Ozone and Biofiltration: Promising Technologies for DBP Removal and T&O Control

Bhavana Karnik, PhD and Sunil Kommineni, PhD, PE, BCEE
Malcolm Pirnie, Inc.,
1700 W. Loop South
Houston, TX 77027

ABSTRACT

There are two popular approaches that the water systems can take to reduce DBPs, DBP precursors and T&O compounds: (i) switching to alternative disinfectants like ozone, chloramines or chlorine dioxide in place of chlorine for primary disinfection and (ii) reducing the DBP precursors (e.g., natural organic matter (NOM)) by using treatment technologies like enhanced coagulation (EC), ozonation or granular activated carbon (GAC) biofiltration. Ozone-assisted GAC biofiltration (OAB) combines the two approaches and provides benefits both in terms of reducing the reliance on chlorine for primary disinfection and removing DBP precursors.

In OAB, application of ozone is expected to breakdown the natural organic matter (NOM) into bioassimilable organic carbon which aides in reducing the DBP precursors, MIB/geosmin and serves as a barrier to emerging contaminants (endocrine disrupting compounds and pharmaceutically-active compounds).

A pilot study was conducted using four, 3-inch diameter filters and two, 8-inch diameter filters filled with granular activated carbon (GAC)/sand and anthracite/sand. The loading rates were 4 gallons/minute-square foot (gpm/sf) or 6 gpm/sf. Ozone was applied in a counter-flow contactor with a residence time of 2-4 minutes and was dissipated in a dissipation system that provided an additional 8-10 minutes of contact time. No residual ozone was present in the water that was applied to the filters. Water samples collected before/after ozonation and biofiltration were analyzed for MIB/Geosmin, TOC, heterotrophic plate counts, and disinfection by-products.

The finding of the study indicated

- The NOM removals measured by Ultraviolet (UV) 254 and dissolved organic carbon (DOC) were higher in GAC biofilters compared to the anthracite biofilters.
- The TTHMs and HAAs concentrations were lower in GAC-biofiltered waters compared to the anthracite-biofiltered waters.
- OAB was successful in removing the T&O compounds from the surface water. Operated at optimum conditions, OAB would be one of the economical alternatives for MIB/Geosmin removal from the potable waters.

This paper will be useful for water treatment professionals including water utility managers, consultants, manufacturer representatives and academic members that are using or considering to use ozone and biofiltration for DBP and T&O control.

KEYWORDS

Ozone, biofiltration, taste and odor, T&O control, DBPs, GAC, MIB, geosmin.

STUDY OBJECTIVES

The goals of pilot testing were:

- To evaluate the effectiveness of GAC biofilters versus anthracite biofilters in the removal of NOM, TTHMs and HAA5
- Removing MIB and geosmin by OAB treatment.

INTRODUCTION

In the past decades, there has been tremendous emphasis on developing solutions for addressing multiple drinking water issues. In the quest to meet stringent regulatory requirements and fulfill customer demands, water purveyors are always on the lookout for promising, economic and feasible technologies.

The Maximum Contaminant Levels (MCLs) for total trihalomethanes (TTHMs) and haloacetic acids (HAA5) are 80 micrograms/liter (µg/L) and 60 µg/L respectively. The algal growth in surface waters lead to earthy/musty odor from the release of methyl-iso-borneal (MIB) and geosmin. The odor threshold for MIB/geosmin is 5-10 nanograms/liter (ng/L).

This report summarizes the objectives, methods and key findings of the pilot study.

METHODOLOGY

A careful evaluation of the design and the operational parameters is necessary in order to introduce any changes to the current treatment processes to achieve enhanced coagulation (EC) and incorporating additional treatment processes such as granular activated carbon (GAC) filter adsorbers and ozone at the City WTPs. In order to develop the design and operating criteria for GAC filter adsorbers and intermediate ozonation (ozonation before filtration) a pilot study was performed over a period of six months. This pilot study was conducted at Squaw Peak Water Treatment Plant (WTP).

This study evaluated a promising approach for removing DBPs and MIB/geosmin. In this approach, ozone is applied as an intermediate oxidant. Ozonation of NOM results in biodegradable products such as organic acids, aldehydes and ketoacids (Siddique et al., 1997). These organic by-products serve as carbon source for bacteria in the biologically active filters. OAB is based on the synergy between ozonation and biofiltration processes.

Figure 1 shows a schematic of the pilot system. As shown in this figure, the pilot facility receives settled water from the full-scale plant.

Details of the pilot filters design and operation are shown in Figure 2. All filters were dual media filters with either GAC/sand or anthracite/sand as the media. The depth of GAC or anthracite was 20-inches. The depth of sand media in each filter was 10-inches. The pilot filters were operated at loading rates of either 4 gpm/sf or 6 gpm/sf. The loading rates at which each filter was operated are shown in parenthesis underneath each pilot filter in Figure 2. Loading rates of 4 gpm/sf and 6 gpm/sf resulted in EBCT of 6.3 minutes and 4.3 minutes, respectively.

The GAC used in the pilot filters was obtained from one of the full-scale plant filters. This GAC was used in the full-scale plant filter for more than three years. The purpose of using aged GAC was to minimize adsorption and evaluate the removal of MIB and geosmin by biofiltration. The filters were acclimated for more than four months prior to performing the experiments. Each experiment was conducted over a period of one-two weeks.

Ozone was applied in a counter-flow contactor with a residence time of 2-4 minutes and was dissipated in another contactor that provided an additional 8-10 minutes of contact time. Sodium thiosulfate was added to the effluent from the ozone dissipation tank to quench residual ozone. No residual ozone was present in the water that was applied to the 3-inch diameter filters. Digital photos of ozonation and biofiltration systems are shown respectively in Figures 3 and 4.

A portion of the settled water is spiked with MIB and geosmin and passed through the large, 8-inch diameter filters. The remaining portion of the water is passed through ozone contact/dissipation system, spiked with MIB/geosmin and passed through the small, 3-inch diameter filters. The MIB and geosmin were continuously spiked into the influent waters to the large and small filters. The targeted MIB and geosmin concentrations in the spiked influent waters to the small and large filters were 25 and 50 ng/L, respectively.

The stock solutions for spiking were prepared using solid MIB and geosmin that was obtained from Wako Chemicals, USA. The MIB and geosmin that was used in this study was not in methanol or other solvents. Since MIB and geosmin are fairly volatile, the stock solutions were stored in gas sampling bags to avoid headspace. The MIB and geosmin concentrations stayed steady in the gas sampling bags over the periods of 1 to 3 weeks (the timeframe over which the bags were getting emptied).

