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CONTROL OF DISINFECTION BYPRODUCTS AND AOC BY PRE-OZONATION AND BIOLOGICALLY-ACTIVE IN-LINE DIRECT FILTRATION

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Introduction

Many utilities in the U.S. are considering use of ozone as a pre-oxidant/disinfectant for the purpose of meeting new disinfection and disinfection byproduct (DBP) regulations. In the Northeast U.S., a large fraction of these utilities will be employing direct filtration, both with and without flocculation, to treat high-quality surface waters. When ozonation is used as a pre-treatment to filtration, substantial improvements in filtered water quality can occur due to higher levels of biological activity within the filter. However, little is known about the effectiveness of this biological treatment for DBP control. Neither is there much known regarding the conditions for best operation of biological filtration. The objective of this study was to determine the effects of pre-ozonation, filtration rate, and the use of chlorinated backwash water on the removal of dissolved organic matter. The organic parameters that were monitored were dissolved organic carbon (DOC), assimilable organic carbon (AOC), and a range of ozonation byproducts and chlorination byproduct precursors.

Experimental

The site of this work was the pilot facility at the West River Water Treatment Plant in Woodbridge, CT. This is a 10 gpm pilot facility comprising two parallel direct filtration trains. Each of the two trains may feed 2-3 dual media filters. This facility is owned and operated by the South Central Connecticut Regional Water Authority. The full-scale West River Treatment Plant is an in-line direct filtration facility, employing dual media anthracite-sand filters. The West River raw water is a low alkalinity (10-15 mg/L $CaCO_3$), low turbidity (~1 NTU), low DOC (~3 mg/L) supply, typical of many New England waters. The pilot plant was run continuously over a period of several months and samples were analyzed for DOC, AOC, and disinfection byproducts on a biweekly basis. Similar analyses were run on the full-scale filter effluent.

Ozone disinfection byproducts that were measured included the low molecular weight aldehydes (formaldehyde to hexanal), two di-aldehydes (glyoxal and methyl glyoxal) and two keto-acids (glyoxalic acid and pyruvic acid). Chlorination byproducts (pentane extractables, haloacetic acids, and chloral hydrate) were measured after laboratory chlorination. Samples were buffered at pH 7.0, dosed with 20 mg/L chlorine and allowed to react for 72 hours in the dark (20°C). A relatively high chlorine dose was chosen (20 mg/L) so that both raw and treated waters would have approximately the same chlorine residual throughout the reaction period.

These organic parameters may be classified into two groups (Figure 1). The TOC, UV absorbance, THM precursors, and Haloacetic acid (HAA) precursors are all indicators of natural organic matter (NOM), especially humic substances. They are represented by relatively hydrophobic (i.e., coagulatable, readily adsorbable), high molecular weight organics. When oxidants are applied to waters containing NOM, these four parameters are either little changed or diminished. In contrast, the AOC, aldehydes, keto-acids, and chloral hydrate precursors are not present in raw waters at very high concentrations. Instead, they tend to be formed as a result of oxidation, expecially with ozone. These compounds are more hydrophilic and of lower molecular weight. It should be recognized that the distinction between these two groups is made to facilitate data interpretation, and not to imply some absolute dichotomy among the various organic parameters. In some cases, ozonation byproducts can be responsible for substantial THM formation, whereas many raw waters contain high concentrations of chloral hydrate precursors.

Samples for analysis of DOC were filtered with a Whatman GF/F glass fiber filter prior to determination. The persulfate-ultraviolet oxidation method (#5310 C., APHA et al., 1989) was used for measuring DOC. UV absorbance at a wavelength of 254 nm was measured on samples that had been filtered through a pre-washed glass-fiber filter (Whatman GF/F). Measurements were made with a double-beam UV-Vis spectrophotometer and 1-cm quartz cells.

The micro-pentane extraction method as described by Koch et al. (1988) was used for determining the THMs (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform) and other neutral halogenated byproducts (i.e., the dihaloacetonitriles, trichloroacetonitrile, 1,1,1-trichloropropanone, 1,1-dichloropropanone, and chloropicrin). The haloacids (primarily dichloroacetic acid and trichloroacetic acid) were determined by a procedure using micro-extraction with methyl-t-butyl ether, and methylation (USEPA method 552: EMSL, 1990; Hwang et al., 1990). Chloral hydrate was analyzed by a method using extraction methyl-t-butyl ether (Met-JMM, 1989). The PFBOA derivatization method proposed by Yamada and Somiya (1989) and subsequently modified by Glaze et al. (1989) and Sclimenti et al. (1990) was used for determining low-molecular-weight aldehydes. Keto-acids were determined by a double derivatization GC method employing diazomethane and PFBOA (Xie and Reckhow, 1992). This was based on the earlier work of Xiong et al., 1991.

Results and Discussion

On February 8, 1992 an experiment was run where both raw water and full-scale filter effluent were ozonated at doses of 0.5-2.0 mg/L and tested for disinfection byproduct precursors. Figure 2 shows the results for the THM precursors. Roughly 50% of the precursors can be removed by coagulation and filtration without the use of ozone. Pre-ozonation achieved approximately the same degree of removal. In the authors' experience this is an exceptionally high THMFP removal by ozone alone, however, prior results have shown this to be characteristic of the West River Water. Ozonation of the filter effluent showed very little loss in THMFP. Apparently, the easily coagulated THM precursors were also those that could be readily destroyed by ozone. The more hydrophilic precursors, were little affected by ozone. The dichloroacetic acid (DCAA) precursors (Figure 3) showed a somewhat different behavior. The DCAA precursors were removed to about the same relative extent by coagulation and filtration. However, pre and post ozonation resulted in little change or even a modest increase.

During the period; May 1 to July 1, 1991, the plant was configured as shown in Figure 4. The ozonated train fed one GAC/sand filter backwashed with non-chlorinated water (#1), and one backwashed with chlorinated water (#2). Similarly, the non-ozonated train fed two GAC/sand filters (one using chlorinated backwash water (#3) and the other not (#4)). An anthracite/sand filter was also placed in line as a control (#5). This treatment sequence differed from the full-scale plant only in the use of chlorine-free backwash water. Breakthrough of the GAC filters, as measured by DOC and UV absorbance, had been observed several months earlier. Average fractional DOC values for this set of runs are shown in Figure 5. Removal across the anthracite/sand filters was about 47% for both the full-scale and pilot-scale (i.e., #5) filters. When GAC/sand was used, the removals were greater. Filters receiving chlorinated backwash water (#2 and #3) showed about 56% DOC removal, and filters not exposed to a chlorine residual (Filters #1 and #4) showed about 63% removal. The readily assimilable fraction of this organic matter (i.e., the AOC) exhibited considerably more variability (Figure 6). Among the trains not receiving ozonated water, filter #4 clearly out-performed the others. Filters backwashed with chlorinated water (#3) or those employing anthracite instead of GAC (#5 and full-scale plant) showed a lower level of AOC removal. Ozonation of the raw water raised the AOC level by more than a factor of two. Subsequent filtration resulted in effective removal by the filter exposed to a chlorine residual (#2) and even greater removal by the filter backwashed with non-chlorinated water (#1).

