

FORMATION AND REMOVAL OF ALDEHYDE IN DRINKING WATER TREATMENT PROCESSES

Xuejun Zhou *
Eastern Research Group, Inc.
110 Hartwell Ave.
Lexington, MA 02173

David A. Reckhow, John E. Tobiason
Department of Civil Engineering
University of Massachusetts at Amherst
Amherst, MA 01003

BACKGROUND

With the concern over formation of THMs from the chlorination of water, engineers and researchers have been looking to alternative disinfectants as a means of controlling by-products in finished waters. Several alternative disinfectants have been suggested and evaluated. Of those alternatives, ozone is becoming increasingly attractive. It is more effective than chlorine at removing *Giardia*, viruses, and certain forms of algae (Sproul 1988). Also, it has been found that ozone can remove taste and odor causing compounds, oxidize manganese and iron, improve flocculation, and perhaps more importantly, it can oxidize THM precursors (Langlais *et al.* 1991). However, ozone can also react with NOM to produce low molecular weight by-products. Aldehydes, a major class of ozonation by-products, are produced when ozone reacts with organic precursors in the water. It is believed that molecular ozone attacks unsaturated carbon-carbon bonds forming epoxide intermediates, and these compounds decompose to form aldehydes. This reaction mechanism was first proposed by Criegee (known as Criegee mechanism) (Glaze *et al.* 1989b). On the other hand, it is possible that aldehydes may also be produced through a pathway involving hydroxyl radicals (Bailey 1978). Although it is reported that aldehydes do not seem to have serious human health effects, they may serve as important components of assimilable organic carbon (AOC) promoting bioactivity in water treatment.

OBJECTIVES AND SCOPE

Little research has been conducted on the formation and removal of aldehydes in drinking waters. Also, little is known of the possible mechanisms of aldehyde formation in natural waters. The first objective of this research was to investigate the effects of ozone dose, pH, and radical scavenger (sodium bicarbonate) concentration on the formation of aldehydes in drinking water

* At the time of this work, Xuejun Zhou was a graduate student at the University of Massachusetts, Department of Civil Engineering.

treatment. A second objective was to investigate the effects of sulfite treatment for the purpose of removing aldehydes. The third objective was to examine the removal of aldehydes by rapid rate filtration in a pilot-scale water treatment plant.

EXPERIMENTAL

BENCH-SCALE STUDIES

1. Model Water Studies

Solutions of extracted fulvic acid were used for most of the model water experiments. This fulvic acid was isolated from Forge Pond (Granby, MA, USA) using hydrophobic resin extraction (Leenheer and Noyes, 1984). These solutions were dosed with ozone under various conditions, and the formation of aldehydes was studied.

A solution of 12.5 mg (DOC)/L of the fulvic acid and 2.5 mM HCO_3^- was prepared at pH 7 for the purpose of investigating the relationship between ozone dose and aldehyde formation. Requisite volumes of freshly-prepared ozone stock solution were first added to a set of 40-mL vials each containing 8 mL of the above fulvic acid solution. A Certain volume of water was added prior to ozone addition in order to make the total volume to 20 mL for each sample after ozone added. After a reaction time of 6 hours, all samples were then analyzed for aldehydes.

In order to study the formation of aldehydes at different HCO_3^- concentrations, and infer OH radical influence, two identical solutions containing 12.5 mg (DOC)/L fulvic acid and pH 7 were prepared. Sodium bicarbonate was added to one giving a total carbonate concentration of 25 mM. The other one did not receive bicarbonate. Each of these two solutions was then divided to a series of 8 mL aliquots, and the requisite amount of water was added in order to make the total volume 20 mL for each sample after ozone addition. These samples were then dosed with different volumes of ozone stock solution. Samples were analyzed for aldehydes after a reaction time of 6 hours.

The pH effect on aldehyde formation was studied in a fourth set of experiments. Two solutions, containing 12.5 mg (DOC)/L fulvic acid, 2.5 mM HCO_3^- , pH at 5 and 9 respectively, were prepared. Like the previous experiment, these two solutions were divided into two series of samples each containing 8mL, and they were spiked with different volumes of freshly-made ozone stock solution. They were then left for 6 hours to react at room temperature prior to analysis.

2. Natural Water Studies

A natural water sample from Quabbin Reservoir (Clinton, MA, USA) was ozonated in the laboratory for the purpose of studying aldehyde formation in a surface water. A phosphate buffer was used to hold the pH of the water at 7. Different prescribed volumes of ozone stock solution were then added to a set of 40 mL vials each containing 10 mL of the Quabbin water (1.5 mg-DOC/L). A certain volume of water was added prior to ozone addition in order to make a final volume of 20 mL for each sample after ozone addition. The reaction was carried out at 20°C in darkness for 6 hours. The residual ozone was quenched using thiosulfate and aldehydes were then measured by taking 20 mL from each solution for PFBHA derivatization. For the purpose of studying the effect of chlorine on aldehyde concentration in the ozonated water, the remaining solutions were then chlorinated at a dose of 7 mg/L. The samples were then incubated in the darkness at 20°C for an additional 48 hours. The residual chlorine was quenched with thiosulfate and aldehydes were measured.

3. Aldehyde Removal Studies

Sulfite is a powerful nucleophile and is known to react with certain aldehydes to form hydroxy sulfonate derivatives. Accordingly, the ability of sulfite to remove aldehydes was studied. Selected aldehydes were dissolved (30 µg/L) into water, and subsequently treated with Na_2SO_3 at a molar ratio of sulfite to aldehyde of 3:2. Samples were collected over time and analyzed for residual aldehydes.

To simulate a real water distribution system, another set of experiments was conducted to determine the effect of chlorination following sulfite addition. After Na_2SO_3 was added, Cl_2 was applied at a molar ratio of 5:1 to the total initial aldehyde. After the desired contact time, the samples were quenched with sodium thiosulfate and re-analyzed for aldehydes.

PILOT-SCALE STUDIES

The formation and removal of aldehydes in certain water treatment processes was investigated at the South Central Connecticut Regional Water Authority's West River Pilot Plant, Woodbridge (CT, USA). This is a 10 gpm dual-train direct filtration plant. This study was part of a larger research project aimed at testing the effects of alternative pre-oxidants and disinfectants on filtration performance (Reckhow *et al.* 1992). Five dual media filters consisting of either GAC/sand or Anthracite/sand were used during this study. A schematic of the plant is shown in Figure 1.

Samples were collected at four different stages of treatment and analyzed for aldehydes (see Figure 1). Some of these samples were chlorinated in the laboratory and re-analyzed. The assimilable organic carbon (AOC) data were collected in parallel with the aldehyde data by McEnroe (1992). These were used to evaluate filter performance and biological activity.

ALDEHYDE ANALYSIS

An aqueous-phase derivatization method, modified by Glaze and coworkers (1989b) from the method of Yamada and Somiya (1989), was used to detect and quantify the aldehydes. A 1-mL volume of an aqueous solution (6 mg/mL) of the derivatization agent -- PFBHA (O-[2,3,4,5,6-pentafluorobenzyl] hydroxylamine hydrochloride, Aldrich Chemical) was added to a 20-mL water sample in a 40-mL amber vial (I-Chem Research, New Castle, DE, USA). It was then placed in water bath (45°C) for 1 hour and 45 minutes to allow the reaction of PFBHA and the aldehydes (derivatization) to reach completion. One or two unique oximes was formed for each aldehyde. These are detectable by gas chromatography using electron capture detection (GC-ECD). After the derivatization, two drops of 18 N of sulfuric acid were added to each sample to quench the residual PFBHA. Then, 2 mL of hexane (containing 400 µg/L 1,2-Dibromopropane (Chem Service, West Chester, PA, USA) as an internal standard) was added to each sample for subsequent liquid-liquid extraction. Each vial was capped tightly and shaken by hand for at least 30 seconds until the micro-extraction reached equilibrium. The vial was allowed to sit for 5 minutes to encourage separation of the two layers. The top organic layer was acidified with 0.1 N sulfuric acid thereby removing residual PFBHA. Next, it was transferred by a disposable Pasteur pipet (Fisher Scientific, Pittsburg, PA, USA) to an auto sampler vial (Hewlett Packard, Co. San Fernando, CA, USA) containing anhydrous Na₂SO₄ as a drying agent. Calibration standards were run every time aldehyde measurements were made. A Hewlett Packard 5890 Gas Chromatograph (GC) equipped with an electron capture detector (ECD) and a methyl phenyl silicone capillary column (DB-5, J&W Scientific, Sclom, CA, USA) was employed to detect and quantify the aldehydes. A schematic of the method is shown in Figure 2. A typical gas chromatogram of the aldehydes studied is shown in Figure 3. The operating conditions and parameters for the GC are listed in Table 1.

