by ozonation. This was confirmed by a maximum formation potential which indicated a 35% average reduction of HAA5 precursors following ozonation (Fig. 10) with raw water and ozone dissipation column effluent concentrations of 120 and 78 μg/L, respectively. Further HAA5 precursor reductions (54–63%) occurred across the biological filters, with effluent concentrations ranging from 44 to 55 μg/L. The highest removal occurred for the biologically spent GAC/sand filter. HAA5, measured by raw water formation potential, consisted of approximately 38% dichloroacetic acid, 51% trichloroacetic acid, 7% chloroacetic acid, 2% bromoacetic acid and 1% dibromoacetic acid. The reductions observed for ozonation followed by biological filtration consisted primarily of reductions in trichloroacetic acid (80%) and dichloroacetic acid (44%). Bromochloroacetic acid (BCAA) occurred at all finished water locations at concentrations averaging 1–2 μg/L. BCAA precursor concentrations averaged 9–10 μg/L at all locations monitored (raw water, ozone dissipation, ozone–sand filter, ozone–anthracite/sand filter and ozone–GAC/sand filter) suggesting that this reaction was bromide-limited.

Total aldehyde formation

While aldehydes are not considered major ozonation by-products, they are of interest because some, such as formaldehyde, are suspected carcinogens. The aldehydes formed during primary and secondary disinfection measured in the effluent of the ozone–chloramine–anthracite/sand filter consisted of 80% formaldehyde, 9% glyoxal, 7% methylglyoxal and 4% acetaldehyde. Propanal and butraldehyde were also observed at a frequency of less than 10% at very low concentrations (1 μg/L). Total aldehyde concentrations increased dramatically across the ozone contactors (Fig. 11), from a background of 4 μg/L in the clarified water to 15 μg/L in the effluent of contactor no. 1, 40 μg/L in the effluent of contactor no. 2 and 54 μg/L in the effluent of contactor no. 3. An average total aldehyde reduction of 50% occurred across the ozone dissipation column due to the presence of biofilm, resulting in an average effluent concentration of 27 μg/L. A further reduction from biological filtration increased the removal to 89%, lowering the average concentration to 6 μg/L with no difference in removal observed for media type.

Following subsequent chloramination of the effluents of the biological filters, total aldehyde concentrations increased to 20–25 μg/L, which was similar to that in the effluent of the chloraminated anthracite/sand filter of 20 μg/L. Despite an indication of some biological activity across the ozone–chloramine–anthracite/sand filter (AOC reduction of 30%), no reduction of total aldehydes was observed, resulting in an average total aldehyde concentration of 46 μg/L. The total aldehydes in the ozone–chloramine–anthracite/sand filter effluent were comprised of those remaining in the ozone dissipation column effluent and those formed from the reaction of precursors with chlorine during the chloramination process. No significant change in total aldehyde concentration was observed after three days of storage at ambient water temperature in the presence of a 2.5-mg/L chloramine residual. A paired comparison of the total aldehydes formed during the chloramination process with those observed for formation potential with free

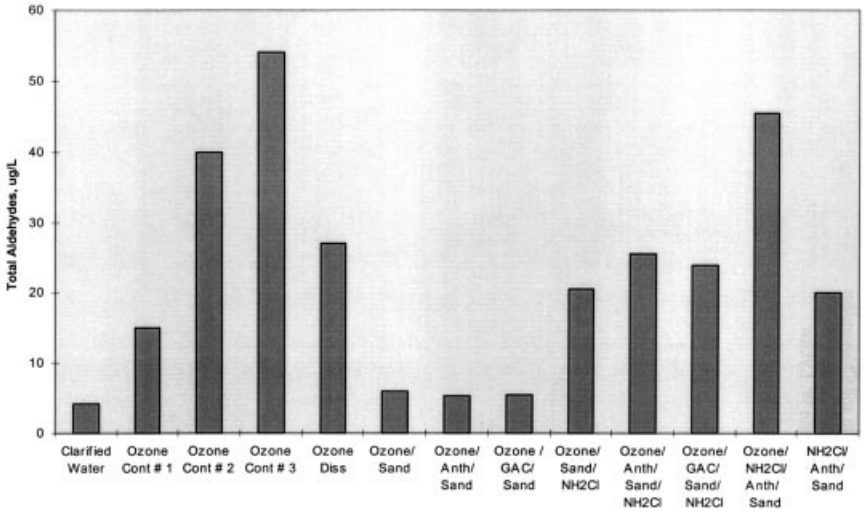

Fig. 11 Total aldehyde formation by ozonation, removal by biological filtration and reformation by chloramination.

