PREOZONATION OF ALGAL LADEN WATERS

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ABSTRACT

Trihalomethanes (THMs) are suspected carcinogens that are formed in the water treatment process upon chlorination of THM precursor compounds. Organic materials such as humic substances and algal biomass have been shown to be THM precursors. This study examines the effect of ozone on these THM precursor compounds in waters that have a high organic load due to the presence of an algal bloom.

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CHAPTER I.

INTRODUCTION

In November 1979, the United States Environmental Protection Agency (USEPA) established, in accordance with the Safe Drinking Water Act (SDWA) of 1974, a Maximum Contaminant Level (MCL) for total trihalomethanes (TTHMs) (1).

Trihalomethanes (THMs) are halogenated organic compounds that are being studied for their possible carcinogenic and other toxic characteristics (2). In water treatment plants, trihalomethanes are formed when trihalomethane precursors in the water come into contact with free chlorine that is added as a disinfectant (2). The MCL that the USEPA has established for total trihalomethanes is 0.10 mg/l (2). This level can be reached by some treatment plants if the raw water contains few dissolved organic compounds. If the MCL is lowered, as is expected, many treatment plants will find it difficult to comply with the standard. Three possible solutions to the problem of THMs in drinking water are;

1. do not add free chlorine to disinfect the water,
2. remove the trihalomethane precursors prior to chlorination, or
3. remove trihalomethanes once they are formed. (2)

The first solution, not to add free chlorine, is not desirable in the U.S. at this time. Free chlorine is relatively inexpensive and disinfects at a higher rate than combined chlorine (NH_2Cl and $NHCl_2$) (3).

Partial removal of the trihalomethane precursors will take place in the treatment plant through coagulation and settling processes. This will not solve the problem in all cases as some treatment plants chlorinate the raw water before it enters the treatment works. In one plant, 60% of the total trihalomethanes were formed in the prechlorination step (4). Various methods to control THM formation have been proposed by the USEPA and others. Among these methods are; use of granular activated carbon (GAC), use of ozone to oxidize THM precursors, and use of combined chlorine as a disinfectant instead of free chlorine. The benefits and detriments of these methods will be presented in following sections (3).

Removal of the trihalomethanes is possible by stripping the trihalomethanes from the water but the free chlorine can continue to react with the remainder of the trihalomethane precursors (3).

In Europe, ozone (O_3) is a commonly used disinfectant. Ozone is a more powerful disinfectant than chlorine and does not form trihalomethanes. On the other hand, ozone cannot protect the distribution system as it decays quickly to oxygen in water and leaves no residual. Some plants use ozone as a primary disinfectant and then add chlorine to protect the distribution system. Ozone also destroys trihalomethane precursors so that subsequent chlorination forms fewer trihalomethanes than if no ozone was used. (5) Ozone is not widely used in the U.S. due to its high cost of generation compared to the cost of generating free chlorine.

During the late summer, many reservoirs are host to algal blooms. As algae are a source of trihalomethane precursors (6,7) it was decided to study the effects of preozonation on the trihalomethane precursors present in an algal bloom.

Trihalomethane formation potential (THMFP), a measure of the total possible THMs in a water sample, was measured before and after ozonation. A decrease in the THMFP would suggest that the THMFP was reduced by the ozone. In addition, dissolved and colloidal organic carbon (DCOC) and chlorophyll a concentration were measured in order to study the oxidation characteristics of ozone. Both batch kinetics and continuous flow tests were performed. In the batch

kinetics tests the variables were ozone dose and level of algae. The level of the algae was measured by the chlorophyll a concentration. High levels of chlorophyll a were used in order to study a "worst case" scenario. In the continuous flow tests pH, ozone dose, and detention times were varied.

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CHAPTER II.

LITERATURE REVIEW

OZONE

PHYSICAL PROPERTIES OF OZONE. Ozone is a very powerful oxidizing agent with a ranking fourth in oxidizing power behind diatomic fluorine gas, followed by F_2O, and free oxygen (O). The boiling point of ozone is -112° C and it is explosive in air in concentrations above 15%. Ozone is relatively stable in air with a half life measured in hours and is relatively unstable in water with a half life measured in minutes. Ozone is 10 to 20 times more soluble in water than is oxygen (8).

The chemistry of aqueous ozone is complicated and will be presented in a later section.

HISTORY OF OZONE USE. Ozone received its name from the Greek word "ozein" which means "to smell". The discovery of ozone is credited to Van Marum who, in 1785, first noted the characteristic odor near an electrical machine (9).

It wasn't until 1840 that ozone was determined, by Schonbein, to be a new substance that several years later

was discovered to be triatomic oxygen, O_3. The first commercial use of ozone was in the disinfection of water (9).

The first major ozonation plant went into operation in 1906 in Nice, France although pilot plants were being operated as early as 1892. By 1936 there were about 100 municipal ozonation plants in France (9). It was reported in 1972 that approximately 8 million people were being supplied ozonated water in France (9).

The first plant to go into operation in the U.S. was in Whiting, Indiana in July 1940. This plant was installed because of taste and odor problems created upon chlorination of the Lake Michigan water (9).

The Schuykill river near Philadelphia was so polluted that the city, in 1949, installed a water treatment plant using ozone to remove manganese, tastes, and odors (9).

TOXICITY TO HUMANS. Ozone, in low concentrations, poses no threat to humans. In fact, the smell of ozone is usually taken as a fresh smell. It is the smell one smells after a thunderstorm. But in higher concentrations, ozone can affect the human body in different ways ranging from discomfort to death in extreme cases. The most common symptom of ozone poisoning, toxicosis, is a dryness of the nose and throat. Reddening and swelling of the eyes is

another common symptom. This symptom can occur with exposure to ozone concentrations of 1 ppm in air. At ozone concentrations between 0.1 and 1.0 ppm it becomes difficult for the vision to adjust to darkness (10).

The most dangerous effects of ozone exposure occur in the respiratory tract. There are three levels of toxicosis with respect to the respiratory system; symptomatic, symptomatic irritant, and severe irritant. Symptomatic refers to the initial stages of toxicosis in which a mild irritation is felt in the nose and throat. The effects of ozone are labeled as symptomatic irritant when the sensations described above become more unpleasant and are usually accompanied by coughing. When exposure to ozone is prolonged or there is a high concentration of ozone in the air, symptoms can become severe. These symptoms relate to the onset of pulmonary edema. Breathing becomes labored and there is pressure and pain felt in the chest. Ozone affects the alveoli in two separate ways. The first effect is edematic swelling. The entrance to the alveoli becomes restricted and breathing becomes difficult. The second effect of ozone on the alveoli is the causing of the alveoli to partially fill with fluid. This fluid decreases the gaseous volumetric capacity of the lung (10).

Clamann and Bancroft tested the effects of ozone on humans at levels of 6 ppm for one hour and 1.2 ppm for 2.5

hours. They tested the subjects taste, smell, blood circulation, blood quality, and respiration. The researchers found that smell was inhibited for short periods of time following exposure. The other tests showed no effect except for respiration. It was found that at 6 ppm, vital capacity decreased to 58% of the original amount. It was also found that total capacity decreased to 80% of original. Since the relationship between vital capacity and total capacity is;

Total Capacity = Vital Capacity + Residual Volume

these tests showed an increase in residual, unusable volume. The effects of exposure lasted for several hours after the tests with no permanent symptoms (10).

Although the effects of exposure to ozone are similar in nature to the effects of exposure to chlorine, there are two main factors that point to ozone as being safer to use than chlorine. The first factor is that ozone is generated on site as it is needed. This factor removes the dangers of transportation and storage that chlorine is subject to. The second factor is that ozone has a half life in air. This means that once a leak is stopped the danger is mostly over. Chlorine is dangerous until it has dispersed (11).

PROPERTIES OF DISINFECTION. Ozone has proved to be a very effective disinfectant. Tests have been performed on bacteria (12,13), viruses (12,14), algae (15), fungi (13), and protozoans (16). In each case ozone proved to be a more powerful disinfectant than chlorine. Ozone doses ranged from 0.01 to 1.3 mg/l. It was found that greater kill efficiencies were found at lower pH's (13). The highest detention time noted was 80 seconds for bacteria (13), five minutes for viruses (12), five minutes for fungi (13), and nine minutes for protozoan cysts (16).

Katzenelson, et al. (12) show a two stage linear relationship between percent surviving bacteria and contact time. The initial kill was on the order of 99.9% in 50 seconds at an ozone dose of 0.04 mg/l and on the order of 99.995% in 10 seconds at an ozone dose of 1.3 mg/l.

Katzenelson, et al. (12) also reported on the ability of ozone to inactivate viruses. The inactivation curves for the viruses also showed the two stage inactivation. Stage one took about 10 seconds at all ozone doses and the inactivation ranged from 99.7% to 99.998% with an ozone dose of 0.01 to 0.26 mg/l.

Farooq, et al. (13) reported on the use of ozone to kill Candida parapsilosis. Percent surviving fungi after 24 seconds detention time in a constant flow reactor was reported to be on the order of 10^{-4} to 10^{-5}.

Roy, Englebrecht, and Chian (14) tested the effects of ozone on six enteroviruses. These viruses, in order of increasing resistance to inactivation by ozone, were; coxsackievirus A9 (Griggs), echovirus 5 (Noyce), coxsackievirus B5 (Faulkner), poliovirus 1 (Mahoney), echovirus 1 (Farouk), and poliovirus 2 (Lansing). The results concur with those of Katzenelson et al. in that a two stage inactivation occurred. Roy, Englebrecht, and Chian found that at an ozone residual of 0.15 mg/l the time for 99% inactivation ranged from 0.12 minutes for coxsackievirus A9 to approximately 4.8 minutes for poliovirus 2.

Ginnocchio (15) reports that preozonation aids in the elimination of algae through filtration. Three filtering methods were used; sand filtration, fine sand filtration, and double layer filtration. The algae studied were; Fragilria crotonensis, Asterionella formosa, Synedra, Tabellaria fenestrata, Cyclotella, Phacotus lenticularis, and Stephanodiscus. The reaction time was 10 minutes. The ozone was dosed at 2 mg/l and after 10 minutes the residual was 0.25 mg/l. Although details are lacking, in each case ozone increased the removal of algae by filtration.

Wickramanayake, et al. (16) tested the effect of ozone on the protozoan cysts Giardia muris and Naegleria gruberi. They found in a batch reactor that after an initial lag of

20 seconds the kill curves were linear with respect to percent surviving versus contact time.

PRACTICAL ASPECTS OF OZONE.

Generation. Ozone is produced in the ozonator by various methods. One method is to excite the oxygen atoms by ultraviolet light. The oxygen molecules will break apart into atomic oxygen. These two atoms will bond onto other oxygen molecules to form ozone. Another method of making ozone is to pass the oxygen through a gap between two charged dielectrics. The electric field produced by an alternating current between the dielectrics causes excitation of the oxygen molecules which split and recombine with oxygen to form ozone (17).

Ozone is most commonly generated on a large scale by passing a current of air, or oxygen, between two electrodes that are subjected to a high voltage alternating current. In nature, ozone is formed by lightning but in industry an arc is undesirable, therefore the electrodes are coated with a dielectric to avoid arcing. The applied voltage usually varies between 8,000 to 20,000 volts. The efficiency of ozone production depends on the temperature, dryness, and purity of the feed gas (18).

There are three general types of ozone generators on the market: plate-type ozonizers, and vertical and

horizontal tube-type ozonizers. Most of the commercial units sold at the present time are of the horizontal tube type (18).

The yield of ozone is found by the following equations.

$$V = C_1 pg$$

$$(Y/A) = C_2 feV^2/d$$

Where:

(Y/A)	is ozone yield per unit area of electrode surface under optimum conditions.
V	is voltage across the discharge gap (peak volts).
p	is gas pressure in the discharge gap (psia).
g	is the width of the discharge gap.
f	is frequency of the applied voltage.
e	is the dielectric constant.
d	is thickness of the dielectric.
C_1	is a constant of proportionality.
C_2	is a constant of proportionality. (19)

The production of ozone uses a large amount of energy. On the average 20 to 30 watt-hours are used to produce one gram of ozone. The variance in energy consumption depends on the size of the unit (18).

Because air contains significant amounts of nitrogen, it must be dried and cooled before passing through the ozonator to reduce accumulation of corrosive by-products such as nitric acid and nitrogen oxides that are created when the dewpoint of the air is above -40°. If oxygen is used as a feed gas, the process of drying and cooling is unnecessary (17).

Aqueous Ozone Chemistry. Since ozone is a gas, transfer to the aqueous phase is necessary for oxidation of aqueous organics. The mass transfer of ozone into the water is limited by stagnant surface effects at the gas-liquid interface. Therefore, fine bubble diffusion is perhaps the most efficient method of gas transfer since it provides a high surface area to volume ratio for ozone bubbles (16).

The overall decomposition of ozone in water is as follows:

$$2O_3 \Longrightarrow 3O_2$$

However, there are many suggested intermediate steps in this process. Peleg, in 1976, summarized several theories regarding the chemistry of ozone in water. Some of the theories date back to the 1930's. Although it is unnecessary to go into detail about the exact reactions, it should be noted that Peleg suggests that the potential species in an aqueous ozone solution include the hydroxyl radical ($OH^{\cdot}$), dissolved ozone (O_3), hydroperoxyl radical ($HO_2^{\cdot}$), oxide radical ($^{\cdot}O^-$), ozonide radical ($^{\cdot}O_3^-$), and possibly free oxygen (O). All the intermediate species are very reactive and have half-lives on the order of milliseconds (20).

Peleg indicates that there are many factors which control the decomposition of ozone in water. Three of the

most important factors are temperature, pH, and alkalinity (20). Hewes and Davison have shown that the rate of ozone decomposition increases as water temperature increases (21). They also varied pH and found that the decay rate of aqueous ozone increased as pH increased. To calculate the rate of ozone decay, k, Hewes and Davison measured the concentration of ozone in the influent and effluent line of a plug flow reactor and assumed second order kinetics.

$$dC/dt = kC^2$$

They plotted $(1/C_{out} - 1/C_{in})$ versus time. The slope of the curve, k, should be constant if the assumption of second order was correct. From their experiments, Hewes and Davison found that ozone decay was second order at temperatures between 10-50°C up to pH 8. Above pH 8 the decay rate was first order. The factor k, in L/(mg-hr), increases by a factor of 183 as the temperature is increased from 10 to 50°C at pH 6. At 40°C the rate constant increases by a factor of 18 from pH 2 to pH 6 (21).

Staehelin and Hoigne also found that between pH 8 and pH 10 the decay rate of ozone was first order. For their experiments, Staehelin and Hoigne studied the half-life $(t_{1/2})$ of ozone in water in the presence of free radical scavengers. It is their theory that the presence of the hydroxyl radicals acts as a catalyst in the decay of ozone to oxygen as such:

$$O_3 + H_2O \Longrightarrow O_2 + 2OH^{\cdot}$$

$$OH^{\cdot} + O_3 \Longrightarrow HO_2^{\cdot} + O_2$$

$$HO_2^{\cdot} + O_3 \Longrightarrow OH^{\cdot} + 2O_2$$

In the presence of free radical scavengers the second and third reactions do not take place (22).