RESULTS AND DISCUSSION

BENCH-SCALE STUDIES

1. Effect of Ozone Dose on Aldehyde Formation

The effects of varying ozone doses (normalized to DOC) on aldehyde formation in ozonated fulvic acid solutions and Quabbin water are shown in Figure 4. The dominant aldehydes were formaldehyde, acetaldehyde, glyoxal and methyl glyoxal. Similar results have been reported by other researchers (Glaze *et al.* 1989b, 1991, Le Lacheur *et al.* 1991, Coleman *et al.* 1992). It can be seen that the fulvic acid solution yielded more formaldehyde and glyoxal per unit DOC than the Quabbin water did at same ozone/DOC ratio. However, the Quabbin water yielded more acetaldehyde and methyl glyoxal than the fulvic acid solution did. It indicates that, the formation of aldehyde is not necessarily directly related to the amount of DOC. Viable aldehyde precursor distributions in different waters may account for the different yields of aldehyde per unit DOC.

From Figure 4, it shows that acetaldehyde reached its maximum concentration at ozone dose/DOC ratio around 1. It is known that ozone can react with aldehydes producing secondary by-products (Glaze *et al.* 1988, Caprio *et al.* 1989). Therefore, both the formation and the destruction of aldehydes by ozone determines the aldehyde concentration in water. In Figure 4, the acetaldehyde precursors may have been exhausted when the ozone dose/DOC ratio reached to 1, and oxidation of the aldehyde may have predominated beyond this point.

2. Effect of pH on Aldehyde Formation

To study the effect of pH on the formation of aldehydes during ozonation, a model water containing extracted fulvic acid was prepared, and then divided into two identical portions. The pH of the two portions was set at 5 and 9 by use of mixed phosphate/carbonate buffers. The same set of ozone doses was applied to both of the water samples. The results indicate that high pH slightly depressed the formation of aldehydes at doses beyond about 3 mg/L (Figure 5). Other aldehydes exhibited the same trend (data not shown).

It is known that ozone decomposition is initiated by hydroxide ion (Langlais *et al.* 1991). Therefore, an increase in pH will enhance ozone decomposition resulting in less molecular ozone in the solution (Tomiyasu, 1985). This reduction in molecular ozone should lead to less production of aldehydes by the Creigee ozonolysis reaction. Although reaction of NOM with hydroxyl radicals may also produce aldehydes, they are not likely to be as dominant a class of by-products as they are for molecular ozone. It is also possible that the formation of hydroxyl radicals could lead to significant loss of aldehydes by oxidation reactions. Reaction of aldehydes with molecular ozone is known to be quite slow (Hoigne and Bader 1983a). At low doses, molecular ozone quickly disappears from solution and its decomposition may be little affected by pH. However, at higher doses, molecular ozone persists for long period of time, and it is more susceptible to the relatively slow reaction with hydroxide. This may explain why differential effects of pH are only seen at higher ozone doses.

3. Effect of Carbonates (Radical Scavengers) on Aldehyde Formation

Figure 6 shows that water with high bicarbonate concentration generally results in lower net aldehyde formation. Other aldehydes exhibited the same trend (data not shown). One possible explanation for this is related to the specific chemistry of bicarbonate radicals. If they are formed in high concentration and they do not produce aldehydes from reaction with NOM or if they readily react with aldehydes to form other oxidated products, their presence would be expected to result in reduced aldehyde concentration. Another possible explanation may be due to the oxidation of aldehydes by molecular ozone at high bicarbonate concentration (Rice, 1992). The possible products may be ketoacids (Xie and Reckhow, 1992a).

4. Effects of Post Chlorination on Aldehyde Concentrations

A set of experiments were conducted to study the effect of chlorine on dialdehydes (glyoxal and methyl glyoxal) due to their presumed high activity. The results are shown in Figures 7 and 8. Results indicate that the reaction kinetics were nearly pseudo-first order with dialdehydes when chlorine was in excess (Figure 7). The rate constants were about 0.05hr^{-1} and 0.24hr^{-1} for glyoxal and methyl glyoxal, respectively. These results are in good agreement with that reported by McKnight and Reckhow (1992). Values of 0.12hr^{-1} and 0.31hr^{-1} for glyoxal and methyl glyoxal respectively, were observed under similar conditions but using chlorine consumption measurements instead of aldehyde residuals.

Secondly, the effect of chlorine addition on aldehyde concentrations in ozonated water was also studied. The results were compared with that for non-chlorinated water samples (Figure 9). The concentration of most aldehydes increased with the addition of chlorine to the ozonated water. It has been reported by others that the chlorination of ozonated water causes increases in aldehyde concentration (Jacangelo *et al.* 1989, Miltner *et al.* 1990). However, the concentrations of glyoxal and methyl glyoxal decreased with the addition of chlorine which is in contrast with the results of Miltner *et al.* (1990). Glaze *et al.* (1991) reported a decrease in methyl glyoxal concentration. From the previous results, it is clear that glyoxal and methyl glyoxal are degraded in the presence of chlorine. If the consumption of glyoxal or methyl glyoxal was faster than their formation during chlorination, the net glyoxal and methyl glyoxal concentrations should decrease in this experiment. This is especially likely for methyl glyoxal given its very rapid reaction with chlorine (Figure 8).

5. Effect of Post-Chlorination on the Reaction between Sulfite and Aldehyde

It was observed that aldehyde concentrations readily decreased with the addition of sulfite; however, after addition of chlorine most of the aldehydes rebounded back to their initial concentrations. However, two compounds, glyoxal and methyl glyoxal did not (Figure 10). It is well known that aldehydes react with sulfite and sulfite to form hydroxy sulfonates (Gerig, 1974). Sulfite reacts very rapidly with chlorine forming sulfate (Cotton *et al.* 1987). This evidently causes the hydroxysulfonate/sulfite equilibrium to shift toward free sulfite thereby releasing aldehydes. This mechanism requires that one assume the hydroxysulfonate forms are not recovered by the PFBHA aldehyde method.

The observation that glyoxal and methyl glyoxal were not totally recovered, and that their concentration kept dropping after recovery, indicates that glyoxal and methyl glyoxal may be reacting with chlorine. This would be expected based on the previous chlorination experiments. Although it is known that dialdehydes significantly react with chlorine, the reaction products are not known. Possible products may include chlorinated aldehydes (Committee of Aldehyde 1981).

PILOT-SCALE STUDIES

The West River Pilot Plant (WRPP) is a direct in-line filtration plant consisting of two parallel trains (10 gpm/train). The schematic of this plant from May 1991 and July, 1991 was presented in Figure 1. Some of the objectives of this project were to study the formation and fate of ozonation by-products (e.g. aldehydes), and to evaluate the effects of different filter media and operating conditions on their removal.

1. Aldehyde concentrations in Raw and Ozonated Waters (5/1 - 7/1/1991)

The ozone dose used in the pilot plant during this period was 1.5 mg/L. The DOC concentration of the raw water from the West River (CT) ranged from 2.3 - 3.5 mg/L, and the pH was between 6.9 and 7.1. The filtration rate was typically 1.5 gpm/sf, and the filters had been in operation for 3 months before the sampling period. DOC and UV absorbance data indicated that the GAC media was exhausted with respect to the adsorption of NOM by this time. Five samplings were conducted during the sampling period. A summary of the concentrations of the major aldehydes formed in this plant from May, 1991 to July, 1991 is listed in Table 2. The aldehyde removal across filter 1 and filter 2 during the same period is listed in Table 3.

The formaldehyde concentration in the raw water was 0.5 - 1.2 $\mu\text{g/L}$, which is slightly lower than the range (1.2 - 13 $\mu\text{g/L}$) reported by Krasner *et al.* (1989) for raw waters from 16 US treatment plants. Table 2 shows that ozonation significantly elevated the concentration of all four aldehydes. The concentration of formaldehyde in the water after ozonation was as high as 11.3 $\mu\text{g/L}$, which is in agreement with the bench-scale results at a similar ozone dose (about 0.5 mg $\text{O}_3/\text{mg C}$) and DOC level (Figure 4). It is also in agreement with the results reported by Glaze *et al.* (1991). Similar results were also reported by Huck *et al.* (1990), Sclimenti *et al.* (1990) and Glaze *et al.* (1989a) using waters with a similar TOC level and ozone dose.

