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Project Summary

Removing Organics from Philadelphia Drinking Water by Combined Ozonation and Adsorption

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Laboratory and pilot scale studies were conducted to investigate the combined unit processes of oxidation by ozonation and adsorption by granular activated carbon (GAC). In addition, the effect of chlorine and chlorine by-products on the ozone and GAC processes was investigated.

The study used Delaware River water that was treated by two coagulation/filtration plants: a full-scale plant operating with a 2 mg/L free chlorine residual and a 30,000 gpd pilot plant operating without any disinfection. The rapid sand filter effluents from each were applied to parallel GAC and O_3/GAC systems. The GAC beds remained in service between 360 and 500 days.

The removal of trace organics substances at the ng/L to μg/L level and the removal of TOC at the mg/L level were carefully monitored along with microbial parameters of biological speciation and growth rates. System comparisons were made using estimated total costs of each unit process, as determined by the carbon regeneration rate needed to maintain various effluent criteria.

This Project Summary was developed by EPA's Municipal Environmental 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

Removing trace organics from drinking water by adsorption onto granular activated carbon (GAC) has been repeatedly demonstrated during pilot plant research studies in Philadelphia, Pennsylvania. Though GAC systems are both technically feasible and operationally manageable, the substantial operating and maintenance costs associated with frequent carbon regeneration could place a severe economic burden on the water utility. Thus the primary concern for the practical use of GAC is to increase its useful bed life for removing trace organic compounds of potential health concern.

This study examines whether ozonation used as a pretreatment to GAC adsorption can increase the useful bed life of GAC sufficiently to justify its cost. The project is based on the fact that ozonation will transform some of the higher-molecular-weight humic substances into more readily biodegradable forms. These lower-molecular-weight organic compounds are then potentially available as a food source for microbes already present on the GAC bed. Preozonation may thus make available more adsorptive sites on the carbon for the less biodegradable, more harmful organic compounds that are poorly oxidized (e.g., chloroform and 1,2-dichloropropane). Preozonation may also help prolong GAC bed life by stripping volatile organic compounds from the process stream.

The present project was conducted on both a pilot and laboratory scale to investi-

gate the technical and economic feasibility of incorporating an ozonation and/or a GAC unit process into a conventional water treatment train to remove trace organics of health concern. The relationship between adsorption and biological activity during water treatment with ozone and GAC was carefully evaluated, as were the effects of prechlorination on these mechanisms. The removal of trace organic substances of health concern at the ng/L to μg/L level and the removal of TOC at the mg/L level were monitored along with microbial paramenters of biological speciation and growth rates. The engineering and economic analyses of the combined treatment systems were made in terms of the following health effects priorities:

Group I. Carcinogens and Suspected Carcinogens listed by
   (1) National Academy of Sciences (3,9)
   (2) National Cancer Institute (10)

Group IA. Mutagens, Teratogens and Promoters listed by
   (1) National Cancer Institute (10)

Group II. Priority Pollutants listed in
   (1) NRDC vs Train (11)

Group III. Other Compounds of Potential Health Effect listed by
   (1) National Academy of Sciences (9)

Group IV. Precursors -- those organic compounds that react with a disinfectant to produce a by-product that falls into groups I - III.

Group V. Humic Substances and Non-Health-Effect Compounds in High Concentration that can compete with.compounds of Groups I through III and cause earlier breakthrough of these compounds on GAC columns.

The specific criteria chosen for GAC regeneration are listed in Table 1. Except for the criteria based on the cumulative breakthrough of 50% of the dissolved organic carbon (DOC) and trihalomethane formation potential (THMFP), all of the criteria investigated are based on the effluent of a single filter, and not on the average effluent of a multiple-filter operation.

