**DEVELOPMENT OF CHLORINE DIOXIDE-RELATED
BY-PRODUCT MODELS FOR DRINKING WATER TREATMENT**

by

Caroline Korn

A thesis submitted in conformity with the requirements
for the degree of Master of Applied Science
Graduate Department of Civil Engineering
University of Toronto

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ABSTRACT

Statistically-designed factorial experiments were conducted using “synthetic” waters to examine the effects of various physical/chemical parameters on chlorine dioxide-related disinfection by-product formation. 2-level factorial experiments were then performed on 7 surface waters and a groundwater collected in Ontario to develop statistically-based model equations capable of predicting chlorine dioxide consumption, chlorite and chlorate formation when dosing with chlorine dioxide. These equations were developed in terms of pH, temperature, chlorine dioxide concentration, reaction time and water organic content. Interaction effects involving the aforementioned parameters were also included in the model equations, improving the accuracy of the predictive equations in fitting measured levels as evaluated through internal and external validations. Chlorine dioxide dose and water organic content were found to be key parameters in developing the predictive equations. Improved correlations between chlorine dioxide consumption, chlorite and chlorate formation with changes in UV_{254} were found to exist on a site- and parameter-specific basis.

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LIST OF ABBREVIATIONS AND SYMBOLS

<	=	less than
>	=	greater than
Δ	=	change in
$^{\circ}\text{C}$	=	degree Celsius
$\mu\text{g/L}$	=	microgram (10^{-6} grams) per litre
AOX	=	adsorbable organic halide
AWWA	=	American Water Works Association
BCAA	=	bromochloroacetic acid
Br^{-}	=	bromide ion
CaCO_3	=	calcium carbonate
CDBAA	=	chlorodibromoacetic acid
Cl^{-}	=	chloride
ClO_2	=	chlorine dioxide
ClO_2^{-}	=	chlorite
ClO_3^{-}	=	chlorate
cm	=	centimeter
Conc.	=	concentration
CT	=	disinfectant concentration * detention time
Ct_x	=	CT value for x% inactivation
D/DBP	=	disinfectant-disinfection by-product
DBAA	=	dibromoacetic acid
DBP	=	disinfection by-product
DCAA	=	dichloroacetic acid
DOC	=	dissolved organic carbon
DOM	=	dissolved organic matter
ESWTR	=	Enhanced Surface Water Treatment Rule
GWDR	=	Groundwater Disinfection Rule
H^{+}	=	hydrogen ion
H_2O	=	water
HAA	=	haloacetic acid
HAA_3	=	monochloroacetic-, dichloroacetic-, trichloroacetic-, monobromoacetic- and dibromoacetic acid
HAA_9	=	HAA_3 + tribromoacetic-, chlorodibromoacetic-, bromodichloroacetic- and bromochloroacetic acid
HOCl	=	hypochlorous acid
ICR	=	Information Collection Rule
IMAC	=	interim maximum acceptable concentration
MAC	=	maximum acceptable concentration
MCAA	=	monochloroacetic acid
MCL	=	maximum contaminant level
MCLG	=	maximum contaminant level goal
MRDL	=	maximum residual disinfectant level

MRDLG	=	maximum residual disinfectant level goal
mg/L	=	milligrams (10^{-3} grams) per litre
NH ₃	=	ammonia
nm	=	nanometer (10^{-9} metres)
NOM	=	natural organic matter
NPOC	=	non-purgeable organic carbon
OCl ⁻	=	hypochlorite ion
OH ⁻	=	hydroxyl radical
R ² -value	=	correlation coefficient
Rxn	=	reaction
SDS	=	simulated distribution system
SDWA	=	Safe Drinking Water Act
SS	=	sum of squares
SEE	=	standard error of the estimate
SSE	=	sum of squares of the errors
TCAA	=	trichloroacetic acid
THM	=	trihalomethane
THMFP	=	trihalomethane formation potential
TOC	=	total organic carbon
TOX	=	total organic halide
TOXFP	=	total organic halide formation potential
TTHM	=	total trihalomethane
TTHMFP	=	total trihalomethane formation potential
UV _x	=	ultra-violet absorbance measured at “x” nm
UVABS	=	ultra-violet absorbance
U.S. or US	=	United States
USEPA	=	United States Environmental Protection Agency
WTP	=	water treatment plant

INTRODUCTION

The use of chlorine as a primary disinfectant has been a common practice. However, it has been observed that during treatment, chlorine reacts with naturally-occurring organic material found in the waters to produce numerous hazardous by-products which are suspected carcinogens. Other disinfectants such as chlorine dioxide (ClO_2) may be considered as viable alternatives to using chlorine. Chlorine dioxide has been found to be effective in inactivating pathogenic organisms including protozoans like *Giardia lamblia* and *Cryptosporidium parvum* (Liyanage *et al.* 1997). Importantly, unlike chlorine, chlorine dioxide does not react with humic substances to form THMs (Lafrance *et al.*, 1993; Lykins and Griesse, 1986; Muttamara *et al.*, 1995; Werdehoff and Singer, 1987; Jun *et al.*, 1996). While employing chlorine dioxide as a disinfectant presents many advantages, concern over the formation of chlorine dioxide-related by-products including chlorite (ClO_2^-) and chlorate (ClO_3^-) do exist. Chlorine dioxide, chlorite and chlorate can lead to hemolytic anemia at low level of exposures while higher levels of exposure can result in an increase in methemoglobin (Gallagher *et al.*, 1994). Consequently, as for most disinfectants, the challenge in disinfection consists of providing adequate protection against pathogenic microbes while producing disinfection by-products (DBPs) which are within regulated guidelines and within levels which are not harmful to human health.

The tradeoff between achieving the necessary disinfection level and the formation of DBPs encourages the development and use of forecasting models (Harrington *et al.*, 1992). While previous research into the development of predictive

by-product formation models for chlorine has been conducted (Amy *et al.*, 1987a; Morrow and Minear, 1987; Hutton and Chung, 1992; Lyn and Taylor, 1993; Hofmann, 1996; Amy *et al.*, 1987b; Adin *et al.*, 1991), such model equations are lacking in the literature for chlorine dioxide-related by-product formation in terms of significant water quality and treatment factors.

Consequently, in view of proposed regulatory limits set in the United States for DBPs such as trihalomethanes, haloacetic acids and chlorite ion (Fed. Reg., 1994) as well as likely future limits to be set for chlorate ion (Pontius, 1991; Health Canada, 1996), the development of equations to predict DBP formation from chlorine dioxide treatment will become increasingly useful. Furthermore, the fact that a maximum residual disinfectant level (MRDL) has been proposed for chlorine dioxide (Fed. Reg., 1994) may also require treatment plants to optimize their systems to ensure a well-operated facility. As such, producing equations capable of predicting chlorine dioxide consumption as well as chlorite and chlorate formation in terms of physical-chemical variables which are related to water quality and chlorine dioxide disinfection treatment (i.e. temperature, pH, chlorine dioxide dose, contact time, organic carbon content) would be beneficial to utility plants in determining the appropriate disinfection strategy. Modeling efforts involving the incorporation of factor interactions via conducting factorial experiments on a number of different water sources has also not been well documented in the literature. It is hoped that this type of design will provide for more accurate predictive DBP formation models when applying chlorine dioxide.

CHAPTER 2

LITERATURE REVIEW

2.1 Regulations

The following section reports on the United States (U.S.) regulations pertaining to the Disinfectant-Disinfection By-Product (D/DBP) rule, briefly on the Surface Water Treatment Rule (SWTR) and on important considerations in regards to the Groundwater Disinfection Rule (GWDR) as well as Canadian regulations which relate to allowable DBP levels. Conflicts will likely surface from the fact that the SWTR inactivation requirements and the extent of DBP formation are dependent on the same variables including pH, temperature, contact time, pretreatment processes and disinfectant type and dose (Dyksen *et al.*, 1988).

2.1.1 U.S. Disinfection By-Product Regulations

A regulatory negotiation ("reg-neg") process originated in 1992 and was concluded in 1994 to develop an Information Collection Rule (ICR), an "enhanced" SWTR as well as a two-phase (Stage 1 and Stage 2) Disinfectant-Disinfection By-Product (D/DBP) rule for disinfectants and their by-products (Fed. Reg., 1994). While the goal of the ICR consists of gathering information which is essential to the development of the ESWTR and D/DBP Rule, the ESWTR would be an expansion of the current SWTR to comprise *Cryptosporidium* (Pontius, 1995).

The proposed D/DBP rule prescribes to community waters systems (CWSs) and nontransient noncommunity water systems (NTNCWSs) where a disinfectant (for either primary or secondary treatment) has been applied at any time or place during the

treatment of drinking water (Fed. Reg., 1994). The rule not only pertains to organic compounds such as trihalomethanes or haloacetic acids but to substances such as chlorite whereby, a maximum contaminant level goal (MCLG) of 0.08 mg/L and a maximum contaminant level (MCL) of 1.0 mg/L have been set for this inorganic byproduct (Table 2.1). The anticipated compliance of chlorite to the rule in public water systems would necessitate three monthly samples where the monthly average must be less than or equal to the MCL (Fed. Reg., 1994). The sampling locations would involve one near the first customer, one representing the average residence time (i.e. in the middle of the distribution system) and one portraying the maximum residence time in the distribution system (i.e. near the end of the distribution system). Although no present regulations have been set for chlorate, due to its health risks, it is anticipated that such guidelines may be introduced in the future.

The proposed D/DBP rule (Fed. Reg., 1994) also regulates against disinfectant residuals (Table 2.2). The MRDLs were set by the reg-neg committee based on a requirement for a sufficient disinfectant residual concentration in the distribution system and on the need to protect human health (Fed. Reg., 1994). Monitoring chlorine dioxide concentrations to check for compliance would be required by CWSs and noncommunity facilities which employ the disinfectant for oxidation or disinfection purposes. Its routine monitoring requirements would involve daily samples taken at the entrance of the distribution system and, under no circumstance, should the MRDL be exceeded for short-term treatment. Depending on the size of the treatment plant and the raw water source, the effective dates for compliance to the rule will be staggered, varying between 18 to 60 months from promulgation of the final rule.

Table 2.1 DBP Standards Proposed in D/DBP Rule (Fed. Reg., 1994)^a

Contaminant	Maximum Contaminant Level Goal (MCLG) (mg/L)	Maximum Contaminant Level (MCL) (mg/L)
Chlorite	0.08 (Stage 1)	1.0 (Stage 1)
Chlorate	NS	NS
Total Trihalomethanes (TTHMs)	NS	0.080 (Stage 1)
	NS	0.040 (Stage 2)
Total Haloacetic Acids (HAA ₅)	NS	0.060 (Stage 1)
	NS	0.030 (Stage 2)
Bromate	0.00 (Stage 1)	0.010 (Stage 1)

Note: NS = Not Specified

TTHMs = Sum of chloroform, bromoform, bromodichloromethane and dibromochloromethane concentrations.

HAA₅ = Sum of mono-, di- and trichloroacetic acids and mono- and dibromoacetic acids.

^a Stage 2 regulations are proposed for systems treating surface or groundwaters directly influenced by surface water (serving communities of over 10 000 people) and are to be based upon results obtained from the Information Collection Rule (Fed. Reg., 1994).

Table 2.2 Disinfectant Standards Proposed in D/DBP Rule (Fed. Reg., 1994)

Disinfectant	Maximum Residual Disinfectant Level Goal (MRDLG) (mg/L)	Maximum Residual Disinfectant Level ^a (MRDL) (mg/L)
Chlorine Dioxide	0.3 (as ClO ₂)	0.8 (as ClO ₂)
Chlorine ^a	4.0 (as Cl ₂)	4.0 (as Cl ₂)
Chloramines ^a	4.0 (as Cl ₂)	4.0 (as Cl ₂)

^a Chlorine and chloramine levels could be exceeded for a short-time period to meet water quality problems. Compliance is based on annual average of monthly averages.

Aside from regulated levels, some water treatment facilities will also have to comply with rules concerning the removal of organic matter (DBP precursors) in the source water which can react with disinfectant residuals to produce DBPs. Systems which are capable of removing a specific Total Organic Carbon (TOC) percentage will be in compliance with the disinfection by-product precursor technique requirement (Fed. Reg., 1994). Such requirements will be necessary for plants which operate conventional processes (i.e. sedimentation, coagulation, flocculation and filtration) and those with softening operations (Fed. Reg., 1994). It goes on to report that treatment plants which treat groundwater not affected by surface waters, or utilize direct filtration, slow sand filtration or diatomaceous earth filters would not have to adhere to such DBP precursor rules. The required TOC % removals using enhance coagulation or softening would be depending on the TOC and alkalinity conditions of the source water (Table 2.3). Certain systems may not have to use enhanced coagulation or softening if they satisfy any one of a number of criteria (Table 2.3). It is specified that systems utilizing chlorine dioxide as a disinfectant, where its generation yield is 95% and the excess chlorine produced is less than 5%, would have to adhere to the TOC removal regulations before any other residual disinfectant is added. It is thought that complying to such chlorine dioxide generating requirements will enable the minimization of chlorate and chlorite production and reduce the availability of free chlorine to react with organics before TOC removal and limit the formation of halogenated organic DBPs (Fed. Reg., 1994).

Based on past regulation trends, it can be anticipated that regulatory DBP levels will become more stringent with time. Consequently, water utilities should remain

Table 2.3 Required % Removal by Enhanced Coagulation for Subpart H Treatment Plants^c Using Conventional Treatment Systems (Fed. Reg., 1994)^b

TOC of Source Water (mg/L)	Alkalinity of Source Water (mg as CaCO ₃ /L)		
	0-60	> 60-120	> 120 ^a
> 2.0-4.0	40.0	30.0	20.0
> 4.0-8.0	45.0	35.0	25.0
> 8.0	50.0	40.0	30.0

^a Systems employing softening must adhere to requirements in given column.

^b Systems which conform to at least one of the following criteria would not have to provide enhanced coagulation:

- Treated water TOC prior to application of continuous disinfection < 2.0 mg/L.
- Source water TOC before any treatment < 4.0 mg/L, alkalinity > 60 mg/L, TTHM < 0.040 mg/L and HAA₅ < 0.030 mg/L.
- Annual TTHM average < 0.040 mg/L and annual HAA₅ average < 0.030 mg/L when chlorine is the disinfectant.
- Systems employing softening (but not using anion exchange) and can remove > 10 mg/L of magnesium hardness (as CaCO₃)

^c Subpart H treatment plant is a plant which treats surface waters and groundwaters under the full or partial influence of surface water.

informed as to legislation developments in order to ensure that future standards will be met by current treatment conditions or that reoptimization of the utility system or implementation of new treatment technologies which may be needed are minimal, economical and feasible.

2.1.2 Chlorine Dioxide Inactivation Potential and Surface Water Treatment Rule

The efficiency of chlorine dioxide in inactivating various waterborne pathogenic microorganisms is of prime importance with respect to its application as a disinfectant in meeting regulatory inactivation levels. The order of increasing resistance of pathogens to chlorine dioxide disinfection is found to be: Bacteria, viruses and protozoan cysts (Sobsey, 1989). Fortunately, as reported by Gates and Harrington (1992), chlorine dioxide is effective in killing viruses, bacteria as well as protozoan cysts (i.e. *Giardia*). It has been found to possess equivalent or superior bacterial (Huang *et al.*, 1997b) and viral (Huang *et al.*, 1997a) inactivation efficiencies to liquid chlorine. Consequently, to attain the same bactericidal effect achieved by liquid chlorine, chlorine dioxide would require a smaller dose and/or a shorter contact time.

In the United States, the Environmental Protection Agency (EPA) promulgated the Surface Water Treatment Rule (SWTR) in 1989. It requires certain microbial inactivation requirements from drinking water treatment facilities whose water sources are either surface waters or groundwaters which are directly influenced by surface waters (USEPA., 1991). It is stipulated that treatment facilities must attain a minimum of 99.9% (3-log) removal and/or inactivation of *Giardia* cysts and a 99.99% (4-log) inactivation and/or removal of enteric viruses. The necessary performance levels are

dependent on the source water characteristics and the site-specific conditions whereby filtration in combination with disinfection or disinfection alone can be employed to meet the required inactivation levels (USEPA, 1991). “CT” values, which consists of multiplying the residual disinfectant concentration (C in mg/L) and the contact time (T in minutes), are used to associate the microbial inactivation required to the given treatment conditions.

Chlorine dioxide efficiency has been found to increase with increasing pH over the pH range encountered in water treatment (Finch *et al.*, 1997; Safe Drinking Water Committee, 1980; Hoff and Geldreich, 1981; Varma *et al.*, 1985; Cronier *et al.*, 1978). Thus, chlorine dioxide would be a viable disinfectant to treat natural waters having a higher pH and particularly for the inactivation of *Cryptosporidium* since ozone and free chlorine are less effective at higher pH levels (Finch *et al.*, 1997). CT values for the *Giardia* cysts and virus inactivation by chlorine dioxide are reported in Table 2.4. Although the values are reported over the 6 to 9 pH range, since there were few data available at other pH levels, the stated CT values for *Giardia* were actually calculated and based on data mostly obtained at pH 7 (USEPA, 1991). The reader is directed to consult the USEPA Guidance Manual (USEPA, 1991) for additional details on how the CT₉₉ and CT_{99.9} *Giardia* and CT virus values were calculated.

2.1.3 Groundwater Disinfection Rule

Groundwaters which are found to not be contaminated with surface water would be regulated under the Groundwater Disinfection Rule (GWDR). The GWDR for groundwater systems is analogous to the SWTR where its development conforms to the

Table 2.4 CT Values for the Inactivation of *Giardia* cysts and Viruses by Chlorine Dioxide For a pH Range between 6 and 9 (USEPA, 1991)

Pathogen	Log Inactivation	Temperature (°C)					
		≤ 1	5	10	15	20	25
<i>Giardia</i> cysts	0.5	10	4.3	4	3.2	2.5	2
	1.0	21	8.7	7.7	6.3	5	3.7
	1.5	32	13	12	10	7.5	5.5
	2.0	42	17	15	13	10	7.3
	2.5	52	22	19	16	13	9
	3.0	63	26	23	19	15	11
Viruses	2.0	8.4	5.6	4.2	2.8	2.1	1.4
	3.0	25.6	17.1	12.8	8.6	6.4	4.3
	4.0	50.1	33.4	25.1	16.7	12.5	8.4

Safe Drinking Water Act (SDWA) requirements to provide safe groundwater for human consumption (Macler, 1996). The GWDR is concerned with illnesses which are transmitted by pathogens which may be found in groundwaters: Different types of viruses (such as hepatitis A agent, rotavirus, Norwalk and Norwalklike agents, coxsackieviruses and echovirus) and a number of bacteria (*Legionella*, *Salmonella*, *Shigella* and *Campylobacter*) (Macler, 1996). The GWDR draft as reported by Grubbs and Pontius (1992), suggests that the utilities which employ a chemical disinfectant would need to provide at least a 0.2 mg/L residual disinfectant concentration in waters at the distribution system entrance. Although certain utilities would treat groundwaters which show susceptibility to contamination, they may escape having to provide a disinfectant if “natural” disinfection of viruses and bacteria is revealed to be satisfactory (Macler, 1996). The reader is advised to consult the GWDR draft as reported by Grubbs and Pontius (1992) for greater details concerning the GWDR.

2.1.4 Canadian Regulations

In Canada, although there are maximum acceptable concentration (MAC), interim maximum acceptable concentration (IMAC) and aesthetic objectives (AO), there are no regulations which are comparable to the SWTR and the D/DBP rule which are found in the United States. In addition, even though one out of three Canadians depends on groundwater supplies, especially in the eastern provinces (Carter Decker and Long, 1992), there is no Canadian equivalent to the GWDR.

In 1986, a Federal-Provincial Subcommittee on Drinking Water was initiated with the purpose of reviewing and revising the guidelines on a continuous basis (Carter

Decker and Long, 1992). The guidelines and recommendations which are proposed are applicable to all publicly and privately operated drinking water supplies. However, they cannot be viewed as legally-enforceable regulations unless promulgated by the appropriate provincial, territorial or federal agency (Health Canada, 1996). While drinking water is regulated by each individual province and territory, the separate provinces have taken on these guidelines as a base for their own regulations (Carter and Decker and Long, 1992). The authors report that only Alberta and Québec have promulgated legally-enforceable standards.

While there is a set MAC for TTHMs at 100 µg/L (based on a yearly average of quarterly sampling), there are no regulations pertaining to chlorine dioxide or its chlorate and chlorite by-products (Health Canada, 1996). Carter Decker and Long (1992) have reported that, in the future, the MAC for TTHMs may possibly be further lowered to 50 µg/L. Chlorine dioxide and other DBPs including chlorite, chlorate, HAAs and bromate are under (or scheduled for) review for possible future regulations (Health Canada, 1996). The timeframe of the above revision process is unknown.

2.2 Chlorine Dioxide in Water Treatment

2.2.1 Chlorine Dioxide Generation

High chlorine dioxide generator efficiencies are important in order to reduce the formation of inorganic by-products and receive applicable CT inactivation credits. The reader is advised to consult the text by White (1992) and journal article written by Aieta *et al.* (1984) for detailed information regarding chlorine dioxide generation methods and chemistry.

In brief, chlorine dioxide is often generated through the reaction of aqueous sodium chlorite and chlorine (Aieta *et al.*, 1984). In its US survey, Dietrich *et al.* (1992) found that, for all of the 32 treatment utilities which responded, the generation of chlorine dioxide consisted of reacting aqueous chlorite (88.2% of the facilities reported using sodium chlorite in the generation process) with chlorine gas or hypochlorous acid. Only a small proportion of the chlorine dioxide production consists of electrochemical generation methods or systems employing sodium chlorite with lactic acid reactions (Gordon and Bubnis, 1995). Sodium chlorite-acid generation methods (such as using sulfuric or hydrochloric acid as the chlorite activator) have been prevalent in producing chlorine dioxide for bench-scale studies in laboratories since the amount of chlorine produced in the chlorine dioxide solution from either acid system is negligible (White, 1992). A number of different chlorine dioxide generation techniques involving the use of sodium chlorite are reported in Table 2.5. The reaction conditions of the chlorine dioxide generator, which have mostly been set by the design of the generator structure, will largely govern to which extent chlorine dioxide, chlorite, chlorate and chlorine are to be found in the product stream of the generator (Aieta *et al.*, 1984). Gordon and Bubnis (1995) report that conditions of high reactant concentrations (no specific levels given) are desirable since the intermediate product (Cl_2O_2) will form quickly and produce chlorine dioxide as the main product (Table 2.5, eqns. 3 and 4). As well, chlorate ion formation would be expected to be minimized by reducing the amount of free hypochlorous acid which is present (Gordon *et al.*, 1990).

Table 2.5 Chlorine Dioxide Generation Methods

Chlorine Dioxide Generation System	Reaction	Chlorine Dioxide Yield	Source
Sodium Chlorite-Gas Chlorine	(1) $2\text{NaClO}_2 + \text{Cl}_{2(g)} \rightarrow 2\text{ClO}_{2(g)} + 2\text{NaCl}$ (2) $\text{Cl}_2 + \text{ClO}_2^- \rightarrow [\text{Cl}_2\text{O}_2] + \text{Cl}^-$ (3) ^a $2[\text{Cl}_2\text{O}_2] \rightarrow 2\text{ClO}_2 + \text{Cl}_2$ Or $[\text{Cl}_2\text{O}_2] + \text{ClO}_2^- \rightarrow 2\text{ClO}_2 + \text{Cl}^-$ (4) ^a $[\text{Cl}_2\text{O}_2] + \text{H}_2\text{O} \rightarrow \text{ClO}_3^- + \text{Cl}^- + 2\text{H}^+$ $[\text{Cl}_2\text{O}_2] + \text{HOCl} \rightarrow \text{ClO}_3^- + \text{Cl}_2 + \text{H}^+$	> 95 % (Aieta and Berg, 1986)	Gordon and Bubnis (1995)
Sodium Chlorite-Aqueous Chlorine	(5) $2\text{NaClO}_2 + \text{Cl}_2 \rightarrow 2\text{ClO}_2 + 2\text{NaCl}$ competing reaction: (6) $\text{NaClO}_2 + \text{Cl}_2 + \text{OH}^- \rightarrow \text{NaClO}_3 + \text{HCl} + \text{Cl}^-$ (7) ^b $2\text{ClO}_2 + \text{HOCl} + \text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 2\text{H}^+ + \text{HCl}$	> 90% for a pH adjusted system > 95% in presence of excess chlorine	Aieta & Berg (1986)
Sodium Chlorite-Hydrochloric Acid	(8) $5\text{NaClO}_2 + 5\text{HCl} \rightarrow 4\text{ClO}_2 + 5\text{NaCl} + \text{HCl} + 2\text{H}_2\text{O}$	≈ 75 %	White (1992)
Sodium Chlorite with Sulfuric Acid	(9) $4\text{NaClO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{Na}_2\text{SO}_4 + 2\text{ClO}_2 + \text{HCl} + \text{HClO}_3 + \text{H}_2\text{O}$ Or $10\text{NaClO}_2 + 3\text{H}_2\text{SO}_4 \rightarrow 8\text{ClO}_2 + 5\text{Na}_2\text{SO}_4 + 2\text{HCl} + 4\text{H}_2\text{O}$	50-55 %	White (1992)

^a The reactions which occur are dependent on the initial reactant concentrations.

^b A side reaction which can result when acceptable yields were attained by providing over 200-300% more chlorine than would be needed by eqn (5).

In a sodium chlorite-chlorine generation process where all the oxidized chlorine compounds can be measured and evaluated in the product stream of the generator, yield can be defined as the ratio between the concentration of chlorine dioxide produced to the theoretical maximum (Aieta *et al.*, 1984). Another point of concern involves the excess chlorine produced from the chlorine dioxide generation process which could lead to the subsequent formation of THMs or reactions with chlorine dioxide or chlorite ion (Gallagher *et al.*, 1994). Expressions to calculate % chlorine dioxide yield and % excess chlorine are provided in Appendix A (equations A.1 and A.2 respectively). Less than 5% excess chlorine should result in the product stream of a well-designed chlorine dioxide generator (Aieta *et al.*, 1984). An average generator efficiency found in the Dietrich *et al.* (1992) study was 88.8% (std = 13.1%) where only 20% of the 32 facilities which responded said they determined their generator efficiency on a daily basis.

The issue of formed contaminants during the chlorine dioxide generation process is that chlorite and chlorate may result in the water treatment effluent. Versteegh *et al.* (1993) found that storage in reservoirs, ozonation, coagulation/rapid filtration and GAC-filtration did not decrease chlorate or chlorite concentrations. Hence, the presence of chlorate and chlorite in the chlorine dioxide generator effluent may lead to these species having important concentrations in the treated water (Hoehn, 1993). Although a correctly-functioning generator can yield 1 to 2% chlorate ion concentrations (Gordon *et al.*, 1990), Gallagher *et al.* (1994) report that improper generator operations can account for nearly 35% of the chlorate concentration in the

distribution system. Consequently, regular monitoring of chlorate concentration and generator efficiency could assist water treatment utilities in determining the true yield of their generators (Dietrich *et al.*, 1992).

Monitoring for and maintaining a high generator efficiency are also significant measures for treatment plants which treat surface waters as well as groundwaters which are under the direct influence of surface waters. Such utilities could obtain CT credits for chlorine dioxide oxidation prior to enhanced coagulation or softening processes if each chlorine dioxide generator is operating at a percent conversion efficiency of 95% or greater and the % excess chlorine is less than 5% (Fed. Reg., 1994). Also, if the resulting efficiency were to be greater than 90% but less than 95% (and the % excess chlorine was greater than 5% but less than 10%) then the facility may accept the CT credit on that day provided that immediate steps be taken to reestablish a 95% or more efficiency and % excess chlorine to be less than or equal to 5% on that day (Fed. Reg., 1994). A treatment utility whose % yield and excess chlorine were less than 90% and greater than 10% respectively could not benefit from a CT credit until subsequent measurements showed the required proper chlorine dioxide yield and excess chlorine.

Hence, research into the effects of varying amounts of chlorine dioxide-related contaminants (i.e. chlorine, chlorate and chlorite) on the formation of DBPs could be useful in evaluating the influences of different chlorine dioxide yield efficiencies.

2.3 Chlorine Dioxide Chemistry and Disinfection By-Products

This section pertains to the chemistry of chlorine dioxide with organic and inorganic materials as well as the formation of DBPs. While a number of organic

DBPs may result from chlorine dioxide treatment, the major by-products of chlorine dioxide have been identified as chlorite, chlorate, chloride as well as chlorine if excess chlorine was used in the preparation of chlorine dioxide (Rice and Gomez-Taylor, 1986).

2.3.1 Chlorine Dioxide Disproportionation Chemistry

Chlorine dioxide, a compound which is part of the oxochlorine family (Aieta and Berg, 1986), is found to be quite stable in acidic as well as neutral mixtures (Rosenblatt, 1978). The reactive nature of chlorine dioxide essentially remains unchanged in the pH range of 2 to 10.5 (Hoigné and Bader, 1994). The reduction of chlorine dioxide (ClO_2) can occur in two stages as shown in eqns. 2.1 and 2.2 (Werdehoff and Singer, 1987). The writers report that while both steps can take place at pH levels less than 2, at pH 7, only the reduction of chlorine dioxide (requiring one valence change) leading to the formation of chlorite is anticipated (eqn. 2.1).

In solutions where the pH is greater than 9 or 10, chlorine dioxide will disproportionate to yield chlorate and chlorite ions as shown in eqn. 2.3 (Rosenblatt, 1978). It is reported by Hazen and Sawyer (1992) that this reaction is not expected to result in considerable yields at pH levels below 8. Gallagher *et al.* (1994) report that in alkaline solutions (pH greater than 9), the rate of formation of chlorate and chlorite will increase with increasing chlorine dioxide concentrations. As noted by Hoehn (1993), applying chlorine dioxide just prior to the addition of lime may result in higher-than-usual chlorate ions concentrations. Also, the disproportionation of chlorine

dioxide may be an important issue in the treatment of groundwaters and surface waters where more efficient microbiological inactivation occurs at greater pH levels (as earlier discussed in Section 2.1.2).

Site-specific characteristics such as the chemical properties of the raw water, nature and concentrations of dissolved organic material and reduced inorganic compounds (such as sulfides, iron and manganese) could influence the persistence of chlorine dioxide residuals by governing whether the chlorine dioxide demand rates will either be fast or slow (Hoehn, 1993). Also, chlorine dioxide-treated water exposed to light can photodecompose to yield chlorate and chlorite ion (Bolyard *et al.*, 1993).

The proportion of consumed chlorine dioxide converted to various inorganic by-products observed by a number of researchers are reported in Table 2.6. In all cases, chlorite was found to be the major inorganic by-product produced, accounting between 40 to 70% of the converted chlorine dioxide. Reported chlorine dioxide conversion percentages to chlorate varied from as low as 5% to 25%.

2.3.2 General Chlorine Dioxide Chemistry with Inorganics Found in Water

Chlorine dioxide can react with a number of inorganic compounds present in surface and groundwaters. It is important to identify such compounds since these substances could exert a chlorine dioxide demand whereby possibly reducing the amount of chlorine dioxide available for disinfection purposes.

Unlike for chlorine, chlorine dioxide is not observed to react with ammonia to form chloramines (Stevens, 1982; Rice and Gomez-Taylor, 1986; Narkis *et al.*, 1995).

Table 2.6 Percentages of Chlorine Dioxide Converted to Various Chlorinated Inorganic By-Products

Experimental Conditions	% as Chlorate	% as Chlorite	% as Chlorine	% as Chloride	Reference
1.5 mg ClO ₂ /L added to Ohio River water which was coagulated, settled and filtered via a dual-media system (pH 7.1 and contact time of 42 hours).	25	50	0	25	Stevens (1982) ^a
0.2 - 1.0 mg ClO ₂ /L added to raw water from the National Water Carrier of Israel (1- 48 hour contact times).	NS	60-65	NS	NS	Limoni <i>et al.</i> (1984)
1.0 mg ClO ₂ /L added to untreated Rinconada water of Santa Clara Valley, CA (pH of 8.28, contact times up to 48 hours after dosing).	Below detection limit	70	ND	ND	Aieta <i>et al.</i> (1984) ^a
1.0 ppm ClO ₂ added to raw water from Lake Kinneret, Israel (temp. of 25°C, contact times of 0.5 to 4.0 hours).	NS	60	NS	NS	Rav-Acha <i>et al.</i> (1985)
1.0-4.0 mg ClO ₂ /L added to Lake Drummond fulvic acids, diluted Northwest River water, diluted finished drinking water, VA (1 to 11 mg/L of TOC, pH 7, contact times up to 100 hrs).	NS	70	NS	NS	Werdehoff and Singer (1987)
0.5-2.0 mg ClO ₂ /L added to Mannheim treatment plant clarified water, Waterloo, ON (TOC of 5.5 mg/L, pH of 7.3 - 8.9, temp. of 1°C to 25°C, contact times of 15 and 60 minutes).	5-10	40-70	NS	NS	Andrews <i>et al.</i> (1997)

Note: NS = Not specified, ND = Not detected

^a Detection limit of 0.045 mg/L for chlorine dioxide, 0.0255 mg/L for chlorate and 0.016 mg/L for chlorine and chlorite.

Further, chlorine dioxide treatment should typically not result in the conversion of bromide to hypobromite ion or in the production of bromoform or bromate (Hoigné and Bader, 1994; Cooper *et al.* 1985; Rav-Acha and Choshen, 1987; Carnimeo *et al.*, 1995). It has been reported by Cooper *et al.* (1985) that the oxidation of bromide to hypobromite ion and hypobromous acid are not thermodynamically favorable (i.e. electrode potential (E) = -0.12 volts). However, Rice and Gomez-Taylor (1986) have reported that a solution containing a high chlorine dioxide concentration of 1.5×10^{-4} M exposed to intense sunlight and in the presence of 1×10^{-4} M bromide ions, could oxidize bromide to bromate and hypobromite.

Chlorine dioxide can oxidize iodide (Hoigné and Bader, 1994; Safe Drinking Water Committee, 1980) in the 5-10 pH range. Hoigné and Bader (1994) report that micromolar concentrations of chlorine dioxide can oxidize 0.03 mM of iodide (pH 8) in a few hundred seconds. The oxidation of iron (Fe^{2+}) and manganese (Mn^{2+}) to Fe^{3+} and Mn^{4+} respectively as well as the oxidation of nitrite to nitrate by chlorine dioxide have also been reported (Hoigné and Bader, 1994; Rice and Gomez-Taylor, 1986). As reported by Hoigné and Bader (1994), the fact that 1 mole of nitrite (1 mM concentration at pH 6) can reduce 2.1 moles of chlorine dioxide should not be overlooked in certain treatment systems since the presence of nitrite can be anticipated from a number of processes or transport in water treatment (i.e. microbiological denitrification). The same authors discuss that the extent to which iron (II) and manganese (II) ions can consume chlorine dioxide in drinking water conditions (i.e. pH 8) is difficult to assess since dissolved organic matter can mask part of the manganese

while the presence oxygen can interfere with the chlorine dioxide oxidation of iron by producing iron(III)-oxide.

2.3.3 Organic DBPs

As for inorganic compounds, organic substances which are also present in source waters can exert a chlorine dioxide demand thus, decreasing the disinfectant potential of chlorine dioxide (Katz *et al.*, 1994). Since chlorine dioxide reacts primarily as an oxidant, few chlorinated organic compounds, either volatile or non-volatile, are expected to be produced (Aieta and Berg, 1986; Narkis *et al.*, 1995). Thus, the main chlorine dioxide DBPs consist of oxidation products as opposed to chlorination ones (Rav-Acha, 1984; Rice and Gomez-Taylor, 1986; Safe Drinking Water Committee, 1980). A summary of the general end-products which can result from reactions between chlorine dioxide and various organic compounds is provided in Table 2.7. The intention of this section is not to discuss all possible chlorine dioxide reactions with different organic substances and their respective DBPs (if interested, the reader is directed to the various literature sources listed in Table 2.7). The main focus of the following discussion will be on halogenated DBP formation, most especially those which are regulated under the D/DBP Rule (Fed. Reg., 1994).

An advantage in utilizing chlorine dioxide as a disinfectant is that, contrary to chlorination, the formation of THMs is not anticipated from chlorine dioxide-organic matter reactions (Lafrance *et al.*, 1993; Lykins and Griese, 1986; Muttamara *et al.* (1995); Werdehoff and Singer, 1987; Jun *et al.*, 1996). For instance, at the St-Rose plant in Laval (Québec), Lafrance *et al.* (1993) report that, since chlorine dioxide has

Table 2.7 General Organic End-Products Resulting from Reactions between Chlorine Dioxide and Various Compounds

Reactant	Products	Reference
Humic and Fulvic acids^a	No or little THMs and some organic haloforms: Carbon tetrachloride, 1,1,1-trichloroethane and 1,2-dichloroethane. Quinones, hydroquinones, aldehydes, ketones, carboxylic acids, some aryl and methyl derivatives of glyoxalic acid and small amounts of phthalic acid, benzoic acid, butanoic acid.	Lafrance <i>et al.</i> (1993); Rav-Acha (1984); Muttamara <i>et al.</i> (1996); Richardson <i>et al.</i> (1994); Carnimeo <i>et al.</i> (1995); Sansebastiano <i>et al.</i> (1995); Jun <i>et al.</i> (1996); Gallagher <i>et al.</i> (1994); Lykins and Griesse (1986); Werdehoff and Singer (1987)
Fulvic acids^b	Benzenepolycarboxylic acid methyl esters, aliphatic dibasic acid dimethyl esters, carboxyphenylglyoxylic acid methyl esters and aliphatic acid monomethyl esters.	Colclough <i>et al.</i> (1983)
Phenol	If phenol in excess: o-chlorophenol, 2,4-dichlorophenol, p-chlorophenol, 2-chlorophenol, 4-chlorophenol, 2,6-dichlorophenol and hydroquinones. If chlorine dioxide in excess: p-benzoquinone.	Wajon <i>et al.</i> (1982); Stevens (1982)
Amines and Olefins	Aldehydes.	Stevens (1982); Rice and Gomez-Taylor (1986)
Amino Acids	Formaldehyde, carbon dioxide, small quantities of benzylic acid, benzoic acid, and mandelic acid and traces of phenylacetaldehyde.	Rice and Gomez-Taylor (1986)
Alkenes	Chlorinated and non-chlorinated compounds	Stevens (1982)
Indene (hydrocarbon)	Trans-1,2-indanediol, cis-1,2-indanediol, 1-hydroxy-2-indanone, cis-2-chloroindan-1-ol and trans-2-chloroindan-1-ol.	Rav-Acha and Choshen (1987)

^a The reported end-products are not discriminatory and pertain as a result of reactions between chlorine dioxide with humic and fulvic acids as a general group.

^b The reported end-products pertain specifically to those resulting from reactions between chlorine dioxide and fulvic acids.

replaced chlorine as a disinfectant, the THMs and other chlorinated organics previously formed by chlorine treatment have been reduced. The THM levels have been below the detection level of 2 µg/L even though the THM formation potential (experimental procedure not given) has varied between 100 µg/L and 200 µg/L. For such results at the Laval treatment plant, Lafrance *et al.* (1993) reported that the excess chlorine produced by the chlorine dioxide generation should not surpass 10%. In a laboratory-scale study conducted on commercial humic acid, Muttamara *et al.* (1995) found that THMs were not detected (detection limit not reported) when a chlorine dioxide dose of 1.5 mg/L was applied to humic acid concentrations as high as 10 mg/L.

Certain nonvolatile halogenated organic substances may be produced from chlorine dioxide disinfection although their overall formation is expected to be minimal (Carnimeo *et al.* 1995) and less than those formed from chlorination (Richardson *et al.*, 1994; Sansebastiano *et al.*, 1995; Werdeoff and Singer, 1987). Carnimeo *et al.* (1995) conducted a pilot-plant study on Sinni River (Italy) water samples (in November, February and June) where chlorine dioxide was employed as a pre-disinfectant (1 mg ClO₂/L applied dose to result in a residual conc. of 0.2 mg Cl/L, pH 7.7-8.2, 20°C). While the Sinni River contained approximately 0.1-2.1 ppb total haloforms (i.e. TTHMs, carbon tetrachloride, 1,1,1-trichloroethane and 1,2-dichloroethane), after chlorine dioxide pre-disinfection, total haloform formation generally between 0.3 and 0.8 ppb was observed.

In regard to HAA formation, Hazen and Sawyer (1992) report that applying “high” chlorine dioxide doses to humic acid-containing waters can result in MCAA and

some DCAA and TCAA formation (no details were given as to what constituted high chlorine dioxide dosages or the level of DBP formation which could be expected).

There are few data which are available concerning the formation of trihalomethanes and total halogenated organics (TOX) resulting from the disinfection of “deep” groundwaters for human consumption (Sansebastiano *et al.*, 1995). The same authors found for two good quality groundwaters with low organic content (no data given) in Italy treated with chlorine dioxide (0.3 mg/L dose at 20°C) produced less TOX compared to sodium hypochlorite (0.3 mg/L) treatment (Figure 2.1).

2.4 Parameter Effects on Chlorine Dioxide Inorganic DBP Formation

Understanding the effects of different water quality parameters (including pH and temperature) as well as chlorine dioxide disinfection treatment variables (including reaction time and the presence of chlorine) on DBP formation will assist in the development of DBP predictive models. The effects of the various parameters on the formation of the chlorine dioxide inorganic DBPs are summarized in Table 2.8.

2.4.1 Chlorine Dioxide Dose and Contact Time

The level and extent of DBP formation will undoubtedly be influenced by the applied chlorine dioxide disinfection dose (Hofmann *et al.*, 1997; Griesse *et al.*, 1993; Werdehoff and Singer, 1987; Oehler *et al.*, 1986; Rav-Acha *et al.*, 1985; Bishop *et al.*, 1985). The required amount of chlorine dioxide to be applied for disinfection will be dependent on the treatment conditions (i.e. temperature and contact time), the level of microbial inactivation to be provided (Hofmann *et al.*, 1997), the chlorine dioxide demand exerted by organic and inorganic compounds in the water and the point of

Figure 2.1 TOX Concentrations in Two Groundwaters in Italy (Adapted from Sansebastiano *et al.*, 1995)

Table 2.8 Summary of Parameter Effects on the Formation of Chlorine Dioxide Inorganic By-Products

Factor	Range Examined	Effect	Reference
pH	2-over 10	<ul style="list-style-type: none"> • ClO_2 remains reactive (pH 2-10.5): forms Cl^- (pH 2) and ClO_2^- (pH 2 and neutral and alkaline pH) and ClO_3^- (neutral and alkaline pH). • ClO_2^- and ClO_3^- proportion ratios not altered in pH range of 7.3 to 8.9. • Increased pH results in increased ClO_2 reaction rate with phenols and humic acids to form ClO_2^-. 	Rosenblatt (1978); Wajon <i>et al.</i> (1982); Werdehoff and Singer (1987); Hoigné and Bader (1994); Freese and Nobel (1995); Hofmann <i>et al.</i> (1997)
Temp.	1°C to 25°C	<ul style="list-style-type: none"> • Greater ClO_3^- and ClO_2^- form at higher temp. (15 to 60-min. contact times). • Greater ClO_3^- and ClO_2^- form at lower temp. (24-hr contact time). 	Oehler <i>et al.</i> (1986); Lafrance <i>et al.</i> (1993); Hofmann <i>et al.</i> (1997)
Contact time	Up to 96 hours	<ul style="list-style-type: none"> • ClO_2^- proportion ratio remains unchanged. • Fast conversion rate of ClO_2 to ClO_2^- in contact time of few hrs. • ClO_2^- decreased with increasing contact time (from 8 to 14 hrs). 	Bishop <i>et al.</i> (1985); Oehler <i>et al.</i> (1986); Rav-Acha <i>et al.</i> (1985); Werdehoff and Singer (1987); Lafrance <i>et al.</i> (1993);
Chlorine Dioxide Dose	0-4 mg/L	<ul style="list-style-type: none"> • Increased ClO_2^- and ClO_3^- formation with higher ClO_2 dose. • Lower or steady ClO_2^- proportion results from higher ClO_2 dosing. 	Griese <i>et al.</i> (1993); Bishop <i>et al.</i> (1985); Werdehoff and Singer (1987); Oehler <i>et al.</i> (1986);
Chlorine	0-200 mg/L	<ul style="list-style-type: none"> • Chlorine applied with ClO_2 will reduce ClO_2^- formation. • Chlorine reacts with ClO_2^- to form Cl^-, ClO_3^- (near neutral and alkaline pH levels) and ClO_2 (acidic and neutral pH levels). 	Noack and Doerr (1978); Rav-Acha <i>et al.</i> (1985); Singer and O'Neil (1987); Gordon (1993); Gallagher <i>et al.</i> (1994)
Organics	1-11 mg/L TOC	<ul style="list-style-type: none"> • ClO_2 residual will be less persistent in waters with high levels of organics: In raw waters, smaller ClO_2:TOC ratios (less than 0.5) resulted in shorter persistence time of the ClO_2 residual in treated water. • ClO_2^- conversion ratio unaffected by increases in TOC while its conc. increases with increasing TOC. 	Werdehoff and Singer (1987); Lafrance <i>et al.</i> (1993); Hoigné and Bader (1994)

application. Possible application points include the raw or presettled water for predisinfection (Carnimeo *et al.* 1995), the water preceding filtration for disinfection (Gordon, 1993) and sometimes, the treated water in the distribution system either alone or in combination with other disinfectants to provide a residual concentration (Hoehn, 1993). Chlorine dioxide treatment concentrations in water treatment have been reported to generally be between 0.1 and 5.0 mg/L (Hofmann *et al.*, 1997; Gordon, 1993; Aieta and Berg, 1984). Hofmann *et al.* (1997) applied chlorine dioxide to a water (water immediately after the sedimentation, coagulation, flocculation processes but prior to disinfection) obtained from the Mannheim treatment plant (Waterloo). The same authors found that to achieve a 3-log *Giardia* inactivation, the required chlorine dioxide dose was usually below 3 mg/L under most conditions (Temp. of 1°C, 10°C, 25°C, pH 7.3 and 8.9 and contact times of 15, 60 and 24-hr simulated distribution system test) except for the 15-minute contact time at 1°C (both pH conditions) case where between 5 and 6 mg/L of chlorine dioxide would be necessary. It is further reported by the authors that, to attain a 0.5-log *Giardia* inactivation requirement (as could be anticipated for large utility plants), the chlorine dioxide dose to be provided would be less than 1.5 mg/L for all tested experimental conditions.

In a pilot plant study conducted on Ohio river source water (water quality characteristics not given), Griesse *et al.* (1993) observed that increased chlorine dioxide dosing from 2 to 5 mg/L added to the rapid mix compartment, resulted in increased chlorite, chlorate and chlorine dioxide residual in the settled (i.e. after alum coagulation and flocculation processes) water (Figure 2.2). Further, Werdehoff and

* Residual concentrations found after a chlorine dioxide contact time of approximately 110 minutes.

Figure 2.2 Chlorine Dioxide Effects on Settled Water Oxychlorine Residual Concentrations (Adapted from Griesse *et al.*, 1993)

Singer (1987) observed that various chlorine dioxide doses (ranging from 1-4 mg/L but mostly below 2 mg/L) consistently produced chlorite ion formed/chlorine dioxide consumed ratios of approximately 70% (Table 2.7) for three types of waters having various TOC concentrations (ranging from 1-11 mg/L) and contact times (ranging up to 96 hours) conditions.

Significantly, it has been reported that applying chlorine dioxide doses which are less than its demand can result in conversions of chlorine dioxide to chlorite which are higher than those where the applied chlorine dioxide doses are greater than the demand (Rav-Acha *et al.*, 1985). The same authors hypothesized that higher chlorine dioxide doses would result in greater amounts of unreacted chlorine dioxide in the treated water thus, reducing the relative proportion of chlorite formation. A bench scale study conducted by Bishop *et al.* (1985) using settled water taken just prior to disinfectant addition at the Chesapeake treatment plant (VA) is likely a good example of applying a chlorine dioxide dose which is less than its demand since the TOC level in the Chesapeake source water have reported to be high (ranging between 20 to 40 mg/L). The same authors found that a chlorine dioxide dose of 1.0 mg/L resulted in a rapid increase in chlorite residual concentration from 0.2 (at time zero) to approximately 0.6 mg/L after a contact time of 4 hours (chlorine dioxide residual was 0.3 mg/L at that time). The chlorite residual increased by only an additional 0.2 mg/L in the next 16 hours (i.e. 20 hours after applying chlorine dioxide). In contrast, Oehler *et al.* (1986) observed that a 0.84 mg/L chlorine dioxide dose (chlorine dioxide present in excess) applied to a model water (0.36 mg C/L, pH = 7.3 and T = 10°C) resulted in

chlorite formation of 0.32 and 0.44 mg/L after approximately 6 and 48 hrs respectively. Hence, a comparison of previous Bishop *et al.* (1985) and Oehler *et al.* (1986) results show, as hypothesized by Oehler *et al.* (1986), the chlorine dioxide/organic matter parameter can affect the proportion of chlorite formation whereby, increased excess of chlorine dioxide results in decreased chlorite formation proportions (further discussed in Section 2.4.4).