Acetaldehyde concentrations in the West River water were lower than the median value reported by Krasner *et al.* (1989) from 36 US water treatment plants (2.6 $\mu\text{g/L}$). In the West River pilot study, the concentration of acetaldehyde in raw water after ozonation is slightly lower than one expected (2.5 - 3 $\mu\text{g/L}$) based on Figure 4, however it is in agreement with the results reported by Gilli *et al.* (1991).

Many researchers have reported that glyoxal concentrations in raw waters are very low, often below the detection limit for the PFBHA method (0.05 $\mu\text{g/L}$). This is substantiated by the West River pilot studies, however, the concentration of glyoxal increased to 3.8 - 14.1 $\mu\text{g/L}$ after ozonation. This is in agreement with the results obtained from the bench-scale studies (Figure 4). Glaze *et al.* (1991) reported that the glyoxal concentrations were between 10 and 20 $\mu\text{g/L}$ after the waters in those treatment plants (TOC = 2.4 - 3.1 mg/L) were ozonated at ozone doses ranging from 1.4 mg/L to 1.6 mg/L. On the other hand,

Miltner *et al.* (1990) reported that only 1.5 µg/L of glyoxal was formed ozonated Ohio River water ($O_3/TOC = 0.8$).

The concentration of methyl glyoxal followed the same trend as that of glyoxal in this research. These results were in agreement with the bench-scale results (Figure 4). They are also in agreement with that reported by Glaze *et al.* (1989b), Yamada and Somiya (1989) and Le Lacheur *et al.* (1991).

2. Aldehyde Removals Across Filtration

In this study, it was observed that rapid rate filtration achieved significant aldehyde removal when fed ozonated water (see Table 3). More than 80% of the formaldehyde and 75% of the acetaldehyde were removed by the GAC filter that was backwashed with non-chlorinated water. Huck *et al.* (1990) reported a similar formaldehyde removal through a filter of anthracite/sand followed by GAC adsorption. Huck and co-workers (1990) also reported that little removal of acetaldehyde was observed across the filter, and in some cases, the concentration of acetaldehyde actually increased. In another study, several water treatment plants using GAC filters (filtration rate = 3.4 - 4.0 gpm/sf) achieved nearly 100% removal of formaldehyde and more than 85% removal of acetaldehyde after filtration (Glaze *et al.* 1991).

The West River Pilot Plant achieved better removal of glyoxal and methyl glyoxal than that of formaldehyde and acetaldehyde. Normally, more than 80% of the dialdehydes in the ozonated water were removed by the GAC filtration process. In the report by Glaze *et al.* (1991), 89% of glyoxal and only 80% of methyl glyoxal were removed in the contrast to nearly 100% removal of formaldehyde in several treatment plants.

The GAC filter backwashed with non-chlorinated water achieved a better removal of aldehydes (especially dialdehydes) as compared to the GAC filter backwashed with chlorinated water. This indicated that biological activity may play an important role in the aldehyde removal and that dialdehydes are probably more biodegradable than formaldehyde and acetaldehyde.

It is interesting to point out that, in some cases, the concentrations of aldehydes in the effluents of filters 3, 4 (GAC media) and filter 5 (anthracite/sand dual media) are higher than in the influent (non-ozonated rapid mix effluent) (Table 2). It is not clear what caused such an increase. Glaze *et al.* (1991) also reported an increase of 30% of formaldehyde across filtration (anthracite/sand) in one plant, and an increase across filtration of 7% of formaldehyde, 20% of acetaldehyde and 20% of glyoxal in a second plant. Huck *et al.* (1990) reported increases in acetaldehyde concentration as great as 10µg/L across a GAC contactor. These authors did not offer an explanation for such increases.

3. Impacts of Process Configuration

The impacts on aldehyde formation and removal by changing process configuration and operational variables in the West River Pilot Plant (WRPP) are discussed in the following section.

An experiment, aimed at studying aldehyde removal by rapid rate filtration, and effects of filtration rate on this removal, was conducted on July 10, 1991. During this period, the DOC of the raw water was 2.3 mg/L, pH was 6.9, and ozone was not applied to either train. In this experiment, a concentrated aqueous solution which contained selected ketoacids and aldehydes (including acetaldehyde, glyoxal and methyl glyoxal) was continuously pumped into the raw water influent to elevate the concentrations of each of aldehydes above the level in the raw water. Because ozone was not applied in this experiment, the aldehyde concentrations in all filter influents (i.e. rapid mix effluents) were similar (Figure 11). This provided a direct comparison of the performance of all five filters.

It was observed that all filters achieved better aldehyde removal at lower filtration rates than they did at higher rates. It is believed that the removal of aldehydes in filtration processes is achieved by adsorption of aldehydes to filter media and/or degradation of aldehydes by microorganisms on filter media (Glaze *et al.* 1991, Huck *et al.* 1990). More contact time will be allowed at a lower filtration rate for adsorption and biodegradation of aldehydes on the surface of the filter media.

It is evident from Figure 11 that filter 1 and filter 4 achieved better removal of aldehydes than filter 2 and filter 3, respectively. Recall that filters 1, 4 and 5 were backwashed with non-chlorinated water, and filters 2 and 3 were backwashed with chlorinated water. The presence of a chlorine residual in the backwash water is likely to have had an adverse effect on bacterial growth attached to the filter media. Thus, the better removal of aldehydes by filters 1 and 4 relative to filters 2 and 3 may be due to the improved biodegradation of aldehydes by the microorganisms in filter 1 and filter 4.

4 Correlations Between Dialdehydes and AOC

It is well known that aldehydes are readily biodegradable. The dialdehydes are apparently more biodegradable than formaldehyde and acetaldehyde. Results from sampling runs conducted at West River Pilot Plant have shown a similar pattern for dialdehyde formation and removal and the formation and removal of AOC (data of Zhou, 1992 and McEnroe, 1992). To further study this correlation, the concentrations of the dialdehydes and AOC values in WRPP water samples from May, 1991 to January, 1992 are plotted in Figure 12. These figures show a strong correlation between AOC and dialdehydes. A correlation test (Student t distribution) showed that the correlation is significant at a level of $\alpha=0.001$. Therefore, these by-products may be useful as surrogates for AOC in ozonated and filtered waters.

CONCLUSIONS

Ozone readily reacted with NOM to form a wide range of low-molecular-weight aldehydes. The formation of these aldehydes was fast, and approached completion within 30 minutes. The major aldehydes formed were formaldehyde, acetaldehyde, glyoxal and methyl glyoxal. The concentrations of the aldehydes increased with increasing ozone dose, however, some aldehydes reached a maximum at a certain intermediate ozone dose. These ozone doses were aldehyde-specific. High pH and high total carbonate concentration led to a decrease in the aldehyde formation.

Aldehydes reacted with sodium sulfite to form hydroxy sulfonate derivatives. This reaction was very fast. However, it was reversible and when chlorine was re-applied, the aldehydes were released from the sulfonate. Chlorine also reacted with certain aldehydes (e.g. glyoxal and methyl glyoxal). The reactions conformed to a classical pseudo-first order when chlorine was in excess. The rate constants were 0.05 and 0.24 hr⁻¹ for glyoxal and methyl glyoxal, respectively.

Aldehydes were readily removed by dual media filtration. They were especially well removed by filters containing biologically activated carbon media. Generally, the removal efficiencies in the West River Pilot Plant were 90%, 82% and 70% for dialdehydes, formaldehyde and acetaldehyde, at a filtration rate of 1.5 gpm/sf, respectively. The removal of aldehydes by filtration was affected by filtration rate. Better aldehyde removal occurred as the filtration rate was lowered. Chlorinated backwash water seemed to substantially decrease aldehyde removal by possibly lowering the bioactivity in the filter.

Strong linear correlations between dialdehyde concentrations and AOC were found.

ACKNOWLEDGEMENTS

This research was conducted in the Department of Civil Engineering, University of Massachusetts at Amherst. The efforts of Boijayanta Bezburua in extracting fulvic acid from Forge Pond water is gratefully acknowledged.

Thanks are due to Compagnie Generale des Eaux and the Syndicat de la Commune de la Banlieue de Paris Pour des Eaux, the National Science Foundation, and South Central Connecticut Regional Water Authority for their Sponsorship of this research.

