United States
Environmental Protection
Agency

Risk Reduction
Engineering Laboratory
Cincinnati, OH 45268

Research and Development

EPA/600/SR-93/136 September 1993

EPA

Project Summary

Disinfection By-Product Formation by Alternative Disinfectants and Removal by Granular Activated Carbon

Wayne E. Koffskey

The effects of the use of alternative disinfection (chlorine, ozone, chloramine, chlorine dioxide) on the formation of halogenated by-products and the removal of these by-products by granular activated carbon (GAC) were evaluated over a 1-yr operational period. Disinfection by-products examined included trihalomethanes (THMs), haloacetic acids (HAAs), haloace-tonitriles (HANs), haloketones (HKs), chloral hydrate (CH), and chloropicrin (CP). Microbiological information was also obtained on the operating systems and included heterotrophic plate count, total coliform, and MS2 coliphage. Other parameters evaluated included total organic carbon (TOC), total organic halide (TOX), and assimilable organic carbon (AOC).

Each of four disinfectant process streams was composed of a 30 min contact chamber followed by a sand column in series with a GAC column, the latter having a 20 min empty bed contact time (EBCT). One of the four disinfectants was applied at the beginning of each process stream. A fifth nondisinfected process stream, consisting of only a sand column in series with a GAC column, was used as a control.

The lowest levels of halogenated disinfection by-products resulted from the combination of preozonation and post chloramination after sand filtration with annual simulated distribution system averages of 27 μg/L of TOX and 12 μg/L for the sum of 18 disinfection by-products. These respective concentrations were further reduced to 13 μg/L and 7 μg/L after GAC treatment. Although ozonation produced significant levels of AOC, sand filtration reduced these levels by an average of 77% to 39 μg/L and subsequent GAC treatment provided a further reduction to 4 μg/L.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Chlorine has been widely used throughout the United States for disinfecting drinking water. During the disinfection process, chlorine reacts with naturally occurring organic matter to form a number of halogenated disinfection by-products. Existing disinfection/disinfection by-product regulations apply only to trihalomethanes with a maximum contaminant level (MCL) of 0.10 mg/L. Anticipated future Federal regulations for disinfection/disinfection by-products will potentially affect most water treatment plants in the United States.

Traditionally, drinking water standards for contaminants are set at the lowest possible, technically and economically feasible number. There must, however, be assurance that drinking water is microbiologically safe, which may mean that a greater risk will have to be accepted from disinfectants and disinfection by-products in the water than for other contaminants. This research project was developed to evaluate the formation of disinfection by-products by alternative disinfectants and their removal by GAC while evaluating the microbiological quality of the treated water. Specific objectives of this project are:

- measure the effects of alternative disinfectants on the formation of halogenated disinfection by-products including the trihalomethanes, the haloacetic acids, the haloacetonitriles, the haloketones, chloral hydrate, and chloropicrin.
- measure the effectiveness of GAC filtration following sand filtration in removing halogenated disinfection by-products and their precursors.
- measure the general microbiological quality of water treated with the alternative disinfectants.
- assess the levels of AOC formed during disinfection with ozone and chlorine.
- evaluate the effectiveness of the alternative disinfectants in the inactivation of MS2 coliphage.

To meet these objectives, a pilot column system consisting of four disinfected process streams (ozone, chlorine dioxide, chlorine, and chloramine) and a nondisinfected process stream was continually operated for one year.

Treatment Plant

Lower Mississippi River water entering the 34 mgd Permutit* treatment plant at Jefferson Parish was dosed with 1 to 6 mg/L diallyldimethylammonium chloride, or dimethylamine polyelectrolyte polymers, or both for clarification, 0.1 to 0.3 mg/L fluosilicic acid (as fluoride) for fluoridation, and 2 mg/L powdered activated carbon for organics control. After clarification via Permutit upflow precipitators, a small portion of clarified water was diverted to a pilot column system and was filtered through one of two pressure sand filters at a hydraulic loading of 1.7 gpm/ft^2. Each sand filter contained 30 in. of 0.45 mm-filter sand and provided an average nondisinfected sand filtered water flow of 8.5 gpm to the rest of the pilot column system.