chlorine over five days at 30 °C (Fig. 12), indicated that a very limited amount of the aldehyde precursors were present, and that essentially all of these precursors reacted with free chlorine to form aldehydes during the 3-min free chlorine contact period of the chloramination process.

Other chlorinated disinfection by-products

Haloacetonitrile formation, consisting of dichloroacetonitrile, trichloroacetonitrile, bromochloroacetonitrile and dibromoacetonitrile (HAN4) was very minimal, averaging only 1–3 μg/L for total acetonitriles at all filtered water locations following chloramination, with the ozonated biofilters having the lowest concentrations. Haloketone (1,2-dichloropropane and 1,1,1-trichloropropane) formation was also minimal, with average concentrations of 0.5–0.7 μg/L for the ozonated biological filters. Haloketone concentrations were slightly higher in the effluent of the ozone–chloramine–anthracite/sand and chloramine–anthracite/sand filters with averages of 1.7 and 1.5 μg/L, respectively. Chloral hydrate exhibited a similar trend, with the ozonated biofilters each averaging 0.3 μg/L, 0.6 μg/L for the ozone–chloramine–anthracite/sand filter and 0.7 μg/L for the chloramine–anthracite/sand filter. The highest concentrations of cyanogen chloride were observed for the ozone–chloramine–anthracite/sand filter, averaging 3.3 μg/L. The chloramine–anthracite/sand filter averaged 0.7 μg/L for cyanogen chloride while the ozonated biosand filters (sand, anthracite/sand and GAC/sand) averaged 0.6, 0.7 and 0.3 μg/L, respectively, suggesting that cyanogen chloride precursors were formed by ozonation but were removed by biofiltration. Chloropicrin was observed at a maximum concentration of only 0.26 μg/L in the effluent of the chloramine–anthracite/sand filter. Chloropicrin concentrations were significantly lower in the effluents of the ozonated filters with average concentrations ranging from 0.04 to 0.09 μg/L.

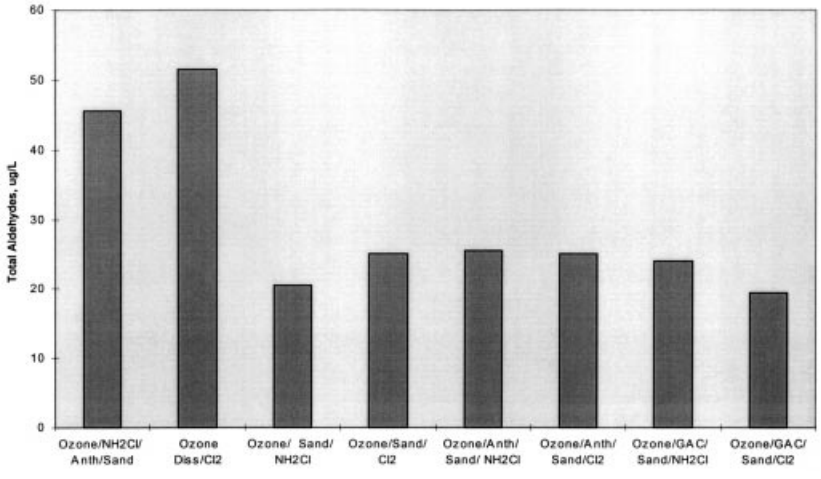

Fig. 12 Comparison of total aldehyde formation by free chlorine and chloramine.