The preceding bench-scale study results reported by Bishop *et al.* (1985) also illustrate the effects of varying contact times on chlorite formation whereas a greater level of chlorite was formed within shorter contact times (i.e. first 4 hours after chlorine dioxide dosing) in comparison to longer contact times (i.e. 20 hours after chlorine dioxide dosing). The implication of varying chlorite formation levels with respect to different contact times in the development of predictive DBP models is that a pertinent selection of the reaction time levels to be investigated is essential to capture the chlorine dioxide conversions to chlorite of interest (i.e. faster conversions at shorter contact times and slower ones at greater contact times). In addition, Oehler *et al.* (1986) observed that chlorine dioxide doses of 0.68, 1.02 and 1.70 mg/L applied to Gallenklinge (Germany) raw water samples (DOC of 3.8 mg/L, T= 15°C) resulted in the respective formation of approximately 0.44 mg/L (in 1 hr), 0.65 mg/L (in 1.1 hrs) and 1.2 mg/L (in 3.5 hrs) of chlorite. Hence, there seems to be a trend where greater chlorine dioxide doses required longer contact times for the conversion of chlorine dioxide to chlorite to go to completion. Interestingly, Lafrance *et al.* (1993) found that for a 14-hour contact time in the distribution system, chlorine dioxide dosing (0.26 to

0.93 mg/L) produced less chlorite (between 0.05 and 0.2 mg/L) than after an 8-hour contact time for all given temperatures (1°C-25°C). The amount of chlorine present in the distribution system was not specified nor was an explanation given to explain the observed decrease.

2.4.2 Chlorine Concentration

The presence of chlorine (either as chlorine, hypochlorous acid and hypochlorite ion) in chlorine dioxide-treated waters may effect the formation of chlorine dioxide by-products (i.e. chlorite, chlorate and chlorite) as well as the residual chlorine dioxide remaining in the finished water. For this reason, chlorine concentration should be considered as a possible significant variable to be included in chlorine dioxide DBP forecasting models.

Noack and Doerr (1978) performed experiments (5 ppm humic acid, $25\pm3^\circ\text{C}$, and 10 ppm chlorine dioxide:chlorine solutions of varying weight ratios) and found that at pH levels of 6.0 and 7.0, higher chlorine/chlorine dioxide ratios provided greater reductions in chlorite concentrations. The same authors observed that from about 5.5 mg/L of chlorite (as NaClO_2) for a 100:0 chlorine dioxide:chlorine mixture, there was a non-linear decrease in chlorite formation with decreasing chlorine dioxide:chlorine mixture ratios (i.e. 60:40, 50:50 and 25:75) to a zero chlorite concentration for the mixture composed entirely of chlorine.

The presence of hypochlorite ion at more alkaline pH levels (i.e. higher than 8) may also affect the formation of DBPs. At pH 9.5, Noack and Doerr (1978) had observed that there was no noticeable chlorite oxidation which correlated with the fact that at this pH level, OCl^- is the dominant chlorine species. This observation is

supported by Aieta and Roberts (1985) who report that, although hypochlorite ion can disproportionate rapidly to chlorate and chloride in hot temperatures (i.e. 80°C) whereby producing high chlorate yields (eqn. 2.4), the oxidation of chlorite by hypochlorite (as shown in eqn. 2.5) is slow in alkaline pH conditions (no details given).

Apart from the reaction between chlorite and hypochlorite ion, chlorate ion can also be produced from the reaction between hypochlorous acid and residual chlorite as presented in eqns. 2.6 (Rav-Acha *al.*, 1985) and 2.7 (Aieta and Roberts, 1985). Singer and O'Neil (1987) conducted an experiment with initial chlorine and chlorite concentrations of about 5 mg/L and confirmed assertions by Werdehoff and Singer (1987) that a reaction between chlorine and chlorite in an oxidant-demand-free dilute solution at pH 7 would yield chlorate as the main resulting compound. Gordon *et al.* (1990) have suggested that averting treatment conditions which can lead to low reaction rates such as high pH levels, low initial reactant concentrations and the presence of free hypochlorous acid (no greater details given) would be efficient in reducing the formation of chlorate ion.

Apart from affecting DBP formation, the presence of chlorine can influence chlorine dioxide residual levels. Rice and Gomez-Taylor (1986) reported that the presence of strong oxidants in solution such as free chlorine and/or ozone could allow for the reoxidation of chlorite back to chlorine dioxide. Hoehn (1993) has reported that

chloramines do not appear to encourage the reformation of chlorine dioxide or the formation of chlorate. Chlorine dioxide reformation can be problematic whereby reacting with organic compounds in households, resulting in undesirable odors at the point of use (Hoehn, 1993).

Chlorine dioxide reformation in the treated water of distribution systems may occur in a near-neutral pH environment from the reaction between chlorite ion (e.g. resulting from the use of chlorine dioxide for pre-oxidant treatment) and the free chlorine which had been applied to ensure a disinfectant residual in the distribution system as shown in eqn. 2.8 (Gallagher *et al.*, 1994). However, it has been reported by Aieta and Roberts (1985) that for chlorine-chlorite reactions, while neutral and alkaline pH levels lend themselves to chlorate formation (as discussed previously), acidic pH levels will encourage chlorine dioxide formation. Gordon (1993) has noted that acidic pH conditions (pH less than 3) would favor the formation of chlorine dioxide through the reaction of chlorine with chlorite as shown in eqn. 2.9. However, such low pH levels are not typical conditions encountered in water treatment processes.

2.4.3 Temperature and pH

Temperature and pH are also important variables which influence chlorine dioxide reactions and thus, DBP levels. Generally, higher temperatures result in higher DBP (i.e. chlorate and chlorite) levels as lower temperatures tend to favor lower DBP formation (Oehler, 1986; Andrews *et al.*, 1997 and Lafrance *et al.*, 1993).

Oehler *et al.* (1986) observed greater chlorine dioxide consumption and chlorite production with increasing temperature. The same authors dosed water samples taken from Gallenklinge (Germany) raw lake water (3.8 mg/L DOC) with chlorine dioxide doses between 0.43 and 1.9 mg/L. After a reaction time of one hour, they found that the chlorite formed as a percentage of chlorine dioxide consumed to be 65% (i.e. 0.28 mg/L) and 43% (i.e. 0.82 mg/L) respectively at 10°C while at 20°C these percentages were respectively, 72% (i.e. 0.31 mg/L) and 58% (1.10 mg/L). The preceding results correlate well with bench-scale study observations by Andrews *et al.* (1997) that up to twice as much chlorite is produced at 25°C than at 1°C for 15 to 60-minute contact times using chlorine dioxide.

Lafrance *et al.* (1993) observed in the distribution system of a treatment plant employing chlorine dioxide that higher chlorite concentrations resulted during the warmer months (18 to 25°C) compared to the colder ones (1 to 12°C). In contrast, although not directly comparable to Lafrance *et al.* (1993) results, Andrews *et al.* (1997) found that in a 24-hour Simulated Distribution System (SDS) test condition (headspace free, in the dark and controlled temperature), the chlorite and chlorate formed were usually found to be 10 to 100% (quantify) greater at 1°C than at 25°C where the higher pH levels (pH 8.9 in contrast to pH 7.3) and greater inactivation levels (*Giardia* log inactivation of 2 or 3 compared to 0 or 1) accompanied the higher formation percentages. It was suggested by Andrews *et al.* (1997) that the necessary chlorine dioxide residual, chlorite rate of formation and level of chlorine dioxide demand will control the extent of chlorite formation at varying temperatures as well as

contact times. In their previous study, Lafrance *et al.* (1993) found in the summer months, chlorine dioxide will disappear very quickly (where only residual chlorite will result in the distribution system extremities) whereas in the winter months, it will react more slowly with organic matter due to the slower reaction rates at lower temperatures compared to those at warmer temperatures. However, due to the fact that it volatilizes at temperatures higher than 10 to 15°C (Gates and Harrington, 1992), disinfecting with chlorine dioxide at lower temperatures might be advantageous in resulting in longer residence times thus, improving its microbial inactivating potential.

For chlorate, the effects of temperature were seen to be influenced by pH (Andrews *et al.*, 1997). The same authors reported that at pH 7.3, the differences between the chlorate formed at 1°C, 10°C and 25°C were small and within the estimated experimental error after 15 and 60-minute contact times. At a pH of 8.9, more chlorate formed at 25°C than at 1°C after 1 hour for the lower *Giardia* inactivation level (below 1-log) even though more chlorate had formed at 1°C comparatively to 25°C after 15 minutes. These results suggest that there may have been a pH-temperature interaction effect on chlorate formation under the given experimental conditions.

The reduction of chlorine dioxide to chlorite had previously been reported to be insignificantly affected by pH in the range of 6 to 9.5 (ambient temperature, 25±3°C) (Noack and Doerr, 1978). However, in the pH range of 6.5 to 8.5, Oehler *et al.* (1986) reported that chlorine dioxide consumption and chlorite formation increased with increasing pH. Experimental results reported by Andrews *et al.* (1997) showed that for the same level of *Giardia* inactivation, normally 20 to 40% more chlorate and

chlorite were formed at pH 8.9 comparatively to pH 7.3. The significance of greater disinfection byproducts could be seen after a SDS test whereby at pH 8.9, the amount of chlorite produced generally exceeded 1 mg/L (proposed MCL for chlorite in the D/DBP rule, Fed. Reg., 1994). Andrews *et al.* (1997) also observed that different pH conditions (i.e. 7.3 and 8.9) did not appear to influence chlorine dioxide conversion ratios to either chlorate and chlorite, generally consisting of approximately 5-10% and 60-70% by weight respectively (Table 2.6).

Further, Hoigné and Bader (1994) reported that the reaction of chlorine dioxide with most kinds of phenols will produce apparent total reaction rate constants which will increase by a factor of 10 per pH increment (in the pH range of 5 to 9). They also observed that the reaction rate constants for humic acid and chlorine dioxide reactions increased by a factor of 3 per pH increment (in the pH range of 4 to 8). The significance of increased reaction rates with increasing pH levels is that higher chlorate and chlorite formation may result within a shorter period of time (i.e. 1 hour) at higher pH levels compared to lower pH levels for the same contact time.

2.4.4 Nature of Source Water

The significance of chlorine dioxide and organic matter reactions lies in the fact that they may lead to the formation of organic as well as inorganic DBPs (Rice and Gomez-Taylor, 1986). Lafrance *et al.* (1993) observed that the amount of chlorite formed is directly proportional to the amount of organic matter (measured as TOC) in the water whereby increased water organic matter result in greater chlorine dioxide

consumption. As such, monitoring the organic content of the water is imperative in developing DBP formation models for chlorine dioxide treatment.

Chlorine dioxide will react with humic acid whereby, if there is an excess of humic acid with respect to the chlorine dioxide, the consumption of chlorine dioxide will be proportional to the chlorine dioxide dose while if chlorine dioxide is in excess, its consumption will be proportional to the organic carbon concentration (Oehler *et al.*, 1986). Moreover, Wajon *et al.*, (1982) observed that chlorine dioxide (3×10^{-4} M at pH 6.92-6.98 and 25°C) and hydroquinone reactions yielded chlorite produced/chlorine dioxide consumed ratio of 1.0 when chlorine dioxide was deficient while this ratio was about 0.70 when chlorine dioxide was in excess. Consequently, as was done by a number of researchers such as Amy *et al.* (1987a) and Di Scipio (1996) in dealing with other disinfectants, observing the DBP formation for various chlorine dioxide/organic matter ratios may be a viable option in developing proper models to reflect the different treatment conditions.

Apart from the fact that chlorine dioxide DBPs will vary with chlorine dioxide/organic matter ratios, it has been documented that the amount of residual chlorine dioxide remaining in the treated water will also be dependent on such ratios (Werdehoff and Singer, 1987). These same researchers observed that smaller chlorine dioxide-TOC ratios in raw waters and fulvic solutions resulted in shorter persistence time for the chlorine dioxide residual in solution (a ratio less than 0.5 resulted in chlorine dioxide being completely consumed within two hours). However, in a

“relatively high quality finished water”, they reported that chlorine dioxide could persist for more than four days for a 0.5-ratio.

Considering more closely the reaction of certain compounds with chlorine dioxide may be useful since certain researchers (i.e. Limoni *et al.*, 1984; Rav-Acha *et al.*, 1985) have used such reactions to explain their observed chlorine dioxide conversion to chlorite. Wajon *et al.* (1982) hypothesized that 2 moles of chlorine dioxide react with 1 mole of phenol (via an electron-transfer pathway) to produce 1 mole of chlorite ion (as simply shown in eqn. 2.10). To account for their 60% to 65% chlorite formation proportion (as reported in Table 2.6), Limoni *et al.* (1984) and Rav-Acha *et al.* (1985) attributed a 50%-fraction of chlorite formation to the presence of humic substances (which make up a major portion of surface waters) having a polyphenolic nature thus, reacting with chlorine dioxide in the manner described by Wajon *et al.* (1982). The same researchers then hypothesized that the remaining 10 or 15% excess chlorite was due to the disproportionation of chlorine dioxide. In contrast, Werdehoff and Singer (1987) could not provide a theoretical explanation for their observed chlorite yield of 70% resulting from TOC levels ranging between 1.7 to 10.7 mg/L in different waters, on the basis that the natural organic substances are too complex in nature and comprised of numerous functional groups.

2.5 Considerations Regarding the Development of Predictive Model Equations

Model equations can be useful tools to administer process control (i.e. information may be obtained faster and cheaper than through regular direct

measurements), evaluate the relative effect of specific parameters on the operation of the process and to conveniently summarize abundant data and compare the treatment efficiency of different water sources (McClellan *et al.*, 1996). Models which can forecast the development of DBPs may be of assistance to utility managers whereby they can establish a basis upon which, economically-sound tradeoffs between source water parameters and water treatment control procedures can be recognized (Hutton and Chung, 1994).

Unlike for chlorine, equations pertaining to the formation of DBPs from chlorine dioxide treatment are not well documented in the literature. Only one model equation concerning chlorine dioxide treatment was found. Lafrance *et al.* (1993) developed an equation (eqn. 2.11) based on a linear relationship between TOC/chlorite and temperature. The researchers employed the equation to estimate the chlorine dioxide required to satisfy its demand (whereby all the chlorine dioxide is assumed to be converted to chlorite and that any excess chlorine dioxide dose will be in free chlorine dioxide form). Although the relationship is influenced by contact time in the finished water storage tank, the equation has been found for a set 12-hour contact time.

$$\text{ClO}_2 = \frac{\text{TOC}}{(-0.482 \cdot T) + 13.76} \quad (2.11)$$

where ClO_2 = Chlorine dioxide concentration required to meet the oxidant demand after a 12-hour contact time, mg/L.

TOC = Total Organic Carbon concentration, mg/L.

T = Water temperature, °C.

Important concepts and thoughts which may have originally been considered in the development of DBP equations upon chlorination could be applicable to chlorine

dioxide DBP formation equations. For instance, Lyn and Taylor (1993) developed nonlinear statistically-based THM as well as chlorine residual models based on bench-scale studies on a groundwater supply to determine whether the Pinellas County (FL) treatment system could comply with present as well as future regulations pertaining to DBP and disinfectant residuals. The development of such models enabled Lyn and Taylor (1993) to identify which parameters, upon their increase, would cause a decrease in chlorine residual concentration as well as cause an increase in THM formation. They considered the Stage 1 proposed D/DBP rule for regulations pertaining to the maximum and minimum chlorine residual requirement (4.0 and 0.2 mg/L respectively) as well as the MCL for THMs (0.08 mg/L). Under the given conditions (0.35-3.5 mg/L nonpurgeable DOC, 5.82-8.75 mg/L chlorine dose at 24°C), the researchers found that for detention times less than or equal to 16.5 hours, the minimum chlorine residual and THM MCL requirements were the limiting factors while for detention times greater than 16.5 hours, the maximum allowable chlorine residual concentration was the limiting criteria. The same type of application could be of great value in the disinfection of surface and groundwaters using chlorine dioxide. Models could be employed to ascertain whether it is the development of chlorate and/or chlorite in contrast to residual chlorine dioxide levels which will be the critical parameter requiring special attention and monitoring. In view of regulatory limits set in the United States for DBPs such as trihalomethanes, haloacetic acids and chlorite ion (Fed. Reg., 1994) as well as likely future limits to be set for chlorate ion (Pontius, 1991; Health Canada, 1996), the development of equations to predict DBP formation (most especially chlorite and chlorate) in terms of physical-chemical variables which

are related to water quality and chlorine dioxide disinfection treatment would become increasingly useful. Furthermore, the fact that the proposed D/DBP Rule (Fed. Reg., 1994) sets a MRDL for chlorine dioxide may also require treatment plants to optimize their systems to ensure a well-operated facility.

Model development can take on two different approaches: General empirical models as well as site-calibrated models (McClellan *et al.*, 1996). While the general empirical models have the advantage of large databases, they may be unreliable if independent variable values are outside the specific data calibration range and the dependent variable may be influenced by other parameters which have not been included in the model formulation (McClellan *et al.*, 1996). The same authors report that such problems may be less prominent in site-specific calibrated models. An advantage to the site-specific models is they may be capable of providing a unique description to a particular location. For example, Hutton and Chung (1992a) included precursor as well as bromide movement based on transport simulation (i.e. hydrodynamic data) in the THMFP model for the Sacramento-San Joaquin Delta (CA).

Models can incorporate a number of different factors or a predictor parameter which reacts similarly to the different factors (McClellan *et al.*, 1996). An example for the latter model would be the use of one DBP compound as a forecaster for other DBPs. Another application of such a model could involve developing predictive chlorite and chlorate model equations by applying a "conversion ratio" coefficient to chlorine dioxide consumption predictions obtained from a statistically-based model equation.

Amy *et al.* (1987b) discuss that the development of predictive DBP formation equations entails formulation, calibration and validation steps. The authors describe that the formulation process consists of establishing the framework of broad-range “functionalities”, calibration involves obtaining equation constants such as from statistical analysis and validation requires testing the model with internal data (obtained from water sources employed to develop model) and especially, external data (obtained from water sources not utilized in the model development stages).

Modeling THM formation as well as other aquatic chemical compounds can be conducted using conventional kinetic or statistically-based empirical models. Amy *et al.* (1987b) report that kinetic models would involve the use of more data (e.g. the disappearance of reactants such as chlorine over time) in order to define the necessary rate law and model calibration. However, a rate law may provide added information as to the possible reaction mechanisms taking place in comparison to empirically-based models.

Kavanaugh *et al.* (1980) developed an empirical model to predict THM formation. Based on an overall stoichiometric expression which describes the reaction between chlorine (i.e. hypochlorous acid) and TOC to yield TTHMs, an expression for the rate of THM formation was developed assuming the rate of TTHM formation order with respect to each variable (i.e. TOC and hypochlorous acid). Upon integrating and manipulating the equation, the rate constants were obtained from linear regression techniques. Considering kinetic and mechanistic observations, Adin *et al.* (1991) also proposed a general mechanism to describe THM formation from the chlorination of

humic materials. For additional details concerning their kinetic model development procedures, the reader is directed to the respective articles written by Kavanaugh *et al.* (1980) and Adin *et al.* (1991). While the model proposed by Adin *et al.* (1991) can be useful in estimating the formation of THM in terms of chlorine and precursor material concentrations at the examined pH and temperature levels (i.e. pH 8 and 20°C), the fact that temperature, pH and the nature of the precursor material are variable, the reaction rate constants would have to be re-evaluated for each water type under their own specific conditions.

The derivation of statistically-based empirical models are said to generally be capable of utilizing routinely-monitored data consisting of initial water quality parameters (i.e. TOC, pH, bromide), temperature, disinfectant dose and DBP concentrations. For this reason, this type of model may be more practical for treatment plants to employ to predict DBP formation given the process conditions of the specific utility plant. To best illustrate the development of statistically-based empirical model, methods and results reported by Amy *et al.* (1987a, 1987b) and Morrow and Minear (1987) will be presented. Amy *et al.* (1987a) conducted a study using a number of natural waters in order to develop statistically-based empirical models (multiple linear or log-log and multiple nonlinear) which would be capable of predicting THM formation resulting from chlorination. The original format of these models is, as reported by the same authors, a multiple-parameter additive form (such as the nonlinear model equations displayed in eqns. 2.12 and 2.13). Although, the log-log model can be retransformed to its multiparameter power function form as shown in eqn. 2.14.

Short-term nonlinear equation applying to reaction times less than 8 hours:

$$\text{TTHM} = -2.46 + 0.315(\text{UVABS} \cdot \text{TOC}) + 0.184 \exp^{0.0762(\text{Temp})} + 0.00611(\text{ClDose})^{1.33} \\ + 0.215(\text{Br})^{1.51} + 1.16(\text{RxnTime})^{0.252} + 0.0887(\text{pH} - 2.6^a) \quad (2.12)$$

Long-term nonlinear equation applying to reaction times greater than 24 hours:

$$\text{TTHM} = -16.9 + 0.849(\text{UVABS} \cdot \text{TOC}) + 0.407 \exp^{0.0834(\text{Temp})} + 0.00678(\text{ClDose})^{1.59} \\ + 0.772(\text{Br})^{1.65} + 9.75(\text{RxnTime})^{0.0707} + 0.402(\text{pH} - 2.6^a) \quad (2.13)$$

Log-log model:

$$\text{TTHM} = 0.00309(\text{UVABS} \cdot \text{TOC})^{0.440}(\text{ClDose})^{0.409}(\text{RxnTime})^{0.265}(\text{TEMP})^{1.06}(\text{pH} - 2.6^a)^{0.715} \\ \times (\text{Br} + 1)^{0.0358} \quad (2.14)$$

where TTHM = Total trihalomethane concentration, $\mu\text{mol/L}$
 TOC = Total organic carbon concentration, mg/L
 UVABS = Ultraviolet absorbance, cm^{-1}
 ClDose = Chlorine dose, mg/L
 Temp. = Temperature, $^{\circ}\text{C}$
 Br = Bromide concentration, mg/L
 RxnTime = Reaction time, hour
 $a =$ Statistically-found coefficient representing the minimum pH at which THM formation begins.

The premise of an additive multiple parameter model is each parameter will have its own incremental contribution to the formation of the DBP which is independent of the action of other variables. The models consisted of separate terms where each term describes the impact of a water quality or treatment parameter under investigation (i.e. temperature, chlorine dose, etc.) on the formation of the THM (the independent variable). Morrow and Minear (1987) and Amy *et al.* (1987a, 1987b) obtained data from experiments resulting from the systematic change of one variable while keeping all the other parameter values constant to their baseline or average values (i.e. ambient pH and bromide levels, chlorine to nonpurgeable organic carbon ratio of 3 and 20°C). Consequently, each variable could be related to the formation of TTHM,

using a linear transform specific to that variable if necessary (log-transformed values may be necessary as was done by Morrow and Minear, 1987) while the other variables have fixed values.

Apart from the chemical rational used in the model formulation, model calibration of the linear and nonlinear models were solely based on statistical analysis involving a least-square strategy in association with an algorithm employed to minimize the total sum of the squares of the errors (SSE) by an iterative system. To develop the nonlinear model proposed by Amy *et al.* (1987a), the determination of the most appropriated relationship between the DBP formation and each independent variable was necessary. For this purpose, various specific linear and nonlinear regressions with certain parts of the original data (i.e. data associated with either a short or long-term reaction time) were performed to derive the model (linear and nonlinear) constants. Morrow and Minear (1987) employed a number of different iterative approaches (Gaussian, Dud and Marguardt and gradient methods) in the derivation of their nonlinear statistically-based empirical models. The reader is directed to the Morrow and Minear (1987) article for more details relating to the previously mentioned iterative approaches. In the nonlinear modeling approach used by Morrow and Minear (1987), they hypothesized that assuming model convergence through minimization of the SSE may result in a deficiency of descriptive statistics.

It was reported that reaction time may affect the impact of each parameter on the formation of THM (Engerholm and Amy, 1983b; Amy *et al.*, 1987a). Thus, Amy *et al.* (1987a) derived a nonlinear model consisting of two sub-models (eqns. 2.12 and

2.13) obtained by performing two different regressions on data associated with either short-term (0.1-8 hours) or long-term reaction times (24-168 hours). In a study conducted by Amy *et al.* (1983a,1983b) on a highly-colored groundwater comprising of bromide and ammonia, three different sub-groups were identified due to the chlorine-ammonia interactions: Chlorine dose greater than, smaller than or equal to the breakpoint chlorine dose. With this in mind, modeling chlorine dioxide DBP formation may also best be accomplished by providing sub-models as they pertain to the different water sources investigated such as developing predictive model equations based on data from surface water experiments only.

The relevance of using two different models can be seen by performing separate sensitivity analyses on each sub-model for each parameter. Based on the incremental contribution of each parameter to the model prediction (as related to the average or baseline value for each parameter), a relative order of significance of the independent variables on DBP formation can be assessed for the short and long term situations. Thus, treatment plants can identify the parameters which, given the reaction time situation, are more critical and requiring more attention. Although the two nonlinear sub-model approach resulted in a SSE which was less than that found for a single equation form (a total SSE of 1102 compared to 2049), the two sub-model strategy can lead to a potential continuity problem at the interface of both sub-model equations (Amy *et al.*, 1987a). The same authors report that because the least-square regression performed on either the short or long-term equation is conducted separately from the other, no provisions are taken to ensure a smooth or continuous curve between them.

Consequently, an observable discontinuity may result (i.e. a decrease or an exaggerated increase from the short-term to the long-term time limit).

Model calibration is an important consideration when developing a model. For instance, recalibration of the model equations proposed by Amy *et al.* (1987a) using data where a positive disinfectant residual concentration resulted was conducted on the assumption that for THM formation potential predictive equations the formation of DBP increases as a function of time and that a residual is maintained for the entire duration (Morrow and Minear, 1987; Amy *et al.*, 1987a; Amy *et al.*, 1990).

The inclusion of precursor-related surrogate parameters (i.e. TOC, UVABS) in the predictive models is dependent on whether a correlation between such surrogates and the formation of DBP can be obtained. Since the reactivity of precursor material can be expected to vary from one water source to another, Amy *et al.* (1987b) had suggested that predictive models should incorporate a combination of precursor-related parameters such as non-volatile TOC (NVTOC), UV absorbance, fluorescence and color. Upon performing a number of simple regressions on the average or baseline data, Amy *et al.* (1987a) found that the multiplicative term UVABS•TOC provided the best precursor-related surrogate parameter in predicting TTHM. The basis of the multiplication of both single surrogates is that TOC constitutes a measure of the amount of precursor while UV absorbance is an indication of the precursor reactivity in producing THMs (Hutton and Chung, 1992).

Upon internal and external validation, Amy *et al.* (1987a) found that the models were the most accurate for the TTHM 1.0-1.5 $\mu\text{mol/L}$ concentration range and tended

to overpredict TTHM formation below this TTHM concentration range and to underpredict at TTHM levels higher than the given range. The internal model validation procedure used by Amy *et al.* (1987a) and also followed by Hutton and Chung (1994) consisted of conducting a linear regression of predicted against measured values. Generally, the log-log linear model yielded predictions which were more accurate than the nonlinear model predictions. In a study conducted on a groundwater, Amy *et al.* (1987b) observed that its models had a tendency to substantially overpredict (between a factor of 6 and 25 times more) the THM formation potential for samples taken from a source having a low organic carbon level but high ammonia level. They hypothesized that such a trend may indicate differences in reactivity between surface and groundwater precursor material.

It is reported by Harrington *et al.* (1992) that differences between predicted and measured values will also encompass errors resulting from the estimates of the various model term components such as contact time, pH, dissolved organic carbon (DOC) and DUV_{254} (data obtained after filtering sample). The same authors report that, typically, differences between UV_{254} and DUV_{254} are more notable than differences between TOC and DOC because turbidity may hinder spectrophotometric measurements of UV absorbance.

As cautioned by Amy *et al.* (1987a), using a model with values found near the extreme boundary conditions will not result in DBP prediction results which are as confident as DBP formation results calculated from parameter levels which are equal or close to their average or baseline values. Morrow and Minear (1987) reaffirm that in

their additive model, it is necessary to employ parameter values which are within the set given boundaries otherwise it may be plausible to attain positive TTHM values in the absence of disinfectant or precursor material.

Eventhough the models suggested by Amy *et al.* (1987a) were calibrated with extreme boundary conditions (i.e. conditions which are less or more favorable to the formation of THMs), such models would not be conducive in predicting extreme conditions of more than one variable since the model does not include terms which directly apply to the modeling of composite (i.e. multiplicative) effects. In fact, the traditional experimental procedure of varying one factor at a time (OFAT) will not offer any information regarding the effects on DBP formation resulting from factor interactions (Anderson and Whitcomb, 1996). In order to capture such interactions, a factorially-designed experiment can be a more efficient and viable alternative to the standard OFAT method (Anderson and Whitcomb, 1996). The statistically-based factorial design method would involve the concurrent variation of experimental factors at their high and low value levels which have been chosen by the experimenter. Experiments which have utilized the two-level factorial design (TLFD) have been conducted and documented by Di Scipio (1996) and Hofmann (1996).

Important factors which are consequential in developing suitable DBP formation models have been summarized in Table 2.9. The choices concerning the model applicability, type, parameter formulation, equation form, experimental approach and statistical strategy will govern the model expression as well as its usefulness and capability of predictive DBP formation. For instance, incorporating factor interaction

Table 2.9 Summary of Important Model Factors in the development of DBP Formation Equations

Factor	Case #1	Reference(s) for Case #1	Case #2	Reference(s) for Case #2
Applicability	General empirical models	Amy <i>et al.</i> (1987a);	Site-calibrated models	Lafrance <i>et al.</i> (1993); Hutton and Chung (1992)
Type	Conventional kinetic models	Kavanaugh <i>et al.</i> (1980); Adin <i>et al.</i> (1991)	Statistically-based empirical models	Amy <i>et al.</i> (1983); Amy <i>et al.</i> (1987a); Amy <i>et al.</i> (1987b); Morrow and Minear (1987); Lyn and Taylor (1993)
Experimental Approach	Varying one factor at a time (OFAT)	Amy <i>et al.</i> (1987a); Amy <i>et al.</i> (1987b); Morrow and Minear (1987); Lyn and Taylor (1993)	Two-level factorial design for factor interaction effects (TLFD)	Di Scipio (1996); Hofmann (1996)
Equation Form	Singular equation	Morrow and Minear (1987)	Sub-Models	Amy <i>et al.</i> (1983); Amy <i>et al.</i> (1987a); Amy <i>et al.</i> (1987b)
Statistical Strategy	Multiple linear regression models	Amy <i>et al.</i> (1987b)	Multiple nonlinear models	Amy <i>et al.</i> (1987a); Morrow and Minear (1987); Lyn and Taylor (1993);
Parameter Formulation	Multiple different factors	Amy <i>et al.</i> (1987a); Amy <i>et al.</i> (1987b); Morrow and Minear (1987); Lyn and Taylor (1993); Hofmann (1996)	Predictor parameter	Amy <i>et al.</i> (1983)

effects into a predictive model via a TLFD will inevitably result in a different model than the model ensuing from employing a standard OFAT experimental approach.

2.6 Surface and Groundwater Characteristics

2.6.1 Groundwaters Not Influenced by Surface Waters

It can be important to identify groundwater sources not under the influence by surface waters since, unlike surface waters and groundwaters which are under the influence of surface waters, their microbiological inactivation requirements are not regulated by the SWTR. Consequently, the groundwaters not under the influence of surface waters may not require any or little disinfection in comparison to surface waters. The evaluation of whether a groundwater is subject to direct surface water contamination would have to be conducted on a site-specific basis (Von Huben, 1991). Indications of groundwaters under the influence of surface waters include the presence of microbial contaminants including *Giardia* cysts, chloroplast-containing algae, animal parasites and insects (Table 2.10) and parameter correlations between variations in water characteristic parameters including pH, temperature, conductivity, turbidity and hardness of the groundwater and nearby surface water (Table 2.10). However, the mixture of a groundwater with a surface water would result in a water to be regulated by the SWTR (Hiltebrand *et al.*, 1991).

2.6.2 Surface and Groundwater Composition Differences

Water quality parameter levels for surface and groundwaters are compared in Table 2.11. Identifying water quality differences between these two water types will be useful in selecting appropriate parameters to include in the predictive model

Table 2.10 Indications of Groundwaters Under the Influence of Surface Waters

Parameter	Groundwaters under the influence of surface waters	Groundwaters not under the influence of surface waters	Reference
Example	springs, shallow wells, infiltration galleries and wells found close to surface waters.	wells located more than 200 ft (60.96 m) from any surface water source, more than 50 ft (15.24 m) deep and properly-constructed ^a .	Von Huben (1991) ^d
Variations in Water Quality	Correlation between sets of water characteristics (i.e. temperature, pH, conductivity, hardness and ferrous ion concentration) variations of groundwater with nearby surface water.	Water quality records show no indication of disease outbreaks, inordinate turbidities, evidence of coliforms in untreated samples or presence of particulate matter which can be linked to surface water.	Von Huben (1991) ^d
Microbial contaminants	Presence of <i>Giardia</i> cysts, live diatoms, blue-green algae, green algae and other chloroplast-containing algae. Presence of Coccidia, fish and animal parasites having a diameter greater than 7µm in diameter, rotifers, insects and insect parts.	Free of <i>Giardia</i> cysts.	Hiltebrand <i>et al.</i> (1991) ^e ; Von Huben (1991) ^d

^a Correctly installed well casing which penetrates the confining layer and is either screened or only unprotected below the layer and is closed to the surface and its surrounding environment.

^b Decisive signs of surface water contamination.

^c Solid but not definite signs of surface water contamination.

^d Von Huben (1991) summarized the U.S. EPA Guidance Manual for compliance with the filtration and disinfection requirements for public water systems using surface water sources (1991)

^e Hiltebrand *et al.* (1991) evaluated groundwaters which are susceptible to *Giardia* and larger protozoan cyst contamination by analyzing particulate results.

Table 2.11 Water Quality Parameters Levels Reported for Surface and Groundwaters

Parameter	Range Reported for Tested Surface Waters	Reference	Range Reported for Tested Groundwaters	Reference
Organic Matter (DOC in mg/L unless otherwise specified)	0.250-20.8	Bruchet <i>et al.</i> (1991); McClellan <i>et al.</i> (1996); Amy <i>et al.</i> (1994); Martin-Mousset <i>et al.</i> (1997)	<0.1-6.13	Bruchet <i>et al.</i> (1991); Amy <i>et al.</i> (1994); Malcolm (1991)
pH	6.1-9.1	Benner <i>et al.</i> (1995); Amy <i>et al.</i> (1987a); Najm <i>et al.</i> (1992); McClellan <i>et al.</i> (1996)	4.2-8.8	Miller <i>et al.</i> (1990); Benner <i>et al.</i> (1995); Bjerg <i>et al.</i> (1995); Senseman <i>et al.</i> (1997)
Temp. (°C)	1-25	Lafrance <i>et al.</i> (1993); McClellan <i>et al.</i> (1996)	8.9-26.6	Miller <i>et al.</i> (1990); Tan and Sudak (1992)
Alkalinity (mg/L as CaCO ₃)	5.50-238	Amy <i>et al.</i> (1994); Najm <i>et al.</i> (1994); Di Scipio (1996)	0-964	Amy <i>et al.</i> (1994); Benner <i>et al.</i> (1995)
Chloride (mg/L)	0.730-131	Aieta <i>et al.</i> (1984); Benner <i>et al.</i> (1995); Amy <i>et al.</i> (1994)	2.2-853	Miller <i>et al.</i> (1990); Amy <i>et al.</i> (1994); Benner <i>et al.</i> (1995); Bjerg <i>et al.</i> (1995);
Bromide (µg/L)	2.50-426	Amy <i>et al.</i> (1987a); Morrow and Minear (1987); Amy <i>et al.</i> (1994); Najm <i>et al.</i> (1994)	2.50-429	Owen <i>et al.</i> (1993); Amy <i>et al.</i> (1994)
Iron (µg/L)	200-1300	Lykins and Griesse (1986); Benner <i>et al.</i> (1995)	0-400000	Miller <i>et al.</i> (1990); Benner <i>et al.</i> (1995); Bjerg <i>et al.</i> (1995)
Manganese (µg/L)	20-700	Aieta <i>et al.</i> (1984); Lykins and Griesse (1986); Benner <i>et al.</i> (1995);	7-30000	Miller <i>et al.</i> (1990); Benner <i>et al.</i> (1995); Bjerg <i>et al.</i> (1995)

equations as well as the suitable experimental conditions to investigate. The parameter ranges consist of values found for a number of geographical areas (including Canada, United States, France and Denmark) and water constitutions (i.e. various ionic strengths, acidity etc.) reported by various researchers. Depending on the surrounding environment, a groundwater can have a very high pH (such as in a limestone region) or may possess an acidic pH due to the presence of a granite terrain (Schwalbaum, 1997). For instance, the author has reported that the pH of groundwater systems can be below pH 6.0 or 5.0 such as in glacial aquifers of the United States midwest or northeast. This concurs with the reported pH values which show that groundwaters can possess a pH as low as 4.2 (Table 2.11). Acidic water can be problematic in that it may acquire high concentrations of heavy metals including copper and lead from water piping systems whereby plausibly resulting in high heavy metal levels leading to human health hazards (Schwalbaum, 1997). Dissolved inorganic compounds including calcium, magnesium, sodium, potassium, bicarbonate, sulfates and chlorides are in greater abundance in comparison to iron, carbonate, nitrate, fluoride and boron in groundwater systems (Schwalbaum, 1997). However, the author specifies that iron and manganese may be more prevalent than calcium and magnesium in acidic groundwaters (such as those resulting from granitic environments). In addition, Hoigné and Bader (1994) have reported that iron (II) and manganese (II) ions can be present in reduced groundwaters or in stratified lake and reservoir hypolimnions. Amy *et al.* (1994) had found that bromide as well as chloride levels in lakes (or reservoirs) were observed to

be lower than those of rivers and groundwaters and attributed this to the unique hydrological constitution of lakes.

Because solar radiation will produce temperature variations upon the terrestrial surface, the type of overlying surface environment as well as the groundwater depth location will influence the range of temperatures over which groundwater temperatures will vary (Bowen, 1986). The author reports that a groundwater which lies beneath a clear area may experience greater annual temperatures and temperature ranges than those beneath a wooded area most probably due to the absence of shade and a layer of organic matter capable of insulating the groundwater from temperature variations. Mazor (1991) has reported that groundwaters can also have temperatures which are either a few degrees above freezing or near boiling point temperatures. To a great extent, this disparity has been attributed by the author to groundwater circulation depth differences and local heat gradient levels. Often, groundwater temperatures will reflect the heat exchanges which take place on the surface of the Earth governed by incoming and outgoing radiation, heat conduction, evaporation, convection as well as chemical and thermonuclear processes occurring in rocks (Matthess and Harvey, 1982). Hydrological conditions and groundwater type can explain certain temperature differences where groundwaters are colder (i.e. in high altitudes and mostly due to snow melt recharges), of similar temperatures (i.e. shallow water cycles circulating at a depth less than 100 m or, infrequently, 200 m) or more than 6°C warmer (i.e. water cycles circulating at considerable depths) than local annual surface temperatures (Mazor, 1991).

While groundwaters tend to possess higher alkalinity and hardness levels compared to rivers and lakes, groundwater organic matter levels will typically be lower (Table 2.11). Organic carbon in natural environmental systems is comprised of dissolved organic carbon (DOC) and particulate organic carbon (POC) substances (Christman *et al.*, 1989). Aquatic organic carbon results from the soil, aquatic microorganisms, and from the contact between water with growing or decaying vegetation from the soil organics (Christman *et al.*, 1989). The DOC component is made up of hydrophobic-acids, -bases and -neutrals and hydrophilic-acids, -bases and -neutrals (Leenheer, 1981). Hydrophobic acids generally consist of humic substances (Aiken, 1985).

Aiken *et al.* (1985) define humic substances as “naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight, and refractory”. There are three primary divisions of humic substances (Aiken *et al.*, 1985): Humin (those which are not soluble at any given pH), fulvic acid (those which are soluble at all pH levels) and humic acids (those which are not soluble in acidic waters, below pH of 2 while they are increasing soluble with higher pH levels). Because dissolved humin does not exist, dissolved humic substances consists of dissolved fulvic and humic acid portions (Malcolm, 1991).

Surface and groundwaters display different DOC concentration levels and DOC composition. It was observed that the DOC levels in groundwaters are lower than those in surface waters. Water will enter the soil surface infiltrating the unsaturated

zone (vadose zone) where soil moisture will provide a considerable barrier to the organic matter at the surface (Thurman, 1985). In addition to DOC levels differences between surface and groundwaters (Table 2.11), greater DOC levels and UV absorbances can result for reservoirs in comparison to river waters (Martin-Mousset *et al.*, 1997). In a study conducted in France, the researchers observed that DOC concentrations for a number of reservoirs to be between 6.8 and 7.8 mg C/L and the DOC levels were between 2.8 and 5.3 mg C/L for the tested rivers samples. The higher reservoir DOC levels were attributed to the transport to the reservoir of terrestrial organic matter and the presence of nitrogenous and phosphoric salts which promote eutrophication whereby increasing the its DOC content.

Hayes *et al.* (1989) report that DOC levels will also vary with respect to climatic zone. DOC concentrations are expected to be greater during the spring months when the soil is damp (Thurman, 1985). He discusses that during the spring runoff in northern temperature climates, the organic matter is cleansed from soil and plant systems in the unsaturated zone. This washing water contains organic carbon and humic substances may be transported to rivers and streams via surface water or may enter the groundwater saturated zone whereby being a significant organic carbon provider to surface and groundwater systems (Thurman, 1985).

Malcolm (1991) described the DOC distribution for rivers and for groundwaters in the United States as shown in Figures 2.3 and 2.4 respectively. It was found that the rivers consisted of about 50% humic compounds (i.e. 45% fulvic acids and 5% humic acids) while the groundwaters consisted of 14.5% humic substances (i.e. 13% fulvic

Figure 2.3 Surface Water DOC Distribution in U.S. Rivers (Malcolm, 1991)

Figure 2.4 Groundwater DOC Distribution in U.S. Aquifers (Malcolm, 1991)

acids and 1.5% humic acids). In their study, Martin-Mousset *et al.* (1997) found that humic substances made up between 51 to 62% of the DOC of the tested reservoir waters while they were found to represent a smaller percentage (between 41 and 50%) of the DOC found in the tested river waters. Apart from the seldom cases where the groundwater contamination is appreciable resulting in the DOC contaminant percentage to be high and notably variable, usually 100% of groundwater DOC is inherently made up of natural organic components (Malcolm, 1991). The DOC of surface waters are less hydrophilic than that of groundwaters (Figures 2.3 and 2.4).

Hence, one would generally expect that applying the same chlorine dioxide dose to a surface and a groundwater would result in greater DBP formation in the surface water due to the higher organic carbon content (and higher humic substance content) found in the surface water.

Thurman and Malcolm (1981) observed that groundwater humic substances consisted of more carbon but less oxygen than those of surface waters. While groundwater humic substances were, on average, comprised of about 60% carbon and 30% oxygen, these percentages for surface water humic substances were found to be on average about 56% and 39% respectively. Thurman (1985) summarizes two hypotheses from his previous research (Thurman, 1979) which could explain the elemental composition differences between the two water types. He suggested that kerogen, which is a source of humic substances in groundwaters, may result from the deposition of organic material with sediments in an aquifer. Since kerogen consists of aliphatic carbon, groundwater humic substances would have a higher carbon

composition than those in surface waters. Secondly, he proposed that microbes may be utilizing humic oxygen as an electron acceptor in anaerobic aquifer conditions resulting in a reduced amount of oxygen present in humic substances of groundwaters.

Whether surface or groundwaters, fulvic acids will constitute the major contributor of organic matter in colored waters (Rook, 1977). Humic substances in groundwater are observed to be less colored per carbon unit than those in surface waters (Thurman, 1985). The reduced color content implies that groundwaters accommodate a lesser amount of chromophores like conjugated double bonds, aromatic rings and phenolic groups (Thurman, 1985). Hence, due to smaller amounts of chromophores, groundwaters would likely display smaller changes in UV_{254} than surface waters which would conceivably have more “reactive” (as measured by UV_{254}) organic content levels.

Upon analyzing a number of different groundwaters in the state of Kansas, Miller *et al.* (1990) found that, even though groundwaters can contain less organic matter than surface waters, their THMFP can also warrant attention especially if lower THM standards were to be set. The authors found that 8% of 50 groundwater samples sites had a THMFP which was greater than 100 $\mu\text{g/L}$ while 56% were greater than 25 $\mu\text{g/L}$ and 90% were greater than 10 $\mu\text{g/L}$. It was noticed that the alluvial aquifers (i.e. aquifer composed of silt, gravel or sand having a depth less than 200 ft or 60.96 m) contained the higher levels of TOC and THMFP (upon chlorination) compared to the unconsolidated and consolidated aquifer and that alluvial aquifers which contained high levels of TOC, ammonium, iron and manganese were at particular risk.

2.7 Research Needs

Upon review of the available literature, some research needs have been identified and are as follows:

1. Evaluation of the effects of various parameters such as pH, temperature and factors which relate to the chlorine dioxide treatment process (i.e. reaction time) on DBP formation resulting from the application of chlorine dioxide to surface or groundwaters has not been significantly researched.
2. While the need to provide a properly-operated chlorine dioxide generator system has been identified, the effects of chlorine dioxide-related contaminants on the formation of DBPs has not been well documented. By assessing the influences of these contaminants on DBP formation, utilities could identify the appropriate chlorine dioxide generator efficiency and treatment conditions which could minimize DBP production and meet regulatory standards.
3. DBP forecasting models in terms of water quality variables and chlorine dioxide treatment parameters is lacking in the literature for surface and groundwaters. The development of such models should help treatment facilities utilizing chlorine dioxide to optimize their treatment systems so as to minimize DBP formation.
4. The evaluation of whether changes in water UV absorbance (measured at 254 nm) can be correlated to chlorine dioxide DBP formation or chlorine dioxide consumption has not been reported in the literature. If such correlations can be provided, utility plants could use information resulting from these trends to predict DBP formation or chlorine dioxide consumption.

CHAPTER 3

EXPERIMENTAL DESIGN

3.1 Overview of Research Objectives

The primary aim of this research was to develop equations which may be used to predict DBP concentrations on the basis of physical-chemical and chlorine dioxide-related disinfection parameters. This was achieved by investigating the effects of physical-chemical parameters on the formation of by-products upon disinfecting with chlorine dioxide by conducting bench-scale factorial experiments using both, “synthetic” and natural waters.

The main objectives of the research consist of the following:

- Objective 1. To investigate the effects of various parameters on the formation of DBPs when disinfecting with chlorine dioxide. The factors examined include pH, temperature, chlorine dioxide: non-purgeable organic carbon content, reaction time, chlorine and chlorate concentrations (from the chlorine dioxide generation process).
- Objective 2. To develop empirically-based equations which are capable of describing DBP formation and which include parameters effects observed to be significant in chlorine dioxide DBP formation.
- Objective 3. To examine whether changes in ultraviolet absorbance (measured at 254 nm) upon applying chlorine dioxide to natural waters can be correlated to chlorine dioxide consumption as well as chlorine dioxide-related DBP formation.

3.2 Outline of Experimental Design

The following section pertains to the experimental approach undertaken to address each objective. The DBPs examined during the evaluation of all three research objectives are shown in Table 3.1. In addition to the typical chlorine dioxide-related inorganic DBPs (i.e. chlorite and chlorate), selected organic DBPs also included those regulated by the proposed D/DBP Rule (i.e. TTHMs and HAAs).

The experiments designed herein (i.e. to address Research Objectives 1 and 2) mainly focused on investigating significant main effects (i.e. those due to individual factors such as pH, temperature, etc.) and two-factor interaction effects (i.e. those due to factor interactions such as pH-temperature, temperature-reaction time) on organic and inorganic DBP formation. As discussed by Box *et al.* (1978), there is a tendency toward an effect hierarchy with respect to the absolute magnitude of factor effects: Main factor effects have a tendency to be greater than 2-factor interactions effects which, in turn, have a tendency to be greater than 3-factor interactions effects, etc. The authors further stated that higher-order interactions can often result in negligible effects and thus, be deemed as insignificant.

3.2.1 Experimental Design - Research Objective 1

A number of physical-chemical factors will affect DBP formation when disinfecting with chlorine dioxide (as described in Section 2.3.3). The main parameters which were investigated to address Research Objective 1 are listed in Table 3.2.

The selected experimental design strategy involved conducting “2-level factorial design” experiments to “screen” selected variables for main and 2-factor interactions

Table 3.1 DBPs and Disinfectant Residual Investigated

Product Type	Compound
Inorganic	Chlorite Chlorate
Organic	TTHMs ^{a,b} HAA ₉ ^c
Disinfectant Residual	Chlorine dioxide

^a TTHMs were examined in Research Objectives 1 and 2.

^b TTHMs = Chloroform, bromodichloromethane, dibromochloromethane, bromoform.

^c HAA₉ = Monochloroacetic-, dichloroacetic-, trichloroacetic-, monobromoacetic- and dibromoacetic acid, tribromoacetic acid, chlorodibromoacetic acid, bromodichloroacetic acid and bromochloroacetic acid.

Table 3.2 Experimental Factors and Levels Investigated in Factorial Experiments of Research Objective 1

Factor	Parameter Values ^a		
	Low Level	"Centerpoint" Level	High Level
pH	5	7	9
Temperature (°C)	4	14.5	25
Chlorine Concentration (mg/L) - Factorial #1 (5.95 mg/L NPOC) - Factorial #2 (2.09 mg/L NPOC)	0 0	0.2 (3.36, NA, NA) 0.07 (3.35, NA, NA)	0.4 (6.72, 22.4, 6.11) 0.14 (6.70, 22.3, 6.09)
Chlorine Dioxide:NPOC Ratio (%)	30	70	110
Chlorate Concentration (mg/L) - Factorial #1 (5.95 mg/L NPOC) - Factorial #2 (2.09 mg/L NPOC)	0 0	0.1 (1.68, NA, NA) 0.035 (1.67, NA, NA)	0.2 (3.36, 11.2, 3.06) 0.07 (3.35, 11.2, 3.04)
Reaction Time (hr)	1	12.5	24

Note: NA = Not applicable

^a Values in parentheses represent concentrations as percentages of NPOC, low and high applied chlorine dioxide concentrations respectively.

effects on DBP formation deemed significant at the 95% confidence level. This approach differed from the One-Factor-At-A-Time (OFAT) method since it allows the simultaneous variation of individual factors in each experimental run. An advantage of factorial designs is that they allow the estimation of additive variable effects along with the calculation of variable interactions or nonadditive effects (Box *et al.*, 1978). Montgomery (1997) reported that since the effect caused by a variable is observed at various levels of the other variable parameters, conclusions which are drawn from the results can be applicable over a range of experimental conditions.