In order to prevent these catalytic reactions from taking place, Staehelin and Hoigne used bicarbonate and carbonate as free radical scavengers. They found that the half-life of ozone in water is dependant upon the pH and on the bicarbonate concentration. Staehelin and Hoigne plotted the half-lives of ozone versus bicarbonate concentrations at pH's of 8, 8.5, 9, 9.5, and 10. As the bicarbonate concentration increased, the half-life of ozone would reach a plateau, the height of which was dictated by the pH. With less bicarbonate the half-life decreases. The data show that pH is more important in determining the half-life than bicarbonate is. At pH 8, and 0.01M bicarbonate (1000 mg/l as $CaCO_3$), the half-life of ozone is 4000 seconds (1 hr 7 minutes). At 10^{-4}M bicarbonate (10 mg/l as $CaCO_3$), the half-life is 2000 seconds (33 minutes 20 seconds). At pH 9, and 0.01M bicarbonate, the half-life is 400 seconds (6 minutes 40 seconds) and at 10^{-4}M it is 300 seconds (5 minutes). At pH 10 the half-life was 40 seconds and the concentration of bicarbonate had little effect (22).

Whether oxidation is aided or hindered by the radical

scavenging is unknown. Oxidation by the hydroxyl radical is faster and less selective than oxidation by aqueous ozone. So the main benefit of radical scavenging is that the ozone will react by less complicated mechanisms.

These three factors, temperature, pH, and alkalinity, will determine the rate of decay of aqueous ozone to oxygen. Since increased temperature and pH increase the rate of decay and increased alkalinity decreases the rate of decay, cold, low to neutral pH, high alkalinity waters would see aqueous ozone as the predominant species.

Methods of Ozone Oxidation. Many researchers concur on the existence of two types of oxidation by ozone. The first is the oxidation of organics directly by ozone and the other is oxidation by one of the free radicals, mainly $OH^{\cdot}$, produced upon decomposition of ozone in water (20,22,23,24).

The hydroxyl radical species, $OH^{\cdot}$, has a higher oxidation potential than dissolved ozone, O_3. The fact that the hydroxyl radical has a higher oxidation potential than ozone could suggest that the powerful oxidation capability of aqueous ozone is due to the hydroxyl radical (20). The reactions due to the oxidation by the hydroxyl radicals are less selective and predominate under basic conditions (25). Hydroxyl oxidation is very fast, on the order of

microseconds (25).

Direct oxidation by ozone, ozonolysis, involves the creation of an ozonide by fixation of an ozone molecule at a double bond (5). The organic molecule is then broken apart by the instability of the ozonide (5).

According to Gomella, a third method of oxidation is "conventional oxidation". Conventional oxidation refers to the oxidation by free oxygen that is liberated from the ozone molecule when it breaks down into diatomic and monatomic oxygen as such:

$$O_3 = O_2 + O \quad (5)$$

The free oxygen produces a high energy oxidation and reacts with most organics in the water, including the cell wall of microorganisms (9). Gomella (5) places more emphasis on the monatomic oxygen atom than Peleg (20) does.

Aqueous ozone, meaning any or all of the possible species discussed above, will react with most organic compounds. The mechanisms of reaction are varied, but in general ozone breaks down aromatic nuclei and cleaves double bonds. As a result of these reactions, ozone makes organic matter more biodegradable (26). The common oxidation products of the organic compounds are generally simpler organic compounds. Only rarely will ozone oxidize an organic compound to carbon dioxide and water (25).

Hoigne and Bader (27,28) conducted experiments to

determine the reaction rate of ozone on various compounds in the presence of free radical scavengers. These conditions would effectively simulate the typical conditions in a water treatment plant. Phenols were shown to have a high reactivity to ozone. Deprotonated organic acids were also highly reactive. Acetic acid reacted so slowly that no rate constant could be determined (27,28). Humic substances are common organic compounds found in the aqueous environment. Although the properties of humic substances are not fully known, Peleg suggests that they contain aromatic and aliphatic components that are arranged in a polymer form. The aromatic components and the double bonds in the aliphatic components are potential oxidation sites (20).

Humic substances will be treated in greater detail in the section on trihalomethane precursors.

TRIHALOMETHANES

DEFINITION. The term trihalomethane (THM) refers to a group of organic compounds similar in structure to methane (CH_4) where three of the four hydrogens are replaced by three atoms of one or more of the elements chlorine, bromine, and/or iodine which are all halogens (2). The ten possible combinations of these three halogens are:

1.	Chloroform	$CHCl_3$
2.	Bromodichloromethane	$CHBrCl_2$

3.	Dibromochloromethane	$CHBr_2Cl$
4.	Bromoform	$CHBr_3$
5.	Dichloroiodomethane	$CHCl_2I$
6.	Dibromoiodomethane	$CHBr_2I$
7.	Chlorodiiodomethane	$CHClI_2$
8.	Bromodiiodomethane	$CHBrI_2$
9.	Bromochloroiodomethane	$CHBrClI$
10.	Iodoform	CHI_3

The main source of THMs in drinking water is the reaction of the chlorine added for disinfection with the aqueous THM precursors (2). The Federal Register reports that chloroform and bromine could be contaminants in the chlorine source (2).

FORMATION AND PRECURSORS. The primary source of trihalomethane precursors in a water supply are the naturally occurring organics in the water such as humic substances and algae as opposed to organics caused by pollution (3). The reaction mechanism and kinetics upon chlorination of THM precursors are largely unknown due to the complexity of the reactions and the unconfirmed molecular structure of the precursors (3,29).

In an aqueous environment, allochthonous trihalomethane precursors commonly arise from humic substances originating from decayed plant matter in the watershed. The sources of autochthonous trihalomethane precursors are highly varied. One source of aqueous THM precursors is the aqueous humic substances which can also be allochthonous or autochthonous.

Other sources of autochthonous THM precursors in a lake environment include algal biomass, extra-cellular products (ECPs), and chlorophyll (7).

In lake environments, the autochthonous humic substances are made up of chains of aliphatic compounds with few aromatic rings. However, the structure of the allochthonous humic substances shows many aromatic rings. Steinberg and Muenster state that in a lake environment the autochthonous form of humic substances is more common than the allochthonous form (29).

Steinberg and Muenster suggest that the primary source of autochthonous humic substances are macrophytes but they concede that it is possible, but not proven, that algal detritus is a source of aliphatic compounds that can polymerize to form humic substances (29).

In contrast, Steelink suggests that autochthonous humic substances may be formed almost exclusively from algal materials. The aromatic components of lignin, Steelink asserts, are the primary building blocks of allochthonous humic substances. Algae, which contain no lignin, cannot contribute aromatic structures to the humic substances. This explains, according to Steelink, why autochthonous humic substances contain mainly aliphatic components (30).

Algal biomass as a source of THM precursors has been studied by Hoehn et al. (6) and the USEPA (7). These

studies showed that components of algal biomass, in addition to being a source of humic substance precursors, are also THM precursors in their original form (6,7).

The EPA reported on tests conducted on three different types of algal cells and ECPs. They found variation in the THMFP between different species. The species tested by the EPA were: Anabaena cylindrica, Pediastrum boryanum, and Scenedesmus quadricauda. The independent variables used by the EPA were: phase of growth cycle, chlorine contact time, species of algae, and chlorine dose. The EPA separated algal cells from algal ECPs and tested each separately. The results were highly varied. THM formation ranged from 0.1 micrograms/liter to 945 micrograms/liter and the only factor that made statistical significance was the phase of growth of the Scenedesmus cells. In the later stage of growth (21 days) Scenedesmus cells showed negligible THM formation potential (6).

Hoehn, et al. (7) also tested chloroform yields from algal biomass. They tested four species of algae; two species of green algae and two species of blue-green algae. The two species of green algae were Chlorella pyrenoidosa and Scenedesmus quadricauda. The two species of blue-green algae were Oscillatoria tenuis and Anabaena flos-aquae. Hoehn, et al. also separated algal cells and ECPs. They tested the THMFP at many different points in the growth

cycle. Although their results were also highly varied, the higher THM yields occurred in the earlier stages of growth. The highest THM yield was 6.7 mg/l for S. quadricauda ECPs when the original culture had a cell count of 10^5 cells/ml. The THM yield from S. quadricauda cells at 9-35 days in the growth cycle was 0.6 - 1.0 mg/l in direct disagreement with the EPA study. This disagreement is one example of the high variety of results from studies on THMFP.

It can be concluded from the results of these experiments that algal biomass (cells and ECPs) is a significant form of aqueous THMFP.

The majority of organics in a lake environment are in the form of detritus in the sediment layer. During an algal bloom, these organics become incorporated into algal biomass which can enter a water treatment plant. There is a complicated relationship between the algae, which consume carbon dioxide and water and produce algal biomass and oxygen through photosynthesis, and bacteria, which consume oxygen and organics (detrital or algal biomass) and produce carbon dioxide and water through the process of respiration (29).

Kuentzal (32) suggests that the logarithmic growth pattern of an algal bloom in an "unpolluted" water is caused by the abundance of carbon dioxide from bacterial respiration as opposed to the abundance of nitrogen and

phosphorous.

These three factors; humic substances as THM precursors, algal biomass as THM precursors, and algal detritus as humic substance precursors, suggest a complicated set of interactions between humic substances and algal biomass in the formation of THM precursors.

HEALTH HAZARDS. Chloroform can enter the body by many different routes including air, food, and water. The intake of chloroform from water can add up to about 90% of the total chloroform intake (3). Once inside the body, chloroform is metabolized to carbon dioxide, chloride ion, phosgene ($COCl_2$), and possibly other metabolites (3). It is possible that these metabolites bind onto the DNA by covalent bonds (2).

Exposure to chloroform can cause central nervous system depression, damage to the liver and kidneys, teratogenicity, and carcinogenicity (3). These responses in mice, rats, and monkeys were observed following doses of chloroform between 30-350 mg/kg body weight (3). It is thought that the brominated THMs are more toxic than the chlorinated ones but existing data are not conclusive (3). Studies have shown that the brominated and iodinated forms of the THMs are more mutagenic than chloroform in Salmonella typhimurium cells (2).

Human epidemiologic data on the effects of THMs on health is not conclusive. However, all the data taken from all the available studies show evidence for concern. The Federal Register asserts that although effects on humans by trihalomethanes are not statistically significant, animal research data is dependable enough to justify setting an MCL for trihalomethanes (2).

The National Academy of Sciences (NAS) concurs with this decision by stating that, "sufficient evidence was available from animal toxicology studies to conclude that exposure to chloroform did pose a risk to human health" (2).

The EPA set 0.10 mg/l for the Interim Maximum Contaminant Level (MCL) for total THMs in finished waters. The Federal Register warns that this MCL "should not be construed as an absolutely 'safe' level, but rather a feasible level achievable with water treatment technology available since 1974" (2).

The Science Advisory Board, the NAS, and the USEPA Carcinogen Assessment Group, using different models for the ingestion of THMs through water, all agree that at the MCL there is an incremental cancer risk of 3-4 per 10,000 people consuming 2 liters of water a day for 70 years (3).

HISTORY OF THM REGULATION. In 1974, it was discovered that trihalomethanes were formed during drinking water

treatment if free chlorine was the disinfectant (3). In 1975, a survey of 80 water utilities showed that all four of the primary THMs, chloroform, bromodichloromethane, dibromochloromethane, and bromoform, were found in finished waters if the treatment process used free chlorine as a disinfectant (3).

Towards the end of 1975, the EPA initiated the National Organics Monitoring Survey (NOMS). This survey examined the THMFP in the water distribution systems of 113 cities. It was found that measuring the THMs at the water treatment plant was inadequate because large quantities of THMs can be formed in the distribution system (2). The Federal Register of November 29, 1979 indicated that the EPA's decision to regulate THMs was based on:

- potential human health risks of chloroform and other THMs;
- the fact that drinking water is the major source of human exposure to THMs;
- the fact that THMs are the most ubiquitous synthetic organic chemicals found in drinking water in the U.S. and are generally found at the highest concentrations of any such chemicals;
- the fact that THMs are introduced in the course of water treatment as byproducts of the chlorination process and thus are readily controllable;
- that low cost and feasible means have been generally available since 1974 to reduce their concentrations in drinking water;
- that monitoring is feasible;

- and that the THMs are also indicative of the presence of a host of other halogenated and oxidized, potentially harmful byproducts of the chlorination process that are concurrently formed in even larger quantities but which cannot be readily characterized chemically. (2)

The iodinated THMs were not included in the regulations due to their chemical instability which makes monitoring difficult. This does not imply that the iodinated THMs are harmless.

On July 14, 1976, the USEPA published an Advance Notice of Proposed Rulemaking (ANPR) to control synthetic organic chemicals in drinking water (3). The proposed rules were published on February 9, 1978. It was suggested that the adoption of an MCL for TTHMs with required monitoring and reporting would be the optimal solution to control THMs. The proposed rules suggested the use of granular activated carbon (GAC) in order to reduce the danger of synthetic organic chemical contamination (3). On July 6, 1978, the USEPA extended the public comment period for the proposed regulations from July 31, 1978 to September 1, 1978. This extension was to allow the public to aid in the documentation and clarification of the proposed rules. The final regulations were published in the Federal Register of November 29, 1979. The USEPA amended the National Interim Primary Drinking Water Regulations by establishing an

interim maximum contaminant level (MCL) of 0.10 mg/l of total trihalomethanes (TTHM). Total trihalomethanes is defined as the summation of the concentrations of the four major trihalomethanes; trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform), in mg/l rounded off to two significant digits (2).

This interim MCL became the MCL in 1986 with the passing of the SDWA amendments (1).

The EPA also stated that the MCL of 0.10 mg/l TTHM is mostly based on current (1974) removal abilities. In the future, the EPA believes that treatment plants will be able to reduce THM levels to as low as 0.010 to 0.025 mg/l and that these values should be set as goals (2).

It should be added that the Federal Government does not require monitoring for THMs in water systems serving less than 10,000 people. The individual states have the authority to regulate these smaller systems (2).

DESTRUCTION/REMOVAL OF THM PRECURSORS AND THMS WITH OZONE. It has already been mentioned that THMs are formed in a series of reactions between aquatic THM precursors and free chlorine. Some of the characteristics of selected THM precursors have been presented. It is not to be inferred that humic substances and algal biomass are

the only THM precursors in drinking water supplies. Humic substances, algal biomass and some of their fundamental components are simply the most common THM precursors in a lake environment. Rice (33) points out that the most common THM precursors in drinking water supplies are the humic, tannic, lignin, chlorophyll and acetogenin substances, all of which are components of either humic substances or algae.

Rice also states the fact that he believes the compounds which contain acetyl moieties are the primary source of THM precursors. Rice cautions that compounds which do not contain an acetyl group can be oxidized by ozone into compounds which do contain an acetyl group. Examples of such compounds include ethanol and methyl secondary alcohols. Therefore it is possible to create THM precursors by use of ozone (33).

The compounds which are oxidized to THM precursors are not common in drinking water supplies. A partial list of such compounds includes hydroquinone, salicylic acid, methoxybenzene, benzaldehyde, and benzoic acid (34).

Destruction of THM precursors is possible by oxidation processes. Although THM precursors are seldom oxidized to carbon dioxide and water, it is possible to oxidize the precursors to non-precursor compounds (33). Even those compounds listed above which can be oxidized to THM precursors can be further oxidized to non-precursor

compounds (34).

Rice presented data from 23 water systems that use ozone. Of these systems, 66% reported a reduction in THMFP by ozone, 26% reported an increase, and 8% had no THMFP either before or after ozonation. Ozone doses ranged from 0.5 - 227 mg/l. Absorbed ozone doses ranged from 0.5 - 17.7 mg/l. The data presented show that ozone concentration, applied or absorbed, is not the primary factor in determining THMFP destruction. The primary factor is the exact chemical nature of the water. Unfortunately, contact times were not given for each situation although Rice states that 12 minutes is "typical". (33)

Rice strongly emphasized the fact that humic acids from one water supply differ greatly in their reactions with oxidants when compared to humic acids from other water supplies (33).

