

COLOR REMOMAL FROM CHURCHILL RIVER WATER
USING
OZONATION, SAND FILTRATION AND CARBON ADSORPTION

BY

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BY

PAUL BARSALOU

A thesis submitted to the Faculty of Graduate Studies of
the University of Manitoba in partial fulfillment of the requirements
of the degree of

MASTER OF SCIENCE

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ABSTRACT

A water treatment process composed of an ozone reactor, a rapid sand filter and a granular activated carbon filter, was employed to reduce the color of Churchill's drinking water supply. Bench scale treatment tests were performed monthly over a 1 year period, while operating parameters such as ozone dosages and residence times were varied. In order to compare treatment efficiencies and to simulate conditions at the treatment facility in Churchill, testing was conducted at 25°C and at 4°C.

Using the results from this study and an extensive literature review, it was concluded that ozone and a granular activated carbon filter reduce color to a greater degree than a carbon filter by itself. A reduction in temperature from 25°C to 4°C or a reduction in empty bed contact times from 20 minutes to 10 minutes in the filter were each shown to decrease the quality of the treatment effluent. This treatment train reduced the apparent color of the raw Churchill River water to below Canada's aesthetic objective limit of 15 color units, in all months except May.

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CHAPTER 1

INTRODUCTION

1.1 PROBLEM

New hydroelectric projects have the benefit of generating electricity for society but in so doing the landscape and drainage patterns in the watershed are altered either permanently or temporarily. This change in drainage patterns affects the local residents to varying degrees; from flooding fishing grounds to decreasing the water quality in a river. As one part of society benefits from electricity generation other segments of the population are adversely affected. If the hydroelectric project produces these negative effects an attempt must be made to mitigate the problem so that people do not have to alter their lifestyle unnecessarily.

The Churchill River Diversion, completed in 1977, reduced the average flow through the Churchill River by approximately 60 %. A dam at Missi Falls raised the level of Southern Indian Lake by approximately 10.6 m and limited the flow through the Churchill River. The diverted water flows out the south end of Southern Indian Lake through a man made channel to the Rat River, which subsequently empties into the Nelson River. Manitoba Hydro found it more economical to divert the water and use it for electricity generation on the Nelson River than to build dams on the Churchill River.

During spring melts, the wetlands surrounding the Churchill River overflow and drain. With a reduced flow in the Churchill River, the concentrated humic materials from

the wetlands are no longer diluted to the same extent as before the diversion. For this reason the water quality in the Churchill River has decreased, causing problems for people using the Churchill River as a source of drinking water.

Since the town of Churchill used the Churchill River as its primary source of drinking water, Manitoba Hydro was responsible for providing a water treatment plant. Unfortunately, the alum coagulation plant installed in Churchill was unable to reduce the color of the water to an acceptable level during these spring melt periods. For this reason Manitoba Hydro is investigating alternate methods of treatment, including a process of ozonation, sand filtration and granular activated carbon adsorption.

1.2 OBJECTIVES

The main objective of this research project was to reduce the color of Churchill's raw drinking water using a bench scale water treatment plant. The processes of ozonation, sand filtration and granular activated carbon adsorption were used for 12 consecutive months to determine the effects of treatment during all 4 seasons. The apparent color removal, efficiency was investigated while varying the empty bed contact time (EBCT) between 10 minutes and 20 minutes, the ozone dosages between 0 mg/l and 6 mg/l and the temperature between 40c and 250c. The effect of the treatment process on other parameters such as total organic carbon (TOC), alkalinity and turbidity were also evaluated.

1.3 SCOPE

The University of Manitoba project was sponsored by Manitoba Hydro in order to find an alternate water treatment process which would decrease the color of Churchill's drinking water to a greater degree than the existing alum coagulation process. It was also important to eliminate the low alkalinity problem during the summer.

In order to accomplish the objectives, a laboratory study was performed over a twelve month period. Raw Churchill River water samples were transported to Winnipeg on a monthly basis so that seasonal changes could be observed. The tests were performed monthly with minimum delay so the water quality characteristics would undergo little change during storage.

The experimental apparatus, discussions and conclusions presented in this thesis have been based on an extensive literature review, experimental data, conversations with professors and other engineers and the author's knowledge of water treatment. Attempts were made to keep the experimental apparatus and procedures constant over the testing period. Since the experiment took place in a location distant from the source of the test water, limited quantities of sample water were transported and tested.

CHAPTER 2

LITERATURE REVIEW

2.1 HUMIC MATERIALS

Humic materials are naturally occurring organic constituents found in surface water, ground water and soils (Amy et al, 1986). These humic materials are actually composed of humic acids, fulvic acids and humins (Josephson, 1982).

Humic substance are amorphous, acidic, predominantly aromatic, hydrophillic, chemically complex polyelectrolytes that range in molecular weight from a few hundreds to tens of thousands (Edwards and Amirtharajah, 1985).

The three different groups can be separated by solubility test in alkali and acid solutions. Humic acid is soluble in alkali solutions but insoluble in acid solutions, fulvic acid is soluble in both alkali and acid solutions and humins are insoluble in both alkali and acid solutions (Edwards and Amirtharajah, 1985). Although the humic materials may be classified according to solubility, their overall molecular structures are a mystery. The structure of each group of humic molecules vary in shape, size and composition (Josephson, 1982).

A study of natural surface waters by Amy et al (1986) in the United States found that approximately 50 % of the soluble organic carbon in water was from humic materials. Of these humic materials fulvic acid was found to be the most predominant, followed by humic acid and humins. Humic

materials are created naturally as wood and leaves decay. In surface water, their origin may be traced to decaying aquatic plants or to run off that has leached the humics out of the surrounding soils. Humics are generally found to be highly concentrated in bogs, marshes and muskeg. When these wet, low lying areas become flooded during a spring melt, the waters rise and drain into local streams or rivers, causing a sudden increase in the concentration of humic materials.

In the natural environment humic substances tend to stay in solution for long periods of time because they are for the most part refractory. The humics are not degraded biologically and removed from natural water courses as easily as some other organics. Since humics easily capture smaller organic and inorganic materials, such as PCB's, DDT and heavy metals, they may in some instances, accumulate excess pollutants and become dangerous.

2.1.1 Color

There are two main problems which arise when humic materials are found in a drinking water source. These materials impart a yellow brown color to the water, thereby making it unappealing and raising questions in the mind of the consumer about water purity. The second reason is related to trihalomethane production during chlorination, which will be discussed in the next section. For these reasons, humic materials are removed from drinking water whenever possible.

As previously mentioned, the humic concentration in

surface water is usually highest during the spring thaw, but it tapers off over the summer months and is at a minimum in the winter with ice cover. The color is also affected by the pH change over the year. With high run off or rain, the existing alkalinity in the water is diluted, causing a decrease in the pH and a decrease in color. If an alkali solution was added to a colored water, the pH would increase and the color would increase significantly.

Color may be measured as true color or apparent color. True color is determined with no pretreatment of the water samples but true color is determined only after the samples have been centrifuged to remove the interfering turbidity or particulate matter. In most good quality surface waters, the apparent color and true color are very similar because the main color causing components are dissolved humic materials, not suspended substances. Some industrial or polluted waters may have suspended solids accounting for the majority of the color, while dissolved substances impart only a fraction of the apparent color (Standard Methods, 1989).

The natural coloration caused by humic materials is generally measured by visual comparison with standards of known color units. One color unit is equal to 1 mg/liter of platinum in the form of chloroplatinate ions. Cobalt ions are added to adjust the hue or tint of the solution to match the water in question. The standard solutions can be used to produce glass color comparison disks which are used much more rapidly for color determination.

A second method for color determination is performed spectrophotometricly. The absorbence of the test water is determined at a number of different wavelengths. This method is more suited for waters colored by industrial pollutants than for natural waters colored by humic materials.

2.1.2 Trihalomethanes

During chlorination of water for disinfection, superchlorination or other purposes, humic materials play an important role in forming trihalomethanes (Oliver and Visser, 1980). Attempts are made to remove organics such as humic materials because they react with chlorine to form carcinogenic trihalomethanes such as chloroform(CHCl_3). In recent years there has been increased concern over trihalomethanes in drinking water so researchers are trying not only to remove more organics, but also using different methods of disinfection which do not create trihalomethanes.

A study done by Abdullah et al (1987) found that not all humic materials produced trihalomethanes to the same extent. They found that trihalomethanes were formed primarily from the reaction of chlorine and humic acids with a molecular weight below 40,000, which represents the low and medium weight fraction of humic material.

2.1.3 Removal Methods

There are many conventional water treatment methods which remove humic material such as alum coagulation, but there is

also a relatively new process of ozonation and carbon adsorption. The conventional coagulation methods are based upon chemical and physical reactions (Abdullah, 1987). For instance, alum is rapidly mixed into the treatment water, an aluminum hydroxide precipitate forms and the color particles attach themselves to the settling flocs, thereby reducing the color. The ozonation and adsorption process tends to reduce the size of the color particles by oxidation so that the activated carbon has an easier time adsorbing the organics. This process will be explained fully in a later section.

2.2 OZONE

2.2.1 Historical Background

Ozone and its smell has been recognized for millennia but it was not until 1906 that it was harnessed for use in a water treatment plant in Nice, France. It was initially used as a disinfectant for the city but its other uses and benefits soon became known. It is now used in over a 1000 water treatment plants all over the world as a disinfectant, and for taste, odour, and color reduction. France, Switzerland and Germany are the three countries which use ozone technology the most; partly because, unlike chlorine, ozone is considered to be a "superior" disinfectant which does not adversely change the taste or smell of water.

2.2.2 Properties

Ozone or tri-atomic oxygen is an unstable blue gas having

a strong characteristic odour. It becomes a liquid at -112°C and freezes at -193°C at atmospheric pressure (Rice and Netzer, 1982). The blue color is seldom seen since the gas is generally produced and used in low concentrations. Both the dark blue liquid and the light blue gas are explosive when ozone constitutes at least 20 % of an exclusively oxygen-ozone mix. These explosions may be initiated by many things such as: changes in pressure or temperature, sparks, catalysts and even the presence of some organic matter (Rice and Netzer, 1982). Since this concentration of ozone is difficult to generate there is little danger of explosions with conventional generators.

Ozone is approximately 13 times as soluble as oxygen in water at standard pressure in the temperature range of 0°C to 30°C . When in the atmosphere or in aqueous solution its half life may vary from seconds to hours. Whether ozone is in water or gas, the half life increases as the pollutant concentration in the carrier fluid decreases. For instance, ozone has a much longer half life in nitrogen gas or distilled water than it does in smog or wastewater. A halflife is the time it takes for 50 % of a substance such as ozone to decompose.

The unstable gas is naturally produced photochemically high up in the earth's stratosphere but it exists in very low concentrations in the lower atmosphere. The chlorofluorocarbons released into the atmosphere by man are catalyzing the destruction of ozone in the high atmosphere

where it is needed and increasing the ozone concentration in the low atmosphere where it is considered a pollutant.

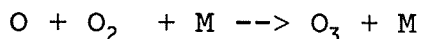
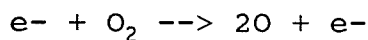
In addition to photochemical generation, ozone is also produced in lightning storms and it is generated electrically by humans for various uses. The generation of ozone is dependant upon many parameters such as pressure, temperature, composition of the surrounding gas and the dew point of the generation gas.

2.2.3 Ozone Generation

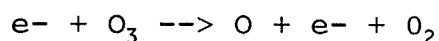
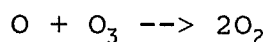
Ozone is produced by humans both intentionally with generators and unintentionally in many electrical appliances or through photochemical action on smog. The electricity travelling through objects such as motor brushes, faulty light switches, high voltage power lines and even photocopying machines produces ozone; albeit in small quantities (Rice and Netzer, 1982). Specially designed electrical generators are used to produce ozone in usable concentrations and in quantities needed for water treatment or industrial uses.

The method commonly used for the creation of ozone is called corona discharge. There are a number of proposed routes for the ozone production reaction but only one path is dominant. The path given by Rice and Netzer (1982) is shown below. The electrons (e^-) coming from the corona discharge collide with diatomic oxygen (O_2) breaking it up into two molecules of molecular oxygen (O) and the initiating electron departs at a lower energy level. The ozone is then produced

by a three body collision between molecular oxygen, diatomic oxygen and any other gas molecule (M).



As mentioned earlier, ozone is relatively unstable so newly produced ozone naturally decomposes back to its original form of diatomic oxygen. In decomposition reactions, either molecular oxygen reacts with ozone to produce two molecules of diatomic oxygen or an energetic electron collides with existing ozone causing it to decompose back to diatomic oxygen, molecular oxygen and the initiating electron. These two decomposition reactions are shown below (Rice and Netzer, 1982).



Since ozone is unstable, its rate of production is actually equal to the rate of ozone produced by the corona minus the ozone destroyed in the corona. The rate of decomposition in the generator is dependent upon many parameters such as temperature and the power density in the corona, so the rate may vary greatly.

2.2.3.1 Electrical Generation

Ozone can be formed in a corona discharge which is,

characterized by a low current electrical discharge across a gas-filled gap at a voltage gradient on the order of the sparking (electrical breakdown) potential of the gap, (Rice and Netzer, 1982).

During discharge, the gas becomes partially ionized; giving off a blue glow. Ozone is produced in this partially ionized gas.

The corona is created with two metallic electrodes that are separated by a small gap with one of the surfaces coated with a dielectric material. Oxygen or air is forced through this gap as a voltage is applied to the electrodes. Energetic electrons cross the dielectric and induce the ozone production and decomposition reactions mentioned earlier. A simple diagram showing the arrangement of a corona cell is given in Figure 1.

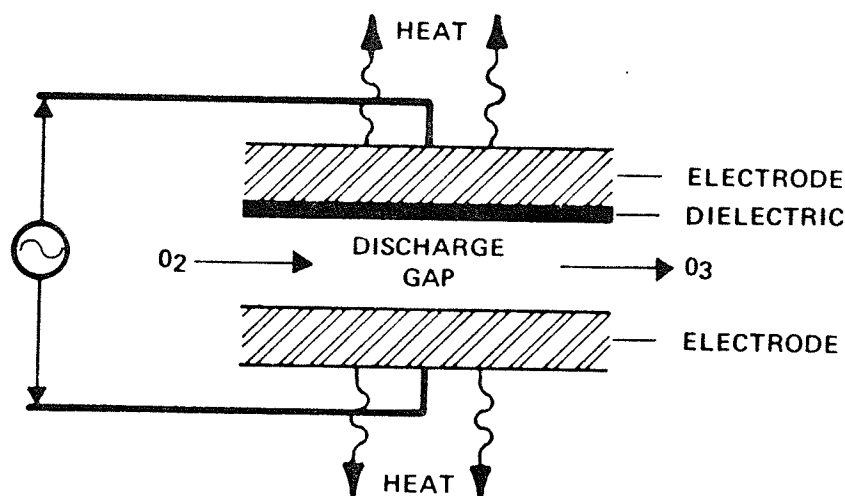


Figure 1: Typical corona cell configuration (Rice and Netzer, 1982).

Ozone generation is inefficient since most of the energy used goes into heat generation with lesser amounts going to ozone generation, light and sound production. Today's generators may vary somewhat in efficiency but the majority of the energy still leaves as heat.

Most generators have corona plates configured either as concentric tubes or flat parallel plates. The design parameters of voltage, capacitance of the discharge plates, the power used and the frequency of alternating current, will not be discussed in depth but certain related items will be mentioned. The main parameters which may be altered in either the tube generators or the plate generators, are the thickness of the dielectrics, the frequency of current modulation and the voltages.

Dielectrics generally range from .5 mm to 3 mm thick and are usually composed of glass or ceramic, laminated onto a metal electrode (Rice and Netzer, 1982). The separation of the plates varies from about 1 mm to 3 mm. The small separation is sometimes difficult to achieve evenly. The generator is easily damaged as the plates may get out of alignment or the dielectric may fail. If the plates are pushed closer together, there will be an increased current flow, causing "hot spots" with subsequent dielectric failure or damage. Typical voltages between the plates range from under 100 volts to over 10,000 volts (Rice and Netzer, 1982).

An ozone generator may be designed for maximum efficiency but unless the electrodes and the gas for ozone production are kept cool, the ozone will decay rapidly back to oxygen in the generator. As the gas in the corona discharge gap is ionized, large amounts of heat are produced. For this reason, the electrode plates must be thin so the heat within the gas may be conducted through the electrodes and out to the cooling

system. At temperatures above 40°C it has been suggested that the ozone decomposition reactions dominate over the ozone production reactions, emphasizing the importance of cooling (Rice and Netzer, 1982). It is generally less expensive to cool the generator than to pay for extra generating capacity, in order to compensate for ozone decomposition.

Ozone production is drastically reduced by humidity and dirt in an ozonator feed gas. When pure oxygen is the feed gas it does not have to be further dried or filtered since the water vapour and dirt is removed in the gas separation process, thereby reducing the dew point of the gas to well below -60°C . Before air is used for generation it must be filtered for dirt and dried with desiccators to reduce the dew point to between -40°C and -60°C . Approximately half as much ozone is produced in air with a dew point of -20°C as is produced in air with a dew point of -60°C .

The increase in ozone yield usually more than compensates for the additional cost of drying the feed gas to such low dew points (Rice and Netzer, 1982).

Depending upon the operating parameters of the ozonator and the efficiency of design, between 1 % and 3 % of ozone is produced by weight in the air and between 2 % and 6 % of ozone is produced in pure oxygen (Rice et al, 1985). The ozonators are then rated by kilograms of ozone produced per kilowatt hour of power consumed by the machine in ozone generation with a given set of parameters. For an ozonator, the ozone production can be altered by varying not only the volume of

gas flowing through the machine but also the pressure of the gas.

2.2.3.2 Other Methods of Ozone Generation

Ozone can also be produced with experimental methods such as ultraviolet radiation and the electrolysis of water. These two methods do produce ozone but at the moment they are not used commercially due to their low yield or their high energy consumption.

Ultraviolet radiation is produced with high energy lamps sending out short wavelength ultraviolet (UV) light. These high energy photons cause photochemical reactions with oxygen, changing it into ozone and other byproducts. At certain wavelengths, UV light is an ideal initiator for the ozone generation reaction. Although the UV light works well, it is difficult to produce the correct wavelength of UV light with any efficiency. Commercially available UV lamps are between .6 % and 1.5 % efficient at producing UV light at the 185 nm wavelength needed to initiate the photochemical reaction (Rice and Netzer, 1982). As the lamps become more efficient the popularity of the method will likely increase greatly.

Generation of ozone through the electrolysis of water is the second experimental method being investigated recently. It is different from the other methods since it generates ozone from a combination of water and oxygen instead of exclusively oxygen gas. At the anode water is transformed into ozone and at the cathode water is produced. The main

advantage of this method is the air feed does not have to be dried in desiccators or filtered. This method has produced ozone concentrations of 30 % to 50 % by mass in oxygen in experiments, but it is still a technology that is more expensive than corona discharge. Because of the high concentration of ozone produced, this method may have special uses despite its increased cost.

2.2.4 Toxicological Effects on Plants and Animals

Although ozone is very useful in water treatment, it is difficult if not dangerous to handle when proper precautions are not taken. In treatment plants there should be detectors and alarms which sound when there are high ozone concentrations in the atmosphere of the plant. Many European plants have detectors in every room which are set to start exhaust fans that rapidly transfer the polluted air to a different location.

Human beings are able to detect ozone at concentrations as low as .01 ppm in air (Rice et al, 1985). Brief exposures to low concentrations are harmless but high concentrations are deadly to humans and other animals as well as plants. Exposure to 1.5 ppm to 2.0 ppm of ozone for a two hour period can effect humans by causing:

...dryness of throat, constrictive chest pains, lessening of mental ability, difficulty in coordinating and articulating, loss of appetite, coughing and 13 percent loss of vital capacity (Rice et al, 1985).

Although ozone harms the body it does not cause carcinogenic,

mutagenic or chromosomal aberrations (Rice et al, 1985).

Ozone has been found to harm agricultural crops. It has been observed that farm crops in areas, high in ozone pollution, are stunted when compared to crops in areas without the ozone pollution. Ozone pollution can be created in the lower atmosphere by photochemical action on smog or by ozone water treatment plants which do not destroy their excess or off-gas ozone.

2.2.5 Ozone Destruction

Whether a water treatment plant using ozone reuses a portion of its off-gas or not, the off-gas should really be treated before it is released into the atmosphere. There are a number of methods which may be used to decrease the ozone concentration and increase the safety of discharging ozonated gas into the atmosphere, such as: catalytic decomposition, heat decomposition, reuse of off-gas, dilution of off-gases and adsorption.

Reusing the off-gas as a method of preozonation serves two purposes. It not only saves money by using as much of the expensively produced ozone as possible but it also decreases the cost of treating the off-gas before releasing it back into the atmosphere. This is not a complete treatment process employed to remove all ozone, but a method of partial treatment which may be used economically with one of the following methods.

Catalytic decomposition, heat decomposition and activated

carbon adsorption are three methods of reducing ozone back to its original form, oxygen gas. The ozone gas is passed through catalysts consisting of palladium, manganese and nickel, whereby ozone decomposes at an accelerated rate. Activated carbon acts in a similar fashion. The ozonated gas flows through an activated carbon filter where the ozone adsorbs and decays at an accelerated rate. Heat treating the off-gas is currently the most common method of ozone destruction throughout the world. The gas is heated and depending upon the temperature and residence time, the ozone decomposes partially or completely. For instance, when heated to 300°C for 1 to 2 seconds there is 100 % decomposition and at 230°C there is only 92 % to 95 % decomposition within 1 minute (Rice and Netzer, 1982).

Another method of off-gas treatment used is dilution with massive quantities of air. Instead of destroying the ozone this "bandaid" solution just spreads the pollution around. To reduce the ozone concentration of a typical off-gas to below .1 ppm, the dilution would have to be with between 5,000 and 10,000 volumes of air. After secondary use of off-gas with subsequent removal of ozone, the dilution factor could be reduced significantly to a more acceptable level.

2.2.6 Kinetics of Ozonation

The reaction kinetics of ozone and solutes in an aqueous solution is quite simple for pure solutions but as the concentration and type of solutes increase so does the

complexity. In a gas environment, ozone reacts directly but in solution, the kinetics become more complex with combinations of direct and indirect reactions. The following section will give generalized kinetics without touching upon the very complex reactions. It is important to understand the parameters that regulate the reaction mechanism in order to use ozone in the best application.

In conventional ozone treatment small dosages of ozone are applied for partial oxidation. At these low dosages, the pollutants generally are not oxidized to end products such as carbon dioxide, water, nitrates and sulphates. With extended ozonation, full mineralization would likely occur, but this is much too expensive for water treatment plants. Some simple solutes may oxidize fully in one step but most organic solutes only get broken up into daughter products on the first oxidation. With extended ozonation the daughter products may in turn become oxidized into further byproducts before full oxidation.

Full oxidation is not necessary in conventional water treatment. Generally one or two oxidations completely changes the characteristics of the target pollutant. In the case of color removal, a simple splitting of the humic molecule might be all that is needed to help with removal.

Once dissolved in water, ozone can follow a number of different reaction pathways. The ozone may react with a solute, it may decompose into another substance which may subsequently react with a solute or it may escape the solution

untouched (Hoigne and Bader, 1976). The path followed depends upon many parameters such as: pH, alkalinity, quantity and type of solutes present.

The direct reaction of ozone with a solute is highly selective and slow by comparison to the radical type reaction. The reaction between the radical produced by decomposition of ozone, with a solute is extremely fast and nonselective. Direct reactions oxidize specific pollutants but the indirect reactions will oxidize almost any solute. The type of oxidation, specific or nonspecific, relies primarily on the rate of decomposition of ozone into radicals.

Ozone decomposes at an accelerated rate as the pH of a system increases or as the concentration of hydroxide ions (OH^-) increases. It becomes more stable at a low pH or at a low OH^- concentration (Gurol and Singer, 1982). If the designers of an ozone reactor wanted to oxidize solutes in a relatively nonselective manner, they could, under special circumstances increase the pH before treatment. On the other hand, the pH could be decreased in order to increase selective oxidations and to increase the ozone half life.

Once ozone decomposes it forms a number of different radicals, of which the hydroxyl radical (OH^\bullet) is the most important. An OH^\bullet radical is one of the most reactive substances found in water, consumed in a reaction within microseconds of being formed. Other radicals playing roles in ozone decomposition are the perhydroxyl radicals (HO_2^\bullet) which disassociates into the superoxide radicals O_2^\bullet (Rice and

Netzer, 1982). These may contribute to oxidations after initial ozone oxidations and the rapid OH^\bullet reactions. As these radicals form they tend to cause chain reactions among themselves and with ozone, initiating ozone decomposition (Hoigne and Bader, 1981). The more radicals formed, the faster ozone decomposes to form radicals, fueling the chain reaction decomposition (Yurteri, 1989).

Both bicarbonate and carbonate ions are considered to be inhibitors which scavenge for OH^\bullet radicals. The inhibitor rapidly consumes OH^\bullet before the radical has a chance to induce further decomposition of ozone. With less radical decomposition initiators in solution, the ozone is not attacked as rapidly and it decomposes at a slower rate. In addition to the alkali scavengers, the three phosphate ions such as H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} act to protect ozone against radicals.

The different reaction mechanisms are illustrated in Figure 2 below. R stands for one of the less important radicals formed after ozone decomposition and S is a scavenger being oxidized.

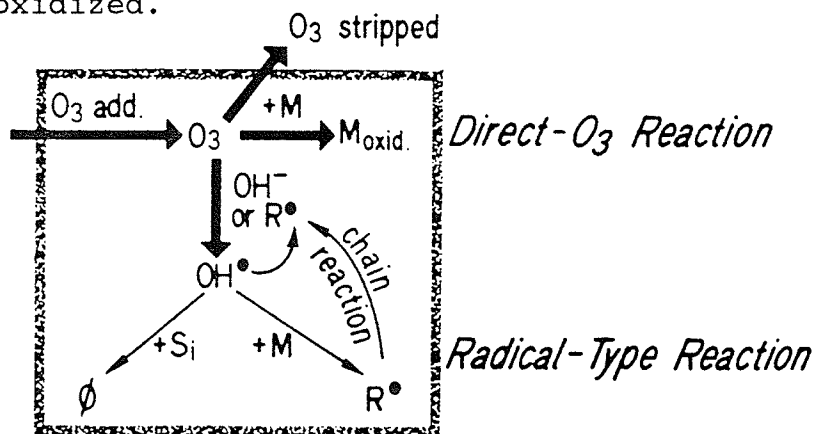


Figure 2: Ozone reaction pathways (Rice and Netzer, 1982).

2.2.6.1 Kinetic Reaction Models

Direct Oxidation by Ozone

Direct oxidation of solutes to a stable end product may take one or many ozone molecules. In the equations below, the variable n represents the stoichiometric factor for the number of molecules M oxidized, for every ozone molecule consumed. The variable K_0 is the rate constant for ozone consumption, K_1 is the overall rate constant, including the stoichiometry and R_1 is the reaction rate.

$$K_1 = n K_0$$

The overall reaction rate then becomes:

$$R_1 = n K_0 [O_3][M]$$

$$R_1 = K_1 [O_3][M]$$

In the case where there is an adequate supply of ozone and oxidizable solutes, the reaction rate is second order, relying on both the concentration of ozone and solute. The order changes if there is either a severe shortage or a great surplus of either substance. In raw wastewater there would be a great supply of oxidizable solutes but a limited supply of ozone in comparison. This changes the reaction to first order since the ozone is consumed almost immediately upon addition. This reaction can be represented by:

$$R_1 = K_1 [O_3]$$

Similarly, a system with surplus ozone but little solutes is also first order, relying upon the concentration of solute.

$$R_1 = K_1 [M]$$

The reaction rate constant of ozone and solutes cannot

be measured without taking precautions against interference from secondary reactions with hydroxyl radicals. The radicals must be eliminated or decreased in number during the measurements, with the use of scavengers such as phosphate buffers or carbonate ions and bicarbonate ions. As previously mentioned, these ions combine with the radicals, forming byproducts which do not support the chain reaction decomposition of ozone. Reaction rate constants for the ozone reaction range from less than $.05/\text{mole} \cdot \text{second}$ for acetic acid and urea to over $2 \times 10^5/\text{mole} \cdot \text{second}$ for 1-Hexene-4-ol.

Ozone oxidizes some compounds more readily than others, depending upon the bonding and chemical characteristics of the molecule. Ozone rapidly attacks the double $\text{C}=\text{C}$ bonds which can be found in many compounds such as olefines and humic acids. Unlike hydroxyl radical reactions, the reaction rate of ozone and different solutes varies greatly (Rice and Netzer, 1985).

Indirect Oxidation By OH° Radicals

Hydroxyl radicals rapidly oxidize solutes with very little selectivity. Many of the solutes which have extremely low reaction constants when being oxidized by ozone, have large reaction constants when being oxidized by hydroxyl radicals. Tests measuring the decomposition of ozone in drinking water have shown that about .5 moles of OH° radicals are produced for every mole of decomposed ozone (Rice and Netzer, 1985). Once the hydroxyl radicals are created kinetic

equations can be used to describe the secondary oxidations. The reaction kinetics are shown below, with R2 being the reaction rate and K2 the reaction rate constant.

$$R2 = K2 [M][OH]$$

Most of these reaction rate constants for K2 are in the 10^9 to 10^{10} /mole*second range but some low weight organics such as urea have rate constants as low as 10^{-6} (Rice and Netzer, 1985). In order to keep the variables consistent with the direct oxidation reactions, the equation was changed to include the ozone concentration.

$$R2 = K3 [M][O_3]$$

The rate constant K3 incorporates the decomposition of ozone in water, the oxidation of solutes in a direct oxidation reaction and the rate of the hydroxyl radical reaction with a solute, making it difficult to calculate.

The total oxidation rate of an ozonation system is given below with K_T being the sum of the direct oxidation rate constant and the radical oxidation rate constant. Although the final equation represents all the ozone related reactions, it is more meaningful to look at the direct and indirect reactions separately, while keeping the pH of the water in mind.

$$RT = K1 [O_3][M] + K3 [O_3][M]$$

$$RT = K_T [O_3][M]$$

The half life of ozone in a number of different aqueous environments was plotted in Figure 3 shown below. This figure shows that the half life of ozone in water decreases as the

solute concentration increases. All four lines plotted on the graph showed significant decreased in half life as the pH decreased. Once the pH rises above 10 the half life of ozone in even the purest waters is still less than a minute.

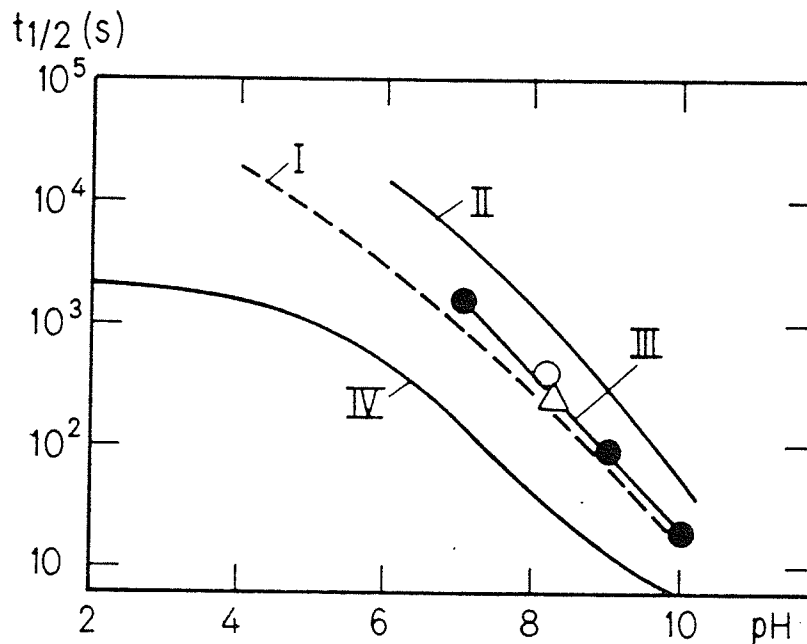


Figure 3: The half life of ozone in a number of different waters. (I) is for distilled water with a phosphate buffer. (II) is for distilled water with 2 mM carbonate and phosphate buffer. (III) is for 70 % Lake Zurich water with various buffers. (IV) is for 70 % municipal wastewater with a borate buffer (Rice and Netzer, 1985).