As reported by Box *et al.* (1978), when considering a two-level factorial design, the effect of a parameter on DBP formation is obtained by varying this factor from a “low” to “high” level (Table 3.2). The investigation of the complete 2-level combination possibilities for the selected 6 variables would have typically required 64 runs (i.e. 2^6) for each water source under examination. Instead of performing all possible parameter combinations when one is examining four or more factors, Montgomery (1997) suggests conducting a *fractional* factorial design which consists of a *fraction* of the maximum number of runs that may be performed. Such a design reduces the number of necessary runs and provides for a more time-efficient and economical experimental strategy, sacrificing mainly higher-order interaction effects which are expected to have minimal importance on DBP formation. To this end, a 2^{6-2} fractional factorial design was utilized. Ultimately, by conducting 16 experimental runs (i.e. $\frac{1}{4}$ fraction of the 64 possible run combinations), all six parameters were examined with respect to DBP formation. A 2^{6-2} factorial experiment can be referred to

as a Resolution IV fractional design whereby each main parameter is respectively “aliased” (i.e. its effect on DBP formation is confounded with another effect) with 5-factor interaction effects (Montgomery, 1997). However, 5-factor interactions were assumed to be negligible with respect to DBP formation thus allowing main factor effects to be identified.

The fractional factorial design formulation caused 2-factor interactions to be confounded with other 2-factor interactions. For instance, if the pH-chlorine dioxide:non-purgeable organic carbon (NPOC) ratio and temperature-reaction time were found to be significant with respect to chlorite formation (at the 0.05 P-value level), it would not be possible to assess with any confidence which 2-factor interaction has caused the observed significant effect without further experimental testing. This being the case, 2-factor interaction results were mainly assessed on a qualitative basis to determine whether they should be included in the later development of DBP predictive models.

Three centerpoints, consisting of midpoints between the low and high levels for each parameter value, were also added to the design (Table 3.2). The purpose of employing centerpoints was two-fold: Providing an estimate of pure error and allowing the assessment of whether curvature was exhibited by the DBP formation data with respect to the parameter variations from their given “low” to “high” levels.

The above-mentioned experimental design was performed using two “synthetic” waters of different NPOC content: ≈ 6.0 mg/L (consistent with NPOC levels found in surface waters), and ≈ 2.0 mg/L (consistent with groundwater NPOC levels). These waters were prepared by adding an appropriate amount of commercial humic acid to

organic-free reagent water to which pH, temperature, chlorine dioxide:NPOC ratio, chlorine concentration, chlorate concentration and reaction time initial parameter levels have been adjusted (Table 3.2) in accordance with “typical” levels reported in the literature (see Table 2.11, Section 2.6.2, Chapter 2).

Although surface and groundwaters may differ in their composition, the same “low” and “high” parameter levels were examined for each water regardless of type and source (Table 3.2). This was done to ensure consistent results, eliminate confounding effects due to different parameter levels for different water sources and allow meaningful water source data comparisons to be made. Also, addressing parameter value ranges encompassing water quality characteristics of both water source types would serve to capture waters of “atypical” composition: Surface waters having water quality characteristics more typically encountered in groundwaters or vice-versa. The “low” pH level of 5 was chosen to reflect groundwaters which could be found in basaltic rock regions. The selected temperature range captured variations for Canadian or Northern American surface water systems. The levels for the other four parameters are associated with the application of chlorine dioxide as a primary disinfectant (generation, dosing, and contact time) and as such, would be similar for both water sources. It should be noted that while similar chlorine dioxide:NPOC ratios were used, because groundwaters typically contain less organic matter than surface waters, their applied chlorine dioxide doses will consequently also be less. The “high” chlorine and chlorate concentration levels represented concentrations which may result from a “non-optimal” chlorine dioxide generation process. Chlorite concentration was not included as a formal factor since chlorite concentrations resulting from chlorine dioxide

generation are relatively insignificant (i.e. 0-5% of chlorine dioxide dosing concentration) when compared to the chlorite which is reported to be produced from chlorine dioxide consumption (typically 50-70% of the chlorine dioxide consumed, see Table 2.6, Chapter 2 for experimental conditions).

Randomization of the trial runs including centerpoints was conducted to ensure the integrity of the factorial design and that uncontrollable factors did not systematically influence the observations or experimental errors associated with the DBP response concentrations (Table 3.3). All 16 experimental runs conducted for a particular source water were performed during the same experimental session. The design and analyses of the factorial experiments were conducted using Design Ease®, a statistically-based software package (Stat-Ease Inc., 1994). An example of its application is presented in Appendix B to provide the reader with a better understanding of the statistical analysis. For additional concepts and details concerning factorial designs, the texts by Box *et al.* (1978) and Montgomery (1997) are recommended. Methods and procedures pertaining to i) the preparation of the synthetic waters and ii) adjustments of parameter level conditions examined during the factorial experiments are presented in Section 4.5 (Chapter 4).

3.2.2 Experimental Design - Research Objective 2

The main focus of this objective consisted of modeling the main chlorine dioxide inorganic by-products (chlorite and chlorate), as well as chlorine dioxide consumption when the disinfectant is applied to raw natural water sources. Since haloacetic acid formation was observed during the synthetic water experiments, HAA

Table 3.3 Randomized Run Arrangement for the Fractional (2^{6-2}) Factorial Experiment - Designed to Address Research Objective 1

Run Number	Factor					
	pH	Temperature	Chlorine Dioxide:NPOC	Chlorine	Chlorate	Reaction Time
1	-1 ^a	+1 ^a	-1 ^a	-1 ^a	-1 ^a	-1 ^a
2	-1	-1	-1	-1	+1	+1
3	-1	-1	-1	+1	+1	-1
4	+1	+1	+1	-1	-1	+1
5	-1	-1	+1	+1	-1	+1
6	-1	+1	+1	-1	+1	+1
7	+1	+1	+1	+1	-1	-1
8	0	0	0	0	0	0
9	-1	+1	-1	+1	-1	+1
10	+1	-1	-1	+1	-1	-1
11	+1	-1	+1	-1	+1	-1
12	0	0	0	0	0	0
13	-1	+1	-1	-1	+1	-1
14	-1	+1	+1	+1	+1	-1
15	+1	-1	+1	+1	+1	+1
16	-1	-1	+1	-1	-1	-1
17	+1	-1	-1	-1	-1	+1
18	0	0	0	0	0	0
19	+1	+1	-1	+1	+1	+1

^a The “-1”, “+1” and “0” respectively represent the factor at its low, high and midpoint value level.

formation was monitored to investigate whether they would form upon chlorine dioxide dosing to natural water matrices. Based on data reported in the literature by various researchers (see Section 2.3.3, Chapter 2), and the preliminary factorial experiment results (see Section 5.7, Chapter 5), trihalomethane formation resulting from chlorine dioxide action is known to be limited. For these reasons, THM formation was only monitored for the duplicated experimental runs (i.e. two pairs) per investigated water source. Attempts were also made to measure bromate formation but experimental difficulties due to analytical interferences caused by the applied phosphate buffer for pH control could not be overcome, thus rendering bromate analysis unfeasible.

The “experimentally-controllable” parameters included in the predictive DBP formation models are reported in Table 3.4. It is believed that the selected parameters were consistent with physical-chemical water quality parameters reported in the literature which are known to influence DBP formation when applying “pure” chlorine dioxide (see Section 2.4, Chapter 2). It is further thought that the parameter selection is in agreement with main parameter and 2-factor interaction identified as significant with respect to chlorite, chlorate and HAA formation during the synthetic water experiments (Chapter 5). Based on the preliminary data, it appeared that expressing chlorite and chlorate formation in terms of the chlorine dioxide demand and organic content separately was more appropriate than expressing these DBPs in terms of a ClO_2 :NPOC ratio. Although organic content can be regarded as an inherent characteristic of each water and thus, cannot be experimentally-controlled like the other parameters listed in Table 3.4, the organic content of each water was monitored in

**Table 3.4 Experimental Factors and Levels Investigated in Factorial Experiments
- Research Objective 2**

Factor	Parameter Values	
	Low Level	High Level
pH	6	9
Temperature (°C)	4	25
Chlorine Dioxide Concentration (mg/L)	1.0	6.0
Reaction Time (hr)	1	24

terms of NPOC as well as UV_{254} and these parameters were also incorporated in the DBP predictive models.

As for the experiments conducted on synthetic waters, the experimental approach followed for the purpose of developing model equations predicting chlorine dioxide consumption, chlorite and chlorate formation in natural waters utilized of a factorial design. In this design, a 2^4 (2 levels, 4 factors) full factorial experiment was performed for each of natural water matrix selected for investigation. The main advantages of this type of design were that main parameters as well as 2-factor interactions which exhibited significant effects on chlorine dioxide consumption as well as chlorite and chlorate formation, could be identified and included in the predictive models. Since the selected experimental design consisted of a full factorial, there were no 2-factor interaction aliasing problems as encountered during the fractional factorial experiments performed on the synthetic waters. Also, this type of design was more time and resource efficient. Since curvature in the chlorite and chlorate data was not found to be significant on a practical basis during the synthetic water experiments (Section 5.9 and Table 5.7, Chapter 5), it was hypothesized that the selected 2-level factorial design would provide the necessary information to develop proper model equations which may be used to predict DBP formation.

The selected “low” and “high” value levels for each investigated parameter (Table 3.4) were based on conditions expected to be encountered in water treatment and were generally consistent with those selected for the factorial designed experiments associated with Research Objective 1. The major difference was that specific chlorine dioxide doses (1.0 and 6.0 mg/L) were applied to each given natural water matrix

(regardless of water organic content). The given chlorine dioxide dose selections provided experimental conditions where organic content (as measured by NPOC) would be greater than the applied chlorine dioxide dose (for the 1.0 mg/L ClO_2 cases) as well as conditions where NPOC would be less than the applied dose (for the 6.0 mg/L ClO_2 cases).

Based on a survey of data from the Ontario Drinking Water Surveillance Program for the period of 1990-1996 provided by the Ministry of Environment and Energy (MOEE), eight natural waters (seven surface waters and one groundwater) were selected so as to represent a wide array of water quality parameter conditions (Table 3.5). The relative geographical locations of the various waters in the province of Ontario are shown in the map depicted in Figure 3.1. The major focus of water selection rested in choosing waters which differed in their organic content levels (expressed as NPOC). The number of water sources (i.e. eight) selected served to provide a more “balanced” statistical analysis in regard to pure error estimation and data “pooling” assessment (both concepts further discussed in this section), given the selected 2^4 factorial design (i.e. 16 trial runs conducted on each natural water).

The factorial experiment trial order which was followed for each natural water is reported in Table 3.6. Trial run randomization was conducted to secure the integrity of the factorial design. While duplication of each trial run would be difficult and time-consuming, two trial runs (said to be “complimentary” since one trial run examined “contrasting” parameter levels of those examined in the other trial run) for each test water were duplicated (see Tables 3.6 and 3.7) to provide an estimation of pure error.

Table 3.5: Summary of Selected Parameter Concentrations for Raw Water Sampling Sites (Monitoring Period: 1990-1996)^{a,b}

Treatment plant	Source	DOC (mg/L)	pH	Alkalinity (mg/L CaCO ₃)	Turbidity (FTU)	Color (TCU)	Iron (µg/L)	Manganese (µg/L)
Brantford	Grand River via Homedale Canal	2.9-7.3 (5.0)	8.08-8.55 (8.36)	147.9-280.6 (207.6)	0.27-96.1 (13.4)	11-38.2 (19.4)	53-670 (232)	3.8-63 (27.8)
Kitchener (Mannheim)	Grand River	3.5-7.8 (5.7)	8.15-8.52 (8.33)	166-281.7 (218)	1.11-130 (14.52)	12-34.5 (14.12)	56-760 (225.6)	10-150 (34.7)
Ottawa (Britannia)	Ottawa River	5.6-6.7 (6.1)	7.07-7.98 (7.61)	17.5-35.5 (24.2)	0.92-15.2 (3.10)	24.6-43 (33.16)	73-790 (179)	5.6-65 (12.9)
Belleville	Bay of Quinte	4.7-6.5 (5.6)	7.96-8.4 (8.19)	89.6-124 (108)	0.45-8.0 (2.80)	10.5-25.4 (17.8)	6.0-2000 (133)	0.32-230 (31.1)
Metro Toronto (R.L. Clark)	Lake Ontario	1.5-2.4 (1.9)	8.11-8.50 (8.25)	96.5-105.7 (100.6)	0.32-13.6 (1.96)	0.50-4.00 (1.83)	6.00-180 (36.1)	0.15-11.0 (3.19)
Windsor	Detroit River	1.4-3.5 (1.9)	8.08-8.42 (8.22)	81.2-143.6 (92.0)	0.93-68 (16.0)	0.2-18.2 (2.17)	22-1700 (272)	1-38.9 (11.0)
Kitchener Well Supply	Groundwater	0.4-2.6 (0.97)	7.84-8.43 (8.10)	230.9-378.6 (300.8)	0.01-2.22 (0.58)	0.2-76.5 (3.72)	6.0-690 (59.8)	9.7-500 (104.7)
Peterborough	Otonabee River	4.5-6.0 (5.25)	7.89-8.28 (8.13)	69.8-95.5 (82.4)	0.42-2.10 (1.17)	10.5-22.5 (15.0)	22.7-78 (41.7)	6.3-74 (18.81)

^a Range of reported values constitute minimum to maximum values while values in parentheses represent average values

^b Reported values constitute measurements obtained at the MOEE laboratories.

Figure 3.1 Geographical Locations of Selected Raw Water Sources in Ontario
(Not to Scale)

Table 3.6 Randomized Run Arrangement for the 2⁴ Factorially-Designed Experiment - Research Objective 2^a

Run Number	Controllable Factor			
	pH	Temperature	Chlorine dioxide Concentration	Reaction Time
1	-1 ^b	+1 ^b	+1	+1
2 ^c	-1	-1	+1	+1
3	+1	-1	-1	-1
4	-1	-1	+1	-1
5	-1	+1	+1	-1
6	+1	+1	-1	+1
7 ^c	+1	+1	-1	-1
8	+1	-1	-1	+1
9	-1	+1	-1	-1
10	+1	+1	+1	+1
11	-1	-1	-1	+1
12	+1	+1	-1	-1
13	-1	-1	+1	+1
14	+1	-1	+1	-1
15	-1	+1	-1	+1
16	-1	-1	-1	-1
17	+1	+1	+1	-1
18	+1	-1	+1	+1

^a Reported duplicated runs are associated with the Brantford water experiment.

^b The “-1” and “+1” respectively represent the factor at its low and high level.

^c Typically, trial runs #2 and #7 were duplicates of the “complimentary” runs.

Table 3.7 Duplicated Trial Runs for Given Water Source - Research Objective 2

Water Source ^a	Duplicated Trial Runs ^b
#1: Brantford	#12 and #13
#2: Ottawa	#9 and #18
#3: Windsor	#11 and #17
#4: Toronto	#10 and #16
#5: Peterborough	#1 and #3
#6: Belleville	#14 and #15
#7: Mannheim surface	#4 and #6
#8: Mannheim groundwater	#8 and #5

^a The ordinal preceding each reported water source refers to the experimental testing order which was followed.

^b Reported trial run numbers refer to the run numbers (and associated parameters conditions) displayed in Table 3.6.

For example, the trial run examining *high* pH, *low* temperature, *low* ClO₂ dose and *high* reaction time conditions can be viewed as “complimentary” to the trial run examining *low* pH, *high* temperature, *high* ClO₂ dose and *low* reaction time conditions. The choice of “complimentary” trial runs ensured that the factorial design maintained its orthogonal property (i.e. balanced array of low and high levels). It was believed that duplication of actual trial runs of the factorial experiment would be more representative of pure error than replication done at only one combination of parameter conditions or at parameter conditions “external” to those part of the factorial experiment such as parameter centerpoint conditions observed during the synthetic water experiments (Chapter 5). The “complimentary” trial runs duplicated during each test water are given in Table 3.7. The different water matrices were tested according to the order reported in Table 3.7. Hence, because two complimentary runs were duplicated during each of the eight water source experiments, each trial run could be duplicated in the 2⁴ factorial design (i.e. 2 trial runs * 8 water sources = 2⁴ or 16 sets of duplicated trial runs). The data resulting from the duplicated trial runs were “pooled” and standard error for various measurements (chlorine dioxide, DBPs and UV₂₅₄) were individually calculated. Additional details as well as a sample calculation of pure error are reported in Appendix F.

Development of predictive model equations was conducted using experimental data pooled from all eight factorially-designed experiments. Hence, unless otherwise noted, each model equation was developed from a data base of 128 different responses. Simple linear regression analyses were conducted on chlorine dioxide consumed,

chlorite and chlorate data with respect to different precursor-related parameters (and combinations thereof) to determine which terms would be adequate in describing water organic content and thus, be included in the predictive models.

Model development was accomplished by performing stepwise multiple linear regressions on the various parameters to obtain term coefficients fitting a Generalized Linear Model (GLM). The reader is directed to consult books by Miller (1990) and Montgomery (1997) for greater detail concerning GLM. Identification of significant effects on chlorine dioxide consumption and chlorite and chlorate formation consisted mainly of the investigation of main as well as 2-factor interaction effects. To examine whether “data pooling” effects may result from “pooling” the results for all eight waters, each water was “coded” with a specific mathematical combination (Table 3.8). Hence, by including these three “pooling factor-codes” (reported for illustrative purposes in Table 3.8 as P1, P2 and P3), significant effects caused by “data-pooling”/water site-specificity (as well as the extent of their significance) could be identified and dealt with by incorporating 2-factor interaction effects involving the water organic content term (elaborated further in Chapter 6).

Each developed equation was tested as to whether the assumptions of error normality, constant variance and independence required by linear regression were met. The log-transformation (base 10) was applied to both the independent (i.e. chlorine dioxide consumed, chlorite and chlorate data) as well as to each dependent variable to more adequately meet the assumption of constant variance. Greater details concerning the statistical analyses involved during model equation development are presented in Chapter 6. Statistical analyses were conducted primarily using Minitab® for Windows

**Table 3.8 Coding Arrangement for Each Water Source Under Examination
- Research Objective 2**

Water Source	3-Level Coding		
	P1	P2	P3
Brantford	–	–	–
Ottawa	+	–	–
Windsor	–	+	–
Toronto	+	+	–
Peterborough	–	–	+
Belleville	+	–	+
Mannheim surface	–	+	+
Mannheim groundwater	+	+	+

Note: Factors P1, P2 and P3 are pooling factors employed to assess if any “data pooling” effects with respect to chlorine dioxide consumption, chlorite and chlorate formation exist.

Student Version, Release 9 statistical package (Minitab Inc., 1995). Design Ease®, Version 3.0.0 (Stat-Ease Inc., 1994) and Excel® (Microsoft Office, version 7.0 for Windows 95) were also employed for simple statistical analyses and various spreadsheet calculations (Excel® only).

Model validation was accomplished by conducting “internal” as well as “external” model validation. Internal model validation involved comparing measured values (from the original data base) to predicted values obtained from the predictive model equations. Data used for “external” model validation were obtained from published reports found in the literature as well as from experiments performed at the University of Toronto. For the external validation based on experimental results, four surface water sources were investigated (Table 3.9): One each from Vancouver (B.C.), Calgary (AB), Brantford (ON) in Canada and Ann Arbor (MI) in the United States. The factor levels which were examined are reported in Table 3.10. Further description and details concerning internal model validations and the external validation experiment are given in Chapter 6.

Equations which may be used to predict chlorite and chlorate formation on the basis of chlorine dioxide consumption estimates were also developed and assessed as to their predictive abilities. Chlorine dioxide to chlorite and chlorate conversion ratios (on a mass basis) were estimated. The “robustness” of these conversion ratios to variations in parameter conditions (pH, temperature, chlorine dioxide concentration and reaction time levels) as well as water sources were assessed via the development of F-statistics (detailed in Chapter 6 and Appendix J). Also, the contributions of all the different parameters involved in the predictive model equations to the “explanatory

Table 3.9 Water Sources Examined During External Validation Experiment

Water Treatment Plant Source	Water Source	NPOC (mg/L)	UV ₂₅₄ (cm ⁻¹)
Vancouver (B.C.)	Seymour Reservoir	1.47	0.043
Calgary (AB)	Glenmore Reservoir from Elbow River	2.05	0.045
Brantford (ON)	Grand River	4.83	0.121
Ann Arbor (MI, USA)	Huron River	5.10	0.141

Table 3.10 Factor Levels Investigated During External Validation Experiment

Parameter	Investigated Level(s)
pH	Ambient
Temperature (°C)	(4 and 20) ^a (6 and 20) ^b
Chlorine Dioxide Concentration (mg/L)	1.51
Reaction Time (hr)	1 and 4

^a Levels investigated for the Calgary, Brantford and Ann Arbor waters.

^b Levels investigated for the Vancouver water only.

power” (defined and further discussed in Chapter 6) of the given equations were also evaluated through statistical means (sample calculation provided in Appendix I).

Methods and procedures pertaining to i) the preparation of the raw waters and ii) adjustments of parameter level conditions examined during the factorial experiments are presented in Section 4.5 (Chapter 4).

3.2.3 Experimental Design - Research Objective 3

The purpose of this research objective was to assess whether chlorine dioxide consumption as well as chlorite, chlorate, or dichloroacetic acid (DCAA) formation can be correlated to changes in (Δ) UV_{254} under various experimental conditions (Table 3.4) such that UV_{254} may be utilized as their sole predictor variable. The investigation of chlorine dioxide consumption as well as chlorite, chlorate and DCAA formation with respect to changes in UV_{254} was conducted via simple linear regression analyses using Excel® spreadsheets (Microsoft Office, version 7.0 for Windows 95). Changes in UV_{254} consisted of subtracting the UV_{254} measured of an oxidized sample for each trial run from the specific UV_{254} measurement obtained from a non-oxidized sample having the pH and temperature conditions as the oxidized sample of interest. Changes in UV_{254} which were smaller than experimental noise were set to a value of 0.001 cm^{-1} (see Section 6.5, Chapter 6 for details). Due to possible UV interferences caused by the presence of chlorite, correlations involving UV_{254} measurements of the oxidized samples which were corrected to account for the chlorite interference (see Section 4.4.1, Chapter 4 and Section 6.5, Chapter 6) were produced. These last correlations were then compared to correlations involving UV_{254} measurements *not* adjusted for

chlorite UV interferences to assess whether the provided UV corrections significantly affected the given different correlations.

Methods and procedures pertaining to UV_{254} measurements (including chlorite correction equation) are discussed in Section 4.4.1 (Chapter 4). Details concerning the statistical procedure analyses are elaborated upon in Section 6.5 (Chapter 6).

CHAPTER 4

MATERIALS AND METHODS

A summary of the analytical methods (including brief descriptions) is presented in Table 4.1. The minimum reported levels (MRLs) for the DBPs under examination in this study are reported in Table 4.2. Flowcharts detailing the procedures to prepare stock solutions and to measure particular DBPs have been included in Appendix C. A quality assurance/quality control (QA/QC) program which included instrument calibration curves and QA/QC charts verifying analyte recoveries was followed. Typical calibration curves and QA/QC charts have been provided in Appendix C.

4.1 Analytical Reagents and Glassware

Reagent water utilized in the experiments was obtained by passing distilled water through a Millipore Milli-Q® filtration UV-Plus system (Millipore Corporation, Bedford, MA). The electrical resistance of the reagent water was never below 18.2 MΩ·cm.

Unless otherwise specified, reagents employed during experimental testing conformed (at the least) to the minimum reagent grade specified by the analytical method of interest. The humic acid, sodium salt technical grade reagent used in the synthetic water experiments was purchased from Aldrich Chemical Co. (Milwaukee, WI). Chlorate standard solution was prepared as recommended by EPA Method 300.0, using sodium chlorate (purity > than 99%) obtained from Aldrich Chemical Company Inc. (Milwaukee, WI). Also as suggested by EPA Method 300.0, the chlorite standard solution was prepared from sodium chlorite (BDH Inc. Toronto, ON). However, since

Table 4.1 Summary of Analytical Methods Employed During Laboratory Testing

Parameter	Analytical Method	Method Description
Chlorine Dioxide	As per Sterling Pulp Chemicals Ltd. (Toronto, ON) ACVK ^a	<ul style="list-style-type: none"> - Sodium thiosulphate titration in the presence of potassium iodide at pH 7.6 and pH 2 - Spectrophotometric analysis using Acid Chrome Violet K (ACVK)
Chlorite, Chlorate and Bromide	USEPA Method 300.0 ^b	<ul style="list-style-type: none"> - Ion chromatographic analysis using a borate H₃BO₃/NaOH eluent^f
TTHM	USEPA Method 551.1 ^c	<ul style="list-style-type: none"> - Liquid-liquid extraction using MtBE as the organic solvent - GC analysis employing ECD
HAA ₉	USEPA Method 552.2 ^d	<ul style="list-style-type: none"> - Liquid-liquid extraction using MtBE then methylation with acidified (sulfuric acid) methanol - GC analysis employing ECD
Chlorine	4500-Cl B ^e	<ul style="list-style-type: none"> - Sodium thiosulfate titration in the presence of potassium iodide
NPOC	5310 C. ^e	<ul style="list-style-type: none"> - Persulfate oxidation using infrared detection
UV ₂₅₄	5910 B ^e	<ul style="list-style-type: none"> - Ultraviolet adsorption measured at 254 nm
pH	As per Manufacturer ^g	<ul style="list-style-type: none"> - Ag/AgCl electrode analysis
Turbidity	As per Manufacturer ^h	<ul style="list-style-type: none"> - Measured as NTU
Alkalinity	2320 B ^e	<ul style="list-style-type: none"> - Sulfuric acid titration
Ammonia	4500-NH ₃ -D ^e	<ul style="list-style-type: none"> - Electrode Method - Standard Additionⁱ
Iron and Manganese	3030 E ^e 3111 B ^e	<ul style="list-style-type: none"> - Nitric Acid digestion - Atomic adsorption using direct air-acetylene flame

^a Developed by Masschelein *et al.* (1989) and investigated by Hofmann *et al.* (1998).

^b In *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA/600/R/93/100, USEPA (1993).

^c In *Methods for the Determination of Organic Compounds in Drinking Water – Supplement I*, EPA/600/4-90/020, NTIS Publ. PB91-146027, USEPA (1993).

^d Method 552.2, Revision 1.0. USEPA (1995).

^e In *Standard Methods for the Examination of Water and Wastewater*, 19th edition (1995).

^f Hautman and Bolyard (1992)

^g VWR Scientific, West Chester, PA

^h Hach Company, Loveland, CO

ⁱ Shugar and Ballinger (1990)

Table 4.2 Summary of Minimum Reporting Levels (MRLs) of Chlorine Dioxide Residual and Disinfection By-Products (DBPs) Investigated

Residual or DBP		MRL (µg/L) ^a
Chlorine Dioxide		40
Chlorite		14
Chlorate		20
TTHM	Chloroform	0.6
	Bromodichloromethane	0.5
	Chlorodibromomethane	0.5
	Bromoform	0.5
HAA ₉	Monochloroacetic acid	1.5
	Dichloroacetic acid	1.0
	Trichloroacetic acid	1.0
	Monobromoacetic acid	1.0
	Dibromoacetic acid	1.0
	Tribromoacetic acid	5.0
	Bromochloroacetic acid	1.0
	Chlorodibromoacetic acid	2.5
	Bromodichloroacetic acid	1.0

^a The reported MRL are "rounded off" values based on MDL values which were determined by (Standard Method 1030E, APHA-AWWA-WEF, 1995; Glaser *et al.* 1981):

$$\text{MDL} = (t) \times (S)$$

Where t = Student t-value for a one-tailed test for a 99% confidence level having N-1 degrees of freedom (i.e. $t = 3.14$ for 7 replicated samples)
 S = Corresponding standard deviation of the N samples
 N = Number of replicated samples

the purity of the sodium chlorite was about 80%, the chlorite standard stock solution was standardized based on a method suggested in an unpublished report by the RioLinda Chemical Company Inc. (Sacramento, CA). The necessary steps to conduct this method (similar to a method employed by Aieta *et al.*, 1984) are reported in Figure C.4, Appendix C. Standards for bromide were prepared with potassium bromide. The standards for total THMs and HAA₉ were each obtained as mixtures of their constituents from Supelco (Toronto, ON). In both cases, the Supelco standard mixtures were prepared in methyl-tert-butyl-ether (MtBE). In addition to the standard solution obtained in mixture form from Supelco for HAA₉, standards for HAA₉ were also prepared from chemicals (solid form) for each individual HAA purchased from Aldrich Chemical Co. (Milwaukee, WI). The standards for iron and manganese were obtained in mixture form (5% nitric acid matrix) from SCP Science (LaSalle, QC). The standard mixture contained not only iron and manganese but also 17 other metals (Q.C. Standard 1, lot number SC 8082305, SCP Science, LaSalle, QC).

Sample vials were cleaned using alkaline detergent, followed by an acid- then tap and deionized water rinses using a Miele Power Set Desinfektor Dishwasher Model G7736. The vials were then rinsed with distilled water prior to being baked at 100°C for a 2-hour time period. Teflon®-lined screw caps with septa were subjected to tap followed by distilled water rinses prior to being baked at 100°C for 2 hours. Glassware (including the 250 mL-amber reactor bottles) employed in chlorine dioxide testing was rendered chlorine dioxide demand-free by soaking the articles in a strong chlorine dioxide solution (i.e. $\approx$ 500-1000 mg/L) and water-rinsed (i.e. tap followed by distilled

water rinses) between uses (Aieta *et al.*, 1984). The reactor bottles and beakers (i.e. not the pipettes, volumetric or Erlenmeyer flasks) were also oven-baked between uses at the same temperature and duration as the sample vials. For added assurance, the 250-mL amber reactor bottles were rendered “chlorine dioxide-ready” as per the above procedure on a periodical basis (i.e. typically if reactor bottles had not been used in a month). Also as suggested by Aieta *et al.* (1984), all chlorine dioxide glassware were kept separately from “general use” lab glassware.

4.2 Chlorine Dioxide

4.2.1 Generation

Chlorine dioxide was generated using a combination of methods proposed by *Standard Methods* (APHA-AWWA-WEF, 1995, Method 2350E), Sterling Pulp Chemicals, Ltd (Toronto, ON) and the Pulp and Paper Research Centre at the University of Toronto (ON). As reported by Andrews *et al.* (1997), the resulting chlorine dioxide generation method culminated in a procedure which improved safety and performance efficiency by incorporating certain aspects and conditions of the previously-mentioned generation techniques. Employing a bench-scale apparatus, chlorine dioxide was formed by slowly mixing a 25% sodium chlorite solution with a 12N sulfuric acid solution. Using a vacuum, the produced chlorine dioxide was purged from the sodium chlorite-sulfuric acid mixture and concentrated in a “chlorine dioxide trap” immersed in a water bath. A potassium iodide (KI) trap was used to react with any escaping chlorine dioxide or chlorine. The resulting chlorine dioxide concentration generally ranged between 2 to 3 g/L, but never exceeded 4 g/L.

Standardization of the chlorine dioxide stock was achieved by following the procedure proposed by Sterling Pulp Chemicals Ltd. (Toronto, ON) and shown in Figure C.1 (Appendix C). In essence, the procedure consisted of titrating a solution composed of the chlorine dioxide stock and potassium iodide with sodium thiosulfate under neutral (pH 7.6) as well as acidic (pH 2) conditions. It is expected that the “neutral” titration captured one-fifth of the chlorine dioxide produced as well as any chlorine which formed during the generation process while the “acidic” titration captured four-fifths of the produced chlorine dioxide and any chlorite present. The purity of the chlorine dioxide stock solutions were determined to be greater than 99%, indicating that the solutions were essentially free from chlorite, chlorate (assessed via Ion Chromatography), and chlorine contamination. Chlorine dioxide solutions were then stored, headspace free in 40 mL-amber vials.

4.2.2 Residual Analyses

Chlorine dioxide residuals in the water samples were measured using the ACVK method developed by Masschelein *et al.* (1989) and recently investigated by Hofmann *et al.* (1998). It is a spectrophotometric method which involved the use of Acid Chrome Violet K dye. This method has been reported by Masschelein *et al.* (1989) and Hofmann *et al.* (1998) to be free from interferences of chlorine, chlorite and chlorate, which could be present in the water samples. The analysis was conducted using a Hewlett Packard* 8452A UV-Visible spectrophotometer equipped with a 5-cm quartz cell. The chlorine dioxide residual concentration is proportional to the difference in absorbance measured at 548 nm of the “control” solution and the chlorine dioxide-

treated sample. The absorbance difference results from the discoloration of the ACVK by chlorine dioxide. For the experiments performed on natural waters, the “control” solution consisted of an aliquot of the water matrix (at the different pH and temperature conditions which were investigated) mixed with the ACVK reagent. For the humic-acid spiked reagent water experiments (i.e. “synthetic” water experiments), the “control” solutions consisted of aliquots of samples where the chlorine dioxide had been removed by purging with helium gas using a gas-dispersion tube for better gas-liquid contact (samples were typically purged for over 10 minutes). Sample dilutions were conducted for cases where the applied chlorine dioxide concentration were equal to or greater than 2 mg/L.

Quality assurance/quality control (QA/QC) consisted of running a reagent water blank (reagent water with ACVK solution) as the first sample of any specific sample run as well as including one (at the very least) as every tenth sample. Providing reagent blanks during the sample runs was essentially done to verify that the glassware and reagents were free from any potential 548 nm absorbance-interfering compounds and that the instrument baseline was not drifting with time. Interim reagent blanks were often run as well for baseline stability checks. A QA/QC standard of 1 mg/L was provided after the first method blank sample and as every tenth sample to verify that the spectrophotometer response was not varying with time. In addition, the chlorine dioxide of each stock bottle used was tested before and after each experiment to confirm that no stock concentration degradation had occurred during the experimental testing periods. A QA/QC chart was developed based on the chlorine dioxide residual concentration recoveries of the QA/QC sample standards and chlorine dioxide stock

check samples to verify that they fell within control limits (upper and lower) of 3 standard deviations of the mean recovery level of the 20 most recent samples (i.e. historical mean) to check that the method and chlorine dioxide stock solution was “in control”. A typical calibration curve and QA/QC chart are provided in Figures C.2 and C.3 respectively. Developing a separate standard curve at 4°C (for the determination of chlorine dioxide residual concentrations in samples held at this temperature) was observed not to be necessary.

4.3 DBP Analyses

4.3.1 Chlorite, Chlorate and Bromide Analyses

Chlorite, chlorate and bromide analyses were conducted in accordance with EPA Method 300.0 (USEPA, 1993). A Dionex® DX 500 ion chromatograph to identify the anions of interests. It should be noted that instead of using a carbonate eluent, a borate eluent was employed. Hautman and Bolyard (1992) report that either eluent can be used for chlorite and chlorate detection. However, the researchers further report that increased sensitivity and reduced baseline noise can be observed when employing the borate eluent resulting in instrument detection limits two to five times lower than those achieved when using a carbonate eluent. An account of the sample preparation and operating conditions relating to the sample analysis by ion chromatography are reported in Figure C.5 of Appendix C.

QA/QC comprised of running a reagent water blank as the first sample of any specific IC sample run as well as including one as every tenth sample. Providing reagent blanks during the sample runs was done to verify that the instrument, reagents and laboratory environment were free from any potential interfering compounds. A

QA/QC sample (provided after each method blank sample) consisted of 0.5 mg/L chlorite, 0.3 mg/L chlorate and 0.1 mg/L bromide (levels representative of expected compound concentrations in tested samples). Providing QA/QC samples allowed for the verification that the IC detector response was not varying with time. A QA/QC chart (based on height counts) was developed to verify that QA/QC samples fell within control limits (upper and lower) of 3 standard deviations of the mean height counts of the 20 most recent samples (i.e. historical mean) to secure that the method was “in control”. Typical calibration curves for chlorite and chlorate are depicted in Figures C.6 and C.8 respectively. Also, a typical QA/QC chart is shown in Figure C.7 for chlorite and Figure C.9 for chlorate. When analyses could not be performed upon sampling, the samples were preserved with ethylenediamine (EDA) as suggested in EPA Method 300.0 (USEPA, 1993). One to two drops of an EDA 45 g/L stock solution was added to the 23 mL-sample vials prior to storing the vials at 4°C until analysis. Samples were rarely stored for more than one week and were typically analyzed within a few days of sampling. A storage method blank and QA/QC sample was provided with the run samples to observe whether storage affected the samples.

For the Toronto, Peterborough, Belleville and Mannheim ground and surface raw waters, an interfering peak adjacent (which was also found in the buffered water blank samples) to the chlorate peak was observed, thus requiring a “correction” to be applied to the chlorate peak for proper concentration evaluation. The correction first involved calculating the “added concentration” caused by the presence of the interfering peak (based on area counts) and subtracting this value from the evaluated chlorate concentration (based on height counts). Applying this correction to a number

of different chlorate-spiked water matrices samples showed that the resulting chlorate concentration was generally within 10% of the spiked chlorate concentration level. Evaluating the chlorate levels in the “uncorrected” chlorate-spiked water matrices samples using either height or area response counts produced near equivalent chlorate concentrations (i.e. concentrations differences typically within ± 0.03 mg/L).

4.3.2 TTHM Analyses

The analyses for TTHMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) was conducted according to a procedure described by EPA Method 551.1 (USEPA, 1993) which involved a liquid-liquid extraction using methyl-tert-butyl-ether (MtBE) as the organic solvent. Measurements were obtained using a Hewlett Packard 5890 Series II Plus[®] gas chromatograph (Hewlett Packard, Mississauga, ON) with electron capture detection (ECD). The Gas Chromatograph (GC) was fitted with a Dura-Bond 5 (DB-5) capillary column (Chromatographic Specialties, Brockville, ON). An account of the sample preparation and operating conditions relating to the sample analyses by the GC are reported in Figure C.10 of Appendix C. Also in Appendix C, a typical calibration curve for the chloroform compound is depicted in Figure C.11.

QA/QC comprised of running a MtBE solvent blank as the first sample of each GC run to determine the purity of the organic solvent in relation to its background concentration of TTHMs. Quality control methods employed in the analyses of TTHMs was similar to those employed for chlorite, chlorate and bromide analyses (Section 4.3.1). The QA/QC standard consisted of 20 $\mu\text{g/L}$ for the synthetic water experiments and 4.31 $\mu\text{g/L}$ for the natural water experiments (i.e. concentration of

each of the four examined THM compounds). A typical QA/QC chart (based on area count) is provided in Figure C.12 (Appendix C).

Also, an internal standard consisting of 1,2-dibromopropane was spiked in each sample. To verify method control, the internal standard area counts were recorded and checked as to whether they fell within $\pm 20\%$ of the mean area count for that particular GC run. Samples were stored at 4°C (for a time period less than 14 days) until sample preparation for GC analyses (Figure C.10, Appendix C). A storage method blank and QA/QC standard was provided with the run samples to observe whether storage affected the samples.

4.3.3 HAA Analyses

Monitoring of the nine HAAs was assessed following USEPA Method 552.2 (1995). The method involved the liquid-liquid extraction of the said DBPs using MtBE as the organic solvent following by their methylation using acidified methanol. Measurements were obtained using a Hewlett Packard 5890 Series II Plus[®] Gas Chromatograph (Hewlett Packard, Mississauga, ON), with electron capture detection (ECD). The GC was fitted with a Dura-Bond 5 (DB-5) capillary column (Chromatographic Specialties, Brockville, ON). An account of the sample preparation and operating conditions relating to the sample analysis by gas chromatograph are reported in Figure C.13 of Appendix C.

QA/QC and sample storage control procedures for the analyses of HAA₉ were similar to those followed for TTHM analyses (Section 4.3.2). The QA/QC standard (for the synthetic water experiments) was a mix of 25.9 µg/L for monochloroacetic acid (MCAA) and dichloroacetic acid (DCAA), 17.2 µg/L for monobromoacetic acid

(MBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA) and chlorodibromoacetic acid (CDBAA) and 8.6 µg/L for dibromoacetic acid (DBAA), tribromoacetic acid (TBAA) and trichloroacetic acid (TCAA). For the natural water experiments, the supplied standard consisted of 8.3 µg/L for MBAA, DCAA, DBAA, BCAA, and TCAA and 16.3 µg/L for MCAA, TBAA, BDCAA and CDBAA. The provided internal standard was 1,2,3-trichloropropane. A typical calibration curve and QA/QC chart for DCAA are depicted in Figures C.14 and C.15 respectively.

4.4 Water Quality Analyses

4.4.1 UV Analyses

UV (ultra-violet) analyses consisted of measuring the UV absorbance (expressed as cm^{-1}) at 254 nm in accordance with Standard Method 5910B (APHA-AWWA-WEF, 1995). Measurements were obtained using a Hewlett Packard® 8452A UV-Visible spectrophotometer with a 1-cm quartz cell (Canlab, location unknown). Each sample was analyzed after passing the sample through a 0.45 µm Gelman acrodisc® CR PTFE syringe filter (Ann Arbor, MI) fitted to a 10-mL glass syringe. Before filtering the samples, the filter and filter assembly were rinsed with reagent water to remove any UV-absorbing organic impurities. The spectrophotometer was zeroed using a filtered reagent water sample (same filtration procedure as previously reported for test samples).

Quality assurance involved measuring the absorbance of an organic-free water blank at least after every 8 or 10 samples. Including organic-free water blanks allowed the verification as to whether the instrument baseline was shifting with time and whether the cell required additional cleaning. Additionally, after measuring the

organic-free water blank, the absorbance of the reagent water contained in a *second* 1-cm quartz cell was measured. Once measured, this *second* cell was set aside with its contents (the reagent water was *not* discarded) until its next absorbance reading so as to allow for better assessment of baseline drifting. Standard error associated with the UV_{254} measurements was estimated from replicated samples which had been performed in duplicate (see Table 3.7, Chapter 3). The spectrophotometer precision was periodically checked using potassium hydrogen phthalate as per Standard Method 5910B (APHA-AWWA-WEF, 1995).

UV absorbance interferences at 254 nm caused by the presence of either chlorite, chlorate and bromide were assessed. The UV absorbance at 254 nm for a 1 mg/L chlorate concentration as well as a 1 mg/L bromide concentration were both found to be within experimental error (i.e. $< 0.002 \text{ cm}^{-1}$). It was observed that chlorite can interfere with UV measurements. An “absorbance correction” which could account for UV interference caused by the presence of chlorite was developed (eqn. 4.1, $R^2 = 0.9978$, chlorite levels equal to or less than 5.0 mg/L were examined).

$$\text{Absorbance correction} = 0.002[\text{Chlorite}] + 0.0001 \quad (4.1)$$

where Absorbance correction = absorbance to be subtracted from the absorbance measured at 254 nm, cm^{-1}

Chlorite = Chlorite conc. in sample (mg/L)

4.4.2 Non-Purgeable Organic Carbon Analyses

Non-Purgeable Organic Carbon (NPOC) was measured at the University of Toronto (Toronto, ON) according to Standard Method 5310C (APHA-AWWA-WEF, 1995) using a O.I. Corporation Model 1010 Total Organic Carbon Analyzer (College

Station, TX). This method employed a persulfate oxidation with infrared detection. NPOC measurements for certain natural raw waters (i.e. Peterborough, Belleville, Manheim surface and groundwater) were conducted at the University of Waterloo (Waterloo, ON) using a Dohrmann DC-180 (Dohrmann division of Rosemount Analytical Inc., Santa Clara, CA) TOC analyzer also according to Standard Method 5310C (APHA-AWWA-WEF, 1995).

Quality assurance typically consisted of running reagent blanks, followed by a tap water sample and a QA/QC standard of known concentration (generally a standard concentration which would be representative of the expected NPOC levels). Calibration and QA/QC standards were prepared with potassium hydrogen phthalate as suggested in Standard Method 5310C (APHA-AWWA-WEF, 1995). NPOC samples which could not be measured upon receipt were acidified to a pH below 2 with a few drops of concentrated sulfuric acid and stored at 4°C until analyses (storage times were always less than 28 days). QA/QC travel standards (also prepared with potassium hydrogen phthalate) were included with the NPOC samples shipped to the University of Waterloo to ensure that the University of Waterloo NPOC results were comparable to the University of Toronto NPOC results. The analysis methods (University of Toronto and University of Waterloo) were deemed “in control” since recoveries of all the potassium biphthalate standard checks were within $100 \pm 10\%$.

4.4.3 pH Analyses

pH was measured using a Ag/AgCl internal reference combination electrode (VWR Scientific Model 8015 Benchtop pH/ISE Meter, West Chester, PA). The pH meter electrode was calibrated on a daily basis using pH 4, 7 and 10 standard buffer

solutions (VWR Scientific, West Chester, PA). As sanctioned by the manufacturer, satisfactory pH meter performance was achieved when a slope between 92% and 102% was obtained.

4.4.4 Alkalinity Analyses

The determination of total alkalinity was conducted according to Standard Method 2320B (APHA-AWWA-WEF, 1995) where samples were titrated until a final sample pH of 4.5 was reached. Quality control involved performing the alkalinity analysis in triplicate whereby successive readings differed by less than 5%.

4.4.5 Turbidity Analyses

Turbidity measurements (in NTU) were obtained using a Hach 2100N Turbidimeter (Hach Company, Loveland, CO). Quality control of turbidity readings was ensured by verifying the turbidimeter calibration using 0-4000 NTU Gelex® secondary turbidity standards (Hach Company, Loveland, CO). The turbidity readings of the Gelex® standards were found to be within 10% of their turbidity values reported by the supplier.

4.4.6 Ammonia Analyses

Ammonia determination was conducted using a VWR Scientific Model 8015 Benchtop pH/ISE Meter (West Chester, PA) accompanied with an ammonia selective electrode. Ammonia measurements and calibration standards, prepared with ammonium chloride, were done in accordance with Standard Method 4500-NH₃-D (APHA-AWWA-WEF, 1995). To eliminate water matrix effects which could interfere with the ammonia measurements, ammonia levels were determined via standard additions as per a standard addition procedure outlined by Shugar and Ballinger (1990).

Standard addition was achieved by adding specific volumes of the ammonium chloride stock solution (1000 $\text{NH}_3\text{-N}$ mg/L) to the water sample. Water samples were acidified to a pH below 2 with concentrated sulfuric acid and stored at 4°C until analyses could be conducted. Sample storage times were less than 28 days.

4.4.7 Iron and Manganese Analyses

Iron and manganese of the raw natural water samples was determined according to Standard Method 3111B (APHA-AWWA-WEF, 1995) using a AAnalyst 100 atomic adsorption spectrometer (Perkin Elmer, Norwalk, CT). This is a flame absorption spectrometry method whereby a sample is directly aspirated into an air-acetylene flame. Iron detection was determined at 248.3 nm while manganese detection was determined at 279.5 nm using the appropriate source lamp for the particular metal of interest. Iron and manganese sample preparation involved digestion of the samples (to convert to the soluble metal form) using nitric acid as required by Standard Method 3030E (APHA-AWWA-WEF, 1995). Digested samples were stored at room temperature until analysis could be conducted. All samples were analyzed within four months after sample digestion.

Calibration standards (0.1-0.5 mg/L) for iron and manganese were prepared from a standard stock solution consisting of a mixture of various metals including iron and manganese (Section 4.1). The instrument was programmed to generate three absorption readings in 5 seconds. Iron and manganese concentrations were based on the average of these three absorbance readings. The Mannheim groundwater and Mannheim surface water spiked with 0.5 mg/L of standard samples were analyzed in duplicate to verify sample reproducibility. QA/QC standards of known concentration

(i.e. 0.1 mg/L and 0.5 mg/L) were also measured with the experimental samples to verify that the instrument was stable (i.e. baseline response not varying with time). In addition, the recoveries of the water matrices spiked with known concentrations of iron and manganese were observed to within $100 \pm 12\%$ of the spiked concentration levels.

4.4.8 Color Analyses

Color measurements for the raw waters obtained from the Brantford, Ottawa Britannia, Windsor and the Toronto R.L. Clark treatments plants were conducted at the Ottawa Britannia WTP in accordance with a spectrophotometric method utilized by plant personnel (measuring filtered samples at 420 nm using a 4-cm path length cell, pH adjusted to 11 with a 1.0M boric acid/0.3M NaOH borate buffer, no other details are known). Determination of color for the four raw waters (i.e. Peterborough, Belleville and Mannheim surface and groundwater) was conducted at the respective treatment facilities by plant personnel whereby the results were sent along with the water shipment. The Peterborough and Mannheim treatment plants used spectrophotometric methods for color detection on filtered raw water samples (both treatment plants employed a “Hach” method where color is determined based on the absorbance reading measured at 455 nm, no other details are known). The Belleville plant utilized a color comparator for its raw water color determination of an unfiltered raw water sample (no greater details with respect to the utilized method are known).

4.5 Water Matrix Preparation for the Factorial Experiments

Experiments performed on “synthetic” as well as natural waters were conducted using oxidant-free 250-mL amber bottles. The “synthetic” waters were prepared by adding an appropriate amount of commercial humic acid (Aldrich Chemical Co.,

Milwaukee, WI) to organic-free reagent water. Once prepared, NPOC concentrations were measured (as per method discussed in Section 4.4.4) to verify that the NPOC water levels were as required. 18-liter plastic carboy containers were rinsed several times (first with tap then with distilled water) prior to being sent to the different water treatment plants to collect the natural water samples. Upon receipt of the carboys, the treatment plants filled the containers with raw water (taken at a point prior to disinfectant addition) and then shipped them back by overnight courier to the water treatment laboratory at the University of Toronto. Upon their arrival, the carboys were stored at 4°C until testing. Experiments were typically conducted on the waters within days (i.e. 2 to 4 days) of receipt.