Parameters such as flow, headloss, turbidity, UV absorbance at 254 nanometers, temperature and pH were measured two-three times per week. Water samples collected before and after ozonation and biofiltration were analyzed for MIB, geosmin, TOC, heterotrophic plate counts (HPCs), bromide, bromate, trihalomethanes (THM) and haloacetic acids (HAA5). The biological filter performance was assessed in terms of the removal of MIB, geosmin, TOC, particulates and microbial parameters.

Figure 1 - Schematic of Pilot Test Facility

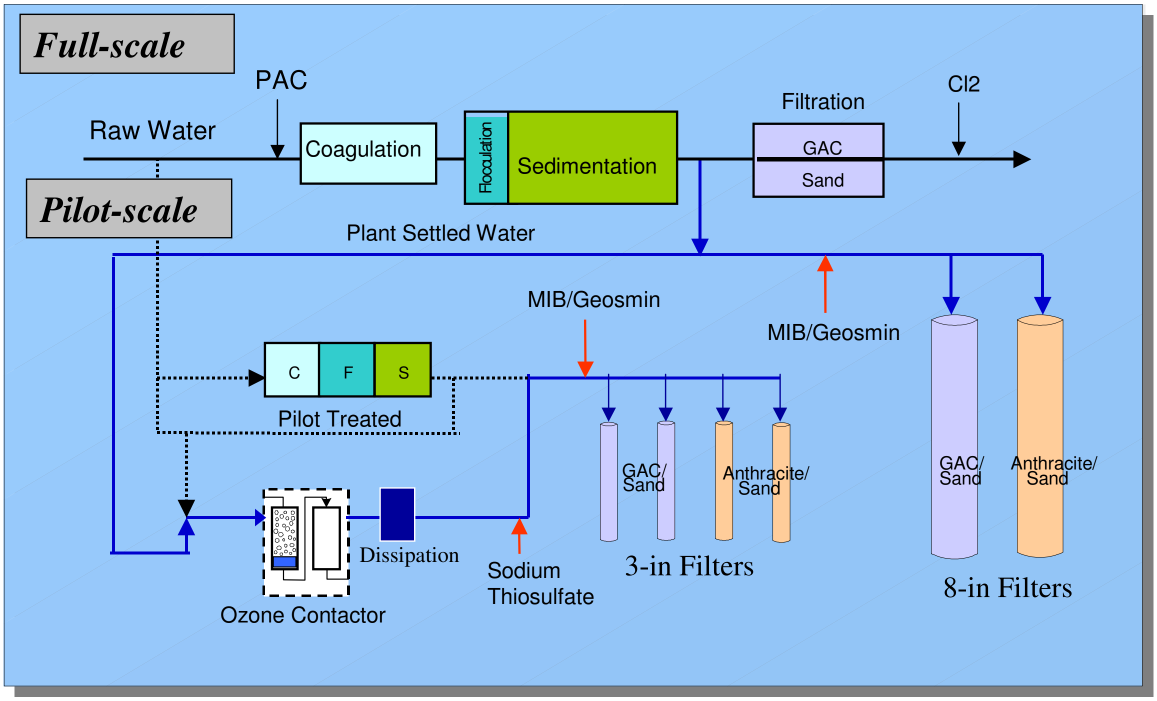


Figure 2 - Dual-Media Pilot Filter Design and Operation

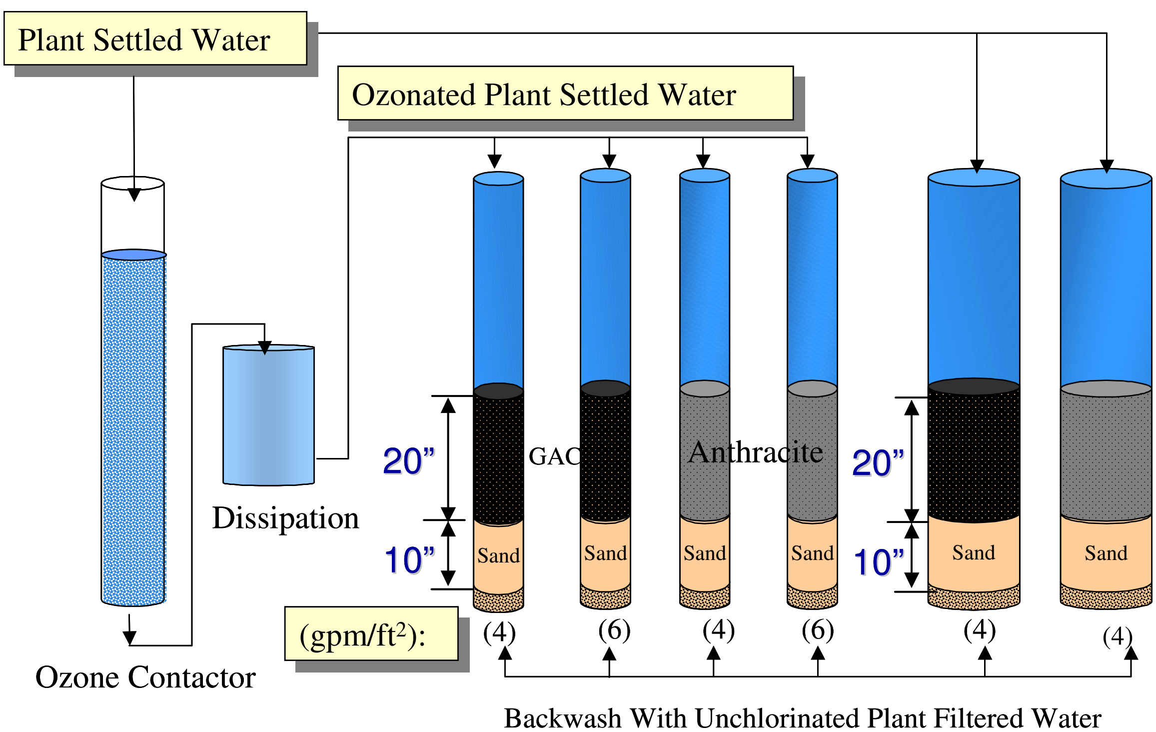


Figure 3 - Pilot Ozonation System

Ozone Generator

Ozone Contactor

Dissipation System

Figure 4 - Pilot Filtration System

3-Inch Diameter Filters

8-Inch Diameter Filters

Sampling Port

RESULTS AND DISCUSSION

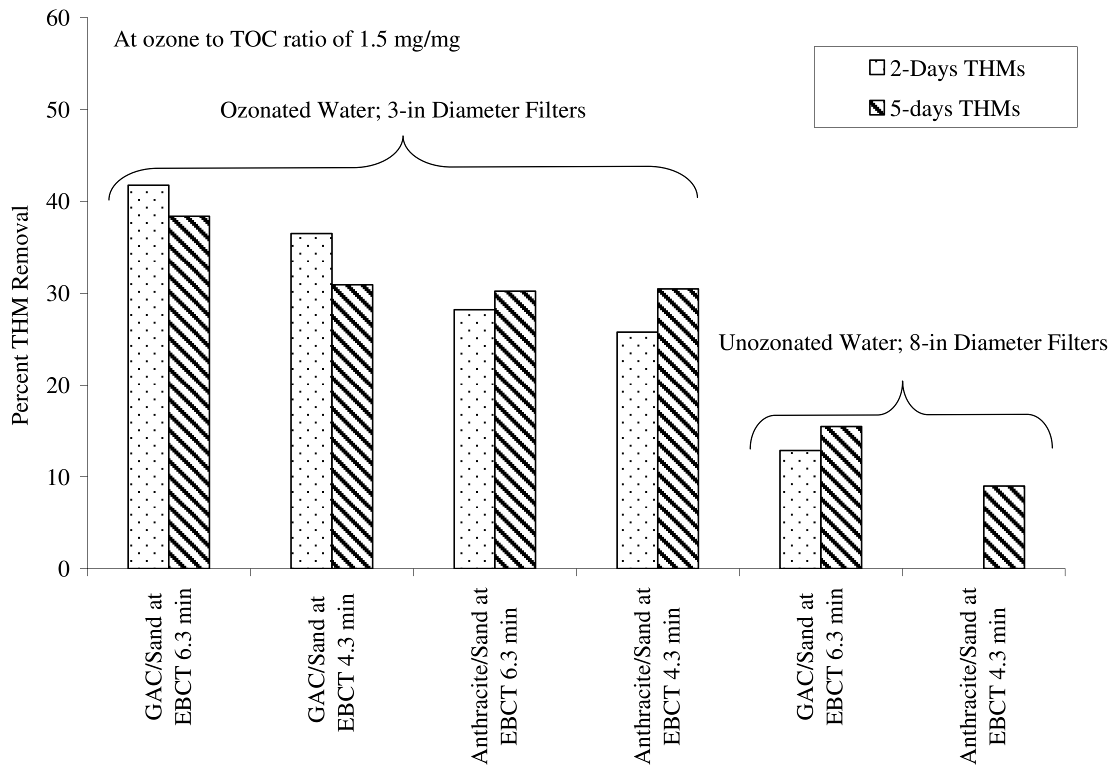
TTHM Removal Results

Samples for TTHM measurement were collected for experiments with ozone to TOC ratio 1.5 mg/mg (high ozone condition). These samples were chlorinated for 2 and 5-days and at the end of incubation period (temperature held at 16^{o}C, temperature typical of distribution system) the amount of chlorine residual maintained was 0.5-1.5 mg/L. The pH was maintained between 7.8-8.0 using phosphate buffer.

