

Modeling Cyanogen Chloride Kinetics in Distribution Systems: A Semi-Batch $C \cdot t$ Protocol for Natural Waters

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Received for Review: 2 February 2000

Accepted for Publication: 24 February 2000

Abstract

Experiments were undertaken with the primary objective of developing kinetic relationships for the formation of cyanogen chloride (CNCl), which could then be integrated into a multi-constituent water quality model. The use of ozone in combination with monochloramine has been reported in the literature to enhance CNCl formation. A procedure to determine $C \cdot t$, a surrogate used to estimate the level of microbial inactivation achieved, was also developed using a semi-batch methodology. Water collected from the Mannheim Water Treatment Plant (WTP) (Waterloo, Ontario, Canada) at 7°C and 20°C was ozonated using a semi-batch procedure to achieve a desired level of inactivation. A series of specific steps were then followed to simulate treatment at the Mannheim WTP as closely as possible at bench-scale. Three different levels of microbial inactivation were selected to simulate 0.5-log *Giardia* inactivation, and both 1.0-log and 3.0-log *Cryptosporidium* inactivation. Kinetic relationships were developed which described CNCl formation as a function of log *Cryptosporidium* inactivation, monochloramine concentration, and time. It was concluded that CNCl formation followed an exponential function of time that depended on both monochloramine concentration and microbial inactivation level.

Key Words

Ozone; Cyanogen Chloride Kinetics; Mannheim Water Treatment Plant; *Cryptosporidium* Inactivation; C-t Protocol; Monochloramine Addition;

Introduction

Ozone use in drinking water treatment has been increasing due to proposed regulations that would lower current regulatory limits on disinfection by-products (DBP) in drinking waters (USEPA, 1994). One of the potential barriers to the widespread implementation of ozone is a lack of understanding

regarding the implications of full-scale application. A methodology for performing bench-scale ozone disinfection experiments has been developed to address this concern. Bench-scale experiments are often used in preliminary assessments prior to ozone implementation at pilot- or full-scale. Since the Surface Water Treatment Rule (SWTR; USEPA, 1991) is based on the $C \cdot t$ (residual concentration \times

contact time) concept for the inactivation of *Giardia* and viruses, the development of a protocol for conducting experiments at bench-scale utilizing real water matrices is required to evaluate disinfection practices in these terms.

A semi-batch bench-scale $C \cdot t$ protocol using natural waters was applied in the evaluation of cyanogen chloride (CNCl) formation kinetics. This research examined the effect of disinfecting to three levels of inactivation (0.5-log *Giardia*, 1-log *Cryptosporidium*, and 3-log *Cryptosporidium*) in terms of $C \cdot t$, on CNCl formation. As well, the subsequent application of 3 levels of chloramination was also investigated. The concentration of CNCl was then measured as a function of time, and kinetic parameters were determined. Experiments such as these could be used by utilities to estimate potential DBP concentrations and evaluate compliance with DBP regulations prior to either the implementation of ozone or increasing its dosage to achieve higher microbial inactivation levels. This research incorporated the results of bench-scale ozonation experiments in the development of CNCl formation equations that may be used to predict the concentration of CNCl reaching a consumer through a water distribution system.

Background

Disinfection

Inactivation of viruses and microorganisms such as *Giardia* and *Cryptosporidium* is a primary objective of drinking water treatment. To this end, the USEPA has promoted the use of a surrogate to estimate the level of microbial inactivation achieved in a given treatment process: the $C \cdot t$ product (USEPA, 1991). The $C \cdot t$ product can be defined knowing only the residual disinfectant concentration C , and the contact time t . Several methods are available for the determination of both C and t in full-scale ozone contactors; these are discussed elsewhere (USEPA, 1991). In this study the relationships between $C \cdot t$ and ozone inactivation of *Giardia* were obtained from the SWTR (USEPA, 1991). $C \cdot t$ values shown in the SWTR were developed using a batch ozonation protocol.

For the purpose of the experiments described herein, ozone was applied to water samples in a semi-batch mode, i.e., ozone was applied to the water sample

directly, as opposed to a batch mode procedure where "pure" water (e.g., Milli-Q™ water) is first ozonated and then added to the sample. The term "semi-batch" is used because the reactor is batch with respect to the water phase but incorporates a continuous ozone gas flow. Batch-type experiments could not be conducted due to the dilution factors associated with the high ozone doses required to overcome the ozone demand. The $C \cdot t$ -inactivation relationship for *Giardia* is given by:

$$\log \frac{N}{N_0} = -k_{\text{Giardia}}[O_3] \cdot t \quad [1]$$

$$k_{\text{Giardia}} = 1.04 \exp 0.0714(T) \quad [2]$$

where $\log \frac{N}{N_0}$ is the log inactivation of viable microorganisms, $[O_3]$ is the ozone residual concentration in water (mg/L), t is the contact time (min), k_{Giardia} is the pseudo first-order reaction rate constant, and T is the temperature (°C). $C \cdot t$ values related to inactivation of *Cryptosporidium* were obtained by applying two relationships developed by Finch *et al.* (1994), which were based on a batch protocol in pure water. The $C \cdot t$ -inactivation relationships for *Cryptosporidium* are presented in Eq. [3] for 7°C and Eq. [4] for 22°C (Finch *et al.*, 1994):

$$\log \frac{N}{N_0} = -0.29[O_3]^{0.68} t^{0.95} \quad [3]$$

$$\log \frac{N}{N_0} = -0.82[O_3]^{0.23} t^{0.64} \quad [4]$$

Using the relationships shown above one can determine the ozone residual concentrations required for a given contact time to achieve a desired level of *Giardia* or *Cryptosporidium* inactivation.

Disinfection By-Products

In general, the use of ozone in combination with post-chloramination has been reported to produce the lowest DBP concentrations when compared to other combinations of ozone, free chlorine, or chloramines (Clark *et al.*, 1994, Lykins *et al.*, 1994, Jacangelo *et al.*, 1989). Ozone treatment usually produces lower levels of halogenated by-products, such as trihalomethanes (THMs) and haloacetic acids (HAAs), with the notable exception of cyanogen chloride (CNCl) and the brominated species such as bromoform, and mono- and di-bromoacetic acid (Shukairy *et al.*, 1994). Ozone

also results in an increased production of oxygenated by-products such as aldehydes and carboxylic acids (Schechter and Singer, 1994, and Weinberg *et al.*, 1993), as well as bromate (Croué *et al.*, 1996, Najm and Krasner, 1995, and Shukairy *et al.*, 1994).

The use of ozone in a treatment train which includes monochloramine addition to provide a distribution system residual has been reported to enhance CNCl formation (Smith and Singer, 1994, Singer *et al.*, 1994, and Jacangelo *et al.*, 1989). Smith and Singer (1994) have suggested that formaldehyde, an ozonation by-product, serves as an intermediate in the CNCl formation pathway by way of a reaction with monochloramine. Although the epidemiology of CNCl is not well understood at the present time, it warrants attention due to the unique synergistic effect of an ozonation by-product (formaldehyde) and monochloramine.

Distribution System Water Quality Modeling

Distribution systems and their associated physical, chemical, and biological components can influence DBP concentrations reaching consumers. THM concentrations can increase, especially in the presence of a free chlorine residual (Baribeau *et al.*, 1994, Clark *et al.*, 1994a, and Lyn and Taylor, 1993). Formaldehyde concentrations have been observed to decrease due to biological interactions (Baribeau *et al.*, 1994, and Levi *et al.*, 1993), however the authors know no research investigating CNCl propagation and reaction in distribution systems.

The simulated distribution system (SDS) methodology described by Koch *et al.* (1991) as well as the uniform formation condition (UFC) procedure (Summers *et al.*, 1996) yield time-dependent DBP concentration data. The SDS and the UFC do not on their own provide the information required for incorporation into a numerical water quality framework. However, the data can be manipulated to provide the desired kinetic relationships. A model that incorporates DBP propagation and the factors that affect the propagation (e.g., chlorine residual concentration) is required to accurately model and predict DBP concentrations reaching consumers.

Numerical water quality models, such as EPANET (USEPA, 1993), are generally capable of describing advective transport and reaction of both water and constituents (e.g., disinfectants, microorganisms, and

DBPs). By contrast, the advection-dispersion equation is a general differential equation that is applied to analyze water quality propagation in pipes and accounts for all common one-dimensional mass transport phenomena which occur in pipeline systems. It has been applied by Axworthy and Karney (1996), Lu *et al.* (1995), and Elshorbagy and Lansey (1994) for the purpose of modeling chlorine propagation in pipes. The advection-dispersion equation with a reaction term is:

$$\frac{\partial C(x,t)}{\partial t} + u \frac{\partial C(x,t)}{\partial x} + D \frac{\partial^2 C(x,t)}{\partial x^2} + \theta(C(x,t)) = 0 \quad [5]$$

where $C(x,t)$ is the constituent (e.g., chlorine) concentration ($\mu\text{g/L}$), x is the longitudinal axis distance (m), t is the time (hrs), u is the mean velocity of flow (m/hr), D is the coefficient of longitudinal diffusion (m^2/hr), and $\theta(C(x,t))$ is the rate of reaction of constituent ($\mu\text{g L}^{-1} \text{hr}^{-1}$). The first term in Eq. [5] accounts for the change in concentration at a point in the system with respect to time. The second term accounts for the advection of the bulk water. The third term accounts for diffusion. Finally, the fourth term accounts for the reaction (formation/decay) of the constituent. When first-order kinetics are used to model constituent decay, the reaction term can be replaced by $\theta(C(x,t)) = kC(x,t)$, where k is the first-order decay constant (hr^{-1}). The reaction term for the bulk water can be determined experimentally as described in this study. More complex reaction terms as developed by Vasconceles *et al.* (1997) to describe pipe wall effects can also be used.