The parameters which were altered to evaluate their effects on DBP formation when employing chlorine dioxide during the natural water experiments were (in the order of variation): Temperature, pH, chlorine dioxide concentration and reaction time. In addition to these parameters, the “synthetic” water experiments also involved spiking the waters with chlorine as well as chlorate.

The 25°C temperature condition was provided by a Precision Scientific Model 815 low-temperature incubator (location unknown), the 14.5°C samples (during “synthetic” water experiments) were attained using a Constant Temperature Control Limited incubator (Aurora, ON) while a McClary (location unknown) incubator/refrigerator provided the 4°C temperature condition. Samples requiring 20°C temperature levels (i.e. samples resulting from the experimental testing of external model validation) were placed in the constant temperature-controlled drinking water laboratory which is held at 20°C $\pm$ 1°C. Thermometers placed in reagent water located

in the various temperature-controlled environments ensured that the temperatures were typically within $\pm 1.0^{\circ}\text{C}$ of the desired temperature. pH adjustments to pH 5, 6, 7 or 9 was achieved through the addition of phosphate buffers as well as the addition of either reagent water:conc. HCl (on a 1:1 volume basis) or 50% (weight/weight) NaOH (to ensure that the added buffer volumes represented less than 1% of the total water sample volume to minimize dilution effects while attaining the desired pH levels). For consistency purposes, buffer solutions were all “phosphate-based”. Buffer solutions were prepared near solubility limits by adding approximately 215 g of potassium dihydrogen orthophosphate to 1.0 L of reagent water followed by the addition of 50% (weight/weight) NaOH (NaOH additions performed “drop-wise” using Pasteur pipettes) to obtain the desired pH buffer value (i.e. pH values of 5, 6, 7 or 9). Due to the nature of the chlorite and chlorate analysis (ion chromatography), precautions were taken to add the least amount of buffer solution to minimize dilution effects but most importantly, to eliminate ion interferences (i.e. due to the phosphate) which could hinder proper chlorite and chlorate analyses. While the various pH levels were generally within ± 0.05 pH units of the desired value, pH checks showed that pH changes which occurred during experiments were typically within ± 0.2 pH units.

Once samples were at the desired temperature and pH, they were decanted into 250 mL-amber chlorine dioxide demand free bottles with minimal headspace (less than 1 mL). The minimal headspace provided the necessary volume for proper mixing. To ensure the integrity of the chlorine dioxide stock by preventing chlorine dioxide losses from volatilization, the chlorine dioxide vials were fitted with Teflon[®]-lined Mininert valves for screwtop vials (Supelco, Toronto, ON). Desired chlorine concentrations

were achieved by spiking with a concentrated “working” chlorine solution (1000 mg/L). The concentrated “working” chlorine solutions were obtained from a commercially available Javex® bleach (5.25% sodium hypochlorite when bottled) dilution, whose chlorine content was evaluated using Standard Method 4500-Cl (APHA-AWWA-WEF, 1995). “Working” chlorine solutions were found to be free of chlorate (i.e. less than 20 µg/L). Desired chlorate concentrations were obtained by spiking with a concentrated sodium chlorate solution (1000 mg/L).

Tests on sample blanks (i.e. non-oxidized samples) were conducted to verify whether the water matrices and employed reagents had “background” concentrations levels of the compounds of interest. It is noted that chloroform was consistently detected in the reagent water blank as well as the sample blanks for all water matrices due to its present in the MtBE solvent. This was dealt with by subtracting the background chloroform concentration (which was typically less than 5 µg/L) from the measured chloroform concentration.

CHAPTER 5

DBP FORMATION RESULTING FROM THE APPLICATION OF CHLORINE DIOXIDE TO SYNTHETIC WATER MATRICES

5.1 Overview

The purpose of these experiments was to identify the parameters having significant effects on DBP formation when dosing “synthetic” water matrices with chlorine dioxide and assess whether 2-factor interactions are important in DBP formation. Parameters having significant effects on DBP formation would be further examined as to their inclusion in the equations designed to predict DBP formation in natural water systems (Chapter 6). A discussion of the disinfection by-product (DBP) formation results (i.e. chlorite, chlorate, THMs and HAAs), arising from the performed factorial experiments is provided in this chapter.

Since the factorial experiments performed on the “synthetic” water matrices were Resolution IV designs, as described in Chapter 3, 2-factor interactions were aliased with one or more 2-factor interactions whereby the effect caused by either interaction could not be differentiated without performing further experimental testing. Such being the case, in lieu of disregarding these 2-factor interactions which could not be “undeniably” deemed as statistically significant, a qualitative analysis as to their effects has been provided to assess their importance on DBP formation.

An example which illustrates the statistical analysis of factorial experiment results has been provided in Appendix B. It should be specified that the main and interaction effects identified as statistically significant are at the 95% confidence interval (CI). As explained in Appendix B, a parameter said to be statistically

significant produces a change in DBP concentration which is beyond the 95% CI of the mean DBP concentration level. Hence, at a discrepancy at the 5% significance level, the observed parameter effect on DBP formation identified as significant is said to be “true” and not due solely to random error.

The water matrices examined in the two experiments differed mainly in their organic content as measured by non-purgeable organic content (NPOC) and UV_{254} (Table 5.1) where NPOC constitutes a surrogate measure of the amount of precursor material while UV absorbance is an indicator of precursor reactivity in forming DBPs such as THMs (Amy *et al.*, 1987a). As reported by Krasner *et al.* (1996), humic content of the NOM is shown through UV_{254} values. The test water involved in Factorial #1 had a NPOC level consistent with those found in surface waters while the NPOC level characterizing Factorial #2 reflected a level typical of groundwaters. These NPOC levels are consistent with values reported in the literature for both water types (refer to Section 2.6.2, Chapter 2).

Low, centerpoint, and high parameter levels as investigated using factorial experiments are shown in Table 5.2. Although the chlorine and chlorate concentration levels differed between factorial experiments, their concentrations, expressed either in terms of a percentage of the water matrix NPOC, or the applied chlorine dioxide concentration, were similar (Table 5.2).

5.2 DBP Formation

The DBP concentration ranges and mean values, which resulted from the various factorially-designed experimental runs for the DBPs under examination, are

Table 5.1 NPOC and UV₂₅₄ Levels of Synthetic Waters^a

Factorial Experiment	Water Parameter	
	NPOC (mg/L)	UV ₂₅₄ (cm ⁻¹) ^b
#1 (1/4 fraction of full factorial: 16 runs)	5.95	2.34 ^c
#2 (1/4 fraction of full factorial: 16 runs)	2.09	0.87 ^d

^a Water matrix consisted of reagent water with commercial humic acid.

^b Measurements obtained using a 5 cm-cell.

^c Value reported for unfiltered raw water sample, measured 14 days after water preparation (3 days at room temperature and 11 days at 4°C).

^d Average value of pH 5 and pH 9 "control" unfiltered water samples, measured 7 days after water preparation (3 days at room temperature and 4 days at 4°C).

Table 5.2 Experimental Factors and Levels Investigated in Factorial Experiments

Factor	Parameter Values ^a		
	Low Level	"Centerpoint" Level	High Level
pH	5	7	9
Temperature (°C)	4	14.5	25
Chlorine Concentration (mg/L) - factorial #1 (NPOC = 5.95 mg/L)	0	0.2 (3.36, NA, NA)	0.4 (6.72, 22.4, 6.11)
- factorial #2 (NPOC = 2.09 mg/L)	0	0.07 (3.35, NA, NA)	0.14 (6.70, 22.3, 6.09)
Chlorine dioxide:NPOC Ratio (%)	30	70	110
Chlorate Concentration (mg/L) - factorial #1 (NPOC = 5.95 mg/L)	0	0.1 (1.68, NA, NA)	0.2 (3.36, 11.2, 3.06)
- factorial #2 (NPOC = 2.09 mg/L)	0	0.035 (1.67, NA, NA)	0.07 (3.35, 11.2, 3.04)
Reaction time (hr)	1	12.5	24

Note: NA = Not applicable

^a Values in parentheses represent concentrations as percentages of NPOC, low and high applied chlorine dioxide concentrations respectively.

shown in Table 5.3. It is observed, especially in Factorial #1, that the resulting average chlorite concentrations were over the MCL of 1.0 mg/L proposed for chlorite by the D/DBP Rule (Fed. Reg., 1994). As anticipated, chlorate formation was less than chlorite formation. The chlorine dioxide residual concentrations were found to be small (average residual concentrations were less than 0.2 mg/L in both factorial experiments). This confirms that the water matrices had a high oxidant demand (i.e. most of the applied chlorine dioxide was consumed) as suggested by the UV_{254} measurements taken for the water matrices indicative of the reactivity of the natural organic matter humic fraction.

The observed low chloroform formation (the only THM detected in all trial runs in both factorial experiments) conforms to findings reported in the literature by many authors (Lafrance *et al.*, 1993; Lykins and Griesse, 1986; Muttamara *et al.*, 1995; Werdehoff and Singer, 1987; Jun *et al.*, 1996) whom report that formation of THMs is not anticipated from chlorine dioxide-organic matter reactions. Dichloroacetic acid (DCAA) was the only HAA compound which was consistently observed above detection limits in all experimental runs for Factorials #1 and #2. Under certain experimental conditions, trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA) and monochloroacetic acid (MCAA) were observed in the factorial experiments. However, their concentrations were observed to be less than 8 $\mu\text{g/L}$ and generally ranged between 1 to 5 $\mu\text{g/L}$. The overall formation of halogenated organic substances from chlorine dioxide disinfection is expected to be minimal (Hazen and Sawyer, 1992;

Table 5.3 DBP and Chlorine Dioxide Concentrations Resulting from Factorial Experiments

Compound	Factorial Experiment					
	#1 (NPOC = 5.95 mg/L)			#2 (NPOC = 2.09 mg/L)		
	Conc. Range ^a	Avg. Conc. ^a	Pure Error ^b	Conc. Range	Avg. Conc.	Pure Error
Chlorite (mg/L)	0.632-4.23	2.31	0.17	0.232-1.40	0.78	0.03
Chlorate (mg/L)	0.088-0.727	0.34	0.01	0.060-0.209	0.12	0.01
Trihalomethanes (µg/L)						
Chloroform	0.4-15.1	4.1	0.1	bdl ^c -3.1	0.7	0.1
Haloacetic acids (µg/L)						
HAA,	5.2-56.3	25.9		0.3-15.2	6.0	
DCAA	4.4-44.1	21.0	1.7	bdl ^d -12.5	4.6	0.5
MCAA	3.9-8.7	NC ^e	NC ^e	ND		
TCAA	ND-2.0	NC ^e	NC ^e	ND		
BCAA	1.6-2.1	NC ^e	NC ^e	1.6-2.1	NC ^e	NC ^e
Residual Chlorine Dioxide (mg/L)	ND-0.23	0.16	0.0037	bdl ^e -0.48	0.12	0.029

Note: ND = Not Detected

NC = Not Calculated (since specific HAA was not detected in all trial runs)

^a Concentration ranges and averages based on data obtained from all experimental trial runs excluding centerpoint data.

^b Pure error reported as the root mean square error based on triplicate centerpoint data (3 points).

^c bdl = below detection limit of 0.6 µg/L

^d bdl = below detection limit of 1.0 µg/L

^e bdl = below detection limit of 0.04 mg/L

Carnimeo *et al.* 1995;) and less than those formed from chlorination (Richardson *et al.*, 1994; Sansebastiano *et al.* 1995; Werdehoff and Singer, 1987).

5.3 Main Parameter Effects on Chlorite Formation

The pH and ClO_2 :NPOC parameters were identified as producing statistically significant effects on chlorite formation (Table 5.4). Since these two factors may “potentially” (due to the aliasing of 2-factor interaction effects, indisputable identification of 2-factor interaction effects is not possible without further experimental testing) be taking part in a significant 2-factor interaction with respect to chlorite formation (Table 5.5), the effect of increasing these individual parameters from their low to high levels on chlorite has been quantified simultaneously as displayed in Figure 5.1. Based on results from both factorial experiments, regardless of pH level, it was evident that increasing the ClO_2 :NPOC ratio from its low to high level (i.e. 0.3 to 1.1) produced substantial increases in chlorite formation (i.e. about 2.7 times more chlorite at the 1.1 ratio than at 0.3). This is not surprising since over 3.5 times more chlorine dioxide was applied at the higher ratio level when compared to the amount dosed to achieve the low ClO_2 :NPOC ratio.

The observation that greater chlorite concentrations ensue from increasing chlorine dioxide doses has been well-documented in the literature (Griese *et al.*, 1993; Werdehoff and Singer, 1987; Andrews *et al.* 1997). The low residual chlorine dioxide concentrations which were observed also provided indications that the oxidant demand was in fact substantial for the test waters involved in the factorial experiments (i.e. average chlorine dioxide residual concentration was only 0.16 and 0.12 mg/L for

Table 5.4 Summary of Main Parameter Effects on DBP Formation

Factorial Exp.	DBP	Factor					
		PH	Temp.	ClO ₂ :NPOC Ratio	Cl ₂ conc.	ClO ₃ ⁻ Conc.	React. Time
#1 NPOC = 5.95 Mg/L	Chlorite	S, I	NS, I	S, I	NS	NS	NS, I
	Chlorate	S, I	NS, I	S, I	NS, I	S	NS
	Chloroform	S, I	NS, I	S, I	NS	S	S
	DCAA	S, I	S	S	NS	NS, I	NS
#2 NPOC = 2.09 Mg/L	Chlorite	S, I	NS	S, I	NS	NS	NS
	Chlorate	S, I	NS, I	S, I	NS	S	NS
	Chloroform	S, I	NS, I	S, I	NS, I	S	S
	DCAA	S, I	NS	S	NS	NS	NS, I

Note: S = Effect found to be significant based on a 95% confidence interval.
 NS = Effect not found to be significant based on a 95% confidence interval.
 I = Parameter involved in one or more significant interaction effect(s).

Table 5.5 Summary of Parameter Interaction Effects on DBP Formation

Fact. Exp.	DBP	Interaction						
		pH-ClO ₂ : NPOC Ratio	Temp.-Rxn Time	pH-Temp.	Temp.-Cl ₂ conc.	pH-ClO ₃ ⁻ conc.	ClO ₂ : NPOC Ratio-Cl ₂ conc	pH-Rxn Time
#1 NPOC = 5.95 Mg/L	Chlorite	S	S	NS	NS	NS	NS	NS
	Chlorate	S	NS	S	S	NS	NS	NS
	Chloroform	S	NS	S	NS	NS	NS	NS
	DCAA	NS	NS	NS	NS	S	NS	NS
#2 NPOC = 2.09 Mg/L	Chlorite	S	NS	NS	NS	NS	NS	NS
	Chlorate	S	NS	S	NS	NS	NS	NS
	Chloroform	S	NS	NS	NS	S	NS	NS
	DCAA	NS	NS	NS	NS	NS	NS	S

Note: S = Effect found to be significant based on a 95% confidence interval.
 NS = Effect not found to be significant based on a 95% confidence interval.

ALIASES for Factorial Experiment #1 and #2:

- pH-ClO₂ to NPOC ratio AND Temperature-Chlorate
- Temperature-Reaction Time AND ClO₂ to NPOC ratio-Chlorine concentration
- pH-Temperature AND ClO₂ to NPOC ratio-Chlorate concentration
- Temperature-Chlorine concentration AND ClO₂ to NPOC conc.-Reaction Time
- pH-Reaction Time AND Chlorine concentration-Chlorate concentration
- pH-Chlorate concentration AND temperature-ClO₂ to NPOC ratio AND chlorine concentration-reaction time

Figure 5.1 pH and ClO_2 :NPOC Ratio Effects on Chlorite Formation

Factorial #1 and Factorial #2 respectively). The relationship between chlorite formation and chlorine dioxide consumption will be further discussed in Section 5.7.

With respect to the effect of variations in pH on chlorite formation, the higher pH condition of 9 led to more chlorite production when compared to pH 5. This trend was more evident at the 1.1 ClO_2 :NPOC ratio. It should be noted that chlorite formation is generally expected to result from the disproportionation of chlorine dioxide to its inorganic DBPs (i.e. chlorite and chlorate), as well as from reactions between chlorine dioxide and organic material present in the water (see Section 2.4.4, Chapter 2). Also, since chlorine dioxide is more unstable at higher pH levels, greater disproportionation of chlorine dioxide is thus anticipated (Rosenblatt, 1978). Similar trends regarding increased chlorite formation with increasing pH have also been reported by Oehler (1986), Andrews *et al.* (1997) and Werdehoff and Singer (1987). The higher chlorite concentrations resulting at the higher pH conditions may have been due to more chlorine dioxide-organic matter reactions at the high pH conditions. As reported by Hoigné and Bader (1994), increasing the pH can increase the reaction rates of chlorine dioxide-humic acid reactions (i.e. increases by a factor of 3 per pH increment in the pH range of 4 to 8). Consequently, these increased reaction rates may have allowed certain reactions at pH 9 to take place within the investigated reaction times (i.e. 1 and 24 hours) which may not have occurred at pH 5.

Hence, based on the preceding observed pH and ClO_2 :NPOC effects on chlorite formation, applying chlorine dioxide doses (most especially in the case of doses which are greater than the water NPOC) to waters preceding treatment processes requiring

high pH levels (such as water softening via lime addition) could be at risk of high chlorite formation which exceeds the proposed 1.0 mg/L MCL in the United States (Fed. Reg., 1994). A better situation would be to dose the water at a lower pH condition. In addition, treatment facilities having to use enhanced coagulation or softening to satisfy the TOC removal regulations before any other residual disinfectant is added (Fed. Reg., 1994) may be helping the optimization of their systems thereby necessitating smaller chlorine dioxide doses thus, minimizing chlorite formation and potentially the production of chlorate and halogenated organic DBPs.

Interestingly, as main parameter effects, neither temperature, reaction time, chlorine and chlorate concentration were found to significantly influence the formation of chlorite at the 95% CI. However, a number of these factors are potentially involved in interaction effects (see Table 5.5).

5.4 Main Parameter Effects on Chlorate Formation

Factorial experiments #1 and #2 produced consistent results whereby in both cases pH, $\text{ClO}_2\text{:NPOC}$ and chlorate concentration have been identified as main factors which exhibit statistically significant effects in chlorate formation (Table 5.4).

Varying the chlorate concentration from its low to high level (0 to 0.2 mg/L for Factorial #1, and 0 to 0.07 mg/L for Factorial #2), was observed to influence final chlorate levels as shown in Figure 5.2. As reported by Versteegh *et al.* (1993), Dixon and Lee (1991) and Griesse *et al.* (1991), once chlorate has been formed, it is typically not removed by other water treatment processes. Thus, once formed, it is likely to remain in solution. Based on this assumption, in order to estimate the chlorate

formation resulting from chlorine dioxide action for the trial runs where chlorate had originally been added, the initial “spiked” chlorate concentration was subtracted from the final chlorate concentration. Subsequent to this calculation, the average chlorate concentrations estimating chlorate formation from chlorine dioxide action for the trial runs spiked with chlorate were found to be 0.251 mg/L and 0.074 mg/L for Factorial #1 and #2 respectively. Considering the average chlorate concentration from the low chlorate concentration level for Factorials #1 and #2 (0.233 mg/L and 0.097 mg/L respectively), both sets (i.e. low and high levels) of chlorate concentrations had relatively comparable results, differing by less than 0.03 mg/L. Consequently, it is presumed that the assumption that the chlorate concentration added to the synthetic water systems was stable in solution is valid.

As for the chlorite analysis, the effects of pH and $\text{ClO}_2\text{:NPOC}$ parameters on chlorate formation were assessed together (Figure 5.3) since the pH- $\text{ClO}_2\text{:NPOC}$ interaction has also been found to “potentially” be statistically significant. Similar to chlorite formation, increasing $\text{ClO}_2\text{:NPOC}$ from 0.3 to 1.1 increased the formation of chlorate. This observation is irrespective of the pH condition but was more evident in the experiment where the water matrix had a NPOC level of 6.0 mg/L. As discussed earlier, the idea is that greater $\text{ClO}_2\text{:NPOC}$ ratios resulted in greater applied chlorine dioxide concentrations which resulted in greater chlorine dioxide consumption, and hence greater disproportionation to chlorite and chlorate. Chlorate formation in terms of chlorine dioxide consumption will be addressed in Section 5.7.

It is also observed from Figure 5.3 that, while a pH variation from 5 to 9 did not seem to greatly influence chlorate formation when $\text{ClO}_2\text{:NPOC}$ was 0.3 (i.e.

Figure 5.2 Chlorate Concentration Effect on Chlorate Formation

Figure 5.3 pH and ClO₂:NPOC Ratio Effects on Chlorate Formation

absolute changes of less than 0.015 mg/L were observed in both factorial experiments), it did have a greater effect on chlorate formation for the high ratio level of 1.1. Interestingly, varying the pH from the 5 to 9 level resulted in a decrease of chlorate of 0.20 mg/L for Factorial #1 and 0.05 mg/L for Factorial #2. It could be hypothesized that, since the water matrix had a high chlorine dioxide demand, higher reaction rates which are typically observed at higher pH conditions (Hoigné and Bader, 1994) allowed for different chlorine dioxide-humic acid pathway reactions as well as side reactions to occur at the higher pH level, resulting in less chlorine dioxide remaining to disproportionate. Since the main objectives of these factorially-designed experiments were to identify, investigate, and model significant effects on chlorine dioxide DBP formation, examining reaction pathways were not conducted and as such, cannot be ascertained with any great certainty. It should be noted that the observation of decreased chlorate formation from increasing pH in the situation where the ClO_2 :NPOC ratio was about 1.1 has not been well documented in the literature. Andrews *et al.* (1997) observed the opposite trend when varying the pH from 7.3 to 8.9 producing an increase in chlorate formation. However, Andrews *et al.* (1997) performed experiments on natural waters systems where it was observed that the pH 9 condition had a higher chlorine dioxide demand and as such, a higher chlorine dioxide concentration was applied at this pH level (see Table 2.6 for additional details concerning their experiments).

Hence, based on the main effects found to be statistically significant and analyzed for scientific relevance, pH, ClO_2 :NPOC and chlorate concentration have

been evaluated as the parameters requiring the most concern in limiting chlorate concentration. While chlorite reduction remains a priority for treatment facilities utilizing chlorine dioxide as a disinfectant, decreasing chlorate concentrations would also be beneficial in obtaining CT credits for chlorine dioxide oxidation prior to enhanced coagulation or softening processes (Fed. Reg., 1994). Indeed, the results obtained display the importance of having high efficiencies when generating chlorine dioxide so as to reduce chlorate formation since once formed it is quite stable and will likely remain in the system. Reducing chlorine dioxide dosing would be expected to not only limit chlorite but also chlorate formation. It may also be best to apply chlorine dioxide to a water having a pH mid-way between these low and high pH levels (i.e. about pH 7) for “acceptable” chlorite and chlorate concentrations which are within regulatory levels. Main effects due to variations in chlorine concentration, temperature and reaction time were not found to be significant in chlorate formation. It should be noted that with CT credits being given to treatment facilities which generate chlorine dioxide with an efficiency greater than 95%, and chlorine dioxide generator suppliers furnishing generators capable of producing chlorine dioxide with efficiencies of 99%, the relevance of the effect of chlorine and chlorate concentrations as formed contaminants in the chlorine dioxide generation process on chlorite and chlorate formation can be expected to become less significant.

5.5 Interaction Effects on Chlorite and Chlorate Formation

With respect to chlorite formation, “potential” statistically-significant interactions include pH-ClO₂:NPOC (which is aliased with temperature-chlorate concentration) for Factorials #1 and #2, and temperature-reaction time (which is aliased

with ClO_2 :NPOC ratio-chlorine concentration) in Factorial #1 only (Table 5.5). 2-factor interactions of significance to chlorate formation were also identified (Table 5.5): pH- ClO_2 :NPOC, pH-temperature and temperature-chlorine concentration (for Factorial #1 only). Their respective aliases are also shown in Table 5.5. Engineering judgment could be employed in determining which interaction caused the observed significant effect. For instance, the interaction of “pH” and “ ClO_2 :NPOC” ratio could be thought as being the significant interaction in chlorite and chlorate production since pH and ClO_2 :NPOC were each found to have statistically significant main parameter effects on both chlorite and chlorate formation. Nonetheless, without experimental justification to validate any such claims, such observations stemming from engineering judgment will have limited applicability. However, since the purpose of the experiments performed on synthetic waters was to identify important parameters in chlorine dioxide-related DBP formation and assess whether 2-factor interactions are important in DBP formation, providing a more qualitative than quantitative evaluation of the 2-factor interactions results will be pursued to address these goals.

Two main observations can be made when contemplating the 2-factor interaction results. Firstly, sufficient data was provided to show that 2-factor interactions can be important in DBP formation when employing chlorine dioxide. For this reason, 2-factor interactions should not be overlooked and thus, should be included in DBP predictive model equations. Secondly, while temperature and reaction time were not observed to have statistically significant effects on both, chlorite and chlorate formation, based on interaction results, these parameters should not be quickly dismissed as having negligible effect on these two chlorine dioxide DBPs. For

instance, temperature was shown to take part in 5 potentially significant effects: Two in chlorite and three in chlorate formation (Table 5.5).

An advantage of performing factorial experiments over the one-factor-at-a-time experimental (OFAT) method when evaluating significant factor effects is observed when “crossover” effect graphs are plotted. The plot displayed in Figure 5.4 was produced to illustrate the temperature-reaction time interaction on chlorite formation and pH-temperature interaction on chlorate formation. The “crossover” effect is seen whereby increasing temperature from 4°C to 25°C at a 1-hour reaction time *increased* chlorite formation while the same increase in temperature at a 24-hour reaction time *decreased* chlorite formation. Hence, even though increasing the temperature factor from its low to high level did not produce a significant effect on chlorite formation, the “crossover” relationship that temperature shares with reaction time resulted in these factors partaking in a potential significant interaction. Consequently, considering such “crossover” 2-factor interaction relationships, had an experiment based on the OFAT method been conducted instead of the performed factorial experiment, temperature and reaction time could have likely been overlooked as being significant in the formation of either chlorite or chlorate.

5.6 HAA and THM Formation

Significant parameter effects on HAA (as DCAA) formation (Figure 5.5) as well as THM (as chloroform) formation (Figure 5.6) observed during Factorial #1 (NPOC = 5.95 mg/L) are presented in this section.

Note: Standard error (std. error) of parameter effects was evaluated as 0.043.

Figure 5.4 Changes in Chlorite Concentration When Varying Temperature (from 4°C to 25°C) and Reaction Time (from 1 to 24 hours) for Experiment #1 (NPOC = 5.95 mg/L)

Figure 5.5 Statistically Significant Main Parameter Effects on DCAA Formation

Figure 5.6 Chloroform Formation for Factorial #1 (NPOC = 5.95 mg/L) and Factorial #2 (NPOC = 2.09 mg/L)

5.6.1 Main Parameter and Interaction Effects on HAA Formation

The formation of HAAs was observed to be below the American D/DBP rule regulations of 60 $\mu\text{g/L}$ (Fed. Reg., 1994). While HAA formation was negligible for Factorial #2 (average concentration of 4.58 $\mu\text{g/L}$), the average DCAA (dichloroacetic acid) which formed in Factorial #1 was 21 $\mu\text{g/L}$ (range of 4.35 to 44.10 $\mu\text{g/L}$). For this reason, a general discussion of the significant main and interaction effects has been provided for Factorial #1 only. The main factors which have been found to have a statistically significant effect on DCAA formation were pH, temperature and $\text{ClO}_2\text{:NPOC}$ ratio (Figure 5.5). Varying pH, temperature and the $\text{ClO}_2\text{:NPOC}$ ratio from their low to high levels (i.e. from 5 to 9, from 4 to 25°C and from 0.3 to 1.1 respectively) produced respective changes in DCAA concentration of -5.36, +4.31 and +27.80 $\mu\text{g/L}$. The fact that higher DCAA concentrations were observed at the higher $\text{ClO}_2\text{:NPOC}$ ratio level is consistent with a discussion reported by Hazen and Sawyer (1992) that in cases where “high” chlorine dioxide doses are applied to waters containing humic acids, formation of MCAA and some DCAA and TCAA may take place (no details were given by the authors as to what constituted high chlorine dioxide dosages or the level of DBP formation which could be expected). As cautioned by Box *et al.* (1978), although an effect has been evaluated as “statistically significant”, this by no means provides an indication as to the “scientific importance” that the effect may have. Henceforth, on a practical basis, changes in the order of ± 5 $\mu\text{g/L}$ in DCAA concentration are quite small considering experimental variation and error,

consequently, reducing the relevance of the effect of pH and temperature on DCAA formation.

With respect to significant interaction effects, only one was identified as being statistically significant: pH-chlorate concentration aliased with temperature- ClO_2 :NPOC and chlorine concentration-reaction time. Consequently, although each of these three possible interactions may possess some theoretical basis, considering the DCAA concentration changes which resulted from either of these 2-factor relationships (each case less than $10 \mu\text{g/L}$) and the magnitudes of the DCAA formation which have resulted from the factorial experiment (Table 5.3), on a practical basis, the significance of these interactions seems small in reference to the given water system.

Hence, with respect to HAA formation resulting from the application of chlorine dioxide, the greatest concern lies with controlling the ClO_2 :NPOC ratio. Treatment facilities operating at high ClO_2 :NPOC ratios whereby higher chlorine dioxide dosages are applied are at greater risk in forming HAAs such as DCAA. However, the DCAA concentration which were observed to form were below regulatory levels as specified in the D/DBP rule (Fed. Reg., 1994).

5.6.2 Parameter Effects on THM Formation

While chloroform was detected above detection limits in all experimental trial runs in both factorial experiments, its formation was less than $15 \mu\text{g/L}$ and was mostly found to range between 1 and $5 \mu\text{g/L}$. The chloroform formation resulting in Factorial #1 is shown in Figure 5.6. Statistically, significant main parameter and interaction effects on chloroform formation can be identified (Table 5.4 and 5.5 respectively). For instance, the four trial runs which ensued in chloroform levels of approximately

15 µg/L (Figure 5.6) were associated with high pH (pH 9) and high ClO_2 :NPOC (1.1) conditions. However, comparing the range and average chloroform concentrations resulting from the Factorial Experiments #1 and #2 (Table 5.3) to the D/DBP rule regulation for TTHMs (Fed. Reg., 1994), main parameter and 2-factor interaction effects deemed statistically significant on THM formation have limited applicability. Due to such low formation levels, chloroform data has not been further investigated to identify significant parameter effects.

5.7 Effect of Chlorine Dioxide Concentration on DBP Formation

Plots of chlorite, chlorate, DCAA and chloroform production in terms of chlorine dioxide consumption based on Factorial Experiments #1 and #2 data are presented in Figures 5.7 through 5.9 respectively. As anticipated, higher DBP concentrations ensued from higher applied chlorine dioxide concentrations. It should also be observed that the DBP concentrations observed at the higher ClO_2 :NPOC ratios were greater than the DBP concentrations observed at the lower ratios. For example, the average chlorite concentration (i.e. 1.22 mg/L) resulting from the 1.1 ClO_2 :NPOC ratio of Factorial #2 was greater than the average chlorite concentration (i.e. 0.99 mg/L) resulting from the 0.3 ClO_2 :NPOC ratio of Factorial #1. This could imply that the magnitude of the applied chlorine dioxide dose plays a greater role in DBP formation than organic matter content of the water matrices. A linear trendline was drawn through the data points. Based on the calculated R^2 -values, the linear trendlines can be said to reasonably predict DBP formation in terms of chlorine dioxide consumption for these three DBPs (Figures 5.7 through 5.9). From the resulting linear equations, the chlorite and chlorate formed (reported as mg/L) from the consumption of

Figure 5.7 Chlorite Formation with Respect to Chlorine Dioxide Consumption

Figure 5.8 Chlorate Formation with Respect to Chlorine Dioxide Consumption

Figure 5.9 DCAA Formation with Respect to Chlorine Dioxide Consumption

chlorine dioxide (reported as mg/L) were about 57% and 6% respectively (y-intercept values were neglected due to their minimal values). These levels conform to percentages reported in the literature: Generally between 50-70% and between 5%-25% of the chlorine dioxide consumed would result as chlorite and chlorate respectively. Table 2.6 should be consulted for details concerning the researcher sources and experimental conditions examined. Given the R^2 values which ensued from the plotted linear trendlines, predictive model equations with respect to chlorite and chlorate formation could, in theory, ensue by first modeling chlorine dioxide consumption then applying these conversion ratio estimates (for example 57% for chlorite and 6% for chlorate). It should be specified that for the chlorate formation plot (Figure 5.8), the reported chlorate concentrations were calculated by subtracting the initially “spiked” chlorate concentration from the resulting final chlorate levels so as to estimate the chlorate produced by chlorine dioxide action. This was based on the assumption that once chlorate is added to a water system, its concentration will not decrease or be reduced (Versteegh *et al.*, 1993; Dixon and Lee, 1991; and Griesse *et al.*, 1991).

5.8 Chlorine Dioxide Disproportionation Percentages

While “average” conversion ratios of chlorine dioxide to its inorganic by-products, as calculated by the slope of the graphs depicted in Figures 5.7 and 5.9 may be useful as initial predictions of the chlorite and chlorate concentrations to expect, analyzing the range of conversion ratios which have resulted from performing factorial experiments provides some useful information. Since the ClO_2 :NPOC ratio and pH

were found to have important effects on chlorite and chlorate formation, the conversion ratios in terms of these low and high parameter levels have been also calculated. As reported in Table 5.6, although the average disproportionation ratios for chlorite were comparable for the different $\text{ClO}_2\text{:NPOC}$ ratios for both factorial experiments, the ratios which were observed varied from about 0.39 to over 0.70. Similar trends were observed for chlorate where average ratios were found to be reasonably similar for the cases where the initially applied chlorate was subtracted (it would be expected that for the cases which were not corrected, the average ratio would vary somewhat). The chlorate formed from the disproportionation of chlorine dioxide has been estimated to vary from about 0.04 to 0.21 (mg/L by mg/L).

The effect of varying pH from its low to high level (from 5 to 9) did not affect the average chlorate conversion ratios, yielding comparable results at these pH conditions. In contrast, the effect of varying pH was to increase the average conversion ratio of chlorine dioxide consumed to chlorite. This trend is assumed to be the result of greater chlorite formation at the higher pH level while the amount of chlorine dioxide consumed at both pH levels was similar (i.e. differences in the average chlorine dioxide concentration consumed at each pH level for both factorial experiments was less than 0.02 mg/L). It is believed that different reactions have taken place at the different pH conditions to yield the said results. Trends resulting from pH changes reported by researchers include that pH (7.3 and 8.9) was not found to significantly influence the conversion ratios for chlorite and chlorate (Andrews *et al.*, 1997). However, developing model equations predicting chlorite and chlorate

Table 5.6 Percentages of Chlorine Dioxide Converted to Chlorite and Chlorate

DBP Produced	Chlorine Dioxide: NPOC ratio	Factorial Experiment			
		#1 (NPOC = 5.95 mg/L)		#2 (NPOC = 2.09 mg/L)	
		Range	Avg.	Range	Avg.
Chlorite	all runs ^a	0.388-0.705	0.580	0.402-0.766	0.585
	1.1	0.457-0.674	0.573	0.470-0.651	0.576
	0.3	0.388-0.705	0.586	0.402-0.766	0.594
Chlorate	all runs ^a	0.0424-0.168	0.0948	0.0446-0.212	0.115
	1.1	0.0424-0.111	0.0777	0.0446-0.0933	0.0729
	0.3	0.056-0.168	0.112	0.103-0.212	0.157
	all runs ^{a,b}	0.0424-0.0804	0.0576	0.0446-0.151	0.0748
	1.1 ^b	0.0424-0.0804	0.0622	0.0446-0.081	0.0566
	0.3 ^b	0.0414-0.0638	0.0530	0.0472-0.151	0.0930

^a Reported concentration ranges and averages based on data obtained from all experimental trial runs excluding centerpoint data.

^b Reported concentration ranges and averages calculated after subtracting the initial "applied" chlorate concentrations from the final chlorate concentrations.

formation by applying a “conversion ratio” (such as those reported in Section 5.8) to chlorine dioxide consumption predictions obtained from developed model equations would require statistical analyses to test the robustness of these conversion ratios given variations of the investigated parameters or water sources.

5.9 Curvature Assessment

Data required to evaluate whether chlorite and chlorate formation exhibited a non-linear relationship with respect to the given parameter variations are reported in Table 5.7. It can be observed (Table 5.7), as was also attested through statistical significance tests, that curvature was not exhibited in the chlorite data (i.e. comparison of the factorial trial runs’ average to the centerpoint runs’ average chlorite concentration). Consequently, it can be assumed that the relation between chlorite formation resulting from the variation of parameters from their low to high levels is linear for the given low and high parameter conditions which were investigated. Even though statistical analyses showed that the difference between the average chlorate concentrations resulting from the 16 trial runs and the 3 centerpoint trial runs was statistically significant, the actual concentration difference was only 0.05 mg/L for Factorial #1 and 0.01 mg/L for Factorial #2 (Table 5.7). Hence, due to these small differences between the average chlorate concentrations, for practical purposes, chlorate formation could also be assumed to result from a linear relation with respect to the given low to high level parameter variations which were examined.

5.10 Chapter Summary

The main parameter and interaction effects identified as statistically significant at the 95% confidence interval for chlorite, chlorate, chloroform and DCAA for

Table 5.7 Curvature Assessment Data

Factorial Experiment	DBP	Avg. DBP Concentration Resulting from the 16 Trial Runs	Avg. DBP Concentration Resulting from the 3 Centerpoints
#1 (NPOC = 5.95 mg/L)	Chlorite	2.31	2.36
	Chlorate	0.34	0.29
#2 (NPOC = 2.09 mg/L)	Chlorite	0.78	0.77
	Chlorate	0.12	0.11

Factorial Experiments #1 (NPOC = 5.95 mg/L) and #2 (NPOC = 2.09 mg/L) are reported in Tables 5.4 and Table 5.5 respectively. The significant effects have been analyzed graphically for chlorite (Figure 5.1), chlorate (Figures 5.2 and 5.3) and DCAA (Figure 5.5).

Generally, chlorite formation was most affected by changes in pH (from 5 to 9) and ClO_2 :NPOC (from 0.3 to 1.1) whereby producing higher concentrations when at their higher levels. In the case of chlorate, in addition to pH and ClO_2 :NPOC ratio, varying chlorate concentration (from 0 to 0.2 mg/L) was also identified as a significant main effect. While increases in ClO_2 :NPOC (from 0.3 to 1.1) and chlorate concentration (from 0 to 0.2 mg/L) produced an increase in chlorate formation, an increase in pH (from 5 to 9) decreased chlorate formation when at the 1.1 ClO_2 :NPOC ratio. Temperature, reaction time, chlorate concentration (for chlorite formation only) and chlorine concentration were not found to significantly influence chlorite and chlorate formation.

Due to interaction aliasing, identification of significant 2-factor interactions could not be ascertained with absolute certainty. However, sufficient data was provided to show that 2-factor interactions can be important in chlorite and chlorate formation. Temperature and reaction time parameters should not be overlooked as being significant in the formation of either chlorite or chlorate due to their involvement in a number of statistically significant 2-factor interactions (temperature most notably).

Due to the low chloroform formation (less than 15 $\mu\text{g/L}$ in all experimental trial runs for Factorial #1 and #2), analysis of significant main and interaction effects was not conducted for this DBP. While DCAA was the most consistent HAA which

formed in the tested waters, statistical analysis was performed on DCAA data obtained from Factorial #1 only. Varying the ClO_2 :NPOC ratio from its low to high level resulted in the greatest change in DCAA concentration (about 28 $\mu\text{g/L}$). Changes in DCAA concentration were too small to confirm any effects caused by variations in pH and temperature. The effect of a significant 2-factor interaction on DCAA was also questionable.

Plots of DBP concentration with respect to chlorine dioxide consumed (Figures 5.7 through 5.9) indicated that increasing chlorine dioxide dosing increased chlorite, chlorate and DCAA formation. Based on plotted linear trendlines, average chlorine dioxide conversion ratios to chlorite and chlorate were estimated at 57% and 6% respectively (on a concentration to concentration basis). Given the R^2 values which ensued from the linear trendlines, modeling chlorine dioxide consumption then applying these conversion ratio estimates (for instance 57% for chlorite and 6% for chlorate) could also, in theory, allow for another approach in developing predictive model equations for chlorite and chlorate (in contrast to modeling these DBPs directly in terms of the various parameters). The reported conversion ratios for chlorite were found to vary from 0.39 to over 0.70 while those for chlorate varied from 0.04 to 0.164. Although varying the ClO_2 :NPOC ratio (from 0.3 to 1.1) and pH (from 5 to 9) did not significantly modify resulting chlorate conversion ratios, variations in pH from 5 to 9 did provide increases in chlorite conversion ratios. For all practical purposes, it was hypothesized that chlorite and chlorate formation could be assumed to result from a linear relationship with respect to the given low to high level parameter variations which were examined.

CHAPTER 6

MODELING DBP FORMATION UPON APPLICATION OF CHLORINE DIOXIDE TO NATURAL WATER MATRICES

6.1 Overview

This chapter presents results obtained from factorially-designed experiments performed using raw natural waters. The principal goal of these factorial experiments was to model DBP, chlorite and chlorate formation as well as chlorine dioxide consumption in terms of significant main parameters (refer to Table 6.1 for list of investigated factors) and 2-factor interactions.

Factorial experiments were performed on seven surface and one groundwater which were obtained from different water treatment plants located in Ontario (see Figure 3.1, Chapter 3). Physical-chemical water quality parameters were recorded to characterize the eight waters (Table 6.2). The organic content of each water was described by measuring the non-purgeable organic carbon (NPOC) level (as mg/L) and the ultra-violet (UV), absorbance at 254 nm (whereby the specific absorbance can subsequently be calculated). Special efforts were made to select waters having a range of NPOC levels. Parameters such as manganese and iron concentrations were also measured since they can exert a chlorine dioxide demand.

The low and high levels of the respective parameters which were examined during the factorial experiments are reported in Table 6.1. The high and low levels reported in Table 6.1 for NPOC and UV_{254} correspond to the lowest and highest levels observed for any of the eight test waters. In addition to monitoring for chlorine dioxide consumption, chlorite and chlorate formation, HAA₉ and TTHMs (for

Table 6.1 Experimental Factors and Levels Investigated in Factorial Experiments Performed on Raw Waters (i.e. Boundary Conditions)

Factor	Parameter Values	
	Lowest Level Examined/Observed^b	Highest Level Examined/Observed^b
pH	6	9
Temperature (°C)	4	25
Chlorine dioxide Concentration (mg/L)	1.0	6.0
Reaction time (hr)	1	24
NPOC (mg/L)	0.60 (groundwater) 2.03 (Toronto) ^a	5.96
UV₂₅₄ (cm⁻¹)	0.009 (groundwater) 0.039 (Toronto) ^a	0.212
NPOC*UV₂₅₄ (mg/L*cm⁻¹)	1.264	0.0054

^a Water obtained from the Toronto R.L. Clark treatment had the lowest NPOC and UV₂₅₄ for the seven surface waters examined in this study.

^b It should be noted that some factors were adjusted to the specified low or high parameter level.

Table 6.2 Water Quality Parameters of Tested Raw Source Waters

Parameter ^a	Water Treatment Plant (water source)							
	Brantford (Grand River via Homedale Canal)	Ottawa Brittania (Ottawa River)	Windsor (Detroit River)	Metro Toronto R.L. Clark (Lake Ontario)	Peterborough (Otonabee River)	Belleville (Bay of Quinte)	Mann- heim Surface water ^b (Grand River)	Mannheim Groundwater ^b (Waterloo groundwater supply, Well K-26)
NPOC (mg/L)	4.29	5.96	2.06	2.03	4.82	4.96	5.71	0.60
UV ₂₅₄ (cm ⁻¹)	0.118	0.212	0.042	0.034	0.136	0.140	0.147	0.009
Specific abs. (cm ⁻¹ /mg/L)	0.028	0.036	0.020	0.017	0.028	0.028	0.026	0.015
pH	8.01	7.21	7.98	8.04	7.80	8.11	7.95	7.57
Alkalinity (mg/L as CaCO ₃)	223.3	33.3	93.7	98.2	80.5	99.5	170.5	265.8
Turbidity (NTU)	2.75	3.91	24.0	2.30	0.73	3.84	6.03	< 0.1
Colour	15.4 TCU	33.1 TCU	5.40 TCU	3.92 TCU	15 TCU	20 app. col. units	21 TCU	no app. colour
Bromide (mg/L)	0.030	0.020	0.022	0.041	< 0.020	< 0.020	0.034	0.027
Iron (mg/L)	0.118	0.254	0.290	0.196	< 0.100	< 0.100	< 0.100	< 0.100
Manganese (mg/L)	< 0.100	< 0.100	< 0.100	< 0.100	< 0.100	< 0.100	< 0.100	< 0.100
Ammonia (mg NH ₃ -N/L)	0.45	< 0.20	< 0.20	< 0.20	< 0.20	< 0.20	0.20	< 0.20

^a Bolded values represent "extreme" parameter conditions (i.e. lowest or highest value recorded for the given parameter)^b Located in Kitchener, Ontario

duplicated samples only) measurements were also taken. Correlations between chlorine dioxide demand, chlorite and chlorate formation and surrogates for precursor-related parameters were investigated. Appendix D contains a number of plots displaying such correlations. Pure error estimates for chlorine dioxide consumed, the monitored DBPs, and UV_{254} measurements are also included in this chapter (a sample calculation can be found in Appendix F).

The development of model equations capable of predicting chlorine dioxide consumption as well as chlorite and chlorate formation was accomplished with the use of stepwise multiple linear regressions fitting a Generalized Linear Model (GLM). The statistical analyses were performed using the statistical software package Minitab®, Student version (Minitab Inc., 1995). A typical statistical data output generated by the software package can be seen in Appendix H. Unless otherwise specified, main and 2-factor interactions having a significant effect on the response variables at the 5% significance level (unless otherwise specified) were included in the predictive models. The standard deviation associated with each model term coefficient for the developed predictive model equations can be found in Appendix E. Each model equation was validated with “internal” (i.e. levels employed as part of the original model data base) as well as with “external” (i.e. levels reported in the literature and levels observed upon testing waters not part of the model development database) response levels. Results pertaining to the experimentally-based “external” validation are presented in table-format in Appendix K. Diagnostic graphs of model residuals can be found in Appendix G while histograms displaying “internal” model validation data are depicted in Appendix H. Sensitivity analyses (described later in this chapter) of the relevant

model equations under given experimental parameter variations were performed (further details and relevant sample calculation can be found in Appendix I). Plots of chlorite and chlorate formation in terms of chlorine dioxide consumption were drawn and conversion ratios calculated. The “robustness” of these conversion ratios were examined with respect to parameter variations as per Table 6.1. A sample calculation for evaluating conversion ratio “robustness” is reported in Appendix J.

UV₂₅₄ measurements taken for trial runs of all tested waters allowed for the examination of possible correlations between chlorine dioxide consumption, chlorite, chlorate, as well as DCAA formation and changes in UV₂₅₄. These results are also presented in this chapter while Appendix L includes a number of these correlation plots.

6.2 Model Formulation

Since research regarding modeling organic and inorganic DBP formation when applying chlorine dioxide is limited, concepts arising from modeling organic DBP (TTHMs) upon chlorination were considered. In their study, Amy *et al.* (1987a), when examining THM formation, transformed both dependent (i.e. response variables) and independent variables to natural-log forms due to results shown by Engerholm and Amy (1983a and b), where such transformations were found to adequately describe TTHM formation. The significance of log-transforming both the response and independent variables is reasonable. For instance, considering the simplistic chlorine dioxide-precursor material reaction depicted in eqn. 6.1, it is logical to assume that

situations may arise whereby either reactant will limit the given reaction, thus suggesting a log relationship with respect to DBP formation.

In addition, log-transformation of the data was useful in this study in meeting the assumption of constant variation which underlies linear regression. An example of this is shown in Figures 6.1 and 6.2 where chlorite formation is plotted against $\text{NPOC} \cdot \text{UV}_{254}$ in untransformed and log-transformed states respectively for the different source waters. To assess the drawn linear regressions, various statistical information has been provided with the figures: R^2 -values (coefficient of estimation which provides an indication as to the percentage of the response level variation explained by the given correlation), s (standard error of the estimate), F -statistic (which tests the hypothesis that both regression coefficients have values of zero) and associated P -values (level of significance at which the given hypothesis can be rejected). Unless otherwise noted, the provided statistical data pertain to the regression performed on the “individual chlorite levels observed by water source case”. The R^2 -value for the regression involving “average chlorite level per water source” case has been given to illustrate that organic content explains a good portion of the variability between average water source chlorite formation.

The eight “columns of data”, displayed in both of these figures, constitute the chlorite formation observed for each of the eight water sources. It can be observed that in the log-transformed case (Figure 6.2), the variation in chlorite levels between the different water sources is reduced (i.e. the eight “columns of data” display greater height length similarities). As such, response variable concentrations (of chlorine

Figure 6.1 Chlorite Formation in terms of $\text{NPOC} \cdot \text{UV}_{254}$

Figure 6.2 Log(Chlorite Formation) in terms of $\text{Log}(\text{NPOC} \cdot \text{UV}_{254})$

dioxide consumed as well as chlorite and chlorate formed) and all parameter levels (Table 6.1) have been log-transformed (base 10).