The following questions are addressed in this report:
1. Can enhanced TOC removal before GAC treatment increase the capacity of the GAC for the trace organics of health concern?
2. Can ozonation as a pretreatment to GAC adsorption increase the useful

bed life of GAC sufficiently to justify its cost?
3. How does prechlorination affect the ozonation process and the GAC adsorption capacity for chlorinated organics and other volatile organics?
4. Can a conventional treatment system be maintained without predisinfection? Can the bacterial integrity of the distribution system be maintained with only post-chlorination?

Process Description

This report provides a detailed analysis of the unit operations of ozonation and GAC treatment when used in combinations of O_3/GAC, O_3/SAND, Cl_2/GAC, Cl_2-O_3/GAC, and no disinfection/GAC following the conventional treatment processes of raw water settling, coagulation,

flocculation, sedimentation, and rapid sand filtration. Figure 1 presents a schematic of the five advance water treatment (AWT) systems evaluated in this study. Two of these systems received their water from the chlorinated rapid-sand-filter effluent of the Torresdale Water Treatment Plant, a conventional coagulation/filtration plant that supplies the City of Philadelphia with half of its daily water requirements. The remaining three AWT systems received the nonchlorinated rapid-sand-filter effluent of a 30,000 gpd pilot plant. The primary difference between the operations of the plants is the fact that only the Torresdale plant chlorinates its process water; the pilot plant does not practice disinfection of any kind. The purpose of using the two plants was to determine the effects of chlorination and chlorine by-
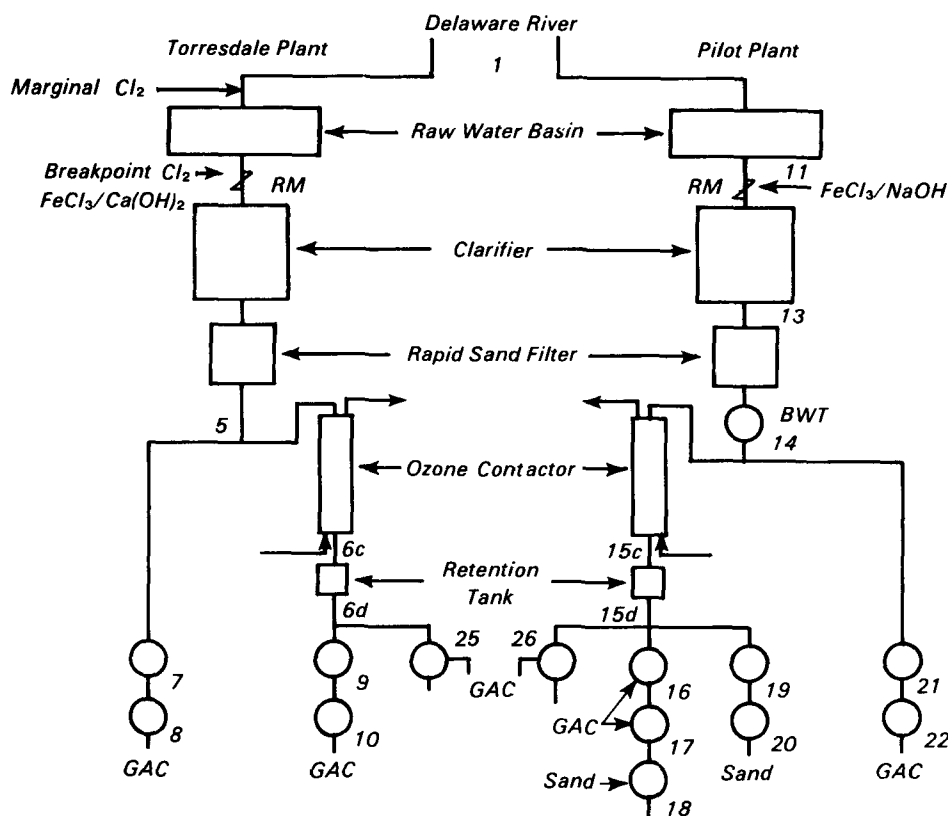
Table 1. Organic Criteria for GAC Regeneration

