Relative Dominance of HAAs and THMs in Treated Drinking Water

Subject Area: Distribution Systems
Relative Dominance of Haloacetic Acids and Trihalomethanes in Treated Drinking Water
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This study was jointly funded for the Microbial/Disinfection By-Products Research Council (M/DBP) by the Awwa Research Foundation (AwwaRF) and the U.S. Environmental Protection Agency (USEPA) under Cooperative Agreement No. CX819540. AwwaRF, M/DBP, and USEPA assume no responsibility for the content of the research study reported in this publication or for the opinions or statements of fact expressed in the report. The mention of trade names for commercial products does not represent or imply the approval or endorsement of AwwaRF, M/DBP, or USEPA. This report is presented solely for informational purposes.

Library of Congress Cataloging-in-Publication Data
Relative dominance of haloacetic acids and trihalomethanes in treated drinking water / prepared by Philip C. Singer … [et al.].
   p. cm.
   Includes bibliographical references.
   ISBN 1-58321-117-9

TD462 .R455 2001
628.1'662--dc21 2001033380

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Awwa Research Foundation
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American Water Works Association
Printed in the U.S.A.

ISBN 1-58321-117-9

Printed on recycled paper.
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FOREWORD

The Awwa Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the industry. The research agenda is developed through a process of consultation with subscribers and drinking water professionals. Under the umbrella of a Strategic Research Plan, the Research Advisory Council prioritizes the suggested projects based upon current and future needs, applicability, and past work; the recommendations are forwarded to the Board of Trustees for final selection. The foundation also sponsors research projects through the unsolicited proposal process; the Collaborative Research, Research Applications, and Tailored Collaboration programs; and various joint research efforts with organizations such as the U.S. Environmental Protection Agency, the U.S. Bureau of Reclamation, and the Association of California Water Agencies.

This publication is a result of one of these sponsored studies, and it is hoped that its findings will be applied in communities throughout the world. The following report serves not only as a means of communicating the results of the water industry’s centralized research program but also as a tool to enlist the further support of the nonmember utilities and individuals.

Projects are managed closely from their inception to the final report by the foundations’ staff and large cadre of volunteers who willingly contribute their time and expertise. The foundation serves a planning and management function and awards contracts to other institutions such as water utilities, universities, and engineering firms. The funding for this research effort comes primarily from the Subscription Program, through which water utilities subscribe to the research program and make an annual payment proportionate to the volume of water they deliver and consultants and manufacturers subscribe based on their annual billings. The program offers a cost-effective and fair method for funding research in the public interest.

A broad spectrum of water supply issues is addressed by the foundation’s research agenda: resources, treatment and operations, distribution and storage, water quality and analysis toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide the highest possible quality of water economically and reliably. The true benefits are realized when the results are implemented at the utility level. The foundation’s trustees are pleased to offer this publication as a contribution toward that end.
Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two principal classes of disinfection by-products resulting from the chlorination of drinking water. Both have been regulated in finished drinking water, and new regulations are expected in the future. A great deal is known about the formation and control of THMs, but much less is known about the behavior of HAAs. Although there are nine bromine- and chlorine-containing HAAs, only five of them are currently regulated. To assist water utilities in complying with future regulations, this report addresses the factors influencing the formation, occurrence, stability, and relative dominance of these two groups of compounds in finished drinking water. All nine HAAs are considered.

Edmund G. Archuleta, P.E.  
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Awwa Research Foundation

James F. Manwaring, P.E.  
Executive Director  
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PREFACE

The Microbial/Disinfection By-Products Research Council was established in 1995 as a vehicle for the selection and funding of research to provide scientific information in the areas of health effects, exposure assessment, risk assessment, and prevention and control of contamination by microbes and disinfection by-products in drinking water. The council is composed of representatives designated by the U.S. Environmental Protection Agency (USEPA), the Awwa Research Foundation (AwwaRF) Board of Trustees, the Association of State Drinking Water Administrators, the National Resources Defense Council, the National Environmental Health Association, or their designees. Sources of funding for this research include the USEPA and AwwaRF, along with other interested parties. The council disburses these funds for research deemed to be of the highest urgency and importance in resolving critical research issues in drinking water.
ACKNOWLEDGMENTS

The authors of this report are indebted to the following water utilities and individuals for their cooperation and assistance in this project:

Metropolitan Water District of Southern California, La Verne, Calif., notably:
Russell Chinn, Donald Bundy, Patrick Hacker, Barry Peterson, Warren Schimpff, Vania Kenanova, Anagha Chitre, Himansu Mehta, Howard Wen, Francis Vergel de Dios, Ming Tan, Katrin Hanley, and Danni Maurizio

American Water Works Services Company, Inc., Voorhees, N.J.