As expected, the other NOM-associated parameters showed results similar to those of the DOC. The THM precursors exhibited a 30-35% decline directly as a result of ozonation (Figure 7). This had little effect on the filtered water THMFP, because the oxidizable fraction was removed by coagulation anyway (refer to Figure 2). There was approximately a 50% removal across the anthracite-sand filters (filter #5 and the plant effluent). This is attributed largely to chemical and physical effects. The improved removal across the GAC-sand filters is likely due to higher levels of biological activity in these filters. The overall result is that filter #5 produced the highest THMFP, followed by filter #3 and then followed by the remaining three. The HAAs showed less direct precursor removal by pre-ozonation (Figure 8 and 9). Filter #5 and the full-scale plant effluent indicated roughly 50% removal of these precursors as well. This suggests that all of these parameters are essentially measuring the removal of the same set of organic compounds (e.g., the humic substances). Improved removal in filters #1-4 as compared to filter #5 reflects the destruction of NOM by biological activity. In general, filter #1 (pre-ozone train, no chlorine backwash) produced the highest quality water. Figure 10 shows a typical data set for one of the low-molecular weight aldehydes, glyoxal. As expected, there is a substantial formation following ozonation. Since the raw water levels were so low, very little was seen in filter #5 effluent and in the full-scale plant effluent, as well as in the effluents for filters #3 and #4. The small increase observed across filter #3 is surprising, but similar increases in the aldehyde concentration have been noted across filters during other phases of this study. Filter #1 showed better removal of glyoxal than filter #2. This is undoubtedly due to higher levels of biological activity in the unchlorinated train.

In the mid-Summer, 1991 an experiment was run where raw water was spiked with a mixture of aldehydes and keto-acids as it entered the pilot plant (Figure 11). Spiked concentrations were about 300 $\mu g/L$ for the keto-acids and 100 $\mu g/L$ for selected aldehydes. The five filters were first run at a hydraulic loading rate of 3.8 m/hr (1.5 gpm/ft^2) until breakthrough of a fluoride tracer and samples were collected. Then the rate was increased to 7.5 and 11.3 m/hr (3.0 and 4.5 gpm/ft^2, respectively) and sampled accordingly. Figure 12 shows the results of glyoxalic acid analysis in the filtered waters. As expected all filters showed increased breakthrough of glyoxalic acid with increasing filtration rate. The filter containing anthracite showed the poorest performance at all filtration rates. The GAC filters exposed to a chlorine residual (#2 and #3) performed slightly better, and the filters not exposed to a chlorine residual were clearly superior. Also, the filter normally receiving ozonated water (#1) out-performed its unozonated counterpart (#4).

Conclusions

1. Conditions favoring biological removal of organic matter include:
   - use of pre-ozonation
   - low filtration rates, or high EBCTs
   - absence of a chlorine residual in the backwash water
   - use of GAC rather than anthracite

2. Removal of DOC, THM precursors, and HAA precursors reflects general removal of natural organic matter. This is largely attributed to physical and chemical effects. Removal of AOC, aldehydes, and keto-acids reflects biodegradation of oxidation byproducts of NOM.

3. Aldehydes and keto-acids may have utility as model biodegradable compounds, indicating the level of biological activity in water treatment systems.

ACKNOWLEDGMENTS

The authors wish to thank Gary Kaminski, Jay Richardson and Stan Barsch for their assistance at the West River Treatment Plant.

LITERATURE CITED

APHA, AWWA, and WPCF (1989) Standard Methods for the Examination of Water and Wastewater, 17th Edition, APHA, Washington.

EMSL (1990) "Methods for the Determination of Organic Compounds in Drinking Water - Supplement I," U.S. EPA, Environmental Monitoring Systems Laboratory, Cincinnati, OH, NTIS #PB91-146027, pp.201-232.

Glaze, W.R., M. Konga, and D. Cancilla, 1989. "Ozonation by-products. 2. Improvement of an Aqueous-Phase Derivatization Method for the Detection of Formaldehyde and Other Carbonyl Compounds formed by Ozonation of Drinking Water," Environ. Sci. Technol., 23:7:838-847.

Hwang, C. et al., 1990. "Method 6000A Disinfection by-products: Chlorine; Haloacetic Acids and Trichlorophenol," draft for inclusion in the 18th Edition of Standard Methods for the Examination of Water and Wastewater.

Koch, B. et al., 1988. "Analysis of Halogenated Disinfection by-products by Capillary Chromatography," Presented at the AWWA Water Quality Technology Conference, November, 1988.

Langlais, B.; D.A. Reckhow; D.R. Brink (1991) Ozone in Water Treatment: Application and Engineering, American Water Works Association Research Foundation, Compagnie Generale des Eaux, Lewis Publ., Chelsea, MI.

Met-JMM (1989) "Disinfection by-products in United States Drinking Waters," Final Report to the U.S. EPA and AMWA; Metropolitan Water District of Southern California, and James M. Montgomery Consulting Engineers, Inc., Volume 2.

Sclimenti, M., S. Krasner, W.H. Glaze, and H.S. Weinberg (1990) "Ozone Disinfection by-products: Optimization of the PFBHA Derivatization Method for the Analysis of Aldehydes," Technology Conference Proc., American Water Works Association, Denver, CO. pp. 477-501.

Xiong, F., J.P. Croue and B. Legube (1991) "Ozone Consumption by Aquatic Fulvic Acids as Precursors of Radical-type Reaction," in Proc. 10th World Ozone Cong., Vol.#1, pp.125-138., International Ozone Assoc., Zurich.

Yamada, H. and I. Somiya (1989) "The Determination of Carbonyl Compounds in Ozonated Water by the PFBOA Method," Ozone: Sci. Eng., 11:2:127-141.

