THE EFFECT OF STRUCTURAL CHARACTERISTICS OF HUMIC SUBSTANCES ON DISINFECTION BY-PRODUCT FORMATION

BY

WELLS WEI-SHIH WU

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1998
ACKNOWLEDGEMENTS

I wish to thank all the members of my advisory committee for their suggestions and support throughout this work. I wish to thank Dr. Paul A. Chadik for his interest and guidance during my graduate studies here. He has been a true mentor. The other members of my advisory committee were also supportive of my research efforts. They provided needed guidance, suggestions and equipment to assist in the accomplishment of this research. I would like to thank Drs. Joseph J. Delfino, Ben L. Koopman, David H. Powell, and John Zoltek, Jr.

Finally, I am very much indebted to my parents; their continual support and encouragement have been invaluable. I thank my wife who encouraged and assisted me every step of the way in this graduate program. Without their help and love, I would not have been able to accomplish this goal.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>ACKNOWLEDGEMENTS</th>
<th>ii</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td><strong>CHAPTERS</strong></td>
<td></td>
</tr>
<tr>
<td>1  INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2  LITERATURE REVIEW</td>
<td>6</td>
</tr>
<tr>
<td>Chlorination of Humic Substances</td>
<td>6</td>
</tr>
<tr>
<td>Chlorination Chemistry</td>
<td>6</td>
</tr>
<tr>
<td>Chlorination By-products</td>
<td>8</td>
</tr>
<tr>
<td>Chlorination Treatment Variables</td>
<td>10</td>
</tr>
<tr>
<td>Chloramination of Humic Substances</td>
<td>14</td>
</tr>
<tr>
<td>Chloramination Chemistry</td>
<td>14</td>
</tr>
<tr>
<td>Chloramination By-products</td>
<td>20</td>
</tr>
<tr>
<td>Chloramination Treatment Variables</td>
<td>24</td>
</tr>
<tr>
<td>The Chemistry of Humic Substances</td>
<td>28</td>
</tr>
<tr>
<td>The Chemistry and Composition of Tea</td>
<td>32</td>
</tr>
<tr>
<td>Disinfection By-products (DBPs)</td>
<td>36</td>
</tr>
<tr>
<td>Trihalomethanes</td>
<td>36</td>
</tr>
<tr>
<td>Haloacetic Acids</td>
<td>39</td>
</tr>
<tr>
<td>Haloacetonitriles</td>
<td>43</td>
</tr>
<tr>
<td>Chlormal Hydrate</td>
<td>46</td>
</tr>
<tr>
<td>Haloketones</td>
<td>48</td>
</tr>
<tr>
<td>Chloropicrin</td>
<td>51</td>
</tr>
<tr>
<td>Cyanogen Halides</td>
<td>55</td>
</tr>
<tr>
<td>The Effects of Structural Characteristics of Humic Substances on DBP Formation</td>
<td>60</td>
</tr>
<tr>
<td>Characterization of Humic Substances</td>
<td>61</td>
</tr>
<tr>
<td>Aquatic Versus Corresponding Soil and Sediment Humic Substances</td>
<td>72</td>
</tr>
<tr>
<td>Structural Characteristics of Humic Substances Versus DBP Formation</td>
<td>77</td>
</tr>
<tr>
<td>3  MATERIALS AND METHODS</td>
<td>85</td>
</tr>
<tr>
<td>Materials</td>
<td>85</td>
</tr>
<tr>
<td>Humic Substances and Tea Samples</td>
<td>85</td>
</tr>
<tr>
<td>Standards and Reagents</td>
<td>87</td>
</tr>
<tr>
<td>Experimental Design</td>
<td>88</td>
</tr>
<tr>
<td>Target Compounds and Parameters</td>
<td>88</td>
</tr>
<tr>
<td>Experimental Design of Chlorination and Chloramination</td>
<td>92</td>
</tr>
</tbody>
</table>
Chlorination of Realistic Instant Tea Samples... 97
In Situ Synthesis of Cyanogen Chloride......... 98
Experimental Procedures of In Situ Synthesis... 98
Analytical Methods.................................. 102
Miscellaneous Analyses and QA/QC Implementation... 102
Structural Characterization and QA/QC Implementation......... 104
EPA Method 551.1 and QA/QC Implementation........ 105
EPA Method 552.2 and QA/QC Implementation........ 108
Cyanogen Halide Analysis and QA/QC Implementation........ 114
GC/MS Analysis and QA/QC Implementation........ 116

4 RESULTS AND DISCUSSION .................... 119
In Situ Synthesis of Cyanogen Chloride........ 119
Disinfectant Demand................................. 125
DBP Formation of Humic Substances.............. 131
Chlorination......................................... 138
Chloramination....................................... 151
The Effect of Structural Characteristics of Humic Substances on DBP Formation........ 156
Elemental Analysis.................................. 156
UV/VIS Spectroscopy................................. 170
Total Acidity Titration.............................. 189
Infrared Spectroscopy.............................. 192
$^{13}$C NMR Spectroscopy............................ 200
DBP Formation of Instant Tea Samples.......... 202
Instant Tea Samples at NPOC of 5 mg/L......... 204
Realistic Instant Tea Samples.................... 209

5 SUMMARY AND CONCLUSIONS .................. 214
Summary............................................. 214
Conclusions........................................ 217
In Situ Synthesis of Cyanogen Chloride........ 217
Structural Characteristics of Humic Substances
   Versus DBP Formation............................ 217
Tea Samples Versus Humic Substances............ 218
Further Research.................................. 218

APPENDIX........................................... 219
REFERENCES........................................ 222
BIOGRAPHICAL SKETCH ......................... 240
Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

THE EFFECT OF STRUCTURAL CHARACTERISTICS OF HUMIC SUBSTANCES ON DISINFECTION BY-PRODUCT FORMATION

By
Wells Wei-Shih Wu
May 1998

Chairman: Paul A. Chadik
Major Department: Environmental Engineering Sciences

The influence of structural characteristics of humic substances on disinfection by-product (DBP) formation was investigated for seven different humic substances in this research. The structural characteristics used in this research included elemental analysis, ultraviolet (UV)/visible spectroscopy, total acidity titration, infrared spectroscopy (IR), and $^{13}$C nuclear magnetic resonance spectroscopy ($^{13}$C NMR). The DBPs studied in this research included trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, chloropicrin, chloral hydrate, cyanogen chloride, and cyanogen bromide.

Water samples prepared from the seven characterized humic substances were studied under a variety of DBP formation conditions. Both chlorination and chloramination experiments were performed. Two pH conditions (7.0 and 8.5)
and two bromide ion concentrations (zero and 250 μg/L) were used in the DBP formation experiments with each humic source.

The hydrogen/carbon ratio of the individual humic substances, a qualitative measurement of aromaticity, correlated with DBP formation for the humic substances investigated. Change in UV absorbance at 254 nm induced by chlorination (ΔUV254) or UV absorbance at 254 nm varied linearly with both DBP formation and chlorine consumption, with the ΔUV254 nm consistently showing better correlation. A linear relationship was observed between aromatic carbon absorption in the 1650 to 1600 cm⁻¹ region of IR spectra at pH 4 and DBP formation as well as chlorine consumption. Based on the results of computation with respect to total acidity, the contribution of COOH group to the hydrogen/carbon ratio of the humic substances studied was not as significant than previously thought. ¹³C NMR data could not be related to DBP formation and chlorine consumption because of insufficient data gathered.

This study also developed the in situ synthesis of cyanogen chloride as a safe and economical aqueous standard.

Furthermore, this research extended the DBP precursor study to instant tea samples. Tea polyphenols, similar to humic substances in both color and structure, were found to react with chlorine to form as much DBPs as the aquatic humic substances under the same formation conditions. Use of boiled water in preparation of instant tea is suggested if the residual free chlorine is high in the tap water.
Natural organic matter (NOM) is a term used to describe the complex matrix of organic material present in natural waters. NOM can be divided into humic and non-humic fractions. The humic fraction is more hydrophobic in character and comprises humic and fulvic acids. The non-humic fraction is less hydrophobic in character and comprises hydrophilic acids, proteins, amino acids, carbohydrates, and so on.

Chlorine is the most widely used oxidant in the United States for water disinfection. Chlorine reacts with NOM and forms disinfection by-products (DBPs). Trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), chloropicrin (CPN), chloral hydrate (CH), cyanogen chloride (CNCl), and cyanogen bromide (CNBr) are all identified chlorination by-products.

In addition to chlorination, chloramination is now a common method of disinfection because it forms much less DBPs as compared to chlorination. Based on a recent survey (Water Quality Division Disinfection Committee, 1992), 20% of the surveyed utilities used some form of the chlorine-ammonia process. It is likely that chloramination will become more popular if the DBP regulations become more
stringent, as expected. Furthermore, chloramination for DBP control, in particular, is receiving much attention because conversion from free chlorination to chloramination is often a viable operational modification for many water systems.

The proposed Disinfectants/Disinfection By-products (D/DBP) Rule was published in July of 1994 by the United States Environmental Protection Agency (USEPA, 1994). This rule, when promulgated, will establish maximum residual disinfectant levels (MRDLs) for several disinfectants and maximum contaminant levels (MCLs) for DBPs. The Stage I MCLs for total trihalomethanes (TTHMs) and five haloacetic acid (HAA5) species are anticipated to be 0.080 mg/L and 0.060 mg/L, respectively. Although the proposed D/DBP Rule does not set limits on HANs, HKs, CPN, CH, CNC1, and CNBr, those DBPs (except CNBr) are among the by-products listed in the USEPA’s Drinking Water Priority Lists (USEPA, 1988; USEPA, 1991). Also, quarterly monitoring of those DBPs (except CNBr) was required in the Information Collection Rule (ICR) (USEPA, 1996). Thus, information concerning their occurrence and formation is of critical interest.

The DBP formation during chlorination and chloramination has been correlated with several non-specific parameters such as dissolved organic carbon (DOC), color, ultraviolet/visible absorbance, chlorine demand, and so on. These parameters, which mainly reflect the concentration of natural organic matter, do not precisely take into account the composition of the humic substance matrix.
Therefore, the influence of structural characteristics of humic substances on DBP formation was investigated for seven different humic substances in this research. Among the seven humic substances, one was from a commercial source (Aldrich), the rest were isolated from several aquatic and their corresponding soil and sediment sources.

The seven isolated humic substances were characterized (Davis, 1993) by a variety of physical and chemical techniques as follows:

- Elemental analysis
- Ultraviolet/visible spectroscopy
- Total acidity titration
- Infrared spectroscopy
- $^{13}$C nuclear magnetic resonance spectroscopy

The water samples prepared from those characterized humic substances were studied in a series of experiments performed under the following conditions:

- Temperature = 25 ± 2°C.
- pH = 7.0 ± 0.1 and 8.5 ± 0.1.
- Bromide ion concentration = zero and 250 µg/L.
- Non-purgeable organic carbon (NPOC) = 5 mg/L.
- Chlorine dose = 12.5 mg/L ($\text{Cl}_2$/NPOC = 2.5).
- Chloramine dose = 6.25 mg/L as $\text{Cl}_2$ ($\text{Cl}_2$/NPOC = 1.25).
- Contact time = 24 hours.

Chlorine and chloramine doses were chosen to achieve the chlorine and chloramine residual concentrations of at least 0.6 mg/L at the end of the 24-hour reaction period for all
samples. The target DBPs in this research and their analytical methods are shown in Figure 1-1.

The objective of this research was to investigate the relationship between the characterization results of the humic substances and the DBP formation under a variety of formation conditions in both chlorination and chloramination. This research presented new information on the relationship between certain structural characteristics of humic substances and DBP formation as well as chlorine consumption.

Furthermore, this research extended DBP precursor study to instant tea samples. The tea polyphenols or tea tannins, as they are called, bear some resemblance to humic substances in both color and structure, as discussed in Chapter 2. Therefore, the free chlorine residual present in tap water, which has shown to be as high as 5.2 mg/L (USEPA, 1994), may react with the tea polyphenols to form DBPs. Two instant tea samples from Lipton and Nestlé were included in this research and were compared to the seven humic substances under the preceding formation conditions. In addition, chlorine consumption as well as DBP formation in realistic instant tea samples chlorinated at a typical level of free chlorine (4 mg/L) were also investigated.
<table>
<thead>
<tr>
<th>Disinfection By-products</th>
<th>Analytical Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Trihalomethanes</strong></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
</tr>
<tr>
<td>Cl–C–H</td>
<td>Cl–C–H</td>
</tr>
<tr>
<td>Br–C–H</td>
<td>Br–C–H</td>
</tr>
<tr>
<td>Cl</td>
<td>Br</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Dichlorobromo</td>
</tr>
<tr>
<td>methane</td>
<td>Dibromochloro</td>
</tr>
<tr>
<td>methane</td>
<td>Bromoform</td>
</tr>
<tr>
<td><strong>Haloacetonitriles</strong></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
</tr>
<tr>
<td>Cl–C–CN</td>
<td>Cl–C–CN</td>
</tr>
<tr>
<td>Br–C–CN</td>
<td>Br–C–CN</td>
</tr>
<tr>
<td>Cl</td>
<td>H</td>
</tr>
<tr>
<td>Trichloro-</td>
<td>Dichloro-</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>Bromochloro-</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>Dibromo-</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>acetonitrile</td>
</tr>
<tr>
<td><strong>Haloketones</strong></td>
<td></td>
</tr>
<tr>
<td>Cl O</td>
<td>Cl O</td>
</tr>
<tr>
<td>Cl–C–C–C–H</td>
<td>Cl–C–C–C–H</td>
</tr>
<tr>
<td>H–H</td>
<td>H–H</td>
</tr>
<tr>
<td>1,1-Dichloro-</td>
<td>1,1,1-Trichloro-</td>
</tr>
<tr>
<td>propanone</td>
<td>propanone</td>
</tr>
<tr>
<td><strong>Haloacetic Acids</strong></td>
<td></td>
</tr>
<tr>
<td>Cl O</td>
<td>Cl O</td>
</tr>
<tr>
<td>H–C–C–OH</td>
<td>Cl–C–C–OH</td>
</tr>
<tr>
<td>H–H</td>
<td>H–H</td>
</tr>
<tr>
<td>Monochloro-</td>
<td>Dichloro-</td>
</tr>
<tr>
<td>acetic acid</td>
<td>Trichloro-</td>
</tr>
<tr>
<td>acetic acid</td>
<td>Monobromo-</td>
</tr>
<tr>
<td>acetic acid</td>
<td>Dibromo-</td>
</tr>
<tr>
<td>acetic acid</td>
<td>acetic acid</td>
</tr>
<tr>
<td><strong>Cyanogen Halides</strong></td>
<td></td>
</tr>
<tr>
<td>Cl–C≡N</td>
<td>Br–C≡N</td>
</tr>
<tr>
<td>Cyanogen chloride</td>
<td>Cyanogen bromide</td>
</tr>
<tr>
<td><strong>Miscellaneous</strong></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>Cl–C–NO₂</td>
</tr>
<tr>
<td>The micro</td>
<td>Lig/Lig Extraction</td>
</tr>
<tr>
<td>Chloropicrin</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1-1. A Diagram for the Structural Formula of DBPs and Their Analytical Methods Used in This Research.
The literature review focuses on the following topics: (1) chlorination of humic substances; (2) chloramination of humic substances; (3) the chemistry of humic substances; (4) the chemistry and composition of tea; (5) disinfection by-products; and (6) the effects of structural characteristics of humic substances on DBP formation.

Chlorination of Humic Substances

A review of published material dealing with the chemistry of chlorination, chlorination by-products, and chlorination treatment variables is presented in this section.

Chlorination Chemistry

Chlorine chemistry. Chlorine hydrolyzes very rapidly in water according to the following reaction:

\[
\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \quad \text{(eq. 2-1)}
\]

Hypochlorous acid is a weak acid that dissociates or ionizes with a dissociation constant ranging from \(1.6 \times 10^{-8}\) at 0°C to \(3.2 \times 10^{-8}\) at 25°C. At pH 7.5 and 25°C, HOCl and OCl\(^-\) are essentially equimolar in concentration:

\[
\text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \quad \text{(eq. 2-2)}
\]
At higher pH values, OCl\(^{-}\) becomes the major form of chlorine; at lower pH values, HOCl becomes dominant.

If sodium or calcium hypochlorite are used as the source of chlorine, they provide hypochlorite ions on dissolution in water. The hypochlorite ion very rapidly establishes equilibrium with hypochlorous acid (eq. 2-2). Although hydrolysis of chlorine gas produces hydrogen ions thus tending to lower the pH, dissolution of hypochlorite salts consumes hydrogen ions in reaching equilibrium thus tending to raise the pH. However, the pH effect is generally very small at the typical milligram-per-liter concentrations of chlorine used in water treatment with moderate alkalinity in the water. Therefore, at the same pH and temperature, the composition of the aqueous solution is the same whether starting with chlorine gas or hypochlorite.

If bromide ion is present, the added chlorine will oxidize the bromide ion rapidly. The overall reaction can be represented as follows:

\[
\text{HOCl} + \text{Br}^- \leftrightarrow \text{HOBr} + \text{Cl}^-
\]

Bromine, as either HOBr or OBr\(^{-}\), will then react with NOM in oxidation and substitution reactions to produce DBPs containing bromine.

**Chlorination chemistry.** Chlorine species are electrophiles and tend to react with electron-rich sites in NOM structures. Activated aromatic rings, aliphatic \(\beta\)-dicarbonyls, and amino nitrogen are examples of electron-rich organic structures (Harrington et al., 1996).
Chlorinated aliphatic compounds could result from aromatic ring rupture or side-chain oxidation of humic molecules followed by halogen substitution. Ring-chlorinated aromatic compounds could survive intact and be detected if the relatively low concentration of chlorine and carbonaceous substrates were used (Seeger et al., 1985). In contrast, de Leer et al. (1985) reported that several chlorinated aromatic acids that were absent at lower Cl\(_2\) dosage were detected at higher Cl\(_2\) dosage.

Nonchlorinated compounds may result from the oxidation of humic substances by chlorine. Christman et al. (1980) found that the presence of the nonchlorinated aromatic products in the extracts of the chlorinated aquatic humic acid indicates chlorine acts as an effective degradation method for humic acid structures. Norwood et al. (1983) chlorinated a natural aquatic fulvic acid and reported that most of the DBPs not containing chlorine are aromatic which could possibly result from the oxidation of fused-ring structures present in the humic (or fulvic) macromolecules. In addition to the nonchlorinated aromatic compounds, Johnson et al. (1982) indicated that the nonchlorinated aliphatic acids may also derive from ring-cleavage of humic substances.

**Chlorination By-products**

The production of DBPs from chlorination of drinking water was not recognized until 1974 when Rook (1974)
demonstrated that chlorination of water containing natural humic substances produced THMs. However, it was soon discovered that most of the chlorine bound to organic compounds resides in the non-volatile fraction of the organic material (Glaze et al., 1979; Rook, 1980). THMs are only a fraction of all of the DBPs. They constitute 22 to 67% of total organic halogen (TOX) depending on the source water (Symons et al., 1982). In fact, all identified DBPs that have been quantified account for about 50% of the TOX contents (Christman et al., 1983; Reckhow and Singer, 1984; Singer and Chang, 1989; Stevens et al., 1990; Singer, 1994). This means that approximately half of the total halogenated DBPs are composed of unidentified halogenated compounds. The unidentified DBPs are either too large in molecular weight to be detected with gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) or cannot be matched with library database spectra.

Stevens et al. (1989b) reported that 782 compounds were detected in the extracts of the chlorinated Fluka humic acid solutions at total organic carbon (TOC) concentrations of 5 to 7 mg/L. Approximately 500 of the 782 compounds could be attributed solely to the chlorination process. Of the 500 byproducts, 196 compounds (either identifiable or unidentifiable) were also found in waters of ten utilities based on GC/MS data. THMs, dihaloacetonitriles, and chloropicrin were not included in the 196-compound list because of their ubiquitous presence.
Despite the fact that researchers have demonstrated that the sum of the commonly identified DBPs such as THMs, HAAs, and HANs accounts for only about 50% of measured TOX, those commonly identified DBPs shown in Figure 1-1 are reported with more frequency and at much higher levels than other DBPs. They are among the EPA’s Drinking Water Priority Lists, and monitoring list in the ICR. Therefore, it calls for more research on their formation.

**Chlorination Treatment Variables**

The formation of DBPs resulting from chlorination is influenced by the following treatment variables:

- Chlorine dosage.
- pH.
- Temperature.
- Reaction time.

The effect of each of the above variables on DBP formation is discussed below in terms of TOX, dissolved organic halogen (DOX), non-purgeable organic halogen (NPOX), or non-purgeable organic chlorine (NPOCl). The effects of chlorination on the identifiable DBPs are compiled in their respective DBP sections as discussed later.

**Chlorine dosage.** The effect of chlorine dosage reported by Fleischacker and Randtke (1983) showed that increasing chlorine dosages with soil and aquatic humic substances as well as a natural water produced increasing concentrations of NPOCl, in some cases reaching a plateau.
Reckhow and Singer (1984) also showed the increasing TOX formation in an aquatic fulvic acid solution with higher chlorine dosages. Stevens et al. (1985) studied a chlorinated Aldrich humic acid solution and reported increasing NPOX and THM concentrations with increasing chlorine dosages.

Luong et al. (1982) proposed that the activation of the humic structure through oxidation reactions produces active sites (TOC*) followed by substitution reactions with oxidant to produce halogenated organics. The increase in the oxidant concentration causes some more difficult-to-halogenate precursor sites to be halogenated, with a corresponding increase in the TOX formation. Since the number of possible active sites is limited, higher oxidant concentration could lead to relatively slower reaction (reacts with some more difficult sites), and eventually reaching a plateau (virtually no difficult sites left).

pH. Some disinfectants (chlorine for instance) are electrophiles and tend to react with electron-rich sites in organic structures of humic substances. pH influences the electron distribution within humic structures and the distribution of aqueous disinfectant species; therefore, pH is an important factor in the interaction between humic substances and disinfectant species. The kinetic competition between hydrolysis, oxidation, and halogenation reactions also establishes pH as an important factor in
determining the DBP species distribution (Harrington et al., 1996).

Chloroform formation can be reduced by disinfecting at a lower pH; however, disinfection at a low pH forms greater concentrations of NPOCl and TOX (Fleischacker and Randtke, 1983; Reckhow and Singer, 1984). Stevens et al. (1985) also showed that the formation of TOX and NPOX were reduced with increasing pH during chlorination.

One explanation for the decrease in TOX formation with increasing pH could be the direct dependence of chlorine speciation. For instance, the concentration of HOCl, which is a better electrophile and a stronger chlorinating agent than the less reactive OCl\(^-\), would increase with decreased pH. Because most of the possible organohalogen-forming reactions involve electrophilic attack of chlorine on organic molecules, it follows that more organohalogen-forming reactions would occur as pH decreases.

**Temperature.** Fleischacker and Randtke (1983) showed that NPOCl concentrations increased with higher temperatures; however, chloroform formation appeared to be more strongly influenced by temperature. Stevens et al. (1985) showed that the NPOX formation increased with increasing temperatures from 4 to 30°C. Summers et al. (1996) investigated the effect of incubation temperature on DOX formation over a temperature range of <10°C to >30°C, and reported that DOX formation increased by 10 to 75 percent.
This increasing NPOX formation with increasing temperature apparently can be explained by the kinetic theory; as the temperature is raised, higher collision frequency of reacting particles and higher probability that the collision is sufficiently energetic for a reaction to occur lead to more DBP formation.

**Reaction time.** The formation of NPOCl as a function of time for a peat fulvic acid and a groundwater was reported by Fleischacker and Randtke (1983); NPOCl formation showed an initial phase of rapid formation followed by a subsequent phase of slower formation and, eventually, a leveling off as any reactant approached depletion. Reckhow and Singer (1984) also demonstrated that TOX increased rapidly in the first few hours and then slowed to a generally steady rate of increase.

These results support the hypothesis that humic substances contain different types of precursor sites or structures; the more reactive sites give rise to TOX formation much more quickly than the less reactive sites. This explains the phenomena of two phases in TOX formation. More reactive sites are halogenated to form substantial linear TOX formation in a relatively shorter term followed by modest increases in TOX concentrations in a relatively longer term, corresponding to slower reaction with less reactive sites.
Chloramination of Humic Substances

A review of published material dealing with the chloramination chemistry, chloramination by-products, and chloramination treatment variables is presented in this section.

Chloramination Chemistry

Chloramine formation. In dilute aqueous solutions (1 to 50 mg/L), chlorine reacts with ammonia in a series of bimolecular reactions to form inorganic chloramines. Chlorine and monochloramine also react with nitrogen-containing organic compounds to form organic chloramines. Chloramines may hydrolyze back to liberate free chlorine (backward reaction in eq. 2-4). These reaction equations are shown as below:

\[
\begin{align*}
\text{HOCl} + \text{NH}_3 & \leftrightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad \text{(eq. 2-4)} \\
\text{HOCl} + \text{NH}_2\text{Cl} & \leftrightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad \text{(eq. 2-5)} \\
\text{HOCl} + \text{NHCl}_2 & \leftrightarrow \text{NCl}_3 + \text{H}_2\text{O} \quad \text{(eq. 2-6)} \\
\text{HOCl} + \text{R-NH}_2 & \leftrightarrow \text{R-NHCl} + \text{H}_2\text{O} \quad \text{(eq. 2-7)} \\
\text{NH}_2\text{Cl} + \text{R-NH}_2 & \leftrightarrow \text{R-NHCl} + \text{NH}_3 \quad \text{(eq. 2-8)} \\
\text{NH}_2\text{Cl} + \text{H}_2\text{O} & \leftrightarrow \text{HOCl} + \text{NH}_3 \quad \text{(eq. 2-9)}
\end{align*}
\]

The formation of these competing reactions is highly dependent upon pH, chlorine ammonia-nitrogen ratio, and to a lesser degree, temperature and contact time.

Inorganic chloramines. Usually monochloramine is the only chloramine that is observed at pH 8 or above when the molar ratio of free chlorine to ammonia is \( \leq 1 \) (\( \text{Cl}_2/\text{NH}_3-\text{N} \leq \))
5:1 by weight). As chlorine continues to be added to the solution at Cl₂/NH₃-N > 5:1, hypochlorous acid reacts with monochloramine to form dichloramine. The formation of trichloramine, or nitrogen trichloride, occurs predominantly at Cl₂/NH₃-N > 7.6:1 or at pH values lower than 4.4. At pH values of 7 to 9, the decomposition of trichloramine is directly dependent on the hydroxyl concentration. Therefore, in potable water systems, trichloramine usually occurs only in trace levels as a nuisance residual following break-point chlorination and rarely as a direct result of routine chloramine treatment operations (Kirmeyer et al., 1993).

Figure 2-1 presents a typical distribution of chloramine species as a function of pH when 2.5 mg/L chlorine is contacted with 0.5 mg/L ammonia-nitrogen (5:1 Cl₂/NH₃-N weight ratio) at 25° C for 2 hours. This figure shows that the relationship between monochloramine and dichloramine is by far the most significant for the pH ranges normally encountered in potable water treatment. As pH reaches 7.0 and greater, almost all of the combined chlorine consists of the monochloramine species; whereas at pH less than 6, the dichloramine species generally accounts for 20 percent or more of the chloramines formed.

Organic chloramines. Equations 2-7 and 2-8 describe the two mechanisms of organic chloramine formation.

The reaction of free chlorine with certain nitrogenous compounds (eq. 2-7) is complex and often occurs much faster than does the reaction of chlorine with ammonia (Wolfe et
Figure 2-1. Distribution of Chloramine Species with pH (2.5 mg/L Chlorine; 0.5 mg/L Ammonia-Nitrogen; Temperature 25°C; Contact Time 2 Hours).

Source:
al., 1985). Therefore, the presence of nitrogenous organic compounds can compete with the formation of inorganic monochloramine.

The active chlorine in chloramines may be transferred to nitrogenous compounds (eq. 2-8). Studies by Isaac and Morris (1980) showed that chlorine can be directly transferred from inorganic chloramines to amino acids and peptides. They observed that with equimolar concentration of NH2Cl (pH 7, 25°C) and several organic nitrogenous compounds, 50 percent of the NH2Cl was converted to organic chloramines in 0.2 to 1.4 days for clean water systems. However, the results of simulations (Yoon and Jensen, 1996) suggested that direct chlorination (eq. 2-7), rather than chlorine transfer (eq. 2-8), is the dominant mechanism of organic chloramine formation in drinking water systems.

**Break-point chlorination.** When break-point chlorination is practiced, the amount and type of residual changes according to the classic textbook curve shown in Figure 2-2. As the Cl2/NH3-N ratio increases, the ammonia molecule becomes progressively more chlorinated, i.e., NH3 → NH2Cl → NHCl2 → NCl3, through reaction equations 2-4, 2-5, and 2-6. With time, the nitrogen in the ammonia and the chlorine residual, primarily in the form of chloramines, are oxidized through a series of reactions that are not entirely understood to nitrogen-containing products, including nitrogen gas, nitrates, nitrous oxide (N2O), nitric oxide (NO), and other reaction end products.
Figure 2-2. Theoretical Breakpoint Chlorination Scheme (1 mg/L Ammonia-Nitrogen; pH 7; Temperature 25°C; Contact Time 2 Hours).

At a Cl₂/NH₃-N ratio of 7.6:1 (or a molar ratio of 3:2), all of the available ammonia is theoretically oxidized to nitrogen gas and other nitrogen-containing products, and combined chlorine residuals are greatly reduced or eliminated. A simplified equation for the overall nitrogen reaction is shown below:

\[ 3\text{Cl}_2 + 2\text{NH}_3 \leftrightarrow \text{N}_2 + 6\text{HCl} \]  

(eq. 2-10)

This phenomenon is known as break-point chlorination because at Cl₂/NH₃-N ratios ≥ 7.6:1, free chlorine is the predominant residual. The actual Cl₂/NH₃-N ratio for break-point for a given water source usually is greater than 7.6:1, depending on the levels of other substances present in the raw water. Once this point is reached, additional chlorine dosage results in an equal and proportional increase in free available chlorine residual, as presented in Figure 2-2.

Chloramination chemistry. DBP formation from chloramination may be interpreted as a special case of chlorination with very low chlorine doses. Cowman and Singer (1996) evaluated the HAA formation during chlorination and chloramination of aquatic humic substances. They assumed that HAA formation was occurring through the reaction of humic substances with small amounts of free chlorine in equilibrium with monochloramine. Such an explanation appeared to agree with the observed predominance
of mono- and dihalogenated HAA species over the trihalogenated forms in chloraminated waters.

**Chloramination By-products**

Presumably, many of the chlorinated DBPs will also be produced by chloramines because of the reasons stated below:

- The hydrolysis of chloramines to hypochlorous acid as in eq. 2-9. However, DBPs should occur in lower concentrations when chloramines are used in place of chlorine because of the low equilibrium concentrations of the hypochlorous acid (Jolley and Carpenter, 1983; Oxenford, 1996).

- The presence of free chlorine that has not yet reacted with ammonia to form chloramines (Arber et al., 1985; Water Quality Division Disinfection Committee, 1992). Pre-chlorination and post-ammoniation is a typical case to this situation.

- The transfer of the chlorine atom from NH₂Cl to the organic compound (Topudurti and Haas, 1991).

Therefore, chloramination is capable of producing the same DBPs as chlorination (Bull and Kopfler, 1991), as listed in Figure 1-1, but at lower levels.

However, of these DBPs, CNCl is believed to be increased to a greater extent when chloramine is used than when chlorine is used (Krasner et al., 1989). The ICR also requires an additional monitoring of CNCl for participating treatment plants using chloramines (USEPA, 1996).
Except CNCl, the rest of the DBPs could be reduced by as much as 80% compared with those produced by chlorination, depending on how the chloramines are formed and applied to the process water (Bull and Kopfler, 1991).

**Chlorination vs. chloramination for DBP surrogates.**

TOX is one of the most commonly reported surrogate parameters for chlorinated DBPs. It is clear that the use of chloramines in place of free chlorine, within the range of conditions most commonly seen in potable water treatment, generally results in lower TOX concentrations in treated water.

For example in natural water, Fleischacker and Randtke (1983) reported monochloramine produced considerably less NPOCl (12 μg Cl/mg TOC) than does free chlorine (130 μg Cl/mg TOC) in a groundwater. A pilot plant study at the Louisville, Kentucky, found that use of chloramines resulted in a mean TOX value 45% lower than the mean TOX value when chlorine was the disinfectant (AWWARF, 1986). The average instantaneous TOX concentration of a treated river water after 30-minute contact period was 117 μg/L when chloramines were used and 263 μg/L when chlorine was used, a relative reduction of about 55% (Lykins et al., 1986). Amy et al. (1990) reported the TOX reductions, between alternate chloramination and chlorination, ranging from 50% to 66% in two treatment plants using groundwaters from the Biscayne Aquifer.
In addition to natural waters, Fleischacker and Randtke (1983) reported combined chlorine, as opposed to free chlorine, produced NPOCl reductions of about 80%, 87%, and 83% for waters prepared from Aldrich humic acid, peat fulvic acid, and groundwater fulvic acid, respectively. Stevens et al. (1985, 1989a) found a NPOX reduction of 85% in a synthetic water prepared from Aldrich humic acid when chloramines were used in place of chlorine. Jensen et al. (1985) compared the reactions of monochloramine and chlorine with an aquatic fulvic acid precursor, and showed that monochloramine produced about one-seventh the TOX that chlorine did. In conclusion, chloramines in place of free chlorine produce lower levels of total chlorinated DBPs.