So the evidence so far is inconclusive. The ability of ozone in the removal of THMFP is based on the exact nature of the organics in the water. There is a high probability that ozone will reduce the THMFP of a water but pilot plant operations should precede incorporation of ozone in a water treatment process to avoid increasing the THMFP.

Ozone does not destroy THMs once they are formed (3). THMs can be removed by aeration (stripping) but this removal is not recommended because although the instantaneous THM

concentration decreases, much of the formation potential and the chlorine residual have not been removed. THMs can then form in the distribution system (3).

PROBLEMS INVOLVED IN THE COMBINATION OF OZONE WITH CHLORINE OR BROMINE

One of the drawbacks associated with disinfection by ozone is the lack of residual to prevent bacterial regrowth in the distribution system. The obvious solution is to first ozonate to disinfect the water then chlorinate to protect the distribution system. There are, however, complications associated with this method as well. One complication is the fact that ozonating the water at the small doses needed for disinfection may cause some of the organics in the water to become trihalomethane precursors. Subsequent chlorination then produces more THMs than would have been created had ozone not been used (3).

Another disadvantage associated with the combination of ozone and chlorine is the fact that if both are present in the water, a series of reactions will take place causing both oxidants to be destroyed (35). The overall reaction with ozone and free chlorine is this;

$$1.23O_3 + OCl^- \Longrightarrow 2O_2 + 0.77Cl^- + 0.23ClO_3^-$$

The hypochlorite ion (OCl^-) reacts with the ozone, but not the hypochlorous acid form (HOCl) (35). The pKa of HOCl is 7.5 which indicates that above pH 7.5 the dominant species is OCl^-. The reaction between ozone and combined chlorine (monochloramine) is as follows;

$$NH_2Cl + 3O_3 \Longrightarrow 2H^+ + NO_3^- + Cl^- + 3O_2 \quad (35)$$

None of the end products have any disinfecting properties except oxygen which will destroy obligate anaerobes. If there is bromine in the water, ozone destruction is increased because in addition to a reaction that parallels the reaction with free chlorine;

$$1.23O_3 + OBr^- \Longrightarrow 2O_2 + 0.77Br^- + 0.23BrO_3^-$$

there is an additional reaction with bromide that causes the reactions to be cyclic.

$$O_3 + Br^- \Longrightarrow O_2 + OBr^- \quad (35)$$

Thus the cycle will continue until all the ozone is used up or until all the bromide and bromine have become bromate (BrO_3^-) (35).

CHAPTER III.

SCOPE OF THE INVESTIGATION

While the literature provides information on ozone oxidation of THM precursors, it does not yield details on the behavior of ozone in algal laden waters. The literature suggests that high ozone doses combined with long detention times would be the most effective method to destroy THMFP (6,7,27). The literature also suggests that low ozone doses may actually increase the THMFP due to the creation of precursors from non-precursor organics present in the water supply (33).

Some water treatment plants preoxidize the raw water. Oxidation of the raw water prevents the growth of algae in the flocculators and settling basins. Most often, in the U.S., chlorine is the oxidant of choice. The chlorine comes into contact with all the organics in the raw water as opposed to only those organics that make it through the treatment system. Thus chlorination of the raw water often increases the level of THMs in the finished water.

This study was initiated to determine the effect that preozonation would have on the THMFP of the raw water. Raw water from the Laramie Water Treatment Plant was ozonated under a given set of conditions and the THMFP was compared to the THMFP of the unozonated sample. The difference between the THMFP of the raw and ozonated water was taken to be a direct measure of the effectiveness of reduction of the THMFP by ozone. Eighteen constant-flow stirred tank reactor (CSTR) tests were conducted. The variables in these tests were; pH, three values; ozone dose, two values; and detention time, three values.

The three values of the pH were; 5, 7, and 9. The pH was adjusted to within +/- 0.2 pH units of these values. The ozone dose values were 1.6 mg/l and 8.3 mg/l. The three values for the detention time were; 10, 20, and 40 minutes.

Four batch kinetics tests were also conducted. The variables in these tests were ozone dose and initial chlorophyll a concentration. The ozone doses were, again, 1.6 and 8.3 mg/l and the approximate chlorophyll a concentrations were 40 and 100 micrograms/l. Chlorophyll a concentrations varied somewhat from experiment to experiment within each range.

CHAPTER IV.

MATERIALS AND METHODS

MATERIALS

RESERVOIR WATER. Water was taken from the influent line of the Laramie Water Treatment Plant and transported to the University of Wyoming Environmental Engineering Lab in a Laramie Water Department truck. Approximately 200 gallons were pumped into a fiberglass reinforced plastic storage tank in the lab. This water was allowed to settle for a few weeks until research commenced. Suspended matter was drained off in order to prevent interference by suspended solid materials.

ALGAE. To provide an inoculum algae was scraped off the walls of the settling tanks of the Laramie Water Treatment Plant and grown in a 200 gallon plastic stock tank. The stock tank was filled with tap water and the algae was added. The suspension was kept mixed with a propeller type of mixer.

Eight grams of solid fertilizer containing nitrogen of an unspecified form, phosphorous as P_2O_7, ferric sulfate,

and potash was added directly to the tank and also placed in a mesh container in the stock tank to provide for slow release of the fertilizer. One hundred grams of ammonium nitrate was added to the water to provide two sources of nitrogen. The approximate concentration of ammonia nitrogen and nitrate nitrogen were 23 mg/l as nitrogen. In addition, 100 grams of enriched Trona (>90% $NaHCO_3$) was added to provide a source of alkalinity. The alkalinity after addition of the Trona was 220 mg/l as $CaCO_3$. As algae grow, they remove dissolved carbon dioxide from the water thereby increasing the pH (31). When the pH in the stock tank rose above 7.5 or so, phosphoric acid was added to reduce it to near pH 5. The increase in the chlorophyll a concentration was taken to be an indication of algal growth.

Light was provided by placing four fluorescent lights and one 250 Watt incandescent light approximately one foot from the water surface. Attempts were made to increase the rate of growth of the algae by giving them a photoperiod and an oxygen supply during that photoperiod. Algae grow in the light but reproduce in the dark so that incorporating a four hour dark period into the diurnal cycle should result in greater biomass production than systems using a constant light source (31). However, this was not observed. In fact, after a few days, the concentration of chlorophyll a in the stock tank began to drop and the photoperiod was

discontinued. The chlorophyll a concentration in the stock tank at the time of the experiments ranged from 70 to 100 micrograms per liter. The algae were identified as being mostly Scenedesmus with some Chlorella and some Anabaena.

TEST WATER. The water used in both the CSTR and batch tests was a mixture of reservoir water and water from the algae stock tank. A dilution of the stock water by the reservoir water was performed in a 50 liter temporary storage tank. Eighteen liters of water from the algae tank was transfered to the storage tank and diluted to 36 liters by the reservoir water in order to produce a test water with the desired chlorophyll a concentration. The test water was then mixed and its pH measured. If needed, adjustments to the pH occurred at this stage. After adjustments to the pH were performed, the alkalinity was measured. The test water was then transferred to the contact chamber/reactor in preparation for the tests.

OZONATOR/CONTACT CHAMBER. The Ozonator used in the experiment was an OREC model 03SP19-0 capable of producing 100 grams of ozone per hour at maximum voltage and oxygen flow. Control of the ozonator output was accomplished through adjustments to the voltage and ozone flow rate. Voltage was adjusted until two amps of current was produced

on the ammeter. The gas flow was increased until adequate mixing was achieved. The gas flow was decreased until cohesion of the bubbles was minimized. Both factors, mixing and bubble cohesion, were determined visually. The flow at which the best balance between these two factors occurred was 4 liters/minute on the flowmeter scale. The actual flow adjusted for the system pressure of 15 psig was 5.4 liters/minute. Approximate settings of the ozonator volt meter required to produce 2 amps were 90 volts using air as the input gas and 70 volts using oxygen as the input gas. Air was used as the feed gas in the "low ozone dose" experiments and oxygen was used as the feed gas in the "high ozone dose" experiments.

The contact chamber/reactor was a four inch diameter glass tube with a capacity of seven liters. Glass was chosen because it does not react with ozone and would provide for visible inspection of mixing and color removal. Test water was introduced into the top of the reactor and removed through an effluent line on the bottom. Ozone was introduced from the bottom of the reactor through a Pyrex ASTM 20-50 C diffuser (see Figure 1). The numbers "20-50" on the diffuser means that this diffuser provides gas bubbles between 20 and 50 microns in diameter. Introduction of ozone to the bottom of the reactor provided for gas flow counter-current to the flow of the test water. This

arrangement provided adequate mixing. In order to determine adequate mixing, a dye test was performed. The reactor was set up as a CSTR and a plug injection of a fluorescent dye, Rhotamine wt, was injected into the influent line. The results of this dye test, reported in appendix E, show that the reactor simulates complete mix very well.

OTHER EQUIPMENT.

Pump. In order to control the influent and effluent flow rates, a Cole-Parmer Masterflex adjustable peristaltic pump with two heads was used. This pump was hooked up to both the influent and effluent liquid lines to provide a constant flow.

Hoses. All hoses for liquid influent and effluent were various diameters of Tygon tubing manufactured by Norton Co.. Ozonator feed gas lines were 1/4" diameter Teflon tubing. Lines for ozone feed were 1/4" diameter Teflon and 3/8" diameter Tygon tubing. Tygon tubing was used due to its flexibility and its resistance to degradation and oxidation by ozone (36).

Flowmeter. A flowmeter was used to measure and maintain a constant test water influent rate. This allowed control of the detention time. The flowmeter used was a

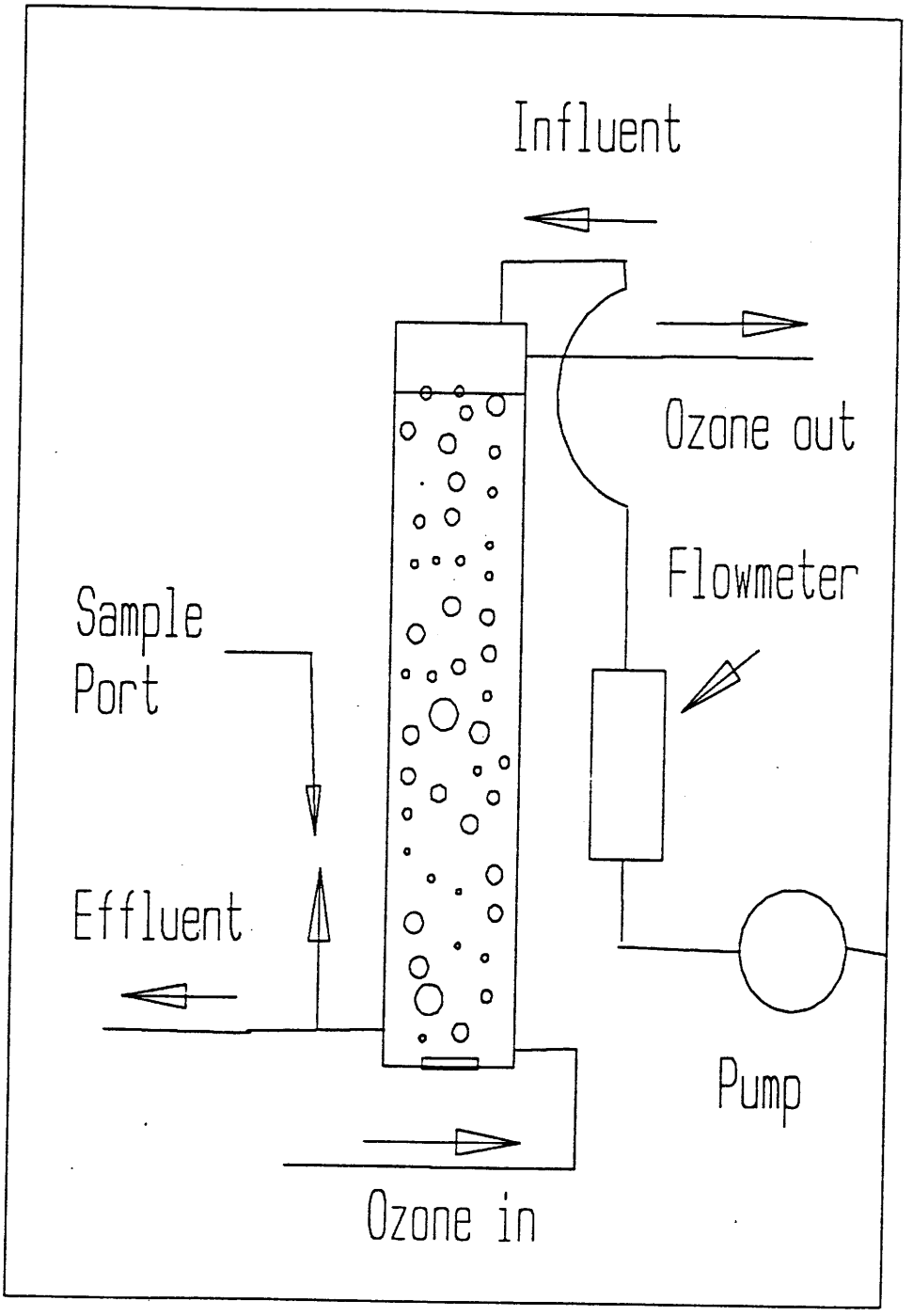


Figure 1. Ozone Contact Chamber/Reactor.

Lab-Crest Mark III flowmeter from Fisher Scientific Co.. Stainless steel and glass floats were used in the 1/4" diameter tube. The steel float was used for the higher flows which would provide for the 10 and 20 minute test water detention times. The glass float was used when the detention time was 40 minutes.

Valves. Fine adjustment of flow rates was accomplished by PVC ball valves which were placed on the high pressure side of the influent line and on the low pressure side of the effluent pump. A PVC ball valve which served as a sampling port was placed at a tee joint at the effluent of the reactor. Rigid PVC was chosen because of its resistance to degradation and oxidation by ozone (37).

METHODS

TEST PROCEDURE FOR BATCH TESTS.

Set up. Test water was transferred from the storage reservoir to the reactor in an 18 liter glass container which was placed on a magnetic mixer and stirred vigorously. Mixing prevented separation and settling of the algae. The test water was then pumped into the reactor to the seven liter mark. Mixing continued for the duration of the test water transfer.

Experiment. Before the ozone was turned on the initial samples were taken. Ozone residual, THM, DCOC, and chlorophyll a were measured. The ozone was then turned on by adjusting the voltage on the ozonator to the desired level and the timer started. Samples were taken at ten, twenty, forty, and 120 minutes. Ozone residual measurements were made at regular intervals. After the last sample was taken the reactor was shut down.

Shut Down. Once the final samples were taken the voltage dial on the ozonator was turned to zero and the feed gas was allowed to flow through the ozonator for three or more minutes to remove residual ozone from the ozonator. The source of gas was turned off and the system pressure dropped to zero. The main power switch on the ozonator was turned to off. The reactor was drained and rinsed with either tap water or distilled water. If more than one experiment was to be run that day the ozonator need not be shut down, except for the gas flow and voltage setting, but the reactor must be drained and rinsed.

TEST PROCEDURE FOR CSTR TESTS.

Set up. Test water was transferred from the storage reservoir to the reactor in two 18 liter glass containers. One of the glass containers was placed on a magnetic mixer

and stirred vigorously. Mixing prevented separation and settling of the algae. Mixing continued for the duration of the experiment. The test water was then pumped into the reactor to the seven liter mark. Test water from the second 18 liter container was added to the first container as needed.