Seasonal variations

Seasonal variations in disinfection by-product formation and removal, as measured by changes in water temperature, were minimal. While others [13,14] have reported reductions and/or a complete loss of biological activity at low water temperature ($\leqslant 10\,^{\circ}C$) following ozonation, no reductions of this type were observed. Relatively constant removals of DOC and AOC were observed across all three biological filters down to 8.5 °C (Figs 13 and 14). Similar removals were observed during a second low temperature period (70 days below 10 °C, minimum 6 °C) with no indication of a reduction in biological filter performance. HPC concentrations in the effluent of the biological filters were also relatively consistent across the entire temperature range (Fig. 15). This was not the case for the HPC concentrations in the effluent of the ozone dissipation column, which dropped off to very low levels below 17 °C. This reduction in HPC correlated with similar reductions in the amount of

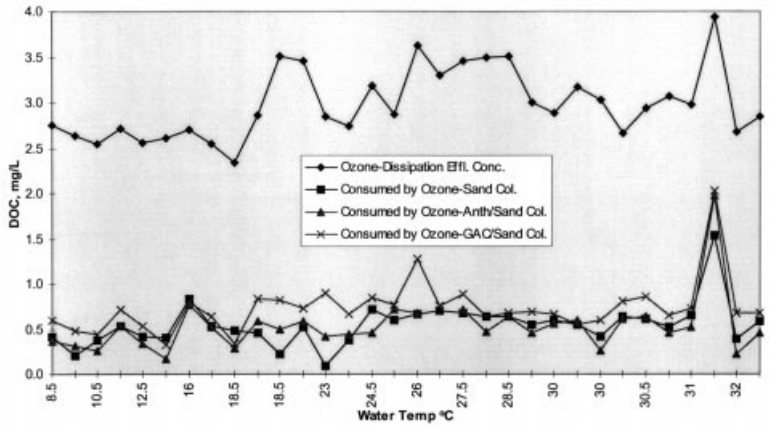

Fig. 13 Variation of DOC consumed by biological filtration with water temperature.

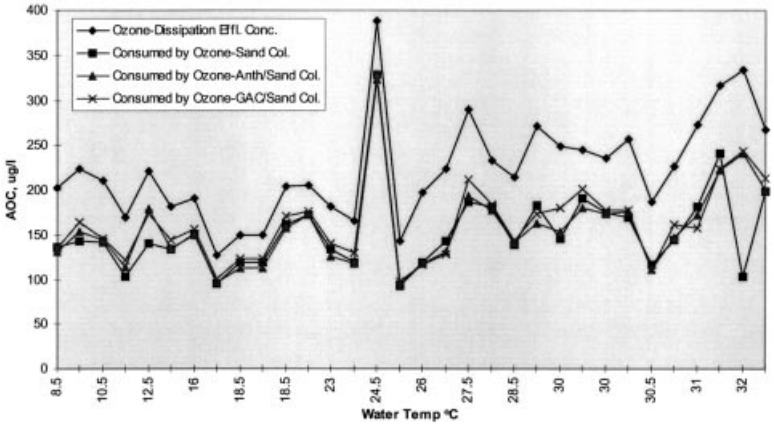

Fig. 14 Variation of AOC consumed by biological filtration with water temperature.

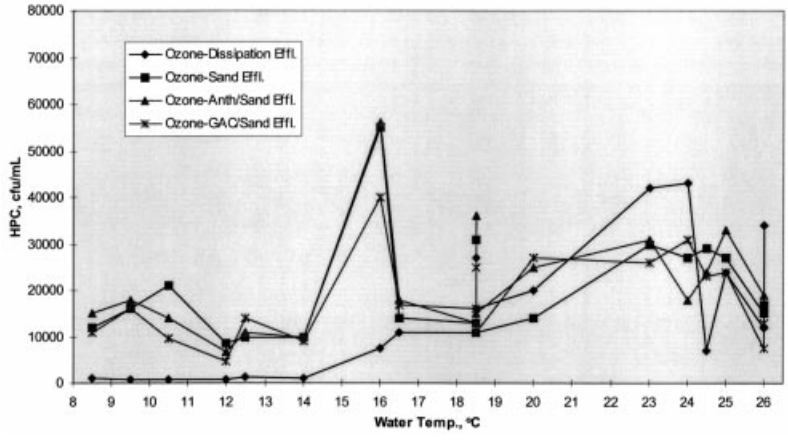

Fig. 15 Variation of HPC in the biological filter effluents with water temperature.

