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Effects of Disinfectants on the Formation of Aldehydes

Megan Dutra

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Effects of Disinfectants on the Formation of Aldehydes

A Master's Project Presented

by

Megan Dutra

Submitted to the Department of Civil and Environmental Engineering of the University of
Massachusetts in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

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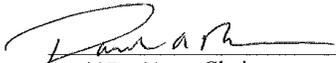
THE EFFECTS OF DISINFECTANTS ON THE FORMATION OF ALDEHYDES

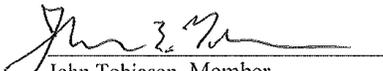
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by

MEGAN DUTRA

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ABSTRACT

Disinfection by-products have been the subject of intense study in the water treatment community due to the established adverse health effects of many known by-products and the postulated adverse health effects of many other known and unknown by-products. Aldehydes are one such group of by-products, containing compounds of both known and postulated health effects. This thesis explores the formation of simple alkyl aldehydes due to different disinfectants; these relationships are important because they can aid in determining possible by-product formation of potentially harmful substances with a particular disinfectant or disinfectant combination. Compounds such as these biodegrade easily, presenting a potential for microbial growth in distribution systems. Water samples were taken from the Atkins Reservoir in Massachusetts and treated at different concentrations with four disinfectants: ozone, chlorine, chlorine dioxide, and ferrate. The samples were analyzed for formaldehyde, glyoxal, methyl glyoxal, and propanal. The highest concentrations produced were for formaldehyde, followed by glyoxal. The greatest concentrations resulted from oxidation using ozone or chlorine dioxide. Ferrate and chlorine produced similar concentrations of these aldehydes. Water samples that had been fortified with sodium bromide before addition of ozone, chlorine dioxide, or ferrate produced higher concentrations than any three of those disinfectants alone. For samples treated with chlorine, longer contact times produced slightly higher increases in formaldehyde and glyoxal concentrations but had no distinct effect on methyl glyoxal. Propanal concentrations were low and barely detectable throughout the study so little information was reported on it.

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1. INTRODUCTION

1.1 Disinfection

Disinfection, the inactivation of viable pathogenic microorganisms, has been used since the early 1900s in water treatment and wastewater treatment. It is used in public systems to protect against waterborne diseases. Many methods of disinfection are currently used and include a variety of chemical oxidants such as chlorine as well as physical processes like ultraviolet irradiation. The disinfection method chosen for a certain water system depends on factors such as the properties of the water being treated, target microorganisms and contaminants, convenience, and expense.

Chemical oxidants such as ozone, chlorine, chlorine dioxide are commonly used for disinfection on a large scale. Ferrate, another disinfectant, is starting to be used, mainly in wastewater. Chlorine, inexpensive and widely available, is the most widely used disinfectant in the US. Ozone is used as a disinfectant as well as an oxidant to control taste and odor problems and can be used to facilitate the removal of iron and manganese. Ozone can inactivate most viruses, bacteria, and protozoa better than chlorine. Since ozone decomposes rapidly, it is often followed by a secondary disinfectant such as chlorine to provide a disinfectant residual. Chlorine dioxide inactivates microorganisms better than chlorine while producing lower concentrations of regulated organic by-products as well. It does form inorganic byproducts such as chlorite (which is regulated by the USEPA) and chlorate and has been shown to produce aldehydes (Dabrowska et al., 2005). Ferrate is a disinfectant of growing interest that has proved to be a powerful oxidant over a wide pH range in addition to its conceivable use as a coagulant (Jiang and Lloyd, 2002).

1.2 Disinfection Byproducts

While disinfection is necessary for controlling pathogens and waterborne diseases, it can also produce unwanted by-products. Disinfection by-products (DBPs) form when disinfectants

react with natural organic matter (NOM) and other compounds in water. NOM is a complex, diverse mixture of organic compounds, with a large portion often composed of humic substances. By reducing the concentration of NOM in water before disinfection occurs, DBPs can be limited.

While hundreds of DBPs have been identified, some major classes include trihalomethanes (THMs), haloacetic acids (HAAs), and aldehydes. Different disinfectants cause different by-products to form; for example, chlorine produces especially high levels of THMs and HAAs while ozone produces high concentrations of aldehydes, ketones and carboxylic acids.

1.3 Aldehydes

The aldehydes targeted for this research are straight-chain, low-molecular-weight organic compounds that can be found naturally in the environment. Some may be the source of taste and odor problems in water. The formation of aldehydes is not fully understood, but it is generally accepted that they form from two pathways: the first is a direct pathway in which the ozone molecules attack carbon-carbon double bonds or aromatic rings in NOM; the second is an indirect reaction involving hydroxyl radicals which form from decomposing ozone (Zhou, 1993, Can and Gurol, 2003). The first pathway has been found to be more important in aldehyde formation. Production of aldehydes depends on many factors such as NOM concentration, pH and temperature of the water, and disinfectant dosage. Many studies have found correlations between assimilable organic carbon (AOC) and aldehyde concentration (Schechter and Singer, 1995, Zhou, 1993), although the relationships are specific to each water.

It has been found by several authors that aldehydes form in direct proportion to ozone dose, but aldehyde destruction is possible at high doses of ozonation (Nawrocki and Kalkowska, 1996, Dabrowska et al., 2005, Can and Gurol, 2003). Some authors have also shown aldehyde formation

with chlorine (Zhou, 1993) and chlorine dioxide (Swietlik et al., 2003, Dabrowska et al., 2002). For example, Dabrowska et al. (2005) showed increased concentrations of aldehydes, especially formaldehyde and acetaldehyde, for three natural waters dosed with chlorine, chlorine dioxide and ozone; with chlorine and chlorine dioxide, the concentrations increased over time. They also found when using chlorine dioxide and chlorine together in different ratios with the same total molar dose, the concentration of generated aldehydes was relatively independent of the ratios. Ramseier et al. (2010) showed connections between ferrate addition and AOC formation, which may indicate a connection between ferrate addition and aldehyde formation as well.

Aldehydes are not regulated under the EPA as certain THMs and HAAs are, however, some aldehydes are included in the USEPA's Contaminant Candidate List for possible future regulation. Formaldehyde is a human carcinogen and glyoxal has been shown to promote stomach tumors (Can and Gurol, 2003). Aldehydes remain a concern due to possible adverse health side effects, their high biodegradability, and the adverse side effects that can occur when aldehydes react with disinfectants to form halogenated byproducts (Schechter and Singer, 1995).

1.4 Research Objectives

The goal of this study was to examine the effects of ozone, chlorine, chlorine dioxide, and ferrate oxidants on the aldehyde concentrations, specifically, formaldehyde, propanol, glyoxal, and methyl glyoxal concentrations, in a natural water. Different doses of each disinfectant, different chlorine contact times, and combinations of the disinfectants were tested. The effects of bromide on aldehyde formation were also examined.

2. METHODS AND MATERIALS

2.1 Addition of chlorine, ozone, chlorine dioxide, sodium bromide, and ferrate

Sodium hypochlorite (NaClO) was used for chlorine dosing. Depending on the volume to be added, chlorine was either dosed directly from the concentrated stock or from a diluted stock of chlorine in Milli-Q water (Millipore Corp, Billerica, MA, US). Samples were buffered to a pH of 7 using a 1 M phosphate buffer solution (sodium phosphate monobasic monohydrate and sodium hydroxide, both from Fisher Scientific, Pittsburg, PA, USA) prior to chlorine dosing. At the appropriate contact time, 40 mL samples were quenched with 45 mg of ammonium chloride (Fisher); if no contact time is noted, samples were quenched at time of analysis (12-24 hours after addition).

Ozone was generated using a Welsbach Ozonator (Type T-408, Welshbach Ozonator Systems Corp., Philadelphia, PA, USA): ozone was bubbled into a borosilicate glass vessel containing Milli-Q water at room temperature for the preparation of a concentration stock solution. The exact concentration of this stock was determined using an Agilent 8453 UV-visible diode-array spectrophotometer and published values for its molar absorptivity. For a 1-cm pathlength and an absorptivity of $3290 \text{ M}^{-1}\text{cm}^{-1}$ at 260 nm this can be simplified as:

$$\text{Conc}_{O_3} \left(\frac{\text{mg}}{\text{L}} \text{ as } O_3 \right) = 14.59 * \text{Absorbance}_{260 \text{ nm}}$$

Ozone was dosed by addition of a requisite volume of the ozone stock solution directly into the sample being treated. This typically resulted in dilution of the sample by no more than 20%. This dilution was not corrected for in the final aldehyde concentration, meaning true aldehyde concentrations would be higher than reported here. After dosing, the samples were held at room temperature for one hour to allow for residual ozone to dissipate.

Chlorine dioxide was generated using Standard Method 4500-Chlorine Dioxide (APHA et al., 2005) and stored at 4°C. Sodium bromide (Fisher) was added directly to samples as a solid. For ferrate dosing, solid potassium ferrate (Aldrich, Milwaukee, WI, USA) was added to samples buffered to a desired pH with 10 mM borate buffer.

2.2 Preparation and preservation of samples.

Water samples were collected from the Atkins Reservoir in Amherst, Massachusetts, on June 1, 2015 in an opaque Nalgene cylindrical container; water quality characteristics of this water

Table 1. Water quality parameters

Parameter	Value
DOC	3.1 mg/L
TOC	3.2 mg/L
UV ₂₅₄	0.0567 cm ⁻¹
pH	6.63
Alkalinity*	2 mg/L as CaCO ₃
Hardness*	8 mg/L as CaCO ₃
Turbidity*	0.4 NTU
Color*	20 Pt-Co

*The values listed for these parameters were not measured for this sample but represent typical values for the Atkins Reservoir.

are shown in Table 1. The container was transported immediately to UMass Amherst and stored in the dark at 4°C. No preservative was added. All samples were filtered through Whatman GF/F glass fiber filters before disinfectant addition, and ferrate samples were filtered again after dosing. Glass bottles ranging from 100 mL to 1 L were used as reacting vessels depending on the experiment. Total organic carbon (TOC) was measured with a Shimadzu Total Organic Carbon Analyzer (Model: TNM-1) in accordance with Standard Methods (APHA et al., 2005).

2.3 Experimental Design

Atkins Reservoir was chosen for the water sample for this study because it is part of the Town of Amherst's water supply system and is typical of water that would be treated using disinfectants for public distribution. Chlorine, chlorine dioxide, and ozone were chosen for examination because they are widely used for drinking water treatment. Ferrate was also used because it is a powerful oxidant, and it could be implemented at a greater number of plants now that it has gained some interest. Bromide was investigated to examine possible catalytic effects on aldehyde formation.

Grab samples were collected at the inlet to Amherst's water treatment plant. Experiments were carried out in glass contacting vessels ranging from 125 mL to 2 L and incubated at room temperature (20°C). Experiments began with the water samples in three or four larger bottles. Sodium bromide and ozone were added to these bottles, if required for the experiment. Water from the larger bottles were then dispensed to smaller vessels for chlorination or ferrate addition. These samples were incubated together and quenched at the appropriate contact time (if chlorine had been added). Samples were dispensed in 40-mL aliquots to amber vials and stored together in the dark at 4°C until the time of analysis (within 48 hours).

Table 2. Chemical compound origins.