Surrogates for DBP precursor material which were examined with respect to their relevance for inclusion in the predictive model equations included NPOC and UV_{254} . Examples of chlorite formation response level variations with respect to these surrogates are shown in Figures 6.3 and 6.4 for the eight investigated water sources. Both regressions produced similar R^2 , s , F-statistic and associated P-values.

In the model equations formulated by Amy *et al.* (1987a) predicting THMFP, the parameter found to best overall represent precursor-related surrogate parameter was $NPOC \cdot UV_{254}$. The same authors discussed the chemical relevance of such a selection where NPOC relates to precursor concentration while UV_{254} gives evidence as to the reactivity of the precursor material with, in their case, chlorine to form TTHM. As such, the response variable response with respect to combinations of both individual organic-precursor surrogate terms such as $NPOC \cdot UV_{254}$ (Figure 6.2 for chlorite) as well as $UV_{254}/NPOC$ (specific absorbance, Figure 6.5 for chlorite) were also investigated. $NPOC \cdot UV_{254}$ displayed a better correlation to chlorite formation when compared to $UV_{254}/NPOC$, and equivalent to correlations for either NPOC and UV_{254} as evaluated by the four aforementioned regression statistics (R^2 , s , F-statistic and P-value). Similar results were observed for chlorine dioxide consumption and chlorate (Figures D.1-D.4 and Figures D.5-D.8 respectively, Appendix D). As such, on the basis of the chemical significance brought forward by Amy *et al.* (1987a) as well as the “added” descriptive information defining precursor material using two surrogates

Figure 6.3 Log(Chlorite Formation) in terms of Log(NPOC)

Figure 6.4 Log(Chlorite Formation) in terms of Log(UV_{254})

Figure 6.5 Log(Chlorite Formation) in terms of Log($\text{UV}_{254}/\text{NPOC}$)

rather than one (i.e. average of both effects based on a geometric mean), $\text{NPOC} \cdot \text{UV}_{254}$ was selected as the parameter defining precursor-related material for all three response variables (i.e. chlorine dioxide, chlorite and chlorate).

When considering the low and high levels examined for the parameters which were experimentally-controlled (Table 6.1), log-transforming the low parameter level for chlorine dioxide concentration and reaction time (i.e. 1.0 mg/L and 1.0 hour respectively) would have resulted in a value of zero. To avoid such situations, instead of using $\log(\text{chlorine dioxide})$ and $\log(\text{reaction time})$, these parameters have been expressed as $\log(\text{chlorine dioxide} + 1)$ and $\log(\text{reaction time} + 1)$ respectively. A similar procedure was described by Amy *et al.* (1987a) for their bromide concentration parameter whereby this concentration would be negative upon ln-transformation.

6.3 Statistically-based Models to Predict Chlorine Dioxide Consumption, Chlorite and Chlorate Formation

Statistically-based models, which may be employed to predict chlorine dioxide consumption as well as chlorite and chlorate formation, as developed in this study, are presented along with their associated statistics in Tables 6.3, 6.4 and 6.5 respectively. For each of these three response variables, empirical models were developed for different model cases which included: i) Significant main factors only (Case A), ii) significant main factor and 2-factor interactions involving experimentally-varied factors only (Case B), iii) significant main and 2-factor interactions (Case C), iv) significant main and 2-factor interactions based on data from the seven tested surface waters only (i.e. neglecting groundwater data) and lastly, iv) Case E (applied to chlorate only), based on data obtained using the seven tested surface waters only and where effects are

Table 6.3 Model Equations Predicting Chlorine Dioxide Consumption and Associated Model Statistical Data

Equation Term	Predictive Model Equation Equations for Log(chlorine dioxide consumption, mg/L)			
	Model A ^a	Model B ^a	Model C ^a	Model D ^a
Coefficient	-0.759	-0.4	-0.435	-0.482
log(pH)	0.353	0.334	0.334	0.338
log(Temp.)	0.174	-0.0355 (NS)	-0.0911 (NS)	-0.0934 (NS)
log(ClO ₂ dose + 1)	0.852	0.251 (NS)	0.422	0.455
log(Rxntime + 1)	0.131	-0.0271 (NS)	-0.0350 (NS)	-0.0288 (NS)
log(NPOC*UV ₂₅₄)	0.360	0.356	0.283	0.162
log(Temperature) *log(ClO ₂ dose + 1)	-	0.366	0.366	0.361
log(ClO ₂ dose + 1) *log(RxnTime + 1)	-	0.276	0.276	0.258
log(NPOC*UV ₂₅₄) *log(Temp.)	-	-	-0.0950	-0.114
log(NPOC*UV ₂₅₄) *log(ClO ₂ dose + 1)	-	-	0.292	0.336
F-statistic; P-value	159.45; < 0.001	138.95; < 0.001	144.97; < 0.001	159.60; < 0.001
R ²	0.871	0.893	0.920	0.934
Standard Error of Estimate (SEE)	0.1404	0.1288	0.1128	0.0822
Sum of Squares of the Errors (SSE)	2.3276	1.9238	1.4507	0.6886
# of Trial Runs	124	124	124	112

- ^a Case A = significant main parameters
Case B = significant main and 2-factor interactions involving experimentally-varied parameters
Case C = significant main and 2-factor interactions
Case D = significant main and 2-factor interactions for 7 tested raw surface waters
- Note: “-” = term not included in given equation
Temp. = temperature, °C ; Rxntime = reaction time, hours
ClO₂dose = chlorine dioxide dose, mg/L
NPOC = non-purgeable organic carbon, mg/L
UV₂₅₄ = UV absorbance @ 254 nm, cm⁻¹
(NS) = P-value of term coefficient was greater than 0.05 (i.e. not significant at a significance level of 0.05)

Table 6.4 Model Equations Predicting Chlorite Formation and Associated Model Statistical Data

Equation Term	Predictive Model Equation Coefficient for log(chlorite, mg/L)			
	Model A ^a	Model B ^a	Model C ^a	Model D ^a
Coefficient	-1.34	-0.996	-0.734	-0.346
log(pH)	0.899	0.899	0.446	-0.070 (NS)
log(Temp.)	0.135	-0.0450 (NS)	-0.0450 (NS)	-0.0253 (NS)
log(ClO ₂ dose + 1)	0.777	0.175 (NS)	0.471	-0.597
log(Rxntime + 1)	0.161	-0.0338 (NS)	-0.0803 (NS)	-0.136
log(NPOC*UV ₂₅₄)	0.425	0.425	0.837	-0.0038 (NS)
log(Temp.) *log(ClO ₂ dose + 1)	-	0.313	0.313	0.293
log(ClO ₂ dose + 1) *log(RxnTime + 1)	-	0.340	0.340	0.393
log(pH) *log(ClO ₂ dose + 1)	-	-	-	1.27
log(NPOC*UV ₂₅₄) *log(pH)	-	-	-0.711	-
log(NPOC*UV ₂₅₄) *log(Temp.)	-	-	-	-
log(NPOC*UV ₂₅₄) *log(ClO ₂ dose + 1)	-	-	0.465	0.670
log(NPOC*UV ₂₅₄) *log(RxnTime + 1)	-	-	-0.0729	-0.161
F-statistic; P-value	106.45; < 0.001	84.91; < 0.001	97.01; < 0.001	182.34; < 0.001
R ²	0.814	0.832	0.892	0.948
Standard Error of Estimate (SEE)	0.1986	0.1900	0.1541	0.0766
Sum of Squares of the Errors (SSE)	4.8107	4.3340	2.7768	0.5919
# of Trial Runs	128	128	128	112

- ^a Case A = significant main parameters
Case B = significant main and 2-factor interactions involving experimentally-varied parameters
Case C = significant main and 2-factor interactions
Case D = significant main and 2-factor interactions for 7 tested raw surface waters
- Note: Temp. = temperature, °C ; Rxntime = reaction time, hours
ClO₂dose = chlorine dioxide dose, mg/L; UV₂₅₄ = UV absorbance @ 254 nm, cm⁻¹
NPOC = non-purgeable organic carbon, mg/L
“-“ = term not included in given equation
(NS) = term coefficient not significant at a significance level of 5%

Table 6.5 Model Equations Predicting Chlorate Formation and Associated Model Statistical Data

Equation Term	Predictive Model Equation Coefficients for log(Chlorate, mg/L)				
	Model A ^a	Model B ^a	Model C ^a	Model D ^a	Model E ^a
Coefficient	-2.47	-2.08	-1.79	-2.33	-1.99
log(pH)	0.780	0.780	0.450	1.05	0.621
log(Temp.)	0.150	-0.0732 (NS)	-0.126	0.323	-0.090 (NS)
log(ClO ₂ dose + 1)	1.161	0.481	0.632	0.079 (NS)	0.698
log(Rxntime + 1)	0.154	-0.0398 (NS)	-0.0863	0.219 (NS)	-0.104
log(NPOC*UV ₂₅₄)	0.197	0.197	0.652	0.145	0.0460 (NS)
log(Temp.) *log(ClO ₂ dose + 1)	-	0.390	0.390	0.389	0.389
log(ClO ₂ dose + 1) *log(RxnTime + 1)	-	0.338	0.338	0.346	0.346
log(pH)*log(Temp.)	-	-	-	-0.523	-
log(pH) *log(ClO ₂ dose + 1)	-	-	-	0.714	-
log(pH) *log(RxnTime + 1)	-	-	-	-0.373	-
log(NPOC*UV ₂₅₄) *log(pH)	-	-	-0.516	-	-
log(NPOC*UV ₂₅₄) *log(Temp.)	-	-	-0.0820	-0.0990	-
log(NPOC*UV ₂₅₄) *log(ClO ₂ dose + 1)	-	-	0.238	0.486	0.486
log(NPOC*UV ₂₅₄) *log(RxnTime + 1)	-	-	-0.0728	-0.119	-0.119
F-statistic; P-value	175.91; < 0.001	165.24; < 0.001	160.85; < 0.001	168.41; < 0.001	207.28; < 0.001
R ²	0.878	0.906	0.938	0.957	0.948
Standard Error of Estimate (SEE)	0.1409	0.1248	0.1027	0.08392	0.09016
Sum of Squares of the Errors (SSE)	2.4227	1.8694	1.2237	0.6853	0.8291
# of Trial Runs	128	128	128	112	112

- ^a Case A = significant main parameters
Case B = significant main and 2-factor interactions involving exp.-varied factors
Case C = significant main and 2-factor interactions
Case D = significant main and 2-factor interactions for 7 tested raw surface waters
Case E = Case D where effects significant at the 1% significance level
- Note: “-” = term not included in given equation
(NS) = term coefficient not significant at a significance level of 5%

deemed significant at the 0.01 significance level. The above model cases were selected so as to observe general model differences when model equations included different 2-factor interactions or were based on data from a specific water type (i.e. surface waters). One can see that Model D (Table 6.5) for chlorate consisted of 14 terms which were significant at the 5% significance level. Since chlorate formation is typically low (i.e. about seven times less than chlorite formation), for practical purposes, Model E was developed for chlorate based on effects deemed significant at the 1% significance level so as to reduce the number of model terms for a more “manageable” predictive equation to result without sacrificing predictability power. It is unclear why so many terms were identified in Model D for chlorate formation.

Chlorite and chlorate models were developed using data obtained in all 128 trial runs, whereas the development of chlorine dioxide models were based on 124 runs (2 measurements were unsuccessful and 2 measurements were statistically shown to be “outlying” values which had great influence on the linear regression and as such, were removed). Pure error estimates (sample calculation provided in Appendix F), arising from the replicated sample levels (see Table 3.7, Chapter 3 for identification of trial runs replicated for given water sources) observed for chlorine dioxide consumed, chlorite, chlorate, dichloroacetic acid and UV_{254} changes, are reported in Table 6.6. Since model development was based on log-transformed values and because this transformation results in similar variances between replicated measurements of chlorine dioxide consumed and associated DBPs when at either high or low concentrations, the pure error assessments for those compounds were conducted on log-transformed data.

Table 6.6 Pure error Estimates of Experimental Variation

Compound	# of Duplicates	Pure Error ^a Estimate	Pure Error ^a Estimate on a % basis
Chlorine Dioxide Consumed	15	0.0260 ^b	$10^{\pm 0.0260} = \approx \pm 6 \%$
Chlorite	14	0.0306 ^b	$10^{\pm 0.0306} = \approx \pm 7 \%$
Chlorate	16	0.0296 ^b	$10^{\pm 0.0296} = \approx \pm 7 \%$
DCAA	13	0.0450 ^b	$10^{\pm 0.0450} = \approx \pm 10 \%$
Change in UV ₂₅₄	15	0.002 ^c	-

^a Pure error reported as standard deviation of the pure error of the measurements

^b Estimate based on log-transformed data where untransformed data in mg/L except for DCAA which was originally expressed in µg/L

^c Estimate based on untransformed data in cm⁻¹

In accordance with Peixoto (1990) and Griepentrog *et al.* (1982), to obtain well-formulated polynomial regression models, hierarchically-inferior terms to significant 2-factor interactions (involving these inferior terms) should also be included in the predictive equations. For instance, if the chlorine dioxide dose-temperature interaction was evaluated as statistically significant (such as was the case for all response variables), then the “chlorine dioxide dose” and “temperature” factors were also included in the model, regardless of whether these parameters were found to have significant effects by themselves (i.e. in these cases, at the specified 5% or 1% level of significance) on DBP formation or chlorine dioxide consumption. It is believed by the preceding researchers that not doing so may lead to incorrect statistical analysis of the data.

For illustrative purposes, a developed equation predicting chlorite formation (Model D) is presented in eqn. 6.2. As previously noted, the developed equations are statistically-based. Hence, they do not provide any information regarding the rate of reaction mechanisms as their kinetically-based equation counterparts do. The model equations presented in this study differ mainly from those developed by other researchers for other disinfectants (Amy *et al.*, 1987a; 1987b; Morrow and Minear, 1987; Lyn and Taylor, 1993) in that they incorporate 2-factor interactions. By doing so, it is anticipated that this will “refine” the parameter effects on DBP formation or disinfectant consumption by the presence of additional terms. For instance, considering equation (6.2), the effect of temperature on chlorite formation has been captured not only singularly but through the temperature-chlorine dioxide concentration

interaction. In addition, providing 2-factor interactions which include $\text{NPOC} \cdot \text{UV}_{254}$ should improve model fit by accounting, as much as they can, for differences between the organic content of different water sources.

$$\log(\text{Chlorite conc, mg/L}) = \quad (6.2)$$

$$\begin{aligned} & - 0.346 - 0.070\log(\text{pH}) - 0.0253\log(\text{Temp.}) - 0.597\log(\text{ClO}_2\text{conc.} + 1) \\ & - 0.136\log(\text{RxnTime} + 1) - 0.0038\log(\text{NPOC} \cdot \text{UV}_{254}) \\ & + 0.293\log(\text{Temp.}) \cdot \log(\text{ClO}_2\text{conc.} + 1) + 0.393\log(\text{ClO}_2\text{conc.} + 1) \cdot \log(\text{RxnTime} + 1) \\ & + 1.27\log(\text{pH}) \cdot \log(\text{ClO}_2\text{conc.} + 1) \\ & + 0.670\log(\text{NPOC} \cdot \text{UV}_{254}) \cdot \log(\text{ClO}_2\text{conc.} + 1) \\ & - 0.161\log(\text{NPOC} \cdot \text{UV}_{254}) \cdot \log(\text{RxnTime} + 1) \end{aligned}$$

General observations can be made upon examining the statistical information pertaining to each formulated model. Considering the progression from Model A to Model D for all three response variables, an increase in the amount of chlorite, chlorate and chlorine dioxide consumption variation explained by the model equations was observed as indicated by increases in R^2 -values (it should be noted that Model D and E were based on fewer data when compared to the other model cases) and decreases in SSE (sum of squares of the errors), SEE (standard error of the estimate) and model constant coefficient (i.e. y-intercepts). This progression should be somewhat expected since the latter model equations encompass more factor terms (by way of 2-factor interactions) which provide added information describing chlorine dioxide consumed or formed chlorite and chlorate. Hence, since Models A and B are lacking certain significant parameter effects on the three response variables thus inevitably reducing their predictive ability, upcoming model validations as well as related discussions will focus on Models C, D and E only.

6.3.1 Internal Model Validations

Prior to analyzing any of the terms which make up the formulated models with any great detail, the models were first assessed to verify that they are well-formulated in that they reasonably satisfy the underlying assumptions of linear regression. Predicted response levels were then compared to measured response levels (i.e. response concentrations which made up the database for model development) to verify that the model equations yielded reasonable predictions and identify any potential shortcomings of the model equations. The three main assumptions underlying linear regression, as reported by McKenzie *et al.* (1995) in the accompanying Student Edition of Minitab® for Windows User's Manual, are that: i) The error constituent should be normally-distributed, ii) have a constant deviation (i.e. constant variation) and iii) should be independently-distributed. Significant violations of any of these three assumptions can influence results implied by the linear regression analysis.

Examples of diagnostic plots based on residual data (i.e. measured - predicted response levels) for Models D (predicting chlorine dioxide consumption and chlorite formation), E (predicting chlorate formation) and C (for all three response variables) which verify these three assumptions are provided in Appendix G (Figures G.1 through G.18). Additional details concerning these diagnostic graphs such as residual standardization are also included in this Appendix. Based on the normalized plots of the standardized residuals (plots G.1, G.4, G.7, G.10, G.13 and G.16, Appendix G), it can be observed that the error components are reasonably normally-distributed. As a "general guideline", the standardized residuals following a normal distribution should

have a mean of zero and standard deviation of one and as such, most of the standardized residuals are expected to have values between -3 and 3 (Montgomery, 1997). The presence of “outlying” points can indicate problems with the predictive potential of the model. It should be noted that intentions were to consider all trial run data unless serious “outlying” data (whose experimental validity were questionable) were identified (four points as for chlorine dioxide) thus necessitating removal. As displayed by the normal plots of the standardized residuals, only a few runs possessed residuals beyond ± 3 (plots G.1, G.4, G.7, G.10, G.13 and G.16, Appendix G). Graphs verifying the constant variance assumption (Figures G.2, G.5, G.8, G.11, G.14 and G.17, Appendix G) resulted mostly in scattered data plots, not showing any evident data trends. For Model C, more variability (i.e. greater differences between predicted and measured levels) was observed at the lowest prediction levels (which were associated to the groundwater source). Based on the time-plots of the standardized residuals (Figures G.3, G.6, G.9, G.12, G.15 and G.18, Appendix G), no “lurking” factors which may affect the results were identified. They did however graphically indicate (via higher residual results) that Model C for chlorite and chlorine dioxide showed some difficulty in fitting the measured levels observed during testing of low NPOC waters: Groundwater (runs 113-128), Toronto (runs 49-60) and Windsor (runs 33-48). Internal model validation will provide information as to whether these “lack-of-fits” are reason for concern. It was thus concluded that assumptions i) to iii) were reasonably met as displayed by the residual diagnostics graphs for Models C, D and E (examples plots displayed in G.1 to G.18, Appendix G). Generally, Models D and E (for chlorate formation) produced the best diagnostics.

Validating the models “internally” with data used in the original database was conducted by using the following three approaches:

1. Perform a regression of predicted responses against measured levels.
2. Develop frequency histograms of % recovery distribution (i.e. Predicted response/Measured response).
3. Develop frequency histograms of residual distribution (i.e. Measured level - Predicted level).

Combining the results of these three analyses should provide the necessary insight into model pertinence and deficiencies. Approach 1 has been applied by Amy *et al.* (1987a) and Morrow and Minear (1987) when validating their model equations predicting THM formation and THMFP respectively upon chlorine application. An analysis of frequency histograms depicting % deviation between predicted (obtained from developed model equations) and measured values has been presented by Greiner *et al.* (1992) in regard to TCAA and DCAA formations and Harrington *et al.* (1992) in regard to organic carbon concentrations. Results of regressions conducted on predicted values against measured values (Approach 1) for Models C, D and E are reported in Table 6.7. Examples of these regression plots are provided in Figures 6.6 to 6.8 for chlorite, chlorate and chlorine dioxide respectively. Removing the data associated with the one tested groundwater from the database (i.e. Models D and E versus Model C) can be observed to have improved the prediction fits (higher R^2 and lower standard error values were obtained). Considering the line slopes, the models have a tendency to underpredict concentrations levels (especially at higher levels). However, considering the y-intercept slope values of the different equations, it is observed that at lower concentrations, overpredictions would typically occur. For instance, when

Table 6.7 Regression Results of Predicted Chlorite and Chlorate Formed as well as Chlorine Dioxide Consumed Against Measured Concentrations Levels for the Developed Predictive Equations

Compound	Model Case	Equation for Predicted Response Level (mg/L)	R²	SEE
Chlorite formed	A (n= 128)	$= 0.223 + 0.732(\text{MC, mg/L})$	0.879	0.3086
	B (n= 128)	$= 0.120 + 0.842(\text{MC, mg/L})$	0.905	0.3089
	C (n=128)	$= 0.0250 + 0.967(\text{MC, mg/L})$	0.931	0.2986
	D (n= 112)	$= 0.0603 + 0.941(\text{MC, mg/L})$	0.941	0.2665
Chlorate formed	A (n= 128)	$= 0.0365 + 0.689(\text{MC, mg/L})$	0.841	0.04661
	B (n= 128)	$= 0.0232 + 0.802(\text{MC, mg/L})$	0.841	0.05416
	C (n=128)	$= 0.0199 + 0.838(\text{MC, mg/L})$	0.888	0.04632
	D (n= 112)	$= 0.0134 + 0.901(\text{MC, mg/L})$	0.912	0.04411
	E (n= 112)	$= 0.0133 + 0.90(\text{MC, mg/L})$	0.899	0.04758
Chlorine Dioxide consumed	A (n= 124)	$= 0.315 + 0.774(\text{MC, mg/L})$	0.901	0.4059
	B (n= 124)	$= 0.155 + 0.882(\text{MC, mg/L})$	0.914	0.4273
	C (n=124)	$= 0.0494 + 0.964(\text{MC, mg/L})$	0.931	0.4140
	D (n= 112)	$= 0.175 + 0.892(\text{MC, mg/L})$	0.930	0.3853
	"Ideal Case"	$= 0.000 + 1.000(\text{MC, mg/L})$	1.00	0.000

Note: MC = Measured concentration levels (mg/L), consisting of concentrations measured as part of the factorial trial runs and which served as the original data base for the development of the different models.

R² = Coefficient of determination/correlation coefficient

SEE = Standard error of the estimate

Figure 6.6 Predicted and Measured Chlorite Formation Levels (Model D, 112 runs)

Figure 6.7 Predicted and Measured Chlorate Formation Levels (Model E, 112 runs)

Figure 6.8 Predicted and Measured Chlorine Dioxide Consumption Levels (Model D, 112 runs)

taking into account the regression equations reported in Figures 6.6 to 6.8, at concentration levels below 1.63 mg/L, 1.03 mg/L and 0.13 mg/L for chlorine dioxide consumed, chlorite and chlorate formed, overpredictions would occur.

All frequency diagrams relating to residual as well as % recovery distributions (Approach 2 and 3) for Models C, D and E (for chlorate only) for chlorine dioxide and the two inorganic DBPs are shown in Appendix H (Figures H.1 to H.14). The percentage of the model database where residuals (evaluated as measured - predicted levels) were within 0 ± 0.2 mg/L and % recoveries (evaluated as predicted levels/measured levels) were within $\pm 20\%$ of the measured values are reported in Table 6.8 for each model case for all three response variables of interest. Progressing from Model C to D or E (for chlorate) resulted in increases in the percentage of the model database falling within the specified ranges. Most notably, using Model case D predicting either chlorine dioxide consumption or chlorite formation, nearly 80% of the predictions were observed to be within 20% of the measured levels. The relevance of developing frequency histograms based on actual residuals can be most evidently seen for chlorate. While between 70 to 78% of the predicted chlorate levels were within $\pm 20\%$ of the measured values, 96.1-100% of the residuals were within 0 ± 0.2 mg/L and 90.6-95.5% were within 0 ± 0.1 mg/L for any given model equation. In the case of chlorate formation, if model validation were assessed on residual distributions, all three models would display excellent accuracies in predicting chlorate formation observed from the given water experiments. It is believed herein that, identifying model equations which are more successful in predicting DBP formation or chlorine dioxide consumption would best be achieved by examining both types of data (i.e. %

Table 6.8 % of Original DataBase where Residuals Fall Within ± 0.2 mg/L and % Recoveries Fall Within $\pm 20\%$ of the Measured Values

Compound	Model case	% of Original Data having a Residual ^a Within 0 ± 0.2 mg/L	% of Original Data having a % Recovery ^b Within $\pm 20\%$ of Measured Level
Chlorine Dioxide Consumed	A (n= 128)	41.1	52.4
	B (n= 128)	50.0	57.3
	C (n= 128)	57.3	66.9
	D (n= 112)	70.0	79.5
Chlorite	A (n= 128)	49.2	39.8
	B (n= 128)	52.3	50.8
	C (n= 128)	64.1	50.0
	D (n= 112)	71.4	77.7
Chlorate^c	A (n= 128)	96.1 (90.6)	50.0
	B (n= 128)	97.8 (89.8)	60.9
	C (n= 128)	98.4 (93.0)	70.3
	D (n= 112)	100.0 (95.5)	77.7
	E (n= 112)	99.1 (94.6)	72.3

^a Residual = Measured level (mg/L) - Predicted level (mg/L)

^b % Recovery = Predicted level (mg/L) / Measured level (mg/L)

^c Values reported in () correspond to % of original database having a 0 to ± 0.1 mg/L residual

recoveries and concentrations differences recorded as residuals). For example, when considering Model C (for chlorite), about 50% of the predictions were observed to be within 20% of the measured values thereby leading one to question the “explanatory” capability of this model. However, if one ponders that approximately 64% of the predictions are within 0 ± 0.2 mg/L of the measured levels, then one should be cautious before quickly dismissing such a model.

On the basis of the model diagnostic and internal model validation checks performed on the given model equations, it is concluded that Models C, D and E were reasonably well-formulated (i.e. met the linear regression assumptions) and complete (in terms of incorporating main as well as 2-level interactions significant at the 5% significance level). However, developed predictive equations based on data from the seven tested surface waters only (i.e. D and E for chlorate formation) were found to exhibit the greatest accuracy in predicting chlorite and chlorate formation/chlorine dioxide consumption observed upon experimental testing of the given test waters. Given the model validation results, Model E predicting chlorate formation which included terms having effects deemed to be significant at the 1% significance level was found to be more “practical” (i.e. consisted of less model terms) than its Model D counterpart but had near similar prediction capabilities. Hence, treatment plant operators would be recommended to employ Model D equations to predict chlorine dioxide consumption (see Table 6.3) and chlorite formation (Table 6.4) and use Model E (Table 6.5) for chlorate formation predictions.

6.3.2 Physical-Chemical Relevance of Model Equations

Typically (apart from 2 interaction terms for Model D predicting chlorate formation), 2-factor interactions solely consisting of experimentally-varied factors deemed statistically significant had regression coefficient values evaluated as being positive. Given the parameter boundary conditions and the model term formulation, the predicted *relative* effect of these terms on the response variable will be to increase its concentration. The theoretical basis of greater chlorine dioxide consumption and chlorite and chlorate formation at higher temperatures, chlorine dioxide doses and reaction times has been well-documented (Table 2.8, Section 2.4, Chapter 2). It should be strongly stressed that the aforementioned increases are simply *relative* predicted level increases (i.e. isolating these specific terms without considering the effect of any other terms included in the given model). If one were interested in evaluating the effect of these specific terms on predicted chlorine dioxide consumed predictions, one would have to specify parameter levels for each and every other model term. A main reason for doing so is that parameters making up either of these 2-factor interactions take part in other term equations which, invariably also have a relative influence on the response variable level outcome. Hence, model users are urged not to make great inferences from individual term equations.

In cases where no chlorine dioxide consumption is observed, chlorite and chlorate production is not expected. With this mind, comparing the model equations predicting chlorine dioxide consumption (Table 6.3) to those predicting either chlorite or chlorate formation (Table 6.4 and 6.5 respectively), it is not unexpected that these

predictive equations consist of similar terms. For instance, in addition to the five main parameter terms, the temperature-chlorine dioxide concentration and chlorine dioxide-reaction time and chlorine dioxide concentration-NPOC*UV₂₅₄ interactions were observed to be significant terms for all three response variables.

When contrasting the predictive model equations for chlorine dioxide consumed, chlorite and chlorate formation, for a given model case, the chlorine dioxide model equations were found to be “less complex” (i.e. consisting of fewer terms). Differences involving 2-factor interactions incorporating experimentally-varied parameters only were observed for the models resulting from the analyses of measured levels from the 7 tested surface waters (i.e. Model cases D and E). One hypothesis for terms found in the chlorite and chlorate formation models and not in the chlorine dioxide model is that they relate to chlorine dioxide disproportionation. Typically, these said “added” terms (involving interactions of experimentally-controlled factors only) generally included pH. As reported in the literature, greater disproportionation of chlorine dioxide to chlorite and chlorate can be expected at higher pH levels (Andrews *et al.*, 1997; Oehler *et al.*, 1986 and Rosenblatt, 1978). Hence, the presence of these terms should not be surprising in predictive chlorite and chlorate equations but not in the equation predicting chlorine dioxide demand. In regards to the “added” terms involving NPOC*UV₂₅₄, these terms may also be attributed to influencing chlorine dioxide disproportionation.

Since Models D and E were observed to produce more accurate predictions of the measured response levels, including 2-factor interactions involving NPOC*UV₂₅₄ in

the formulated models did indeed help in improving the model fits. This suggest that these terms will thus, “adjust” the response prediction level in accordance with water organic content. The reader should be cautious in making any great deductions from isolated $\text{NPOC} \cdot \text{UV}_{254}$ terms without considering the other model $\text{NPOC} \cdot \text{UV}_{254}$ interaction terms since they more likely than not, act as a group to provide the necessary adjustment.

6.3.3 Sensitivity Analyses

Due to the nature of the predictive equations (i.e. logarithmic form) and the presence of 2-factor interactions, the evaluation of parameter effects on predicted concentrations is more involved than model equations which are based on untransformed data or consisting of main parameter effects only. The fact that the equations are in a log-transformed state, changes in parameter conditions (i.e. such as varying the pH from 6 to 9) essentially result in percentage changes in the predicted response concentrations. As such, performing any type of sensitivity analysis would be specific to the parameter levels selected to conduct the given examination. Furthermore, to evaluate the effect caused by a parameter which takes part in one or more 2-factor interactions, one would inevitably need to quantify the other parameter taking part in the said interaction(s) as is implied by the fact that the observed effect is an “interactive” one. For these reasons, each treatment facility which utilizes these models would be urged to assess “model sensitivity” to parameter variations under their own water and treatment conditions. In order to provide the reader with some understanding on the “functionalities” of the developed equations, a sensitivity analysis

example will be presented along with an evaluation of the contribution of each parameter to the explanatory “power” of the given equations.

A sensitivity analysis example pertaining to chlorine dioxide consumption (using Model D), chlorite formation (using Model D) and chlorate formation (using Model E) is graphically displayed in Figure 6.9, 6.10 and 6.11 respectively. The parameter levels selected for the experimentally-controlled parameters (reported in Figures 6.9 to 6.11) represent either typical or average values of the low and high parameter levels investigated during the factorial experiments. The displayed results illustrate the effect on response variable predictions of varying one parameter level while the other factors remain at a set “baseline” value.

It can be seen that progressing from waters having low NPOC and UV_{254} levels to waters having higher NPOC and UV_{254} levels, ensued in greater predictions regarding chlorine dioxide consumed as well as chlorite and chlorate formed. This was anticipated since the higher NPOC and UV_{254} waters showed a greater demand for chlorine dioxide whereby producing higher DBP levels for these said waters. As one could intuitively foresee, the greatest change in predicted response levels resulted from a variation in chlorine dioxide dose.

Contrasting sensitivity analyses results obtained using Model C with those obtained from using Model D or E (for chlorate) allowed for a general examination of the effect of including the groundwater data on the development of predictive equations and subsequently, on response variable concentrations (Table I.2, Appendix I). In comparison to Model C, predictions resulting from Model D for chlorine dioxide and chlorite, and Model E for chlorate were greater for low NPOC and UV_{254} waters

Note: Groundwater = Mannheim groundwater; Mannheim = Mannheim surface water

Baseline conditions:

pH = 7.5, Temp. = 14.5°C, ClO₂ dose = 3.5 mg/L and rxn time = 12.5 hrs

Trial pH: 8

Trial temp.: 20°C

Trial ClO₂ dose: 2.5 mg/L

Trial reaction time: 8 hrs

Figure 6.9 Sensitivity Analysis Example for ClO₂ Consumed, Model D

Note: Groundwater = Mannheim groundwater; Mannheim = Mannheim surface water

Baseline conditions:

pH = 7.5, Temp. = 14.5°C, ClO₂ dose = 3.5 mg/L and rxn time = 12.5 hrs

Trial pH: 8

Trial temp.: 20°C

Trial ClO₂ dose: 2.5 mg/L

Trial reaction time: 8 hrs

Figure 6.10 Sensitivity Analysis Example for Chlorite Formation, Model D

Note: Groundwater = Mannheim groundwater; Mannheim = Mannheim surface water

Baseline conditions:

pH = 7.5, Temp. = 14.5°C, ClO₂ dose = 3.5 mg/L and rxn time = 12.5 hrs

Trial pH: 8

Trial temp.: 20°C

Trial ClO₂ dose: 2.5 mg/L

Trial reaction time: 8 hrs

Figure 6.11 Sensitivity Analysis Example for Chlorate Formation, Model E

(Toronto and Windsor), were similar for mid-ranging NPOC and UV_{254} levels (Brantford) and were lower for high NPOC and UV_{254} waters (Peterborough, Belleville, Mannheim surface and Ottawa). These trends suggest that including the groundwater in the database (as was the case in Model C), “drove” the linear regressions downward at the low NPOC* UV_{254} level thereby resulting in a steeper regression line. This provides some indication that the groundwater exhibited high leverage thereby having an important influence on the model regressions. As a result, model equation C tends to overpredict at high NPOC* UV_{254} and underpredict at low. It is unclear whether this situation arises due to the smaller and/or nature of the organic content found in the groundwater. Since the Brantford water had a mid-range NPOC* UV_{254} level, the response predictions for this water will experience less variance than waters at the NPOC* UV_{254} boundary levels such as Ottawa or Toronto. Hence, it is highly likely that the developed model equations will have a greater applicability for waters having a mid-range NPOC* UV_{254} level similar to the level recorded for the Brantford water.

The percent (%) contribution of each parameter to the “explanatory power” of a given predictive equations has been calculated. The explanatory power of an equation may be defined as the variation in the measured levels (which were part of the original database) explained by the model equations, as determined by the regression sum of squares (SS). The % contributions to the explanatory power of the equation for a given parameter (i.e. pH, temperature, chlorine dioxide dose, reaction time and NPOC* UV_{254}) is, in essence, the gain in adding the terms containing the specific parameter to the equation R^2 -value. These % contributions should not be confused

with the % contributions of these same parameters to the response variable (i.e. chlorine dioxide consumed, chlorite and chlorate formed) concentrations predicted by these equations as they are not necessarily interchangeable. The % contributions were calculated using eqn. 6.3. A sample calculation is provided in Appendix I. All calculated % contributions (for either Models D and E) were found to be statistically significant based on calculated F-statistics (F-values provided in Appendix I, Table I.1).

$$\% \text{ contribution} = ((A-B)/A) * 100\% \quad (6.3)$$

where A = Regression sum of squares (SS) with all terms

B = Regression sum of squares (SS) without terms involving specific factor

The percent contribution of the examined parameters are graphically shown in Figure 6.12, 6.13 and 6.14 for chlorine dioxide consumption (Model D), for chlorite formation (Model D) and for chlorate formation (Model E) respectively. As can be seen by these figures, the sum of the contribution of all the individual parameter contributions is greater than 100%. This is due to the fact that the 2-factor interactions have been accounted for twice during the calculations. For instance, the temperature-chlorine dioxide concentration interaction will be accounted in the “temperature” as well as “chlorine dioxide concentration” % contribution calculations. For this reason, the difference between the “sum of all contributions” and 100% can be attributed to the contribution of the 2-factor interactions. For example, for Model case D for chlorite formation (Figure 6.13), the 2-factor interactions have contributed 14.7% to the model equation explanatory power as calculated from the regression sum of squares values.

Figure 6.12 Model D (ClO_2): % Contribution of Parameter Effects (Main and 2-Factor Interactions) to Regression SS (Sum of Contributions = 106.1%)

Figure 6.13 Model D (Chlorite): % Contribution of Parameter Effects (Main and 2-Factor Interactions) to Regression SS (Sum of Contributions = 114.7%)

Figure 6.14 Model E (Chlorate): % Contribution of Parameter Effects (Main and 2-Factor Interactions) to Regression SS (Sum of Contributions = 106.7%)

Based on the % contribution results, the parameters have been ordered as to their relative importance in terms of their contributions to equation explanatory power:

For Chlorine Dioxide Consumption (Model D):

$\text{ClO}_2 \text{ dose} > \text{NPOC} * \text{UV}_{254} > \text{Temperature} * > \text{Reaction Time} * > \text{pH}$

For Chlorite Formation (Model D):

$\text{ClO}_2 \text{ dose} > \text{NPOC} * \text{UV}_{254} > \text{Reaction Time} > \text{pH} * > \text{Temperature} *$

For Chlorate Formation (Model E):

$\text{ClO}_2 \text{ dose} > \text{NPOC} * \text{UV}_{254} > \text{Reaction Time} > \text{Temperature} > \text{pH}$

Note: * indicate a pair of parameter % contributions within 1 % of each other.

Based on the given results for the observed experimental data, chlorine dioxide concentration and $\text{NPOC} * \text{UV}_{254}$ had the greatest contributions while pH had the smallest when developing the above model equations.

6.3.4 DBP Model Predictions Based on Conversion Ratios of Chlorine Dioxide Consumed to Chlorite and Chlorate

Chlorite as well as chlorate formation was plotted with respect to chlorine dioxide consumption (Figures 6.15 and 6.16 respectively). As shown by the correlation coefficients, linear trendlines adequately fit the experimental data. Based on these linear regressions, it is found that approximately 68% and 9% (as described by the regression slope coefficients, neglecting the y-intercept values) of the chlorine dioxide consumed is converted to chlorite and chlorate respectively (on a mass basis). These conversion ratios are consistent with those reported in the literature by other researchers (see Table 2.6, Chapter 2) and relatively comparable to those found during the synthetic water experiments (57% and 6% respectively). Since the trendline R^2 -

Figure 6.15 Chlorite Formation With Respect to Chlorine Dioxide Consumption For Natural Test Water Factorial Experiments (n= 126 cases)

Figure 6.16 Chlorate Formation With Respect to Chlorine Dioxide Consumption For Natural Test Water Factorial Experiments (n= 126 cases)

values are deemed satisfactory, the possibility exists to predict chlorite and chlorate formation by applying the above conversion ratios subsequent to predicting chlorine dioxide consumption using the developed model equations (Table 6.3). Hence, the approach first consisted of predicting chlorine dioxide consumption using Model D since this model was found to be most accurate. Secondly, and if necessary, the predicted chlorine dioxide consumption levels were corrected to account for overpredictions (i.e. if predicted ClO_2 values $>$ applied ClO_2 dose used to obtain the prediction then the predicted ClO_2 levels are to be “defaulted” to the applied ClO_2 dose values). Subsequently, the appropriate conversion ratios (i.e. 68% for chlorite and 9% for chlorate) were applied to the chlorine dioxide consumption predictions.

Regression equations pertaining to chlorite and chlorate formation in terms of chlorine dioxide consumption obtained for a particular parameter condition (i.e. high pH condition, low temperature condition etc.) are presented in Table J.1 while those pertaining to the specific water sources are reported in Table J.2 (both tables are shown in Appendix J). It can be observed that the reported slope coefficients for chlorite and chlorate formation generally had values within $68\% \pm 13\%$ and $9\% \pm 5\%$ for these respective DBPs. Additional details are provided in Appendix J concerning the effects of potential “outlying points” on certain regression fits (i.e. R^2 -values).

F-statistics were developed to verify whether employing the 68% and 9% conversion ratios for chlorite and chlorate formation in terms of chlorine dioxide consumption (see Figures 6.15 and 6.16) produced a residual sum of squares (RSS) which was significantly different from the RSS calculated from regression equations for either a given parameter level or water source. A sample calculation is provided in

Appendix J. Based on the developed F-statistics and associated P-values (Table J.3, Appendix J), statistically-significant differences (at the 5% significance level) between RSS were observed upon varying pH, reaction time and water source (i.e. biggest conversion ratio differences observed for waters of low organic content such as Windsor, Toronto and the groundwater) while for chlorate, when varying chlorine dioxide concentration or water source. However, on a practical engineering basis, regression slope differences within 10-13% and 6% of the chlorine dioxide conversion ratios respectively observed for chlorite and chlorate formation are small enough to be tolerated. Thus, chlorite and chlorate formation predicted in terms of chlorine dioxide consumption based on a conversion ratio of 68% and 9% (mass by mass) respectively, irrespective of parameter level and water source was conducted since such practices were deemed reasonable on a practical basis.

Based on frequency histograms of residuals and % recoveries (Plots H.15-H.18, Appendix H), chlorite and chlorate formation predictions (using the chlorine dioxide consumption Model D and associated conversion ratio) for the measured DBP levels used during model development were not very promising: For chlorite, 66% of the residuals were within 0 ± 0.2 mg/L while 67% of the recoveries were within 80 to 120% of the measured value while these percentages for chlorate were respectively found to be 99% and 41%. After comparing these values with those reported in Table 6.8 for the chlorite and chlorate model equations directly incorporating parameter effects (i.e. pH, temperature, etc.), it is concluded that the chlorite and chlorate predictions via chlorine dioxide consumption estimates were less accurate. Moreover, on a site-specific basis (Table 6.9), predicting either chlorite or chlorate formation

Table 6.9 Number of Trials Runs Having Percent Recoveries between 80% and 120% of the Measured Chlorite and Chlorate Levels

Water source (NPOC, mg/L; UV ₂₅₄ , cm ⁻¹)	Chlorite			Chlorate	
	Model D	From 0.68* (ClO ₂ pred. From Model D)	From 0.68* (Measured ClO ₂)	Model E	From 0.09* (ClO ₂ pred. From Model D)
Brantford (4.29; 0.118)	11	12	13	14	10
Ottawa (5.95; 0.212)	9	8	10	9	3
Windsor (2.06; 0.042)	14	9	10	14	9
Toronto (2.03; 0.034)	13	7	7	13	7
Peterborough (4.82; 0.136)	13	12	14	15	7
Belleville (4.96; 0.140)	12	12	13	13	6
Mannheim Surface (5.71; 0.148)	16	15	16	11	4
Mannheim Groundwater (0.60; 0.009)	N/A	N/A	N/A	N/A	N/A
Total^a	88 out of 112	75 out of 112	83 out of 112	89 out of 112	46 out of 112

Note N/A = Not applicable (i.e. groundwater data was not included in the model development of Model D for chlorine dioxide and chlorite or Model E for chlorate)

^a "Grand" total of number of trial runs determined as 16*7 (i.e. 16 different trial runs tested for each of the seven surface waters)

after first estimating chlorine dioxide consumption did not produce great (if any) enhancement in prediction accuracy when compared to Model D or E predicting chlorite (Table 6.4) and chlorate (Table 6.5) formation directly from the given parameter effects.

Essentially, the chlorite and chlorate predictions can be as good as the chlorine dioxide consumption predictions. For instance, based on results in Table 6.9, it is observed that a greater number of predicted chlorite concentrations were within 20% of the measured levels when predicting chlorite levels by applying the 68% conversion ratio to *measured* chlorine dioxide consumed values versus *predicted* chlorine dioxide consumed levels using Model D (Table 6.3). It is also hypothesized that there may be a “compounding” of errors whereby the error from inaccurate chlorine dioxide consumption predictions is “combined” with the error in estimating the conversion ratios. This “compounding” of errors may have caused more inaccuracies (i.e. less predictions falling within 20% of the measured levels) in the chlorite and chlorate predictions versus predictions from the model D and E respectively (see Tables 6.4 and 6.5). Further, the above results (results presented in Figures G.15-G.18 compared to those reported in Table 6.8) may be demonstrating that terms which are associated with chlorine dioxide disproportionation and not necessarily chlorine dioxide consumption (i.e. such as the pH-chlorine dioxide concentration interaction for chlorite) are important in obtaining more accurate chlorite and chlorate predictions.

Thus, to predict chlorite and chlorate formation, treatment plant operators using the models would be recommended to employ model equations developed directly from

parameter effects (Models D and E respectively) for more adequate capture of the “site-specificity” of their water’s organic content.

6.3.5 External Validations of Predictive Model Equations

The final step of model assessment involved performing external model validations. This consisted of testing the accuracy of the model equations in predicting measured levels of chlorine dioxide consumed and chlorite and chlorate formed which were not part (i.e. “external”) of the original database of measured response levels employed for model development. These validations allowed the evaluation of the general applicability of the predictive model equations for parameter conditions which are different from those examined during the raw water factorial experiments (Table 6.1). Two data sources were employed for the external validation: i) Conc. levels resulting from experiments conducted separately from those performed for model development and, ii) levels which have been reported in the literature.

6.3.5.1 Experiment Data

The “external” water sources used during experimental testing included waters obtained from regions outside the province of Ontario (Table 6.10): Michigan (USA), British Columbia and Alberta. A groundwater (from Guelph, ON) had also been obtained however, the observed levels of chlorine dioxide consumption (<0.18 mg/L), chlorite (< 0.12 mg/L) and chlorate (<0.03 mg/L) formation were too limited for pertinent comparisons to be made with predicted values thus, these values have not been included herein. The external validation experiment of all four waters was conducted on the same day. The raw water samples were sent to the laboratory from the various treatment plants in 18-liter carboys. Upon their arrival, the carboys were

Table 6.10 Experimental Factors and Levels Investigated During External Validation Experiment

Water Source	Parameter Condition			
	pH ^a	Temperature (°C)	Chlorine Dioxide dose (mg/L)	Reaction Time (hour)
Vancouver (NPOC = 1.47 mg/L; UV ₂₅₄ = 0.043 cm ⁻¹)	6.57	6	1.51	1
	6.57	6	1.51	4
	6.68	20	1.51	1
	6.68	20	1.51	4
Calgary (NPOC = 2.05 mg/L; UV ₂₅₄ = 0.045 cm ⁻¹)	8.37	4	1.51	1
	8.37	4	1.51	4
	8.46	20	1.51	1
	8.46	20	1.51	4
Brantford (NPOC = 4.83 mg/L; UV ₂₅₄ = 0.121 cm ⁻¹)	7.79	4	1.51	1
	7.79	4	1.51	4
	7.87	20	1.51	1
	7.87	20	1.51	4
Ann Arbor (NPOC = 5.10 mg/L; UV ₂₅₄ = 0.141 cm ⁻¹)	7.78	4	1.51	1
	7.78	4	1.51	4
	7.70	20	1.51	1
	7.70	20	1.51	4

^a Ambient pH level measured when sample had attained its test temperature.

stored at 4°C (all waters were stored for less than one week) until “testing day”, except for the Vancouver (B.C.) water which arrived in the laboratory on “testing day” and as such, was not stored. Examined parameter conditions are reported in Table 6.10. pH measurements were taken when water samples had attained their desired temperature levels (explaining the slight pH level differences reported in Table 6.10 for each water source). The NPOC and UV_{254} levels of these raw waters were measured (Table 6.10). Further details concerning the experimental procedure undertaken to perform this experiment are given in Section 4.5 (Chapter 4).

As can be seen by the results presented in Figures 6.17 to 6.19, on a general basis, model predictions for chlorine dioxide consumption as well as chlorite and chlorate formation fit measured levels reasonably well. Predictions resulting from Model C were also calculated for the given water sources since this model equation evolved from the testing of waters having NPOC levels encompassing the NPOC levels recorded for “external” water sources (Table K.1, Appendix K). Results shown graphically in Figures 6.17 to 6.19 are also reported in table form in Table K.1 (Appendix K). It can be observed that Models D (for chlorine dioxide consumption and chlorite formation) and E (for chlorate formation), models developed based on surface water data only, had better predicting capabilities than Model C (developed from surface and groundwater data). While assessing whether level predictions fell within $\pm 20\%$ of the measured levels was a sensible means of evaluation for chlorine dioxide consumption and chlorite formation, performing such an evaluation with respect to chlorate formation would be less effective due to the small observed yield for this DBP. Nonetheless, it can be noticed that differences between measured and

Figure 6.17 External Validation Experimental Results, Model D: Comparison of Measured and Predicted Chlorine Dioxide Consumption Levels (chlorine dioxide dose of 1.51 mg/L, ambient pH condition)

Figure 6.18 External Validation Experimental Results, Model D: Comparison of Measured and Predicted Chlorite Formation Levels (chlorine dioxide dose of 1.51 mg/L, ambient pH condition)

Figure 6.19 External Validation Experimental Results, Model E: Comparison of Measured and Predicted Chlorate Formation Levels (chlorine dioxide dose of 1.51 mg/L, ambient pH condition)

predicted chlorate levels were typically well below 0.06 mg/L indicating good predictive model equations capabilities. It should be pointed out that Model D more than adequately predicted both chlorine dioxide consumption and chlorite formation for the water from Vancouver, B.C. even though the lowest NPOC and UV_{254} observed for the seven surface waters (i.e. 2.03 mg/L and 0.038 cm^{-1} respectively) which constituted the Model D database were higher than the levels observed for the Vancouver water. Hence, Model D predictions which were obtained by extrapolation also seemed to be reasonable close to the measured levels.