formaldehyde removed across the ozone dissipation column. With influent concentrations of 34–41 μg/L, removal decreased from 30 μg/L at 18.5 °C, to 16 μg/L at 12.5 °C and to 4 μg/L at 9.5 °C. While this loss of biological activity correlated with a lower water temperature, it was attributed to the further penetration of the ozone residual down the ozone dissipation column at lower water temperatures. While an ozone residual was never observed in the effluent of the ozone dissipation column (method detection limit = 0.002 mg/L), penetration of the ozone residual was observed by the visual movement of the biofilm interface up and down the column as water temperature increased and decreased. At low water temperature with an influent ozone concentration of only 0.20–0.25 mg/L, the biofilm interface was near the bottom of the dissipation column. It is important to note that had the ozone dissipation column not been present in the system, a reduction of biological activity would have been observed for all of the biological filters at low water temperatures.

Heterotrophic bacteria, total coliform and MS2 coliphage

Heterotopic bacteria concentrations, as measured by heterotopic plate count (HPC), averaged 31 000 and 34 000 CFU/mL in the effluent of the biological sand and anthracite/sand filters, with maximums of 330 000 and 200 000 CFU/mL, respectively. As observed in previous studies [1,2] the biological GAC/sand filter had considerably lower counts, averaging 16 000 CFU/mL with a maximum of 49 000 CFU/mL. These relatively high heterotrophic bacteria concentrations were effectively neutralised by relative short contact with free chlorine. Weekly monitoring of HPC following 1, 2, 3 and 4 min of free chlorine contact in the disinfection pipe loop indicated that 1 min of free chlorine contact reduced average HPC to less than 50 CFU/mL. A further reduction to approximately 10 CFU/mL was observed for 3 min of free chlorine contact at all water temperatures. Any additional contact time produced no further reduction. The relative short free chlorine contact time required to reduce HPC to acceptable concentrations may make biological filtration more appealing to those utilities who have been reluctant to consider its use.

Along with high heterotrophic plate counts, total coliform bacteria were also often observed in the effluents of the biological filters at low concentrations. The percentage of positive samples observed was 17, 23 and 18% for the ozone–sand, ozone–anthracite/sand and ozone–GAC/sand filters. The average total coliform count was 2 CFU/100 mL for each biological filter with a maximum count of 5 CFU/mL. As with HPC, these low total coliform concentrations are easily neutralised by a brief contact with free chlorine.

MS2 coliphage assays were employed to evaluate virus reductions across the ozone contact and dissipation system. Each month, an MS2 coliphage seed containing approximately 2–3 $\times 10^{10}$ PFU/mL was continuously fed into the nondisinfected clarified water prior to entering the first ozone contact chamber. An average influent phage assay of 7.67×10^6 PFU/mL was reduced by 2 logs each across contactor no. 1 (5.76×10^4 PFU/mL) and contactor no. 2 (397 PFU/mL) with an additional log removal for contactor no. 3 (32 PFU/mL) and the dissipation column (7 PFU/mL) for a total removal of 6 logs. Combined with the 2-log virus removal achieved through conventional treatment, a total virus removal of 8 logs was achieved by the inclusion of ozonation into the treatment train. These results are in relative agreement with the ozone *CT* tables for *Giardia* and virus inactivation contained in the Surface Water Treatment Rule Guidance Manual [3].

