



Project Summary

Alternative Disinfectants and Granular Activated Carbon Effects on Trace Organic Contaminants

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A study was conducted to evaluate the effects of alternative disinfectants on drinking water quality at Jefferson Parish, Louisiana, and the ability of granular activated carbon (GAC) to remove disinfection byproducts and specific organic compounds. Bacteriological information was collected on the influent and effluent of sand and GAC columns.

Four parallel pilot-column process streams were dosed with a different disinfectant (ozone, chlorine dioxide, monochloramine, and chlorine) and compared with a fifth pilot-column stream that was not disinfected. After 30 minutes of disinfectant contact time, the water in each process stream was passed through parallel sand, GAC, and duplicate GAC filters, each with 20 minutes of empty bed contact time (EBCT). Samples collected from each process stream were analyzed for total organic carbon (TOC), total organic halide (TOX), 10 volatile organics, 65 solvent-extractable hydrocarbons, 26 chlorinated hydrocarbon insecticides, heterotrophic plate count (HPC), total coliforms, and dissolved oxygen. To simulate distribution conditions, aliquots of each column effluent were dosed with monochloramine and free chlorine and analyzed for TOX and 10 volatile organics after storage for 5 days at river water temperature.

The process train that yielded the least dissolved organic contaminants was predisinfection with ozone followed by GAC filtration and postdisinfection with monochloramine.

This Project Summary was developed by EPA's Water Engineering Research 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

The Mississippi River along with its tributaries drains nearly two-thirds of the continental United States and supplies a source of drinking water to many cities located along its banks, including Jefferson Parish. The waters of the Mississippi River and its tributaries also receive vast quantities of industrial and municipal wastes as well as agricultural run-off that create various levels (ng/L) of trace organic contamination. In addition, significantly higher levels ($\mu\text{g/L}$) of organic contamination form when chlorine is used in disinfection. Therefore, a research project, funded jointly by the U.S. Environmental Protection Agency (EPA) and Jefferson Parish, was initiated to determine the effect of applying various disinfectants (ozone, chlorine dioxide, monochloramine, and chlorine) to clarified and filtered water followed by GAC adsorption.

Pilot-Column Plant

At the raw water intake of Jefferson Parish (located on the east bank above the mouth of the Mississippi River), raw water is pumped to four separate treatment plants. Nondisinfected clarified water was applied to the pilot-column

plant by the Permutit III plant (Figure 1).

Raw river water was clarified with diallyldimethylammonium chloride and/or dimethylamine type cationic polymers and fluoridated with fluosilicic acid before entering the pilot-column system. The clarified water was then filtered through one of two pressure sand filters and divided into five process streams.

Each disinfected process stream consisted of a 30-minute disinfectant contact chamber followed by parallel filtration through a sand column, a GAC column, and a duplicate GAC column. The duplicate column was used to determine variability between GAC columns within the same process stream. The configuration of the non-disinfected process stream was identical to that of the disinfected process streams except that the disinfectant contact chamber was eliminated.

All materials used to construct the pilot-column system (pumps, pressure sand filters, plumbing, contact chambers, and columns) were composed of stainless steel, teflon, or glass. Plastic flow totalizers were installed at the end of each process stream, but all samples were taken upstream. Each pilot column was constructed from 6-in. ID \times 10-ft glass pipe with 150 lb/in.² stainless steel flange ends and a teflon/stainless steel screen underdrain. The pilot columns

were charged with 6.8 ft of either sand or GAC media to obtain a 20-minute EBCT with a flow of 0.5 gpm.

Each disinfectant contact chamber was constructed from 12.75-in. OD (0.18-in. wall) stainless steel pipe with stainless steel blind flanged or capped ends. The chlorine dioxide, monochloramine, and chlorine contact chambers were 10 ft in height in order to produce 30 minutes of disinfectant contact time with a flow of 2 gpm. The ozone contact chamber was 11 ft in height and designed for countercurrent operation with the water entering at the top of the contact chamber and the ozone gas stream entering on the bottom. The water and ozone gas influent lines were oriented such that the influent water would be in contact with the ozone gas stream for 30 minutes. Ozone gas exiting the contact chamber was reduced by passage through a heated pelletized nickel oxide column to prevent condensation.

Ozone was generated from compressed dry air using an electrically powered ozone generator with a maximum output capacity of 0.25 lb/day. Chlorine dioxide was generated using two solutions, one containing sodium chlorite and sodium hypochlorite and the other containing sulfuric acid. Adding a 50% excess of sulfuric acid adjusted the pH of the final solution to 4.