REFERENCES

- Bailey, S. P. (1978) Ozonation in Organic Chemistry, Volume I, Olefinic Compounds, Trahonovsky W., Ed. Academic Press, Chapter IV.
- Caprio, V. *et al.* (1989) "Glyoxal Ozonation Process In Aqueous Solution" Ozone Sci. & Eng., Vol. 11, No. 3, pp. 271-280
- Coleman, W. E. *et al.* (1992) "Ozonation/Post-Chlorination Of Humic Acids: A model For Predicting Drinking Water Disinfection By-products" Ozone Sci. & Eng., Vol. 14, pp. 51-69.
- Committee on Aldehyde (1981) Formaldehyde and Other Aldehydes National Academy Press, Washington D. C.
- Gerig J. T. (1974) Introductory of Organic Chemistry, Academic Press. pp. 204-220.
- Gilli, G. *et al.* (1991) "Water Disinfection: A Relationship Between Ozone and Aldehydes Production" Ozone Sci. & Tech. Vol. 13, No. 3, pp. 231-241.
- Glaze, W. H. *et al.* (1989a) "Evaluation of Ozonation By-products from Two California Surface Waters" J. AWWA Vol. 81, No. 8, pp. 66-73.
- Glaze, W. H. *et al.* (1989b) "Ozonation By Products 2. Improvement of an Aqueous-Phase Derivatization Method for the Detection of Formaldehyde and Other Carbonyl Compounds Formed by the Ozonation of Drinking Water", ES&T, Vol. 23, pp. 838-847.
- Glaze, W. H. *et al.* (1991) "Trends in Aldehyde Formation and Removal Through Plants Using Ozonation and Biological Active Filters", Proceeding, AWWA Annual Conference, June 1991, Philadelphia, PA.
- Hoigne, J., Bader H. (1983a) "Rate Constant of Reactions of Ozone with Organic and Inorganic Compounds in Water I. Non-Dissociating Organic Compounds", Water Res., Vol 17, No. 2, pp. 173-184.
- Hoigne, J., Bader H. (1983b) "Rate Constant of Reactions of Ozone with Organic and Inorganic Compounds in Water II. Dissociating Organic Compounds" Water Res., Vol 17, No. 2, pp. 185-197.
- Huck, P. M. *et al.* (1990) "Formation and Removal of Selected Aldehydes in a Biological Drinking Water Treatment Process", Water SRT-Aqua., Vol. 39, pp. 321-333.

- Jacangelo, J. G. *et al.* (1989) "Ozonation: Assessing Its Role in the Formation and Control of Disinfection By-Products", J. AWWA, Aug. pp. 74-84.
- Krasner, S. *et al.* (1989) "The Occurrence of Disinfection By-products in US Drinking Water" J. AWWA, Vol. 81, No. 8, pp. 41-53
- Langlais, B., Reckhow, D.A., Brink, D. R., (1991) Eds. Ozone in Water Treatment - application and Engineering, Lewis Publishers Inc. pp. 2-8, pp. 60-70.
- Leenheer, J.A., Noyes, T.I. (1984) "A Filtration and Column-Adsorption System for Onsite Concentration and Fractionation of Organic Substances from Large Volumes of Water", U.S. Geological Survey Water-Supply, paper 2230.
- Le Lacheur R. M., Singer, P. C., Charles, M. J. (1991) "Disinfection By-products in New Jersey Drinking Water", Proceeding, AWWA Ann. Conf. June, 1991, Philadelphia, PA.
- McEnroe, R.L. (1992) "Preozonation and In-line Direct Filtration: Impacts on the Bacterial Regrowth Potential", M.S. Thesis, Univ. of Mass., Dept of Civil Eng.
- McKnight, A., Reckhow, D. A. (1992) "Chlorine Reactions of Ozonation By-products Model Compound Studies" poster presented at the Envir. Chem. Div., ACS National Meeting, April, 1992, San Francisco, CA
- Miltner, B. *et al.* (1990) "Pilot-Scale Investigation of the Formation and Control of Disinfection By-Product", Proceeding, AWWA Annual Conference, June 1990, Cincinnati, OH.
- Reckhow, D. A. *et al.* (1992) "Control of Disinfection Byproducts and AOC by Pre-ozonation and Biologically-active In-line Direct Filtration" Proceeding AWWA Annual Conference, Vancouver, Canada, 1992
- Rice, R.G. (1992) personal communication.
- Sclimenti, M. J. *et al.* (1990) "Ozone Disinfection By-products: Optimization Of The PFBHA Derivatization Method For The Analysis Of Aldehydes" Proc. AWWA WQTC, Nov. 11 1990, San Diego, CA.
- Sproul, O. J. (1988) "Ozonation: Recent Advances and Research needs" Proceeding AWWA Denver, CO.
- Tomiyasu, H., Fukutomi, H. and Gordon, G. (1985) "Kinetics and Mechanism of Ozone Decomposition in Basic Aqueous Solution" J. Inorg. Chem., Vol. 24, pp. 2962-2966.

- Xie, Y., Reckhow, D.A. (1992a) "Formation of Ketoacids in Ozonated Drinking Water" Ozone Sci. & Eng., Vol.14, No.3, pp. 269-275
- Xie, Y., Reckhow, D. A. (1992b) "Identification of Trihaloacetaldehydes in Ozonated and Chlorinated Fulvic Acid Solutions" Analyst, in press.
- Yamada, H., Somiya, I. (1989) "The Determination of Carbonyl Compound in Ozonated Water by the PFBOA Method", Ozone Sci. & Engrg., Vol. 11, pp. 127-141.
- Zhou, X. (1992) "Formation and Removal of Aldehyde in Drinking Water Treatment Processes" M.S. Thesis, Dept. of Civil Eng., Univ. of Mass.

Table 1 GC Operating Conditions for Aldehyde Analysis

PARAMETER	VALUE
Column:	
Type	DB-5
Length	30 m
Internal Diameter (I.D.)	0.25 mm
Film thickness	1 μ m
Carry Gas	Nitrogen
Carry Gas Flow Rate	2.8 ml/min.
Oven Temperature Program:	
Initial Temperature	60 $^{\circ}$ C
Initial Holding Time	1 min.
Temperature Ramping Rate	4 $^{\circ}$ C/min.
Final Temperature	200 $^{\circ}$ C
Final Holding Time	8 min.
Injector:	
Mode	Splitless
Purge Time	0.5 min.
Injector Temperature	200 $^{\circ}$ C
Volume of Injection	1 μ L
Detector:	
Type	ECD
Detector Temperature	275 $^{\circ}$ C
Makeup Gas Flow Rate	30 ml/min.

Table 2 Aldehyde Concentrations ($\mu\text{g/L}$) in the WRPP ** (5/1/91-7/1/91)

	Formald.	Acetald.	Glyoxal	M-Glyoxal
Raw Water ##	0.5 - 1.2	0.2 - 0.5	0.1 - 0.5	0.2 - 0.4
Rapid Mix Eff.(No O_3)	0.5 - 1.0	0.2 - 0.5	0.2 - 0.5	0.1 - 0.6
Post Ozone	6.2 - 11.3	1.6 - 2.1	3.8 - 14.1	2.9 - 8.1
Rapid Mix Eff. (O_3)	6.1 - 11.2	1.1 - 1.7	6.1 - 12.4	3.6 - 8.0

** Ozone dose = 1.5 mg/L, filtration rate = 1.5 gpm/sf, 5 samplings.

Raw water DOC = 2.3 - 3.5 mg/L

Table 3 Aldehyde Removal (%) across Filters 1 and 2 in the WRPP (5/1-7/1/91)

	Formald.	Acetald.	Glyoxal	M-Glyoxal
GAC Filter 1 Effluent				
(Non- Cl_2 Water Backwash)	81 (10) *	75 (8)	92 (5)	90 (5)
GAC Filter 2 Effluent				
(Cl_2 Water Backwash)	76 (12)	70 (10)	81 (5)	80 (5)

* the number in parentheses is the standard deviation.



