Evaluation of ozone as primary disinfectant at the A. H. Weeks WTP, Windsor, Ontario.

Juliann. Sladic
University of Windsor

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Evaluation of Ozone as Primary Disinfectant at The A.H. Weeks WTP, Windsor, ON

By

Juliann Sladic

A Thesis
Submitted to the Faculty of Graduate Studies and Research
Through the Department of Civil & Environmental Engineering
In Partial Fulfillment of the Requirements for
The Degree of Master of Applied Science at the
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Abstract

The presence of certain pathogenic protozoa such as Cryptosporidium parvum oocyst in drinking water sources made the water treatment industry consider the use of disinfectants that are more effective than chlorine, such as ozone (Jasim, 1999). The Windsor Utilities Commission (WUC) in Windsor, Ontario, Canada, is in the process of implementing ozone (pre-coagulation ozonation) as primary disinfectant at the A. H. Weeks Water Treatment Plant. The system is designed to provide a 2-log (99%) Cryptosporidium inactivation credit. Ozone demand and decay in water is significantly affected by raw water quality, specifically, temperature, pH, and total organic carbon (TOC). The objective of this study was to conduct bench-scale ozone demand and decay experiments to determine the decay rate constant (k), the corresponding ozone half-life, and the 60-second residual value for the raw water during different operating conditions. The study also investigated the effective contact time (T_{10}) provided by the ozonation system through tracer studies. The results indicate that first-order kinetics could be used to describe the ozone decay rate. The results demonstrate that an increase in ozone dose is proportional to the 60-second residual value, and is also proportional to the ozone half-life. Also, an increase in temperature and/or an increase in pH accelerate the ozone decay rate corresponding to a short half-life time. The addition of the rapid mix and two flocculation basins to the original contacting unit significantly increased the effective contact time, which is required for Cryptosporidium inactivation. The hydraulic efficiency (T_{10}/T) of the original contactor improved with the addition of baffled walls. In order to establish the disinfection requirements of the full-scale plant and assist in
optimizing the ozonation process the log integration method was used to calculate the 
disinfection efficiency (CT product). The CT requirement of 2-log (99%) 
*Cryptosporidium* inactivation was achieved using the lowest initial ozone dose for 
temperature 5 °C and temperature 21 °C with the additional baffled wall contactor-rapid 
mixer-two flocculation system.
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Chapter

1.

Background

1.1 Introduction

The primary goal for any drinking water industry is to provide their community with water that is both palatable and potable. Safe drinking water results from the application of treatment processes to the source water along with disinfection. A typical conventional water treatment plant (WTP) employs rapid mixing, flocculation, sedimentation, filtration, and disinfection to remove color, turbidity, taste and odor, and bacteria (Davis et al., 1998). Disinfection of water to eliminate or inactivate bacteria, viral particles, and parasites is the most important step in the drinking water treatment process. Even though filtration or coagulation-flocculation-sedimentation may reduce pathogens this is not generally their primary goal (Haas, 2000). To date, the most commonly used disinfectant in the drinking water industries is chlorine (Finch et al., 1994). Chlorine as a primary disinfectant first dates back to 1902 in Middelkerke, Belgium (EPA, 1999). There exist many incidents where pathogens have not been properly inactivated and enter the drinking water system. Even with chlorine application such occurrences exist. The protozoan parasite Cryptosporidium oocyst is one type of pathogen that may resist chlorine treatment. Chlorine has been shown to be an extremely poor biocide for Cryptosporidium oocysts (Oppenheimer et al., 1997). This pathogen causes cryptosporidiosis, which affects the gastrointestinal track of mammals, including humans. In North America, waterborne outbreaks of cryptosporidiosis have occurred 19
times throughout the period of 1971 to 1994 and in all of these cases the drinking water was the pathway to the consumer and also chlorine was used as the primary disinfectant (Chauret, 2000). The most serious outbreak to date of cryptosporidiosis occurred in 1993 in Milwaukee, Wisconsin where approximately 400,000 people were affected (Craun et al., 1998). In Canada the most recent outbreaks of cryptosporidiosis occurred in North Battleford, Saskatchewan (2001) (Henton, 2001) and, in Collingwood, Ontario (1996) where no filtration existed and the water was disinfected with chlorine (Frey et al., 1998).

It is well known that Cryptosporidium oocysts are ubiquitous in natural water (Chauret, 2000) and have been detected in pristine surface water, groundwater, filtered drinking water, and contaminated lakes (Craun et al., 1998). The oocyst is resistant to conventional chemical disinfectants and can even pass through a filtration unit. Testing for Cryptosporidium can be difficult and unreliable since no surrogate or indicator microorganism exists (Chauret, 2000).

Chlorine is also a concern for a drinking water supplier due to its association with carcinogenic disinfection by-products such as trihalomethanes (THMs). THMs are formed when the water containing an organic precursor is chlorinated. There are four different compounds of THMs, which have been regulated since 1979, including chloroform, bromodichloromethane, dibromochloromethane, and bromoform. In the United States, the regulation for total THMs (TTHMs) includes a maximum contaminant level (MCL) stage 1 of 0.080 mg/L, and a MCL stage 2 of 0.040 mg/L (Pontius, 1998). In Ontario, Canada the maximum acceptable level for THMs is 0.100 mg/L (MOE, 2000).
With recent outbreaks of cryptosporidiosis caused by the *Cryptosporidium parvum* oocysts, and the stringent regulations of chlorinated disinfection by-products, alternative methods and/or disinfectants are required. An alternative method/disinfectant making promising advancements is ozone.

1.2 Ozone in Drinking Water Treatment

The use of ozone for the treatment of drinking water is well recognized and has been practiced for nearly a 100 years in Europe (Larocque, 1999). The first full-scale application of ozone in drinking water treatment occurred in 1893 at Oudshoorn, Netherlands (Langlais et al., 1991). Ozonation plants grew rapidly throughout Europe with majority being located in France and many using it as a primary disinfectant. In the early 1900’s, ozone was recognized to improve taste and odor, remove color, and oxidized iron and manganese in a water source. In the 1960’s effects of ozone on coagulation were explored where ozone enhanced particle removal (Langlais et al., 1991). In the 1980’s ozone application was for disinfection by-product control (THMs) and biological stabilization (Langlais et al., 1991).

Presently, ozonation is viewed for those earlier discoveries as well as for THM control, enhanced coagulation, pesticide removal, oxidation of total organic carbon (TOC), inactivation of *Giardia* and *Cryptosporidium* cysts, combining ozonation with ultraviolet (UV) radiation or hydrogen peroxide (H$_2$O$_2$) for advanced oxidation of refractory organics, and controlling bacterial re-growth in the distribution systems (Rice, 1999). Today in North America, especially in the United States (U.S.), there has been an increase in ozone installation at many water treatment plants (Rice, 1999). More than 100 U.S.
plants have switched to ozone in the past ten years (AWWARF, 2000). Much of this outcome may have resulted from the 1986 Safe Drinking Water Act Amendments and its evolution of new drinking water regulations with respect to disinfection and disinfection by-products, and outbreaks of Cryptosporidium. In Canada, Larocque (1999) reports that approximately 68 municipal treatment plants have installed ozonation with the majority located in Quebec. Presently, much of the ozone installations in Canada are based on the research and regulatory practices conducted in the United States (Larocque, 1999).

Ozone has the highest oxidation potential and is the single most powerful disinfectant amongst the conventional chemicals used in water treatment. The disinfection effectiveness is measured through the CT product. The CT concept relates the product of disinfectant concentration (C) times contact time (T) to specific numerical levels for each type of regulated microorganism at a pH and temperature (Rice, 1999). Ozone has the lowest CT values amongst chlorine, chlorine dioxide, and monochloramine; and can achieve inactivation levels in minimal time (Rice, 1999). Table 1-1 compares the CT value of ozone with common conventional disinfectants for 2-log (99%) inactivation for various microorganisms (Langlais et al., 1991).

Many are installing ozonation with a target level inactivation credit for Cryptosporidium even though this microorganism is presently unregulated in North America (Rakness et al., 2000). There have been a few studies of ozone inactivation of Cryptosporidium (Finch et al., 1994). Finch et al. (1994) studied ozone inactivation of Cryptosporidium parvum and Giardia lamblia in similar laboratory conditions and found that Cryptosporidium parvum was more difficult to inactivate. It was observed that
Cryptosporidium requires 14 to 58 times more effort at 25 °C than that for Giardia lamblia (Finch et al., 1994).

**Table 1-1 CT Values (mg-min/L) for 99% Inactivation of Microorganisms with Disinfectants at 5°C**

(Langlais et al., 1991)

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Free Chlorine (pH 6 to 7)</th>
<th>Chloramine (pH 8 to 9)</th>
<th>Chloride Dioxide (pH 6 to 7)</th>
<th>Ozone (pH 6 to 7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. Coli</td>
<td>0.034 – 0.05</td>
<td>95 – 180</td>
<td>0.4 – 0.75</td>
<td>0.02</td>
</tr>
<tr>
<td>Polio 1</td>
<td>1.1 – 2.5</td>
<td>770 - 3750</td>
<td>0.2 – 6.7</td>
<td>0.1 – 0.2</td>
</tr>
<tr>
<td>Rotavirus</td>
<td>0.01 – 0.05</td>
<td>3810 – 6480</td>
<td>0.2 – 2.1</td>
<td>0.006 – 0.06</td>
</tr>
<tr>
<td>Phage f2</td>
<td>0.08 – 0.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G. lamblia cysts</td>
<td>47 -&gt; 150</td>
<td>-</td>
<td>-</td>
<td>0.5 – 0.6</td>
</tr>
<tr>
<td>G. muris cysts</td>
<td>30 – 630</td>
<td>1400</td>
<td>7.2 – 18.5</td>
<td>1.8 – 2.0</td>
</tr>
</tbody>
</table>

Finch et al. (1994) found contact time to be more important than residual ozone concentration for Cryptosporidium inactivation but with the maintenance of sufficient ozone residual during the contact time. For this reason, when designing an ozonation system for Cryptosporidium inactivation it may be more appropriate to speak in terms of combinations of ozone residual concentration and contact time (Schulz et al., 2000).
Many researchers have noted that the linear Chick-Watson model, which is the underlying theory for the CT concept (i.e. Effluent Method), inaccurately predicts disinfection credit for ozone (Coffey et al., 1994; Finch et al., 1994). The effluent method is said to underestimate the required CT value (AWWARF, 2000). A better approach is to use a model that accounts for disinfectants that decay over time such as the Log Integration model. The United States Environmental Protection Agency’s Guidance Manual for the Surface Water Treatment Rule (SWTR), which provides guidance for CT calculations, also suggests the use of models other than the Chick-Watson that better evaluates disinfection with ozone (Langlais et al., 1991).

1.3 Full-scale Application
The Windsor Utilities Commission (WUC), Windsor, ON, Canada operates a conventional drinking WTP. In 1994, it upgraded its total capacity from 227 ML/d to 454 ML/d with the construction of a second water treatment plant, A.H. Weeks Plant. The construction of the A.H. Weeks WTP included the provision of ozonation in the future, which was designed for taste and odor control. Presently, the WUC is implementing the use of pre-coagulation ozonation at the A.H. Weeks WTP with a primary disinfection target of 2-log (99%) Cryptosporidium inactivation. The total inactivation/removal goal from all treatment barriers for the A.H. Weeks WTP, including primary disinfection with ozone, is 4-log (99.99%) Cryptosporidium.

Any utility considering ozone needs to characterize the raw water quality along with the ozonation process (Hoigné, 1994). This involves an experimental approach of bench-scale testing to determine the ozone demand/decay of a water source, and tracer studies to
determine the effective contact time provided by the ozonation system. Prior to the
design of the WUC ozonation system, no such studies existed. The information obtained
from these two studies will be used to calculate CT values for 2-log (99%) Cryptosporidium inactivation according to log integration methodology. The findings of
this research will also assist the design engineers in determining the optimal ozone dose,
the application points of ozone injectors, and the proper contactor configuration in order
to meet the design target.