Experiment. To begin the experiment the reactor effluent valve was opened and the test water circulated through the reactor. At this point the initial samples were taken for ozone residual, THM, DCOC, and chlorophyll a from the sample port. Using the peristaltic pump controls, the flow rate was adjusted to a preselected value that would provide for the desired test water detention time in the reactor. Gas flow through the ozonator was adjusted to 4 lpm at 15 psig. The voltage on the ozonator was set to the desired amount and the timer was started. The effluent from the reactor flowed to drain when samples were not being taken. Figure 2 shows the flow diagram of the experiments. DCOC and Chlorophyll a samples were taken at the end of each detention time. Ozone residual measurements were taken every ten minutes. The experiment proceeded until three detention times had elapsed. At that point it was decided that steady state conditions had been reached. Final samples were then taken and the system was shut down.

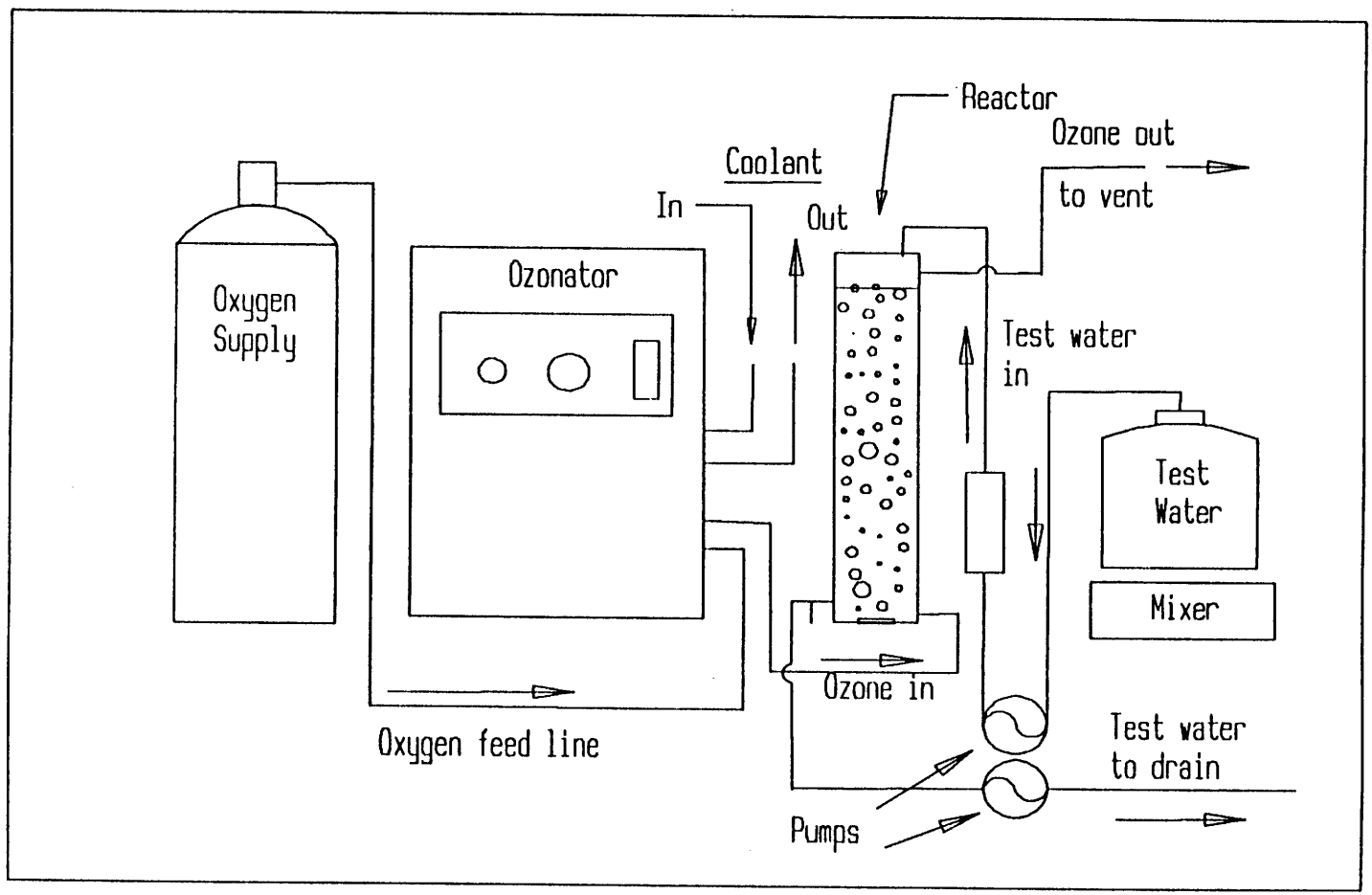


Figure 2. Experiment Flow Diagram.

Shut down. Once the final samples are taken the pump was shut off. The voltage dial on the ozonator was turned to zero and air/oxygen was allowed to flow through the ozonator for three or more minutes to remove residual ozone from the ozonator. The source of gas was turned off and the system pressure dropped to zero. The main power switch on the ozonator was turned to off. The reactor was drained and rinsed with either tap water or distilled water. If more than one experiment was to be run that day the ozonator need not be shut down, except for the gas flow and voltage setting, but the reactor must be drained and rinsed.

CHAPTER V.

ANALYTICAL PROCEDURES

pH AND ALKALINITY

The pH of the test water was measured with a Fisher Accumet Model 425 Digital Ion/pH meter calibrated at pH7. The alkalinity test was performed as in Standard Methods for the Examination of Water and Wastewater (38). The titrant was 0.1 N HCl, the sample volume was 200 ml and the titration end point was pH 4.5 in all cases. The ph and alkalinity were measured once per test. If adjustments to the pH were necessary, the alkalinity was measured after the adjustments.

OZONE RESIDUAL

The ozone residual was measured according to the Indigo method described by H. Bader and J. Hoigne (39). Sample size varied from 2 ml to 20 ml. It was found that the green color of the test water interfered slightly with the absorbance readings so a sample of the test water was used in addition to the distilled water for determination of the blank. Sample size must remain constant or the color of the

test water may interfere with the readings. The ozone residual was calculated using two analysis per sample. Typical volumes of test water were 5 ml and 10 ml per analysis. The reported ozone residual is the average of these two values. Ozone residual is reported in units of milligrams per liter (mg/l).

TRIHALOMETHANE FORMATION POTENTIAL

Trihalomethane samples were prepared by adding 0.2 ml of Clorox to 40 ml Vari-Clean Sample Storage vials (No. 13510 from Pierce). Trihalomethane (THM) samples were stored at 20° C for seven or more days and then turned into the Wyoming State Agricultural Labs for THM analysis. The vials were pre-cleaned by Pierce specifically for THM samples and were fitted with Teflon and silicon discs inside open top screw caps. Three vials were filled per sample in order that one of the bottles could be measured for chlorine residual and two independent THM analyses could be performed per sample. The State Labs analyzed the samples by the purge and trap method with a halide specific detector. It was found after the first few analysis that the concentration of chloroform was greater than the concentration of the other three THMs by at least 2 log scales. Therefore, only the concentrations of chloroform were measured. THMFP is reported in units of milligrams per

liter (mg/l).

DISSOLVED AND COLLOIDAL ORGANIC CARBON

Dissolved and colloidal organic carbon (DCOC) measurements were made with an Astro Model 1850 Total Organic Carbon-Total Carbon Analyzer. Samples were stored in 200ml French square bottles and acidified with phosphoric acid to pH<2. The samples were then stored at 5°C until the time of analysis. The TOC analyzer was calibrated with an acetone solution. Acetone was chosen as the standard because of ease in preparation and reproducability of results. The range used on the TOC analyzer was 0.1-100 ppm as carbon. The samples were filtered through a 0.45 micron filter and purged with nitrogen for three minutes to remove carbon dioxide which would interfere with analysis. Samples were then injected into the analyzer with a glass syringe. Four analysis per sample were conducted. The reported DCOC value is the average of these four values. If the variance in the readings was greater than 5%, the TOC analyzer was recalibrated and the analysis was repeated. The analyzer provided a readout in both digital and hard copy form. DCOC is reported in units of milligrams per liter (mg/l).

CHLOROPHYLL a

Chlorophyll a was measured as described in the Handbook

of Common Methods in Limnology (40). The water sample, which varied in volume from 0.5 to 50 ml, was filtered through a 0.7 micron blank filter. The filter was then dissolved in a 90% acetone solution. The fluorescence of the acetone/chlorophyll a solution was measured on a fluorometer and the chlorophyll a concentration was determined by cross referencing the fluorometer reading with fluorometer readings of known chlorophyll a concentrations from a calibrated fluorescence/chlorophyll a graph. The Fluorometer was a Turner Corp. model 110 Fluorometer equipped with a F4T5/B Straight Tube Lamp with lamp adapter. The primary filter was a 5-60 and the secondary filter was a 2-64 both by Turner Corporation. The fluorometer was calibrated using chlorophyll a purchased from Sigma Chemical Company. Standards were prepared and the fluorometer was calibrated on the 1x, 3x, and 10x scales. For the batch kinetics tests, one sample was taken per sample time. For the CSTR tests, one sample of the initial conditions was taken and two samples of the final conditions were taken. All the samples were analyzed on the 1x, 3x, and 10x scales of the fluorometer. The reported value is the average of the readings from these three scales. Chlorophyll a is reported in units of micrograms per liter.

CHAPTER VI.

STATISTICAL METHODS

In order to determine the predictability of the reactions of THM precursors with ozone, attempts were made to model the results with linear models. These models show the variation of the dependent variable being tested against independent variables controlled in the study. The models were created on the SAS statistics package by the General Linear Model Procedure (PROC GLM) command. This package gave the results of a Least Squares Regression and determined the fit and the significance of the model.

The Least Squares Method determines the equation for the best fit line. The example given below shows the calculations for a best fit line in two dimensions. If more than two dimensions are to be used, matrix calculation methods must be applied. The basic form of the Least Squares Regression Model is

$$y' = B_0 + B_1 x$$

where y' = the expected value of the dependent variable,
x = the independent variable,
B_0 = the y intercept, and
B_1 = the slope of the line.

The slope of the line is determined by the following equation.

$$B_1 = (n*Sxy - Sx*Sy)/(nSx^2 - (Sx)^2)$$

where n = the number of samples in the data,
Sxy = the sum of the product $x*y$,
Sx = the sum of the independent variable,
Sy = the sum of the dependent variable, and
Sx^2 = the sum of the square of the independent variable.

The y intercept is determined by the following equation.

$$B_0 = \text{mean}(y) - B_1*\text{mean}(x)$$

where mean(y) = the arithmetic mean of the dependent variable and
mean(x) = the arithmetic mean of the independent variable.

The next step after determining the best fit model is to determine the significance of the model, the significance of the independent variables, and the fit of the line.

The significance of the model is determined by the F value. The F distribution is a one-tailed normal distribution that determines if at least one of the B's, except B_0 is not equal to zero. In this example there is only one other B, B_1. If any one of the B's are not equal to zero then at least one independent variable has an influence on the value of y'. The exact F value needed for a certain statistical significance depends on the number of

degrees of freedom in the model and in the error. If the calculated F value is greater than the F value required for the significance, say 95%, then the model is accepted. It follows that the greater the F value, the higher the significance of the model. It is also possible to determine what the significance of the model is from the F value. The F value is the ratio of the mean square of the model divided by the mean square of the error.

$$F = \text{mean square/mean square error}$$

The mean square is determined by dividing the Sum of Squares (SS) of the model by the Degrees of Freedom (DF). The Sum of Squares of the model is simply;

$$SS = \text{Sum}(y - \text{mean}(y))^2$$

The degrees of freedom is equal to the number of independent variables in the model. The Sum of Squares of the Error (SSE) is determined by the following equation.

$$SSE = \text{Sum}(y - y')^2$$

The degrees of freedom is equal to the sample size minus the number of B's, two in this example.

The significance of each independent variable is determined by the T ratio. The T ratio works on the same principle as the F value except that it is a two tailed normal distribution and each independent variable is individually tested for significance. The T ratio is the estimate of B divided by the error in the estimate. As with

the F value, the greater the T ratio, the higher the significance of that particular independent variable. The estimate of B (B_1 in the two dimensional case) is the same value as was determined in the Least Squares Regression. The error in the estimate (EE) is found as in the following equation.

$$EE = s/(\text{sqrt}(Sxx))$$

where $s = \text{sqrt}(SSE/(n-2))$ and
$Sxx = (nSx^2 - (Sx)^2)/n$.

The absolute value of the T ratio is compared to the value needed depending on the significance required, the degrees of freedom in the estimate, and the degrees of freedom in the error. If the T ratio is equal to or greater than this predetermined value, the independent variable is accepted. As with the F value, it is possible to determine the significance of the independent variable from the T ratio.

The goodness of fit of the model is determined by the coefficient of determination (R^2). The value of R^2 is determined as in the following equation.

$$R^2 = 1 - (SSE/SS)$$

If no statistics were available, the expected value of the dependent variable would have to be determined by the mean of the dependent variable. The coefficient of determination indicates the improvement, if any, that the Least Squares Model has on predicting the expected value of the dependent

variable. An R^2 of 0 indicates that predicting the expected value of the dependent variable with the Least Square Model is no more accurate than using the mean of the the dependent variable to determine the expected value. An R^2 of 1 indicates that the model predicts the expected value of the dependent variable with negligible error.

By using the F value, the T ratio, and the coefficient of determination, it is possible to accept or reject the significance of a given model or a given variable in that model. This decision making capability allows for increased flexibility and accuracy in the ability to predict the expected value of the dependent variable.

CHAPTER VII.

RESULTS AND DISCUSSION

BATCH KINETICS TEST RESULTS.

Four batch kinetic experiments were performed. Kinetic experiments were done to ascertain possible reaction models and to determine the behavior of ozone-algal mass reactions over an extended time period. Ozone dose and initial chlorophyll a concentration were the only independant variables. The raw data are plotted in Figures 3-6 and will be discussed below.

The initial conditions for these tests are as follows. At the low chlorophyll a concentrations (approximately 40 microg/l) in tests 1 and 2, the THMFP is approximately 3 mg/l and the DCOC is approximately 6 mg/l. At the high chlorophyll a concentrations (approximately 100 microg/l) in tests 3 and 4, the THMFP is approximately 6.5 mg/l and the DCOC is approximately 9 mg/l.

Statistical analysis indicates strong two way correlations between initial THMFP, initial DCOC, and initial chlorophyll a. The correlation between initial THMFP and initial DCOC was 0.91 (1.00 being perfectly

correlated). The correlation between initial THMFP and initial chlorophyll a was 0.987, and the correlation between chlorophyll a and DCOC was 0.895. These high correlations suggest that the initial THMFP can be predicted if the initial chlorophyll a and DCOC are known. The regression model shows that the initial THMFP can be modeled as such;

$$THMFP = 0.21*DCOC + 43.5*chlorophyll\ a$$

with an R^2 of 0.997 and a confidence of 99.7%. Therefore, as initial DCOC and chlorophyll a increase, initial THMFP also increases. In this case, the units for THMFP, DCOC, and chlorophyll a are all in mg/l. Due to the fact that THMFP, DCOC, and chlorophyll a have different responses to ozone, the THMFP could not be accurately modeled by DCOC and chlorophyll a. Once the experiment was started, the resulting models included time as an independent variable which caused a lower significance. Attempts to predict the linear response of ozone residual, THMFP, DCOC, and chlorophyll a with respect to ozone dose, initial chlorophyll a concentration, and contact time were unsuccessful. Thus, for example, chlorophyll a and DCOC can be used to estimate THMFP for unozonated waters but not for ozonated samples.