A series of mass-transport equations (similar to Eq. [5]) can be set up and solved simultaneously to model the transport of several constituents. The reaction term in each equation may be a function of another constituent's concentration. A water quality model that incorporates multi-constituent transport as well as inter-constituent reactions is capable of more accurately predicting distribution system dynamics and kinetics than one which ignores these terms. This paper describes the methodology used in the development of the inter-constituent reaction terms.

Analytical Methods

Ozone

Ozone was produced using a 1.2 lb/day (0.54

kg/day) ozone generator¹. All connecting tubing was of either 316 stainless steel or TeflonTM. All appurtenances were 316 stainless steel or TeflonTM-lined. A custom-made 2.9-L glass reactor² was used for all semi-batch ozonation experiments. Two 500-mL PyrexTM gas-washing bottles served as potassium iodide (KI) traps, which were required for the determination of both applied ozone dose and off-gas concentrations. A constant ozone gas flow rate of 0.3 L/min was used for all experiments; applied doses were achieved by varying the length of ozonation application time.

The ozone concentration in the supply gas was determined using the ozone demand/requirement—semi batch method (*Standard Method* 2350 E, APHA, AWWA, and WEF, 1995). Three potassium iodide (KI) trap tests were conducted to determine the applied ozone dose prior to commencing an experiment. An acceptable error between the three tests was set at a standard deviation of 2% (maximum error was 1.9%). Ozone off-gas concentration was determined by routing the ozone through a KI trap following the reactor.

Residual ozone concentration in the water was measured using the indigo colorimetric method (*Standard Method* 4500-O₃ B, APHA, AWWA, and WEF, 1995). The spectrophotometric procedure employed a Hewlett-Packard Diode Array Spectrophotometer, Model 8452A³, equipped with a flow through cell utilizing a 1-cm path length and a peristaltic pump Model 89052B³. Ozonated water was added to a 100-mL volumetric flask containing indigo until the color was almost completely dissipated. A modification to the indigo colorimetric method conducted in this research is described as follows. The volume of sample V added to the 100-mL flask was determined by adding known amounts of Milli-QTM water following the ozonated water sample addition. The volume of sample V is :

$$V = 100 - \text{Volume of Indigo} - \text{Volume of Milli-Q}^{\text{TM}} \quad [6]$$

This method was preferred over that described in *Standard Methods* due to its shorter sampling time. A modified indigo method as described by Williams

and Darby (1992) was used to account for suspended material in the ozonated real water. This method involves taking an absorbance reading of an indigo blank (indigo in Milli-QTM), an ozonated water sample, and an ozonated water sample with indigo. The difference in absorbance ΔA represents the difference between the indigo blank plus the ozonated water sample, and the water sample with indigo. That is:

$$\Delta A = \text{Indigo blank} + \text{Ozonated water sample} - \text{Ozonated water with indigo} \quad [7]$$

$$\text{mg O}_3/\text{L} = \frac{100 \times \Delta A}{f \times b \times V} \quad [8]$$

where b is the path length of cell (cm), V is the volume of sample (mL), and $f = 0.42$.

Prior to use, the 2.9-L reactor was made ozone-demand-free by contacting the glassware with water containing a measurable ozone residual.

Cyanogen Chloride

Cyanogen chloride (CNCl) concentrations were determined using a liquid-liquid extraction procedure as described by the Metropolitan Water District of Southern California (1994). Ascorbic acid (20 mg) was added (to provide dechlorination) to each 40-mL sample vial prior to sampling. A 25-mL aliquot of sample water was added to each sample vial. Approximately 10 g of sodium sulfate (Na₂SO₄) and 4 mL of the extraction solvent, methyl tert-butyl ether (MtBE), containing an internal standard 1,2-dibromopropane (1,2-DBP), was then added to the sample vial. The sample vials were sealed, shaken for 7 minutes, and allowed to stand for 10 minutes prior to transferring the MtBE layer to 1.5-mL autosampler vials. Analysis was always conducted within 48 hours of sample collection (typically within 6 hours). A Hewlett Packard 5890 Series II PlusTM Gas Chromatograph³, fitted with an HP-5 capillary column³ (30m length, 0.250mm inside diameter) and an electron capture detector (ECD) was used for all analyses. The minimum reporting level (MRL) for CNCl was determined to be 0.25 $\mu\text{g/L}$. The temperature program was as follows: 35°C for 1 minute, followed by 10°C/min to 120°C. The injector and detector temperatures were 157°C and 300°C, respectively.

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Chlorine Residual

Free chlorine, monochloramine, and total chlorine measurements were conducted with amperimetric titration (*Standard Method* 4500-Cl D, APHA, AWWA, and WEF, 1995) using a Wallace & Tiernan™ Series A-790 amperimetric titrator⁴.

Monochloramine was formed by adding an ammonia chloride (NH₄Cl) solution to chlorine in a ratio of 5:1 total chlorine (mg Cl₂/L): ammonia (NH₃ as mg N/L).

All glassware that came into contact with either a free chlorine or a monochloramine residual was made chlorine demand free. This was achieved by contacting the glassware with a 10 mg Cl₂/L chlorine solution prepared in distilled water for at least 3 hours.

Experimental Protocol

A protocol which allows the generation of bench-scale operational curves that relate applied dose to a desired level of *Giardia* and *Cryptosporidium* inactivation was developed first. The resulting curves allow an experimenter to apply ozone to achieve a desired level of microbial inactivation. Separate curves must be developed for waters which have different water quality characteristics (i.e., ozone demand). Curve characteristics may also be dependent on reactor configuration and ozone flow rates into the reactor. The second part of this section describes the protocol that was used to develop the DBP kinetic relationships.

Applied Dose-Inactivation Relationships

Ozone was initially applied at a dose which was anticipated to be near to that required to provide a desired level of *Giardia* or *Cryptosporidium* inactivation. An appropriate starting point was an applied ozone dose to organic carbon ratio of 1:1. Ozone decay was measured over time by taking a series of ozone residual measurements using the indigo colorimetric method. The $C \cdot t$ product was then calculated for 6 applied doses (as described in subsequent sections). Relationships between applied dose and the level of inactivation of *Giardia* or *Cryptosporidium* were developed using relevant $C \cdot t$

t -inactivation equations (Eqs. [1] to [4]). A range of typical inactivation requirements was selected based on a review of the SWTR Rule (USEPA, 1991) and the proposed Enhanced SWTR (ESWTR) Rule (USEPA, 1994b). The desired levels of inactivation for each microorganism are listed in Table I for disinfection conducted at 7°C and 20°C. Experiments were conducted at 7°C since $C \cdot t$ -inactivation relationships have been reported for this temperature (Finch *et al.*, 1994). The ambient temperature of the laboratory in which the experiments were performed was 20±1°C and as such was selected to perform the higher temperature experiments. $C \cdot t$ -inactivation relationships developed by Finch *et al.* (1994) at 22°C were directly applied since a 2°C difference would not result in significant error.

To evaluate the $C \cdot t$ product, the residual ozone concentration was measured over time following the termination of ozone gas flow into a semi-batch reactor. Information gained from decay tests include the order of decay (typically first order), and the decay coefficient, k_{O_3} . The equation describing first-order decay is shown below:

$$[O_3]_t = [O_3]_0 \exp(-k_{O_3} \cdot t) \quad [9]$$

where $[O_3]_t$ is the ozone residual concentration (mg O₃/L) at time t , $[O_3]_0$ is the initial ozone residual concentration (mg O₃/L), k_{O_3} is the ozone decay coefficient (min⁻¹), and t is the contact time (min). In cases where ozone follows a first order decay, Eq. [9] can be solved for k_{O_3} to determine the decay coefficient, as shown below:

$$k_{O_3} = \frac{-\ln\left(\frac{[O_3]_t}{[O_3]_0}\right)}{t} \quad [10]$$

Concentration C

Two methods were investigated to calculate the concentration term $[O_3]$ of the $C \cdot t$ product as discussed in the following paragraphs. Method 1, as described by Finch *et al.* (1994), utilized Eq. [11] to evaluate $[O_3]$, the integrated ozone residual concentration.