1.4 Objectives Of The Thesis

The specific objectives of this research were as follows:

- To develop ozone demand/decay data at different ozone dosages for various
  combinations of raw water temperature and pH;

- To evaluate the effective contact time, \( T_{10} \), of the ozonation process in order to
  establish the hydraulic efficiency ratio, \( T_{10}/T \), and

- To project CT values for 2-log (99%) Cryptosporidium inactivation credit.

1.5 Scope

The study was done in conjunction with the Windsor Utilities Commission, WUC, in
Windsor, Ontario. The scope of this study involved:

- Bench-scale ozonation testing at various ozone dosages (1.5, 2, and 3 mg/L) for
  the Detroit River raw water source, based on various combinations of temperature
  and pH (5 °C/7.7, 5 °C/8.1, 21 °C/7.7, 21 °C/8.1, respectively).
The indigo colorimetric method, Method 4500-O₃ (B.) of Standard Methods (APHA, 1999), was used to calculate the concentration of ozone residual in the water samples.

The step input test was used for the full-scale tracer studies. The study was first performed on the original contactor basin designed for taste and odor control. Next, the study included the addition of the rapid mixer and the first two flocculation basins to the original contactor basin. Finally, the original contactor basin with the addition of stainless steel baffled walls was investigated.

Calculate CT values based on the results from the bench-scale ozone demand/decay studies and the tracer studies using the Log Integration method.
Chapter 2.

Literature Research

2.1 Introduction

2.1.1 Properties of Ozone
Ozone is a metastable molecule produced from oxygen (O₂) having the chemical symbol O₃ and a molecular weight of 47.992 grams per mole. Its density is 1.5 times that of oxygen and is 12.5 times more soluble in water. The following lists some of the physical properties of ozone (NRC, 1987):

- Colorless gas
- Pungent odor detected at levels as low as 0.01 to 0.05 ppm
- Unstable at ambient temperatures
- Solubility in water of 0.494 m³/m³ at 0 °C.
- Density in the gaseous state is 2.144 g/L.

2.1.2 Application of Ozone
Ozone is a powerful oxidant. It’s oxidation potential (E⁰) of 2.07 V is much greater than that of chlorine, which has an E⁰ of only 1.36 V (Brown et al., 1991). Ozone can oxidize inorganics such as iron, manganese, hydrogen sulfide, bromide, and organics including pathogens (bacteria, virus, Giardia, and Cryptosporidium), and solvents, pesticides, color, and taste and odor (Rice, 1999).
Ozone does not impart taste and odor to water and it does not provide a residual for bacterial stability of treated water in transit in the distribution system. An alternative disinfectant such as chlorine is used for the protection of possible bacterial growth in the distribution network. Post-chlorination after ozonation can reduce the chlorine demand of water thus reducing the formation of halogenated by-products which chlorine alone produces (Rice, 1999).

The use of ozone can produce disinfection by-products (DBPs). Similar to chlorine, ozone reacts with inorganics and organics in the water supply to form undesirable and possibly harmful by-products. The DBPs formed when ozone reacts with certain organic matter include aldehydes, ketoacids (oxoacids), carboxylic acids, etc. The WUC, which conducted a pilot study in 1996, concluded that these organic by-products were very low (Cervi, 1996) when ozone reacted with the organics in the Detroit River raw water source. Ozone reacting with inorganic matter particularly bromide, which is present naturally in water, can form bromate. Bromate is a suspected carcinogen and is regulated in Canada by The Canadian Federal – Provincial Committee on Environmental and Occupational Health. The listed interim maximum acceptable concentration (IMAC) for bromate in drinking water is 10 μg/L. Similarly, the United States Environmental Protection Agency (USEPA) regulation for bromate ions includes maximum contaminant level goals (MCLGs) of 0 mg/L, and a maximum contaminant level (MCL) stage 1 of 0.010 mg/L (Pontius, 1998). Pilot-scale studies conducted at the WUC for pre-coagulation ozonation of the Detroit River water source in order to meet 2-log (99%) Cryptosporidium inactivation concluded that bromate levels were within the IMAC at the following optimal conditions: an ozone dose application between 2 and 3 mg/L, a contact
time of 9 minutes, and initial bromide concentrations of less than 30 ug/L (Guerrieri, 2000).

The use of ozone for the treatment of water dates back to the early 1900’s when the European’s were first to discover ozone’s disinfection properties. In Canada, ozone application first occurred in 1954 in Ste. Therese, Quebec for disinfection of drinking water (Laroque, 1999). The largest ozone installation to date is at the Charles des Baillots drinking water treatment plant in Montreal, Quebec. In the United States (U.S.) ozone application dates back to the early 1900s at which time its use in the drinking water industry grew slowly until the mid-1980s. Stricter regulation arising in the US created an increase in ozone installation at many U.S. water treatment plants. From 1982 to mid-1997, 200 US drinking water treatment plants where using ozone or advanced oxidation (i.e. the combination of ozone plus UV radiation or hydrogen peroxide (H₂O₂)) (Rice, 1999). As for the Canadians, the growing awareness and use of ozone arises from the US and their research with the Unites States Environmental Protection Agency (USEPA), American Water Works Association (AWWA), AWWA Research Foundation (AWWARF), and the International Ozone Association (IOA) (Laroque, 1999).

2.1.3 Generation of Ozone
Ozone is an unstable molecule and is generated on site of a water treatment center. It is generally formed by, combining an oxygen atom with an oxygen molecule. The reaction for ozone formation from elemental oxygen is an endothermic reaction and requires considerable input of energy written in the following form (Langlais et al., 1991):

\[ 3O_2 \rightarrow 2O_3 \ (\Delta H^\circ \text{at 1 atm} = +284.5 \text{ kJ/mol}) \]
Ozone generation occurs through the application of an electrical discharge to a carrier gas of oxygen (i.e. pure oxygen or dry air). A standard unit consists of a gas source (oxygen or air), dust filters, gas dryers, ozone generators, contacting units, and off-gas destruction units. Presently, corona discharge in a dry process gas containing oxygen is the most widely used method of ozone generation in water treatment. Basically, the oxygenated gas flows through an electric field of high potential sufficient to generate a “corona” discharge between electrodes where the oxygen bond (O-O) splits and reacts with molecular oxygen to form ozone (Langlais et al., 1991). This basic concept is depicted in Figure 2-1 (Hunter, 2000).

The feed gas must be a clean and dry supply of oxygen molecules to the generator(s) at a controlled rate and pressure. Moisture in the feed gas affects the ozone production yield (i.e. minimizing the yield) and also leads to the formation of nitric acid, which can corrode the generator(s) (Langlais et al., 1991). A popular feed gas is vaporized liquid oxygen better known as LOX.

2.1.4 Ozone Contactors
Ozone diffusers are responsible for transferring ozone gas into water. The mass transfer of ozone into water is based on the two-film theory (Langlais et al., 1991). The transfer efficiency can be affected by such factors as bubble size, diffuser depth, ozone feed-gas concentration, and ozone demand/decay characteristics (AWWARF, 2000). The diffusers are located within a contactor basin, where ozone reacts with the water constituents. A contactor basin is composed of individual cells.
Figure 2-1 Ozone Generation – Corona Discharge Method (Hunter, 2000)
Generally in the first cell of a contactor, ozone is introduced into the water, and the remaining cells acts as reactive cells. The majority of a disinfection credit (i.e. CT value) is accounted for in the reactive cells of a contactor.

2.1.5 Ozone Reactions and Decay
Ozone can react with compounds in aqueous solutions (e.g. water) by two types of reactions. The first is a direct reaction involving molecular ozone. The second way is through an indirect reaction with the radical species that form when ozone decomposes in water, with the hydroxyl radical (OH) becoming the most important oxidant formed. The OH has a higher oxidation potential than ozone making it a very powerful oxidant. The following diagram illustrates these two general reactions of ozone in water, where $S_i$ represents all compounds in water (Langlais et al., 1991).

\[
\begin{align*}
+ S_i & \rightarrow \text{Products} \\
O_3 & \rightarrow + \text{OH}^- \rightarrow \text{OH (radical)} + S_i \rightarrow \text{Products}
\end{align*}
\]

The two reactions compete for substrate. The ozone molecule is said to react rather selectively and slowly with species/contaminants in the water supply whereas the radical species reacts very quickly and non-selectively thus playing an important role in oxidation (Richards, 1994; Langlais et al., 1991). Both ozone and its many decomposition products are powerful oxidizing agents.

The spontaneous decomposition of ozone occurs through a chain process that can be initiated, promoted, and inhibited by many compounds in the raw water source. The
stability of ozone is affected by pH, UV light, ozone concentration, and concentration of radical scavengers (Hoigné, 1994). In pure water, where no other initiators exist, the self-decomposition of ozone is initiated by reaction with the hydroxide ion (OH\(^{-}\)). In raw water sources, initiation involves those compounds capable of inducing the formation of a superoxide ion (O\(_{2}^{\cdot}\)) from an ozone molecule such as the hydroxide ion (OH\(^{-}\)), hydroperoxide ions (HO\(_{2}^{\cdot}\)), iron (Fe\(^{2+}\)), ultraviolet radiation at 253.7 nm, and humic substances (Langlais et al., 1991). Promoters include those molecules capable of regenerating the O\(_{2}^{\cdot}\) from the hydroxyl radical such as O\(_{3}\), humic substances, aryl groups, formic acid, glyoxylic acid, primary alcohols, humic acids, and phosphates (Langlais et al., 1991). Inhibitors include those compounds capable of consuming the OH without regenerating the O\(_{2}^{\cdot}\) such as bicarbonate and carbonate ions, alkyl groups, tertiary alcohols, and humic substances (Langlais et al., 1991). Since the exact mechanism and reactions that occur during decomposition of ozone have not been established (EPA, 1999) the following is the mechanistic model described by the Hoigné, Staehelin and Bader (Langlais et al., 1991):

\[
\begin{align*}
O_3 + OH^- & \rightarrow O_2^{\cdot} + HO_2 & k_1 = 7 \times 10^1 \text{ M}^{-1} \text{ s}^{-1} \\
HO_2 & \leftrightarrow H^+ + O_2^{\cdot} & k_2 \text{ (ionization constant)} = 10^{-4.8} \\
O_3 + O_2^{\cdot} & \rightarrow O_3^- + O_2 & k_2 = 1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \\
O_3^- + H^+ & \leftrightarrow HOO_3 & k_3 = 5.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad ; \quad k_3 = 2.3 \times 10^2 \text{ s}^{-1} \\
HO_3 & \rightarrow OH + O_2 & k_4 = 1.1 \times 10^5 \text{ s}^{-1} \\
O_3 + OH & \rightarrow HO_4 & k_5 = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}
\end{align*}
\]
\[
\text{HO}_4 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{\textit{k}_6 = 2.8 \times 10^4 \text{s}^{-1}}
\]

\[
\text{HO}_4 + \text{HO}_4 \rightarrow \text{H}_2\text{O}_2 + 2 \text{O}_3
\]

\[
\text{HO}_4 + \text{HO}_3 \rightarrow \text{H}_2\text{O}_2 + \text{O}_3 + \text{O}_2
\]

The treatment objective generally dictates which reaction, either the direct or indirect reactions, will be of relevance. For the case of disinfection, the direct pathway is desirable since the \text{O}_3 molecule is very selective and slow, and the concentration of aqueous ozone is relatively high (Urfer et al., 1999; EPA, 1999). Labatiuk et al. (1994) demonstrates this with \textit{Giardia muris} cysts. They observed a greater inactivation of \textit{Giardia muris} cysts when little decomposition of ozone occurred over the duration of the experiment (Labatiuk et al., 1994).

The decay of ozone in natural waters can be generally expressed as a first-order kinetic reaction (AWWARF, 2000). This reaction is first-order in ozone concentration, at a given pH and measured in presence of excess radical scavengers (Urfer et al., 1999, Langlais et al., 1991). Many researchers have observed that when an initial dose of ozone is introduced into water a two-staged first-order kinetic process occurs (Richards, 1994; Rakness et al., 1999; Langlais et al., 1991). Figure 2-2 illustrates the two-staged first-order plot.