These two solutions were pumped together and received in-line mixing in small generating tower constructed of teflon shavings and glass. All components that came into contact with chlorine dioxide were made of teflon or glass. This method generated a 96% yield of chlorine dioxide. Chlorine gas was fed to both the monochloramine and chlorine process streams using teflon eductors. Ammonia was added in the form of an ammonium hydroxide solution by pumping into the chloramine process stream ahead of the chlorine eductor.

Disinfectant Effectiveness

After 30 minutes, ozone residuals averaged 0.5 mg/L as O₃ and chlorine dioxide 0.5 mg/L as ClO₂. The average 30-minute residual for chlorite was slightly higher than that of chlorine dioxide at 0.6 mg/L as ClO₂. Essentially all of the chlorite resulted from the reduction of chlorine dioxide during the 30-minute contact period. This was determined by data generated from the chlorine dioxide demand analyses performed in a batch mode using deionized carbon filtered water and nondisinfected pilot-column influent water. The average concentrations of chlorine dioxide constituents in deionized carbon filtered water were 1.6 mg/L ClO₂, 0.0 mg/L ClO₂⁻, 0.2 mg/L Cl₂, 0.1 mg/L NH₂Cl, and 0.1 mg/L NHCl₂. Those residuals observed after 30 minutes of contact time with the influent water of the pilot column were 0.7 mg/L ClO₂, 0.6 mg/L ClO₂⁻, 0.1 mg/L Cl₂, 0.2 mg/L NH₂Cl, and 0.1 mg/L NHCl₂. An average chlorine dioxide demand of 0.9 mg/L as ClO₂ was seen with 0.6 mg/L or 67% reduced to chlorite.

Thirty-minute monochloramine residual averaged 2.1 mg/L as NH₂Cl or 1.4 mg/L as Cl₂. A dichloramine residual was also observed averaging 0.4 mg/L as NHCl₂. The average 30-minute chlorine residual for the chlorine process stream was 1.0 mg/L as Cl₂ with an average monochloramine residual of 0.2 mg/L as NH₂Cl and an average dichloramine residual of 0.3 mg/L as NHCl₂. The presence of 0.1 to 0.2 mg/L of naturally occurring ammonia nitrogen produced chloramines.

After 30 minutes of disinfectant contact time, ozone exhibited the highest level of disinfection followed by chlorine dioxide and chlorine whereas monochloramine was somewhat less effective. Chlorine dioxide, chlorine, and monochloramine became equally

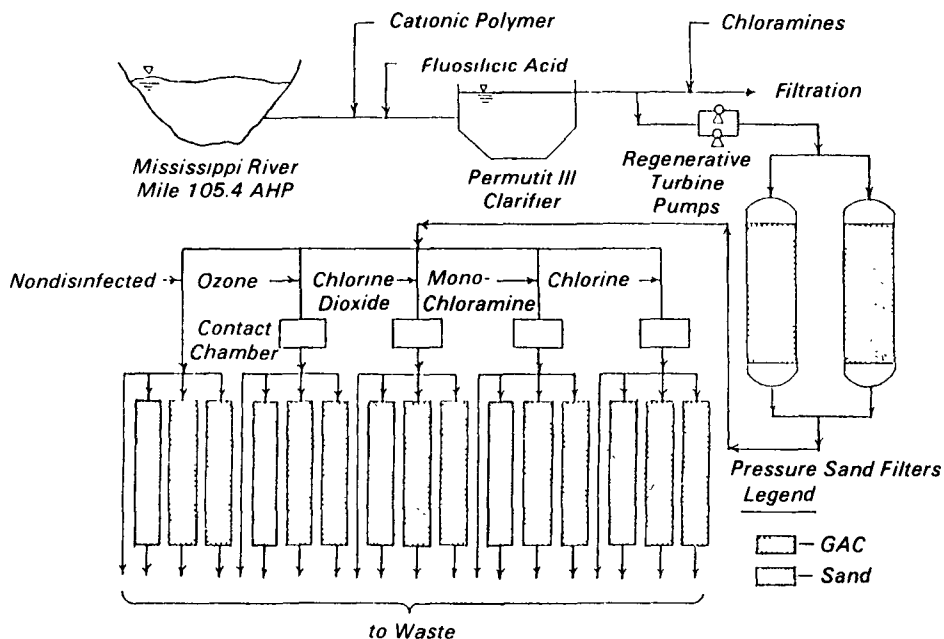


Figure 1. Pilot-column system flow schematic

effective after filtration through the sand columns. As ozonated water passed through the sand column, the geometric mean for the HPC rose from 8 to 4594 CFU/mL, indicating a biologically activated sand column. Whereas the geometric means for the HPC increased across the sand columns for all of the disinfected process streams, it decreased for the nondisinfected process stream. Because each disinfectant became ineffective in the first portion of each GAC column, the geometric mean of the HPC in the effluent of each disinfected GAC column increased to a level similar to that observed for the nondisinfected influent water of the pilot-column system. Most of the colonies picked from the heterotrophic plates were gram positive. Of the gram negative bacteria identified, *Pseudomonas*, *Alcaligenes*, *Moraxella*, and *Acinetobacter calcoaceticus* were observed most frequently. Some positive coliforms were observed, especially at the beginning of the study.

