

REMOVAL OF DISINFECTION BYPRODUCTS BY FILTRATION IN A PILOT-SCALE OZONE PLANT

David A. Reckhow, Patricia Byrnes Jaeger, Qing-wen Zhu, Yuefeng Xie,
Jon Weiner, James K. Edzwald
Department of Civil Engineering
University of Massachusetts
Amherst, MA 01003

Bruce Johnson
CH2M Hill
Boston, MA 02144

Introduction

Concerns over pending disinfection byproduct regulations have led many utilities in the US to consider the use of ozone as an alternative to chlorine. Ozone does not lead to the formation of chlorinated organic byproducts, and it is both a powerful oxidant and disinfectant. While the use of ozone may not preclude the need for chlorine, it can alleviate the need to add chlorine at the head of the plant. Ozone can also produce some secondary effects which translate to improved finished water quality and enhanced performance of subsequent processes (e.g., Langlais *et al.*, 1991). Many of these secondary effects result in lower disinfection byproduct precursor concentrations in the finished water. The combined effects of delayed addition of chlorine and improved DBP precursor removal can be very effective at reducing DBP concentrations at the tap.

One concern over the use of ozone is its tendency to enhance the biodegradability of natural organic matter. Unless controlled within the plant, organic nutrients can enter the distribution system and encourage bacterial re-growth. Biologically-active granular media filters offer an opportunity to reduce the organic nutrient concentration and thereby improve the biological stability of the water. Recent research suggests that the surface of activated carbon encourages biological colonization. Biodegradation occurs on such media in competition with adsorption. After exhaustion of the adsorptive capacity of the activated carbon, biodegradable organic compounds can still be removed by the attached bacteria (e.g., Servais *et al.*, 1991). Although bioregeneration of the GAC (biodegradation of previously adsorbed compounds) has been shown to occur in model systems (Speitel and DiGiano, 1987), arguments can be made against this mechanism for many other types of solutes (Xiaojian *et al.*, 1991).

In response to the surface water treatment rule and the disinfection byproduct rule, the Massachusetts Water Resources Authority (MWRA) initiated a pilot treatment program of its Wachusett Reservoir supply. The authority retained CH2M Hill Consulting Engineers and the University of Massachusetts for the purpose of conducting a 4-season pilot study on this water source. This paper attempts to describe the more important results regarding the removal of disinfection byproducts (DBPs), byproduct precursors, and assimilable organic

carbon (AOC). The data are summarized in a concise fashion so that they might be useful to other utilities and researchers examining the use of ozone with granular media filtration.

Materials and Methods

The pilot plant is a 90 gpm facility with three main parallel trains: direct filtration (DF); dissolved air flotation (DAF); and contact adsorption clarification (CAC) (Figure 1). The CAC unit operates like an upflow roughing filter, and it contains granular activated carbon (GAC). Each train feeds a set of three filters typically containing 6 feet of 1.4 mm anthracite (mono-media I), 6 feet of 1.6 mm anthracite (mono-media II), and 3 feet of 1.0 mm anthracite over 1 foot of 0.5 mm sand (dual-media). The filter columns were constructed of 4-inch-diameter clear-PVC. An additional set of filters, designated "acclimated" or "accl.", were made biologically active by long-term continuous operation. These contained 6 ft. of 1.4 mm anthracite, 3 ft of 1.0 mm F300 GAC¹ (coal-based) over 1 ft of sand; and 6 ft. of 1.2 mm Nuchar B² (wood-based). Starting in October, 1991, these filters were fed raw water in an upflow mode. This allowed them to be operated between seasons when the pilot plant was not staffed. As needed, the acclimated filters were plumbed to receive water from any one of the three trains.

Preozone doses fell within the range of 1.0 to 1.7 mg/L, depending on the day, and the testing season. The chosen dose was applied to all trains, and provided a residual of 0.20 to 0.25 mg/L in the contactor effluent. Filtration rates for all runs reported here were constant at 6 gpm/ft². The DAF unit was operated at 4 gpm/ft² throughout. Pilot runs chosen for intensive sampling for DBPs were those deemed near optimal. Although coagulants and doses changed from one sampling day to another, they were generally uniform across treatment trains. For both the first (6 Feb) and second (17-20 Feb) Winter sampling periods, 0.75 mg/L of PACl was being used as the primary coagulant. In the Spring (14 May), 8 mg/L of ferric chloride was used, and in the Summer (4 Aug), it was 5 mg/L of alum. Raw water temperatures varied from about 2°C in Winter, to 10°C in Spring and up to 20°C in Summer.

The pilot plant treated water from Wachusett Reservoir. This is a low DOC, low turbidity source, typical of many New England waters (Table 1). The reservoir also experiences periodic algal blooms, causing problems with tastes and odors. The plant was operated for 6 weeks at a time during four seasons from September 1991 to August 1992. Samples were collected once per season, except in the winter (February) when four sets of samples were collected.

Assimilable organic carbon (AOC) was measured on as many samples as the UMass laboratory capabilities would allow; typically 12 per run. The ozone disinfection byproducts that were measured included three keto-acids (glyoxalic acid, pyruvic acid, and ketomalonic acid). Chlorination byproducts (pentane extractables, haloacetic acids, and chloral hydrate) were measured after laboratory-scale chlorination. Formation potential 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

¹Calgon Corp., Bridgewater, NJ.

²Westvaco Corp., Covington, VA.

would have approximately the same chlorine residual throughout the reaction period. Samples collected for the simulated distribution system test were dosed with 4 mg/L chlorine and held for 2 days. This dose provided a residual of about 1 mg/L at the end of the incubation period. All other conditions were the same.

Table 1. Wachusett Reservoir Raw Water

Water Quality Parameter	Avg. Value	Units
Turbidity	0.4	NTU
Alkalinity	7	mg/L
Hardness	14	mg/L
pH	7.0	
DOC	3.1	mg/L

Assimilable organic carbon was measured using a modification of Van der Kooij's method as described by Kaplan and Bolt (1988). Samples were inoculated with both strains P17 and NOX. 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 with diazomethane (USEPA method 552: EMSL, 1990; Hwang *et al.*, 1990). Chloral hydrate (CH) was analyzed by a method using extraction with methyl-t-butyl ether (Met-JMM, 1989). Ketoacids were determined by a double derivatization GC method employing diazomethane and PFBOA (Xie and Reckhow, 1992). This latter method was based on the earlier work of Xiong *et al.*, 1991.

Results and Discussion

Raw Water Precursors and Removal by Ozonation

Raw water quality in the Wachusett Reservoir showed little change over the period from February to August, 1992. For example, the dichloroacetic acid formation potential was 70 µg/L in the winter, 63 µg/L in the spring and 65 µg/L in the Summer. Table 2 summarizes the concentrations of the four major precursors measured in this study. Pre-ozonation altered some of these values by a substantial amount. Table 1 shows that the percent removals ranged from an average of 45% for TCAA precursors to 35% for THM

precursors to 10% for DCAA precursors. The order and relative effectiveness of ozone at destroying these three precursors is identical to that which has been reported from laboratory studies (Reckhow *et al.*, 1986). The fourth precursor type, chloral hydrate, exhibited an average increase of 60% following ozonation. The fact that ozonation increases chloral hydrate formation has been known for several years, and it is attributed to ozone's tendency to form carbonyl compounds.

Table 2. DBP Precursor Concentrations in the Wachusett Reservoir
Raw Water and Impacts of Pre-ozonation

Precursor	Raw Water Conc. ($\mu\text{g/L}$)	% Removal by Ozone
THMFP	140	45
DCAA-FP	66	10
TCAA-FP	98	35
CH-FP	24	-60

General Trends in Filtered Water Quality

The run on August 4, 1992 presents a typical set of results for this pilot plant (Figures 2-8). On this day, samples were collected from the mono-media filters on all three trains. The anthracite in the mono-media filter on the DAF train had been replaced with fresh GAC in May, but the other two still contained the original anthracite media. Also, the three acclimated filters were receiving floated water, and samples were collected from each. On this day the Raw Water AOC was low as compared to the spring (21.4 mg/L vs 40 mg/L). This may have been due to the higher temperatures which could accelerate AOC utilization in the reservoir, and keep the steady state level low. As always, ozonation caused a large increase in AOC, especially NOX growth (Figure 2). The mono-anthracite filter in the direct filtration train showed relatively poor removal, typical of the low biological activity expected for anthracite. Dissolved air flotation showed very little AOC removal (DAF train; filter influent). Compounds responsible for ozone-produced AOC are likely to be of low molecular weight and not amenable to removal by coagulation and settling or flotation. In this particular sample, the NOX organisms did not grow. The mono-GAC filter showed good performance, probably due in part to abiotic adsorption for this relatively new media. All three biological activated carbon (BAC) or "acclimated" filters showed substantial drops in AOC as well. The mono-anthracite was the least effective of the three and the Nuchar B appeared to be the more effective of the two GAC filters. This latter trend is not thought to be significant, because the

previous pilot run showed slightly better removal by the F300. The contact adsorption clarifier was probably reaching DOC breakthrough, but not fully biologically-active, and therefore it did not remove AOC as well as the other GAC media.

The keto-acid data (Figure 3) were qualitatively similar to the AOC data. After ozonation the total keto-acid concentration was found to be consistently in the range of 69 μ g/L to 75 μ g/L. Some removal occurred across the DAF unit, especially for ketomalonic acid. This has been observed by the authors elsewhere, and the mechanisms are uncertain. The only non-acclimated, non-adsorbing filter (DF mono-media anthracite) was the least effective at removing keto-acids. Among the acclimated filters, the two GAC units were identical and quite effective. The mono-anthracite filter was only slightly less effective. Although not as well aged as the acclimated filters, the CAC media was still able to effectively remove keto-acids.

Trihalomethane data showed about a 26% reduction in precursors across ozonation on this day (Figure 4). Dissolved air flotation resulted in additional removal. The direct filtration effluent was only slightly better in quality than the floated water, suggesting similar chemistries with little biodegradation in either system. However, the filters on the DAF line did remove substantially more precursor material. The non-acclimated monomedia-GAC filter was clearly the best (still strongly adsorbing). Among the acclimated filters, the two containing GAC showed the best performance. Any differences in performance that existed between the two carbons (Nuchar B and F300) were minor. The CAC unit was showing signs of breakthrough. However, the quality of the filter influent was still quite good. In fact, it did not appear that the filter on the CAC train was removing any additional precursor material.

The haloacid (HAA) data showed nearly the same trends as the THMs (Figures 5 and 6). The principal difference was in the immediate effect of ozone. Trichloroacetic acid precursors were destroyed to a greater extent by ozone, and dichloroacetic acid precursors to a lesser extent. Nevertheless, both sets of precursors are more hydrophobic and less biodegradable than the AOC. Figure 7 shows an example of the data collected using a simulated distribution system test for determining precursors. Because the same low chlorine dose was used on all samples, only filter effluents were tested. Conclusions drawn from this figure are identical to those from the formation potential data. For this reason, only formation potential data will be shown.

Chloral hydrate precursors represent a class of compounds that include biodegradable ozonation byproducts as well as other, more refractory natural organic matter. As expected, ozonation produced an increase in Chloral hydrate precursors (Figure 8). Removal of these precursors throughout the pilot plant closely mirrored the THM and HAA data.