2.2.6.2 Oxidation of Humic Substances

Recently ozone has been employed in water treatment systems for color removal. The ozone attacks the unsaturated double carbon-carbon bonds and breaks the color molecule or humic material into smaller pieces. It rapidly cleaves the unsaturated groups, leaving ketones, aldehydes and acids, depending upon the concentration of ozone and the ozonation period (Rice et al, 1985). Once the humic substance has been

oxidized and the molecule is broken up, the color is reduced. The smaller molecules are more easily removed from solution by adsorption than are the larger molecules.

With the low ozone dosages used in water treatment one would not expect much of a total organic carbon (TOC) reduction. In fact, studies found very little change in TOC with low ozone dosages. Grasso et al (1989) reports that ozone dosages of .75 mg/l tended to increase TOC but the increasing effect levelled off at a concentration of 1.5 mg/l.

2.2.7 Trihalomethane Formation Potential

Trihalomethanes are formed when organics are chlorinated, creating potentially dangerous substances in a water supply. Ozone affects the structure of organics, as mentioned in previous sections, so it follows that ozone would also affect the reaction between organics and chlorine.

In small dosages, ozone does not significantly change the organic carbon concentration. On the other hand, high ozone concentrations tend to oxidize more fully, reducing some organics to end products such as: water, carbon dioxide and other stable products. Ozone is rarely applied in this high concentration for conventional water treatment because it is much too expensive.

It appears that the trihalomethane formation potential (THMFP) is affected by ozonation but researchers are not sure exactly how. In a study of 26 measurements taken at laboratories and treatment plants using ozone; 19 showed a

decrease in trihalomethanes with ozone, 6 showed an increase with ozone and 1 had no effect (Rice et al, 1985). In a second study by LePage (1985) the THMFP was found to decrease with ozone dosages but occasionally substantial increases were also observed. The reason for the increase in THMFP in both studies is unknown.

By itself, ozone reduces the organics concentration significantly and has a tendency to reduce the THMFP, but granular activated carbon with or without ozone, reduces the organic concentration drastically, thereby decreasing the THMFP. There are other methods of water treatment beside carbon adsorption, such as coagulation, which also decrease the organic concentrations in water.

2.2.8 Disinfection

One of the benefits of using ozone in water treatment is its excellent disinfecting properties. Ozone rapidly reacts in water creating oxidized products, hydroxyl radicals, hydroperoxyl radicals, superoxide radicals and hydrogen peroxide. The oxidizing ability of most of these substances damages bacterial cells and other microorganisms. The ozone and the radicals formed by ozone decomposition, react quickly so they do not stay in the water system long enough to harm the consumer. The ozone is able to disinfect the water at the treatment plant but the water may become contaminated with disease causing organisms during storage or transportation to the consumer.

It has been reported by Roy et al (1981) that ozone is a much stronger disinfectant than either chlorine or chlorine dioxide. Ozone disinfects as well as the other two chemicals in much shorter periods and at lower concentrations. For instance polio viruses were inactivated with an ozone concentration of .05 mg/liter to .45 mg/liter within 2 minutes but .5 mg/liter to 1.0 mg/liter of chlorine was required to inactivate the viruses in 1.5 to 2 hours (Roy et al, 1981).

Ozone is seldom used as the sole disinfectant for a water distribution network because it does not leave a residual disinfectant. However, ozone can be used in combination with long lasting disinfectants such as chlorine or chlorine dioxide. By using ozone as the initial disinfectant a lower concentration of chlorine can be used as a residual disinfectant, thereby decreasing the chlorine concentration available for trihalomethane formation.

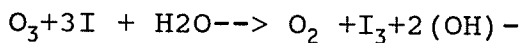
The byproducts of chlorine and organics have been increasingly investigated but there has been little investigation into the products produced from low dosage ozonation of organics. Although it is not expected, the byproducts of ozonation may be as dangerous as trihalomethanes, so further studies must be performed to identify the byproducts.

2.2.9 Ozone Measurement

There are many methods used to determine the concentration of ozone such as: iodometric oxidation,

ultraviolet spectrophotometry, leuco crystal violet, diethyl-p-phenylenediamine (DPD), syringaldazine (FACTS), indigo blue, amperometric bare electrodes and amperometric steady state membrane electrodes (Rice and Netzer, 1982). The sixteenth edition of Standard Methods for the Examination of Water and Wastewater (Standard Methods) recommends the iodometric oxidation method and the seventeenth edition recommends the ultraviolet spectrophotometric method. Both iodometric and spectrophotometric methods will be discussed in addition to the indigo blue method. None of the analytical methods mentioned are ideal for ozone determination in all situations but some are more accurate than others, using less equipment and time. The methods become more refined as ozone becomes more frequently used in the laboratory and in industry so an "ideal" method may arise in the future which may be capable of analyzing the highly reactive and unstable gas without problems.

Iodometric oxidation used to be the preferred method for analysis but the UV spectrophotometric method is now preferred because of greater accuracy over a greater range of concentrations. Standard Methods lists the accuracy of the iodometric method as being $\pm 1\%$, however I think a more realistic value would be closer to 5% . In the iodometric oxidation procedure, gas containing ozone is bubbled into a 2% potassium iodine solution. Oxidation of iodide to iodine and the reduction of ozone to oxygen is shown in the equation below (Gordon et al, 1989).



This equation represents the reaction of ozone with iodide at a neutral pH. Unfortunately, the stoichiometry and products of oxidation changes somewhat as the pH changes, thereby reducing the accuracy of the procedure. The iodine concentration is then determined by one of several methods such as titration with sodium thiosulphate after acidification. The thiosulphate reduces the iodide back to iodine and the ozone is calculated with the assumed stoichiometry and volume of titrant.

Buffers are often added to reduce interferences and to keep the reaction stoichiometry more constant. Various authors suggest different buffers because the buffer may also add to the interferences and change the stoichiometry. Rice and Netzer (1982) suggest using a potassium iodide solution buffered with .1 M boric acid to eliminate inaccuracy. It has been suggested that through buffer addition, when the desired one to one stoichiometry is achieved between ozone and iodide, it is only achieved through a combination of reactions with different stoichiometries (Gordon et al, 1989). With or without buffers, stoichiometries of between .65 and 1.5 have been observed, at a range of pH (Gordon et al, 1989).

In the ultraviolet spectrophotometric method of ozone measurement, ozone is detected by its adsorption of light in the range of wavelengths from 240 nm to 300 nm. The peak absorption point is at 254.7 nm. This method can be used for measurement in both air and aqueous solutions. By using the

Beer-Lambert principles it is possible to measure dissolved ozone down to a concentration of .2 mg/l (Rice and Netzer, 1982). Standard Methods lists this procedure as having an error as low as 1 % in laboratory conditions.

This analytical method also has shortcomings such as; interferences caused by the turbidity and dissolved substances in natural waters. Often dissolved organics, such as humic materials and inorganics, absorb the wavelength of light being measured which result in inaccurate measurements. Even though the measurements of ozone concentrations in raw water may be somewhat inaccurate, this method still provides an online method of measurement which can be very useful. When using pure or relatively pure water, this method gives fast, accurate results.

Another spectrophotometric method of analysis measures the bleaching action of ozone on indigo-blue dye. Below a pH of 3.0, the indigo blue dye is bleached and then tested in a spectrophotometer for its absorbance at 600 nm (Gordon et al, 1989). A known volume of ozonated water is mixed with a known quantity of dye. Therefore, the precision of the test relies on the precision of the spectrophotometer and on the measurement of the initial blue dye before bleaching. Ozone detection to as low as 3 ug/l is possible if every precaution is taken to eliminate interferences (Gordon et al, 1989).

2.3 RAPID SAND FILTRATION

In water treatment, rapid sand filters are generally used

for filtering out the suspended flocs after coagulation or for removing suspended solids in direct filtration of raw water (Peavy et al, 1985). Filtration removes some turbidity and some pathogenic organisms. Rapid sand filters have short residence times of roughly 10 to 20 minutes with backwashing when headlosses increase above a certain level.

In the treatment process of ozonation, sand filtration and granular activated carbon adsorption, the sand filter not only removes suspended solids but it also dissipates the residual ozone. The sand filter helps eliminate residual ozone before the water flows to the granular activated carbon adsorption unit. While in the sand filter, the small quantity of residual ozone continues to react and eliminate itself. If the water being treated contained ozone and it passed into the carbon filter, the ozone would oxidize the carbon, with subsequent loss of adsorption material (Rice and Robson, 1982). The granular particles are reduced in size over a period of time until new carbon must be added to the filter.

Sand filtration does not remove true color to any great extent. It removes the color produced by suspended solids, reducing apparent color, without affecting the soluble color molecules. The filter material removes most of the sediment by straining, keeping the sediment in place with very weak electrochemical van der Waal's forces (Peavy et al, 1985).

Depending upon the size of the sand grains, different amounts of solids will be removed, with the finer grained sand corresponding with higher removal than coarse grained sand.

Although the small grains filter better, they also become clogged more rapidly, causing more frequent backwashing. Sometimes a dual or multi-media filter is employed since it may filter fine material, yet it does not become clogged as fast. In single media filters most of the sediment becomes trapped at the surface but with multimedia filters, containing various sizes and types of aggregate, the sediment travels deeper into the material, thereby extending the period between backwashing.

Backwashing is done to remove foreign material collected during the filter run. The flow through a rapid sand filter is reversed so that the water flows up through the bed, fully agitating the particles and removing the dirt. The bed is fluidized until it expands by about 50 %, or a lower backwash rate may be used in combination with other turbulence creating mechanisms like water jets at the surface or air injectors (ASCE, 1969).

Downflow filters are used almost exclusively in North America but some places like the Soviet Union use upflow filters. An advantage of an upflow filter is the sediment goes from coarse base material up to the very fine material, giving extended filter runs. A disadvantage is that as the headloss increases, the bed begins to expand, with loss of efficiency and possible short circuiting.

2.4 GRANULAR ACTIVATED CARBON ADSORPTION

As the concern over the quality of drinking water and

the effluent quality of wastewater increases, activated carbon is being used more frequently. Through the mechanism of adsorption, activated carbon removes soluble organic and inorganic micropollutants from water. It is being used increasingly both in full scale water treatment plants and in point of use package plants for individual homes.

Activated carbon can be produced from any raw organic material high in carbon content such as wood, coal, coconut shells, and petroleum coke (Deithorn and Mazzone, 1986). The carbonaceous material is initially dehydrated, at temperatures of about 170°C. Occasionally zinc chloride or phosphoric acid is employed for further dehydration (Benefield et al, 1982). This drives off impurities such as methanol and tar, causing the material to decompose, producing a char. As the volatile substances are driven off they produce an elaborate network of very fine pores in the char. The char is heated to between 750°C and 950°C in the presence of a mixture of air, carbon dioxide and steam in order to activate the carbon. Before activation the pores are clogged with the products of decomposition so the activation step cleans out the dirty pores, expands the pore network and the pore size, readying the carbon for adsorption.

Depending upon the pore size, the granular activated carbon has varying uses. Carbon used to remove gaseous pollutants possess very small pores, whereas carbon used to remove liquid phase pollutants has larger pore sizes with a greater variation in pore size. Gas phase carbon will mainly

have pore sizes of about 10 angstroms but aqueous phase carbon will have pore sizes ranging from less than 10 angstroms to pores greater than 10 000 angstroms across (Deithorn and Mazzoni, 1986).

The pore size indicates the type of pollutant or adsorbate that can be removed, but the iodine number and the molasses number indicate the surface area of the internal pores. The iodine test measures the adsorption of the adsorbate iodine, making it possible to estimate the pore area. Since iodine is a relatively small molecule it is adsorbed into almost all pores, whether they are large or small. On the other hand, the molasses test is performed using molasses as the adsorbate, possessing large molecules unable to penetrate small pores. By looking at both the iodine and the molasses numbers, a person can decide if the carbon has many small pores, possessing a high iodine number and a low molasses number or whether the carbon has large pores possessing both a high molasses number and a high iodine number. For liquid phase carbon adsorption, iodine numbers are generally between 500 m^2/gram and 1000 m^2/gram of carbon and the molasses numbers vary from 200 m^2/gram to 400 m^2/gram of carbon.

Since activated carbon is generally used in a filter which is backwashed periodically, the carbon must be strong enough to resist the destructive agitation of washing. The resistance to abrasion is named the abrasion number. In comparing different carbons it is useful to look at this

parameter since it could indicate how long the carbon can be used and regenerated (Perrich, 1981).

2.4.1 Activated Carbon Sizes

Once charred carbon is activated, it is either finely ground for use as powdered activated carbon or it is roughly ground for use as granular carbon. Granular carbon is used in activated carbon filters and it is regenerated periodically to reactivate the carbon. Powdered carbon is mixed into the water flow, flocculated, settled and subsequently disposed of due to inherent trouble in regenerating fine material economically.

Powdered activated carbon is ground so that between 95 % and 100 % of the carbon will pass through .149 mm openings or a # 100 mesh sieve and between 50 % and 95 % passes through a # 325 mesh (Benefield et al, 1982). Granular carbon particles are much larger with different sizes purchased for different uses. The sizes are given by a system such as 12/40 and 8/30. For instance, particles passing through a # 12 mesh sieve and being retained on a # 40 mesh sieve are given the label 12/40.

2.4.2 Adsorption Mechanisms

Adsorption is a process that removes soluble substances from solution and concentrates them at an interface. In the case of granular activated carbon adsorption, solutes are taken out of an aqueous solution, bound to the surface of the

carbon particle and drawn inside the carbon pore openings. Although there are three adsorption mechanisms working on activated carbon, two of them predominate over the third. The two main types are physical adsorption and chemical adsorption with the third type being exchange or electrochemical adsorption.

Physical adsorption is a relatively nonspecific and reversible process if the concentration of solutes in solution change. For instance, if a system containing carbon, water and a solute are in equilibrium and the solute concentration is changed, some of the adsorbed solute may go back into solution with agitation. The forces responsible for this physical attraction are the weak van der Waal's forces. The adsorbate may condense on the carbon particle in one layer or in many layers with each particle free to move around on the surface.

The process of chemical adsorption is site specific and is much less reversible than physical adsorption. Adsorbates attach themselves to specific sites on the carbon particle with forces similar in strength to molecular binding forces (Benefield et al, 1982). Unlike physical adsorption, chemical adsorption can only occur in a layer that is one molecule or one adsorbate layer thick. In other words, the adsorbate becomes strongly adsorbed to specific sites on the carbon surface, unable to move until the carbon is regenerated at very high temperatures.

Electrochemical adsorption is a process where by

electrical charges attract and hold a solute at the surface of the carbon particle. Electrostatic charges on a carbon particle attract ions of an opposite charge to the carbon surface in a process similar to ion exchange (Sawyer and McCarty, 1978). Ions with greater valences tend to adsorb more easily than ions of a low valence, as do ions with smaller radii.

Whether the adsorption of a solute is physical, chemical or exchange, the solute must still follow three steps in the adsorption process (EPA, 1973). At the exterior, a solute crosses through a surface film barrier and secondly it is drawn to the pore spaces of the carbon particle. Finally, the solute is adsorbed into the interior pore spaces in the carbon particle. Since the internal surface area of the particle is immense, the majority of the adsorbents could be found within the particle instead of on the surface.

2.4.3 Factors Affecting Adsorption

There are many factors which affect both the rate of adsorption and the quantity of solute which can adsorb to the activated carbon. Factors such as the size of the adsorbate molecules, temperature, solubility of the adsorbate, pH, agitation and characteristics of the activated carbon effect the adsorption. Even though each of these factors may tend to decrease or increase solubility by itself, all of the factors must be weighed in order to understand how they work together.

The size of the adsorbate molecules can be a major factor affecting adsorption. If the target adsorbates are all similar or smaller in size than the pores in the activated carbon, then the sizes will likely not hinder or affect adsorption significantly. However, in the case of color removal, where the color molecules or humic materials are very large, the size of the pore may seriously limit adsorption. If an activated carbon was used that possessed small pore openings, very little of the humic material could adsorb before the pore openings would get clogged. The color would prematurely break through the carbon filter and costly regeneration would result because carbon with inappropriately sized pores was used.

The temperature of an adsorption system affects the rate and degree of adsorption. An increase in temperature, increases the speed at which the reaction or adsorption takes place, but it also decreases the degree of adsorption. Although these two parameters tend to combine, their affects can be countered. At high temperatures, when the adsorption is rapid but the degree of adsorption is low, the adsorption unit should have a low residence time with frequent regeneration of the carbon material. At low temperatures the residence time in the carbon would be increased and the unit would not have to be regenerated as often.

Solubility of an adsorbent often affects the adsorption of the solute. An adsorbent with very low solubility generally does not want to stay in solution, so it is more

easily adsorbed than a substance such as sucrose, possessing a high solubility. Easily dissolved substances generally have a strong affinity towards water, whereas barely soluble substances have a low affinity towards water, making them easier to adsorb (Benefield et al, 1982).

The pH of an adsorption system affects adsorption differently depending upon the characteristics of the adsorbate. The pH of a system often determines the solubility of an adsorbate. The more soluble the substance is at a certain pH the lower the adsorbability. A pH adjustment making a substance less soluble, causes a decrease in its affinity for water, making it more readily adsorbable. As an example, humic acids are not only less soluble at a low pH but they are also more easily adsorbable (Weber et al, 1983).

The degree of agitation in a water system controls, to some degree, the rate of adsorption. Water and activated carbon mixtures with a high degree of agitation have higher adsorption rates than quiescent systems. Mixing the adsorption system decreases the thickness of the surface film of liquid around the carbon particles in addition to causing increased contact between adsorbent and adsorbate. The diffusion of an adsorbate through the surface film would increase but the mixing would not affect the diffusion of the adsorbate into the pore network of the particle. Therefore, with little mixing, the surface film diffusion is the adsorption limiter, whereas with well mixed systems there is plenty of adsorbate at the pore openings but the diffusion

into the pores becomes the adsorption limiting step.

The size of the adsorbent or the activated carbon particle helps determine the rate of adsorption. The rate of adsorption is affected by the external surface area of the particle. For instance, there is more rapid adsorption in powdered activated carbon than there is in granular activated carbon. Although the total adsorptive capacity of activated carbon is essentially the same gram per gram for a given carbon, the adsorption rate increases with external surface area and with carbon particle size reduction.

2.4.4 Adsorption Isotherms

In order to quantify the adsorptive characteristics of activated carbon, isotherm tests are performed. The isotherm relates the concentration of solute in solution to the mass of solute adsorbed onto specific weights of activated carbon. Each isotherm is produced by conducting a number of batch adsorption tests, employing a sample water and varying activated carbon dosages.

Depending upon the type and size of the carbon particles, the system is mixed for a long or short period. Powdered carbon is usually mixed for 1 or 2 hours but granular carbon is mixed for much longer depending upon the grain size. Often granular carbon is pulverized before testing in order to speed up the adsorption reactions by increasing the external surface area of the particles.

The isotherm can measure the removal of many different

quantities such as chemical oxygen demand (COD), total organic carbon (TOC), 5 day biochemical oxygen demand (BOD_5) or even color (Perrich, 1981). TOC is often the parameter chosen since the TOC values can easily be measured with the correct equipment and TOC is an all encompassing measurement, relatively unaffected by biodegradability or refractory substances. The TOC, for instance is measured before and after the adsorption tests and the results are gathered together to form a mathematical isotherm relationship.

There are a number of isotherms used to quantify adsorption data. Of the many isotherms in existence the three most popular ones are the Langmuir isotherm, the Freundlich isotherm and the Bramaaur-Emmete-Teller (BET) isotherms, listed in order of increasing complexity. Many isotherms are used because they are all based on assumptions or empirical data, with none of them truly representing all of what occurs in reality. For this reason, it may be necessary to try a number of different isotherms before a good relationship is found. Often a series of adsorption tests produce a line composed of more than one slope, corresponding to different phases. Sometimes, the data does not fit any of the isotherms very well.

The Langmuir isotherm is based upon the assumption that there are a fixed number of adsorption sites per unit of surface area on a particular carbon particle, with all adsorption sites being equally attractive in terms of energy (Metcalf and Eddy, 1979). It is also based upon the

assumption that adsorption is reversible with all adsorption being physical not chemical. The particles reach equilibrium once the rate of solute adsorption is equivalent to the rate of desorption. The adsorption rate is proportional to the difference between the amount of solute that is adsorbed at a particular solute concentration and the amount of solute than can be adsorbed onto the carbon surface at that same solute concentration (Benefield et al, 1982). The Langmuir equation is given below, with X equal to the amount of solute adsorbed, M equal to the weight of adsorbate, C equal to the concentration of solute remaining in solution after adsorption, while A and B are constants determined from the plotted results.

$$\frac{1}{X/M} = \frac{1}{B} + \frac{1}{ABC}$$

The Freundlich isotherm is an empirical equation, also based upon assumptions about the adsorption mechanisms. Freundlick assumes the carbon surface is heterogeneous, with different types of adsorption sites (Benefield et al, 1982). Each type or class of site is assumed to follow the Langmuir isotherm assumptions. The Freundlick equation is given below with X, M and C being the same as in the Langmuir isotherm and the constants K and N are determined from the graphed data.

$$\log (X/M) = \log(K) + 1/N*\log(C)$$

The third type of isotherm, BET, is based upon the assumption that molecules can adsorb in layers more than one molecule thick. Similar to the Langmuir isotherm, the carbon

surface is assumed to possess uniform adsorption sites with equal attraction to solutes with adsorption sites that are mutually exclusive. Also, the energy of adsorption is assumed to hold the first layer of adsorbates but all subsequent layers are held onto the adsorbent by the condensation energy of the adsorbate (Benefield et al, 1982). The BET isotherm is given below with the variables C, X and M having the same values as in the Langmuir isotherm, X_m equal to the amount of solute adsorbed in forming a complete monolayer, C_s equal to the saturation concentration of the solute and A equal to a constant describing the energy of interaction between the solute and the carbon surface.

$$\frac{C}{(C_s - C) X/M} = \frac{1}{A * X_m} + \frac{A - 1}{A * X_m}$$

2.4.5 Regeneration

Periodically, when the adsorptive capacity is exhausted, activated carbon must either be replaced or regenerated. Granular carbon is seldom disposed of when exhausted because it is more economical, at least in water treatment plants, to reuse the carbon after regeneration. The carbon may be removed from the adsorption unit either in its entirety for batch regeneration or it can be removed from the bottom of the filter in a moving bed system.

The most popular method of carbon regeneration is by a thermal process in the presence of some oxidizing substances such as water vapour, carbon dioxide and oxygen. The regeneration temperature varies depending on the type of

solutes adsorbed: wastewater solutes, industrial pollutants or solutes from drinking water purification. Patrick et al (1982) suggests regeneration at 850°C (1550°F) for drinking water carbon and 962°C (1750°F) for wastewater and industrial pollutants. If too low a temperature is used, not all the solutes are oxidized and the fine pores within the carbon stay partially clogged. Equally as destructive and wasteful, very high temperatures tend to oxidize and destroy the carbon.

Regeneration occurs in three phases: drying, pyrolysis and gasification. Wet carbon is initially dried at approximately 100°C and then it is heated to between 402°C and 542°C (750°F to 1000°F) in the absence of oxygen for pyrolysis. During pyrolysis, volatile organics escape the carbon and nonvolatile adsorbates become pyrolysed ash which remains in the carbon pore structure, to be removed in the gasification phase. Gasification takes place at the peak chosen temperature of 850°C for drinking water carbon, in the presence of limited quantities of steam and oxygen. This selectively oxidizes the solutes in the pore structure and activates the carbon for reuse.

If done carefully, there will be a 5 % to 10 % loss of carbon in the regeneration phase (Metcalf and Eddy, 1979). The regenerated carbon will have almost the same adsorptive characteristics as the original carbon, with a slow build up of ash in the pore structure and a reduction in the number of micropores with each regeneration. The reactivation is usually done in multiple hearth furnaces (Perrich, 1981).

The regeneration process is very costly due to the high temperatures required for oxidation and gasification of adsorbed solutes. Not only is the regeneration required, but the carbon that is either lost or oxidized must be replaced with virgin carbon. In an economic analysis performed by Cairo et al (1982) using pilot plant results, it was found the 80 % of the annual cost of the plant operation was used for regenerating the carbon and for purchasing replacement carbon. Of the 80 %, half of the cost was attributed to carbon loss during regeneration or in transportation to the furnace.

Generally, granular activated carbon is regenerated but it is difficult to thermally regenerate powdered activated carbon. Over the years powdered carbon has been disposed of after adsorption but since its use is increasing, more refined methods of regeneration are being investigated. Methods used by Clifford et al (1983) recover between 60 % and 80 % of the original carbon mass, while actually increasing the adsorption capacity per unit weight.

A more modern and experimental method of activated carbon regeneration is performed chemically. Two types of chemicals are needed. One must be an inorganic chemical that can oxidize adsorbates and regenerate the carbon, while the second chemical must be organic with solubilizing powers capable of removing solutes from the pore network. The efficiency of this type of regeneration depends upon the pore sizes and upon the size of the adsorbates. Martin and Ng (1985) found that the regenerant had difficulty in removing the lower weight

adsorbates in the micropores. The small adsorbates could travel deeper into the pore network wedging themselves in the micropores, staying out of reach from regenerative chemicals.

2.4.6 Adsorption and Water Treatment

Activated carbon is used increasingly in water treatment for adsorption of organic micropollutants which cause color, odour and taste problems. The adsorption process is also used for dechlorination in both the home and water treatment plants.

Granular activated carbon and powdered activated carbon remove the organics which cause color, odour and taste, and in so doing they also reduce the trihalomethane formation potential. Adsorption reduces the concentration of organics remaining in solution, which would have been available to react with chlorine to form trihalomethanes. Carbon adsorption not only removes the biodegradable organic fraction in polluted water but it also removes the refractory organic portion that is generally left untouched in biological purification. Very few water treatment processes can remove biodegradable and refractory organics to the same extent as adsorption.

Activated carbon has been used both in the home and in full scale treatment plants for dechlorination. For home use activated carbon columns are utilized to remove micropollutants and to dechlorinate the water by removing the chlorine residuals added by the water treatment plants for

disinfection. Some treatment plants use high chlorine dosage for breakpoint chlorination. The chlorine removes or combines with ammonia to create chloramines which are subsequently removed by the carbon filters. This process of breakpoint chlorination and dechlorination is more often used to polish wastewater treatment plant effluents than for drinking water treatment.

In drinking water treatment, color molecules are adsorbed into the carbon pores, thereby decreasing the true color of the water. Provided the pores in the carbon are in the medium to large size range, the low to medium weight humic and fulvic color molecules are easily adsorbed. The large color molecules may not adsorb onto the carbon because they are too large to fit into the carbon pore network. If color is not removed efficiently by the carbon particles, an oxidant such as ozone or even potassium permanganate may be employed to cleave the molecules into smaller, easier to adsorb molecules.

Compounds causing taste and odour are generally smaller than the large humic materials and therefore adsorb more readily. The main odour causing compounds are the amines, ammonia, diamines, hydrogen sulfide, mercaptans, organic sulfides and skatoles (Metcalf and Eddy, 1979). In countries such as Canada, where there is a significant ice cover during the winter, the taste and odour problems usually occur in the spring and summer, with few problems in the cooler fall and winter.

Since these water quality problems are often seasonal,

the most economical method of removing the troublesome compounds might also be seasonal. If there is an existing coagulation, flocculation and sedimentation process, powdered activated carbon may be added with a minimum change of infrastructure. This intermittent addition of powdered carbon may be less expensive than using granular activated carbon columns year around when color, taste and odour removal is not necessary. When the problems are encountered throughout the entire year or when the objective is to reduce the organic carbon concentration for trihalomethane reduction, it might be most economical to use granular activated carbon with regeneration furnaces for the carbon.

2.5 BIOLOGICALLY ACTIVATED CARBON

The 3 step process of ozonation, sand filtration and granular activated carbon adsorption has the potential to support biological activity on the activated carbon. The adsorption unit removes pollutants through adsorption as well as through biological removal. The ozone cleaves the organics, reducing them from a heavy nonbiodegradable form, into lighter and more biologically attractive substances (Neulrug, 1985). Biological removal of adsorbates extends the life of the carbon filters, thereby reducing the cost of operation. The microbes utilize adsorbed material for substrate, freeing the adsorption site for another adsorption. Biologically activated carbon is used in Europe, where the water temperatures are not extreme and the bacteria grow more

readily.

The ozonation or oxidation phase serves two purposes; it not only reduces the size of the heavy organics but it also aerates the water, supplying oxygen to the bacteria in the carbon filter. In waters with few refractory organics the ozonation may be replaced by some other type of oxidation or even aeration. The oxidant must not be allowed to reach the biologically activated carbon or it will continue to oxidize not only the organics but also the granular carbon and the much wanted bacteria.

The second phase is the rapid sand filtration of the oxygenated or oxidized water. The sand filter provides sites for ozone decomposition, it removes suspended solids which would foul up the activated carbon and it also gives the water extra time for the oxidant to finish reacting before entering the carbon. The sand also polishes the water by reducing turbidity somewhat.

The biologically activated carbon (BAC) unit is the third and the most important phase of the treatment process. The first two phases extend the life of the activated carbon and help polish the water, but they are not the main sources of purification. When the process is initially started the removal is only through adsorption but as bacteria become adsorbed to the carbon surface and multiply, the biological removal increases. The biological activity takes a widely varying length of time to become established; depending upon the concentration of solutes, the type of solutes in solution,

the temperature and many other factors. Rice and Robson (1982) suggest that biological activity takes several weeks to develop.

The bacteria are too large to enter the small carbon pores so they attach themselves to the macropores, accounting for about 1% of the total pores. The macropores are mainly located on the surface of the particle and they branch out into smaller micropores within the particle, as shown in Figure 4.

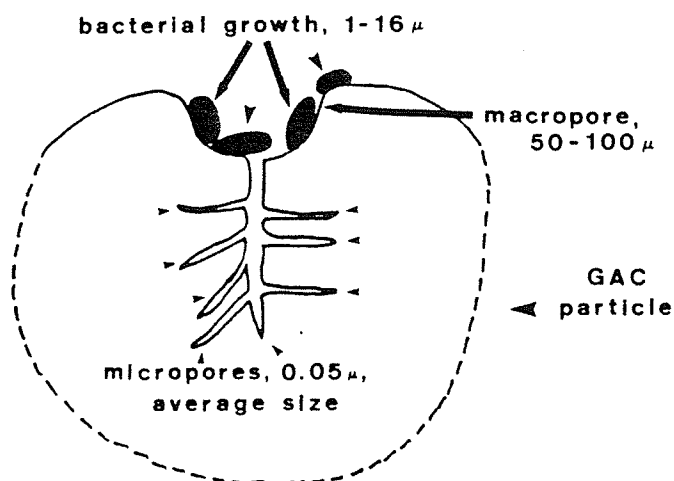


Figure 4: Representation of activated carbon particle showing bacteria and pores (Rice and Robson, 1982).