The first stage is marked by a sudden depletion of ozone within the first few seconds of introduction (Hoigné et al., 1994). This portion is referred to as the apparent initial ozone demand and is caused by those substances readily oxidized by ozone, such as organic and inorganic compounds (Urfer et al., 1999).
Schulz et al. (1999) showed that the raw water (TOC = 3.9 mg/L) ozone demand was 2 to 4 time higher than the settled water (TOC = 1.5 mg/L) ozone demand. Removing approximately 60% of the TOC through coagulation and settling significantly reduced the ozone demand (Schulz et al., 1999). Following the ozone demand stage is a slower decay in ozone, which behaves according to first-order kinetics. Elovitz et al. (2000) showed that for a temperature range of 5 °C and 15 °C a fast reaction phase precedes the principle first-order phase. First-order kinetics with respect to ozone is mathematically expressed by the following equation (Rakness et al., 1999):

\[
[O_3]_t = [O_3]_{start} e^{-kt}
\]

OR
\[-k = \frac{\ln \left( \frac{[O_3]}{[O_3]_{\text{start}}} \right)}{t}\]

Equation 1

Where: \(k\) (minutes\(^{-1}\)) is the first-order rate constant, \([O_3]_t\) (mg/L) is the concentration of the ozone residual at time, \(t\), \([O_3]_{\text{start}}\) (mg/L) is the starting concentration of the ozone residual, and \(t\) (minutes) is the reaction time (Rakness et al., 1999).

The half-life, which relates to the stability of dissolved ozone, represents the time taken for the residual ozone concentration to decrease to half of its starting value (Bonnelye et al., 1997). The following is the half-life equation for first-order kinetics (Langlais et al., 1991):

\[t_{1/2} = \frac{\ln(0.5)}{-k}\]

Equation 2

Where: \(t_{1/2}\) (minutes) is the half-life, and \(k\) (minutes\(^{-1}\)) is the first-order decay rate constant.

The half-life value is characteristic of the raw water source and the conditions of ozonation (Richard, 1994).

The two parameters, ozone demand and half-life time (i.e. independent of each other) (Hoigné et al., 1994), are important parameters and will be used for modeling the
disinfection requirements for 2-log (99%) Cryptosporidium inactivation for pre-coagulation ozonation, as discussed later.

2.1.6 Operational Conditions on Ozone Decay

The reduction of dissolved ozone concentration depends on different parameters of the water source such as temperature, pH, alkalinity, nature and concentration of organic matter, iron (II) Fe$^{2+}$, manganese (II) Mn$^{2+}$, bromide ion Br$^{-}$, and also the concentration of ozone added (Richard, 1994). Since these conditions greatly influence the stability of ozone the disinfection requirements (i.e. CT value) will also be affected (EPA, 1999). The following are the parameters relevant to the findings of this research.

Temperature

The solubility of ozone and its reaction rates causing ozone to decay is dependent upon temperature (i.e. direct reaction and indirect reaction of ozone) (Hoigné, 1994; Urfer et al., 1999). The solubility of ozone in water at a partial pressure increases in concentration with decreasing temperatures. Figure 2-3 illustrates the solubility of ozone in water at pH 7 (Masschelein, 2000). When temperatures rises, ozone is less soluble and less stable in water but the reaction rate with the substrate increases (Langlais et al., 1991). Elovitz et al. (2000) studied the effect of varying reaction temperatures on the rate of ozone depletion at an initial dose of 1 mg/L and pH 8.0 and found that the rates increased with increasing temperatures.
$pH$

The decomposition of ozone, hence the decay rate, is affected by the pH value of the water. The presence of hydroxide anions (OH$^-$) and H$_2$O$_2$ in water can both initiate the decomposition of ozone (Hoigné, 1994). Lowering the pH decreases the concentration of OH$^-$ and H$_2$O$_2$ thus producing a stabilizing effect on molecular ozone (i.e. direct reaction) (Urfer et al., 1999). Low pH values ($< pH 7$) favor the direct reaction pathway whereas high pH values ($> pH 8$) favor the indirect reaction pathway. At a pH range of 6 - 9, Elovitz et al. (2000) demonstrated that the rate of ozone depletion increases with increasing pH. The high rates of decay are somewhat expected by considering the hydroxide-initiated ozone decomposition reaction (Elovitz et al., 2000).
**Alkalinity**

In most natural waters, between pH 6 – 9, alkalinity is the concentration of bicarbonate ions (HCO$_3^-$) plus the concentration of carbonate ions (CO$_3^{2-}$) (Davis *et al*., 1998). The OH radicals, which act as chain carriers for the decomposition of ozone in water, are consumed by carbonate and bicarbonate ions. This decelerates the decomposition process by not generating O$_2^-$ or other species that initiate the process (Urfer *et al*., 1999; Hoigné, 1994), which significantly increases the stability of the ozone molecule (i.e. causes a decrease in ozone depletion). Elovitz *et al.* (2000) showed a two-fold decrease in the rate of ozone depletion when the carbonate alkalinity was increased from 0 to 1.5 mM.

### 2.1.7 Ozone Dose

The rate of ozone decay varies with the applied ozone concentration in surface water and in ground water (Richard, 1994). Park *et al.* (1999) showed how the decay rate constant, $k$, decreased exponentially with an increase of ozone dose from 1 to 6 mg/L. This observation may be due to the accelerated promotion reaction between ozone and the secondary promoters (i.e. hydrogen peroxide) (Park *et al*., 1999). The peculiarity of this behavior of natural water raises the importance to test a range of ozone dose levels for a treatment process (Richard, 1994).

### 2.1.8 Reactions with Organics

Organics in water are from either natural or human sources (Langlais *et al*., 1991). Total organic carbon (TOC), which measures total organic content, is composed primarily of two fractions: dissolved organic carbon (DOC) (i.e. fulvic and humic acids), and particulate organic carbon (POC) (Becker *et al*., 1996). Ozonation of organics occurs through direct reactions with molecular ozone and the OH radical (Elovitz *et al*., 2000).
The following illustrates the two modes of ozone oxidation of organics where $S_i$ represents the organic matter in water (Langlais et al., 1991):

\[
\begin{align*}
\text{Products (}k_1\text{)} \\
O_3 + S_i &\quad \overset{}{\xrightarrow{\text{initiation}}} \quad \text{OH + Products (}k_2\text{)} \\
\text{Products (}k_3\text{)} &\quad \overset{}{\xrightarrow{\text{termination}}} \quad S_i + OH \\
\text{OH}_2 + \text{Products (}k_4\text{)} &\quad \overset{}{\xrightarrow{\text{propagation}}}
\end{align*}
\]

Dissolved organic matter (DOM), measured as DOC, can cause an instantaneous ozone demand; it can either inhibit or accelerate the chain reaction of ozone decomposition by scavenging or transforming the OH radical, respectively; it can scavenge the OH radical which can account for un-oxidized pollutants; can be a precursor for disinfection by-products formation; and it can cause fouling in the distribution system (Hoigné, 1994). Reckhow et al. (1992) preformed ozonation experiments on various fractions of DOM and observed that humic and fulvic acid fractions were responsible for most of the ozone consumption.

### 2.2 CT Concept

In 1989, the USEPA implemented the Surface Water Treatment Rule (SWTR) requiring surface waters to ensure removal/inactivation of at least 3-log (99.9%) *Giardia* cysts and 4-log (99.99%) of enteric viruses (Guidance Manual, 1989). The SWTR uses the CT concept (called the Effluent method) to predict inactivation efficiencies of
microorganisms by disinfection (Langlais et al., 1991). The CT concept sets specific numerical values for the product of concentration of disinfectant (C; mg/L) times the contact time (T; minutes) to each regulated microorganisms at a specified temperature and pH level encountered in most treatment facilities (Rice, 1999). The numerical CT values are related to the number of log-inactivation of the microorganisms involved (Rice, 1999).

The evolution of the CT concept is based on the Chick-Watson rule, where a constant product of C and T are required for the inactivation (Urfer et al., 1999), which is described by the following relationship (Liyanage et al., 1997):

\[
\log\frac{N}{N_0} = -kC^nT
\]

Equation 3

Where: \(k\) is a reaction rate constant found experimentally; \(N_0\) and \(N\) are the number of infectious oocysts initially and after the contact time \(T\), respectively; \(C\) is the concentration of the disinfectant; and \(n\) is an empirical constant (Liyanage et al., 1997).

The SWTR guidance manual (1989), which provides guidelines for a simple and conservative calculation of CT value (i.e. Effluent Method), provides ozone CT values for desired inactivation levels for Giardia and viruses (AWWARF, 2000). Since Cryptosporidium is unregulated therefore no CT values exist for this microorganism at a specified temperature and pH level. Determining Cryptosporidium CT values has been the prime focus for many researchers. Table 2-1 reports the ozonation requirements for Cryptosporidium inactivation cited in literature (EPA, 1999).
### Table 2-1 Summary of Ozonation Requirements for 99% Inactivation of Cryptosporidium Oocysts (EPA, 1999)

<table>
<thead>
<tr>
<th>Species</th>
<th>C (mg/L)</th>
<th>T (min.)</th>
<th>Temperature</th>
<th>CT (mg min/°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. baileyi</td>
<td>0.6</td>
<td>4</td>
<td>25</td>
<td>2.4</td>
<td>Langlais et al., 1990</td>
</tr>
<tr>
<td>C. parvum</td>
<td>0.5</td>
<td>18</td>
<td>7</td>
<td>9.0</td>
<td>Finch et al., 1993</td>
</tr>
<tr>
<td>C. parvum</td>
<td>0.77</td>
<td>6</td>
<td>Room</td>
<td>4.6</td>
<td>Peeters et al., 1989</td>
</tr>
<tr>
<td>C. parvum</td>
<td>1.0</td>
<td>5 &amp; 10</td>
<td>25</td>
<td>5 - 10</td>
<td>Korich et al., 1994</td>
</tr>
</tbody>
</table>

The CT requirements reported in Table 2-1 vary from study to study which adds uncertainty to design CT requirements for a specific application (EPA, 1999).

Finch et al. (1994) showed that the inactivation requirements for Cryptosporidium were 14 to 58 times greater than for Giardia at 25 °C. This study based CT values for Cryptosporidium to the Giardia CT values listed in Appendix O of the SWTR by applying a multiplier between 5 and 20 (Schulz et al., 2000). Finch et al. (1997), also studied ozone disinfection on the inactivation of Cryptosporidium and demonstrated that the Chick-Watson approach is not a suitable method for disinfection process design due to overestimation of the disinfection requirements. Assuming that C°T is a constant,
which is the case in the Chick-Watson model, excludes the fact that disinfectants react and decay over the contact time (Finch et al., 1997).

The SWTR guidance manual suggests the use of mathematical modeling instead of the effluent method for determining ozone CT values. A better approach is to use site-specific methods, which are less conservative and predict the efficiency of ozone inactivation (CT value) more accurately (AWWARF, 2000). One type of site-specific model is the log integration model (Coffey et al., 1994). This model takes into account the hydraulic characteristics, and the ozone demand/decay results. This study will use the log integration model to calculate the CT values for Cryptosporidium using the result from the ozone demand/decay and tracer studies. The log integration model takes the following form (Rakness et al., 2000):

\[
CT = T_{10} \frac{C_{\text{inal}}}{k} \times (e^{-kx} - 1)
\]

\[
\ln \left( \frac{C}{C_{\text{inal}}} \right) = -k \frac{t}{T}
\]

Where: \(T_{10}\) (minutes) is the detention time at which 10% of the water passes through the basin, which is determined through a tracer study, \(T\) (minutes) is the hydraulic detention time (HDT) calculated by dividing the volume of the contactor by the flow rate, \(T_{10}/T\) is the hydraulic efficiency ratio (< 1.0), \(C_{\text{inal}}\) (mg/L) is the initial concentration of ozone residual, \(C\) (mg/L) is the concentration of the ozone residual at some downstream

Equation 4
location, \( k \) (minutes\(^{-1}\)) is the ozone decay rate, and \( t \) (minutes) is the contact time between the initial ozone residual and some downstream ozone residual (NSF International, 1999).