Characterization of Organic Matter

TOC *UV abs* *THM Precursors* *Haloacetic Acid Precursors*	Associated with Natural Organic Matter
AOC *Aldehydes* *Keto-acids* *Chloral Hydrate Precursors*	Associated with Ozonation Byproducts

Figure 1. NOM-Associated Measurements vs OBP-Associated Measurements

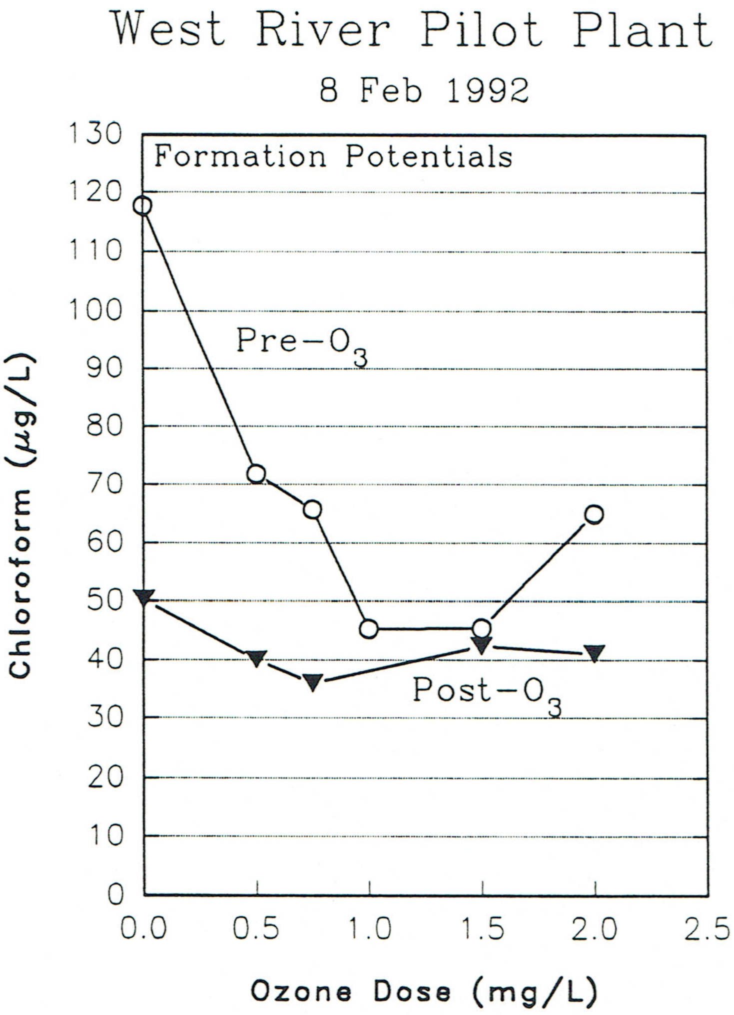

Figure 2. Effect of Pre- and Post-ozonation on THM Precursors.

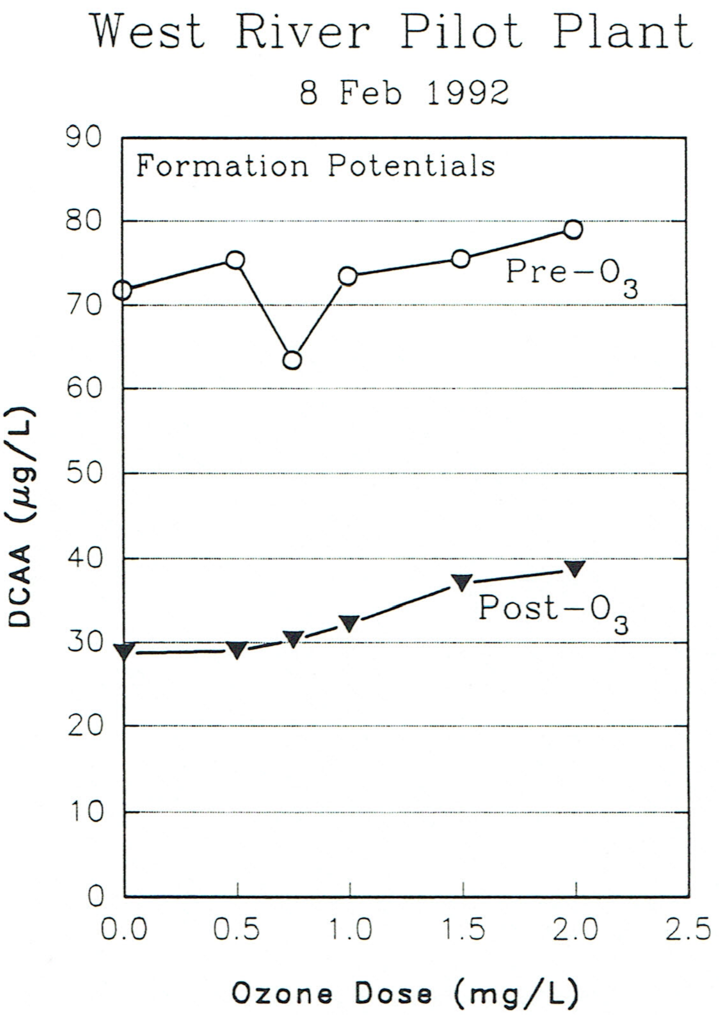

Figure 3. Effect of Pre- and Post-ozonation on Dichloroacetic Acid Precursors.