Illinois American Water Company, East St. Louis, Ill.: Esther Dundore, Tim Elliot, and Brent Gregory

City of Durham, N.C.: George Carter

Indianapolis Water Company, Indianapolis, Ind.: Dan Moran and Rick Giltner

Manatee County Public Works Department, Bradenton, Fla.: Bruce MacLeod

City of Groton Department of Utilities, Groton, Conn.: Richard Stevens

Seattle Public Utilities District, Seattle, Wash.: David Hilmoe

Palm Beach County Water Utilities, West Palm Beach, Fla.: Eugenia Carey

Fairfax County Water Authority, Herndon, Va.: Heather Jenkins

Washington Suburban Sanitary Commission, Laurel, Md.: Betsy Hallman

Antelope Valley East Kern Water District, Quartz Hill, Calif.: Maureen Smith

City of Raleigh, N.C.: Larry McMillan

Gulf Coast Water Authority, Texas City, Texas: Robert Istre

City of Houston, Texas: Jim Greenlee and Roger Hulbert

In addition, Alexa Obolensky of the Philadelphia (Pa.) Water Department; Steve Via of the American Water Works Association (AWWA); and Christianne Nagel, Roger Gorges, and Charles Kroner of the University of North Carolina all assisted in various ways in the performance of this work.

The authors also wish to acknowledge the suggestions of the Project Advisory Committee: Richard Miltner, an environmental engineer with the USEPA in Cincinnati, Ohio; John Rissel,
Water Quality Supervisor with the Brick Township Municipal Utility in Brick, N.J.; and Salome Freud of the New York City Department of Environmental Protection. We gratefully acknowledge the support of Dr. Kenan Ozekin of Awwa Research Foundation who served as project officer.

We thank the American Chemical Society for allowing us to use Figures 2.2, 2.3, 2.9, 2.11, 2.12, and 2.13, and Table 2.7, which appeared in a paper titled “Quantification of Nine Haloacetic Acids Using Gas Chromatography With Electron Capture Detection” by Brophy, Weinberg, and Singer in ACS Symposium Series Volume 61, Natural Organic Matter and Disinfection By-Products (ISSN 00097-6156), and AWWA for allowing us to use Figures 6.1, 6.2, 6.5, 6.6, 6.7, 6.8, 6.9, 6.10, 6.11, 6.12, 6.13, 6.14, 6.21, 6.22, 6.23, and 6.24, which were published in the Proceedings of the 2000 AWWA Water Quality Technology Conference as part of a paper by Baribeau, Krasner, Chinn, and Singer (2000a) titled “Impact of Biomass on the Stability of Haloacetic Acids and Trihalomethanes in a Simulated Distribution System.”

Sara Lachenman of the University of North Carolina at Chapel Hill assisted in preparing this final report.
EXECUTIVE SUMMARY

Public health concern about the disinfection process was first raised more than 25 years ago with the identification of chloroform and other trihalomethanes (THMs) in chlorinated drinking water. Since that time, hundreds of chemical by-products of the disinfection process (called DBPs) have been found in treated drinking water. The most prevalent chlorination by-products by weight are the THMs, followed by the haloacetic acids (HAAs), chloral hydrate, haloacetonitriles, haloketones, and chloropicrin. Between 20 and 60 percent of the halogenated materials resulting from chlorination are accounted for by these compound classes, of which the concentrations of the THMs and HAAs tend to comprise more than 50 percent on a weight basis.

THMs in finished drinking water have been regulated since 1979. When this project began, the U.S. Environmental Protection Agency (USEPA) was planning to tighten the regulation on THMs and to regulate HAAs as well. Since then, the USEPA has promulgated Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule, which establishes maximum contaminant levels (MCLs) of 0.080 mg/L (80 µg/L) for total THMs (TTHMs) and 0.060 mg/L (60 µg/L) for five of the haloacetic acids (HAA5). The five HAAs are monochloroacetic acid (ClAA), monobromoacetic acid (BrAA), dichloroacetic acid (Cl₂AA), trichloroacetic acid (Cl₃AA), and dibromoacetic acid (Br₂AA). The second stage of the D/DBP Rule, expected to be promulgated in May 2002, listed 0.040 mg/L (40 µg/L) and 0.030 mg/L (30 µg/L) as placeholders for the THM and HAA MCLs, respectively. However, recent negotiations suggest that the MCLs for TTHMs and HAA5 will remain at 80 and 60 µg/L, respectively, but that compliance will be based on a different monitoring regimen than that currently in place.