⁴ Wallace & Tiernan, Inc., 25 Main St., Belleville NJ, 07109-3057

$$[O_3]_{\text{int}} = \exp\left(\frac{\ln[O_3]_0 + \ln[O_3]_f}{2}\right) \quad [11]$$

where $[O_3]_{\text{int}}$ is the integrated ozone residual concentration (mg O_3 /L), and $[O_3]_f$ is the final ozone residual concentration (mg O_3 /L).

Method 2 was used to calculate the average ozone residual concentration $[O_3]_{\text{avg}}$ over the contact time and is adapted from Langlais *et al.* (1991).

$$[O_3]_{\text{avg}} = \left(\frac{[O_3]_0}{k_{O_3} \cdot t} \times (1 - \exp(-k_{O_3} \cdot t))\right) \quad [12]$$

Either $[O_3]_{\text{avg}}$ or $[O_3]_{\text{int}}$ was then substituted for $[O_3]$ in Eqs. [1], [3], or [4] to estimate the level of inactivation. Eq. [12] was derived by integrating the first-order decay equation (Eq. [9]) with respect to time t and then dividing by t to determine the average ozone residual concentration.

Time t

The equation used to estimate contact time in the semi-batch reactor was derived from the first-order decay equation (Eq. [9]). Solving Eq. [9] for t and setting $[O_3] = 0.01$ mg/L, the contact time is estimated as:

$$t = \frac{-\ln\left(\frac{0.01}{[O_3]_0}\right)}{k_{O_3}} \quad [13]$$

The value $[O_3]_f = 0.01$ mg/L was selected for two reasons. First, this is the lowest residual that can be reliably measured using the indigo colorimetric method. Second, a residual below this concentration will not contribute significantly to the $C \cdot t$ product and hence to the inactivation credit achieved due to ozone disinfection.

The contact time t exerts only a limited effect on the $C \cdot t$ product as defined by the SWTR since there are equivalent exponent values on the C and t . The t terms cancel, with time t only remaining in the exponential term as shown in Eq. [14].

$$C \cdot t = [O_3] \times t = \left(\frac{[O_3]_0}{k_{O_3} \cdot t} \times (1 - \exp(-k_{O_3} \cdot t))\right) \quad [14]$$

Contact time has a more pronounced effect on the C

$\cdot t$ product when the equations developed by Finch *et al.* (1994) are utilized (Eqs. 3 to 4). This is due to the non-equivalent exponent values on the C and t terms. The relative magnitude of the exponents can weight the $C \cdot t$ product more heavily towards either the concentration or time term.

Bulk Water Protocol

Ozone was applied to the water samples in a semi-batch mode to achieve a pre-selected *Giardia* or *Cryptosporidium* inactivation level as shown in Table I. When the required ozonation time was complete, the flow of ozone into the reactor was terminated. The ozone residual was allowed to dissipate until it was below measurable limits (<0.01 mg O_3 /L using the indigo colorimetric method described earlier). Subsequently, 800 mL of ozonated water was transferred from the reactor to each of three narrow-neck 2.5-L amber-glass carbuoys. Chlorine was then added to the water to provide nominal total chlorine residuals of 0.45, 1.8, and 4.2 mg Cl_2 /L after 20±2 hours of contact time. The treated water was incubated at either 7°C or 20°C. Experiments were conducted at 7°C or 20°C due to the availability of *Cryptosporidium* inactivation relationships using $C \cdot t$ at these temperatures (Finch *et al.*, 1994).

Once the chlorine contact period was complete, 1600 mL of groundwater was added to the treated water. The mixture of ground and surface waters (ratio of 2:1) was selected to simulate the typical protocol used at the Mannheim WTP, Ontario, Canada. The addition of groundwater to the treated-water resulted in a dilution of the chlorine residual by a factor of three. Residuals of 0.15, 0.6, and 1.6 mg Cl_2 /L were sought. The residual concentrations were selected following a review of available literature to represent a range of typical chlorine residual concentrations observed upon entry into a water distribution system. The 2.5-L carbuoys were not sealed headspace free (a total of 2.4 L of water was added) to maintain the proper proportions of surface and ground water. Monochloramine was formed by adding an ammonia chloride solution to the chlorinated water to achieve a mass ratio of 5:1 Cl_2 : NH_3 as N, as per Mannheim WTP protocol. The ammonia solution was prepared by adding ammonium chloride to pH 8 buffered Milli-Q™ water.

Table I: Desired Inactivation Levels and Associated C · t Products

Level of Microbial Inactivation	Microbe	Log Inactivation	C · t	7°C $C^{0.68}t^{0.95}$	20°C $C^{0.23}t^{0.64}$
Low	<i>Giardia</i>	0.5	0.29 ^a	-	-
Medium	<i>Crypto</i>	1.0	-	3.4 ^b	-
High	<i>Crypto</i>	3.0	-	10.3 ^b	-
Low	<i>Giardia</i>	0.5	0.10 ^a	-	-
Medium	<i>Crypto</i>	1.0	-	-	1.22 ^b
High	<i>Crypto</i>	3.0	-	-	3.7 ^b

^a Based on SWTR (USEPA, 1991).

^b Based on Finch *et al.* (1994).

Table II: Results of Water Quality Analysis for the Mannheim WTP and Well K21

Parameter	Units	WTP	Well K21
pH		7.28	7.69
NPOC	mg C/L	4.8	2.1
Alkalinity	mg CaCO ₃ /L	118±2.9	275±2.5
Turbidity	NTU	3.5	0.15
UV-254	cm ⁻¹	0.088±0.003	0.0050±0.0001
Bromide	µg/L	<20	<20

The water from the 2.5 L carbuoys was then subdivided into seven headspace-free 250-mL bottles, to simulate successive distribution system residence times of 0, 1, 2, 3, 8 days. Analysis of the water for at least one residence time in each experiment was performed in duplicate and one other bottle was filled to serve as a backup.

The incubation temperature was calculated as the weighted average of temperatures of the ozonated/chlorinated water and the groundwater. Groundwater was added at 10°C since this represented the typical year round temperature of the groundwater source. Treated water was either at 7°C or 20°C, the temperatures at which the water was ozonated. Therefore, the incubation temperatures were 9°C (for the 7°C disinfected water) and 13.3°C (for the 20°C disinfected water). The complete protocol for the bulk water experiments is summarized in Figure 1.

Results and Discussion

Water Quality

For the purpose of conducting bench-scale experiments, "treated water" was collected at a post-settling (pre-ozonation) location from the Mannheim WTP, Waterloo, Ontario, Canada. Groundwater was collected at the same time from Waterloo's well K21. The water quality parameters for both waters are shown in Table II. Groundwater was mixed with surface water in a ratio of 2:1 prior to entering the distribution system at the Mannheim WTP. Groundwater was added to ozonated/chlorinated water in a ratio of 2:1 following a 1 day contact period, prior to ammonia addition.

Applied Dose-Inactivation Relationships

A first-order ozone decay coefficient k_{O_3} was

determined for each ozone decay kinetic test. The decay coefficients are listed in Table III for experiments performed at 7°C and 20°C. A plot of decay coefficients vs. applied ozone dose was developed as shown in Figure 2. Well-defined relationships are observed to exist between the first-order decay coefficients and the applied dose at each temperature. Until demand is met, there is no measurable residual and the decay is undefined. Recall that "ozone demand" is defined as the point where an ozone residual is measurable. Ozone consumed during the "demand" period is reacting with material that is quickly oxidized; however, some reactive material remains. The decay coefficient decreases as the applied ozone dose increases. A lower decay coefficient indicates that there is less material to react with the residual ozone. The ozone decay coefficient will approach its auto-decomposition value as all the ozone oxidizable compounds have reacted. That is, ozone will decay at the rate it would if there were no material remaining in the water to react with. Similar results have been reported by Oke *et al.* (1996), who developed mathematical relationships between various water quality characteristics and ozone decay rates. Since ozone decay does not follow a simple first-order decay relationship over a range of different doses, the incorporation of the decay coefficient into equations describing ozone residual concentration and contact time is beneficial. Because of the non-simple ozone first-order decay, Method 2 as described earlier, was selected to calculate ozone residual concentration. It is not as straightforward as Method 1, but it does incorporate more information about the decay kinetics by inclusion of decay coefficient term k_{O_3} .

The decay coefficients k_{O_3} and initial ozone residuals $[O_3]_0$ can be entered into Equation [13] to determine the contact time t . The average ozone residual $[O_3]_{avg}$ can be determined using Equation [12], if k_{O_3} , $[O_3]_0$, and t are known. Concentration and time may then be defined as $[O_3]_{avg}$ and t , respectively.