Changes in Performance over Time

All three acclimated filters were sampled for the first time during the Winter pilot run. Because of the large number of samples collected in February, it was not possible to measure AOC from these filters. Nevertheless, the keto-acid data provide valuable insight into the biological activity of the filter media. Figure 9 shows that both the mono-anthracite and the Nuchar B filters were removing a substantial amount of the keto-acids (recall that the post-ozone value was typically 70 μ g/L. However, the filter containing the F300 media was less

effective. This suggests that the coal-based GAC had developed biological activity more slowly than the anthracite. This is the reverse of what has been observed elsewhere (Krasner *et al.*, 1993). All values were low for the CAC train, because the CAC unit was removing keto-acids by itself. These same trends were seen with the chloral hydrate precursors (Figure 10), and to a lesser extent, the trichloroacetic acid precursors (Figure 11). The reason that the chloral hydrate precursors responded more strongly to changes in biological activity than the TCAA precursors, is thought to be due to their greater inherent biodegradability. This will be further discussed in the next section.

Despite the poorer performance of the F300 in February, by May it was comparable to the wood-based carbon (Figure 12), and superior to the anthracite. All three acclimated filters were operating more effectively in May, and these trends continued through August (Figure 3). The reasons the wood-based GAC appeared to develop biological activity earlier than the coal-based carbon are not known. The greater bed depth (6ft vs 3 ft) or the larger and more regular pore structure of the wood-based carbon may play a role. An explanation for why anthracite would develop biological activity more quickly than the GAC, might lie in the competitive nature of substrate uptake. Before the GAC can become exhausted with respect to adsorption, strongly adsorbed compounds might not be available for uptake by the microorganisms (e.g., DeWaters and DiGiano, 1990; Xiaojian *et al.*, 1991). Thus, growth could be retarded until the GAC becomes exhausted. In contrast, anthracite media would not suppress the substrate concentration. Therefore, growth could begin immediately. This mechanism may be superimposed over surface effects on bacterial attachment which would favor the GAC over anthracite. The net effect may depend on organic loading rates, temperature, and the nature of the dissolved organic carbon.

Even the non-acclimated filters showed signs of developing a small degree of biological activity. Figure 13 illustrates the lack of biological activity of these filters in the early runs. None of the keto-acids was removed through DAF, and only a portion of the ketomalonic acid was removed through filtration. Nevertheless, in May the DAF mono-anthracite filter showed an improvement (Figure 12), and by August the DF mono-anthracite filter was removing keto-acids as well (Figure 3). Improved removal of chloral hydrate precursors over time was also observed for the non-acclimated filters. This was not the case for the other chlorination byproduct precursors.

Summary of Process Performance

In an effort to summarize the large volume of data collected during this project, removal efficiencies across the various filters were calculated and averaged. Table 3 shows the results of these calculations. In general all DBP formation potential data from February to August were used in obtaining the numbers in Table 3 with the following exceptions (SDS could not be used, since filter influents were not measured). Only February chloral hydrate data were used for the non-acclimated filters, because subsequent data from these filters suggested some biological removal of these compounds. Only the later data (May-August) were used for characterizing the acclimated filters. This was done to ensure that the numbers

in Table 3 represented a mature biological system. Because the ultimate performance of the two acclimated GAC filters was nearly indistinguishable, their data were pooled.

Dissolved air flotation resulted in a 38% removal of TCAA precursors and 27% or less for the other precursors. The 13% average for TTHM precursors is probably low; a more accurate value may be closer to 26% as observed for the August run.

The combination of DAF and anthracite mono-media filtration resulted in nearly the same precursor removal as direct filtration with an anthracite mono-media filter. This is expected, since the extent of organics removal in these abiotic systems is primarily controlled by their chemistry (i.e., the chemistry of coagulation) and not the physical means of particle separation. Precursor removal in the non-acclimated filters followed a well-defined hierarchy similar to that previously reported for coagulation. The TCAA precursors were removed to the greatest extent (avg: 61%). Next came the DCAA precursors (40%), followed closely by the THM precursors (37%). The least easily coagulated were the chloral hydrate precursors (avg: 29%). Reckhow and Singer (1984; 1990) showed that TCAA precursors were among the most readily coagulated of the DBP precursors, because they were most strongly associated with the hydrophobic organic fractions (i.e., humic acids). In their work, DCAA precursors were much less easily removed, and they were followed by the THM precursors. Although they didn't study chloral hydrate precursors, they did look at precursors to another carbonyl-containing byproduct, 1,1,1-trichloropropanone. These compounds were the least easily removed of all, probably due to their low molecular weight. The same may be true for chloral hydrate precursors, since they are produced by ozonation like trichloropropanone precursors, and are highly biodegradable.

Table 3. Average Precursor Removal from Wachusett Pilot Studies*

Treatment Process or Change in Process	TTHM	DCAA	TCAA	Chloral Hydrate
<i><u>% Removal across Process</u></i>				
DAF alone	13	27	38	20
DAF+ Anthr. Filtr.	37	40	65	27
Anthr. Filtr.	37	40	58	30
Accl. Anthr. Filtr.	49	54	70	67
Accl. GAC Filtr.	62	65	76	78
<i><u>Additional % Removal from Change</u></i>				
Acclimation (Anthr.)	12	14	9	38
Anthr. → GAC	13	9	6	11

*Calculated as the difference between the concentration in the ozone contactor effluent and the indicated process effluent divided by the concentration in the ozone contactor effluent

The acclimated anthracite mono-media filter exhibited superior performance to the non-acclimated filter. Percent removals are shown in Table 3. Benefits accrued from acclimation may be better visualized by examining the difference between the removals across the acclimated filters and the non-acclimated filters. These numbers are shown in the second-to-last row in Table 3. Most strongly affected by acclimation are the chloral hydrate precursors. An additional 38% of these compounds could be removed by biological activity on the filter. This further supports the assertion that the chloral hydrate precursors are the most biodegradable of the DBP precursors. Next in line were the DCAA and THM precursors at 14% and 12%, respectively. The TCAA precursors (9%) appeared to be the least biodegradable. Miltner *et al.* (1992) also compared an acclimated anthracite filter with a non-biologically active control. They found an additional removal of $20 \pm 14\%$ for THM precursors and $28 \pm 10\%$ for total haloacid precursors due solely to acclimation of this media.

The importance of providing acclimation time, and avoiding contact with disinfectants is well recognized. Krasner *et al.* (1993) showed that up to 100 days may be needed for anthracite filters to develop the ability to biologically degrade aldehydes. Weinberg *et al.* (1993) noted that among the 6 plants they studied that used anthracite filter media, only the one that had been operating for an extended period in full-scale, and had not been subject to chlorine or ozone residuals, showed good removal of aldehydes. Reckhow *et al.* (1992) observed that even residual chlorine in the backwash water can inhibit biological activity.

The small difference in the effect of acclimation on TCAA precursors as compared to the THMs and DCAA may or may not be significant. Considering that the TCAA precursors are most strongly associated with the highly recalcitrant humic acids (Reckhow *et al.*, 1990), one would expect them to be very slowly degraded. On the other hand, these same humic acids are among the most reactive fraction with respect to ozone (Reckhow *et al.*, 1993), leading to partial oxidation, fragmentation, and possibly more rapid biodegradation. If the increase in biodegradability occurs more readily than the destruction of TCAA precursor sites, ozone could have an especially large impact on the biological removal of TCAA formation potential. Recent research (Shukairy *et al.*, 1992; Speitel *et al.*, 1993) indicates that total haloacid precursors (TCAA + DCAA) are more biodegradable than THM precursors. Differences between these studies and the Wachusett study include temperature, media contact time, raw water quality and pretreatment. Regarding the latter, TCAA precursors are so extensively removed by coagulation (up to 65% in this study) that the remaining precursors may not be representative of what was present in the raw water.

Additional improvements in precursor removal could be realized by replacing anthracite media with GAC in biologically-active filters. This is shown by the numbers in the bottom row of Table 3. These numbers are equal to the difference between the percent removal across the acclimated GAC filters and the acclimated anthracite filters. On average, a 10% improvement was observed with GAC. As before, the TCAA precursors were the least affected by the improved biological system. The ability of GAC to remove AOC better than anthracite is well documented (e.g., LeChevallier *et al.*, 1992), and this seems to carry over to a wide variety of DBP precursors (see also Miltner and Summers, 1992). As an example, Price *et al.* (1993) indicated that at East Bay Municipal District's Sobrante Pilot Plant, about 5% additional THMFP removal occurs with GAC/sand versus anthracite/sand (both following

ozonation), and the benefits of GAC at Tampa's Hillsborough River Pilot Plant are somewhat greater. Table 3 shows that a 13% improvement was observed in this study for THMFP. The overall removals across coagulation and biologically-active GAC filtration in this study ranged from 62% for THM precursors (compare with 54% from LeChevallier *et al.*, 1992) to 78% for chloral hydrate precursors.

Relative Byproduct Concentrations

The determination of relative precursors concentrations can sometimes provide useful information for systems that have a long history of THM monitoring, but little data on other byproducts, such as HAAs (Reckhow and Singer, 1990). Figure 14 shows the ratio of the formation potential for total haloacids (TCAA + DCAA) to total trihalomethanes for the May 14 sampling date. The raw water ratio is nearly 1.1 $\mu\text{g}/\mu\text{g}$, which is typical of many natural waters. Although subsequent treatment reduces the TCAA to a greater extent than the TTHMs, the reverse is true for DCAA. This results in little net change in the HAA/TTHM ratio. A dark line is drawn in Figure 14 at the 0.75 $\mu\text{g}/\mu\text{g}$ mass ratio. This represents the ratio of the proposed MCLs for the haloacids and THMs. All the bars fall above this line indicating that the haloacids will determine compliance for this water at pH 7. Dichloroacetic acid will be the major contributing species. Figure 15 shows that similar ratios are observed for low-dose, SDS conditions. Again, DCAA is the principal haloacid. There is a very slight tendency for DCAA to become more important as the chlorine dose is lowered. These data suggest, for example, that the pH could be elevated a certain extent for corrosion control, without endangering compliance. As pH is increased above 7, TTHM formation generally increases, while the TCAA formation decreases (e.g., Reckhow and Singer, 1985). Dichloroacetic acid formation is not strongly affected by pH.

Conclusions

1. Preozonation alone resulted in a 10% removal of DCAA precursors, 35% removal of TTHM precursors, and a 45% removal of TCAA precursors.
2. As expected, precursor removal was dependent on the biological activity of the filter media, and was not substantially affected by use of DAF prior to filtration. Non-acclimated filters removed 29% of the chloral hydrate precursors, 37% of the THM precursors, 40% of the DCAA precursors, and 61% of the TCAA precursors.
3. The coal-based, F300 required more time to achieve good biological activity than the wood-based, Nuchar B. However, once both were operating in a biological mode, their performances were comparable. The anthracite filter achieved good biological activity earlier than the F300 filter. During this time it outperformed the GAC media. However, once biological activity was established, the GAC media was clearly superior.