The adsorbates must pass by the bacteria on their way into the fragile micropores. At this point, the bacteria have easy access to the solutes, removing them from solution and using them as substrate. If the particles are physically adsorbed and the concentrations of solutes in solution changes, some adsorbed particles may desorb, once again leaving the pore network by exiting near the bacteria in the

macropore. The bacteria also secrete enzymes into the pores (Rice and Robson, 1982). With sufficient oxygen supply the small enzymes can partially oxidize the adsorbates in the pores and possibly change their adsorption characteristics. Once again, the partially degraded adsorbate may be released from the micropores and possibly be utilized by the bacteria.

Nitrification is performed to some degree in biologically activated carbon. Provided the autotrophic bacteria have large quantities of oxygen available, ammonia is oxidized by *Nitrosomonas* to nitrites and then rapidly oxidized by *Nitrobacter* to nitrates (Rice and Robson, 1982). Denitrification is not performed in aerobic carbon filters so nitrates stay as the end product without reduction to nitrogen gas.

Biological activity is encouraged by slightly longer residence times than what would normally be necessary for adsorption alone. With longer periods between backwashing, bacterial colonies have a greater chance of attaching themselves and reproducing, without being washed away by shear forces. Once the biological activity becomes established, large numbers of bacteria are swept out with backwashing and with the water being treated. The disinfecting action of the ozone or the oxidizing effect of an oxidant is eliminated by the biological activity on the carbon. Some of the BAC organisms leave the activated carbon and enter the water flow, reinoculating the water with bacteria. The water would need to be disinfected and given a residual such as chlorine before

the water would be safe for distribution.

As already discussed, biological activity extends the life of activated carbon and to a varying degree reduces the frequency of regeneration. Since each system is different, one cannot make a sweeping statement that biologically activated carbon lasts a certain number of times longer than plain granular activated carbon columns. However, it is safe to say biological activation can significantly extend the life of the carbon.

The temperature of the water not only affects the type of bacteria but also the rate of reproduction and pollutant assimilation for the bacteria (Rice and Robson, 1982). Psychophilic bacteria predominate in the range of 4°C to 10°C, mesophilic bacteria predominate in the range of 20°C to 40°C and thermophilic bacteria predominate between 50°C and 55°C. In general, the lower the temperature, the lower the metabolic rate of the bacteria. At about zero degrees, very little activity will exist except for the most hardy of bacteria. As with any biological unit, most microorganisms are inhibited by heavy metals such as zinc, copper, mercury, lead, chromium and many chlorinated compounds.

There are a wide variety of bacteria which can live in the activated carbon. Analysis of the bacteria living in Philadelphia's granular carbon filter show that the most populous geni are Pseudomonas and Bacillus (Rice and Robson, 1982). The genus and species of the different bacteria will not be included because it is sufficient to say that the

bacteria found in the filters generally have no pathogenic effect on man.

CHAPTER 3

MATERIALS AND METHODS

3.1 APPARATUS

An existing down flow rapid sand filter and a down flow carbon adsorption unit were employed but the remaining parts of the apparatus were either constructed or assembled by the author. All the units were composed of clear glass or acrylic plastic with tygon connecting tubing.

An Ozonair ozonator (by Canatraco Ltd.) was used for ozone generation in air instead of pure oxygen. Compressed Medical Air was used not only because the gas had virtually no moisture but also because it was possible to supply a constant flow of air at an appropriate pressure which was not attainable with a conventional compressor or air pump. The air flowed through the ozonator for ozone generation and then through a Fisher Scientific Mark III Flowmeter (cat. no. 11-164-50) for gas flow measurement.

From the flow meter, the gas flowed through an improvised tygon sparger positioned in the ozonator. The sparger was made out of a clamped piece of tygon tubing with 4 fine needle holes for gas bubble release. The ozonation reactor was 9.5 cm in diameter and 38 cm in height, with ports on both sides at the 15.5 and 30.8 cm height, corresponding to a 1 liter and a 2 liter volume. The top of the cylindrical ozonator had a flanged end which was clamped closed with C-clamps, creating an air tight container, except for the ports. A plastic baffle was used to separate the reactor into two sections,

with a 2 cm space left at the bottom for water passage. The gas flowed in through a hole in the lid to a tygon sparger hanging down to the bottom of the ozonator and off-gas was collected through an exit port in the lid. The water being treated flowed into the reactor on the same side as the sparger, flowed under the baffle, up the other side and out a port to the sand filter.

The rapid sand filtration unit and the carbon adsorption unit were cylindrical with a 9.5 cm internal diameter. From the bottom up, the sand filter was composed of 2 overlapping fiberglass screens, a 1 cm thick layer of garnet support sand and an 18 cm thick layer of filter silica sand with an average size of .67 mm and a uniformity coefficient of 1.3. Similarly, the carbon adsorption unit contained 2 overlapping fiberglass screens, a 1 cm thick layer of garnet support sand and an 18 cm thick layer of 12x40 granular activated carbon. For a list of the activated carbon characteristics provided by the supplier see Table D2 in the appendix. Each filter screen was supported by a 4 mm plastic plate with 4 mm holes drilled into it. The water exited down through the support plate into a 20 mm high water collection space before it flowed out the bottom of the filter unit through tygon tubing. The influent water flowed down through a port at the top of the unit and after filtration it exited at the bottom through the tygon tubing. Depending upon the flow, the water head above the filters and the freeboard varied but the flow remained constant. The water being treated flowed through the

sand filter causing a few cm headloss, with subsequent flow to the activated carbon unit and a similar head loss. Effluent from the activated carbon unit was collected in a beaker for analysis.

Any off-gas from ozonation was collected in a large plastic garbage bag that had been taped closed to create a flexible air tight container. Once full, the bag was left idle for a day to allow for ozone decomposition and later released into the atmosphere.

Ozonated air was bubbled through a series of glass jars, containing a 2 % potassium iodide solution, in order to measure the ozone concentration in both the off-gas and the ozonation gas. Gas was bubbled into one jar and its off-gas flowed out to the second jar where it bubbled through the same solution and out to the gas collection bag. These solutions were acidified and titrated with sodium thiosulphate to measure the ozone concentration that was in the gas.

In order to measure the quantity of ozone removed during ozonation of sample water, a 1.05 liter cylinder was manufactured with a 9.5 cm internal diameter. The cylinder was created to simulate the ozone reactor while making the conditions more conducive to ozone measurement. It possessed a rapidly clamped air tight lid with an access port for a gas sparger and an access port for gas collection and ozone measurement.

Pumping was performed with a Masterflex Cole-Parmer multispeed pump fitted with a size 18 head. Pump tubing was

inspected every four months for damage and wear. A Shimpo Tachometer was used to correlate the pump speed with the flow rate so that future flow settings could be rapidly set with the tachometer instead of with time volume measurements.

Water treatment was performed at room temperature, approximately 25°C and at approximately 4°C to simulate Churchill treatment conditions. The target temperatures varied by up to 2°C during the test. The cold tests were carried out while the sand filter, the carbon unit and the ozonator were positioned in a large plastic water bath filled either with ice or snow. The experimental set up is shown in Figure 5. Figure 6 shows the sand filter, the activated carbon unit and the ozonator being kept at about 4°C. A schematic of the experimental apparatus is shown in Figure 7.

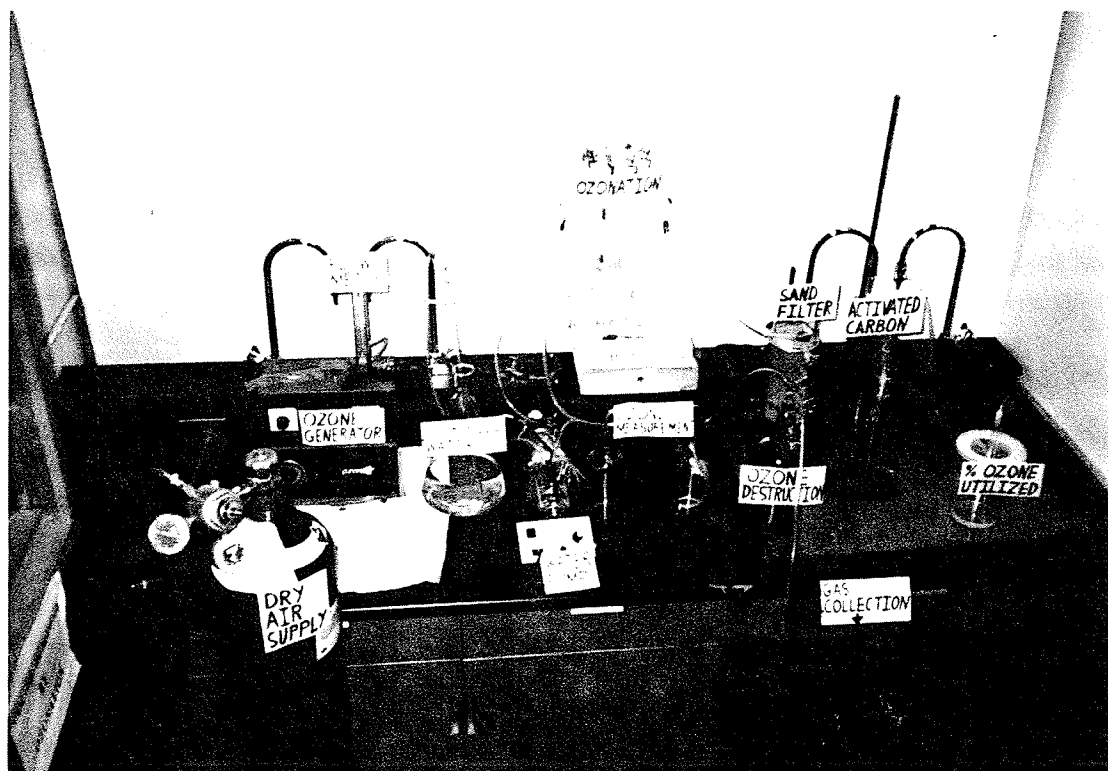


Figure 5: Experimental arrangement.

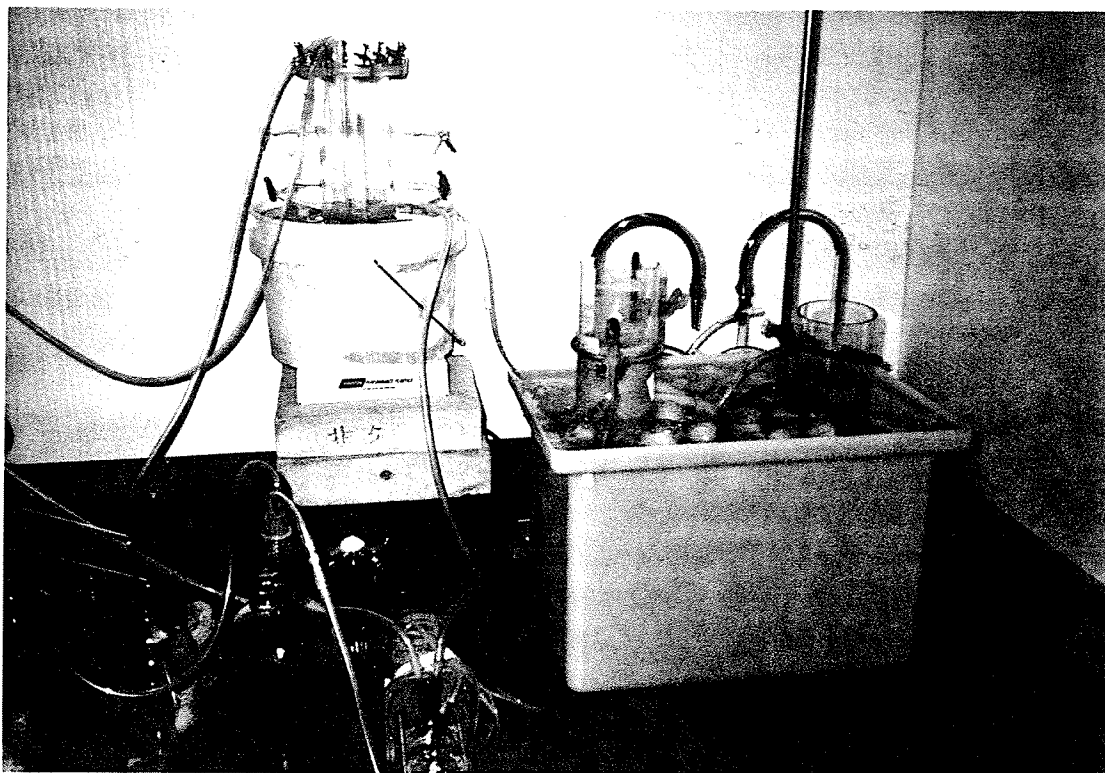


Figure 6: Refrigeration of the experimental arrangement.

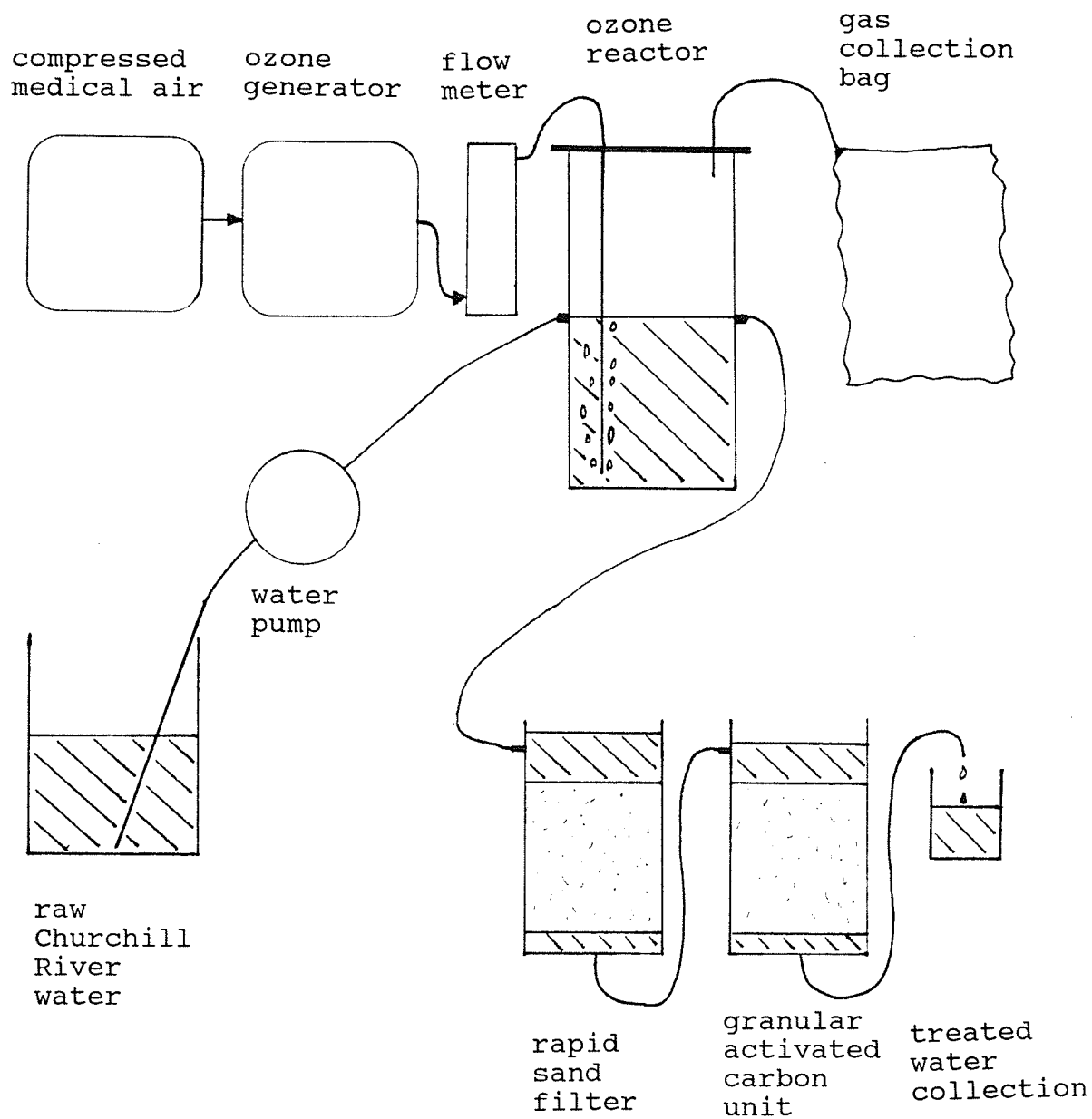


Figure 7: Schematic showing experimental arrangement.

3.2 PROCEDURE

The monthly water testing was generally performed within two weeks of receiving the raw Churchill water. Raw water was collected directly from the Churchill River intake pipe. The raw water was stored in a 4°C refrigeration chamber until it was used for testing. Room temperature tests were performed after the water warmed up to room temperature (25°C), usually 3 hours, and cold tests were initiated with no warm up time. In fact, the cold water was kept in a Erlenmeyer flask which was placed in a tub of snow or ice for refrigeration, helping to ensure a constant temperature during the tests.

Since there was a limited quantity of water available, a limited number of water treatment tests were conducted in each month. Between 7 and 11 full treatment tests were performed each month, giving a minimum of 3 tests at each flow rate. It would have been better to perform a minimum of 4 or 5 tests at each flow but due to experimental problems sometimes it was not possible. From May to November, the monthly tests were carried out at room temperature, with two different flow rates. During December, the tests were conducted at the higher rate of flow with half the tests at 4°C and the other half at room temperature. From January to April the tests were performed at 4°C with the two different flow rates.

The testing program was designed to compare results at two different water flow rates while varying the ozone dosages. The two flow rates corresponded to empty bed contact

times (EBCT) of 10 minutes and 20 minutes in each of the three units. The 10 minute EBCT corresponded to a water flow rate of 100 ml/minute and an overflow rate of 14 litres/minute*m² and the 20 minute EBCT corresponds to a flow rate of 50 ml/minute and an overflow rate of 7 litres/minute*m². The experiments were conducted with ozone dosages ranging between 0 mg/l and about 6 mg/l.

At the beginning of each water treatment experiment the main valve on the medical air tank was fully opened and the valve on the regulator was slowly opened until the gas flow reached 50 ml/minute as it bubbled through a sparger. Adjustment of the regulator was required periodically throughout the experiment to keep the flow constant. After turning the ozonator on, a constant rate of production was generally achieved after approximately three hours of operation or warm up time. During this stabilization period the ozonated gas was bubbled into the ozone measurement bottles containing water and the off-gas was collected in the plastic collection bag. The bag was capable of containing the gas used during approximately 15 hours of ozone generation before being emptied.

Once stabilized, the ozone concentration in the ozonated air was measured using a 2 % potassium iodide solution, as described in the sixteenth edition of Standard Methods. To ensure that there was constant ozone production, the ozone concentration was measured a second and third time at roughly 10 minute intervals. If the ozone concentration was either

too high or too low the ozonator dial was moved accordingly to alter the gas production. After adjusting the ozonator, approximately one hour of stabilization time was required provided it had been operating for a minimum of three hours. The stabilization time was provided so the ozone generator plates had time to achieve an equilibrium temperature and therefore ozone production.

Not all of the ozone bubbled in the ozone reactor was removed from solution by the sample water so a test for the percent ozone removal from the gas flow was performed. This test was conducted in series while the special ozone reactor, the ozone measurement bottles and the collection bag were connected in series. One litre of sample water, at either 4°C or 25°C was measured into the percent removal reactor, the vessel was clamped closed and the off-gas was collected for ozone measurement. Each 1 litre sample was ozonated for 10 minutes and then a further 10 minutes to simulate the 10 and 20 minute ozonation periods used in the treatment tests. The off-gas was bubbled through the potassium iodide solutions for ozone measurement in each period. The ozone removed by the water was calculated as the difference between the equilibrium concentration and the off-gas concentration.

Once the true ozone dosage was calculated, the gas was bubbled into the ozone reactor for a continuous flow water treatment test. The water was ozonated and then it flowed by a combination of pressure and gravity to the sand filter and subsequently to the activated carbon filter. Generally, about

5 liters of Churchill water was used in each experiment. The effluent was collected from the activated carbon filter, with the first 4.75 liters being discarded, while the final .25 liters was collected as testing water. This was done so that a sample was collected that truly represented the correct ozone dosages and the correct empty bed contact times.

The true ozone dosages were varied from 0 mg/l or no ozone to about 6 mg/l of ozone. Generally two tests were performed in a row, one 10 minute EBCT test and one 20 minute EBCT, which reduced the time used in restabilizing the ozonator. To ensure constant ozone production, the ozone concentration was measured in between tests. If the concentration had changed the ozonator was allowed to restabilize and it was retested. As a control, the water treatment tests were also conducted at the high and low flow rate, without ozone application for each month.

The .25 liter sample of treated Churchill water was subjected to numerous test to measure the water quality characteristics of the treated water and they were compared to the raw water. These results were graphed to indicate a trend or an optimum ozone dosage for color, turbidity and TOC removal. Water testing was performed within a couple hours of completing the treatment tests so that certain parameters did not have a chance to change with exposure to the atmosphere.

3.3 ANALYTICAL TECHNIQUE

Ozone Measurement

The ozone concentration was determined by bubbling the ozonated air through potassium iodide traps as described in the sixteenth edition of Standard Methods (1985). A 2 % solution of potassium iodide (KI), was used to react with the ozone during ozone calibration tests. After ozonated gas was bubbled into a 200 ml sample of KI solution for 4 minutes, at a gas flow rate of 50 ml/minute, the solution was transferred to a beaker and acidified with 10 ml of 1 N H_2SO_4 or sulfuric acid to reduce the pH to below 2. The ozone liberated the iodine, thereby changing the solution from clear to yellow. Sodium thiosulphate titrant or .005 M $\text{Na}_2\text{S}_2\text{O}_3$ was added until the yellow color almost disappeared, at which point 2 ml of a .5 % starch solution was added, turning the solution blue. Titration continued until the blue color disappeared.

To insure there were no impurities in the newly made KI solution, such as free iodine, iodate or traces of reducing agents, blank tests were conducted on each batch of KI solution. While observing for a color change, 10 ml of 1 N H_2SO_4 and 2 ml of starch indicator were transferred into 200 ml of KI solution. If a blue color change appeared, the solution was titrated with the thiosulphate until clear. If no color change occurred, it was titrated with .005 N iodine solution until a blue color appeared and back titrated with thiosulphate to eliminate the blue color. The equation below was used for the ozone concentration calculation.

$$\text{mgO}_3/\text{l} = \frac{(A+B) * .005 \text{ M Na}_2\text{S}_2\text{O}_3}{\text{ml of KI solution}} \times 24\,000$$

A= ml of titrant for sample

B= ml titrant for blank

- If the solution turned blue with acid addition the sign is - and B is the volume of thiosulphate
- If there was no color change with acid addition the sign is + and B is the volume difference of iodine titrant minus the thiosulphate titrant.

Apparent Color Measurement

The apparent color of the raw and treated Churchill waters were measured using a Hellige Aqua Tester. This method is mentioned in the seventeenth edition of Standard Methods (1989) in article 2120 B. The Aqua Tester uses a color wheel or disk which was factory calibrated against platinum cobalt standards. Two nessler tubes are filled, one with deionized water and the other with sample water. Once placed in the tester, the color disk was rotated until the shade of the sample tube was reproduced or copied by the deionized water tube and the color disk. This allowed for rapid color measurement.

Turbidity Measurement

Turbidity measurements were performed with a nephelometer (model DRT15B) made by HF Instruments. Instead of using the old Jackson Candle Turbidimeter which is only accurate for

liquids of high turbidity, nephelometric units were used as described by 2130 B in the seventeenth edition of Standard Methods (1989). The nephelometer was accurate for waters with less than one nephelometric turbidity units (NTU) so it would be ideal for potable water testing. Before each test, the nephelometer was calibrated using a .1 NTU standard and subsequent measurements were performed by filling a special test tube with sample water and placing it in the machine for turbidity measurement.

Alkalinity

Alkalinity was measured by titrating to neutralize acid destroying ions, as described in 2320 B in the seventeenth edition of Standard Methods (1989). About 5 drops of phenolphthalein indicator was mixed into each 50 ml water sample, turning the solution pink if the pH was above 8.3 and having no color affect at pH below 8.3. The solution was titrated with .02 N H_2SO_4 or sulfuric acid until the pH dropped to 8.3 and the indicator became clear. This titrant volume was called the phenolphthalein point. After the addition of methyl purple, the titration continued until the pH was reduced to 4.5 and the methyl purple indicator changed from green to royal purple. The titrations were initially performed both potentiometrically and by color indicator method. Since they yielded identical results the color indicator method was chosen for simplicity and more rapid titrations.

The three common forms of alkalinity are: carbonate ions, bicarbonate ions and hydroxide ions. The equation below was used to calculate the alkalinity and Table 1 was used to differentiate between the different types of alkalinity.

Table 1: Alkalinity relationships (Standard Methods, 1989).

RESULT OF TITRATION	HYDROXIDE ALKALINITY AS CaCO ₃	CARBONATE ALKALINITY AS CaCO ₃	BICARBONATE CONCENTRATION AS CaCO ₃
P = 0	0	0	T
P < 1/2 T	0	2P	T - 2P
P = 1/2 T	0	2P	0
P > 1/2 T	2P - T	2(T - P)	0
P = T	T	0	0

$$\text{Alkalinity, mgCaCO}_3/\text{l} = \frac{.02 \text{ N} \times 50,000 \text{ mg/mole} \times \text{Titrant(ml)}}{\text{ml of sample}}$$

Organic Carbon

Organic carbon was measured using a Dorhman DC-80 carbon analyzer as mentioned in 5310 C in the seventeenth edition of Standard Methods (1989). Once the machine's instructions are followed for power up, reagent production, and calibration, the water samples were injected into the machine. Total carbon (TC) analysis was performed without pretreatment but total organic carbon (TOC) analysis was conducted only after acidification to pH 2 and five minutes of air sparging. Total inorganic carbon (TIC), was the difference between the total and the organic carbon. When using the low range needed for these tests, 1 ml of sample water was injected into the analyzer at a time. Single tests were performed unless

unexpected results were produced, at which point retesting was performed.

Water Hardness

The hardness was measured by using a EDTA titration method as described in 2340 C in the seventeenth edition of Standard Methods (1989). Total hardness and calcium hardness were measured with the use of different buffers and indicators, manufactured by BETZ Inc. The difference between the two forms of hardness was the magnesium hardness.

Hardness was measured using 50 ml samples, which were magnetically mixed in porcelain dishes. A dipperful of HACH buffer, adjusting the pH to 10, and BETZ indicator were mixed into the water sample to create a dark purple color. The solution was titrated with ethylenediaminetetraacetic acid or EDTA until the color became dark blue. The calcium hardness procedure called for 2 ml of calcium buffer solution, 1 N NaOH, and one dipperful of BETZ indicator, mixed with 50 ml of sample water. The EDTA was added with continuous mixing until the sample changed from pink to purple. In each case, the volume of titrant was used in the following equations to calculate the appropriate hardness.

$$\begin{array}{l} \text{mg/l of Calcium} \\ \text{or Total Hardness} = \frac{\text{ml of EDTA titrant}}{\text{ml of sample water}} \times 1000 \\ \text{mg/l as CaCO}_3 \end{array}$$

$$\text{Magnesium Hardness} = \text{Total Hardness} - \text{Calcium Hardness}$$

PH

The pH of the raw and treated waters were determined by using a glass electrode probe as mentioned in 4500-H B of the seventeenth edition of Standard Methods (1989). The pH meter was calibrated at pH 7 and 10 using buffer solutions prepared by Fisher Scientific, prior to pH measurement.

Adsorption Isotherm

The granular activated carbon adsorption isotherm was produced using a method similar to the one given in Benefield et al (1982). The isotherm characterized the removal of total organic carbon in the month of April 1990 for raw Churchill water. A number of tests were performed until the approximate carbon dosage range was chosen.

Three hundred milliliter of sample water were deposited into each of the nine 500 ml flasks. The carbon dosages were preweighed and rapidly poured into each flask. All of the flasks were secured to a shaker table for 24 hours of continuous mixing. Carbon dosages varied from 0 mg/300ml sample to 1500 mg/300ml sample. The TOC of the raw water and the batch test water were compared and manipulated using an appropriate isotherm as shown in the analysis section of this thesis.

CHAPTER 4

RESULTS

The results of the monthly raw water testing for the water quality parameters are given in Table A1 to A3 in Appendix A. The only missing data is for June and July turbidity measurements, during which time the nephelometer was broken. The monthly results are also graphed in Figures A1 through A6 in Appendix A to indicate the variations throughout the year.

Data showing the percent of ozone removed from the ozonation gas is given in Table B1 and B2 in Appendix B. The data in Table B1 was produced at 25°C with both 10 and 20 minute empty bed contact times (EBCT) using the water sample from December. Table B2 is a combination of tests performed at 4°C using January and February water samples, with both 10 and 20 minute EBCT. The data from Table B1 is graphed in Figure B2 and Table B2 is graphed in Figure B2. The vertical scale is the percent ozone removed from the ozonated gas and the horizontal scale is the initial dosage applied to the water. The true dosage is the initial ozone dosage multiplied by the percent ozone removed.

In order to produce an equation which best represented the points in each graph, computer regression was performed. Regression was performed using orders from 1 to 10 and second order regression was found to give the best fit. The lines were not used beyond the last point but they were used between zero and the first point on the graph. The computer generated

second order regression line equations are listed below each graph.

Tables C1 and C2 in Appendix C summarize the monthly water treatment data. Again the only data missing is for the turbidity measurements during the months of June and July. Although all the data was collected, only the most pertinent data for TOC, TC, TIC, apparent color and turbidity were graphed for each month, in order to reduce what is already a large number of graphs. These graphs are given in order by month starting with Figure C1 and ending with Figure C46 in Appendix C.

Granular activated carbon isotherm results are given in Table D1 and they are graphed in Figure D1 of Appendix D. A best fit line was drawn through the points on the graph, excluding the final three points. This gives a slope of 1.31 with a Y intercept of .0024. The results were used with the Freundlich equation as given below since this model gave the closest fit line.

Freundlick equation

$$\log \frac{X}{(M)} = \log K + \frac{1}{n} \log C$$

$$\log \frac{X}{M} = \log .0024 + .76 \log C$$

CHAPTER 5

DISCUSSION

Ozonation of the Churchill River water samples was performed primarily to reduce the amount of color causing materials in the water by oxidizing the unsaturated bonds in the humic acids and fulvic acids. It is not known whether the ozone did react with the unsaturated bonds as predicted but the experimental data did indicate that the ozone helped to reduce the color significantly. The degree of additional color removal due to ozonation, above the removal by filtration and adsorption, varied from month to month.

The process of oxidizing the humic materials and reducing the size of the material is supposed to encourage adsorption. By reducing the size of the high weight humic molecules, the broken molecules were more apt to fit in the adsorption sites within the carbon particle. In this way, the carbon will remove more of the humic materials than it would otherwise. This suggestion is supported by the observed tendency for more color causing substances, presumably heavy weight humic materials, to be removed when ozone is used in the treatment tests.

Ozone was also expected to oxidize the organics in the water, transforming the refractory organics into smaller, more easily biodegradable ones. This would be beneficial if the activated carbon unit had biological activity, similar to the process called biologically activated carbon or BAC. Since these tests were performed on a continuous basis for only a

few hours at a time during a two week period every month, accurate results on biological activity are non-existent. The carbon unit was not only operated in a semi-batch method, but in between tests it was stored at approximately 25°C. This temperature would support a much higher biological activity than a carbon unit would at 2°C in Churchill. Tests for biological activity would have to be performed in Churchill due to the large amount of water which would be necessary for meaningful results. At 2°C in Churchill there would still be some biological activity, since bacteria are acclimated to cold temperatures in that region. However, at this temperature it would take many weeks for a sufficiently large bacterial population to develop, if at all.

A side benefit to the ozonation process is the disinfection by oxidation. Since ozone is an extremely strong oxidant it would inadvertently disinfect the water being treated. In this instance disinfection is only an additional benefit of ozonation, which may reduce the final chlorine dose to some degree and provide a backup disinfection system in case the chlorinator malfunctions.

