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EFFECT OF PRE-OZONATION ON ORGANICS REMOVAL BY IN-LINE DIRECT FILTRATION

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ABSTRACT

A pilot-scale study of the effects of pre-ozonation on the performance of in-line direct filtration was carried out. Performance measures included filtered water turbidity, unit filter run volumes, and organics in filtered waters: DOC, UV254, AOC and DBPs. Continuous operation of four dual media GAC/sand filters with and without pre-ozonation and chlorinated backwash and a dual media anthracite/sand filter were compared to full-scale performance. Pre-ozonation frequently results in longer filter runs, causes a two-fold increase in raw water AOC and has little effect on raw water DOC. GAC/sand filters consistently reduced the AOC in the ozone train to levels below that of the full-scale plant and also provided 25 % lower DOC levels as compared to anthracite/sand filters. The effect of ozone and filtration on chlorinated DBPs followed overall DOC removal while DBPs created by ozonation followed AOC removal trends.

KEYWORDS

Direct filtration; pre-ozonation; assimilable organic carbon; dissolved organic carbon; disinfection by-products.

INTRODUCTION

In direct filtration facilities for the treatment of drinking water, the removal of dissolved organic constituents is controlled by chemical addition (oxidants and coagulants), mixing processes (rapid and slow), particle deposition in granular media filters, and sorption and biodegradation in the filter. The type and dose of any pre or intermediate oxidants and the types and doses of coagulants affect the nature of dissolved and particulate organic substances, their incorporation into particles which may be removed by filtration and their removal by sorption or biodegradation. The objective of this paper is to examine the effects of pre-ozonation on the removal of organic substances and on the general performance of in-line (no flocculation) direct filtration. Organic substance removal was determined by measurement of several parameters: dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV254), assimilable organic carbon (AOC) and disinfection by-products (DBPs).

The work has involved conducting pilot-scale filtration experiments using a pilot facility located inside the West River Treatment Plant (WRTP). The 0.46 m^3/s (10.4 million gallon/day) capacity WRTP is an in-line direct filtration facility including potassium permanganate addition, coagulation with alum (or ferric chloride) and cationic polymer, dual media (anthracite/sand) filters, and disinfection with free chlorine. Raw water for the WRTP is taken from three impoundments of the West River. The relatively high quality raw water is characterized (average values) by low turbidity (1 NTU), low DOC (3 mg/L), and low alkalinity and hardness (i.e., 20 mg/L as $CaCO_3$). The pilot facilities and the WRTP are owned and operated by the South Central Connecticut Regional Water Authority (SCCRWA) headquartered in New Haven, Connecticut.

The SCCRWA is investigating the use of alternative pre-oxidants in order to improve treated water quality and to comply with various recent and soon to be enacted federal drinking water regulations. For example, ozonation may be appropriate for achieving required disinfection effectiveness and for reducing the formation of some disinfection by-products (DBPs). While the use of ozonation is relatively common in Europe, it is not utilized extensively in the United States. It is well known that ozonation can affect coagulation and filtration, oxidize reduced metals (Fe, Mn), and cause the organic matter in a water to become more biodegradable (Langlais et al., 1990). Thus the focus of this study has been the impact of pre-ozonation and biologically active filters on organics removal and filtration performance.

EXPERIMENTAL METHODS

The pilot experiments involved operation of two parallel treatment trains. Samples were collected at various locations along the pilot treatment trains and from the full-scale plant. The pilot trains did not include a pre-contact tank for permanganate addition as is practiced in the full-scale plant but could include one or two contactors for pre-ozonation. Ozone was generated from air and applied in a counter-current manner in a 0.3 m diameter by 3 m tall tank (nominal 5 minute hydraulic detention time at a water flow of 38 L/min). In 1991, the pilot plant was operated continuously and included four granular activated carbon/sand (GAC/S) dual media filters and one anthracite/sand (A/S) dual media filter; one train included pre-ozonation while the other did not. In the pre-ozone train, ozonated water was coagulated and applied to two parallel GAC/S filters, one of which (#1) was backwashed with non-chlorinated water (full-scale filter effluent) while the other (#2) received chlorinated backwash water (1.3 mg/L free chlorine). Coagulated water from the no ozone train was applied to three parallel filters, two of which had GAC/S media, one (#3) with chlorinated backwash and one (#4) with non-chlorinated backwash. The third filter for the no-ozone train had anthracite/sand media and had non-chlorinated backwash. Chlorinated backwash was only used for filters 2 and 3 and only until 10 July 1991. The coagulant doses being used in the full-scale plant were also used in the pilot plant: 10-12 mg/l of alum in combination with 0.5-1.5 mg/l of polymer.