While for the higher organic carbon-containing waters (i.e. Brantford (ON) and Ann Arbor (MI)), the calculated levels had a tendency to underpredict chlorine dioxide consumption, chlorite and chlorate formation, these underpredictions were still within 20% of the measured levels.

6.3.5.2 Literature Data

Information required to perform appropriate validations arising from data published in the literature were found to be limited; only references which reported NPOC levels were employed (Table 6.11). In certain cases, some parameter conditions were not reported in the literature. In order to employ the predictive model equations, values for such parameters have been assumed. The assumed UV_{254} levels were based on levels observed with respect to the NPOC levels recorded for the different water sources tested throughout this thesis work (Figure 6.20).

As observed for the external validation experiments, predictions from Model D (E for chlorate formation) for chlorine dioxide consumption and chlorite formation fit the measured levels reported in the literature fairly well. Upon comparing the results

Table 6.11 External Model Validation Results Based on Concentration Levels Reported in the Literature

Reference	Water Source	Concentration ^a (mg/L)			Parameter Condition				
		Chlorine Dioxide Consumed	Chlorite	Chlorate	pH	Temp. (°C)	ClO ₂ Dose (mg/L)	React. Time (hrs)	NPOC* UV ₂₅₄ (mg/L*cm ⁻¹)
Karpel <i>et al.</i> (1996)	Plant B (River water)	N/A	1.15 (0.68)	0.21 (0.08)	7.4	Dec. '92 "10"	2.0	8.0	2.7**0.069"
			1.07 (0.75)	0.14 (0.09)				14.0	
			1.12 (0.77)	0.14 (0.09)				17.0	
Aieta <i>et al.</i> (1984)	Sacramento San Joachin Delta water(CA)	> 0.955 (0.88)	0.724 (0.59)	< 0.255	8.2	"20"	1.0	2.0	3.3**0.088"
		> 0.955 (1.01)	0.732 (0.71)	< 0.255				48.0	
Werdehoff and Singer (1987)	-Diluted Raw Northwest River water (VA)	0.87 (0.73)	0.63 (0.47)	N/A	7	room ^b	1.0	1.0	2.1**0.050"
	-Finished Drinking water (VA)	2.0 (1.53)	1.46 (0.99)	N/A	7	room ^b	2.0	6.0	5.2**0.149"
			0.65 (0.81)	0.50 (0.65)	N/A	7	room ^b	1.0	20.0
Oehler <i>et al.</i> (1986)	Gallenklinge raw water, Struttgard (Germany)	1.28 (1.07)	0.68 (0.68)	N/A	"7"	15	1.70	1.0	3.8**0.104"
		0.95 (0.84)	0.65 (0.56)	N/A	"7"	15	1.02	1.0	
		0.65 (0.72)	0.45 (0.50)	N/A	"7"	15	0.68	1.0	
		1.68 (1.15)	1.03 (0.75)	N/A	"7"	15	1.70	4.0	
		1.00 (0.88)	0.69 (0.59)	N/A	"7"	15	1.02	4.0	
		0.68 (0.74)	0.47 (0.50)	N/A	"7"	15	0.68	4.0	

Note: N/A = Not available, Values reported in " " are assumed levels

^a Values in () are levels predicted by Model D for chlorine dioxide consumed and chlorite formation and Model E for chlorate formation

^b Room temperature was assumed to be 20°C

Figure 6.20 UV₂₅₄ Measurements With Respect to Water Source NPOC Observed During Raw Water and External Model Validation Experiments

in Figures 6.17-6.19 and Table K.1 (Appendix K) with Table 6.11, it is seen that predictions from Model D (E for chlorate) were more accurate in fitting the measured levels found experimentally than the measured levels reported in the literature. However, it is likely that, model predictions based on literature data were influenced by assumptions made concerning parameter condition values so as to employ the different model equations thus, conceivably not reflecting the “true” parameter conditions at hand.

6.3.5.3 Applicability of Model Equations

It was concluded that the model equations based on surface water data only (i.e. Models D and E) exhibit reasonable prediction capabilities. However, model users applying the predictive equations to high organic carbon content waters (over 3.8 mg/L of NPOC) or reaction times found to be between 1 and 24 hours (especially over 4 hours) should do so with care. Based on results reported in Figures 6.17-6.19 and Table 6.11, for higher organic carbon-containing waters like Brantford (ON), Ann Arbor (MI), Northwest water (VA) and Gallenklinge water (Germany), calculated levels were found to underpredict chlorine dioxide consumption, chlorite and chlorate formation. Predictions resulting from the previously-noted reaction time cases also tended to underpredict chlorine dioxide consumption, chlorite and chlorate formation (evidently more prevalent for waters having higher NPOC levels). This last observation may indicate that, in certain occurrences, chlorine dioxide consumption as well as DBP formation may follow a more non-linear response in regards to reaction time. Due to the fact that a number of parameter level assumptions were made, one

cannot make concrete conclusions regarding differences between predicted and measured levels for the literature data-based external validation.

6.3.6 Considerations and Limitations of Predictive Model Equations

It should be stressed that the applicability of the developed model equations would best be limited to parameter levels within “boundary conditions”, established mostly by the low and high levels investigated for each parameter during the factorial experiments (Table 6.1). Any user of the models presented herein would be discouraged from applying the models at levels for the given factors (whether it be $\text{NPOC} \cdot \text{UV}_{254}$ or any of the experimentally-controlled parameter) which are beyond the tested ranges. If one would still do so, resulting predictions would come about as extrapolations of model equations since model development was not based on those factor levels. Extra care should also be exercised when applying the model equations to parameter conditions (especially in the case of reaction time) which are found to be between the low and high parameter levels investigated for model development (Table 6.1): Predicted levels may be lower than “actual” levels due to possible non-linear responses to parameter variations. It would be recommended that if a predicted negative concentration level were to appear upon application, then this level be defaulted to zero. In addition, if predicted concentrations are greater than the applied chlorine dioxide doses (as could occur in predicting chlorine dioxide consumption and to some extent, chlorite formation), the predicted levels should be defaulted to the applied chlorine dioxide dose. Since the developed predictive model equations are log-based and incorporate 2-factor interactions, treatment plant operators would be strongly urged to assess “model

sensitivity” in regards to either chlorine dioxide consumption or chlorite and chlorate formation to parameter variations under their own parameter and water conditions.

6.4 Organic DBP Formation

As earlier discussed in Chapter 5, while the major drawbacks of applying chlorine dioxide as a disinfectant is the formation of its inorganic chlorite and chlorate by-products, organic HAA (i.e. HAA₉) and THM (TTHMs) DBPs were monitored to examine their formation when treating raw water systems.

Only limited halogenated organic by-product formation when using chlorine dioxide has been reported in the literature by such researchers as Carnimeo *et al.* (1995), Richardson *et al.*, (1994), Sansebastiano *et al.* (1995) and Werdeoff and Singer, (1987). Similarly to results reported earlier for the synthetic water experiments (Section 5.6, Chapter 5), dichloroacetic acid (DCAA) was the HAA most consistently observed in the water sources examined. Its concentration levels were always below the 60 µg/L regulatory level proposed in the American D/DBP rule (Fed. Reg., 1994). Other HAAs such as monochloroacetic acid (MCAA), bromochloroacetic acid (BCAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA) and chlorodibromoacetic acid (CDBAA) were also sometimes observed however, their presence was inconsistent from water to water and their concentrations were low, typically ranging from “below detection limit” to 3 µg/L and rarely exceeding 5 µg/L. For these reasons, the following section will pertain to a discussion of DCAA formation only.

One of the main conclusions drawn from the chlorine dioxide experiments performed on synthetic waters with respect to controlling HAA formation (Chapter 5) was to limit the applied chlorine dioxide dose:NPOC ratio (i.e. limiting the applied chlorine dioxide dose). For this reason, the observed DCAA concentrations as a function of terms of applied chlorine dioxide dose and natural water NPOC has been presented (Figure 6.21). The DCAA concentrations have also been plotted against natural water UV_{254} for a better contrast of DCAA formation observed for the eight different water sources (as seen by the eight “columns” of data displayed in Figure 6.22). One can take notice that the DCAA levels recorded when a 1.0 mg/L chlorine dioxide dose was applied were typically below 5 $\mu\text{g/L}$, and were found to be below the detection limit of 1 $\mu\text{g/L}$ for the natural test waters having NPOC levels below 2 mg/L (most notably for the groundwater).

The only DCAA formation of significance resulted from dosing the Peterborough (NPOC=4.82 mg/L; UV_{254} =0.136 cm^{-1}), Belleville (NPOC= 4.96 mg/L; UV_{254} =0.140 cm^{-1}), Mannheim surface (NPOC=5.71 mg/L; UV_{254} =0.148 cm^{-1}) and most especially Ottawa (NPOC=5.95 mg/L; UV_{254} =0.212 cm^{-1}) waters with 6.0 mg/L of chlorine dioxide yielding average DCAA levels of 7.51, 7.78, 5.75 and 24.15 $\mu\text{g/L}$ respectively. It should be noted that the previously-mentioned average DCAA levels pertained to a chlorine dioxide dose of 6 mg/L while conditions for pH, temperature and reaction time were either at either their low or high levels (Table 6.1). The fact that the 6.0 mg/L chlorine dioxide dosing of the Mannheim surface water (NPOC=5.71 mg/L; UV_{254} =0.148 cm^{-1}) yielded lower DCAA levels than the Peterborough (NPOC=4.82 mg/L; UV_{254} =0.136 cm^{-1}) and Belleville

Note: The eight “columns of data” which are displayed, constitute DCAA formation levels observed for each of the eight water sources.

Figure 6.21 DCAA Formation In Terms of Test Water NPOC

Note: The eight “columns of data” which are displayed, constitute DCAA formation levels observed for each of the eight water sources.

Figure 6.22 DCAA Formation In Terms of Test Water UV₂₅₄

(NPOC = 4.96 mg/L; UV_{254} = 0.140 cm^{-1}) waters suggests that the type of organic content may be a greater issue than the amount of organic content present in the test waters. It is hypothesized that in the case of the Ottawa water (NPOC = 5.95 mg/L; UV_{254} = 0.212 cm^{-1}), more NPOC-chlorine dioxide reactions took place which resulted in greater DCAA formation than in the other investigated waters.

Hence, as previously suggested by Hazen and Sawyer (1992) applying a “high chlorine dioxide dose” to a water having relatively high NPOC and UV_{254} levels such as the Ottawa water (NPOC = 5.95 mg/L; UV_{254} = 0.212 cm^{-1}) can lead to DCAA formation important enough to warrant some concern and special attention. However, while DCAA has been observed experimentally to result from chlorine dioxide-organic matter reactions such as in the case of the Ottawa water, it should be noted that under the same experimental conditions, chlorite formation was found to be typically between 2 to 4 mg/L. Those concentrations are much greater than the proposed 1 mg/L MCL for chlorite (Fed. Reg., 1994). As such, it is anticipated that meeting the suggested chlorite MCL requirement would be of more concern than the formation of DCAA. Hence, given the DCAA results obtained, treatment plants operating at a chlorine dioxide dose of 1.0 mg/L (or even applying a high dose of 6 mg/L to low organic content waters of 2 mg/L) could expect to produce only very limited (if any) amounts of DCAA (i.e. 5 μ g/L) and as such, would best concentrate their efforts in minimizing chlorite and chlorate formation.

Monitoring of TTHM formation resulted in the observation of extremely limited amounts of chloroform (Table 6.12). Hence, as reported by a number of authors in the

Table 6.12 Chloroform Formation Observed During Factorial Experiments on the Natural Water Systems

Water Tested	Parameter Condition				Chloroform conc. ^{c,d} (µg/L)
	pH	Temp. (°C)	ClO ₂ dose (mg/L)	Reaction Time (hr)	
Mannheim Groundwater	6	25	6.0	1	N/A ^a
Mannheim Groundwater	9	4	1.0	24	1.09
Toronto ^b	6	4	1.0	1	1.69
Toronto ^b	9	25	6.0	24	2.52
Windsor	6	4	1.0	24	1.33
Windsor	9	25	6.0	1	2.35
Brantford	6	4	6.0	24	1.52
Brantford	9	25	1.0	1	0.97
Peterborough	6	25	6.0	24	1.09
Peterborough	9	4	1.0	1	1.12
Belleville	6	25	1.0	24	1.45
Belleville	9	4	6.0	1	1.93
Mannheim Surface	6	4	6.0	1	1.30
Mannheim Surface	9	25	1.0	24	1.16
Ottawa	6	25	1.0	1	1.59
Ottawa	9	4	6.0	24	1.46

^a N/A = Not available due to lost sample

^b 1.05 µg/L of bromoform also detected in this sample (detection limit = 0.5 µg/L)

^c Chloroform detection limit = 0.6 µg/L

^d Reported chloroform concentrations are averages of duplicated samples

literature including Lafrance *et al.*, 1993; Lykins and Griesse, 1986; Muttamara *et al.*, 1995; Werdehoff and Singer, 1987 and Jun *et al.*, 1996, chlorine dioxide-organic material reactions are expected to yield only insignificant amount of trihalomethanes. It should be noted that raw water bromide levels did not exceed 41 $\mu\text{g/L}$. While brominated THMs were rarely observed, water treatment plants treating waters containing higher bromide levels would be urged to verify that brominated THMs formation would also be minimal when applying chlorine dioxide to their waters.

6.5 UV Analyses

As demonstrated earlier in this chapter section, and as reported by such researchers as Amy *et al.* (1987) and Morrow and Minear (1987), DBP formation (and chlorine dioxide consumption) can be correlated to the light absorbed by natural waters at a wavelength of 254 nm. The electrons “promoted” once a molecule absorbs light make up the functional group known as chromophores (Korshin *et al.*, 1987b). Typically, chromophores are associated with the natural organic matter (NOM) humic fraction (Korshin *et al.*, 1997b). Recknow *et al.* (1990) reported that humic substances generally are aromatic in nature. It was on the basis that since NOM aromaticity is associated with both UV absorbance as well as DBP formation, there likely exists a relationship between UV absorbance and DBP formation that Korshin *et al.* (1997a) examined the relationship between UV absorption changes and THM formation upon chlorination. Korshin *et al.* (1997b) had observed a good correlation between chloroform formation and UV_{254} changes (ΔUV_{254}) when chlorinating four independent

water sources (i.e. DOC 2.0 to 3.6 mg/L) at a dose of 16 mg/L, pH of 7.00 and reaction times between 2 and 72 hours.

This section examines whether chlorine dioxide consumption as well as the formation of either chlorite, chlorate and dichloroacetic acid (DCAA) can be correlated with UV_{254} changes (ΔUV_{254}) when dosing natural waters with chlorine dioxide under various experimental conditions. The purpose of this investigation is to assess whether the observed changes in UV_{254} reflect the effects of pH, temperature, chlorine dioxide concentration and reaction time such that the ΔUV_{254} may be utilized as a sole predictor variable for DBP formation and consumption.

Chlorine dioxide consumption, chlorite, chlorate and DCAA as a formation of ΔUV_{254} are illustrated in Figures 6.23, 6.24, 6.25 and 6.26 respectively for data “pooled” from all eight natural waters. Similar to Korshin *et al.* (1997a, 1997b), no data transformations have been performed on the data sets. In addition, pure error associated with ΔUV_{254} was estimated on untransformed data (Table 6.6). It was believed that this would be more useful when assessing whether observed changes exceeded pure error (i.e. experimental noise), as opposed to expressing pure error on a percentage basis. While skewness of the pure error estimate could be caused by different variances for different absorbance levels when considering non-transformed data, the fact that the experimental noise was evaluated as only 0.002 cm^{-1} (Table 6.6) seems to indicate that any variance skewness (if any) was not of concern. For these graphs, ΔUV_{254} values which were below experimental noise (i.e. below 0.002 cm^{-1}) have been assigned an absorbance reading of 0.001 cm^{-1} . This was done to equally

Figure 6.23 Chlorine Dioxide Consumption With Respect to ΔUV_{254} (UV_{254} Changes Below 0.002 cm⁻¹ Adjusted to 0.001 cm⁻¹)

Figure 6.24 Chlorite Formation With Respect to ΔUV_{254} (UV_{254} Changes Below 0.002 cm⁻¹ Adjusted to 0.001 cm⁻¹)

Figure 6.25 Chlorate Formation With Respect to ΔUV_{254} (UV_{254} Changes Below 0.002 cm^{-1} Adjusted to 0.001 cm^{-1})

Figure 6.26 DCAA Formation With Respect to ΔUV_{254} (UV_{254} Changes Below 0.002 cm^{-1} Adjusted to 0.001 cm^{-1})

account for no change (i.e. zero absorbance) as well as a change of 0.002 cm^{-1} which are both arguably represented by ΔUV_{254} values of less than 0.002 cm^{-1} . Plots of unadjusted values of UV_{254} changes below 0.002 cm^{-1} are displayed in Appendix L (Figures L.1 to L.4). Also displayed in Appendix L (Figures L.5 to L.12) are plots where reported UV_{254} changes are based on absorbance measurements upon performing a certain correction (Section 4.4.1, Chapter 4) for chlorite absorbance interferences. Comparing these different plots (i.e. Figures 6.23 to 6.26 to those shown in Figures L.1-L.12, Appendix L), it can be observed that performing the various corrections (i.e. accounting for chlorite absorbances and experimental noise), while somewhat improving the regression fits, did not alter the data trendlines or regression coefficients significantly. In all cases, UV_{254} changes observed for the groundwater were all found to be within experimental error.

For practical purposes, the discussion provided herein will pertain to the ΔUV_{254} values shown in Figures 6.23 to 6.26. The y-intercept coefficients for the chlorine dioxide, chlorite and chlorate graphs were all positive while for DCAA, they were negative (crossing the x-axis at about 0.002 cm^{-1}). Consequently, it may be assumed that chlorine dioxide consumption as well as chlorite and chlorate formation also occurs without any destruction in absorbance when measured at 254 nm. Interestingly, taking the ratio of the chlorite or chlorate y-intercepts to the chlorine dioxide y-intercept, values of approximately 65% and 9.5% respectively are obtained. These values are consistent with the conversion ratios observed from plots of chlorite and chlorate formation with respect to chlorine dioxide consumption (Figures 6.15 and 6.16). Hence, correlations for these three response variables against ΔUV_{254} appear to

have maintained the integrity of the systems being examined. For the case of DCAA, similar observations were made to those reported by Korshin *et al.* (1997b) with respect to chloroform formation upon chlorination, the regression line did not go through the origin but crossed the x-axis at a positive ΔUV_{254} value. As suggested by Korshin *et al.* (1997b) for chloroform formation upon chlorination, before the formation of DCAA, chlorine dioxide likely destroys chromophores thereby producing other by-product intermediates or destroys inorganic chromophores which would only subsequently (if at all) lead to organic DBP formation (such as DCAA).

Statistical data shown in Figures 6.23 through 6.26 indicate that the various regression equations, when data has been “pooled” from different water sources, were found to be statistically significant (i.e. based on F- and t-statistic and associated P-values). However, the variation in chlorine dioxide consumption as well as chlorite and chlorate formation explained by linear regression were less than adequate as displayed by R^2 -values of less than 0.70. Moreover, one can visually see from these plots that there is a lot of data scatter about the linear regression trendlines. For instance, ΔUV_{254} values between 0.02-0.025 resulted in chlorite formations ranging from approximately 0.25 to over 2 mg/L (Figure 6.24).

The fact that variations in chlorine dioxide consumption and chlorite and chlorate formation were not especially well explained by the linear trendlines was somewhat expected. As shown in the predictive model equations (Tables 6.3 to 6.5), parameters such as pH, temperature, chlorine dioxide concentration and reaction time as well as interactions of these parameters have significant effects on the consumption

of chlorine dioxide or chlorite and chlorate formation. In addition, the percent contributions of these factors to the “explanatory power” of the predictive model equations showed that they were significant (Table I.1). Consequently, the fact that the correlation coefficients for these three response variables are low (below 0.70) appears to indicate that there are effects which are not sufficiently represented in the UV_{254} changes.

Other possible explanations as to this “lack of fit” in the data may be that chlorine dioxide reacted with other compounds present in the water or underwent disproportionation into its inorganic by-products, as per eqn. 6.4 reported by Rosenblatt (1978).

While equation (6.4) may predominantly occur at pH 9 or pH 10, it shows that chlorine dioxide-organic compound reactions are not the sole sources of chlorite and chlorate formation, and that the extent of the reaction depicted in equation (6.1) may be different under given experimental conditions such as temperature, chlorine dioxide dose or reaction time. In essence, a logical premise would be that, although chlorine dioxide-organic compound (most specifically humic substances) reactions generally constitute the foundation of chlorite and chlorate formation, there are other routes for the formation of these *inorganic* by-products (as well as for chlorine dioxide consumption). Discussions presented in Section 6.4 and Section 5.6 (Chapter 5) reported that chlorine dioxide concentration as well as organic content were the most significant factors in DCAA formation. However in contrast to chlorite and chlorate,

the formation of *organic* DBPs such as DCAA (or chloroform formation with respect to UV_{254} changes upon chlorination as reported by Korshin *et al.* (1997a, b)), would largely require these inorganic disinfectants to react with organic compounds. With these facts in mind, the general linear correlation coefficient associated with DCAA formation with respect to ΔUV_{254} (i.e. when pooling data from different test waters) can be anticipated to be greater than for chlorine dioxide consumption or chlorite and chlorate formation. Indeed, in the case of DCAA formation, there was not as much “data scattering” and the R^2 -values (of adjusted or unadjusted data plots) were higher (they were about 0.80).

Since data scattering when pooling data from different sources was observed to be significant, especially for chlorine dioxide consumption and chlorite and chlorate formation, “site-specific” plots of the data have been produced. Plots for chlorite and DCAA are shown in Figures 6.27 and 6.28 respectively. Similar plots for chlorine dioxide consumption and chlorate formation can be found in Appendix L (Figures L.13 and L.14 respectively). The data show that DBP formation as well as chlorine dioxide consumption with respect to ΔUV_{254} is largely site-specific. With the exception of the Mannheim surface water, a general trend appears to be that waters having higher initial UV_{254} levels (Table 6.2) display greater UV_{254} changes. One could assume that source waters containing more chromophores would have greater potentials for chlorine dioxide consumption and by extension, chlorite, chlorate and DCAA formation. Although, this appears to be general trend and not necessary a rule, as shown when

Figure 6.27 Chlorite Formation With Respect to ΔUV_{254} on a Site-Specific Basis (UV_{254} Changes Below $0.002 cm^{-1}$ Adjusted to $0.001 cm^{-1}$)

Figure 6.28 DCAA Formation With Respect to ΔUV_{254} on a Site-Specific Basis (UV_{254} Changes Below $0.002 cm^{-1}$ Adjusted to $0.001 cm^{-1}$)

comparing the Mannheim surface water ($UV_{254} = 0.148$) to the Peterborough and Belleville water (i.e. UV_{254} of 0.136 and 0.140).

Upon examining the various plots, one can observe a “conglomeration” or “plateau” of data points at approximately 1.0 mg/L, 0.7 mg/L, 0.05 mg/L and 4 μ g/L for chlorine dioxide consumed, chlorite, chlorate and DCAA respectively (see Figures 6.23-6.26). As reported in Table 6.1, each source water was initially dosed with either 1.0 or 6.0 mg/L of chlorine dioxide. As such, most of these “plateau” points are associated with a chlorine dioxide dosing of 1.0 mg/L, as shown in Figures 6.29 and 6.30 in regards to, respectively, chlorite and DCAA formation (see Figures L.15 and L.17, Appendix L, for graphs relating to chlorine dioxide and chlorate formation) where data points relating to this one dose have been isolated. This “plateau” effect could possibly be attributed to the fact that, (especially for the waters having a NPOC of greater than 4 mg/L), most (if not all) of the applied chlorine dioxide has been consumed (Figure L.15, Appendix L) whereby a “ceiling” with respect to DBP formation was reached. It should be noted that for DCAA, this “ceiling” effect is not as prominent and its formation is very limited (i.e. generally below 5 μ g/L). In contrast to these water matrices where the chlorine dioxide:NPOC ratio was below 0.5, most of the published results which describe chloroform formation in terms of UV changes (whether at 254 or 272 nm) upon chlorination were performed at chlorine dioxide:NPOC ratios which were greater than 4 (Korshin *et al.*, 1997a; 1997b).

Interestingly, with respect to the Ottawa data (Figures 6.29, 6.30, L.15 and L.17, Appendix L), it can be seen that the eight data points are divided into two groups

Figure 6.29

Chlorite Formation With Respect to ΔUV_{254} on a Site-Specific Basis
For a ClO_2 Dose of 1.0 mg/L (UV_{254} Changes Below 0.002 cm⁻¹
Adjusted to 0.001 cm⁻¹)

Figure 6.30

DCAA Formation With Respect to ΔUV_{254} on a Site-Specific Basis
For a ClO_2 Dose of 1.0 mg/L (UV_{254} Changes Below 0.002 cm⁻¹
Adjusted to 0.001 cm⁻¹)

of “similar” ΔUV_{254} values (cm^{-1}): In the range of 0.014 or 0.025. Data points associated with a UV_{254} change of 0.025 were obtained at a temperature of 25°C while those at the lower UV_{254} change were obtained at a temperature of 4°C. This suggests that a temperature difference may have promoted different chlorine dioxide-NOM reactions thereby yielding different chromophore destruction levels but similar chlorine dioxide consumption and DBP (chlorite, chlorate and DCAA) formation. Due to this “plateau” effect, one would be urged to be cautious in formulating conclusions regarding chlorine dioxide consumption and DBP formation based on UV_{254} changes alone especially in cases where the chlorine dioxide dose:NPOC ratio is low, resulting in the applied disinfectant/oxidant to be nearly or completely consumed.

Chlorite formation data resulting from a chlorine dioxide dose of 6.0 mg/L for three specific waters are presented in Figure 6.31 since they exhibited a high correlation to ΔUV_{254} . Plots for chlorine dioxide consumed and chlorate formation can be found in Appendix L (Figures L.16 and L.18). Unlike the lower chlorine dioxide dose (i.e. 1.0 mg/L), one can observe a linear trend (note that the chlorine dioxide dose:NPOC ratios are greater than 1.0 in these cases) for chlorite formation as well as chlorate and chlorine dioxide consumption. When considering the Peterborough, Belleville and Mannheim surface waters, at the 6.0 mg/L and given pH (either 6 or 9), linear trendlines having high correlation coefficients (i.e. R^2 -values greater than 0.93) were exhibited (note that only four pairs of data points make up each correlation). Korshin *et al.* (1997b), also obtained good correlations for a given chlorine dose and pH condition with respect to chloroform formation. In the case of DCAA formation

Figure 6.31 Chlorite Formation With Respect to UV₂₅₄ Changes on a Site-Specific Basis for a ClO₂ Dose of 6.0 mg/L (UV₂₅₄ Changes Below 0.002 cm⁻¹ Adjusted to 0.001 cm⁻¹)

(Figure 6.30), a different trend was observed: Each test water resulted in roughly the same DCAA yields irrespective of the observed UV_{254} change. This variability in the destruction of chromophores (as evaluated in terms of UV_{254} changes) producing generally constant yields of DCAA tends to signify that the predominance of the chlorine dioxide-NOM reactions are leading to other byproduct formation (such as chlorite) and do not typically favor haloacetic acid formation.

This section demonstrates that ΔUV_{254} analyses may have a certain application in water treatment as a predictor variable for disinfectant consumption or DBP formation. However, such practices would be extremely site-specific and would likely have greater potential for cases where the disinfectant/oxidant was applied in excess to organic content and at specific experimental conditions such as pH and even disinfectant/oxidant dose (so as to avoid “ceiling effects” on DBP formation or disinfectant consumption which would limit the pertinence of ΔUV_{254} as a predictor variable). Each treatment facility would have to conduct their own UV analysis to confirm whether correlations between chlorine dioxide demand and chlorite, chlorate and DCAA formation and ΔUV_{254} exist. Treatment plant facilities would also be urged to verify whether measured chlorite levels significantly interfere with any of their UV_{254} measurements.

6.6 Chapter Summary

This chapter has presented a discussion concerning the development and application of model equations to predict chlorine dioxide consumption as well as chlorite and chlorate formation. These models contain terms representing pH, temperature, chlorine dioxide concentration, reaction time as well as water organic

content (as described by $\text{NPOC} \cdot \text{UV}_{254}$). 2-factor interaction effects involving the aforementioned parameters were also included in the model equations and found to improve the accuracy of the model equations in fitting the measured response variable concentrations. Parameter or interaction effects deemed as statistically significant at the 5 % significance level have been incorporated in the predictive model equations. A model incorporating parameter effects which are significant at the 1 % significance level in terms of chlorate formation was found to be more practical/manageable than the other developed equations (i.e. included less terms) while sacrificing very little in terms of predictive equation explanatory power. For these reasons, that model equation would be the best choice to predict chlorate formation. Pertinent model equations were shown to have “adequate” predictive powers through internal and external validations. The development of model equations based on data from the seven surface waters examined (groundwater data excluded) provided “better-fitting” predictive model equations: Nearly 80% of the predictions for chlorine dioxide consumption and chlorite and chlorate formation were observed to be within 20% of the measured levels (i.e. levels forming the model databases). It was found that over 90% of the chlorate levels predicted by all of the developed models were within ± 0.1 mg/L of the measured levels used in the model database. Chlorine dioxide concentration and $\text{NPOC} \cdot \text{UV}_{254}$ (i.e. water organic content) were found to be key parameters when developing the chlorite and chlorate formation as well as chlorine dioxide consumption model equations. The average conversion of chlorine dioxide consumed to chlorite and chlorate, on a mass basis was found to be approximately 68% and 9% respectively. While these effects were found to be tolerable on a “practical engineering basis”,

varying pH (from 6 to 9), reaction time (from 1 to 24 hours) and water source in the case of chlorite and varying chlorine dioxide concentration (from 1.0 to 6.0 mg/L) and water source in the case of chlorate were found to have statistically-significant impacts on the preceding conversion ratios. For the natural waters examined, THM formation was negligible (1 to 3 $\mu\text{g/L}$) and consisted almost exclusively of chloroform in the tested samples. Dichloroacetic acid (DCAA) was the most consistent HAA observed during testing. With the exception of one case where a 6.0 mg/L chlorine dioxide dose was applied to Ottawa River water (NPOC = 5.95 mg/L, $\text{UV}_{254} = 0.212 \text{ cm}^{-1}$), the typical DCAA formation was observed to be below 10 $\mu\text{g/L}$ and was found to be below 5 $\mu\text{g/L}$ when applying a chlorine dioxide dose of 1.0 mg/L.

Changes in UV_{254} (ΔUV_{254}) observed for the one groundwater (NPOC = 0.60 mg/L, $\text{UV}_{254} = 0.009 \text{ cm}^{-1}$) were found to be within experimental noise. Upon “pooling” data from all eight test waters, a better correlation resulted between DCAA formation and ΔUV_{254} (R^2 -values of 0.81-0.84) than for chlorine dioxide consumption, chlorite and chlorate formation where there was significant data scattering (R^2 -values of 0.44-0.67). In cases where the applied chlorine dioxide was nearly or completely consumed, ΔUV_{254} values were not observed to have a significant effect on either chlorine dioxide consumption, chlorite, chlorate or DCAA formation whereby different values for UV_{254} changes were recorded for similar yields of the four previously-mentioned response variables (approximately 1.0 mg/L, 0.7 mg/L, 0.05 mg/L and below 5 $\mu\text{g/L}$ respectively). Improved correlations between chlorine dioxide consumption or chlorite and chlorate formation with changes in UV_{254} were found to be both site- and parameter-specific. For certain waters (Peterborough,

Belleville and Mannheim surface), at a chlorine dioxide dose of 6.0 mg/L, and a given pH level (pH 6 or 9), chlorine dioxide consumption, chlorite and chlorate formation were observed to be highly correlated to UV_{254} changes.

CHAPTER 7

CONCLUSIONS

7.1 DBP Formation Resulting From the Application of Chlorine Dioxide to Synthetic Water Matrices

Factorial experiments were conducted using synthetic water matrices (NPOC water levels of approximately 6.0 and 2.0 mg/L) to examine chlorite, chlorate, haloacetic acid and trihalomethane formation following the application of chlorine dioxide (ClO_2). The synthetic waters were prepared by adding appropriate amounts of commercial humic acid to organic-free reagent water. Parameter effects on DBP formation which were investigated included pH, temperature, ClO_2 :NPOC ratio and reaction time. The presence of chlorine and chlorate concentrations, as they result during the chlorine dioxide generation process, were also examined as to their effects on chlorine dioxide DBP formation.

The following conclusions may be made from the experimental results:

1. Chlorite formation was most influenced by changes in pH (from 5 to 9) and ClO_2 :NPOC ratio (from 0.3 to 1.1) whereby higher formation was observed at higher levels.
2. In addition to pH and ClO_2 :NPOC ratio, chlorate concentration was also identified as exhibiting a significant main effect (at the 5% significance level) on chlorate formation.
3. Reaction time and temperature (most notably) were involved in a number of statistically significant 2-factor interaction effects in the formation of either chlorite or chlorate (at the 95% significance level).

4. Chlorite and chlorate formation increased linearly with respect to chlorine dioxide consumption: Average chlorine dioxide conversion ratios to chlorite and chlorate were estimated at about 57% and 6% (mass basis) respectively.
5. DCAA was the HAA most consistently observed. Varying the ClO_2 :NPOC ratio from its low to high level (for the 6.0 mg/L NPOC water) resulted in the greatest change in DCAA concentration (about 28 $\mu\text{g/L}$).
6. Trihalomethane formation was limited: Chloroform (the only observed THM) formation was $< 15 \mu\text{g/L}$ in all experimental trial runs.

7.2 Modeling Chlorite and Chlorate Formation Upon Application of Chlorine Dioxide to Natural Water Matrices

2-level factorial experiments were conducted on raw water matrices to develop statistically-based model equations capable of predicting chlorite and chlorate formation upon chlorine dioxide application. Model equations were developed for chlorine dioxide consumption as well as chlorite and chlorate formation on the basis of measured levels recorded for eight different water sources (7 surface waters and one groundwater) originating in Ontario. Parameters included in the developed model equations either as main or as part of 2-factor interaction(s) consisted of pH, temperature, chlorine dioxide dose, reaction time and $\text{NPOC} \cdot \text{UV}_{254}$ (term used to describe water organic content). Chlorine dioxide doses were in the typical range of those which would provide *Giardia* inactivation. Development of the predictive model equations involved applying a log-transformation (base 10) to the response and all independent variables. Measurements of TTHMs (for duplicated samples only) and HAA_9 were also recorded. The following conclusions may be made:

1. The inclusion of 2-factor interactions effects in the model equations improved the accuracy of the model equations in fitting the measured response variable concentrations regarding chlorine dioxide consumed as well as formed chlorite and chlorate. Inclusion of 2-factor interactions encompassing $\text{NPOC} \cdot \text{UV}_{254}$ provided “adjustments” to account for site-specific responses.
2. Through internal and external model validations, model equations based on the seven surface waters data only (i.e. groundwater data excluded) provided “better-fitting” predictive model equations.
3. Chlorine dioxide concentration and $\text{NPOC} \cdot \text{UV}_{254}$ (i.e. water organic content) were the most significant parameters when developing equations to predict chlorite and chlorate formation as well as chlorine dioxide consumption.
4. The average conversion of chlorine dioxide consumed to chlorite and chlorate (mass basis) was estimated as approximately 68% and 9% respectively.
5. Dichloroacetic acid (DCAA) was the most consistent HAA observed during testing. Typical DCAA formation was observed to be below 10 $\mu\text{g/L}$.
6. TTHM formation, typically only chloroform, was negligible (1 to 3 $\mu\text{g/L}$).
7. Upon “pooling” data from all test waters, a better correlation resulted between DCAA formation and ΔUV_{254} values (R^2 of 0.81-0.84) than between chlorine dioxide consumption, chlorite and chlorate formation and UV_{254} changes where there was significant data scattering (R^2 of 0.44-0.67).
8. Improved correlations between chlorine dioxide consumption, chlorite and chlorate formation with changes in UV_{254} were found to exist on a site- and parameter-specific basis.

CHAPTER 8

RECOMMENDATIONS

1. Verification of model applicability at full- and pilot-scale would assess whether predictive model equations developed from bench-scale experiments adequately capture treatment plant conditions and responses.
2. Reducing the chlorine dioxide (ClO_2) dose and water organic content would provide the most efficient means for treatment plants to minimize chlorite, chlorate and haloacetic acid formation upon ClO_2 application.
3. The experimental protocol conducted for this study to develop model equations predicting ClO_2 demand, chlorite and chlorate formation should be applied to clarified waters and then, both sets of model equations (i.e. pertaining to raw and clarified waters) compared.
4. Future work should consider incorporating more than 2 levels for each investigated parameter in order to identify any possible non-linear DBP formation or oxidant-demand responses to the different parameter variations.
5. Due to the presence of 2-factor interactions and the logarithmic-nature of the equations, those employing the model equations developed herein should perform their own sensitivity analysis with respect to predicting DBP formation or ClO_2 demand upon given parameter level changes (i.e. comparing DBP formation in summer months vs. winters).
6. The investigation of DBP formation upon ClO_2 application preceding chlorination or chloramination should be conducted.

7. Future work should examine the formation of brominated DBPs (i.e. bromate and brominated organics) upon ClO_2 dosing of high-bromide level waters.
8. Future work should involve examining whether the chlorine dioxide dosages investigated as part of this study are adequate to achieve satisfactory inactivation of more resistant pathogens such as *Cryptosporidium parvum*.

REFERENCES

- Adin, A., J. Katzhendler, D. Alkaslassy and Ch. Rav-Acha. 1991. Trihalomethane Formation in Chlorinated Drinking Water: A Kinetic Model. *Wat. Res.*, 25(7), 797-805.
- Aieta, E.M. and J.D. Berg. 1986. A Review of Chlorine Dioxide in Drinking Water Treatment. *Jour. AWWA*, 78(6), 62-72.
- Aieta, E.M. and P.V. Roberts. 1985. The Chemistry of Oxo-Chlorine Compounds Relevant to Chlorine Dioxide Generation. In *Water Chlorination: Chemistry, Environmental Impact and Health Effects*. Vol. 5. Edited by R.L. Jolley, R.J. Bull, W.P. Davis, S. Katz, M.H. Roberts, Jr. and V.A. Jacobs. Lewis Publishers, Chelsea, MI, pp. 783-794.
- Aieta, E.M., P.V. Roberts and M. Hernandez. 1984. Determination of Chlorine Dioxide, Chlorine, Chlorite, and Chlorate in Water. *Jour. AWWA*, 76(1), 64-70.
- Aiken, G.R. 1985. Isolation and Concentration Techniques for Aquatic Humic Substances. In *Humic Substances in Soil, Sediment and Water*. G.R. Aiken, D.M. McKnight, R.L. Wershaw and P. MacCarthy. Eds. John Wiley & Sons, Inc, New York, NY, pp. 363-385.
- Aiken, G.R., D.M. McKnight, R.L. Wershaw and P. MacCarthy. 1985. An Introduction to Humic Substances in Soil, Sediment, and Water. In *Humic Substances in Soil, Sediment and Water*. G.R. Aiken, D.M. McKnight, R.L. Wershaw and P. MacCarthy. Eds. John Wiley & Sons, Inc, New York, NY, pp. 1-9.
- American Public Health Association, American Water Works Association and Water Environment Federation (APHA-AWWA-WEF). 1995. Standard Methods for the Examination of Water and Wastewater, 19th Edition. Washington, D.C.
- Amy, G.L., P.A. Chadik and Z.K. Chowdhury. 1987a. Developing Models for Predicting Trihalomethane Formation Potential and Kinetics. *Jour. AWWA*, 79(7), 89-97.
- Amy, G.L., W.J. Cooper, K. Kasfian and P.H. King. 1983. A Mathematical Model for Trihalomethane Formation in a Highly Colored Groundwater Containing Ammonia and Bromide. *Preprints Div. Envir. Chem., Amer. Chem. Soc.*, 23(1), 171-174.

- Amy, G.L., R.A. Minear and W.J. Cooper. 1987b. Testing and Validation of a Multiple Nonlinear Regression Model for Predicting Trihalomethane Formation Potential. *Wat. Res.*, 21(6), 649-659.
- Amy, G., M. Siddiqui, W. Zhai, J. DeBroux and W. Odem. 1994. Survey of Bromide in Drinking Water and Impacts on DBP Formation. AWWA Res. Fdn., Denver, CO, 90 pp.
- Anderson, M.J. and P.J. Whitcomb. 1996. Optimize Your Process-Optimization Efforts. *Chemical Engineering Progress*, December, 51-60.
- Andrews, R.C., R. Hofmann and R. Di Scipio. 1997. Drinking Water Treatment to Minimize Disinfection By-Products and Ensure Microbiological Control. Report Submitted to Environmental Health Centre, Health Canada. 246 pp.
- Bacon, J.M. and W.A. Oleckno. 1985. Groundwater Contamination. A National Problem with Implications for State and Local Environmental Health Personnel. *J. Environ. Health*, 48(3), pp. 116-121.
- Benner, S.G., E.W. Smart and J.N. Moore. 1995. Metal Behavior During Surface-Groundwater Interaction, Silver Bow Creek, Montana. *Environ. Sci. Technol.*, 29(7), 1789-1795.
- Bishop, M.M., D.A. Cornwell, J.A. Morris. 1985. Chlorine Dioxide and Process Evaluation for Disinfection and Trihalomethane Control. In *Proc. American Water Works Association Water Quality Technology Conference*, Dec. 8-11, Houston, TX, pp. 365-382.
- Bjerg, P.L., K. Rügge, J.K. Pedersen and T.H. Christensen. Distribution of Redox-Sensitive Groundwater Quality Parameters Downgradient of a Landfill (Grindstend, Denmark), *Environ. Sci. Technol.*, 29(5), 1387-1394.
- Bolyard, M., P. Snyder Fair and D. P. Hautman. 1993. Sources of Chlorate Ion in US Drinking Water. *Jour. AWWA*, 85(9), 81-88.
- Bowen, R. 1986. Groundwater, Second Edition. Elsevier Applied Science Publishers, New York, NY. 427 pp.
- Box, G.E.P., W.G. Hunter and J.S. Hunter. 1978. Statistics for Experimenters. John Wiley & Sons, Inc., Toronto, ON. 653 pp.
- Bruchet, A., K. N'Guyen, M.F. Legrand and J. Mallevalle. 1991. Variation in Organic and Organoleptic Water Quality During Treatment of Artificially Recharged Groundwater. *Jour. AWWA*, 83(3), 63-70.

- Carnimeo, D., R. Di Marino, F. Donadio, L. Liberti, E. Ranieri, M. Pitzurra and A. Savino. 1995. Comparison between H_2O_2 /UV and ClO_2 Disinfection of Drinking Water. *Water Supply*, 13(2), 159-169.
- Carter Decker, K. and B.W. Long. 1992. Canada's Cooperative Approach to Drinking Water Regulation. *Jour. AWWA*, 84(4), 120-128.
- Christman, R.F., D.L. Norwood and Y. Seo. 1989. Oxidative Degradation of Humic Substances from Freshwater Environments. In *Humic Substance II- In Search of Structure*. Edited by M.H.B. Hayes, P. MacCarthy, R.L. Malcolm and R.S. Swift. John Wiley & Sons Ltd, New York, NY, pp. 33-67.
- Colclough, C.A., J.D. Johnson, R.F. Christman and D.S. Millington. 1983. Organic Reaction Products of Chlorine Dioxide and Natural Aquatic Fulvic Acids. In *Water Chlorination: Environmental Impact and Health Effects*, Vol. 4, bk. 1. Edited by R.L. Jolley, W.A. Brungs, J.A. Cotruvo, R.B. Cumming, J.S. Mattice and V.A. Jacobs, Lewis Publishers, Chelsea, MI, pp. 219-229.
- Cooper, W.J., R.G. Zika and M.S. Steinhauer. 1985. Bromide-Oxidant Interactions and THM Formation: A Literature Review. *Jour. AWWA*, 77(4), 116-121.
- Cronier, S., P.V. Scarpino and M.L. Zink. 1978. Chlorine Dioxide Destruction of Viruses and Bacteria in Water. In *Water Chlorination: Environmental Impact and Health Effects*. Vol 2. Edited by R.L. Jolley, H. Gorchev and D.H. Hamilton Jr. Ann Arbor Science Publishers, Ann Arbor, MI, pp. 651-658.
- Di Scipio, R. 1996. Assessment of Disinfection By-Product Formation When Employing Ozone for the Inactivation of *Giardia lamblia* and *Cryptosporidium parvum*. M. A. Sc. Thesis. University of Toronto.
- Dietrich, A.M., M.P. Orr, D.L. Gallagher and R.C. Hoehn. 1992. Tastes and Odors Associated With Chlorine Dioxide. *Jour. AWWA*, 84(6), 82-88.
- Dixon, K.L. and R.G. Lee. 1991. The Effect of Sulfur-Based Reducing Agents and GAC Filtration on Chlorine Dioxide By-products. *Jour. Awwa*, 83(5), 48-55
- Dyksen, J.E., D.J. Hildebrand and R.F. Racczko. 1988. SDWA Amendments: Effects on the Water Industry. *Jour. AWWA*, 80(1), 30-35.
- Engerholm, B.A. and G.L. Amy. 1983a. A Predictive Model for Chloroform Formation from Humic Acid. *Jour. AWWA*, 75(8), 418-423.

- Engerholm, B.A. and G.L. Amy. 1983b. An Empirical Model for Predicting Chloroform Formation from Humic and Fulvic Acids. In *Water Chlorination: Environmental Impact and Health Effects*. Vol. 4, Bk. 1. Edited by R.L. Jolley, W.A. Brungs, J.A. Cotruvo, R.B. Cumming, J.S. Mattice and V.A. Jacobs. Ann Arbor Science Publishers, Chelsea, MI, pp. 243-252.
- Federal Register (Fed. Reg.). 1994. Vol. 59, No. 145, pp. 33668-38858. Proposed Rules: Part II & III, Environmental Protection Agency, United States. Friday, July 29, 1994.
- Finch, G.R., L.R.J. Liyanage and M. Belosevic. 1995. Effect of Chlorine Dioxide on *Cryptosporidium* and *Giardia*. In *Chlorine Dioxide: Drinking Water, Process Water and Wastewater Issues, Proc. Third International Symposium*, AWWA, New Orleans, LA, pp. 23-32.
- Finch, G.R., J. Bradbury, L. Gyürék and L.R.J. Liyanage. 1997. Synergistic Effects of Disinfectants on Waterborne Pathogens. In *Proc. of the CSCE-ASCE Environmental Engineering Conference*, Edmonton, AB, July. 22-26, pp. 655-666.
- Freese, S.D. and G.D. Knobel. 1995. Chlorine Dioxide: Problems of Analysis. *Water Supply*, 13(2), 83-92.
- Gallagher, D.L., R.C. Hoehn and A.M. Dietrich. 1994. Sources, Occurrence and Control of Chlorine Dioxide By-Product Residuals in Drinking Water. AWWA Res. Fdn., Denver, CO. 184 pp.
- Gates, D. and R. Harrington. 1992. Drinking Water Disinfection Practices: Chlorine Dioxide in the Nineties. In *Proceedings of the Fifth National Conference on Drinking Water*, Winnipeg, MA, Sept. 13-15, pp. 339-363.
- Glaser, J.A., D.L. Forest, G.D. McKee, S.A. Quave and W.L. Budde. 1981. Trace Analyses for Wastewaters. *Environ. Sci. Technol.*, 15(12), 1426-1435.
- Gordon, G. 1993. Water Chemistry of the Oxy-Chlorine Species. In *Chlorine Dioxide: Drinking Water Issues, Proc. Second International Symposium*, AWWA, Houston, TX, pp. 15-25.
- Gordon, G., L. Adam and B. Bubnis. 1995. Minimizing Chlorate Ion Formation. *Jour. AWWA*, 87(6), 97-105.
- Gordon, G. and B. Bubnis. 1995. Chlorine Dioxide Chemistry Issues. In *Chlorine Dioxide: Drinking Water, Process Water and Wastewater Issues, Proc. Third International Symposium*, AWWA, New Orleans, LA, pp. 1-15.

- Gordon G., B. Slootmaekers, S. Tachiyashiki and D.W. Wood III. 1990. Minimizing Chlorite Ion and Chlorate Ion in Water Treated With Chlorine Dioxide. *Jour. AWWA*, 82(4), 160-165.
- Greiner, A.D., A. Obolensky and P.C. Singer. 1992. Technical Note: Comparing Predicted and Observed Concentrations of DBPs. *Jour. AWWA*, 84(11), 99-102.
- Griepentrog, G.L., J.M. Ryan and L.D. Smith. 1982. Linear Transformations of Polynomial Regression Models. *The American Statistician*, 36(3) Part 1, 171-174.
- Griese, M.H., K. Hauser, M. Berkemeier and G. Gordon. 1991. Using Reducing Agents to Eliminate Chlorine Dioxide and Chlorite Ion Residuals in Drinking Water. *Jour. AWWA*, 83(5), 56-61.
- Griese, M.H., J.J. Kaczur and G. Gordon. 1993. Combined Methods for the Reduction of Oxychlorine Residuals in Drinking Water. In *Chlorine Dioxide: Drinking Water Issues, Proc. Second International Symposium*, AWWA, Houston, TX, pp. 89-124.
- Grubbs, T.R. and R.W. Pontius. 1992. USEPA Releases Draft Ground Water Disinfection Rule. *Jour. AWWA*, 84(9), pp. 25, 27, 29 and 31.
- Harrington, G.W., Z.K. Chowdhury and D.M. Owen. 1992. Developing a Computer Model to Simulate DBP Formation During Water Treatment. *Jour. AWWA*, 84(11), 78-87.
- Hautman, D.P. and M. Bolyard. 1992. Using Ion Chromatography to Analyze Inorganic Disinfection By-products. *Jour. AWWA*, 84(11), 88-93.
- Hayes, M.H.B., P. MacCarthy, R.L. Malcolm and R.S. Swift. 1989. In *Humic Substance II- In Search of Structure*. Edited by M.H.B. Hayes, P. MacCarthy, R.L. Malcolm and R.S. Swift. John Wiley & Sons Ltd., New York, NY, pp. 3-31.
- Hazen and Sawyer Environmental Engineers and Scientists. 1992. *Disinfection Alternatives for Safe Drinking Water*. Van Nostrand Reinhold, New York, NY. 518 pp.
- Health Canada. 1996. *Guidelines for Canadian Drinking Water Quality*, Sixth Edition. Canada Communications Group- Publishing, Ottawa, ON.