Pilot Columns

The filtered water was split into five process streams, one for each of the four disinfectants and another nondisinfected process stream used as a control. Each disinfected process stream consisted of a 30-min disinfectant contact chamber followed by series filtration through a sand column and a GAC column. The nondisinfected process stream consisted of only a sand column in series with the GAC column.

Each disinfectant contact chamber was constructed with the use of a 12-in. diameter stainless steel pipe that was 10 ft high, except for the ozone contact chamber that was 11 ft high. The sand and GAC columns were constructed from 10-ft sections of 6-in. diameter glass pipe. All pilot column components were constructed from stainless steel, glass, and teflon. The sand columns were charged with 30 in. of 0.45-mm filter sand, and the GAC columns were charged with 6.8 ft of 12 x 40 mesh GAC to achieve a 20-min EBCT at a flow of 0.5 gpm. Each column was operated at a hydraulic loading of 2.5 gpm/ft^2 and was backwashed only when necessary to achieve the desired flow rate. No media loss was observed during backwashing. The GAC used in this study was Ceca GAC 40 and was selected after a thorough evaluation of various types of GAC.

During the course of the operational period, water temperatures ranged from 3 to 29 °C. After the addition of the various disinfectants, slight variations in pH were observed. On the average, the pH of the chlorine dioxide contact chamber effluent decreased 0.6 units to pH 7.0 whereas that for the chlorine and chloramine contact chambers increased 0.1 and 0.2 units to pH 7.7 and 7.8, respectively. No change in pH was observed for the ozone process stream.

A 96% yield of chlorine dioxide was generated by the in-line mixing of hypochlorite/chlorite and sulfuric acid solutions before its injection into the process stream. Chloramines were formed within the process stream with the injection of hypochlorite followed within a few seconds by ammonium hydroxide. The average 30-min demands for each disinfectant determined during the operational period are compared in Table 1 along with their average disinfectant contact chamber effluent residual concentrations. Although residual concentrations were measured as chlorine using the DPD titrimetric method, they are reported as the specific disinfectant indicated, not as free chlorine. The ozone residual dissipated completely across the sand column, but the other three disinfectant residuals were only slightly reduced. No residual species of any disinfectant were observed in the effluent of the GAC columns.

Pilot Column Performance

Microbiological Effectiveness

At the dosages used, all of the disinfectants reduced total coliforms to acceptable levels. With heterotrophic bacteria, however, all disinfectants except chloramines reduced the levels to below 100. Other organisms may not have been as effectively controlled by all disinfectants. For instance, during one study when MS2 Coliphage was spiked into the pilot plant, chloramines were ineffective for this virus indicator. Future studies at Jefferson Parish will apply the concentration x time (C•t) concept for determining disinfectant efficiency.

Halogenated By-Product Control

During the 1-yr operation of the pilot plant, two surrogate parameters that give an indication of organic concentrations, including halogenated by-products, were evaluated: TOC and TOX. The average TOC concentrations in the disinfectant contact chamber effluents were 3.1, 2.9, 3.2, 3.2 and 3.2 mg/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively. A slight reduction in TOC averaging 0.3 mg/L was indicated across the ozone contact chamber, whereas the concentration of TOC remained fairly constant for the other disinfectants. TOC was further reduced across the ozone sand column by an average of 0.8 mg/L when compared with the nondisinfected influent. Based on the levels of heterotrophic bacteria in the effluents of the ozone contact chamber and ozone sand column, the reduction of TOC across the ozone contact chamber appears to have resulted primarily from oxidation and that across the ozone sand column can be attributed to biodegradation.

With an average nondisinfected TOX influent concentration of 25 µg/L, TOX concentrations increased significantly after 30 min of disinfectant contact time to 86 µg/L for chlorine dioxide, 99 µg/L for chloramine, and 246 µg/L for chlorine.