Parameter	Criteria Investigated
DOC	Effluent levels of: 0.5, 1.0, 1.5, and 2.0 mg/L
DOC, THMFP	50% cumulative breakthrough
Chloroform	Effluent levels of: 1, 10, and 100 μg/L
1,2-Dichloropropane	Effluent levels of: 1 and 5 μg/L
All volatile organic compounds with average concentration $\geq$ 0.1 μg/L	Average time to: Initial breakthrough 100% breakthrough

Figure 1. Schematic of the five advanced water treatment systems evaluated

products on the AWT systems investigated. Following conventional treatment, the rapid-sand-filter effluents of the Torresdale and pilot plants were applied to the ozone and the carbon contactors.

Both ozone systems used cocurrent flow, in which both the ozone gas and water enter the contactors from the bottom. For the diffusion of the ozone gas into water, a porous dome diffuser was used. The contactors were constructed of 316L stainless steel pipe that was 13 feet high and had an inside diameter of 10 in. To the extent possible, the two contacting systems were operated under identical conditions. Following ozonation, stainless steel retention tanks provided the ozonated water with sufficient contact time to yield an ozone residual below detectable limits. These tanks maximize the ozone/water contact time and minimize the possibility of oxidizing the carbon granules. A centrifugal pumping system then transfers the water from the retention tanks to the O_3/GAC and the O_3/SAND systems.

Conventional Treatment

Significant differences were observed in the DOC and THMPF effluent levels from the two conventional treatment systems. In fact, by postponing chlorination until after rapid sand filtration, the pilot plant conventional treatment processes reduced THMFP by a third during the 1-year period of study.

Two factors appear to have been primary influences. First, the two clarification systems varied greatly in their ability to remove DOC from their process streams. For example, the pilot plant clarifier (an upflow sludge contactor without clarification) removed nearly three times the DOC removed through the Torresdale clarification system (transverse flow-through paddle flocculators and sedimentation basins with chlorination). Second, a portion of the DOC normally found in the Delaware River Estuary was readily degraded by the bacteria present in the pilot plant conventional treatment train. Bacterial degradation of organics was only a factor in the pilot plant system, since the Torresdale plant inhibited bacterial growth through prechlorination.

In addition to THMFP and DOC reductions, postponing the chlorination process should be considered for another reason: Prechlorination at Torresdale appears to produce many more nonpolar compounds (both chlorinated and nonchlorinated), as observed from the broad spectrum analysis of extracts from macroreticular resin accumulators. These compounds could arise from oxidation and/or substitution of low-molecular-weight organics and high-molecular-weight humics by chlorine.

The operational integrity of the pilot plant was maintained continuously for more than 2 years without any predisinfection. With a covered raw water basin, clarifier, and rapid sand filters, no large algae blooms or filter-clogging bacteria were noted. But bacterial levels were high throughout the system, and higher forms of animal life (e.g., fresh water shrimp) were occasionally observed in the rapid sand filters during the summer months. Bench-scale testing indicated that satisfactory disinfection of the pilot plant water could be achieved with post-chlorination.

Ozonation Systems

The ozonation process affected the level of organic compounds (both natural and synthetic) in the Delaware River water through two mechanisms: oxidation and volatilization. To monitor this removal, TOC, UV adsorbance at 254 nm (A254), THMFP, and specific-compound chromatography were used. Stripping was the dominant mechanism for removing the specific volatile organic compounds below a C-8 hydrocarbon (as determined by the purge and trap method for both chlorinated and nonchlorinated water). Above the C-8 hydrocarbons, stripping still predominated for the chlorinated influent, but oxidation was the predominant mechanism for removing organics in the nonchlorinated influent (as determined by the XAD resin isolation method).

Many of the more hazardous organic substances found in the water supply are low-molecular-weight organic compounds that remain stable upon ozonation. Typically, these compounds have Henry's law coefficients greater than 1×10^{-3} atm-m^3/mole and may thus be easily stripped from the water. A good example of this class of volatile compound is chloroform.