In general, the batch kinetics tests demonstrated that the higher the ozone dose, the greater the removal of THMFP. This result agrees with the literature. On the other hand,

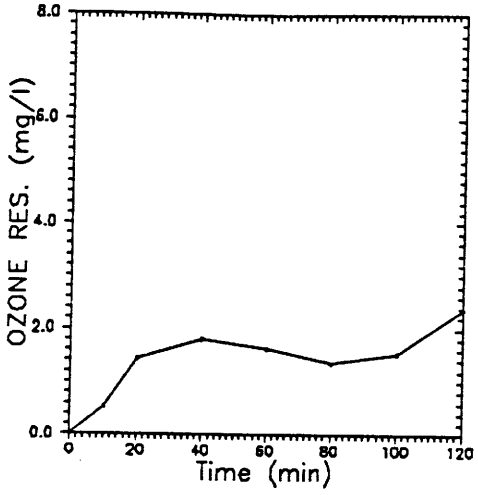


Figure 3a. Ozone Residual versus Time.

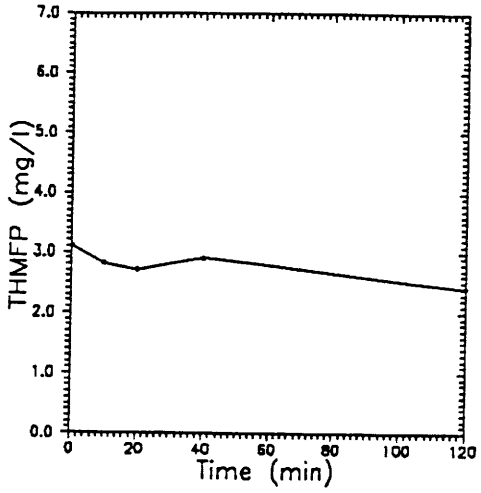


Figure 3b. THMFP versus Time.

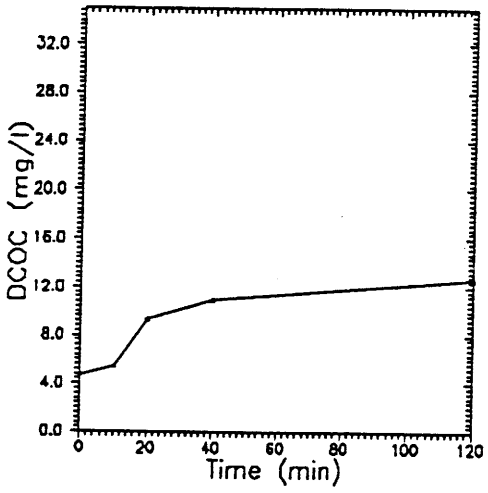


Figure 3c. DCOC versus Time.

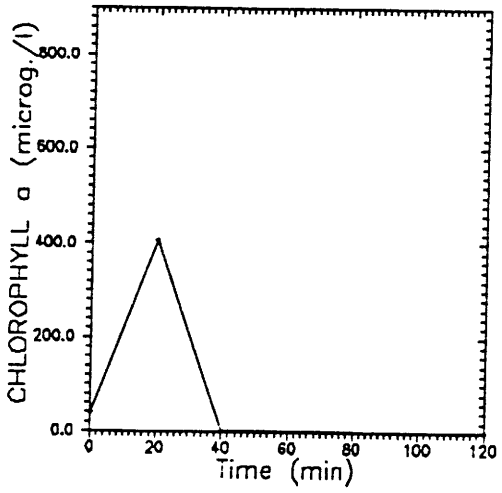


Figure 3d. Chlorophyll a versus Time.

Figure 3. Batch Kinetics Test #1
Low Initial Chlorophyll
Low Ozone Dose.

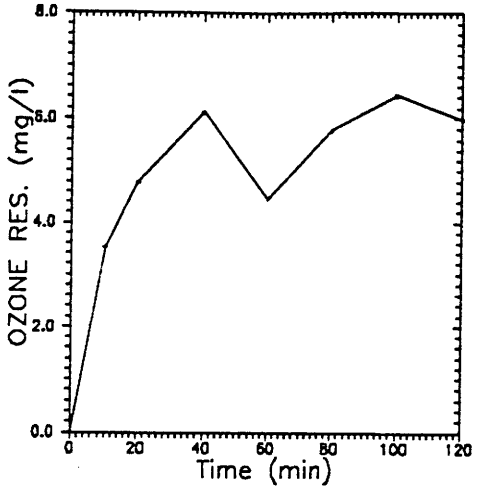


Figure 4a. Ozone Residual versus Time.

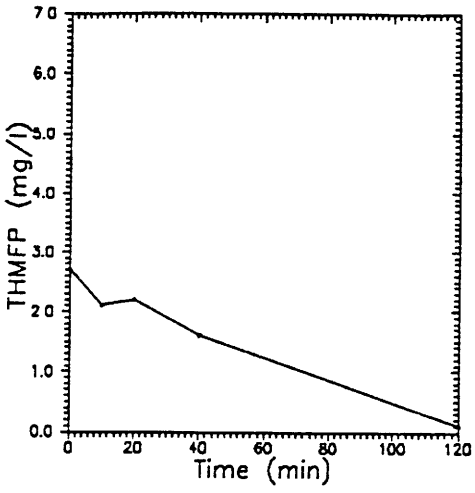


Figure 4b. THMFP versus Time.

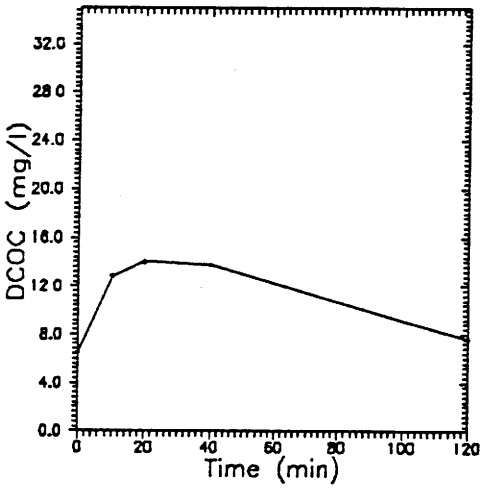


Figure 4c. DCOC versus Time.

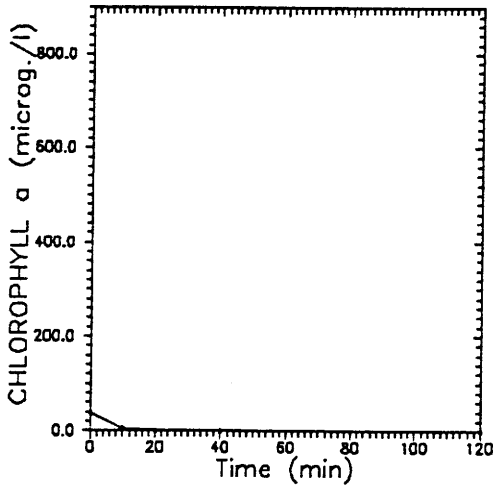


Figure 4d. Chlorophyll a versus Time.

Figure 4. Batch Kinetics Test #2
Low Initial Chlorophyll
High Ozone Dose.

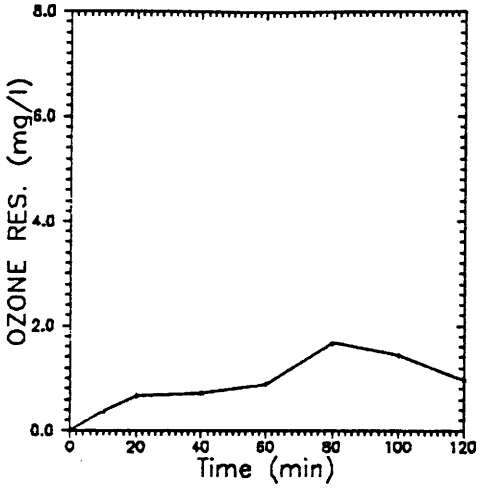


Figure 5a. Ozone Residual versus Time.

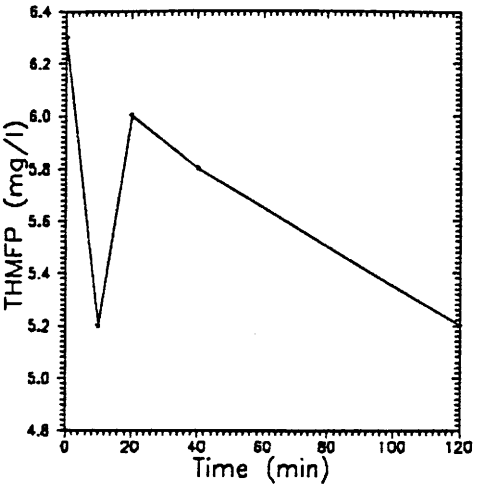


Figure 5b. THMFP versus Time.

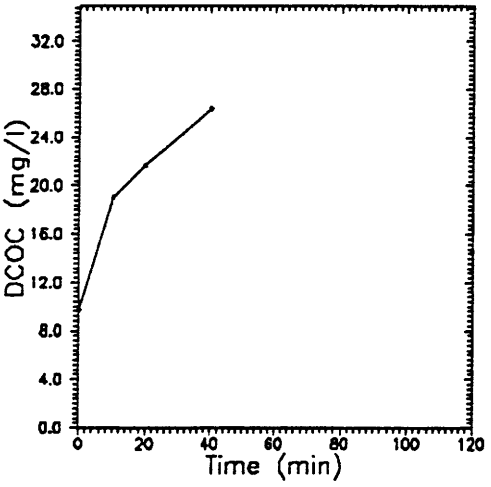


Figure 5c. DCOC versus Time.

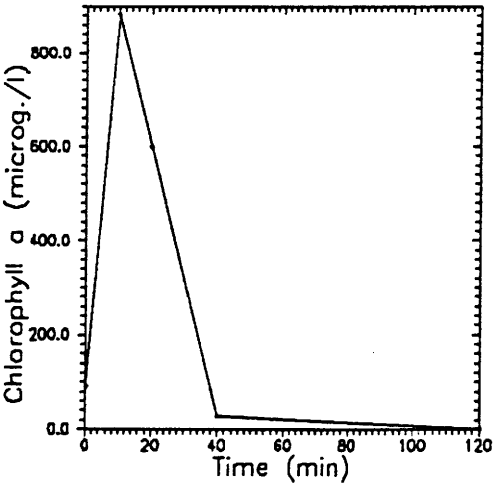


Figure 5d. Chlorophyll a versus Time.

Figure 5. Batch Kinetics Test #3
High Initial Chlorophyll
Low Ozone Dose.

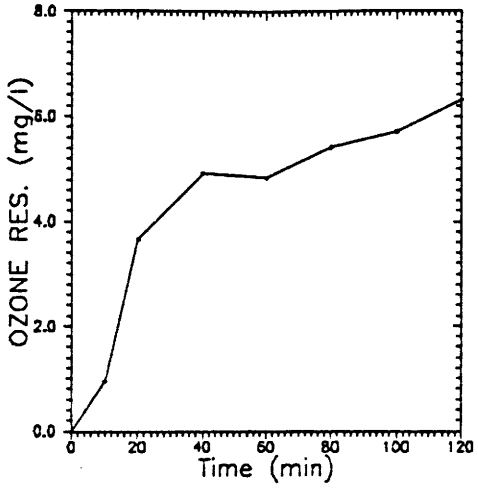


Figure 6a. Ozone Residual versus Time.

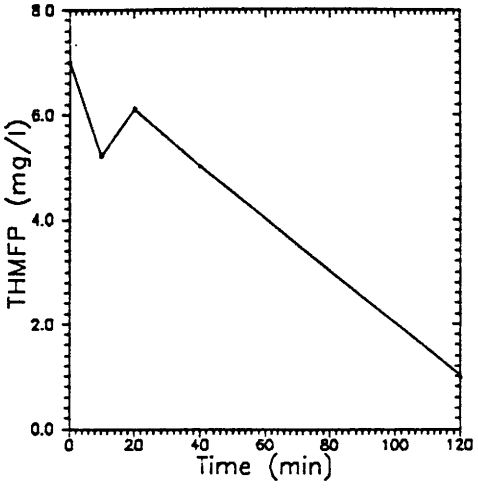


Figure 6b. THMFP versus Time.

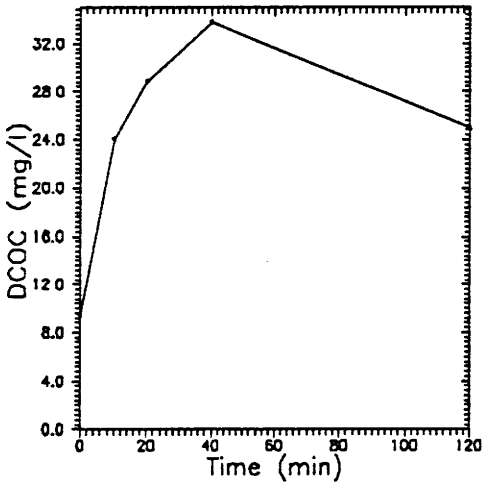


Figure 6c. DCOC versus Time.

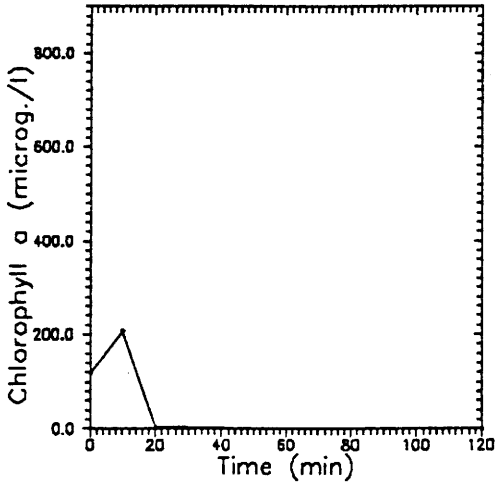


Figure 6d. Chlorophyll a versus Time.

Figure 6. Batch Kinetics Test #4
High Initial Chlorophyll
High Ozone Dose.

as can be seen in figures 3b and 5b, low ozone dose did not significantly remove THMFP.

The increase in DCOC could be caused by the breaking down of larger organic compounds into colloidal or dissolved states. This phenomenon has been reported in many studies (33,34,41).

Rice (33) and Veenstra (41) suggest that increases in DCOC can occur at the same time as decreases in the THMFP. This observation can result from the fact that organic carbon is rarely oxidized by ozone to carbon dioxide and water while THM precursors can be oxidized to non-precursor compounds. Therefore, exposure of organic material to ozone will result in dissimilar responses of the DCOC and THMFP parameters.

An additional explanation for the increases in DCOC occurring at the same time as decreases in THMFP is possible. The filtering of the DCOC samples results in the retention of intact cells on the filter. In the initial (t=0) samples, the organic carbon is largely tied up in intact cells. After exposure to ozone, many of the cells were probably lysed and much of the cellular contents passed through the filter and were detected by the TOC analyzer. The DCOC would then be observed to increase upon exposure of algal cells to ozone.

Another interesting phenomenon noted in these

experiments is the temporary increase in the THMFP and chlorophyll a concentrations. The responses of the THMFP to contact with ozone (figures 3b, 4b, 5b, and 6b) consistently showed an initial drop in THMFP followed by an increase peaking at approximately 20 minutes. This increasing of the THMFP was subsequently followed by a sharp decline. On the other hand, in most cases chlorophyll a showed no initial decline (figures 3d, 4d, 5d, 6d). Instead it increased steadily before dropping off.