Figure 1 Schematic of the South Central Connecticut Regional Water Authority West River Pilot Plant at Woodbridge (CT)

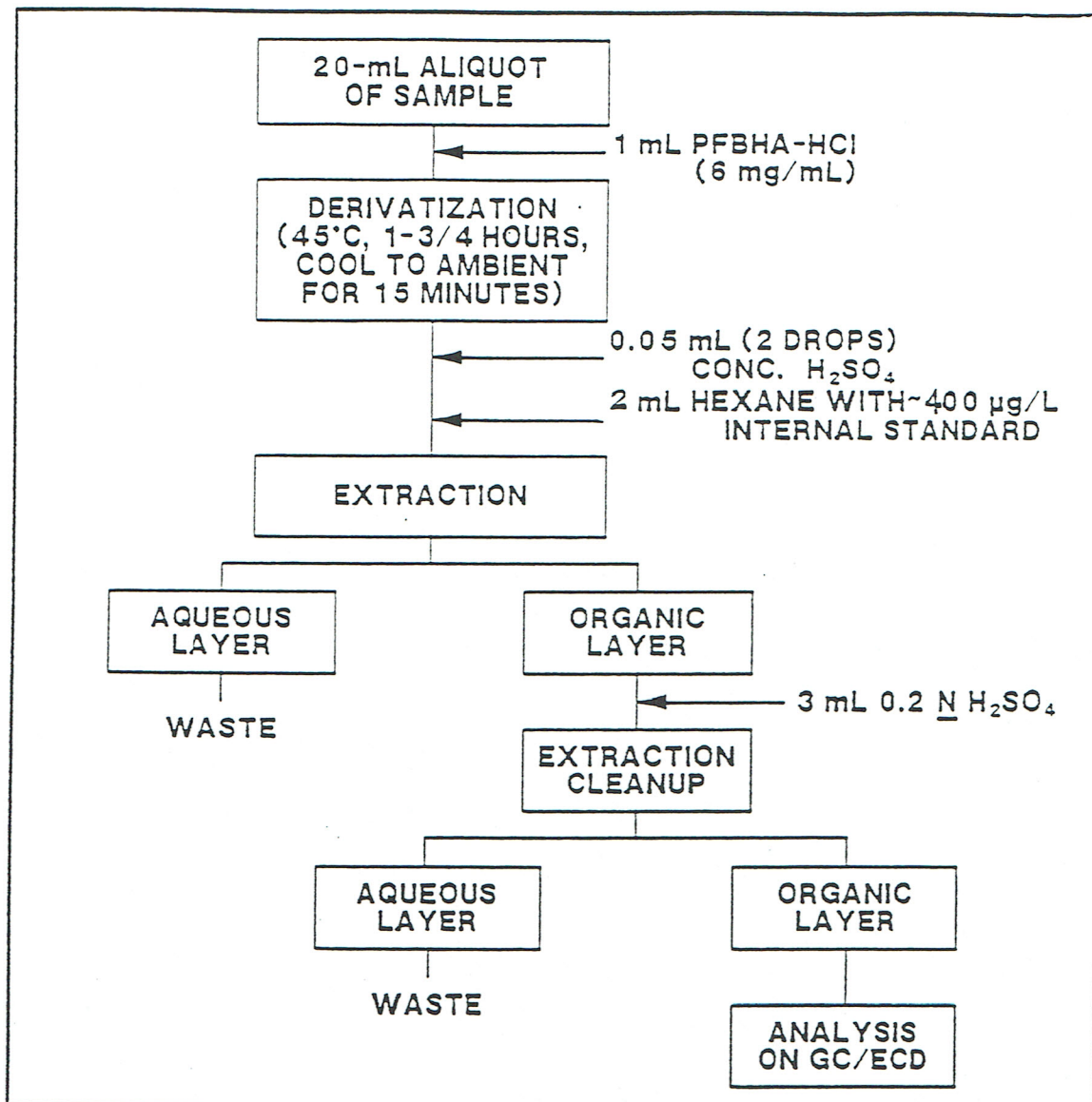


Figure 2 Schematic of Analytical Method for Aldehydes

(Modified from Scimienti *et al.* 1990)