The same trend seen for TOC was also observed for TOX where an average reduction of 33% occurred in the ozone contact chamber to produce an average effluent concentration of 16 µg/L with a further reduction to 11 µg/L across the ozone sand column. Treatment of the sand filtered effluents with free chlorine followed by a 5-day storage to simulate the distribution system significantly increased TOX

Table 1. Average Disinfectant Contact Chamber Demands and Residuals

	Average 30-min disinfectant demand (mg/L)	Process stream average disinfectant contact time (min)	Process stream average disinfectant residuals (mg/L)
Ozone	2.5	30	0.5
Chlorine dioxide	0.7	30	0.5
Chlorine	1.8	30	1.0
Monochloramine	0	30	2.2

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

concentrations for all process streams (557, 540, 339, and 379 µg/L for nondisinfected, chlorine, ozone, and chlorine dioxide, respectively).

The THMs reacted as expected with no significant concentrations (1 µg/L average) observed in the disinfectant contact chamber and sand column effluents for the nondisinfected, ozone, and chlorine dioxide process streams. An average THM concentration of 3 µg/L occurred in the chloramine disinfectant contact chamber and sand column effluents whereas that in the chlorine contact chamber effluent averaged 39 µg/L and increased to 49 µg/L across the chlorine sand column. By maintaining a chloramine residual for 5 days, the terminal THM concentrations increased slightly to an average of 8.5, 3.2, 4.2, and 9.4 µg/L for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams, respectively. Similar treatment and storage with free chlorine produced relatively high terminal THM concentrations for the nondisinfected and chlorine process streams with average concentrations of 236 and 225 µg/L. When compared with the nondisinfected sand column effluent, terminal THMs were 35% and 41% less when ozone and chlorine dioxide were used during pretreatment, i.e., average concentrations of 154 and 138 µg/L, respectively. As expected, GAC reduced all concentrations until the columns became saturated in 60 to 80 days.

The haloacetic acids followed the same trend as seen with THMs except at a lower concentration. The highest concentrations were formed by using free chlorine, which mainly produced dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and bromochloroacetic acid (BCAA). Chloroacetic acid (CAA), bromoacetic acid (BAA), and dibromoacetic acid (DBAA) were also formed to some extent. Average instantaneous concentrations for DCAA were 0.9, 1.7, 3.7, 1.1, and 13 µg/L for the nondisinfected, chlorine dioxide, chloramine, ozone, and chlorine process streams after sand filtration, respectively. Five-day terminal values for the same process streams with free chlorine were 60, 44, 38, and 60 µg/L for the nondisinfected, chlorine dioxide, ozone, and chlorine streams, respectively.

Similar treatment of the sand filter effluents with chloramine and a 5-day storage period resulted in only slightly elevated DCAA concentrations. The slight concentration increase is similar to that seen for THMs during similar treatment with chloramine suggesting that both were formed by free chlorine during in-situ formation of chloramine. GAC adsorption produced continued removals of 80% or greater of DCAA after steady-state was reached at about 150 days of operation. After 5-day storage with free chlorine, GAC steady-state was reached in about 250 days for DCAA with average removals after steady-state of 48%, 73%, 53%, 46%, and 51% for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively. Similar observations for all unit processes were also seen for TCAA.

Relatively low concentrations of HANs were formed across each process stream with chlorine producing the highest levels which averaged 3.1 µg/L total HANs. An average of less than 1 µg/L of HANs was observed across the other process streams. The predominant HAN was dichloroacetonitrile (DCAN) followed by bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), and trichloroacetonitrile (TCAN). Treatment of the chlorine sand column effluent with additional free chlorine and subsequent 5-day storage produced an average concentration of 1.9 µg/L of DCAN, which was the same as that of the sand column effluent suggesting that all DCAN precursors had reacted. No consistent breakthrough of the HANs was observed through any GAC column except that of the chlorine process stream, which was still removing over 95% of the influent HANs at the end of the 1-yr operational period.