4. Acclimation of the anthracite filter media improved the removals of all precursors tested. Incremental benefits of acclimation ranged from 9-38% additional precursor removal. Chloral hydrate precursors were most susceptible to biological removal.
5. Use of acclimated GAC/sand filters in place of acclimated anthracite/sand filters produced additional benefits in precursor removal in the range of 6-13%. The overall precursor removals by the acclimated GAC/sand filters were 62% for the THMs, 65% for DCAA, 76% for TCAA and 78% for chloral hydrate.
6. The ratio of HAA precursors to TTHM precursors in the Wachusett Raw water was about 1.1 $\mu\text{g}/\mu\text{g}$. Upon ozonation, this ratio increased slightly. Following coagulation and filtration, it fell, but still remained in the vicinity of 0.9 $\mu\text{g}/\mu\text{g}$. DCAA precursors became predominant after treatment. When comparing parallel trains for precursor removal, the formation potential test and the simulated distribution system test showed the same trends.

Acknowledgements

The authors wish to thank Michael S. Switzenbaum and Rebecca McEnroe for their help with AOC analysis and interpretation. Thanks also go to Roger Yorton for supervising the operation of the Wachusett Pilot Plant. This work was conducted with the support of the Massachusetts Water Resources Authority

Literature Cited

- DeWaters, J.E. and F.A. DiGiano, 1990. "The Influence of Ozonated Natural Organic Matter on the Biodegradation of a Micropollutant in a GAC Bed," Jour. Am. Wat. Wrks. Assn. 82:8:69-75
- 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.
- 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.
- Kaplan, L.A. and T.L. Bolt, 1988. "Measurement of Assimilable Organic Carbon in Water Distribution System by a Simplified Bioassay Technique," Proc. 16th Annual AWWA Wat. Qual. Techn. Conf., Amer. Wat. Wrks. Assn., Denver, CO., p.475.
- Koch, B. et al., 1988. "Analysis of Halogenated Disinfection by-products by Capillary Chromatography," Presented at the AWWA Water Quality Technology Conference, November, 1988.
- Krasner, S.W., M.J. Scilimenti, and B.M. Coffey, 1993. "Testing Biologically Active Filters for Removing Aldehydes Formed During Ozonation," Jour. Am. Wat. Wrks. Assn. 85:5:62-71.

Langlais, B., D.A. Reckhow and 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.

Le Chevallier, M.W., W.C. Becker, P. Schorr and R.G. Lee, 1992. "Evaluating the Performance of Biologically Active Rapid Filters," Jour. Am. Wat. Wrks. Assn. 84:4:136-146.

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.

Miltner, R.J. and R.S. Summers, 1992. "A Pilot-scale Study of Biological Treatment," Proc. 1992 Am. Wat. Wrks. Assn. Annual Conf., pp.181-198

Miltner, R.J., R.S. Summers, J.Wang, J. Swertfeger, and E.W. Rice, 1992. "The Response of Biological Filters to Backwashing," Proc. 1992 Wat. Qual. Techn. Conf., pp657-680, Am. Wat. Wrks. Assn., Denver, CO.

Price, M.L., R.W. Bailey, A.K. Enos, M. Hook and S.W. Hermanowicz, 1993. "Evaluation of Ozone/Biological Treatment for Disinfection Byproducts Control and Biologically Stable Water," Ozone: Sci. & Eng. 15:2:95-130.

Reckhow, D.A., P. Bose, B. Bezbarua, E. Hesse, and A. MacNeill. 1993. "Transformations of Natural Organic Material During Preozonation," Final Project Report to USEPA (Grant #CR-814663-01-0; Leown A. Moore, Project Officer).

Reckhow, D.A., B. Legube and P.C. Singer, 1986. "The Ozonation of Organic Halide Precursors: Effect of Bicarbonate," Water Research, 20(8):987-998.

Reckhow, D.A. and P.C. Singer, 1984. "Removal of Organic Halide Precursors by Pre-ozonation and Alum Coagulation," Journal of the American Water Works Association, Vol. 76, No. 4, pp. 151-157.

Reckhow, D.A. and P.C. Singer, 1985. "Mechanisms of Organic Halide Formation During Fulvic Acid Chlorination and Implications with Respect to Pre-ozonation," in Water Chlorination: Environmental Impact and Health Effects, Vol. 5, pp. 1229-1257, (Lewis Publishers, Inc., Chelsea, MI.).

Reckhow, D.A. and P.C. Singer, 1990. "Chlorination Byproducts in Drinking Waters: From Formation Potentials to Finished Water Concentrations," Journal of the American Water Works Association, 82:4:173-180.

Reckhow, D.A., P.C. Singer and R.L. Malcolm, 1990. "Chlorination of Humic Materials: Byproduct Formation and Chemical Interpretations," Environmental Science & Technology, 24:11:1655-1664.

Reckhow, D.A., J.E. Tobiason, M.S. Switzenbaum, R. McEnroe, Y. Xie, Q-W. Zhu, X. Zhou, P. McLaughlin and H.J. Dunn, 1992. "Control of Disinfection Byproducts and AOC by Pre-Ozonation and Biologically-Active In-line Direct Filtration," Proc. 1992 Am. Wat. Wrks. Assn. Annual Conf., pp.

Servais, P., G. Billen, C. Ventresque, and G.P. Bablon, 1991. "Microbial Activity in GAC Filters at the Choisy-le-Roi Treatment Plant," Jour. Am. Wat. Wrks. Assn. 83:2:62-68.

Shukairy, H.M., R.J. Miltner and R.S. Summers, 1992. "Control of Disinfection By-products and Biodegradable Organic Matter Through Biological Treatment," Revue des Sciences de l'Eau, 5:special:1-15.

Speitel, G.E. Jr. and F.A. DiGiano, 1987. "The Bioregeneration of GAC Used to Treat Micropollutants," Jour. Am. Wat. Wrks. Assn. 79:1:64-73.

Speitel, G.E. Jr., J.M. Symons, A.C. Diehl, H.W. Sorensen, and L.A. Cipparone, 1993. "Effect of Ozone Dosage and Subsequent Biodegradation on Removal of DBP Precursors," *Jour. Am. Wat. Wrks. Assn.* 85:5:86-95.

Weinberg, H.S., W.H. Glaze, S.W. Krasner, and M.J. Scilimenti, 1993. "Formation and Removal of Aldehydes in Plants That Use Ozonation," *Jour. Am. Wat. Wrks. Assn.* 85:5:72-85.

Xiaojian, Z, W. Zhansheng and G. Xiasheng, 1991. "Simple Combination of Biodegradation and Carbon Adsorption - The Mechanism of the Biological Activated Carbon Process," *Wat. Res.* 25:2:165-172.

Xie, Y. and D.A. Reckhow, 1992. "Formation of Ketoacids in Ozonated Drinking Water," *Ozone: Sci. & Eng.*, 14:269-275.

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.