Chemical	Source
Formaldehyde	Fisher [§]
Propanal	Aldrich [†]
Glyoxal	Aldrich
Methyl Glyoxal	Aldrich
KHP	Fisher
PBFHA	Aldrich
H ₂ SO ₄	Fisher
Hexane	Fisher
DBP	Fisher

[§]Fisher Scientific, Pittsburg, PA, USA

[†]Aldrich Chemical, Milwaukee, WI, USA

2.4 Extraction and measurements of aldehydes

The procedures outlined in Standard Methods 6252. Disinfection By-Products: Aldehydes (Proposed) (APHA et al., 2005) were used for the aldehyde analysis. Chemical sources are displayed in Table 2. Standards of formaldehyde, propanal, glyoxal, and methyl glyoxal were prepared volumetrically in acetonitrile for stock solutions and, from these stock solutions, an additive mixture containing all four aldehydes was prepared weekly. Five calibration standards were prepared daily from the additive standard solution in Milli-Q water with concentrations ranging from 2 µg/L to 40 µg/L. Example standard curves are included in the Appendix.

Samples were analyzed in duplicate when available sample volumes allowed. Samples (20 ml each in 40 mL amber vials) were buffered with 200 mg potassium hydrogen phthalate (KHP, $C_8H_5KO_4$) each before addition of 1 milliliter of 15 mg/mL O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) derivatizing agent (prepared fresh daily gravimetrically in Milli-Q water). Samples were incubated in a 35°C water bath for 2 hours. Samples were cooled for 10 minutes and the reaction quenched with two drops of concentrated sulfuric acid. Four milliliters of hexane solvent containing 100 µg/L 1,2-dibromopropane (DBP, internal standard) was added to each vial and the samples were shaken for 3.5 minutes. After settling for five minutes, the top hexane layer was drawn and added to a smaller vial containing 3 mL of 0.2 N sulfuric acid. The vials were shaken for 30 seconds and settled for five minutes. The top hexane layers were again drawn and placed in gas chromatograph (GC) autosampler vials. If not used immediately, vials could be stored for up to 14 days in the dark at 4°C.

An Agilent 6890N GC with an electron capture detector was used for the analysis. The gas chromatograph injector was set to 180°C with the split valve open at 0.5 min and the split flow at 50 mL/min. A fused silica DB-5 capillary column (30 m long, 0.25-mm internal diameter, 0.25-

μm film thickness, J&W Scientific) was used with helium carrier gas (flow of 1.5 mL/min at 100°C) and the following temperature program: 50°C for 1 minute, rising at 4°C/min to 220°C, and finally rising at 20°C to 250°C. The detector was set to 300°C with a nitrogen make-up gas flow of 27 mL/min.

3. RESULTS AND DISCUSSION

3.1 Effects of ozonation on aldehyde formation

The impact of ozonation on aldehydes was investigated by ozonating the Atkins Reservoir water using the batch method described above; the results are shown in Figure 1. Concentrations of formaldehyde, glyoxal, and methyl glyoxal increased with increasing ozone dose. Propanol concentrations were consistently low (<1 $\mu\text{g/L}$) and are not reported here. The increase in all three aldehydes for the 2 mg/L ozone dose was greater than for the 4 mg/L dose, suggesting that, at higher ozone doses, the yield of aldehydes per milligram of ozone is reduced or aldehydes are further oxidized (e.g. to organic acids) by elevated ozone doses.

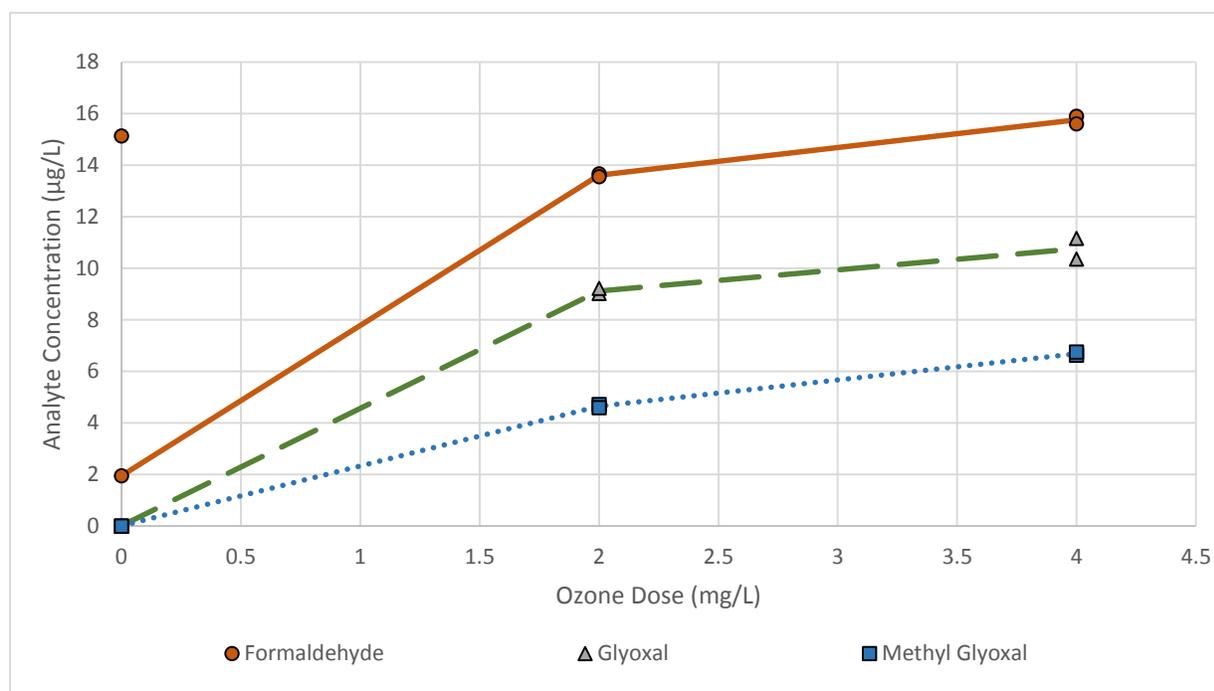


Figure 1. Aldehyde concentrations when Atkins Reservoir water was treated with ozone only. Each point shows a replicate measurement. Lines designate replicate averages (excluding outliers).

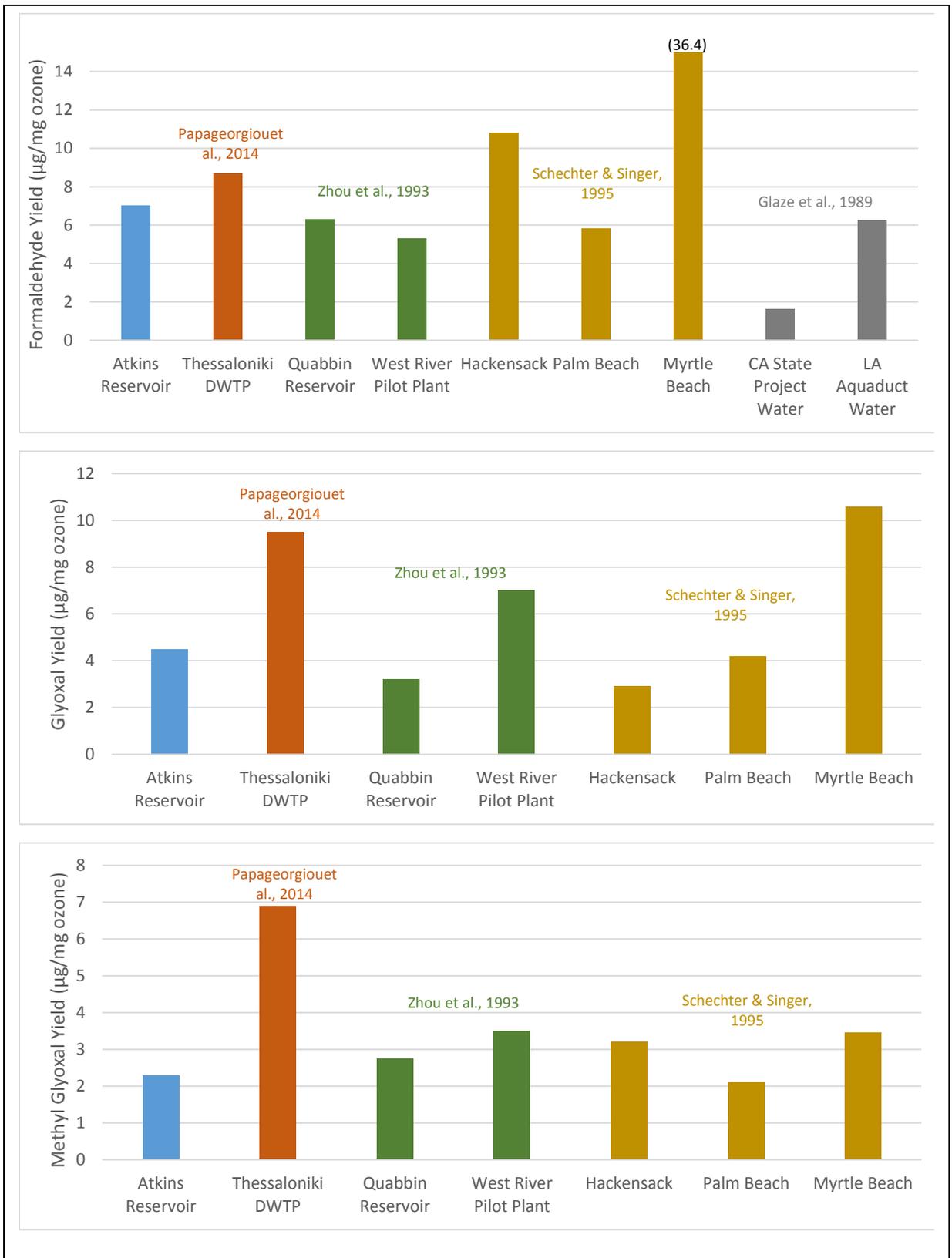


Figure 2. Aldehyde yields due to ozonation from this study compared to previously documented data.

The data above fall within in the range of previously published aldehyde concentrations (see Figure 2). The most similar yields are from Palm Beach (Schechter & Singer, 1995), the LA Aquaduct Plant (Glaze et al., 1989), and the Quabbin Reservoir (Zhou, 1993). Schechter & Singer recorded average formaldehyde, glyoxal, and methyl glyoxal increases of 6 $\mu\text{g/L}$, 4 $\mu\text{g/L}$ and 2 $\mu\text{g/L}$, respectively, using Palm Beach water with semi-batch ozonation. Zhou used ozone doses up to 4 mg/L with water from the Quabbin Reservoir in Massachusetts and found formaldehyde increased up to 10 $\mu\text{g/L}$, glyoxal up to 4 mg/L, and methyl glyoxal up to 6 $\mu\text{g/L}$. Glaze documented averages of 6 $\mu\text{g/L}$, 10.5 $\mu\text{g/L}$, and 3.5 $\mu\text{g/L}$ for formaldehyde, glyoxal and methyl glyoxal respectively at the Los Angeles Aqueduct Filtration Plant. The variety of yields in Figure 2 shows how broad the range of aldehyde production is for ozonated waters.