West River Pilot Plant
May-July, 1991

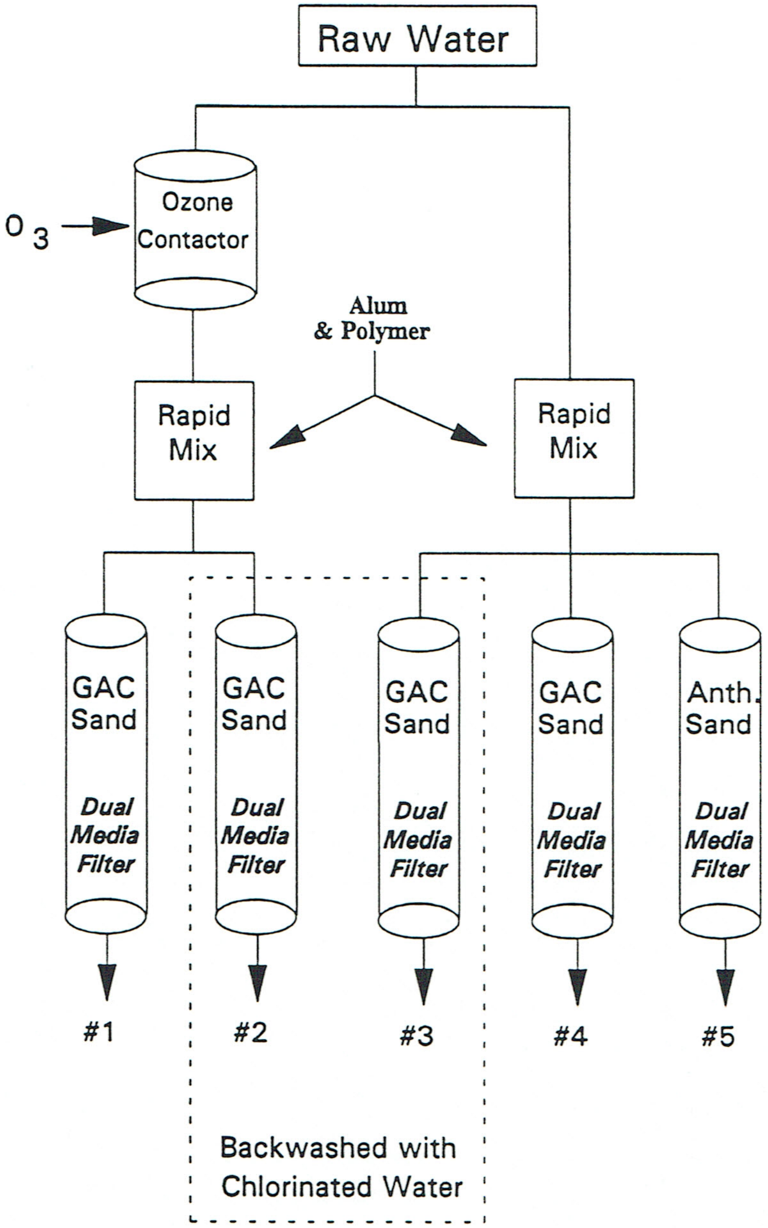

Figure 4. Schematic Diagram of the West River Pilot Plant during May and June of 1991.

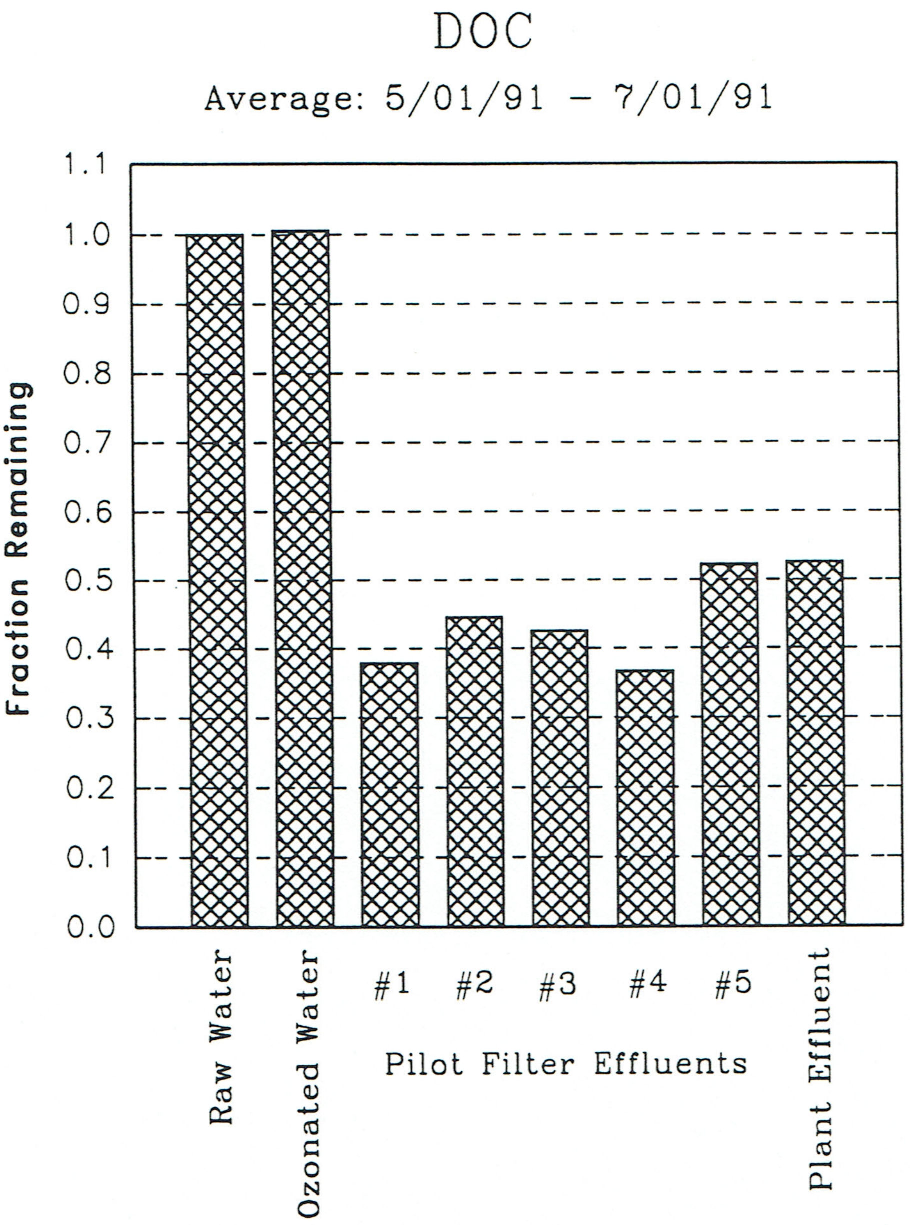

Figure 5. Relative DOC in the West River Pilot Plant: Data from May 1, 1991 to July 1, 1991.