- Hiltebrand, D.J., Z.K. Chowdhury and L.A. Wanchow. 1991. The Impact of the Surface Water Treatment Rule on Groundwater. *Jour. AWWA*, 83(3), 52-54.
- Hoehn, R.C. 1993. Chlorine Dioxide Use in Water Treatment: Key Issues. In *Chlorine Dioxide: Drinking Water Issues, Proc. Second International Symposium*, AWWA, Houston, TX, pp. 1-14.
- Hoff, J.C. and E.E. Geldreich. 1981. Comparison of the biocidal Efficiency of Alternative Disinfectants. *Jour. AWWA*, 73(1), 40-44.
- Hofmann, R. 1996. Minimising Chlorination and Chloramination DBPs while Ensuring Microbiological Control. M. A. Sc. Thesis. University of Toronto.
- Hofmann, R., R.C. Andrews and Q. Ye. 1997. Chlorite Formation when Disinfecting Drinking Water to *Giardia* Inactivation Requirements Using Chlorine Dioxide. Presented at *Proc. of the Sixth National Conference on Drinking Water*, Edmonton, AB, July. 23-25.
- Hofmann, R., R.C. Andrews and Q. Ye. 1998. Comparison of Spectrophotometric Methods for Measuring Chlorine Dioxide in Drinking Water. *Environmental Technology.*, 19, 761-773.
- Hoigné, J. and H. Bader. 1994. Kinetics of Reactors of Chlorine Dioxide (OClO) in Water- I. Rate Constants for Inorganic and Organic Compounds. *Wat. Res.*, 28(1), 45-55.
- Huang, J., L. Wang, N. Ren, X.-L. Liu, R.-F. Sun and G. Yang. 1997a. Disinfection Effect of Chlorine Dioxide on Viruses, Algae and Animal Planktons in Water. *Wat. Res.*, 31(3), 455-460.
- Huang, J., L. Wang, N. Ren, F. and J. Ma. 1997b. Disinfection Effect of Chlorine Dioxide on Bacteria in Water. *Water Res.*, 31(3), 607-613.
- Hutton, P.H. and F.I. Chung. 1992a. Simulating THM Formation Potential in Sacramento Delta, Part I. *Journal of Water Resources Planning and Management*, 118(5), 513-529.
- Hutton, P.H. and F.I. Chung. 1992b. Simulating THM Formation Potential in Sacramento Delta, Part II. *Journal of Water Resources Planning and Management*, 118(5), 530-541.
- Hutton, P.H. and F.I. Chung. 1994. Bromine Distribution Factors in THM Formation. *Journal of Water Resources Planning and Management*, 120(1), 1-16.

- Jun, W.-L., Y. Zuobin, C. Xinpei, G. Ming and C. Fuhuan. 1996. Trihalomethanes Formation in Water Treated with Chlorine Dioxide. *Wat. Res.*, 30(10), 2371-2376.
- Karpel Vel Leitner, N., J. De Laat, M. Doré and H. Suty. 1996. The Use of ClO_2 in Drinking Water Treatment: Formation and Control of Inorganic By-Products (ClO_2^- , ClO_3^-). In *Disinfection By-Products in Water Treatment (The Chemistry of Their Formation and Control)*. Edited by R.A. Minear and G.L. Amy. CRC Press, Lewis Publishers, Boca Raton, FL. 502 pp.
- Katz, A., N. Narkis, F. Orshansky, E. Friedland and Y. Kott. 1994. Disinfection of Effluent by Combinations of Equal Doses of Chlorine Dioxide and Chlorine Added Simultaneously Over Varying Contact Times. *Wat. Res.*, 28(10), 2133-2138.
- Kavanaugh, M.C., A.R. Trussell, J. Cromer and R. Rhodes. 1980. An Empirical Kinetic Model of Trihalomethane Formation: Applications to Meet the Proposed THM Standard. *Jour. AWWA*, 72(10), 578-582.
- Korshin, G.V., C.-W. Li and M.M. Benjamin. 1997a. The Decrease of UV Absorbance as an Indicator of TOX Formation. *Wat. Res.*, 31(4), 946-949.
- Korshin, G.V., C.-W. Li and M.M. Benjamin. 1997b. Monitoring the Properties of Natural Organic Matter Through UV Spectroscopy: A Consistent Theory. *Wat. Res.*, 31(7), 1787-1795.
- Krasner, S.W., J.-P. Croué, J. Buffle and E.M. Perdue. 1996. Three Approaches for Characterizing NOM. *Jour. AWWA*, 88(6), 66-79.
- Lafrance, P, D. Duchesne, N. Arcouette and M. Prévost. 1993. The Use of ClO_2 : Case Study of Laval. In *Chlorine Dioxide: Drinking Water Issues, Proc. Second International Symposium*, AWWA, Houston, TX, pp. 147-162.
- Leenheer, J.A. 1981. Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic Carbon from Natural Waters and Wastewaters. *Environ. Sci. Technol.*, 15(5), 578-587.
- Limoni, B., E. Choshen (Goldstein) and Ch. Rav-Acha. 1984. Determination of Oxidants Formed Upon the Disinfection of Drinking Water With Chlorine Dioxide. *J. Environ. Sci. Health*, A19(8), 943-947.
- Lykins Jr., B.W. and M.H. Griesse. 1986. Using Chlorine Dioxide for Trihalomethane Control. *Jour. AWWA*, 78(6), 88-93.

- Lyn, T.L. and J.S. Taylor. 1993. Modeling Compliance of Chlorine Residual and Disinfection By-Products. In *Proc. American Water Works Association Water Quality Technology Conference*, Miami, FL, Nov. 7-11, pp. 513-523.
- MacIer, B.A. 1996. Developing the Ground Water Disinfection Rule. *Jour. AWWA*, 88(3), 47-55.
- Malcolm, R.L. 1991. Factors to be Considered in the Isolation and Characterization of Aquatic Humic Substances. In *Humic Substances in the Aquatic and Terrestrial Environment*. H. Boren, B. Allard and A. Grimvall. Eds. Springer-Verlag, New York, NY, pp. 9-36.
- Martin-Mousset, B., J.P. Croué, E. Lefebvre and B. Legube. 1997. Distribution and Characterization of Dissolved Organic Matter of Surface Waters. *Wat. Res.*, 31(3), 541-553.
- Masschelein, W.J., Fransolet, G., Laforge, P. and Savoir, R. (1989). Determination of Residual Ozone or Chlorine Dioxide in Water with ACVK - An Updated Version. *Ozone Sc. & Eng.*, 11, 209-215.
- Matthess, G and J.C. Harvey (translated by). 1982. The Properties of Groundwater. Wiley-Interscience. New York, NY. 406 pp.
- Mazor, E. 1991. Applied Chemical and Isotopic Groundwater Hydrology. Open University Press, Great Britain. 274 pp.
- McClellan, J.N., D.A. Reckhow, J.E. Tobiason, J.K. Edzwald and A.F. Hess. 1996. Empirical Models for Chlorination By-Products: Four Years of Pilot Experience in Southern Connecticut. In *Water Disinfection and Natural Organic Matter, Characterization and Control*. Edited by R.A. Minear and G.L. Amy. ACS Symposium Series 649. American Chemical Society. Washington, DC. pp. 26-47. (394 pp. total)
- McKenzie, J., R.L. Schaefer and E. Farber. 1995. The Student Edition of MINITAB® for Windows User's Manual. Addison-Wesley Publishing Company, Inc. Reading, MA.
- Miller, R.E., S.J. Randtke, L.R. Hathaway and J.E. Denne. 1990. Organic Carbon and THM Formation Potential in Kansas Groundwaters. *Jour. AWWA*, 82(3), 49-62.
- Minitab Inc. 1995 The Student Edition of Minitab® for Windows software. Release 9. Addison-Wesley Publishing Company, Inc. Reading, MA.

- Montgomery, D.C. 1997. Design and Analysis of Experiments. Fourth Edition. John Wiley & Sons, Inc., Toronto, ON. 704 pp.
- Morrow, C.M. and R.A. Minear. 1987. Use of Regression Models to Link Raw Water Characteristics to Trihalomethane Concentrations in Drinking Water. *Wat. Res.*, 21(1), 41-48.
- Muttamara, S., C.I. Sales and Z. Gazali. 1995. The Formation of Trihalomethane from Chemical Disinfectants and Humic Substances in Drinking Water. *Wat. Supply*, 13(2), 105-117.
- Myers, R.H. 1990. Classical and Modern Regression with Applications, 2nd Edition. The Duxbury Advanced Series in Statistics and Decision Sciences. PWS-KENT Publishing Company, Boston, MA. 488 pp.
- Najm, I.N., N.L. Patania, J.G. Jacangelo and S.W. Krasner. 1992. Evaluating Surrogates: For Disinfection By-Products. *Jour. AWWA*, 86(6), 98-106.
- Narkis, N., A. Katz, F. Orshansky, Y. Kott and Y. Friedland. 1995. Disinfection of Effluents by Combinations of Chlorine Dioxide and Chlorine. *Wat. Sci. Tech.*, 31(5/6), 105-114.
- Noack, M.G. and R.L. Doerr. 1978. Reactions of Chlorine, Chlorine Dioxide and Mixtures Thereof With Humic Acid: An Interim Report. In *Water Chlorination: Environmental Impact and Health Effects*. Vol 2. Edited by R.L. Jolley, H. Gorchev and D.H. Hamilton Jr. Ann Arbor Science Publishers, Ann Arbor, MI, pp. 49-58.
- Oehler, K.E., A. Köhler and A. Schüttler. 1986. Formation of Chlorite During Raw Water Treatment With Chlorine Dioxide and the Removal of Chlorite by Water Treatment. *Wat. Supply*, 4(3), 127-139.
- Owen, D.M., G.L. Amy and Z.K. Chowdhury. 1993. Characterization of Natural Organic Matter and Its Relationship to Treatability. AWWA Res. Fdn., Denver, CO, 230 pp.
- Peixoto, J.L. 1990. A Property of Well-Formulated Polynomial Regression Models. *The American Statistician*, 44(1), 26-30.
- Pontius, F.W. 1991. Disinfectant-Disinfection By-Product Rule Update. *Jour. AWWA*, 83(12), 24-115.
- Pontius, F.W. 1995. An Update of the Federal Drinking Water Regs. *Jour. AWWA*, 87(2), 48-58.

- Ransome, M.E., T.N. Whitmore and E.G. Carrington. 1993. Effect of Disinfectants on the Viability of *Cryptosporidium parvum* Oocysts. *Water Supply*, 11, 103-117.
- Rav-Acha, Ch. 1984. The Reactions of Chlorine Dioxide with Aquatic Organic Materials and their Health Effects. *Wat. Res.*, 18(11), 1329-1341.
- Rav-Acha, Ch. And E. Choshen. 1987. Aqueous Reactions of Chlorine Dioxide with Hydrocarbons. *Environ. Sci. Technol.*, 21(11), 1069-1074.
- Rav-Acha, Ch., A. Serri, E. (Goldstein) Choshen and B. Limoni. 1985. Disinfection of Drinking Water Rich in Bromide With Chlorine and Chlorine Dioxide, While Minimizing the Formation of Undesirable By-Products. *Wat. Sci. Tech.*, 17(4/5), 611-621.
- Reckhow, D.A., P.C. Singer and R.L. Malcolm. 1990. Chlorination of Humic Materials: Byproduct Formation and Chemical Interpretations. *Environ. Sci. Technol.*, 24(11), 1655-1664.
- Rice, R.G. and M. Gomez-Taylor. 1986. Occurrence of By-Products of Strong Oxidants Reacting with Drinking Water Contaminants- Scope of the Problem. *Environ. Health Persp.*, 69, 31-44.
- Richardson, S.D., A.D. Thruston, Jr. and T.W. Collette. 1994. Multispectral Identification of Chlorine Dioxide Disinfection Byproducts in Drinking Water. *Environ. Sci. Technol.*, 28(4), 592-599.
- Rook, J.J. 1977. Chlorination Reactions of Fulvic Acids in Natural Waters. *Environ. Sci. Technol.*, 11(5), 478-482.
- Rose, J.B. 1988. Occurrence and Significance of *Cryptosporidium* in Water. *Jour. AWWA*, 80(2), 53-58.
- Rosenblatt, D.H. 1978. Chlorine Dioxide: Chemical and Physical Properties. In *Ozone/Chlorine Dioxide Oxidation Products of Organic Materials*. Edited by R.G. Rice and J.A. Cotruvo. Ozone Press, Cleveland, OH, pp. 332-343.
- Safe Drinking Water Committee 1980. The Disinfection of Drinking Water. In *Drinking Water and Health*, Vol. 2, National Academy Press, Washington, D.C., 393 pp.

- Sansebastiano, G., V. Rebizzi, E. Bellelli, F. Sciarrone, S. Reverberi, S. Saglia, A. Braccaioli and P. Camerlengo. 1995. Total Halogenated Organic (TOX) Measurement in Ground Waters Treated with Hypochlorite and with Chlorine Dioxide. Initial Results of an Experiment Carried Out in Emilia-Romagna (Italy). *Wat. Res.*, 29(4), 1207-1209.
- Schwalbaum, W.J. 1997. Understanding Groundwater. Nova Science Publishing Inc. Commack, NY. 190 pp.
- Senseman, S.A., T.L. Lavy and T.C. Daniel. 1997. Monitoring Groundwater for Pesticides at Selected Mixing/Loading Sites in Arkansas. *Environ. Sci. Technol.*, 31(1), 283-288.
- Shugar, G.J. and J.T. Ballinger. 1990. Chemical Technicians' Ready Reference Handbook, 3rd Edition. McGraw-Hill Inc., New York, NY. 889 pp.
- Singer, P.C., W.K. O'Neil. 1987. Technical Note: The Formation of Chlorate From the Reaction of Chlorine and Chlorite in Dilute Aqueous Solution. *Jour. AWWA*, 79(11), 75-76.
- Sobsey, M.D. 1989. Inactivation of Health-Related Microorganisms in Water by Disinfection Processes. *Wat. Sci. Tech.*, 21(3), 179-195.
- Stat-Ease Inc. 1994. Design Ease®. Version 3.0.0. Minneapolis, MN.
- Stat-Ease Inc. 1994. Design Ease® 3.0 Reference Manual. Minneapolis, MN.
- Stevens, A.A. 1982. Reaction Products of Chlorine Dioxide. *Environ. Health Persp.*, 46, 101-110.
- Tan Lo and R.G. Sudak. 1992. Removing Color From a Groundwater Source. *Jour AWWA*, 84(1), 79-87.
- Thurman, E.M. 1979. Isolation, Characterization, and Geochemical Significance of Humic Substances from Groundwater: PhD. Thesis, University of Colorado, Boulder. (not seen)
- Thurman, E.M. 1985. Humic Substances in Groundwater. In *Humic Substances in Soil, Sediment and Water*. G.R. Aiken, D.M. McKnight, R.L. Wershaw and P. MacCarthy. Eds. John Wiley & Sons, Inc, New York, NY, pp. 87-103.
- Thurman, E.M. and R.L. Malcolm. 1981. Preparative Isolation of Aquatic Humic Substances. *Environ. Sci. Technol.*, 15(4), 463-466.

- Triska, F.J., V.C. Kennedy and R.J. Avanzino. 1989. Retention and Transport of Nutrients in a Third-Order Stream in Northwestern California: Hyporheic Processes. *Ecology*, 70(6), 1893-1905.
- USEPA. 1991. 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 (1993). Determination of Inorganic Anions by Ion Chromatography, Revision 2.1. In *Methods for the Determination of Inorganic Substances in Environmental Samples*, EPA/600/R/93/100.
- USEPA (1993). Determination of Chlorination Disinfection ByProducts and Chlorinated Solvents in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection. In *Methods for the Determination of Organic Compounds in Drinking Water - Supplement I*, EPA/600/4-90/020, NTIS Publ. PB91-146027, pp. 170-199.
- USEPA (1995). Method 552.2, Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection, Revision 1.0. National Exposure Research Laboratory, Office of Research and Development. Cincinnati, OH.
- Varma, M.M., G. Torrence, R.C. Chawla and H. Okrend. 1985. Relative Disinfection Potentials of Chlorine and Chlorine Dioxide in Drinking Water. In *Water Chlorination: Chemistry, Environmental Impact and Health Effects*. Vol. 5. Edited by R.L. Jolley, R.J. Bull, W.P. Davis, S. Katz, M.H. Roberts, Jr. and V.A. Jacobs. Lewis Publishers, Chelsea, MI, pp. 783-794.
- Versteegh, J.F.M., J. Hrubec and R.F.M.J. Cleven. 1993. Chlorite and Chlorate in Drinking Water: DBP's or Environmental Pollutants? In *Proc. American Water Works Association Annual Conference*, San Antonio, TX, June 6-10, pp. 231-249.
- Von Huben, H. 1991. Surface Water Treatment- The New Rules. ISBN 0-89867-536-7. AWWA. Denver, CO. 40-45.
- Wajon, J.E., D.H. Rosenblatt and E.P. Burrows. 1982. Oxidation of Phenol and Hydroquinone by Chlorine Dioxide. *Environ. Sci. Technol.*, 16(7), 396-402.
- White, G.C. 1992. The Handbook of Chlorination and Alternative Disinfectants. Third Edition. Van Nostrand Reinhold, New York, NY. 1308 pp.

Werdehoff, K.S. and P.C. Singer. 1987. Chlorine Dioxide Effects on THMPF, TOXFP, and the Formation of Inorganic By-Products. *Jour. AWWA*, 79(9), 107-113.

APPENDIX A

**EQUATIONS TO CALCULATE
CHLORINE DIOXIDE GENERATOR EFFICIENCY**

Appendix A: Equations to calculate Chlorine Dioxide Generator Efficiency

Generating chlorine dioxide from a sodium chlorite-chlorine generation process where all the oxidized chlorine compounds can be measured and evaluated in the generator's product stream, yield can be calculated by taking the ratio between the chlorine dioxide concentration produced and the theoretical chlorine dioxide concentration maximum as shown in eqn. A.1 (Aieta *et al.*, 1984).

$$\text{Yield} = \frac{[\text{ClO}_2]}{[\text{ClO}_2] + [\text{ClO}_2^-] + (67.45/83.45)[\text{ClO}_3^-]} \times 100\% \quad (\text{A.1})$$

where $[x]$ = concentration of substance x, measured in the product stream (mg/L)
 67.45/83.45 = ratio of chlorite to chlorate molecular-weight ratio

Since the chlorite used in the generator will emerge as chlorine dioxide, chlorite, chlorate or chlorine dioxide and considering that the maximum amount of chlorine dioxide produced is equivalent to the amount of chlorite fed into the generator system, the above expression can represent the conventional theoretical yield definition (Aieta *et al.*, 1984).

An expression for the calculation of excess chlorine is shown in eqn. A.2 (Gordon, 1993).

$$\% \text{ Excess Cl}_2 = \frac{[\text{Cl}_2]}{0.525\{[\text{ClO}_2] + [\text{ClO}_2^-] + (0.808)[\text{ClO}_3^-]\}} \times 100\% \quad (\text{A.2})$$

APPENDIX B

EXAMPLE FOR ANALYZING AND INTERPRETING FACTORIAL RESULTS PERTAINING TO SYNTHETIC WATER EXPERIMENTS

Appendix B: Example for Analyzing and Interpreting Factorial Results Pertaining to Synthetic Water Experiments

While statistics texts such as Box *et al.* (1978) and Montgomery (1997) should be consulted for details concerning full or fractional factorial designs, the example provided in the following discussion is for illustrative purposes regarding analysis and interpretation of factorial experiments results. Design Ease[®] (Stat-Ease Inc., 1994) software package was employed in the design and analysis of the factorial experiments. The example presented herein pertains to factor effects as they relate to chlorite DBP formation resulting from the factorial experiment performed on the “synthetic” water having a NPOC concentration of 5.95 mg/L. The factors and levels which were investigated during the synthetic water experiments are reported in Table B.1. The chlorite concentration was measured for each sample in conformity with the randomized experimental run order shown in Table B.2. The design information pertaining to the selected 2^{6-2} fractional factorial design is displayed in Figure B.1. Three centerpoints (parameter values midway between the high and low parameter values for each factor) were added to the design to provide estimates of pure error and data curvature (i.e. investigation as to whether DBP formation responds in a linear fashion when the factors are varied from their respective low to high levels).

Once the chlorite concentrations were entered in the software package, the effects on chlorite concentration were calculated by taking the change in chlorite concentration from the “low” to “high” level of the given factor. Hence, due to its balanced arrangement (i.e. equal number of low and high levels), the 2^{6-2} fractional

Table B.1 Experimental Factors and Levels Investigated in Factorial Experiments

Factor	Parameter Values ^a		
	Low Level	"Centerpoint" Level	High Level
pH	5	7	9
Temperature (°C)	4	14.5	25
Chlorine Concentration (mg/L)			
- factorial #1 (NPOC = 5.95 mg/L)	0	0.2	0.4
- factorial #2 (NPOC = 2.09 mg/L)	0	0.07	0.14
Chlorine dioxide:NPOC Ratio (%)	30	70	110
Chlorate Concentration (mg/L)			
- factorial #1 (NPOC = 5.95 mg/L)	0	0.1	0.2
- factorial #2 (NPOC = 2.09 mg/L)	0	0.035	0.07
Reaction time (hr)	1	12.5	24

Table B.2 Randomized Run Arrangement for the 2⁶⁻² Factorial Experiment

Run Number	Factor					
	pH	Temperature	Chlorine Dioxide:NPOC	Chlorine	Chlorate	Reaction Time
1	-1 ^a	+1 ^a	-1 ^a	-1 ^a	-1 ^a	-1 ^a
2	-1	-1	-1	-1	+1	+1
3	-1	-1	-1	+1	+1	-1
4	+1	+1	+1	-1	-1	+1
5	-1	-1	+1	+1	-1	+1
6	-1	+1	+1	-1	+1	+1
7	+1	+1	+1	+1	-1	-1
8	0	0	0	0	0	0
9	-1	+1	-1	+1	-1	+1
10	+1	-1	-1	+1	-1	-1
11	+1	-1	+1	-1	+1	-1
12	0	0	0	0	0	0
13	-1	+1	-1	-1	+1	-1
14	-1	+1	+1	+1	+1	-1
15	+1	-1	+1	+1	+1	+1
16	-1	-1	+1	-1	-1	-1
17	+1	-1	-1	-1	-1	+1
18	0	0	0	0	0	0
19	+1	+1	-1	+1	+1	+1

^a The "-1", "+1" and "0" respectively represent the factor at its low, high and midpoint value.

1/4 Replicate of 6 factors in 16 experiments					
6 Factors: A, B, C, D, E, F					
Factor Generator					
E = ABC					
F = BCD					
Defining Contrast					
I = ABCE = BCDF = ADEF					
Word Lengths of Contrast					
1	2	3	4	5	6
0	0	0	3	0	0
Resolution IV					
A L I A S E S					
A = BCE = DEF					
B = ACE = CDF					
C = ABE = BDF					
D = AEF = BCF					
E = ABC = ADF					
F = ADE = BCD					
AB = CE					
AC = BE					
AD = EF					
AE = BC = DF					
AF = DE					
BD = CF					
BF = CD					
ABD = ACF = BEF = CDE					
ABF = ACD = BDE = CEF					

Figure B.1 Design Information Concerning the 2^{6-2} Fractional Factorial Design

factorial design used to address objective 1 involved 8 variations of each variable from its “low” to “high” value. In truth, as reported by Anderson and Whitcomb (1996), average parameter effects are calculated as the difference between the average chlorite concentrations observed when the factor was at its respective high and low levels (eqn. B.1).

$$\text{Variable effect on chlorite conc.} = \text{Mean } Y_+ - \text{Mean } Y_- \quad (\text{B.1})$$

where Y_+ = Mean chlorite conc. resulting from variable at the “high” or “+” level
 Y_- = Mean chlorite conc. resulting from variable at the “low” or “-” level

Using Design Ease®, a normal distribution plot of the main factor and 2-factor interaction effects on the production of chlorite was produced to validate the statistical assumptions of equal variance and normality as well as identify which of these variables is/are significant in chlorite formation (Figure B.2). A normal distribution plot can be generated by ranking the effects in increasing order (i.e. from the lowest to the highest) then calculating the cumulative probability values (Anderson and Whitcomb, 1996; Montgomery, 1997).

As cautioned in the Design Ease® Instruction Manual (Stat-Ease Inc., 1994), the plotted straight line should be placed through the “center set of points”, whereby the midpoint of the line corresponds to an effect of zero. In other words, the data points which lie on the fitted line represent near-zero effects, displaying normal scatter (noise) or an estimation of experimental error. However, since centerpoints were added to the factorial design, the statistical package can pool the pure error estimated from the centrepoints with the error estimated from the parameter and interaction effects which have been assessed to be non-significant by the user. The data points which are

Figure B.2 Normal Probability Plot of Effects on Chlorite Formation (Where A = pH, B = Temperature, C = Chlorine Dioxide:NPOC ratio, F = Reaction Time, AC = Interaction of pH and Chlorine Dioxide:NPOC ratio, BF = Interaction of Temperature and Reaction Time).

considered as “outliers” (i.e. points not positioned on the fitted line and found either to the lower left-hand or upper right-hand part of the line) are said to have significant effects on DBP formation beyond random experimental error. Based on Figure B.2 results, the following significant parameter effects have been identified: pH (factor A), chlorine dioxide:NPOC ratio (factor C), pH and chlorine dioxide:NPOC ratio interaction (factor AC) and the temperature-reaction time interaction (factor BF). In order to assess the level of significance of each of these effects, an analysis of variance (ANOVA) was performed on the given data using the Design Ease[®] statistical package (Stat-Ease Inc., 1994). It should be noted that no data transformations were necessary to obtain a more applicable statistical validation.

Characteristic ANOVA results using the Design Ease[®] statistical package (Stat-Ease Inc., 1994) are displayed in Figure B.3. While a number of different statistical information are provided, attention should be especially drawn to the various probability values: The model, curvature, lack of fit and factor probability values. Indeed, the data under the “PROB > F” (i.e. the probability of obtaining the reported F-value if the null hypothesis is true) and “PROB > |t|” (i.e. the probability of obtaining the t-value from a two-tailed t-distribution test if the null hypothesis is true) column headings were especially useful in assessing the significance of the different effects on chlorite formation. Based on the small “PROB > F” value for the model coefficients (i.e. < 0.0001), the null hypothesis that factor effects can be explained by random error alone was rejected (as can be concurred by viewing Figure B.2). The “PROB > |t|” value for each investigated factor effect is an indication as to whether

 Analysis of Chlorite

SOURCE	SUM OF SQUARES	DF	MEAN SQUARE	F VALUE	PROB > F
MODEL	30.30997	6	5.0517	167.49	< 0.0001
CURVATURE	0.00524	1	0.0052	0.17	0.6847
RESIDUAL	0.33177	11	0.0302		
*LACK OF FIT	0.27128	9	0.0301	1.00	0.5958
*PURE ERROR	0.06050	2	0.0302		
COR TOTAL	30.64698	18			

ROOT MSE	0.17367	R-SQUARED	0.99
DEP MEAN	2.31763	ADJ R-SQUARED	0.98
C.V. %	7.49343	PRED R-SQUARED	0.97

Predicted Residual Sum of Squares (PRESS) = 0.9935

* Residual = Lack-Of-Fit + Pure Error

FACTOR	COEFFICIENT ESTIMATE	DF	STANDARD ERROR	t FOR H0 COEFFICIENT=0	PROB > t
INTERCEPT	2.310437	1	0.043418		
A	0.303312	1	0.043418	6.99	< 0.0001
B	-0.010063	1	0.043418	-0.23	0.8210
C	1.327312	1	0.043418	30.57	< 0.0001
F	-0.033812	1	0.043418	-0.78	0.4525
AC	0.160938	1	0.043418	3.71	0.0035
BF	-0.116063	1	0.043418	-2.67	0.0217
CENTER POINT	0.045563	1	0.109265	0.42	0.6847

Final Equation in Terms of Uncoded Factors

Chlorite = - 0.21178 + 0.01084*pH + 0.01106*Temperature + 1.91008 * ClO2-TOC rt.
 + 0.01100*Reaction T. + 0.20117*pH*ClO2-TOC rt.
 - 0.00096*Temperature*Reaction T.

Figure B.3 Analysis of Variance (ANOVA) and Model Equation Results Pertaining to Chlorite Formation

the null hypothesis that the observed parameter effect on DBP formation is “true” and not due solely to random error can be rejected. It can be seen from the “PROB > |t|” values (Figure B.3) that the effects identified as significant in Figure B.2, are so at the 95% confidence level. In other words, there is a 5% chance that the effect believed to be a “true” effect could actually be explained by random error.

The presence of centerpoints is not expected to influence the factor effects on DBP formation. To evaluate whether there was curvature in the chlorite data with respect to the given parameter variations, the average chlorite concentration from the three centrepoint runs was compared to the average chlorite concentration found from the 16 trial runs. Based on the PROB > F value of 0.6847 which transpired upon this curvature calculation, data curvature can be said to be insignificant since the probability value is greater than 0.1 (equivalent to a 90% confidence level). Finally, the “lack of fit” Prob > F value provided an assessment of whether the error evaluated from the effects deemed to be insignificant is statistically different from the error evaluated from the replicated centrepoints. Design Ease® manual (Stat-Ease Inc., 1994) reports that models having small p-values are not appropriate models. Based on the obtained p-value of 0.5958 and assuming a 90% confidence level is adequate, it can be concluded that there is no significant lack of fit about the fitted model.

Although model development was addressed in Research Objective 2, Design Ease® (Stat-Ease Inc., 1994) can produce a model which predicts chlorite formation based on coefficient estimates (associated with either “coded” or “uncoded” factors) provided for the significant and nonsignificant effects. While the model in terms of “coded” factors requires that either “-1” or “+1” be entered when the factor

is respectively at its low or high level value, the “uncoded”-factor model requires actual variable values (such as 4°C for the temperature factor) be entered in the formulated predictive chlorite equation. The model equation in terms of the “uncoded” factors is shown in Figure B.3.

Once the data had been analyzed using the ANOVA method, it was important to ascertain that the factorial design and the ANOVA statistical analysis are valid whereby, the random errors are normally- and independently-distributed random variables each possessing a zero mean and variance of σ^2 . To this end, two residual plots were drawn: A normal probability plot of residuals as well as a graph of the residuals versus predicted response. The normal probability plot of residuals (a residual is defined as the difference between observed and predicted values) was obtained similarly to the normal plot depicted in Figure B.2. As can be seen by the normal plot of the studentized residuals in Figure B.4, a straight line can be drawn through the data points which indicate that the errors terms are indeed normally-distributed (mild point scattering can be expected). The scatter observed from the plot of studentized residuals versus predicted values (Figure B.5) implied that no observable change in variation was witnessed with increasing predicted values. If either or both of these tests had not provided the results to confirm the above-mentioned assumptions, the raw data may be transformed using a specific mathematical transformation such as a power or base 10 log transformation and then statistically re-analyzed. Plotting residuals with trial run order can be useful in determining whether there were any “lurking” factors which affected the given results. As can be seen from Figure B.6, the residual data are randomly distributed about zero indicating that there does not

appear to be any lurking factors influencing the chlorite data. Once the assumptions have been validated, the results from the ANOVA statistical method are assumed to be sound and well-founded.

Finally, the last step involved the interpretation of the significant effects on chlorite formation. For this purpose, main effect and interaction graphs of the significant effects on chlorite formation were developed. It should be mentioned that the plot of a main effect which was also found to take part in an interaction with another factor (for instance, pH was found to produce a significant effect on its own as well as part of a “potentially” significant interaction effect with chlorine dioxide:NPOC ratio) was not drawn since conclusions drawn from such a plot may be misleading. Consequently, the effect of pH on chlorite formation was assessed simultaneously with variations in chlorine dioxide:NPOC ratio on the same graphical plot. Results pertaining to factor effects on chlorite formation as well as on the formation of the other examined DBPs are presented and discussed in Chapter 5.

Figure B.4 Normal Plot of Studentized Residuals

Figure B.5 Residuals Versus Predicted Value of Chlorite Formation

Figure B.6 Residuals Versus Trial Run Number

APPENDIX C

**ANALYTICAL METHOD FLOWCHARTS AND
QA/QC CHARTS**

Appendix C: Analytical Method Flowcharts and QA/QC Charts

Figure C.1 Flowchart of Chlorite Stock Solution Preparation Method

Chlorine Dioxide Stock Titration Preparation:

Add 25 mL of a 10% w/v KI solution and 15 mL of a pH 7.6 phosphate buffer to a 250 mL-erlenmeyer flask containing about 50 mL of reagent water

Add 5 mL of the ClO_2 stock solution
(insure that the pipette tip is immersed in the solution
before blowing out contents to reduce ClO_2 losses due to volatilization)

Titrate solution with 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ solution until iodine color disappears.
Record titrant volume. (volume of neutral titration, N)

Add 10 mL of 4N H_2SO_4 to titrated solution.
Titrate solution with 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ until iodine color becomes light yellow.
Add starch indicator solution. Continue titrating with 0.1N $\text{Na}_2\text{S}_2\text{O}_3$ solution.
Record titrant volume. (volume of acidic titration, A)

Chlorine Dioxide Concentration (g/L) Calculation:

$$\frac{(N + A)\text{mL} * 0.1\text{EQ Na}_2\text{S}_2\text{O}_3/\text{L} * 67.5 \text{ g ClO}_2/\text{EQ}}{\text{mL sample} * 5(e^-\text{Na}_2\text{S}_2\text{O}_3/e^-\text{ClO}_2)}$$

Chlorine Dioxide Stock Purity (%):

$$5A/(4(N + A)) * 100\%$$

If $T = 5A/4$ then ClO_2 pure of chlorine and chlorite

If $T < 5A/4$ then ClO_2^- and ClO_2 in solution

If $T > 5A/4$ then Cl_2 and ClO_2 in solution

Figure C.2 Procedure for Standardization of Chlorine Dioxide Stock Solution

Figure C.3 Flowchart of Method for Sample Preparation and Analysis of Chlorite, Chlorate and Bromide

Sample Collection:

For processing expediency and minimization of transfer losses, prior to sampling,
Measure total volume using reagent water which 20 mL-vial can contain.
(Perform on at least 7 different sample vials)

Place approximately 30 mg ($\approx$ 2 micro-spatula spoonfuls) of NH_4Cl into
each 20 mL-vial for sample gathering. Fill each 20 mL-vial completely
(i.e. to the very top) with sample. Store vials at 4°C until sample preparation.

Sample Preparation:

Transfer each sample from its 20 mL-vial to a 40 mL-vial.
Add 5 mL of MtBE then add 8 g of Na_2SO_4 .

Invert and shake vigorously for 30 seconds.
Lie vial on its side until all vials are prepared.

Place all vials in a covered vial holder. Manually hand shake all vials vigorously
for 3 minutes. Let vials stand (over 3 minutes time) until organic and water layer
separation is attained.

Using a Pasteur pipette, deliver approximately 2 mL of the MtBE layer into a GC vial.
Store in dark (temp. less than 4°C) until sample analysis.

GC-ECD Analysis:

30m x 0.25mm x 0.25 μm DB-5 capillary column; injection: 1 μL , splitless;
injector @ 200°C , detector @ 300°C ; helium gas carrier (1.0 mL/min @ 35°C)
oven: 35°C for 10 min. to 80°C @ $5^\circ\text{C}/\text{min.}$, hold for 2 min.;
to 100°C @ $10^\circ\text{C}/\text{min.}$, hold for 2 min.;

Figure C.4 Flowchart of Method for Sample Preparation and Analysis of THMs

Sample Collection:

For processing expediency and minimization of transfer losses, prior to sampling,
Measure total volume using reagent water which 20 mL-vial can contain.
(Perform on at least 7 different sample vials)

Place approximately 30 mg ($\approx$ 2 micro-spatula spoonfuls) of NH_4Cl into
each 20 mL-vial for sample gathering. Fill each 20 mL-vial completely
(i.e. to the very top) with sample. Store vials at 4°C in dark until sample preparation.

Sample Preparation:

Transfer each sample from its 20 mL-vial to a 40 mL-vial. Add 1.5 mL of conc.
 H_2SO_4 . Add 4 mL of MtBE. Add 8 g ($3/4$ of a tbsp) of Na_2SO_4 . Invert and shake
vigorously for 30 seconds to break clumps. Lie vial on its side until all vials are
prepared. Place all vials in a covered vial holder. Manually hand shake all vials
vigorously for 5 minutes. Let vials stand (5 minutes) until layer separation.

Deliver at least 3 mL of the MtBE layer to a 15 mL-vial. Add 1 mL of 10% H_2SO_4 in
Methanol solution to each of these vials. Place in a water bath at 50°C for 2 hours.

Remove from water bath and let samples cool to ambient temperature.
Add 4 mL of a saturated NaHCO_3 solution. Hand shake each vial for 1 minute.
Open vials periodically to vent CO_2 . Allow samples to stand for about 5 minutes.
Using a Pasteur pipette, deliver approximately 2 mL of the MtBE layer into a GC vial.
Store in dark (temp. less than 4°C) until sample analysis.

GC-ECD Analysis:

30 m x 0.25 mm x $1\ \mu\text{m}$ DB-5 capillary column; injection: $2\ \mu\text{L}$, splitless;
injector @ 200°C , detector @ 300°C ; helium gas carrier ($1.2\ \text{mL/min}$ @ 35°C)
oven: 35°C for 10 min. to 100°C @ 2°C/min. , hold for 4 min.;
to 120°C @ 10°C/min. , hold for 4 min.;

Figure C.5 Flowchart of Method for the Sample Preparation and Analysis of HAAs

Figure C.8 Typical Calibration Curve for Chlorite Measurements

Figure C.9 Typical Chlorite QA/QC Chart (0.5 mg/L Chlorite)

Figure C.10 Typical Calibration Curve for Chlorate Measurements

Figure C.11 Typical Chlorate QA/QC Chart (0.3 mg/L Chlorate)

Figure C.12 Typical Calibration Curve for Chloroform Measurements

Figure C.13 Typical Chloroform QA/QC Chart (20 $\mu\text{g/L}$ Chloroform)

Figure C.14 Typical Calibration Curve for Dichloroacetic Acid Measurements

Figure C.15 Typical Dichloroacetic Acid QA/QC Chart (10 $\mu\text{g/L}$ Dichloroacetic acid)

APPENDIX D

CHLORINE DIOXIDE CONSUMPTION AND CHLORATE FORMATION IN TERMS OF VARIOUS ORGANIC CONTENT SURROGATES

Appendix D: Chlorine Dioxide Consumption and Chlorate Formation in Terms of Various Organic Content Surrogates

This appendix contains plots of chlorine dioxide consumption (Figures D.1 to D.4) as well as chlorate formation (Figures D.5 to D.8) in terms of a number of organic content surrogate parameters: Non-Purgeable Organic Content (NPOC), ultra-violet absorbance at 254 nm (UV_{254}), specific ultra-violet absorbance ($UV_{254}/NPOC$) and $NPOC \cdot UV_{254}$. All graphs report data which have been log-transformed (base 10). Along with the regression trendlines, other statistical information which are reported are correlation coefficient (R^2 -values), F-statistic and P-value associated with the linear regression equation and standard error (sse). These plots shown trends which are similar to those exhibited for chlorite formation in terms of the same surrogates (graphs displayed in Chapter 6). It is seen that the correlation of chlorine dioxide consumption and chlorate formation with either NPOC, UV_{254} and $NPOC \cdot UV_{254}$ showed comparable and reasonable linear regression fits. Based on the reported statistical information, the correlation with respect to $UV_{254}/NPOC$ resulted in a worse linear fit than the other organic precursor surrogate parameters.

Figure D.1 Log(Chlorine Dioxide Consumption) in terms of Log(NPOC)

Figure D.2 Log(Chlorine Dioxide Consumption) in terms of Log(UV₂₅₄)

Figure D.3 Log(Chlorine Dioxide Consumption) in terms of Log(NPOC*UV₂₅₄)

Figure D.4 Log(Chlorine Dioxide Consumption) in terms of Log(UV₂₅₄/NPOC)

Figure D.5 Log(Chlorate Formation) in terms of Log(NPOC)

Figure D.6 Log(Chlorate Formation) in terms of Log(UV_{254})

Figure D.7 Log(Chlorate Formation) in terms of Log(NPOC $\cdot$ UV $_{254}$)

Figure D.8 Log(Chlorate Formation) in terms of Log(UV $_{254}$ /NPOC)

APPENDIX E

**STANDARD DEVIATIONS ASSOCIATED WITH
THE COEFFICIENT TERMS OF THE DIFFERENT
MODEL EQUATIONS PREDICTING CHLORINE
DIOXIDE CONSUMPTION, CHLORITE AND CHLORATE
FORMATION**

**Appendix E: Standard Deviations Associated with the Coefficient Terms
of the Different Model Equations Predicting
Chlorine Dioxide Consumption, Chlorite and Chlorate Formation**

Table E.1 Standard Deviations Associated with Coefficient Terms of Model
Equations Predicting Chlorine Dioxide Consumption^a and Associated
Statistical Data

Equation Term	Standard Deviations			
	Model A ^b	Model B ^b	Model C ^b	Model D ^b
Coefficient	0.1334	0.1431	0.1282	0.09778
log(pH)	0.1438	0.1319	0.1156	0.08118
log(Temp.)	0.03169	0.06777	0.06302	0.04860
log(ClO ₂ dose + 1)	0.04639	0.1326	0.1202	0.09240
log(Rxntime + 1)	0.02301	0.04935	0.04939	0.03301
log(NPOC*UV ₂₅₄)	0.01796	0.01652	0.04939	0.05763
log(Temperature) *log(ClO ₂ dose + 1)	-	0.1068	0.09358	0.07172
log(ClO ₂ dose + 1) *log(RxnTime + 1)	-	0.07785	0.06819	0.05204
log(NPOC*UV ₂₅₄) *log(Temp.)	-	-	0.05303	0.04224
log(NPOC*UV ₂₅₄) *log(ClO ₂ dose + 1)	-	-	0.03615	0.06180
F-statistic; P-value	159.45; < 0.001	138.95; < 0.001	144.97; < 0.001	159.60; < 0.001
R ²	0.871	0.893	0.920	0.934
Standard Error of Estimate (SEE)	0.1404	0.1288	0.1128	0.0822
Sum of Squares of the Errors (SSE)	2.3276	1.9238	1.4507	0.6886
# of Trial Runs	124	124	124	112

^a Model equations predicting chlorine dioxide consumption are reported in Table 6.3

^b Case A = significant main parameters

Case B = significant main and 2-factor interactions involving experimentally-varied parameters

Case C = significant main and 2-factor interactions

Case D = significant main and 2-factor interactions for 7 tested raw surface waters

Note: “-” = term not included in given equation

Temp. = temperature, °C ; Rxntime = reaction time, hours

ClO₂dose = chlorine dioxide dose, mg/L

NPOC = non-purgeable organic carbon, mg/L

UV₂₅₄ = UV absorbance @ 254 nm, cm⁻¹

Table E.2 Standard Deviations Associated with Coefficient Terms of Model Equations Predicting Chlorite Formation^a and Associated Statistical Data

Equation Term	Standard Deviation			
	Model A ^b	Model B ^b	Model C ^b	Model D ^b
Coefficient	0.1855	0.2060	0.2041	0.1750
log(pH)	0.1993	0.1908	0.2027	0.1916
log(Temp.)	0.04411	0.09843	0.07979	0.04239
log(ClO ₂ dose + 1)	0.06452	0.1925	0.1617	0.2754
log(Rxntime + 1)	0.03200	0.07142	0.6160	0.03285
log(NPOC*UV ₂₅₄)	0.02333	0.02232	0.1851	0.04384
log(Temp.) *log(ClO ₂ dose + 1)	-	0.1552	0.1258	0.06682
log(ClO ₂ dose + 1) *log(RxnTime + 1)	-	0.1126	0.09127	0.04848
log(pH) *log(ClO ₂ dose + 1)	-	-	-	0.3020
log(NPOC*UV ₂₅₄) *log(pH)	-	-	0.2055	-
log(NPOC*UV ₂₅₄) *log(Temp.)	-	-	-	-
log(NPOC*UV ₂₅₄) *log(ClO ₂ dose + 1)	-	-	0.06652	0.05757
log(NPOC*UV ₂₅₄) *log(RxnTime + 1)	-	-	0.03299	0.02856
F-statistic; P-value	106.45; < 0.001	84.91; < 0.001	97.01; < 0.001	182.34; < 0.001
R ²	0.814	0.832	0.892	0.948
Standard Error of Estimate (SEE)	0.1986	0.1900	0.1541	0.0766
Sum of Squares of the Errors (SSE)	4.8107	4.3340	2.7768	0.5919
# of Trial Runs	128	128	128	112

^a Model equations predicting chlorite formation are reported in Table 6.4

^b Case A = significant main parameters

Case B = significant main and 2-factor interactions involving experimentally-varied parameters

Case C = significant main and 2-factor interactions

Case D = significant main and 2-factor interactions for 7 tested raw surface waters

Note: Temp. = temperature, °C ; Rxntime = reaction time, hours

ClO₂dose = chlorine dioxide dose, mg/L; UV₂₅₄ = UV absorbance @ 254 nm, cm⁻¹

NPOC = non-purgeable organic carbon, mg/L

“-“ = term not included in given equation

Table E.3 Standard Deviations Associated with Coefficient Terms of Model Equations Predicting Chlorate Formation^a and Associated Statistical Data

Equation Term	Predictive Model Equation Coefficients for log(Chlorate, mg/L)				
	Model A ^b	Model B ^b	Model C ^b	Model D ^b	Model E ^b
Coefficient	0.1316	0.1353	0.1375	0.2991	0.1063
log(pH)	0.1415	0.1253	0.1351	0.3376	0.09676
log(Temp.)	0.03130	0.06465	0.05660	0.2015	0.04992
log(ClO ₂ dose + 1)	0.04579	0.1264	0.1078	0.3008	0.1014
log(RxnTime + 1)	0.02271	0.04691	0.04107	0.1462	0.03870
log(NPOC*UV ₂₅₄)	0.01655	0.01466	0.1271	0.6436	0.05164
log(Temp.) *log(ClO ₂ dose + 1)	-	0.1019	0.08386	0.07299	0.07870
log(ClO ₂ dose + 1) *log(RxnTime + 1)	-	0.07394	0.06085	0.05296	0.05710
log(pH)*log(Temp.)	-	-	-	0.2255	-
log(pH) *log(ClO ₂ dose + 1)	-	-	-	0.3299	-
log(pH) *log(RxnTime + 1)	-	-	-	0.1636	-
log(NPOC*UV ₂₅₄) *log(pH)	-	-	0.1370	-	-
log(NPOC*UV ₂₅₄) *log(Temp.)	-	-	0.03032	0.04299	-
log(NPOC*UV ₂₅₄) *log(ClO ₂ dose + 1)	-	-	0.04435	0.06289	0.06781
log(NPOC*UV ₂₅₄) *log(RxnTime + 1)	-	-	0.02200	0.03119	0.03363
F-statistic; P-value	175.91; < 0.001	165.24; < 0.001	160.85; < 0.001	168.41; < 0.001	207.28; < 0.001
R ²	0.878	0.906	0.938	0.957	0.948
Standard Error of Estimate (SEE)	0.1409	0.1248	0.1027	0.08392	0.09016
Sum of Squares of the Errors (SSE)	2.4227	1.8694	1.2237	0.6853	0.8291
# of Trial Runs	128	128	128	112	112

^a Model equations predicting chlorate formation are reported in Table 6.5

^b Case A = significant main parameters

Case B = significant main and 2-factor interactions involving exp.-varied factors

Case C = significant main and 2-factor interactions

Case D = significant main and 2-factor interactions for 7 tested raw surface waters

Case E = Case D where effects significant at the 1% significance level

Note: "-" = term not included in given equation

APPENDIX F

PURE ERROR SAMPLE CALCULATION

Appendix F: Pure Error Sample Calculation

This appendix describes how pure error was calculated for measured levels of chlorine dioxide consumed, chlorite, chlorate and DCAA produced as well as change in UV_{254} observed during experiments performed on natural waters. For illustrative purposes, a sample calculation is also provided herein. Since model development and data analysis was conducted on log-transformed (base 10) data, pure error calculations were thus also performed on log-transformed data. However, in the case of UV_{254} measurements, pure error was based upon raw absorbance readings. As originally discussed in Chapter 3, two “complimentary” trial runs for each of the eight test waters were duplicated to provide an estimation of pure error. An example of “complimentary” runs (i.e. trial runs having “contrasting” parameter levels being examined) would be one trial run consisting of *high* pH, *low* temperature, *low* ClO_2 dose and *high* reaction time while the other run would consist of *low* pH, *high* temperature, *high* ClO_2 dose and *low* reaction time. The choice of “complimentary” trial runs ensured that the factorial design maintains its orthogonal property (i.e. balanced array of low and high levels). Hence, because eight water sources were investigated, each trial run could be duplicated. The data resulting from the duplicated trial runs (16 sets of 2 duplicated runs) were “pooled” and the standard deviation of the pure error for the compound measurements of interest was calculated using eqn. F.1 reported by Box *et al* (1978).

$$s^2 = \frac{v_1(s_1)^2 + v_2(s_2)^2 + \dots + v_g(s_g)^2}{v_1 + v_2 + \dots + v_g} \quad (\text{F.1})$$

where s^2 = estimate of run variance from pooled data
 $(s_i)^2$ = sample variance of duplicated set "i"
 v_i = degrees of freedom of duplicated set "i"
 g = set of experimental conditions

The calculation of pure error associated with the measured chlorate levels is presented. Based on the spreadsheet results (Table F.1):

where v_i = 1 degree of freedom per duplicated set "i" (i.e. replicates are in pairs)
 g = 16 set of experimental conditions

Therefore,
$$s^2 = \frac{1(s_1)^2 + 1(s_2)^2 + \dots + 1(s_g)^2}{16}$$

$$s^2 = \frac{0.01406}{16} \text{ (sum of } s^2 \text{ of all duplicated sets, see Table F.1)}$$

$$s^2 = 0.0008788$$

$$\text{standard deviation, } s = 0.02964 \text{ (based on log data)}$$

This standard deviation can be converted to a percentage (i.e. rate, R) by:

Let X = chlorate, mg/L
 pure error = log(R)

$$\log(X \cdot R) = \log(X) + \log(R)$$

then taking the inverse-log of either side,

$$(X \cdot R) = 10^{[\log(X) + \log(R)]} = X \cdot 10^{\pm \log(R)}$$

Therefore,
$$R = 10^{\pm 0.02964}$$

The experimental error expressed as the standard deviation of the pure error associated with the measured chlorate conc. levels is $\approx \pm 7\%$.