The level of *Giardia* inactivation can be determined by substituting $[O_3]_{avg}$ and t into Equation [1]. This procedure is described in detail by Romain (1996). Similarly, the level of *Cryptosporidium* inactivation can be determined by substituting $[O_3]_{avg}$ and t into Equation [3] for tests conducted at 7°C and Equation [4] for 20°C tests. Applied dose-inactivation relationships were developed for both *Giardia* and

Cryptosporidium at 7°C and 20°C. Operational relationships between *Giardia* and *Cryptosporidium* inactivation and applied dose are shown in Figures 3 and 4, respectively. Contact times used in the experiments ranged from 1.5 to 38 minutes for the 7°C temperature water, and 0.9 to 16 minutes for the 20°C temperature water. These relationships may then be used to determine the applied dose to obtain a desired level of inactivation (Table IV).

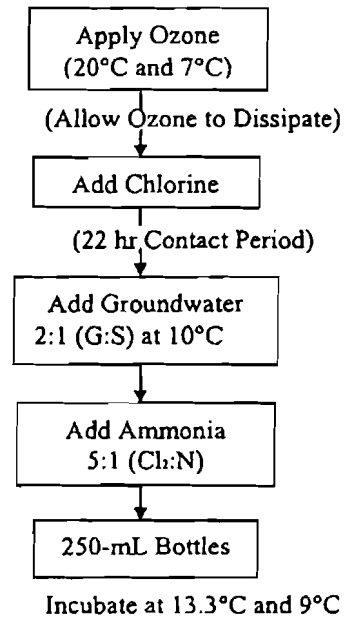


Figure 1: Summary of Bulk Water Experimental Protocol

Bulk Water Experiments

Three experiments were conducted at the high temperature (20°C ozonation and 13.3°C incubation) while two experiments were conducted at the low temperature (7°C ozonation and 9°C incubation). Both desired and achieved log inactivations are shown in Table V. The operational curves served well when estimating applied ozone dosages at 20°C for the 3-log *Cryptosporidium* and 0.5-log *Giardia* inactivation levels. A +0.2-log inactivation error was observed when attempting to obtain a desired 1-log *Cryptosporidium* inactivation. The operational curves did not estimate inactivations at 7°C.

Table III: Summary of Ozone Residual Decay Experiments

Applied Ozone (mg O ₃ /L)	[O ₃] ₀ (mg O ₃ /L)	Decay Coefficient			No. of Observations
		<i>k</i> _{O₃} (min ⁻¹)	<i>T</i> _{1/2} ^a (min)	R ²	
Ozonation at 7°C					
2.0	0.84	0.115	6.0	0.989	9
1.5	0.48	0.205	3.4	0.941	6
1.35	0.47	0.273	2.5	0.990	6
1.2	0.38	0.473	1.5	0.974	5
1.0	0.26	0.499	1.4	0.994	3
0.7	0.08	1.38	0.5	1.000	2
Ozonation at 20°C					
4.85	1.36	0.308	2.3	0.945	7
4.0	0.92	0.370	1.9	0.970	5
2.4	0.55	0.682	1.0	0.988	3
1.8	0.34	0.949	0.7	1.000	3
1.5	0.18	1.539	0.5	1.000	2
1.17	0.04	1.517	0.5	1.000	2

$$^a \text{ Half-life, } T_{1/2} = \frac{\ln 2}{k_{O_3}}$$

Table IV: Required Applied Ozone Doses for Desired Inactivations

Microbe	Desired Log Inactivation	Applied Dose (mg O ₃ /L)		Reference Figure
		7°C	20°C	
<i>Giardia</i>	0.5	0.96	1.32	3
<i>Crypto</i>	1.0	1.43	1.84	4
<i>Crypto</i>	3.0	2.0	4.2	4

Chlorine Modeling

Free chlorine, monochloramine, and total chlorine concentrations were measured throughout the course of all bulk water experiments. Following the addition of ammonia, monochloramine was the dominant species constituting 83±15% and 93±4% of the total chlorine residual for the 13.3°C and 9°C

incubation temperature experiments, respectively. The error term is the standard deviation of all data points divided by the average residual.

Zero-, first-, and second-order curves were fit to the experimental monochloramine data. Only monochloramine was modeled since it represented most of the total chlorine residual present. Also,

monochloramine in natural waters has been shown to react to form CNCl (Smith and Singer, 1994, and Jacangelo, *et al.*, 1989) and therefore is of primary interest. Relationships for zero-, first-, and second-order reactions are shown as Equations [15], [16] and [17], respectively.

$$\frac{d[\text{NH}_2\text{Cl}]}{dt} = -k \quad [15]$$

$$\frac{d[\text{NH}_2\text{Cl}]}{dt} = -k[\text{NH}_2\text{Cl}] \quad [16]$$

$$\frac{d[\text{NH}_2\text{Cl}]}{dt} = -k[\text{NH}_2\text{Cl}]^2 \quad [17]$$

where $[\text{NH}_2\text{Cl}]$ is the monochloramine concentration ($\text{mg Cl}_2/\text{L}$), t is the time (hrs), and k is the decay coefficient.

The decay coefficient for each reaction order was determined for all experimental data by minimizing the error of the sum of squares. The sum of the squares of the difference between the value determined utilizing either the zero-, first-, or second-order equations and the experimentally measured value are minimized. Equation [18] is an example of the minimizing function for first-order decay.

$$S_{\min} = \text{minimize} (\Sigma ([\text{NH}_2\text{Cl}]_{\text{observed}} - [\text{NH}_2\text{Cl}]_{\text{predicted}})^2) \quad [18]$$

where:

$$[\text{NH}_2\text{Cl}]_{\text{predicted}} = [\text{NH}_2\text{Cl}]_0 \exp(-kt) \quad [19]$$

The least squares analysis was performed using a commercial spreadsheet⁵. The results of the least-squares analysis are shown in Table VI. First-order decay was selected to model monochloramine kinetics since it had the lowest sum of squares. R-squared values were only calculated for the first-order models since the zero- and second-order models were not examined further. The R-squared values are quite low indicating a low correlation between data and the first-order models. A possible explanation for this result is that zero-order reaction kinetics were observed to more appropriately characterize monochloramine residual decay at very low levels ($<0.1 \text{ mg Cl}_2/\text{L}$).

Monochloramine first-order decay coefficients of $1.0\text{--}1.5 \times 10^{-3} \text{ min}^{-1}$ have been reported by Haas *et*

al. (1996) and are of the same order of magnitude as those measured in this research ($1.27\text{--}1.63 \times 10^{-3} \text{ min}^{-1}$).

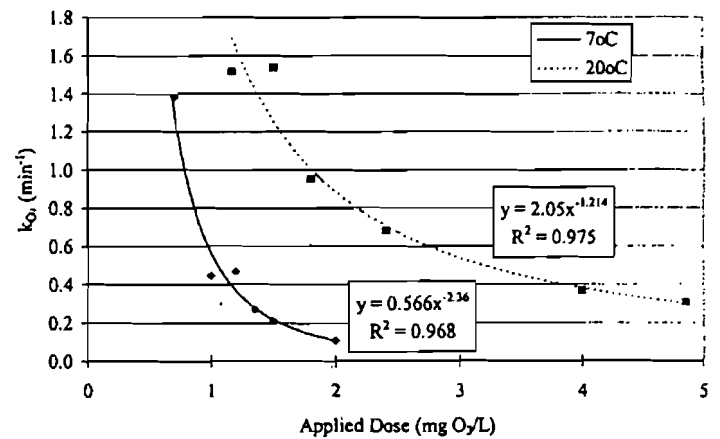


Figure 2: First-Order Decay Coefficient, k_{O_3} , vs. Applied Dose for both 7°C and 20°C.

Cyanogen Chloride Modeling

Multi-Constituent Cyanogen Chloride Model

Three multi-constituent models were developed on the basis of Equation 20.

$$\frac{d[\text{CNCl}]}{dt} = k^* [\text{NH}_2\text{Cl}]^\alpha (\text{Inact})^\beta \exp\left(-\frac{E}{RT}\right) \exp(-\delta \cdot t) \quad [20]$$

where $[\text{CNCl}]$ is the cyanogen chloride concentration ($\mu\text{g}/\text{L}$), t is the contact time (hrs), k^* is the reaction rate coefficient (determined experimentally), $[\text{NH}_2\text{Cl}]$ is the monochloramine residual concentration ($\text{mg Cl}_2/\text{L}$), Inact is the negative log inactivation ($\text{Inact} = \ln\left(\frac{N}{N_0}\right)$) of

Cryptosporidium (dimensionless), E is the activation energy (J), T is the temperature (K), R is the gas constant (8.314 J/K), and α , β & δ are experimentally determined coefficients (dimensionless). The form of this equation is similar to one proposed by McKnight and Reckhow (1992) for chlorine and acetaldehyde decay. The term, Inact , in Equation [20] is used in lieu of an initial formaldehyde concentration. Formaldehyde is a suspected intermediate in the formation of CNCl (Smith and Singer, 1994). The use of this surrogate is justified if formaldehyde formation is considered to be a function of inactivation (inactivation is a function of applied dose) and formaldehyde is assumed to behave according to first-order kinetics.