The increase in the THMFP can be explained by the degradation of non-precursor organic compounds into THM precursors or by the lysis of algal cells causing the release of THM precursors. Either process could require a lag time before the effects are observed. During this time a decline in THMFP would be observed as noncellular THMFP is destroyed. Then as cells lyse or non-precursor substances are oxidized to precursor substances, an increase in the THMFP would be detected. These precursor substances are subsequently oxidized to non-precursor substances. These results show that with "sufficient" exposure to ozone, destruction of THM precursors will occurr. The "sufficient" level of exposure to ozone is a function of the exact nature and concentration of the THM precursors, the exact nature and concentrations of the other organics in the water, and the inorganic nature of the water.

The apparent increase in the chlorophyll a concentration is to be expected since chlorophyll a is measured by its fluoresence property. The fluoresence can be increased by stressing the chlorophyll by partial oxidization. The fluoresence occurs when the chlorophyll returns to its reduced state (42). Further oxidation would likely result in destruction of the chlorophyll. Consequently, when algal cells are exposed to ozone, the apparent increase in chlorophyll a concentration can be caused by the fluorescent response of chlorophyll a to oxidant related stressing of the molecule.

The data from each test were also plotted in Figures 7-10 with the vertical axis representing the fraction of the given parameter remaining (C_t/C_0) where C_t is the concentration of the variable at any time and C_0 is the initial concentration of the same variable. A linear fit to these plots would indicate a first order response of this parameter to ozonation. It was attempted to fit the data in figures 7-10 to a such a model. It was found that fraction remaining of THMFP was modeled fairly well. The regression equation was;

$$\text{Log}((\text{THMFP}_t)/(\text{THMFP}_0)) = -1.052*10^{-3}*\text{TIME}*\text{DOSE}$$

with a confidence of 99.99% and an R^2 of 0.90. This means

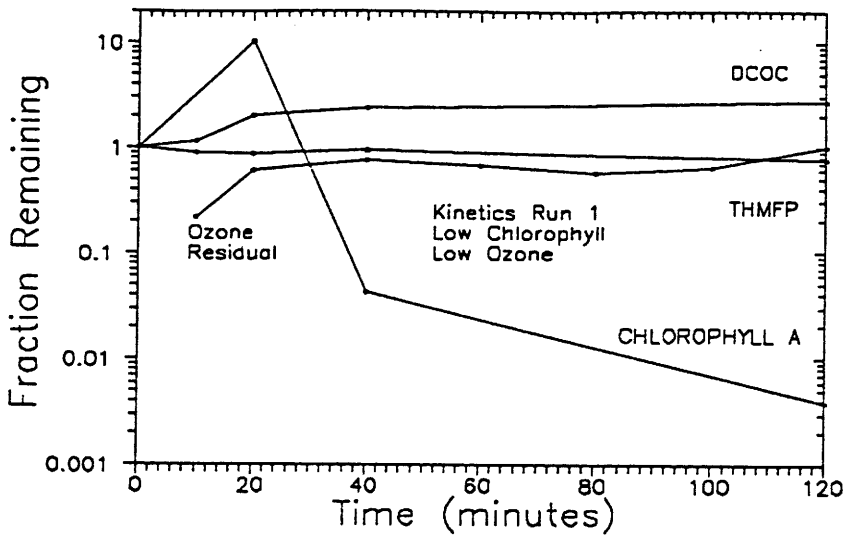


Figure 7. Fraction Remaining Batch Kinetics Test #1.

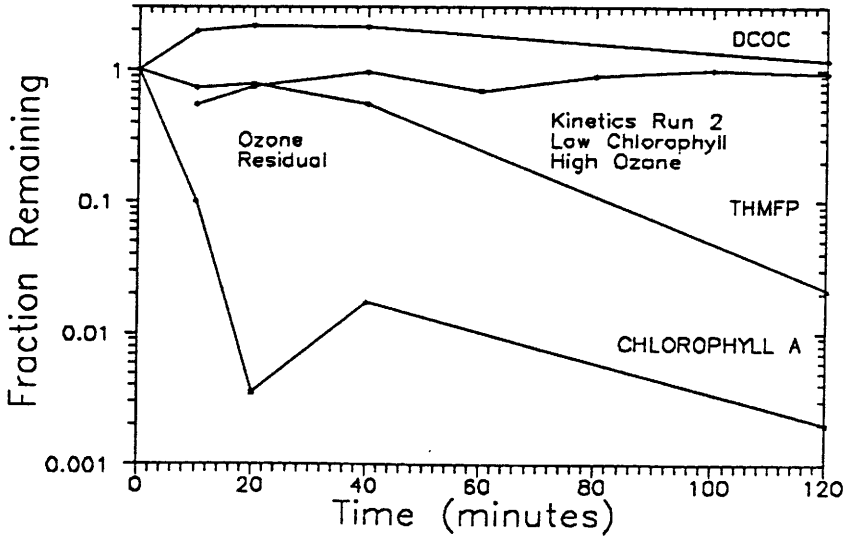


Figure 8. Fraction Remaining Batch Kinetics Test #2.

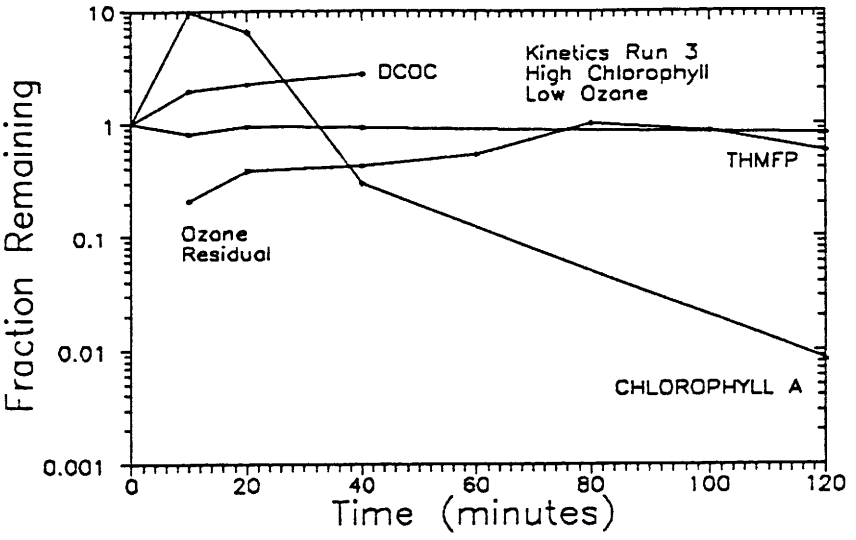


Figure 9. Fraction Remaining Batch Kinetics Test #3.

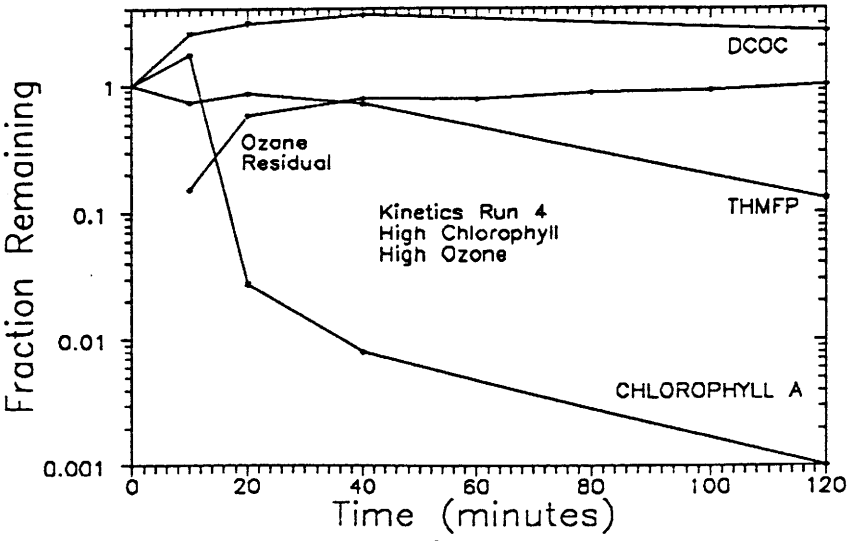


Figure 10. Fraction Remaining Batch Kinetics Test #4.

that as the variable (TIME*DOSE) increases, the THMFP decreases. The other dependant variables (DCOC, ozone residual, and chlorophyll a) did not fit a first order model as closely as did THMFP. For example,the best model for log fraction remaining of chlorophyll a,

$$\text{Log}((CHL_t)/(CHL_0)) = 0.78 - 0.02*\text{TIME} - 0.2*\text{DOSE}$$

had an R^2 of 0.73 and a confidence of 99.99%. This equation shows that as the time or dose is increased, the chlorophyll a decreases. Although the R^2 term is not exceptionally high, the confidence limit shows that there is a strong trend in the data. It is this trend that can be modeled, not necessarily the exact fraction of chlorophyll a remaining. In the batch experiments the ozone residual varied throughout the duration of the tests. The maximum value of the ozone residual (C_{max}) usually occurred near the end of the run when much of the ozone demand had been satisfied. The best model for the log fraction of maximum ozone residual ($\log(C_t/C_{max})$) had an R^2 of 0.18 and a confidence level of 73.5%. The model for the log fraction remaining for DCOC had an R^2 of 0.12 and a confidence of 85.5%. These models are not regarded as reliable since the trends show confidence levels less than 95%.

These experiments show that ozone can be used for the destruction of THM precursors but that high doses and long detention times are needed if the ozone is applied to raw

water that has a high initial THMFP.

CSTR TEST CONDITIONS.

Eighteen CSTR experiments were conducted where ozone dose, pH, and detention time were varied. The test conditions are shown in Table 1.

Table 1. CSTR Test Conditions.

pH	Dt (min.)	Ozone Dose*	Ozone Residual*	Alkalinity**	Test #
5.3	10	low	0.87	25.0	2
6.8	10	low	0.40	107.5	1
9.1	10	low	0.03	267.5	9
4.6	20	low	1.63	2.5	3
7.1	20	low	0.48	125.0	5
8.9	20	low	0.44	237.5	8
5.1	40	low	1.41	12.5	4
6.6	40	low	0.92	100.0	6
8.9	40	low	0.79	252.5	7
5.3	10	high	2.74	25.0	16
7.4	10	high	1.68	132.5	17
8.7	10	high	0.74	212.5	18
5.1	20	high	4.76	20.0	13
6.6	20	high	3.04	95.0	11
8.9	20	high	1.33	220.0	15
5.4	40	high	5.47	27.5	12
7.1	40	high	3.61	120.0	10
9.0	40	high	2.66	215.0	14

* milligrams/liter
** milligrams/liter as Calcium Carbonate

It was expected that the greatest removal of THMFP, DCOC, and chlorophyll a would take place at the higher ozone doses and longer detention times. As will be shown,

this was not always the case.

The data were fit to a general linear model which had the form of:

$$Y = B_0 + B_1X_1 + B_2X_2 + \ldots + B_nX_n$$

where

B_i = a constant
X_i = Detention time, Ozone Dose, pH, or Predicted Ozone Residual or combinations of said
Y_i = Decrease in: THMFP, DCOC, or Chlorophyll a.

The number of variables was kept small in each model tested. If large numbers of variables were included in a given model, the model could give a false high coefficient of determination (R^2) and confidence limit. Variables which showed significance were included in a general model. This general model was then tested for significance. Due to the fact that including too many variables would decrease the reproducability of the final model, the number of variables was kept at three or less. Although in later sections only the top ten ranked removal conditions are reported, all eighteen data points were used in the predictor models. All the data are presented in appendix B.

Because the ozone residual was a dependant variable it was not possible to use it as an independent variable in the modeling process. Hence, it was necessary to model the ozone residual and use the predicted values as the

independent variable in the general model for the decrease in Y. The regression model for the predicted ozone residual (Res.) to be included in the general model was;

Res. = 0.82*Dose + 0.01*Dose*Time - 0.095*Dose*pH

with a confidence interval of 99.99% and an R^2 of 0.98. This model suggests that as the ozone dose is increased, the ozone residual also increases. This model also suggests that at lower pH values, the ozone residual is greater than at higher pH values at the same ozone dose. This concurs with the literature (20,21,22,23,24).

DECREASE IN THMFP

Table 2 shows ten of the experiments ranked in descending order of decrease in THMFP.

From Table 2 we can see that the highest ranked test for THMFP removal is test #14 where high ozone dose, long detention time, and high pH were used. This result was expected (27,33,34). However, the second highest ranked test for THMFP removal (#18) occurred under the same conditions as the first except that the shortest detention time was involved. In addition, the third ranked test (#7) had the same conditions as the first except that the low ozone dose was used. Out of the top five conditions, three are high pH, three are 40 minute detention time, and three are low ozone dose.

Table 2. Reduction in THMFP

Rank	Test #	THMFP* Before	THMFP* After	Decrease in THMFP*
1	14	2.5	1.4	1.1
2	18	2.6	1.6	1.0
3	7	2.1	1.1	1.0
4	5	2.7	1.1	0.9
5	4	2.0	1.1	0.9
6	3	1.9	1.1	0.8
7	13	2.2	1.6	0.6
8	12	1.8	1.2	0.6
9	15	2.6	2.1	0.5
10	10	2.1	1.6	0.5

* milligrams/liter

The statistical model shows high a confidence level in the trend of the data but a large variation. The best fit model for the reduction in THMFP was:

$$\text{Decrease in THMFP} = 0.016 * \text{Time}$$

The linear model had a coefficient of determination (R^2) of 0.4 with a confidence of 99.6%. This means that as the detention time is increased, THMFP decreases. Again, this model is very good at representing the trend of the data but cannot be used to predict the exact decrease in THMFP under a given set of conditions. Although the relative reduction in THMFP is not very great, the absolute reduction is. The top ten ranked conditions show removals of THMFP that are 5-11 times the MCL. The NOM survey (2) showed that THMFPs at the consumers tap ranged from 0.08 to 0.8 mg/l without the use of ozone. The studies reported here show that ozone

can reduce the THMFP by 0.5 to 1.1 mg/l. Therefore, in almost all cases, the incorporation of ozone into the water treatment systems of the surveyed cities would enable compliance with the MCL of 0.10 mg/l. It can be concluded from these observations that ozone can remove significant amounts of THMFP.

DECREASE IN DISSOLVED AND COLLOIDAL ORGANIC CARBON.

The data are shown in descending order of dissolved and colloidal organic carbon (DCOC) removal in Table 3.

Table 3. Reduction in DCOC

Rank	Test #	DCOC* Before	DCOC* After	Decrease in DCOC*
1	2	46.0	42.3	3.7
2	10	0.0	0.0	0.0
3	11	0.0	0.0	0.0
4	8	12.7	14.4	-1.7
5	12	0.0	3.0	-3.0
6	16	6.0	9.5	-3.5
7	14	9.7	13.5	-3.8
8	15	9.0	13.6	-4.6
9	4	8.9	14.2	-5.3
10	18	5.2	11.5	-6.3

* milligrams/liter

It was expected that the conditions that allowed the most THMFP removal would also permit the greatest removal of DCOC. This, however, was not the case. The conditions under which removal of DCOC was maximized (in fact the only

situation that provided a positive removal) was the conditions of low pH, low ozone dose, and shortest detention time. This set of conditions was expected to show the least DCOC removal since it represented the lowest opportunity for oxidation of the organics in the water. However, it is possible that, although the ozone dose was too low to lyse algal cells, it was great enough to oxidize noncellular organics.