Although volatilization plays a major role in removing the lower-molecular-weight organic compounds, it was of little significance to overall DOC removal. Only a small percentage (<1%) of the DOC reductions may be accounted for by the volatilization of chloroform and other easily stripped organics, as determined by performing mass balances across the contactors. Most DOC removal observed during ozonation resulted from the complete oxidation of organics to carbon dioxide.

GC profiles of volatile and semi-volatile organics provided evidence of the production of many organic compounds of unknown identity and unknown health concern during ozonation. Acetone was the only organic compound confirmed by GC/MS to be produced at detectable levels during the ozonation process. Since acetone is both highly volatile and biodegradable, it was not found in high concentrations in the O_3/GAC or O_3/SAND system effluents.

Prechlorination appeared to produce compounds that were more resistant to further oxidation by ozone (as measured by DOC, A254, and THMFP). This fact was most notable for THMFP. Although THMFP levels were consistently reduced when nonchlorinated water was ozonated, the ozonation of prechlorinated water caused both increases and decreases in THMFP. Averaged through the study period, ozonation increased the THMFP levels of prechlorinated water. Thus to oxidize organics by means of ozone, the applied water should not be predisinfected with chlorine.

Adsorption Systems

GAC systems remove both mg/L concentration of DOC and THMFP and ng/L to μg/L concentrations of trace organics of health concern. Within this framework, each of the four adsorption systems operated during the pilot-scale testing encountered varying levels of applied organic loads. In general, however, the following trend developed:

GAC(TP) > O_3/GAC(TP) > GAC(PP) > O_3/GAC(PP)

where TP = Torresdale plant and PP = pilot plant

The GAC(TP) system experienced the highest organic loads, and the O_3/GAC(PP) system experienced the lowest. This trend was observed for all of the organic parameters measured, including DOC and the volatile and semivolatile organics measured by the purge and trap and the MRR accumulator methods, respectively. The pilot plant adsorption systems experienced lower applied organic loads compared with the Torresdale plant systems for the reasons outline above for the conventional treatment processes. Organic levels decreased through the ozonation systems because of the production of carbon dioxide, the subsequent biodegradation of the partially oxidized products, and the volatilization of trace organics. In general, preozonation affected the concentration and types of organics applies to the GAC beds less than did the changes made in conventional treatment processes.

Sand has been used in this study as an inert medium control in which biological TOC removal can be observed separately from the combined adsorption/biological TOC removal observed on GAC. The basis for using sand beds in this manner was

developed in bench- and pilot-scale testing, which determined that the rate of biological TOC removal on sand was equivalent to that on GAC. Thus by comparing GAC, O_3/GAC, and O_3/SAND systems during steady-state DOC removal conditions, it was possible to estimate the relative contributions of adsorption and rapid biodegradation. It was thus determined that while preozonation increased overall DOC removal, no synergistic removal of DOC by the combined effects of adsorption and biodegradation were observed in the preozonated GAC systems.

The O_3/GAC and the GAC systems all proved capable of removing odoriferous compounds from the process water. This reduction was nearly complete and appeared to be unaffected by the length of time the carbon bed remained in service, the type of water applied, or seasonal or temporal changes. The use of ozone, either alone or in conjunction with GAC treatment, proved to be of little additional benefit in reducing the odor threshold.

Preozonation did not significantly alter the bed life of the adsorption systems when bed life was based on limiting the effluent levels of trihalomethanes, 1,2-dichloropropane and 10 other volatile organic compounds with average influent concentrations greater then 0.1 μg/L. The effect of preozonation on the time to both initial and 100% breakthrough for these compounds varied among compounds and systems, but maintaining GAC columns on line beyond 100% breakthrough always resulted in a chromatographic effect, in which the instantaneous effluent concentrations exceeded the influent concentrations. The chromatographic effect was frequently observed for chloroform through both the GAC and O_3/GAC systems. But the GAC systems retained the chloroform adsorbed before bed exhaustion, whereas the net adsorption of chloroform onto the O_3/GAC systems decreased nearly to zero following breakthrough. This result may have been due to the production of unidentified low-molecular-weight organics through the ozonation process; these organics then compete for the available adsorptive sites.