⁵ Microsoft Excel 5.0 Solver, Microsoft Corp., Redwood WA

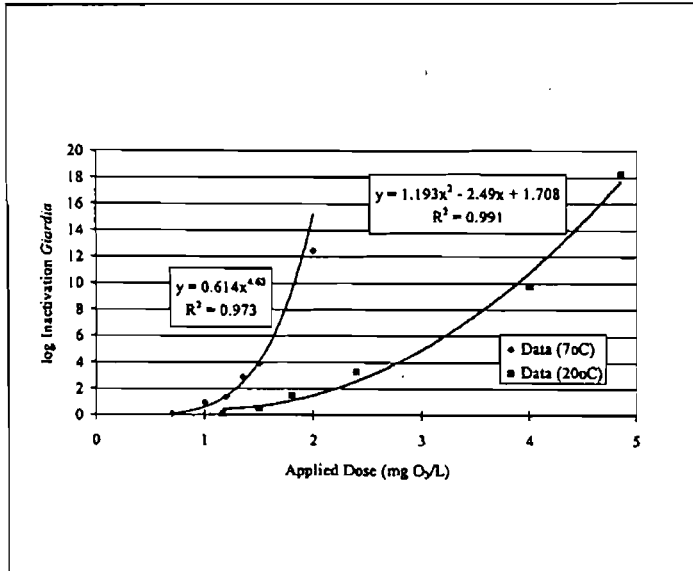


Figure 3: Operational Relationship Between Inactivation and Applied Dose for *Giardia* at both 7°C and 20°C.

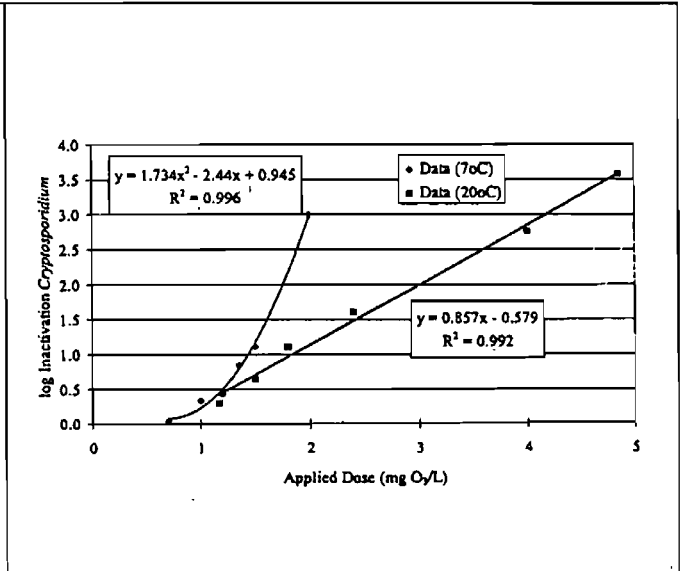


Figure 4: Operational Relationship Between Inactivation and Applied Dose for *Cryptosporidium* at both 7°C and 20°C.

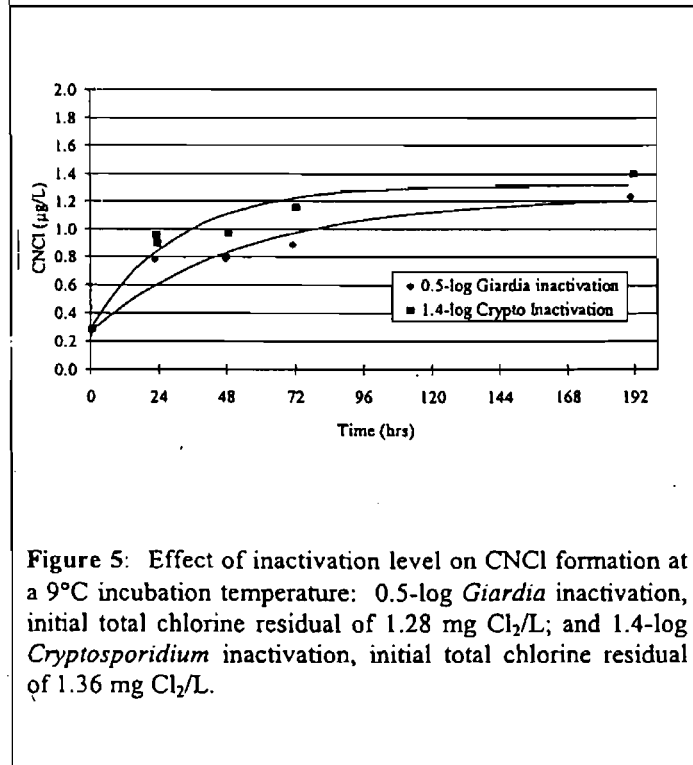


Figure 5: Effect of inactivation level on CNCI formation at a 9°C incubation temperature: 0.5-log *Giardia* inactivation, initial total chlorine residual of 1.28 mg Cl₂/L; and 1.4-log *Cryptosporidium* inactivation, initial total chlorine residual of 1.36 mg Cl₂/L.

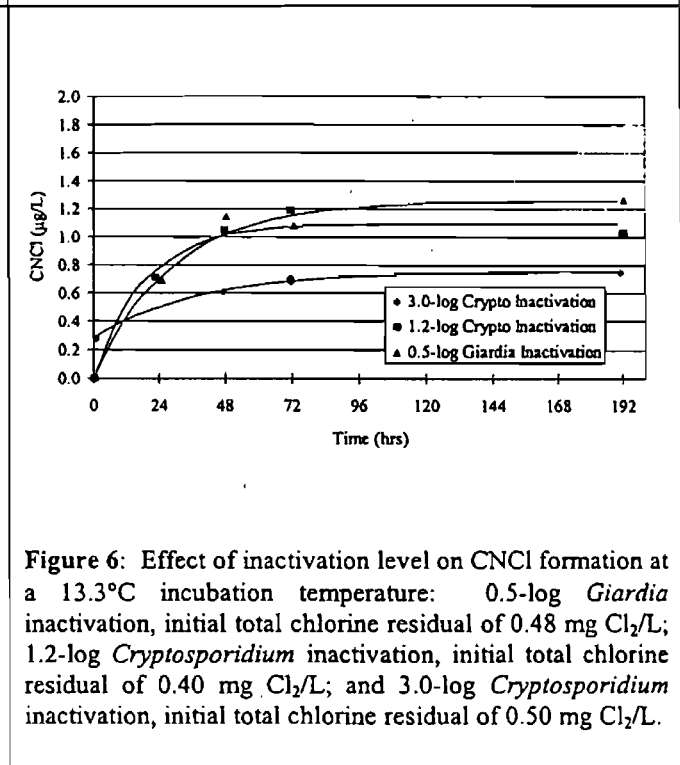


Figure 6: Effect of inactivation level on CNCI formation at a 13.3°C incubation temperature: 0.5-log *Giardia* inactivation, initial total chlorine residual of 0.48 mg Cl₂/L; 1.2-log *Cryptosporidium* inactivation, initial total chlorine residual of 0.40 mg Cl₂/L; and 3.0-log *Cryptosporidium* inactivation, initial total chlorine residual of 0.50 mg Cl₂/L.

Table V: Desired and Experimentally Achieved Log Inactivations for Bulk Water Experiments

Exp #	Target Organisms	Log Inactivations		[O ₃] ₀ (mg O ₃ /L)	k _{O₃} (min ⁻¹)	Trans O ₃ (mg O ₃ /L)	η _{Trans} (%)
		Achieved	Desired				
20°C Disinfection							
1, 2, 3	<i>Crypto</i>	3.0	3.0	0.74	0.30	1.27	31
4, 5, 6	<i>Giardia</i>	0.50	0.50	0.12	0.89	0.62	47
7, 8, 9	<i>Crypto</i>	1.18	1.00	0.25	0.71	0.64	35
7°C Disinfection							
10, 11, 12	<i>Crypto</i>	1.4	3.0	0.39	0.14	0.92	46
13, 14, 15	<i>Giardia</i>	0.50 ^a	0.50	NA	NA	0.62	63

^a Assumed due to insufficient data points.

NA Not Available

Table VI: Monochloramine Modeling Results for Bulk Water Experiments

Reaction Order	Minimum Sum of Squares	k (hr ⁻¹)	R ²
9°C Bulk Water Experiments			
Zero	0.41	1.78 × 10 ⁻³	NA
First	0.23	1.27 × 10 ⁻³	0.58
Second	0.28	1.69 × 10 ⁻³	NA
13.3°C Bulk Water Experiments			
Zero	0.24	1.02 × 10 ⁻³	NA
First	0.10	1.63 × 10 ⁻³	0.29
Second	0.15	1.48 × 10 ⁻³	NA

NA Not Available—R² values for zero and second order were not evaluated.