In the literature, it is was mentioned that ozone should not be allowed to reach the activated carbon because there may be a reaction with subsequent loss of activated carbon. A number of methods were used to detect a residual ozone concentration either coming out of the ozonator or out of the rapid sand filter. At high ozone dosages, a very low concentration was detected entering the sand filter but at no

point was ozone detected entering the carbon filter. The methods used for detection included odour detection, gently mixing out flowing water with a potassium iodide solution and ozone detection vials produced by HACH.

During backwash of the carbon adsorption unit and the sand filter very little particulate matter was washed out. The backwashing was performed primarily to remove suspended solids and to prevent significant biological activity and dirt build up on the plastic filter containers, not to alleviate excess headloss.

The adsorption process is the primary color removal mechanism being employed to remove the unwanted organics during high color periods. Color removal is the most difficult during the spring months when the run off from the melting snow drains from the swamp or muskeg areas surrounding the Churchill river. The existing alkalinity in the Churchill river is diluted by spring melt water. Since snow contains very little alkalinity it acts to dilute the existing alkalinity. Unfortunately, the low alkalinity water occurs at the same time as the muskeg areas flood and release their humic materials into the water flow.

Although this low alkalinity period would likely not have a great effect on the ozone and adsorption treatment process, it would significantly effect other treatment processes such as alum coagulation. Alum consumes alkalinity as it is dissolved in water being treated. During high color periods, the alum dose might not be as effective as it should because

not all the alum can react to coagulate the impurities in the water. During the periods of low alkalinity and high color, the alum dosage may have to be cut back or excess alum may stay in solution instead of precipitating. At this time the answer would be to either leave the coloured water or to add alkalinity in the form of sodium bicarbonate or some other alkali compound. This would end up being costly in addition to increasing the ion content of the water.

Three sets of percent ozone removal tests were performed to determine the actual ozone dosage during treatment. The first tests were performed in December with 25°C water, the second set was in January and February at 4°C and the final group was in March and April, also at 4°C. As can be seen in the graphs provided, the first and second experiments matched quite well but the third set was quite different. The tygon tube used for sparging in these experiments was also changed at the beginning of the third set of tests, further raising the question of accuracy. For these reasons the first two sets of data were used and the third set was left unused but included in Figure B3.

The treatment processes used in the experiment are influenced both negatively and positively by the extremely low treatment water temperature in Churchill, 2°C. The carbon adsorption rate decreases with a decrease in temperature whereas the ozone transfer from the ozonation gas to the sample water increased as the temperature decreased.

The adsorption rate decreased with temperature but this

can be compensated by increasing the EBCT of an adsorption unit. The experiments showed that an EBCT of 20 minutes was more effective than 10 minutes, in removing apparent color, turbidity and organic carbon. Before a person would decide upon the contact time to be used in a treatment plant, the cost and benefits would have to be weighed. Is it worth designing a large plant with a very long contact time to satisfy the spring treatment requirements or should the plant be designed less expensively for winter requirements? Perhaps the answer would be somewhere between the two extremes, but that would be decided upon at a later date.

Since the temperature of the water being treated in Churchill stays constant at approximately 2°C all year around, temperature variation is not a variable which could seriously affect the treatment process from month to month. In designing a treatment plant for Churchill, winter and summer temperature variations would not have to be taken into account.

As already mentioned, ozone is removed from a gas-flow more readily at low temperatures than at high temperatures. As temperatures decreased, the solubility of the ozone increases although the ozone decomposition rate and ozone reaction rate decreased. The experimental data supports the statement that ozone dissolves more readily at low temperatures but it was not observed whether the dissolved ozone reacted at a lower rate with a decrease in temperature. The ozone removed from the ozonation gas was measured but it

was not possible to observe the rate of ozone decomposition or ozone utilization to form a conclusion on the utilization rate.

Ozonation before filtration and adsorption did not always decrease the TOC to a greater extent than just filtration and adsorption. Sometimes the TOC would increase yet other times it would stay the same with no general trend to be observed. As explained earlier, the TOC was expected to decrease slightly with increased ozone dosages due to oxidation and increased adsorption.

Throughout the year of testing, air flow stability was a problem. Many compressed air sources and flow measurement methods were experimented with before deciding upon the final apparatus, with a flow meter in series with a Medical Compressed Air tank fitted with a low pressure regulator. This final set up was still somewhat unreliable at times but it was the best available. In order to regulate the pressure and flow further, a sparging apparatus composed of tygon tubing was used with repeatable results. For this reason it was assumed that the improvised sparger did not cause problems with the test but it made them possible and more accurate.

During testing, occasionally the set up did not flow or operate as expected. Sometimes, ozonated gas being bubbled into the ozone reactor did not create enough pressure to expel the sample water, allowing the water level in the reactor vessel to increase. Since the author was constantly monitoring the test, the problem was rapidly rectified, by

tightening the reactor lid to allow pressure generation from influent gas. Sometimes tygon tubes were inadvertently clamped during adjustment thereby impeding water flow. These problems were fixed easily and detected easily, with few mishaps too great to correct. At times when parameters were not followed closely or when mistakes were made, the test was performed again.

Due to the occasional instability of air flow, the error in ozone measurement and possible fluctuation in ozone generation, I would estimate the ozone dosages may have an error as high as 10 %. However, the values for apparent color, turbidity, alkalinity, PH, organic carbon, and total carbon are expected to be below 5 %.

CHAPTER 6

CONCLUSIONS

Based on the water treatment tests performed monthly over a one year period, the following conclusions have been formed:

1. The bench scale treatment train composed of an ozone reactor, a rapid sand filter and an activated carbon adsorption unit reduced the apparent color, turbidity and organic carbon of the Churchill River water samples.
2. The treatment process decreased the color of the raw water to below 15 apparent color units, the objective limit, in all of the months except May, when the initial color was at a high of 120 color units. During May the effluent apparent color was reduced to between 15 and 20 apparent color units using the 20 minute EBCT.
3. When comparing water quality characteristics after treatment for both the 10 and 20 minute EBCT, it was concluded that the longer contact time was more effective at improving the water quality characteristics than the short one.
4. Adsorption in the GAC unit was the primary removal mechanism for organic carbon, turbidity and color removal.

5. The rapid sand filter had a very minor effect on water quality in this bench scale experiment because settled water was used instead of fresh water directly from the river source. The water was agitated before testing but not all of the sediment was resuspended. It is expected that the actual raw water flow in Churchill possesses a greater quantity of suspended solids so the rapid sand filter would become more useful than in the laboratory. The overflow rate corresponding to the 20 minute contact time was $7 \text{ litres/m}^2 \cdot \text{minute}$ and the overflow rate corresponding to the 20 minute contact time was $14 \text{ litres/m}^2 \cdot \text{minute}$.
6. Although the organic carbon is removed by adsorption, the inorganic carbon is left relatively unchanged during treatment.
7. In most of the test months, the samples treated with ozone, filtration and adsorption had a lower effluent apparent color than the water treated with just filtration and adsorption.
8. TOC values after ozonation, sand filtration and carbon adsorption do not differ significantly from those with just sand filtration and carbon adsorption. Therefore, ozone should not be employed solely for TOC reduction.

9. A greater percentage of ozone is removed from ozonated gas through a combination of decomposition, oxidation or dissolution in the water at 4°C than 25°C.
10. As the ozone concentration in the ozonation gas increases the percent ozone removed by the Churchill River water decreases.
11. The water treatment process used tended to lower the effluent alkalinity during most months.
12. Biological activity on the activated carbon either at 4°C in the laboratory or at 2°C in Churchill probably will not be great enough to significantly extend the periods between regeneration. It should be assumed that adsorption will be the only organic removal mechanism operating within the carbon bed.
13. Ozone gas should be used very carefully, whether it is in a laboratory or in a water treatment plant since its strong oxidizing characteristics affects plants and animals as well as aquatic pollutants.
14. In future tests the ozone concentration should be measured with an in line monitor instead of 2 % potassium iodide traps leaves this would significantly increase the ease of ozone measurement.

CHAPTER 7

RECOMMENDATIONS FOR FURTHER STUDY

Based upon the information gathered for this thesis, I would suggest that a future study should investigate using intermittent dosages of powdered activated carbon together with Churchill's alum coagulation process. During most months of the year alum coagulation is capable of treating Churchill's water and reducing the color to acceptable limits. In the high color, high flow, low alkalinity spring and summer months, powdered carbon may be used in conjunction with the existing alum coagulation. It could be flocculated and mixed with the alum and collected with the aluminum hydroxide flocs. This may cause more wear and tear on the equipment but in the short term it may be a relatively inexpensive answer to the color problem.

BIBLIOGRAPHY

- Amy, Gary L., Paul A. Chadik, Raymond A. Sierka, and William J. Cooper. "Ozonation of Aquatic Organic Matter and Humic Substances: An Analysis of Surrogate Parameters for Predicting Effects on Trihalomethane Formation Potential." Environmental Technology Letters, Volume 7, 1986, pp. 99-108.
- Annesini, M. C., F. Gironi, M. Ruzzi and C. Tomei. "Adsorption of Organic Compounds onto Activated Carbon." Water Research, Volume 21, Number 5, 1987, pp. 567-571.
- Anselme, Christophe, I. H. Suffet, and J. Mallevalle. "Effects of Ozonation on Tastes and Odors." Journal AWWA, October 1988, pp. 45-51.
- APHA, AWWA and WPCF. Standard Methods for the Examination of Waste and Wastewater. APHA, Sixteenth Edition, USA, 1985.
- APHA, AWWA and WPCF. Standard Methods for the Examination of Waste and Wastewater. APHA, Seventeenth Edition, USA, 1989.
- ASCE, AWWA and CSCE. Water Treatment Plant Design. AWWA, Denver, Colorado, USA, 1969.
- Bablon, Guy P., Claire Ventresque and Roger Ben Aim. "Developing a Sand-GAC Filter to Achieve High-Rate Biological Filtration." Journal AWWA, December 1988, pp 47-53.
- Baker, M. N., and Michael J. Taras. The Quest for Pure Water. Volume 1, Second Edition, AWWA, USA, 1981.
- Benefield, Larry D., Joseph F. Judkins and Barron L. Weand. Process Chemistry for Water and Wastewater Treatment. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, USA, 1982.

- Brodard, E., J. P. Duguet, J. Mallevalle and M. Roustan.
"A New Method To Dissolve Ozone into Water: Deep U Tube." Environmental Technology Letters, Volume 7, 1986, pp. 469-478.
- Bull, Richard J. "Toxicological Problems Associated With Alternative Methods of Disinfection." Journal AWWA, December 1982, pp. 642-648.
- Cairo, Patrick R., James T. Coyle, John J. Davis, Howard M. Neukrug, Irwin H. Suffet and Arnold Wicklund.
"Evaluating Regenerated Activated Carbon Through Laboratory and Pilot-Column Studies." Journal AWWA, February 1982, pp. 94-102.
- Chrostowski, Paul C., Andrea M. Dietrich and Irwin H. Suffet. "Laboratory Testing of Ozonation Systems Prior to Pilot-Plant Operations." Ozone in Water Treatment-Applications, Operations, and Technology. AWWA, USA, 1985, pp. 97-102.
- Clifford, Dennis, Philip Chu and Albert Lau. "Thermal Regeneration of Powdered Activated Carbon (PAC) and PAC-Biological Sludge Mixtures." Water Research, Volume 17, Number 9, 1983, pp. 1125-1138.
- Craig, R.F. Soil Mechanics. Fourth Edition, Van Nostrand Reinhold (UK) Co. Ltd., Great Britain, 1987.
- Culp, Russell L. and Robert M. Clark. "Granular Activated Carbon Installations." Journal AWWA, August 1983, pp. 398-405.
- De Laat, J., F. Bouanga, M. Dore and J. Mallevalle.
"Influence of Bacterial Growth in Granular Activated Carbon Filters on the Removal of Biodegradable and of Non-Biodegradable Organic Compounds." Water Research, Volume 19, Number 12, 1985, pp. 1565-1578.
- Decoret, C., J. Royer, B. Legube, and M. Dore.
"Experimental and Theoretical Studies of the Mechanism of the Initial Attack of Ozone on Some Aromatics in Aqueous Medium." Environmental Technology Letters, Volume 5, 1984, pp. 207-218.

- Deithorn, Robert T. and Anthony F. Mazzoni. "Activated Carbon What it is, How it Works." Water Technology, Volume 9, Number 8, November 1986, pp. 26-29.
- Den Blanken, John G. "Microbial Activity in Activated Carbon Filters". Journal of the Environmental Engineering Division, ASCE Proceedings, April 1982, pp. 405-425.
- Dowbiggin, William B. and Philip C. Singer. "Effects of Natural Organic Matter and Calcium on Ozone-Induced Particle Destabilization." Journal AWWA, June 1989, pp. 77-84.
- Edwards, Gerald A., and A. Amirtharajah. "Removing Color Caused by Humic Acids." Journal AWWA, March 1985, pp. 50-57.
- El-Rehaili, Abdullah M. and Walter J. Weber Jr. "Correlation of Humic Substance Trihalomethane Formation Potential and Adsorption Behavior to Molecular Weight Distribution in Raw and Chemically Treated Waters." Water Research, Volume 21, Number 5, 1987, pp. 573-582.
- Elia, Victor J., C. Scott Clark, Kevin T. McGinnis, Terence E. Cody and Riley N. Kinman. "Ozonation in a Wastewater Reuse System: Examination of Products Formed." Journal WPCF, July 1978, pp. 1727-1732.
- Environmental Protection Agency. Process Design Manual for Carbon Adsorption. EPA, USA, 1973.
- Evans, Francis L. III. Ozone in Water and Wastewater Treatment. Ann Arbor Science Publishers Inc, USA, 1972.
- Farooq, Shaukat, Richard S. Engelbrecht and Edward S. K. Chian. "Process Considerations in Design of Ozone Contactor for Disinfection." Journal of the Environmental Engineering Division, ASCE Proceedings, October 1978, pp. 835-847.

- Glaze, William H. "Drinking-Water Treatment with Ozone." Environment Science and Technology, Volume 21, Number 3, 1987, pp. 224-230.
- Glaze, William H. and James L. Wallace. "Control of Trihalomethane Precursors in Drinking Water: Granular Activated Carbon With and Without Preozonation." Journal AWWA, February 1984, pp. 68-75.
- Gordon, Gilbert, Kerwin Rakness, David Vornehm and Delmer Wood. "Limitations of the Iodometric Determination of Ozone." Journal AWWA, June 1989, pp. 72-76.
- Graese, Sandra L., Vernon L. Snoeyink and Ramon G. Lee. "Granular Activated Carbon Filter - Adsorber Systems." Journal AWWA, December 1987, pp. 64-68.
- Grasso, Domenic, Walter J. Weber Jr. and John A. DeKam. "Effects of Preoxidation With Ozone on Water Quality: A Case Study." Journal AWWA, June 1989, pp. 85-92.
- Greenberg, Arnold E. "Public Health Aspects of Alternative Water Disinfectants." Journal AWWA, January 1981, pp. 31-40.
- Gurol, Mirat D. "Factors Controlling the Removal of Organic Pollutants in Ozone Reactors." Journal AWWA, August 1985, pp. 55-60.
- Gurol, Mirat D. and Phillip C. Singer. "Kinetics of Ozone Decomposition: A Dynamic Approach." Environment Science and Technology. Volume 16, Number 7, 1982, pp. 377-383.
- Harrington, Gregory W., Francis A. DiGiano. "Adsorption Equilibria of Natural Organic Matter After Ozonation." Journal AWWA, June 1989, pp. 93-102.
- Hillman, Bette. "The Chlorination Question. Highlights of the Recent Conference in California." Environment Science and Technology, Volume 16, Number 1, 1982, pp. 15A-18A.

- Hoigne, J. and H. Bader. "The Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions." Water Research, Volume 10, 1976, pp. 377-386.
- Hoigne, J. and H. Bader. "Rate Constants of Reactions of Ozone With Organic and Inorganic Compounds in Water I Non-Dissociating Organic Compounds." Water Research, Volume 17, 1983, pp. 173-183.
- Hoigne, J. and H. Bader. "Rate Constants of Reactions of Ozone With Organic and Inorganic Compounds in Water II Dissociating Organic Compounds." Water Research, Volume 17, 1983, pp. 185-194.
- Hyde, Robert A., Don G. Hill, Tom F. Zabel and Terry Burke. "Replacing Sand with GAC in Rapid Gravity Filters." Journal AWWA, December 1987, pp. 33-38.
- Josephson, Julian. "Humic Substances." Environment Science and Technology, Volume 16, Number 1, 1982, pp. 20A-24A.
- Josephson, Julian. "Stratospheric Ozone: Changing Forcasts." Environment Science and Technology, Volume 16, Number 6, 1982, pp. 328A-331A.
- Keller, James W., Robert A. Morin and Timothy J. Schaffernoth. "Ozone Disinfection Pilot-Plant Studies at Laconia, N. H." Journal AWWA, December 1974, pp. 730-733.
- Kirkham, Michael and Associates. "First Iowa Ozone Plant On-Line." Journal AWWA, August 1985, pp. 93-94.
- Kuhn, W., H. Sontheimer, L. Steiglitz, D. Maier and R. Kurz. "Uses of Ozone and Chlorine in Water Utilities in the Federal Republic of Germany." Ozone in Water Treatment-Applications, Operations, and Technology. AWWA, USA, 1985, pp. 79-84.
- Lambert, S. D. and N. J. D. Graham. "Adsorption Methods for Treating Organically Coloured Upland Waters." Environmental Technology Letters, Volume 10, 1989, pp. 785-798.

- LePage, Wilfred L. "A Treatment Plant Operator Assesses Ozonation." Journal AWWA, August 1985, pp. 44-48.
- Liao, Wenta, Russell F. Christman, J. Donald Johnson and David S. Millington. "Structual Characterization of Aquatic Humic Material." Environment Science and Technology, Volume 16, Number 7, 1982, pp. 403-409.
- Lykins Jr., Benjamin W., Robert M. Clark and Jeffrey Q. Adams. "Granular Activated Carbon for Controlling THMs." Journal AWWA, May 1988, pp. 85-92.
- Maloney, Stephen W., I. H. Suffet, Keith Bancroft and Howard M. Neukrug. "Ozone-GAC Following Conventional US Drinking Water Treatment." Journal AWWA, August 1985, pp. 66-73.
- Martin, R. J. and W. J. Ng. "Chemical Regeneration of Exhausted Activated Carbon - II." Water Research, Volume 19, Number 12, 1985, pp. 1527-1535.
- McCreary, John J. and Vernon L. Snoeyink. "Characterization and Activated Carbon Adsorption of Several Humic Substances." Water Research, Volume 14, 1980, pp. 151-160.
- Metcalf & Eddy, Inc. Wastewater Engineering: Treatment Disposal Reuse. Second Edition, McGraw-Hill Book Company, USA, 1979.
- Monk, Robert D.G., Robert Y. Yoshimura, Micheal G. Hoover and Sherry H. Lo. "Prepurchasing Ozone Equipment." Journal AWWA, August 1985, pp. 49-54.
- Narkis, Nava, Alberto M. Wachs and Malka Schneider. "Ozone Effect on Nitrogenous Matter in Effluents." Journal of the Environmental Engineering Division, ASCE Proceedings, October 1977, pp. 887-891.
- Neulrug, Howard M., Matthew G. Smith, Stephen W. Maloney and Irwin H. (Mel) Suffet. "Biological Activated Carbon - At What Cost?" Ozone in Water Treatment- Applications, Operations, and Technology. AWWA, USA, 1985.

- Oliver, Barry G. and Simon A. Visser. "Chloroform Production From the Chlorination of Aquatic Humic Material: The Effect of Molecular Weight, Environment and Season." Water Research, Volume 14, 1980, pp. 1137-1141.
- Peavy, Howard S., Donald R. Rowe and George Tchobanoglous. Environmental Engineering. McGraw-Hill Book Company, USA, 1985.
- Perrich, Jerry R. Activated Carbon Adsorption for Wastewater Treatment. CRC Press, Inc., USA, 1981.
- Peyton, Gary R. and William H. Glaze. "Destruction of Pollutants in Water With Ozone in Combination With Ultraviolet Radiation. 3. Photolysis of Aqueous Ozone." Environment Science and Technology, Volume 22, Number 7, 1988, pp. 761-767.
- Randtke, Stephen J. and Christopher P. Jepsen. "Effects of Salts on Activated Carbon Adsorption of Fulvic Acids." Journal AWWA, February 1982, pp. 84-93.
- Randtke, Stephen J. and Vernon L. Snoeyink. "Evaluating GAC Adsorptive Capacity." Journal AWWA, August 1983, pp. 406-413.
- Rapinat, Michel. "Recent Developments in Water Treatment in France." Ozone in Water Treatment- Applications, Operations and Technology. AWWA, USA, 1985, pp. 71-78.
- Renner, Robert C. and Kerwin L. Rakness. "Ozone Design Considerations for Water Treatment." Ozone in Water Treatment- Applications, Operations, and Technology. AWWA, USA, 1985.
- Rice, Rip G., C. Michael Robson, G. Wade Miller and Archibald G. Hill. "Uses of Ozone in Drinking Water Treatment." Journal AWWA, January 1981, pp. 44-56.
- Rice, Rip G. and C. Michael Robson. Biological Activated Carbon, Enhanced Aerobic Biological Activity in GAC Systems. Ann Arbor Science Publishers, USA, 1982.

- Rice, Rip G. and Aharan Netzer. Handbook of Ozone Technology and Applications. Volume 1, Ann Arbor Science Publishers, USA, 1982.
- Rice, Rip G. and G. Wade Miller. "The Use of Ozone in Non-Conventional Treatment Techniques for Controlling Organics in Drinking Water." Ozone in Water Treatment-Applications, Operations, and Technology. AWWA, USA, 1985, pp. 47-70.
- Roberts, Paul V. and R. Scott Summers. "Performance of Granular Activated Carbon for Total Organic Carbon Removal." Journal AWWA, February 1982, pp. 113-118.
- Rosen, Harvey M. "Ozone Applications: A Water Reuse Review." Ozone in Water Treatment- Applications, Operations and Technology. AWWA, USA, 1985, pp. 17-46.
- Roy, Dipak, E. S. K. Chian and R. S. Engelbrecht. "Kinetics of Enteroviral Inactivation by Ozone." Journal of The Environmental Engineering Division, ASCE Proceedings, October 1981, pp. 887-901.
- Sanks, Robert L. Water Treatment Plant Design For the Practicing Engineer. Ann Arbor Science Publishers, USA, 1978.
- Sawyer, Clair N. and Perry L. McCarty. Chemistry for Environmental Engineering. McGraw-Hill Book Company, Third Edition, USA, 1978.
- Schalekamp, Maarten. "Comparisons Between Two Ozone Plants With Normal and Increased Frequency as Well as of the Effect Between a Dosage of 1 Milligramme Resp. 5 Milligrammes of O₃ per Litre." Ozone in Water Treatment- Applications, Operations, and Technology. AWWA, USA, 1985, pp. 83-94.
- Servais, Pierre, Gilles Billen and Marie-Claude Hascoet. "Determination of the Biodegradable Fraction of Dissolved Organic Matter in Waters." Water Research, Volume 21, Number 4, 1987, pp. 445-450.

- Sotelo, J. L., F. J. Beltran, F. J. Benitez and J. Beltran-Heredia. "Henry's Law Constant for the Ozone-Water System." Water Research, Volume 23, Number 10, 1989, pp. 1239-1246.
- Weber Jr., Walter J., Thomas C. Voice and Abdullah Jodellah. "Adsorption of Humic Substances: The Effects of Heterogeneity and System Characteristics." Journal AWWA, December 1983, pp. 612-619.
- Weber Jr., Walter J. and Edward H. Smith. "Simulation and Design Models for Adsorption Processes." Environment Science and Technology, Volume 21, Number 11, 1987, pp. 1040-1049.
- Weng, Cheng-nan, Donald L. Hoven and Barry J. Schwartz. "Ozonation: An Economic Choice for Water Treatment." Journal AWWA, November 1986, pp.83-89.
- Wiesner, Mark R., John J. Rook and Francois Fiessinger. "Optimizing the Placement of GAC Filtration Units." Journal AWWA, December 1987, pp.39-49.
- Yurteri, Coskum. Removal of Organic Pollutants by Ozonation: Kinetics and Reactor Design. Drexel University of Philadelphia, Pennsylvania, 1989.

APPENDIX A

Table A1: Turbidity, apparent color, pH and alkalinity of the raw water. Testing occurred from May 1989 to April 1990.

MONTH	TURBIDITY NTU	APPARENT COLOR	pH	ALKALINITY HCO ₃ ⁻
MAY	24.0	120	6.6	39
JUNE		60	8.1	56
JULY		55	7.6	79
AUGUST	3.2	45	7.1	90
SEPTEMBER	3.5	55	7.7	83
OCTOBER	3.3	55	7.7	80
NOVEMBER	3.9	40	7.7	82
DECEMBER	3.0	25	7.7	88
JANUARY	2.7	20	7.6	88
FEBRUARY	1.6	25	7.4	90
MARCH	2.5	20	7.6	94
APRIL	2.4	25	7.7	94

Table A2: Raw water hardness. Testing occurred from May 1989 to April 1990.

MONTH	TOTAL HARDNESS mg/l CaCO ₃	CALCIUM HARDNESS mg/l CaCO ₃	MAGNESIUM HARDNESS mg/l CaCO ₃
MAY	42	33	9
JUNE	56	42	14
JULY	69	50	19
AUGUST	78	56	22
SEPTEMBER	76	58	18
OCTOBER	80	58	22
NOVEMBER	86	64	22
DECEMBER	87	65	22
JANUARY	99	68	31
FEBRUARY	95	70	25
MARCH	98	70	28
APRIL	96	72	24

Table A3: Total carbon, organic carbon and inorganic carbon of the raw water. Testing occurred between May 1989 and April 1990.

MONTH	TOTAL CARBON mg/l	ORGANIC CARBON mg/l	INORGANIC CARBON mg/l
MAY	24.0	15.0	9.0
JUNE	24.7	11.5	13.3
JULY	25.4	11.1	14.3
AUGUST	29.2	10.9	18.3
SEPTEMBER	28.3	12.0	16.3
OCTOBER	30.9	12.3	18.6
NOVEMBER	29.8	11.0	18.8
DECEMBER	38.1	11.2	26.9
JANUARY	22.4	7.3	15.1
FEBRUARY	29.0	8.1	20.9
MARCH	28.7	7.5	21.2
APRIL	30.1	8.2	21.9

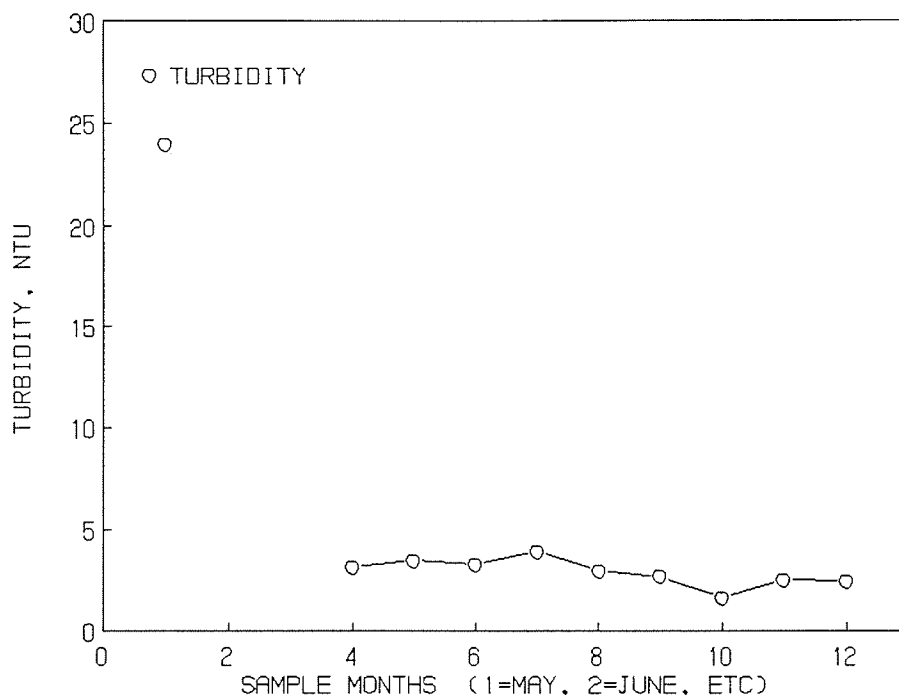


Figure A1: Turbidity of the raw water.

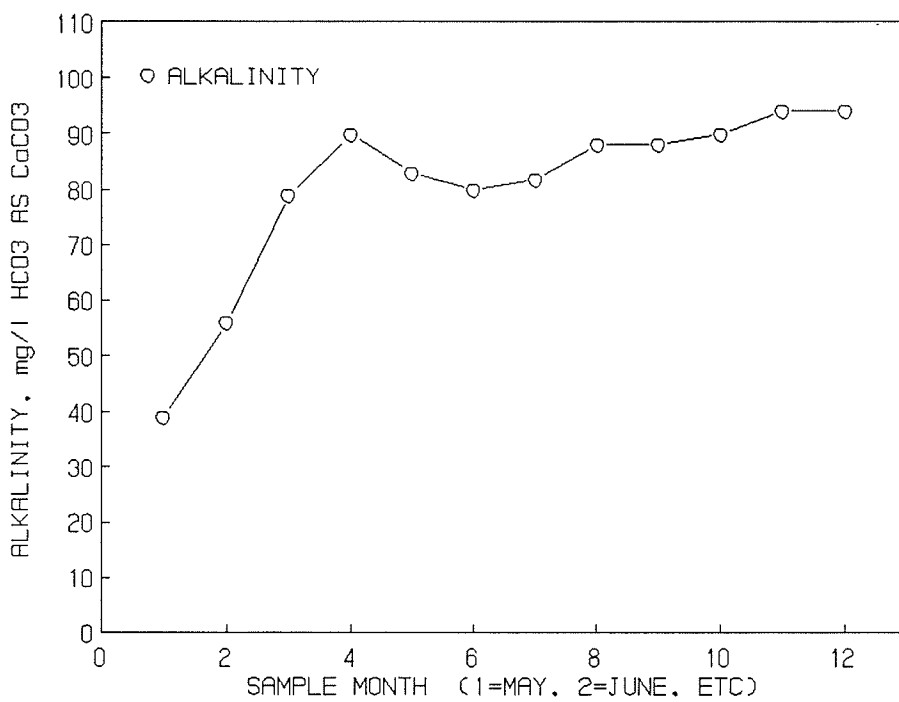


Figure A2: Alkalinity of the raw water.

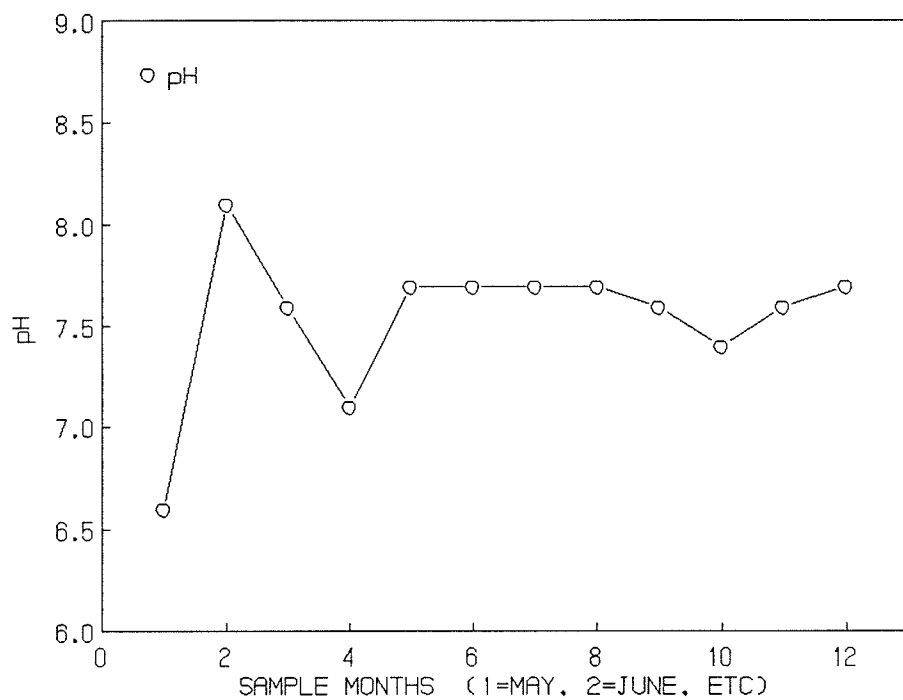


Figure A3: pH of the raw water.