The 2-day and 5-day TTHM concentrations in the plant settled water were between 20-30 µg/L. At the baseline condition (at ozone to TOC ratio of 0.25 mg/mg) did not result in any significant reduction in THM concentrations. The TTHM results for the higher ozone dosage experiment are shown in Figure 5. The percent TTHM removals were calculated using the plant settled water THM as the reference to filtered water TTHMs. At this ozone dosage (at ozone to TOC ratio of 1.5 mg/mg), higher TTHM removals were observed in filters that received ozonated water compared to unozonated water. The 2-day and 5-day THM removals were 25-40 percent and 30-40 percent, respectively. The higher TTHM reduction in unozonated filters is attributed to the higher biomass and the associated biological activity.

Increasing the ozone-TOC ratio may have resulted in more conversion of TOC to smaller molecular weight organics (possibly of non-humic nature) that is more biodegradable and also less reactive in forming THMs (Sinha, 1997). Higher THM removals were observed in GAC/sand filters compared to anthracite/sand filters and this attributed to higher biological activity in GAC compared to anthracite media filters.

Figure 5 - THMs removals in filters that received ozonated (at ozone/TOC of 1.5 mg/mg) and unozonated settled waters

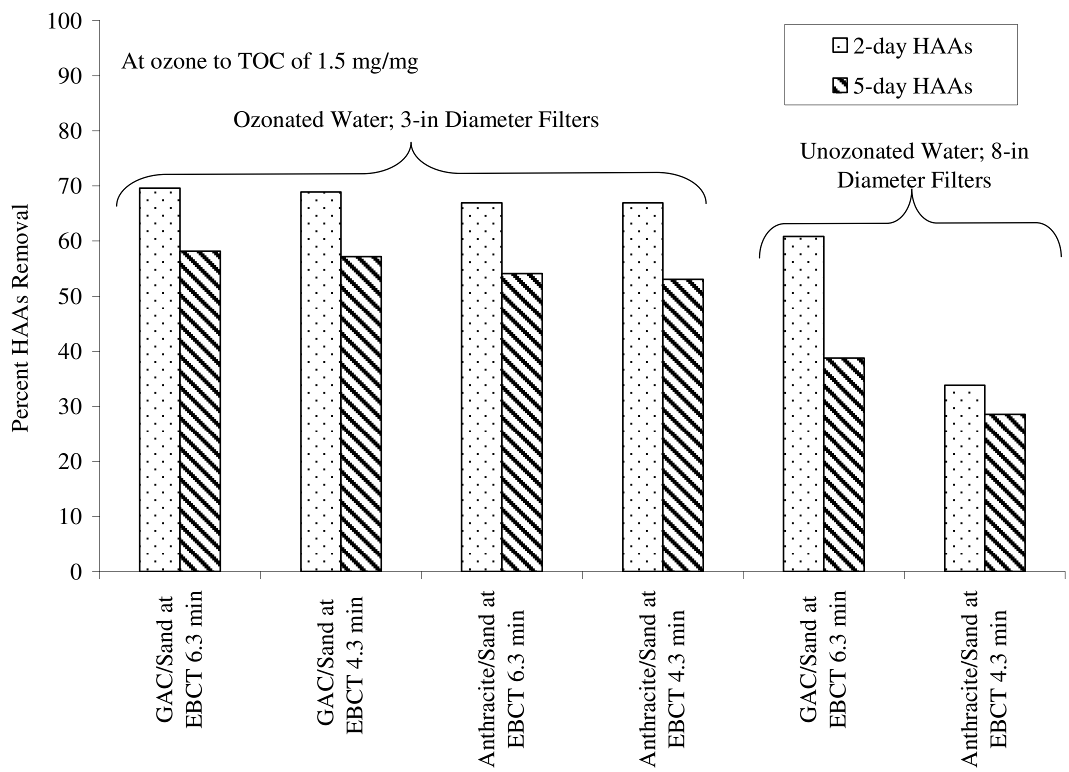


HAA5 Removal Results

The 2-day and 5-day HAA5 were also measured on samples that were collected for experiments with ozone to TOC ratio of 0.25 mg/mg (baseline condition) and 1.5 mg/mg (high ozone condition). Similar to TTHM samples, chlorination was performed at pH between 7.8-8.0 using phosphate buffer and incubated at 16 ^{o}C with the targeted chlorine residual was 0.5-1.5 mg/L.