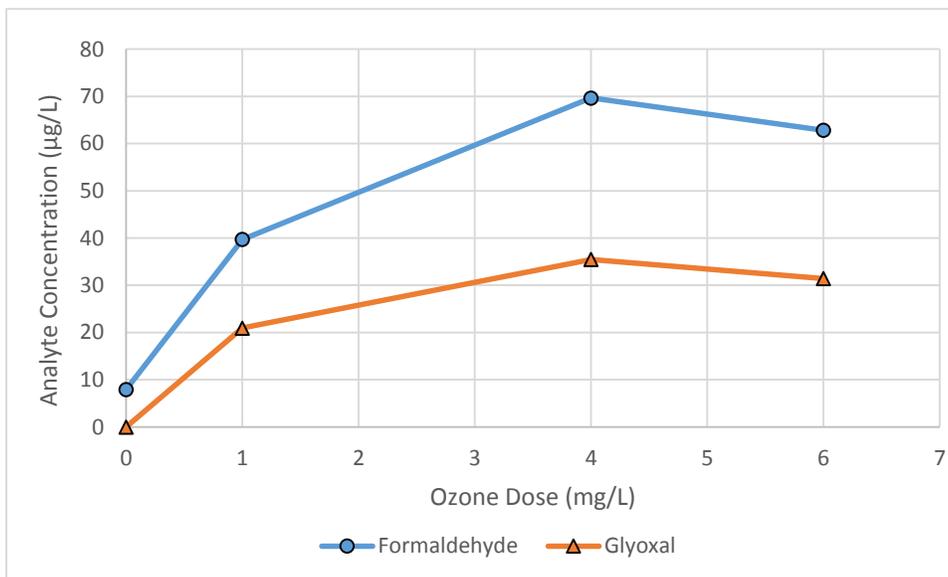


Figure 3. Water samples, fortified with 300 $\mu\text{g/L}$ sodium bromide, dosed with different ozone doses, and finished with 6 mg/L chlorine.

A sample of Atkins water, fortified with 300 $\mu\text{g/L}$ NaBr, was ozonated at different ozone doses before treatment with 6 mg/L Cl_2 (Figure 3). Similar to the results shown in Figure 1, the concentrations of formaldehyde and glyoxal increased at a decreasing rate as ozone dose increased until the point that the destruction rate of the aldehydes overcame the production rate. The

concentrations seen from pretreating with sodium bromide are much greater than with ozonation alone. Propanal and methyl glyoxal did not appear in significant concentrations. Bromide is known to act as a catalyst in many oxidation reactions in water treatment (Gunten, 2003), although other authors have not found any effect (Schechter and Singer, 1995). It appears from these results that bromide catalyzes the formation of aldehydes.

3.2 Effects of chlorine on aldehyde formation

Atkins Reservoir water samples were also treated with chlorine under varying conditions to evaluate the effects of chlorine on aldehyde formation. Two replicate experiments were performed with the second experiment using the same water stored for a week longer at 4°C. The second experiment also included more sampling points than the first. The higher concentrations in the first experiment may be reflective of these differences, as the chlorine stock may have degraded in the time between the two experiments. The top graphs of the pairs below show the results from the first experiment, and the bottom graphs show the results from the second experiment. Each graph shows the concentrations of the aldehydes when the chlorine was quenched at different chlorine contact times under the same ozonation condition; each pair of graphs corresponds to a different ozonation condition, either 0 mg/L, 2 mg/L, or 4 mg/L ozone dose.

3.2.1 Formaldehyde

When the Atkins Reservoir water was treated only with chlorine (Figure 4), formaldehyde concentrations increased 1-1.3 µg/L at 3 mg/L Cl₂ and 4.3-5.4 at 6 mg/L Cl₂. The formaldehyde increase between chlorine contact times was less than 0.2 at 3 mg/L Cl₂ dose and 0.4-0.6 µg/L at a dose of 6 mg/L.

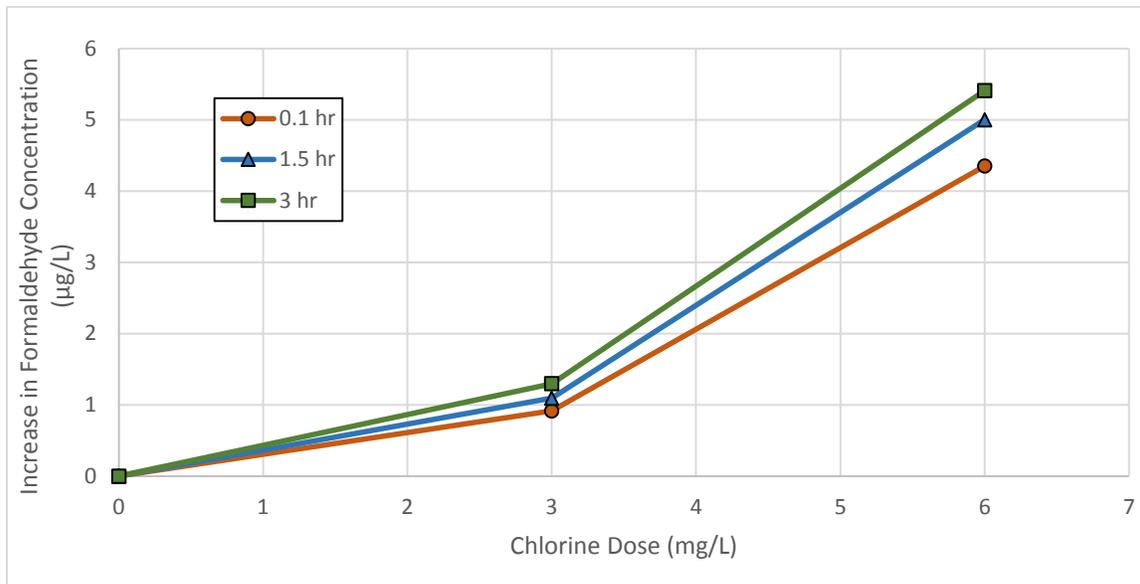


Figure 4. Formaldehyde increases when Atkins Reservoir water was treated with chlorine only.

In Figure 5, results from the two replicate experiments are shown for the Atkins Reservoir water pretreated with 2 mg/L ozone before chlorine addition. In the first replicate, formaldehyde increased by 3 to 4 µg/L when 3 mg/L Cl₂ was used and by 4 µg/L when 6 mg/L Cl₂ was used. For a 3 mg/L Cl₂ dose, the 3-hour contact time concentration was 1 µg/L higher than the 0.1-hour contact time. In the second replicate, formaldehyde increased by 0.6-0.9 µg/L when 3 mg/L Cl₂ was used and by 1.1-1.8 µg/L when 6 mg/L Cl₂ was used. In this experiment, the longer contact times showed lower increases, although the difference was small (<0.2 µg/L); the exception was the 0.1-hour contact time, which had a drop off for the 6 mg/L Cl₂ dose that didn't follow the trend of the other data.

In Figure 6, two replicate experiments are shown for the Atkins Reservoir water pretreated with 4 mg/L before chlorine treatment. In the first, formaldehyde increased by 7-9.5 µg/L for a 3 mg/L Cl₂ dose and 7.8 mg/L Cl₂ dose. In the second experiment, formaldehyde increased by 1-1.5 µg/L for the 3 mg/L Cl₂ dose. For the 6 mg/L Cl₂ dose, the 1.5-hour and 3-hour contact time data

points only showed increases of 3 $\mu\text{g/L}$, whereas the 0.1-hour showed an increase of 20 $\mu\text{g/L}$ and is likely an outlier. There was no prevalent trend with contact time, which were all within 0.5 $\mu\text{g/L}$ of one another (with the exception of the mentioned outlier point).

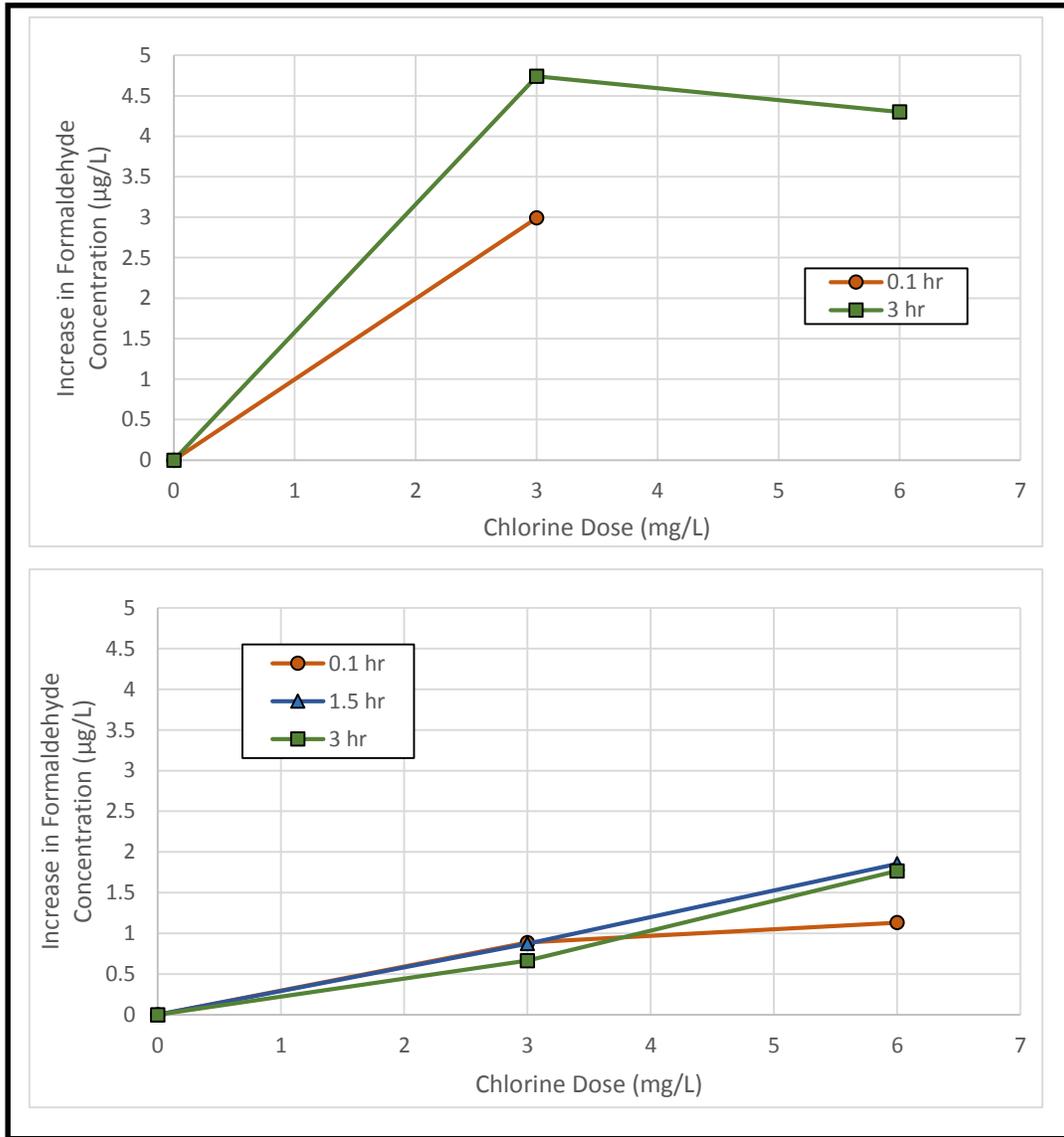


Figure 5. Formaldehyde increases in two replicate experiments with Atkins Reservoir water pretreated with 2 mg/L ozone before chlorine addition. (Different symbols represent different chlorine contact times.)