Table F.1 Calculation of Run Variance from Pooled Replicated Data for Chlorate Formation

Tested Water	Dup. #	Parameter Condition					Log10 of Chlorate conc. (mg/L)	std. dev. of dup.	(std. dev of dup.) ^2
		pH	Temp. (deg.C)	ClO ₂ dose (mg/L)	Rxn Time (hrs)	Chlorate Conc. (mg/L)			
Brant-ford	1	6	4	6	24	0.268	-0.572	0.003359	1.1E-05
	1	6	4	6	24	0.265	-0.577		
	2	9	25	1	1	0.066	-1.183	0.058868	0.00347
	2	9	25	1	1	0.079	-1.100		
Ottawa	3	9	4	6	24	0.498	-0.302	0.028946	0.00084
	3	9	4	6	24	0.454	-0.343		
	4	6	25	1	1	0.069	-1.161	0.002599	6.8E-06
	4	6	25	1	1	0.069	-1.164		
Windsor	5	6	4	1	24	0.046	-1.337	0.005868	3.4E-05
	5	6	4	1	24	0.047	-1.328		
	6	9	25	6	1	0.138	-0.862	0.007699	5.9E-05
	6	9	25	6	1	0.134	-0.872		
Toronto	7	9	25	6	24	0.244	-0.613	0.011341	0.00013
	7	9	25	6	24	0.253	-0.597		
	8	6	4	1	1	0.035	-1.457	0.068231	0.00466
	8	6	4	1	1	0.028	-1.553		
Peter-borough	9	6	25	6	24	0.494	-0.306	0.006042	3.7E-05
	9	6	25	6	24	0.504	-0.297		
	10	9	4	1	1	0.063	-1.199	0.010174	0.0001
	10	9	4	1	1	0.061	-1.214		
Belle-ville	11	6	25	1	24	0.046	-1.339	0.009405	8.8E-05
	11	6	25	1	24	0.047	-1.325		
	12	9	4	6	1	0.244	-0.612	0.000598	3.6E-07
	12	9	4	6	1	0.244	-0.613		
Mann-heim surface	13	9	25	1	24	0.070	-1.153	0.054329	0.00295
	13	9	25	1	24	0.059	-1.230		
	14	6	4	6	1	0.128	-0.893	0.041005	0.00168
	14	6	4	6	1	0.112	-0.951		
Ground-water	15	6	25	6	1	0.052	-1.282	0.000933	8.7E-07
	15	6	25	6	1	0.052	-1.284		
	16	9	4	1	24	0.034	-1.465	0.000000	0
	16	9	4	1	24	0.034	-1.465		
Sum of (std. Deviation)^2 =									0.01406

APPENDIX G

DIAGNOSTIC CHECKS OF MODEL RESIDUALS

Appendix G: Diagnostic Checks of Model Residuals

To ensure that t-tests, F-tests and interval estimates ensuing from the multiple linear regressions are valid, three main assumptions underlying linear regression must be verified (McKenzie *et al.*, 1995, Student Edition of Minitab® for Windows User's Manual). These assumptions regard the error component whereby requiring it to be normally- and independently-distributed, have a constant standard deviation. The diagnostic plots performed to verify these assumptions are reported in Table G.1. These plots were obtained using the Minitab® software package (Student Edition for Windows, 1995). A discussion pertaining to the results displayed in these plots is provided in Chapter 6. For further statistical details concerning these plots, the reader is directed to consult statistical books such as Box *et al.* (1978) and Montgomery (1997). The description of each model case for which these diagnostic model checks were conducted for is reported in Table G.2. The trials runs associated with the eight test waters are identified in Table G.3. Diagnostic graphs of model equation residuals related to chlorite formation (Figures G.1-G.6), chlorate formation (Figures G.7-G.12) and chlorine dioxide consumption (G.13-G.18) are reported in Sections G.1, G.2 and G.3 respectively.

Table G.1 Diagnostics Model Checks Performed to Assess Linear Regression Assumptions

Assumption	Diagnostic Check	Desired graph outcome to meet assumption
Errors are normally-distributed	Normal distribution plot of standardized residuals	- Data points should form a straight line
Errors have constant variance	Plot of standardized residual against predicted log(response variable level)	- Data points should be scattered (no obvious trends should be seen)
Errors are independently-distributed	Plot of standardized residual against run number	- Data points should be scattered (no obvious trends should be seen)

Note: Standardized Residual for a given point calculated as:

$[\log(\text{measured response}) - \log(\text{predicted response})] / \text{standard deviation of this point}$

where standard deviation of point = $(\text{MSE} - (\text{standard deviation of point fit})^2)^{1/2}$
MSE = mean square error

Table G.2 Description of Model Cases

Model Case	Number of Trial Runs for Model Development	Description
A	128 (124 for ClO ₂ model)	- Only significant main factors included
B	128 (124 for ClO ₂ model)	- Significant main factors and 2-factor interactions which include experimentally-varied factors only ^a
C	128 (124 for ClO ₂ model)	- Significant main factors and 2-factor interactions ^a
D	112	- Significant main factors and 2-factor interactions ^a - Employing data obtained from the 7 tested surface waters only
E	112 (for chlorate only)	- Significant main factors and 2-factor interactions ^b - Employing data obtained from the 7 tested surface waters only

^a Effects significant at the 5% significance level

^b Effects significant at the 1% significance level

Table G.3 Trial Runs Associated with Each Tested Water Source

Water Source	Trial Runs
Brantford	1 to 16
Ottawa	17 to 32
Windsor	33 to 48
Toronto	49 to 64
Peterborough	65 to 80
Belleville	81 to 96
Mannheim Surface	97 to 112
Groundwater	113 to 128

G.1 Diagnostic Plot Checks for Model Equations Predicting Chlorite Formation

CASE C:

Figure G.1 Normal Probability Plot of Standardized Residuals

Figure G.2 Standardized Residuals vs Predicted Chlorite

Figure G.3 Standardized Residuals vs Trial Run Order

CASE D:

Figure G.4 Normal Probability Plot of Standardized Residuals

Figure G.5 Standardized Residuals vs Predicted Chlorite

Figure G.6 Standardized Residuals vs Trial Run Order

Section G.2 Diagnostic Plot Checks for Model Equations Predicting Chlorate Formation

CASE C:

Figure G.7 Normal Probability Plot of Standardized Residuals

Figure G.8 Standardized Residuals vs Predicted Chlorate

Figure G.9 Standardized Residuals vs Trial Run Order

CASE E:

Figure G.10 Normal Probability Plot of Standardized Residuals

Figure G.11 Standardized Residuals vs Predicted Chlorate

Figure G.12 Standardized Residuals vs Trial Run Order

G.3 Diagnostic Plot Checks for Model Equations Predicting Chlorine Dioxide Formation

CASE C:

Figure G.13 Normal Probability Plot of Standardized Residuals

Figure G.14 Standardized Residuals vs Predicted ClO_2 consumed

Figure G.15 Standardized Residuals vs Trial Run Order

CASE D:

Figure G.16 Normal Probability Plot of Standardized Residuals

Figure G.17 Standardized Residuals vs Predicted ClO_2 consumed

Figure G.18 Standardized Residuals vs Trial Run Order

APPENDIX H

**FREQUENCY DIAGRAMS OF
“INTERNAL” MODEL VALIDATION RESULTS**

Appendix H: Frequency Diagrams of “Internal” Model Validation Results

This appendix contains “internal” model validation curves for the developed predictive models for chlorite (ClO_2^-) and chlorate (ClO_3^-) formation as well as chlorine dioxide (ClO_2) consumption. The description of each model case is reported in Table H.1.

The validation curves (Figures H.1 to H.18) consist of histograms which report on the number of runs (i.e. frequency) where the concentration residuals as well as the % recoveries fall within given ranges. Residuals were found as the differences between the measured and predicted concentrations levels (meas. conc. – pred. conc., both in mg/L). Percent recoveries were obtained by taking the ratios of the predicted to measured concentration levels (Pred. conc./meas. conc., both in mg/L).

Table H.1 Description of Model Cases

Model Case	Number of Trial Runs for Model Development	Description
C	128 (124 for ClO ₂ model)	- Significant main factors and 2-factor interactions at 5% significance level
D	112	- Significant main factors and 2-factor interactions at 5% significance level - Employing data obtained from the 7 tested surface waters only
E	112 (for chlorate only)	- Significant main factors and 2-factor interactions at 1% significance level - Employing data obtained from the 7 tested surface waters only
F	124	- ClO ₂ ⁻ (mg/L) = 0.6815(ClO ₂ predicted by Model C where predicted ClO ₂ < or = ClO ₂ dose) - ClO ₃ ⁻ (mg/L) = 0.0904(ClO ₂ predicted by Model C where predicted ClO ₂ < or = ClO ₂ dose)

Note: Conversion ratios of chlorine dioxide to chlorite (0.6815) and to chlorate (0.0904) were determined from experimental data (see Chapter 6 for details).

Figure H.1 “Internal” Model Validation for Chlorite Formation, case C: Frequency Histogram of Residual Data

Figure H.2 “Internal” Model Validation for Chlorite Formation, case C: Frequency Histogram of % Recoveries

Figure H.3 “Internal” Model Validation for Chlorite Formation, case D:
Frequency Histogram of Residual Data

Figure H.4 “Internal” Model Validation for Chlorite Formation, case D:
Frequency Histogram of % Recoveries

Figure H.5 “Internal” Model Validation for Chlorate Formation, case C: Frequency Histogram of Residual Data

Figure H.6 “Internal” Model Validation for Chlorate Formation, case C: Frequency Histogram of % Recoveries

Figure H.7 “Internal” Model Validation for Chlorate Formation, case D: Frequency Histogram of Residual Data

Figure H.8 “Internal” Model Validation for Chlorate Formation, case D: Frequency Histogram of % Recoveries

Figure H.9 “Internal” Model Validation for Chlorate Formation, case E:
Frequency Histogram of Residual Data

Figure H.10 “Internal” Model Validation for Chlorate Formation, case E:
Frequency Histogram of % Recoveries

Figure H.11 “Internal” Model Validation for Chlorine Dioxide Consumption, case C: Frequency Histogram of Residual Data

Figure H.12 “Internal” Model Validation for Chlorine Dioxide Consumption, case C: Frequency Histogram of % Recoveries

Figure H.13 “Internal” Model Validation for Chlorine Dioxide Consumption, case D: Frequency Histogram of Residual Data

Figure H.14 “Internal” Model Validation for Chlorine Dioxide Consumption, case D: Frequency Histogram of % Recoveries

Figure H.15 "Internal" Model Validation for Chlorite Formation, case F: Frequency Histogram of Residual Data

Figure H.16 "Internal" Model Validation for Chlorite Formation, case F: Frequency Histogram of % Recoveries

Figure H.17 “Internal” Model Validation for Chlorate Formation, case F: Frequency Histogram of Residual Data

Figure H.18 “Internal” Model Validation for Chlorate Formation, case F: Frequency Histogram of % Recoveries

APPENDIX I

RESULTS AND SAMPLE CALCULATIONS RELATED TO THE SENSITIVITY ANALYSES OF MODEL EQUATIONS

Appendix I: Results and Sample Calculations Related to the Sensitivity Analyses of Model Equations

Percent (%) contributions of each parameter to the explanatory power of the given predictive equations were calculated for comparison purposes. A sample calculation has been provided. For a “cleaner” presentation, all figures and tables are provided *after* the sample calculation. This appendix also includes the sensitivity analyses results with respect to relevant model equations predicting chlorine dioxide consumption, chlorite and chlorate formation (refer to Table I.2). The different % contributions were calculated by comparing the residual sum of squares (RSS) for the given model equation to the RSS resulting for the regression equation where all the terms associated with a specific parameter were removed. Hence, the % contribution (i.e. gain of adding these terms to the equation) to the explanatory power of the equation for a specific parameter is calculated as:

$$\% \text{ contribution} = ((A-B)/A) * 100\%$$

where A = Regression sum of squares with all terms

B = Regression sum of squares without terms involving specific factor

(NOTE: A - B = SS contribution of removed terms to regression SS)

These % contributions should not be confused with the % contributions of these parameters to the response variable levels predicted by these equations as they are not necessarily interchangeable. Results of the regression analyses for Model C and D for chlorite formation (i.e. including main as well as 2-factor interactions having significant effects on chlorite formation at the 5% significance level) are respectively shown in Figures I.1 and I.2. The output displayed in Figure I.1 is a typical predictor

table and ANOVA statistical output when performing regression analysis using Minitab®, Student Version (Minitab Inc., 1995). It can be seen that the display consists of a table of “predictor variables” containing statistical information pertaining to the various model terms (i.e. standard deviation, t-statistic and P-value), standard error of the estimate and R^2 values, an ANOVA reporting on the model statistics, the sequential sum of squares for each predictor terms as well as unusual observations which may have some influence on the regression such as observations having standardized residuals beyond ± 2 .

The results of regression analysis for Model Case D for chlorite formation when the pH, temperature, chlorine dioxide concentration, reaction time, NPOC*UV₂₅₄ and 2-factor interactions terms have been removed are displayed in Figures I.3 to I.8 respectively. For simplicity, only statistical data pertaining to the Analysis of Variance (ANOVA) are reported in Figures I.2 to I.8. Based on the previously reported equation to calculate the % contribution of each parameter to the explanatory power of, in this case, Model case D to predict chlorite formation, the following % contribution results were obtained (see Figures I.2 to I.8):

pH:	$[(10.6850 - 10.2038)/10.6850]*100\% = 4.5\%$
Temperature:	$[(10.6850 - 10.2117)/10.6850]*100\% = 4.4\%$
Chlorine Dioxide Concentration:	$[(10.6850 - 3.1395)/10.6850]*100\% = 70.6\%$
Reaction Time:	$[(10.6850 - 9.3121)/10.6850]*100\% = 12.8\%$
NPOC*UV ₂₅₄ :	$[(10.6850 - 8.2911)/10.6850]*100\% = 22.4\%$
Sum of All Contributions	$= 4.5 + 4.4 + 70.6 + 12.8 + 22.4 = 114.7\%$

$$\% \text{ Contribution of 2-factor interactions} = 114.7 - 100 = 14.7\% \checkmark$$

(NOTE= each 2-factor interaction is accounted for twice in above calculations)

Check for % contribution of 2-factor interactions:

$$\text{2-factor interactions:} \quad [(10.6850 - 9.1034)/10.6850]*100\% = 14.8\% \checkmark$$

Each calculated % contribution can be assessed as to its significance as to whether the % contribution statistically differs from zero. This was accomplished using the following developed F-Statistic (Myers, 1990):

$$\text{F-Statistic} = \frac{(\text{SS, removed terms})/\# \text{ of terms removed}}{\text{SSE, full model}/\text{DFE, full}}$$

where SS, removed terms = Sequential sum of squares contributing to regression sum of squares
 # of terms removed = # of terms containing the parameter of interest
 SSE, full model = Error sum of squares of full model
 DFE, full = Degrees of freedom associated with SSE, full model

All % contributions associated with Models C, D and E were found to be statistically significant based on calculated F-statistics (Table I.1). For example, the F-Statistics for the % contributions associated with the pH and temperature factors are found as (Model C, chlorite formation):

For pH

SS, removed terms = 10.6850 (Figure I.2) - 10.2038 (Figure I.3) = 0.4812
 # of terms removed = 2 (pH and pH-ClO₂ dose interaction)
 SSE, full model = 0.5919 (Figure I.2)
 DFE, full = 101 (Figure I.2)

For Temperature

SS, removed terms = 10.6850 (Figure I.2) - 10.2117 (Figure I.4) = 0.4733
 # of terms removed = 2 (Temp. and Temp.-ClO₂ concentration interaction)
 SSE, full model = 0.5919 (Figure I.2)
 DFE, full = 101 (Figure I.2)

As such, $F\text{-Statistic}_{(\text{pH})} = \frac{0.4812/2}{0.5919/101} = 41.05$

$$F\text{-Statistic}_{(\text{temperature})} = \frac{0.4733/2}{0.5919/101} = 40.38$$

Consulting F-Tables (such as in Montgomery, 1997), for $\text{DOF1} = 2$ and $\text{DOF2} = 101$
for $F\text{-Statistic}_{(\text{pH})} = 41.05$

and for $F\text{-Statistic}_{(\text{temperature})} = 40.38$

the associated P-value $= < 0.001$

Consequently, both % contributions have values which statistically differ from zero (based on a selected significance level of 5%).

Predictor	Coef	Stdev	t-ratio	p
Constant	-0.7340	0.2041	-3.60	0.000
log(pH)	0.4460	0.2027	2.20	0.030
log(Temp.)	-0.04496	0.07979	-0.56	0.574
log(ClO ₂ dose+1)	0.4708	0.1617	2.91	0.004
log(React.+1)	-0.08026	0.06160	-1.30	0.195
log(TOC*UV ₂₅₄)	0.8367	0.1851	4.52	0.000
log(Temp.)*log(ClO ₂ dose+1)	0.3133	0.1258	2.49	0.014
log(ClO ₂ dose+1)*log(React.+1)	0.34007	0.09127	3.73	0.000
log(pH)*log(NPOC*UV ₂₅₄)	-0.7109	0.2055	-3.46	0.001
log(ClO ₂ dose+1)*log(NPOC*UV ₂₅₄)	0.46453	0.06652	6.98	0.000
log(React.+1)*log(NPOC*UV ₂₅₄)	-0.07292	0.03299	-2.21	0.029

s = 0.1541 R-sq = 89.2% R-sq(adj) = 88.3%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	10	23.0226	2.3023	97.01	0.000
Error	117	2.7768	0.0237		
Total	127	25.7994			

SOURCE	DF	SEQ SS
log(pH)	1	0.8024
log(Temp.)	1	0.3671
log(ClO ₂ dose+1)	1	5.7154
log(React.+1)	1	0.9994
log(TOC*UV ₂₅₄)	1	13.1043
log(Temp.)*log(ClO ₂ dose+1)	1	0.1472
log(ClO ₂ dose+1)*log(React.+1)	1	0.3295
log(pH)*log(NPOC*UV ₂₅₄)	1	0.2839
log(ClO ₂ dose+1)*log(NPOC*UV ₂₅₄)	1	1.1573
log(React.+1)*log(NPOC*UV ₂₅₄)	1	0.1159

Unusual Observations

Obs.	log(pH)	log(ClO ₂ -)	Fit	Stdev.Fit	Residual	St.Resid
29	0.778	-0.4474	-0.1127	0.0449	-0.3347	-2.27R
45	0.778	-0.1670	-0.4870	0.0392	0.3200	2.15R
55	0.778	-0.3276	-0.6356	0.0407	0.3080	2.07R
61	0.778	-0.1652	-0.5185	0.0407	0.3533	2.38R
64	0.954	0.3076	-0.0100	0.0407	0.3175	2.14R
119	0.778	-1.6669	-1.0799	0.0691	-0.5871	-4.26R
123	0.778	-1.3664	-0.8692	0.0691	-0.4971	-3.61R
127	0.954	-1.0275	-0.7405	0.0691	-0.2871	-2.08R

R denotes an obs. With a large st. resid.

Figure I.1 Statistical Output for Developed Model C Predicting Chlorite Formation

Table I.1 Statistical Results Assessing the Significance of Model Equation
Parameter Terms Contribution to the Regression Sum of Squares for the
Given Factors Examined in this Study

Compound	Model Case	Parameter Terms Relating to ^a					
		pH	Temp.	ClO ₂ dose	Reaction Time	NPOC* UV ₂₅₄	2-factor interactions
Chlorite	D	41.06	40.38	257.51	78.09	102.12	53.98
Chlorate	D	15.79	20.98	359.64	39.97	62.49	20.75
	E	41.20	31.51	385.74	44.35	70.16	31.28
Chlorine Dioxide	D	14.66	33.15	268.17	47.83	80.24	21.70

^a For the reported F-statistics, all P-values were found to be < 0.001

s = 0.07655 R-sq = 94.8% R-sq(adj) = 94.2%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	10	10.6850	1.0685	182.34	0.000
Error	101	0.5919	0.0059		
Total	111	11.2768			

TERM	DF	SEQUENTIAL SS
log(pH)	1	0.3771
log(Temp.)	1	0.3606
log(ClO ₂ dose + 1)	1	6.1504
log(React. + 1)	1	0.8014
log(Temp.)*log(ClO ₂ dose + 1)	1	0.1127
log(ClO ₂ dose + 1)*log(React. + 1)	1	0.3849
log(ClO ₂ dose + 1)*log(NPOC*UV ₂₅₄)	1	2.1204
log(React. + 1)*log(NPOC*UV ₂₅₄)	1	0.2734
log(NPOC*UV ₂₅₄)	1	0.0000
log(pH)*log(ClO ₂ dose + 1)	1	0.1041

Figure I.2 Statistical Output for Developed Model D Predicting Chlorite Formation

s = 0.1021 R-sq = 90.5% R-sq(adj) = 89.7%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	8	10.2038	1.2755	122.44	0.000
Error	103	1.0730	0.0104		
Total	111	11.2768			

TERM	DF	SEQ SS
log(Temp.)	1	0.3606
log(ClO ₂ dose + 1)	1	6.1504
log(React. + 1)	1	0.8014
log(Temp.)*log(ClO ₂ dose + 1)	1	0.1127
log(ClO ₂ dose + 1)*log(React. + 1)	1	0.3849
log(ClO ₂ dose + 1)*log(NPOC*UV ₂₅₄)	1	2.1204
log(React. + 1)*log(NPOC*UV ₂₅₄)	1	0.2734
log(NPOC*UV ₂₅₄)	1	0.0000

Figure I.3 Statistical Output for Developed Model D Predicting Chlorite Formation Where Terms Involving pH Have Been Removed

s = 0.1017 R-sq = 90.6% R-sq(adj) = 89.8%

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	8	10.2117	1.2765	123.43	0.000
Error	103	1.0651	0.0103		
Total	111	11.2768			

TERM	DF	SEQ SS
log(pH)	1	0.3771
log(ClO ₂ dose + 1)	1	6.1504
log(React. + 1)	1	0.8014
log(ClO ₂ dose + 1)*log(React. + 1)	1	0.3849
log(ClO ₂ dose + 1)*log(NPOC*UV ₂₅₄)	1	2.1204
log(React. + 1)*log(NPOC*UV ₂₅₄)	1	0.2734
log(NPOC*UV ₂₅₄)	1	0.0000
log(pH)*log(ClO ₂ dose + 1)	1	0.1041

Figure I.4 Statistical Output for Developed Model D Predicting Chlorite Formation Where Terms Involving Temperature Have Been Removed

$s = 0.2771$ $R\text{-sq} = 27.8\%$ $R\text{-sq(adj)} = 24.4\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	5	3.13954	0.62791	8.18	0.000
Error	106	8.13731	0.07677		
Total	111	11.27685			

TERM	DF	SEQ SS
log(pH)	1	0.37708
log(Temp.)	1	0.36063
log(React. + 1)	1	0.80140
log(NPOC*UV ₂₅₄)	1	1.41387
log(React. + 1)*log(NPOC*UV ₂₅₄)	1	0.18656

Figure I.5 Statistical Output for Developed Model D Predicting Chlorite Formation Where Terms involving Chlorine Dioxide Concentration Have Been Removed

$s = 0.1374$ $R\text{-sq} = 82.6\%$ $R\text{-sq(adj)} = 81.4\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	7	9.3121	1.3303	70.42	0.000
Error	104	1.9647	0.0189		
Total	111	11.2768			

TERM	DF	SEQ SS
log(pH)	1	0.3771
log(Temp.)	1	0.3606
log(ClO ₂ dose + 1)	1	6.1504
log(Temp.)*log(ClO ₂ dose + 1)	1	0.1127
log(ClO ₂ dose + 1)*log(NPOC*UV ₂₅₄)	1	2.1204
log(NPOC*UV ₂₅₄)	1	0.0869
log(pH)*log(ClO ₂ dose + 1)	1	0.1041

Figure I.6 Statistical Output for Developed Model D Predicting Chlorite Formation Where Terms involving Reaction Time Have Been Removed

$s = 0.1694$ $R\text{-sq} = 73.5\%$ $R\text{-sq(adj)} = 71.7\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	7	8.2911	1.1844	41.26	0.000
Error	104	2.9858	0.0287		
Total	111	11.2768			

TERM	DF	SEQ SS
log(pH)	1	0.3771
log(Temp.)	1	0.3606
log(ClO ₂ dose + 1)	1	6.1504
log(React. + 1)	1	0.8014
log(Temp.)*log(ClO ₂ dose + 1)	1	0.1127
log(ClO ₂ dose + 1)*log(React. + 1)	1	0.3849
log(pH)*log(ClO ₂ dose + 1)	1	0.1041

Figure I.7 Statistical Output for Developed Model D Predicting Chlorite Formation Where Terms Involving $\text{NPOC} \cdot \text{UV}_{254}$ Have Been Removed

$s = 0.1432$ $R\text{-sq} = 80.7\%$ $R\text{-sq(adj)} = 79.8\%$

Analysis of Variance

SOURCE	DF	SS	MS	F	p
Regression	5	9.1034	1.8207	88.79	0.000
Error	106	2.1735	0.0205		
Total	111	11.2768			

TERM	DF	SEQ SS
log(pH)	1	0.3771
log(Temp.)	1	0.3606
log(ClO ₂ dose + 1)	1	6.1504
log(React. + 1)	1	0.8014
log(NPOC*UV ₂₅₄)	1	1.4139

Figure I.8 Statistical Output for Developed Model D Predicting Chlorite Formation Where Terms Involving 2-Factor Interactions Have Been Removed

Table I.2 Chlorine Dioxide Consumed, Chlorite and Chlorate Formed as Predicted by Model Equations for Given Experimental Conditions: Sensitivity Analyses Results

Water Source (NPOC,mg/L; UV ₂₅₄ , cm ⁻¹)	Model Case ¹									
	C					D (E for Chlorate)				
	Case #1	Case #2	Case #3	Case #4	Case #5	Case #1	Case #2	Case #3	Case #4	Case #5
Mannheim Groundwater (0.60; 0.009)	0.44	0.45	0.50	0.39	0.42	0.74	0.76	0.84	0.67	0.70
	0.21	0.24	0.22	0.20	0.18	0.49	0.51	0.51	0.51	0.40
	0.08	0.09	0.09	0.07	0.07	0.07	0.07	0.07	0.06	0.06
Toronto (2.03; 0.034)	1.11	1.14	1.21	0.91	1.05	1.40	1.43	1.53	1.15	1.32
	0.64	0.69	0.67	0.54	0.58	0.92	0.97	0.97	0.81	0.82
	0.13	0.14	0.14	0.10	0.12	0.12	0.12	0.12	0.09	0.11
Windsor (2.06; 0.042)	1.21	1.24	1.31	0.98	1.14	1.48	1.51	1.61	1.21	1.40
	0.70	0.76	0.74	0.58	0.64	0.98	1.03	1.03	0.84	0.87
	0.13	0.14	0.14	0.10	0.12	0.12	0.13	0.13	0.10	0.11
Brantford (4.29; 0.118)	2.30	2.35	2.43	1.76	2.17	2.29	2.34	2.43	1.75	2.17
	1.52	1.58	1.59	1.15	1.42	1.53	1.60	1.61	1.16	1.43
	0.18	0.19	0.19	0.13	0.17	0.19	0.19	0.20	0.13	0.18
Peterborough (4.82; 0.136)	2.53	2.58	2.66	1.91	2.38	2.45	2.50	2.58	1.85	2.31
	1.70	1.76	1.79	1.28	1.59	1.63	1.71	1.72	1.21	1.53
	0.19	0.20	0.20	0.14	0.18	0.20	0.21	0.21	0.14	0.19
Belleville (4.96; 0.14)	2.58	2.64	2.72	1.95	2.43	2.48	2.54	2.61	1.88	2.35
	1.74	1.80	1.83	1.30	1.64	1.65	1.74	1.74	1.22	1.56
	0.20	0.20	0.20	0.14	0.18	0.20	0.21	0.21	0.14	0.19
Mannheim Surface (5.71; 0.148)	2.77	2.83	2.91	2.08	2.61	2.61	2.66	2.74	1.96	2.46
	1.89	1.96	1.99	1.41	1.78	1.74	1.82	1.83	1.27	1.65
	0.20	0.21	0.21	0.14	0.19	0.21	0.22	0.22	0.14	0.20
Ottawa (5.96; 0.212)	3.21	3.28	3.35	2.38	3.02	2.88	2.95	3.01	2.13	2.72
	2.26	2.31	2.38	1.64	2.14	1.92	2.02	2.03	1.36	1.84
	0.22	0.22	0.23	0.15	0.19	0.23	0.24	0.24	0.15	0.22

Note:

Case #1: pH = 7.5, Temp. = 14.5°C, ClO₂ dose = 3.5 mg/L and react. time = 12.5 hrs

Case #2: Case #1 with pH = 8 instead of 7.5

Case #3: Case #1 with Temp. = 20°C instead of 14.5°C

Case #4: Case #1 with ClO₂ dose = 2.5 mg/L instead of 3.5 mg/L

Case #5: Case #1 with react. time = 8 hrs instead of 12.5 hrs

^a Order of reported concentrations (all concentrations in mg/L):

- Chlorine dioxide consumed
- chlorite formed
- chlorate formed

APPENDIX J

SAMPLE CALCULATION FOR F-STATISTIC TESTING “ROBUSTNESS” OF CONVERSION RATIOS OF CHLORINE DIOXIDE CONSUMED TO EITHER CHLORITE AND CHLORATE

Appendix J: Sample Calculation for F-Statistic Testing “Robustness” of Conversion Ratios of Chlorine Dioxide Consumed to Either Chlorite and Chlorate

Regression equations (i.e. with or without considering a y-intercept) pertaining to chlorite and chlorate formation in terms of chlorine dioxide consumption obtained for a given parameter condition (i.e. high pH condition, low temperature condition etc.) are presented in Table J.1 while those pertaining to a specific water source are reported in Table J.2. Special attention was brought to equations based on Toronto data for chlorite formation (due to their R^2 -values of 0.555 and 0.584, Table J.2). With respect to chlorate formation, equations pertaining to a chlorine dioxide concentration of 1.0 mg/L (R^2 -values of 0.441 and 0.237, Table J.1) as well as those pertaining to the groundwater data case (slope coefficient values of 0.4, Table J.2) were also considered. An investigation of these regressions showed that removing a potential “outlying” data point from the data series of interest improved the R^2 -values, and for the chlorate groundwater data system, a regression slope which was more compatible with the equations resulting for the other examined water sources (Tables J.1 and J.2). It should be noted that low chlorine dioxide consumed and chlorate formation levels resulted during the experimental testing of the groundwater or when applying a chlorine dioxide dose of 1.0 mg/L to any of the tested waters. As such, even small variations about these low concentration levels can result in less accurate fits (as reported by smaller R^2 -values).

The “robustness” of the conversion ratios of chlorine dioxide consumed to either chlorite and chlorate observed during the experiments performed on the natural waters, was assessed. This was done by testing whether these conversion ratios,

Table J.1 Chlorite and Chlorate Formation With Respect to Chlorine Dioxide Consumption under Given Experimental Conditions

Parameter Condition	Chlorite		Chlorate	
	Equations ^a for Chlorite conc. (mg/L) in Terms of ClO ₂ consumed (mg/L)	R ²	Equations ^a for Chlorate conc. (mg/L) in Terms of ClO ₂ consumed (mg/L)	R ²
Low pH (pH 6)	= 0.633(ClO ₂ cons.) - 0.0309 = 0.6225(ClO ₂ cons.)	0.947 0.946	= 0.0947(ClO ₂ cons.) - 0.0178 = 0.0886(ClO ₂ cons.)	0.941 0.935
High pH (pH 9)	= 0.7359(ClO ₂ cons.) - 0.0367 = 0.7251(ClO ₂ cons.)	0.971 0.971	= 0.0868(ClO ₂ cons.) + 0.0163 = 0.0916(ClO ₂ cons.)	0.795 0.791
Low Temperature (4°C)	= 0.6663(ClO ₂ cons.) + 0.0161 = 0.6725(ClO ₂ cons.)	0.918 0.918	= 0.0906(ClO ₂ cons.) - 0.0022 = 0.0897(ClO ₂ cons.)	0.902 0.902
High Temperature (25°C)	= 0.716(ClO ₂ cons.) - 0.1087 = 0.6859(ClO ₂ cons.)	0.967 0.964	= 0.0903(ClO ₂ cons.) + 0.0012 = 0.0907(ClO ₂ cons.)	0.823 0.823
Low ClO ₂ dose (1.0 mg/L)	= 0.5951(ClO ₂ cons.) + 0.0598 = 0.6606(ClO ₂ cons.)	0.770 0.760	= 0.0387(ClO ₂ cons.) + 0.0229 = 0.0638(ClO ₂ cons.) without "outlying" point = 0.0432(ClO ₂ cons.) + 0.0184 = 0.0633(ClO ₂ cons.)	0.441 0.237 0.566 0.433
High ClO ₂ dose (6.0 mg/L)	= 0.7138(ClO ₂ cons.) - 0.1185 = 0.683(ClO ₂ cons.)	0.932 0.930	= 0.0795(ClO ₂ cons.) + 0.0487 = 0.0922(ClO ₂ cons.)	0.776 0.748
Low Reaction time (1 hour)	= 0.6555(ClO ₂ cons.) - 0.0294 = 0.6432(ClO ₂ cons.)	0.915 0.915	= 0.0909(ClO ₂ cons.) - 0.0087 = 0.0873(ClO ₂ cons.)	0.838 0.838
High Reaction time (24 hours)	= 0.7052(ClO ₂ cons.) - 0.0257 = 0.6983(ClO ₂ cons.)	0.965 0.964	= 0.0891(ClO ₂ cons.) + 0.0096 = 0.0917(ClO ₂ cons.)	0.836 0.851

^a For each parameter condition, an equation involving a y-intercept followed by an equation without one are reported.

Table J.2 Chlorite and Chlorate Formation With Respect to Chlorine Dioxide Consumption Equations for Tested Water Sources

Water Source	Chlorite		Chlorate	
	Equations ^a for Chlorite conc. (mg/L) in Terms of ClO ₂ consumed (mg/L)	R ²	Equations ^a for Chlorate conc. (mg/L) in Terms of ClO ₂ consumed (mg/L)	R ²
Brantford	= 0.6757(ClO ₂ cons.) + 0.1217 = 0.716(ClO ₂ cons)	0.942 0.937	= 0.0923(ClO ₂ cons.) - 0.0145 = 0.0874(ClO ₂ cons)	0.973 0.969
Ottawa	= 0.7075(ClO ₂ cons.) - 0.22113 = 0.6593(ClO ₂ cons)	0.983 0.977	= 0.0888(ClO ₂ cons.) - 0.026 = 0.0831(ClO ₂ cons)	0.943 0.937
Windsor	= 0.5136(ClO ₂ cons.) + 0.0635 = 0.5487(ClO ₂ cons)	0.767 0.763	= 0.1233(ClO ₂ cons.) - 0.0524 = 0.0943(ClO ₂ cons)	0.897 0.830
Toronto	= 0.5506(ClO ₂ cons.) + 0.1695 = 0.716(ClO ₂ cons) without "outlying" point = 0.5227(ClO ₂ cons.) + 0.1272 = 0.5994(ClO ₂ cons.)	0.584 0.555 0.802 0.777	= 0.0971(ClO ₂ cons.) - 0.0152 = 0.0879(ClO ₂ cons)	0.942 0.930
Peterborough	= 0.7459(ClO ₂ cons.) - 0.1336 = 0.7027(ClO ₂ cons)	0.978 0.973	= 0.1097(ClO ₂ cons.) - 0.0391 = 0.0971(ClO ₂ cons)	0.978 0.959
Belleville	= 0.6795(ClO ₂ cons.) - 0.06899 = 0.657(ClO ₂ cons)	0.986 0.984	= 0.1050(ClO ₂ cons.) - 0.0345 = 0.0937(ClO ₂ cons)	0.930 0.914
Mannheim Surface	= 0.7875(ClO ₂ cons.) - 0.1491 = 0.7444(ClO ₂ cons)	0.979 0.975	= 0.1006(ClO ₂ cons.) - 0.0277 = 0.0926(ClO ₂ cons)	0.859 0.851
Mannheim Groundwater	= 0.5118(ClO ₂ cons.) + 0.02880 = 0.5738(ClO ₂ cons)	0.825 0.801	= 0.439(ClO ₂ cons.) - 0.0168 = 0.403(ClO ₂ cons) without "outlying" point = 0.128(ClO ₂ cons.) + 0.0319 (avg. ClO ₃ conc. = 0.055 (std 0.00))	0.795 0.784 0.189

^a For each parameter condition, an equation involving a y-intercept followed by an equation without one are reported.

resulting from the analysis of all experimental data (irrespective of parameter condition), significantly (on a statistical basis) differed from the conversion ratios resulting at specific conditions (i.e. low or high level) of the different experimentally-varied factors (i.e. pH, temperature, chlorine dioxide concentration and reaction time). This was accomplished using the following developed F-statistic (Myers, 1990):

$$F\text{-statistic} = \frac{(RSS1 - RSS2)/DOF1}{RSS2/DOF2}$$

where RSS1 = Residual Sum of Squares obtained when employing equation predicted from regression performed on all experimental data

RSS2 = Residual Sum of Squares obtained when employing equations A and B predicted from regressions performed on experimental data where parameter condition was at the low condition (i.e. Equation A) and on experimental data where parameter condition is at the high condition (i.e. Equation B)

DOF1 = Degrees of freedom = a - b

a = total number of terms involved in both equations employed in the calculation of RSS2

b = total number of terms involved in equation employed in the calculation of RSS1

DOF2 = Degrees of freedom = n - a

n = total number of data points

note for each data point,

$$RSS = [(\text{measured conc.}) - (\text{conc. predicted from regression trendline})]^2$$

The calculated F-statistics are reported in Table J.3. The application of the above equation could best be illustrated with a sample calculation. As such, the F-statistic to test the robustness of the chlorine dioxide consumed to chlorite conversion ratio (on a mass basis) with respect to variations of pH from its low to high tested conditions (i.e. pH 6 and pH 9 respectively) during the natural water experiments is presented. The linear trendline resulting upon regressing the measured chlorite levels against the corresponding measured chlorine dioxide consumed levels of all available

Table J.3 “Robustness” of Chlorite and Chlorate Produced to Chlorine Dioxide Consumed ratios to Variations of Given Parameters

Parameter or Condition	Chlorite		Chlorate	
	F-Statistic	P-value	F-Statistic	P-value
pH	13.37	< 0.001	1.67	0.194
Temperature	1.86	0.155	0.028	> 0.25
Chlorine Dioxide Concentration	1.60	0.207	9.21	< 0.001
Reaction time	2.81	0.0459	0.69	> 0.25
“Pooling” of Data from All Eight Waters	3.08	< 0.001	7.77 2.40 ^a	< 0.001 0.0093 ^a

^a Values are associated with case where Mannheim groundwater data is excluded (i.e. only data observed for the seven surface water are considered).

experimental data is shown in Figure J.1 (reproduced from Chapter 6). The linear regression trendlines resulting from the trial runs where pH = 6 and from the trial runs where pH = 9 are displayed in Figure J.2. The F-statistic was calculated as per the following equation:

$$\text{F-statistic} = \frac{(\text{RSS1} - \text{RSS2})/\text{DOF1}}{\text{RSS2}/\text{DOF2}}$$

where RSS1 = 7.802
 RSS2 = 2.952 (for pH = 6) + 2.919 (for pH = 9) = 5.871
 DOF1 = a - b
 a = 4 (two equations, each described by a slope and y-intercept)
 calculation of RSS2
 b = 1 (one equation described by a slope coefficient)
 DOF1 = a - b = 4 - 1 = 3
 n = 126
 DOF2 = n - a = 126 - 4 = 122

Hence,

$$\begin{aligned}\text{F-statistic} &= \frac{(7.802 - 5.872)/3}{5.871/122} \\ &= 13.367\end{aligned}$$

Consulting F-Tables (such as in Montgomery, 1997), for DOF1 = 3 and DOF2 = 122

for F-statistic = 13.367

the associated P-value = < 0.001

As such, there is a statistical difference between RSS1 and RSS2 (based on a selected significance level of 5%).

Figure J.1 Chlorite Formation With Respect to Chlorine Dioxide Consumption Observed during the Natural Test Water Factorial Experiments (n = 126 cases)

Figure J.2 Chlorite Formation With Respect to Chlorine Dioxide Consumption Observed during the Natural Test Water Factorial Experiments where pH = 6 (n = 62 cases) or pH = 9 (n = 64 cases)

APPENDIX K

**RESULTS OF EXTERNAL VALIDATION EXPERIMENT
IN TABULAR FORM**

Appendix K: Results of External Validation Experiment in Tabular Form

Table K.1 Predictive Model Equation Validations Using Measured Levels "External" to the Original Database

Water Source ^a	Parameter Condition			ClO ₂ consumed (mg/L)			Chlorite (mg/L)			Chlorate (mg/L)		
	pH ^b	Temp. (°C)	React. time (hr)	Meas.	Pred. Model C	Pred. Model D	Meas.	Pred. Model C	Pred. Model D	Meas.	Pred. Model C	Pred. Model E
Vancouver (1.47; 0.043)	6.57	6	1	0.50	0.48 P	0.62	0.40	0.25	0.39 P	0.041	0.038	0.041
	6.57	6	4	0.60	0.51 P	0.66 P	0.44	0.28	0.48 P	0.047	0.043	0.048
	6.68	20	1	0.78	0.59	0.78 P	0.46	0.28	0.44 P	0.053	0.045	0.045
	6.68	20	4	0.88	0.63	0.83 P	0.62	0.32	0.54 P	0.074	0.051	0.053
Calgary (2.05; 0.045)	8.37	4	1	0.47	0.55 P	0.67	0.29	0.37	0.45	0.042	0.051	0.050
	8.37	4	4	0.60	0.59 P	0.72 P	0.56	0.42	0.54 P	0.054	0.061	0.056
	8.46	20	1	0.44	0.71	0.89	0.49	0.43 P	0.53 P	0.058	0.057	0.058
	8.46	20	4	0.98	0.76	0.95 P	0.70	0.49	0.63 P	0.082	0.069	0.065
Brantford (4.83; 0.121)	7.79	4	1	0.95	1.02 P	1.00 P	0.83	0.68 P	0.66 P	0.102	0.070	0.070
	7.79	4	4	1.39	1.09	1.07	0.98	0.72	0.69	0.130	0.075	0.074
	7.87	20	1	1.35	1.16 P	1.14 P	1.00	0.78	0.76	0.120	0.076	0.078
	7.87	20	4	> 1.47	1.24 P	1.22 P	1.24	0.83	0.81	0.130	0.081	0.083
Ann Arbor (5.10; 0.141)	7.78	4	1	1.11	1.09 P	1.05 P	0.75	0.73 P	0.69 P	0.070	0.073	0.073
	7.78	4	4	1.30	1.17 P	1.12 P	1.02	0.78	0.71	0.086	0.077	0.076
	7.70	20	1	1.36	1.22 P	1.17 P	0.93	0.83 P	0.79 P	0.083	0.078	0.080
	7.70	20	4	> 1.47	1.30 P	1.25 P	1.15	0.88	0.82	0.098	0.082	0.084

Note: All trial runs involved the application of a 1.51 mg/L chlorine dioxide dose.

P = Predicted levels within $\pm 20\%$ of the measured levels, conducted for chlorine dioxide consumption and chlorite formation only.

^a Values reported in () are, respectively, the NPOC (in mg/L) and UV₂₅₄ (in cm⁻¹) levels for the given water source.

^b Ambient pH levels measured when sample had attained its test temperature.

APPENDIX L

**PLOTS OF CHLORINE DIOXIDE CONSUMPTION AND
DBP FORMATION WITH RESPECT TO
CHANGES IN UV_{254}**

Appendix L: Plots of Chlorine Dioxide Consumption and DBP Formation With Respect to Changes in UV_{254}

This appendix thus, contain graphs which support the discussion provided in Chapter 6 pertaining to the investigation as to whether chlorine dioxide consumption as well as DBP formation (i.e. chlorite, chlorate and DCAA). Correlations resulting subsequent to unadjusted or adjusted for experimental error (refer to Chapter 6 for additional details) and/or chlorite UV_{254} interferences (refer to Chapter 4 for additional details) are displayed in Figures L.1 through L.12. It is seen that, while UV_{254} adjustments for either experimental error or chlorite interferences did improve the linear trendline fits (as evidenced by higher R^2 values), the slope coefficients were not significantly affected. Chlorine dioxide consumption and chlorate formation in terms of UV_{254} changes on site- as well as parameter specific basis are presented in Figures L.13 to L.18. As mentioned in Chapter 6, they show similar trends displayed by chlorite formation with respect to UV_{254} whereby improved correlations are observed when isolating the data from individual water sources as well as under given experimental conditions (i.e. specific chlorine dioxide concentration and pH levels).

Figure L.1 Chlorine Dioxide Consumption With Respect to ΔUV_{254}
(Unadjusted UV_{254} for Pure error and Chlorite Interferences)

Figure L.2 Chlorite Formation With Respect to ΔUV_{254}
(Unadjusted UV_{254} for Pure error and Chlorite Interferences)

Figure L.3 Chlorate Formation With Respect to ΔUV_{254}
(Unadjusted UV₂₅₄ for Pure error and Chlorite Interferences)

Figure L.4 DCAA Formation With Respect to ΔUV_{254}
(Unadjusted UV₂₅₄ for Pure error and Chlorite Interferences)

Figure L.5 Chlorine Dioxide Consumption With Respect to ΔUV_{254}
(Adjusted for Chlorite UV Interference only)

Figure L.6 Chlorite Formation With Respect to ΔUV_{254}
(Adjusted for Chlorite UV Interference only)

Figure L.7 Chlorate Formation With Respect to ΔUV_{254}
(Adjusted for Chlorite UV Interference only)

Figure L.8 DCAA Formation With Respect to ΔUV_{254}
(Adjusted for Chlorite UV Interference only)

Figure L.9 Chlorine Dioxide Consumption With Respect to ΔUV_{254}
(Adjusted UV_{254} for Pure error and Chlorite Interferences)

Figure L.10 Chlorite Formation With Respect to ΔUV_{254}
(Adjusted UV_{254} for Pure error and Chlorite Interferences)

Figure L.11 Chlorate Formation With Respect to ΔUV_{254}
(Adjusted UV_{254} for Pure error and Chlorite Interferences)

Figure L.12 DCAA Formation With Respect to ΔUV_{254}
(Adjusted UV_{254} for Pure error and Chlorite Interferences)

Figure L.13 Chlorine Dioxide Consumption With Respect to ΔUV_{254} on a Site-Specific Basis (UV_{254} Changes Below 0.002 cm⁻¹ Adjusted to 0.001 cm⁻¹)

Figure L.14 Chlorate Formation With Respect to ΔUV_{254} on a Site-Specific Basis (UV_{254} Changes Below 0.002 cm⁻¹ Adjusted to 0.001 cm⁻¹)

Figure L.15 Chlorine Dioxide Consumption With Respect to Δ Changes on a Site-Specific Basis for a ClO_2 Dose of 1.0 mg/L (UV_{254} Changes Below 0.002 cm⁻¹ Adjusted to 0.001 cm⁻¹)

Figure L.16 Chlorine Dioxide Consumption With Respect to UV_{254} Changes on a Site-Specific Basis for a ClO_2 Dose of 6.0 mg/L (UV_{254} Changes Below 0.002 cm⁻¹ Adjusted to 0.001 cm⁻¹)

Figure L.17 Chlorate Formation With Respect to ΔUV_{254} on a Site-Specific Basis for a ClO_2 Dose of 1.0 mg/L (UV_{254} Changes Below 0.002 cm^{-1} Adjusted to 0.001 cm^{-1})

Figure L.18 Chlorate Formation With Respect to UV_{254} Changes on a Site-Specific Basis for a ClO_2 Dose of 6.0 mg/L (UV_{254} Changes Below 0.002 cm^{-1} Adjusted to 0.001 cm^{-1})