Regulation of only five of the nine bromine- and chlorine-containing HAAs is based on occurrence data, although research findings suggest that some of the other, nonregulated bromine-containing HAAs may be present at appreciable concentrations, even in waters with low bromide concentrations. The Information Collection Rule (ICR), which became effective in July 1997, provided for the collection of a large array of water quality and treatment data, including THM and HAA concentrations within water treatment plants and in water distribution systems. Although systems were encouraged to collect data for all nine bromine- and chlorine-containing HAAs, only the collection of data for six HAAs (the regulated HAA5 along with bromochloroacetic acid, BrClAA) was required.
Although THM levels have been shown to exceed HAA levels in some water systems, the reverse is true in others. THM formation has been studied extensively, and THMs have been shown to be stable in water distribution systems. HAAs are less well studied, and their kinetics of formation and stability are not as well characterized. They appear to be formed faster than THMs, some of the species are thought to decompose at elevated pH values, and some of the species are believed to be biodegraded in the absence of a chlorine residual. Additionally, bromine incorporation into HAAs appears to parallel that of bromine incorporation into THMs, but this has not been demonstrated to a significant degree in actual distribution systems.

Factors expected to influence the relative distribution of HAAs and THMs in treated drinking water are

- pH of chlorination and distribution
- Temperature
- Bromide concentration
- Chemical characteristics of natural organic material (NOM) in the water (e.g., specific ultraviolet absorbance [SUVA] of the water, hydrophilic versus hydrophobic distribution of the dissolved organic carbon in the water)
- Contact time
- Type of disinfection scenario (e.g., chlorination only, chlorination/chloramination, or ozonation/chlorination)
- Potential for biodegradation of HAAs

To understand the underlying causes of the relative differences in THM and HAA formation in different waters, controlled studies must be conducted in which the various factors contributing to these differences are investigated.

**RESEARCH OBJECTIVES**

The objectives of this project were to investigate the relative occurrence of HAAs and THMs in treated drinking waters and to determine water quality, treatment, and distribution system conditions that influence their relative concentrations.
APPROACH

All four bromine- and chlorine-containing THM species (THM4, equivalent to what is typically referred to as TTHMs) and all nine bromine- and chlorine-containing HAAs (called HAA9 in this report) were measured as part of this investigation. The project consisted of chlorination experiments on a variety of different waters under controlled laboratory conditions, measurements made in selected full-scale water treatment systems (within the treatment plant as well as in the distribution system), and a comprehensive assessment of THM and HAA occurrence based on an analysis of the first 12 months of ICR data.

The study had five major components:

1. A laboratory phase of controlled investigations to assess the stability of the different HAA species under various solution conditions. Before conducting this phase of the study, existing methods for the analysis of HAA9 were investigated and a modified derivatization method for HAA9 analysis was developed and validated.

2. A bench-scale, controlled laboratory chlorination study in which six waters with differing NOM characteristics from different regions of the United States were chlorinated under various solution conditions. The bench-scale studies also included chlorination before and after optimal coagulation of the waters, and hydrophobic/hydrophilic fractionation of the NOM and chlorination of these fractions.

3. Analysis of ICR data to examine the relative occurrence of HAA and THM concentrations in finished drinking water, and an evaluation of factors influencing the relative dominance of these two principal classes of DBPs. As part of this analysis, a theoretical model was developed and validated that allows for the prediction of bromodichloroacetic acid (BrCl$_2$AA), dibromochloroacetic acid (Br$_2$ClAA), and tribromoacetic acid (Br$_3$AA) concentrations, the three missing HAAs (HAA3) for which mandatory monitoring was not conducted as part of the ICR.

4. A full-scale plant study to assess the distribution and speciation of THMs and HAAs in a variety of waters from geographically diverse regions, with differing water quality, treatment, and distribution system characteristics. In this phase of the study, samples of treated water were collected at various locations in the treatment plant and distribution system.
system of 10 utilities across the United States. An attempt was made to pair the utilities in such a manner that the two treatment plants drew water from the same water source but used different treatment scenarios.