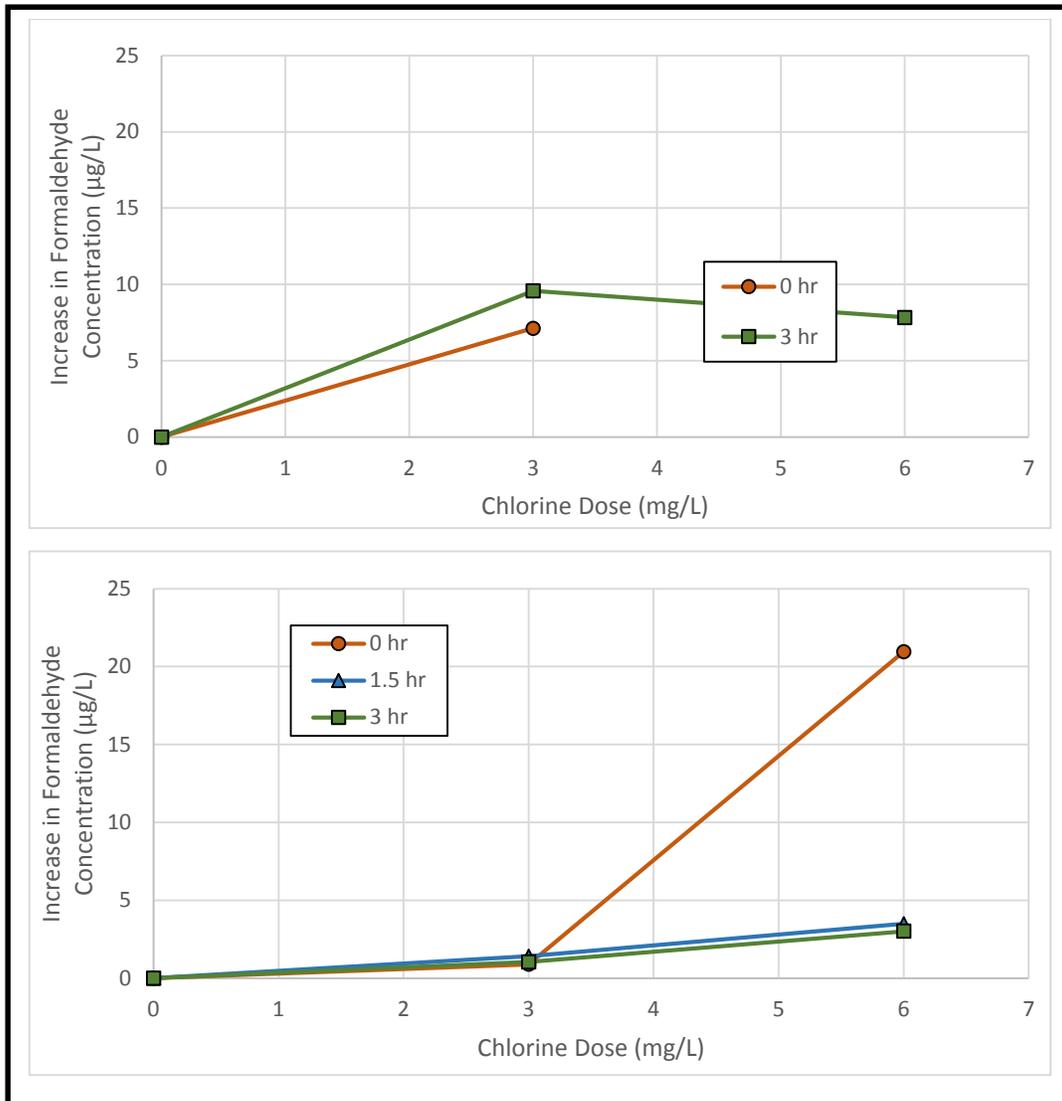


Figure 6. Formaldehyde increases in two replicate experiments with Atkins Reservoir water pretreated with 4 mg/L ozone before chlorine treatment.

3.2.2 Glyoxal

In the first replicate experiment with no ozone added (Figure 7), the glyoxal concentration increased by 1.3-2 µg/L for the 3 mg/L Cl₂ dose but only by 1.2 µg/L for the 6 mg/L Cl₂ dose. In the second experiment, glyoxal increased almost linearly with increasing chlorine dose by 0.4-0.5 µg glyoxal per mg of chlorine dose. It also increased with increasing chlorine contact time, although all the values for the same chlorine dose were within 0.7 µg/L of one another.

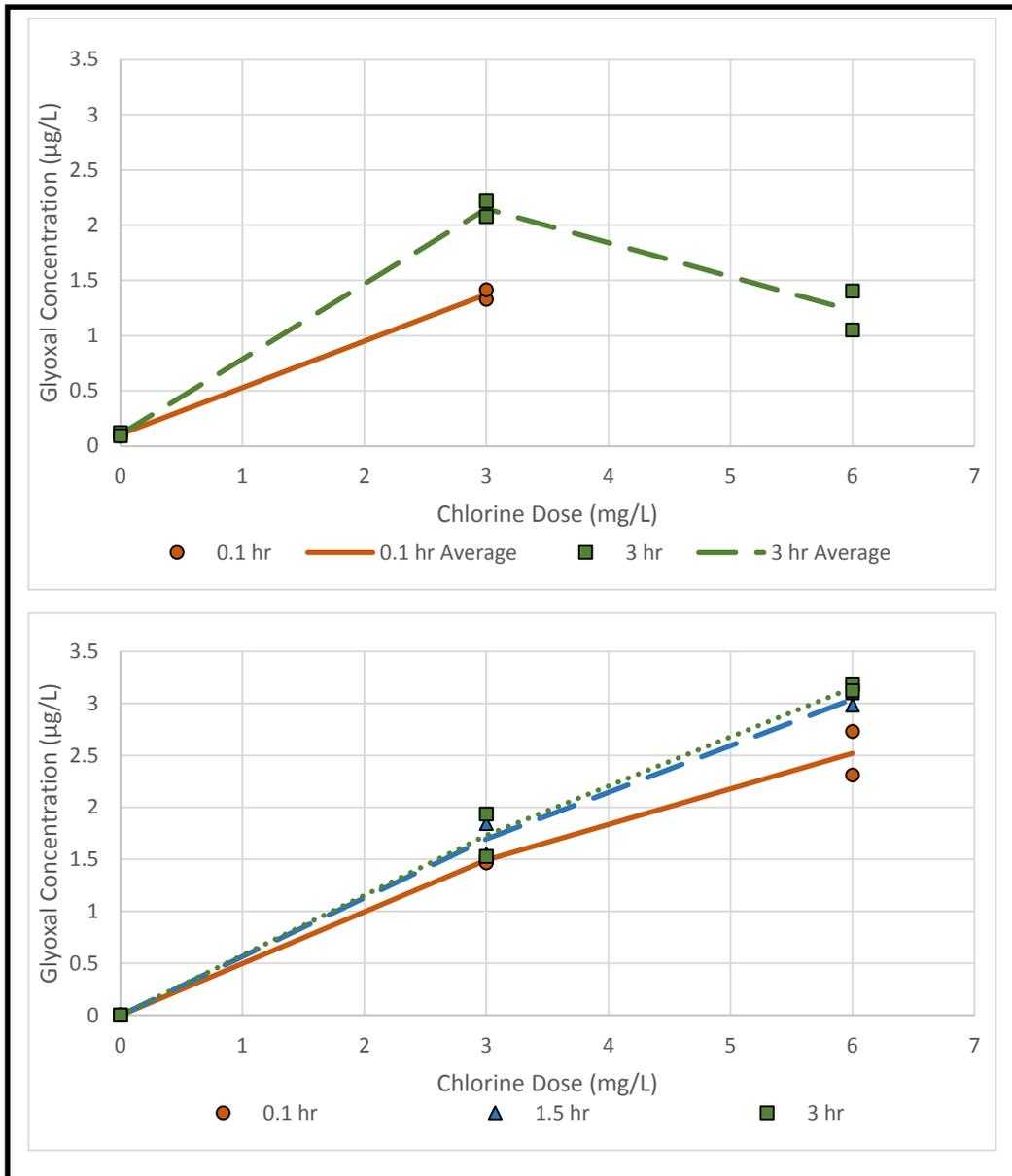


Figure 7. Glyoxal concentrations in two replicate experiment with Atkins Reservoir water treated with chlorine only.

In the first replicate experiment with an ozone dose of 2 mg/L used (Figure 8), the glyoxal concentration increased between 2.2 and 2.5 µg/L with chlorine dose and chlorine contact time for both the 3 and 6 mg/L Cl₂ doses. The 3-hour contact time was slightly higher (0.3 µg/L) and the 0.1-hour contact time. In the second experiment, glyoxal concentration increases by 0.5-2 µg/L for

the 3 mg/L Cl₂ and by 3-5 µg/L when the dose was increased to 6 mg/L. No trend stood out for the different chlorine contact times.

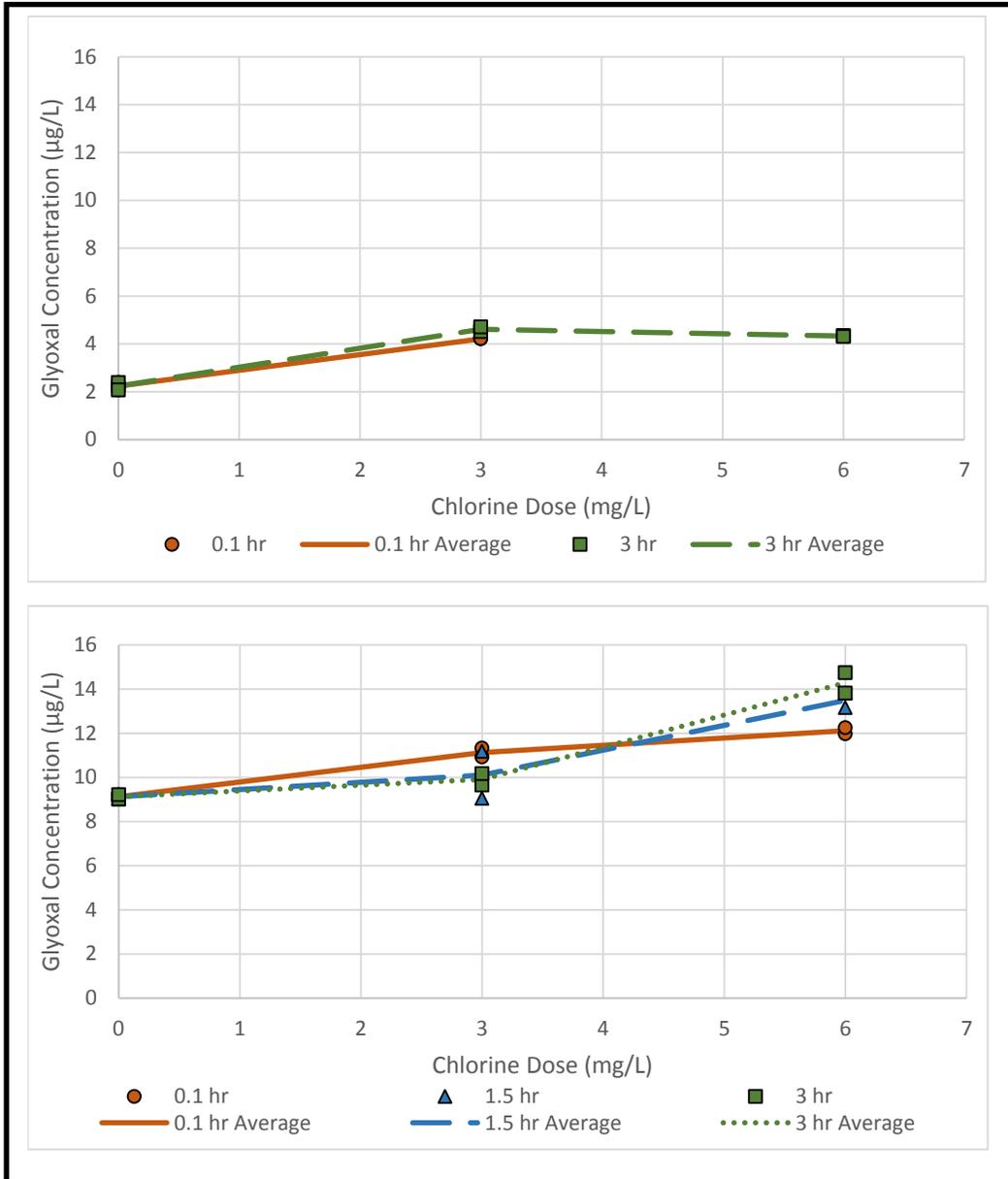


Figure 8. Glyoxal concentrations in two replicate experiments with Atkins Reservoir water pretreated with 2 mg/L ozone before chlorine addition.