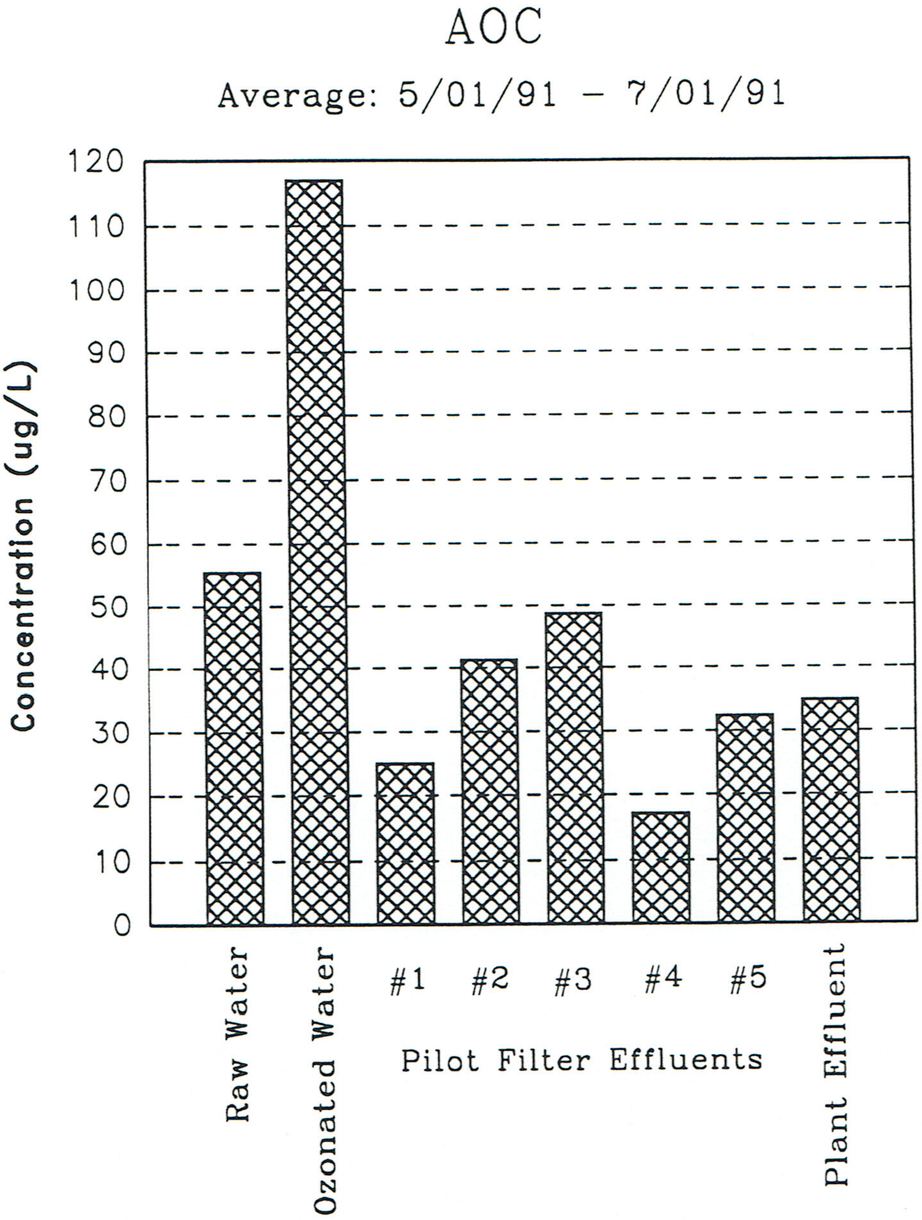

Figure 6. Assimilable Organic Carbon in the West River Pilot Plant: Data from May 1, 1991 to July 1, 1991.

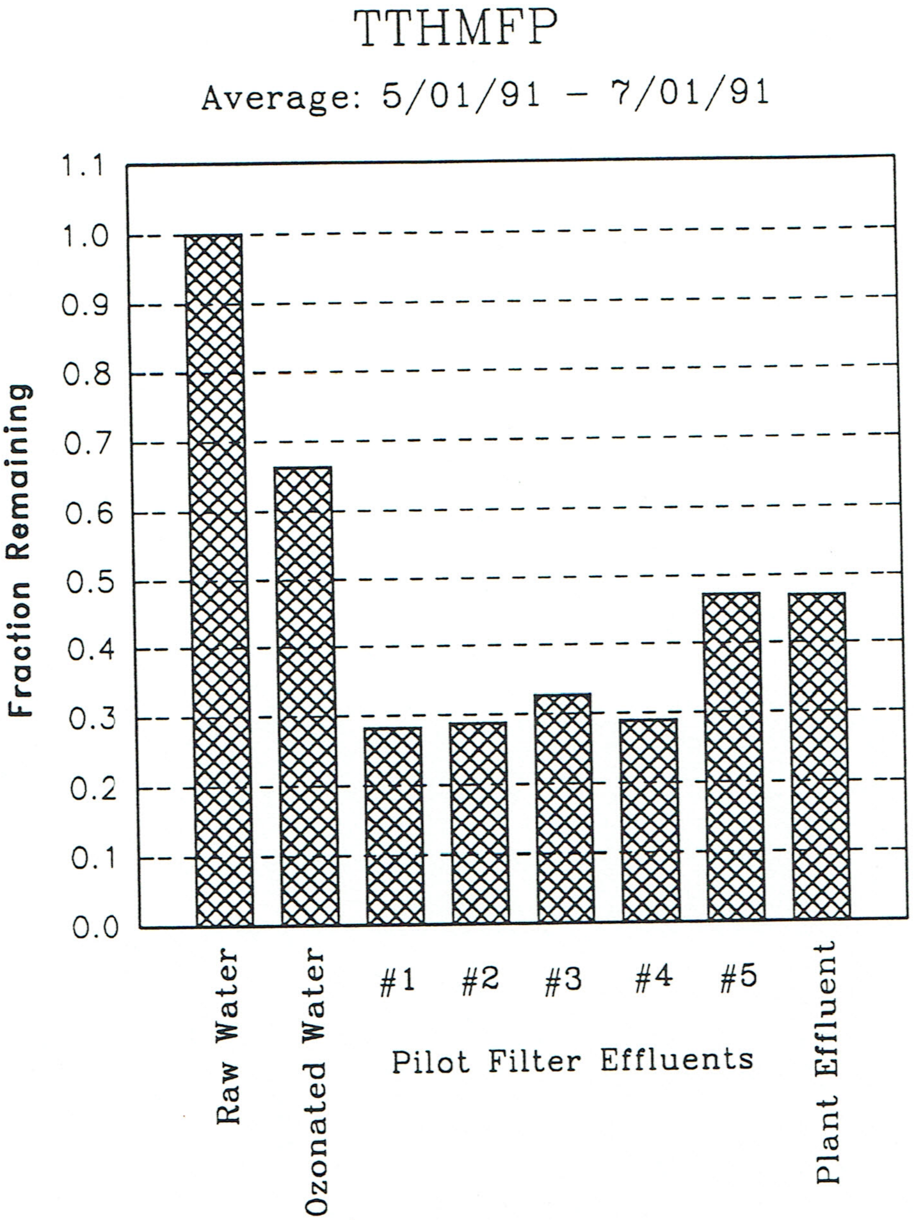

Figure 7. Relative TTHMFP in the West River Pilot Plant: Data from May 1, 1991 to July 1, 1991 (Raw Water TTHMFP = 190 μg/L).