AWWARF (2000) demonstrated that the log integration method more accurately predicted disinfection than the more commonly used effluent method. Figure 2-4 depicts the CT value calculation for an ozone profile using the log integration method and the effluent method (Rakness et al., 2000). The log integration method incorporates the ozone first-order kinetics profile thus better estimating the true level of inactivation.

### 2.2.1 Ozone and Cryptosporidium

Waterborne outbreaks of *Cryptosporidium parvum* (*C. parvum*) oocysts, have been documented in Canada and the U.S. (Liyanage et al., 1997). *C. parvum* is a protozoa parasite known to infect humans with cryptosporidiosis. This disease can be life threatening for those individuals who have a suppressed immune system (Pontius, 1998).

The 1993 cryptosporidiosis outbreak in Milwaukee, WI was the turning point for drinking water treatment methods and research. Many studies showed that practical water treatment plant doses of chlorine, monochloramine, and UV radiation were ineffective for controlling *C. parvum* (Liyanage et al., 1997). Removal by filtration is also difficult due to the small size of the oocysts (4 - 5 \(\mu\)m) (Langlais et al., 1991). Many researchers have showed that ozone is the single most effective disinfectant against *C. parvum* (Liyanage et al., 1997).
Figure 2-4 Calculating CT Value - Effluent Method versus the Log Integration Method (Rakness et al., 2000)
Presently, there is no federal drinking water regulation of *Cryptosporidium* oocyst inactivation in the U.S. or in Canada (Rakness *et al.*, 2000). But many water utilities are implementing *Cryptosporidium* inactivation based on anticipated regulatory guidance from the U.S. Enhanced Surface Water Treatment Rule (ESWTR) (November 1998) and levels desired by the water treatment facilities (Schulz *et al.*, 2000).

### 2.2.2 Ozonation Process
Designing a system for primary disinfection places importance on both the ozone dose and the contact time requirements (Langlais *et al.*, 1991).

**Ozone Dose**
The applied ozone concentration should be an amount that is sufficient enough to provide and maintain a residual for the contact time required for 2-log (99%) *Cryptosporidium* inactivation (Langlais *et al.*, 1991). The rate of ozone decay will considerably affect the CT value for a given contactor. Testing all possible variations in water quality (i.e. temperature, pH, and organic concentration) is important to understand the changes on the decay rate constants, since changes in k occur with seasonal variations (Hunter, 2000). The results of the ozone demand/decay study will also provide insight into the sizing of the ozone generators and contacting system, and the application point(s) of ozone injectors in the contactor (Langlais *et al.*, 1991, Rakness *et al.*, 1999). Rakness *et al.* (1999) recommends analyzing bench-scale or pilot-scale decay data using a contactor operation model in order to develop design criteria for ozone generators and contactor size.
**Contact Time**

The contact time provided during the ozone process greatly influence the CT value. The "T" in CT is taken to be $T_{10}$, which represents the time that 90% of the water will be exposed to the disinfectant or that 10% of the water has passed through the contactor (AWWARF, 2000).

$T_{10}$ is determined through field tracer studies. Tracer studies also provide information of the flow configuration existing in a process unit. Ozone contactor configuration can range from an almost continuously stirred tank reactor (CSTR) to an almost ideal plug flow reactor (PFR) (Teefy, 1996). Ozone contactors are generally non-plug flow reactors, but they can approach plug flow behavior by increasing their depth to length ratio through the addition of baffles (Urfer et al., 1999). Since baffled wall addition increases $T_{10}$, therefore the hydraulic efficiency, which is described by the ratio $T_{10}/T$, also increases.

$T_{10}/T$ ratio, which is referred to as the short-circuiting factor and provides information on the hydraulic efficiency of the contacting system, is normally less than 1.0 for ozone contactors. Table 2-2 relates the hydraulic efficiency condition with the expected $T_{10}/T$ ratio (Teefy, 1996; Hannoun et al., 1998).
<table>
<thead>
<tr>
<th>Hydraulic Efficiency</th>
<th>Expected $T_{10}/T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor</td>
<td>0.3</td>
</tr>
<tr>
<td>Average</td>
<td>0.5</td>
</tr>
<tr>
<td>Superior</td>
<td>0.7</td>
</tr>
<tr>
<td>Perfect (Plug Flow)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Chapter 3.

Experiments

The research presented in this thesis examined the ozone demand and ozone decay rates in the Detroit River water source at bench scale settings and also the effective contact time of the full-scale ozonation process through tracer studies. The experiments were conducted with the Water Division of the WUC. The results from these experiments were needed to establish the disinfection requirements of the full-scale plant and to assist in optimizing the ozonation system.

3.1 Background – The A.H. Weeks WTP and The Detroit River
The A.H. Weeks WTP, which serves three municipalities with a total population of 230,000, has a total capacity of 454 ML/d. Figure 3-1 shows the location of the WTP in the city of Windsor, and the intake of the raw water. The raw water is drawn from the Detroit River, which connects Lake St. Clair to Lake Erie. The raw water quality includes low turbidity, ranging from 4 to 10 NTU (Nephelometric Turbidity Unit) with the occasional spikes, low color (< 5 TCU (True Color Unit)), low TOC usually between 1.6 and 2.1 mg/L, and moderate hardness of 100 to 150 mg/L as CaCO₃ (Calcium Carbonate).
Figure 3-1 Location of the A.H. Weeks WTP (Alarcon-Herrera, 1994)
3.2 Bench-Scale Tests for Ozone Demand/Decay

This study and the parameters investigated are representative of the conditions that are most likely to be encountered in the full-scale start up of the ozonation process for the A.H. Weeks WTP. The temperatures investigated, 5 °C and 21 °C, approximately, represent the two extreme values, which were critical for designing the primary disinfection system. The pH levels of 8.1 and 7.7 represent the natural raw water pH and the adjusted pH achieved in the summer months with the addition of carbon dioxide, respectively. The initial ozone doses studied represent the range of ozone concentrations most likely to be used for the proposed contact time in order to achieve 2-log (99%) Cryptosporidium oocysts inactivation.

3.2.1 Experimental Scope

The experiments were conducted at bench-scale settings at four combined conditions of temperature and pH, 5 °C and 7.7, 5 °C and 8.1, 21 °C and 7.7, and 21 °C and 8.1, respectively. Three levels of ozone dosages were evaluated for each of the temperature/pH conditions; the studied ozone dosages were approximately 1.5 mg/L, 2.0 mg/L, and 3.0 mg/L. The experiments were conducted from September 2000 to February 2001. A water bath (hot and cold) was used to maintain the raw water temperature, and sulfuric acid was used to adjust pH. The raw water parameters monitored during each experimental run included, temperature, pH, TOC, alkalinity, turbidity, and hardness. Table 3-1 displays the temperature and pH studied and the associated raw water parameters encountered during the ozone demand/decay study.
Table 3-1 Raw Water Conditions-Ozone Demand/Decay Study

<table>
<thead>
<tr>
<th>Date</th>
<th>pH</th>
<th>Temperature °C</th>
<th>TOC mg/L as C</th>
<th>Alkalinity mg/L as CaCO3</th>
<th>Hardness mg/L as CaCO3</th>
<th>Turbidity NTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-Nov</td>
<td>8.09</td>
<td>21*</td>
<td>1.5</td>
<td>86</td>
<td>112</td>
<td>13</td>
</tr>
<tr>
<td>22-Nov</td>
<td>8</td>
<td>21*</td>
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<tr>
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</tr>
<tr>
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* Adjusted values. pH with sulfuric acid and temperature with controlled water baths.

3.2.2 Ozone Generation
The ozone generator from the ENWIN Pilot Plant was used to generate the highly concentrated stock solution. Ozone was generated using a PCI Ozone & Control Systems, Inc (West Caldwell, NJ) GL-1 Laboratory Ozone Generator. Ambient air ozone concentrations were monitored using PCI LC-12 ozone monitor. The generator output and off-gas line ozone levels were measured using a PCI HC-12 ozone monitor. The oxygen source was from (99.6 % pure grade) oxygen gas (2.6Zero – PRAXAIR). Ozone in the off-gas line, was destroyed by a PCI OD-2 ozone destruct unit equipped with a preheater.
3.2.3 Ozone Residual Analysis
The ozonated water and indigo reagent II mixture’s absorbance was measure with a spectrophotometer (Spec 20 D) at a wavelength of 600 nm using a 1 cm cell path length.

3.2.4 Equipment/Instruments
The glassware, which was of laboratory grade, used for the experiments, was made demand free by acid washing in a solution of distilled water and nitric acid. The materials in contact with ozone (i.e. tubing, caps, and tapes) were made from Teflon. Brinkmann Bottletop Dispensers (Brinkmann Instruments, Inc., Mississauga, ON), which was a compatible instrument for ozone, were used for delivering the ozone stock solution and the ozonated water. The warm water bath (Aquabath™ – Labline Instruments, Inc., Melrose Park, IL) was equipped with a thermometer. The cool water bath, which was designed by the researcher, uses ice cubes, a continuous flow of tap water, and a thermometer.

3.2.5 Procedure
The bench-scale ozone decay experiments where conducted at the WUC and at the ENWIN Laboratory, Windsor, ON, Canada.

The indigo colorimetric method’s spectrophotometric procedure, Method 4500-O₃ (B.) of Standard Methods (APHA, 1999), was used to measure the concentrations of the dissolved ozone residual in the water source. An ozone stock solution was prepared by bubbling an oxygen carrier gas containing 8 % ozone (by weight) it into distilled water for approximately 25 to 30 minutes. The decay of ozone in the stock solution was minimized through the use of an ice bath. Figure 3-2 shows the setup used to generate the ozone stock solution.
A residual of the ozone stock solution was determined prior to its delivery to the raw water batch reactor. Typically ozone stock solution concentrations varied from 25 mg/L to 40 mg/L of ozone.

The sample reactor contained 1 L of raw water from the Detroit River. The raw water’s temperature and pH were conditioned either with a warm water bath or cool water bath and/or pH addition of sulfuric acid (0.02 N H₂SO₄), respectively. While stirring, a predetermined volume was delivered from the ozone stock solution into the sample reactor. Figure 3-3 shows the setup of the ozone decay study.

The stirrer was stopped after 10 seconds of delivery and the first sample was drawn at the 20 seconds mark. Approximately 5 to 10 mL of this ozonated water sample was delivered to a volumetric flask containing 4 mL of indigo reagent II. Additional samples were drawn from the ozonated water flask every 20 seconds up to 1 minute and every minute thereafter.

3.2.6 Operational Conditions Analysis
The raw water parameters such as pH, temperature, and turbidity, were measured on-line and directed to a computer software package developed by Electrical & Systems Advanced Control Inc (ESAC) ( Tillsonburg, ON). TOC was measured according to the persulfate-ultraviolet oxidation method, Method 5310 (C.) Standard Methods (APHA, 1999). Alkalinity and hardness were measured according to Method 2320 (B.) and Method 2340 (B.) & (C.), respectively, Standard Methods (APHA, 1999). The pH levels for the adjusted raw water samples were measured using a pH/ion/conductivity meter (Accumet® model 50, Fisher Scientific).
Figure 3-2 Ozone Stock Solution Generation Set-up

Figure 3-3 Bench-scale Ozone Demand/Decay Set-up
3.2.7 Calculations

The ozone residuals in the samples were determined by the method described by Rakness et al. (1999):

\[
\frac{mgO_3}{L} = \frac{TSV \times \Delta A}{f \times b \times V}
\]

\textit{Equation 5}

Where \( TSV \) (mL) is the total sample volume, which is equal to the ozonated sample volume plus the indigo volume, \( \Delta A \) is the difference in absorbance between the ozonated sample and the blank, \( f (0.42 \pm 0.01 \text{ cm/mg/L}) \) is the sensitivity coefficient, \( b \) (cm) is the path length of the cell, and \( V \) (mL) is the volume of ozonated water sample.

The following was the approach taken to calculate the ozone residual and its corresponding half-life for each ozone stock solution and ozonated water sample.