In the first replicate experiment with an ozone dose of 4 mg/L used (Figure 9), the glyoxal concentration increased by 2.6-5.6 µg/L for the 3 mg/L Cl₂ dose and by 2.7 µg/L for the 6 mg/L

Cl₂ dose. Glyoxal concentration increases 1.2 µg/L or less in the second replicate for the 3 mg/L Cl₂ dose and 2 µg/L or less for the 6 mg/L Cl₂ dose. There was also no chlorine contact time trend.

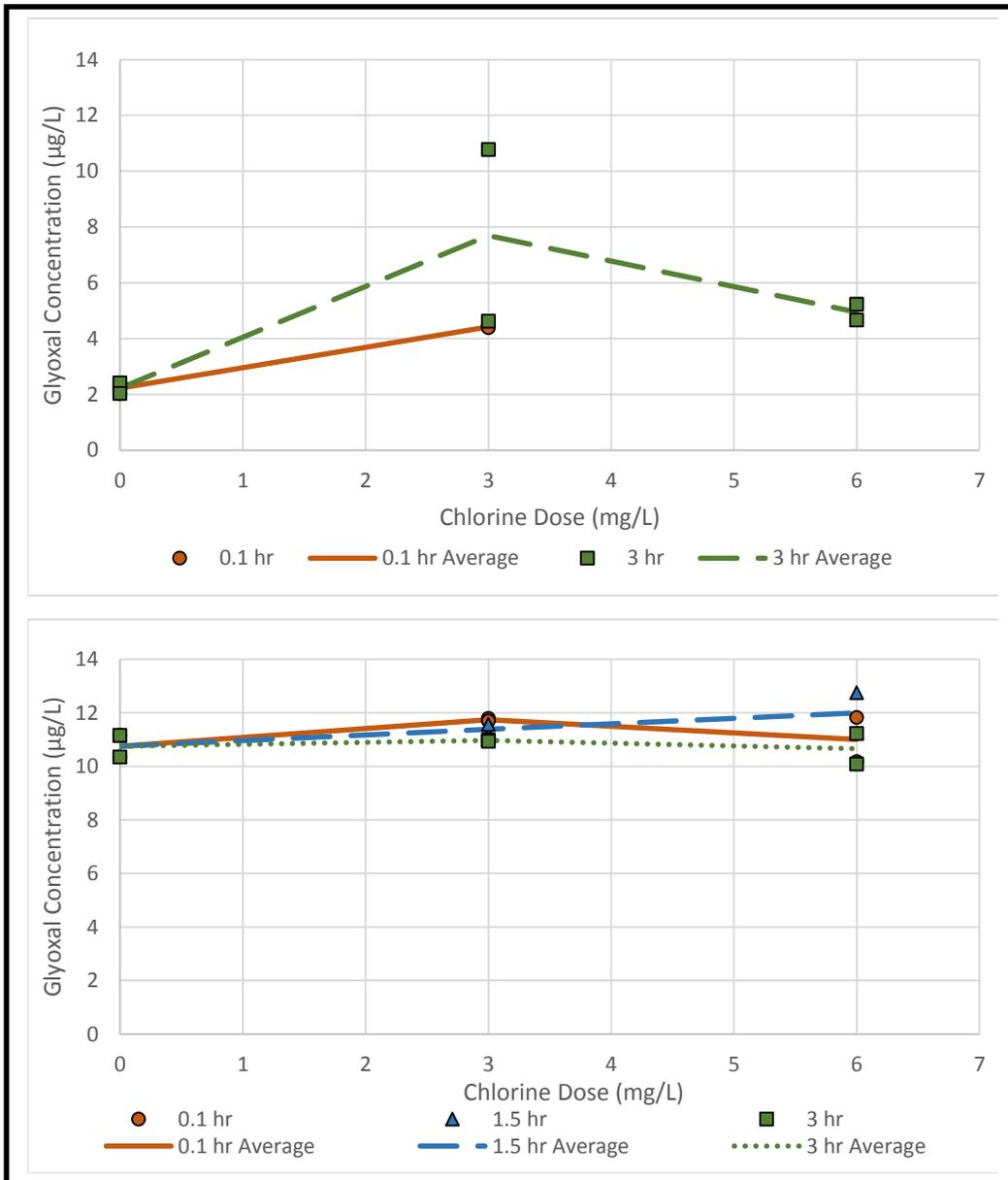


Figure 9. Glyoxal concentrations in two replicate experiments with Atkins Reservoir water pretreated with 4 mg/L ozone before chlorine addition.

3.2.3 Methyl Glyoxal

For methyl glyoxal, the concentrations for the samples with no ozone dose were lower than 1 µg/L and are not reported here.

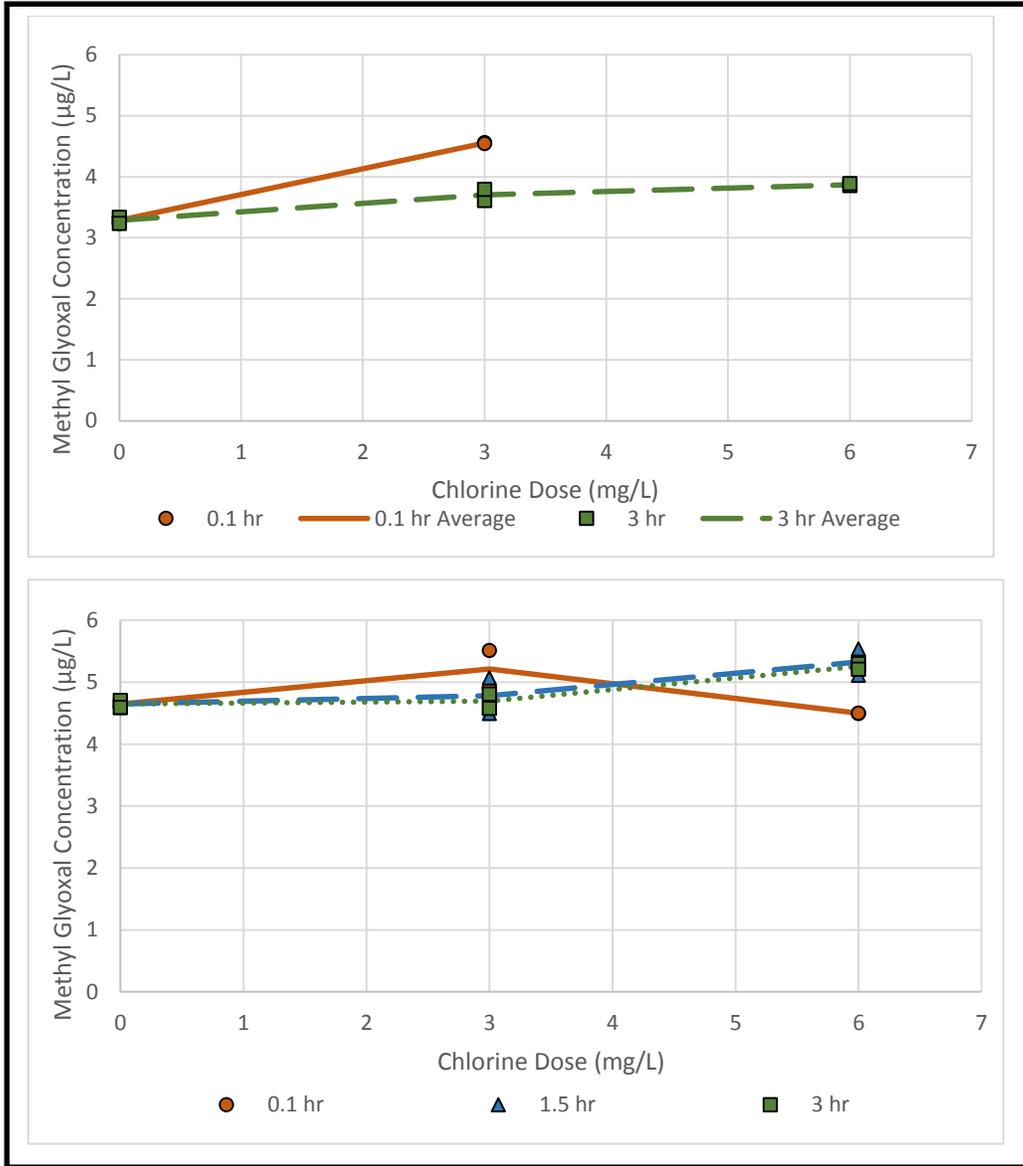


Figure 10. Methyl glyoxal concentration for two replicate experiments with Atkins Reservoir water pretreated with 2 mg/L ozone before chlorine addition.

Figure 10 shows the results for methyl glyoxal from the replicate experiments with the 2 mg/L ozone pretreatment. In the first experiment, methyl glyoxal concentration increases between

0.5 $\mu\text{g/L}$ and 1 $\mu\text{g/L}$ for the 3 mg/L Cl_2 chlorine dose and by 0.6 $\mu\text{g/L}$ for the 6 mg/L dose. In the second experiment, concentrations for both doses rose under 0.7 $\mu\text{g/L}$, and no trends in chlorine contact time were observed.