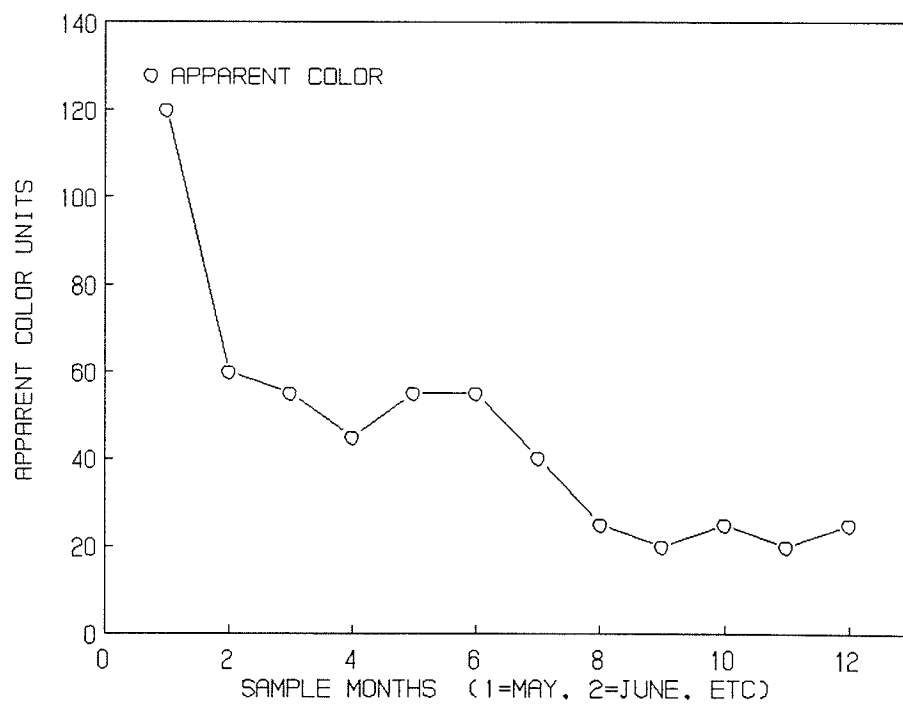


Figure A4: Apparent color of the raw water.

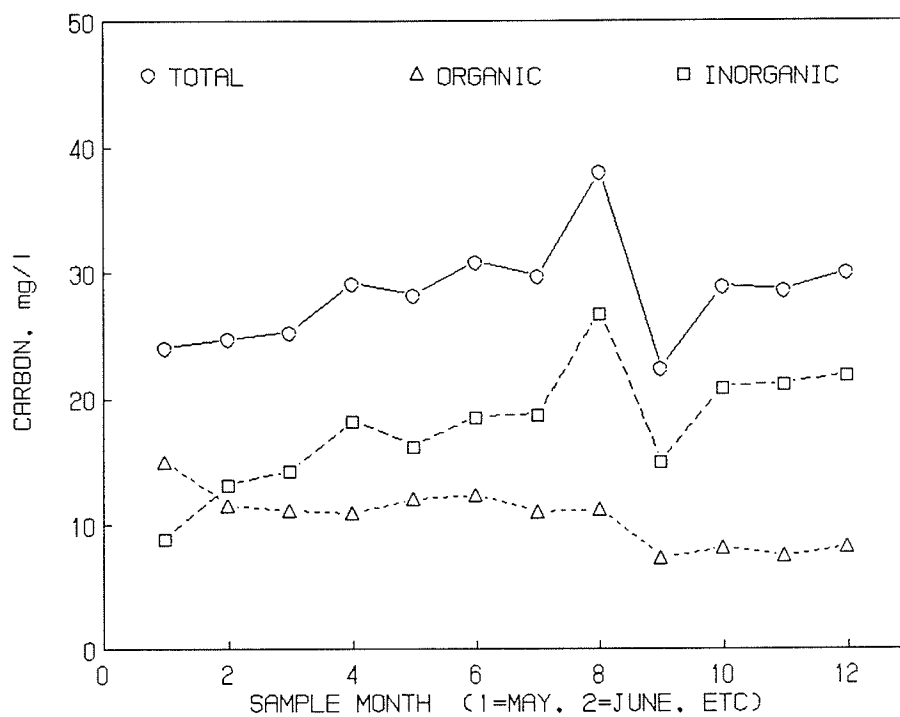


Figure A5: Total carbon, organic carbon and inorganic carbon of the raw water.

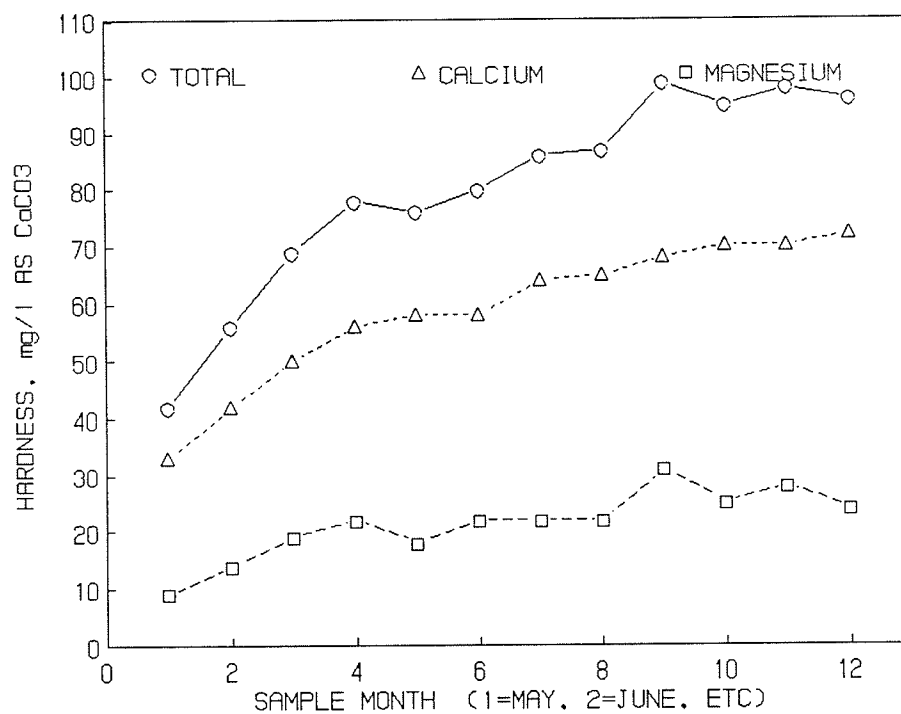


Figure A6: Hardness of the raw water.

APPENDIX B

Table B1: Percent ozone removed from gas flow during ozonation at 25°C using the December sample water.

INITIAL OZONE DOSAGE mg/l	OZONE REMOVED DURING TREATMENT mg/l	PERCENT OZONE REMOVED DURING OZONATION, %	OZONATION PERIOD MINUTES
0.72	0.65	90	10
1.91	1.41	74	10
2.73	1.83	67	10
4.77	2.34	49	10
1.44	1.33	95	20
3.82	2.56	67	20
5.46	3.60	66	20
9.54	4.39	46	20

Table B2: Percent ozone removed from gas flow during ozonation at 4°C using January and February sample water.

INITIAL OZONE DOSAGE mg/l	OZONE REMOVED DURING TREATMENT mg/l	PERCENT OZONE REMOVED DURING OZONATION, %	OZONATION PERIOD MINUTES
0.95	0.95	100	10
1.55	1.40	90	10
1.80	1.64	91	10
2.55	2.01	79	10
3.23	2.16	67	10
4.43	2.92	66	10
5.10	2.70	53	10
6.10	3.42	56	10
1.91	1.91	100	20
3.10	2.79	90	20
3.60	3.17	88	20
5.10	3.72	73	20
6.45	4.00	62	20
8.85	5.58	63	20
10.20	5.20	51	20

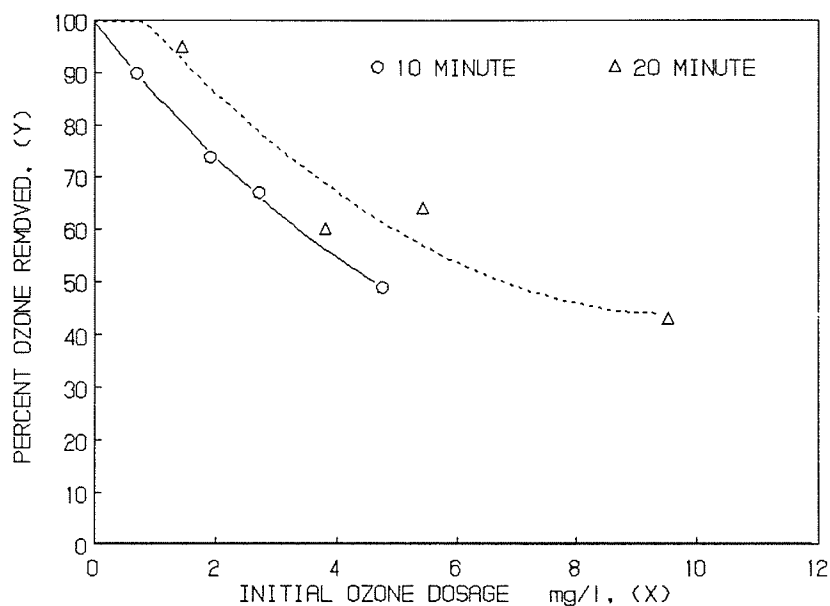


Figure B1: Percent ozone removed from the gas flow during ozonation at 25°C using the December water sample.
 $Y(10 \text{ minutes}) = 99.77 - 174.63 \cdot X/12 + 118.75 \cdot (X/12)^2$
 $Y(20 \text{ minutes}) = 110.86 - 165.10 \cdot X/12 + 101.92 \cdot (X/12)^2$

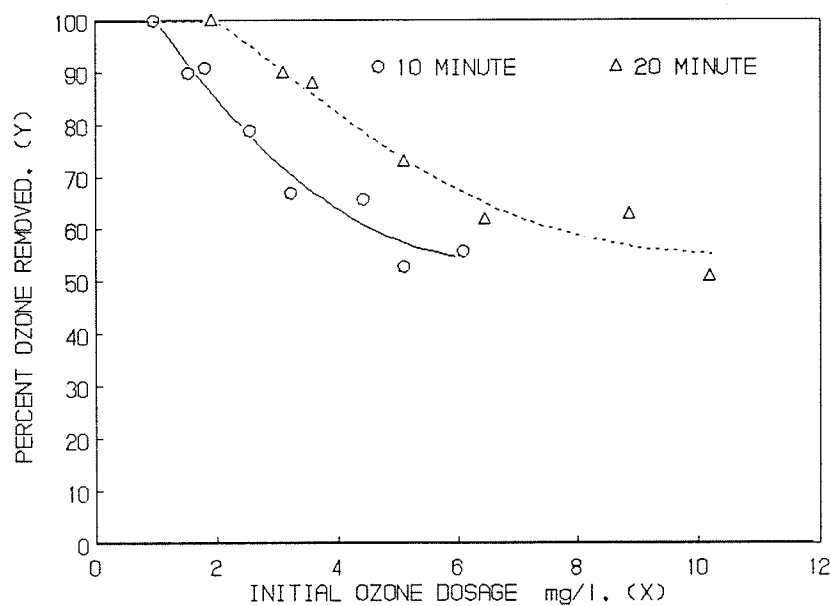


Figure B2: Percent ozone removed from the gas flow during ozonation at 4°C using the January and February water samples.
 $Y(10 \text{ minutes}) = 118.05 - 234.29 \cdot X/12 + 216.12 \cdot (X/12)^2$
 $Y(20 \text{ minutes}) = 122.02 - 145.35 \cdot X/12 + 77.10 \cdot (X/12)^2$

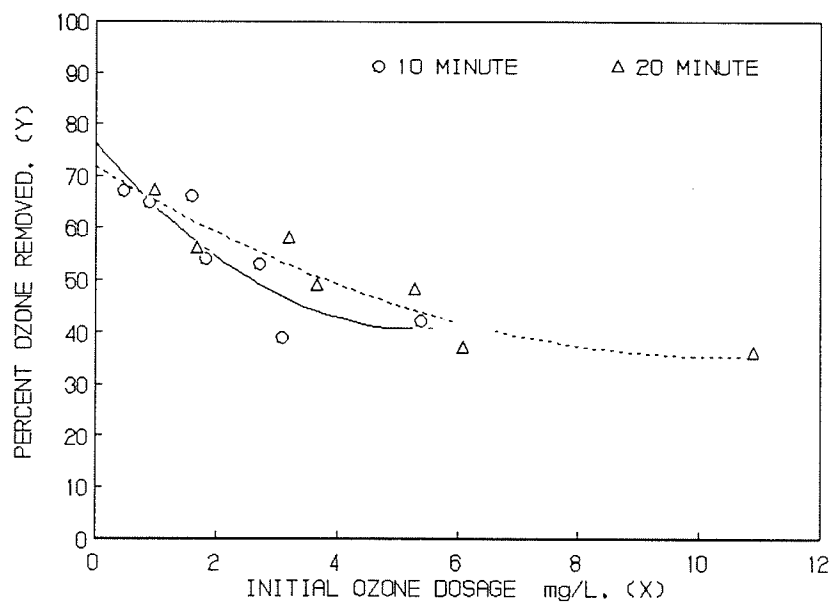


Figure B3: Percent ozone removed from the gas flow during ozonation at 4°C using the March and April water samples.

$$Y(10 \text{ minutes}) = 76.21 - 161.11 \cdot X/12 + 183.22 \cdot (X/12)^2$$

$$Y(20 \text{ minutes}) = 71.62 - 83.27 \cdot X/12 + 47.98 \cdot (X/12)^2$$

APPENDIX C

Table C1: Monthly treated water data.

MONTH	OZONATION TIME MINUTES	TEMP C	OZONE DELIVERED mg/l	CARBON mg/l			pH
				TC	TOC	TIC	
MAY	10	25	0.00	11.9	1.76	10.1	7.0
MAY	10	25	1.10	13.1	1.47	11.6	6.8
MAY	10	25	2.28	13.7	2.65	11.1	7.0
MAY	20	25	0.00	9.1	1.03	8.1	7.4
MAY	20	25	1.13	14.8	1.02	13.7	7.2
MAY	20	25	2.39	8.9	0.88	8.0	6.9
MAY	20	25	2.97	11.2	1.47	9.7	6.7
JUNE	10	25	0.00	14.4	2.10	12.3	6.8
JUNE	10	25	0.73	12.5	1.97	10.5	6.7
JUNE	10	25	1.66	12.0	1.84	10.1	6.7
JUNE	20	25	0.00	10.5	2.04	8.4	6.9
JUNE	20	25	1.60	8.5	0.93	7.6	7.7
JUNE	20	25	2.74	10.6	1.10	9.5	6.8
JULY	10	25	0.00	15.2	1.60	13.6	6.6
JULY	10	25	1.26	14.0	0.78	13.2	6.6
JULY	10	25	2.16	15.0	0.90	14.1	6.7
JULY	20	25	0.00	14.0	1.10	12.9	7.7
JULY	20	25	1.33	12.9	1.14	11.8	7.5
JULY	20	25	1.97	14.1	1.20	12.9	7.0
JULY	20	25	2.54	16.1	1.30	14.8	7.0
JULY	20	25	3.15	12.5	1.10	11.4	7.0
AUGUST	10	25	0.00	16.6	1.80	14.8	6.7
AUGUST	10	25	1.30	14.5	1.70	12.8	7.1
AUGUST	10	25	1.93	15.6	1.20	14.4	7.4
AUGUST	20	25	0.00	14.3	1.40	12.9	6.7
AUGUST	20	25	1.41	20.9	1.20	19.7	7.6
AUGUST	20	25	2.56	14.9	1.50	13.4	7.1
AUGUST	20	25	3.23	19.7	1.20	18.5	7.3
SEPTEMBER	10	25	0.00	22.7	1.18	21.5	7.0
SEPTEMBER	10	25	0.65	17.1	1.14	16.0	7.1
SEPTEMBER	10	25	1.36	14.4	1.25	13.2	6.9
SEPTEMBER	10	25	2.32	16.6	1.15	15.5	7.1
SEPTEMBER	20	25	0.00	19.8	1.60	18.2	
SEPTEMBER	20	25	1.32	17.3	1.05	16.3	6.8
SEPTEMBER	20	25	2.28	16.2	1.10	15.1	7.0
SEPTEMBER	20	25	3.85	15.9	0.90	15.0	7.2

Table C1: Continued.

MONTH	OZONATION TIME MINUTES	TEMP C	OZONE DELIVERED mg/l	CARBON mg/l			pH
				TC	TOC	TIC	
OCTOBER	10	25	0.00	19.3	0.96	18.3	7.1
OCTOBER	10	25	1.00	20.3	1.24	19.1	7.5
OCTOBER	10	25	1.53	23.4	1.28	22.1	6.8
OCTOBER	10	25	1.97	19.5	0.89	18.6	7.0
OCTOBER	10	25	2.29	19.8	1.02	18.8	7.4
OCTOBER	20	25	0.00	20.5	0.93	19.6	7.0
OCTOBER	20	25	1.90	20.4	1.00	19.4	7.3
OCTOBER	20	25	2.75	19.4	1.17	18.2	6.7
OCTOBER	20	25	3.99	21.5	0.94	20.6	7.1
NOVEMBER	10	25	0.00	20.2	1.01	19.2	7.0
NOVEMBER	10	25	1.63	21.4	1.32	20.1	7.0
NOVEMBER	10	25	1.70	20.6	1.07	19.5	7.8
NOVEMBER	10	25	2.31	20.7	0.86	19.8	7.4
NOVEMBER	20	25	0.00	23.7	0.99	22.7	7.1
NOVEMBER	20	25	2.93	21.3	0.88	20.4	7.5
NOVEMBER	20	25	2.98	19.3	1.37	17.9	7.2
NOVEMBER	20	25	3.95	19.6	1.06	18.5	7.5
DECEMBER	10	4	0.00	27.6	1.29	26.3	7.8
DECEMBER	10	4	0.72	26.2	2.20	24.0	7.7
DECEMBER	10	4	1.90	26.5	1.53	25.0	7.8
DECEMBER	10	4	2.93	27.3	2.00	25.3	7.8
DECEMBER	10	25	0.00	25.6	1.73	23.9	7.3
DECEMBER	10	25	0.65	27.0	2.20	24.8	7.5
DECEMBER	10	25	1.81	26.4	1.20	25.2	7.7
DECEMBER	10	25	2.33	27.9	1.50	26.4	7.7
JANUARY	10	4	0.00	18.4	2.50	15.9	7.7
JANUARY	10	4	1.41	17.0	0.96	16.0	7.8
JANUARY	10	4	2.13	17.1	0.89	16.2	7.8
JANUARY	10	4	2.69	17.2	0.67	16.5	7.9
JANUARY	10	4	3.17	17.3	0.74	16.6	7.9
JANUARY	20	4	0.00	17.6	2.60	15.0	7.8
JANUARY	20	4	2.77	16.7	0.89	15.8	7.8
JANUARY	20	4	4.12	17.0	0.82	16.2	7.8

Table C1: Continued.

MONTH	OZONATION TIME MINUTES	TEMP C	OZONE DELIVERED mg/l	CARBON mg/l			pH
				TC	TOC	TIC	
FEBRUARY	10	4	0.00	22.9	1.12	21.8	7.2
FEBRUARY	10	4	1.18	23.7	0.97	22.7	7.4
FEBRUARY	10	4	1.82	21.1	1.41	19.7	7.5
FEBRUARY	10	4	3.01	23.0	1.00	22.0	8.0
FEBRUARY	20	4	0.00	24.6	1.14	23.5	7.1
FEBRUARY	20	4	1.22	21.8	0.81	21.0	7.9
FEBRUARY	20	4	2.03	22.9	0.96	21.9	7.3
FEBRUARY	20	4	3.18	22.1	1.41	20.7	7.6
FEBRUARY	20	4	4.36	21.7	0.86	20.8	7.7
MARCH	10	4	0.00	22.7	1.22	21.5	7.7
MARCH	10	4	1.46	23.2	1.00	22.2	7.8
MARCH	10	4	1.91	22.4	1.08	21.3	7.6
MARCH	20	4	0.00	23.0	1.26	21.7	7.6
MARCH	20	4	1.40	24.0	1.37	22.6	7.5
MARCH	20	4	2.90	22.9	1.23	21.7	7.8
MARCH	20	4	3.84	23.3	0.90	22.4	7.6
APRIL	10	4	0.00	23.7	1.50	22.2	7.6
APRIL	10	4	0.70	24.0	1.49	22.5	7.7
APRIL	10	4	1.47	24.1	1.46	22.6	7.6
APRIL	10	4	2.15	27.9	1.31	26.6	7.6
APRIL	10	4	3.01	25.1	1.30	23.8	7.8
APRIL	20	4	0.00	23.6	1.04	22.6	7.6
APRIL	20	4	1.59	23.8	1.08	22.7	7.7
APRIL	20	4	2.72	24.0	1.36	22.6	7.6
APRIL	20	4	4.00	24.9	15.1	23.4	7.5

Table C2: Monthly treated water data.

MONTH	OZONE DELIVERED mg/l	OZONE DOSAGE TIME MINUTES	TURBID- ITY NTU	ALKALINITY mg/l AS CaCO ₃	APPARENT COLOR UNITS	
					INITIAL	FINAL
MAY	0.00	10	6.0	40	120	30
MAY	1.10	10	8.0	38	120	25
MAY	2.28	10	7.0	48	120	30
MAY	0.00	20	1.4	40	120	20
MAY	1.13	20	4.0	52	120	15
MAY	2.39	20	3.4	40	120	20
MAY	2.97	20	4.4	40	120	15
JUNE	0.00	10		50	60	7
JUNE	0.73	10		34	60	5
JUNE	1.66	10		36	60	5
JUNE	0.00	20		32	60	12
JUNE	1.60	20		34	60	7
JUNE	2.74	20		36	60	5
JULY	0.00	10		64	55	10
JULY	1.26	10		56	55	10
JULY	2.16	10		54	55	10
JULY	0.00	20		62	55	5
JULY	1.33	20		60	55	5
JULY	1.97	20		64	55	5
JULY	2.54	20		68	55	5
JULY	3.15	20		58	55	5
AUGUST	0.00	10	1.1	74	45	5
AUGUST	1.30	10	1.0	74	45	5
AUGUST	1.93	10	1.4	74	45	5
AUGUST	0.00	20	1.0	70	45	5
AUGUST	1.41	20	1.8	96	45	5
AUGUST	2.56	20	1.2	72	45	7
AUGUST	3.23	20	1.2	80	45	5
SEPTEMBER	0.00	10	2.6	104	55	5
SEPTEMBER	0.65	10	2.4	68	55	5
SEPTEMBER	1.36	10	2.3	74	55	5
SEPTEMBER	2.32	10	2.2	76	55	5
SEPTEMBER	0.00	20	2.6	84	55	5
SEPTEMBER	1.32	20	2.3	64	55	5
SEPTEMBER	2.28	20	2.2	76	55	5
SEPTEMBER	3.85	20	2.4	76	55	5

Table C2: Continued.

MONTH	OZONE DELIVERED mg/l	OZONE DOSAGE TIME MINUTES	TURBID- ITY NTU	ALKALINITY mg/l AS CaCO ₃	APPARENT COLOR UNITS	
					INITIAL	FINAL
OCTOBER	0.00	10	2.8	74	55	12
OCTOBER	1.00	10	2.7	74	55	7
OCTOBER	1.53	10	2.8	76	55	7
OCTOBER	1.97	10	2.8	74	55	7
OCTOBER	2.29	10	2.8	74	55	7
OCTOBER	0.00	20	2.6	72	55	10
OCTOBER	1.90	20	2.6	74	55	12
OCTOBER	2.75	20	2.5	70	55	7
OCTOBER	3.99	20	2.4	74	55	7
NOVEMBER	0.00	10	3.4	72	40	7
NOVEMBER	1.63	10	3.2	74	40	5
NOVEMBER	1.70	10	3.2	78	40	5
NOVEMBER	2.31	10	3.1	80	40	5
NOVEMBER	0.00	20	3.4	88	40	5
NOVEMBER	2.93	20	3.0	80	40	5
NOVEMBER	2.98	20	3.2	73	40	5
NOVEMBER	3.95	20	3.4	78	40	5
DECEMBER	0.00	10	2.4	84	25	7
DECEMBER	0.72	10	3.2	78	25	7
DECEMBER	1.90	10	2.3	84	25	7
DECEMBER	2.93	10	4.2	84	25	7
DECEMBER	0.00	10	2.2	78	25	5
DECEMBER	0.65	10	2.4	76	25	5
DECEMBER	1.81	10	4.0	80	25	5
DECEMBER	2.33	10	2.3	82	25	5
JANUARY	0.00	10	2.5	84	20	7
JANUARY	1.41	10	3.4	86	20	5
JANUARY	2.13	10	2.4	86	20	7
JANUARY	2.69	10	2.3	86	20	5
JANUARY	3.17	10	2.4	88	20	5
JANUARY	0.00	20	2.4	86	20	5
JANUARY	2.77	20	2.4	86	20	5
JANUARY	4.12	20	2.3	90	20	5

Table C2: Continued.

MONTHLY	OZONE DELIVERED mg/l	OZONE DOSAGE TIME MINUTES	TURBID- ITY NTU	ALKALINITY mg/l AS CaCO ₃	APPARENT COLOR UNITS	
					INITIAL	FINAL
FEBRUARY	0.00	10	1.3	80	25	7
FEBRUARY	1.18	10	2.0	84	25	5
FEBRUARY	1.82	10	1.3	92	25	5
FEBRUARY	3.01	10	1.2	90	25	5
FEBRUARY	0.00	20	1.3	82	25	7
FEBRUARY	1.22	20	1.6	90	25	7
FEBRUARY	2.03	20	1.8	84	25	5
FEBRUARY	3.18	20	1.4	92	25	5
FEBRUARY	4.36	20	1.2	86	25	5
MARCH	0.00	10	2.0	92	20	10
MARCH	1.46	10	1.9	92	20	5
MARCH	1.91	10	1.9	94	20	5
MARCH	0.00	20	2.4	92	20	10
MARCH	1.40	20	1.8	92	20	5
MARCH	2.90	20	1.8	92	20	5
MARCH	3.84	20	1.7	96	20	5
APRIL	0.00	10	2.8	92	25	5
APRIL	0.70	10	2.0	94	25	5
APRIL	1.47	10	1.7	94	25	5
APRIL	2.15	10	1.9	96	25	5
APRIL	3.01	10	1.8	92	25	5
APRIL	0.00	20	1.9	92	25	5
APRIL	1.59	20	2.2	94	25	5
APRIL	2.72	20	1.6	92	25	5
APRIL	4.00	20	2.1	90	25	5

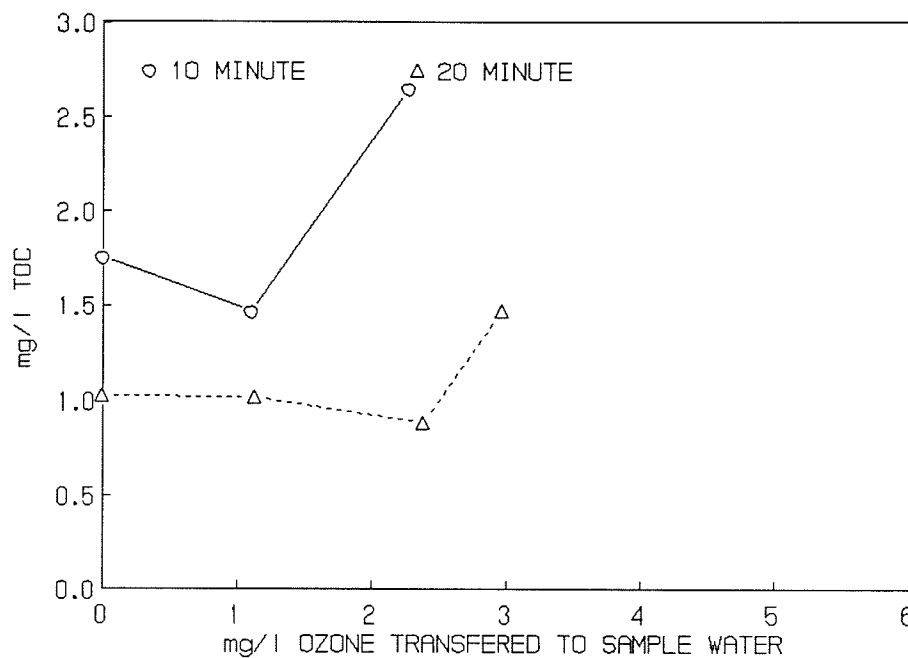


Figure C1: **May water sample.** TOC after treatment with both 10 and 20 minute contact times at 25°C. Initial TOC was 15.0 mg/l.

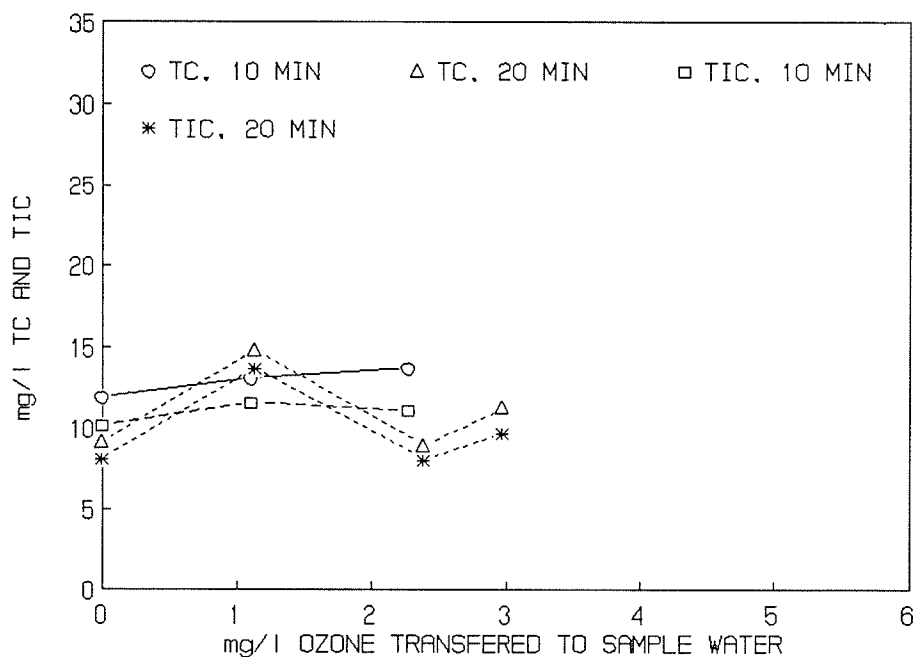


Figure C2: **May water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 25°C. Initial TC was 24.0 mg/l and TIC was 9.0 mg/l.