Organic Products

TOC and TOX surrogates were evaluated during this study. After 30-minute disinfection contact time, average TOC concentrations were 3.3, 3.0, 3.3, 3.4, and 3.3 mg/L for nondisinfected, ozone, chlorine dioxide, monochloramine, and chlorine, respectively. After sand filtration, the ozone stream showed a 0.5 mg/L concentration reduction. The TOC concentrations of the other streams were comparable to their influent values. GAC effluent concentrations at steady state (180 days) were 2.7 mg/L TOC for all disinfection streams except ozone (2.2 mg/L).

Average instantaneous TOX concentrations after 30-minute disinfectant contact time were 25, 15, 85, 117, and 263 $\mu\text{g/L}$ for nondisinfected, ozone, chlorine dioxide, monochloramine, and chlorine, respectively. TOX byproducts were formed after disinfectant addition except for the ozonated stream, where an average 10 $\mu\text{g/L}$ reduction was seen. Instantaneous TOX concentrations in the sand column effluents were comparable to their respective influents. GAC effluent instantaneous TOX concentrations were influenced by the amount applied to the columns. Higher influent produced higher effluent concentrations.

Flame ionization detection and electron capture chromatograms provided an overall indication of the effect of using various disinfectants. Compared

to nondisinfected water, chlorination produced the most peaks followed by chloramination, chlorine dioxide, and ozone. (Figures 2 and 3).

For the volatile organics detected (trihalomethanes, 1,2-dichloroethane, dichloromethane, trichloroethylene, 1,1,2-trichloroethane, and carbon tetrachloride), only the trihalomethanes were affected by disinfection. Average trihalomethane concentrations after 30 minutes of contact time were 1, 1, 1, 4, and 34 $\mu\text{g/L}$ for nondisinfected, ozone, chlorine dioxide, monochloramine, and chlorine, respectively. GAC removed the trihalomethanes formed by chlorination for about 60 days until breakthrough and for about 80 days for those formed by chloramination.

The nonvolatile organics identified in the pilot system influent consisted of 28 chlorinated hydrocarbons, 16 alkylbenzenes, 8 alkanes, 7 phthalates, 6 chlorobenzenes, 3 nitrobenzenes, 2 alkylaldehydes, tributylphosphate, triphenylmethane, 4-nonylphenol, and d-fenchone.

The herbicide atrazine and the insecticide alachlor were present in the influent to the pilot system throughout the study. Influent atrazine concentrations ranged from 23 to 249 ng/L with an average of 80 ng/L. The influent atrazine concentration was not affected by chlorine dioxide, chloramine, or chlorine disinfection. Compared with the nondisinfected influent, however, ozonation removed an average of 83% of the atrazine. Alachlor levels in the nondisinfected influent of the pilot column ranged from 13 to 593 ng/L with an average of 127 ng/L. Alachlor was also unaffected by chlorine dioxide, chloramine, or chlorine disinfection, but its concentration was reduced an average of 84% by ozonation.

Other chlorinated hydrocarbon insecticides (CHIs) were evaluated as a total sum of all the individual CHIs monitored during the study except atrazine and alachlor. The total CHI concentration in the nondisinfected influent ranged from 18 to 88 ng/L with an annual average of 36 ng/L. The concentration of these sub-

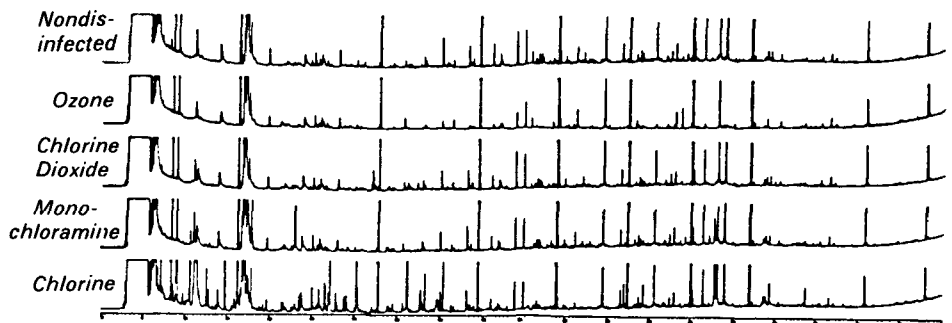


Figure 2. Flame ionization GC profiles after disinfection (runday 87).