A. Determination of the absorbance of the blank:

First, a standardized curve was developed based on the indigo reagent II solution. This was achieved by adding, to a 100 mL volumetric flask, known volumes of indigo reagent II solution to known volumes of distilled water and measuring the absorbancy. The absorbancy was measured with a spectrophotometer at a wavelength of 600 nm using a 1 cm cell path length. Figure 3-4 is a standard curve developed for an indigo reagent II solution prepared on December 11/00.
B. Determination of the ozone residual in the stock solution:

1. The equation of the line from the standardized curve represents the absorbance of the blank (e.g. $y = 2.0551x - 0.0001$). This equation of the line was assumed to be linear for the entire range of ratios tested. The maximum ratio (indigo: total sample) used in the bench-scale study was 0.9. The absorbance of the blank was determined by finding the fraction of indigo solution volume to total sample volume (i.e. "x"). For example, if the volume of indigo reagent II solution was 45 mL and the sample volume of the ozone stock solution was 5 mL, then the value $x = 45 \text{ mL} / 50 \text{ mL} = 0.9$. This value substituted into the equation of a line ($y = 2.0551(0.9)-0.0001$) gives a value of 1.849 for the absorbance of the blank.
2. The absorbance of the sample (the mixture of the 45 mL indigo solution and 5 mL ozone stock solution) was measured with a spectrophotometer. Example: the absorbance of sample = 0.295.

The values above were substituted into Equation 5 to determine the ozone residual of the sample. Example: TSV = 45 + 5 = 50 mL; A = 1.849 - 0.295 = 1.554; \( f = 0.42 \) /cm/mg/L; \( b = 1 \) cm, and \( V = 5 \) mL. From Equation 5, the ozone residual is the following:

\[
\frac{mgO_3}{L} = \frac{50 \times 1.554}{0.42 \times 5 \times 1} = 37.0 \text{ mg/L}
\]

C. Determination of the ozone residual in the raw water samples:

The same procedure was followed for determining the sample residuals as for the stock residuals. Example: 5 mL of the ozonated raw water was added to the 4 mL of indigo reagent II solution. The absorbance of the blank was first determined by finding the fraction \( x = 4\text{mL}/9\text{mL} = 0.4444 \), and substituting this value into the equation of the line (absorbance of blank = 0.913). The absorbance of the sample at the 20 seconds mark (the mixture of 4mL and 5 mL) read a value of 0.293. The ozone residuals for all samples were determined using Equation 5.

Example at \( t = 20 \) seconds: TSV = 4 + 5 = 9 mL; \( A = 0.913 - 0.293 = 0.620; \) \( f = 0.42 \) /cm/mg/L; \( b = 1 \) cm; and \( V = 5 \) mL. From Equation 5 the residual ozone concentration at time 20 seconds was the following:

\[
\frac{mgO_3}{L} = \frac{9 \times 0.620}{0.42 \times 5 \times 1} = 2.66 \text{ mg/L}
\]
D. Determination of the ozone decay rate constant, \( k \), and the half-life:

The following equation represents first-order kinetic and was used to calculate the decay rate constant, \( k \):

\[
-k = \frac{\ln \left( \frac{[O_3]}{[O_3]_{60\text{sec.}}} \right)}{(t - 60\text{sec.})}
\]

*Equation 6*

Where: \( k \) (minutes\(^{-1}\)) is the first-order decay rate constant; \( [O_3] \) (mg/L) is the concentration of the ozone residual at time, \( t \); \( [O_3]_{60\text{sec.}} \) (mg/L) is the concentration of the ozone residual at 60 seconds; and \( t \) (minutes) is time.

To calculate the corresponding ozone half-life the following equation was used:

\[
t_{1/2} = \frac{\ln(0.5)}{-k}
\]

*Equation 7*

The initial ozone dose \( [O_3]_{dose} \) (mg/L), of the ozonated raw water sample, was calculated according to the following equation:

\[
[O_3]_{dose} = \frac{[O_3]_{stock} \times \text{Volume of stock transferred}}{\text{Volume of stock transferred} + \text{Volume of Raw Water}}
\]

*Equation 8*
Where: \([O3]_{stock}\) (mg/L) is the concentration of the ozone stock solution, *Volume of the stock transferred* (mL) is the volume stock solution added to raw water flask, and *Volume of Raw Water* = 1 L.

3.2.8 Sensitivity Coefficient, \(f\)

The indigo colorimetric standard method for measuring ozone is based on the reaction of ozone with indigo trisulfonate. This method is fast, sensitive and precise due to a high molar absorptivity \((\varepsilon_{600\text{nm}} = 20,000 \, \text{M}^{-1} \, \text{cm}^{-1}\) for 80 - 85% pure indigo) of the indigo trisulfonate (Gordon *et al.*, 2000). The constant value, \(f\), in the equation for calculating ozone residual is called the sensitivity coefficient and equals 0.42 cm/mg/L. The sensitivity coefficient is based on the slope of an ozone calibration curve for a source of indigo, which is 80 – 85% pure and has a molar absorptivity of 20,000 M\(^{-1}\) cm\(^{-1}\) (Gordon *et al.*, 2000). They showed that the assumption that all indigo sources have constant molar absorptivities (i.e. sensitivity coefficients) results in unacceptable levels of measurements. The molar absorptivity determined by Gordon and co-authors might be as much as 25% lower than that presumed by standard methods which accounts for higher ozone residual readings (Rakness *et al.*, 2001). Gordon *et al.* (2000) observed that the reagent purity varies and the indigo stock solution degrades over time.

They developed a method to correct for the varied \(f\) value. The following was the procedure used to measure the \(f\) value for the indigo stock solution prepared for the experiments in this thesis (Gordon *et al.*, 2000):

- Using a spectrophotometer at 600 nm, measure the absorbance of a mixture of 10 mL indigo stock solution in a 100 mL volumetric flask and dilute its volume with
distilled water (Note: Gordon and co-authors referred to the indigo reagent II as the indigo stock solution).

- Calculate the molar absorptivity using the following equation:

\[
Molar \text{ Absorptivity} = \frac{Absorbance}{pathlength \times [Indigo \text{ stock solution}]}
\]

*Equation 9*

Where: *path length* is 1 cm, and *[Indigo stock solution]* is the molar concentration = 1.248(10)^{-5} M (Molar).

- Calculate the sensitivity coefficient, \( f \), using the following equation:

\[
f = \frac{molar \text{ absorptivity}}{MW \text{ indigo} \times grams \text{ of indigo}} \times \frac{sample \text{ volume}}{total \text{ volume}}
\]

*Equation 10*

Where: *MW indigo* is the molecular weight of potassium indigo trisulfonate (C_{16}H_{7}N_{2}O_{11}S_{3}K_{3}) = 616.74 g/mol, *grams of indigo* = 770 mg, *sample volume* = 10 mL indigo reagent II solution, and *total volume* = 100 mL (indigo II plus distilled water).

Table 3-2 displays the molar absorptivities and sensitivity coefficients calculated for the various indigo reagent II solutions prepared for this study.

It was observed that the sensitivity coefficient, hence the molar absorptivity, varied with indigo reagent II solution. The corrected sensitivity coefficients varied from 0.33 to 0.41 cm/mg/L, which corresponds to molar absorptivities ranging between 15,593 and 19,345
cm/M. The error that would have resulted from assuming a constant sensitivity coefficient was as much as 22 % and as low as 3 % below the value of 0.42 cm/mg/L. Rakness et al. (2001) showed that using the constant $f$ to calculate ozone residual under-reported the actual values by 10 to 25 %, which would effect the ozone concentration required for target disinfection (Rakness et al., 2001).

<table>
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<th>Molar Absorptivity</th>
<th>Percent Error</th>
<th>$f$</th>
<th>Percent Error</th>
</tr>
</thead>
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<td>%</td>
<td>/cm/mg/L</td>
<td>%</td>
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3.2.7 Calculations were repeated using the adjusted $f$ values.
3.3 Tracer Study

In order to design for 2-log (99%) Cryptosporidium inactivation at the A.H. Weeks WTP, adjustments were required to extend the contact time. The contact time was increased by installing stainless steel baffled walls to the original contactor basin, and incorporating the two flocculation basins to the ozonation system. The original contactor basin contains concrete baffled walls only. The effective contact time, $T_{10}$, and the hydraulic efficiency ratio, $T_{10}/T$, were established for the ozonation system through tracer studies.

3.3.1 Experimental Scope

The tracer study was divided into three phases. The first phase included the existing ozone contactor basin with concrete baffled walls designed for taste and odor control. The second phase included the rapid mixer and two flocculation basins to the original contactor basin. The third phase accounted for the original contactor basin with additional stainless steel baffled walls. The tracer studies were conducted using the step input test and were preformed at the existing plant flow rates.

3.3.2 Procedure

The tracer study followed the procedures outlined by Teefy (1996), and Muylwyk (2000). The tracer material used was hydrofluosilicic acid ($\text{H}_2\text{SiF}_6$). $\text{H}_2\text{SiF}_6$ stock solution, which is in liquid form, had a specific gravity of 1.223 with a solution composition of fluoride equal to 23.2 % by mass. First, jar tests were performed with the tracer chemical ($\text{H}_2\text{SiF}_6$) and the coagulant and coagulant aid, Alum and PERCOL LT-22, respectively, which are used at the A.H. Weeks WTP. The purpose of the jar test was to give consideration to whether the tracer will react with these chemicals used in the water treatment process. The jar test procedure is in Appendix A.
A step input tracer test was performed, which requires continuous addition of the tracer material (H₂SiF₆) at a constant dosage upstream from the contactor inlet. A step input feed allows tracer response to be monitored while the tracer material is injected (i.e. increasing mode step input test) and after it is no longer fed to the process tank (i.e. decreasing mode step input test). Figure 3-5 shows the tracer chemical feed point and the sampling points with the corresponding basins.

The tracer material was feed into the process tank with laboratory grade pumps, which were adjusted according to the raw water flow rate during the testing. The pumps were calibrated with a graduated cylinder and a stopwatch several times prior to testing. The background or naturally occurring fluoride concentration present in the raw water, which is approximately 0.15 mg/L F, was measured during each tracer study. The added fluoride concentration from the H₂SiF₆ stock solution was approximately 0.8 mg/L F.

The feed of the tracer material and test duration was conducted long enough to achieve equilibrium (C₀ (m)). The tracer response was monitored after stopping the chemical feed (i.e. decreasing mode step input test) which generated a second curve that was used to confirm the original results.

The sampling consisted of grab samples every minute for the duration of the tracer test. Table 3-3 and Table 3-4 summarizes the details of each individual tracer study and the basin dimension with their corresponding volumes.
Figure 3-5 Tracer Study- Basins and Sampling Points
Table 3-3 Tracer Study Parameters

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<th>Location</th>
<th>Date</th>
<th>Q (raw water)</th>
<th>Q (tracer feed)</th>
<th>[F] background</th>
<th>[Co]</th>
<th>Tracer stopped</th>
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<td></td>
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<td>mL/min</td>
<td>mg/L</td>
<td>mg/L</td>
<td>min.</td>
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[Tracer stock solution] = 232,000 mg/L as F

Table 3-4 Tracer Study - Basin's Dimensions and Volume

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<td>6</td>
<td>1.575</td>
<td>9.5</td>
<td>6.8</td>
<td>101.745</td>
</tr>
<tr>
<td>7</td>
<td>1.55</td>
<td>9.5</td>
<td>6.8</td>
<td>100.13</td>
</tr>
<tr>
<td>8</td>
<td>1.2</td>
<td>9.5</td>
<td>6.8</td>
<td>77.52</td>
</tr>
<tr>
<td>9 (rapid mixer)</td>
<td></td>
<td></td>
<td></td>
<td>175</td>
</tr>
<tr>
<td>10 (floc#1)</td>
<td></td>
<td></td>
<td></td>
<td>670</td>
</tr>
<tr>
<td>11 (floc#2)</td>
<td></td>
<td></td>
<td></td>
<td>670</td>
</tr>
</tbody>
</table>

3.3.3 Fluoride Analysis

The concentrations of fluoride in the samples (C\text{measured}) were measured using Method 4500-F (D) Standard Methods (APHA, 1999).
3.3.4 Calculations

The measured concentrations \( C_{\text{measured}} \) were adjusted for background fluoride concentration \( C_{\text{background}} \) according to the following equation (Teeffy, 1996):

\[
C_{\text{adjusted}} = C_{\text{measured}} - C_{\text{background}}
\]

*Equation 11*

The adjusted concentrations \( C_{\text{adjusted}} \) were normalized either by dividing them with the steady-state concentration \( C_o \) \((m)\), which was determined graphically, or dividing them by the calculated concentration \( C_o \) \((c)\), which was determined by a mass balance around the desired process basin, according to the following equation (Teeffy, 1996):

\[
C_{\text{normalized}} = \frac{C_{\text{adjusted}}}{C_o}
\]

*Equation 12*

The normalized concentrations \( C_{\text{normalized}} \) were plotted versus sample time to generate the F curve, where the F curves graphically generates the \( T_{10} \) value. For an increasing mode step input test, a horizontal line was drawn from the y-axis \( (C_{\text{adjusted}}/C_o) \) at 0.10 into the curve and then vertically down to the x-axis (Time), which corresponds to the \( T_{10} \) value. For a decreasing mode step input test, a horizontal line was drawn from the y-axis at 0.90 into the curve and then vertically down to the x-axis (Time).