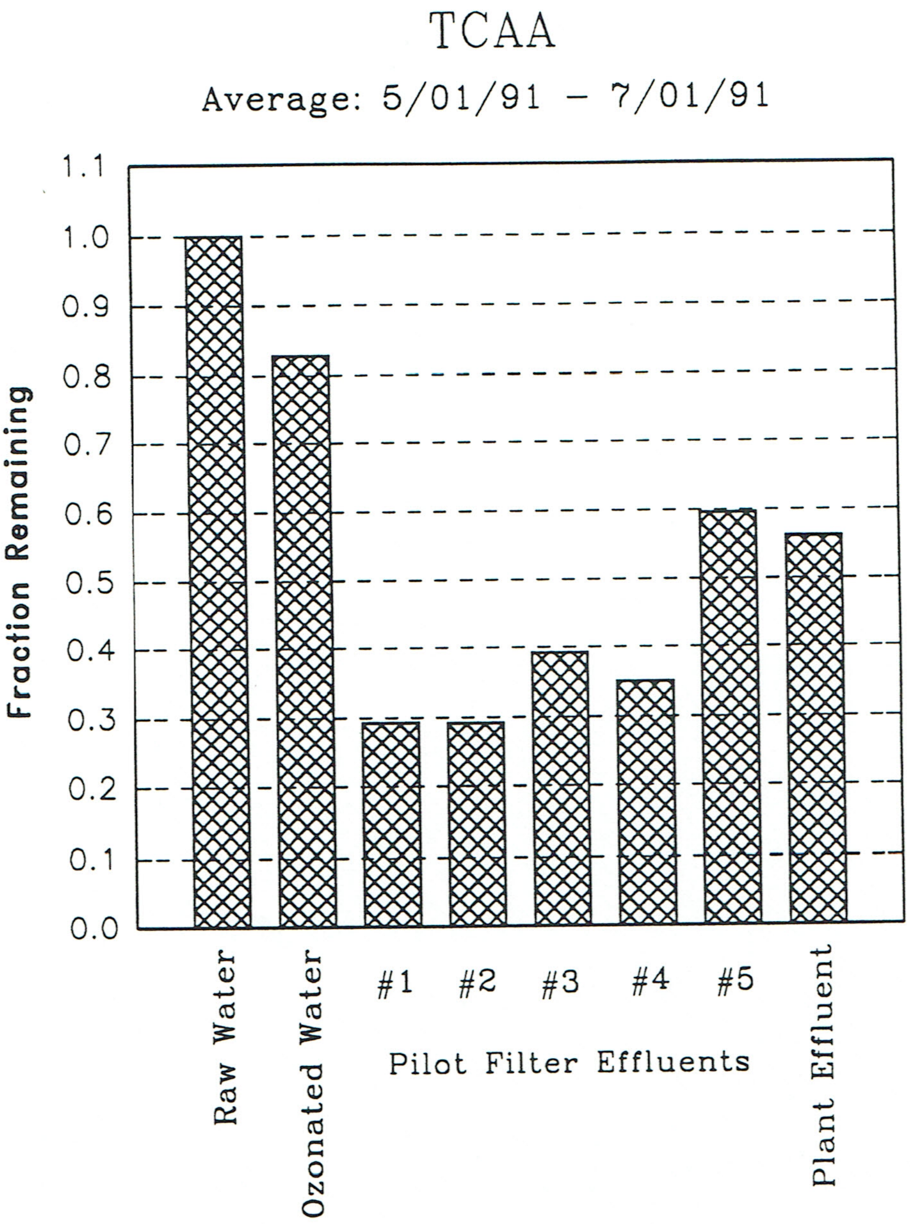

Figure 8. Relative TCAA Formation Potential in the West River Pilot Plant: Data from Ma 1, 1991 to July 1, 1991.