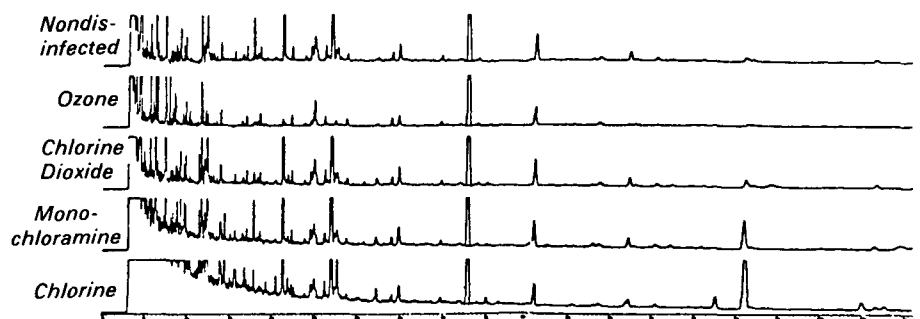


Figure 3. Electron capture GC profiles after disinfection (runday 87).

stances was unchanged after disinfection except for ozonation, which produced an average total CHI reduction of 57%.

The total alkylbenzene concentration in the nondisinfected influent ranged from 59 to 10,300 ng/L with an average of 590 ng/L. Thirty minutes of disinfectant contact time with chlorine dioxide, chloramine, and free chlorine produced an increase in the total alkylbenzene concentration of 11%, 14%, and 100%, respectively. Treatment with ozone, however, reduced the total alkylbenzene concentration by 52%. The total alkane concentration in the nondisinfected influent averaged 50 ng/L with a range of 10 to 150 ng/L. Ozonation reduced the concentration of the total alkanes by an average of 35%. Addition of the other disinfectants had no effect on the total alkane concentration.

The total phthalate concentrations in the nondisinfected influent ranged from 70 to 470 ng/L with an average of 180 ng/L. Ozonation produced an average total phthalate reduction of 11%. No significant changes in total phthalate levels occurred for the other disinfectants. Total chlorobenzene concentrations in the nondisinfected influent ranged from 4 to 304 ng/L with an average of 100 ng/L. Nitrobenzene concentrations ranged from a minimum of 0.1 ng/L for 2-nitrotoluene to 260 µg/L for 2,4-dinitrotoluene. Ozonation produced an average of 68% concentration reduction for total chlorobenzene and 61% for total nitrobenzene. Conversely, chlorination resulted in a 75% increase in total chlorobenzene and a 43% increase in total nitrobenzene.

Two alkylaldehydes, octanal and nonanal, were quantified. The total concentration of these two constituents for

the nondisinfected influent ranged from below detection (<0.1 ng/L) to 37 ng/L with an average of 14.4 ng/L. An average uniform increase in the total alkylaldehyde of 144% was observed in the ozonation system, whereas a relatively nonuniform increase of 56% occurred for the chlorine system relative to the nondisinfected influent. No significant changes in the concentration of total chlorobenzene, total nitrobenzene, and the alkylaldehydes were noted for the other disinfectants.

Sand filtration had some effect on the total alkylbenzenes, total phthalates, total chlorobenzenes, and total alkylaldehydes, with lower concentrations in the effluent as compared to the influent. On the average, GAC removed the chlorinated hydrocarbons 90% to 97%, total alkylbenzenes 40% to 45%, total alkanes 44% to 52%, total chlorobenzenes 93% to 96%, and total nitrobenzenes 81% to

92% for the 1-year operational period. The removal of total phthalates by GAC averaged 44% to 50% for about 250 days before the ozonated stream broke through.

Ozone appears to be the disinfectant of choice because lower concentrations of organics were detected during its use. More research is needed, however, to understand what happens to the organics after ozonation. Are these organics oxidized and destroyed; are they converted to other organics that are more biodegradable; are they more water soluble and not extractable, making them difficult to detect?

The full report was submitted in partial fulfillment of Cooperative Agreement No. CS806925 by Jefferson Parish, Louisiana, Department of Public Utilities, under the sponsorship of U.S. Environmental Protection Agency.

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The complete report, entitled "Alternative Disinfectants and Granular Activated Carbon Effects on Trace Organic Contaminants," (Order No. PB 87-146 700/AS; Cost: \$24.95, subject to change) will be available only from:

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