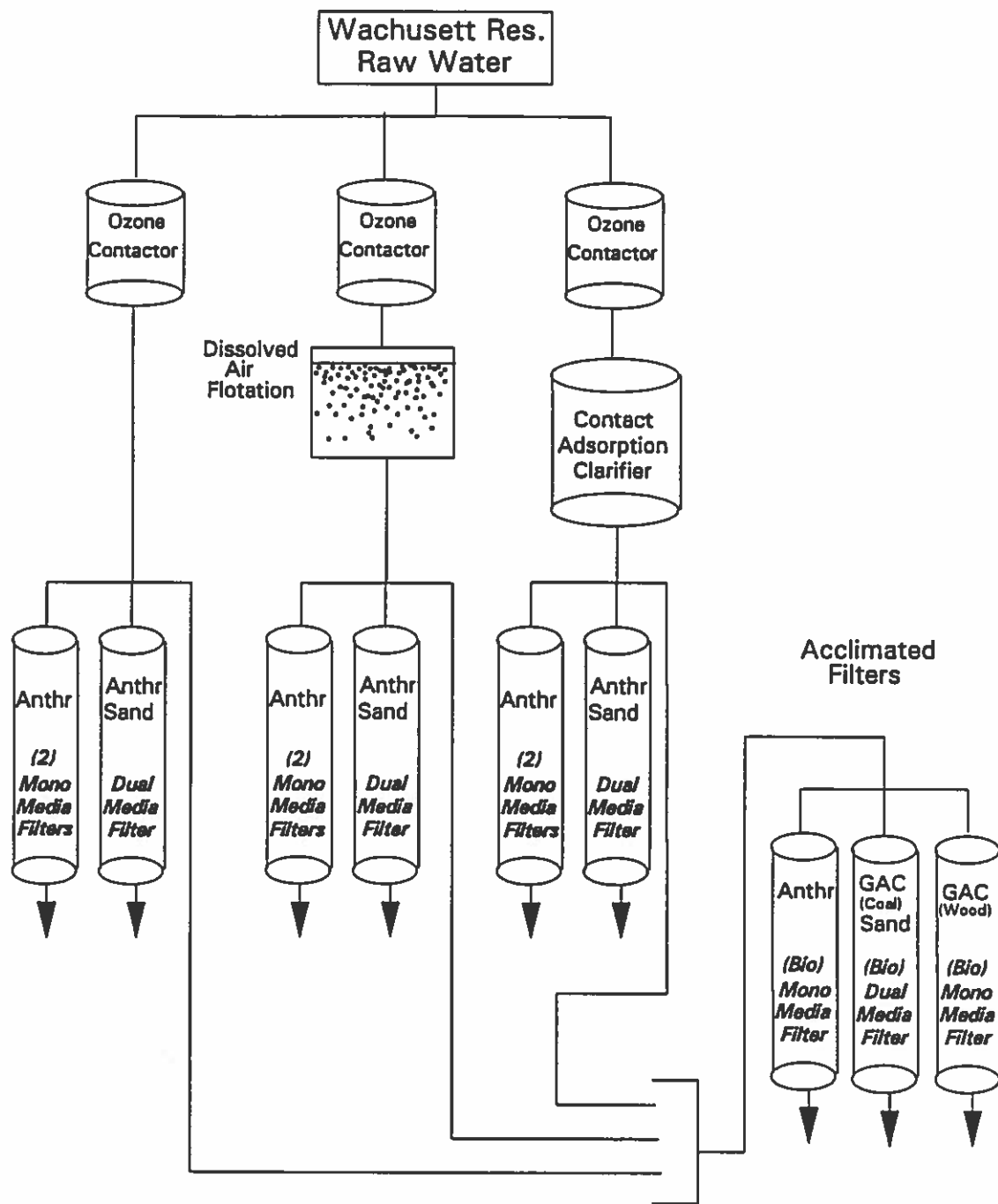


Figure 1. Process Schematic for the Wachusett Reservoir Pilot Plant

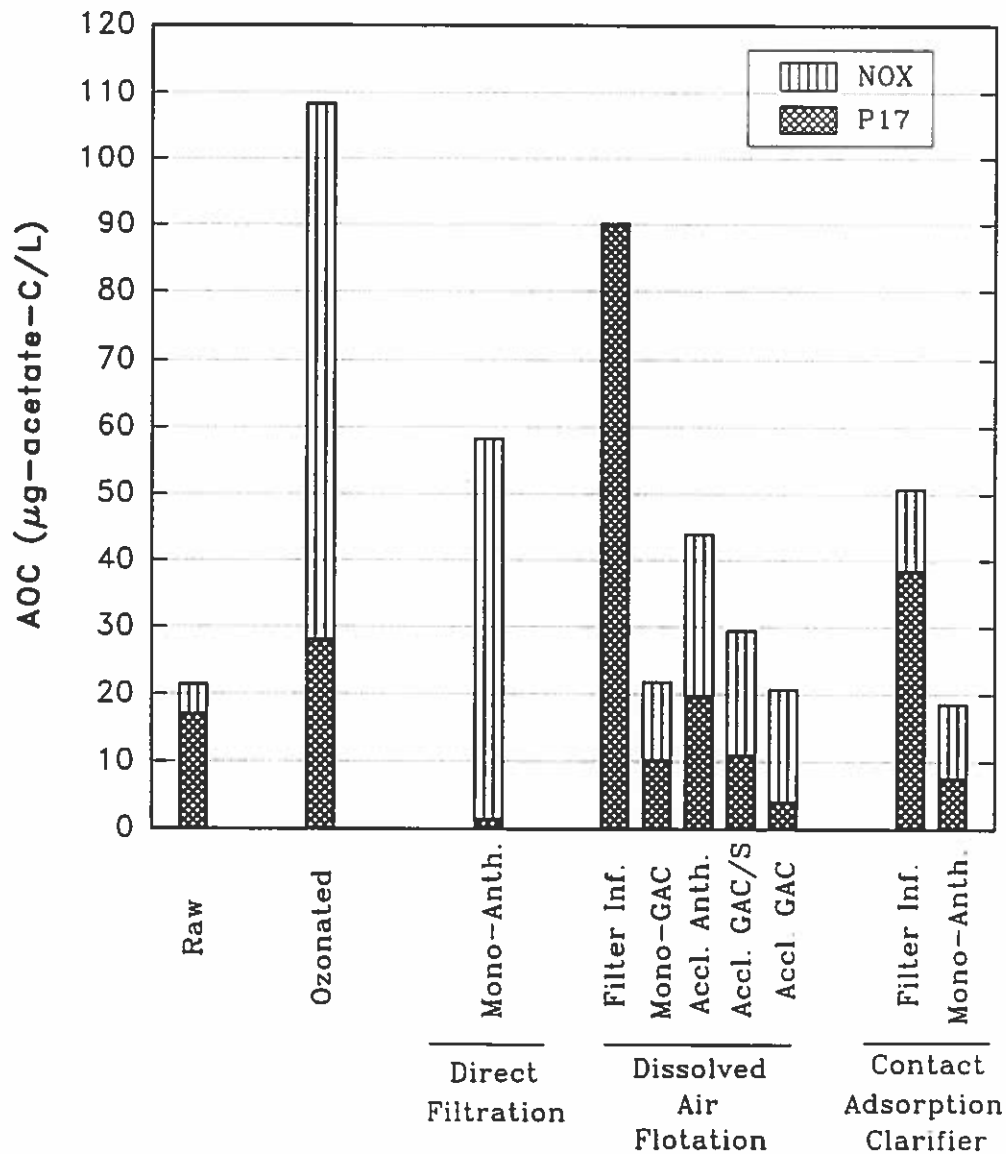


Figure 2. Assimilable Organic Carbon Concentrations at Various Stages of Treatment on August 4, 1992. (All are filter effluents unless otherwise indicated; Mono-GAC=fresh mono-media GAC filter with F300; Accl. Anth.=acclimated mono-media anthracite filter; Accl. GAC/S=acclimated GAC/Sand dual-media with F300; Accl. GAC=acclimated GAC mono-media filter with Nuchar B)

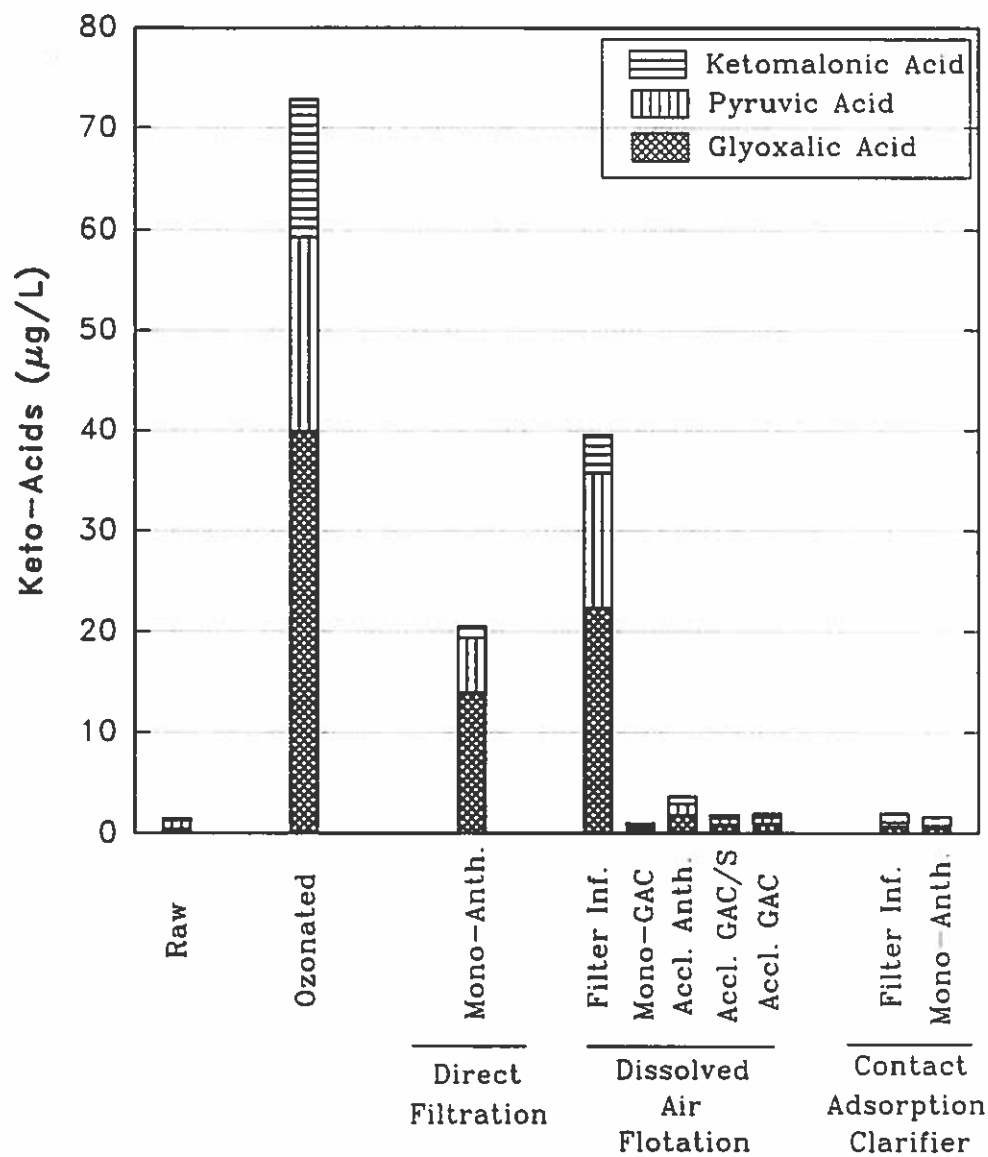


Figure 3. Keto-acids at Various Stages of Treatment on August 4, 1992. (All are filter effluents unless otherwise indicated; Mono-GAC=fresh mono-media GAC filter with F300; Accl. Anth.=acclimated mono-media anthracite filter; Accl. GAC/S=acclimated GAC/Sand dual-media with F300; Accl. GAC=acclimated GAC mono-media filter with Nuchar B)

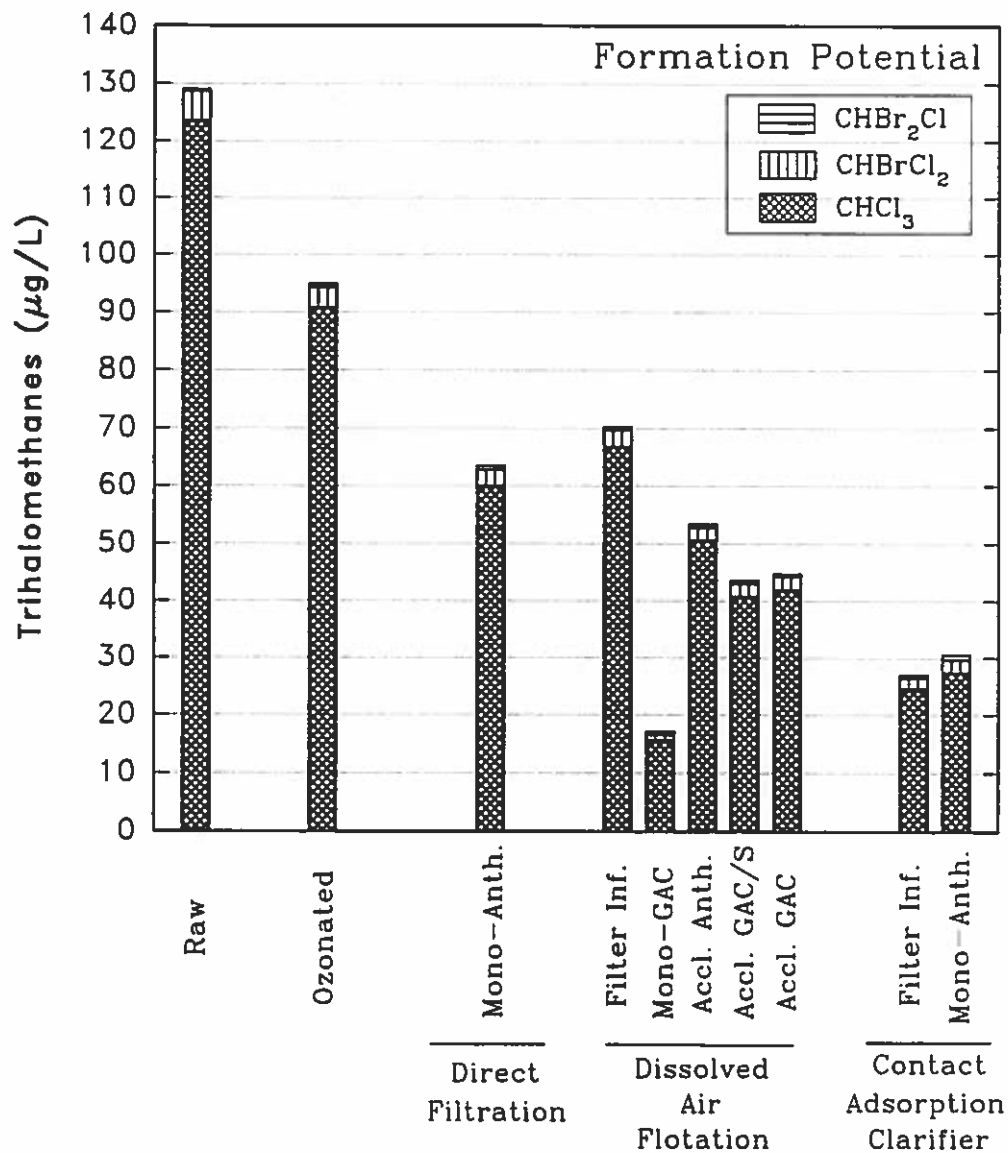


Figure 4. Trihalomethane Formation Potential at Various Stages of Treatment on August 4, 1992. (All are filter effluents unless otherwise indicated; Mono-GAC=fresh mono-media GAC filter with F300; Accl. Anth.=acclimated mono-media anthracite filter; Accl. GAC/S=acclimated GAC/Sand dual-media with F300; Accl. GAC=acclimated GAC mono-media filter with Nuchar B)