Water quality analyses were conducted at three locations: on-site at the WRTP; by the SCCRWA laboratory; and at the UMass Environmental Engineering laboratories. On-site analyses included turbidity, ultraviolet light absorbance at 254 nm wavelength (UV254), temperature, pH, ozone transfer efficiency, aqueous ozone residual, and filter headloss. The SCCRWA laboratory conducted flavor profile analyses as well as some total organic carbon (TOC) and heterotrophic plate count (HPC) analyses. Measurements of manganese (Mn), dissolved organic carbon (DOC), assimilable organic carbon (AOC), aldehydes, ketoacids, and formation potential for chlorinated DBPs (pentane extractables (PE), haloacetic acids and chloral hydrate) were made at the UMass laboratories.

Although a detailed description of each analytical method is not possible in this paper, key features of selected methods are presented. Samples for DOC and UV254 analyses were filtered through a pre-washed glass fiber filter (Whatman GF/C). DOC samples were then acidified, sparged with nitrogen and analyzed using the UV-persulfate oxidation method with a Dohrmann DC 80 instrument. AOC was determined using a modification of the van der Kooij et al. (1982) method developed by Kaplan (Standard Methods, 1990). The method involves simultaneous inoculation and growth of two bacterial strains, P17 and NOX. For this work, bacterial growth (CFU) was converted to equivalent carbon concentrations based on published yield values for growth on an acetate substrate (van der Kooij et al., 1989). Disinfection by-products were determined using gas chromatography following appropriate sample extraction and derivatization procedures (Koch et al., 1988; Hwang et al., 1990; Glaze et al. 1989).

RESULTS AND DISCUSSION

Results for the effects of pre-ozonation on general filter performance and the removal of DOC, AOC, and DBP precursors are presented and discussed.

General Filter Performance. Pre-oxidation with 0.5-1.5 mg/L of applied ozone usually does not have a large impact on general filter performance as assessed by filtered water turbidity and headloss development. Results from earlier pilot studies at the WRTP involving intermittent filter runs indicated that pre-ozonation sometimes resulted in significantly longer filter run times due to decreased head loss development or a delay in turbidity breakthrough (Tobiason et al., 1992). Results of this earlier work also showed that pre-ozonation did not alter the required doses of alum and polymer for good treatment. Ozonation often causes a very slight reduction in filtered water turbidity as compared to no oxidation or to the full-scale plant (i.e., 0.01 - 0.02 NTU less at levels of 0.01 to 0.05 NTU).

The results from continuous pilot plant operation in 1991 have shown limited effects of pre-ozonation on filtered water turbidity and headloss development. Turbidity data from dates when sampling for organic analyses was undertaken are shown in Figure 1. These results, and the daily data, indicate that pre-ozonation (1.5 mg/L applied except for 3.0 mg/L on 3 Oct. 91) had no consistent effect on raw water turbidity, that turbidity following rapid mix was similar for the pilot trains and the full-scale plant (increase due to coagulant addition and precipitation of organic matter), and that the filtered waters all had similar low turbidities in the range of 0.01 to 0.03. Results of particle size distribution analyses (2 to 120 microns, 15 channels) typically show that the filtered water from the ozone train has a somewhat lower particle number concentration than the no-ozone train or the full-scale plant.