The 2-day and 5-day HAA5 concentrations in the plant settled water were between 8-12 µg/L. For all samples, the HAA levels were much below the regulatory limit of 80 µg/L. Summarized in Figure 6 are the percent HAA5 removals for the high ozone-TOC experiment. Intermediate ozonation was able to result in HAA5 removal of 50-70 percent. These high HAA5 removals at high ozone dose are attributed to the oxidation of large molecular-sized organics to form small molecular-sized, non-humic, biodegradable organics that may have been removed more effectively by the biologically active filters. The findings of this study are in agreement with earlier studies that found reduced TTHM and HAA5 formation in waters that were either ozonated prior to filtration (intermediate ozonation) or ozonated prior to coagulation/sedimentation/filtration (pre-ozonation) (Siddique et al.1997; Chiaket et al., 2002).

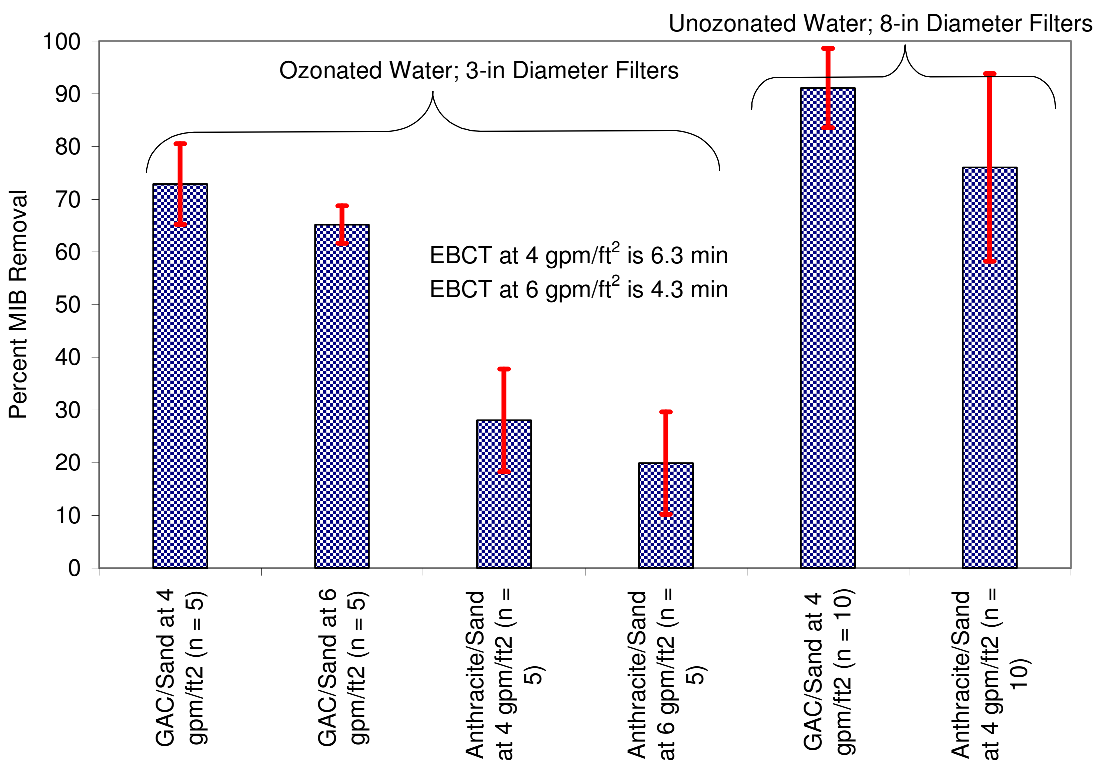
Figure 6 - HAA5 removal in filters that received ozonated (at ozone/TOC of 1.5 mg/mg) and unozonated settled waters



Effect of Filter Design and Operation on MIB Removal

Shown in Figure 7 are the average, MIB percent removals for the various filter designs and operational conditions (varying EBCTs and with and without ozone). The data shown in Figure 5 for the small filters is for baseline operation conditions with ozone to TOC ratio of 0.25 mg/mg. The number of observations used for calculating the average and error are shown in parenthesis underneath each bar (e.g., n = 5 means 5 data points). In both ozonated (small) and unozonated (large) filters, high MIB removals were observed in GAC/sand filters compared to anthracite/sand filters. The GAC filters are known to support more biological activity than anthracite filters by providing the physical support structure (Wang et al., 1995). The enhanced biological activity may be the cause for higher MIB removals in GAC filters compared to the anthracite filters. Higher EBCTs (6.3 min) showed slightly better MIB removal compared to lower EBCTs (4.3 min) for both GAC/sand and anthracite/sand filters. Higher EBCTs provide higher residence time for biological uptake.

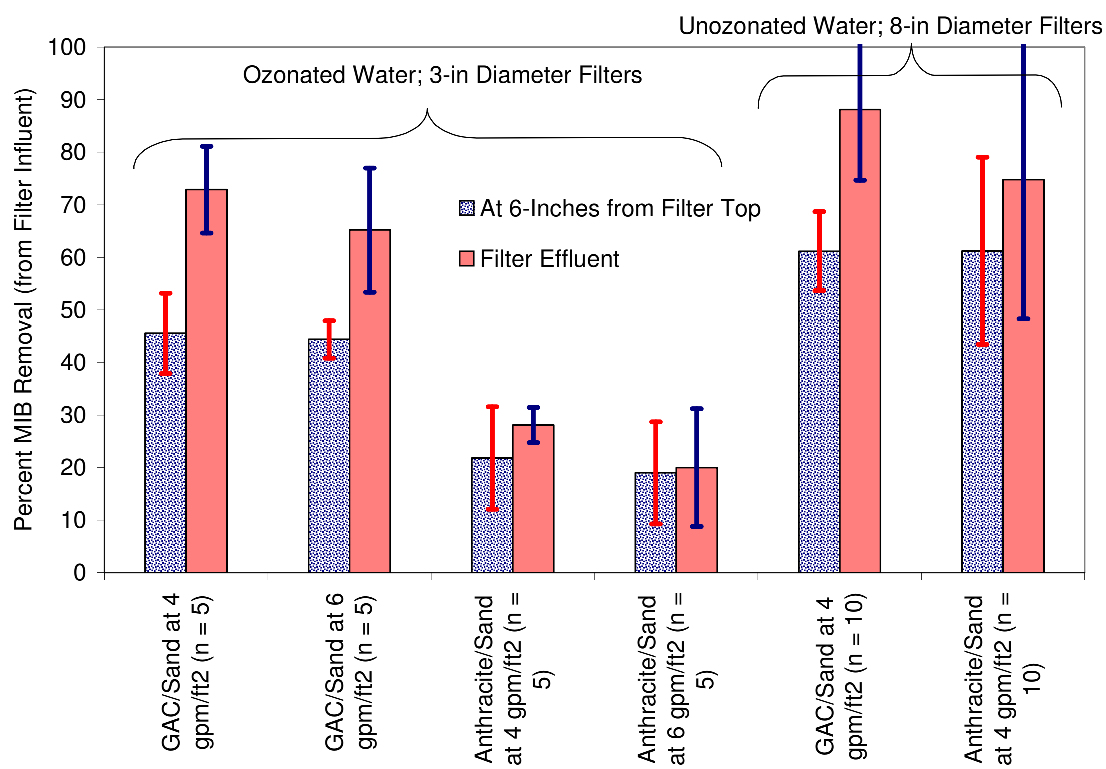
Figure 7 - Percent MIB Removals in GAC/Sand and Anthracite/Sand Filters that Received Ozonated and Unozonated Waters at EBCTs between 4.3-6.3 minutes