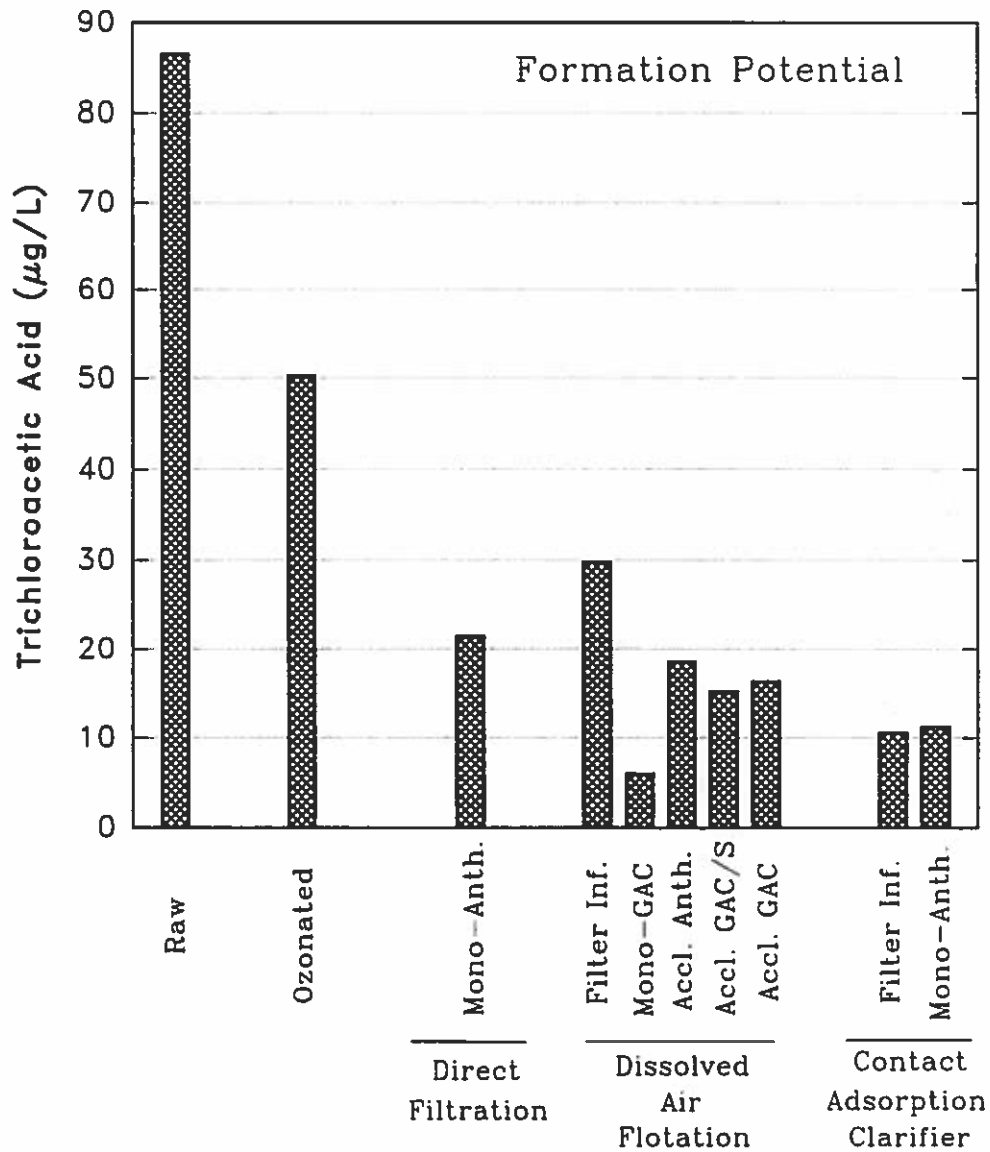


Figure 5. Trichloroacetic Acid Formation Potential at Various Stages of Treatment on August 4, 1992. (All are filter effluents unless otherwise indicated; Mono-GAC=fresh mono-media GAC filter with F300; Accl. Anth.=acclimated mono-media anthracite filter; Accl. GAC/S=acclimated GAC/Sand dual-media with F300; Accl. GAC=acclimated GAC mono-media filter with Nuchar B)

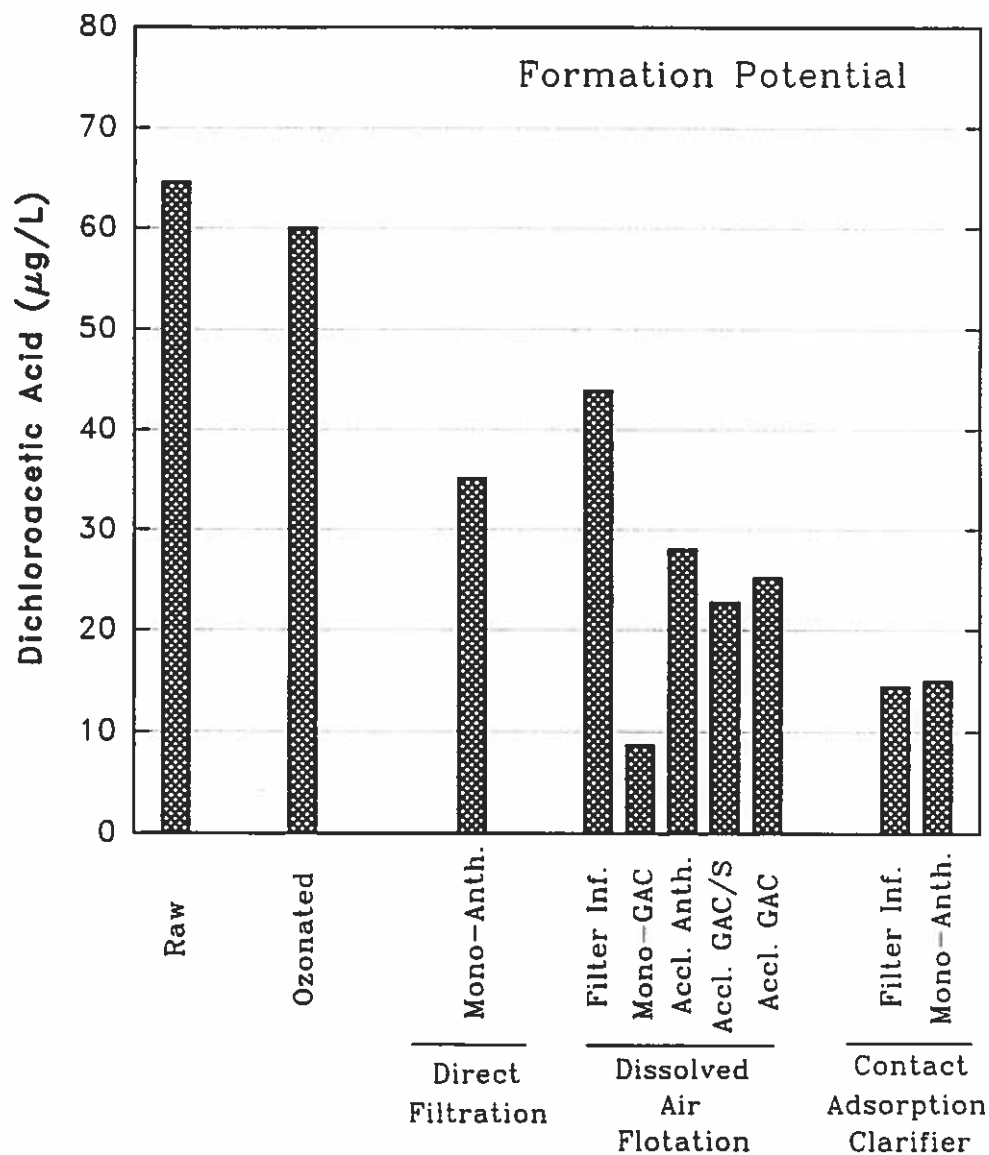


Figure 6. Dichloroacetic Acid Formation Potential at Various Stages of Treatment on August 4, 1992. (All are filter effluents unless otherwise indicated; Mono-GAC=fresh mono-media GAC filter with F300; Accl. Anth.=acclimated mono-media anthracite filter; Accl. GAC/S=acclimated GAC/Sand dual-media with F300; Accl. GAC=acclimated GAC mono-media filter with Nuchar B)