The effects of treatment on headloss development are shown in the form of unit filter run volumes (UFRV), the volume of water filtered per unit surface area of filter prior to backwashing. For this study, backwashing and UFRV results are based on the development of 2.4 m (8.0 feet) of headloss. Average UFRV data for approximately monthly periods for the five pilot filters and the full-scale plant in 1991 are shown in Figure 2. During this period, the pilot filters were operated at a filtration rate of either 3.7 or 7.3 m/hr (1.5 or 3.0 gpm/sq ft) while the full-scale plant operated between 5.4 and 7.3 m/hr. The data in Figure 2 require explanation. First, it is important to note that filters 2 and 3 were backwashed with chlorinated water from start-up in January until 10 July 1991. On this date, these two filters were taken out of operation due to excessive headloss development, as indicated in Figure 2 by the steady and extensive decline in UFRV relative to the other filters that begins in April. Although filter 2 received pre-ozonated water and filter 3 did not, their behavior was similar, suggesting that the chlorinated backwash caused the problem. It was also observed that these filters lost more media than the other filters and that this was associated with foaming during backwashing. A sieve analysis of filter media samples from all the GAC/S

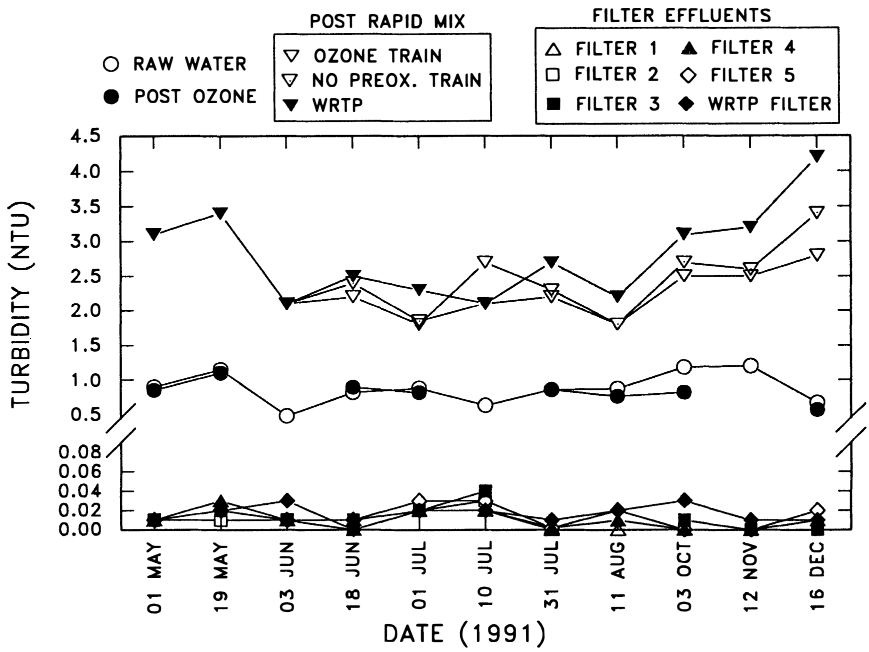

Fig. 1 Summary of turbidity for 1991 sampling dates.