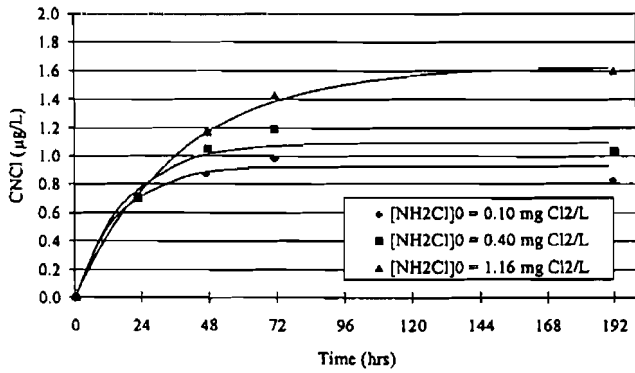


Figure 7: Effect of initial monochloramine concentration on CNCI formation at a 13.3°C incubation temperature and a 1.2-log *Cryptosporidium* inactivation.

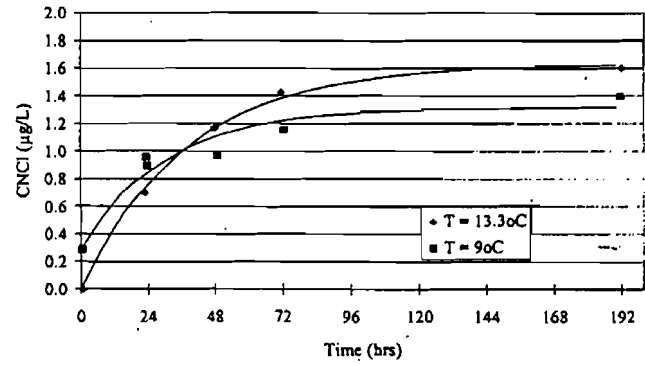


Figure 8: Effect of incubation temperature on CNCI formation: 13.3°C incubation experiments had a 1.2-log *Cryptosporidium* inactivation and an initial total chlorine residual of 1.16 mg Cl₂/L, and 9° incubation experiments had a 1.4-log *Cryptosporidium* inactivation and an initial total chlorine residual of 1.36 mg Cl₂/L.

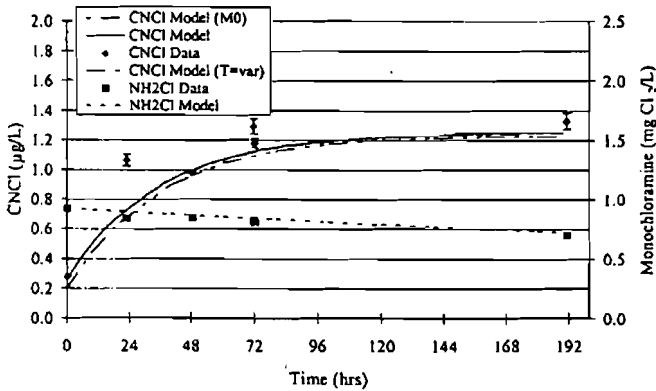


Figure 9: 1.4-log *Cryptosporidium* inactivation, initial total chlorine residual of 1.06 mg Cl₂/L, incubation temperature of 9°.

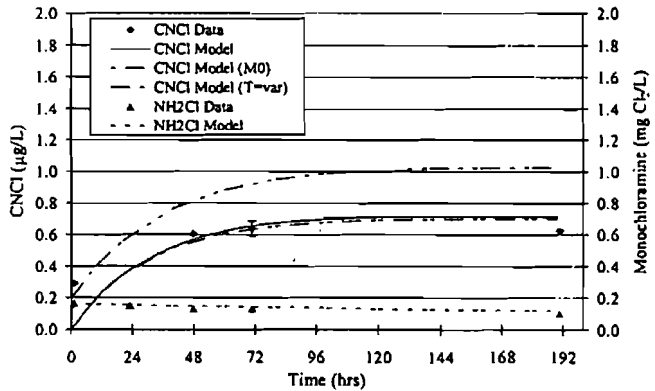


Figure 10: 3-log *Cryptosporidium* inactivation, initial total chlorine residual of 0.24 mg Cl₂/L, incubation temperature of 13.3°.

The form of Equation [20] is that expected for the product of two exponentially decaying compounds (CNCl and formaldehyde).

Isothermal equations were developed to model CNCl formation at each temperature and an equation was also developed to model CNCl over a range of temperatures (between 9°C and 13.3°C). Isothermal models do not include the Arrhenius temperature modification term, $\exp\left(-\frac{E}{RT}\right)$. An integrated form

of the equation which was used to evaluate the coefficients in Equation 20 is shown below.

$$[\text{CNCl}] = \frac{k^*}{\delta} [\text{NH}_2\text{Cl}]^\alpha (\text{Inact})^\beta \exp\left(-\frac{E}{RT}\right) \cdot (1 - \exp(-\delta t)) + \text{Const} \quad [21]$$

where Const is an integration constant. It is important to note that the level of inactivation is expressed in terms of *Cryptosporidium* inactivation. For *Giardia* inactivation experiments, the level of *Cryptosporidium* inactivation achieved during the same experiment must be used as the input value. For example, 0.19-log and 0.76-log *Cryptosporidium* inactivations represent 0.5-log *Giardia* inactivations at 7°C and 20°C, respectively.

The coefficients in Equation [21] were evaluated using Solver⁵. Detailed calculations have been previously presented by Romain (1996). The coefficients for these equations are shown in Table VII. The standard deviation, s , of the models as calculated using Equation [22] (Box *et al.*, 1978) are 0.13 µg/L and 0.15 µg/L for the temperatures of 9°C and 13.3°C, respectively.

$$s = \sqrt{\frac{S_{\min}}{n - k}} \quad [22]$$

where n is the number of measured data points, and k is the number of parameters being fitted.

An exponential value (α and β in Equations [20] and [21]) approaching zero indicates that monochloramine residual concentration and log *Cryptosporidium* inactivation have less weight in the CNCl formation equation. A positive exponent indicates a proportional relationship between CNCl formation and the variable, and a negative exponent indicates an inversely proportional relationship. Using the values for β at 13.3°C from Table VII

(-0.40) in Equations 20 and 21 would indicate that higher levels of *Cryptosporidium* inactivation result in lower CNCl concentrations. This is counterintuitive since CNCl formation has been hypothesized to result from an intermediate reaction with formaldehyde, an ozonation by-product (Smith and Singer, 1994). Formaldehyde formation has also been reported to increase with increasing ozone dose (Andrews, 1993, and Zhou *et al.*, 1992). An increase in formaldehyde production with an increase in ozone dose would imply an increase of CNCl since formaldehyde serves as an intermediate in CNCl production. Smith and Singer (1994) and Andrews (1993) reported increased CNCl formation with increased dose. Smith and Singer (1994) also report that there exist other intermediates which are involved in the CNCl formation reaction, including CH₂=NCl. Oxidation of an intermediate in the CNCl formation pathway of this specific water matrix may occur resulting in the inverse relationship between inactivation level and CNCl formation at 13.3°C. If an intermediate compound that is limiting the reaction is not in excess, CNCl formation may be dampened.

Table VII: Coefficients for Isothermal CNCl Formation Equations

Coefficient	9°C	13.3°C
k^*	0.027	0.045
α	-0.056	0.134
β	0.126	-0.40
δ	0.028	0.031
E	0 ^a	0 ^a
Const	0.26 ^b	0 ^c

^a Setting $E = 0$ results in $\exp\left(-\frac{E}{RT}\right) = 1$, thus

producing an isothermal model.

^b Const was set to 0.26 µg/L, the average $[\text{CNCl}]_0$ in Experiments 4 and 5.

^c Const was set equal to 0 µg/L, the average initial $[\text{CNCl}]$ concentration.

A positive β associated with the 9°C experiments does not contradict the negative value observed for the 13.3°C experiments. The inactivation levels in

the low temperature experiments do not cover the range of inactivations achieved for the high temperature experiments (0.5-log *Giardia* inactivation to 3.0-log *Cryptosporidium* inactivation for the 13.3°C experiments compared to 0.5-log *Giardia* inactivation to 1.4-log *Cryptosporidium* inactivation for the 13.3°C experiments). There was negligible difference in CNCl formation in the 13.3°C experiments when comparing 0.5-log *Giardia* inactivation to 1.2-log *Cryptosporidium* inactivation. The effect of the level of inactivation on CNCl formation at 9°C and 13.3°C is shown in Figures 5 and 6, respectively. An increase in CNCl formation is observed for an increasing inactivation level for the 9°C experiments, while a decrease in CNCl formation is observed for an increasing inactivation level for the 13.3°C experiments. It can be concluded from these results that increasing the level of inactivation at the high temperature will result in lower CNCl concentrations reaching the consumer. At low temperatures, an increase in inactivation would result in higher CNCl concentrations reaching the consumer.

Monochloramine concentration had a significant effect on CNCl formation at 13.3°C as illustrated by the an $\alpha = 0.14$. This is as expected. The exponent term on the 9°C experiments was not significant and had a negligible effect on CNCl formation. The effect of monochloramine residual on CNCl formation is shown in Figure [7] for 13.3°C temperature experiments.