The MIB removals in GAC/sand filters for ozonated (small) and unozonated (large) waters were respectively 65-73 percent and 91 percent. The large filters received unozonated, plant settled water spiked with 25 ng/L of MIB/geosmin since the beginning of the study. The small filters received varyingly processed (e.g., varying ozone dosages, MIB/geosmin concentrations) plant settled water. Another difference in operation of the small and large filters was in backwashing. The small and large filters were backwashed using plant filtered water (Figure 2). Backwashing was able to expand the small filter media by 50 percent (bed expansion). On the other hand, due to physical limitations (pipe that carried filtered water to the pilot facility), only 30 percent bed expansion was achieved during backwashing of the large filters. These operational differences between the small and large filters may have played some role in the MIB removals that were observed.

Figure 8 shows the percent MIB removals as a function of the filter depth. The percent MIB removals were calculated as a function of MIB concentration in the filter influents. As shown by the data presented in Figure 8, most of the MIB removal occurred in the top 6-inches of the filter media. Some additional removal of MIB occurred in the bottom 24-inches of the filter. The high MIB removal in the top 6-inches is also indicative of the biological uptake.

Figure 8 - A Comparison of Percent MIB Removals in Samples Collected at 6-inches from the Filter Top and in Filter Effluents

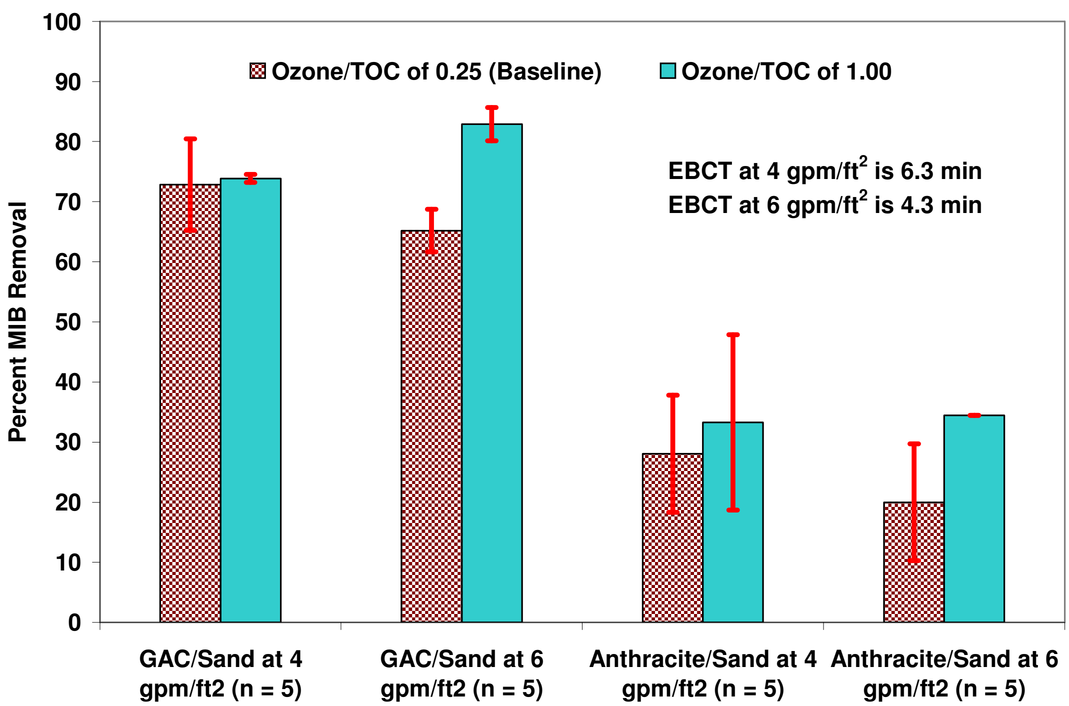


Effect of Ozone Dose on MIB Removal

Ozone addition to the plant settled water would breakdown some of the larger, natural organics into smaller, more biodegradable organic molecules. The presence of smaller organics is expected to enhance the biological activity in the filters and thereby result in higher MIB removals. Note that MIB was spiked after ozone addition, prior to filtration to the small filter influents.

The percent MIB removals for ozone to TOC mass ratios of 0.25 and 1.0 are shown in Figure 9. In all the filters, higher ozone dose resulted in higher MIB removals (by about 1-14 percent) supporting the hypothesis that ozone addition would enhance the biological uptake of MIB. Addition of ozone excessively may result in total oxidation (conversion to CO_2 and water) of organics. For T&O control, ozone should be applied at low ozone-TOC ratios to take advantage of the biological oxidation.