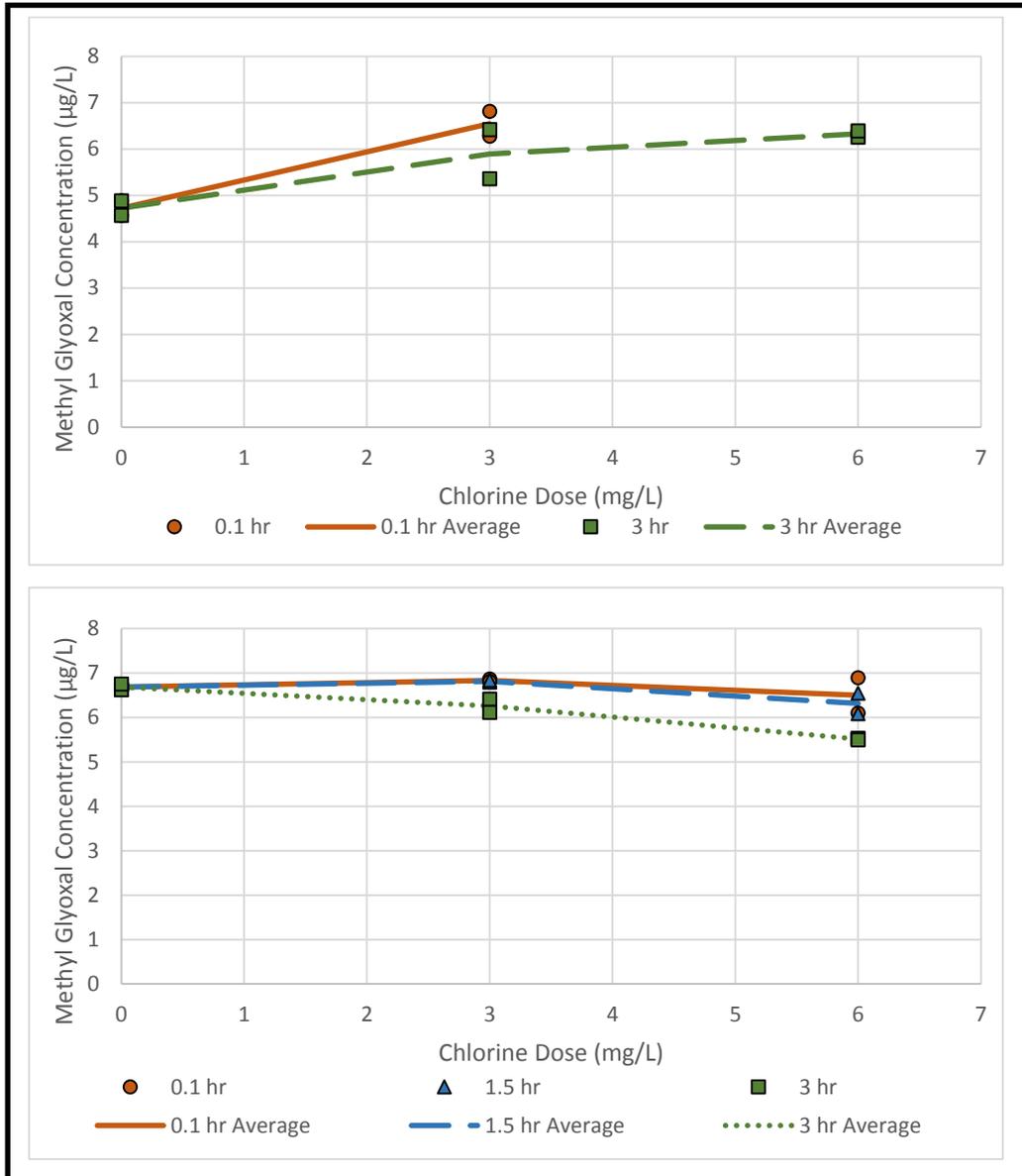


Figure 11. Methyl glyoxal concentrations in two replicate experiments with Atkins Reservoir water pretreated with 4 mg/L ozone before addition of chlorine.

In the first experiment with an ozone dose of 4 mg/L used (Figure 11), the methyl glyoxal concentration increased by 1.3-2 $\mu\text{g/L}$ at the 3 mg/L Cl_2 dose and by 1.7 $\mu\text{g/L}$ for the 6 mg/L dose.

In the second experiment, the results show a decrease in concentration (up to 0.5 µg/L for 3 mg/L and up to 1 µg/L for the 6 mg/L dose) with increasing chlorine dose. In both, concentrations increase with decreasing chlorine contact time.

Overall, chlorine addition cause methyl glyoxal concentrations to increase. Methyl glyoxal concentrations decreased at higher chlorine doses in some—but not all—cases. Longer contact times generally showed a decrease in methyl glyoxal concentration, possibly due to the degradation of methyl glyoxal overcoming its rate of production by chlorine.

3.2.4 Propanal

In all the chlorine experiments, propanal was only detected in low concentrations (2 µg/L or less) and was not reported here. It would appear, from this, then propanol is not produced in great quantities in response to chlorination.

3.2.5 Summary

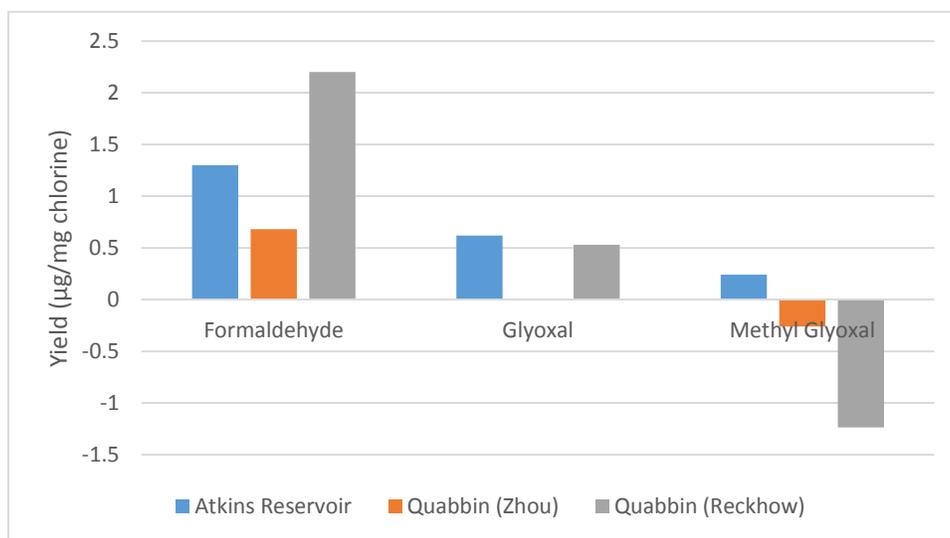


Figure 12. Aldehyde yields from chlorination in this study compared to previously documented data.

The overall yield results of the chlorination experiments are summarized in Figure 12. The yields for formaldehyde and glyoxal from chlorine treatment are within the general range of other published data, however, the range of yields varies considerably (even within the same water source, e.g. Quabbin Reservoir). In addition, the methyl glyoxal yield for this study is positive, but the other studies report negative yields. Only one set of data in this study (water pretreated 4 mg/L ozone) showed a definite negative trend for methyl glyoxal.

The relationship between chlorine contact time, chlorine dose, and aldehyde concentrations was not consistent across all experiments or aldehydes. Longer contact times increased formaldehyde concentrations in most cases, but the increases were mostly minor (1 or 2 $\mu\text{g/L}$). Glyoxal showed the same trend in about half the data, but the increases were likewise small. Methyl glyoxal showed the opposite trend (decreased concentration for longer chlorine contact times); this is not surprising as the other studies in Figure 12 showed a decrease in methyl glyoxal with chlorine dose. This decrease for only methyl glyoxal likely occurs when chlorine reacts with the compound's methyl group, forming chlorinated by-products through additional reactions.

Increases in aldehyde concentrations were greater per milligram of ozone for the 2 mg/L dose than the 4 mg/L dose, indicating that the bulk of aldehyde formation happens at lower doses of ozone. This likely happens due to the limited amount of carbon available in the samples for oxidation: as the aldehyde precursor concentration became depleted, the rate of aldehyde production would slow. Because of this, it is possible that a greater difference in formation would be demonstrated if chlorine contact times were studied using lower doses of ozone.

3.3 Effects of chlorine dioxide on aldehyde formation

The effects of chlorine dioxide on aldehyde formation were explored by dosing the Atkins reservoir water with chlorine dioxide at different doses after the water had been fortified with 300 µg/L NaBr and finishing it with 6 mg/L chlorine (Figure 13).

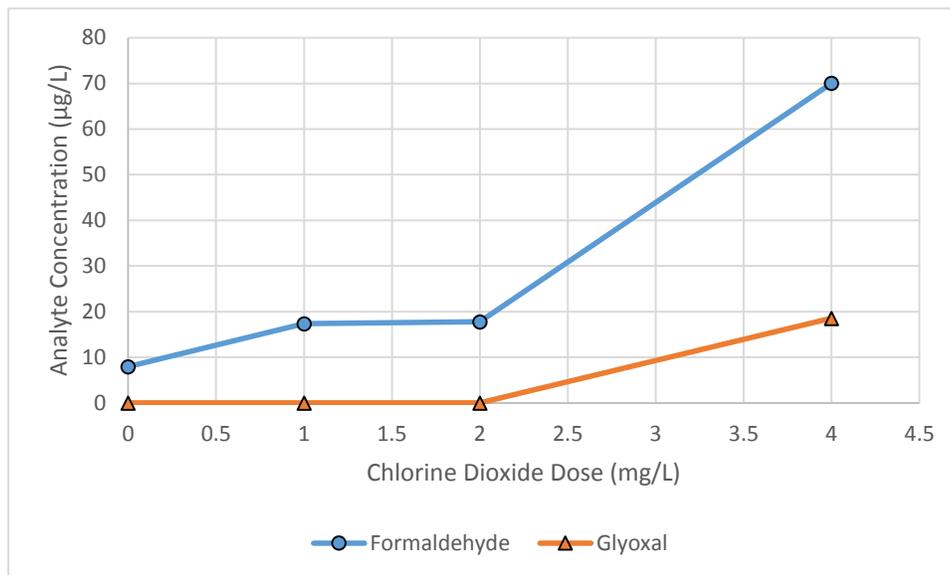


Figure 13. Aldehyde concentrations when Atkins Reservoir water was fortified with 300 µg/L NaBr, treated with varying levels of chlorine dioxide, and finished with 6 mg/L chlorine.

Only formaldehyde and glyoxal were formed in measurable concentrations in this experiment. Glyoxal was only seen when the highest chlorine dioxide dose (4 mg/L) was used, increasing in concentration to 20 µg/L. Formaldehyde doubled when 1 mg/L chlorine dioxide was used and the concentration when 4 mg/L was used increased to seven times the original concentration. However, the concentration remained the same when a 2 mg/L dose was used as it was when a 1 mg/L dose was used.

In Dabrowski et al. (2002), the authors found increases in total aldehyde concentration of up to 30 µg/L for doses of chlorine dioxide between 0 and 9 mg/L on a surface water (Bagdanka River) in Poland. In addition, the ICR report (2002) found only up to 9 µg/L formaldehyde in 21

surface water plants using chlorine dioxide. Both of these are considerably lower than the results seen here, which reach a maximum increase of 60 $\mu\text{g/L}$ of formaldehyde alone.

3.4 Effects of ferrate on aldehyde formation

Atkins Reservoir water was dosed with ferrate to investigate its impact on aldehyde concentration. The samples were adjusted to two pH values (6.2 and 7.5) because ferrate degrades differently at different pH. Results are shown in Figures 14 and 15.

At both pH values, formaldehyde concentration increased, with the increase being greater for the 3 mg/L dose than the 6 mg/L dose in both cases. Glyoxal increased at both pH for the 3 mg/L dose, but the increase was greater at a pH of 6.2. At pH 7.5, glyoxal concentration remained the same for a dose of 6 mg/L while, at pH 6.2, glyoxal concentration continued to rise another 5 $\mu\text{g/L}$. At pH 6.2, methyl glyoxal was present at approximately 2 $\mu\text{g/L}$ at both doses of ferrate; at 7.5, propanol was present between 2 $\mu\text{g/L}$ and 2.5 $\mu\text{g/L}$ at both doses.