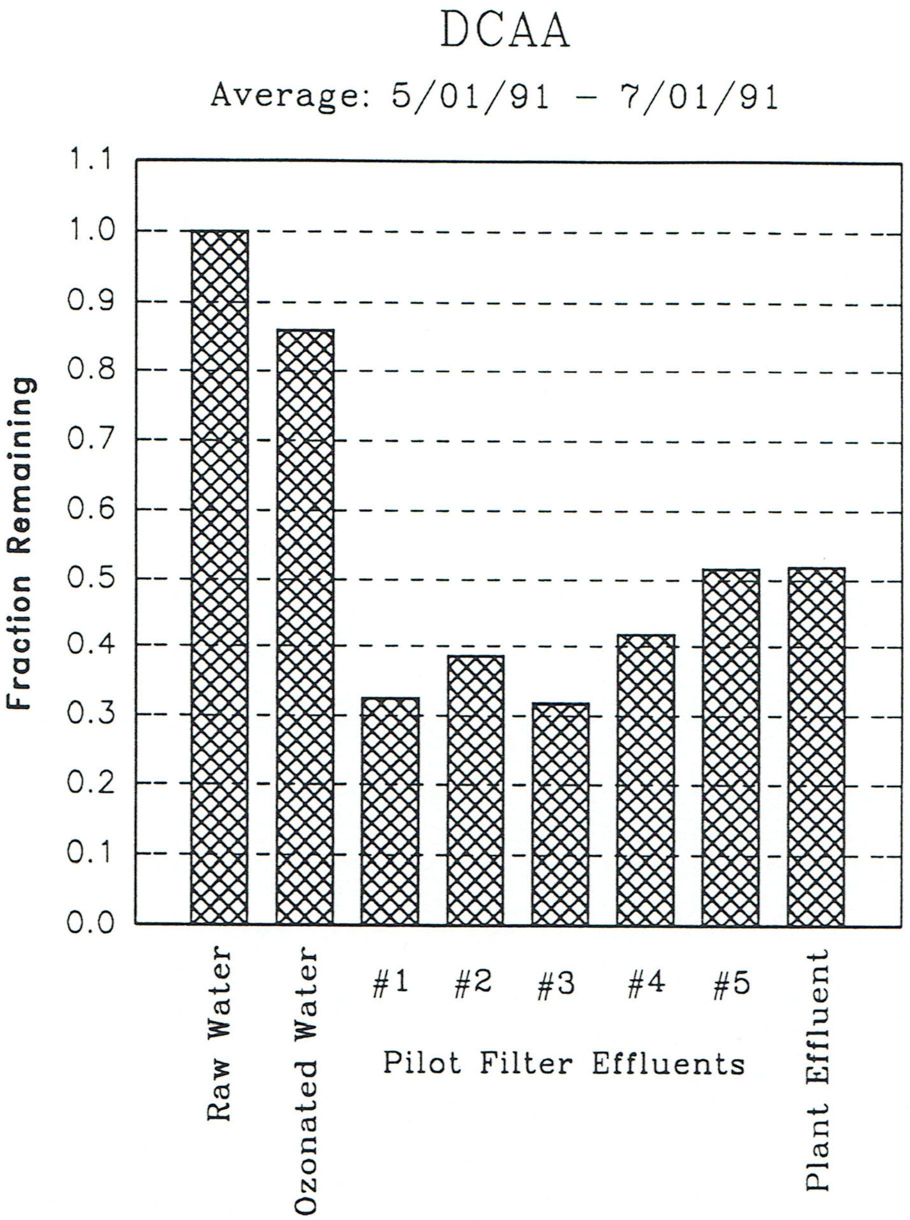

Figure 9. Relative DCAA Formation Potential in the West River Pilot Plant: Data from May 1, 1991 to July 1, 1991.

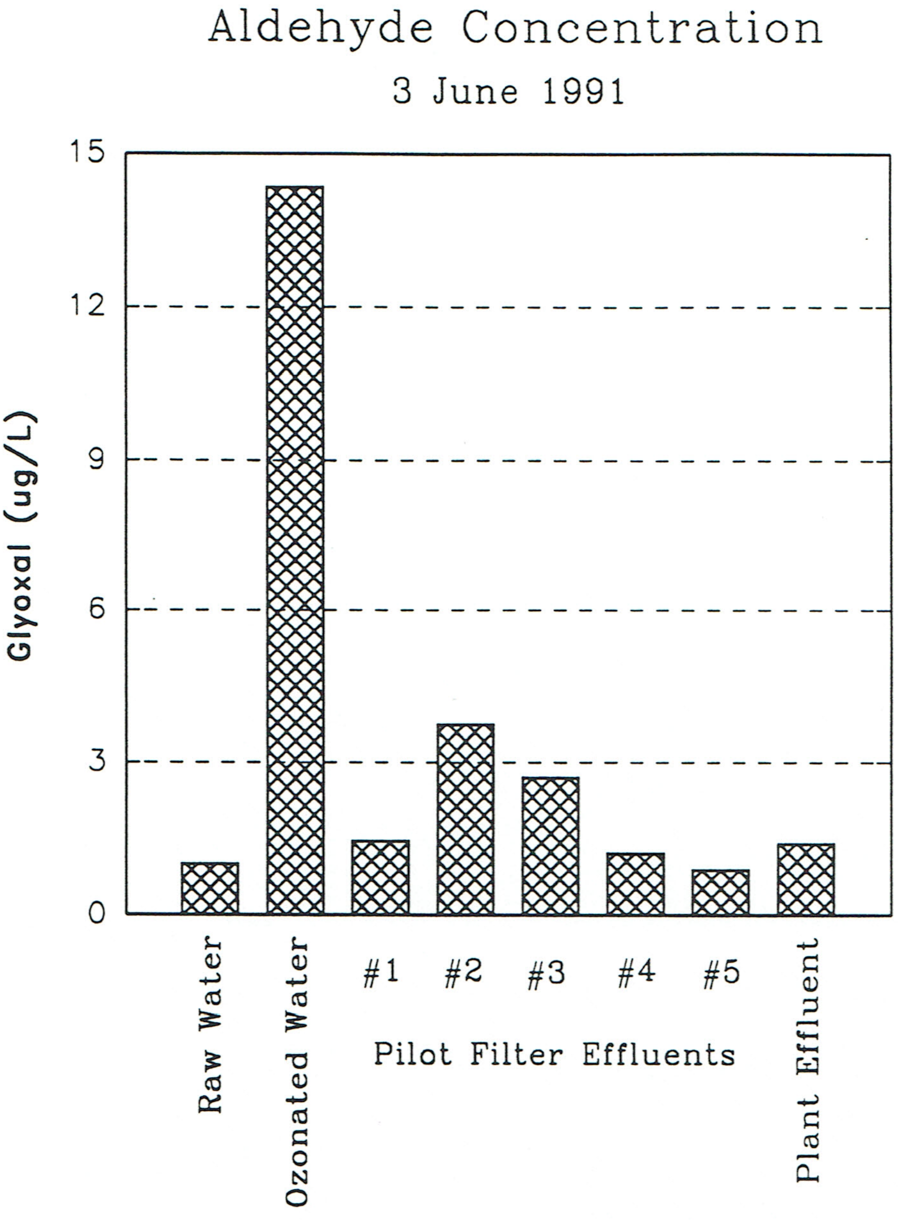

Figure 10. Glyoxal Concentrations in the West River Pilot Plant: Data from June 3, 1991.