5. Two controlled biostability studies in which annular reactors and biologically active filters were used to evaluate the biodegradability of different HAA species under different treatment and distribution conditions. The annular reactor study was conducted at the Weymouth Treatment Plant of the Metropolitan Water District of Southern California; the reactors were fed chlorinated, chloraminated, dechlorinated, and dechloraminated finished water, and were operated during warm-water and cold-water seasons. The biological filtration study was conducted at one of Illinois American Water Company’s facilities in East St. Louis, Ill. Three types of filters were examined—aged granular activated carbon (GAC) filters, virgin GAC filters, and conventional sand filters. The raw water was chlorinated or chloraminated and the behavior of THMs and HAAs across the filters was monitored for 10 months.

In all phases of this study, all four bromine- and chlorine-containing THMs and all nine bromine- and chlorine-containing HAAs were measured.

CONCLUSIONS

This project has shown that several significant water quality and treatment factors influence the relative distribution of HAAs and THMs in treated drinking water, as well as the relative distribution of species within both of these major DBP groups. All nine bromine- and chlorine-containing HAAs were studied in this project to obtain a complete assessment of overall HAA occurrence and HAA9 behavior relative to the four bromine- and chlorine-containing THMs. The study of all nine HAA species was made possible only after the existing HAA6 analytical methodology was modified to allow for more precise and more robust analysis of the remaining HAA3 species. A standard analytical procedure for HAA9 was developed.

Conclusions reached in this project are described below.

pH was a principal factor controlling the distribution of HAAs and THMs and thus the relative dominance of HAAs and THMs in finished drinking water. HAA9 concentrations tended
to decrease with increasing pH, whereas THM4 concentrations tended to increase with increasing pH. However, among the HAA species, the formation of the trihalogenated acetic acid species decreased with increasing pH, whereas the formation of the dihalogenated acetic acid species was relatively independent of pH. The bromine-containing species in each class of HAAs behaved in the same manner with respect to pH as their chlorine-containing counterparts.

In the controlled laboratory chlorination studies, the formation of THM4 was higher than the formation of HAA9 at pH 8, and the reverse was true at pH 6. This was found for the chlorination of raw and coagulated waters, and for the chlorination of both the hydrophobic and hydrophilic fractions.

The results from analysis of the first 12 months of ICR data showed that chlorinated surface water systems with filtered water pH values less than 7 (and therefore presumed to be chlorinated at pH values less than 7) had higher HAA9/THM4 ratios than systems with filtered water pH values greater than 8. This was observed for filtered water, finished water at the point of entry to the distribution system, and water from average distribution system locations.

The results from sampling at the 10 full-scale water treatment plants showed that HAA concentrations exceeded THM concentrations only when chlorination was practiced after coagulation at pH values less than 6.5–7.0, or for chlorination of raw waters with high concentrations of hydrophobic NOM. For all other cases, THM concentrations exceeded HAA concentrations.

The characteristics of the NOM in the water being chlorinated had a major impact on the relative distribution of THMs and HAAs. In general, waters with high hydrophobic organic carbon concentrations and high SUVA values tended to produce more HAAs (relative to THMs) than waters with low SUVA values, which were dominated by hydrophilic organic carbon.

In the controlled laboratory chlorination experiments, the waters with higher SUVA values produced slightly higher HAA9/THM4 ratios. In addition, the slightly stronger correlation observed between haloacetic acid formation potential and SUVA compared to that for trihalomethane formation potential and SUVA suggests that the HAA precursors are more aromatic in nature than the THM precursors. The hydrophobic fractions from almost all waters gave higher formation potentials for dihalogenated acetic acids (X₂AA), trihalogenated acetic acids (X₃AA), and THM4 than the corresponding hydrophilic fractions from the same water, which is consistent with the SUVA findings. These results confirm earlier work indicating that
hydrophobic carbon, which is rich in aromatic content and phenolic hydroxyl groups, is the main precursor of DBPs. The HAA9/THM4 ratio was higher in the hydrophobic fractions than in the hydrophilic fractions at pH 8, but no significant difference was observed at pH 6. The results suggest that aliphatic carbon may play a more important role in THM formation than in HAA formation.

Along these same lines, in the controlled laboratory chlorination experiments, coagulation removed substantial amounts of DBP precursors and shifted the distribution of HAA and THM species. In general, the waters with higher SUVA values, which usually contained more hydrophobic and aromatic carbon, were more amenable to coagulation. For all the controlled laboratory experiments, coagulation removed more ultraviolet absorbance at 254 nm than total organic carbon (TOC), thereby lowering the SUVA values. For the high-SUVA waters, HAA9 precursors were removed to a greater degree than THM4 precursors. These results are consistent with the belief that HAA precursors are more hydrophobic and aromatic than THM precursors.