If the top five ranked conditions are examined, it can be seen that the actual results are similiar to the expected results. One of the top five had a high pH, two had a neutral pH, and two had a low pH. Two of the top five were 40 minute detention time, two were 20 minutes, and one was ten minutes. Three of the top five had a high ozone dose. The linear model for the decrease in DCOC;

Decrease in DCOC = -4.6*Ozone Residual

had a coefficient of determination (R^2) of 0.25 and a confidence of 97%. This model suggests that DCOC increases as the ozone residual increases. As with the decrease in THMFP model, this model can only predict the trend of the data. Due to the fact that DCOC and THMFP have opposite responses to exposure to ozone, the change in DCOC should not be taken as being representative of the change in THMFP. Similarly, the reduction in the THMFP should not be taken as indicative of the level of organics removed.

Only one set of test conditions actually resulted in a decrease in DCOC. All other cases tested showed an increase in DCOC. This increase could be caused by the same factors that resulted in the rise of DCOC that occurred in the batch reactor tests. It is possible to increase the concentration of dissolved and colloidal organics by breaking down the organics that were retained by the filter in the unozonated samples.

Another difficulty in the interpretation of the TOC data lay in the zero values of TOC in tests 10, 11, and 12. In some cases, samples which contained algal biomass yielded no detectable dissolved and colloidal organic carbon. This phenomenon may be due to limitations in the TOC analyzer. The lower range of the analyser is 0.1 mg/l and readings at the detection limits have occurred. These zero values were unexpected and may have biased the resulting models.

DECREASE IN CHLOROPHYLL A.

The experiments are ranked in descending order of chlorophyll a removal in Table 4.

The situation for greatest chlorophyll a removal was high ozone dose, longest detention time, and low pH. Out of the top five results only one was high pH while two were neutral and two were low pH. Three of the top five conditions had the longest detention time while the other

two conditions had the intermediate detention time. All of the top five ranked tests used a high ozone dose.

Table 4. Reduction in Chlorophyll a

Rank	Test #	Chlor. a* Before	Chlor. a* After	Decrease in Chlor. a*
1	13	48.9	2.5	46.4
2	10	47.7	2.0	45.7
3	12	39.8	0.7	39.1
4	11	47.1	13.0	34.1
5	14	31.5	4.2	27.3
6	4	47.6	35.8	11.8
7	6	39.5	28.9	10.6
8	7	47.8	38.4	9.4
9	16	34.6	27.7	6.9
10	15	23.7	22.6	1.1

* micrograms/liter

The model for the decrease in chlorophyll a,

Decrease in Chlorophyll a = 2.4*Time -15.8*pH + 8*Dose,

had an R^2 0.845 and a confidence of 99.99%. In other words, as detention time and ozone residual increase, more chlorophyll a is destroyed and as pH decreases less chlorophyll a is destroyed.

The models for predicting the response of chlorophyll a to exposure to ozone had a higher confidence interval and a higher degree of correlation than the models for predicting the response of THMFP and DCOC had.

RELATIONS BETWEEN THMFP AND TOC/DCOC.

Some reports in the literature have attempted to define the relationship between THMFP and TOC. Yamada et al. (33), in testing the effect of preozonation on the THM formation potential of various organic compounds, presented THMFP in the form of micrograms of $CHCl_3$ yielded per milligram TOC. Their data range from 0 to 2,168 micrograms/milligram depending on the organic compound being studied. They concluded that there is a relationship between TOC and THMFP but that the specific relationship depends on the exact nature of the organic compound being studied.

Hoehn, et al. (7) found no consistent pattern between THMFP and TOC in algal biomass. However, they conclude from their data that the algae in the earlier phase of growth have a higher THMFP/TOC than when the culture was in the later stages of growth.

The exact nature of the organic compounds and the stage of growth of the algae in the experiments reported here are unknown. It is assumed that the algae used in these experiments represented all stages of growth. No effort was made to control growth stage. Using the same type of ratio employed by Yamada et al., the THMFP/DCOC ratio (micrograms/milligram) was found to have a 95% confidence interval of 0 to 584 before ozonation and 0 to 344 after ozonation. These large confidence intervals suggest that

using DCOC will provide a somewhat insecure method of predicting the THMFP of a given water.

SUMMARY

Four batch reactor experiments and eighteen CSTR experiments were conducted in order to determine the effect of ozone on algal laden waters. When interpreting the results it is imperative to recall that the THMFPs that were studied are very high due to the presence of the algal bloom. These conditions represent a "worst case" scenario. If ozone can significantly reduce the THMFP of waters under these extreme conditions, then ozone is a valid means of THMFP removal year round. The response to exposure to ozone of certain parameters such as dissolved and colloidal organic carbon, chlorophyll a, and, most importantly, THM formation potential were studied.

Samples were taken during the batch kinetics tests initially and at 10 minutes, 20 minutes, 40 minutes, and 120 minutes. In the CSTR tests, the reactor was set up in such a way as to provide a counter-current flow between the test water and the ozone gas flow. Samples were taken from the CSTR tests initially and after each detention time until steady state was assumed to have been reached (three detention times).

The values of the THMFP of the samples were in the range

of 1 to 2.7 ppm even in the ozonated samples. The values of the THMFP in the batch tests that had a high initial chlorophyll concentration were near 7 mg/l. The chlorine dose was very high in order to achieve a maximum THMFP. It was interesting to note that the conditions that were most favorable for the removal of THMFP were not necessarily the optimal conditions for removal of DCOC.

Statistical analysis on the data showed that due to the small sample size, modeling of most of the parameters could not be accomplished with much accuracy. It was possible to model the trend of the data of log fraction remaining THMFP in the batch tests and ozone residual, decrease in THMFP, decrease in DCOC, and decrease in chlorophyll a in the CSTR tests.

CHAPTER VIII.

CONCLUSIONS

Based on the absolute reductions of THMFP in all the tests reported here and the fact that only two of eighteen CSTR conditions increased the THMFP it is concluded that ozone can significantly reduce the THMFP of all waters including those experiencing an algal bloom.

Although detention time, ozone dose, pH, and ozone residual are all factors that effect the ability of ozone to oxidize THM precursors, the most significant factor is the detention time.

All the independent variables (detention time, ozone dose, pH, and ozone residual) had positive correlations with decrease in THMFP. This means that optimal THM precursor removal occurs at long detention time, high ozone dose, high pH and high ozone residual.

The THMFP in unozonated waters can be predicted using the chlorophyll a and DCOC concentrations. The instruments and methods used for determining the chlorophyll a and DCOC are less expensive than those used to determine THMFP. In addition, the chlorophyll a and DCOC tests can be performed

within 24 hours of sampling whereas the test for THMFP requires a seven day incubation of the samples.

CHAPTER IX.

RECOMMENDATIONS

1. Although the tests reported here show that ozone is effective in the removal of THMFP, the level of exposure to ozone (dose and detention time) required for sufficient THMFP removal must be determined for each individual situation.

2. The optimal location(s) of ozonation in the treatment works should also be determined. Although not shown in these experiments it is likely that ozonation of settled water with or without preozonation is the optimal location of ozonation to reduce THMFP. This theory can be confirmed by running parallel water treatment pilot water treatment plants in which one plant incorporates ozone while the other does not. This study is imperative for further understanding and quantification of the uses of ozone for the reduction of THMFP.

3. If air is to be the feed gas, it should be dried with $CaCl_2$ (36) to prevent buildup of corrosive by-products in

the ozone generator. It is also important to vent the off gas from the reactor so as not to expose the operator to potentially toxic ozone fumes.

4. The exact ozone dose should be determined. This determination can be accomplished by measurement of the concentration of ozone in the supply lines versus the concentration of ozone in the off gas. This would allow a calculation of milligrams of ozone consumed per milligram decrease in THMFP.

5. It would also be wise to get algal counts and bacteria counts in the test water. These counts would allow testing of correlation between chlorophyll a and cell counts and THMFP and cell counts.

6. Future studies should determine the effect of temperature on ozonation. All the tests in the experiments reported here were done at room temperature. Tests should be run at temperatures closely simulating raw water conditions, such as 4-15°C.

7. The effect of the level of algae should be investigated further. The CSTR tests in this study were conducted at one high level of algae. Tests that determine the ability of

ozone to remove THM precursors at lower levels of algae should be conducted. Conditions that include chlorophyll a concentrations in the range of 0 - 20 micrograms per liter should be investigated.

8. Another important phenomenon to be examined in further studies is the conditions that cause ozone to increase the THMFP. This knowledge is critical for the safe use of ozone in water treatment systems.

9. Due to the fact that many researchers claim that ozone residual is a more important factor than ozone dose in the reduction of THMFP by ozone, the ozone residual should be held constant at different levels. Suggested ozone residuals for further studies are; 0.5 mg/l, 2 mg/l, and 5 mg/l. The first level was chosen because it is a commonly used level of ozone residual used for disinfection. Studies at the other two levels will allow scientists to determine the optimal ozone residual for THMFP removal.

10. Some researchers claim that radical scavenging by carbonate and bicarbonate ions is an important factor in aqueous ozone chemistry and hence ozone oxidation. Therefore, studies that fix the concentrations of carbonate and bicarbonate at known values will enable scientists to

determine the effect of radical scavenging by carbonate species on oxidation of THM precursors by ozone.

APPENDIX A.

DATA FOR FIGURES 3-6.

Batch Test #1. Low Initial Chlorophyll, Low Ozone Dose.

Time (min.)	Ozone Residual (mg/l)	THMFP (mg/l)	DCOC (mg/l)	Chlorophyll a (microg/l)
0	0	3.1	4.7	39.3
10	0.52	2.8	5.4	
20	1.43	2.7	9.3	405.3
40	1.80	2.9	10.9	1.7
120	2.37	2.4	12.6	0.15

Batch Test #2. Low Initial Chlorophyll, High Ozone Dose.

Time (min.)	Ozone Residual (mg/l)	THMFP (mg/l)	DCOC (mg/l)	Chlorophyll a (microg/l)
0	0	2.7	6.5	37.8
10	3.51	2.1	12.8	3.88
20	4.76	2.2	14.0	0.13
40	6.11	1.6	13.7	0.45
120	5.97	0.1	7.6	0.08

Batch Test #3. High Initial Chlorophyll, Low ozone Dose.

Time (min.)	Ozone Residual (mg/l)	THMFP (mg/l)	DCOC (mg/l)	Chlorophyll a (microg/l)
0	0	6.3	9.7	92.1
10	0.36	5.2	19.0	881.8
20	0.66	6.0	21.7	597.3
40	0.71	5.8	26.3	27.3
120	0.95	5.2		0.76

Batch Test #4. High Initial Chlorophyll, High Ozone Dose.

Time (min.)	Ozone Residual (mg/l)	THMFP (mg/l)	DCOC (mg/l)	Chlorophyll a (microg/l)
0	0	7.0	9.4	119.3
10	0.95	5.2	24.0	206.5
20	3.64	6.1	28.8	3.27
40	4.92	5.0	33.8	0.94
120	6.31	1.0	24.9	0.12

APPENDIX B.

CSTR TEST RESULTS.

Test #	pH	Dt*	Ozone Dose (**)	Ozone Resid. (**)	THMFP Bef. (**)	THMFP Aft. (**)	CHla Bef. (***)	Chla Aft. (***)	DCOC Bef. (**)	DCOC Aft. (**)
1	6.8	10	Low	0.40	2.4	2.6	54.2	119.3	10.7	18.5
2	5.3	10	Low	0.87	2.1	1.9	31.2	95.3	46.0	42.3
3	4.6	20	Low	1.63	1.9	1.1	43.7	65.9	12.5	18.8
4	5.1	40	Low	1.41	2.0	1.1	47.6	35.8	8.9	14.2
5	7.1	20	Low	0.48	2.0	1.1	58.1	86.9	6.5	13.7
6	6.6	40	Low	0.92	0.1	1.1	39.5	28.9	0.0	7.2
7	8.9	40	Low	0.79	2.1	1.1	47.8	38.4	0.1	14.7
8	8.9	20	Low	0.44	2.3	2.0	35.8	131.7	12.7	14.4
9	9.1	10	Low	0.03	2.1	2.1	43.5	179.1	0.2	7.2
10	7.1	40	High	3.61	2.1	1.6	47.7	2.0	0.0	0.0
11	6.6	20	High	3.06	1.6	1.6	47.1	13.0	0.0	0.0
12	5.4	40	High	5.47	1.8	1.2	39.8	0.7	0.0	3.0
13	5.1	20	High	4.76	2.2	1.6	48.9	2.5	9.5	97.4
14	9.0	40	High	2.66	2.5	1.4	31.5	4.2	9.7	13.5
15	8.9	20	High	1.33	2.6	2.1	23.7	22.6	9.0	13.6
16	5.3	10	High	2.74	2.4	2.3	34.6	27.7	6.0	9.5
17	7.4	10	High	1.68	2.5	2.3	42.1	57.2	4.2	10.7
18	8.7	10	High	0.74	2.6	1.6	31.3	104.7	5.2	11.5

(*) minutes
(**) milligrams/liter
(***) micrograms/liter

APPENDIX C.

CSTR TESTS
OZONE RESIDUAL (mg/l)

Test #	Time 5	10	20	30	40	50	60	70	80	90	100	110	120
1	0.4	0.3	0.4	0.5									
2	0.7	0.9	0.8	1.2									
3	1.0	1.2	1.5	1.9	1.9	1.7	2.0						
4	1.0	1.0	2.0	1.6	1.3	1.6	1.0	1.5	1.1	1.4	1.6	1.9	1.3
5	0.2	0.1	0.8	0.3	0.7	0.7	0.7						
6		0.5	0.9	1.2	1.2		1.2		1.4		0.8		1.2
7	0.0	0.0	0.6		1.0		0.8		0.6		1.9		1.4
8	0.5	1.0	0.2	0.5	0.2	0.5	0.3						
9	0.0	0.0	0.0	0.1									
10	1.7	2.5	3.3	4.0	3.9		4.5				3.3		
11	1.8	2.7	3.2	3.6	3.5	3.3	3.2						
12		4.7	4.7	5.3	5.0		5.3		5.3		5.5		
13	3.9	4.8	4.8	5.0	5.0	4.8	5.0						
14		0.6	2.1	2.9	3.1		3.7		3.6		3.9		3.5
15		0.2	1.1	1.9	1.4	1.4	1.9						
16	1.9	2.9	3.0	3.2									
17	0.7	1.5	2.0	2.5									
18	0.2	0.3	1.1	1.2									