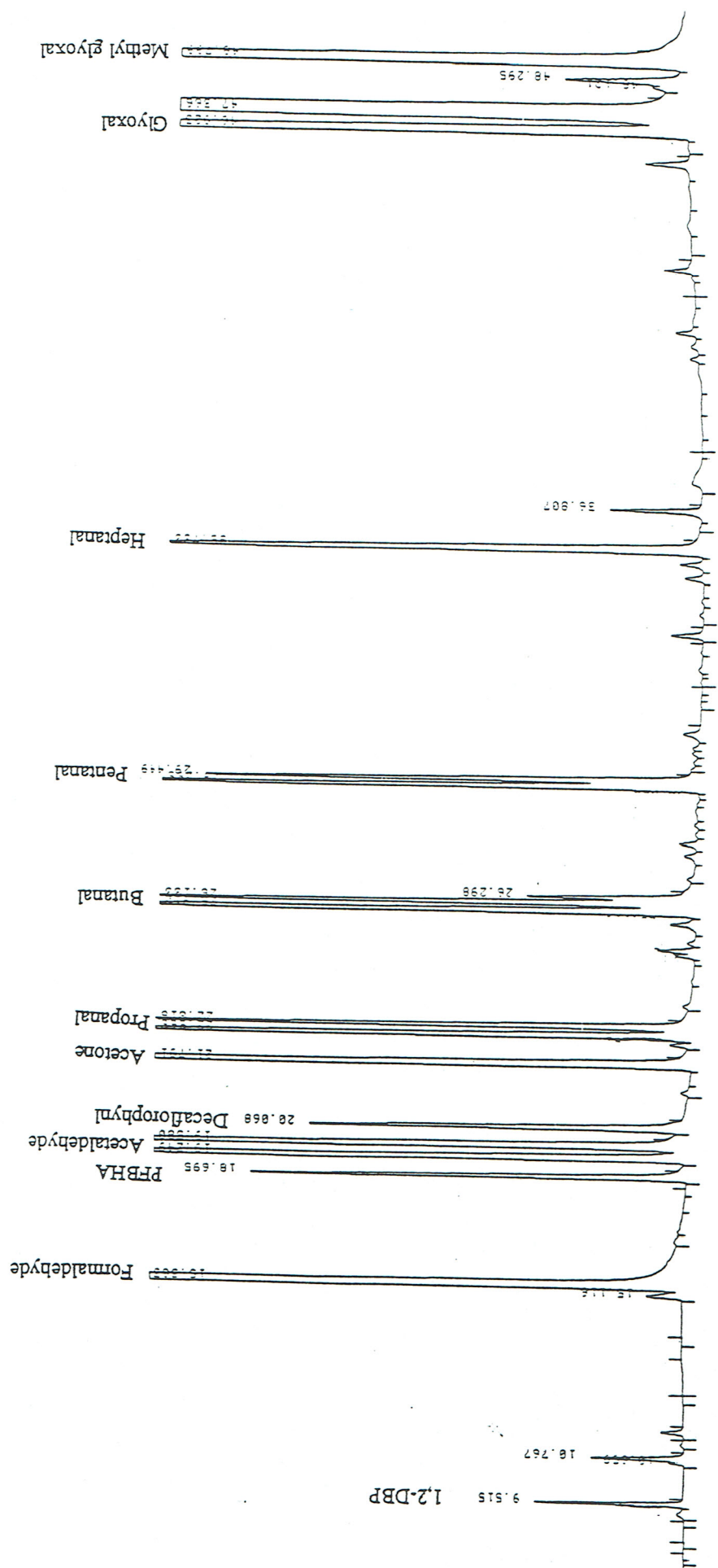


Figure 3 Gas-chromatogram of the Derivatized Aldehydes Studied

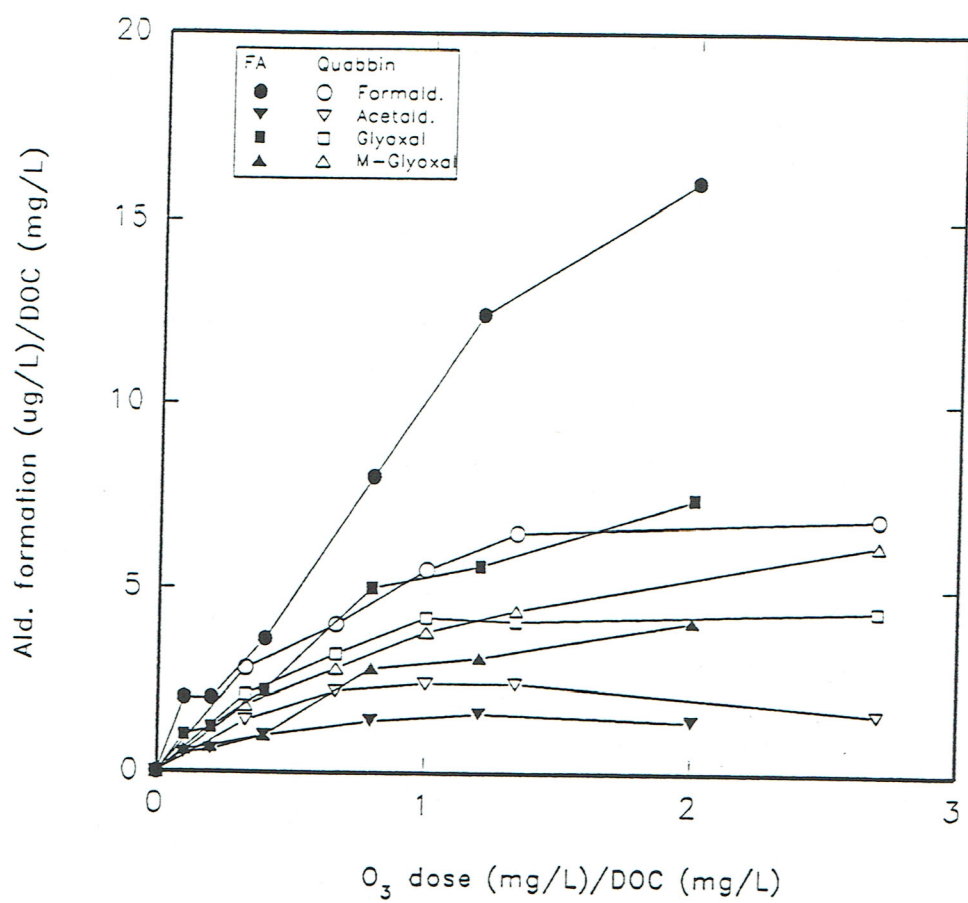


Figure 4 Effect of Ozone Dose on Aldehyde Formation for An Aquatic Fulvic Acid (FA) and Quabbin Reservoir Water

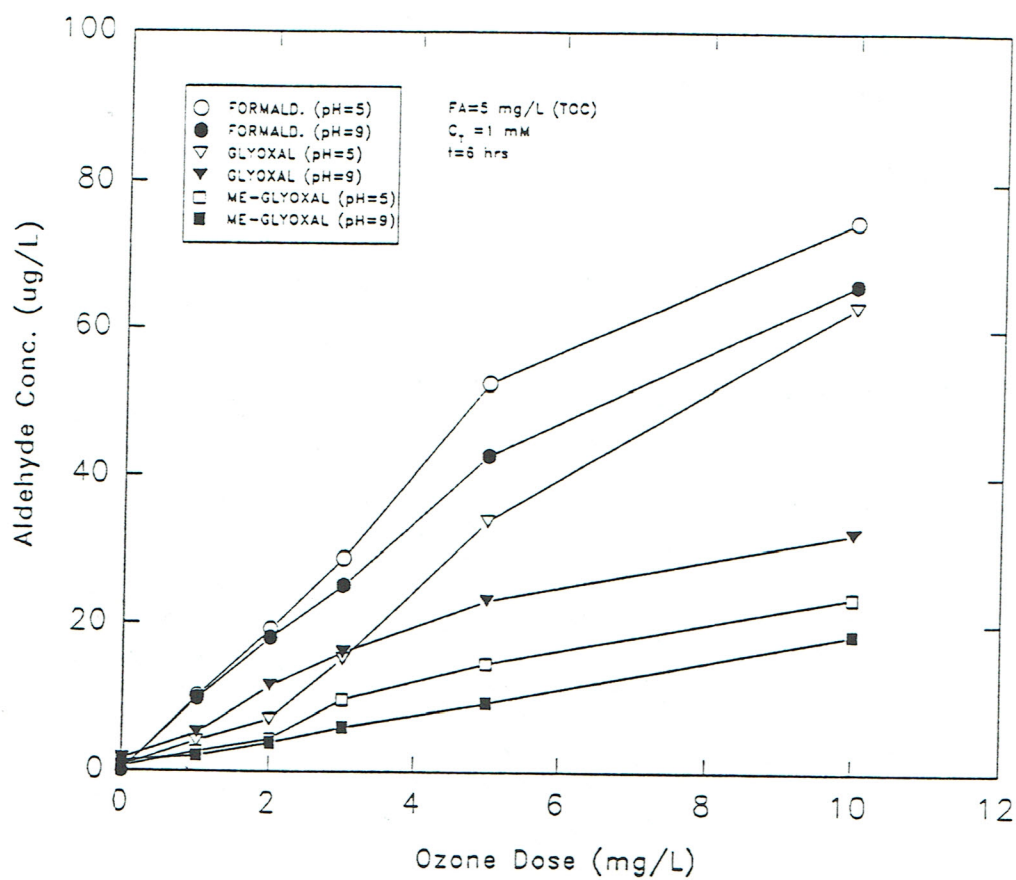


Figure 5 Effect of pH on Aldehyde Formation (Aquatic Fulvic Acid)

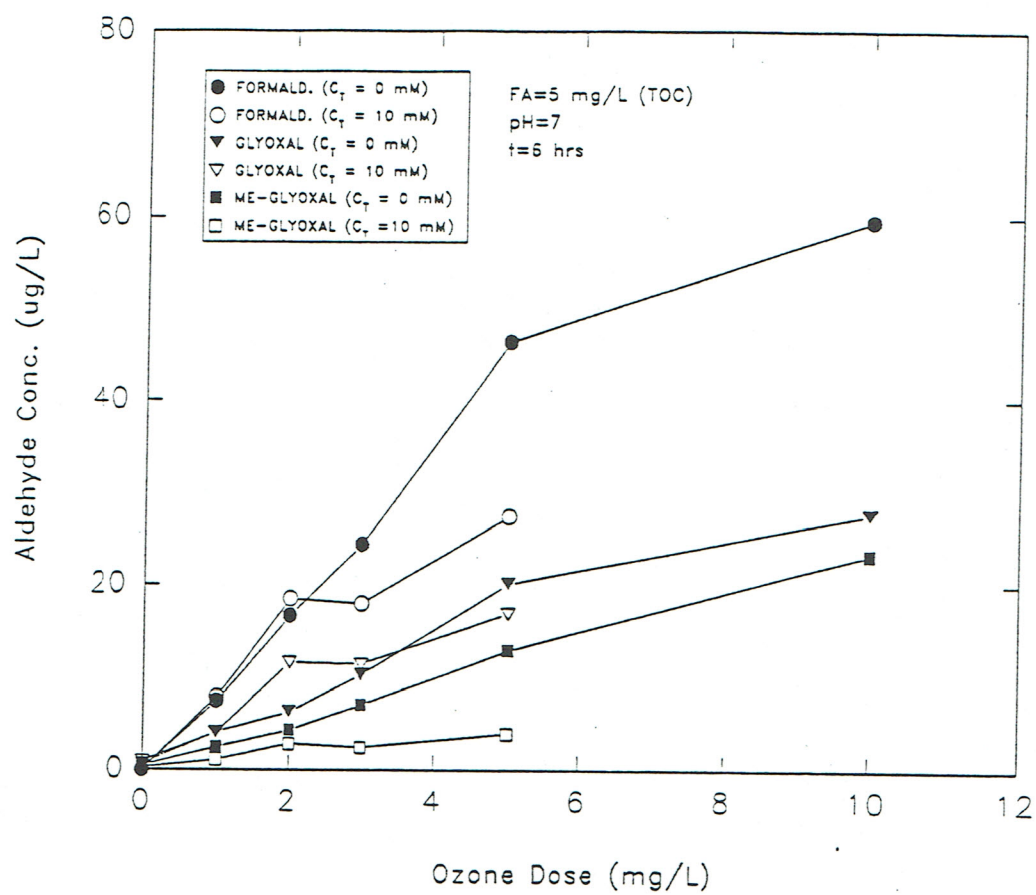


Figure 6 Effect of Carbonates on Aldehyde Formation (Aquatic Fulvic Acid)