The results of the tracer studies were used in the log integration method to calculate the inactivation credits of Cryptosporidium oocyst in Chapter 4.
Chapter 4.

Results & Discussion

4.1 General
In this chapter, the results have been presented in three sections. In the first section, the data obtained from the bench scale ozone demand and decay experiments are described. The second section describes the data obtained from the full-scale tracer. The final section describes the CT values resulting from the above two studies and the calculation procedure.

4.2 Ozone Demand and Decay Study

4.2.1 Water Quality
The raw water parameters measured during the ozone demand/decay experiments are displayed in Table 3-1 (Chapter 3). Alkalinity and hardness, which were consistent with the levels expected in the Detroit River, ranged from 82 to 96 mg/L as CaCO₃, and 100 to 140 mg/L as CaCO₃, respectively. TOC was fairly consistent except for the occasional lows and highs, ranging from 0.5 mg/L to 3.2 mg/L. Turbidity levels varied the most from 3.4 NTU to 21.1 NTU.

4.2.2 Condition: Temperature 21 °C & pH 8.1
Three working days, November 20, 22, and 23, 2000, represent the bench-scale ozone demand/decay results for this condition. The initial ozone dose ranged from 1.35 to 3.76 mg/L. The ozone residual for each initial ozone dose was plotted against time. The data
obtained on November 22, 2000 is represented in Figure 4-1. Figure 4-1 illustrates a decrease in dissolved ozone residual with time.

![Ozone Residual Profile vs. Time](image)

**Figure 4-1 Ozone Residual vs. Time Profile: T=21°C & pH 8.1**

A two phase ozone decomposition was observed. This finding was consistent with other researchers who also observed a two phase phenomena, which is common for natural water sources (Hoigné et al., 1994; Rakness et al., 1998). Ozone decays quickly within the first few seconds of introduction. This initial decay represents the ozone demand of the water source, which is generally due to organics and inorganics that react quickly with ozone (Roustan et al., 1998). Hoigné et al. (1994) defines the ozone demand phase as the difference between the introduced ozone dose and the measured value of ozone residual several seconds after introduction, approximately between 0 and 20 seconds. The second phase, which follows the initial demand, is marked by a decrease in ozone decay. This
phase represents the moderate to slow reactions of ozone with constituents in water (Roustan et al., 1998); it is also the portion of the decay representing first-order kinetics (Langlais et al., 1991). Rakness et al. (1998) observed that the initial ozone residual decayed faster between 20 seconds and 60 seconds and noted that after the 1 minute mark ozone residual decayed at a defined rate. The data obtained in this study was represented according to a 60 seconds instantaneous ozone demand, and the first-order kinetic constant and half-life were calculated using the 60 seconds ozone residual value as the starting dose. The 60 seconds ozone demand ranged from 0.67 m g/L to 1.34 m g/L. Figure 4-2 represents the semi-log (natural logarithm) plot of the exponential decay of ozone with time for the data obtained on November 22, 2000.

![First-Order Decay Profile](image)

*Figure 4-2 First-Order Decay Profile: T=21 °C & pH 8.1*
The straight-line forms indicated ozone decay in the Detroit River raw water source can be described by first-order reaction kinetics. Figure 4-1 and Figure 4-2 both show a variation in ozone decay with varied initial ozone dose. Increasing the ozone dose decreased the decay rate constant, \( k \), thus increasing the half-life time. Similar results have been observed by Richard (1994), Bonnellye et al. (1997), and Park et al. (1999). The decay rate constants, which relates to the 60 seconds residual values of 0.61 mg/L to 2.75 mg/L, were between 1.317 minutes\(^{-1}\) and 0.115 minutes\(^{-1}\). This corresponds to half-life times between 0.53 and 6.02 minutes. Figure 4-3 and Figure 4-4, both show an increase in 60 seconds ozone residual and half-life with increased ozone dose, respectively for November 22, 2000.

![Graph](image)

*Figure 4-3 60 seconds Ozone Residual vs. Ozone Dose: T=21 °C & pH 8.1*
4.2.3 Condition: Temperature 21 °C and pH 7.7
These experiments were conducted on December 1, 4, 6, and 11, 2000. The initial ozone dose varied between 1.59 mg/L to 3.71 mg/L. Figure 4-5 displays the results from December 1, 2000 for the decay of ozone versus time for varied initial ozone dosage.

Figure 4-6, which where the results from December 1, 2000, shows that first-order kinetics was applicable and the decay rate constant decreased with increased ozone dose. The 60 seconds instantaneous demand varied from 0.50 mg/L to 1.47 mg/L. The decay rate constant for the 60 seconds ozone residual between 0.62mg/L to 2.70 mg/L were between 1.147 minutes⁻¹ and 0.105 minutes⁻¹ which corresponds to half-life times from 0.60 to 9.06 minutes. Figure 4-7 and Figure 4-8, both show an increase in 60 seconds ozone residual and half-life with increased ozone dose, respectively for December 1, 2000.
Figure 4-5 Ozone Residual vs. Time Profile: T=21 °C & pH 7.7

Figure 4-6 First-Order Decay Profile: T=21 °C & pH 7.7
60sec. Ozone Residual vs. Ozone Dose
pH 7.7 : T= 21°C

\[
y = 0.7853x - 0.0626
R^2 = 0.9364
\]

Figure 4-7 60 seconds Ozone Residual vs. Ozone Dose: T=21 °C & pH 7.7

Half-life vs. Ozone Dose
pH 7.7 : T= 21°C

\[
y = 2.3804x - 3.0782
R^2 = 0.8352
\]

Figure 4-8 Half-life vs. Ozone Dose: T=21 °C & pH 7.7
4.2.4 Condition: Temperature 5 °C and pH 8.1
These experiments were conducted on December 7, and 14, 2000 and on January 25, February 1 and 22, 2001. The initial ozone dose varied between 1.75 mg/L to 3.48 mg/L. Figure 4-9 displays the results from February 1, 2001 for the decay of ozone versus time. The 60 seconds instantaneous ozone demand varied between 0.19 mg/L to 0.82 mg/L. The ozone demand concentrations for temperature 21 °C and pH 8.1 were slightly higher than for temperature 5 °C and pH 8.1 values. This observation indicates that temperature has an important effect on the rate at which ozone decays. For similar water quality, increased temperatures increase the rate of ozone decay (Richard, 1994). Figure 4-10 shows the first-order kinetic rate constants variation with initial ozone dose for the data collected on February 1, 2001. The 60 seconds ozone residual values varied from 1.30 mg/L to 3.09 mg/L. The first-order rate constant was between 0.213 minutes⁻¹ and 0.036 minutes⁻¹, corresponding to half-life times between 3.2 minutes and 19.5 minutes. Figure 4-11 and Figure 4-12, both show the increase in 60 seconds ozone residual and half-life with increased ozone dose, respectively for February 1, 2001.
Ozone Residual Profile vs. Time
T=5°C : pH 8.1

Time; minutes

- 1.86mg/L
- 2.41mg/L
- 3.48mg/L

Figure 4-9 Ozone Residual vs. Time Profile: T=5°C & pH 8.1

First-Order Decay Profile
T=5°C : pH 8.1

Time; minutes

- 1.86mg/L
- 2.41mg/L
- 3.48mg/L

Figure 4-10 First-Order Decay Profile: T=5°C & pH 8.1
Figure 4-11 60 seconds Ozone Residual vs. Ozone Dose: T=5°C & pH 8.1

Figure 4-12 Half-life vs. Ozone Dose: T=5°C & pH 8.1
4.2.5 Condition: Temperature 5 °C and pH 7.7
These experiments were conducted on December 8 and 12, 2000, and February 6, 23, and 26, 2001. The initial ozone dose varied between 1.47 mg/L to 4.12 mg/L. Figure 4-13 represents the decay of ozone verses time for varied initial ozone dose on December 8, 2000.

![Ozone Residual Profile vs. Time](image)

*Figure 4-53 Ozone Residual vs. Time Profile: T=5 °C & pH 7.7*

The 60 seconds instantaneous ozone demand varied between 0.01 mg/L to 1.36 mg/L. Figure 4-14, which is the data resulting from December 8, 2000, shows how increasing the initial ozone dose decreases the first-order kinetic rate constants.
The 60 seconds ozone residual values varied from 1.01 mg/L to 3.55 mg/L. The first-order rate constants ranged from 0.133 minutes\(^{-1}\) to 0.02 minutes\(^{-1}\), corresponding to half-life times between 5.2 minutes and 35 minutes. The half-life of ozone at pH 7.7 was considerably longer than at pH 8.1. A decreased pH level decreases the rate of ozone decay, which is due to a lower concentration of OH\(^-\) in the water source (Hoigné, 1994). Hoigné (1994) showed that the fraction of hydroxide anions and \(\text{H}_2\text{O}_2\), both initiating ozone decomposition, decrease by one order of magnitude per lowered pH unit. Figure 4-15 and Figure 4-16, both show the increase in 60 seconds ozone residual and half-life with increased ozone dose, respectively for December 8, 2000.
Figure 4-15 60 seconds Ozone Residual vs. Ozone Dose: $T=5^\circ C$ & $pH 7.7$

Figure 4-16 Half-life vs. Ozone Dose: $T=5^\circ C$ & $pH 7.7$
4.2.6 Summary: Ozone Demand and Decay Data

Using the data from each of the four conditions tested, a best-fit line was determined to estimate the 60 seconds ozone residual for an ozone dose, and the half-life for an ozone dose. The equations are the following:

Condition: Temperature 21 °C and pH 8.1

\[ [O_3]_{60sec.} = 0.8942 \times [O_3]_{dose} - 0.6899 \]

\[ T_{1/2} = 1.1862 \times [O_3]_{dose} - 0.8 \]

Condition: Temperature 21 °C and pH 7.7

\[ [O_3]_{60sec.} = 0.7908 \times [O_3]_{dose} - 0.4064 \]

\[ T_{1/2} = 2.2364 \times [O_3]_{dose} - 1.3188 \]

Condition: Temperature 5 °C and pH 8.1

\[ [O_3]_{60sec.} = 0.8332 \times [O_3]_{dose} - 0.0461 \]

\[ T_{1/2} = 2.6318 \times [O_3]_{dose} + 6.3961 \]

Condition: Temperature 5 °C and pH 7.7

\[ [O_3]_{60sec.} = 0.9242 \times [O_3]_{dose} - 0.2734 \]

\[ T_{1/2} = 5.3386 \times [O_3]_{dose} - 2.7949 \]

Where: \([O_3]_{60sec.}\) (mg/L) is the 60 second ozone residual; \([O_3]_{dose}\) (mg/L) is the ozone dose; and \(T_{1/2}\) (minutes) is the half-life. Figures 4-17 and 4-18 display the plots for 60 seconds residual and half-life for an ozone dose between 1.5 and 3.5 mg/L from the lines of best-fit.
60 Second Residual Summary

Ozone Dose, mg/L

2.5
2
1.5
1
0.5
0

60 sec. Residual, mg/L

● 21 C/8.1
△ 21 C/7.7
+ 5 C/8.1
■ 5 C/7.7

Figure 4-67 60 seconds Ozone Residual Summary

Ozone Half-life Summary

Ozone Dose, mg/L

25
20
15
10
5
0

Ozone Half-life, minutes

● 21 C/8.1
△ 21 C/7.7
+ 5 C/8.1
■ 5 C/7.7

Figure 4-18 Ozone Half-life Summary
The effect of temperature is clearly pronounced in these plots. At a given ozone dose and pH level, 60 seconds residual is much higher at temperature 5 °C than at temperature 21 °C. A similar observation is made for half-life. Colder water temperatures generally convey slower rates of ozone decay. The reaction rates, which cause ozone to decay, are temperature dependent. The relationship between reaction rates (ozone decay rates) and temperature (5 °C and 21 °C) were developed with the Arrhenius equation. A graph of ln k versus 1/T was produced for pH 8.1 and pH 7.7 for the two temperatures. Figure 4-19 displays a linear relationship between ln k versus 1/T for pH 8.1 and pH 7.7.