Only two haloketones, 1, 1, 1-trichloropropanone (TCP) and 1, 1-dichloropropanone (DCP) were detected with the highest concentration (1 to 2 µg/L) being observed in the chlorine process stream. Post chlorination of the sand column effluents followed by 5-day storage produced similar TCP concentrations of 2.1, 2.5, 4.2, and 2.5 µg/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams, respectively. Although consistent breakthroughs of these haloketones were observed across the GAC columns, removals remained above 85% throughout the one-year operational period.

CH was formed predominantly in the chlorine process stream with an average contact chamber effluent concentration of 2.9 µg/L that increased to 4.5 µg/L across the sand filter because of an additional 30 minutes chlorine contact time. The CH concentrations in the effluent of the chloramine contact chamber and sand column were identical and averaged 0.25 µg/L. CH was detected intermittently in the contact chamber and sand column effluents of the chlorine dioxide, ozone, and nondisinfected process streams at average concentrations ranging from 0.01 to 0.07 µg/L. Post-treatment of the sand column effluents with free chlorine and storage for 5 days produced CH concentrations averaging 79, 55, 45, and 75 µg/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams, respectively. Similar treatment with chloramine produced average concentrations of 0.03 to 0.3 µg/L. GAC adsorption removed all of the CH throughout the project in all process streams.

The concentrations of CP in the effluents of the disinfection contact chambers and the sand columns were the same, averaging 0.004, 0.004, 0.015, 0.038, and 0.43 µg/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively. Chlorination and 5-day storage of the sand column effluents produced concentrations averaging 1.3, 7.7, 1.4, and 1.3 µg/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams, respectively. Preozonation appears to have produced an increase in CP precursors. Only slight increases in CP concentrations were observed after similar chloramine treatment and storage of the sand column effluents with average concentrations of 0.03, 0.04, 0.11, and 0.09 µg/L for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams, respectively. No consistent breakthrough of CP above 0.003 µg/L was observed across the GAC column of any process throughout the operational period.

Summary

From these data, one might conclude that ozonation before sand filtration and chloramination after sand filtration will solve the halogenated by-product problem. Although this is true, the total effect of disinfection must be evaluated. For instance, although ozone shows promise and may be a viable disinfection alternative, the increased AOC produced must be controlled before entering the distribution system. This can be done by biostabilization of the water during treatment before distribution. Average AOC concentrations at Jefferson Parish are shown in Table 2. After ozonation, 166 µg/L of AOC is present. Sand filtration provides some biostabilization by reducing the AOC to 39 µg/L; in the GAC effluent AOC is reduced to 4 µg/L which is comparable to the AOC concentration (5 µg/L) in the chlorine contact chamber effluent. Ozonation by-products such as aldehydes, ketones, and acids are also a concern. Although chloramines may be the disinfectant of choice to provide a distribution system disinfection residual, it may not provide the desired disinfection effectiveness in all cases.

The full report was submitted in fulfillment of Cooperative Agreement NO. CR814033 by the Jefferson Parish, Louisiana Department of Public Utilities under the sponsorship of the U.S. Environmental Protection Agency

Table 2. *Average AOC Concentration at Jefferson Parish, LA*

Treatment	*AOC, ug/L*
Nondisinfection	*10*
O_3 Contact chamber	*166*
O_3-Sand	*39*
O_3-Sand-GAC	*4*
Cl_2 Contact chamber	*5*
Cl_2-Sand-GAC	*3*

☆U.S. GOVERNMENT PRINTING OFFICE: 1993 - 750-071/80075

Wayne E. Koffskey is with the Jefferson Parish, Louisiana Department of Water, Jefferson Parish, LA 70121.
***Benjamin W. Lykins, Jr.** is the EPA Project Officer (see below).*
The complete report, entitled "Disinfection By-Product Formation by Alternative Disinfectants and Removals by Granular Activated Carbon," (Order No. PB93-222214AS; Cost: $36.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use
$300

EPA/600/SR-93/136

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35