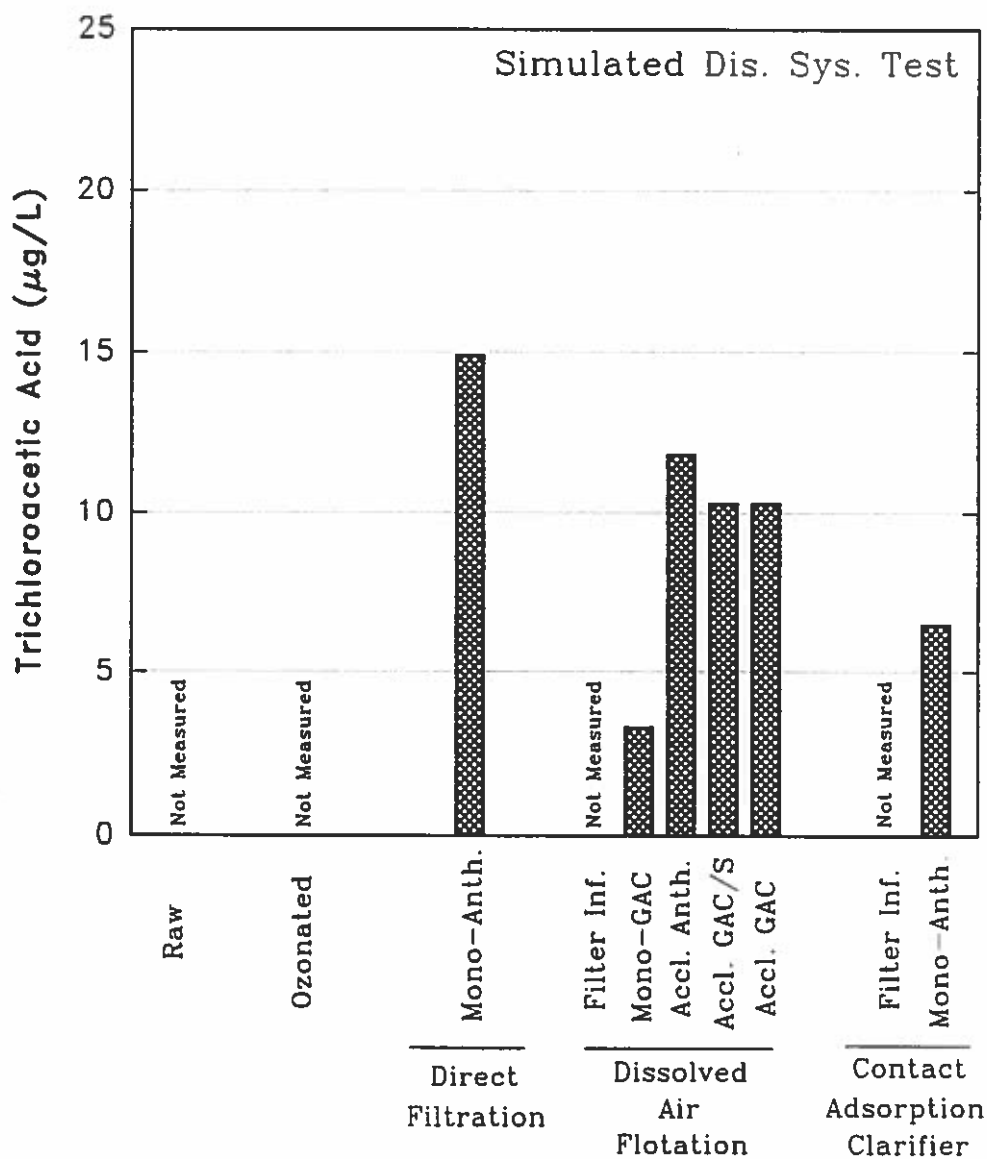


Figure 7. Trichloroacetic Acid Formation from the Simulated Distribution System Test in the Pilot Filter Effluents on August 4, 1992. (All are filter effluents unless otherwise indicated; Mono-GAC=fresh mono-media GAC filter with F300; Accl. Anth.=acclimated mono-media anthracite filter; Accl. GAC/S=acclimated GAC/Sand dual-media with F300; Accl. GAC=acclimated GAC mono-media filter with Nuchar B)

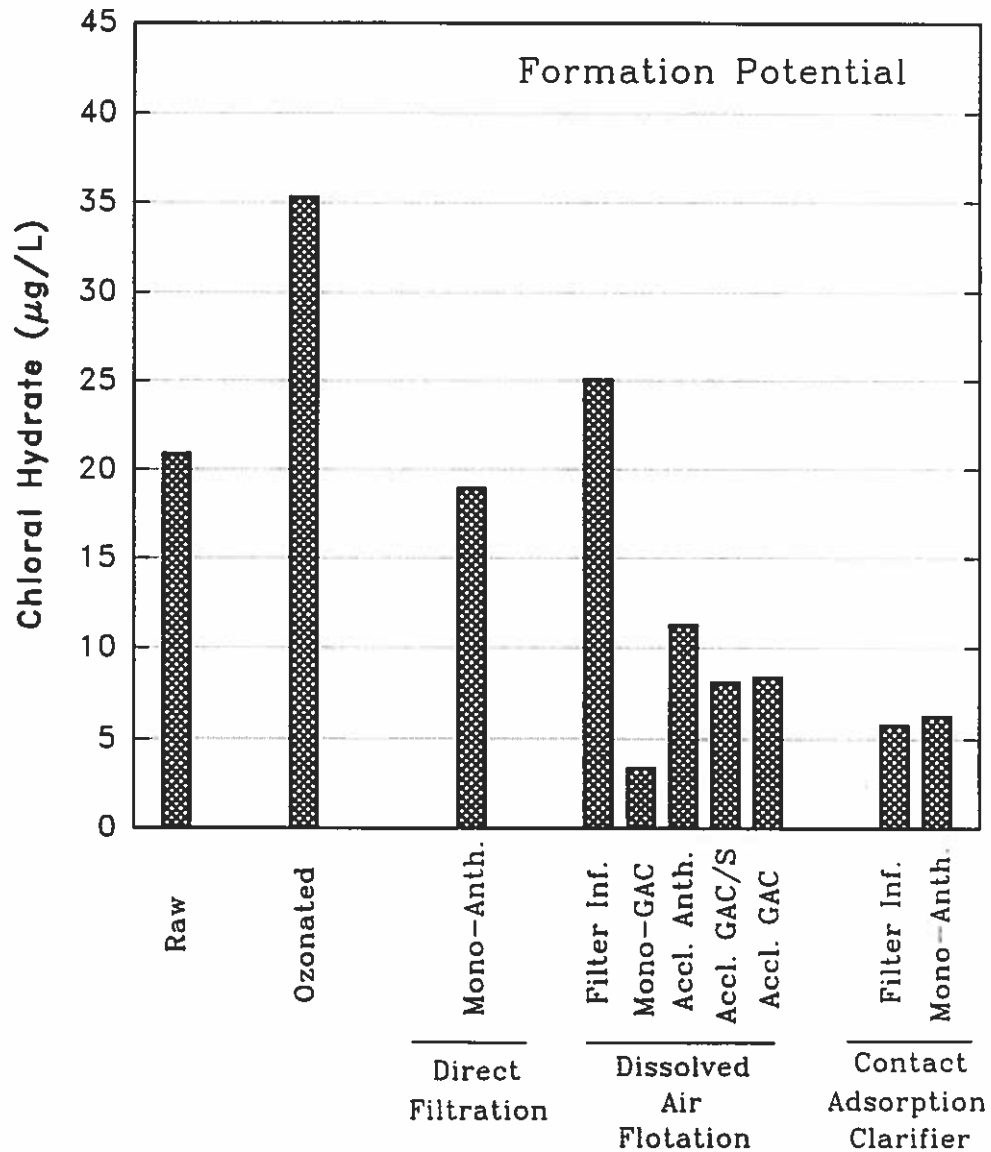


Figure 8. Chloral Hydrate Formation Potential at Various Stages of Treatment on August 4, 1992. (All are filter effluents unless otherwise indicated; Mono-GAC=fresh mono-media GAC filter with F300; Accl. Anth.=acclimated mono-media anthracite filter; Accl. GAC/S=acclimated GAC/Sand dual-media with F300; Accl. GAC=acclimated GAC mono-media filter with Nuchar B)

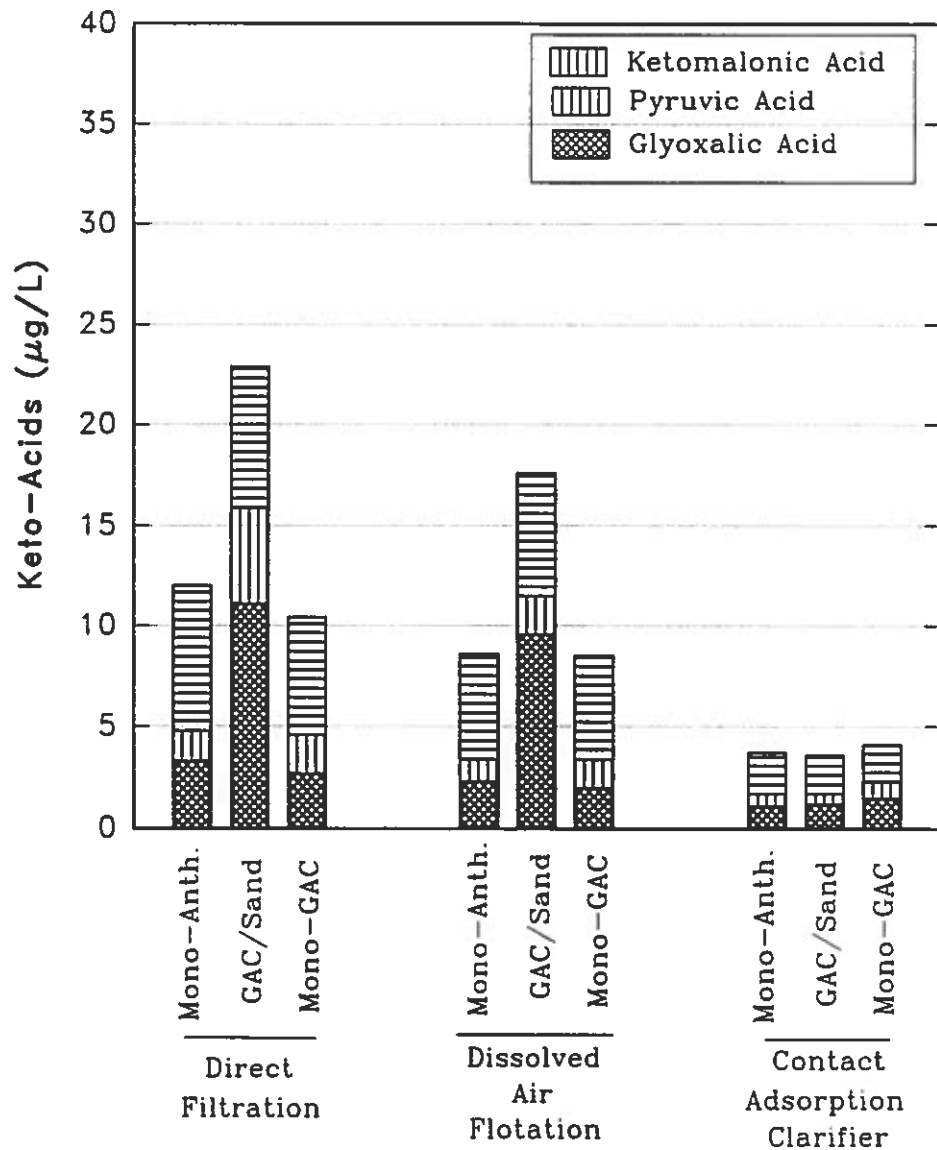


Figure 9. Keto-acid Concentrations in the Effluents of the Three Acclimated Filters for the Period February 17-20, 1992. (Mono-Anth.=mono-media anthracite filter; GAC/Sand=dual-media filter with F300 and sand; Mono-GAC=mono-media filter with Nuchar B)