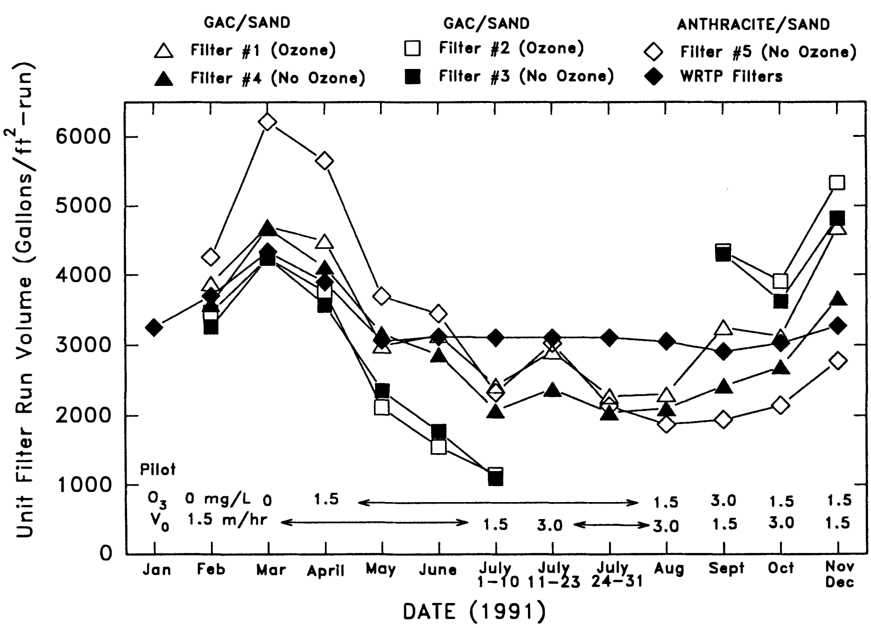

Fig. 2 Unit filter run volumes by month during 1991.
(N.B. 1000 gallons/ft2 $\simeq$ 41.4 m^3/m^2)

filters showed that the effective size (ES) of the chlorinated backwash filters had decreased relative to the non-chlorinated filters (0.51 - 0.61 mm versus 0.81 - 0.87 mm) and that the uniformity coefficient (UC) had increased (2.2 versus 1.85). The non-chlorinated filters had not changed significantly from their original size classification. The sieve analysis results account for the greater headloss and shorter UFRVs for filters 2 and 3. These filters were placed back in service in September with new and larger GAC media (8 X 20, 1.07 mm ES, 1.53 UC). The results in Figure 2 indicate that the ozone train filters (1 and 2) often exhibit longer UFRVs than their non-ozone counterparts (3 and 4). The difference in UFRV appears to be more for the smaller GAC (8 X 30, #1 and 4) and for lower filtration rates. The difference can be quite consisitent on a daily basis. For example, daily results for the period 15 October to 10 November 1991 (7.5 m/hr rate) are shown in Figure 3. The effects of GAC size and ozone are apparent. The 8 X 20 GAC typically yields significantly longer UFRVs than the full-scale plant, however, the effects of ozone are not always significant. For example, during a recent (March 1992) period of constant 7.3 m/hr filtration, there was no difference in UFRVs between the ozone and no ozone trains.

Dissolved Organic Carbon and UV254. The effects of pre-ozonation and filter media type on natural organic matter removal are investigated by measurements of DOC and UV254, frequently a useful surrogate for DOC for a given source water. The results of UV254 analyses for various sampling dates in 1991 are shown in Figure 4. The results show that raw water levels were reduced by 30 to 40 % by ozonation alone (1.5 mg/L applied, 3.0 mg/L on 3 Oct 91) and that the effect of ozonation is apparent in the consistently lower filtered water UV254 values for the ozone train GAC/S filters (1 and 2) as compared to the no ozone train (3 and 4). The results also show that the UV254 levels for the full-scale WRTP and the A/S pilot filter (5) filtered waters are the same, indicating the ability of the pilot filter to simulate full-scale water quality. In addition to the ozonation effect, note that the GAC/S filters without pre-ozone always have lower UV254 than the A/S filters. This appears to be a steady state result as most of the GAC/S filter results are for periods after general breakthrough of DOC and UV254. The exception is for 3 October 1991, two weeks after the re-start of filters 2 and 3 with virgin GAC media. Thus the GAC/S filters cause a reduction in UV254 due to sorption and/or biodegradation.