CONCLUSIONS

The following conclusions were derived from the operational and analytical data obtained during this study:

- Ozonation at a level of 3 logs for *Giardia* removal produced an associated virus removal of 6 logs, as measured by MS2 coliphage. The combined inactivation achieved for conventional treatment and ozonation was a 5.5-log calculated removal for *Giardia* and an 8-log measured removal for virus, which should be sufficient to meet any perceived increase in microbial inactivation which may result from the ESTWR.
- The concentration of disinfection by-products produced by disinfection with ozone to achieve 3 logs of *Giardia* removal, when combined with biological filtration and monochloramine (3 mg/L) as the secondary disinfectant, were well below all of the proposed requirements of the Disinfectants and Disinfection By-products Rule (Table 2). This includes the requirement for TOC reduction by enhanced coagulation based on alkalinity and source water TOC concentration. The THM and HAA6 average concentrations formed during treatment were 6 and 9 μg/L, respectively, which are well below the proposed THM/HAA5 concentrations of the D/DBPR for both Stage 1 at 80/60 μg/L THM/HAA and Stage 2 at 40/30 μg/L THM/HAA. The total chlorinated by-products produced by ozonation, biological filtration and chloramine secondary disinfection (excluding TOX) was only 17 μg/L. Similar pretreatment using free chlorine as the secondary disinfectant in the distribution system was ineffective in meeting the Stage 1 requirements of the D/DBP Rule.
- The elevated BDOC, AOC and total aldehyde concentrations produced by ozonation were effectively reduced by biological filtration with relatively short empty bed contact times (5–9 min). The removal of these organic constituents, as well as the biological activity on the filters, were unaffected by low (6–10 °C) water temperature. The BDOC, AOC and total aldehyde concentrations remaining after biological filtration were equivalent to those produced by the *in situ* generation of chloramine. Thus, the use of

Table 2 Comparison of the annual average effluent water quality for each process stream

Water quality parameter	Chloramine–anthracite/sand filtration	Ozone–chloramine–anthracite/sand filtration	Ozone–sand filtration*–chloramine	Ozone–anthracite/sand filtration*–chloramine	Ozone–GAC/sand filtration*–chloramine
DOC, mg/L	3.19	2.86	2.43†	2.44†	2.26†
BDOC‡, mg/L	0.45	0.77	0.5	0.47	0.42
AOC, μg/L	60	154	70	66	59
TOX μg/L	155	107	94	99	86
THM, μg/L	7	2	6	6	6
HAA6§, μg/L	15	9	9	9	9
HAN4, μg/L	3.1	2.4	1.2	1.2	1.2
Haloketones, μg/L	1.5	1.7	0.6	0.7	0.5
Chloral hydrate, μg/L	070	0.60	0.30	0.30	0.30
Chloropicrin, μg/L	026	0.04	0.09	0.08	0.06
CNCl, μg/L	0.7	3.3	0.6	0.7	0.3
Aldehydes, μg/L	20	46	21	26	24

* Biological filtration.
†Meets D/DBP proposed enhanced coagulation removal requirements.
‡BDOC at ambient water temperature.
§ HAA5 and bromochloroacetic acid.

biological filtration following ozonation effectively reduced any potential for increased biological regrowth in the distribution system which may be derived from elevated concentrations of biodegradable organic carbon created during ozonation.

- The elevated heterotrophic plate counts resulting from biological filtration were effectively reduced to 10 CFU/mL with only 3 min of free chlorine contact.
- The DOC reduction achieved via ozonation and subsequent biological filtration had essentially no effect on THM and HAA by-product formation when chloramines were employed for secondary disinfection.
- Biological filtration following ozonation prevented the formation of elevated concentrations of TOX, aldehydes and cyanogen chloride through precursor reduction. TOX formed via chloramination was reduced approximately 80 μg/L for each mg/L DOC removed by ozonation and biological filtration prior to chloramination.
- Ozonation followed by biological filtration with both sand, anthracite/sand, and spent GAC/sand filter media and subsequent chloramination (3 min free chlorine contact) resulted in the formation of similarly low concentrations of disinfection by-products, with annual averages of 6 μg/L for THM and 9 μg/L for HAA6. Although the spent GAC/sand media produced in slightly elevated removals of DOC (5%), TOX (7%) and AOC (6%) resulting from the adsorption equilibrium, the additional benefit provided by GAC as an adsorptive nonregenerable biological media is insufficient to offset its higher initial and maintenance costs.

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