Based on the aforementioned discussion, chloramines produce lower but still significant quantities of TOX (or in terms of NPOX or NPOCl) relative to chlorine. Table 2-1 demonstrates that chloramines produce from 9 to 37% as much TOX (or in terms of NPOX or NPOCl) as chlorine under the same reaction conditions.

**Chlorination vs. chloramination for identifiable DBPs.** In addition to the 91 to 63% TOX reduction, chloramines are known to produce only very small amounts of identifiable DBPs. For example, less than 3% of the chloroform produced by chlorine was formed by chloramine at oxidant levels of \( \leq 20 \) mg/L (Fleischacker and Randtke, 1983). Stevens et al. (1985) reported that THM formation was reduced by 95% when chloramines were used. Cowman and Singer (1996) reported
<table>
<thead>
<tr>
<th>Substances</th>
<th>Conditions</th>
<th>Chloramine-Produced TOX/Cl₂-Produced TOX</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peat fulvic acid</td>
<td>Time = 100 hours</td>
<td>13*</td>
<td></td>
</tr>
<tr>
<td>Groundwater</td>
<td>Chlorine dosage = 20 mg/L</td>
<td>9*</td>
<td></td>
</tr>
<tr>
<td>Groundwater fulvic acid</td>
<td></td>
<td>17*</td>
<td></td>
</tr>
<tr>
<td>Secondary effluent</td>
<td></td>
<td>37*</td>
<td></td>
</tr>
<tr>
<td>Aquatic fulvic acid</td>
<td>pH = 9, TOC = 21 mg/L</td>
<td>13.7 (Cl₂ = 10.5 mg/L)</td>
<td>Jensen et al., 1985.</td>
</tr>
<tr>
<td></td>
<td>Time = 24 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Monochloramine dosage = 210 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Free chlorine dosage = 10.5 mg/L &amp; 102.9 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.3 (Cl₂ = 102.9 mg/L)</td>
<td></td>
</tr>
<tr>
<td>Aldrich humic acid</td>
<td>pH = 4.7 to 11.5, TOC = 5 mg/L</td>
<td>11 - 18</td>
<td>Stevens et al., 1985 &amp; 1989a.</td>
</tr>
<tr>
<td></td>
<td>Time = 144 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chloramine dosage = 22.9 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Free chlorine dosage = 20 mg/L</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* In terms of NPOCl
# In terms of NPOX
about 90 to 95% reductions of the total micromolar HAA formation when waters containing aquatic fulvic acids were disinfected with monochloramine as opposed to free chlorine. Because approximately one half of the compounds that make up TOX are not readily identified, treatment variations that reduce TOX levels do not always have the same effect on respective identifiable DBPs. Although the TOX parameter is a powerful monitoring tool, it is inherently a non-specific parameter that provides no indication of specific compounds. Therefore, more research is needed to identify the identifiable DBPs found in drinking water after chloramination. The literature review of the effects of chloramination on identifiable DBPs is compiled in the respective DBF sections.

**Chloramination Treatment Variables**

The formation of DBPs resulting from chloramination is influenced by the following treatment variables:

- Point of ammonia application.
- Mixing.
- Chloramine dosage.
- Chlorine:ammonia-nitrogen ratio.
- pH.
- Temperature.

The effects of each of the above variables on DBP formation are discussed below.
**Point of ammonia application.** The point of ammonia application to form chloramines in a treatment process can significantly affect DBP level. There are four basic ways to add chlorine and ammonia to form chloramines as described below:

- Pre-formed addition, where chlorine and ammonia are mixed together and then added to the water.
- Concurrent addition, where chlorine and ammonia are added very close to one another in the treatment process.
- Pre-ammoniation (or post-chlorination).
- Post-ammoniation (or pre-chlorination).

It is well established that contacting water with free chlorine results in considerably higher DBP levels than does contact with chloramines, and that DBP formation is time dependent. Therefore, reducing the free chlorine contact time prior to ammonia addition will help minimize DBP formation.

The pre-formed addition, although minimizing the free chlorine contact time, is not practiced in full-scale treatment plants (Kirmeyer et al., 1993); however, it has been used in laboratories (Jensen et al., 1985; Cowman and Singer, 1996) and pilot tests (Arber et al., 1985) which could provide true comparison between chlorination and chloramination.

**Mixing.** Mixing and reaction times for chloramine formation can impact the DBP formation by controlling the form and availability of the disinfecting species.
Rapid and complete mixing between ammonia and free chlorine minimizes the contact time free chlorine has with DBP precursors. Assuming complete mixing, at neutral pHs of 7 to 9 and temperatures of 20 to 25°C, the reaction of ammonia and free chlorine to form monochloramine takes from 0.07 to about 3 seconds, almost immediately eliminating the potential contact between free chlorine and DBP precursors (Kirmeyer et al., 1993).

**Chloramine dosage.** Fleischacker and Randtke (1983) reported that DBP formation relative to chloramine dosage is not a linear relationship. NPOCl formed rapidly at lower concentrations of monochloramine while NPOCl increased at a much slower rate at higher concentrations of chloramines. They also found that chloramine dosages of more than 20 mg/L in several raw waters with different precursor types did not result in additional increases in NPOCl formation. This phenomenon has been discussed in chlorination sections using active sites proposed by Luong et al. (1982).

Typically, chlorine and ammonia are not applied at dosages that produce a total chlorine residual of greater than 5 mg/L. Typical dosages of chloramine in drinking water treatment facilities range from 1.5 to 2.7 mg/L, and surveyed occurrence and median concentrations range from 0.1 to 5.5 and 1.1 to 1.8 mg/L, respectively (USEPA, 1994). Within the range of chloramine residuals, chloramine dosage does not appear to be a significant factor in DBP formation;
rather, it is the chlorine:ammonia-nitrogen ratio used that is more significant, as discussed below.

**Chlorine:ammonia-nitrogen ratio.** The Cl$_2$:NH$_3$-N ratio has been shown to directly influence the amount of DBP formed. Kirmeyer et al. (1993) found that Cl$_2$:NH$_3$-N mass ratios usually ranges from 3:1 to 5:1 in a survey on chloramination practices of 30 water utilities. Therefore, it may be anticipated that if Cl$_2$:NH$_3$-N mass ratios are optimized for the chloramine formation (3:1 to 5:1), DBP formation can be minimized. Arber et al. (1985) showed that THMs, DCAN, and TOX remained quite low before breakpoint (Cl$_2$:NH$_3$-N < 7.6:1), then increased dramatically above the 7.6:1 ratio. Furthermore, the amounts of THMs, DCAN, and TOX formed at far to the left of breakpoint (Cl$_2$:NH$_3$-N < 5:1, monochloramines predominate) were about half the amounts produced at just to the left of breakpoint (5:1 < Cl$_2$:NH$_3$-N < 7.6:1, dichloramines predominate).

**pH.** Fleischacker and Randtke (1983) showed that NPOCl formation increased sharply as the pH decreased when combined chlorine was used. This finding suggests that monochloramine is more reactive at lower pH, perhaps converting to dichloramine (Figure 2-1), or that monochloramine slowly and partially hydrolyzes to HOCl, which is then influenced by pH as discussed in chlorination sections. Stevens et al. (1989a) also reported that the concentration of NPOX formed at pH 7.5 was found to be about two-thirds of the NPOX concentration formed at pH 5.9 after
chloramination, regardless of the incubation time, whereas THM levels remained low and unchanged with increasing pH.

**Temperature.** Increasing temperatures increase the DBP formation during chloramination. Fleischacker and Randtke (1983) reported NPOCl formations of 82, 92, and 133 µg/L at temperatures of 3, 20, and 30°C, respectively, for water with a TOC of 3 mg/L chloraminated at pH 7.0 and contacted for 100 hours. The results of a pilot study practicing chloramination also indicated that TOX formation increased significantly as the temperature was increased from 7 to 25°C (AWWARF, 1986). The increasing organic halogen formation with increasing temperature has been previously discussed in chlorination sections.

The Chemistry of Humic Substances

Humic substances are the decay products of plants, animals, microorganisms, and their wastes. They are geomacromolecules whose structures are not well defined and, accordingly, cannot be described in unambiguous structural terms. As a result, humic substances must be defined operationally.

There are three major fractions of humic substances operationally defined in terms of their solubilities (Aiken et al., 1985):

- Humin: That fraction of humic substances that is not soluble in water at any pH value.
• Humic acid: That fraction of humic substances that is not soluble in water under acidic conditions (pH < 2), but becomes soluble at higher pH.

• Fulvic acid: That fraction of humic substances that is soluble in water under all pH conditions.

The gross chemical and physical properties of humic acid and fulvic acid are listed in Table 2-2 (Schnitzer and Khan, 1972). Two hypothetical chemical structures of humic acid and fulvic acid are shown in Figure 2-3 (Schnitzer and Khan, 1972; Stevenson, 1994).

It is now well established that the practice of chlorination in drinking water treatment produces numerous organic DBPs. Humic substances occurring naturally in water serve as major precursors for reaction with chlorine to produce a variety of DBPs, a large percentage of which are halogenated (Glaze et al., 1979; Christman et al., 1980; Christman et al., 1983; Miller and Uden, 1983; Seeger et al., 1985).

Humic materials have a wide range of molecular weights and sizes, ranging from a few hundred to as much as several hundred thousand daltons. Substantial evidence shows that humic substances consist of a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, ketone, and quinone groups. The structures of fulvic acids are somewhat more aliphatic and
Table 2-2. Physical and Chemical Properties of Humic and Fulvic Acids.

<table>
<thead>
<tr>
<th>Property</th>
<th>Humic Acids</th>
<th>Fulvic Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental composition (% by weight)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>50-60</td>
<td>40-50</td>
</tr>
<tr>
<td>H</td>
<td>4-6</td>
<td>4-6</td>
</tr>
<tr>
<td>O</td>
<td>30-35</td>
<td>44-50</td>
</tr>
<tr>
<td>N</td>
<td>2-4</td>
<td>&lt;1-3</td>
</tr>
<tr>
<td>S</td>
<td>1-2</td>
<td>0-2</td>
</tr>
<tr>
<td>Solubility in strong acid (pH=1)</td>
<td>Not soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>Molecular weight range</td>
<td>Few 100 → several million</td>
<td>180 → 10,000</td>
</tr>
<tr>
<td>Functional group distribution</td>
<td>Percent of oxygen in indicated functional group</td>
<td></td>
</tr>
<tr>
<td>carboxyl -COOH</td>
<td>14-45</td>
<td>58-65</td>
</tr>
<tr>
<td>phenol -OH</td>
<td>10-38</td>
<td>9-19</td>
</tr>
<tr>
<td>alcohol -OH</td>
<td>13-15</td>
<td>11-16</td>
</tr>
<tr>
<td>carbonyl -C=O</td>
<td>4-23</td>
<td>4-11</td>
</tr>
<tr>
<td>methoxyl -O-CH₃</td>
<td>1-5</td>
<td>1-2</td>
</tr>
</tbody>
</table>

Hypothetical structure of humic acid showing free and bound phenolic OH groups, quinone structures, oxygen as bridge units, and carboxyls variously placed on aromatic rings.

Type structure of fulvic acid showing the hydrogen bonds.

Figure 2-3. Two Hypothetical Chemical Structures of Humic Acid And Fulvic Acid.

References:

less aromatic than humic acids; and fulvic acids are richer in carboxylic acid, phenolic, and ketonic groups.

The Chemistry and Composition of Tea

The tea polyphenols or tea tannins, as they are called, bear some resemblance to humic substances in both color and structure, as discussed in the next section. Therefore, chlorine residual present in tap water may react with the tea polyphenols to form DBPs. The four national surveys of free chlorine residuals in drinking water compiled in the D/DBP Rule proposal (USEPA, 1994) showed that the occurrence of free chlorine residual in drinking water ranged up to 5.2 mg/L. Therefore it is very likely that reactions between free chlorine residual and tea polyphenols can take place during the preparation of instant tea, since un-boiled tap water is used in most occasions. Actually, a review paper on published information has shown that chlorine undergoes oxidation/substitution reactions with several model food compounds and forms by-products with potential toxicity (Fukayama et al., 1986).

Second only to water, tea is the most widely consumed beverage in the world today with annual per capita consumption exceeding 40 liters (International Tea Committee, 1990). There are three general types of tea produced: green (unfermented), oolong (partially fermented), and black (fully fermented). Instant tea, usually a powder, is generally prepared by the aqueous extraction of black tea
followed by concentration and drying. It is also possible to make instant tea from green tea; however, this kind is not common in the North America. Instant tea is manufactured in several countries, but production and consumption in the United States is greater than in the rest of the world (Kirk-Othmer Encyclopedia, 1983).

To the best of my knowledge, the studies on this topic that indicates the number and identity of all possible DBPs formed during the preparation of instant tea have not yet been identified previously. It was shown in our laboratory that instant (black) tea is a good precursor of THMs, HAAs, and other DBPs.

Chemistry of Tea. The outstanding chemical characteristic of tea flush is its very high concentration of polyphenolic material. Their approximate amounts in fresh leaf, green and black teas are in the range of 30-35%, 10-25%, and 8-21%, respectively (Lunder, 1992). The most important of polyphenols are a group of flavanols which usually constitutes 20-30% of the dry matter. The flavanols of tea belong to the group known as catechins (Kirk-Othmer Encyclopedia, 1983). In addition to flavanols, tea contains other polyphenols, caffeine, amino acids and others. A representative analysis of fresh leaf is given in Table 2-3a (Sanderson, 1972). The polyphenolic composition of tea is shown in Table 2-3b (Lunder, 1992).

The manufacturing process converts freshly harvested leaf to products of commerce. Black tea is the result of
Table 2-3. The Composition of Tea.
(a) Composition of Tea Flush.
(b) Polyphenolic Composition of Tea.
(c) Composition of Black Tea Leaves.

(a)

<table>
<thead>
<tr>
<th>Composition</th>
<th>% of Dry Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flavanols (Catechins)</td>
<td>17-30</td>
</tr>
<tr>
<td>Flavonols and Flavonol Glycosides</td>
<td>3-4</td>
</tr>
<tr>
<td>Leucoanthocyanins</td>
<td>2-3</td>
</tr>
<tr>
<td>Polyphenolic Acids and Depsides</td>
<td>~5</td>
</tr>
<tr>
<td>Total Polyphenols</td>
<td>~30</td>
</tr>
<tr>
<td>Caffeine</td>
<td>3-4</td>
</tr>
<tr>
<td>Amino Acids</td>
<td>~4</td>
</tr>
<tr>
<td>Simple Carbohydrates</td>
<td>~4</td>
</tr>
<tr>
<td>Organic Acids</td>
<td>~0.5</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>~13</td>
</tr>
<tr>
<td>Protein</td>
<td>~15</td>
</tr>
<tr>
<td>Ash</td>
<td>~5</td>
</tr>
<tr>
<td>Cellulose</td>
<td>~7</td>
</tr>
<tr>
<td>Lignin</td>
<td>~6</td>
</tr>
<tr>
<td>Lipids</td>
<td>~3</td>
</tr>
<tr>
<td>Pigments</td>
<td>~0.5</td>
</tr>
<tr>
<td>Volatiles</td>
<td>0.01-0.02</td>
</tr>
</tbody>
</table>


(b)

<table>
<thead>
<tr>
<th>Unprocessed Tea (Green Tea)</th>
<th>%W/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flavanols (Catechins)</td>
<td>17-30</td>
</tr>
<tr>
<td>Flavonols and Flavonol Glycosides</td>
<td>3-4</td>
</tr>
<tr>
<td>Phenolic Acids</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fermented Tea (Black Tea)</th>
<th>%W/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thearubigins</td>
<td>15-20</td>
</tr>
<tr>
<td>Theaflavins</td>
<td>1-2</td>
</tr>
<tr>
<td>Bisflavonols</td>
<td>2-4</td>
</tr>
<tr>
<td>Phenolic Acids</td>
<td>4</td>
</tr>
<tr>
<td>Unchanged Flavanols</td>
<td>1-3</td>
</tr>
<tr>
<td>Flavonols and Flavonol Glycosides</td>
<td>2-3</td>
</tr>
</tbody>
</table>

### Table 2-3. Continued.

(c)

<table>
<thead>
<tr>
<th>Composition</th>
<th>mg/g Dry Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td>4.0</td>
</tr>
<tr>
<td>Catechin</td>
<td>2.3</td>
</tr>
<tr>
<td>Epicatechin</td>
<td>4.1</td>
</tr>
<tr>
<td>Epicatechin Gallate</td>
<td>8.0</td>
</tr>
<tr>
<td>Epigallocatechin</td>
<td>10.5</td>
</tr>
<tr>
<td>Epigallocatechin Gallate</td>
<td>16.6</td>
</tr>
<tr>
<td>Flavonol Glycosides</td>
<td>0.5</td>
</tr>
<tr>
<td>Theaflavin</td>
<td>2.5</td>
</tr>
<tr>
<td>Theaflavin Gallate A</td>
<td>1.7</td>
</tr>
<tr>
<td>Theaflavin Gallate B</td>
<td>2.4</td>
</tr>
<tr>
<td>Theaflavin Digallate</td>
<td>2.5</td>
</tr>
<tr>
<td>Thearubigens</td>
<td>59.4</td>
</tr>
<tr>
<td>Protein</td>
<td>150</td>
</tr>
<tr>
<td>Fiber</td>
<td>300</td>
</tr>
<tr>
<td>Amino Acids</td>
<td>40</td>
</tr>
<tr>
<td>Ash</td>
<td>50</td>
</tr>
<tr>
<td>Carbohydrate</td>
<td>70</td>
</tr>
</tbody>
</table>

promoting the oxidation of fresh leaf catechins by atmospheric oxygen through catalysis by tea polyphenolase. The most significant change that occurs during the manufacture of black tea is the conversion of the colorless catechins to a complex mixture of orange-yellow to red-brown substances and the development of a large number of volatile compounds. During the formation of black tea, ca 15% of tea catechins remain unchanged and ca 10% are oxidized to theaflavin, theaflavic acid, and bisflavanol. About 75% of the catechins are converted to a complex, poorly defined, highly color, incompletely separated group of substances known as thearubigens whose molecular weight ranges from 700 to 40,000 (Kirk-Othmer Encyclopedia, 1983). The general composition of black tea leaves is presented in Table 2-3c (Balentine, 1992).

Figure 2-4 shows some typical structures of catechin, theaflavin, theaflavic acid, bisflavanol and thearubigen. Dihydroxybenzene moieties with two free meta-positioned OH-groups have been hypothesized to be responsible for the formation of chloroform (Rook, 1977; de Leer et al., 1985); therefore, all compounds in Figure 2-4 appear to be DBP precursors.

Disinfection By-products

Trihalomethanes

THMs are major DBPs of chlorination, and are also formed in lesser concentrations with chloramine. It has
Acid hydrolysis of thearubigen fractions results in the formation of cyanidin and delphinidin.

Figure 2-4. Some Typical Structures of the Polyphenols—Catechin, Theaflavin, Theaflavic Acid, Bisflavanol, and Thearubigen Found in Black Tea.

been noted in the 1970s that THMs can be formed from humic substances (Rook, 1974). THMs also can be formed from algae (Hoehn et al., 1980; Wardlaw et al., 1991), from polyhydroxyaromatics (tannins and lignins), proteins, aminoacids (Bruchet et al., 1990), or from certain model compounds such as resorcinol, and dihydroxybenzoic acids (Norwood et al., 1980; Rook, 1980).

**Occurrence and concentrations during chlorination and chloramination.** Symons et al. (1975) reported the results of the first national survey for the presence of THMs in 80 drinking waters with concentrations ranging from 0 to 482 µg/L. The American Water Works Association Research Foundation conducted a national survey of the THM concentrations in 727 utilities and showed that the range of THM concentrations was 0 to 360 µg/L with a median of 39 µg/L (McGuire and Meadow, 1988). Krasner et al. (1989) studied the occurrence of DBPs (including THMs) in 35 utilities across the United States; although the data were not given numerically, the median concentrations of THMs in those supplies were around 40 µg/L.

In addition to natural waters, the findings on THM formation from the chlorination/chloramination of humic substances can be found elsewhere. For example, chloroform was produced by either chlorination or chloramination of a groundwater fulvic acid (TOC = 3 mg/L), but less than 3% of the chloroform produced by chlorination was formed by chloramine at oxidant levels of ≤20 mg/L (Fleischacker and
Randtke, 1983). Stevens et al. (1985) also reported that THM formation was reduced by 95% when chloramines were used in stead of chlorine for a water containing 5 mg/L Aldrich humic acid.

**pH effects.** The increasing trend for THM formation with increasing pH has been well documented (Rook, 1976; Stevens et al., 1989a).

**Bromide ion concentration effects.** Luong et al. (1982) have demonstrated that bromine may favorably compete with chlorine in THM formation even when the chlorine concentration is high compared with the Br⁻ concentration. Several researchers (Minear et al., 1980; Luong et al., 1982; Symons et al., 1993) have observed a variation in the distribution of chlorinated and brominated THM species as a function of initial Br⁻ concentration when all other reaction conditions were held constant.

**Haloacetic Acids**

The most frequently identified DBPs, in addition to THMs, are HAAs. A national survey indicated that THMs were the by-products present in the highest concentrations in finished drinking water, with HAAs present at approximately 50% of the total THMs (Krasner et al., 1989). Similar to THMs, HAAs are formed in lesser concentrations with chloramine than free chlorine for either actual drinking water practice (Koch and Krasner, 1989) or aquatic humic substances (Cowman and Singer, 1996).
There are totally nine HAAs as shown in Figure 1-1. They are monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCBA).

Occurrence and concentrations during chlorination and chloramination. For instance in natural water, Uden and Miller (1983) identified DCAA and TCAA in two municipal tap waters. A survey of ten water supplies showed TCAA concentrations ranging from 4 to 54 μg/L (Norwood et al., 1985). Singer and Chang (1989) found that the ranges of TCAA and DCAA in six distribution systems were 15 to 103 μg/L and 8 to 79 μg/L, respectively. A study of the occurrence of DBPs in U.S. drinking waters presented HAA data in the form of quarterly median values for all supplies (practiced either chlorine, chloramine, chlorine dioxide, or ozone). The quarterly median ranges for MCAA, DCAA, TCAA, BCAA, and DBAA were <1.0 to 1.2 μg/L, 5.0 to 7.3 μg/L, 4.0 to 6.0 μg/L, <0.5 μg/L, 0.9 to 1.5 μg/L, respectively (Krasner et al., 1989). Stevens et al. (1990) reported, in their ten utility survey, that DCAA was found in all the utilities while MCAA and TCAA were also found, but in less frequency.

HAAs were also found in chlorinated solutions containing humic substances. Rook (1977) chlorinated a solution containing peat-derived humic acid and identified DCAA as one of the reaction products. Christman et al.
(1983) and Norwood et al. (1983) investigated the chlorination of aquatic humic material and reported MCAA, DCAA, and TCAA. Seeger et al. (1985) chlorinated solutions of three humic acids containing 5 to 6 mg TOC/L and an highly colored water from a south Florida lake that contained 28 mg TOC/L. MCAA, DCAA, and TCAA were found in all samples, while BCAA was identified only in the Florida lake water.

Formation of all nine HAAs has been reported by analysis of the chlorination of phenol in the presence of Br\(^-\) (Ireland et al., 1988). Pourmoghaddas et al. (1993) have also identified all nine HAAs as products of laboratory chlorination of a commercial humic acid in the presence of Br\(^-\). Cowman and Singer (1996) evaluated the influence of Br\(^-\) during the chlorination and chloramination of aquatic humic substances and identified all nine HAAs. They also reported the speciation changes and 90 to 95% reductions of the total micromolar HAA formation in chloraminated waters compared to chlorinated waters.

**pH effects.** Miller and Uden (1983) determined that the chlorination pH had only a small effect on the DCAA formation; however, TCAA concentrations were significantly lower when pH increased. Formation of DCAA was also found to be relatively independent of pH, while the amounts of TCAA formed at pH 5 and 7 were similar, but the amount produced at pH 9.4 was greatly reduced at any given reaction time (Stevens et al., 1989a).
Pourmoghaddas et al. (1993) assessed the roles of Br⁻ and pH in the HAA formation and showed a general trend of HAA decreases with increasing pH for all nine HAAs except DCAA and the un-quantified MCAA. Cowman and Singer (1996) showed that the sums of total nine HAA formation decreased with increasing pH from 6 to 8, in two chlorinated waters containing aquatic humic substances.

**Bromide ion concentration effects.** Krasner et al. (1989) studied 35 utilities, and demonstrated a change in HAA species distribution as a result of seasonal variation of Br⁻ concentration. Empirical equations for individual HAAs as functions of independent water quality variables including Br⁻ concentration were derived from databases which covered raw waters with diverse water quality characteristics, but no experiments were performed to examine the effects of varying the Br⁻ concentration on HAA formation (Montgomery Watson, 1993). Symons et al. (1994) reported shifts in the HAA species distribution as a result of alternative treatments of Lake Houston water with natural and spiked Br⁻, and Shukairy et al. (1994) reported ozone effects on HAA species distribution in chlorinated Ohio River water with variable Br⁻ concentration. However, TBAA, BDCAA, and DBCAA were not reported in these studies because stable standards could not be obtained.

Pourmoghaddas et al. (1993) evaluated the influence of Br⁻ on the formation and species distribution of HAAs under controlled conditions during chlorination of waters prepared
from Aldrich humic acid. Nine HAAs were found in their research, but MCAA could not be accurately quantified. Cowman and Singer (1996) evaluated the influence of Br during the chlorination and chloramination of humic substances extracted from natural waters with XAD-8 resin and identified all nine HAAs. Wu and Chadik (1997) chlorinated a Biscayne Aquifer water containing an ambient bromide ion and showed that the molar yield of HAAs increased as the initial bromide ion concentration increased. Concentrations of total HAAs, brominated, and mixed HAAs (BCAA, BDCAA, and DBCAA) increased substantially, while chlorinated HAAs decreased slightly, with the addition of bromide ion.

**Haloacetonitriles**

The presence of HANs in chlorinated water supplies consists of dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN), chlorobromoacetonitrile (BCAN), and trichloroacetonitrile (TCAN). There have been no reports of the occurrence of monochloroacetonitrile, monobromoacetonitrile, and tribromoacetonitrile in chlorinated drinking waters. According to two surveys (Oliver, 1983; Krasner et al., 1989), HANs represented about one tenth of the concentration of THMs found in drinking water samples.

**Occurrence and concentrations during chlorination and chloramination.** For instance in natural water, Trehy and
Bieber (1981) measured dihaloacetonitrile concentrations as great as 42 μg/L in a Florida water supply along with the brominated analogs, BCAN and DBAN. Oliver (1983) conducted an HAN survey in 10 Canadian water supplies and showed the ranges of DCAN and BCAN were from 0.3 to 8.1 and < 1.8 ppb, respectively. A study of the occurrence of DBPs (including HANS) in U.S. drinking waters has been reported by Krasner et al. (1989). The values reported for total HANs were the quarterly medians of 2.8, 2.5, 3.5, and 4.0 μg/L, respectively for four quarters. Reding et al. (1989) also investigated the occurrence of HANs in 29 U.S. drinking waters practicing free chlorine disinfection and showed that DCAN ranged from 0.2 to 24 μg/L; BCAN ranged from 0.2 to 10 μg/L; and DBAN ranged from 0.2 to 11 μg/L. Stevens et al. (1990) conducted a study of DBPs at 10 utilities. One or more dihaloacetonitriles were detected in the 10 waters investigated, and the concentrations were all reported as < 10 μg/L.

While TCAN has been reported to be present in low concentrations in several water systems (Keith et al., 1983), it has not been detected in the two systematic monitoring surveys (Koch and Krasner, 1989; Stevens et al., 1990). This is probably due to its significant rate of hydrolysis and the rate increases with increasing pH (Croue and Reckhow, 1989). Because most drinking waters in the United States are somewhat alkaline, TCAN is not likely to occur with any regularity. Krasner et al. (1989) reported
quarterly TCAN medians of < 0.029 µg/L in the 35 surveyed utilities.

HANs are also formed with chloramines, but at lower concentrations. Jacangelo et al. (1989) reported that the levels of HANs ranged from 30 to 16 µg/L when free chlorine was used in two utilities as opposed to 18 to about 1 µg/L at the two plants when chloramination was practiced.

In addition to natural waters, HANs were also found in chlorinated solutions containing humic substances. Oliver (1983) reported the formation of dihaloacetonitriles resulting from the chlorination of nitrogen containing aquatic fulvic acid and algae solutions. Coleman et al. (1984) investigated the chlorination DBPs of Fluka humic acid and Ohio River humic substance at the same chlorine and TOC concentrations. The formation of DCAN, TCAN, DBAN, and BCAN was observed. About 20 times more DCAN was produced upon chlorination of the Fluka humic acid than the Ohio River humic substance. They speculated that this may be due to a difference in the nitrogen content of the two humic substances (N, 0.7% for the Fluka humics; undetermined for the Ohio River humics).

**pH effects.** Similar to the base catalyzed hydrolysis of TCAN, dihaloacetonitriles (DCAN, BCAN, and DBAN) also undergo gradual hydrolysis with increasing pH. The hydrolysis rates were reported in the order DCAN > BCAN > DBAN by Bieber and Trehy (1983). Stevens et al. (1989a), in an Ohio River water chlorination experiment, showed that
DCAN formation was higher at pH 5; DCAN formed within 4 hours then decayed over time to < 5 μg/L at pH 7; DCAN hardly formed at pH 9.4. They proposed a formation-decay competing reaction based on the data at pH 7.

Bromide ion concentration effects. The effect of bromide ion concentration on the formation of HANs was investigated by Coleman et al. (1984). They found the degree of bromine incorporation into HANs appeared to be directly related to the amount of Br⁻ present during chlorination. Krasner et al. (1996) studied the impact of Br⁻ and DOC on HAN speciation, and showed that the impact was similar to that observed for THMs and HAAs. In addition, the sum of the HANs divided by the total THM level was fairly constant: a range of 6.1 to 9.8%, with an average of 7.4% and a standard deviation of 1.1%.

Chloral Hydrate

A number of haloaldehydes have been detected in chlorinated solutions containing humic substances, but the only one occurring in finished drinking waters with any regularity is trichloroacetaldehyde, which exists in water as chloral hydrate (Bull and Kopfler, 1991). CH was the fourth most abundant chlorinated by-products after THMs, HAAs, and HANs found in the 35 utilities based on quarterly median values (Krasner et al., 1989).

Occurrence and concentrations during chlorination and chloramination. For instance in natural water, Uden and
Miller (1983) investigated the occurrence of CH in chlorinated tap water of two utilities serving Amherst, MA. The CH concentrations of the two waters were reported as 7.2 and 11.9 μg/L, respectively. Jacangelo et al. (1989) investigated the effect of alternate disinfectants on the CH formation and reported that the CH levels were increased by preozonation and decreased by chloramination. A survey of the occurrence of DBPs (including CH) in 35 U.S. drinking waters has been reported by Krasner et al. (1989). The quarterly medians of CH concentrations for all supplies were reported as 1.8, 3.0, 2.2, and 1.7 μg/L, respectively. Stevens et al. (1990) conducted a study of DBPs at 10 utilities; and estimated CH concentrations of > 10 μg/L but < 100 μg/L in all of the surveyed waters.

In addition to natural waters, CH was also found in chlorinated solutions containing humic substances. Christman et al. (1983) identified CH in chlorinated solutions containing aquatic humic substances. Miller and Uden (1983) observed the CH presence in chlorinated fulvic acid solution and examined several parameters on its formation including pH which will be discussed in pH section. Kopfler et al. (1985) investigated the chlorination of Fluka humic acid and identified CH along with other chloroaldehydes.

**pH effects.** Miller and Uden (1983) chlorinated fulvic acid solutions and showed that CH concentration increased steadily from pH 4 to pH 7 at which point its concentration
decreased with increasing pH. They concluded that this drop in CH concentration at high pHs is due to its instability (decomposed to chloroform) in basic medium. Stevens et al. (1989a) chlorinated an Ohio River water and also showed that CH undergoes hydrolysis to chloroform at basic pHs. They concluded that the competing reactions of formation and hydrolysis make prediction of actual CH levels in distribution system difficult.

Bromide ion concentration effects. Xie and Reckhow (1992a) identified the presence of brominated trihaloacetaldehydes by GC/MS. They also reported increasing brominated trihaloacetaldehyde concentrations with increasing Br\(^-\) in pre-ozonated and post-chlorinated fulvic acid solutions.

Haloketones

HKs were the fifth most abundant chlorinated by-products after THMs, HAAs, HANs, and CH found in the 35 utilities based on quarterly median values (Krasner et al., 1989). The identification of HKs in chlorinated natural waters and humic acid solutions has revealed twenty different kinds of HKs present as compiled by Bull and Kopfler (1991). They also reported that even though a variety of C3-C5 chloroketone congeners and a trichlorocyclopentenedione may occur in water, only 1,1-dichloropropanone (DCPO) and 1,1,1-trichloropropanone (TCPO) exist in significant amounts in finished water. In
literature, DCPO and TCPO were sometimes called 1,1-
dichloroacetone and 1,1,1-trichloroacetone, respectively.