The UV254 results are somewhat mirrored by results for DOC measurements for the same period (Figure 5). One difference is that there is not a consistent decrease in DOC following ozonation, a result in accord with the ozonation conditions of approximately 0.5 mg ozone absorbed per mg of DOC (for a 1.5 mg/L ozone dose). The results for 23 February and 3 October illustrate the need to operate GAC/S filters for considerable time periods prior to assessing DOC removal; in both cases the filters had recently (2 - 4 weeks) been placed in operation with new GAC so the DOC levels are very low. In contrast to the UV254 results, the DOC levels in the GAC/S filtered waters are similar for both the ozone and no-ozone trains. However, the effect of the GAC media is apparent as DOC levels in GAC/S filter effluents are generally lower than in A/S filtered waters. As with the UV254 data, results for the WRTP and the pilot A/S filter (5) are very similar. Average DOC levels at various treatment steps for the period 1 May to 1 July 1991 are shown in bar graph form in Figure 6, clearly illustrating the effects noted in the above discussion. Note also that the DOC levels for filters 2 and 3 are somewhat higher than for filters 1 and 4, perhaps reflecting negative effects of chlorinated backwash on biodegradation and DOC removal.

Assimilable Organic Carbon. AOC is one measure of the biodegradable organic matter in a water and is an indicator of biological stability with respect to regrowth in distribution systems (Huck, 1990;LeChevallier et al., 1991). The West River supply is relatively stable with respect to biodegradation as evidenced by a mean raw water AOC value of approximately 50 μg/L of acetate-C equivalents (combined P17 and NOX). The raw water AOC ranges from 25 to 100 μg/L of acetate-C equivalents with typically 60 to 90 % attributed to P17 growth. Pre-ozonation increases AOC by a factor of 2 on average (1.5 to 4 range) and increases the fraction attributed to NOX growth. Results of the earlier (1990) intermittent pilot experiments

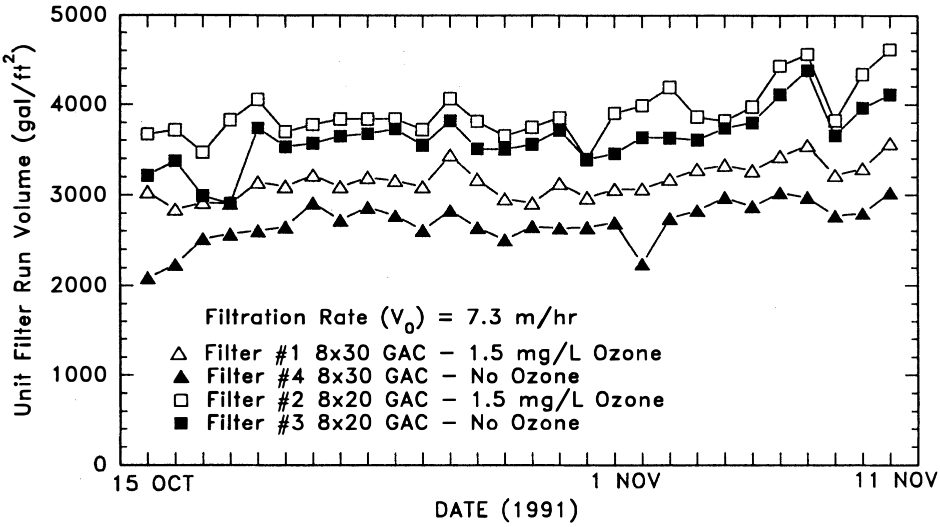

Fig. 3 Daily unit filter run volumes for GAC/sand pilot filters.