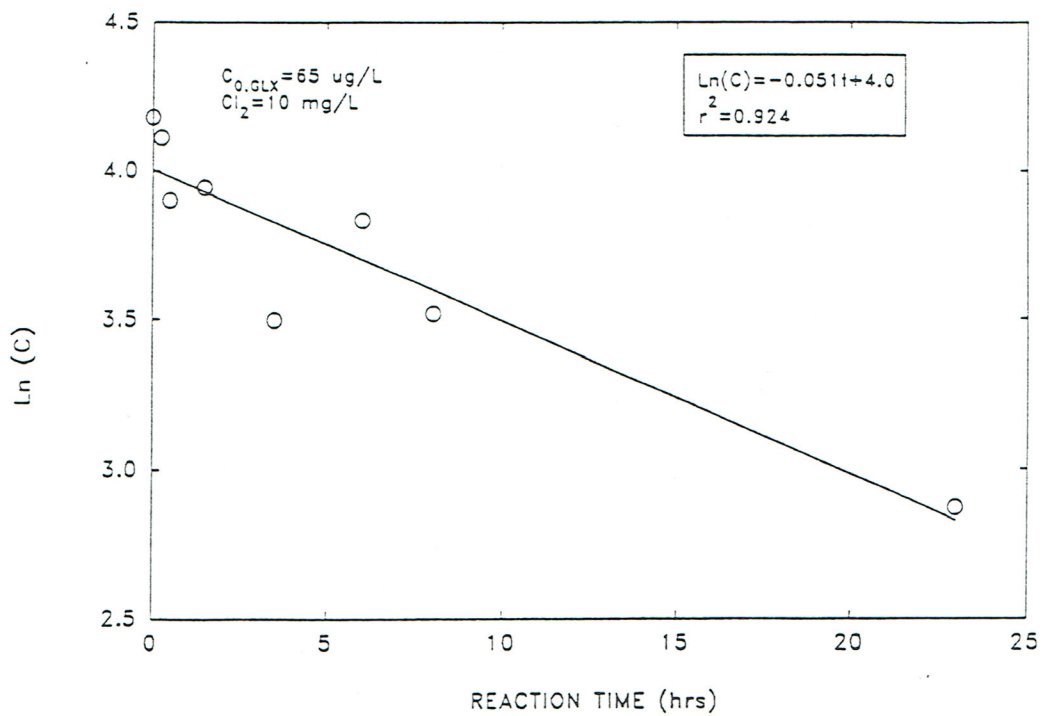


Figure 7 Reaction Rate of Glyoxal with Chlorine

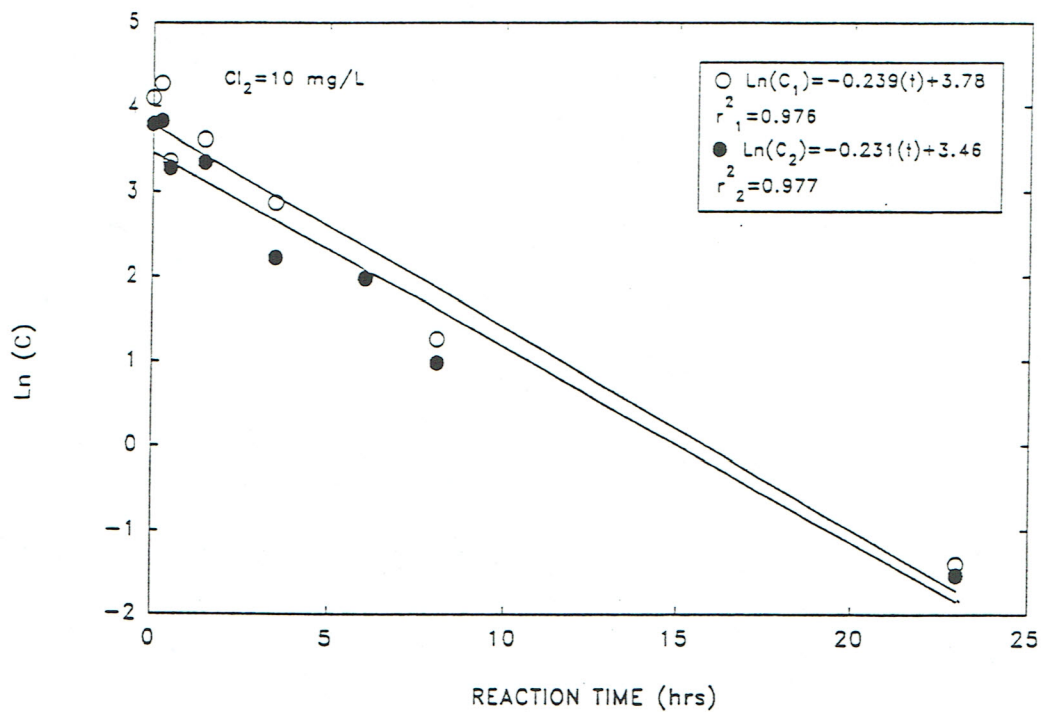


Figure 8 Reaction Rate of Methyl Glyoxal with Chlorine

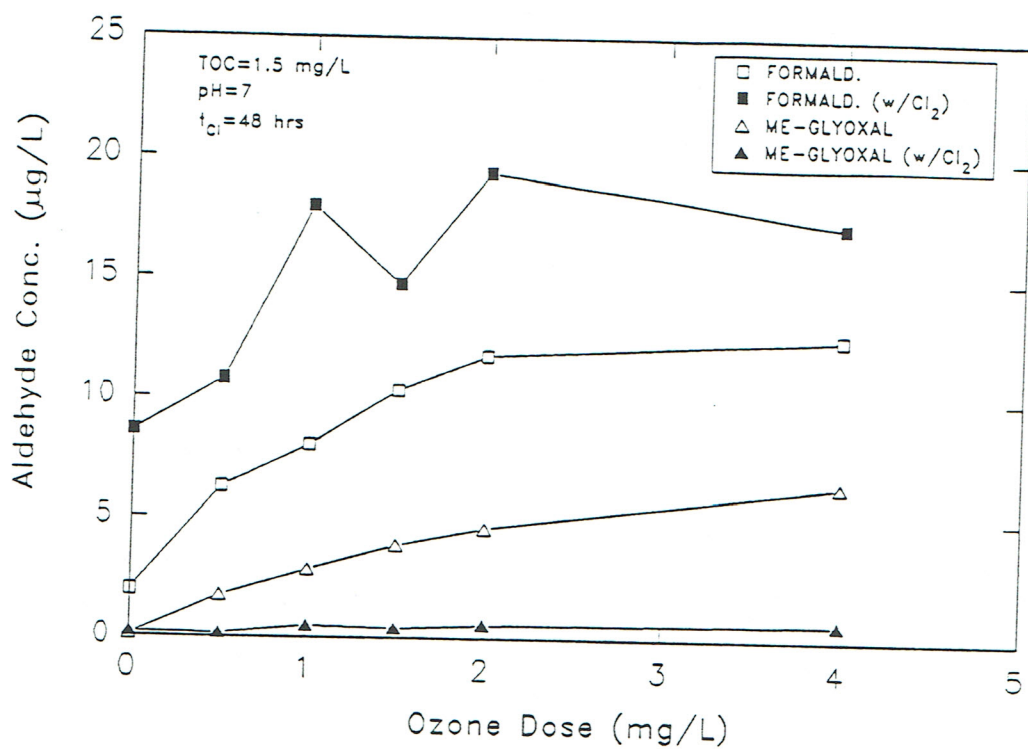


Figure 9 Effects of Ozonation and Post-Chlorination on Aldehyde Concentrations

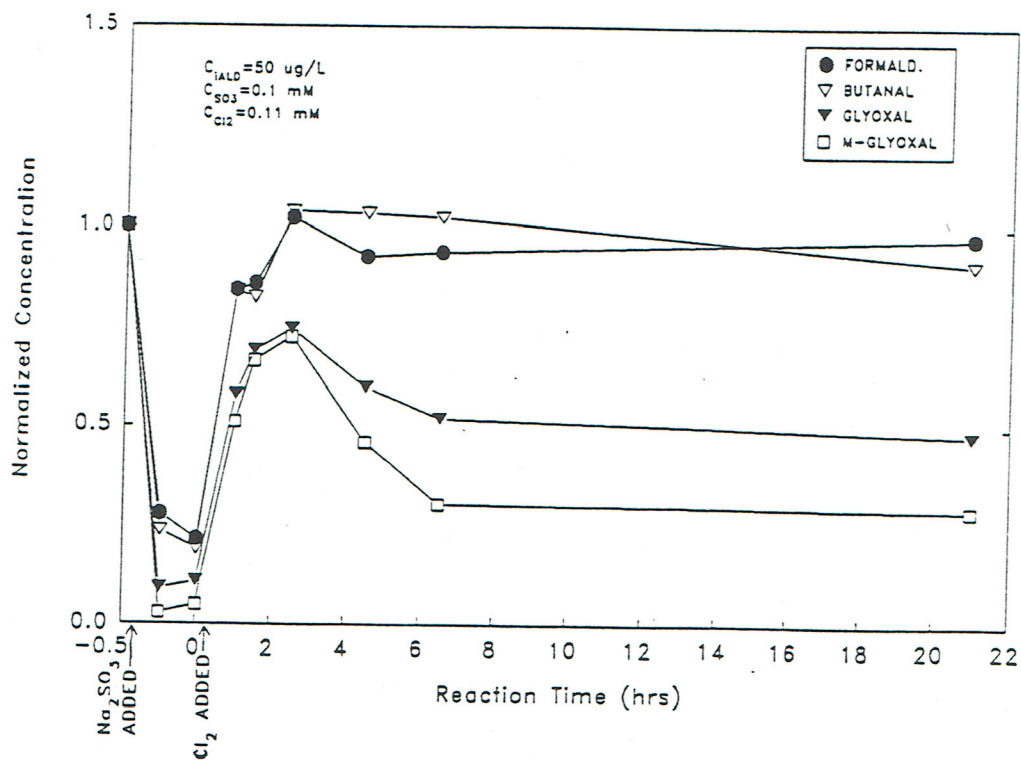