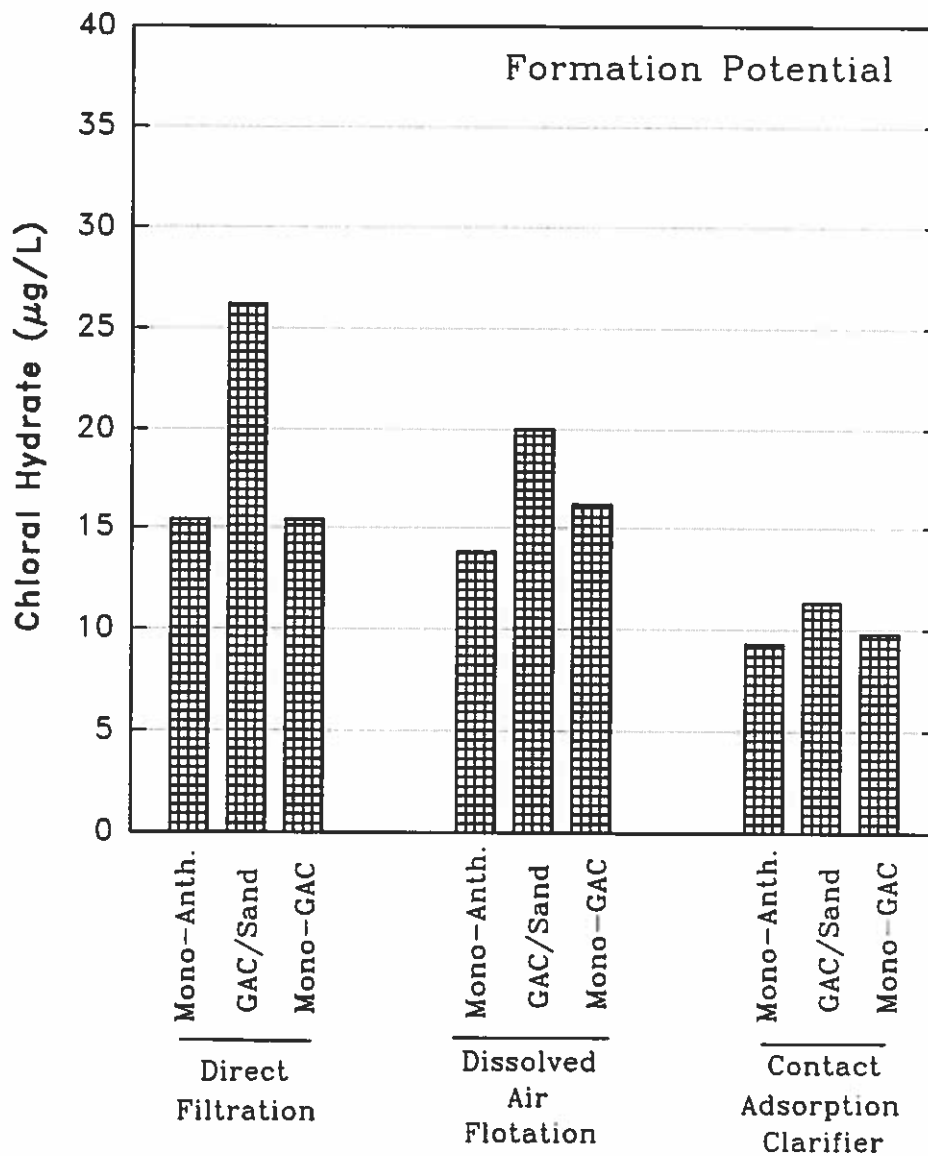


Figure 10. Chloral Hydrate Formation Potential in the Effluents of the Three Acclimated Filters for the Period February 17-20, 1992. (Mono-Anth.=mono-media anthracite filter; GAC/Sand=dual-media filter with F300 and sand; Mono-GAC=mono-media filter with Nuchar B)

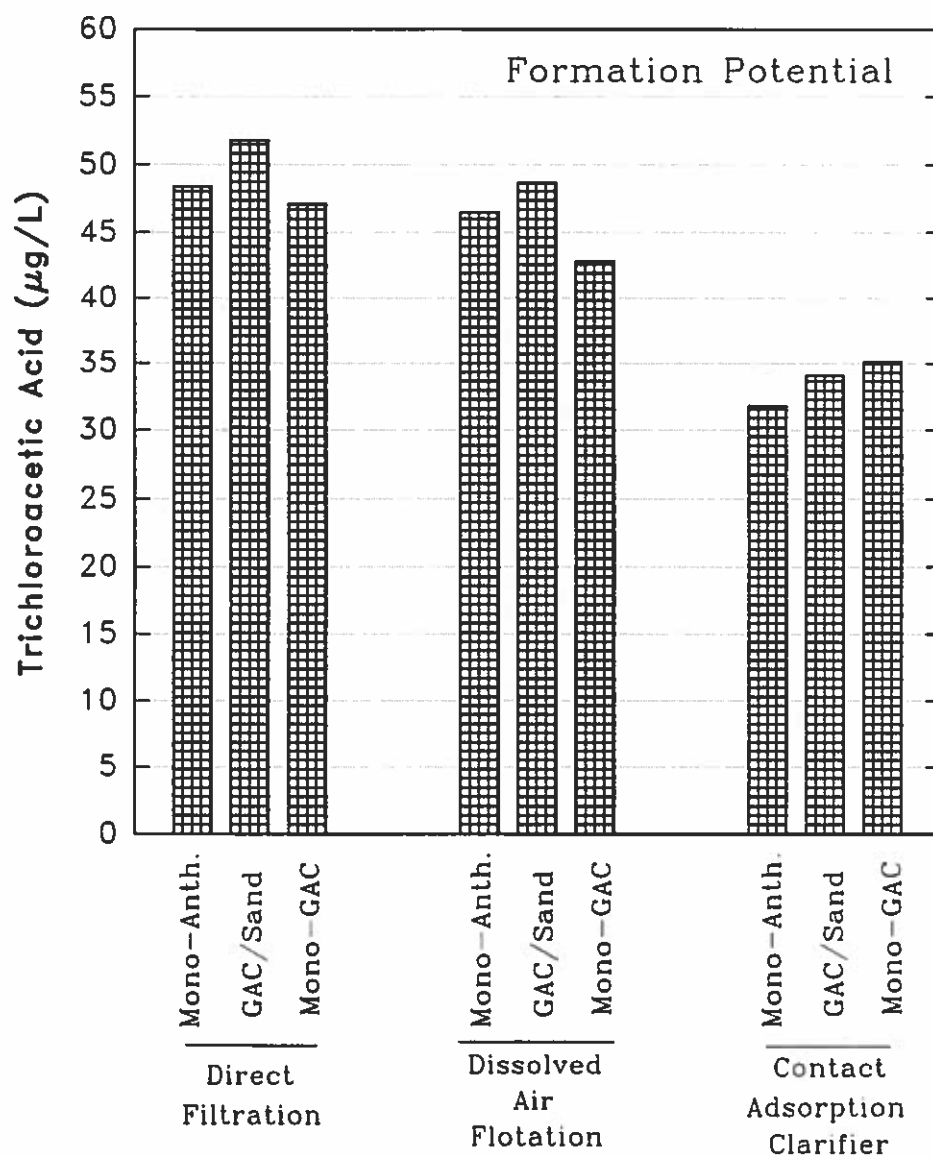


Figure 11. Trichloroacetic Acid Formation Potential in the Effluents of the Three Acclimated Filters for the Period February 17-20, 1992. (Mono-Anth.=mono-media anthracite filter; GAC/Sand=dual-media filter with F300 and sand; Mono-GAC=mono-media filter with Nuchar B)

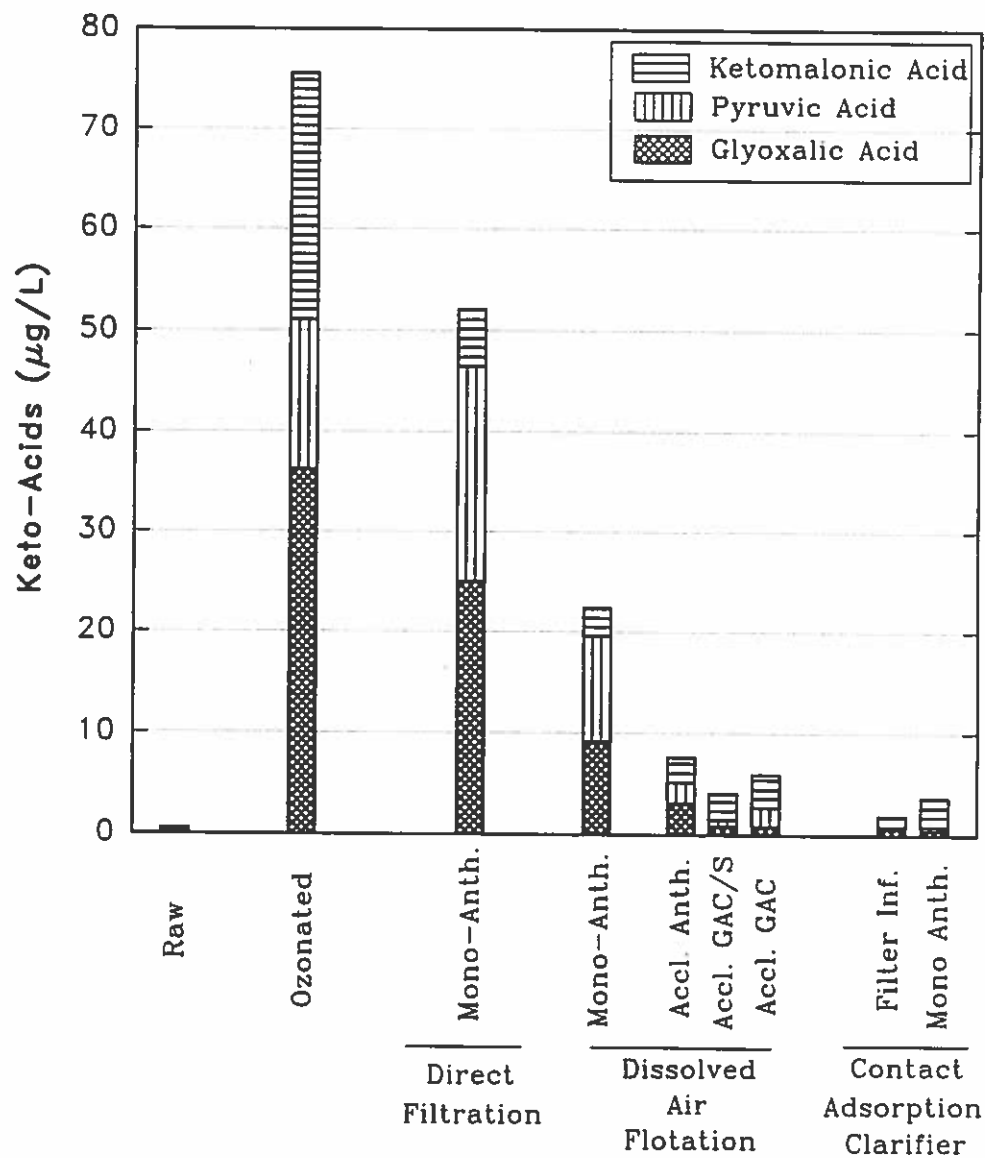


Figure 12. Keto-acid Concentrations at Various Stages of Treatment on May 14, 1992. (All are filter effluents unless otherwise indicated; Accl=acclimated; GAC/S=dual media filter with F300 and sand; GAC=mono-media filter with Nuchar B)