Cost Considerations

Several advanced water treatment schemes (Figure 2) were investigated to determine the economic feasibility of each to attain selected levels of organic removal at the Torresdale Water Treatment Plant. The results and operating parameters from the pilot-scale investigations were used as a basis for this economic feasibility study. The treatment processes investigated were
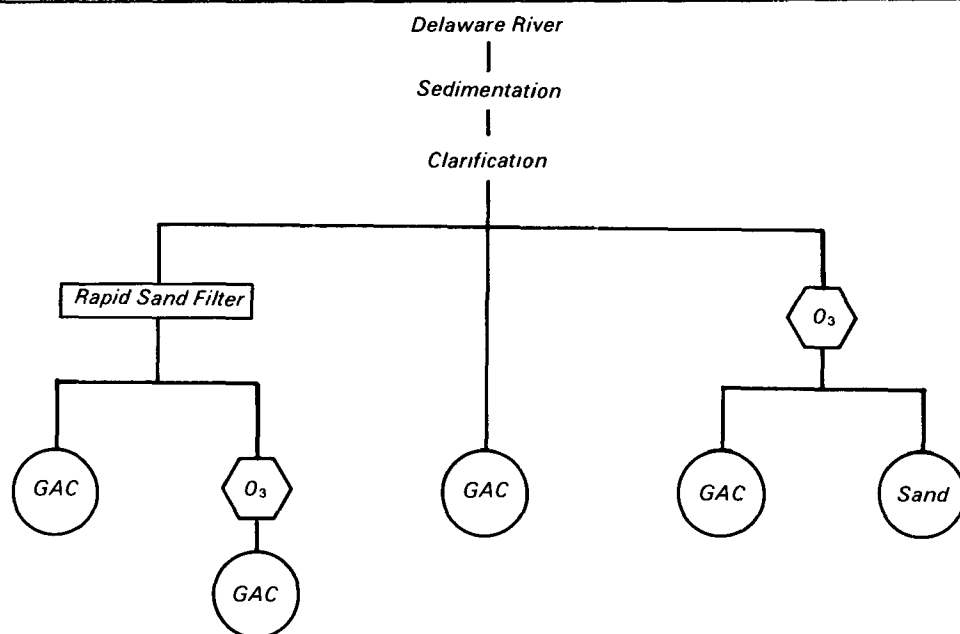

Figure 2. Advanced water treatment alternatives

GAC alone, GAC preceded by ozone (O_3/GAC), and ozone followed by sand filtration (O_3/SAND). Though both chlorinated and nonchlorinated systems were investigated, no consideration was given to any of the costs associated with modifications to the conventional treatment processes of the Torresdale plant to allow for a nonchlorinated treatment process. Table 2 lists the assumptions used in developing the costs.

To calculate the total costs of each of the treatment schemes, three unit processes were examined separately to determine the capital and operations and maintenance (O&M) costs associated with each: GAC postfiltration contactors, GAC filter/adsorbers, and ozone generators and contactors. In addition, the costs associated with carbon regeneration and/or replacement were examined. The economics of each process were affected by the capital,

Table 2. System Design Considerations

Flow			
Peak	480 mgd		
Average	282 mgd		

GAC Contactors	Post Filter	Filter/Adsorber
EBCT (min.)	15	13.8
Surface loading rate (gpm/ft^2)	4.9	2.0
Contactor construction	common wall concrete	common wall concrete (existing)
Number of contactor pairs	25	47
GAC bed depth (ft.)	10	3.75

Ozone System	
Ozone dose (Avg.)	2 mg/L
Contact time (min.)	20
Contactor construction	reinforced concrete (18 ft. deep, 2:1 length to width)