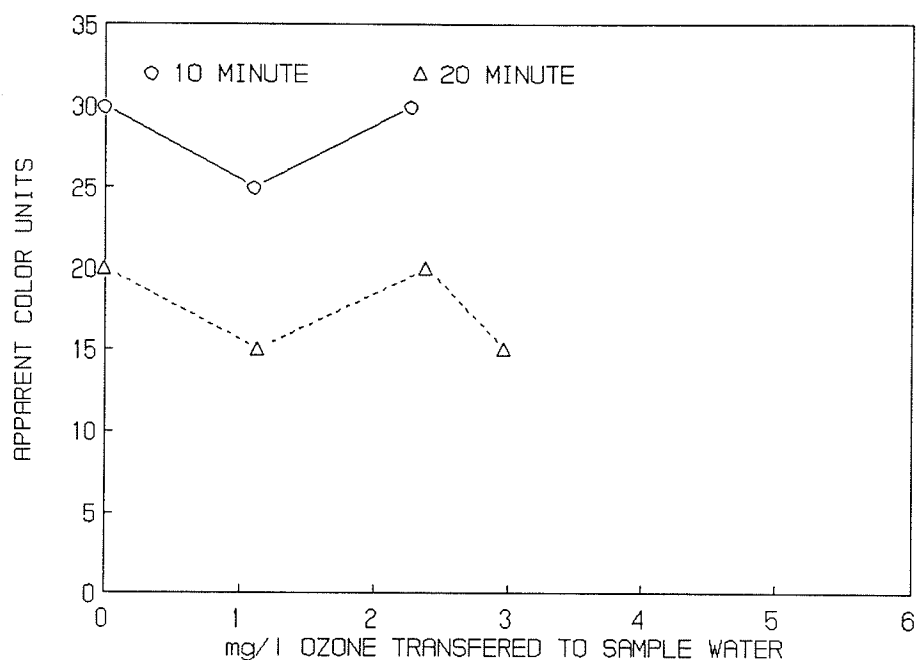


Figure C3: **May water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 25°C. Initial apparent color was 120 color units.

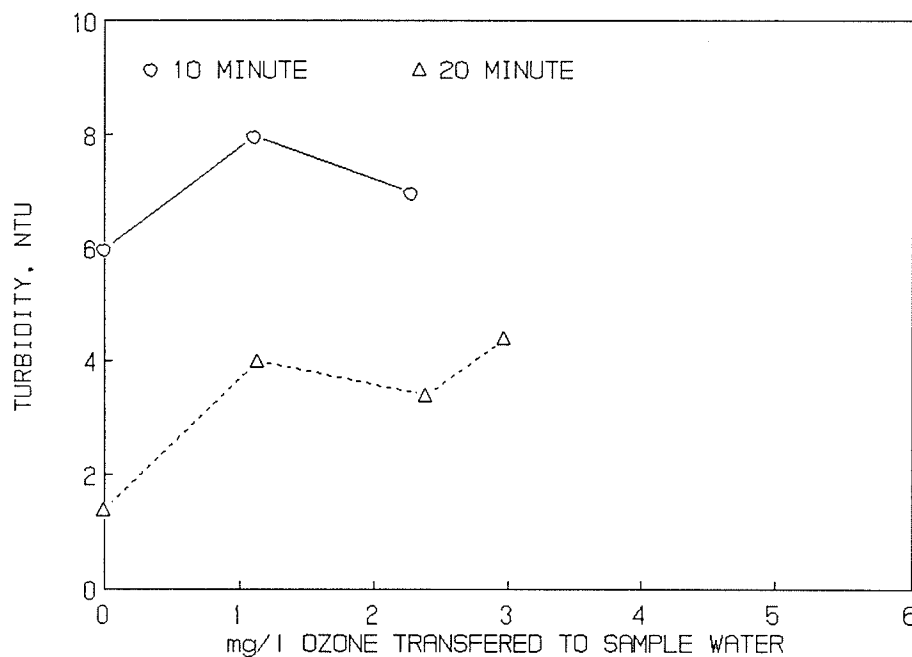


Figure C4: **May water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 25°C. Initial turbidity of 24.0 NTU.

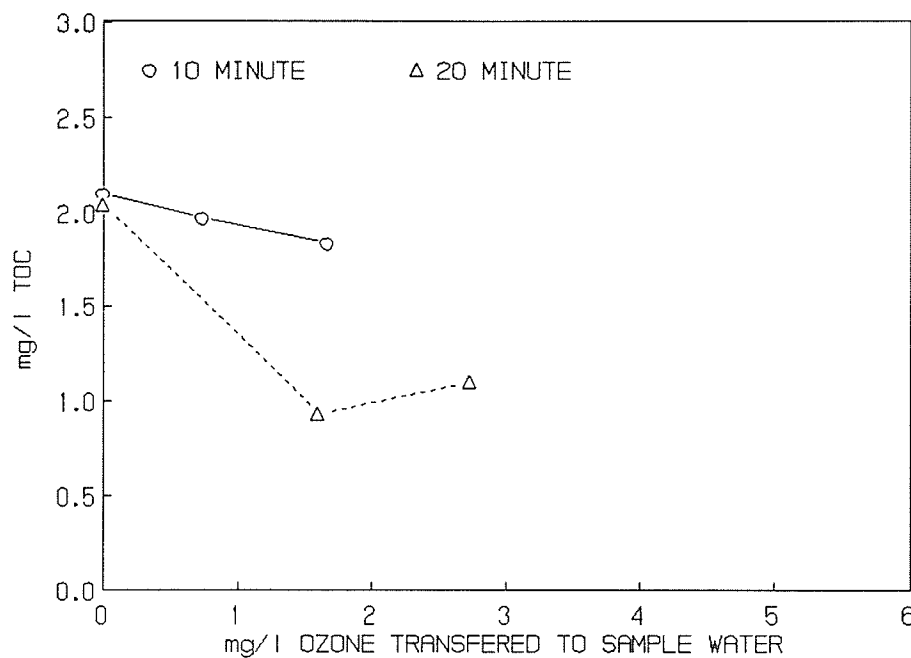


Figure C5: **June water sample.** TOC after treatment with both 10 and 20 minute contact times at 25°C. Initial TOC was 11.5 mg/l.

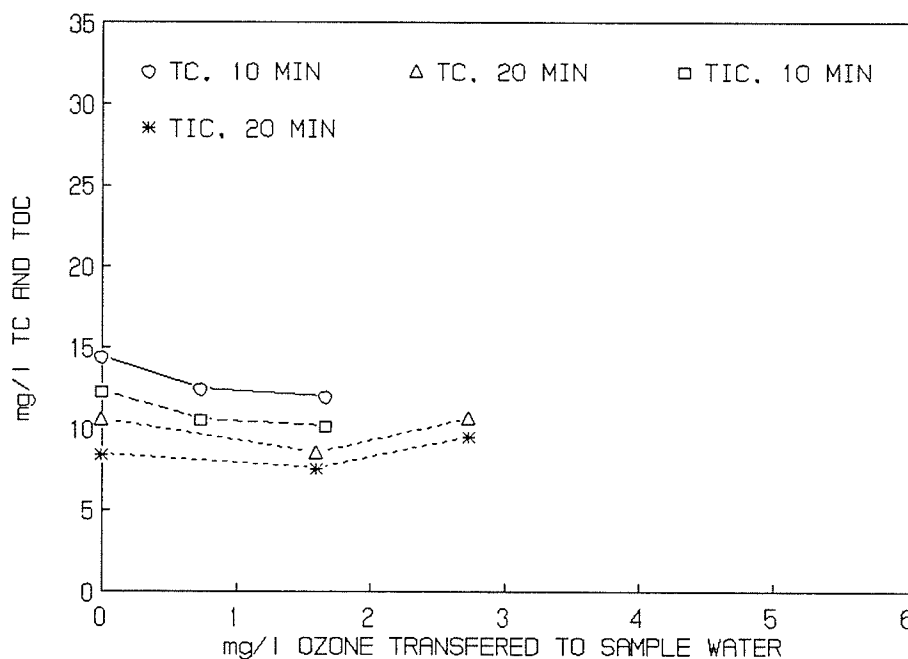


Figure C6: **June water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 25°C. Initial TC was 24.7 mg/l and TIC was 13.3 mg/l.

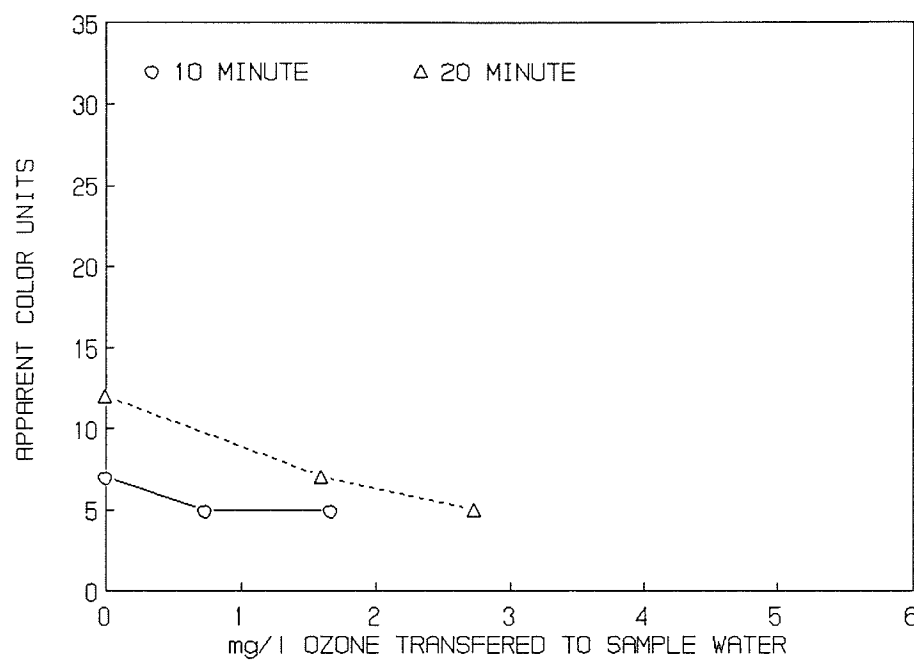


Figure C7: **June water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 25°C. Initial apparent color was 60 color units.

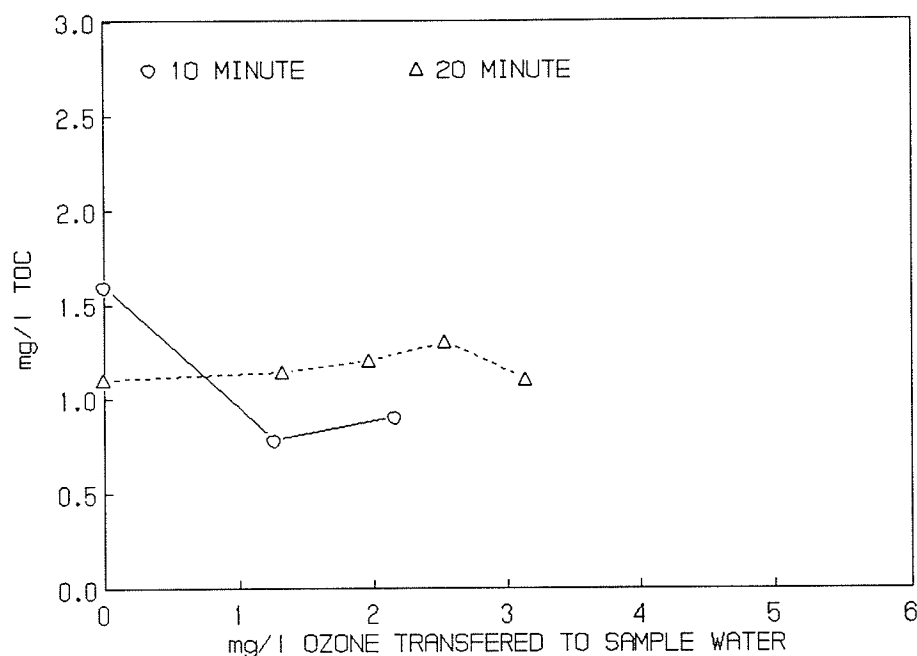


Figure C8: **July water sample.** TOC after treatment with both 10 and 20 minute contact times at 25°C. Initial TOC was 11.1 mg/l.

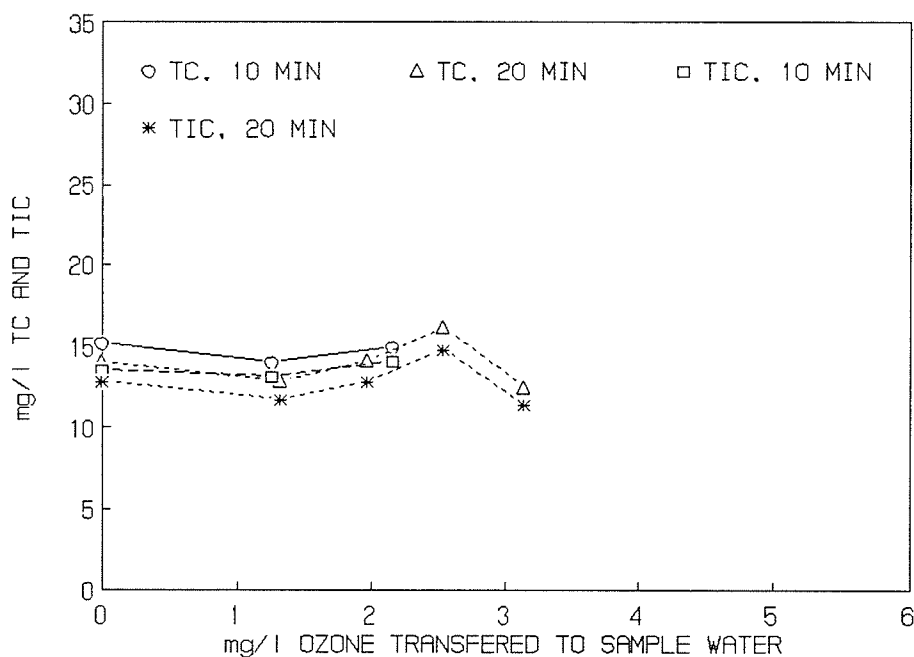


Figure C9: **July water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 25°C. Initial TC was 25.4 mg/l and TIC was 14.3 mg/l.

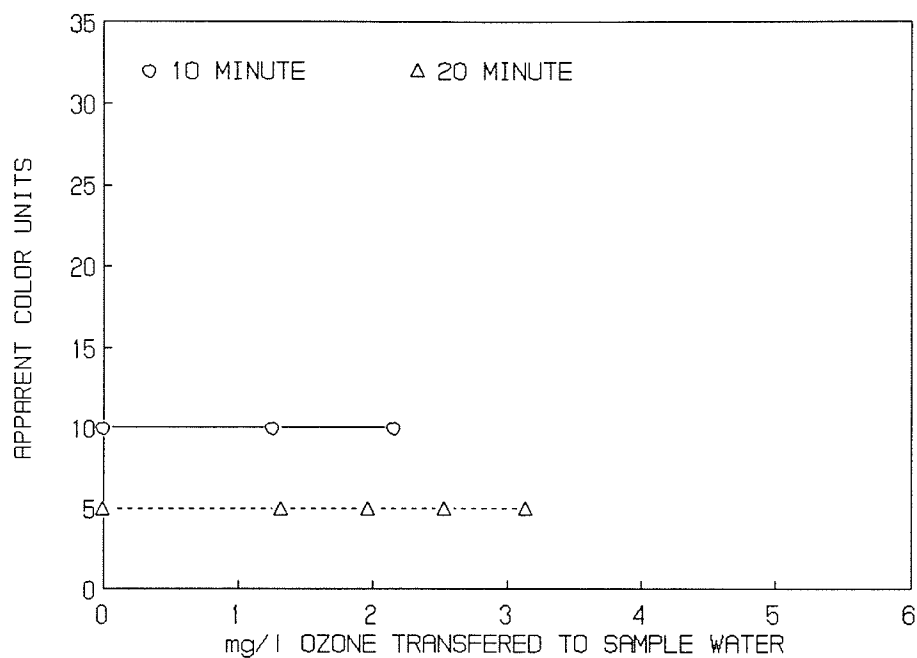


Figure C10: **July water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 25°C. Initial apparent color was 55 color units.

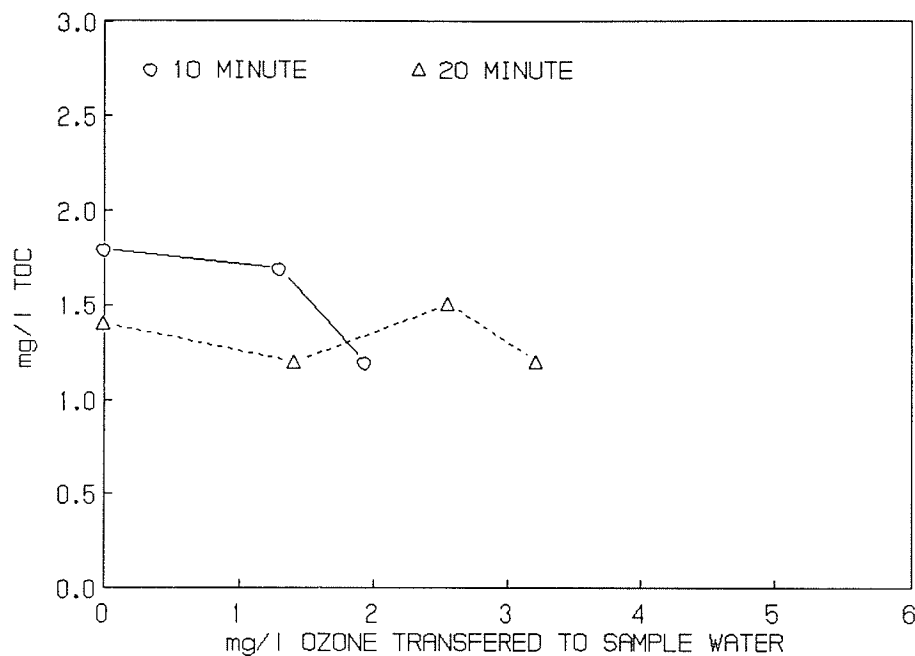


Figure C11: **August water sample.** TOC after treatment with both 10 and 20 minute contact times at 25°C. Initial TOC was 10.9 mg/l.

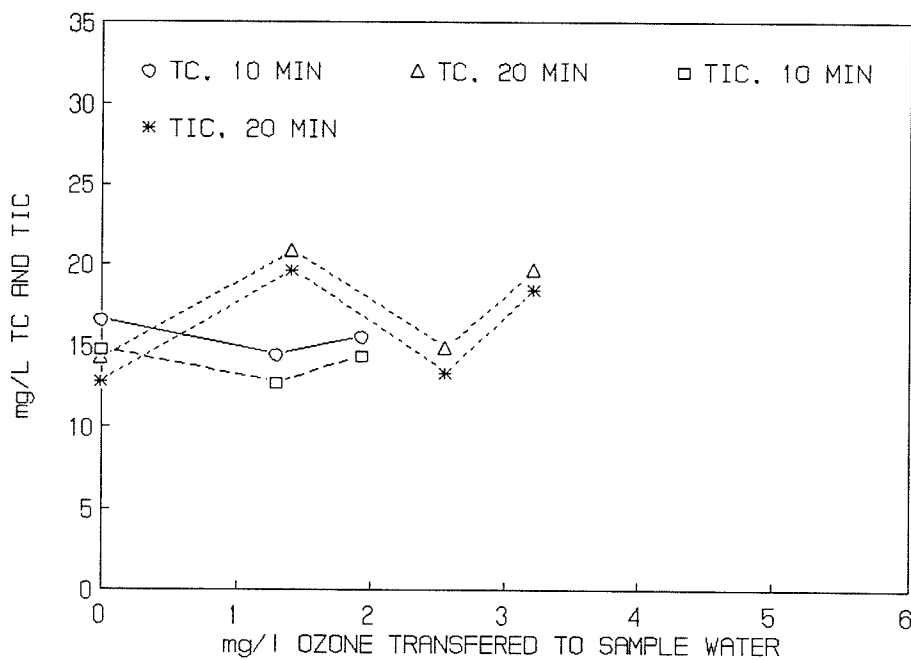


Figure C12: **August water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 25°C. Initial TC was 29.2 mg/l and TIC was 18.3 mg/l.

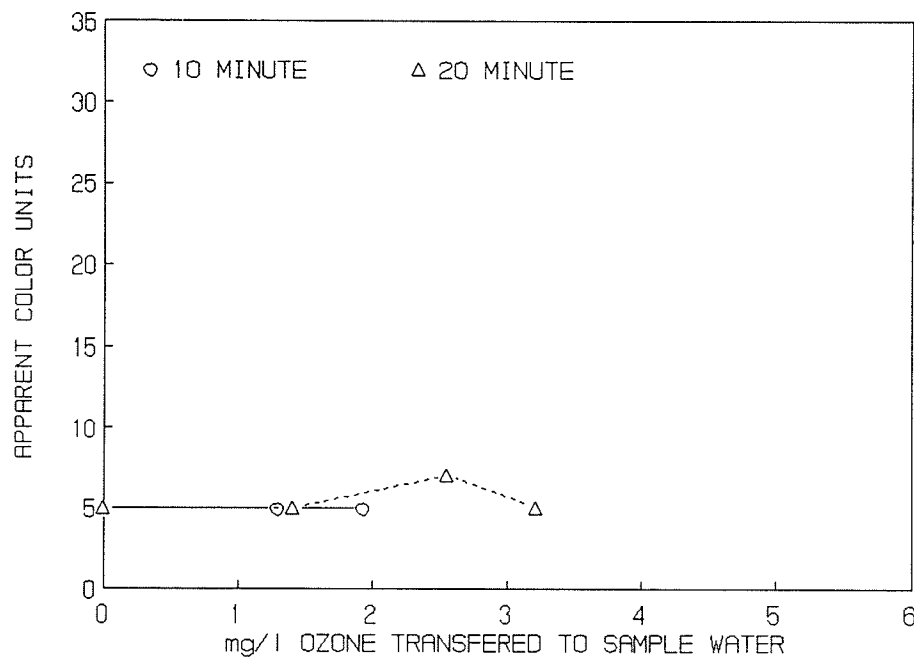


Figure C13: **August water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 25°C. Initial apparent color was 45 color units.

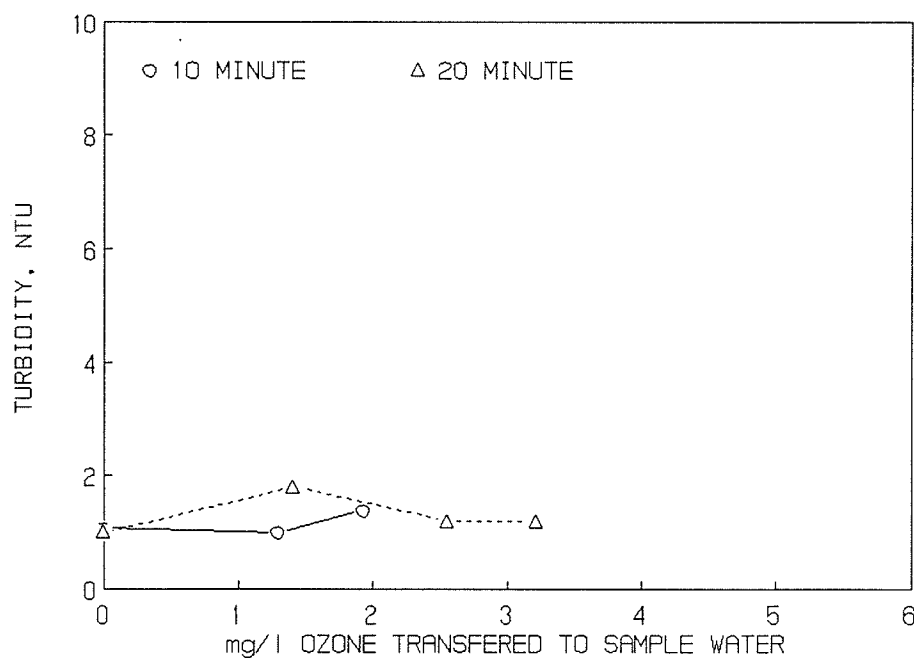


Figure C14: **August water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 25°C. Initial turbidity was 3.2 NTU.

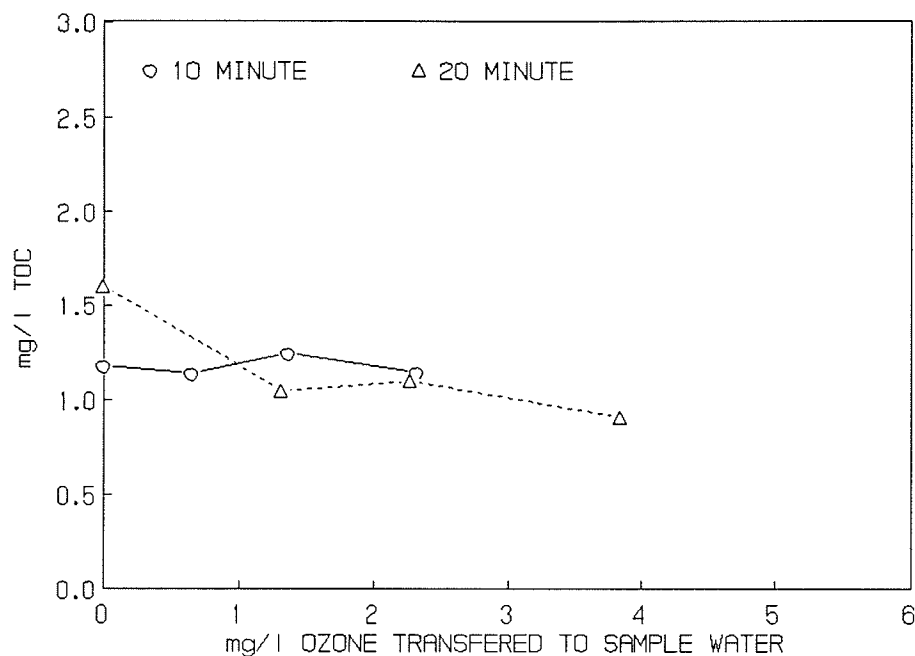


Figure C15: **September water sample.** TOC after treatment with both 10 and 20 minute contact times at 25°C. Initial TOC was 12.0 mg/l.

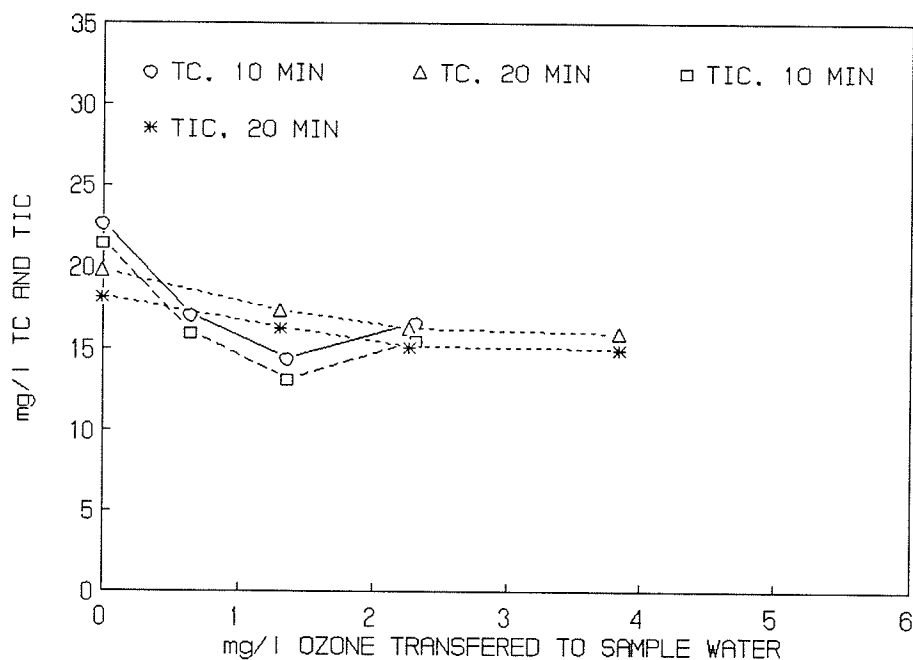


Figure C16: **September water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 25°C. Initial TC was 28.3 mg/l and TIC was 16.3 mg/l.

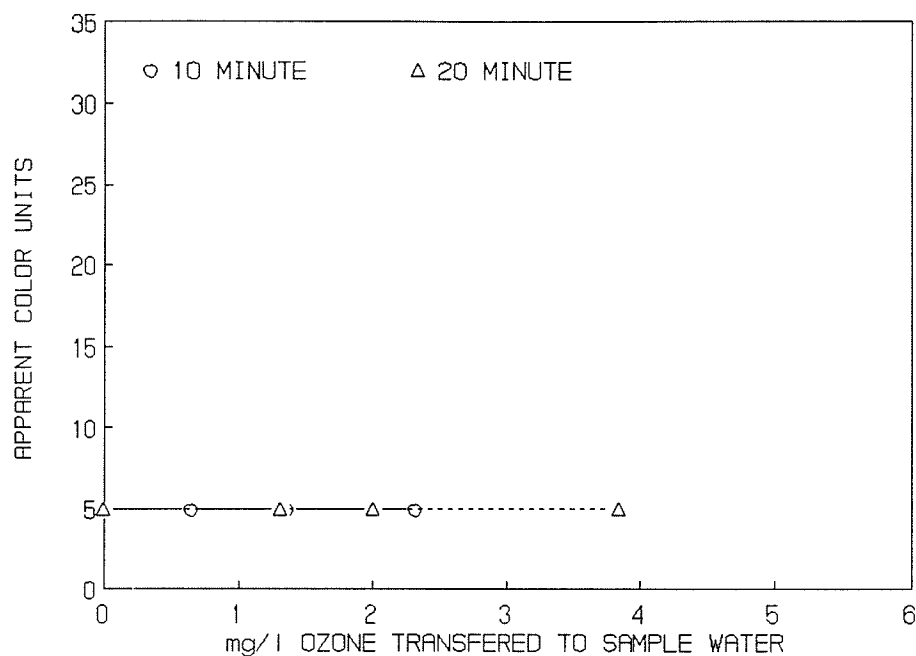


Figure C17: **September water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 25°C. Initial apparent color was 55 color units.

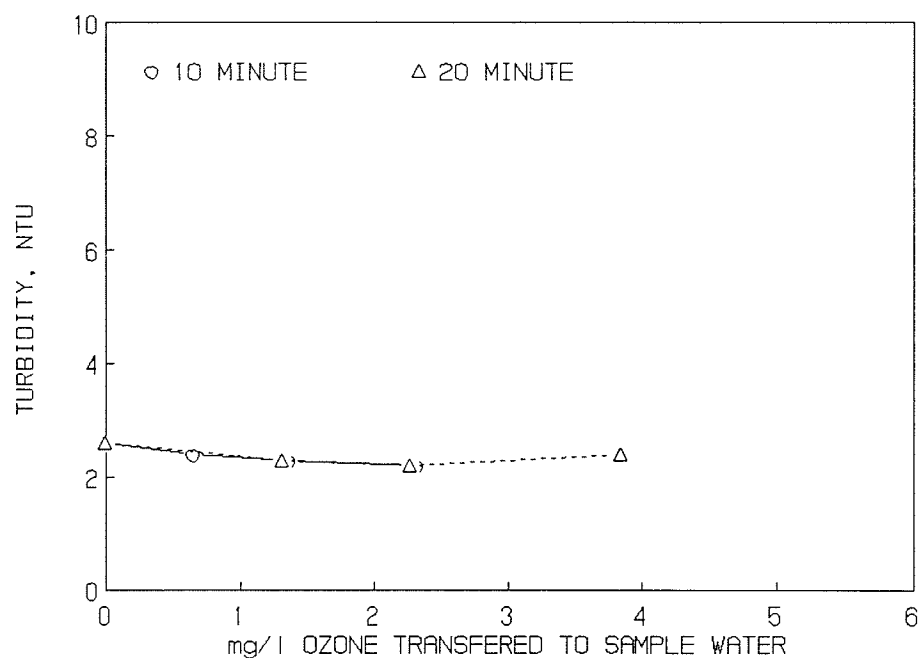


Figure C18: **September water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 25°C. Initial turbidity was 3.5 NTU.