HKs, as target DBPs by themselves, are intermediates to
chloroform formation. Gurol et al. (1983) studied
chloroform formation from the base-catalyzed hydrolysis of
TCPO in the absence of chlorine. They found that in the
presence of chlorine, an additional pathway existed that
greatly increased the rate of chloroform production.
Reckhow and Singer (1985) also studied the role of TCPO as
an intermediate in the chloroform formation, and in one
experiment they estimated that 7.5% of the chloroform
produced passed through the TCPO intermediate.

Occurrence and concentrations during chlorination and
chloramination. For instance in natural water, Geiger et
al. (1976) reported the formation of TCPO and other HKs in
chlorinated Lake Zurich water. Suffet et al. (1976)
identified TCPO by GC/MS from the drinking water of two
river water supplies. Koch and Krasner (1989) reported the
total HK (DCPO and TCPO) concentrations ranged from 0.49 to
1.7 μg/L in waters of the Metropolitan Water District of
Southern California. A survey of the occurrence of DBPs
(including HKs) in U.S. drinking waters has been reported by
Krasner et al. (1989). The medians of sums of DCPO and TCPO
for all supplies were reported as 1.4, 0.94, 1.0, and 1.8
μg/L, respectively for four quarters. Stevens et al. (1990)
conducted a study of DBPs at 10 utilities; and TCPO occurred
in half of the surveyed utilities. The concentrations were
all reported at < 10 μg/L except one case the concentration was reported at 10 to 100 μg/L.

In addition to natural waters, HKs were also found in chlorinated solutions containing humic substances. Coleman et al. (1984) investigated the chlorination of Fluka humic acid and Ohio River humic substance. The formation of DCPO and TCPO was observed. TCPO was found to be the fourth abundant DBP formed after chloroform, DCAA, and TCAA in unbuffered humic acid solutions chlorinated at pH 7 (Meier et al., 1985). Legube et al. (1989) also found TCPO in chlorinated aquatic fulvic acid solutions.

**pH effects.** Coleman et al. (1984) reported that when humic acid was chlorinated at pH above 9.3, no chlorinated propanones were formed. Croue and Reckhow (1989) showed a significant decomposition rate of TCPO at pH 8.5. Stevens et al. (1989a) chlorinated an Ohio River water and showed that TCPO formation was higher at pH 5; < 2 μg/L at pH 7; and not detected at pH 9.4.

**Bromide ion concentration effects.** The effect of bromide ion concentration on the formation of HKs was investigated by Coleman et al. (1984). They reported the formation of 1,1-dibromo-1-chloro-2-propanone and 1,1,1-tribromo-2-propanone in the chlorinated Fluka humic acid solution in the presence of bromide ion.
Chloropicrin

CPN, with synonyms of trichloronitromethane, nitrotrichloromethane, and nitrochloroform, is frequently formed when waters are disinfected with chlorine. CPN is a strong irritant; therefore, it was used as a warfare gas.

CPN can be formed from nitrogenous organic compounds such as amino acids, from humic substances, or from certain non-nitrogenous organics such as phenol and resorcinol in the presence of nitrites as discussed below.

Occurrence and concentrations during chlorination and chloramination. For instance in natural water, Coleman et al. (1976) published one of the earliest reports of the presence of CPN in 3 of 5 chlorinated drinking water supplies with concentrations ranging from 0.4 to 3 µg/L. Duguet et al. (1985) also identified CPN formation in two water treatment plants that used various treatment processes including chlorination at some stage. The highest CPN concentration observed in one of the two plants with a high organic carbon content (8 to 14 mg/L) was 2.4 µg/L during sand filtration.

Hoigne and Bader (1988) found that chlorination of two lake waters with DOC of 1.5 mg/L and 4 mg/L produced about 0.4 and 2 µg/L CPN, respectively. Thibaud et al. (1988) investigated CPN formation of seven chlorinated surface waters. The range of concentrations was 1.9 to 3.3 µg/L, with both mean and median being 2.5 µg/L. They also demonstrated that the high-molecular-weight organic matter
(≥ 500 apparent molecular weight) in two waters produced an average of 90% of CPN formed.

A study of the occurrence of DBPs (including CPN) in U.S. drinking waters has been reported by Krasner et al. (1989). The values reported for CPN were the quarterly medians of 0.16, 0.12, 0.10, and 0.10 μg/L, respectively for four quarters. The levels of CPN observed in two chloraminated distribution systems were also given, ranging from 0.44 to 0.59 μg/L and 0.16 to 0.20 μg/L, respectively.

Reding et al. (1989) also investigated the occurrence of CPN in 29 U.S. drinking waters practicing free chlorine disinfection and showed occurrences of CPN correlated positively with THM occurrences. CPN was found in 25 of the 29 utilities ranging from <0.2 to 5.6 μg/L in treatment plants and <0.2 to 1.5 μg/L in distribution systems, respectively.

Stevens et al. (1990) conducted a study of DBPs at 10 utilities. CPN was detected in 8 of the 10 finished waters investigated, and the concentrations were all reported as <10 μg/L. Nieminski et al. (1993) studied 14 chlorinated drinking waters in Utah and found CPN only in trace amounts (<0.10 to 0.6 μg/L) compared to other DBPs.

In addition to natural waters, CPN was also found in chlorinated solutions containing amino acids and humic substances. Duguet et al. (1985) referred to a Japanese literature by Sayato et al. showing that CPN can be formed by the action of chlorine on amino acids. Duguet et al.
(1985) also investigated the formation of CPN resulting from the chlorination of nitrogen containing fulvic (N, 0.25%) and humic acid (N, 0.4%) solutions in the presence and absence of nitrite and nitrate ions. They found that the amount of CPN formed increased with the presence of nitrite (but not nitrate), which may indicate the need for a mineral source of nitrogen to form CPN. This effect was more pronounced for a fulvic acid solution than in a natural water. They determined that in the presence of nitrite about 1.8 μg of CPN was formed per mg carbon in Contech fulvic acid while only about 0.8 μg of CPN was formed per mg carbon in the Cholet natural water, both at contact time of 120 hours. They also chlorinated one natural water and one humic acid solution in the presence of ammonium to determine the effect of chloramination on CPN formation. The chlorinated natural water which contained 0.35 mg/L nitrite and 0.8 mg/L ammonium showed slight formation before break-point but marked increase after break-point. However, the chlorinated humic acid solution which contained 45 mg/L ammonium showed that the beginning of the appearance of CPN coincided with the start of the breakdown of monochloramine (Cl2/NH3-N mass ratio about 4) and CPN content remained low and tended to diminish after break-point, which may be due to the lack of nitrogen present in a usable form (i.e. nitrite).

The results by Thibaud et al. (1987) indicated that chlorination of some non-nitrogenous organic compounds such
as phenol and resorcinol in the presence of nitrites can lead to CPN formation; however, CPN was not detected during monochloramination using those two precursors in the presence of nitrites.

Thibaud et al. (1990) showed that chlorination of aquatic humic substances can lead to CPN formation. Moreover, the production of CPN, which varied from 0.2 to 0.7 µg/mg carbon, may be explained by the presence of functional nitrogen groups in the humic structures and by the presence of nitrogenous compounds (amino acids, proteins) associated with humic material.

**pH effects.** Duguet et al. (1985) reported that for humic acids that are good precursors at pH 11, their CPN formation at pH 7 seemed to require an appropriate mineral nitrogen form. Thibaud et al. (1987) showed that during chlorination of phenol in the presence of nitrite, CPN production increased with increasing pH, but resorcinol showed a reverse trend.

However, it was reported by Croue and Reckhow (1989) that CPN is subject to base-catalyzed hydrolysis. Furthermore, Krasner et al. (1990) studied the pH effects on stability of bromopicrin in aqueous solutions and showed that higher pH somewhat decreased bromopicrin concentrations in a holding study. They explained that bromopicrin may be similarly vulnerable to alkaline conditions.

**Bromide ion concentration effects.** The effect of bromide ion concentration on the formation of CPN was
investigated by Thibaud et al. (1988). They found the addition of bromide ion led to reduced yields of chloropicrin resulting from the chlorination of nitrophenols, aquatic fulvic acids, and two natural waters. However, the formation of brominated nitromethanes, which were found from nitrophenol precursors, were not detected in chlorinated natural waters nor in chlorinated fulvic acid solutions under their analytical conditions.

Krasner et al. (1990) studied a series of pilot tests that compared ozone and PEROXONE treatment with and without ammonium and bromide ion addition. When waters with ambient bromide ion levels (0.3 to 0.4 mg/L) was ozonated, bromopicrin was either not detected or was detected up to a maximum of 1 µg/L. When waters spiked with bromide ion up to a total of 1 mg/L was ozonated, bromopicrin was produced at a level of ≤ 2 µg/L.

Cyanogen Halides

CNCl and CNBr are the two commonly found cyanogen halides in drinking waters. There is some evidence suggesting that CNCl may be formed in greater amounts during chloramination than when free chlorine is utilized as discussed below.

Occurrence and concentrations during chlorination and chloramination. For instance in natural water, three water supplies in Japan found that CNCl was formed by the addition of hypochlorous acid in the presence of ammonium ion.
Furthermore, CNCl formation was at a maximum when the reaction mixture contained relatively high Cl₂/NH₃-N mass ratio (in the range of 8.0 to about 9.0), and the maximum yield of CNCl increased as increasing amounts of hypochlorous acid were added (Ohya and Kanno, 1985). Jacangelo et al. (1989) reported that the CNCl formation was influenced by the final disinfectant. Their data indicated that for those disinfection schemes that employed chloramines, CNCl levels were approximately 8 to 15 times greater than those that employed chlorine as a final disinfectant. Krasner et al. (1989), in a DBP survey of 35 water utilities, found the median value for CNCl at utilities that used only free chlorine was 0.4 µg/L in finished water, whereas those utilities that pre-chlorinated and post-ammoniated had a median CNCl value of 2.2 µg/L in finished water. They also reported a significant difference between the median CNCl concentration for all chloraminated waters (regardless of the order of chemical addition) of 1.6 µg/L and the median CNCl concentration for all chlorinated waters of 0.4 µg/L. Miltner et al. (1990) reported CNCl concentrations that ranged from 1.6 to 2.5 µg/L at utilities using chloramines whereas CNCl was not detected when free chlorine was the final disinfectant. In a study of ten utilities, Stevens et al. (1990) detected CNCl at only one utility; the only utility which was using chlorammines.

In addition to natural waters, CNCl and CNBr were found in an aquatic fulvic acid chloramination experiment (Xie and
The greater amounts of CNCl formed during chloramination of a humic acid at higher initial ammonium ion concentrations were also reported (Ohya and Kanno, 1985). Research in Japan showed that CNCl was sometimes formed in the presence of certain amino acids and hypochlorous acid. But CNCl was always formed in the presence of the amino acids tested when chloramine was used (Hirose et al., 1988).

However, the evidence suggesting that CNCl and CNBr form in greater amounts during chloramination than chlorination may be due to the low chemical stability of CNCl and CNBr to chlorine. A holding study showed that the half-life of CNCl in the presence of only 1 mg/L free chlorine residual at pH 7 is about 30-40 minutes, whereas in the absence of free chlorine the compounds are stable for hours (Xie and Reckhow, 1992b). Therefore, chlorination of the precursors could produce equal or more CNCl and CNBr, as opposed to chloramination. However, those cyanogen halides formed may be quickly destroyed by chlorine.

**pH effects.** Krasner et al. (1989) referred to a personal communication with Fair and stated that CNCl may degrade at high pH. In Fair's study of CNCl stability, reagent water was buffered at pH values of 5, 7, and 9. CNCl broke down immediately at pH 9 and it broke down after three days at the other pH levels. Furthermore, CNCl in unbuffered reagent water was stable, implying that buffers may have caused the degradation in addition to high pH.
The stability of CNCl has also been discussed by Bailey and Bishop (1973a, 1973b) and Xie and Reckhow (1992b). They concluded that high pH as well as the presence of sulfite and free chlorine cause degradation of CNCl.

**Bromide ion concentration effects.** The effect of bromide ion concentration on the formation of CNBr was investigated by chloraminating a series of fulvic acid solutions containing varying amounts of bromide ion (Xie and Reckhow, 1993). Under the conditions of this study, a shift from CNCl formation to CNBr formation was reported. Furthermore, the molar sum of the two cyanogen halides appeared to be little changed over the bromide ion ranges from 0 to 2 mg/L.

**The effects of application points of chlorine and ammonia on CNCl formation.** In a study by J.M. Montgomery (1991), lower CNCl values were recorded in bench-scale studies (0.2 µg/L to 0.3 µg/L) using concurrent addition of chlorine and ammonia than at a full-scale treatment plant using pre-chlorination and post-ammoniation (1 µg/L to 5 µg/L). The researchers postulated that a strong pre-oxidant (i.e., chlorine or ozone) used to form the appropriate precursor may be necessary for CNCl formation. Krasner et al. (1991) also reported that higher pre-chlorination times of 15 and 60 minutes prior to ammonia addition produced more CNCl than lower pre-chlorination times of ≤ 5 minutes prior to ammonia addition. They concluded that pre-chlorination may result in higher overall CNCl production if the
initially produced CNCl can be stabilized by post-ammoniation.

Some drawbacks of commercial CNCl standards. CNCl is highly toxic and very volatile (boiling point: 13.1°C). In addition to its hazardous nature, CNCl is also expensive; recent quotes for a lecture bottle of gaseous CNCl were $2200/0.7 lb and $700/0.5 lb from two companies.

Existing protocols for preparing stock standards of CNCl from a gaseous source call for absorbing 10 to 50 cc of CNCl gas into 10 ml of methanol and determining the mass transferred gravimetrically (Flesch and Fair, 1989; Xie and Reckhow, 1993). Although no sophisticated instrumentation is needed for this procedure, great care must be taken to ensure quantitative transfer and no gas leakage. CNCl standards with concentrations ranging from 100 μg/mL to 2000 μg/mL can also be purchased in a methanol solution with a shelf life of three months from the production date (Wu et al., 1997). However, Flesch and Fair (1989) found that the stock CNCl standards in methanol with similar concentrations prepared in their laboratory had a useful life of only five weeks. In addition, since no externally prepared verifiable standard is available for CNCl, the same standards that have been used for calibration have also been used as quality control standards (Flesch and Fair, 1989). The aforementioned commercial standards in a methanol solution are not true externally prepared standards because they are prepared from commercial CNCl gas (Wu et al., 1997).
In light of the hazardous nature and high cost of aqueous CNCl preparation from gas standards and the limited shelf life of prepared standards in a methanol solution, an alternative method of in situ synthesis of CNCl was developed as part of this dissertation research to provide a safe and economical aqueous CNCl standard.

The Effects of Structural Characteristics of Humic Substances on DBP Formation

The concentration of DBPs formed during chlorination and chloramination has been correlated with various non-specific parameters such as raw water DOC, color, UV absorbance, chlorine demand, and so on. These parameters, which mainly reflect the concentration of natural organic matter, do not precisely take into account the various compositions of humic substance matrix.

The nature and extent of interaction between humic substances and disinfectant species depend on numerous structural factors. For example, some disinfectants (chlorine for instance) are electrophiles and tend to react with electron-rich sites in organic structures of humic substances. Therefore, the structural characteristics of humic substances play an important role in determining the amounts and species of DBPs formed.

The literature review on the relationship between certain structural characteristics of humic substances and DBP formation is therefore focused on: (1) the review of the characterization of the humic substances studied in this
research by a variety of chemical techniques; (2) the relationship between the source of aquatic humic substances and their corresponding soil and sediment humic substances; and (3) the examination of the relationship between structural characteristics of humic substances and DBP formation.

Characterization of Humic Substances

Seven humic substances with a wide range of structure and composition were studied in this research. A variety of different humic sources isolated from water, soil, and sediment were chosen to increase the variation in reaction between disinfectants and measured compositional characteristics. The humic substances were characterized in a former study (Davis, 1993) and were used in this study to investigate whether their structural composition could be used to predict their reaction with disinfectants. The investigation of the structural characteristics of the humic substances used in this research was carried out using the following analytical techniques by Davis (1993):

- Elemental Analysis
- Ultraviolet/Visible (UV/VIS) Spectroscopy
- Total Acidity Titration
- Infrared (IR) Spectroscopy
- $^{13}$C Nuclear Magnetic Resonance ($^{13}$C-NMR) Spectroscopy

The collection, isolation, and characterization of the humic substances as well as their QA/QC measures were discussed in more detail by Davis (1993).
Elemental analysis. Elemental analyses of C, H, and N were carried out by catalytic combustion of the samples in an oxidizing atmosphere followed by separation and quantification of the resulting CO₂, H₂O and N₂. The oxygen content was determined by difference (from 100%) based on the C, H, and N content, after these values had been corrected for moisture and ash content. The moisture and ash content of each humic substance were measured by drying and ignition, respectively.

The results of these analyses presented in Table 2-4 show little variation of elemental compositions for the humic substances investigated; except that the nitrogen composition of the Newnans Lake sediment was substantially higher (2.51%) than the nitrogen composition of other humic substances in this study, perhaps reflecting the eutrophic nature of this lake.

UV/VIS spectroscopy. Absorbance measurements were recorded at 254 (UV254), 272 (UV272), 465 (VIS465), and 665 (VIS665) nm for all humic substances investigated. Solutions were prepared by dissolving each humic substance in 10 mL of 0.01 M NaCl, then adjusted to pH 7. Measurements were performed using 1.0 cm cells with 0.01 M NaCl, pH 7 as a reference. The results are presented in Table 2-5.

The ratio of absorbances at 465 and 665 nm (E₄/E₆) of a given humic substance has been correlated with some structural properties for different humic substances. The
Table 2-4. The Elemental Analysis and Composition of the Humic Substances* and Instant Tea Samples Studied in This Research.

Moisture, ash, and elemental analyses are expressed as percent by weight. Elemental composition, expressed in moles, appears in parentheses.

<table>
<thead>
<tr>
<th>Source</th>
<th>Moisture</th>
<th>Ash%</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O‡</th>
<th>H/C~</th>
<th>H/O~</th>
<th>O/C~</th>
<th>N/C~ (x10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich Humic Acid</td>
<td>2.06</td>
<td>1.50</td>
<td>50.83</td>
<td>3.57</td>
<td>0.60</td>
<td>45.00</td>
<td>0.84</td>
<td>1.27</td>
<td>0.66</td>
<td>0.10</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>0.81</td>
<td>15.6</td>
<td>42.34</td>
<td>4.76</td>
<td>2.51</td>
<td>50.39</td>
<td>1.35</td>
<td>1.51</td>
<td>0.89</td>
<td>0.51</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>2.60</td>
<td>12.6</td>
<td>47.67</td>
<td>4.41</td>
<td>0.74</td>
<td>47.19</td>
<td>1.11</td>
<td>1.49</td>
<td>0.74</td>
<td>0.13</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>1.65</td>
<td>1.15</td>
<td>49.41</td>
<td>3.69</td>
<td>0.77</td>
<td>46.13</td>
<td>0.90</td>
<td>1.28</td>
<td>0.70</td>
<td>0.13</td>
</tr>
<tr>
<td>St. Marys River</td>
<td>0.62</td>
<td>0.43</td>
<td>51.17</td>
<td>3.82</td>
<td>0.61</td>
<td>44.41</td>
<td>0.90</td>
<td>1.38</td>
<td>0.65</td>
<td>0.10</td>
</tr>
<tr>
<td>Orange Heights GWS</td>
<td>1.20</td>
<td>2.35</td>
<td>50.48</td>
<td>4.10</td>
<td>0.49</td>
<td>44.93</td>
<td>0.97</td>
<td>1.46</td>
<td>0.67</td>
<td>0.08</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>0.28</td>
<td>6.62</td>
<td>50.23</td>
<td>4.60</td>
<td>0.79</td>
<td>44.38</td>
<td>1.10</td>
<td>1.66</td>
<td>0.66</td>
<td>0.13</td>
</tr>
<tr>
<td>Lipton Tea</td>
<td>8.21</td>
<td>31.5</td>
<td>54.22</td>
<td>6.34</td>
<td>2.29</td>
<td>37.15</td>
<td>1.40</td>
<td>2.73</td>
<td>0.51</td>
<td>0.36</td>
</tr>
<tr>
<td>Nestlé Tea</td>
<td>8.56</td>
<td>17.7</td>
<td>57.84</td>
<td>6.81</td>
<td>4.56</td>
<td>30.79</td>
<td>1.41</td>
<td>3.54</td>
<td>0.40</td>
<td>0.68</td>
</tr>
</tbody>
</table>

* By Davis (1993).
# Elemental analyses are corrected for moisture and ash content.
† Represents approximate inorganic content.
‡ Calculated by difference.
§ Groundwater.
~ Molar ratios.
Table 2-5. Ultraviolet and Visible Spectral Analysis Results of the Humic Substances* Studied in This Research.

<table>
<thead>
<tr>
<th>Source</th>
<th>Absorptivity L/(g Humic Carbon·cm)</th>
<th>E4/E6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>254 nm</td>
<td>272 nm</td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>74.72</td>
<td>67.76</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>35.57</td>
<td>31.79</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>63.29</td>
<td>55.59</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>46.53</td>
<td>39.90</td>
</tr>
<tr>
<td>St. Marys River</td>
<td>53.12</td>
<td>46.48</td>
</tr>
<tr>
<td>Orange Heights GW§</td>
<td>47.49</td>
<td>40.80</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>46.21</td>
<td>39.95</td>
</tr>
</tbody>
</table>

* By Davis (1993).
§ Groundwater.
ratios of E4/E6 have been investigated extensively for soil humic substances (Schnitzer and Khan, 1972; Chen et al., 1977) and for aquatic humic substances (Thurman, 1985a). The ratio varies for humic substances extracted from different sources (Schnitzer and Khan, 1972). The ratio has been reported to be in the range of 2 to 5 for soil humic acids, 8 to 10 for soil fulvic acids, and ~5 to 22 for aquatic fulvic acids (Thurman, 1985a).

Based on the E4/E6 ratios in Table 2-5 and the aforementioned criteria, the commercial, soil, and sediment humic substances are predominately humic acids, and the four aquatic humic substances are predominately fulvic acids. It has been reported that extractable humic substances from soil are predominately humic acids (Stevenson, 1994), and aquatic humic substances generally consist of 85% or higher fulvic acids in rivers, streams, lakes, and groundwater (Thurman, 1985a).

**Total acidity titration.** The Ba(OH)_2 titration method was used to measure the total acidity. The humic substance was allowed to equilibrate for 24 hours with Ba(OH)_2 solution under a nitrogen atmosphere. During this period, the humic substance containing acidic functional groups reacted with the Ba^{++} ions and precipitated. The sample was then filtered to remove the precipitate, and the resulting filtrate was titrated with HCl to a pH of 8.4. The total acidity of the humic substance was calculated by difference
based on the initial Ba(OH)$_2$ concentration and the equivalents of Ba(OH)$_2$ remaining in the filtrate.

The results of total acidity of the humic substances are presented in Table 2-6. The acidic nature of humic substances has been attributed to both COOH and acidic OH groups (presumed to be phenolic OH), with COOH being the most important (Stevenson, 1985). Aquatic humic substances generally contain more acidic functional groups than soil derived humic substances (Schnitzer and Khan, 1972; Thurman, 1985a). However, the commercial, soil and sediment humic substances shown in Table 2-6 appear to contain amounts of COOH and acidic OH groups in close proximity to the aquatic humic substances.

Infrared spectroscopy. IR spectra of humic substances are the result of the absorption of IR radiation by a complex mixture of molecules; therefore, the resulting IR spectra contain a variety of bands which are indicative of the different functional groups. The quantitative IR measurements in this research used an internal standard, KSCN, to compensate for the variation in sample preparation and instrumental operation between different samples. The internal standard approach allows a direct quantitative comparison of specific functional group compositions among the different humic substances.

The IR spectroscopy was carried out by the cast film technique (Davis, 1993). It involves applying a solution of the humic sample containing a fixed amount of KSCN to an IR
Table 2-6. Total Acidity Analysis Results of the Humic Substances* Studied in This Research.

<table>
<thead>
<tr>
<th>Source</th>
<th>meq H⁺/g Humic #</th>
<th>meq H⁺/g Humic C §</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich Humic Acid</td>
<td>7.37</td>
<td>14.50</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>8.42</td>
<td>19.88</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>8.90</td>
<td>18.66</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>8.40</td>
<td>17.00</td>
</tr>
<tr>
<td>St. Marys River</td>
<td>9.24</td>
<td>18.06</td>
</tr>
<tr>
<td>Orange Heights GW§</td>
<td>7.83</td>
<td>15.50</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>7.61</td>
<td>15.15</td>
</tr>
</tbody>
</table>

* By Davis (1993).
# Normalized to the mass of the humic substance.
§ Normalized to the carbon mass of the humic substance.
$ Groundwater.
transparent plate followed by evaporation of the solvent to dryness. The IR spectrum was recorded from the dried deposit in an evacuated sample chamber of an IR spectrometer.

The IR spectral adsorption band frequency ranges for functional group components of humic substances are presented in Table 2-7. The IR data of the humic substances obtained at pH 4 and pH 11 are shown in Table 2-8. There are fewer peaks in the IR spectra recorded at pH 11 than at pH 4, because at elevated pH the peak for -COOH shifts to a lower frequency that combines with peaks of other functional groups (Davis, 1993). The normalized peak heights of the humic substances investigated in this study indicate that there were significant differences in their structure and composition. A discussion of assigning absorption bands to respective functional groups will be presented later.

13C-NMR spectroscopy. NMR spectroscopy, like other spectroscopic techniques, is dependent on the interaction of electromagnetic radiation with nuclear, atomic, or molecular species (Wershaw, 1985). The nucleus in an atom is partially shielded by its electrons from interaction with the externally applied magnetic field. The shielding in an organic compound is a function of the chemical environment in the vicinity of the nucleus. In other words, different functional groups in organic molecules have different electronic distributions, thus, causing their nuclei to resonate at characteristic frequencies. The displacement of the resonance frequency of a particular nucleus in a

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400-3200</td>
<td>O-H stretch from COOH and COH</td>
</tr>
<tr>
<td>3100-2800</td>
<td>C-H stretch from CH, CH₂, and CH₃</td>
</tr>
<tr>
<td>2700-2400</td>
<td>O-H stretch from strongly H-bonded COOH</td>
</tr>
<tr>
<td>1700</td>
<td>C=O stretch from COOH</td>
</tr>
<tr>
<td>1650-1600</td>
<td>aromatic C=C vibration; C=O stretch from H-bonded conjugated ketones; and COO⁻ asymmetric stretch</td>
</tr>
<tr>
<td>1400</td>
<td>OH and C-O deformation from alcoholic and phenolic OH; and COO⁻ symmetric stretch</td>
</tr>
<tr>
<td>1220-1200</td>
<td>C-O stretch and OH bending from COOH</td>
</tr>
<tr>
<td>1050-1020</td>
<td>C-O stretch of poly-saccharides; and Si-O stretch from silicate impurities</td>
</tr>
<tr>
<td>925</td>
<td>O-H bend; carboxylic acid dimers</td>
</tr>
</tbody>
</table>
Table 2-8. The Mean Infrared Absorption Peaks Ratios of the Humic Substances* to KSCN
(Based on the Average of 100 Repetitive Scans) Studied in This Research.
(a) Normalized to the Humic Substance Mass (mg KSCN/mg humic).
(b) Normalized to the Humic Substance Carbon Mass (mg KSCN/mg humic C).

<table>
<thead>
<tr>
<th>Source</th>
<th>pH 4</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3400-3200</td>
<td>3000-2900</td>
<td>2900-2800</td>
<td>2700-2400</td>
<td>1700</td>
<td>1650-1600</td>
<td>1400</td>
<td>1220-1200</td>
<td>1050-1000</td>
<td>925</td>
<td></td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>0.223</td>
<td>0.267</td>
<td>0.246</td>
<td>0.148</td>
<td>0.710</td>
<td>0.520</td>
<td>0.237</td>
<td>0.589</td>
<td>0.522</td>
<td>0.399</td>
<td></td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>0.329</td>
<td>0.334</td>
<td>0.389</td>
<td>0.218</td>
<td>0.888</td>
<td>0.372</td>
<td>0.298</td>
<td>0.603</td>
<td>0.663</td>
<td>0.439</td>
<td></td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>0.163</td>
<td>0.152</td>
<td>0.155</td>
<td>0.103</td>
<td>0.430</td>
<td>0.284</td>
<td>0.231</td>
<td>0.224</td>
<td>0.241</td>
<td>0.188</td>
<td></td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>0.169</td>
<td>0.203</td>
<td>0.219</td>
<td>0.125</td>
<td>0.685</td>
<td>0.300</td>
<td>0.295</td>
<td>0.415</td>
<td>0.384</td>
<td>0.258</td>
<td></td>
</tr>
<tr>
<td>St. Marys River</td>
<td>0.127</td>
<td>0.150</td>
<td>0.163</td>
<td>0.128</td>
<td>0.510</td>
<td>0.293</td>
<td>0.258</td>
<td>0.315</td>
<td>0.289</td>
<td>0.219</td>
<td></td>
</tr>
<tr>
<td>Orange Heights GW$</td>
<td>0.158</td>
<td>0.166</td>
<td>0.148</td>
<td>0.113</td>
<td>0.448</td>
<td>0.289</td>
<td>0.238</td>
<td>0.282</td>
<td>0.218</td>
<td>0.197</td>
<td></td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>0.182</td>
<td>0.247</td>
<td>0.233</td>
<td>0.145</td>
<td>0.709</td>
<td>0.238</td>
<td>0.261</td>
<td>0.360</td>
<td>0.373</td>
<td>0.292</td>
<td></td>
</tr>
<tr>
<td>pH 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>0.197</td>
<td>0.168</td>
<td>0.142</td>
<td>nd</td>
<td>nd</td>
<td>0.741</td>
<td>0.873</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>0.118</td>
<td>0.177</td>
<td>0.145</td>
<td>nd</td>
<td>nd</td>
<td>0.457</td>
<td>0.471</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>0.111</td>
<td>0.069</td>
<td>0.048</td>
<td>nd</td>
<td>nd</td>
<td>0.554</td>
<td>0.397</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>0.151</td>
<td>0.113</td>
<td>0.091</td>
<td>nd</td>
<td>nd</td>
<td>0.553</td>
<td>0.570</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>St. Marys River</td>
<td>0.123</td>
<td>0.128</td>
<td>0.115</td>
<td>nd</td>
<td>nd</td>
<td>0.672</td>
<td>0.565</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Orange Heights GW$</td>
<td>0.171</td>
<td>0.153</td>
<td>0.128</td>
<td>nd</td>
<td>nd</td>
<td>0.710</td>
<td>0.594</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>0.147</td>
<td>0.155</td>
<td>0.139</td>
<td>nd</td>
<td>nd</td>
<td>0.595</td>
<td>0.465</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
</tbody>
</table>

* By Davis (1993).
$ Groundwater.
Table 2-8. Continued.

(b)

<table>
<thead>
<tr>
<th>Source</th>
<th>3400-3200</th>
<th>3000-2900</th>
<th>2900-2800</th>
<th>2700-2400</th>
<th>1400</th>
<th>1650-1600</th>
<th>1400</th>
<th>1220-1200</th>
<th>1050-1000</th>
<th>925</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>0.439</td>
<td>0.526</td>
<td>0.483</td>
<td>0.291</td>
<td>1.398</td>
<td>1.023</td>
<td>0.467</td>
<td>1.160</td>
<td>1.027</td>
<td>0.785</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>0.779</td>
<td>0.790</td>
<td>0.919</td>
<td>0.516</td>
<td>2.099</td>
<td>0.879</td>
<td>0.704</td>
<td>1.424</td>
<td>1.567</td>
<td>1.039</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>0.341</td>
<td>0.319</td>
<td>0.325</td>
<td>0.215</td>
<td>0.902</td>
<td>0.595</td>
<td>0.484</td>
<td>0.469</td>
<td>0.505</td>
<td>0.395</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>0.342</td>
<td>0.411</td>
<td>0.443</td>
<td>0.252</td>
<td>1.386</td>
<td>0.608</td>
<td>0.597</td>
<td>0.840</td>
<td>0.777</td>
<td>0.522</td>
</tr>
<tr>
<td>St. Marys River</td>
<td>0.247</td>
<td>0.292</td>
<td>0.319</td>
<td>0.250</td>
<td>0.996</td>
<td>0.571</td>
<td>0.504</td>
<td>0.615</td>
<td>0.564</td>
<td>0.429</td>
</tr>
<tr>
<td>Orange Heights GWS</td>
<td>0.313</td>
<td>0.328</td>
<td>0.293</td>
<td>0.224</td>
<td>0.886</td>
<td>0.572</td>
<td>0.472</td>
<td>0.559</td>
<td>0.432</td>
<td>0.391</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>0.362</td>
<td>0.492</td>
<td>0.464</td>
<td>0.288</td>
<td>1.411</td>
<td>0.474</td>
<td>0.520</td>
<td>0.716</td>
<td>0.743</td>
<td>0.581</td>
</tr>
<tr>
<td>pH 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>0.394</td>
<td>0.335</td>
<td>0.284</td>
<td>nd</td>
<td>nd</td>
<td>1.481</td>
<td>1.744</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>0.332</td>
<td>0.407</td>
<td>0.407</td>
<td>nd</td>
<td>nd</td>
<td>1.280</td>
<td>1.321</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>0.267</td>
<td>0.145</td>
<td>0.114</td>
<td>nd</td>
<td>nd</td>
<td>1.328</td>
<td>0.952</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>0.310</td>
<td>0.231</td>
<td>0.187</td>
<td>nd</td>
<td>nd</td>
<td>1.133</td>
<td>1.168</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>St. Marys River</td>
<td>0.241</td>
<td>0.251</td>
<td>0.225</td>
<td>nd</td>
<td>nd</td>
<td>1.318</td>
<td>1.107</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Orange Heights GWS</td>
<td>0.346</td>
<td>0.310</td>
<td>0.259</td>
<td>nd</td>
<td>nd</td>
<td>1.439</td>
<td>1.205</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>0.314</td>
<td>0.330</td>
<td>0.297</td>
<td>nd</td>
<td>nd</td>
<td>1.269</td>
<td>0.992</td>
<td>nd</td>
<td>nd</td>
<td></td>
</tr>
</tbody>
</table>

* By Davis (1993).
$ Groundwater.
molecule from the position for the unshielded atom is referred to as the chemical shift. Chemical shift frequencies are generally reported relative to a standard (often tetramethylsilane, TMS), and are usually reported in ppm (Wershaw, 1985).