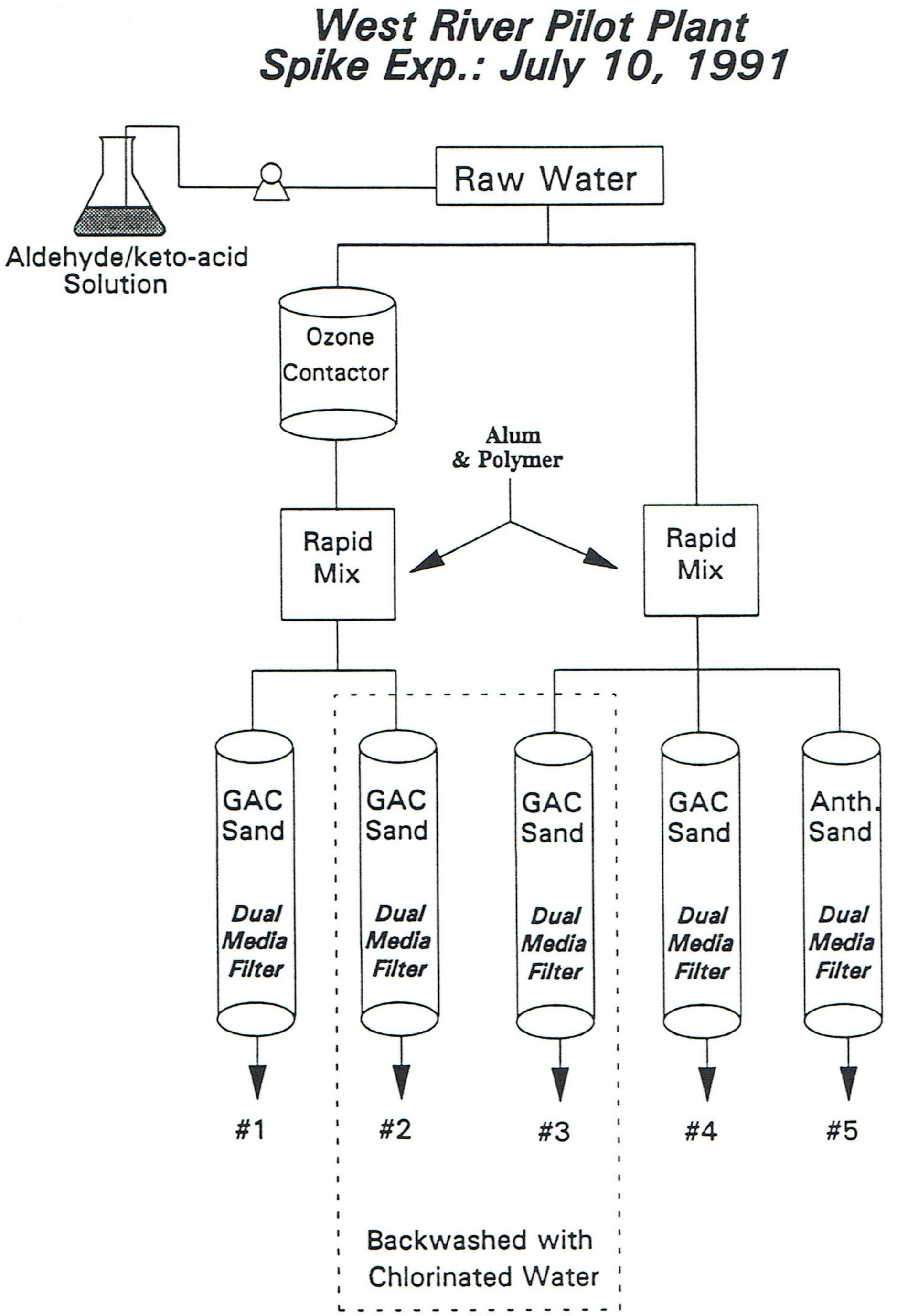

Figure 11. Schematic Diagram of the West River Pilot Plant during July Spike Experiment.

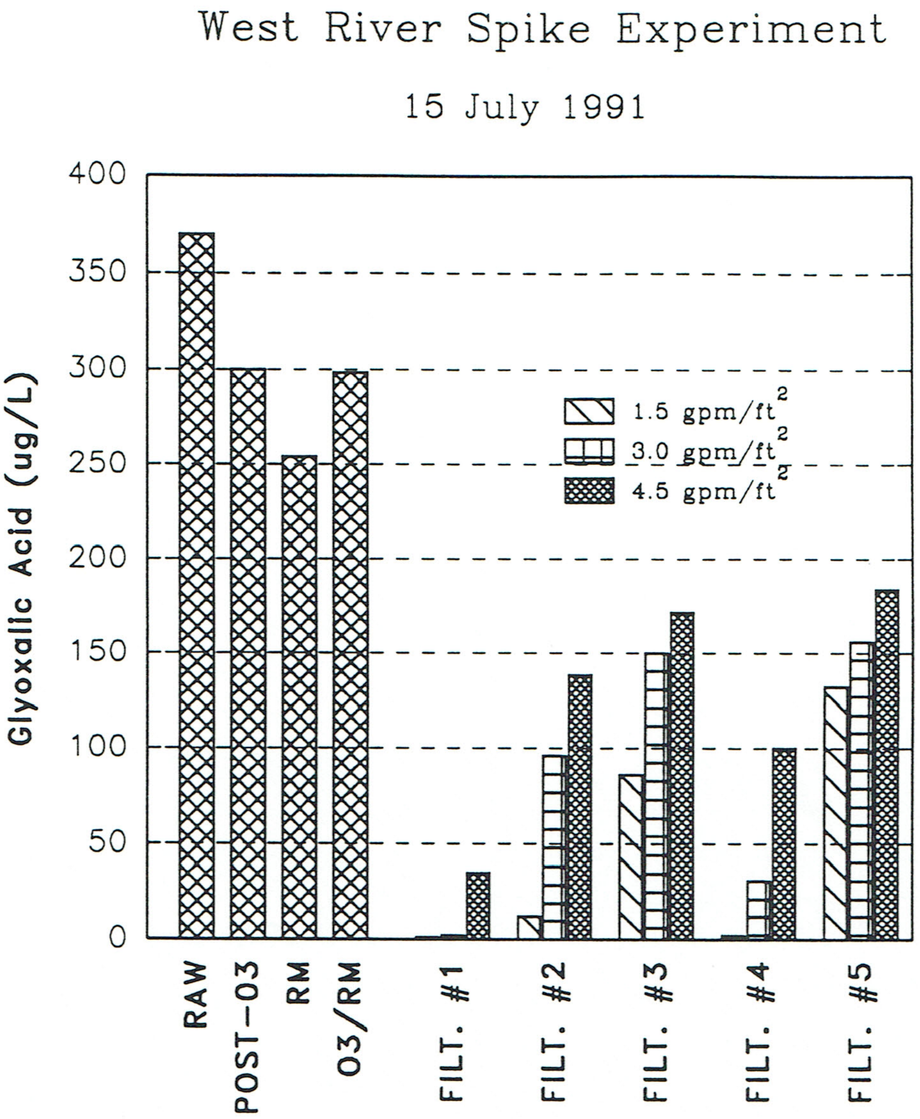

Figure 12. Effect of Filtration Rate and Clorine Backwash on Removal of Glyoxalic Acid.