Figure 9 - Effect of Ozone Dose on MIB Removal in Dual-Media Filters

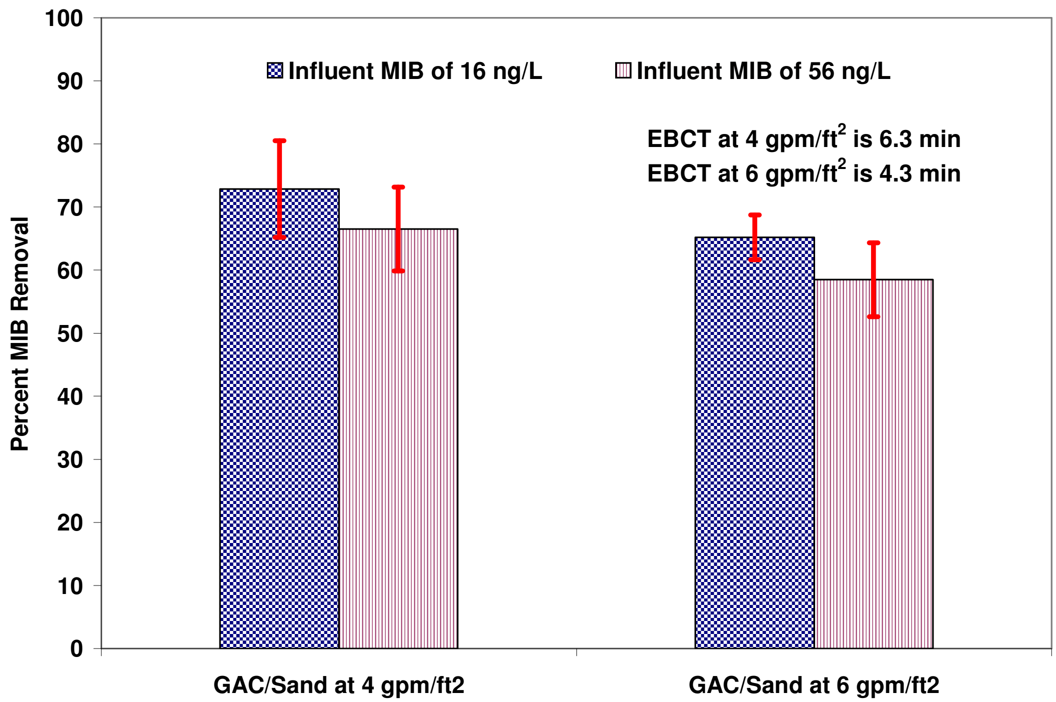


Effect of Influent Concentration on MIB Removal

The historical MIB concentrations in the WTP source water varied between 10 and 60 ng/L. Two experiments were conducted to evaluate the effect of influent MIB concentrations on the filter performance. The influent MIB concentrations tested included 16 ng/L and 56 ng/L. For both these experiments, ozone was applied at a mass ratio of 0.25 to the influent TOC. The results for these tests are summarized in Figure 10.

The MIB removal percentages for influent MIB of 56 ng/L were between 58 and 67 percent. These MIB removal percentages are slightly lower (6-7 percent) than those observed under baseline conditions. Increasing MIB concentrations does not seem to affect the filter performance significantly. This observation also supports biological uptake being the predominant mechanism compared to adsorption for MIB removal.

Figure 10 - Effect of Influent MIB Concentration on MIB Removal in GAC/Sand Filters



Geosmin Removal Results

Geosmin concentrations were also monitored in the filter influents and effluents. Even though the stock solution had geosmin, the concentrations of geosmin were less than 6 ng/L in the filter influents and less than detection limit (2 ng/L) in the filter effluents. Efforts to increase geosmin concentrations by increasing the amount of stock solution spiked also did not yield the targeted 25 ng/L and 50 ng/L in the large and small filter influents, respectively. Volatilization loss could be the cause for the low concentrations of geosmin that were measured in the filter influents. Previous studies have shown geosmin to readily oxidize and biodegrade compared to MIB.

Other Organics Removal Results

Organic removal by the pilot filters was monitored in terms of TOC and ultraviolet (UV) 254 nanometer (nm) absorbances. Figure 11 shows the TOC box-and-whisker plots for raw, plant settled ozonated and filtered waters. The solid line in the box indicates the median and the hatched line shows the mean or average. The data shown in Figure 11 is a summary of 24 data points collected over the duration of testing for each sample location (e.g., raw water, plant settled water). The GAC/sand filters performed slightly better than anthracite/sand filters in terms of the TOC removal. Ozonation did not lower the TOC indicating that the applied dosages of ozone did not result in total oxidation.

The UV254 nm results are shown in Figure 12. The data shown in Figure 10 was synthesized from 44 independent measurements taken over the course of testing. UV254 absorbances were measured as part of the field parameters and therefore there were more readings compared to the TOCs. Similar to the TOC results, lower UV254 absorbances were observed in the GAC/sand filter effluents compared to the anthracite sand filters. The UV254 absorbances represent smaller organics in the water. The lower UV254 absorbances in GAC/sand filter effluent were possibly due to higher uptake of smaller organics by the bacterial population in the biologically active filters.

Figure 11 - TOC Results for Raw, Plant Settled, Filter Influent (Ozonated Water) and Filter Effluents