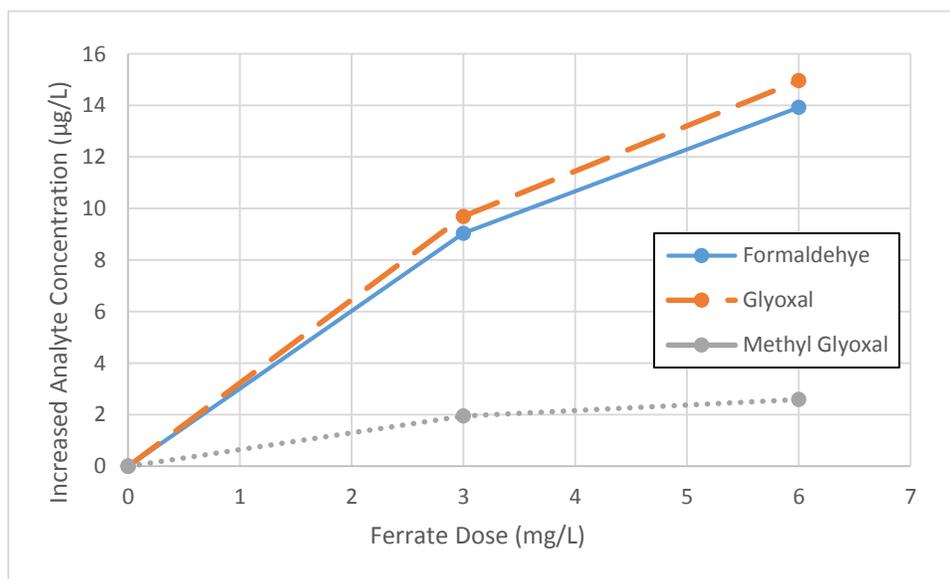


Figure 14. Aldehyde increases from Atkins Reservoir water buffered to a pH of 6.2 and treated with ferrate.

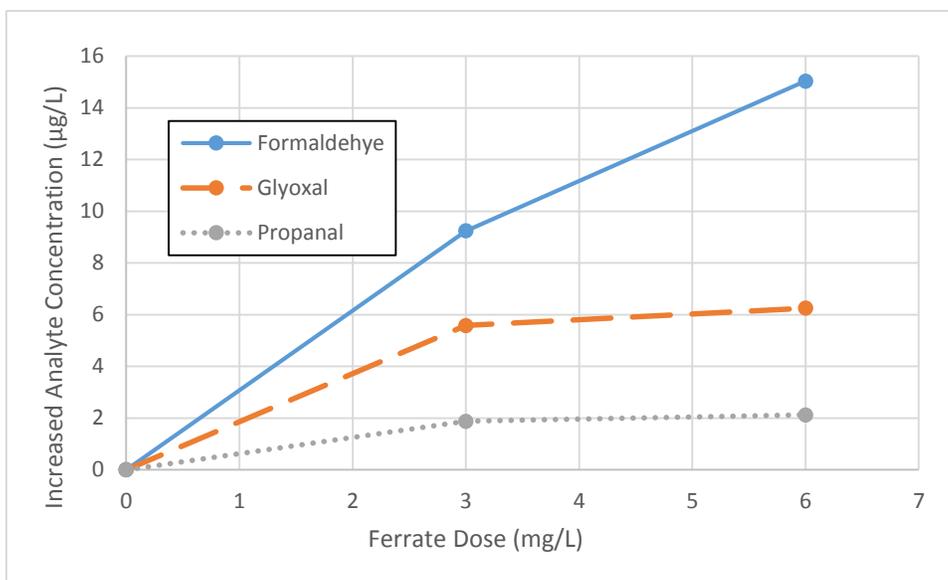


Figure 15. Aldehyde increases from Atkins Reservoir water buffered to a pH of 7.5 and treated with ferrate.

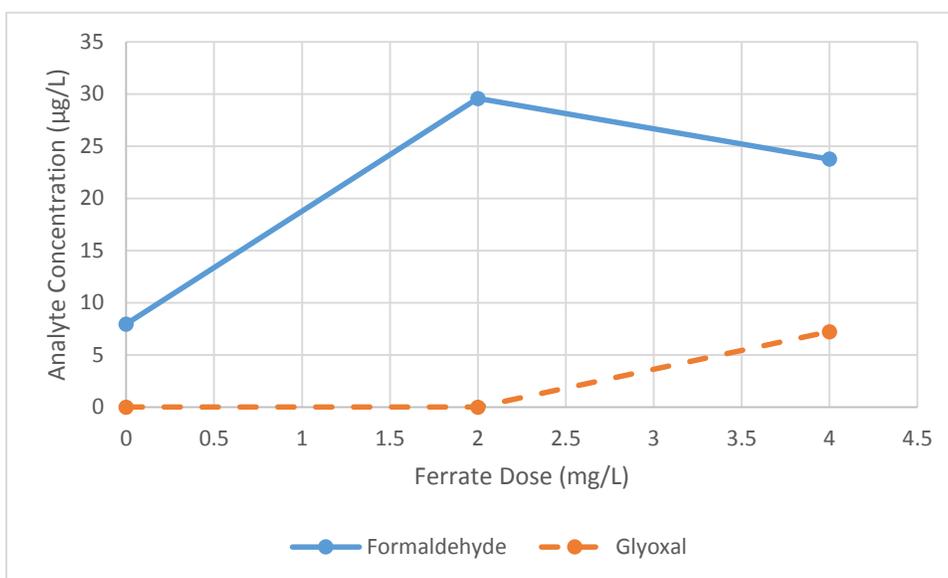


Figure 16. Aldehyde concentrations from Atkins Reservoir water fortified with sodium bromide and treated with ferrate (pH 7.5).

Ferrate was also used with Atkins Reservoir water that was fortified with 300 µg/L NaBr and finished with 6 mg/L Cl₂ (Figure 16). Only formaldehyde and glyoxal formed at measurable concentrations. At a dose of 2 mg/L of ferrate, formaldehyde increased by more than three times its original concentration, but decreased by 20% when a dose of 4 mg/L was applied. Glyoxal was

not seen until the higher ferrate dose of 4 mg/L was used, at which it was found at a concentration of 7 µg/L.

4. CONCLUSION

This research was performed to better characterize the consequences of several different disinfectants on the formation of aldehydes in a natural water. As aldehydes are a potential health concern and are still under investigation, it is important to understand what situations may produce higher concentrations of aldehydes. Figure 17 shows a summary graph of average aldehyde formation from this study.

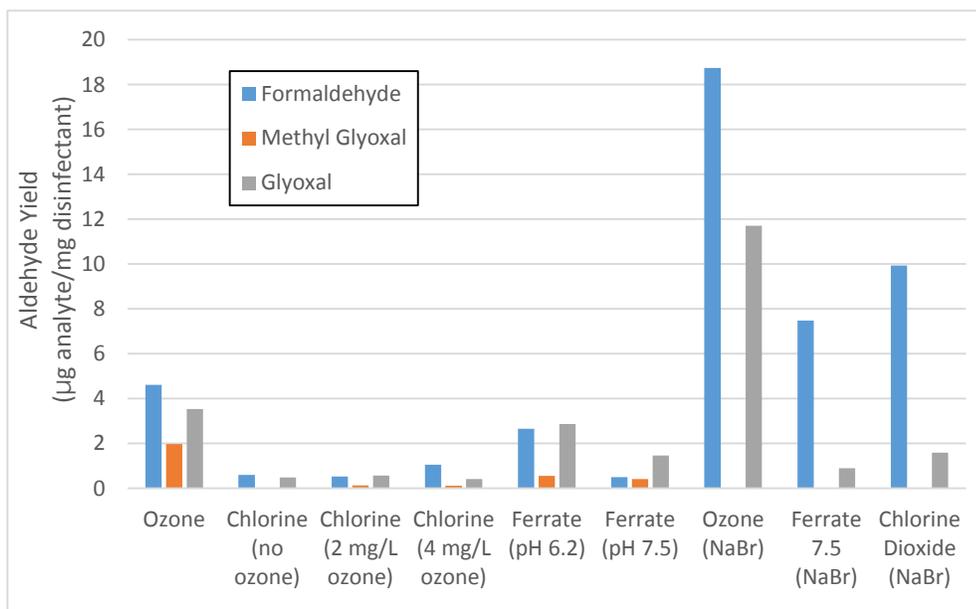


Figure 17. Average aldehyde yields of different aldehydes using different treatment scenarios. Formations from chlorine are averaged from all contact times. Outliers are excluded.

From the results of the experiments performed, a few general observations can be made. When treated with ozone alone, concentrations of formaldehyde, glyoxal, and methyl glyoxal increased with ozone dose, and the increases were greater at lower doses of ozone. At the highest ozone dose tested, formaldehyde and glyoxal concentrations decreased. This is likely due to diminished aldehyde formation and higher rates of aldehyde destruction (e.g. oxidation).

For formaldehyde, glyoxal, and methyl glyoxal, concentrations increased with dose at lower chlorine doses but decreased at higher doses. For both formaldehyde and glyoxal,

concentrations also increased with longer contact times, although this trend was weaker for glyoxal. For methyl glyoxal, concentrations decreased with longer contact times, presumably due to reaction of chlorine with this compound and the formation of chlorinated by-products.

Chlorine dioxide produced increased concentrations of formaldehyde and glyoxal. The relationship was stronger for formaldehyde, and the concentrations produced were greater than when chlorine was used.

Ferrate produced more aldehydes than chlorine did, but not as much as chlorine dioxide or ozone. Formaldehyde formed equally at both pH levels when the water samples were dosed with ferrate. While glyoxal formed at both pH levels when dosed with ferrate, concentrations were higher for a pH of 6.2. Methyl glyoxal was only measurable for a pH of 6.2.

While little experimentation was performed using sodium bromide in this study, it would seem that the use of sodium bromide in some of the experiments described above produced more aldehydes than expected with just the disinfectants used alone. It appears the catalyzing effects of bromide increased aldehyde formation in the fortified samples.

Combining the results of this study with those from previously published work, it would seem that the formation of aldehydes cannot be predicted easily from simple parameters such as DOC, oxidant dose, and pH. Ozonation appears to form the greatest amounts of aldehydes, followed by chlorine dioxide, ferrate, and finally chlorine. The relationship of aldehyde concentration to ozone dose appears to differ at lower doses, with lower doses providing more linear results that become asymptotic and reach a maximum concentration. It appears dependent on some characteristics of a particular water, but the exact relationship remains elusive. Previously suggested indicators such as TOC and AOC have had mixed results, but parameters such as these are the most likely to prove successful.