Solid state $^{13}$C NMR spectroscopy was used for functional group analysis of the humic substances studied in this research (Davis, 1993). Due to limited access to the NMR spectrometer, only a portion of the total number of humic substances were analyzed using this method (Davis, 1993). An internal standard (Delrin) $^{13}$C NMR technique, similar to the internal standard method described earlier for the IR analyses, was practiced to quantify the $^{13}$C response based on per unit carbon. The data obtained from the $^{13}$C NMR analysis shown in Table 2-9 indicate differences in the composition of the humic substances investigated. The assignments of the chemical shift regions in the NMR spectra to different functional groups are consistent with those reported in the literature (Harrington et al., 1996).

Aquatic Versus Corresponding Soil and Sediment Humic Substances

Interest in the role of humic substances on DBP formation is naturally confined to aquatic humic substances. However, the objective of this research was to investigate how characteristics of humic substances can be relate to DBP formation. Therefore, in addition to the aquatic humic substances, the characterized commercial (from Aldrich) and
Table 2-9. Functional Group Percent Composition of the Humic Substances Studied in This Research as Determined by $^{13}$C NMR.

<table>
<thead>
<tr>
<th>Source</th>
<th>Functional Group (PPM)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich Humic Acid</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Orange Heights Soil*</td>
<td>48.6</td>
<td>20.6</td>
<td>5.4</td>
<td>21.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Santa Fe River*</td>
<td>53.6</td>
<td>15.5</td>
<td>3.9</td>
<td>18.1</td>
<td>7.2</td>
</tr>
<tr>
<td>St. Marys River*</td>
<td>48.9</td>
<td>18.0</td>
<td>5.2</td>
<td>18.6</td>
<td>8.7</td>
</tr>
<tr>
<td>Orange Heights GWS*</td>
<td>53.3</td>
<td>15.7</td>
<td>4.3</td>
<td>16.5</td>
<td>8.4</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* By Davis (1993). Chemical shift ranges were re-integrated to be consistent with Harrington et al. (1996).
§ Groundwater.
Orange Heights soil as well as Newnans Lake sediment humic substances were included in this research.

Confidence in the use of the readily available commercial humic substance in DBP formation tests was based on a comparative study and on research found in the literature using commercial humic substances. Seeger et al. (1985) reported, in a comparative study using GC/MS, "Few differences in the types of compounds formed from the chlorination of the different sources of humic acids" from four different sources (Aldrich, Fluka, Black Lake, and an unconcentrated highly colored Florida lake water). Numerous studies using commercial humic substances were also performed elsewhere (Fleischacker and Randtke, 1983; Coleman et al., 1984; Stevens et al., 1985, 1989a, 1989b; Pourmoghaddas et al., 1993).

Although Seeger et al. (1985) have come to the conclusion that no major differences were found in the types of by-products produced with the different sources of humic substances used, they did not attempt to quantitate the compounds produced from the different sources.

The soil and sediment humic substances were included in this research because they are likely partial sources of their corresponding aquatic humic substances as discussed below:

Sources of aquatic humic substances. Allochthonous source means organic carbon from land or outside the aquatic system. These sources may be separated into two categories,
from soil and from plants. Autochthonous source means organic carbon produced within the aquatic system, for example, algae, algal excretions, and macrophytes (Thurman, 1985a).

It has been reported that humic substances in rivers and streams are of allochthonous origin from soil and plant matter; humic substances in lakes have both terrestrial and aquatic (autochthonous) origins; and humic substances found in some shallow groundwaters are carried in from soil and plant matter with precipitation (Thurman, 1985a). There is no consensus regarding the primary source of NOM in water; however, in this context related to drinking water treatment, NOM essentially derives from soil (Gjessing, 1994). Aiken and Cotsaris (1995) also indicated that "Much of the DOC present in surface waters is allochthonous material originating in the soils of the watershed".

Aiken et al. (1991) have reported evidence for the diffusion of aquatic fulvic acid from lake sediments to the overlying water. Thurman (1985b) has indicated that one of humic substance sources in groundwater originates in overlying soils. Steelink (1985) has pointed that the surface waters (marshes, bogs, rivers, and streams) contain humates similar to their soil counterparts based on O/C ratios. As previously stated, based on the E4/E6 ratios in Table 2-5, the commercial, soil, and sediment humic substances are predominately humic acids, and the four aquatic humic substances are predominately fulvic acids.
However, the St. Marys River sample did not fall in the E4/E6 ratio range reported for fulvic acids. The St. Marys River sample was obtained at a time when the river was at flood stage (Davis, 1993); therefore, its E4/E6 ratio being between humic and fulvic acid values may indicate a terrestrial source (more humic acid) during the flood stage.

The soil and sediment humic substances studied in this research were from Orange Heights soil and Newnans Lake bottom sediment. Their corresponding aquatic humic substance counterparts were from Orange Heights groundwater and Newnans Lake, respectively. In light of the aforementioned discussion, the soil and sediment humic substances are likely partial sources of their corresponding aquatic humic substances. Therefore, the soil and sediment humic substances were included in this research.

Furthermore, based on the characterization results, the soil and sediment humic substances were found to have high carboxylic acid content, approximately the same as the aquatic humic substances. For example, the data in Table 2-6 appear to show that the soil and sediment humic substances contain amounts of COOH and acidic OH (COOH being the most important) near to the aquatic humic substances. From the results in Table 2-8 and Table 2-9, the soil and sediment humic substances were also found to have high carboxylic acid content in proximity to the aquatic humic substances. Therefore, considering the relationship between solubility and carboxyl groups, the soil and sediment humic substances
are likely, at least, partial sources of their corresponding aquatic humic substances.

**Structural Characteristics of Humic Substances Versus DBP Formation**

There are only limited data on the relationship between DBP formation and fundamental chemical characteristics of humic materials. The available information is categorized as follows.

**Elemental analysis.** Ratios of elemental composition are often used to compare different humic substances; therefore, the atomic ratios of H/C, H/O, O/C and N/C have been included with the data presented in Table 2-4. The H/C ratio has often been used to indicate the degree of aromaticity (a small value) or aliphaticity (a large value) of humic substances (Thurman, 1985a). The H/C ratio thus appears to be a qualitatively useful parameter for comparing the aromaticities of humic materials (Rice and MacCarthy, 1991).

The activated aromatic structures such as phenolics have been reported to be especially reactive with chlorine producing large amounts of chlorinated byproducts from model compound studies (Norwood et al., 1980; De Laat et al., 1982; Reckhow and Singer, 1985) and from humic substances (Reckhow et al., 1990; Harrington et al., 1996). Therefore the relationship between H/C ratio and the degree of aromaticity of humic substances may be correlated with DBP formation.
However, due to the fact that humic substances are complex mixtures, a comprehensive analysis considering more than one characterization results may be needed in order to draw some generalization with stronger standing. For example, a small H/C ratio may indicate that the humic substance contains a large number of carbon to carbon double bonds; but the reasoning has been questioned because it does not consider the contribution of carbon to oxygen double bonds to the H/C ratio since both COOH and -HC=CH- have the same H/C ratio. The presence of a high concentration of COOH groups would adversely affect the use of atomic H/C as a measure of -HC=CH- (Perdue, 1984; Gauthier et al., 1987; Rice and MacCarthy, 1991). Therefore, the degree of aromaticity indicated by H/C ratio should be viewed with caution.

In terms of relationship between DBP formation and percent elemental composition, Reckhow et al. (1990) reported that DCAN formation in chlorinations of ten aquatic humic substances correlated well with nitrogen content in the humic substances. However, Smith and Singer (1994) showed that CNCl formation in the different chlorinated model waters prepared from five aquatic humic substances did not correlate well with the nitrogen content of the humic substances. Thibaud et al. (1990) reported that CPN formation in the three humic substances studied did not vary linearly with the nitrogen content.
**UV/VIS spectroscopy.** UV254 is often a good surrogate parameter both for DOC and for THM formation potential (Edzwald et al., 1985; Singer and Chang, 1989); therefore, its use has been included in Standard Method 5910 UV-Absorbing Organic Constituents (APHA, 1995). Studies using raw and treated natural waters have shown excellent correlations between THM formation potential and UV254 (Singer et al., 1981; Edzwald et al., 1985). In the modeling of natural waters for DBP formation, several researchers (Amy et al., 1987; Owen et al., 1992) have found that DOC*UV254 (the "reactive" fraction of the overall organic content) often resulted in the best fit among the variable forms representing NOM. Specific UV254 absorbance (UV254/TOC) has also been shown to correlate with THM yield (Edzwald, et al., 1985; Krasner, 1994).

DBP formation can also be correlated with the change in UV254 absorption ($\Delta$UV254) induced by chlorination. Korshin et al. (1996) reported a strong correlation ($r^2 = 0.95$) between chloroform formation and the $\Delta$UV254 after chlorination of a reservoir water for a range of reaction times, DOC concentrations, and chlorine doses. The same research group later reported that the change in UV272 absorption ($\Delta$UV272) and $\Delta$UV254 correlated linearly with the amount of TOX formed, for a wide range of water quality conditions and reaction times (Korshin et al., 1997a; 1997b).
The E4/E6 ratio has been correlated with an index of humification or aging of humic substances (Thurman, 1985a). For example, humic acids, which are thought to be more mature, have a lower E4/E6 ratio than fulvic acids; and this lower E4/E6 ratio is a measure of humification (Schnitzer and Khan, 1972). The E4/E6 ratio has also been reported to be inversely correlated with the degree of condensation (Stevenson, 1994): lower ratios reflect relatively higher degree of condensation of aromatic constituents; higher ratios infer the presence of relatively more aliphatic (less aromatic) structures. However, Chen et al. (1977) found no evidence to support this hypothesis. For the soil humic substances investigated by Chen et al. (1977), the strongest correlation ($r = -0.95$, $p = 0.01$) was found to be between E4/E6 ratio and reduced viscosity (related to molecular weight). In a general way, there is a greater molecular weight for humic acid over fulvic acid, and humic acid has a lower E4/E6 ratio (Thurman, 1985a). Reckhow et al. (1990) have reported that aquatic humic acids produce more DBPs than aquatic fulvic acids extracted from the same source water on a per carbon basis.

In summary, the E4/E6 ratio has been correlated with humification (aging), with degree of condensation of aromatic constituents, with aromaticity (or aliphaticity), and with molecular weight. In light of the aforementioned discussion, the E4/E6 ratio may be correlated with DBP formation.
Total acidity titration. Humic substances have been reported to complex both divalent and trivalent metal ions (Stevenson, 1994). As previously stated, the acidic nature of humic substances is attributed to both COOH and acidic OH groups (presumed to be phenolic OH), with COOH being the most important. The oxygen containing functional groups have been reported as ligands primarily responsible for metal ion binding by humic substances (Stevenson, 1994). The acidic character of humic substances can therefore be related with metal binding capacity. This relationship may be useful in the predictive analysis of humic-metal binding. It may play a role in treatment such as charge neutralization mechanisms in coagulation. However, it may not be so useful in DBP formation prediction since DBP formation in this research was carried out in buffer solution in which no divalent or trivalent metal ions were present. To the best of the author’s knowledge, the relationship between total acidity and DBP formation has not been previously identified in water chemistry settings.

As discussed previously, a small H/C ratio may indicate that the humic substance contains a large number of carbon to carbon double bonds; but the reasoning has been questioned because it does not consider the contribution of carbon to oxygen double bonds to the H/C ratio since both COOH and -HC=CH- have the same H/C ratio. The total acidity titration result may be combined with the H/C ratio to calculate the contribution of carbon to oxygen double bonds
of COOH groups to the H/C ratio. It will be discussed in Chapter 4 in more detail.

**Infrared spectroscopy.** The quantitative IR technique used an internal standard to compensate for the variation in sample preparation and instrumental operation between different samples (Davis, 1993). Therefore the normalized (to internal standard) IR measurements listed in Table 2-8 allow a direct quantitative comparison of specific functional group compositions among the different humic substances.

The absorbance in the 1650 to 1600 cm\(^{-1}\) region of the spectra has been attributed to a combination of aromatic carbon, carboxylate anion, and ketonic carbon (Table 2-7). However, in the spectra recorded at pH 4, there should be very little contribution from carboxylate anion. The \(^{13}\)C-NMR spectra indicate that there was very little or no ketonic carbon in these humic substances (Table 2-9); numerous \(^{13}\)C-NMR studies have also found very little or no ketonic carbon present in the humic substances investigated as compiled by Davis (1993, p.141-p.142). Therefore, it leads to the conclusion that the mean IR absorption in the 1650 to 1600 cm\(^{-1}\) region of spectra at pH 4, for these humic substances investigated in this research, was due primarily to aromatic carbon (Davis, 1993). The aromaticity of humic substances obtained from the mean IR absorption in the 1650 to 1600 cm\(^{-1}\) region of spectra at pH 4 may therefore be correlated with DBP formation.
$^{13}$C-NMR spectroscopy. The results of aliphatic, aromatic, phenolic, carboxylic, and carbonyl contents of the humic substances by $^{13}$C-NMR are shown in Table 2-9. The relationship between activated aromatic structures and DBP formation as well as chlorine reactivity has been referenced before. The activated aromatic structures such as phenolics have been reported to be especially reactive with chlorine producing large amounts of chlorinated byproducts from model compound studies (Norwood et al., 1980; De Laat et al., 1982; Reckhow and Singer, 1985). Reckhow et al. (1990) showed a linear relationship between chlorine consumption and calculated activated aromatic content for the ten humic substances tested. Harrington et al. (1996) indicated that phenolic carbon content was the best indicator of reactivity between NOM and chlorine. However, not all aromatic structures are activated. An estimation of activated aromatic content is discussed in the comprehensive analysis.

Comprehensive analysis. There is no direct measure of the activated aromatic content of humic substances; however, one can estimate their concentration on a probabilistic basis. It was assumed that only OH- and nitrogen-substituted aromatics are important and that additional substitutions on the aromatics (either electron donating or electron withdrawing) are of lesser importance (Reckhow et al., 1990). The final form of the calculation of activated aromatic content (Act Ar-R) was developed by Reckhow et al. (1990) to include the terms such as aromatic carbon content.
(Ar-C), phenolic group content (Ar-OH), nitrogen content (N), and carbon content (C) as described below:

\[
[\text{ActAr-R}] = \frac{[\text{Ar-C}]}{6} \left[ 1 - \left( 1 - \frac{[\text{Ar-OH}]}{[\text{Ar-C}]} \right)^6 \left( 1 - \frac{[\text{N}]}{[\text{C}]} \right)^6 \right] \quad (\text{eq. 2-11})
\]

\( \Delta \text{UV254} \) was reported to be an estimation of the destruction of activated aromatic rings which leads to chlorinated byproduct formation (Korshin et al., 1996). The experiment-derived estimation of the destruction of activated aromatic rings by Korshin et al. may not be the same as the equation-derived values developed by Reckhow et al. More research regarding the relationship between \( \Delta \text{UV254} \) and eq. 2-11 is needed.
CHAPTER 3
MATERIALS AND METHODS

Materials

Humic Substances and Tea Samples

Humic substances. Of the seven humic substances studied in this research, one was from a commercial source (Aldrich Chemical Co., Milwaukee, WI), the rest were isolated from several aquatic sources and their corresponding soil and sediment sources. The seven isolated humic substances were extracted and characterized by Davis (1993) as stated in Chapter 2. The aquatic humic substances were obtained from two blackwater rivers in Florida: the Santa Fe River and the St. Marys River. Additional aquatic humic substances were obtained from an eutrophic lake (Newnans Lake) and a surficial groundwater source in a planted pine forest (Orange Heights). The aquatic humic substances were extracted through XAD-8 column, and eluted by backflushing with 0.1 M NaOH; the 0.1 M NaOH solutions of concentrated aquatic humic substances were then eluted through a cation exchange column to convert the humic substances to the H+ form (Davis, 1993). The soil and sediment humic substances were obtained from Orange Heights soil and from Newnans Lake bottom sediment, respectively. The soil and sediment humic substances and commercial humic substances...
substance (Aldrich) were extracted from the solid matrices using 0.5 M NaOH; and the supernatants were decanted and centrifuged. After centrifugation, the supernatants were filtered through 0.45 μm pore size nylon filters, and passed though a cation exchange column as the aquatic humic substances (Davis, 1993). All aquatic, soil, sediment and commercial humic substances studied were frozen at -40°C and freeze dried to provide the humic substances in dried form.

As discussed in Chapter 2, interest in the role of humic substances on DBP formation is naturally confined to aquatic humic substances. However, the objective of this research was to investigate how characteristics of humic substances can be relate to DBP formation. Therefore, in addition to the aquatic humic substances, the characterized soil, sediment, and commercial humic substances were included in this research.

Based on characterization results, the soil and sediment humic substances were found to have high carboxylic acid content. Therefore, in light of the relationship between solubility and carboxyl groups, they are likely partial sources of their corresponding aquatic humic substances as examined in Chapter 2.

Confidence in the use of the readily available commercial humic substance in DBP formation tests was based on the comparative studied reported by Seeger et al. (1985) and on research found in the literature using commercial
humic substances (Fleischacker and Randtke, 1983; Coleman et al., 1984; Stevens et al., 1985, 1989a, 1989b; Pourmoghaddas et al., 1993) as discussed in Chapter 2.

**Tea samples.** The two instant tea samples, Lipton Natural Decaf Iced Tea Mix (Thomas J. Lipton, Inc., Englewood Cliffs, NJ) and Nestea (Nestlé Beverage Co., San Francisco, CA), were obtained from a local supermarket. According to the labels, they were 100% unsweetened instant tea powder without any addition of flavorants. The tea samples were only characterized in terms of elemental analysis and UV spectroscopy, as opposed to the humic substances.

**Standards and Reagents**

**Standards.** DBP calibration standards of EPA Method 551.1 used in this research were purchased from ULTRA Scientific (North Kingstown, RI) for THM components and AccuStandard Inc. (New Haven, CT) for the non-THM components, respectively. DBP calibration standard of EPA Method 552.2 used in this research was purchased from Supelco Inc. (Bellefonte, PA). ±1,2-dibromopropane (97% pure, internal standard used for EPA Method 551.1 and micro-liquid/liquid extraction technique for cyanogen halides) and 1,2,3-trichloropropane (99% pure, surrogate standard used for EPA Method 551.1 and internal standard used for EPA Method 552.2) were purchased from Aldrich Chemical Co. (Milwaukee, WI). The surrogate standard for EPA Method
552.2 (2-bromopropionic acid) was obtained from Supelco Inc. CNCl standards were in situ synthesized in this laboratory or purchased in a methanol solution from Protocol Analytical Supplies, Inc. (Middlesex, NJ). The in situ synthesized CNCl standard has been demonstrated to be comparable with the purchased commercial standards (Wu et al., 1997). CNBr was purchased from Fisher Scientific Co. (Pittsburgh, PA) as solid crystals.

Reagents. All other chemicals employed in this study were reagent grade or better (Fisher Scientific Co., Pittsburgh, PA). The reagent water used was Type 1 water (APHA, 1995) produced by Barnstead NANOpure ultrapure water system (Dubuque, Iowa). The purity of potassium cyanide used was certified as 100% by the manufacturer. Chloramine T used in this study contained at least 12% active chlorine. Sodium hypochlorite solutions prepared from reagent grade NaOCl were used as a source of free chlorine.

Experimental Design

Target Compounds and Parameters

Target compounds. The target compounds of DBPs were shown in Figure 1-1.

Parameters. The water samples prepared from those characterized humic substances and tea samples were studied in a series of experiments performed under the following conditions:

- Temperature = 25 ± 2°C.
• pH = 7.0 ± 0.1 and 8.5 ± 0.1.
• Bromide ion concentration = zero and 250 µg/L.
• Non-purgeable organic carbon (NPOC) = 5 mg/L.
• Chlorine dose = 12.5 mg/L (Cl₂/NPOC = 2.5).
• Chloramine dose = 6.25 mg/L as Cl₂ (Cl₂/NPOC = 1.25).
• Contact time = 24 hours.

Chlorine and chloramine doses were chosen to achieve the chlorine and chloramine residual concentrations of at least 0.6 mg/L at the end of the 24-hour reaction period for all samples.

The rationales for using the preceding parameters are discussed as follows:

The temperature of 25°C and pH 7 were chosen according to the Standard Method 5710B Trihalomethane Formation Potential (APHA, 1995). A pH 8.5 was set to reflect the influence of the Lead and Copper Rule on distribution system pH. Seasonal averages of Br⁻ for 100 utilities in USA were reported to range from 2 to 429 µg/L (Amy et al., 1994). The Br⁻ concentration of 250 µg/L was chosen in this research to give a sufficiently high impact on species distribution between chlorinated and brominated DBPs, while keeping the Br⁻ concentration within a reasonable range.

A general equation describing DBP formation can be expressed below:

precursors + disinfectants → DBPs

The disinfectants, providing a driving force, react with precursors through oxidation and substitution to form DBP.
It has been well known that increasing dosages of chlorine or chloramine produce increasing DBP concentrations, in some cases reaching a plateau.

A concern at initial stage of this research was in choosing the proper common chlorination and chloramination driving force in subsequent experiments to investigate the effect of structural characteristics on DBP formation among different humic substances. The Uniform Formation Condition (UFC) developed by Summers et al. (1996) specified incubation time of 24 hours and chlorine dose adjusted to achieve the desired chlorine residual concentrations of 1 ± 0.4 mg/L at the end of the 24-hour reaction period. This approach gives a good approximation of achieving a chlorine residual typical of distribution system conditions. The UFC method was described by the authors as "a means for direct DBP formation comparisons among different waters"; however, it fails to provide a common chlorination driving force among different waters since it does not take into account the differences in the respective chlorine demand in the waters of different chemical character.

In contrast to UFC, researchers in some recent studies used a common initial chlorine dose for the waters investigated and studied DBP formation (Reckhow et al., 1990; Pourmoghaddas et al., 1993; Cowman and Singer, 1996). Although a common initial dosage does not provide the same chlorination driving force among different waters without considering the respective chlorine demand, the method
greatly simplifies the laboratory chlorination procedures. Furthermore, several researchers have reported two phases in DBP formation; substantial linear DBP formation in a shorter term followed by modest increases in DBP concentrations in a relatively longer term (Luong et al., 1982; Fleischacker and Randtke, 1982; Miller and Uden, 1983; Amy et al., 1985). Therefore, the common chlorine dosage may provide a common chlorination driving force at the most productive stage of DBP formation than the common chlorine residual after 24 hours as proposed by Summers et al.

This dissertation was to investigate the effects of structural characteristics of humic substances on DBP formation; therefore, fixed initial free chlorine and combined chlorine concentrations were practiced in this study. Based on the chlorine residual data shown in Figure 4-3, a common free chlorine dosage of 12.5 mg/L established residual chlorine concentrations of at least 0.6 mg/L at the end of 24-hour reaction period for all samples, which is within the lower end of the target chlorine residual range (1.0 ± 0.4 mg/L) in the UFC. Chloramine dose was set to be half of the free chlorine dose based on the study reported by Jensen et al. (1985) and based on the combined chlorine residual data shown in Figure 4-4 that chloramine demand is usually less than free chlorine demand. In a recent study, Cowman and Singer (1996) used similar Cl₂/NPOC ratios (8/4 in chlorinations, 4/4 in chloraminations) to study HAA formation in waters containing aquatic humic substances.
Confidence in the use of the free chlorine/NPOC ratio of 2.5 was also based on the numerous DBP formation studies reported elsewhere using similar doses (Amy et al., 1985; Reckhow et al., 1990; Pourmoghaddas et al., 1993). The chloramine as Cl₂/NPOC ratio of 1.25 in the chloramination experiments was practiced in order to achieve sufficient DBP detection sensitivity since chloramination forms much less DBPs as opposed to chlorination, while keeping the dosage in a reasonable range for application to water treatment utilities.

Experimental Design of Chlorination and Chloramination

The major experiments of this study were performed according to the following design.

Preparation of humic and tea samples. The preparations of humic substances were performed according the following procedures. About 100 mg of humic substance were dissolved in 900 mL of reagent water that contained 20 mL of 1.00 N NaOH. The aquatic humic substances (except Newnans Lake’s) dissolved immediately upon slightly shaking. The complete dissolution of Newnans Lake aquatic humic substance was achieved by stirring for 10 minutes on a magnetic stirrer. The commercial, soil, and sediment humic substances were prepared in a similar manner, but with 30-minute stirring. Twenty mL of 1.00 N H₂SO₄ were then added to each solution and mixed. The solutions of commercial, soil, and sediment humic substances were observed to be completely dissolved
after such preparation procedures; however, they were further filtered with pre-washed 0.45 μm membrane filters. Those solutions were brought to 1 L with reagent water in a volumetric flask and refrigerated at 4°C in the dark until use. Standard Method 5310 B Combustion Infrared Method (APHA, 1995) was used to measure NPOC using a Dohrmann DC-190 TOC Analyzer (Cincinnati, OH). NPOC and UV254 were periodically monitored throughout the experimental period; and no degradation of the water quality was noted. The solutions of equal carbon concentration (NPOC = 5 mg/L) of humic samples were prepared by diluting volumetrically the stock solutions in reagent water every time before use.

Tea samples were prepared in a different manner. Tea powder of each instant tea brand was dissolved in reagent water only. After determining the exact mass to make NPOC of 5 mg/L, tea solutions were freshly made in this manner before use.

**Preparation of chlorine solution.** Free chlorine solution was prepared from reagent grade NaOCl. The standardized stock hypochlorite solution and free chlorine dosing solution were prepared according to the procedures in Standard Method 5710 B Trihalomethane Formation Potential.

Pre-formed monochloramine was prepared by dropwise addition of equal volumes of NaOCl dosing solution (5000 mg/L as Cl2) into a buffered NH4Cl solution at pH 9.0 (4773 mg/L as NH4Cl) in a well-stirred Erlenmeyer flask on ice in a concentration ratio of 4 mg Cl2 to 1 mg N. Preliminary
experiment and literature review (Smith and Singer, 1992; Cowman and Singer, 1996) showed that the resulting solution had at least 96% conversion of free chlorine into monochloramine and no residual free chlorine was detected. Monochloramine solutions were prepared fresh on the day of each chloramination.

The free chlorine and monochloramine concentration were measured by Standard Method 4500-Cl G DPD Colorimetric Method (APHA, 1995) using a Spectronic 21 UV spectrophotometer (Milton Roy Co., Ivyland, PA).

**Chlorination and chloramination experiments.** All samples were brought to room temperature prior to chlorination or chloramination. Bromide ion concentration of 250 µg/L was added as NaBr into the batch of samples to investigate Br⁻ effects. The waters were buffered to pH of 7.0 ± 0.1 and 8.5 ± 0.1 with a phosphate buffer and a mixed buffer (phosphate buffer mixed with borate buffer), respectively. The use and the preparation of the buffer systems were according to Standard Method 5710 B Trihalomethane Formation Potential (APHA, 1995). The appropriate amount of 1.0 N NaOH was added to adjust pH to 8.5 for samples with mixed buffer.

Chlorination was conducted in borosilicate glass vials (nominally 40 mL) sealed with teflon-faced septa. Each experiment was conducted with five vials. The first two vials were used for chlorine residual analysis and UV254 measurement, respectively, at the end of the 24-hour
reaction period. The remaining vials were used for EPA Method 551.1, EPA Method 552.2, and micro-liquid/liquid extraction for cyanogen halide measurements. At the end of the 24-hour reaction period, different dechlorinating agents were added to terminate the DBP formation according to different methods used. Ammonia chloride was added to the vials for analyses of both EPA Methods 551.1 and 552.2 to produce a concentration of 100 mg/L in the samples. The addition of ammonia chloride converts free chlorine to monochloramine as a dechlorination mechanism. For the cyanogen halide measurements, 2.5 mg of ascorbic acid and 0.1 mL of 1.0 N H₂SO₄ were added to the 40-mL sample to quench chlorine and to preserve cyanogen halides, respectively.

A preliminary experiment on all of the humic and tea samples had shown that a separate dechlorination scheme using sodium sulfite for CH was not necessary because the recoveries of CH quenched with ammonia chloride were the same as the recoveries of CH quenched with sodium sulfite for the matrices used in this research.

Chloramination was performed in a similar manner to chlorinations using the freshly prepared monochloramine solutions as mentioned before.

No dechlorinating agent was added to the samples in chloramination for EPA Method 551.1 and EPA Method 552.2 analyses. The two methods specify the use of ammonium chloride as the dechlorinating agent for chlorinated
samples, and the two methods do not call for the removal of monochloramine prior to extraction. Therefore, at the end of the 24-hour reaction period the samples in chloramination were stored as they were at 4°C. Although Koch and Krasner (1989) reported that "monochloramine did not react with humic or fulvic acids to form PE-DBPs during the 3-day holding period while the samples were stored at 4°C", all the samples in chloraminations were extracted on the next day. However, the addition of ascorbic acid to dechloraminate the samples for cyanogen halide measurement was practiced in this research as specified in the method (Sclimenti et al., 1994).

The DBPs formed were determined by EPA Method 551.1, EPA Method 552.2, and micro-liquid/liquid extraction for cyanogen halide using a Perkin Elmer (Norwalk, CT) AutoSystem GC equipped with an electron capture detector (ECD). Selected samples were analyzed using a GC/MS (5840A GC/5985 MS, Hewlett Packard, San Fernando, CA) for confirmation.

**UV/VIS spectroscopy.** All water samples before and after chlorination as well as chloramination were analyzed by Standard Method 5910 UV-Absorbing Organic Constituents (APHA, 1995) for UV254 absorbance using a Perkin Elmer Model 552 double beam grating spectrophotometer (Norwalk, CT). In chlorinated waters, residual chlorine was quenched with sodium sulfite at a dose equal to 100% of stoichiometric requirement based on the residual chlorine data; however, no
dechloraminating agent was added for chloraminated waters. The decrease in UV254 ($\Delta$UV254) of each sample was determined by the difference of two measurements, one before chlorination or chloramination, the other one after.

**Chlorination of Realistic Instant Tea Samples**

**Target compounds.** The target compounds of DBPs in the chlorinated realistic instant tea samples were the same as shown in Figure 1-1; in addition, TOX was included as a nonspecific DBP measurement.

**Chlorination experiment.** The NPOC of the tea samples used in the previously discussed chlorination and chloramination experiments was 5 mg/L. The chlorination experiment discussed here extended to realistic instant tea samples of NPOC = 925 mg/L and 1175 mg/L, respectively, for Lipton and Nestlé tea samples. The aforementioned high NPOC concentrations were obtained by dissolving 2.9573 g of tea powder to 1 L of Type 1 reagent water (APHA, 1995) at room temperature adjusted to pH 7 by phosphate buffer (1 teaspoon of 0.7 g to 8 fl. oz. water, according to the preparation suggestion on labels).

The proposed maximum residual free chlorine level was 4.0 mg/L (USEPA, 1994); and all instant tea samples were prepared to waters containing 4.0 mg/L free chlorine in an open container to simulate the possibly highest level of free chlorine that tea drinkers will encounter in the future. The free chlorine contact time was initially set to
be four hours. However, as discussed in Chapter 4, the free chlorine dissipated instantaneously; therefore, virtually no contact time longer than one minute was needed in this research.

The free chlorine residual was measured by Standard Method 4500-Cl D Amperometric Titration Method (APHA, 1995) using a CL Titrimeter Model 397 (Fisher Scientific Co., Pittsburgh, PA). The DBPs formed were determined by EPA Method 524.2 using a GC/MS (5840A GC/5985 MS, Hewlett Packard, San Fernado, CA) and EPA Method 625 using a GC/MS (AutoSystem GC/QMASS, Perkin Elmer, Norwalk, CT). The former is a P&T GC/MS method, and the latter is a liquid/liquid extraction followed by GC/MS analysis. TOX analysis was performed by Chemist Elizabeth Kennelley at QST Environmental Co. (Gainesville, FL) using Standard Method 5320 B Adsorption-Pyrolysis-Titrmetric Method (APHA, 1995).

**In Situ Synthesis of Cyanogen Chloride**

CNCl standards are expensive and difficult to acquire. An in situ synthesis of CNCl was developed as part of the doctoral research. A technical note regarding the in situ CNCl synthesis was accepted for publication in *Water Research* (Wu et al., 1997).