Figure 10 Effect of Sulfite and Chlorine on Aldehyde Concentrations

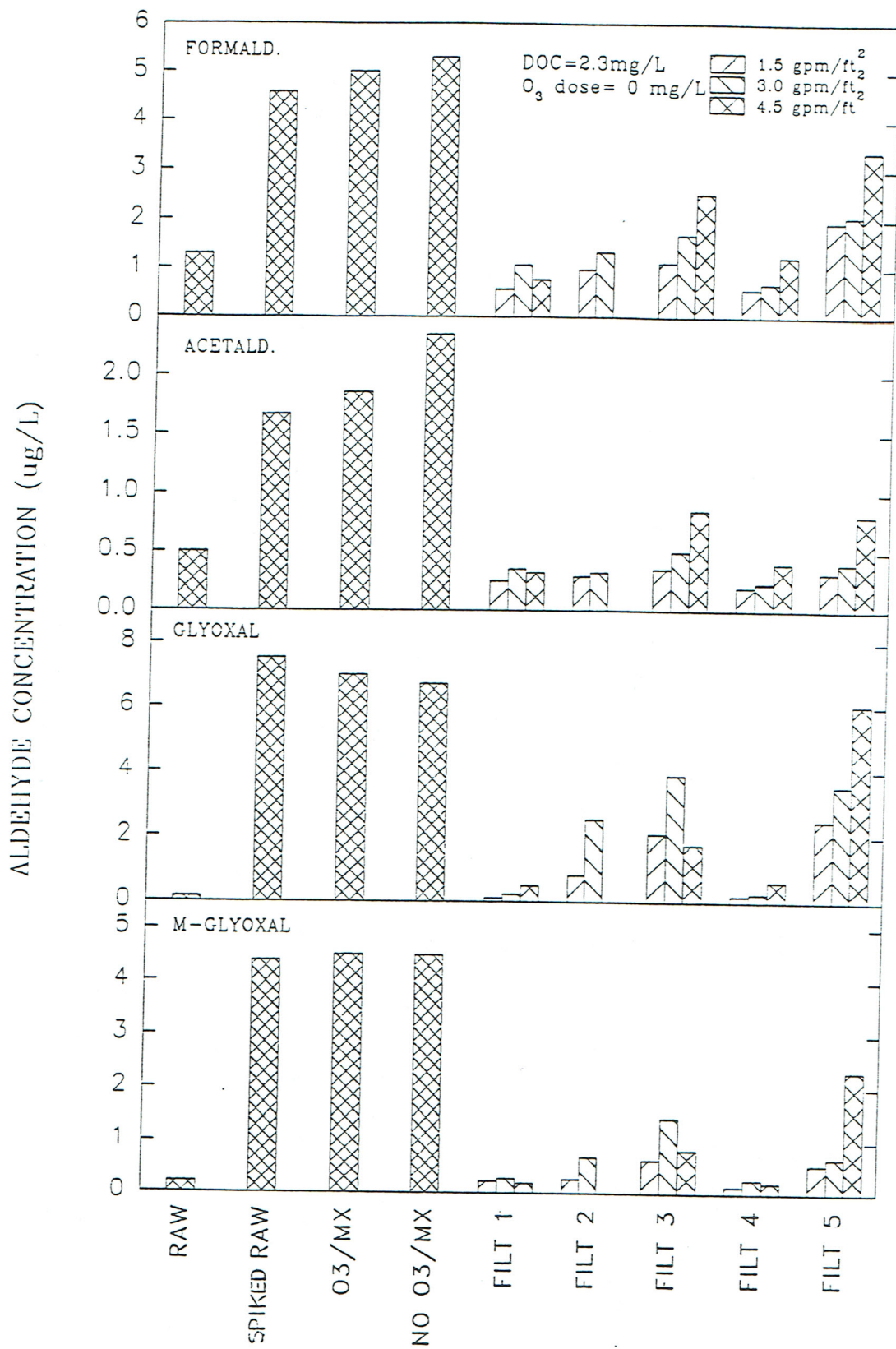


Figure 11 Results from West River Pilot Run Using Amended Raw Water

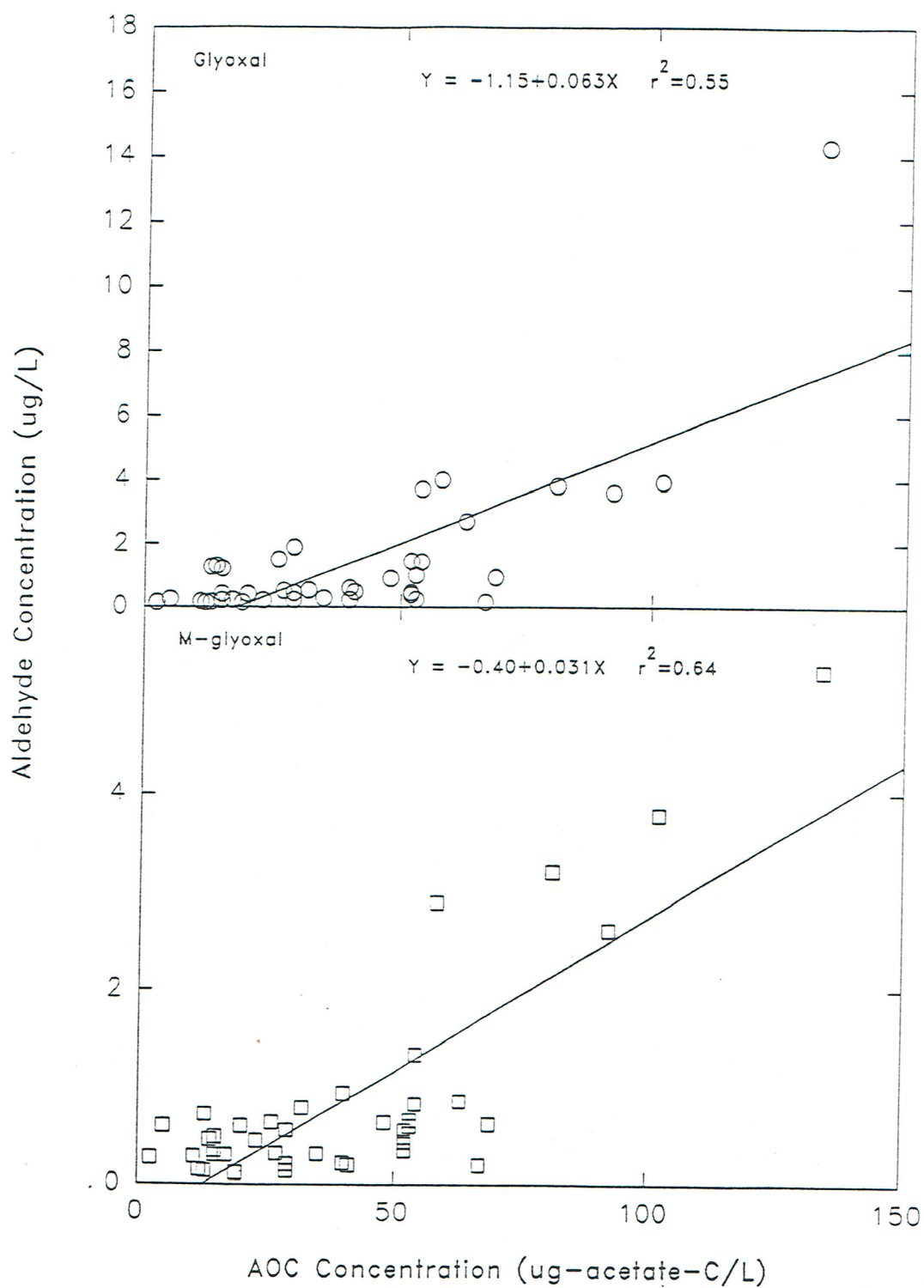


Figure 12 Correlation Between AOC and Glyoxal and Methyl Glyoxal Concentrations (AOC Data from McEnroe, 1992)