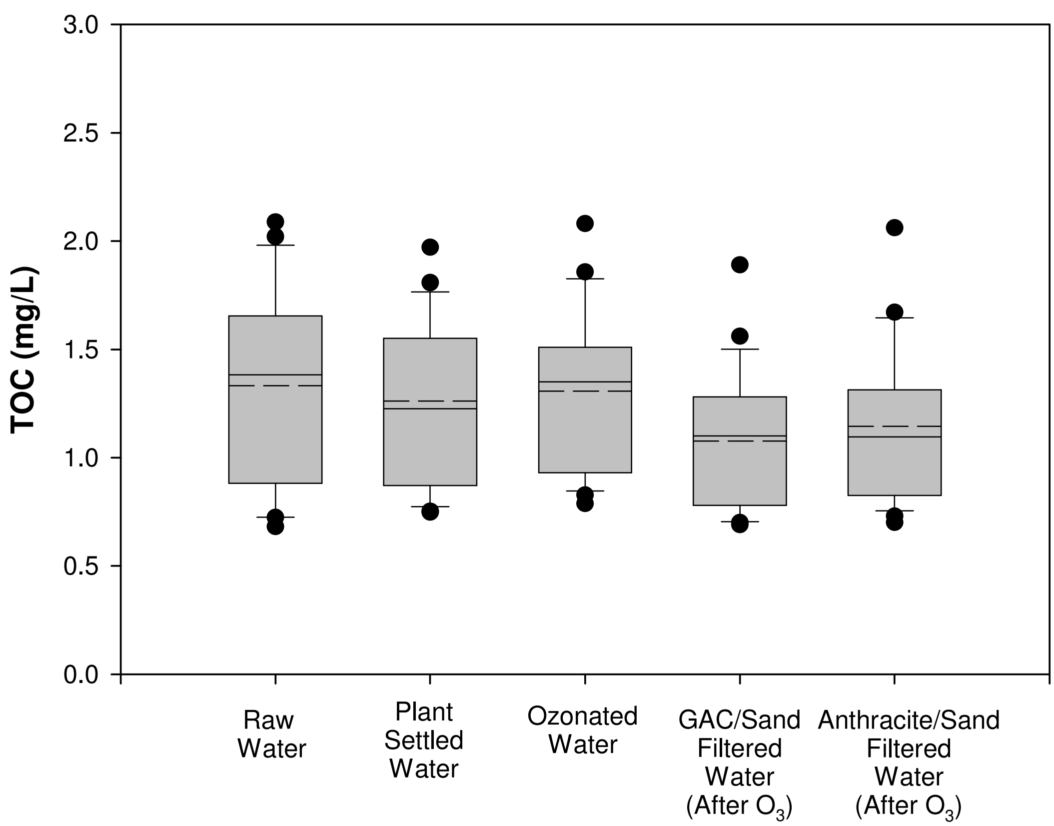
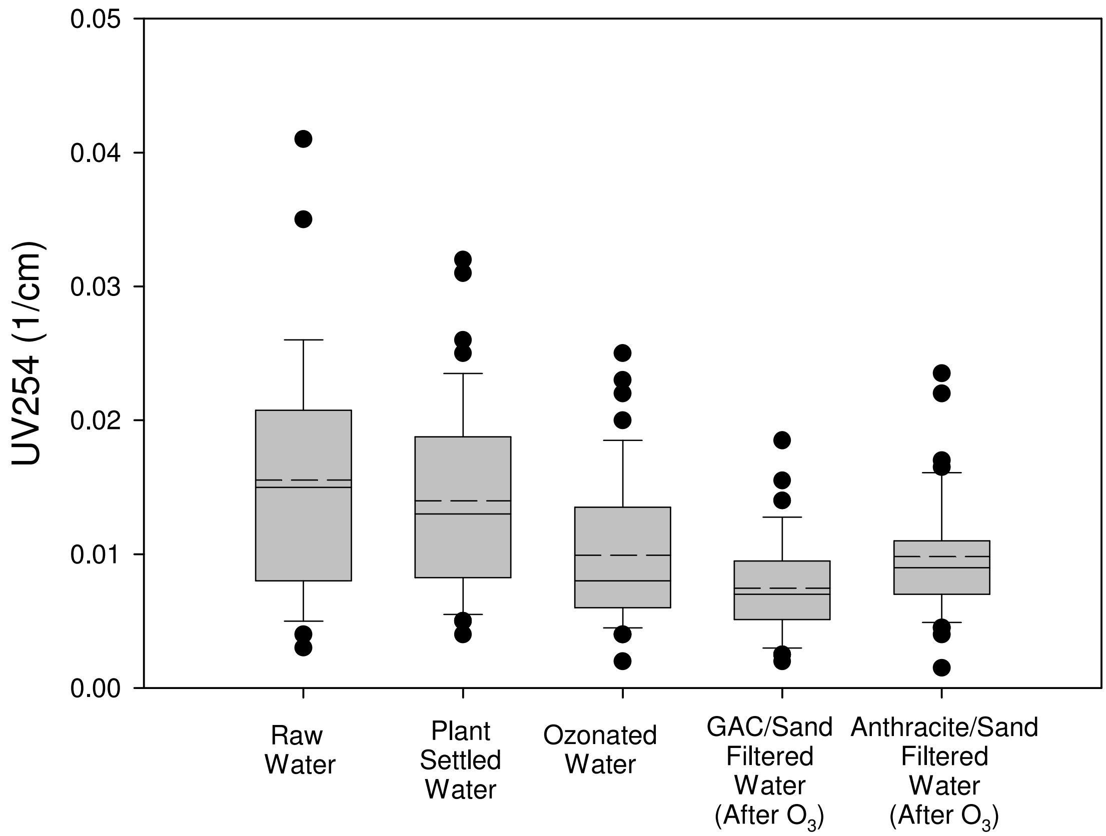


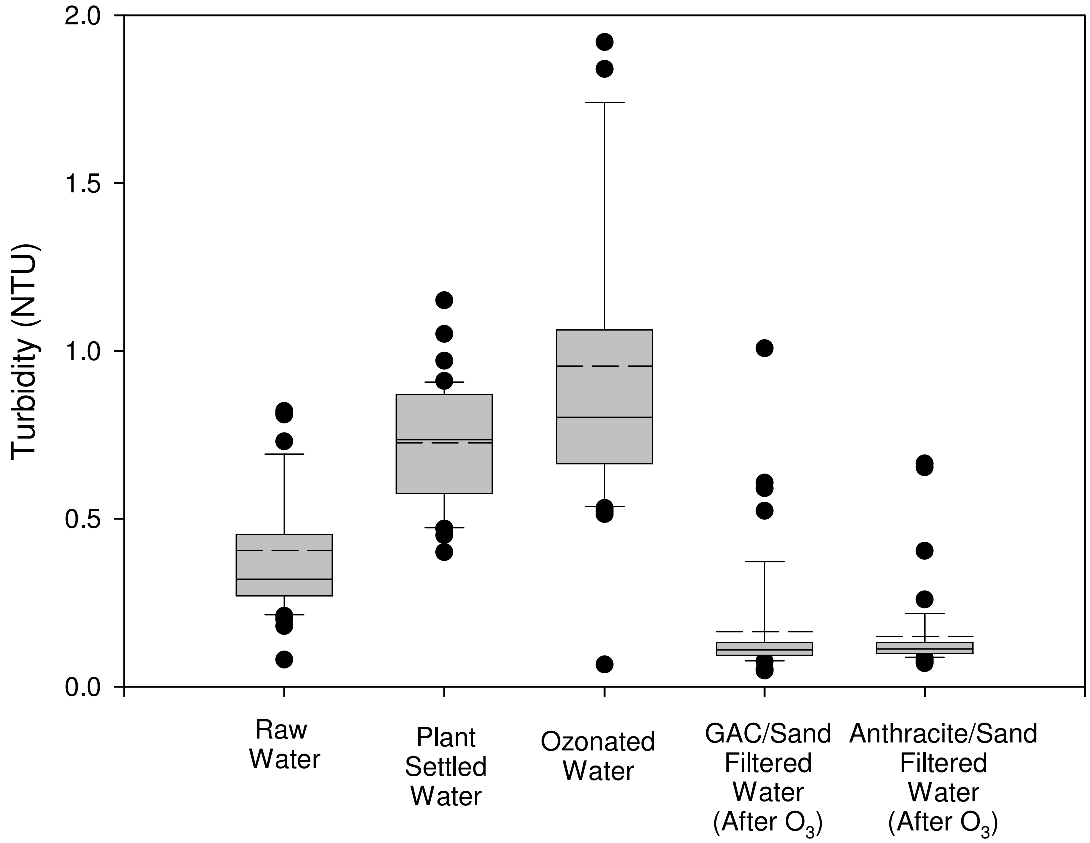
Figure 12 - UV254 Results for Raw, Plant Settled, Filter Influent (Ozonated Water) and Filter Effluents



Particulates Removal Results

Particulates removal in the pilot filters was monitored in terms of turbidity. The turbidity results are shown in Figure 13. The data shown in Figure 13 is a summary of 44 data points for each location. The raw water turbidities were less than 0.5 nephlometric turbidity units (NTU). The settled water turbidities were between 0.5 and 1.0 NTU. The higher turbidities in settled water compared to the raw water is due to the carryover of PAC and alum floc. Both GAC/sand and anthracite/sand filters reduced the turbidities in the filtered waters to less than 0.2 NTU. Ozonation and biofiltration did not compromise the quality of the water in terms of turbidity. The target for turbidities in the WTP filtered water is ≤ 0.3 NTU. Our pilot filters produced filtered water that met the 0.3 NTU target. It should be noted that the filters were backwashed once every 24-30 hours similar to the full-scale plant. Backwashing was performed for periods of 15-20 minutes, until the backwash water was visibly clear of particles.