**Experimental Procedures of In Situ Synthesis**

In light of the hazardous nature and high cost of aqueous CNCl preparation from gas standards and the limited
shelf life of prepared standards in a methanol solution (Protocol, Middlesex, NJ), an alternative method of in situ synthesis of CNCl was developed to provide a safe and economical method to generate calibration and quality control standards. The method consists of stoichiometrically oxidizing cyanide with chlorine to produce CNCl.

$$\text{KCN + HOCl} \rightarrow \text{CNCl + KOH}$$

This quantitative conversion of cyanide to CNCl is used as an intermediate step in the analysis of cyanide in Standard Method 4500-CN⁻ E Colorimetric Method (APHA, 1995).

By carefully weighing potassium cyanide as the CNCl precursor and adjusting pH, a theoretical amount of aqueous CNCl standard can be generated in situ. Furthermore, at higher pH (pH > 8.5), CNCl hydrolyzes to cyanate ion which has only limited toxicity. Hence the disposal problems of unused CNCl generated by this method can be minimized by simply raising pH. Although Method 4500-CN⁻ E has been historically accepted for cyanide analysis, the use of the intermediate, CNCl, as a standard has not been previously identified in water treatment settings.

A phosphate buffer as described in Method 4500-CN⁻ J Cyanogen Chloride was used instead of acetate buffer specified in Method 4500-CN⁻ E. The use of a buffer is necessary because the stability of CNCl is pH dependent. At alkaline pH, CNCl rapidly hydrolyzes to cyanate ion.

Krasner et al. (1989), referring to a personal communication
with Fair, stated that CNCl may degrade at high pH. In Fair’s study of CNCl stability, reagent water was buffered at pH values of 5, 7, and 9. CNCl degraded immediately at pH 9, and after three days at the other pH levels. Furthermore, CNCl in unbuffered reagent water was stable, implying that buffers may have caused the degradation in addition to high pH. Therefore, the dosage of phosphate buffer used in this in situ generation was only half of the dosage specified in Standard Method 4500-CN⁻ J. Preliminary experiments showed that use of this lower buffer dosage adequately controlled the pH at 5.0 after the addition of up to 5.0 mg/L hypochlorite or up to 400 mg/L chloramine T for up to 4 days in capped headspace-free vials at 4°C in the dark.

The preparation of reagents and the experimental design of the in situ synthesis is shown schematically in Figure 3-1. For laboratories first using this method, it is advisable to check the free chlorine residual at least once after adding ascorbic acid to ensure that the chlorine residual has been completely eliminated. Chloramine T, potassium cyanide and phosphate buffer solutions were refrigerated and maintained their stability for at least one week. Method 4500-CN⁻ E does not require the refrigeration of the potassium cyanide solution but for convenience all solutions were refrigerated in this study.

Calibration CNCl standards were prepared by volumetrically diluting a commercial CNCl standard in a
Preparation of Reagents (Refrigerated After Use)

Phosphate buffer: NaH$_2$PO$_4$, 6 g add reagent water to 100 ml

Free Chlorine solution*: NaOCl solution

(Chloramine T solution:
  chloramine T, 1 g add reagent water to 100 ml)*

Stock cyanide standard:
  KCN, 0.212 g add reagent water to 100 ml

*Chlorine dose can be either free chlorine or chloramine T alternatively.

The Experimental Design

Stock cyanide standard (1 ml = 0.847 mg CN$^-$)
  - Take 1 ml stock cyanide standard.
  - Dilute it to 1 L using reagent water.

Primary cyanide standard (1 ml = 0.847 μg CN$^-$)
  - Take 5 ml primary cyanide standard.
  - Dilute it by about 30 ml reagent water.
  - Add 4 ml phosphate buffer.
  - Add NaOCl solution to achieve Cl$_2$ dosage between 0.5 to 5 mg/L in the 50 ml aliquot. (Or add 2 ml chloramine T solution).
  - Immediately bring to 50 ml with reagent water in a volumetric flask.

  - Stopper, mix by gentle inversion twice.
  - Let stand exactly 2 minutes.
  - After 2 minutes, add 25 mg ascorbic acid to quench residual chlorine.
  - Stopper, let stand for 30-40 seconds with occasional gentle inversions.

This is the primary CNCl standard (200 μg/L) which may be diluted to calibration standard concentrations with reagent water in volumetric flasks. Calibration standards are stored in capped headspace-free vials at 4°C in the dark.

Figure 3-1. The Preparation of Reagents and the Experimental Design of the In Situ Synthesis.
methanol solution (Protocol, Middlesex, NJ). These standards were then analyzed immediately after preparation. The synthesized calibration standards were calibrated by and compared to the commercial standards. The synthesized calibration standards (either generated by chloramine T or hypochlorite) were also analyzed immediately after preparation, and only freshly prepared calibration standards were used except in the stability study.

The CNCl standards were analyzed by two methods: a purge-and-trap (P&T) GC/MS analysis (Flesch and Fair, 1989) and a micro-liquid/liquid extraction (μ-LLE) GC/ECD technique (Sclimenti et al., 1994).

Analytical Methods

Miscellaneous Analyses and OA/OC Implementation

Miscellaneous analyses. The NPOC, chlorine residual, UV254, and TOX measurements were performed according to Standard Methods (APHA, 1995) as referenced before.

Standard Method 5910 UV-Absorbing Organic Constituents does not specify the need of dechlorinating sample before taking UV measurements. However, for UV254 measurements after chlorinations, free chlorine residual was quenched with sodium sulfite at a dose equal to 100% of stoichiometric requirement based on the residual chlorine data. No dechloraminating agent was added to samples for UV254 measurements after chloramination.
QA/QC implementation. To achieve QA/QC requirements, several different measures were performed for respective analysis. A laboratory blank was prepared and run with each batch of samples. For NPOC analyses, at least three replicate injections were made for each sample. At least 20% (2 in 9) of all samples taken for chlorine residual and UV254 measurements were analyzed concurrently as duplicate samples. An independent verification standard of free chlorine standard (Voluette Free Chlorine Standard, Hach Co., Loveland, CO) was used to verify the calibration and overall performance of chlorine analysis. For UV254 determination, two replicate measurements were made for each sample. TOX analyses of realistic instant tea samples were performed at QST Environmental Co. as stated previously. A laboratory blank, three realistic tea samples (Lipton, Nestlé, and Nestlé spiked with 250 \( \mu \)g/L bromide ion), and a chlorinated water containing Aldrich humic substance were sent to QST Environmental Co. Nestlé tea spiked with 250 \( \mu \)g/L bromide ion served as a duplicate measurement for Nestlé tea since incorporated bromine bound to organics, if any, was read as chloride in TOX analysis. The TOX result of the Aldrich sample should be approximately twice the amount of the sum of all identified DBPs (Christman et al., 1983; Reckhow and Singer, 1984; Singer and Chang, 1989; Stevens et al., 1990; Singer, 1994) which was determined independently in this dissertation research.
Structural Characterization and QA/QC Implementation

As discussed in Chapter 2, tea polyphenols, like humic substances, are complex mixtures, and some of which are poorly defined macromolecules. In order to understand the reactions between chlorine and tea polyphenols on a fundamental level, as well as to correlate the observed DBP yields and chlorine consumption with the characterization results, tea samples obtained from two different sources were characterized in terms of elemental analysis and UV spectroscopy.

Characterization method. Elemental analyses of C, H, and N were carried out by Engineer Melvyn A. Courtney with a Carlo Erba Model 1106 CHN Analyzer (Milan, Italy) in the Chemistry Department Spectroscopic Services at the University of Florida. The moisture and ash content of each tea sample were measured by drying and ignition, respectively, according to (Davis, 1993). UV254 measurements were performed as previously described.

QA/QC implementation. The elemental analyses, moisture and ash content of the two tea samples were determined in duplicate. The average for each of these determinations are included in Table 2-4. The elemental compositions in Table 2-4 have been corrected for moisture and ash content; and the oxygen content was determined by difference (from 100%) based on the C, H, and N content, after these values had been corrected for moisture and ash content. The QA/QC
requirements for UV measurement were practiced as previously stated.

EPA Method 551.1 and OA/OQ Implementation

Summary of EPA Method 551.1. In EPA Method 551.1 (USEPA, 1995a), a 50 mL sample aliquot is extracted with 5 mL methyl-tert-butyl-ether (MTBE). Two μL of the extract is then injected into a GC/ECD. Aqueous calibration standards are also extracted and analyzed in a manner similar to samples in order to compensate for any extraction losses. This research basically followed EPA Method 551.1, but the volumes of sample and MTBE used followed EPA Method 551 (USEPA, 1990). Namely, a 35 mL sample aliquot was extracted with 2 mL MTBE in this research because the chlorinations and chloramination were conducted in borosilicate glass vials with nominal 40 mL volume. A schematic diagram for the procedures of the modified EPA Method 551.1 used in this research is presented in Figure 3-2.

All samples were extracted using a mechanical shaker (Eberbach Corp., Ann Arbor, MI). After sample extraction, a two μL aliquot of the finished extract was analyzed on a Perkin Elmer AutoSystem GC/ECD. Analytical separation was achieved with a 0.53 mm i.d., 30-meter fused silica capillary column (DB-5ms) with 1.5 μm film thickness (J & W Scientific, Folsom, CA). Table 3-1 summarizes the operating conditions and the retention times observed for GC/ECD analyses.
35 mL preserved sample, lab blank, or standard

- Add 40 μL surrogate standard (1,2,3-trichloropropane, 1000 μg/mL in MTBE)
- Add 2 mL MTBE
- Add 14 g Na₂SO₄ (Before using a batch of Na₂SO₄, place in muffle furnace at 400°C for up to 4 hours)
- If a series of samples are being prepared for extraction, immediately after the addition of Na₂SO₄, the sample should be recapped, agitated and placed in a secure horizontal position with the undissolved Na₂SO₄ distributed along the length of the vial

- Extract by a mechanical shaker for 12 min on a fast setting

- Allow the phases to separate for about 2 min
- Use a graduated pipet, transfer 1 mL MTBE to an autosampler vial
- Add 10 μL internal standard (± 1,2-dibromopropane, 200 μg/mL in acetone) into the MTBE extract
- Cap the autosampler vial. The analytes are stable up to 14 days when stored in a freezer at < -10°C

2 μL of the extract for GC/ECD analysis

Figure 3-2. A Schematic Diagram for the Procedures of the Modified EPA Method 551.1 Used in This Research.
Table 3-1. Retention Time Data and Chromatographic Conditions of GC/ECD.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Retention Times (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>5.01</td>
</tr>
<tr>
<td>Trichloroacetonitrile</td>
<td>7.08</td>
</tr>
<tr>
<td>Dichlorobromomethane</td>
<td>9.38</td>
</tr>
<tr>
<td>Chloral Hydrate</td>
<td>9.54</td>
</tr>
<tr>
<td>Dichloroacetonitrile</td>
<td>10.76</td>
</tr>
<tr>
<td>Dichloropropanone</td>
<td>11.14</td>
</tr>
<tr>
<td>Chloropicrin</td>
<td>14.57</td>
</tr>
<tr>
<td>Dichloroacetonitrile</td>
<td>15.71</td>
</tr>
<tr>
<td>Dichloropropanone</td>
<td>16.78</td>
</tr>
<tr>
<td>± 1,2-dibromopropane (internal standard)</td>
<td>17.35</td>
</tr>
<tr>
<td>Bromoform</td>
<td>18.06</td>
</tr>
<tr>
<td>Dichloroacetonitrile</td>
<td>19.16</td>
</tr>
<tr>
<td>1,2,3-trichloropropane (surrogate standard)</td>
<td>20.04</td>
</tr>
<tr>
<td>EPA Method 551.1#</td>
<td>20.16</td>
</tr>
<tr>
<td>Monochloroacetic acid</td>
<td>13.03</td>
</tr>
<tr>
<td>Monobromoacetic acid</td>
<td>16.75</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>17.35</td>
</tr>
<tr>
<td>2-bromopropionic acid (surrogate standard)</td>
<td>18.31</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>21.46</td>
</tr>
<tr>
<td>Bromochloroacetic acid</td>
<td>21.89</td>
</tr>
<tr>
<td>1,2,3-trichloropropane (internal standard)</td>
<td>22.35</td>
</tr>
<tr>
<td>Tribromoacetic acid</td>
<td>29.03</td>
</tr>
<tr>
<td>Bromochloroacetic acid</td>
<td>29.73</td>
</tr>
<tr>
<td>Tribromoacetic acid</td>
<td>39.04</td>
</tr>
<tr>
<td>Tribromoacetic acid</td>
<td>46.60</td>
</tr>
</tbody>
</table>

Micro-Liquid/Liquid Extraction}%

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Retention Times (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyanogen chloride</td>
<td>2.09</td>
</tr>
<tr>
<td>Cyanogen bromide</td>
<td>3.62</td>
</tr>
<tr>
<td>± 1,2-dibromopropane (internal standard)</td>
<td>8.52</td>
</tr>
</tbody>
</table>

GC/ECD: DB-5ms, 0.53 mm i.d., 30-meter fused silica capillary column with 1.5 μm film thickness. Injector temp. = 200°C (150°C for %). Detector temp. = 260°C. He linear velocity = 25 cm/sec at 35°C. Makeup N2 flow rate = 30 ml/min.

Program: #Hold at 35°C for 12 min, ramp to 190°C at 8°C/min and hold for 3 min.
*Hold at 35°C for 10 min, ramp to 75°C at 5°C/min and hold for 15 min, ramp to 100°C at 5°C/min and hold for 5 min, ramp to 200°C at 5°C/min and hold for 2 min.
*Hold at 30°C for 1 min, ramp to 120°C at 10°C/min, ramp to 190°C at 35°C/min and hold for 1 min.
QA/QC implementation. All data generated during the analyses followed EPA Method 551.1. All laboratory work followed good laboratory practices and, in principle, followed the QA/QC outlined in the Method. The following QA/QC measures were performed such as method blank, triplicate experiments, matrix spikes, continuing calibration checks, monitoring surrogate/internal standards, and estimating method detection limits (MDLs) based on seven replicate injections. The MDL of each analyte in GC/ECD analyses is presented in Table 3-2 based on the results of the seven replicate laboratory fortified blanks. The tabular QA/QC data regarding precision, spike recovery, and surrogate recovery are presented in Tables 3-3 and 3-4 for chlorination and chloramination, respectively.

EPA Method 552.2 and QA/QC Implementation

Summary of EPA Method 552.2. EPA Method 552.2 (USEPA, 1995b) involves liquid-liquid extraction of the acidified water sample with MTBE, methylation by the addition of acidic methanol at 50°C for two hours, and analysis by GC/ECD. Aqueous calibration standards are also extracted and analyzed in a manner similar to samples in order to compensate for any extraction losses. In EPA Method 552.2, a 40 mL acidified and salted sample aliquot is extracted with 4 mL MTBE. Two μL of the extract is then injected into a GC/ECD. This research basically followed EPA Method
Table 3-2. Method Detection Limit (MDL) of Each Target DBP Determined by GC/ECD Based on the Results of the Seven Replicate Laboratory Fortified Blanks.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>MDL (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA Method 551.1</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.80</td>
</tr>
<tr>
<td>Trichloroacetonitrile</td>
<td>0.02</td>
</tr>
<tr>
<td>Dichlorobromomethane</td>
<td>0.21</td>
</tr>
<tr>
<td>Chloral Hydrate</td>
<td>0.03</td>
</tr>
<tr>
<td>Dichloroacetonitrile</td>
<td>0.13</td>
</tr>
<tr>
<td>Dichloropropanone</td>
<td>0.05</td>
</tr>
<tr>
<td>Chloropicrin</td>
<td>0.03</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>0.30</td>
</tr>
<tr>
<td>Bromochloroacetonitrile</td>
<td>0.03</td>
</tr>
<tr>
<td>Trichloropropanone</td>
<td>0.04</td>
</tr>
<tr>
<td>Bromoform</td>
<td>0.32</td>
</tr>
<tr>
<td>Dibromoacetonitrile</td>
<td>0.03</td>
</tr>
<tr>
<td>EPA Method 552.2</td>
<td></td>
</tr>
<tr>
<td>Monochloroacetic acid</td>
<td>2.47</td>
</tr>
<tr>
<td>Monobromoacetic acid</td>
<td>0.16</td>
</tr>
<tr>
<td>Dichloroacetic acid</td>
<td>0.63</td>
</tr>
<tr>
<td>Trichloroacetic acid</td>
<td>0.65</td>
</tr>
<tr>
<td>Bromochloroacetic acid</td>
<td>0.25</td>
</tr>
<tr>
<td>Dibromoacetic acid</td>
<td>0.09</td>
</tr>
<tr>
<td>Bromodichloroacetic acid</td>
<td>0.22</td>
</tr>
<tr>
<td>Dibromochloroacetic acid</td>
<td>0.46</td>
</tr>
<tr>
<td>Tribromoacetic acid</td>
<td>0.73</td>
</tr>
<tr>
<td>Micro-Liquid/Liquid Extraction</td>
<td></td>
</tr>
<tr>
<td>Cyanogen chloride</td>
<td>0.65</td>
</tr>
<tr>
<td>Cyanogen bromide</td>
<td>0.96</td>
</tr>
</tbody>
</table>
# Table 3.3

The DBP Formation QA/QC Results of Chlorination.

(a) In the Absence of Bromide Ion.

(b) In the Presence of 250 µg/L Bromide Ion.

**Surro%**: Surrogate Recovery.

**RSTD**: relative standard deviation.

### (a)

<table>
<thead>
<tr>
<th><strong>rw 7</strong></th>
<th><strong>Sites</strong></th>
<th><strong>CIB</strong></th>
<th><strong>PCIB</strong></th>
<th><strong>CIC</strong></th>
<th><strong>PCIC</strong></th>
<th><strong>CIB/CIC</strong></th>
<th><strong>PCIB/PCIC</strong></th>
<th><strong>TOPO</strong></th>
<th><strong>CIB/TOPO</strong></th>
<th><strong>DRB</strong></th>
<th><strong>NODR</strong></th>
<th><strong>MAB</strong></th>
<th><strong>TCA</strong></th>
<th><strong>TOA</strong></th>
<th><strong>RIB</strong></th>
<th><strong>NODR</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td><strong>MLE</strong></td>
<td>255.13</td>
<td>0.24</td>
<td>23.97</td>
<td>17.80</td>
<td>2.82</td>
<td>0.68</td>
<td>1.07</td>
<td>119.52</td>
<td>6.81</td>
<td>119.52</td>
<td>5.91</td>
<td>93.19</td>
<td>288.22</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
</tr>
<tr>
<td><strong>Avr. RSTD</strong></td>
<td><strong>MLE</strong></td>
<td>2.12%</td>
<td>0.76%</td>
<td>5.43%</td>
<td>6.05%</td>
<td>9.16%</td>
<td>10.20%</td>
<td>5.10%</td>
<td>14.20%</td>
<td>3.60%</td>
<td>9.62%</td>
<td>13.60%</td>
<td>13.62%</td>
<td>12.29%</td>
<td>9.62%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>91.8%</td>
<td>93.3%</td>
<td>96.4%</td>
<td>96.4%</td>
<td>91.8%</td>
<td>96.4%</td>
<td>91.8%</td>
<td>123.3%</td>
<td>123.3%</td>
<td>91.8%</td>
<td>96.4%</td>
<td>91.8%</td>
<td>96.4%</td>
<td>91.8%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>8.2%</td>
<td>6.7%</td>
<td>11.2%</td>
<td>2.49%</td>
<td>9.28%</td>
<td>4.33%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>113.1%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>15.2%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>35.8%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### (b)

<table>
<thead>
<tr>
<th><strong>rw 8.5</strong></th>
<th><strong>Sites</strong></th>
<th><strong>CIB</strong></th>
<th><strong>PCIB</strong></th>
<th><strong>CIC</strong></th>
<th><strong>PCIC</strong></th>
<th><strong>CIB/CIC</strong></th>
<th><strong>PCIB/PCIC</strong></th>
<th><strong>TOPO</strong></th>
<th><strong>CIB/TOPO</strong></th>
<th><strong>DRB</strong></th>
<th><strong>NODR</strong></th>
<th><strong>MAB</strong></th>
<th><strong>TCA</strong></th>
<th><strong>TOA</strong></th>
<th><strong>RIB</strong></th>
<th><strong>NODR</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td><strong>MLE</strong></td>
<td>350.04</td>
<td>0.00</td>
<td>27.83</td>
<td>3.09</td>
<td>3.20</td>
<td>2.82</td>
<td>0.13</td>
<td>96.45%</td>
<td>11.37</td>
<td>63.75</td>
<td>22.62</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Avr. RSTD</strong></td>
<td><strong>MLE</strong></td>
<td>6.46%</td>
<td>0.26%</td>
<td>2.46%</td>
<td>2.24%</td>
<td>2.35%</td>
<td>2.20%</td>
<td>1.15%</td>
<td>6.74%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>99.54%</td>
<td>116.4%</td>
<td>121.4%</td>
<td>92.3%</td>
<td>95.4%</td>
<td>110.1%</td>
<td>93.4%</td>
<td>121.4%</td>
<td>92.3%</td>
<td>89.8%</td>
<td>109.6%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>0.46%</td>
<td>0.01%</td>
<td>38.00</td>
<td>1.79</td>
<td>0.40</td>
<td>0.02</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>5.74%</td>
<td>3.00%</td>
<td>8.20%</td>
<td>8.03%</td>
<td>5.24%</td>
<td>1.50%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>0.03%</td>
<td>0.03%</td>
<td>3.97</td>
<td>0.16</td>
<td>0.07</td>
<td>0.00</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>34.76%</td>
<td>4.04%</td>
<td>56.90</td>
<td>5.80</td>
<td>56.90</td>
<td>5.80</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>2.00%</td>
<td>0.00%</td>
<td>8.24%</td>
<td>3.06%</td>
<td>8.24%</td>
<td>3.06%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>105.64%</td>
<td>116.1%</td>
<td>121.0%</td>
<td>30.73%</td>
<td>105.64%</td>
<td>116.1%</td>
<td>121.0%</td>
<td>30.73%</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### (c)

<table>
<thead>
<tr>
<th><strong>rw 8.5</strong></th>
<th><strong>Sites</strong></th>
<th><strong>CIB</strong></th>
<th><strong>PCIB</strong></th>
<th><strong>CIC</strong></th>
<th><strong>PCIC</strong></th>
<th><strong>CIB/CIC</strong></th>
<th><strong>PCIB/PCIC</strong></th>
<th><strong>TOPO</strong></th>
<th><strong>CIB/TOPO</strong></th>
<th><strong>DRB</strong></th>
<th><strong>NODR</strong></th>
<th><strong>MAB</strong></th>
<th><strong>TCA</strong></th>
<th><strong>TOA</strong></th>
<th><strong>RIB</strong></th>
<th><strong>NODR</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average</strong></td>
<td><strong>MLE</strong></td>
<td>180.46</td>
<td>0.00</td>
<td>24.73</td>
<td>37.54</td>
<td>3.24%</td>
<td>3.24</td>
<td>3.24%</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
<td><strong>RIB</strong></td>
<td><strong>NODR</strong></td>
</tr>
<tr>
<td><strong>Avr. RSTD</strong></td>
<td><strong>MLE</strong></td>
<td>3.99%</td>
<td>0.28%</td>
<td>3.99%</td>
<td>0.28%</td>
<td>3.99%</td>
<td>0.28%</td>
<td>3.99%</td>
<td>0.28%</td>
<td>3.99%</td>
<td>0.28%</td>
<td>3.99%</td>
<td>0.28%</td>
<td>3.99%</td>
<td>0.28%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>101.28%</td>
<td>100.76%</td>
<td>102.4%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td>98.93%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>7.50%</td>
<td>5.00%</td>
<td>7.50%</td>
<td>5.00%</td>
<td>7.50%</td>
<td>5.00%</td>
<td>7.50%</td>
<td>5.00%</td>
<td>7.50%</td>
<td>5.00%</td>
<td>7.50%</td>
<td>5.00%</td>
<td>7.50%</td>
<td>5.00%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>127.24%</td>
<td>126.0%</td>
<td>127.24%</td>
<td>126.0%</td>
<td>127.24%</td>
<td>126.0%</td>
<td>127.24%</td>
<td>126.0%</td>
<td>127.24%</td>
<td>126.0%</td>
<td>127.24%</td>
<td>126.0%</td>
<td>127.24%</td>
<td>126.0%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>5.20%</td>
<td>6.00%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>125.76%</td>
<td>126.0%</td>
<td>126.0%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>6.25%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>real and deviation recovery</strong></td>
<td><strong>MLE</strong></td>
<td>7.50%</td>
<td>6.25%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td>6.25%</td>
<td>7.18%</td>
<td><strong>RIB</strong></td>
</tr>
<tr>
<td><strong>spike recovery</strong></td>
<td><strong>MLE</strong></td>
<td>107.6%</td>
<td>105.5%</td>
<td>78.04%</td>
<td>107.6%</td>
<td>105.5%</td>
<td>78.04%</td>
<td>107.6%</td>
<td>105.5%</td>
<td>78.04%</td>
<td>107.6%</td>
<td>105.5%</td>
<td>78.04%</td>
<td>107.6%</td>
<td>105.5%</td>
<td><strong>RIB</strong></td>
</tr>
</tbody>
</table>

**Note**: Below Detection Limit
| Site  | p2    | p5     | rt    | rpm   | DCM  | DCO  | CFP  | CBF/120 | DRG  | DRG  | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average | Spike recovery | Average |
|-------|-------|--------|-------|-------|------|------|------|---------|------|------|---------|----------------|---------|----------------|---------|----------------|---------|----------------|---------|----------------|---------|----------------|---------|----------------|---------|----------------|---------|----------------|---------|----------------|---------|
|       |       |        |       |       |      |      |      |         |      |      |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |
| M30  | 7.26  | 2.68   | 2.35  | 2.50  | 2.67 | 2.58 | 2.50 | 2.20    | 2.50 | 2.50 | 2.50   | 2.50            | 2.50    | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   |
|       |       |        |       |       |      |      |      |         |      |      |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |
| M30  | 2.86  | 2.86   | 2.86  | 2.86  | 2.86 | 2.86 | 2.86 | 2.86    | 2.86 | 2.86 | 2.86   | 2.86            | 2.86    | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   |
|       |       |        |       |       |      |      |      |         |      |      |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |
| M30  | 7.26  | 2.68   | 2.35  | 2.50  | 2.67 | 2.58 | 2.50 | 2.20    | 2.50 | 2.50 | 2.50   | 2.50            | 2.50    | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   | 2.50            | 2.50   |
|       |       |        |       |       |      |      |      |         |      |      |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |                |         |
| M30  | 2.86  | 2.86   | 2.86  | 2.86  | 2.86 | 2.86 | 2.86 | 2.86    | 2.86 | 2.86 | 2.86   | 2.86            | 2.86    | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   | 2.86            | 2.86   |

* Below Detection Limit
552.2, but the volumes of sample and MTBE used were 30 mL and 4 mL, respectively, because the chlorinations and chloramination were conducted in borosilicate glass vials with nominal 40 mL volume. A schematic diagram for the procedures of the modified EPA Method 552.2 used in this research is presented in Figure 3-3.

All samples were extracted using a mechanical shaker (Eberbach Corp., Ann Arbor, MI). After sample extraction, a two µL aliquot of the finished extract was analyzed on a Perkin Elmer AutoSystem GC/ECD. Analytical separation was achieved with a 0.53 mm i.d., 30-meter fused silica capillary column (DB-5ms) with 1.5 µm film thickness. Table 3-1 summarizes the operating conditions and the retention times observed for GC/ECD analyses.

**QA/QC implementation.** All data generated during the analyses followed EPA Method 552.2. All laboratory work followed good laboratory practices and, in principle, followed the QA/QC outlined in the Method. The following QA/QC measures were performed such as method blank, triplicate experiments, matrix spikes, continuing calibration checks, monitoring surrogate/internal standards, and MDLs based on seven replicate injections. The MDL of each analyte in GC/ECD analyses is presented in Table 3-2 based on the results of the seven replicate laboratory fortified blanks. The tabular QA/QC data regarding precision, spike recovery, and surrogate recovery are
30 mL preserved sample, lab blank, or standard

- Add 40 μL surrogate standard (2-bromopropionic acid, 50 μg/mL in MTBE)
- Add at least 2 mL conc. H₂SO₄ to lower pH < 0.5
- Quickly add ca. 2 g CuSO₄·5H₂O and shake until dissolved
- Quickly add 12 g Na₂SO₄* and shake for 3-5 min until almost all is dissolved (*See pretreatment in Figure 3-2)
- Add 4 mL MTBE

Extract by a mechanical shaker for 30 min on a fast setting

- Allow the phases to separate for about 5 min
- Use a graduated pipet, transfer 3 mL MTBE to a conical vial
- Add 1 mL of 10% H₂SO₄ in methanol

Methyleate extract in the capped conical vial at 50°C for 2 hr in a heating block

- Remove the vial from the heating block, allow it to cool before removing the cap
- Add 4 mL saturated NaHCO₃ soln to the vial in 1 mL increments
- Shake the vial for 2 min, venting frequently
- Transfer 1 mL MTBE phase to an autosampler vial
- Add 10 μL internal standard (1,2,3-trichloropropane, 1000 μg/mL in MTBE) into the MTBE extract
- Cap the autosampler vial. The extract is stable up to 7 days at ≤ 4°C or up to 14 days at ≤ -10°C

2 μL of the extract for GC/ECD analysis

Figure 3-3. A Schematic Diagram for the Procedures of the Modified EPA Method 552.2 Used in This Research.
presented in Tables 3-3 and 3-4 for chlorination and chloramination, respectively.

Cyanogen Halide Analysis and QA/QC Implementation

**Summary of cyanogen halide analysis.** The cyanogen halides were analyzed by the micro-liquid/liquid extraction (μ-LLE) followed by GC/ECD analysis (Sclimenti et al., 1994). In the μ-LLE method, a 30 mL sample aliquot is extracted with 4 mL MTBE. The extract is then injected into a GC/ECD. Aqueous calibration standards are also extracted and analyzed in a manner similar to samples in order to compensate for any extraction losses. This research basically followed the μ-LLE method. However, a P&T GC/MS method (Flesch and Fair, 1989) was also used during the method development of the in situ synthesis of CNCl. Sclimenti et al. (1996) have shown that the two methods are comparable. A schematic diagram for the procedures of the μ-LLE method used in this research is presented in Figure 3-4.

All samples were extracted using a mechanical shaker (Eberbach Corp., Ann Arbor, MI). After sample extraction, a two μL aliquot of the finished extract was analyzed on a Perkin Elmer AutoSystem GC/ECD. Analytical separation was achieved with a 0.53 mm i.d., 30-meter fused silica capillary column (DB-5ms) with 1.5 μm film thickness. Table 3-1 summarizes the operating conditions and the retention times observed for GC/ECD analyses. For confirmation
30 mL preserved sample, lab blank, or standard

- The sample should have been preserved by adding 0.1 mL of 1 N H₂SO₄ and 0.1 mL of freshly prepared 0.142 M ascorbic acid solution

- Add 4 mL MTBE

- Add 10 g muffled Na₂SO₄* (*See pretreatment in Figure 3-2)

- If a series of samples are being prepared for extraction, immediately after the addition of Na₂SO₄, the sample should be recapped, agitated and placed in a secure horizontal position with the undissolved Na₂SO₄ distributed along the length of the vial

Extract by a mechanical shaker for 10 min on a fast setting

- Allow the phases to separate for about 4 min

- Use a graduated pipet, transfer 1 mL MTBE to an autosampler vial

- Add 10 µL internal standard (± 1,2-dibromopropane, 10 µg/mL in MTBE) into the MTBE extract

- Cap the autosample vial. The analytes are stable up to 2-3 days when stored at ≤ 4°C

2 µL of the extract for GC/ECD analysis

Figure 3-4. A Schematic Diagram for the Procedures of the Micro-Liquid/Liquid Extraction for Cyanogen Halides Used in This Research.
purposes and during the method development of the in situ synthesis of CNCl, selected samples were analyzed using EPA Method 524.2 P&T GC/MS analysis.

**QA/QC implementation.** All data generated during the analyses followed the μ-LLE method. All laboratory work followed good laboratory practices and, in principle, followed the QA/QC outlined in the method. The following QA/QC measures were performed such as method blank, triplicate experiments, matrix spikes, continuing calibration checks, monitoring internal standards, and estimating MDLs based on seven replicate injections. The MDL of each analyte in GC/ECD analyses is presented in Table 3-2 based on the results of the seven replicate laboratory fortified blanks. The tabular QA/QC data regarding precision, spike recovery, and surrogate recovery are presented in Tables 3-3 and 3-4 for chlorination and chloramination, respectively.

**GC/MS Analysis and QA/QC Implementation**

For confirmation purposes, selected samples with NPOC = 5 mg/L and realistic tea samples were analyzed using two GC/MS methods—EPA Methods 524.2 and 625.

**Summary of EPA Method 524.2.** EPA Method 524.2 (USEPA, 1995c) involves extraction of the volatile organic compounds by bubbling an inert gas through the aqueous sample; trap of the purged volatile organic compounds by suitable sorbent
materials, and GC/MS analysis by desorbing the trapped compounds into a capillary column.

A Hewlett Packard P&T GC/MS (5840A GC/5985 MS) system was used for this method. Analytical separation was achieved with a 0.32 mm i.d., 30-meter fused silica capillary column (DB-624) with 1.8 μm film thickness.