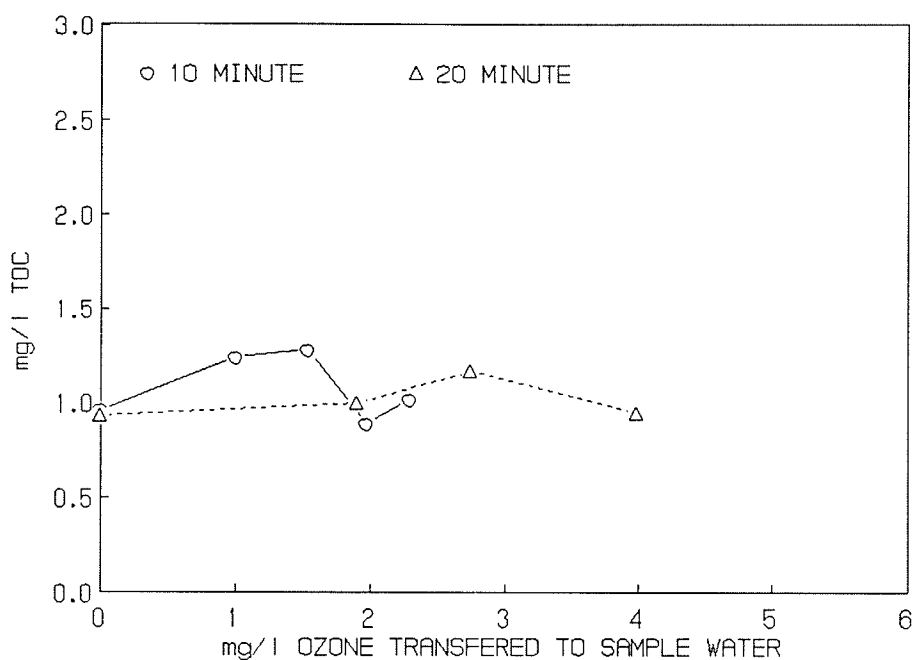


Figure C19: **October water sample.** TOC after treatment with both 10 and 20 minute contact times at 25°C. Initial TOC was 12.3 mg/l.

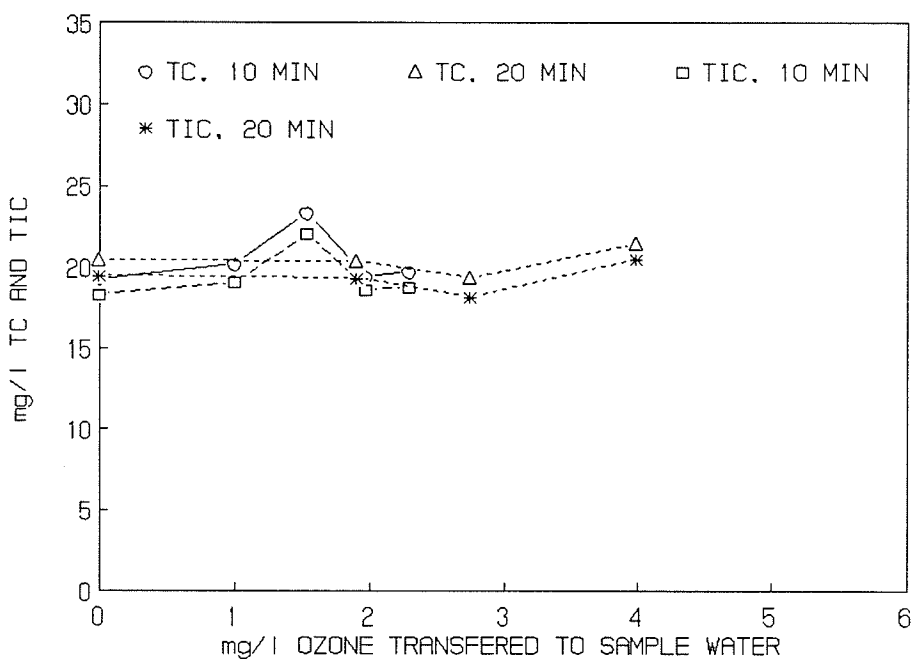


Figure C20: **October water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 25°C. Initial TC was 30.9 mg/l and TIC was 18.6 mg/l.

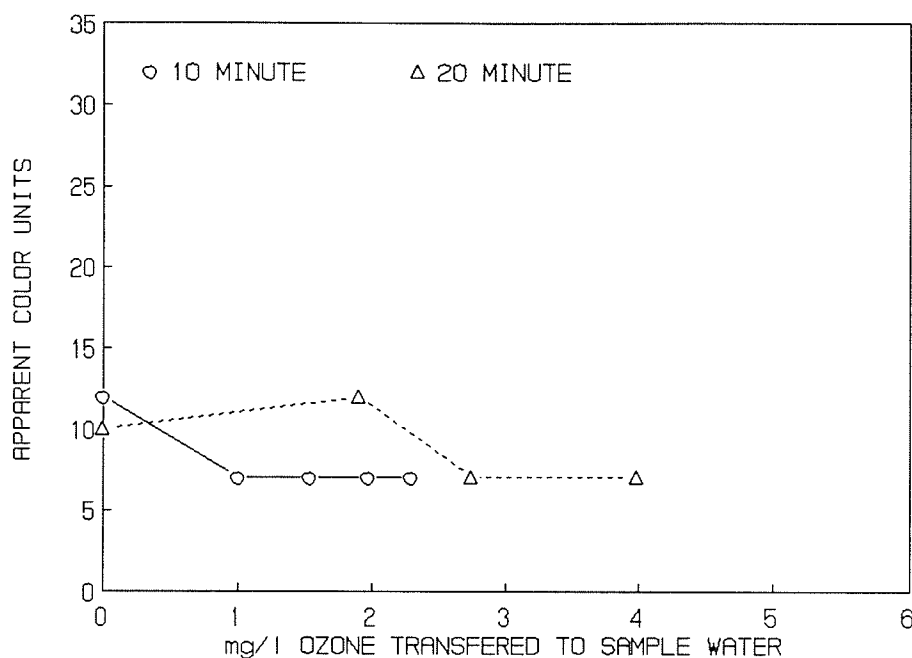


Figure C21: **October water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 25°C. Initial apparent color was 55 color units.

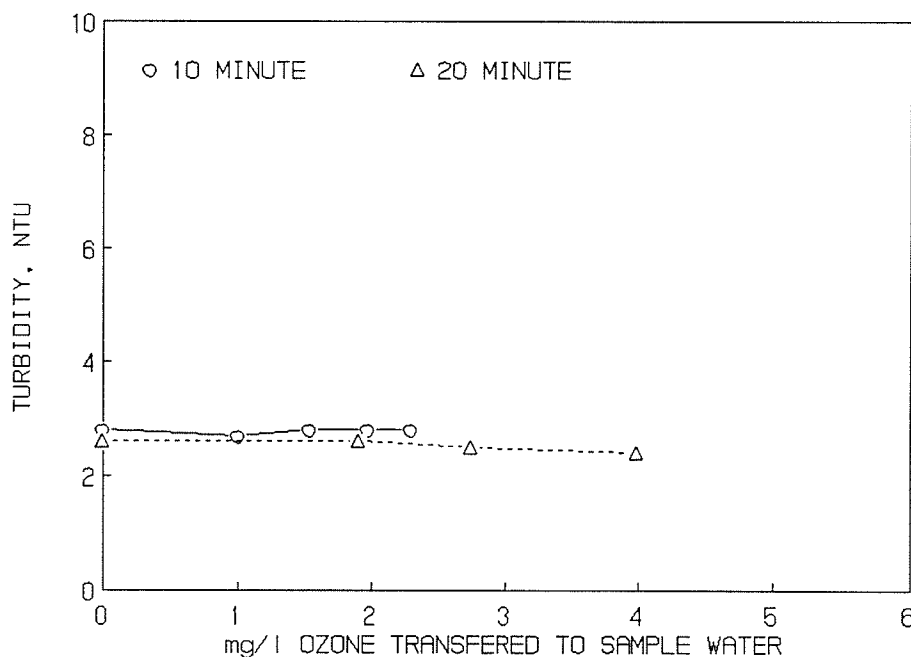


Figure C22: **October water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 25°C. Initial turbidity was 3.3 NTU.

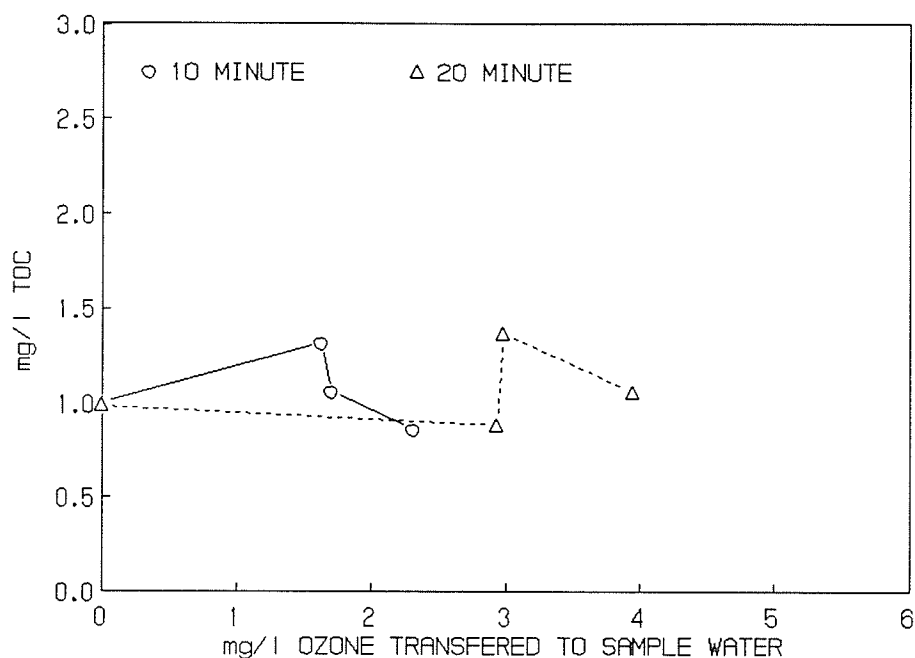


Figure C23: **November water sample.** TOC after treatment with both 10 and 20 minute contact times at 25°C. Initial TOC was 11.0 mg/l.

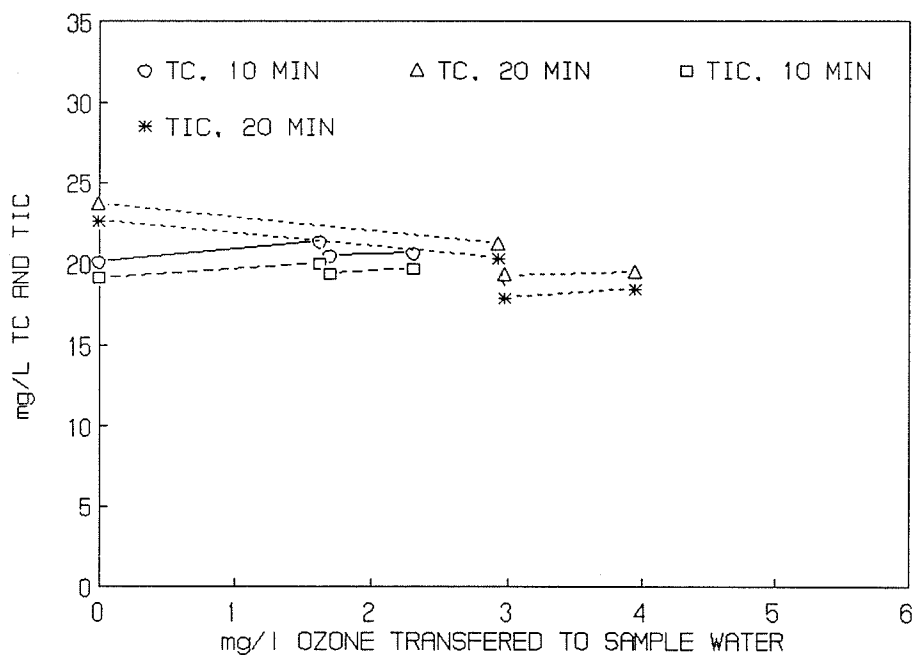


Figure C24: **November water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 25°C. Initial TC was 29.8 mg/l and TIC was 18.8 mg/l.

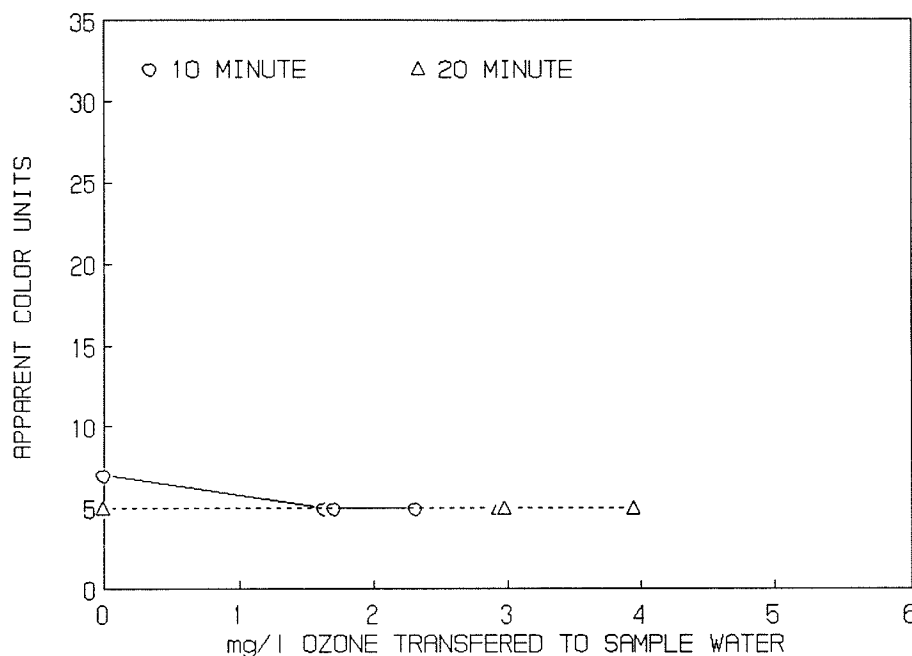


Figure C25: **November water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 25°C. Initial apparent color was 40 color units.

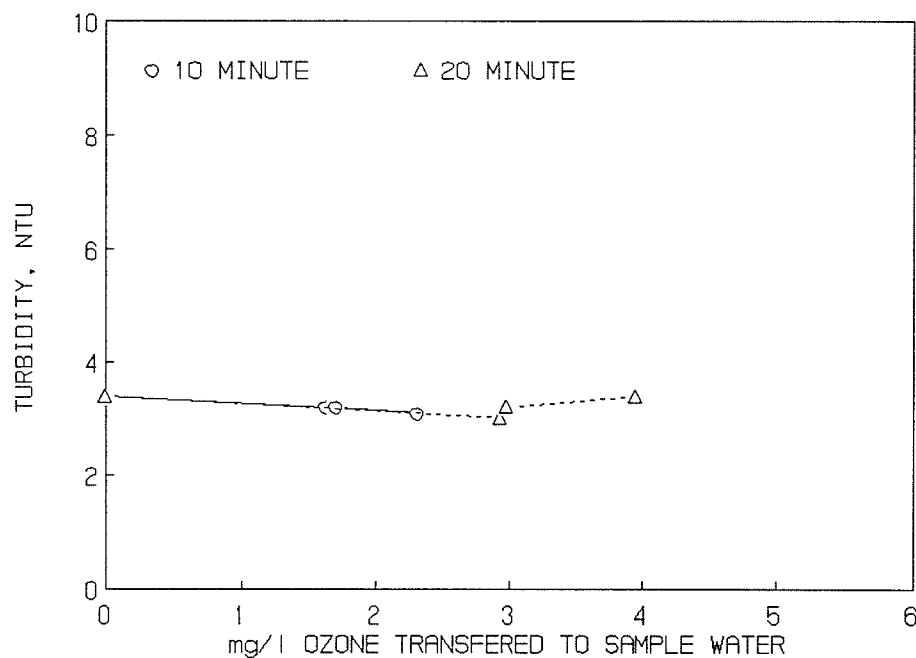


Figure C26: **November water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 25°C. Initial turbidity was 3.9 NTU.

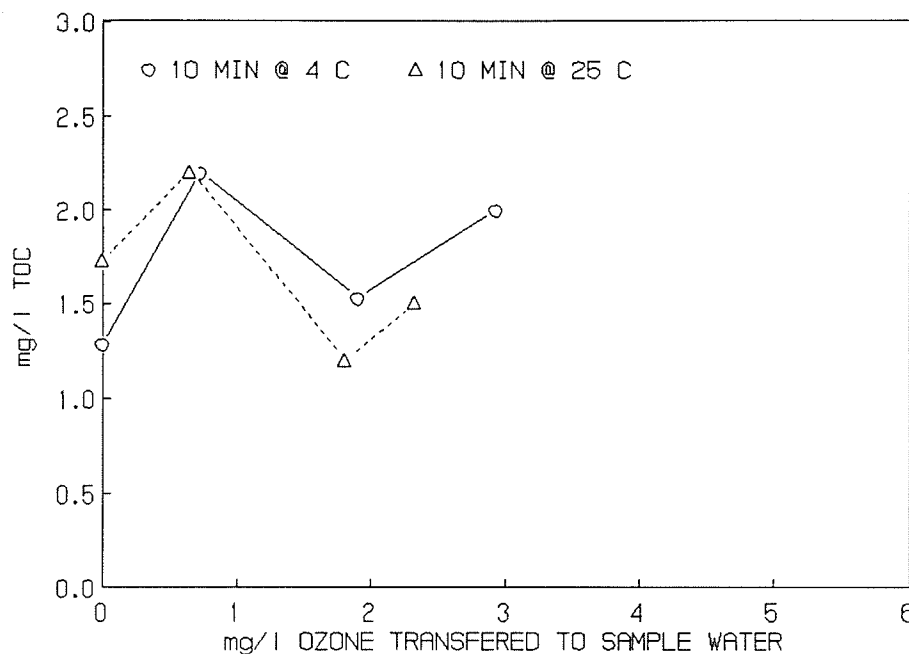


Figure C27: **December water sample.** TOC after treatment at 4°C and 25°C using a 10 minute contact time at 25°C. Initial TOC was 11.2 mg/l.

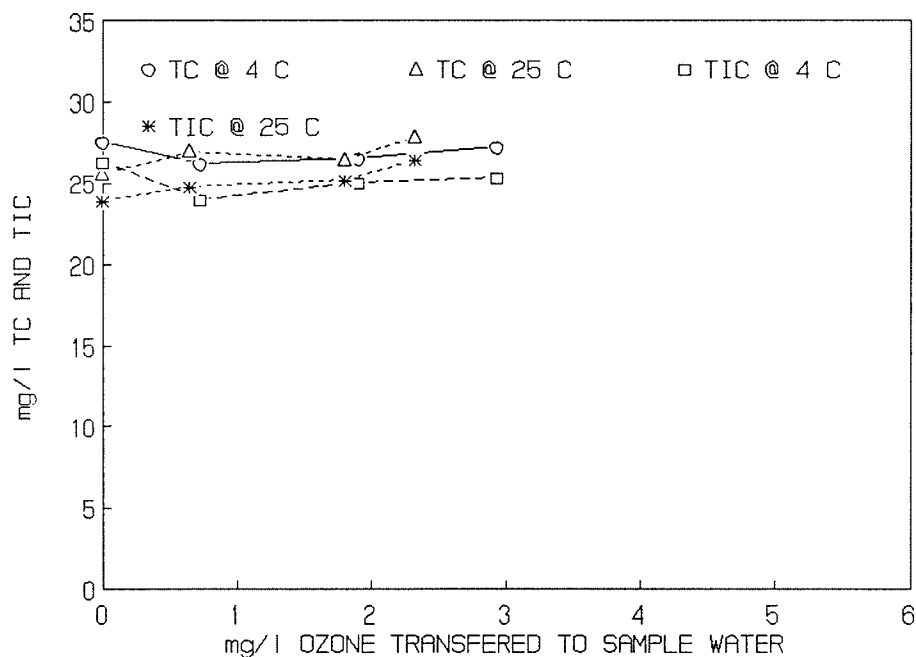


Figure C28: **December water sample.** TC and TIC after treatment at 4°C and 25°C using a 10 minute contact time. Initial TC was 38.1 mg/l and TIC was 26.9 mg/l.

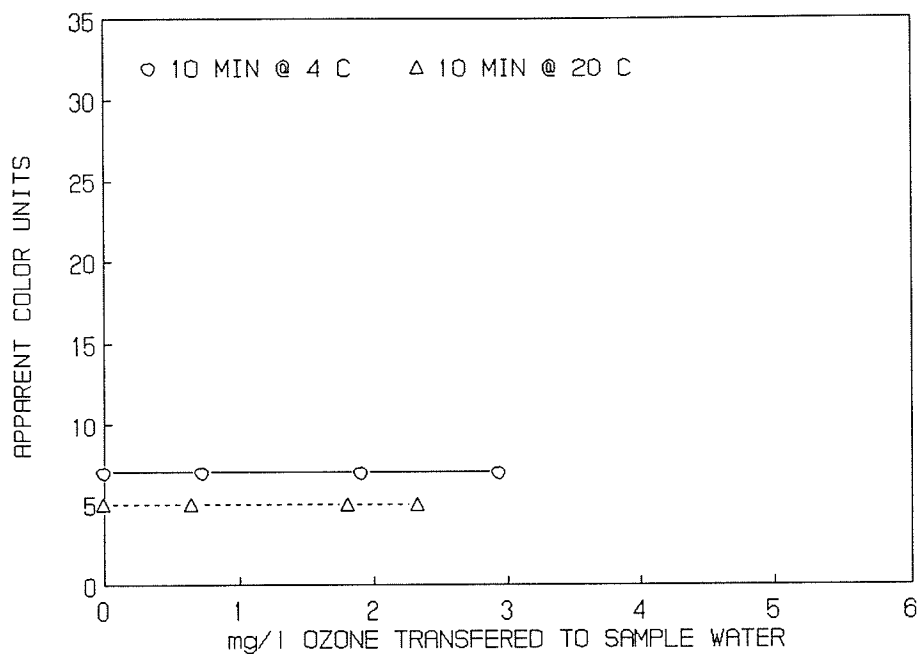


Figure C29: **December water sample.** Apparent color after treatment at 4°C and 25°C using a 10 minute contact times. Initial apparent color was 25 color units.

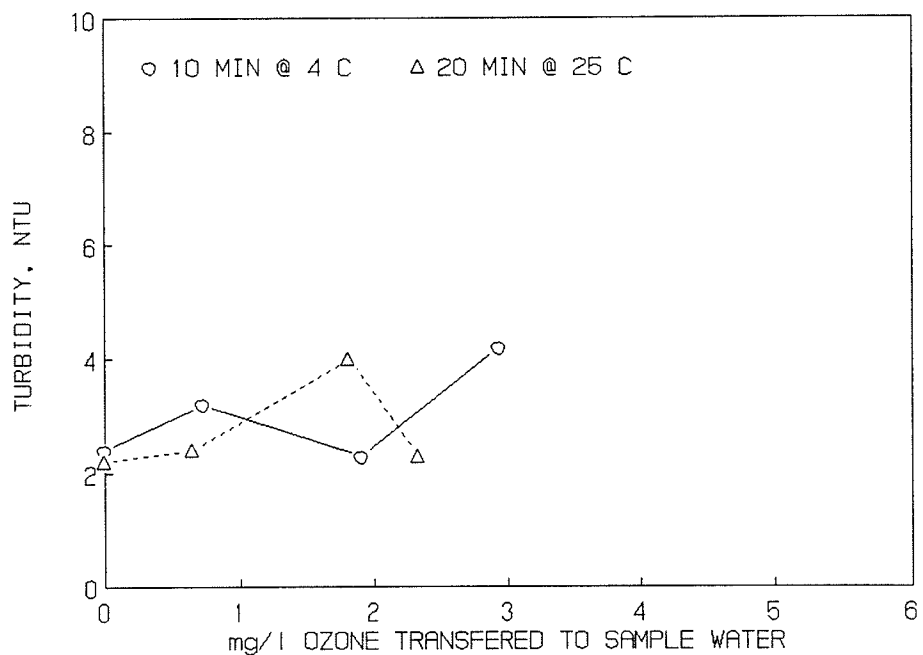


Figure C30: **December water sample.** Turbidity after treatment at 4°C and 25°C using a 10 minute contact time. Initial turbidity was 3.0 NTU.

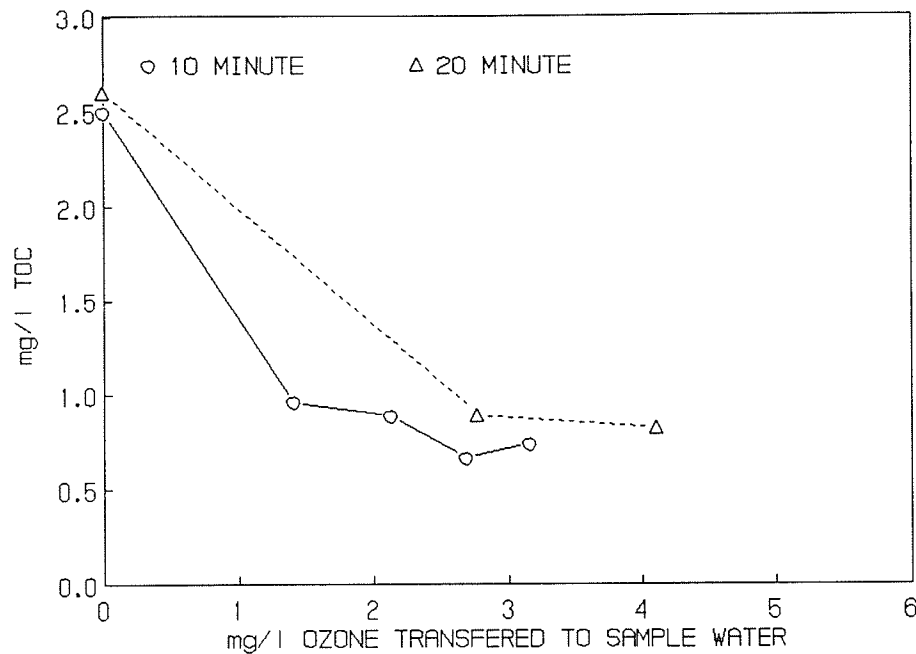


Figure C31: **January water sample.** TOC after treatment with both 10 and 20 minute contact times at 4°C. Initial TOC was 7.3 mg/l.

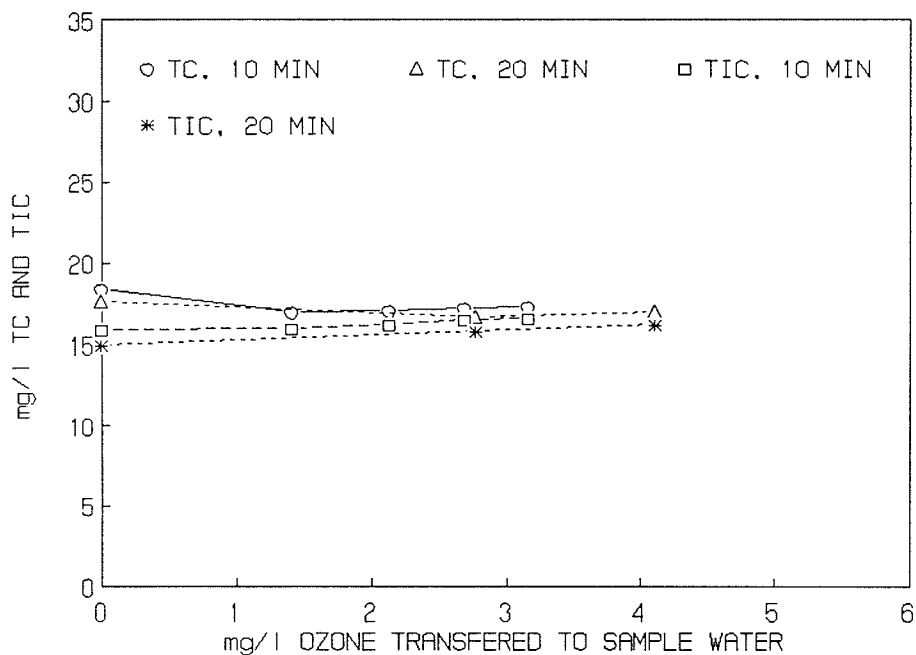


Figure C32: **January water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 4°C. Initial TC was 22.4 mg/l and TIC was 15.1 mg/l.

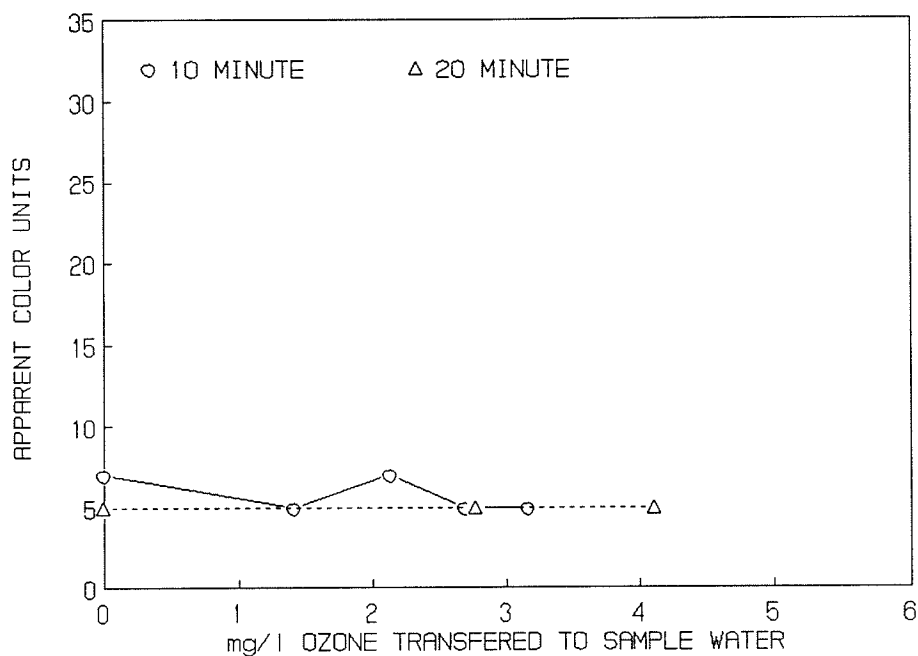


Figure C33: **January water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 4°C. Initial apparent color was 20 color units.