The coefficient associated with the time term (δ in $\exp(-\delta t)$) is essentially the same for both temperatures (≈ 0.28). This indicates that residence time effects on CNCl formation are independent of temperature.

Equation [23] represents the general CNCl formation model incorporating a variable temperature term.

$$\frac{d[\text{CNCl}]}{dt} = 0.056[\text{NH}_2\text{Cl}]^{0.114}(\text{Inact})^{-0.012} \exp\left(-\frac{1560}{RT}\right) \exp(-0.027t) \quad [23]$$

Equation 23, developed using Solver, was observed to be highly unstable. The lack of stability was probably due to the relatively small range of temperatures (a 4.3° difference) used in the experiments. A larger range of temperatures may be

required to develop temperature dependent equations.

Single Constituent Cyanogen Chloride Model

A model was developed which could be used without a numerical water quality model framework. The single constituent model is shown below.

$$[\text{CNCl}] = \frac{k^*}{\delta} [\text{NH}_2\text{Cl}]_0^\alpha (\text{Inact})^\beta (1 - \exp(-\delta t)) + \text{Const} \quad [24]$$

where $[\text{NH}_2\text{Cl}]_0$ is the initial monochloramine residual concentration (mg Cl_2/L). Equation 24 is the integrated form of Equation 20 with $\exp\left(-\frac{E}{RT}\right) =$

1. Coefficients in Equation [24] were determined using the same methodology as the multi-constituent model. The single constituent models for incubation temperatures of 9°C and 13.3°C are shown in Equations [25] and [26], respectively.

$$[\text{CNCl}] = 0.95[\text{NH}_2\text{Cl}]_0^{-0.035}(\text{Inact})^{0.126} (1 - \exp(-0.028t)) + 0.26 \quad [25]$$

$$[\text{CNCl}] = 1.41[\text{NH}_2\text{Cl}]_0^{0.153}(\text{Inact})^{-0.38} (1 - \exp(-0.033t)) \quad [26]$$

Incorporation of the Arrhenius temperature modification term to develop a single constituent equation which could account for temperature variations was not sought following the problems with convergence in formulating the multi-constituent model. Equations [25] and [26], once developed for a specific water, can be utilized as a quick "back of envelope" calculation to determine potential CNCl concentrations reaching consumers if residence time is known. An individual can simply substitute the desired inactivation level, Inact, the monochloramine concentration entering the distribution system, $[\text{NH}_2\text{Cl}]_0$, and the residence time t from the treatment plant to the point of interest.

The accuracy of the single constituent model however may be questionable since it lacks the incorporation of pipe wall effects that could be accounted for by a calibrated numerical water quality model. Pipe wall effects on CNCl formation/decay were not identified at the time of this research but can be determined by conducting a

sampling program and subsequent numerical water quality model calibration. It is hypothesized by the authors that CNCI formation may be dampened due to the biodegradation of formaldehyde (an intermediate serving as a precursor in CNCI formation) by biological activity in the bulk fluid and the biofilm on pipe walls (Baribeau *et al.*, 1994, and Levi *et al.*, 1993). The reduction in the availability of formaldehyde may decrease CNCI formation, if formaldehyde is the limiting substance in the CNCI formation pathway. If CNCI formation is reduced by pipe wall biofilm, the stand-alone model will predict higher CNCI concentrations reaching consumers than actually occur. The single constituent model would therefore provide conservative estimates of CNCI concentrations reaching consumers.

Summary of Bulk Water Experiments

Two example plots of CNCI formation as predicted by the isothermal multi-constituent models (CNCI Model) using Equation 20 with $T = 0$, the single constituent model (CNCI Model (M0)) which was developed using only initial monochloramine concentrations using Equations [25] and [26], and the general form of the multi-constituent model (CNCI Model (T=Var)) are shown in Figures 9 and 10. The first-order monochloramine decay model is also plotted on each graph (NH₂Cl Model) to illustrate the correlation between the reduction in monochloramine concentration and the formation of CNCI.

As shown in Figures 9 and 10, CNCI formation is predicted accurately by both the isothermal model and the single constituent model. Monochloramine data is accurately modeled using the first order decay model. The general multi-constituent model, however, does not predict CNCI formation accurately for the high temperature experiments while producing an accurate model representing low temperature experimental data. The isothermal equations predicting CNCI concentration were compared to the observed CNCI concentrations in Figure 11. The points were normally distributed with an R^2 of 0.6. If the points in the upper left hand corner were eliminated, an R^2 of 0.86 would be calculated.

After reviewing all CNCI data and the equations which were used to model CNCI formation the following observations may be reported.

1. Monochloramine concentration had less of an effect on low temperature CNCI formation than on high temperature formation.
2. The low temperature isothermal model (9°C) predicts a proportional relationship between CNCI formation and inactivation level while the high temperature isothermal model (13.3°C) predicts an inverse relationship.

When all data are used to develop the general CNCI formation equation (Equation [23]) two numerical phenomena will occur: the proportional and inverse relationships with respect to CNCI formation and inactivation level will almost cancel each other out as shown in Equation [23] by the Inact exponent equal to -0.012 , the proportional effect of monochloramine concentration on CNCI formation will be dampened by the slightly inverse relationship predicted by the low temperature experimental data. Because of these phenomena, a general CNCI formation predictive equation would poorly model CNCI formation over many of the experimental conditions investigated in this research.

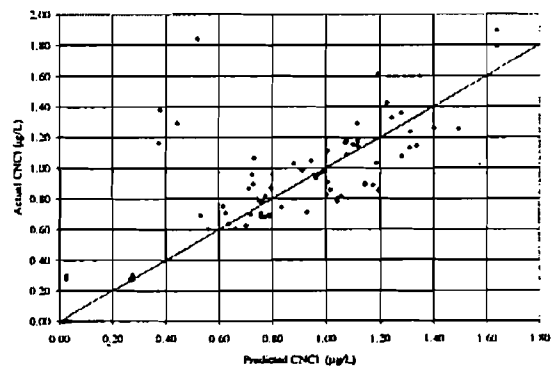


Figure 11: Comparison of predicted and actual mean cyanogen chloride (CNCI) concentrations for all experiments.

Conclusions

Experiments were conducted to develop DBP and disinfectant residual kinetic relationships with the aim of incorporating them into a multi-constituent water quality model. General conclusions are listed below:

Future Work

1. A inverse relationship was observed between log inactivation of *Cryptosporidium* and CNCl formation at 13.3°C, indicating that an increase in ozone dose to meet higher levels of *Cryptosporidium* inactivation will result in lower CNCl concentrations in the distribution system. It has been hypothesised that an intermediate in the CNCl formation pathway other than formaldehyde was oxidized in this specific water during ozonation, thus limiting CNCl formation.
2. The isothermal multi-constituent CNCl formation equations developed in this study are of a form that may be incorporated into a water quality model. Advection-dispersion equations including the CNCl formation and monochloramine decay terms at 9°C are shown in Equations 27 and 28, respectively.

$$\frac{\partial[\text{CNCl}]}{\partial t} + u \frac{\partial[\text{CNCl}]}{\partial x} + D \frac{\partial^2[\text{CNCl}]}{\partial x^2} + 0.027[\text{NH}_2\text{Cl}]^{-0.056}(\text{Inact})^{0.126} \exp(-0.028t) = 0 \quad [27]$$

$$\frac{\partial[\text{NH}_2\text{Cl}]}{\partial t} + u \frac{\partial[\text{NH}_2\text{Cl}]}{\partial x} + D \frac{\partial^2[\text{NH}_2\text{Cl}]}{\partial x^2} - 1.27 \times 10^{-3}[\text{NH}_2\text{Cl}] = 0 \quad [28]$$

Advection-dispersion equations including the CNCl formation and monochloramine decay terms at 13.3°C are shown in Equations [29] and [30], respectively.

$$\frac{\partial[\text{CNCl}]}{\partial t} + u \frac{\partial[\text{CNCl}]}{\partial x} + D \frac{\partial^2[\text{CNCl}]}{\partial x^2} + 0.045[\text{NH}_2\text{Cl}]^{0.134}(\text{Inact})^{-0.40} \exp(-0.031t) = 0 \quad [29]$$

$$\frac{\partial[\text{NH}_2\text{Cl}]}{\partial t} + u \frac{\partial[\text{NH}_2\text{Cl}]}{\partial x} + D \frac{\partial^2[\text{NH}_2\text{Cl}]}{\partial x^2} - 1.63 \times 10^{-3}[\text{NH}_2\text{Cl}] = 0 \quad [30]$$

3. Monochloramine decay was observed to be best described by first-order decay kinetics when compared to zero- and second-order decay kinetics.
4. An experimental protocol was developed which can be used to investigate additional constituents with the goal of developing a total water quality model that can accurately predict constituent propagation throughout a distribution system.