Summary of EPA Method 625. In EPA Method 625 (USEPA, 1982), semi-volatile organic compounds are serially extracted with methylene chloride at pH greater than 11 and again at pH less than 2 using a separatory funnel. The methylene chloride extract is dried and concentrated to a volume of 1 mL which is then injected into a GC/MS. This research basically followed EPA Method 625 with two exceptions—using MTBE as extraction solvent and omitting pH adjustment to greater than 11. The modifications were made according to Method 552.2 since only confirmation of HAAs was needed.

A Perkin Elmer AutoSystem GC/QMASS system was used for this method. Analytical separation was achieved with a 0.25 mm i.d., 30-meter fused silica capillary column (DB-5ms) with 1 μm film thickness.

QA/QC implementation. All data generated during the analyses followed respective Methods. All laboratory work followed good laboratory practices and, in principle, followed the QA/QC outlined in the Methods. However, the following QA/QC measures were not performed such as matrix spikes, continuing calibration checks, and monitoring
surrogate recovery since no quantitation was made for samples for confirmation only. The two aforementioned GC/MS instruments were routinely operated, tuned, and maintained by the staff of Analytical Services Laboratory in the Department of Environmental Engineering Sciences.
CHAPTER 4
RESULTS AND DISCUSSION

The analytical results and discussion regarding (1) in situ synthesis of CNCl; (2) disinfectant demand; (3) DBP formation of humic substances; (4) effect of structural characteristics of humic substances on DBP formation; and (5) DBP formation of instant tea samples will be provided in this chapter.

In Situ Synthesis of Cyanogen Chloride

CNCl standards were synthesized in situ in this research as a safe and economical method of standard preparation. A comparison of commercial and synthesized standards is provided in Table 4-1. Standard Student t test procedures indicated that each synthesized standard mean concentration was not significantly different from the commercial standard mean concentration at a level of significance of 0.05.

Stability tests were performed by preparing diluted standards following the synthesis procedure and analyzing the standards after selected storage durations. Figure 4-1 (a) shows the time-storage study of the hypochlorite generated CNCl. Synthesized standards of 20 μg/L were prepared for triplicate analyses across a four-day time
Table 4-1. Comparison of Commercial and Synthesized Standards of Cyanogen Chloride.
(a) Micro-LLE/GC-ECD Method.
(b) P&T/GC-MS Method.

Calibration was based on commercial standards. Values shown are mean ± standard deviation in μg/L based on 5 replicates at each prepared concentration of 1, 10, and 20 μg/L.

(a)

<table>
<thead>
<tr>
<th>Standard Source</th>
<th>Prepared Concentration (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Commercial</td>
<td>1.40 ± 0.20</td>
</tr>
<tr>
<td>Synthesized with hypochlorite</td>
<td>1.62 ± 0.10</td>
</tr>
<tr>
<td>Synthesized with chloramine-T</td>
<td>1.56 ± 0.16</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Standard Source</th>
<th>Prepared Concentration (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Commercial</td>
<td>1.36 ± 0.07</td>
</tr>
<tr>
<td>Synthesized with chloramine-T</td>
<td>1.47 ± 0.15</td>
</tr>
</tbody>
</table>
Figure 4-1. The Stability Tests of Synthesized Standards with ±10% Control Limits.
(a) Hypochlorite Generated CNCl (20 μg/L).
(b) Chloramine T Generated CNCl (10 μg/L and 20 μg/L).
Concentrations of CNCl appeared to be stable for at least two days and began decreasing thereafter falling below the 10% control line after 4 days. Figure 4-1 (b) summarizes the results of the stability tests for chloramine T generated CNCl at concentrations of 10 and 20 μg/L. Figure 4-1 (b) shows that the synthesized standards were stable for at least one hour since the time interval between each run (including purge, GC analysis, and oven cool down) was approximately 60 minutes. Although replicate analyses were not run for the stability test using chloramine T as the chlorinating agent, both concentration levels exhibited a similar trend.

Since the free chlorine generated CNCl was stable for days, it may be suitable as a calibration standard or a QC check sample for a typical working period of at least eight hours without repeated synthesis if properly sealed headspace-free. The calibration curve of the free chlorine generated CNCl shown in Figure 4-1 (a) used a chlorine dosage of 2.5 mg/L. Since the concentration of CNCl generated is limited by the amount of the cyanide precursor present, the hypochlorite dose may not be critical. To demonstrate this, 20 μg/L CNCl standards generated with 0.5, 1, 2.5, and 5 mg/L of hypochlorite were prepared and analyzed. As shown in Figure 4-2, these synthesized standards agreed to within ±10%. The rationale for using 0.5 mg/L free chlorine as the lowest dosage was to ensure a
Figure 4-2. The 20 μg/L CNCl Calibration Standards Synthesized with Different Dosages of Free Chlorine.
positive free chlorine residual after the immediate chlorine demand (0.23 mg/L) of the cyanide ion was satisfied.

As discussed above, the chloramine T generated CNCl appeared to be stable for at least one hour. Although its usefulness in extended use over time may be limited, the fresh aliquot can be repeatedly synthesized in less than 10 minutes. Furthermore, the use of chloramine T avoids the extra steps of preparing and standardizing free chlorine solution.

The chemistry of chloramine T deserves some discussion to help explain the instability of chloramine T generated CNCl. In aqueous solution, chloramine T reacts as if it were a hypochlorite (Wilson and Wilson, 1960):

$$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NClNa} + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 + \text{NaOCl} \quad (\text{eq. 4-1})$$

Therefore exact apparent free chlorine concentration resulted from chloramine T hydrolysis could not be determined because chloramine T undergoes equilibrium reaction in aqueous solution.

The 2 ml chloramine T added to the 50 ml aliquot produced about 3.5 to 4 mg/L "instantaneous" free chlorine measured by Hach DPD Free Chlorine Powder Pillow. The "instantaneous" free chlorine residual was measured by taking the color reading immediately after the DPD powder was added, but the reading increased with time. The rationale for using 5 mg/L free chlorine as the highest dosage (Figure 4-2) was to encompass the ambiguous chlorine concentration from chloramine T.
The stability of CNCl has been discussed by Bailey and Bishop (1973a; 1973b) and Xie and Reckhow (1992). They concluded that high pH as well as the presence of sulfite and free chlorine causes degradation of CNCl. None of these factors was present in the controlled synthesis process (free chlorine was quenched after CNCl generation). The cause for the relative instability of chloramine T generated CNCl was not experimentally investigated because hypochlorite generated CNCl was found to be stable for several days. However, the instability of chloramine T generated CNCl may be caused by the \( \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2 \) as shown in eq. 4-1 or by the product formed after chloramine T reacted with ascorbic acid. However, this point needs more research.

**Disinfectant Demand**

The humic substances and instant tea samples used in this research were:

- Aldrich (Aldrich)
- Newnans Lake sediment (NLS)
- Orange Heights soil (OHS)
- Santa Fe River (SFR)
- St. Marys River (St MR)
- Orange Heights DOC (OH DOC)
- Newnans Lake DOC (NL DOC)
- Lipton Natural Decaf Iced Tea Mix (Lipton)
- Nestlé Tea (Nestea)
Preliminary chlorination and chloramination experiments were run to determine the appropriate chlorine and chloramine dosages for subsequent DBP formation experiments. DBP formation was not measured in these preliminary experiments. For the first set of the experiments, humic substances and tea samples were dissolved in pH 7 ± 0.1 buffer solutions and chlorinated with sodium hypochlorite at 25°C in the absence of light and bromide ion. At the end of 24 hours, samples were analyzed for chlorine residuals. For the second set of the experiments, chloramination was performed in a manner similar to chlorination. The two sets of experiments were studied under a series of conditions:

- **Temperature** = 25 ± 2°C.
- **pH** = 7.0 ± 0.1.
- **Bromide ion concentration** = zero.
- **Non-purgeable organic carbon (NPOC)** = 5 mg/L.
- **Chlorine dose** = 6, 9, and 12.5 mg/L (Cl₂/NPOC = 1.2, 1.8, and 2.5, respectively).
- **Chloramine dose** = 3, 4.5, and 6.25 mg/L as Cl₂ (Cl₂/NPOC = 0.6, 0.9, and 1.25, respectively).
- **Contact time** = 24 hours.

Three chlorine/NPOC levels were performed to investigate the effect of chlorine dosages on the extents to which chlorine reacted with the humic substances and tea samples.

The data shown in Figure 4-3 and Figure 4-4 indicate that there were strong similarities among the shapes of the
Figure 4-3. The Free Chlorine Residual as a Function of Cl₂/NPOC Ratio from the Seven Humic Substances and the Two Tea Samples in the Absence of Bromide Ion at pH 7 After 24 Hours.
Figure 4-4. The Chloramine Residual as a Function of Cl$_2$/NPOC Ratio from the Seven Humic Substances and the Two Tea Samples in the Absence of Bromide Ion at pH 7 After 24 Hours.
chlorine residual curves of the humic substances and tea samples with respect to the chlorine/NPOC ratios.

In the chlorination experiments (Figure 4-3), 12.5 mg/L chlorine dose (Cl₂/NPOC = 2.5) established residual chlorine concentrations of at least 0.6 mg/L at the end of 24-hour reaction period for all samples. The lowest free chlorine concentration of 0.6 mg/L (Nestea) is within the target chlorine residual range (1.0 ± 0.4 mg/L) in the proposed Uniform Formation Conditions (Summers et al., 1996). Although the free chlorine residuals of other sources exceeded Uniform Formation Conditions, this dosage (12.5 mg/L) was used thereafter in subsequent DBP formation experiments as discussed in Chapter 3 (the rationales for using the chlorine dose). In the chloramination experiments (Figure 4-4), the highest chloramine dose of 6.25 mg/L as Cl₂ (Cl₂/NPOC = 1.25) was practiced thereafter in subsequent DBP formation experiments in order to achieve sufficient DBP detection sensitivity since chloramination forms much less DBPs compared to chlorination.

The Nestea and Aldrich samples at Cl₂/NPOC of 1.2 and 1.8 consumed all the free chlorine applied. Except for these two samples, the slopes of the humic substances and Lipton tea sample increased progressively as the chlorine doses increased, indicating that chlorine demand increases with increasing chlorine doses (Symons et al., 1996). The ratio of the change in chlorine residual to the change in chlorine dose indicates the chlorine demand associated with
each humic substance. The ratio of one is interpreted as no chlorine demand for the particular substance. For ratios of less than one; the higher the ratio, the less the free chlorine demand by the particular substance. If the Aldrich and Nestea samples were excluded, the aforementioned ratios between Cl₂/NPOC of 1.8 and 2.5 ranged from 0.52 mg/mg for Lipton to 0.85 mg/mg for NLS. These values (calculated from the slopes of Figure 4-3, with exclusion of NPOC) are all less than one, indicating that there was still some chlorine demand at the higher chlorine doses—either in oxidation and/or substitution reactions.

The smallest ratio of 0.52 mg/mg shows that the chlorine demand is substantial for the Lipton sample at the higher chlorine doses. Assuming the Aldrich and Nestea samples began to show some minute free chlorine residuals at Cl₂/NPOC of 1.8, the aforementioned ratios between Cl₂/NPOC of 1.8 and 2.5 were 0.46 mg/mg for Aldrich and 0.23 mg/mg for Nestea. In the Aldrich and Nestea samples, the ratios would be larger if free chlorine residuals became measureable at Cl₂/NPOC greater than 1.8; however, the ratios probably would not exceed 0.52 mg/mg. As will be discussed later in Table 4-4 (a), the chlorine demands for Aldrich and Nestea were the two highest values. In light of this, the chlorine demands at the higher chlorine doses were substantial for the Aldrich, Lipton, and Nestea samples.

Figure 4-3 and Figure 4-4 show that there was a significant difference in chlorine demands among the humic
substances and tea samples. Further data analyses shown later indicate that there was also a significant difference among the humic substances and tea samples with respect to DBP yields and chlorine consumption.

**DBP Formation of Humic Substances**

After the results of the preliminary chlorination and chloramination experiments were obtained, the water samples prepared from those characterized humic substances and tea samples were studied in a series of experiments performed under the following conditions:

- Temperature = 25 ± 2°C.
- pH = 7.0 ± 0.1 and 8.5 ± 0.1.
- Bromide ion concentration = zero and 250 μg/L.
- Non-purgeable organic carbon (NPOC) = 5 mg/L.
- Chlorine dose = 12.5 mg/L (Cl₂/NPOC = 2.5).
- Chloramine dose = 6.25 mg/L as Cl₂ (Cl₂/NPOC = 1.25).
- Contact time = 24 hours.

Chlorine and chloramine doses were chosen to achieve the chlorine and chloramine residual concentrations of at least 0.6 mg/L and 2.4 mg/L, respectively, at the end of the 24-hour reaction period for all samples as indicated in Figures 4-3 and 4-4.

Tables 4-2 and 4-3 summarize the DBP formation results for chlorination and chloramination, respectively, under the aforementioned conditions. In Tables 4-2 and 4-3, total THMs, total HAAs, and total HANs are abbreviated as THM4,
### Table 4-2. The DBP Formation Data (In Mass Unit: µg/L) of Chlorination.

(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.

CNCl and CNBr were below detection limit (BDL).

#### (a)

| Sites     | CHCl3 | CHCl2Br | CHBr2Cl | CHBr3THM | TCA | DCA | BCA | DBA | HAN | DCPO | TCPO | CH | CBF | MCAA | MCAA | MCAA | MCAA | MCAA | BCAA | TCAA | TCAA | TCAA | TCAA | TCAA | DBAA | BDCAA | BDCAA | BDAA | BDAA | BDAA | BDAA |
|-----------|-------|---------|---------|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| PH 7      |       |         |         |          |     |     |     |     |     |     |     |     |     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Aldrich   | 440.68 | 21.1 |     |     |     |     |     |     |     |     |     |     |     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| NLS       | 264.19 | 0.24 | 16.70 | 16.94 | 0.62 | 10.07 | 33.97 | 2.68 | 8.91 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CMS       | 369.29 | 0.10 | 5.67 | 5.77 | 0.51 | 8.54 | 18.54 | 0.23 | 7.45 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| SFR       | 397.44 | 0.09 | 5.51 | 5.60 | 0.83 | 10.08 | 20.05 | 0.84 | 10.02 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| St MR     | 373.85 | 0.08 | 4.65 | 4.73 | 0.69 | 11.73 | 28.85 | 0.26 | 13.64 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| OH DOC    | 391.71 | 0.07 | 5.97 | 5.04 | 0.74 | 14.22 | 22.41 | 0.44 | 9.74 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| NL DOC    | 373.94 | 0.09 | 5.17 | 5.26 | 0.95 | 12.27 | 23.06 | 0.24 | 8.72 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Lipton    | 368.58 | 0.07 | 4.62 | 4.69 | 0.54 | 2.26 | 44.22 | 0.16 | 13.86 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Nestea    | 413.38 | 0.09 | 3.64 | 36.73 | 0.47 | 2.16 | 43.52 | 0.07 | 11.73 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |

#### (b)

| Sites     | CHCl3 | CHCl2Br | CHBr2Cl | CHBr3THM | TCA | DCA | BCA | DBA | HAN | DCPO | TCPO | CH | CBF | MCAA | MCAA | MCAA | MCAA | MCAA | BCAA | TCAA | TCAA | TCAA | TCAA | TCAA | TCAA | DBAA | BDCAA | BDCAA | BDAA | BDAA | BDAA | BDAA |
|-----------|-------|---------|---------|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| PH 8      |       |         |         |          |     |     |     |     |     |     |     |     |     |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Aldrich   | 556.01 | 0.06 | 2.30 | 2.36 | 0.28 | 0.12 | 18.79 | 0.48 | 11.53 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| NLS       | 353.64 | 0.08 | 3.59 | 3.67 | 0.32 | 0.13 | 23.78 | 2.88 | 11.39 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| CMS       | 425.65 | 0.07 | 2.16 | 2.23 | 0.36 | 0.12 | 27.02 | 0.20 | 7.64 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| SFR       | 420.14 | 0.03 | 1.70 | 1.73 | 0.42 | 0.14 | 23.91 | 0.66 | 10.48 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| St MR     | 476.08 | 0.03 | 1.80 | 1.83 | 0.49 | 0.21 | 38.09 | 0.20 | 11.48 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| OH DOC    | 464.22 | 0.02 | 1.88 | 1.90 | 0.56 | 0.22 | 88.69 | 0.45 | 32.22 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| NL DOC    | 442.42 | 0.05 | 1.98 | 2.03 | 0.51 | 0.20 | 29.64 | 0.22 | 10.12 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Lipton    | 376.77 | 0.06 | 6.22 | 6.28 | 0.13 | 0.04 | 61.01 | 0.12 | 11.28 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Nestea    | 432.66 | 0.05 | 2.87 | 5.92 | 0.16 | 0.04 | 54.80 | 0.11 | 14.68 |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |

* BDL
<table>
<thead>
<tr>
<th>PH 7</th>
<th>Sites</th>
<th>CHC13</th>
<th>CHC12Br</th>
<th>CHC12Br2</th>
<th>CHC12Br3</th>
<th>THM4</th>
<th>TCAC</th>
<th>DCAM</th>
<th>BCGA</th>
<th>DBAA</th>
<th>HAAM4</th>
<th>DCPO</th>
<th>DCPH</th>
<th>CPH</th>
<th>MCA</th>
<th>MBAA</th>
<th>MBCA</th>
<th>DCAA</th>
<th>TCAA</th>
<th>BCAA</th>
<th>DBAA</th>
<th>BDCAA</th>
<th>DBCA</th>
<th>TBA</th>
<th>HA69</th>
<th>CHC1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich</td>
<td>8.84</td>
<td>*</td>
<td>*</td>
<td>8.84</td>
<td>*</td>
<td>1.65</td>
<td>*</td>
<td>*</td>
<td>1.65</td>
<td>4.97</td>
<td>0.15</td>
<td>0.11</td>
<td>0.20</td>
<td>20.25</td>
<td>0.83</td>
<td>*</td>
<td>*</td>
<td>45.65</td>
<td>6.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NLS</td>
<td>9.19</td>
<td>*</td>
<td>*</td>
<td>9.19</td>
<td>*</td>
<td>1.66</td>
<td>*</td>
<td>*</td>
<td>1.66</td>
<td>4.81</td>
<td>0.19</td>
<td>0.24</td>
<td>0.88</td>
<td>4.47</td>
<td>28.29</td>
<td>0.69</td>
<td>*</td>
<td>*</td>
<td>33.45</td>
<td>7.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ONS</td>
<td>7.75</td>
<td>*</td>
<td>*</td>
<td>7.75</td>
<td>*</td>
<td>1.28</td>
<td>*</td>
<td>*</td>
<td>1.28</td>
<td>3.64</td>
<td>0.14</td>
<td>0.11</td>
<td>0.35</td>
<td>4.95</td>
<td>28.06</td>
<td>0.73</td>
<td>*</td>
<td>*</td>
<td>33.74</td>
<td>5.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SFR</td>
<td>6.35</td>
<td>*</td>
<td>*</td>
<td>6.35</td>
<td>*</td>
<td>1.29</td>
<td>*</td>
<td>*</td>
<td>1.29</td>
<td>5.46</td>
<td>0.19</td>
<td>0.14</td>
<td>0.38</td>
<td>8.11</td>
<td>33.18</td>
<td>0.95</td>
<td>*</td>
<td>*</td>
<td>42.20</td>
<td>6.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St MR</td>
<td>7.11</td>
<td>*</td>
<td>*</td>
<td>7.11</td>
<td>*</td>
<td>1.19</td>
<td>*</td>
<td>*</td>
<td>1.19</td>
<td>6.97</td>
<td>0.18</td>
<td>0.14</td>
<td>0.23</td>
<td>10.13</td>
<td>35.42</td>
<td>0.85</td>
<td>*</td>
<td>*</td>
<td>46.40</td>
<td>5.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH DOC</td>
<td>8.59</td>
<td>*</td>
<td>*</td>
<td>8.59</td>
<td>*</td>
<td>1.24</td>
<td>*</td>
<td>*</td>
<td>1.24</td>
<td>7.05</td>
<td>0.20</td>
<td>0.12</td>
<td>0.21</td>
<td>7.54</td>
<td>39.75</td>
<td>1.05</td>
<td>*</td>
<td>*</td>
<td>48.34</td>
<td>5.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NL DOC</td>
<td>9.06</td>
<td>*</td>
<td>*</td>
<td>9.06</td>
<td>*</td>
<td>1.30</td>
<td>*</td>
<td>*</td>
<td>1.30</td>
<td>5.98</td>
<td>0.23</td>
<td>0.16</td>
<td>0.38</td>
<td>7.84</td>
<td>26.54</td>
<td>0.64</td>
<td>*</td>
<td>*</td>
<td>35.02</td>
<td>5.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lipton</td>
<td>7.58</td>
<td>*</td>
<td>*</td>
<td>7.58</td>
<td>*</td>
<td>1.41</td>
<td>*</td>
<td>*</td>
<td>1.41</td>
<td>0.72</td>
<td>0.01</td>
<td>0.26</td>
<td>10.16</td>
<td>14.16</td>
<td>0.34</td>
<td>*</td>
<td>*</td>
<td>47.46</td>
<td>4.77</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nestea</td>
<td>9.97</td>
<td>*</td>
<td>*</td>
<td>9.97</td>
<td>*</td>
<td>0.97</td>
<td>*</td>
<td>*</td>
<td>0.97</td>
<td>0.80</td>
<td>0.01</td>
<td>0.42</td>
<td>20.79</td>
<td>45.51</td>
<td>0.38</td>
<td>*</td>
<td>*</td>
<td>66.58</td>
<td>4.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PH 8.5</th>
<th>Sites</th>
<th>CHC13</th>
<th>CHC12Br</th>
<th>CHC12Br2</th>
<th>CHC12Br3</th>
<th>THM4</th>
<th>TCAC</th>
<th>DCAM</th>
<th>BCGA</th>
<th>DBAA</th>
<th>HAAM4</th>
<th>DCPO</th>
<th>DCPH</th>
<th>CPH</th>
<th>MCA</th>
<th>MBAA</th>
<th>MBCA</th>
<th>DCAA</th>
<th>TCAA</th>
<th>BCAA</th>
<th>DBAA</th>
<th>BDCAA</th>
<th>DBCA</th>
<th>TBA</th>
<th>HA69</th>
<th>CHC1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich</td>
<td>7.23</td>
<td>*</td>
<td>*</td>
<td>7.23</td>
<td>*</td>
<td>0.21</td>
<td>*</td>
<td>*</td>
<td>0.21</td>
<td>1.41</td>
<td>0.03</td>
<td>*</td>
<td>4.59</td>
<td>19.89</td>
<td>0.19</td>
<td>*</td>
<td>*</td>
<td>46.57</td>
<td>4.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NLS</td>
<td>5.12</td>
<td>*</td>
<td>*</td>
<td>5.12</td>
<td>*</td>
<td>0.28</td>
<td>*</td>
<td>*</td>
<td>0.28</td>
<td>1.54</td>
<td>0.07</td>
<td>*</td>
<td>3.01</td>
<td>21.62</td>
<td>0.17</td>
<td>*</td>
<td>*</td>
<td>48.50</td>
<td>5.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ONS</td>
<td>5.29</td>
<td>*</td>
<td>*</td>
<td>5.29</td>
<td>*</td>
<td>0.14</td>
<td>*</td>
<td>*</td>
<td>0.14</td>
<td>1.07</td>
<td>0.03</td>
<td>*</td>
<td>3.00</td>
<td>15.31</td>
<td>0.21</td>
<td>*</td>
<td>*</td>
<td>48.52</td>
<td>4.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SFR</td>
<td>4.42</td>
<td>*</td>
<td>*</td>
<td>4.42</td>
<td>*</td>
<td>0.15</td>
<td>*</td>
<td>*</td>
<td>0.15</td>
<td>1.49</td>
<td>0.03</td>
<td>*</td>
<td>3.86</td>
<td>21.95</td>
<td>0.25</td>
<td>*</td>
<td>*</td>
<td>26.06</td>
<td>4.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SC MR</td>
<td>4.59</td>
<td>*</td>
<td>*</td>
<td>4.59</td>
<td>*</td>
<td>0.19</td>
<td>*</td>
<td>*</td>
<td>0.19</td>
<td>2.07</td>
<td>0.05</td>
<td>*</td>
<td>7.41</td>
<td>17.35</td>
<td>0.44</td>
<td>*</td>
<td>*</td>
<td>25.20</td>
<td>4.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH DOC</td>
<td>5.06</td>
<td>*</td>
<td>*</td>
<td>5.06</td>
<td>*</td>
<td>0.17</td>
<td>*</td>
<td>*</td>
<td>0.17</td>
<td>2.12</td>
<td>0.04</td>
<td>*</td>
<td>9.58</td>
<td>18.25</td>
<td>0.30</td>
<td>*</td>
<td>*</td>
<td>32.00</td>
<td>3.83</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NL DOC</td>
<td>4.48</td>
<td>*</td>
<td>*</td>
<td>4.48</td>
<td>*</td>
<td>0.12</td>
<td>*</td>
<td>*</td>
<td>0.12</td>
<td>1.47</td>
<td>0.03</td>
<td>*</td>
<td>3.26</td>
<td>17.79</td>
<td>0.18</td>
<td>*</td>
<td>*</td>
<td>21.23</td>
<td>4.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lipton</td>
<td>3.87</td>
<td>*</td>
<td>*</td>
<td>3.87</td>
<td>*</td>
<td>0.24</td>
<td>*</td>
<td>*</td>
<td>0.24</td>
<td>0.21</td>
<td>0.65</td>
<td>*</td>
<td>10.39</td>
<td>21.01</td>
<td>0.16</td>
<td>*</td>
<td>*</td>
<td>31.58</td>
<td>3.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nestea</td>
<td>3.61</td>
<td>*</td>
<td>*</td>
<td>3.61</td>
<td>*</td>
<td>0.14</td>
<td>*</td>
<td>*</td>
<td>0.14</td>
<td>0.38</td>
<td>0.24</td>
<td>*</td>
<td>12.06</td>
<td>23.39</td>
<td>0.26</td>
<td>*</td>
<td>*</td>
<td>35.71</td>
<td>3.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3. The DBP Formation Data (In Mass Unit: mg/L) of Chloramination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 mg/L Bromide Ion.
CNBr was below detection limit (BDL).
HAA9, and HAN4, respectively. Representative GC/ECD chromatograms are included in Appendix A. The QA/QC results of the DBP measurements and tea characterization were already discussed in Chapter 3.

The results of chlorine demands and UV254 measurements associated with Tables 4-2 and 4-3 are listed in Tables 4-4 and 4-5, respectively.

When bromide ion is present, the added chlorine oxidizes the bromide ion rapidly to bromine as represented in eq. 2-3 (free chlorine demand exerted by Br⁻: 0.9 mg Cl₂/mg Br⁻). Bromine thus formed is able to react with humic substances as either oxidizing or substituting (preferentially) agents. In oxidation reactions, the corresponding bromide ion is produced, and the bromide ion so formed is reconverted to bromine with a further loss of chlorine. The standard DPD method measures free chlorine and free bromine expressed in terms of Cl₂ in chlorination situations; and chloramine and bromamine are also expressed in term of Cl₂ in chloramination conditions. Table 4-4 presents the overall halogen (Cl₂ + Br₂) demand after 24-hour reaction under different bromide ion concentrations and shows that total halogen consumption increased with added bromide ion.

ΔUV254 was reported to be an estimation of the destruction of activated aromatic rings which leads to chlorinated byproduct formation (Korshin et al., 1996). Table 4-5 (a) shows that chlorination induced substantial
Table 4-4. Chlorine and Chloramine Demands of the Humic Substances and Instant Tea Samples Studied in This Research.
(a) Chlorination.
(b) Chloramination.

(a) Chlorine Demand (mg/L)

<table>
<thead>
<tr>
<th>Source</th>
<th>Chlorine Demand (mg/L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Br⁻ = 0 μg/L</td>
<td>Br⁻ = 250 μg/L</td>
<td>pH 7</td>
<td>PH 8.5</td>
<td>pH 7</td>
<td>PH 8.5</td>
<td></td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>10.94</td>
<td>9.57</td>
<td>11.10</td>
<td>9.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>6.76</td>
<td>6.00</td>
<td>7.00</td>
<td>6.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>6.22</td>
<td>6.11</td>
<td>6.42</td>
<td>6.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>6.43</td>
<td>6.26</td>
<td>6.74</td>
<td>6.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Marys River</td>
<td>7.53</td>
<td>6.98</td>
<td>7.78</td>
<td>7.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orange Heights GW*</td>
<td>6.32</td>
<td>5.56</td>
<td>6.51</td>
<td>5.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>7.53</td>
<td>7.50</td>
<td>7.82</td>
<td>7.66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lipton Tea</td>
<td>9.20</td>
<td>8.65</td>
<td>9.50</td>
<td>8.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nestlé Tea</td>
<td>10.72</td>
<td>10.03</td>
<td>11.00</td>
<td>10.30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Groundwater.

(b) Chloramine Demand (mg/L)

<table>
<thead>
<tr>
<th>Source</th>
<th>Chloramine Demand (mg/L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Br⁻ = 0 μg/L</td>
<td>Br⁻ = 250 μg/L</td>
<td>pH 7</td>
<td>PH 8.5</td>
<td>pH 7</td>
<td>PH 8.5</td>
<td></td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>1.98</td>
<td>1.41</td>
<td>2.81</td>
<td>1.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>1.62</td>
<td>0.99</td>
<td>1.83</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>1.20</td>
<td>0.52</td>
<td>1.41</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>1.30</td>
<td>0.89</td>
<td>1.51</td>
<td>1.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Marys River</td>
<td>1.62</td>
<td>0.89</td>
<td>2.19</td>
<td>1.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orange Heights GW*</td>
<td>1.83</td>
<td>0.99</td>
<td>1.90</td>
<td>1.67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>1.68</td>
<td>0.84</td>
<td>1.98</td>
<td>1.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lipton Tea</td>
<td>2.40</td>
<td>1.99</td>
<td>2.50</td>
<td>2.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nestlé Tea</td>
<td>3.08</td>
<td>2.35</td>
<td>3.59</td>
<td>2.81</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Groundwater.
Table 4-5. UV254 Measurements and ΔUV254 Values of the Humic Substances and Instant Tea Samples Studied in This Research.
(a) Chlorination.
(b) Chloramination (CLN).

<table>
<thead>
<tr>
<th>Source</th>
<th>UV Absorbance (cm(^{-1})) at 254 nm</th>
<th>ΔUV254 (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Chlorination</td>
<td>After Chlorination</td>
</tr>
<tr>
<td></td>
<td>pH 7</td>
<td>pH 8.5</td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>0.445</td>
<td>0.452</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>0.195</td>
<td>0.198</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>0.364</td>
<td>0.369</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>0.246</td>
<td>0.255</td>
</tr>
<tr>
<td>St. Marys River</td>
<td>0.262</td>
<td>0.265</td>
</tr>
<tr>
<td>Orange Heights GW#</td>
<td>0.263</td>
<td>0.266</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>0.240</td>
<td>0.241</td>
</tr>
<tr>
<td>Lipton Tea</td>
<td>0.093</td>
<td>0.100</td>
</tr>
<tr>
<td>Nestlé Tea</td>
<td>0.115</td>
<td>0.123</td>
</tr>
</tbody>
</table>

# Groundwater.
Table 4-5. Continued.

(b) Table 4-5. Continued.

<table>
<thead>
<tr>
<th>Source</th>
<th>UV Absorbance (cm⁻¹) at 254 nm</th>
<th>Before CLN</th>
<th>After CLN</th>
<th>After CLN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH 7</td>
<td>pH 8.5</td>
<td>pH 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br⁻ = 0 µg/L</td>
<td></td>
<td>Br⁻ = 250 µg/L</td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.445</td>
<td>0.452</td>
<td>0.425</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.195</td>
<td>0.198</td>
<td>0.187</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.364</td>
<td>0.369</td>
<td>0.350</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.246</td>
<td>0.255</td>
<td>0.225</td>
</tr>
<tr>
<td>St. Marys River</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.262</td>
<td>0.265</td>
<td>0.250</td>
</tr>
<tr>
<td>Orange Heights GW#</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.263</td>
<td>0.266</td>
<td>0.244</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.240</td>
<td>0.241</td>
<td>0.219</td>
</tr>
<tr>
<td>Lipton Tea</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.093</td>
<td>0.100</td>
<td>0.093</td>
</tr>
<tr>
<td>Nestlé Tea</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.115</td>
<td>0.123</td>
<td>0.115</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source</th>
<th>ΔUV254 (cm⁻¹)</th>
<th>Before CLN</th>
<th>After CLN</th>
<th>After CLN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH 7</td>
<td>pH 8.5</td>
<td>pH 7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Br⁻ = 0 µg/L</td>
<td></td>
<td>Br⁻ = 250 µg/L</td>
</tr>
<tr>
<td>Aldrich Humic Acid</td>
<td>*</td>
<td>0.02</td>
<td>0.002</td>
<td>0.015</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>*</td>
<td>0.008</td>
<td>0</td>
<td>0.014</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>*</td>
<td>0.014</td>
<td>0</td>
<td>0.011</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>*</td>
<td>0.021</td>
<td>0.003</td>
<td>0.014</td>
</tr>
<tr>
<td>St. Marys River</td>
<td>*</td>
<td>0.012</td>
<td>0.004</td>
<td>0.011</td>
</tr>
<tr>
<td>Orange Heights GW#</td>
<td>*</td>
<td>0.019</td>
<td>0.004</td>
<td>0.015</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>*</td>
<td>0.021</td>
<td>0.001</td>
<td>0.017</td>
</tr>
<tr>
<td>Lipton Tea</td>
<td>*</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nestlé Tea</td>
<td>*</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Groundwater.