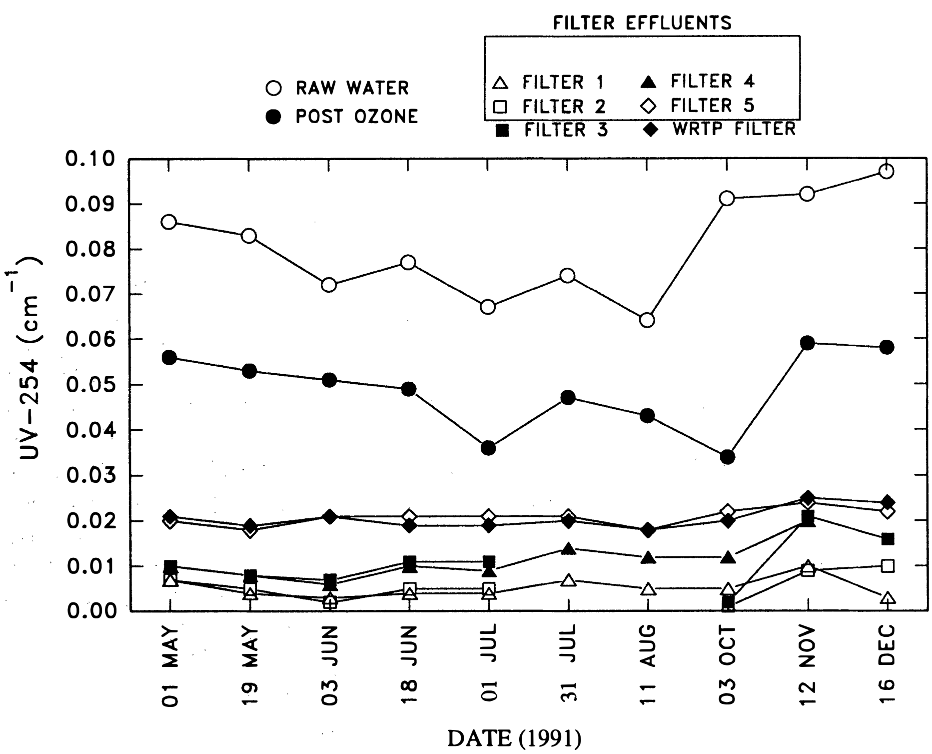

Fig. 4 Summary of UV254 for 1991 sampling dates.

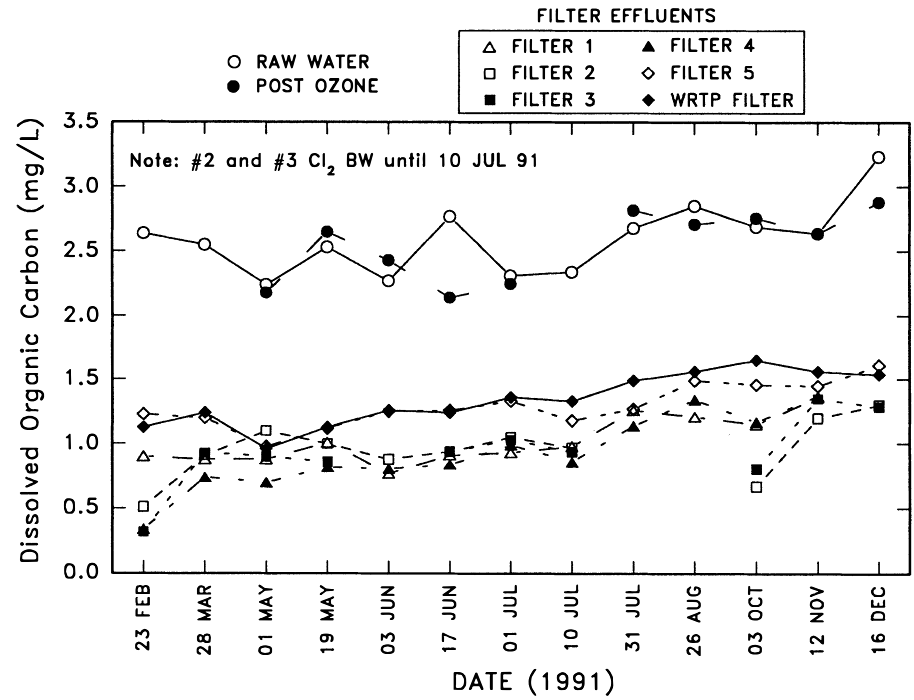

Fig. 5 Summary of dissolved organic carbon results.