A natural extension to this research is to incorporate the advection-dispersion equations which include CNCl formation and monochloramine decay terms into a numerical multi-constituent water quality framework. The complete model could then be calibrated using field data. The calibrated model could then be used to determine hydraulic, and pipe wall effects on CNCl formation within a distribution system. In addition, the model could be expanded to include more variables which may have an effect on CNCl formation such as precursor material (organic carbon), concentrations of constituents such as formaldehyde and other DBPs, as well as water quality characteristics such as pH. Seasonal water quality variations in addition to waters obtained from other sources should also be investigated in terms of applied dose-inactivation and CNCl formation relationships.

Fundamental work is required to further investigate the factors which affect cyanogen chloride kinetics. It is unknown at what ratio of free chlorine to monochloramine that cyanogen chloride will form as opposed to decay.

Acknowledgments

The authors wish to acknowledge Hankin Atlas Ozone Systems Ltd. for the loan of an ozone generator and monitors, technical support, and providing partial financial support through a Natural Sciences and Engineering Research Council (NSERC) Industrial Scholarship. NSERC Canada is also acknowledged for providing direct financial assistance for this research. The authors acknowledge the Regional Municipality of Waterloo including the personnel at the Mannheim WTP, specifically Franklyn Smith and Brian Pett, who contributed both time and energy in support of this research. In addition, the authors acknowledge Professor Susan Andrews, University of Waterloo, Ontario, Canada, Department of Civil Engineering, for providing advice concerning the cyanogen chloride extraction method.

References

- American Public Health Association, American Water Works Association, and Water Environment Federation. 1995. Standard Methods for the Examination of Water and Wastewater. 19th Ed.

- APHA, AWWA, and WEF, Washington DC.
- Andrews, S.A. Organic By-Product Formation from the Ozonation and Chlorination of Aquatic Natural Organic Matter. Ph.D. Thesis. University of Alberta, Edmonton AB, Canada. 332 p., (1993).
- Axworthy, D.H. and Karney, B.W. Modelling Low Velocity/High Dispersion Flow in Water Distribution Systems. *J. Water Resour. Plng. and Mgmt*, 122(3), 218-221, (1996).
- Baribeau, H., Prevost, M. and LaFrance, P. Evolution of Oxidants and Disinfection By-products in Distribution Systems. *Proc. AWWA Ann. Conf.*, June 19-23, New York NY, 153-165, (1994).
- Box, G.E.P., Hunter, W.G. and Hunter, J.S. Statistics for Experimenters. An Introduction to Design, Data Analysis, and Model Building. John Wiley & Sons, Toronto, Canada. 653 p, (1978).
- Clark, R.M., Lykins, B.W., Block, J.C., Wymer, L.J. and Reasoner, D.J. Water Quality Changes in a Simulated Distribution System. *J. Water SRT-Aqua*, 43(6), 263-277, (1994).
- Croue, J.P., Koudjonou, B.K. and Legube, B. Parameters Affecting the Formation of Bromate Ion During Ozonation. *Ozone: Sci. & Engrg.*, 18(1), 1-18, (1996).
- Elshorbagy, W. and W. Lansey, W. Dynamic Modeling of Water Quality in Water Distribution Systems. Computers in the Water Industry. *Proc. AWWA Computer Conference*. April 10-13, Los Angeles CA, 457-465, (1994).
- Finch, G.R., Black, E.K., Gyurek, L.L. and Belosevic, M. Ozone Disinfection of Giardia and Cryptosporidium. American Water Works Association Research Foundation, Denver CO, (1994).
- Haas, C.N., Joffe, J., Anmangandla, U., Jacangelo, J.C. and Heath, M. Water Quality and Disinfection Kinetics. *J. Amer. Wat. Wks. Assoc.*, 88(3), 95-103, (1996).
- Jacangelo, J.G., Patania, N.L., Reagan, K.M., Aieta, E. M., Krasner, S.W. and McGuire, M.J. Ozonation: Assessing Its Role in the Formation and Control of Disinfection By-Products. *J. Amer. Wat. Wks. Assoc.*, 81(8), 74-84. (1989).
- Koch, B., Krasner, S.W., Scilimenti, M.J. and Schimpff, W.K. Predicting the Formation of DBPs by the Simulated Distribution System. *J. Amer. Wat. Wks. Assoc.*, 83(10), 62-70, (1991).
- Levi, Y., Jammes, C., Kienne, L. Hochereau, C. and Dumoutier, N. Stability of Disinfection By-products in Drinking Water Distribution System. Presented at the AWWA Water Quality Technology Conference, November 7-11, Miami FL, (1993).
- Lu, C., Biswas, P. and Clark, R.M. Simultaneous Transport of Substrates, Disinfectants and Micoorganisms in Water Pipes. *Water Research*, 29(3), 881-894, (1995).
- Lykins, Jr., B.W., Koffskey, W.E. and Patterson, K.S. Alternative Disinfectants for Drinking Water Treatment. *J. Environ. Engrg.*, 120, 745-758, (1994).
- Lyn, T.L. and Taylor, J.S. Modeling Compliance of Chlorine Residual and Disinfection By-products. Presented at the AWWA Water Quality Technology Conference, November 7-11, Miami FL, (1993).
- McKnight, A. and Reckhow, D.A. Reactions of Ozonation Byproducts with Chlorine and Chloramines. *Proc. AWWA Ann. Conf.*, Water Research, June 18-22, Vancouver BC, 399-409, 1992.
- Metropolitan Water District of Southern California (MWDSC). Analysis of Cyanogen Halides: A Micro-Liquid-Liquid Extraction. Draft. 16 p, (1994).
- Najm, I.N. and Krasner, S.W. Effects of Bromide and NOM on By-Product Formation. *J. Amer. Wat. Wks. Assoc.*, 87(1), 106-115, (1995).
- Oke, N.J., Smith, D.W. and Zhou, H. An Empirical Analysis of Ozone Decay Kinetics in Natural Waters. International Ozone Association Pan American Group Annual Conference, Sept. 8-11, Ottawa ON, 285-297, (1996).
- Romain, D.E. Modelling Impacts of Ozone Disinfection on Distribution System Water Quality. M.A.Sc. Thesis. University of Toronto, Toronto ON, Canada. 230 p, (1996).
- Schecter, D.S. and Singer, P.C. Formation of Aldehydes During Ozonation. *Ozone: Sci. & Engrg.*, 17(1), 53-69, (1994).
- Shukairy, H.M., Miltner, R.J. and Summers, R.S. Bromide's Effect on DBP Formation, Speciation and Control: Part 1, Ozonation. *J. Amer. Wat. Wks. Assoc.*, 86(6), 72-87, (1994).
- Singer, P.C., Harrington, G.W., Cowman, G.A., Smith,

- E., Schechter, D.S. and Harrington, L.J. Impact of Ozonation on the Formation of Chlorination and Chloramination By-products. Proc. AWWA Ann. Conf., Water Research, June 19-23, New York NY, 921-940, (1994).
- Smith, M.E. and Singer, P.C. Impact of Ozonation on Cyanogen Chloride Formation. AWWA Water Quality Technology Conference, November 6-10, San Francisco CA, 925-945, (1994).
- Summers, R.S., Hooper, S.M., Shukairy, H.M., Solarik, G. and Owen, D.. Assessing DBP Yield: Uniform Formation Conditions. J. Amer. Wat. Wks. Assoc., 88(6), 80-93, (1996).
- USEPA National Primary Drinking Water Regulations; Disinfectants and Disinfection Byproducts; Proposed Rule. Federal Register, 59(145), 38668, (1994).
- USEPA National Primary Drinking Water Regulations; Enhanced Surface Water Treatment Requirements; Proposed Rule. Federal Register, 59(145), 38832, (1994b).
- USEPA. EPANET Users Manual. Risk Reduction Engineering Laboratory, Cincinnati OH. 107 p, (1993).
- USEPA. Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources. Science and Technology Branch of the Office of Drinking Water, USEPA. Available from AWWA. 492 p, (1991).
- Vasconcelos, J.J., Rossman, L.A., Grayman, W.M., Boulos, P.F. and Clark, R.M. Kinetics of Chlorine Decay. J. Amer. Wat. Wks. Assoc., 89(7), 54-65, (1997).
- Weinberg, H.S., Glaze, W.H., Krasner, S.W. and Scilimenti, M.J. Formation and Removal of Aldehydes in Plants That Use Ozonation. J. Amer. Wat. Wks. Assoc., 85(5), 72-85, (1993).
- Williams, M.E. and Darby, J.L.. Measuring Ozone by Indigo Method: Interference of Suspended Material. J. Enviro. Engrg., 118(6), 988-993, (1992).
- Zhou, X., Reckhow, D.A. and Tobiason, J.E. Formation and Removal of Aldehydes in Drinking Water Treatment Processes. Proc. AWWA Water Quality and Technology Conference, Toronto, Ontario, Nov. 15-19, 1992, Toronto ON, 291-315, (1992).