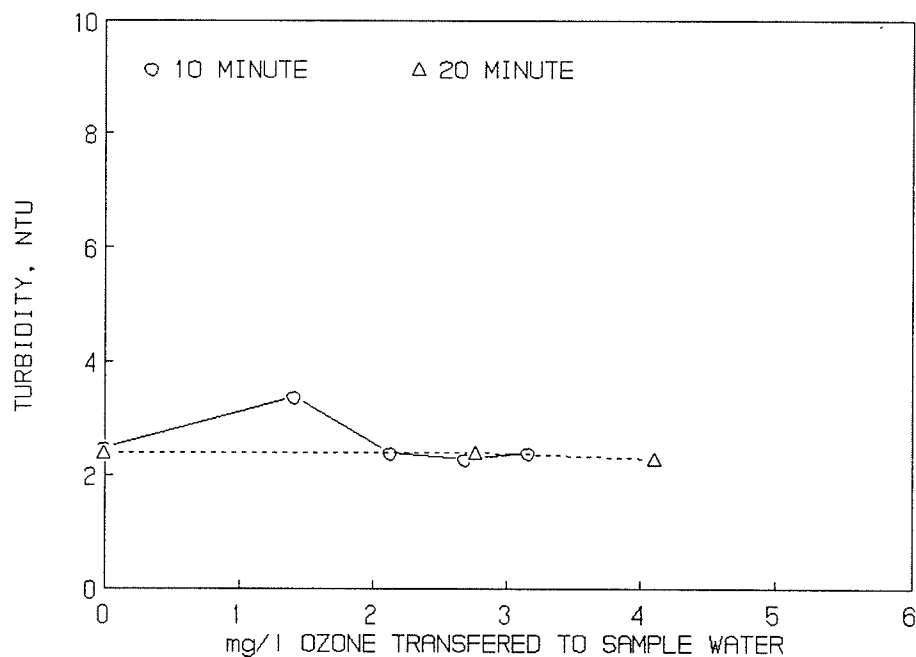


Figure C34: **January water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 4°C. Initial turbidity was 2.7 NTU.

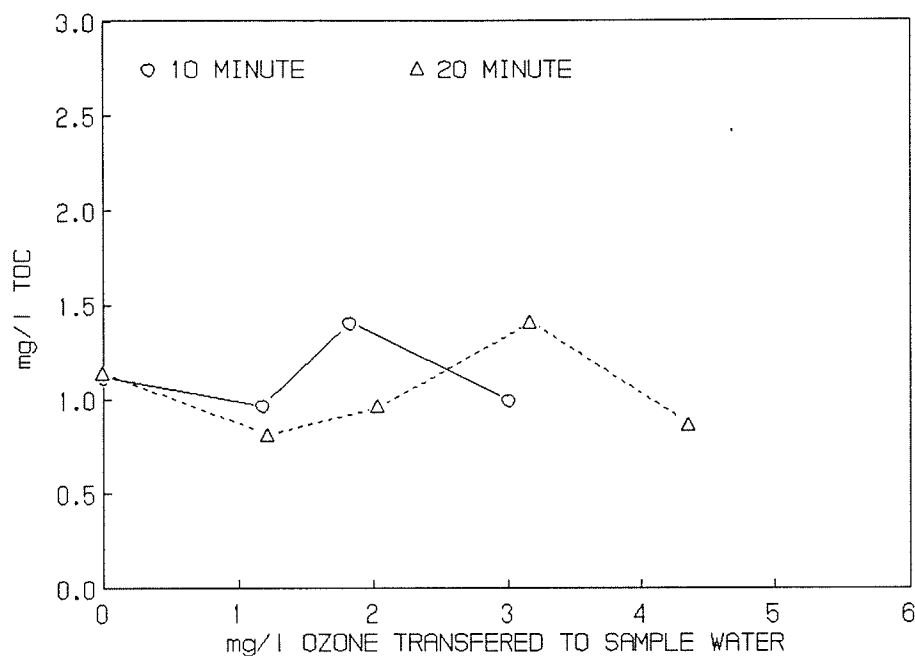


Figure C35: **February water sample.** TOC after treatment with both 10 and 20 minute contact times at 4°C. Initial TOC was 8.1 mg/l.

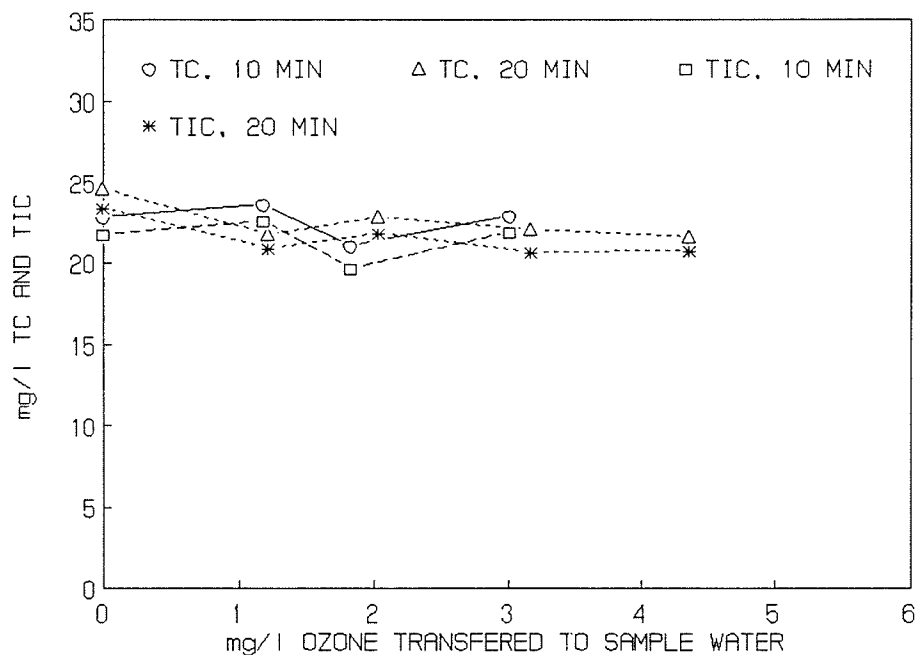


Figure C36: **February water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 4°C. Initial TC was 29.0 mg/l and TIC was 20.9 mg/l.

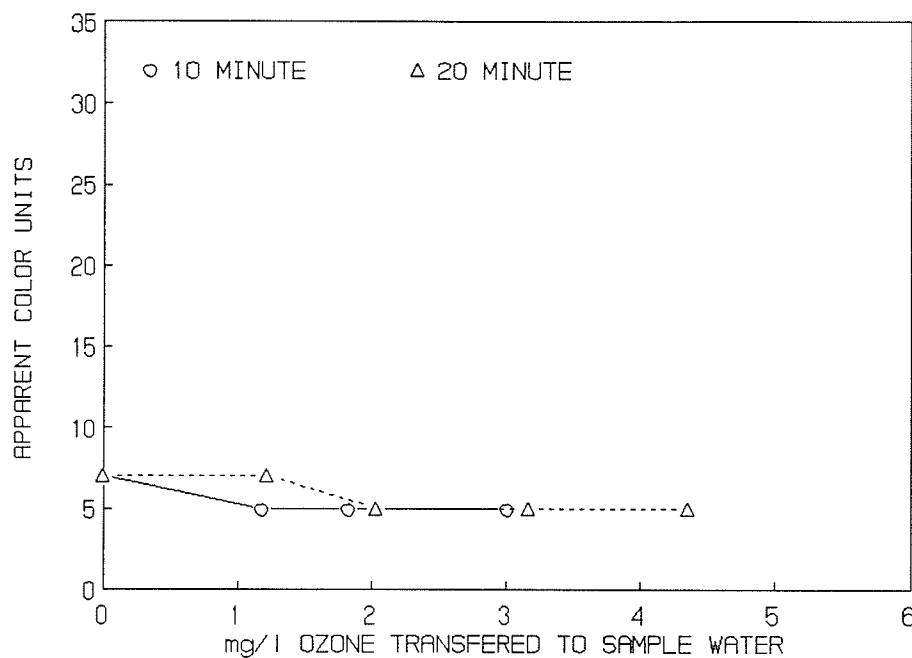


Figure C37: **February water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 4°C. Initial apparent color was 25 color units.

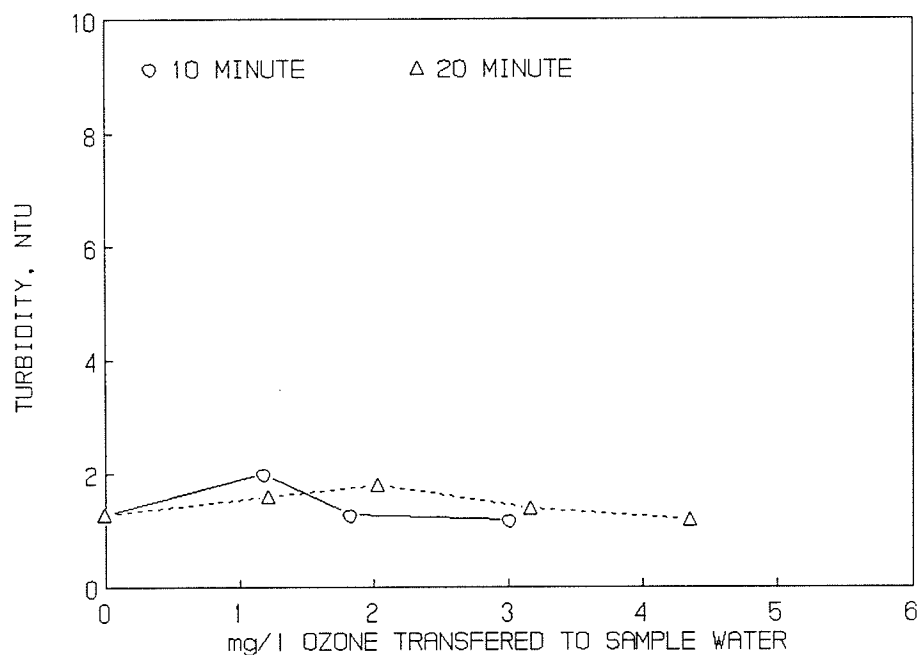


Figure C38: **February water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 4°C. Initial turbidity was 1.6 NTU.

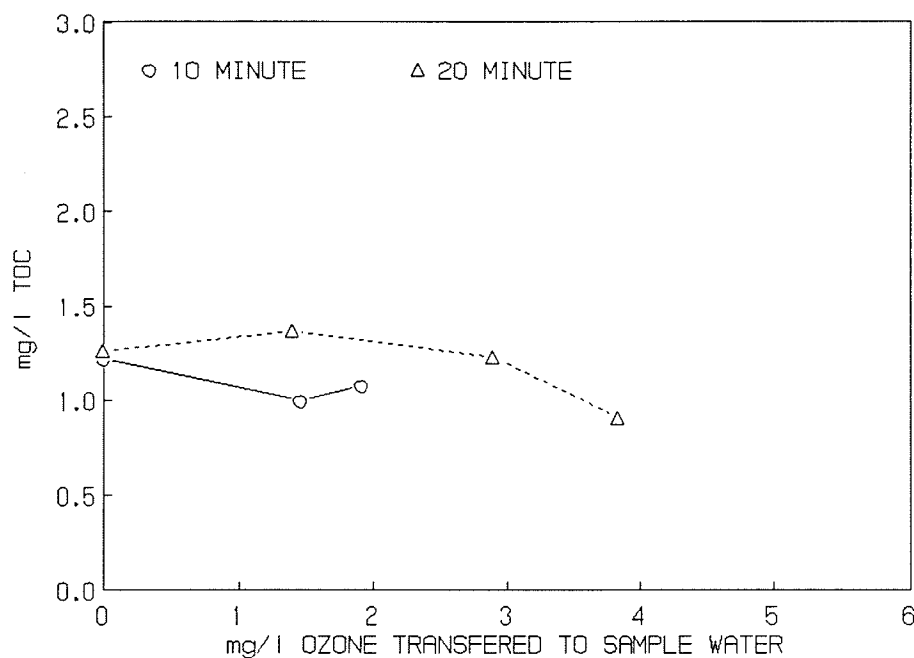


Figure C39: **March water sample.** TOC after treatment with both 10 and 20 minute contact times at 4°C. Initial TOC was 7.5 mg/l.

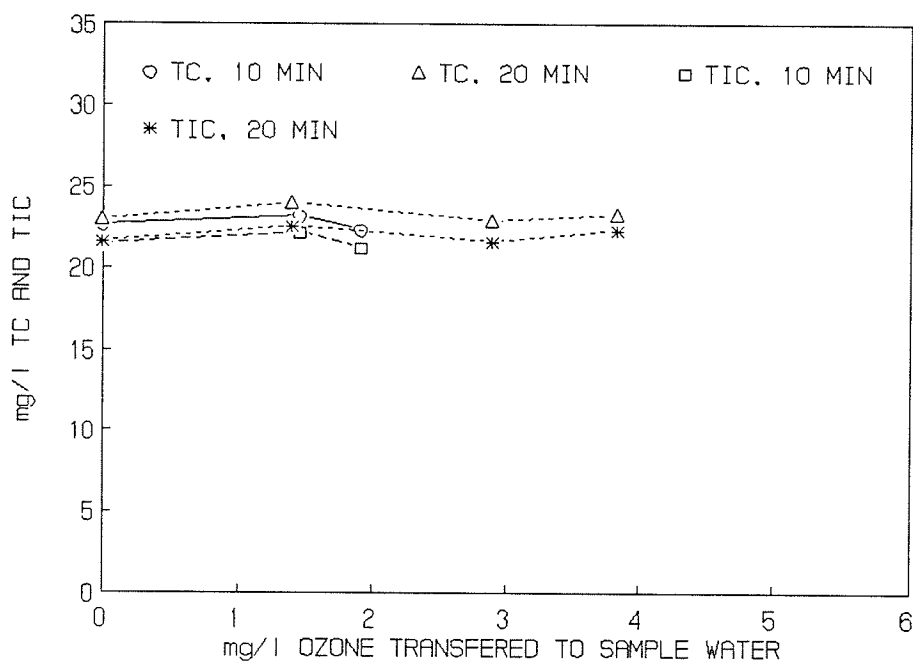


Figure C40: **March water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 4°C. Initial TC was 28.7 mg/l and TIC was 21.2 mg/l.

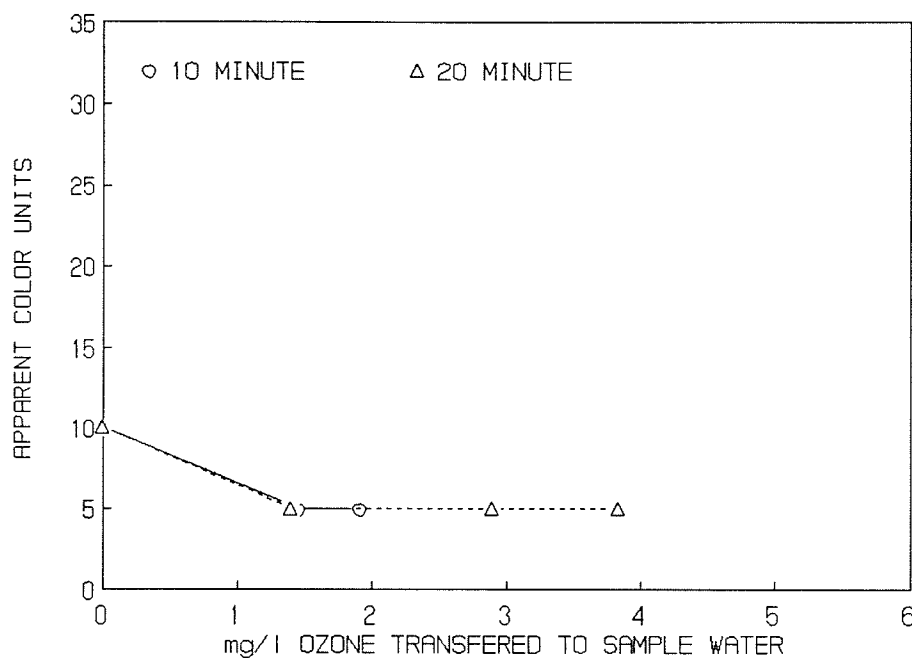


Figure C41: **March water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 4°C. Initial apparent color was 20 color units.

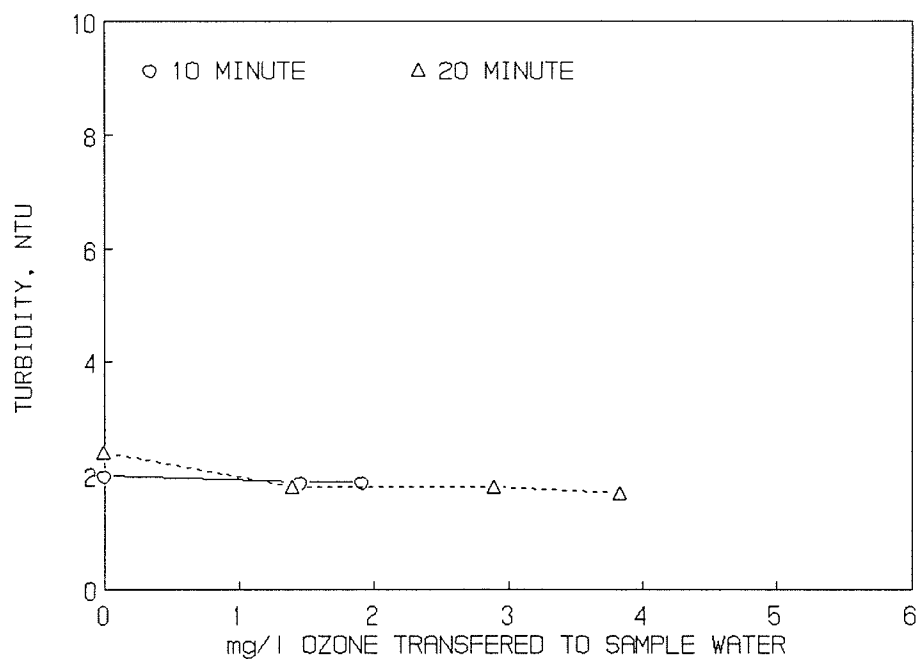


Figure C42: **March water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 4°C. Initial turbidity was 2.5 NTU.

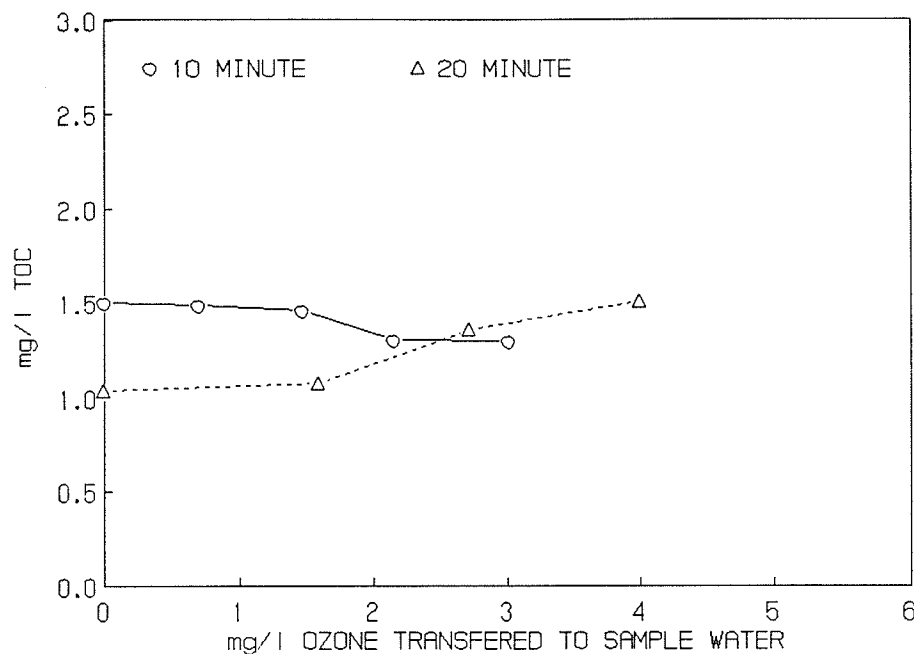


Figure C43: **April water sample.** TOC after treatment with both 10 and 20 minute contact times at 4°C. Initial TOC was 8.2 mg/l.

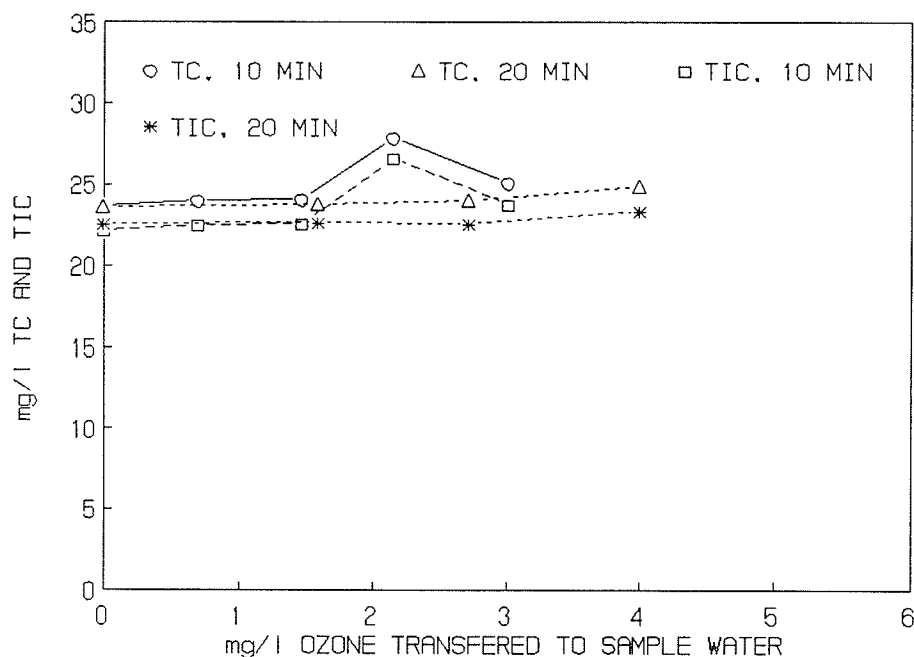


Figure C44: **April water sample.** TC and TIC after treatment with both 10 and 20 minute contact times at 4°C. Initial TC was 30.1 mg/l and TIC was 21.9 mg/l.

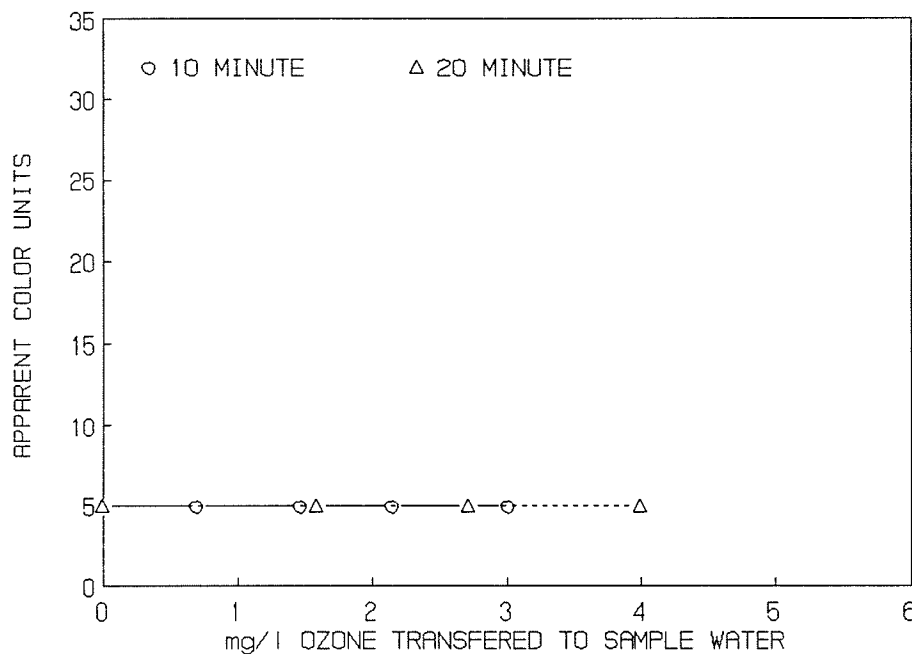


Figure C45: **April water sample.** Apparent color after treatment with both 10 and 20 minute contact times at 4°C. Initial apparent color was 25 color units.

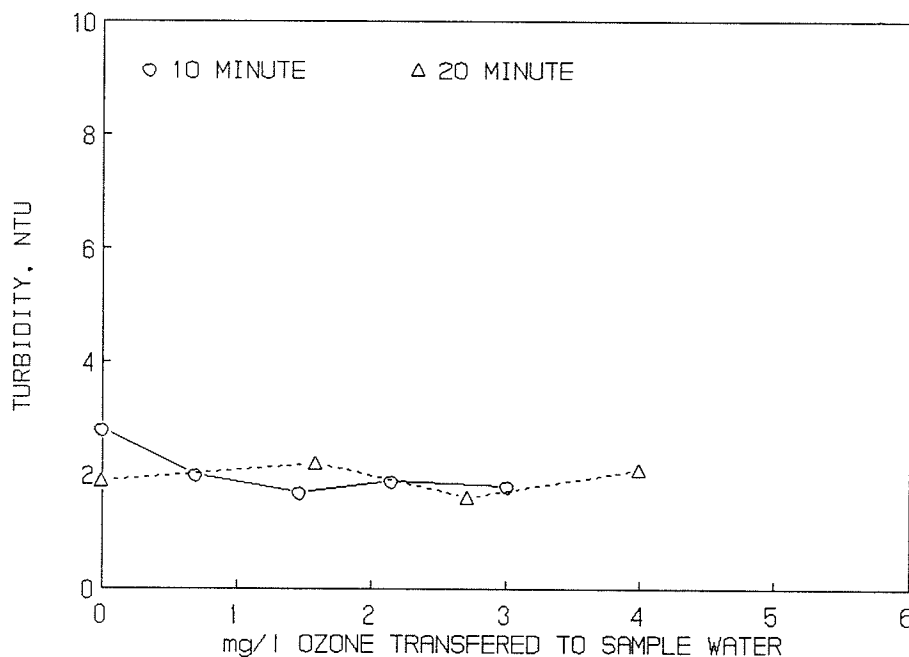


Figure C46: **April water sample.** Turbidity after treatment with both 10 and 20 minute contact times at 4°C. Initial turbidity was 2.4 NTU.

APPENDIX D

Table D1: Carbon adsorption isotherm using TOC with the Freundlich model. Initial TOC was 8.50 mg/liter. The tests were performed using sample water from April, 1990.

TEST #	WEIGHT OF CARBON mg	VOLUME LITERS	M CARBON DOSAGE mg/l	C FINAL TOC mg/l	X TOC REMOVED mg/l	X/M
1	0	.300	0	8.50	0.00	.0000
2	100	.300	333	5.52	2.98	.0089
3	200	.300	667	4.10	4.40	.0066
4	300	.300	1000	2.90	5.60	.0056
5	400	.300	1333	2.32	6.18	.0046
6	600	.300	2000	1.49	7.01	.0035
7	800	.300	2667	1.28	7.22	.0027
8	1000	.300	3333	1.23	7.27	.0022
9	1500	.300	5000	1.22	7.28	.0015

Figure D1: Activated carbon isotherm.

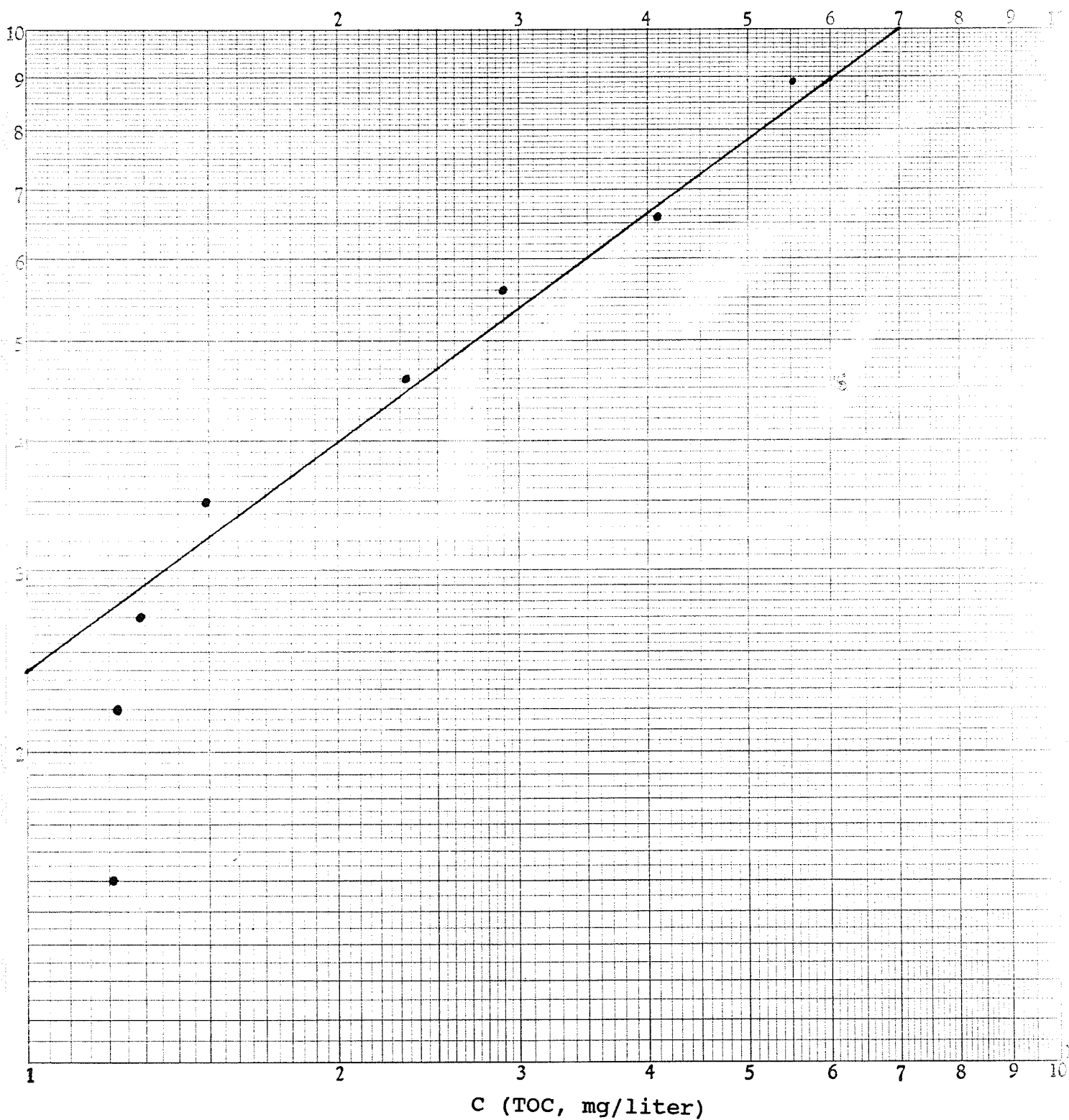


Table D2: Activated carbon characteristics from the manufacturer

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TYPICAL PROPERTIES OF HYDRODARCO
GRANULAR CARBONS

HYDRODARCO 3000

Bulk Density, lbs/cu.ft.*	24
Particle Density Wetted in Water, g/ml	1.4
Pore Volume, ml/g	1
Total Surface Area (N ₂ BET Method), m ² /g	625
Iodine Number	600
Molasses Number	350

Specifications

Sieve Analysis (U.S. Sieve Series), %	
+8 mesh	8 max.
-30 mesh	5 max.
+12 mesh	----
-40 mesh	----
Mean Particle Diameter, mm	1.4-1.6
Effective Size, mm	0.8-1.0
Uniformity Coefficient	1.9 or less
Abrasion Number, % retention (NBS Method)	70 min.
Moisture, % as packed	8 max.

*Used to calculate volume requirements.

Safety

CAUTION, avoid inhalation of excessive carbon dust. No problems are known to be associated in handling this material. However, dust may contain greater than 1.0% silica (quartz). Long term inhalation of high dust concentrations can lead to respiratory impairment. Use forced ventilation or a dust mask when necessary for protection against airborne dust exposure (see Code of Federal Regulations-Title 29, Subpart Z, par. 1910.1000 Table Z-3).