5. REFERENCES

- American Public Health Association, American Water Works Association, Water Environment Federation (2005). Standard Methods for the Examination of Water and Wastewater.
- Can, Z. S., & Gurol, M. (2003). Formaldehyde Formation During Ozonation of Drinking Water. *Ozone: Science & Engineering*, 25: 41-51.
- Dabrowska, A., Swietlik, J., Nawrocki, J. (2002). Formation of aldehydes upon ClO₂ disinfection. *Water Research* 37: 1161-1169.
- Dabrowska, A., Hordern, B. K., Nawrocki, J. (2005). Aldehydes Formation During Water Disinfection By Ozonation and Chlorination Process. *Global NEST Journal* 7.1: 61-71.
- Glaze, W. H., Koga, M., Cancilla, D., Wang, K., McGuire, M. J., Liang, S., Davis, M. K., Tate, C. H., Aieta, E. M. (1989). Evaluation of Ozonation By-products From Two California Surface Waters. *American Water Works Association* 81.8: 66-73.
- Jiang, J. and Lloyd, B. (2002). Progress in the development and use of ferrate(VI) salt as an oxidant and coagulant for water and wastewater treatment. *Water Research* 36: 1397-1408.
- McGuire, M. J., McLain, J. L., Obolensky, A. (2002). Information Collection Rule Data Analysis. AWWA Research Foundation and American Water Works Association.
- Nawrocki, J. and Kalkowska, I. (1996). Formation and Determination of Aldehydes—Ozonation By-products. *Chemical Analysis* 41.3: 447-454.
- Papageorgiou, A., Voutsas, D., Papadakis, N. (2014). Occurrence and fate of ozonation by-products at a full-scale drinking water treatment plant. *Science of the Total Environment* 481: 392-400.
- Ramseier, M. K., Peter, A., Traber, J., von Gunten, U. (2010). Formation of assimilable organic carbon during oxidation of natural waters with ozone, chlorine dioxide, chlorine, permanganate, and ferrate. *Water Research* 45: 2002-2010.
- Schechter, D. S. and Singer, P. C. (1995). Formation of Aldehydes During Ozonation. *Ozone: Science & Engineering* 17.1: 53-69.
- Swietlik, J., Dabrowska, A., Raczyk-Stanislawiak, U., Nawrocki, J. (2003). Reactivity of natural organic matter fractions with chlorine dioxide and ozone. *Water Research* 38: 547-558.
- von Gunten, U. (2003). Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Research* 37: 1469-1487.
- Zhou, X. (1993). Formation and Removal of Aldehydes in Drinking Water Treatment Processes. University of Massachusetts at Amherst.

6. APPENDIX

Figures A1 through A4 show sample calibration curves for formaldehyde, propanol, glyoxal and methyl glyoxal. Curves were forced through zero and R^2 values were always 0.96 or higher. “IS” in these graphs refers to the internal standard.

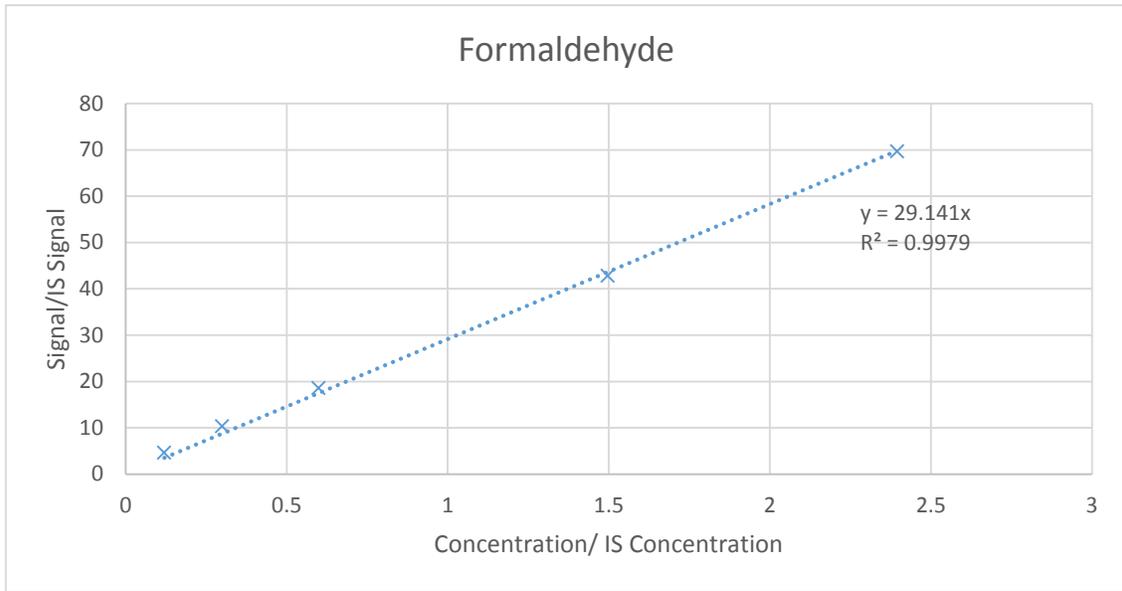


Figure A 1. Example of formaldehyde standard curve.

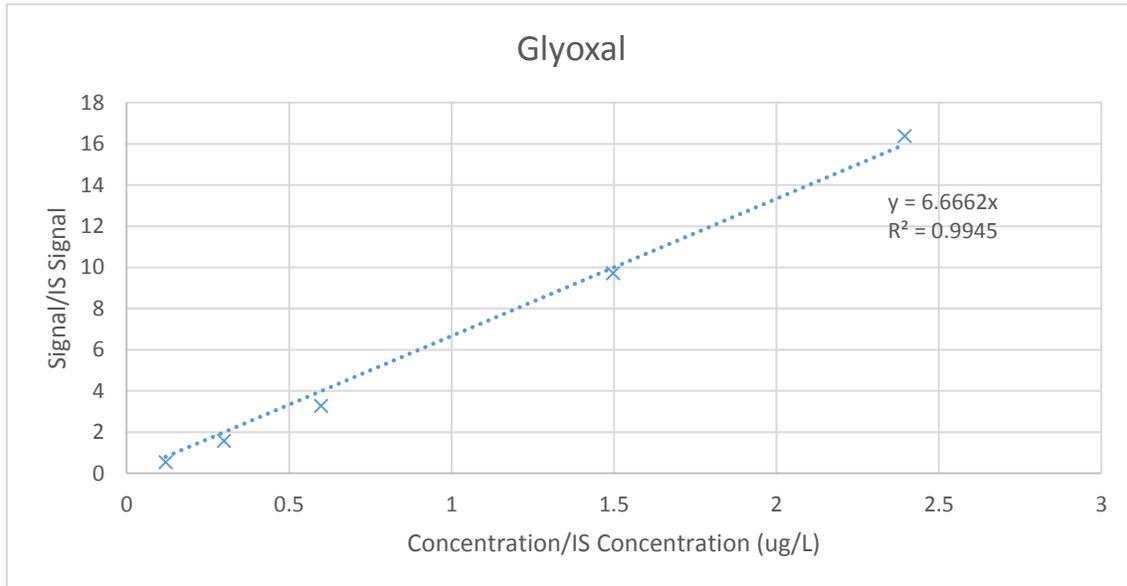


Figure A 2. Example of glyoxal standard curve.

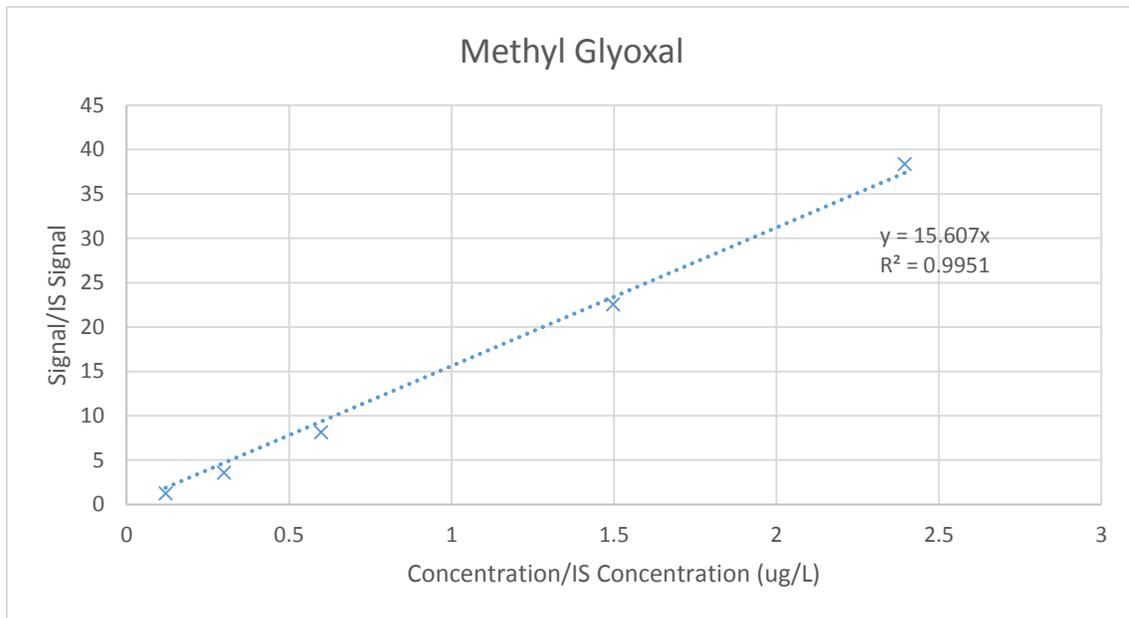


Figure A 3. Example of formaldehyde standard curve.

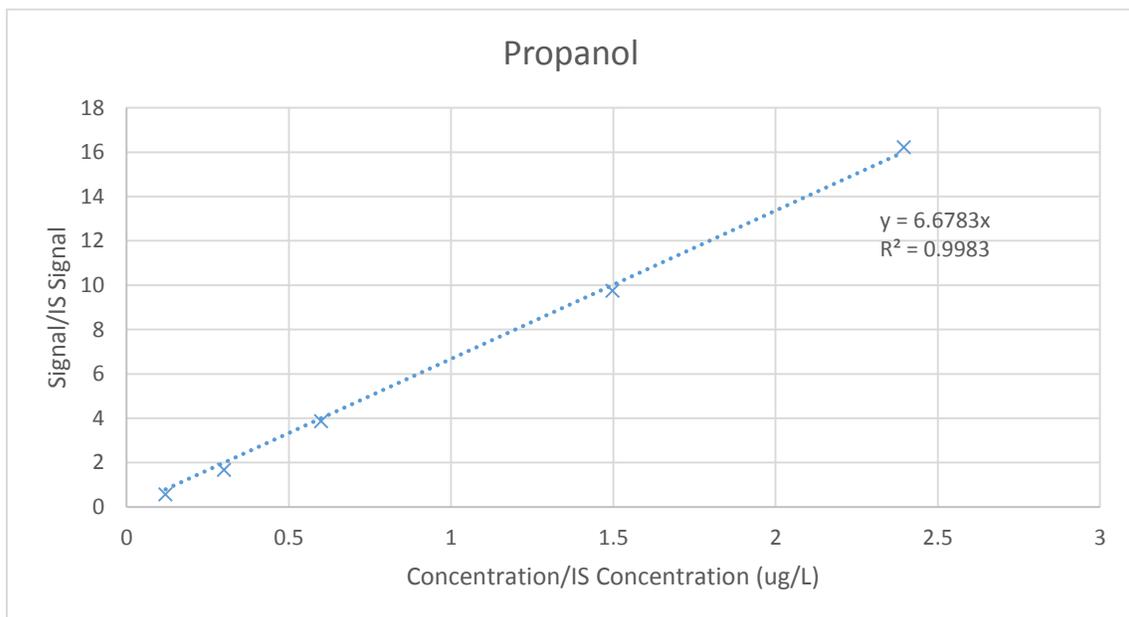


Figure A 4. Example of formaldehyde standard curve.