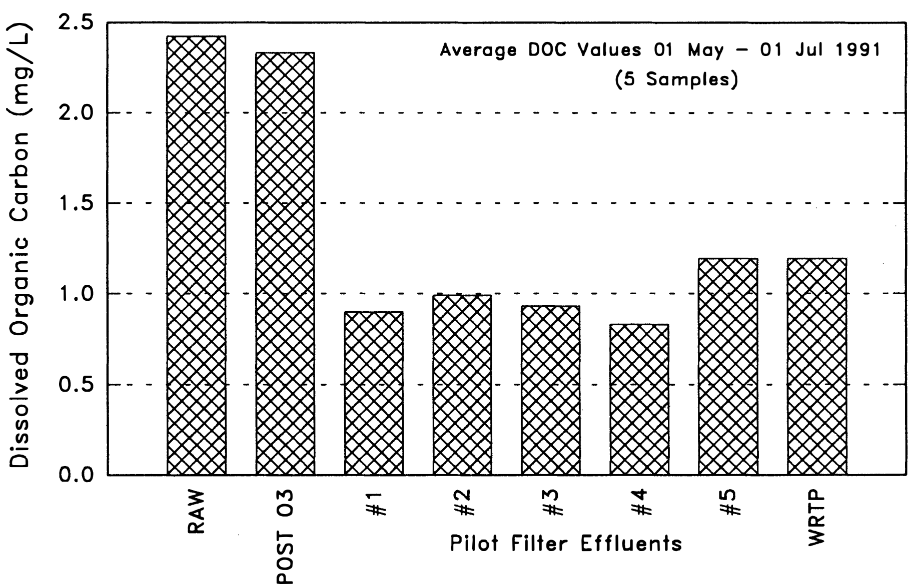

Fig. 6 Average DOC across treatment, 01 May - 01 July 1991.

show that filtration of pre-ozonated water through non-biologically active A/S filters results in AOC levels that remain significantly greater than levels in filtered water from the full scale plant. In contrast, results from the continuous pilot experiments in 1991 show that biologically active GAC/S filters (without chlorine backwash) that receive pre-ozonated water achieve a reduction in AOC to levels below that of non-ozonated waters filtered with conventional dual media. This is shown in Figure 7 where average AOC levels for the period 1 May to 1 July 1991 are shown as a function of treatment step. Note again that poorer organic removal is found for the GAC/S filters with chlorinated backwash (2 and 3) than for their non-chlorinated partners (1 and 4). A review of all the AOC results indicates that water temperature and filtration rate did not have a large impact on AOC removal.

A comparison of AOC and DOC removal by GAC/S filtration of pre-ozonated water and by A/S filtration of non-ozonated water is shown in Table 1. For AOC, the results show that A/S filtration does not achieve significant AOC removals on average. However, despite a doubling of AOC by ozonation, the biologically active GAC/S filters achieve AOC levels that are less variable and approximately one half the level of the A/S filtered water. The DOC results show that preozonation does not significantly alter the DOC level and that GAC/S filtered water DOC levels are approximately 25 % lower than A/S filtered waters. The difference between the relative magnitude of the treatment effects for AOC and DOC is most likely a result of the relatively small fraction of the total DOC that the AOC represents.

Disinfection By-Products. The DBP results include two general classes of organics; precursors for chlorinated organics, as measured by a chlorinated DBP formation potential (Cl-DBPFP), and oxidation (especially ozonation) by-products (OBPs), as measured by instantaneous aldehyde and ketoacid concentrations. In general it is found that the effects of treatment on Cl-DBPFP follow the DOC results while effects on OBPs follow AOC results. An exception is the direct effect of ozonation on some components of the Cl-DBPFP of the raw water.For the West River supply, pre-ozonation results in a 15-40 percent reduction in trihalomethane formation potential. The magnitude of the ozone effect on CL-DBPFP is significantly reduced for filtered waters, reflecting a higher fractional removal of THM precursors than of overall DOC by coagulation. Thus the reduction in DOC achieved by the GAC/S filters as compared to the A/S filters is also approximately found for Cl-DBPFP.