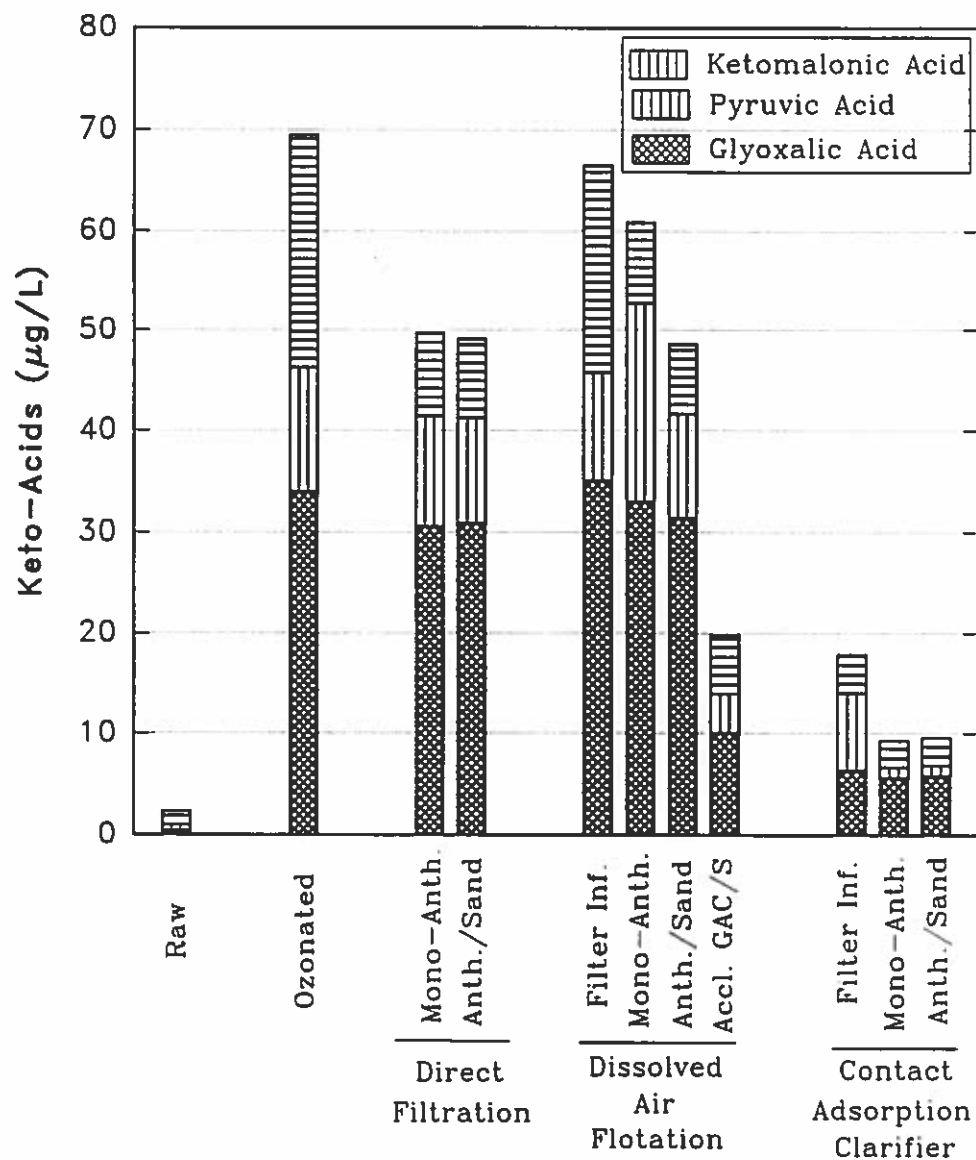


Figure 13. Keto-acid Concentrations at Various Stages of Treatment on February 6, 1992. (All are filter effluents unless otherwise indicated; Accl. GAC/S=acclimated dual-media filter with F300 and sand)

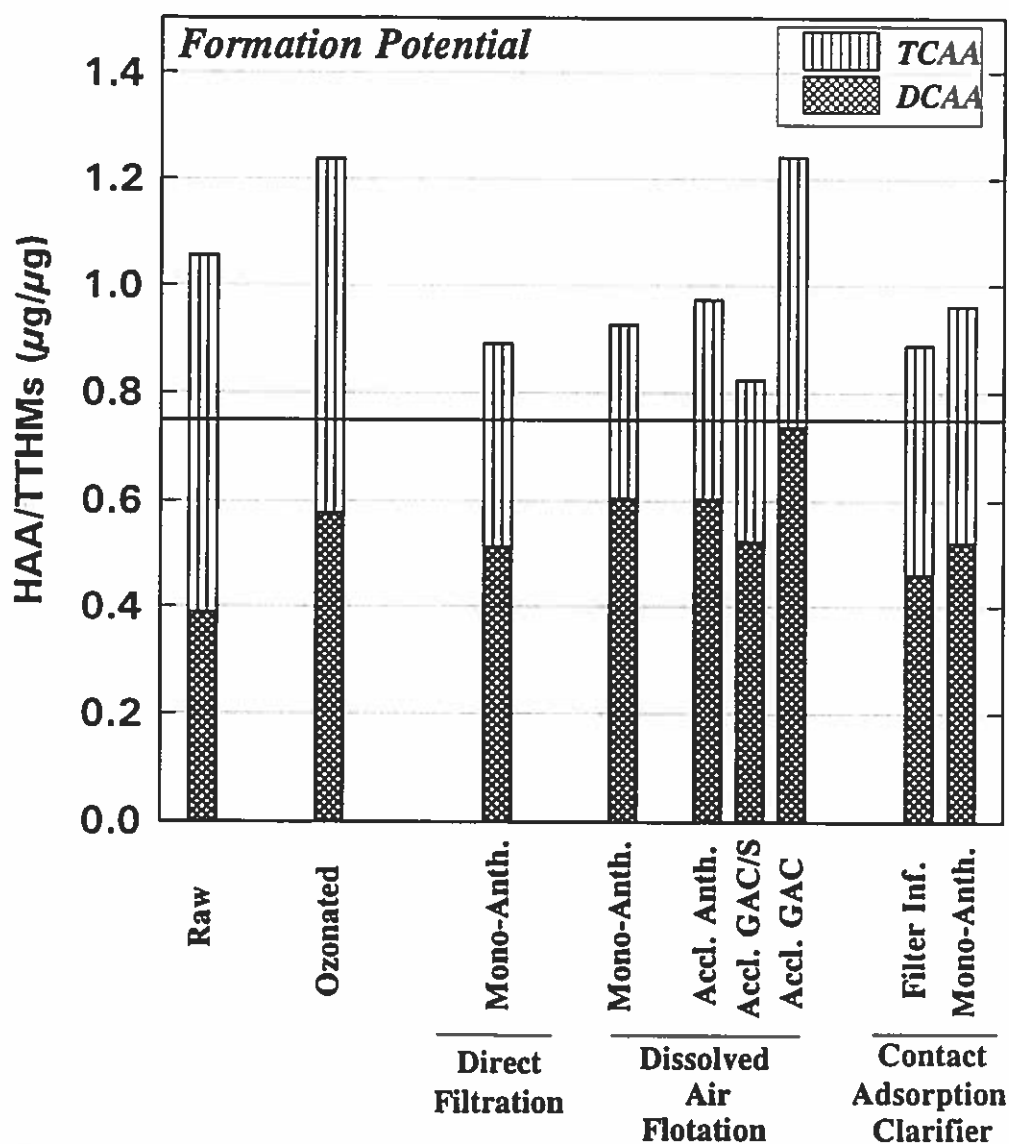


Figure 14. Haloacid to Trihalomethane Formation Potential Ratios at Various Stages of Treatment on May 14, 1992. (All are filter effluents unless otherwise indicated; Accl=acclimated; GAC/S=dual media filter with F300 and sand; GAC=mono-media filter with Nuchar B)

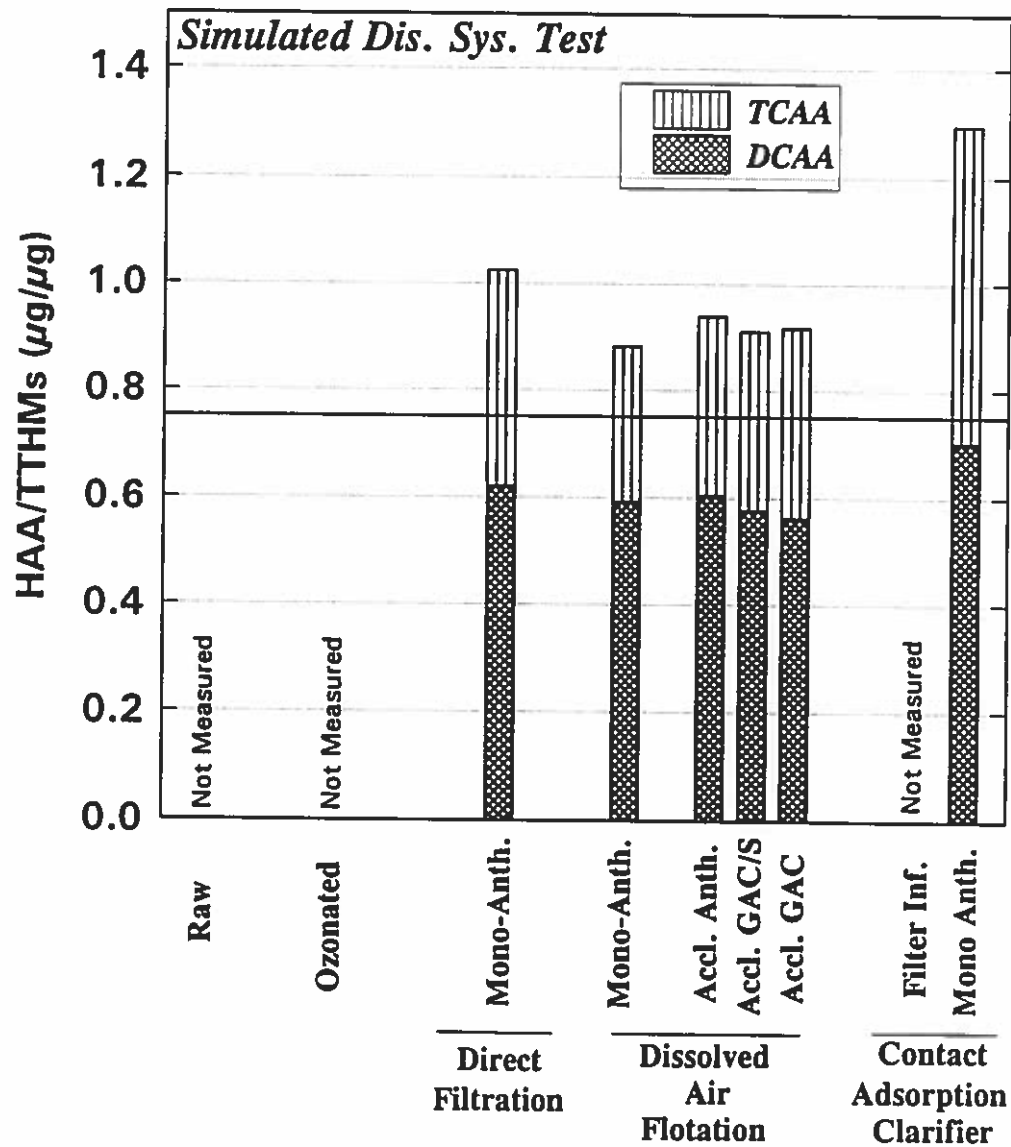


Figure 15. Haloacid to Trihalomethane Simulated Distribution System Test Ratios at Various Stages of Treatment on May 14, 1992. (All are filter effluents unless otherwise indicated; Accl=acclimated; GAC/S=dual media filter with F300 and sand; GAC=mono-media filter with Nuchar B)