![Ln k vs. 1/T - Arrhenius Plot](image)

**Figure 4-19 Arrhenius Plot**

The activation energy (E_a) for pH 7.7 and pH 8.1 was 55.32 kJ/mol and 79.32 kJ/mol, respectively. As the magnitude of E_a increases, the reaction rate k, decreases (Brown et
al., 1991). The $E_a$ under conditions representative of water treatment (i.e. low ozone residual concentrations, and the auto-decomposition of ozone is an apparent first-order reaction) ranges from 100 to 40 kJ/mol, and is higher at lower pH values (Langlais et al., 1991). The activation energies, which are empirical $E_a$, obtained for temperatures 5 °C and 21 °C, were within the range reported in literature. The decreased pH level from 8.1 to 7.7 resulted in a decreased $E_a$, and decreased reaction rates, which was not in agreement with literature. The pH range studied, which was small, may have contributed to this finding.

The effect of pH on ozone decay was not clearly defined for 60 seconds ozone residual and ozone dose relationship as they were for half-life and ozone dose relationship. For the same water temperature, the effect of pH on 60 seconds ozone residual was not clearly defined. This study describes the instantaneous ozone demand as the difference between the ozone dose and the 60 seconds residual. The instantaneous ozone demand may be consistent with the characteristics of the water source and irrelevant to the variation in pH level. Elovitz et al. (2000) did not observe a clear trend for pH variation with the initial phase of ozone decomposition. They attribute this to the inability to sample short reaction times, which is the case for the initial ozone demand phase (Elovitz et al., 2000). The half-life and ozone dose summary plot better illustrates the effect of pH for the same water temperature. Increasing the pH level results in higher rates of ozone depletion, corresponding to short half-life times.

Rakness et al. (1999) used the relationships from 60 seconds residual with ozone dose and half-life with ozone dose to project ozone residual profile and CT value for plant-
scale ozone contactors. They also assessed the usefulness of bench-scale results in projecting ozone dose by comparing projected verses measured dose to achieve equivalent CT value. The results from this study will be used to determine the required ozone dose to achieve 2-log (99%) *Cryptosporidium* inactivation for the full-scale plant. Bench-scale testing generally provides good estimation of full-scale dose requirements and can be used to develop optimized contactor and generator design criteria for meeting the disinfection objectives (Rakness *et al.*, 1999).

### 4.3 Tracer Study

This study determined the contact time $T_{10}$, and the hydraulic efficiency $T_{10}/T$, for the following:

- The original contactor basin containing concrete baffled walls (taste and odor control),
- The addition of the rapid mix basin and the first two flocculation basins to the original contactor, and
- The installation of additional baffled walls (stainless steel) to the original contactor.

#### 4.3.1 Jar Tests

Appendix A contains the results from the jar test. It was observed that a loss of 4.8 % or 0.08 mg/L as F resulted in the coagulated water sample. Fluoride is known to react with coagulants such as alum and possibly ferric salts and cationic polymers (Teeby, 1996). These reactions appear to be reversible and are not instantaneous. The change in concentration was considered to be minimal and testing was continued with $\text{H}_2\text{SiF}_6$. 

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4.3.2 Original Contactor Basin
The tracer studies, for the original contactor basin, were performed on July 14, 17 and 21, 2000. The volume of the original contactor is 762.28 m$^3$. The raw water flow during the tracer study was 67.5, 61, and 69 m$^3$/min, corresponding to a hydraulic detention time (HDT) or T of 11.3, 12.5, and 11.1 minutes, respectively. Figure 4-20 through Figure 4-22 display the normalized fluoride concentrations with sample time (i.e. F curve).

![Graph of Original Contactor July 14/00](image)

*Figure 4-20 F Curve – Original Contactor Basin*
Figure 4-21 F Curve – Original Contactor Basin

Figure 4-22 F Curve – Original Contactor Basin
The water flow rate of 67.5 m³/min resulted in a T₁₀ of 4.5 minutes and a T₁₀/T ratio of 0.40. The flow rate of 61 m³/min gave a T₁₀ of 5.5 minutes and a T₁₀/T ratio of 0.44. The final water flow rate of 69 m³/min resulted in a T₁₀ of 5 minutes and a T₁₀/T ratio of 0.45. According to Teefy (1996), a T₁₀/T ratio between 0.3 and 0.5 relates to a basin with poor to average hydraulic efficiency.

4.3.3 Original Contactor + Rapid Mixer and Two Flocculation Basins
These tests were performed on July 26, and August 14, 2000. The volume of the rapid mixer plus the contactor is 937.28 m³. The raw water flow rate of 77 and 79 m³/min/train corresponding to the HDT of 12.2 and 11.9 minutes, a T₁₀ of 6.5 and 7 minutes, and a T₁₀/T ratio of 0.53 and 0.59, respectively, as shown in Figure 4-23 and Figure 4-24.

![Contactor (Original) → Rapid Mixer](image)

Figure 4-23 F Curve – Original Contactor–Rapid Mix System
Figure 4-24 F Curve – Original Contactor–Rapid Mix System

The hydraulic efficiency slightly improved with the addition of the rapid mixer basin to the original contactor. The contact time significantly increased with the addition of the rapid mix basin, which was expected.

Figure 4-25 and Figure 4-26 display the results with the inclusion of the flocculation basins to the original contactor and rapid mixer.
Figure 4-25 F Curve – Original Contactor–Rapid Mix–Flocculation System

Figure 4-26 F Curve – Original Contactor–Rapid Mix–Flocculation System
The volume of the contactor-rapid mix-two flocculation system is 2277.28 m$^3$. The raw water flow rates of 77 and 79 m$^3$/min/train correspond to a HDT of 29.6 and 28.8 minutes, a $T_{10}$ of 12 and 13 minutes, and a $T_{10}/T$ ratio of 0.41 and 0.45, respectively. The additional volume provided by the two flocculation basins significantly increased the effective contact time, $T_{10}$, but reduced the hydraulic efficiency. The reduction in hydraulic efficiency may be attributed to the absence of baffled walls in the flocculation basin, which can result in stagnant water and/or re-circulation zones (Hannoun et al., 1998). Teefy (1996) reports a $T_{10}/T$ ratio between 0.1 and 0.3 for un-baffled basins.

The WUC decided to incorporate the rapid mixer and the flocculation basins to ozonation system for an increased contact time. The WUC also decided to install stainless steel baffled walls to the original contactors; this will improve the hydraulic efficiency and increase the contact time of the ozonation system.

4.3.4 Baffled Contactor Basin
These tests were done on March 13, and 20, 2001, and were only performed on the baffled wall contactor. The contactor volume remained the same with a value of 762.28 m$^3$. The raw water flow rates of 54.5 and 50 m$^3$/min/train corresponds to a HDT of 14 and 15.3 minutes, a $T_{10}$ of 10 and 12 minutes, and a $T_{10}/T$ ratio of 0.71 and 0.79, respectively, as shown in Figure 4-27 and Figure 4-28.
Baffled Contactor
March 13/01

Figure 4-27 F Curve – Original Contactor with Additional Baffled Walls

Baffled Contactor
March 20/01

Figure 4-28 F Curve – Original Contactor with Additional Baffled Walls
A significant improvement in both contact time and the hydraulic efficiency was observed for the contactor containing stainless steel baffled walls. The hydraulic efficiency ratio significantly increased corresponding to superior baffling conditions ($T_{10}/T > 0.7$) (Hannoun et al., 1998). The higher the $T_{10}/T$ (i.e. approaches 1.0) the more effective the disinfection since the flow behaves according to plug flow conditions (Hannoun et al., 1998).

Table 4-1 displays the results from the tracer study and Table 4-2 displays the calculated $T_{10}$ and $T_{10}/T$ based on average and maximum water flow rates for the full-scale WTP. The latter were calculated according the Guidance Manual’s equation, which assumes constant volume was maintained within the basin studied (Teefy, 1996). Using either the average or maximum water flow rates the $T_{10}$ value doubles for the stainless steel baffled wall contactor.

<table>
<thead>
<tr>
<th>Location</th>
<th>Date</th>
<th>flow/train m3/min.</th>
<th>$T_{10}$ min.</th>
<th>$T$ min.</th>
<th>$T_{10}/T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3 Contactor</td>
<td>7/14/00</td>
<td>67.5</td>
<td>4.5</td>
<td>11.29</td>
<td>0.40</td>
</tr>
<tr>
<td>O3 Contactor</td>
<td>7/17/00</td>
<td>61</td>
<td>5.5</td>
<td>12.50</td>
<td>0.44</td>
</tr>
<tr>
<td>O3 Contactor</td>
<td>7/21/00</td>
<td>69</td>
<td>5</td>
<td>11.05</td>
<td>0.45</td>
</tr>
<tr>
<td>O3 Cont.-Rapid mix</td>
<td>7/26/00</td>
<td>77</td>
<td>6.5</td>
<td>12.17</td>
<td>0.53</td>
</tr>
<tr>
<td>O3 Cont.-Rapid mix</td>
<td>8/14/00</td>
<td>79</td>
<td>7</td>
<td>11.86</td>
<td>0.59</td>
</tr>
<tr>
<td>O3 Cont.-Floc #2</td>
<td>7/28/00</td>
<td>77</td>
<td>12</td>
<td>29.58</td>
<td>0.41</td>
</tr>
<tr>
<td>O3 Cont.-Floc #2</td>
<td>8/14/00</td>
<td>79</td>
<td>13</td>
<td>28.83</td>
<td>0.45</td>
</tr>
<tr>
<td>O3 Contactor w/baffling</td>
<td>3/13/01</td>
<td>54.5</td>
<td>10</td>
<td>13.99</td>
<td>0.71</td>
</tr>
<tr>
<td>O3 Contactor w/baffling</td>
<td>3/20/01</td>
<td>50</td>
<td>12</td>
<td>15.25</td>
<td>0.79</td>
</tr>
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</table>
Table 4-2 Tracer Study Results based on Average and Maximum Water Flow Rates