Carbon	
Cost	$0.70/lb
Loss/regeneration	7% (by weight)

Financing	
Bond interest rate	12%
Amortization period	25 years
Bond issue cost	40% of capital
Inflation for O&M	10% per year

O&M, and financial costs. All costs investigated were based on the Torresdale plant design flow of 282 mgd and an empty bed contact time (EBCT) of 13.8 min. for sand filter replacement (filter/adsorber mode) and 15 and 30 min. for the post contactor mode. Figure 3 presents the total first-year costs for the advanced water treatment systems at various carbon regeneration frequencies. More specifically, total first-year costs based on the bed life necessary to maintain various DOC, THMFP, chloroform, and DCP effluent criteria were also developed.

Conclusions

● Enhanced TOC removal before treatment does not appear to increase the adsorptive capacity of the GAC for the trace organics of health concern.

● The cost of preozonation is not sufficiently offset by the lowered GAC operating costs associated with less frequent GAC regenerations, when the removal of the halogenated, volatile organic compounds is the controlling criteria. For TOC reductions, preozonation may be cost effective, depending on the exact criteria chosen.

● Chlorination appears to produce compounds resistant to further oxidation by ozone and should thus be applied only after ozonation.

● Chlorination and ozonation each affect the adsorptive capacity of the specific organic compounds differently.

● GAC effluents were effectively disinfected with chlorine. No bacterial regrowth was found after 5 days.

● There were no operational problems associated with maintaining a conventional treatment system on line for over 2 years without any type of pre-disinfection.

The full report was submitted in fulfillment of Cooperative Agreement No. CR806256 by the Philadelphia Water Department under the sponsorship of the U.S. Environmental Protection Agency.
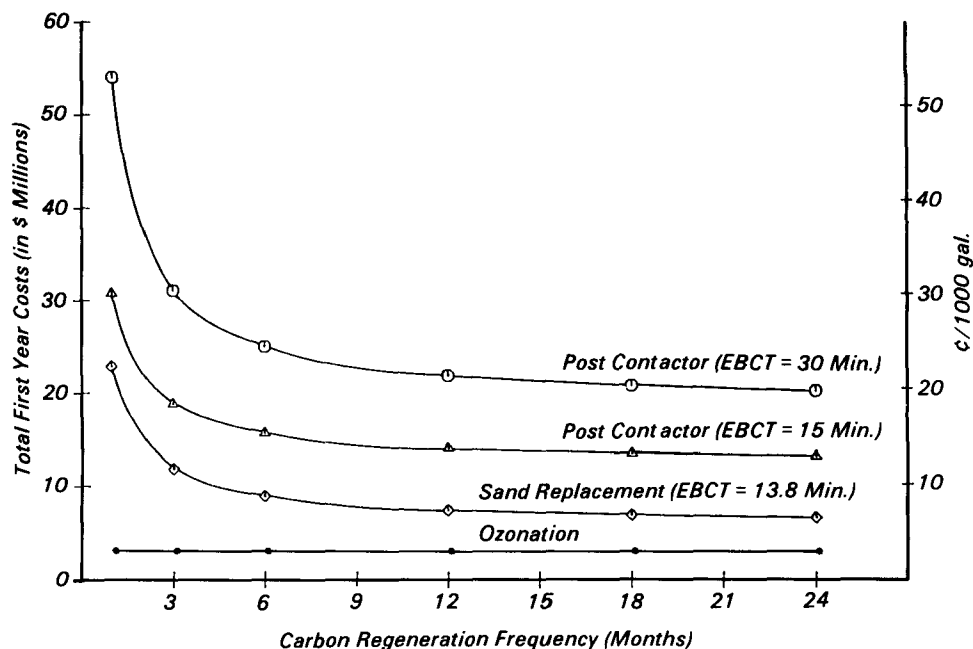

Figure 3. Advanced water treatment total cost for first year

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