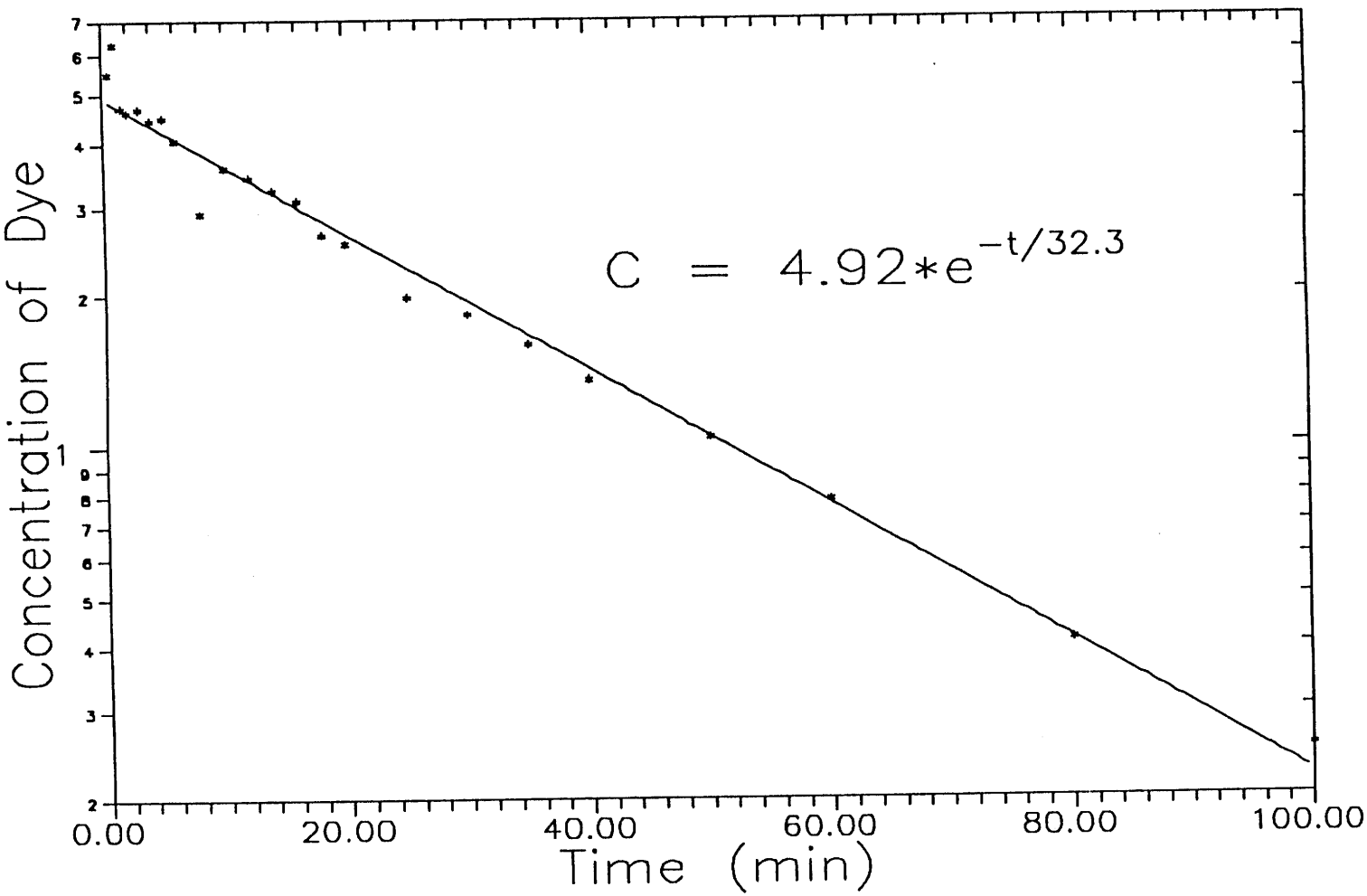
APPENDIX D.

CSTR TESTS DCOC

Test	Time (*Detention Time)			
#	0	1	2	3
1	10.6	15.2	15.6	18.5
2	46.0	39.5	39.7	42.3
3	12.5	17.6	17.6	18.8
4	8.9	13.2	13.5	14.2
5	6.5	12.8	13.6	13.7
6	0.0	5.1	8.4	7.2
7	0.1	12.9	13.8	14.7
8	12.7	14.9	15.5	14.4
9	0.2	9.3	7.2	7.1
10	0.0	0.1	0.0	0.0
11	0.0	0.5	0.0	0.0
12	0.0	0.0	6.8	3.0
13	9.4	3.7	4.7	97.4
14	9.7	21.6	18.8	13.5
15	8.9	16.5	16.0	13.6
16	6.0		11.4	9.5
17	4.2	9.2	10.4	10.6
18	5.2	10.6	12.1	11.5

APPENDIX E.
CSTR DYE TEST

Time (min)	Fluorometer Reading	
0	0	
0.5	5.49	Dt set at 30 minutes
1	6.29	
1.5	4.71	Volume = 7 liters
2	4.61	
3	4.69	Air flow = 2 lpm
4	4.45	
5	4.49	Regression Line:
6	4.06	Significance = 99.99%
8	2.92	R^2 = 0.985
10	3.58	
12	3.43	
14	3.24	
16	3.08	
18	2.64	
20	2.54	
25	1.98	
30	1.83	
35	1.59	
40	1.35	
50	1.04	
60	0.78	
80	0.41	
100	0.25	


Concentration of Dye
Time (min)
C = 4.92*e^-t/32.3
0.00
20.00
40.00
60.00
80.00
100.00
1
2
3
4
5
6
7
8
9

APPENDIX F.
MATHEMATICAL MODELS

This appendix shows some of the mathematical models that were used to determine the reproducability of the results. This appendix is arranged as such,

$$Y = B_0 + B_1X_1 + \ldots + B_nX_n$$

where Y = Model
B = Estimate
X = Parameter.

The value of PR>F is the probability of an occurrence greater than the F value. The F value is the ratio of the mean square of the model and the mean square of the error. These values are not shown here. A PR>F of 0.05 is analogous to a 95% confidence interval. The value of PR>T is the probability of an occurrence greater than the absolute value of the T ratio. The T ratio is the ratio between the estimate and the standard error of the estimate. These values are not shown here. A PR>T of 0.05 is analogous to a confidence interval of 95%.

BATCH KINETICS MODELS

Model: Initial THMFP PR>F = 0.15 R^2 = 0.98

Parameter	Estimate	PR>T
Intercept	0.45	0.79
DCOC	0.12	0.75
Chlor a	0.05	0.23

Model: THMFP PR>F = 0.0001 R^2 = 0.90
Log Fraction Remaining

Parameter	Estimate	PR>T
Time*Dose	-0.001	0.0001

Model: THMFP PR>F = 0.0001 R^2 = 0.89
Log Fraction Remaining

Parameter	Estimate	PR>T
Intercept	-0.044	0.51
Time	0.001	0.20
Dose	0.013	0.27
Time*Dcse	-0.001	0.0001

Model: Chlorophyll a PR>F = 0.0001 R^2 = 0.73
Log Fraction Remaining

Parameter	Estimate	PR>T
Intercept	0.78	0.0408
Time	-0.02	0.0001
Dose	-0.17	0.0045

Model: DCOC PR>F = 0.15 R^2 = 0.12
Log Fraction Remaining

Parameter	Estimate	PR>T
Intercept	0.14	0.14
Chlor a	0.002	0.15

Model: DCOC PR>F = 0.11 R^2 = 0.24
Log Fraction Remaining

Parameter	Estimate	PR>T
Intercept	0.081	0.41
Chlor a	0.002	0.11
Time	0.002	0.13

Model: Ozone Residual PR>F = 0.27 R^2 = 0.18

Parameter	Estimate	PR>T
Intercept	-0.5741	0.01
Time	0.0042	0.35
Time*Dose	0.0002	0.75

Model: Ozone Residual PR>F = 0.10 R^2 = 0.18

Parameter	Estimate	PR>T
Intercept	-0.574	0.01
Time	0.005	0.10

CSTR MODELS

Model: Ozone Residual PR>F = 0.0001 R^2 = 0.98

Parameter	Estimate	PR>T
Dose	0.824	0.0001
Dose*Time	0.009	0.0001
Dose*pH	-0.095	0.0001

Model: Decrease in THMFP PR>F = 0.004 R^2 = 0.40

Parameter	Estimate	PR>T
Time	0.016	0.004

Model: Decrease in THMFP PR>F = 0.72 R^2 = 0.14

Parameter	Estimate	PR>T
Intercept	0.55	0.63
pH	-0.05	0.73
Time	0.0003	0.98
Dose	-0.285	0.45
Ozone Residual	0.189	0.40

Model: Decrease in THMFP PR>F = 0.85 R^2 = 0.41

Parameter	Estimate	PR>T
Intercept	-2.50	0.89
pH	0.70	0.85
Time	-0.01	0.70
Dose	-0.16	0.57
Residual	0.32	0.55
Alkalinity	-0.02	0.72
Alk.*Alk.	0.00	0.85
pH*Alk.	-0.002	0.93
Dose*Alk.	0.001	0.49
Residual*Alk.	-0.002	0.68
Time*Alk.	0.000	0.56

Model: Decrease in THMFP PR>F = 0.87 R^2 = 0.40

Parameter	Estimate	PR>T
Intercept	-6.10	0.89
pH	2.44	0.86
Time	-0.04	0.65
Dose	-0.47	0.55
Residual	0.80	0.61
Alkalinity	-0.05	0.78
pH*pH	-0.21	0.85
pH*Dose	0.07	0.53
pH*Residual	-0.10	0.67
pH*Alk.	0.006	0.78
pH*Time	0.007	0.63

Model: Decrease in THMFP PR>F = 0.90 R^2 = 0.37

Parameter	Estimate	PR>T
Intercept	-5.28	0.76
pH	0.84	0.81
Time	-0.03	0.55
Dose	0.07	0.81
Residual	3.27	0.77
Alkalinity	-0.008	0.87
Residual*pH	-0.287	0.90
Residual*Dose	-0.21	0.31
Residual*Residual	0.013	0.97
Residual*Alk.	0.005	0.89
Residual*Time	0.005	0.84

Model: Decrease in THMFP PR>F = 0.84 R^2 = 0.36

Parameter	Estimate	PR>T
Intercept	-6.24	0.71
pH	1.02	0.75
Time	-0.03	0.52
Dose	0.98	0.78
Residual	2.13	0.33
Alkalinity	-0.01	0.81
Dose*Dose	0.00	
pH*Dose	-0.20	0.77
Dose*Residual	-0.22	0.44
Dose*Alk.	0.004	0.75
Dose*Time	0.002	0.82

Model: Decrease in THMFP PR>F = 0.97 R^2 = 0.28

Parameter	Estimate	PR>T
Intercept	7.73	0.66
pH	-1.67	0.65
Time	-0.01	0.99
Dose	0.31	0.47
Residual	-1.05	0.35
Alkalinity	0.02	0.71
pH*Time	0.03	0.86
Time*Time	-0.003	0.33
Time*Dose	-0.007	0.73
Time*Residual	0.030	0.48
Alkalinity*Time	0.000	0.93

Model: Decrease in DCOC PR>F = 0.03 R^2 = 0.25

Parameter	Estimate	PR>T
Ozone Residual	-4.59	0.03

Model: Decrease in DCOC PR>F = 0.13 R^2 = 0.77

Parameter	Estimate	PR>T
Intercept	-184.56	0.77
pH	38.27	0.78
Time	0.92	0.47
Dose	3.08	0.77
Residual	-19.92	0.33
Alkalinity	0.10	0.96
Alk.*Alk.	0.004	0.72
pH*Alk.	-0.19	0.77
Dose*Alk.	-0.02	0.74
Residual*Alk.	0.17	0.28
Time*Alk.	-0.007	0.38

Model: Decrease in DCOC PR>F = 0.75 R^2 = 0.48

Parameter	Estimate	PR>T
Intercept	-473.22	0.75
pH	161.30	0.75
Time	3.19	0.37
Dose	7.96	0.77
Residual	-71.19	0.22
Alkalinity	-2.14	0.71
pH*pH	-12.98	0.75
pH*Dose	-1.12	0.76
pH*Residual	10.62	0.23
pH*Alk.	0.27	0.70
pH*Time	-0.47	0.36

Model: Decrease in DCOC PR>F = 0.13 R^2 = 0.77

Parameter	Estimate	PR>T
Intercept	-130.26	0.75
pH	27.86	0.72
Time	-1.47	0.19
Dose	-2.82	0.67
Residual	93.12	0.72
Alkalinity	-0.38	0.74
Residual*Residual	-14.31	0.15
Residual*pH	-18.50	0.72
Residual*Dose	4.02	0.38
Residual*Alk.	0.17	0.85
Residual*Time	1.42	0.05

Model: Decrease in DCOC PR>F = 0.14 R^2 = 0.72

Parameter	Estimate	PR>T
Intercept	-127.11	0.77
pH	18.29	0.82
Time	-1.40	0.23
Dose	34.91	0.69
Residual	21.63	0.68
Alkalinity	-0.13	0.91
Dose*Dose	0.00	
pH*Dose	-2.86	0.87
Dose*Residual	-9.54	0.19
Dose*Alk.	-0.06	0.85
Dose*Time	0.68	0.02

Model: Decrease in DCOC PR>F = 0.36 R^2 = 0.66

Parameter	Estimate	PR>T
Intercept	435.71	0.35
pH	-84.50	0.39
Time	-8.58	0.63
Dose	13.93	0.23
Residual	-64.73	0.05
Alkalinity	1.04	0.49
pH*Time	2.10	0.60
Time*Time	-0.06	0.46
Time*Dose	-0.26	0.65
Time*Residual	1.47	0.21
Alkalinity*Time	-0.027	0.66

Model: Dec. in Chlor. a PR>F = 0.0001 R^2 = 0.85

Parameter	Estimate	PR>T
Time	2.42	0.0001
pH	-15.83	0.0001
Ozone Dose	8.06	0.0001

Model: Dec. in Chlor. a PR>F = 0.003 R^2 = 0.93

Parameter	Estimate	PR>T
Intercept	347.13	0.56
pH	-88.89	0.49
Time	1.63	0.18
Dose	12.75	0.22
Residual	-6.36	0.73
Alkalinity	0.79	0.63
Alk.*Alk.	-0.005	0.66
pH*Alk.	0.16	0.80
Dose*Alk.	-0.001	0.98
Residual*Alk.	-0.05	0.71
Time*Alk.	0.01	0.13

Model: Dec. in Chloro. a PR>F = 0.004 R^2 = 0.93

Parameter	Estimate	PR>T
Intercept	813.28	0.57
pH	-267.17	0.58
Time	-2.09	0.54
Dose	13.71	0.60
Residual	15.66	0.77
Alkalinity	3.92	0.49
pH*pH	16.76	0.66
pH*Dose	-0.02	1.00
pH*Residual	-4.65	0.57
pH*Alk.	-0.42	0.54
pH*Time	0.78	0.14

Model: Dec. in Chloro. a PR>F = 0.0005 R^2 = 0.96

Parameter	Estimate	PR>T
Intercept	-5.14	0.99
pH	-9.43	0.91
Time	4.09	0.01
Dose	6.06	0.41
Residual	236.38	0.40
Alkalinity	-0.36	0.77
Residual*Residual	3.67	0.71
Residual*pH	-60.50	0.29
Residual*Dose	5.22	0.30
Residual*Alk.	1.30	0.19
Residual*Time	-0.79	0.26

Model: Dec. in Chloro. a PR>F = 0.009 R^2 = 0.87

Parameter	Estimate	PR>T
Intercept	-164.96	0.82
pH	10.81	0.94
Time	3.57	0.10
Dose	-36.77	0.81
Residual	9.09	0.92
Alkalinity	-0.33	0.87
Dose*Dose	0.00	
pH*Dose	9.32	0.75
Dose*Residual	0.74	0.95
Dose*Alk.	-0.16	0.74
Dose*Time	-0.35	0.43

Model: Dec. in Chlor. a PR>F = 0.0002 R^2 = 0.97

Parameter	Estimate	PR>T
Intercept	-792.47	0.05
pH	142.79	0.09
Time	33.01	0.04
Dose	-5.25	0.54
Residual	40.05	0.11
Alkalinity	-2.60	0.05
pH*Time	-6.19	0.07
Time*Time	0.01	0.90
Time*Dose	0.68	0.15
Time*Residual	-1.76	0.07
Alkalinity*Time	0.10	0.06

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