ΔUV254 = UV254 before chlorination (or chloramination) - UV254 after chlorination (or chloramination)
change in UV254; and the ΔUV254 values of each humic and tea sample at the same pH were essentially the same with or without bromide ion, supporting the finding reported by Symons et al. (1987) that the presence of bromide ion during free chlorination did not appreciably change the amount of TOX produced in μmole/L. Table 4-5 (a) also shows smaller ΔUV254 values of each humic and tea sample at pH 8.5 compared to those at pH 7, which again supports research performed elsewhere that TOX formation decreased with increasing pH as discussed in Chapter 2.

Table 4-5 (b) shows that chloramination induced lesser change in UV254 compared to chlorination, which is consistent with the finding reported by Fleischacker and Randtke (1983) that chloramine produced considerably less NPOCl than did free chlorine. Some trends with respect to bromide ion and pH similar to chlorination were also observed in chloramination, but with less regularity. Since only minor changes of absorbance occurred upon chloramination, very precise UV absorbance measurements were critical.

Chlorination

Table 4-2 summarizes the DBP results of chlorination of the seven humic substances. Total THM and total HAA concentrations were greater for the commercial humic substance (ranging from 441 to 565 μg/L for THM4; ranging from 414 to 606 μg/L for HAA9) than for the extracted
aquatic, soil, and sediment humic substances with the lowest DBP formation associated with the NLS (ranging from 218 to 361 μg/L for THM4; ranging from 197 to 371 μg/L for HAA9). The range of specific THM yields found in this research (44-113 μg of THM4/mg of NPOC) falls in the range reported by Oliver and Thurman (1983) for a set of eight extracted aquatic humic substances from natural waters (25-179 μg of total THMs/mg of TOC). The specific HAA yield found in this research ranged from 39 to 123 μg of HAA9/mg of NPOC.

If the commercial (Aldrich) as well as soil and sediment (OHS and NLS) humic substances were excluded, the specific THM and specific HAA yields found in this research ranged from 72 to 100 μg of THM4/mg of NPOC and from 41 to 119 μg of HAA9/mg of NPOC, respectively. This observation may suggest that for chlorinated natural waters containing humic substances as primary DBP precursors, HAA9 formed may be present at approximately the same levels as the THM4 if all the nine HAAs are considered.

The proposed D/DBP rule addresses only five HAAs (HAA5), and the ICR requires monitoring of six HAAs (HAA6). However, this research has shown that three HAA compounds (TBAA, BDCAA and DBCAA) that will not have MCLs or have monitoring requirements contributed to the total HAA (HAA9) concentrations to some extent. Figure 4-5 shows the mass concentrations of HAA5, HAA6 and HAA9 for chlorination of different aquatic humic substances. The HAA9 concentrations exceed the HAA5 concentrations by more than 27 to 33%-a
Figure 4-5. HAA5, HAA6, and HAA9 Formation of Different Aquatic Humic Substances after 24-Hour Chlorination in the Presence of 250 μg/L Bromide Ion at pH 7.
finding that is similar to the findings of Wu and Chadik (1997).

In addition to THMs and HAAs, all the other target compounds listed in Figure 1-1 were found in chlorinated waters except cyanogen halides. As stated previously in Chapter 2, the presence of free chlorine causes degradation of cyanogen chloride. Xie and Reckhow (1992b) reported, in a holding study, that the half-life of CNCl in the presence of only 1 mg/L free chlorine residual at pH 7 is about 30-40 minutes. The free chlorine residuals of all samples in this research were at least 0.6 mg/L at the end of the 24-hour reaction period. Therefore, even though CNCl may have been initially produced, it also may have been degraded later by residual free chlorine. Although the stability of CNBr in the presence of free chlorine has not been clearly defined, the CNBr produced may be degraded as well.

pH effects. The increasing trend for THM formation and decreasing trend for HAA formation with increasing pH have been well documented as discussed in Chapter 2. The two trends were also shown in this research as presented in Figure 4-6. The n, n', and n" values in Figure 4-6 will be discussed later. For all chlorinated waters at pH 7 with or without the presence of bromide ion, the molar ratios of HAA9 to THM4 ranged from 0.86 to 1.13, with an average of 1.02 and a standard deviation of 0.09. However, for all chlorinated waters at pH 8.5 with or without the presence of bromide ion, the molar ratios of HAA9 to THM4 ranged from
Figure 4-6. DBP Formation at Different pHs and Bromide Ion Concentrations for the Seven Humic Substances in Chlorination.

(a) THMs with $n$ Values.
(b) HANs with $n'$ Values.
(c) HAAs with $n''$ Values.
0.37 to 0.63, with an average of 0.53 and a standard deviation of 0.10. Data shown in Figure 4-6 suggest base catalyzed hydrolysis of HANs since the HAN4 concentrations at pH 8.5 were lower than at pH 7.0. This was particularly evident for the NLS sample. Error bars on Figure 4-6 provide an estimate of the uncertainty associated with these measurements, but the statistical significance of the difference could not be quantified since replicate experiments were only conducted for the NLS and St MR samples. Base catalyzed hydrolysis of HKs was also suggested by the data shown in Table 4-2. CPN is similarly vulnerable to alkaline conditions (Croue and Reckhow, 1989). The base catalyzed hydrolysis was less obvious for CPN reported in this research; probably due to the generally low concentrations found. CH showed a rather irregular formation trend with respect to pH. Stevens et al. (1989a) chlorinated an Ohio River water and showed that CH initially formed most rapidly at pH of 9.4 compared to pHs 7 and 5; but the rate of hydrolysis of CH at this high pH quickly exceeded the rate of formation, and consequently, the CH concentration at pH of 9.4 decreased with time. They concluded that the competing reactions of formation and hydrolysis make prediction of actual CH levels in distribution systems difficult.

**Bromide ion concentration effect.** The effect of bromide ion in chlorination was studied in this research. Figure 4-6 shows that the total micromolar formation of
THM4, HAN4, and HAA9 was fairly constant as the bromide ion concentration increased to 250 µg/L. The increase in bromide ion concentration to 250 µg/L caused changes in the THM species distribution—decreasing chloroform concentrations with increasing bromine-containing THM concentrations (Table 4-2)—a finding consistent with research performed elsewhere. The constant micromolar THM formation with bromide ion addition found in this research is not in line with the expected trend of increasing THM yield with increasing bromide ion concentration reported by Oliver (1980) and Symons et al. (1993). However, the bromide ion ranges reported in the two aforementioned studies were very wide: 0–25 mg/L (Oliver) and 0–6 mg/L (Symons et al.).

To assess the amount of bromine substitution in THMs, an incorporation factor n, defined (Symons et al., 1996) as follows, is used:

\[ n = \frac{\text{THMBr} \, (\mu\text{mol/L})}{\text{TTHM} \, (\mu\text{mol/L})} \]

where THMBr is the sum of molar concentrations of bromine incorporated in the THM species that contain Br, and TTHM represents the sum of molar concentrations of the total number of THM species. Therefore,

\[ \text{THMBr} = (1\times\text{CHCl}_2\text{Br}) + (2\times\text{CHClBr}_2) + (3\times\text{CHBr}_3) \]

Thus, \( n = 0 \) corresponds to the formation of only chloroform (virtually no ambient bromide ion present); whereas \( n = 3 \) corresponds to THM formation exclusively as bromoform.
(extremely high ambient bromide ion present, not found in natural fresh waters).

Values of THM bromine incorporation factor are shown in Figure 4-6 (a) and indicate that the degree of bromine incorporation was very low at the conditions used in this research: NPOC = 5 mg/L, Br⁻ = 250 µg/L, and Cl₂ dose = 12.5 mg/L. On the other hand, Symons et al. (1993, Figure 16) reported bromine incorporation factors as high as 2.65 with bromide ion as high as 6 mg/L at similar conditions of organic carbon concentration = 5 mg/L and Cl₂ dose = 20 mg/L. Therefore the bromine incorporation caused by the realistic bromide ion concentration of 250 µg/L used in this research was markedly different than the wide bromide ranges used by Symons et al. (1993).

The relative insensitivity of HAA9 formation to changes in bromide ion concentration as shown in Figure 4-6 (c) is consistent with the finding reported by Cowman and Singer (1996). The addition of bromide ion led to reduced yields of HKs, CH, and CPN as indicated in Table 4-2. As discussed in Chapter 2, when bromide ion is present, brominated analogs of those DBPs are formed, but they were not quantitated in this research.

The HAN analog to n for the THMs in this study is defined as follows:

\[ n' = \frac{\text{HANBr}_2 \ (\mu\text{mol/L})}{\text{THAN} \ (\mu\text{mol/L})} \]

where HANBr₂ is the sum of molar concentrations of bromine incorporated in the two HAN species that contain Br,
and THAN represents the sum of molar concentrations of the total number of HAN species. Therefore,

\[ \text{HANBr}_2 = (1\times\text{BCAN}) + (2\times\text{DBAN}) \]

Likewise, the HAA analog to \( n \) for the THMs in this study is defined as follows:

\[ n'' = \frac{\text{HAABr}_6}{\text{HAA}_9} \]

where HAABr6 is the sum of molar concentrations of bromine incorporated in the six HAA species that contain Br, and HAA9 represents the sum of molar concentrations of the total number of HAA species. Therefore,

\[ \text{HAABr}_6 = (1\times\text{MBAA}) + (2\times\text{DBAA}) + (3\times\text{TBAA}) + (1\times\text{BCAA}) + (1\times\text{BDCAA}) + (2\times\text{DBCAA}) \]

The higher \( n \) can be translated to higher bromine incorporation into THM species, so do \( n' \) and \( n'' \) for HAN and HAA species, respectively. Figure 4-6 shows that there were some variation of the bromine incorporation factors among different samples. Aldrich consistently showed lowest bromine incorporation factors, while Newnans Lake samples (NL DOC or NLS) tended to show highest bromine incorporation factors.

Bromine incorporation in THM as well as HAN and HAA formation and the variability in the bromine incorporation factors as a function of the type of humic substances can be better understood by examining the reactivity of the humic substances to form DBPs. HOBr is a stronger halogenating agent compared to chlorine species even when the chlorine concentration is in excess (Luong et al., 1982); and the
reaction between humic material and HOBr is faster compared to humic material and chlorine species (Oliver, 1980). A mechanistic metaphor describes HOBr, a stronger halogenating agent, is analogous to a "bully", while HOCl, a weaker halogenated agent, is analogous to a "mob" (Symons et al., 1996). Thus metaphorically speaking, a few bullies are out-competing a mob for active sites in humic structures.

In DBP formation, chlorine and bromine species tend to attack the activated aromatic rings in humic structures. One semiquantitative measure of the active sites in humic structures is UV254. Aldrich humic substance has the highest UV254 (Table 4-5); therefore, HOCl can compete more favorably with HOBr in solutions containing Aldrich humic substance whose smallest bromine incorporation factors indicate little limitation of active sites. The NLS and NL DOC with the two lowest UV254 represent a contrasting situation; therefore, the two samples tended to show highest bromine incorporation factors. Figure 4-7 illustrates the aforementioned observation. The correlation coefficient for HANs was the poorest among others because nitrogen content, an important factor in HAN formation (Reckhow et al., 1990), was not considered in this graph.

Another way to examine the relationship between DBP formation and Br⁻ concentration is through the ratio of free available chlorine to bromide ion concentration. The free available chlorine concentration changes as it oxidizes organic matter. Since it cannot be calculated at every
Figure 4-7. Relationship Between Bromine Incorporation Factors and UV254 for the Seven Humic Substances in Chlorination.
(a) At pH 7.
(b) At pH 8.5.
moment during the incubation, the average free available chlorine concentration, defined (Symons et al., 1996) as follows, is used to represent the extent of free available chlorine "driving the THM and HAA formation reaction during incubation":

\[ Cl^+ = \frac{(\text{initial Cl}_2 + \text{residual Cl}_2)}{2} \]

Symons et al. (1996) indicated that the molar ratio of the initial \( Br^-/Cl^+ \) plays an important role in bromine substitution during THM and HAA formation. As the \( Br^-/Cl^+ \) ratio increases, more bromine becomes available for oxidation and substitution, and because bromine is more reactive in substitution reactions than chlorine, greater bromine incorporation may be expected. Wu and Chadik (1997) also reported that as the \( Br^-/Cl^+ \) ratio increases, bromine incorporation in HAAs increases accordingly.

The observation mentioned above was primarily derived from bromide ion spiked samples with the same origin of organic precursor (a water from a single source). Figure 4-8 shows that the correlation between \( Br^-/Cl^+ \) ratio and bromine incorporation was not significant among different organic precursors even at the same NPOC concentration. Further data analyses examined later indicate that there was a significant difference between chlorine species and humic substances with respect to DBP yield. The reaction between HOBr "bullies" and DBP precursors was, as indicated in Figure 4-8, also influenced by the nature of humic substances.
Figure 4-8. Relationship Between Bromine Incorporation Factor and Br⁻/Cl⁺ Ratio for the Seven Humic Substances in Chlorination.
(a) At pH 7.
(b) At pH 8.5.
Chloramination

Table 4-3 summarizes the DBP results of chloramination of the seven humic substances. Both quantitative formation and speciation of the DBPs were dramatically different in chloraminated waters compared to chlorinated waters. Chloramination produced less than 5% of the THM4 produced by chlorination, and HAA9 formation by chloramination was from 86-95% lower than the HAA9 concentration produced by chlorination. DCAA was the principal HAA species formed from chloramination, but observed concentrations did not exceed 40 μg/L. Some brominated HAA species were observed from chloramination in the presence of 250 μg/L bromide ion, principally MBAA, DBAA, and BCAA. Formation of the trihalogenated HAAs was greatly suppressed by chloramination. Namely, the dihalogenated HAAs were the principal species formed, while trihalogenated HAAs were the minor species. Therefore, DCAA formation may continue to be an issue even in chloraminated waters.

The suppression of trihalogenated DBP formation was also observed in the formation of HANs and HKs. TCAN, while detected in chlorinated waters, was below detection limit in all chloraminated samples. In chloramination, TCPO concentrations greatly decreased, but DCPO concentrations increased compared to chlorination.

The aforementioned finding supports the interpretation of DBP formation in chloramination as a special case of
chlorination with very low chlorine doses present (Jolley and Carpenter, 1983; Cowman and Singer, 1996; Oxenford, 1996). In chloramination, DBP formation may be occurring through the reaction between humic substances and small amounts of free chlorine in equilibrium with chloramines. Such an explanation, in terms of HAA, HAN, and HK formation reported in this research, appears to agree with the observed predominance of dihalogenated DBP species over the trihalogenated forms in chloraminated waters.

All the target compounds listed in Figure 1-1 were found in chloraminated waters except TCAN and CNBr. TCAN formation was less than 0.25 μg/L in chlorinated waters (Table 4-2). The absence of TCAN in chloramination is not surprising since HANs are formed at lower amounts with chlorammines as discussed in Chapter 2.

CNBr was not detected in any of the chloraminated samples. In light of the low CNBr MDL of 0.96 μg/L, it was concluded that any small concentrations of CNBr formed should be detected. The formation of CNBr (up to ~ 0.12 μM) was reported by chloraminating a series of fulvic acid solutions (DOC = 5 mg/L) containing varying amounts of bromide ion (Xie and Reckhow, 1993). However, under the conditions of their study, a two-hour chlorination preceded a 48-hour chloramination. Krasner et al. (1991) reported the presence of CNBr in the pilot plant which used ozone and PEROXONE in preoxidation and used chloramines as a final disinfectant. The postulate of a strong pre-oxidant (i.e.,
chlorine or ozone) used to form the appropriate precursor for CNCl formation has been discussed in Chapter 2. While pre-chlorination may result in higher overall CNCl production, a strong pre-oxidant may be required for CNBr formation, which was not practiced in this research.

**pH effects.** Figure 4-9 (a) shows that the increasing trend for THM formation with increasing pH was not observed in the chloramination investigated. Arber et al. (1985) showed that the amounts of THMs formed at far to the left of breakpoint (Cl₂:NH₃-N < 5:1, monochloramines predominate) were about half the amounts produced at just to the left of breakpoint (5:1 < Cl₂:NH₃-N < 7.6:1, dichloramines predominate). Although the chloramine dosages applied at both pH conditions were the same, the actual chloramine species were different. Figure 2-1 shows that as pH reaches 8.5, almost all of the combined chlorine consists of the monochloramine species; whereas at pH 7, the dichloramine species generally accounts for five percent of the chloramines formed. The presence of more dichloramine at pH 7 may lead to more THM formation.

Except THMs, other DBP formation was consistent with research performed elsewhere. Figure 4-9 (b) and (c) as well as Table 4-3 shows decreasing concentrations of HAAs, HANs, HKs, CH, CPN, and CNCl with increasing pH.

**Bromide ion concentration effect.** Figure 4-9 shows that the total micromolar formation of THMs, HANs, and HAAs was fairly constant over the range of bromide ion...
Figure 4-9. DBP Formation at Different pHS and Bromide Ion Concentrations for the Seven Humic Substances in Chloramination.

(a) THMs with n Values.
(b) HANs with n' Values.
(c) HAAs with n" Values.
concentration reported in chloramination. The reduced yields of HKs, CH, and CPN as the addition of bromide ion were also observed as indicated in Table 4-3.

To assess the amount of bromine substitution in THMs, HANs, and HAAs, incorporation factors n, n', and n'' are also shown in Figure 4-9. If chloramination is viewed as a special case of chlorination with very low chlorine doses present, the Br⁻/Cl⁺ ratios in chloramination should be higher than their counterparts in chlorination. According to the previous discussion that as the Br⁻/Cl⁺ ratio increases for the organic precursor of the same origin, greater bromine incorporation may be expected. Therefore, in chloramination at pH 7, greater n, n', and n'' values (Figure 4-9) were observed compared to chlorination at the same pH (Figure 4-6) with only a few exceptions. However, the comparison between the waters in chlorination and chloramination both at pH 8.5 exhibited a rather irregular trend. The exception and irregularity may be due to the different degree of activation of the humic structure through oxidation reactions (Luong et al., 1982) between chlorination and chloramination. The higher chlorine concentration found in chlorination halogenates both active precursor sites and some more difficult to halogenate precursor sites. The small amounts of free chlorine in equilibrium with monochloramine may only react with the most active sites, which leads to different reacting properties of precursor materials between chlorination and
chloramination even though the apparent precursor materials are the same.

**The Effect of Structural Characteristics of Humic Substances on DBP Formation**

In the following discussion, efforts were made to correlate the observed DBP yields with the characterization results. Considering the complex nature of humic substances and the relatively limited data set, good correlations were not always obtained between certain structural characteristics and DBP formation. Selected modifications to the correlation variables allowed improved goodness-of-fit, as measured by the coefficient of determination ($r^2$) for linear correlation. These modifications were made based on sound chemical intuition regarding the character of humic material and its effect on DBP formation.

The humic substance characteristics including elemental analysis, UV/VIS spectroscopy, total acidity titration, IR spectroscopy, and $^{13}$C NMR were listed in Table 2-4 through Table 2-9 (excluding Table 2-7). The relationship between the humic substance characteristics and DBP formation as well as chlorine consumption was examined in this section.

**Elemental Analysis**

The results of elemental analysis presented in Table 2-4 show little variation of elemental compositions for the humic substances investigated; except that the nitrogen composition of the NLS was substantially higher than the
nitrogen composition of other humic substances in this study. Reckhow et al. (1990) reported the DCAN concentration correlated well with the nitrogen content in their chlorinated waters containing humic substances in the absence of bromide ion. This dissertation research extended the correlation analysis to more DBPs formed in chlorination as well as chloramination and included DBP formation in the presence of bromide ion.

In chlorination, Figure 4-10 shows that DCAN and the sum of the two species (DCAN and TCAN) correlated well with organic nitrogen content of humic substance in the absence of bromide ion. The correlation between TCAN and organic nitrogen content is questionable even though the regression coefficient is high because of the low TCAN concentrations reported. Figure 4-11 illustrates that DCAN, BCAN, and the sum of the four target HANs correlated well with the organic nitrogen content in the presence of 250 μg/L bromide ion. The correlations between TCAN as well as DBAN and organic nitrogen content is questionable because of the low concentrations detected.

Examination of Figures 4-10 and 4-11 in the organic-N range of 3 to 6 μM reveals a poorer correlation between the organic-N and DBP formation in that range. The single point of NLS (organic-N of 21.2 μM or 296 μg/L) largely influences the regression coefficient. Considering the complexity of the reactions between the oxidants and the humic substances under investigation and the inherently broad nature of the
Figure 4-10. Relationship Between HAN Formation and Organic Nitrogen Content for the Seven Humic Substances in the Absence of Bromide Ion at pH 7 in Chlorination (some points are overlapping).
Figure 4-11. Relationship Between HAN Formation and Organic Nitrogen Content for the Seven Humic Substances in the Presence of 250 μg/L Bromide Ion at pH 7 in Chlorination (some points are overlapping).
nitrogen moiety in the humic substances, the narrow organic-N range of 3 to 6 μM (50 to 80 μg/L) may not grant a reasonable differentiation in terms of increasing N-containing DBP concentrations. To compare this observation with the finding reported by other researchers, Figure 4-10 was therefore redrawn in mass unit as showed in Figure 4-12. A figure showing the effect of organic-N in humic substances on HAN formation expressed in mass unit (Reckhow et al., 1990) is presented in Figure 4-12 as an inset on the upper left corner. For the narrow organic-N range between about 80 to 130 μg/L reported in their study, a reasonable correlation could not be obtained among those fulvic acids.

From another point of view, a much higher nitrogen content like that of NLS may indicate an ultimate trend of increasing HAN concentrations if some humic substances should contain much higher nitrogen content. Rice and MacCarthy (1991) reported nitrogen contents (expressed as weight percent) ranging from 0.50 to 7.00% for soil humic acids with a mean of 3.6%; from 0.45 to 5.87% for soil fulvic acids with a mean of 2.6%; from 0.63 to 7.97% for freshwater humic acids with a mean of 2.6%; from 0.47 to 8.16% for freshwater fulvic acids with a mean of 2.3%. Although the NLS nitrogen content (2.51% expressed as weight percent) is substantially higher than those of other humic substances in this study (Table 2-4), it is still within the ranges reported by Rice and MacCarthy (1991).
Figure 4-12. Relationship Between HAN Formation and Organic Nitrogen Content for the Seven Humic Substances in the Absence of Bromide Ion at pH 7 in Chlorination.

While the aforementioned regression equations are interesting from a predictive standpoint, they fail to take into account variabilities among the humic structures with respect to their reactivity to chlorine. As discussed in Chapter 2, ΔUV254 was reported to be an estimation of the destruction of activated aromatic rings which leads to chlorinated byproduct formation (Korshin et al., 1996). Therefore, a more appropriate relationship would be between N-containing DBP/ΔUV254 and organic-N/organic-C (Figures 4-13 and 4-14). Indeed, this approach gives better correlations based on regression coefficients compared to Figures 4-10 and 4-11. An inset on the upper left corner of Figure 4-13 will be discussed later. This approach also gives better correlations for those points around 0.01 organic-N/organic-C ratio in Figures 4-13 and 4-14 (or around 5 μM organic-N in Figures 4-10 and 4-11). If the NLS point was excluded, the regression equations of HAN Sum of Figures 4-10, 4-13, 4-11, and 4-14, respectively, can be expressed as follows:

\[
\begin{align*}
\text{Figure 4-10} & : y = -1.00 \times 10^{-4}x + 5.05 \times 10^{-2} \quad r^2 = 2.11 \times 10^{-4} \\
\text{Figure 4-13} & : y = 35.645x + 0.240 \quad r^2 = 0.294 \\
\text{Figure 4-11} & : y = -1.33 \times 10^{-3}x + 5.80 \times 10^{-2} \quad r^2 = 8.99 \times 10^{-2} \\
\text{Figure 4-14} & : y = 39.185x + 0.186 \quad r^2 = 0.429
\end{align*}
\]

The molar ratio of organic-N/organic-C gives a better account of the availability of nitrogen moiety in humic structures for the reactions between oxidants and humic
Organic-N/Organic-C (molar ratio):

- TCAN: $y = 0.632x + 0.001 \quad r^2 = 0.990$
- DCAN: $y = 58.986x - 0.033 \quad r^2 = 0.982$
- HAN Sum: $y = 59.618x - 0.032 \quad r^2 = 0.982$

Figure 4-13. Relationship Between HAN Formation/ΔUV254 and the Ratio of Organic Nitrogen to Organic Carbon for the Seven Humic Substances in the Absence of Bromide Ion at pH 7 in Chlorination.

Figure 4-14. Relationship Between HAN Formation/ΔUV254 and the Ratio of Organic Nitrogen to Organic Carbon for the Seven Humic Substances in the Presence of 250 μg/L Bromide Ion at pH 7 in Chlorination.
substances. Since all the samples in this research were 5 mg/L NPOC samples, molar organic-N content may effectively represent molar ratio of organic-N/organic-C. The molar ratio was used here to make a direct comparison to a figure reported by Reckhow et al. (1990). They reported an improved correlation between DCAN/TOX ratio and the ratio of organic-N/organic-C shown as an inset in Figure 4-13. The replacement of TOX by ΔUV254 in Figures 4-13 and 4-14 still shows a comparable result, experimentally indicating ΔUV254 is a good estimation of activated aromatic ring destruction which leads to organic halogen formation.

The same approach (N-DBP/ΔUV254 vs. N/C) was used to investigate other nitrogen containing DBPs. Figure 4-15 shows that CPN concentration correlated well with the nitrogen content. The correlation is slightly better in (a), probably because the brominated analog, bromopicrin, was not quantitated in (b). The correlation between humic substance nitrogen content and CNCl formation resulting from chloramination is presented in Figure 4-16. The correlation in (b) is not significant, probably because the brominated analog, CNBr, was not included.

However, the correlation between those points around 0.01 organic-N/organic-C ratio in Figures 4-15 and 4-16 appears to be lower. If the NLS point (organic-N/organic-C ratio of 0.051) was excluded, the regression equations of Figures 4-15 and 4-16 can be expressed as follows:

Figure 4-15 (a) \( y = 3.276x - 0.007 \quad r^2 = 0.096 \)
Figure 4-15. Relationship Between CPN Formation/ΔUV254 and the Ratio of Organic Nitrogen to Organic Carbon for the Seven Humic Substances at pH 7 in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
Figure 4-16. Relationship Between CNCl Formation/A\text{UV254} and the Ratio of Organic Nitrogen to Organic Carbon for the Seven Humic Substances at pH 7 in Chloramination.

(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 \( \mu \)g/L Bromide Ion.
(b) \( y = 0.897x + 0.010 \) \( r^2 = 0.052 \)

\[
\text{Figure 4-16 (a) } y = -72.629x + 6.435 \quad r^2 = 0.012
\]
\[
\text{(b) } y = -164.746x + 7.906 \quad r^2 = 0.078
\]

Then the correlations between CPN as well as CNCl concentration and organic-N/organic-C ratio were not significant.

Similar to the case of HANs, current data suggest that a much higher nitrogen content may lead to an ultimate trend of increasing CPN and CNCl concentration. However, a reasonable differentiation in terms of increasing CPN and CNCl formation could not be obtained from the narrow organic-N range of 50 to 80 \( \mu g/L \) reported in this research.

The H/C ratio has often been used to indicate the degree of aromaticity (a small value) or aliphaticity (a large value) of humic substances (Thurman, 1985a). In other words, H/C ratio is inversely proportional to aromaticity. As discussed in Chapter 2, the H/C ratio thus appears to be a qualitatively useful parameter for comparing the aromaticities of humic substances (Rice and MacCarthy, 1991); and aromaticity of humic substances correlates well with DBP formation and chlorine consumption.

The correlation between C/H ratio and THM as well as HAA formation is presented in Figure 4-17; C/H ratio, instead of H/C ratio discussed above, was used here in order to obtain a positive correlation. The correlations between C/H ratio and the formation of THMs and HAAs were remarkably
Figure 4-17. Relationship Between DBP Formation and C/H Molar Ratio for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
good considering the only qualitative nature of C/H ratio and the wide variation in source characteristics.

Figure 4-18 illustrates the correlation between C/H ratio and chlorine consumption for the seven humic substances in chlorination. For waters investigated under the conditions used in this research, a good linear relationship between chlorine consumption and C/H ratio characterizing the entire data set could not be obtained. All regressions in Figure 4-18 were not significant at \( p < 0.05 \). Reckhow et al. (1990) indicated that the tendency of an organic molecule to react with aqueous chlorine is probably less sensitive to specific molecular structure than is its tendency to form any specific DBPs like THMs; therefore it is more likely that the correlation between structural properties and chlorine consumption is generally stronger. However, the poorer correlation shown in Figure 4-18 compared to Figure 4-17 contrasts with the relationship reported by Reckhow et al. (1990). No explanation for this finding is apparent. To the best of the author's knowledge, the correlation between C/H ratio and chlorine consumption has not been previously studied in water chemistry settings. Additional research is clearly warranted to fully evaluate this finding.

**UV/VIS Spectroscopy**

UV254 is often a good surrogate parameter for DBP formation potential (Edzwald et al., 1985; Singer and Chang,
Figure 4-18. Relationship Between Chlorine Consumption and C/H Molar Ratio for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
Figure 4-19 illustrates the correlation between THM and HAA formation and UV254. The regression fitting results were not as impressive as the correlations reported by Edzwald et al. (1985) (THMs vs. UV254 for raw waters, $r^2 = 0.82-0.94$) as well as Singer and Chang (1989) (THMs vs. UV254 for raw waters, $r^2 = 0.799$). However, the correlations reported in this research are certainly consistent with the claim that THM formation correlates well with UV254; and the regressions reported in Figure 4-19 were significant at $p < 0.05$. The inferior regression coefficients may be attributed to the limited data ($n = 7$) included in this research compared to the two aforementioned studies ($n = 42-54$ by Edzwald et al.; $n = 42$ by Singer and Chang).

As discussed in Chapter 2, initial UV254 measured before disinfection may only characterize the possible amount (viewed as potential) of activated aromatic ring in a particular organic matrix to form DBPs; but it does not represent the actual estimation of activated aromatic ring destruction which leads to DBP formation (viewed as reactivity). The relationship between initial UV254 measured before chlorination and $\Delta$UV254 is illustrated in Figure 4-20. The figure shows that even though there was a linear correlation between UV254 and $\Delta$UV254, some variation did occur. Therefore, it is advantageous to use $\Delta$UV254 to replace UV254 in correlation analysis. Figure 4-21 is a plot of THM and HAA formation versus $\Delta$UV254; this approach
Figure 4-19. Relationship Between DBP Formation and UV254 for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
Figure 4-20. Relationship Between Initial UV254 and ΔUV254 for the Seven Humic Substances in Chlorination. (a) In the Absence of Bromide Ion. (b) In the Presence of 250 µg/L Bromide Ion.
Figure 4-21. Relationship Between DBP Formation and ΔUV254 for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
consistently gives better correlations compared to those in Figure 4-19. However, it should be noted that although ΔUV254 was used to correlate with DBP formation, ΔUV254 per se is not a structural characteristic of humic substances.

Korshin et al. (1996) have proposed that if the reactions between chlorine and the aromatic rings it attacks have a constant DBP yield for a water from a single source, then a fixed ΔUV254 should correspond to a fixed amount of that DBP formed. However, this observation could not be extended to waters with wide variation in source characteristics used in this research. The relationship between the concentration of DBPs formed per unit ΔUV254 and UV254 is presented in Figure 4-22. THM and HAA yields per unit change in UV254 tended to decrease with increasing UV254. Figure 4-23 further illustrates that THM and HAA yields per unit change in UV254 also tended to decrease with increasing ΔUV254. This observation may be concluded that the larger number of active sites in NOM associated with higher UV254 (or higher ΔUV254 according to the relationship revealed in Figure 4-20) may lead to relatively less degree of chlorine substitution and, therefore, higher degree of chlorine oxidation if considered as per unit change in UV254.

The correlation between UV254 and chlorine consumption for the seven humic substances in chlorination is presented in Figure 4-24; all regressions were significant at $p < 0.05$. Figure 4-25 illustrates a plot of ΔUV254 versus
Figure 4-22. Relationship Between DBP Formation (μM)/ΔUV254 and UV254 for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
Figure 4-23. Relationship Between DBP Formation ($\mu$M)/$\Delta$UV254 and $\Delta$UV254 for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 $\mu$g/L Bromide Ion.
Figure 4-24. Relationship Between Chlorine Consumption and UV254 for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
Figure 4-25. Relationship Between Chlorine Consumption and ΔUV254 for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
chlorine consumption; and again this approach consistently gives better correlations compared to those in Figure 4-24. As discussed previously in Figures 4-17 and 4-18, the correlation between C/H ratio and chlorine consumption was poorer compared to that between C/H ratio and DBP formation. However, the correlation between UV254 (or ΔUV254) and chlorine consumption was comparable with that between UV254 (or ΔUV254) and DBP formation. Although Reckhow et al. (1990) stated that the correlation between structural properties and chlorine consumption is generally stronger than that between structural properties and DBP formation, the correlation coefficients reported in the paired figures, (Figures 19 and 24) and (Figures 21 and 25), were close to each other. It may indicate that UV254 and ΔUV254 are qualitative indicators for both chlorine consumption and DBP formation.