<table>
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<tr>
<th>Location</th>
<th>Date</th>
<th>Flow/train m3/min.</th>
<th>T10 min.</th>
<th>T min.</th>
<th>T10/T</th>
<th>Flow/train m3/min.</th>
<th>T10 min.</th>
<th>T min.</th>
<th>T10/T</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3 Contactor</td>
<td>7/14/00</td>
<td>43.75</td>
<td>6.94</td>
<td>17.42</td>
<td>0.40</td>
<td>86.8</td>
<td>3.50</td>
<td>8.78</td>
<td>0.40</td>
</tr>
<tr>
<td>O3 Contactor</td>
<td>7/17/00</td>
<td>43.75</td>
<td>7.67</td>
<td>17.42</td>
<td>0.44</td>
<td>86.8</td>
<td>3.87</td>
<td>8.78</td>
<td>0.44</td>
</tr>
<tr>
<td>O3 Contactor</td>
<td>7/21/00</td>
<td>43.75</td>
<td>7.89</td>
<td>17.42</td>
<td>0.45</td>
<td>86.8</td>
<td>3.97</td>
<td>8.78</td>
<td>0.45</td>
</tr>
<tr>
<td>O3 Cont.-&gt;Rapid mix</td>
<td>7/28/00</td>
<td>43.75</td>
<td>11.44</td>
<td>21.42</td>
<td>0.53</td>
<td>86.8</td>
<td>5.77</td>
<td>10.80</td>
<td>0.53</td>
</tr>
<tr>
<td>O3 Cont.-&gt;Rapid mix</td>
<td>8/14/00</td>
<td>43.75</td>
<td>12.64</td>
<td>21.42</td>
<td>0.59</td>
<td>86.8</td>
<td>6.37</td>
<td>10.80</td>
<td>0.59</td>
</tr>
<tr>
<td>O3 Cont.-&gt;Floc #2</td>
<td>7/28/00</td>
<td>43.75</td>
<td>21.12</td>
<td>52.05</td>
<td>0.41</td>
<td>86.8</td>
<td>10.65</td>
<td>26.24</td>
<td>0.41</td>
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<td>O3 Cont.-&gt;Floc #2</td>
<td>8/14/00</td>
<td>43.75</td>
<td>23.47</td>
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<td>0.45</td>
<td>86.8</td>
<td>11.83</td>
<td>26.24</td>
<td>0.45</td>
</tr>
<tr>
<td>O3 Contactor w/taffling</td>
<td>3/13/01</td>
<td>43.75</td>
<td>12.46</td>
<td>17.42</td>
<td>0.71</td>
<td>86.8</td>
<td>6.28</td>
<td>8.78</td>
<td>0.71</td>
</tr>
<tr>
<td>O3 Contactor w/taffling</td>
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<td>86.8</td>
<td>6.91</td>
<td>8.78</td>
<td>0.79</td>
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4.4 CT values

The results from the bench-scale ozone demand/decay study and the tracer study were used to calculate the CT values for Cryptosporidium inactivation using the log integration method. The projected CT values were based on the summary plots of 60 seconds residual versus ozone dose and half-life verses ozone dose, and maximum water flow rate's T10 and T10/T.

The following example was the approach used to calculate CT value (Rakness et al., 1999):

- The summary plot of 60 seconds ozone residual versus ozone dose was used to determine the 60 seconds ozone residual. The projected 60 seconds ozone residual was 0.65 mg/L for an initial ozone dose of 1.50 mg/L at condition temperature 21 °C and pH 8.1 (0.65 mg/L = 0.8942(1.50) – 0.6899).

- The summary plot of half-life versus ozone dose was used to determine the half-life value. An initial ozone dose of 1.50 mg/L at condition temperature 21°C and...
pH 8.1 corresponds to a projected half-life of 0.98 minutes (0.98 min. = 1.1862(1.50)− 0.8). The decay rate was determined using first-order kinetics. The decay rate was 0.7078 minutes⁻¹ for a half-life of 0.98 minutes.

The WUC ozonation plant will add ozone to the first cell of the baffled wall contactor basin. Figure 2-29 displays the contactor’s configuration. The ozone consumed in the first cell is not available in the form of a measurable residual to satisfy the disinfection requirements (Schulz et al., 2000). CT credits are based on those cells within a contactor of detectable ozone residual (i.e. reactive flow cells). The CT calculation in this study used the outlet ozone residual from cell 1 as the initial concentration ($C_{initial}$) in the log integration equation. The HDT, at maximum water flow rate, in the first cell of the baffled wall contactor is 1.15 minutes. Therefore the ozone residual at the outlet of cell 1 was 0.59 mg/L and was calculated according to the following equation (Rakness et al., 1999):

$$C_{outlet\ cell\ 1} = \frac{C_{60sec}}{1-kt}$$

Equation 13

Where: $k$ is the ozone decay rate, $C_{60sec}$ is the ozone residual at 60 seconds, and $t$ is the difference between the HDT of cell 1 and 60 seconds (i.e. 1.15 minutes − 1 minute = 0.15 minutes).
Figure 4-29 Contactor Basin Configuration at the A.H. Weeks WTP
The $T_{10}/T$ for the baffled wall contactor was 0.75, and the HDT from the end of cell 1 to the end of cell 8 (the outlet of the contactor basin) was 7.62 minutes with a volume of 662.15 m$^3$. The CT value was 0.62 mg-min/L calculated using the log integration method.

- The log inactivation credit was determined by multiplying the CT value with the proposed Cryptosporidium inactivation rate based on research from CH2M Hill (North York, ON), which has the following form (Hunter, 2000):

$$K_{Cryptos} = 0.1497 \exp(0.0311 \times T)$$

Equation 14

Where: $T$ is the water temperature = 21 °C.

The calculated Cryptosporidium log inactivation was 0.18. The performance ratio (PR) was 0.09, which was calculated by dividing the calculated log inactivation by the required (i.e. 2 log for the WUC ozonation process) log inactivation. The acceptable operating PR range for the WUC is 0.9 and 1.2. Any value above or below the PR range requires adjustment.

- The above procedure and calculations were repeated for all conditions studied.

Table 4-3 displays the information used to determine the CT values in the following sections.
### Table 4-3 CT Calculation Variables

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<th>Basin(s)</th>
<th>Volume m³</th>
<th>Max. Flow Rate m³/min/Train</th>
<th>T10/T</th>
<th>HDT min.</th>
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#### 4.4.1 Summary

Table 1 in Appendix B summarizes the calculated CT values. Figures 4-30 through 4-33, which displays the four combined conditions of temperature and pH, show the relationship between Cryptosporidium log inactivation and ozone dose for the hydraulic efficiencies and their related basin(s).

For all four combinations of temperature and pH, the target disinfection of 2-log (99%) Cryptosporidium inactivation was not achieved for the original contactor basin. In order to achieve target disinfection levels, C, T or both should be increased. Increasing C would raise operating costs; it could result in high concentrations of disinfection by-products, which may exceed current standards (Hannoun et al., 1998). Increasing the contact time by adding the rapid mixer and two flocculation basins to the original contactor was an effective measure for three of the four combined conditions of temperature and pH.
Figure 4-30 Log Inactivation vs. Ozone Dose: \( T = 21 ^\circ C \) & pH 8.1

Figure 4-31 Log Inactivation vs. Ozone Dose: \( T = 21 ^\circ C \) & pH 7.7
Figure 4-32 Log Inactivation vs. Ozone Dose: $T=5^\circ C$ & pH 8.1

Figure 4-33 Log Inactivation vs. Ozone Dose: $T=5^\circ C$ & pH 7.7
The addition of stainless steel baffled walls to the original contactor basin had substantially increased the CT value and the log inactivation credit when compared with the original contactor containing concrete baffled walls. An increase in hydraulic efficiency from 0.43 to 0.75 significantly improved disinfection (i.e. plug-flow behavior).

All four operating conditions achieved 2-log (99%) Cryptosporidium inactivation credit with the additional baffled wall contactor-rapid mixer-two flocculation system. The condition, temperature 5 °C and pH 7.7, achieved 2-log (99%) Cryptosporidium inactivation with the lowest initial ozone dose using this system of basins. The initial ozone dose approximately ranged from 1.7 mg/L to 2.1 mg/L, corresponding to PRs between 0.9 and 1.2. For the same system of basins, the condition temperature 5 °C and pH 8.1, achieved PRs between 0.9 and 1.2 for initial ozone concentrations greater than 1.7 mg/L and less than 2.5mg/L. The condition, temperature 21 °C and pH 7.7 achieved the desired PR with initial ozone doses ranging from approximately 2.5 mg/L to 3.0 mg/L. The condition, temperature 21 °C and pH 8.1 achieved 2 log (99%) Cryptosporidium inactivation with concentrations of initial ozone greater than 3.0mg/L.

Low water temperatures reduce the rate of ozone diffusion through the microorganism surface thus the [ozonation] system requires higher ozone concentrations, higher contact times, or both (Urfer et al., 1999). This study achieved target CT values at reduced initial ozone concentrations for the lower water temperature (5 °C). The effect of lower temperatures on engineering parameters is less than it might appear; the associated slower decay rate and lower water demand during lower water temperatures (i.e. winter months) lead to an increased HDT in the contacting systems (Urfer et al., 1999).
Improved inactivation was observed for the reduced pH level (i.e. pH 7.7). In all cases, 2-log (99%) Cryptosporidium inactivation was achieved with reduced initial ozone dose for pH 7.7. At low pH levels the direct pathway of molecular ozone dominants; the direct pathway is said to be relevant for disinfection purposes due to it’s slow and selective reactions with constituents (Urfer et al., 1999). At high pH levels, the indirect reaction pathway with the OH radical reacts quickly with many types of dissolved species and can be scavenged before they encounter particles such as microorganisms (Urfer et al., 1999).
Conclusions & Recommendations

5.1 Conclusions

The following conclusions were drawn for this study:

- The ozone decay rate was well approximated with first-order kinetics for the Detroit River raw water source.

- Assuming a constant sensitivity coefficient resulted in an under estimation of the ozone residuals by 3 to 22%, which would effect the concentration in order to meet a require target of disinfection.

- The four combinations of temperature and pH studied in order of greatest rate of ozone decay (shorter half-life times) to lowest rate of ozone decay (longer half-life times) are 21 °C /pH 8.1, 21 °C /pH 7.7, 5 °C /pH 8.1, and 5 °C /pH 7.7.

- Increasing ozone dose from 1.5 mg/L to 3.0 mg/L decreased the rate of ozone decay and thus increased the 60-second ozone residual and increased the half-life time.

- The tracer studies provided the effective contact times and the hydraulic efficiencies in order to calculate the CT value.
Additional contact time provided by the rapid mixer and two flocculation basins increased the CT value and hence achieved the required target disinfection without increasing ozone dose concentration.

Improved hydraulic efficiencies and hence improvements in disinfection were reported with the installation of stainless steel baffled walls in the original contactor basin.

Required target disinfection, for both operating temperatures 21 °C and 5 °C, was achieved with the additional baffled wall contactor-rapid mixer-two flocculation system of basins.

The lower pH level, 7.7, was more effective in achieving desired levels of inactivation with lower ozone dose than pH 8.1.

5.2 Recommendations
Develop ozone demand/decay data for digressive raw water quality events. This will help to define the range of water quality conditions expected to produce maximum ozone decay rates for the A.H. Weeks water supply.

Develop the Indigo Reagent II Standard Curve for ratios intended in the study. This should better predict the absorbance of the blank across the range of interest.

Develop the hydraulic efficiency for the rapid mix and the flocculation basins incorporating the baffled wall contactor (i.e. concrete plus stainless steel baffles). This will better predict the disinfection efficiency of the ozonation system.
Calculate CT using the recently developed Integrated Disinfection Framework (IDDF) method. This method is considered more accurate than either the effluent or log integration method (Rakness et al., 2000).
References


Urfer, D., P. Huck, G.A. Gagnon, D. Mutti, and F. Smith “Modeling Enhanced Coagulation to Improve Ozone Disinfection” Journal AWWA, March (1999),
Appendix A Jar Testing Results

**Apparatus:** Standard fluoride sample, approximately 1.5 mg/L; distilled water sample; raw water sample; coagulated raw water sample; and jar testing apparatus.

**Procedure:** The standard solution was added to the distilled water jar, raw water jar, and the coagulated water jar. The mixers were at maximum speed for 2 minutes and then reduce to 20 – 30 rpm for the 2 hours of testing. A sample was drawn from each jar apparatus at the following sample times: 0, 1, and 2 hours.

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<th>Measured Fluoride Concentrations</th>
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<td>Distilled water + standard</td>
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<tr>
<td>Raw water sample + standard</td>
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<td>Coagulated sample (Alum + PERCOL) + Standard</td>
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<td>Natural Background Fluoride</td>
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## Appendix B  CT value Calculations

### Table B-1 CT Value Data

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<th>Ozone Dose</th>
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<th>O3Res@75sec mg/L</th>
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VITA AUCTORIS

NAME: Juliann Sladic

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DATE OF BIRTH: October 23, 1976

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