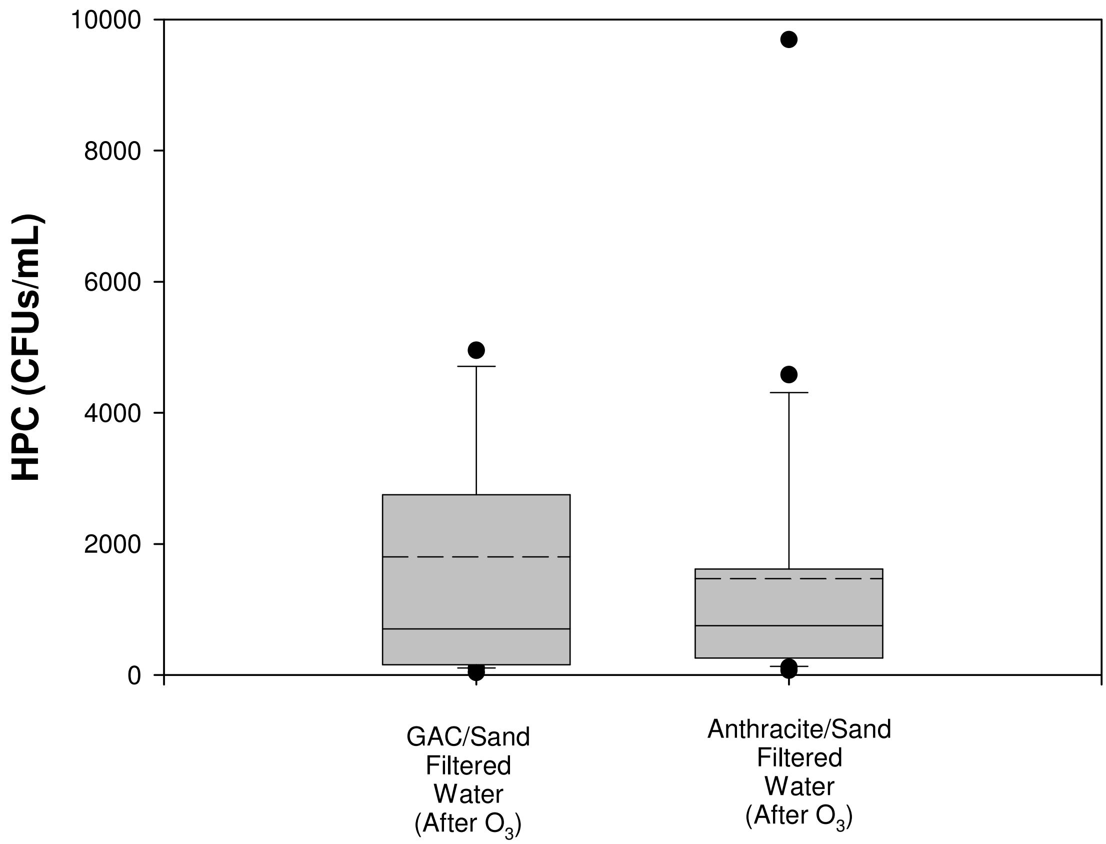
Figure 13 - Turbidity Results for Raw, Plant Settled, Filter Influent (Ozonated Water) and Filter Effluents



Microbial Results

The bacterial populations in the filter effluents were monitored during the testing period. A summary of the HPC results is shown in Figure 14. The HPCs in GAC/sand filter effluents were higher than those measured in the anthracite/sand filter effluents. Samples of media at the end of testing were sent to the University of Colorado, Boulder for biomass analysis. The media samples were collected at different depths to estimate the biological activity as a function of filter depths. The biomass results are being awaited.

Figure 14 - HPC Results for GAC/Sand and Anthracite/Sand Filtered Waters



CONCLUSIONS

Higher MIB removals were observed in GAC/sand filters compared to anthracite/sand filters. The MIB removals were a function of EBCT; higher EBCTs achieved higher MIB removal. Most of the MIB removal occurred in the top 6-inches of the filter indicating predominance of biological oxidation as opposed to adsorption (to GAC media). Increased ozone dose resulted in slightly enhanced MIB removal. Influent MIB concentration had minimal affect on the MIB removed.

The GAC/sand filters outperformed anthracite/sand filters in terms of TOC and UV254 reductions. Both GAC/sand and anthracite/sand filters produced water with turbidities less than 0.2 NTU. Higher HPCs were observed in GAC/sand filters compared to anthracite/sand filters. Filter media samples are being analyzed for viable biomass using phospholipids analysis. The biomass results will help in understanding the extent of biological activity in each filter.

ACKNOWELDGEMENTS

The authors would like to acknowledge AwwaRF for funding this project. This study was funded under AwwaRF Project #2775 "*Ozone Enhanced Biofiltration for Geosmin and MIB Removal*". The Project Officer is Dr. Djanette Khiari, AwwaRF.

REFERENCES

Chiaket T., P. C. Singer, A. Miles, M. Moran and C. Pallota (2002) Effectiveness of Coagulation, Ozonation and Biofiltration in Controlling DBPs, *Journal of American Water Works Association,* v. 94, No.12, p. 81-95.

Siddique M.S., Amy G. L. and Murphy B.D. (1997) Ozone Enhanced Removal of Natural Organic Matter from Drinking Water Sources, *Water Research*, v.31, No. 12, pp. 3098-3106.

Sinha, S., Amy, G., Sohn, J. (1997) Reactivity of Natural Organic Matter (NOM) Fractions in Forming Chlorinated Disinfection-by-Products (DBPs), in Proceedings, Annual Meeting of American Water Works Association, Atlanta, Georgia.

Wang J. Z., Summers S. R. and Miltner R.J. (1995) Biofiltration Performance: Part-1, Relationship to Biomass, *Journal of American Water Works Association*, v. 87, No. 12, pp. 55-63.

DISCLAIMER