The question remaining for the application of the ΔUV254 in the DBP formation investigation of humic substances is: whether or not ΔUV254 is a better surrogate than chlorine consumption. Chlorine consumption has been shown to be a reasonably good indicator of the extent of DBP production (Singer et al., 1995). To further address this question, the correlation between chlorine consumption and DBP formation (Figure 4-26) was compared with the correlation between ΔUV254 and DBP formation (Figure 4-21). In all of these comparisons made at each pH and with or without bromide ion, ΔUV254 was consistently a better
Figure 4-26. Relationship Between DBP Formation and Chlorine Consumption for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
surrogate for DBP formation than was chlorine consumption, based on the regression coefficient \( (r^2) \). Further statistic analysis shows that not all regressions in Figure 4-26 were significant at \( p < 0.05 \). This observation can be easily explained by that \( \Delta U V 254 \) may be more representative of destruction of activated aromatic rings which leads to chlorinated byproduct formation, while chlorine consumption is rather a composite measurement due to not only chlorine substitution but also chlorine oxidation. For a natural water, chlorine demand may be further related to other inorganic and organic compounds that are not involved in DBP formation.

The \( E_4/E_6 \) ratio has been discussed in Chapter 2: lower ratios reflect relatively higher degree of condensation of aromatic constituents; lower ratios indicate larger reduced viscosity (related to larger molecular weight); and lower (higher) ratios imply the presence of relatively more aromatic (less aliphatic) structures. While it has been reported that aromaticity of humic substances correlates well with DBP formation and chlorine consumption (Reckhow et al., 1990; Harrington et al., 1996) and that molecular weight (size) correlates well with THM formation (Oliver and Thurman, 1983), there are not enough data available to conclude the contribution of the degree of condensed aromatic rings to the aforementioned correlations.

The correlation between \( E_6/E_4 \) and THM as well as HAA formation is presented in Figure 4-27; \( E_6/E_4 \) ratio, instead
Figure 4-27. Relationship Between DBP Formation and E6/E4 Ratio for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
of E4/E6 ratio discussed above, was used here in order to obtain a positive correlation. There did not appear to be any significant correlation between E6/E4 and formation of THMs as well as HAAs based on the poor correlation coefficients; all regressions in Figure 4-27 were not significant at p < 0.05.

In contrast, the chlorine consumption varied somewhat linearly and showed better correlation with E6/E4 ratio as shown in Figure 4-28. Chen et al. (1977) have concluded that humic substances contain aromatic rings; but the occurrence of significant concentrations of aromatic structures exclusively or even largely composed of condensed rings is unlikely. However, even though the presence of the condensed rings may not play an important role, the improved correlation between chlorine consumption and E6/E4 ratio may better represent the chlorine demand including that due to the destruction of condensed aromatic rings, which did not necessarily lead to DBP formation.

However, if the NLS (E6/E4 = 0.24) was excluded from Figure 4-27, improved correlations between E6/E4 and DBP formation can be observed as showed in Figure 4-29; and the regressions of THMs were significant at p < 0.05. Ertel and Hedges (1983) reported a linear correlation \( r^2 = 0.85 \) between the E4/E6 ratios and the H/C ratios for seventeen terrestrial and synthetic humic acids; and Davis (1993) reported that the E4/E6 ratios were also correlated with the H/C ratios for the humic substances studied in this
Figure 4-28. Relationship Between Chlorine Consumption and E6/E4 Ratio for the Seven Humic Substances in Chlorination.

(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
Figure 4-29. Relationship Between DBP Formation and E6/E4 Ratio for the Six Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
research. The relationship was further illustrated by combining data of Ertel and Hedges (1983) and from Nissenbaum and Kaplan (1970) with the results from Davis' dissertation (1993); and the relationship showed that the marine humic acids and the NLS humic substance appeared above the other humic substances in a figure correlating E4/E6 ratios in x-axis with H/C ratios in y axis (Figure 3.2, Davis, 1993). Ertel and Hedges (1983) have reported that marine humic acids had low E4/E6 ratios compared to their H/C ratios, implying that the aromaticity estimated by E4/E6 ratios may be higher compared to the aromaticity estimated by H/C ratios for marine humic substances. The low E4/E6 ratios for marine humic substances were reported due to pigment absorption near 665 nm (Nissenbaum and Kaplan, 1970). Lake sedimentary humic substances are similar to marine humic substances in their H/C ratio (Ishiwatari, 1985); and sedimentary humic substances from some eutrophic lakes were reported to contain chromophore groups due to plant-derived pigments (Klavins and Apsite, 1997). Therefore, the E4/E6 ratio of NLS might overestimate the aromatic content compared to that by H/C ratio. In light of this, the aromaticity estimated by E4/E6 ratio of NLS was probably anomalous and should not be included in the DBP comparison deduced from aromaticity.

Further examination of Figure 4-29 in the E6/E4 range of 0.14 to 0.23 (five points) reveals a poorer correlation between the E6/E4 ratio and the DBP formation in that range.
The single point of Aldrich may largely influence the regression coefficient. If both Aldrich and OHS were excluded from Figure 4-29, the correlation for the remaining four points of aquatic humic substances is rather poor, indicating that there is no linear relationship between the E6/E4 ratio of the studied aquatic humic substances and the DBP formation. Several researchers have investigated the E4/E6 ratio of aquatic humic substances; and these studies reached no conclusions on the relationship of E4/E6 ratio to the structure of aquatic humic substances (Thurman, 1985a).

Total Acidity Titration

The H/C ratio has often been used to indicate the degree of aromaticity as discussed previously; however, the reasoning has been questioned because it does not consider the contribution of carbon to oxygen double bonds to the H/C ratio since both COOH and -HC=CH- have the same H/C ratio (Rice and MacCarthy, 1991).

As discussed in Chapter 2, the acidic nature of humic substances is attributed to both COOH and acidic OH groups (presumed to be phenolic OH), with COOH being the most important. Davis (1993) reported that the IR data for the carboxylic acid content (1700 cm⁻¹) of these humic substances studied in this research correlated well with their total acidity values \( r = 0.80, p < 0.01 \), indicating that the phenolic content was low compared with the amount of carboxylic acid. Assuming the number of acidic OH groups
is negligible compared to that of COOH group (assuming total acidity is entirely attributable to COOH), a new H/C ratio with exclusion of COOH group can be derived by solving the following two equations with all terms expressed in units of mmole/L:

\[ C_{rest} + C_{COOH} = C = 5/12 \]  
\[ H/C = \frac{(H_{rest} + H_{COOH})}{C} = \frac{(H_{rest} + H_{COOH})}{(5/12)} \]

Where \( C_{COOH} \) stands for the amount of carbon existing in the COOH group; and \( C_{rest} \) represents the total carbon with exclusion of \( C_{COOH} \). Similarly, \( H_{COOH} \) stands for the amount of hydrogen existing in the COOH group; and \( H_{rest} \) represents the total hydrogen with exclusion of \( H_{COOH} \). Recall that the NPOC in solutions containing the studied humic substances was 5 mg/L, 5/12 represents the carbon concentration expressed in mmole/L.

There is an equal number of carbon and hydrogen in the COOH group; therefore, the eq. 4-2 can be rearranged to:

\[ C_{rest} = 5/12 - H_{COOH} \]

By rearranging eq. 4-3, \( H_{rest} \) can be determined:

\[ H_{rest} = H/C \times 5/12 - H_{COOH} \]

Assuming the total acidity consists of only the COOH group, \( H_{COOH} \) can be derived from the total acidity reported previously in Chapter 2. The modified H/C ratio \( (H_{rest}/C_{rest}) \) can therefore be calculated and listed in Table 4-6 along with H/C ratio and total acidity.

It is apparent that the difference between H/C ratio and \( H_{rest}/C_{rest} \) ratio was very small based on the results of
Table 4-6. Total Acidity, H/C Ratio, and $H_{rest}/C_{rest}$ Ratio of the Humic Substances Studied in This Research.

<table>
<thead>
<tr>
<th>Source</th>
<th>Total Acidity$^%$ (meq H$^+$/g Humic C)</th>
<th>H/C Ratio</th>
<th>$H_{rest}/C_{rest}$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich Humic Acid</td>
<td>14.50</td>
<td>0.84</td>
<td>0.81</td>
</tr>
<tr>
<td>Newnans Lake Sediment</td>
<td>19.88</td>
<td>1.35</td>
<td>1.46</td>
</tr>
<tr>
<td>Orange Heights Soil</td>
<td>18.66</td>
<td>1.11</td>
<td>1.14</td>
</tr>
<tr>
<td>Santa Fe River</td>
<td>17.00</td>
<td>0.90</td>
<td>0.87</td>
</tr>
<tr>
<td>St. Marys River</td>
<td>18.06</td>
<td>0.90</td>
<td>0.87</td>
</tr>
<tr>
<td>Orange Heights GWS</td>
<td>15.50</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td>Newnans Lake</td>
<td>15.15</td>
<td>1.10</td>
<td>1.12</td>
</tr>
</tbody>
</table>

$^\%$ Normalized to the carbon mass of the humic substance.
$^\S$ Groundwater.
computation summarized in Table 4-6. In other words, the contribution of COOH group to the H/C ratio was not so significant as previously thought. The correlation between $C_{\text{rest}}/H_{\text{rest}}$ and THM as well as HAA formation is presented in Figure 4-30; $C_{\text{rest}}/H_{\text{rest}}$ ratio, instead of $H_{\text{rest}}/C_{\text{rest}}$ ratio discussed above, was used here to obtain a positive correlation. The correlations between $C_{\text{rest}}/H_{\text{rest}}$ ratio and the formation of THMs and HAAs were generally slightly better compared to those in Figure 4-17.

**Infrared Spectroscopy**

The quantitative IR technique used an internal standard to compensate for the variation in sample preparation and instrumental operation between different samples (Davis, 1993). Therefore the normalized (to internal standard) IR measurements listed in Table 2-8 allow a direct quantitative comparison of specific functional group compositions among the different humic substances.

As discussed in Chapter 2, the absorbance in the 1650 to 1600 cm$^{-1}$ region of the spectra has been attributed to a combination of aromatic carbon, carboxylate anion, and ketonic carbon (Table 2-7). However, in the spectra recorded at pH 4, there should be very little contribution from carboxylate anion. The $^{13}$C-NMR spectra indicate that there was very little or no ketonic carbon in these humic substances (Table 2-9); numerous $^{13}$C-NMR studies have also found very little or no ketonic carbon present in the humic
Figure 4-30. Relationship Between DBP Formation and Crest/Hrest Molar Ratio for the Seven Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 μg/L Bromide Ion.
substances investigated as compiled by Davis (1993, p.141-p.142). In addition, water absorbs in the 1650 to 1600 cm\(^{-1}\) region; however, the preparation of samples as discussed in Chapter 2 likely precluded the presence of water interference. Therefore, it leads to the conclusion that the mean IR absorption in the 1650 to 1600 cm\(^{-1}\) region of spectra at pH 4, for these humic substances investigated in this research, was due primarily to aromatic carbon (Davis, 1993).

As previously discussed, aromaticity of humic substances correlates well with DBP formation and chlorine consumption. The mean IR absorption for NLS in the 1650 to 1600 cm\(^{-1}\) region of spectra at pH 4 was only second to Aldrich (Table 2-8b), implying the aromaticity of NLS was probably among the highest values; however, it is opposite to the finding inferred by its highest H/C ratio (Table 2-4). The spectra of the humic substances studied in this research contained significant peaks in the 1650 to 1600 cm\(^{-1}\) region; the peaks were centered at 1610 ± 5 cm\(^{-1}\) in the spectra recorded at pH 4, with the exception of the NLS which was closer to 1650 cm\(^{-1}\) (Davis, 1993). Aromatic C=C vibration has been reported to absorb over this entire range (Stevenson, 1994); however, electron withdrawing substituents and asymmetric substitution are known to shift the aromatic C=C frequency to near 1600 cm\(^{-1}\) (Bellamy, 1975). Considering the degree of substitution proposed for humic substances (Stevenson, 1985), the aromatic carbon
vibration would be expected to occur near 1600 cm\(^{-1}\) in these substances (Schnitzer, 1978; Thurman, 1985a). Therefore, the mean IR absorption in the 1650 to 1600 cm\(^{-1}\) region of spectra at pH 4 for NLS was probably anomalous.

The correlation between aromatic carbon absorption in the 1650 to 1600 cm\(^{-1}\) region of IR spectra at pH 4 and THM as well as HAA formation is presented in Figure 4-31; the anomalous high-ash-content NLS has been excluded from this figure. Statistic analysis shows that the regressions between the DBP formation and the IR absorption were significant at \(p < 0.05\) except for HAA formation in the presence of bromide ion. Therefore the IR absorption appeared to be a qualitatively useful parameter for comparing the aromaticities of humic substances and its effects on THM formation. The correlation between aromatic carbon absorption in the 1650 to 1600 cm\(^{-1}\) region of IR spectra at pH 4 and chlorine consumption is shown in Figure 4-32; and again the correlation between the mean IR peak height ratio and chlorine consumption was comparable with that between the mean IR peak height ratio and DBP formation.

Rook (1977) proposed that carboxylic functional group formation in HAAs, based on the proposed pathway of chlorination of resorcinol-type moiety of fulvic acids, was by hydroxide attack on carbonyl carbon of the chlorinated intermediate carbanion with a cleavage as indicated by dotted line b:
Figure 4-31. Relationship Between DBP Formation and Mean IR Peak Height Ratio in the 1650 to 1600 cm\(^{-1}\) Region at pH 4 for the Six Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
Figure 4-32. Relationship Between Chlorine Consumption and Mean IR Peak Height Ratio in the 1650 to 1600 cm\(^{-1}\) Region at pH 4 for the Six Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 \(\mu g/L\) Bromide Ion.
However, the possibility of HAAs obtaining the carboxylic functional group from the humic substances per se can not be ruled out. As previously discussed that the mean IR absorption in the 1650 to 1600 cm\(^{-1}\) region of spectra of the humic substances studied at pH 4 was primarily due to aromatic carbon since there should be very little contribution from carboxylate anion; accordingly, the mean IR absorption in the same region of spectra at pH 11 was therefore due to the combination of aromatic carbon and COO\(^-\) (Davis, 1993). If HAA formation should involve, in addition to the aromatic content, the carboxylic functional group from the humic structures, the IR absorption at pH 11 may show a stronger correlation with HAAs compared to the IR absorption at pH 4 shown in Figure 4-31. Figure 4-33 shows the correlation between the DBP formation and the IR absorption at pH 11. Based on the \(r^2\) values, the inclusion of carboxylic functional group in IR absorption at pH 11 consistently resulted in poorer correlation for THMs since THM formation is not typically associated with carboxylic content; however, the correlation for HAAs also tended to be
Figure 4-33. Relationship Between DBP Formation and Mean IR Peak Height Ratio in the 1650 to 1600 cm$^{-1}$ Region at pH 11 for the Six Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
poorer, indicating that the proposed pathway by Rook may adequately explain at least some stages of the HAA formation.

IR spectroscopy can obtain a great deal of structural information from a small sample. The sample size required to obtain an IR spectrum is 1 to 10 mg (Stevenson, 1994). This small sample size is an advantage since the amount of extracted humic substances usually is limited. The $^{13}\text{C}-\text{NMR}$ spectroscopy discussed later also provides functional group information, but it requires sample sizes $\geq 100$ mg (Stevenson, 1994).

$^{13}\text{C}-\text{NMR}$ Spectroscopy

As discussed in Chapter 2, the phenolic carbon content is a good indicator of reactivity between humic substances and chlorine. Correlations were evaluated between the results of phenolic carbon content of the humic substances, estimated by $^{13}\text{C}-\text{NMR}$, and DBP formation as well as chlorine consumption. Due the limited access to the NMR spectrometer, only four of the seven humic substances used in this study were analyzed using this method (Davis, 1993). Correlation coefficients for the relationship between THM as well as HAA formation and phenolic carbon content are shown in Figure 4-34. The regressions between phenolic carbon content and DBP formation were not significant at $p < 0.05$ probably because of the limited data set of only four humic substances and/or the analytical imprecision of $^{13}\text{C}-\text{NMR}$
Figure 4-34. Relationship Between DBP Formation and Phenolic Carbon Content for the Four Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
method. Similarly, a linear relationship between chlorine consumption and phenolic carbon content characterizing the entire data set could not be obtained as shown in Figure 4-35; the regressions were not significant at p < 0.05.

**DBP Formation of Instant Tea Samples**

As previously discussed, the results of the two instant tea samples were included and compared to the four aquatic humic substances under the same formation conditions:

- Temperature = 25 ± 2°C.
- pH = 7.0 ± 0.1 and 8.5 ± 0.1.
- Bromide ion concentration = zero and 250 µg/L.
- Non-purgeable organic carbon (NPOC) = 5 mg/L.
- Chlorine dose = 12.5 mg/L (Cl₂/NPOC = 2.5).
- Chloramine dose = 6.25 mg/L as Cl₂ (Cl₂/NPOC = 1.25).
- Contact time = 24 hours.

The first part of the following discussion was based on the aquatic humic substances and instant tea samples of all at NPOC = 5 mg/L. Then the second part of the discussion extended to realistic instant tea samples of NPOC = 925 mg/L and 1175 mg/L, respectively, for Lipton and Nestlé tea samples. The aforementioned high NPOC concentrations were obtained by dissolving 2.9573 g of tea powder to 1 L of Type 1 reagent water (APHA, 1995) at room temperature adjusted to pH 7 by phosphate buffer (1 teaspoon of 0.7 g to 8 fl. oz. water, according to the preparation suggestion on labels).
Figure 4-35. Relationship Between Chlorine Consumption and Phenolic Carbon Content for the Four Humic Substances in Chlorination.
(a) In the Absence of Bromide Ion.
(b) In the Presence of 250 µg/L Bromide Ion.
**Instant Tea Samples at NPOC of 5 mg/L**

**Chlorination.** Figure 4-36 shows that the two tea samples formed as much THMs, HAAs, and HANs as the aquatic humic substances under the same reaction conditions. It is interesting to note that the UV254 absorbances of the two tea samples (ranging from 0.093 to 0.123 cm⁻¹) are considerably lower than the values of those aquatic humic substances (ranging from 0.240 to 0.266 cm⁻¹), while the tea samples still formed concentration of DBPs comparable to the aquatic humic substances. The addition of 250 µg/L bromide ion resulted in formation of THMs, HAAs, and HANs similar to Figure 4-36, and therefore not presented here. It is also interesting to note that the higher chlorine demands for the two tea samples compared to the aquatic humic substances (Figure 4-3) did not result in higher DBP formation, indicating that the oxidation reactions are probably favored over substitution reactions for the tea samples compared to the aquatic humic substances. This observation will be further discussed later. However, Figure 4-36 also shows that the Nestea sample formed higher concentrations of THMs and HAAs than the Lipton sample, which is consistent with the prediction based on chlorine consumption. The higher chlorine demand of the Nestea sample than that of the Lipton sample may be attributed to the higher N content in the Nestea (Table 2-4) and its larger UV254 absorbance.
Figure 4-36. The Comparison of THM, HAA, and HAN Formation Between the Tea Samples and the Aquatic Humic Substances in the Absence of Bromide Ion.
(a) pH 7 with UV254 Absorbance (㎝⁻¹).
(b) pH 8.5 with UV254 Absorbance (㎝⁻¹).
In addition to THMs, HAAs, and HANs, all the other target compounds listed in Figure 1-1 were found in chlorinated tea samples except cyanogen halides as indicated in Table 4-2. The instability of cyanogen halides in the presence of free chlorine has been discussed, and the absence of cyanogen halides was expected.

Figure 4-37 shows that CH concentrations reported in the tea samples were consistently higher than those found in the aquatic humic substances, perhaps implying haloaldehydes were favored chlorinated by-products in the chlorination of tea polyphenols. However, the formation of HKs and CPN in the tea samples was less compared to the aquatic humic counterparts. Reckhow et al. (1990) have reported that TCPO (DCPO not quantitated in their research) was the only DBP that showed higher yields for the fulvic fractions over the corresponding humic fractions; and a higher methyl ketone content in the fulvic fraction was proposed to be responsible for the higher TCPO yields. Figure 2-4 shows the typical structures of the polyphenols found in black tea; none of which contains methyl ketone moieties. The lower CPN concentration found in tea samples is noteworthy because the higher N content in the tea samples resulted in higher HAN formation but lower CPN formation compared to the extracted humic substance samples. It has been discussed in elemental analysis section that a reasonable correlation between N content and CPN formation could not be obtained.
Figure 4-37. The Comparison of CH, HKs, and CPN Formation Between the Tea Samples and the Aquatic Humic Substances in the Absence of Bromide Ion.

(a) pH 7 with UV254 Absorbance (cm$^1$).
(b) pH 8.5 with UV254 Absorbance (cm$^1$).
among those humic substances with a narrow organic-N range; but a much higher nitrogen content like that of NLS may indicate an ultimate trend of increasing CPN concentrations if some humic substances should contain much higher nitrogen content. The N contents of the two tea samples were comparable with that of NLS, but no corresponding comparably high CPN concentrations like those of NLS were reported.

Chloramination. For the two tea samples, chloramination produced less than 2.4% of the THM4 produced by chlorination; and HAA9 formation by chloramination was from 82.6-91.2% lower than the HAA9 concentration produced by chlorination. In addition to THMs and HAAs, all the target DBPs listed in Figure 1-1 were found in chloraminated waters containing tea samples except TCAN and CNBr. TCAN formation was less than 0.09 µg/L in chlorinated tea samples (Table 4-2). The absence of TCAN in chloraminated tea samples is not surprising since HANs are formed at lower amounts with chloramines as discussed in Chapter 2. The absence of CNBr is consistent with the results of the humic substances, indicating that the postulate of a strong pre-oxidant (i.e., chlorine or ozone) used to form the appropriate precursor for CNBr may be required for CNBr formation from the tea samples.

In summary, based on the results obtained for tea samples of NPOC = 5 mg/L, data suggest that refilling teacup by tap water may not be wise even though it helps the drinker to get the most of the tea out and make the
following teacup washing easier. The refilling by tap water may achieve low NPOC to common values found in raw drinking water and cause substantial formation of THMs, HAAs, and other identifiable DBPs in the diluted tea solution.

**Realistic Instant Tea Samples**

The chlorine consumption as well as DBP formation in the realistic instant tea samples were discussed below.

The proposed maximum residual free chlorine level of 4.0 mg/L (USEPA, 1994) was used in the instant tea preparation to simulate the possibly highest level of free chlorine that tea drinkers will encounter in the future. The free chlorine residual was measured by Standard Method 4500-Cl D Amperometric Titration Method (APHA, 1995); this method, although introduced specifically for water analysis, was used in this study for free chlorine determination in the tea samples. Standard Methods states that the amperometric titration "is the method of choice because it is not subject to interference from color, turbidity, iron, manganese, or nitrite nitrogen". Repeated analyses showed that the free chlorine of 4 mg/L present in Lipton and Nestea tea samples was quickly dissipated. The quick disappearance of free chlorine was expected due to both its reactivity and the large number of organic compounds found in tea samples (NPOC = 1000 mg/L).

Because the Cl₂/NPOC ratio of the reaction mixture was comparatively small (ca. 4/1000 mg/mg) as opposed to those
normally encountered in water treatment (0.5/1 to 3/1 mg/mg), the DBPs formed, if any, were not likely to be extensively chlorinated or oxidized. In other words, reaction products were not likely to be small fragments of larger molecules and their identification by GC or GC/MS might not be possible. It was assumed that much of the organically bound halogen in this realistic tea study occurred in unidentified halogenated macromolecules. Preliminary GC/MS analyses for the chlorinated realistic tea samples were not successful. P&T GC/MS analysis for volatile organics of the realistic tea samples encountered serious peak overlapping interference and broadly unresolved humps on chromatograms, probably due to the vast amounts of volatile organic aroma present in tea. Serious foaming was observed in liquid/liquid extraction for semi-volatile organic analysis; in addition, the apparent denaturation of tea components (floc-like or cloud-like) to naked eyes in acidified samples made any subsequent procedures difficult.

The unidentifiable DBPs formed were either too large in molecular weight to be separated by GC column or could not be concentrated due to aforementioned analytical difficulties. However, those byproducts might be simple to detect by TOX. Korshin et al. (1997a) reported that approximately 15% of the 7 day TOX in their water samples was produced in the first half minute of reaction, and concluded that the virtually instantaneous appearance of TOX, although not documented before, is possible during the
chlorine/organic reaction. The results of TOX analysis of the realistic tea samples are listed in Table 4-7 which shows that TOX formed during the preparation of instant tea using realistic free chlorine dose exceeded the Swiss limit of TOX of 25 μg/L as referenced by Fleischacker and Randtke (1983), although there is no current federal regulations in the United States.

The TOX found in the tea samples may pose a very strong potential threat to the health of instant tea drinkers because TOX may well be just as toxic as THMs and HAAs or may break down into smaller, more toxic compounds. However, this point needs more research.

The non-chlorinated by-products in the realistic tea samples deserve some discussion. As discussed previously, the oxidation reactions are probably favored over substitution reactions for the tea samples compared to the aquatic humic substances. Therefore, non-chlorinated by-products may result from the oxidation of tea polyphenols by chlorine more preferably than aquatic humic substances. This may causes change of the integrity of tea beverage. Black and green teas, among other 22 vegetables investigated, have been ranked high for their antioxidant capacities (Cao et al., 1996). However, their antioxidant capacities may be destroyed by reacting with chlorine residual (an oxidant) in tap water. In addition, although little is known about the human health effects of the non-chlorinated oxidized tea content, they are of great interest.
Table 4-7. The Results of TOX Analysis of the Realistic Tea Samples Studied in This Research.

<table>
<thead>
<tr>
<th>Source</th>
<th>TOX (µg/L as Chloride)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lipton</td>
<td>196.1</td>
</tr>
<tr>
<td>Nestea</td>
<td>163.8</td>
</tr>
<tr>
<td>Nestea spike§</td>
<td>192.4</td>
</tr>
</tbody>
</table>

§ Nestea spiked with 250 µg/L bromide ion.
because they are ingested in significant amounts by human
due to the large amounts of polyphenolic compounds in tea.
Average tea consumption is 7 to 9 g/day/person in Ireland
and the United Kingdom, 4.5 to 7 g/day/person in Hong Kong,
New Zealand and Turkey, and about 1 g/day/person in the
United States and China (WHO, 1991). Since polyphenolic
material in black teas are about 10-20%, total polyphenolic
ingestion in humans is in the range of 0.15 to 1
g/day/person.

In light of this, use of boiled water in preparation of
instant tea is suggested if the residual free chlorine is
determined to be high in the particular distribution system.
CHAPTER 5
SUMMARY AND CONCLUSIONS

Summary

The DBP formation during chlorination and chloramination has been correlated in the research literature with several non-specific parameters such as raw water DOC, color, UV absorbance, chlorine demand, and so on. These parameters, which mainly reflect the concentration of natural organic matter, do not precisely take into account the various compositions of humic substance matrices.

The influence of structural characteristics of humic substances on DBP formation was investigated for seven different humic substances in this research. Among the seven humic substances, one was from a commercial source, the rest were isolated from several aquatic and their corresponding terrestrial and sedimentary sources. The seven isolated humic substances were characterized (Davis, 1993) by a variety of physical and chemical techniques as follows:

- Elemental analysis
- Ultraviolet/visible spectroscopy
- Total acidity titration
- Infrared spectroscopy
- $^{13}$C nuclear magnetic resonance spectroscopy
The water samples prepared from those characterized humic substances were studied in a series of experiments performed under the following conditions:

- Temperature = 25 ± 2°C.
- pH = 7.0 ± 0.1 and 8.5 ± 0.1.
- Bromide ion concentration = zero and 250 μg/L.
- Non-purgeable organic carbon (NPOC) = 5 mg/L.
- Chlorine dose = 12.5 mg/L (Cl₂/NPOC = 2.5).
- Chloramine dose = 6.25 mg/L as Cl₂ (Cl₂/NPOC = 1.25).
- Contact time = 24 hours.

The DBFs studied in this research included THMs, HAAs, HANs, HKS, CPN, CH, CNCl, and CNBr.

Furthermore, this research extended DBP precursor study to instant tea samples. The two tea samples investigated were found to react with chlorine to form DBPs. The data show that the tea samples formed as much DBPs as the aquatic humic substances under the same formation conditions.

This study also developed an in situ synthesis of CNCl as a safe and economical aqueous standard, and demonstrated that the synthesized CNCl standards are comparable with available commercial standards.

This dissertation research on the relationship between the structure and composition of humic substances and their effect on DBP formation is one of only a few such investigations reported to date. The results presented in this dissertation add to the relatively small amount of information currently available on using chemical
characterization of humic substances to predict DBP formation.

HAN and CPN formation in chlorination and CNCl formation in chloramination were correlated with organic nitrogen content in humic structures. A stronger correlation between the nitrogen-containing DBPs and the organic nitrogen content was further demonstrated by considering the change in UV absorption at 254 nm ($\Delta$UV254) and the molar ratio of nitrogen to carbon.

A qualitative measurement of aromaticity, H/C ratio, correlated with DBP formation for the humic substances investigated. UV254 and $\Delta$UV254 varied linearly with both DBP formation and chlorine consumption, with $\Delta$UV254 consistently showed better correlation. A linear relationship was observed between aromatic carbon absorption in the 1650 to 1600 cm$^{-1}$ region of IR spectra at pH 4 and DBP formation as well as chlorine consumption.

Based on the results of computation with respect to total acidity, the contribution of COOH group to the H/C ratio of the humic substances studied was not as significant than previously thought.

The instant tea samples formed as much DBPs as the aquatic humic substances under the same formation conditions. The tea experiment also extended to realistic concentrations of tea solution. The TOX formed during the preparation of instant tea using realistic free chlorine dose (4 mg/L) exceeded the Swiss limit of TOX of 25 $\mu$g/L,
although there is no current federal regulations in the United States.

**Conclusions**

**In Situ Synthesis of Cyanogen Chloride**

CNCl standards synthesized using the protocols developed in this research should be comparable with available commercial standards.

Only microgram quantities of this hazardous substance will be generated in situ and may be safely converted to the relatively innocuous cyanate ion immediately after use by simply raising the pH.

**Structural Characteristics of Humic Substances Versus DBP Formation**

There likely will be a significant difference in DBP formation and chlorine consumption among humic substances from a variety of sources.

The hydrogen/carbon ratio of the individual humic substances, a qualitative measurement of aromaticity, can be correlated with DBP formation. ΔUV254 or UV254 should vary linearly with both DBP formation and chlorine consumption, with the ΔUV254 nm consistently showing better correlation. The aromaticity deduced from the 1650 to 1600 cm⁻¹ region of IR spectra at pH 4 is likely to correlate with THM formation and chlorine consumption, but not necessarily with HAA formation during the free chlorination of humic substances.
Based on the results of computation with respect to total acidity, the contribution of COOH group to the hydrogen/carbon ratio of the humic substances studied may not be significant.

**Tea Samples Versus Humic Substances**

Instant tea powders may form as much DBPs as aquatic humic substances under the same reaction conditions, although the concentration of tea used for consumption typically is much higher than the concentration of humic substances in natural waters. At typical tea concentrations, substantial levels of TOX will be generated if free chlorine is present in the water used to make the tea.

Use of boiled water in preparation of instant tea is suggested if the residual free chlorine is high in the tap water.

**Further Research**

The complex nature of humic substances requires a large data set for statistically significant conclusions to be obtained about their effect on DBP formation. Continuing interest in the role of humic substances and how their composition can be related to DBP formation is needed. Further research using humic substances from different watersheds, representing other water qualities and geographic locations, will be important.
APPENDIX
REPRESENTATIVE GC/ECD CHROMATOGRAMS
Figure A-1. Two Typical Chromatograms Showing the GC/ECD Analyses of EPA Method 551.1.
Figure A-2. Two Typical Chromatograms Showing the GC/ECD Analyses of EPA Method 552.2.
REFERENCES


BIOGRAPHICAL SKETCH

Wells Wei-Shih Wu was born in Kaohsiung, Taiwan, on October 10, 1965. He graduated with a Bachelor of Science degree in chemistry in June 1988 at National Taiwan University, Taipei, Taiwan. After two years of military service, he worked as a full-time research assistant in the Graduate Institute of Environmental Engineering, National Taiwan University, for one year. He served as an environmental chemist on a major research project studying drinking water quality improvement, which was funded by the Environmental Protection Administration of the Taiwan Government.

He continued his education at the University of Florida beginning in 1991. He received his Master of Science degree in environmental engineering sciences with an emphasis on water chemistry in 1993. He is a Ph.D. candidate in the Department of Environmental Engineering Sciences at the University of Florida, studying the effect of structural characteristics of humic substances on disinfection by-product formation.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Paul A. Chadik, Chairman
Assistant Professor of
Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Joseph J. Delfino
Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Ben L. Koopman
Professor of Environmental Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

David H. Powell
Associate Scientist of Chemistry
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

John Zoltek, Jr.
Professor of Environmental Engineering Sciences

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1998

Winfred M. Phillips
Dean, College of Engineering

Karen A. Holbrook
Dean, Graduate School