Ozonation by-products include the relatively biodegradable aldehydes (formaldehyde, acetaldehyde) and ketoacids (pyruvic acid, glyoxylic acid, ketomalonic acid). Results indicate that the OBPs formed by ozonation are readily removed by biologically active GAC/S filters to levels as low as found in non-ozonated filtered waters. Further evidence of the importance of biodegradation and the negative impact of chlorinated backwash was found when some of the OBPs were added to the pilot plant raw water in a spike experiment. The results showed that removal increased with decreasing filtration rate and that removal was worst for the filters receiving chlorinated backwash and best for the ozone train GAC/S filter without chlorinated backwash.

CONCLUSION

In general, pre-ozonation does not have a large impact on the classical performance of the in-line West River filtration plant. Increased filter run times are frequently, but not always, found for filters with pre-ozonation as compared to filters without pre-ozonation. The 8 X 20 GAC/S dual media filter performed well, achieving significantly longer filter run times than the full-scale plant. The effects of pre-oxidation with ozone on organics removal by in-line direct filtration depend on the organic parameter being measured, the media type and the biological activity of the filters. DOC levels were consistently lower for GAC/S filter effluents as compared to A/S filters but the impact of pre-ozonation was small. The AOC

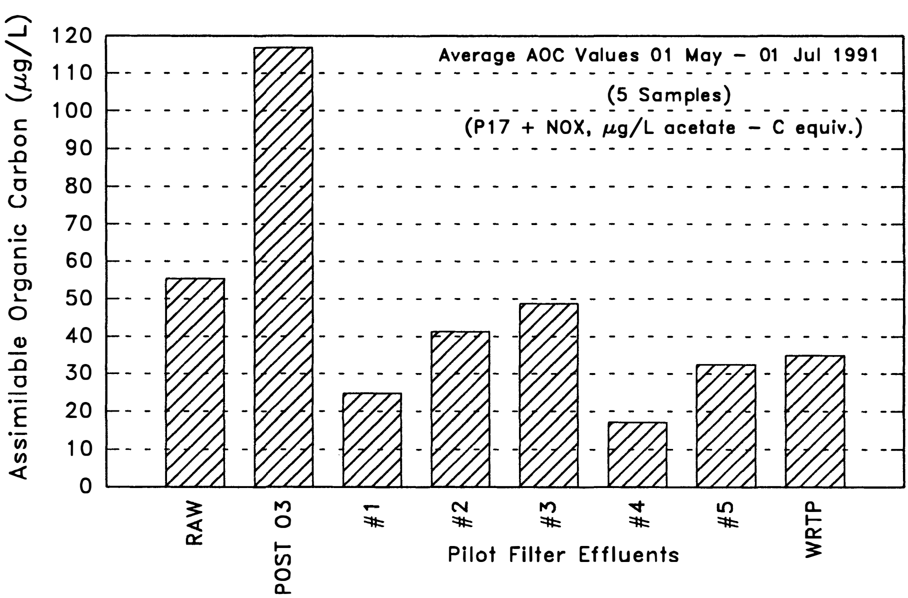

Fig. 7 Average AOC across treatment, 01 May - 01 July 1991.

TABLE 1 Summary of AOC and DOC Results

Sample	AOC[1] (µg/L) Mean	AOC[1] (µg/L) S.D.	AOC[1] # Samples	DOC[2] (mg/L) Mean	DOC[2] (mg/L) S.D.	DOC[2] # Samples
Raw	52	25	10	2.6	0.29	11
Post-O_3	95	25	10	2.5	0.31	11
Filter Effluents:						
O_3-GAC/S	24	9	8	1.1	0.19	11
WRTP	45	34	8	1.4	0.29	11

S.D.: Standard deviation.

1. AOC: Assimilable organic carbon, µg/L acetate-C equiv, P17 + NOX.

2. DOC: Dissolved organic carbon.

content of the raw water was often doubled by ozonation but this level was quickly reduced to less than that of non-ozonated filtered water by biologically active GAC/S filters. Chlorinated disinfection by-product precursor removal largely followed overall DOC removal while the ozone by-product levels followed AOC results.

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