Similar findings were observed for the full-scale water treatment facilities in that HAA9 concentrations were found to exceed THM concentrations only for waters with high hydrophobic organic carbon concentrations or for waters that were chlorinated at reduced pH values after coagulation.

In addition, both the controlled laboratory study and the field study showed that, by removing only organic carbon and having no impact on the concentration of bromide, coagulation altered the Br/TOC ratio of the waters and shifted the distribution of HAAs and THMs toward the bromochloro and brominated species.

Temperature had a significant impact on the relative dominance of HAAs and THMs. Analysis of the ICR data indicated that, for surface water treatment plants using only free chlorine, the HAA9/THM4 ratio increased with decreasing temperature and, consistent with that finding, HAA9/THM4 ratios were found to be lowest in the winter months (January–March) and highest in the summer months (July–September).

The concentration of bromide in water, particularly the Br/TOC ratio, had a marked impact on the distribution of bromine-containing HAAs and THMs. As the Br/TOC ratio increased, the mole fractions of bromine-containing species increased significantly whereas the reverse occurred for the species containing only chlorine. This was observed for HAAs as well as for THMs.
The controlled laboratory chlorination studies found that the hydrophilic fractions exhibited consistently higher reactivity with bromine than the hydrophobic fractions. Bromine was found to be more reactive in substitution reactions and was incorporated into HAA and THM species faster than chlorine. Increasing pH increased the incorporation of both bromine and chlorine into THM and HAA species but did not change the relative distribution of bromine to chlorine within those species.

As part of this study, a model was developed to predict the formation of the three trihalogenated bromine-containing species that are not part of the regulated HAA5 species and for which limited data are available in the ICR database, notably BrCl₂AA, Br₂ClAA, and Br₃AA. The model indicates that BrCl₂AA, Br₂ClAA, and Br₃AA are present in similar proportions to Cl₃AA, on a mole fraction basis, as CHBrCl₂, CHBr₂Cl, and CHBr₃, respectively, are present relative to CHCl₃ formation. Consequently, the model allows calculation of BrCl₂AA, Br₂ClAA, and Br₃AA (collectively HAA3) concentrations from knowledge of the concentrations of the individual THM species and Cl₃AA. The model was verified using the limited HAA9 data from the ICR database, and was shown to represent data from the selected full-scale water systems examined in this study reasonably well.

Although HAAs have been reported in the literature to form more rapidly than THMs, the controlled laboratory chlorination results showed that the relative distribution of HAA9 and THM4 was reasonably consistent throughout the 72-hour reaction period at both pH 6 and pH 8. The results did show, however, that among the HAA species, the X₃AA/X₂AA ratio increased with increasing contact time at both pH values. This ratio increased particularly rapidly during the first 8 hours of chlorination, and remained essentially unchanged after 24 hours.

Analysis of the ICR data for surface water treatment systems using only free chlorine showed that the HAA9/THM4 ratio was highest in the filtered water, lower in the finished water, and even lower in the distribution system at average hydraulic residence times. Use of chloramines in the distribution system was found to maintain the same relative distribution of HAAs to THMs as in the finished water at the point of entry to the distribution system. Essentially, chloramination of finished water stops subsequent THM and HAA formation.

The fact that HAA species are biodegradable and THM species are not may also have a significant impact on the relative distribution of THMs and HAAs. The annular reactor studies, conducted in the presence and absence of a free chlorine or combined chlorine residual, showed
clearly that when the residual was absent, the dihalogenated acetic acids were biodegraded under warm-water conditions. The trihalogenated acetic acid species, however, were not biodegraded under similar conditions, nor were the THMs. In cold water, the X$_2$AAs were stable because of slower reaction kinetics, but may also be biodegraded if longer hydraulic residence times are provided. In the presence of a free chlorine residual, both classes of HAA species, as well as the THMs, continued to form.

In the in-depth full-scale plant evaluation, it was also found that HAAs can be removed by GAC filtration, presumably by biodegradation processes within the GAC bed. The extent of removal depends on water temperature and the residual chlorine concentration. Removal of HAAs was greatest when water temperatures were high and residual chlorine concentrations were low. Dihaloacetic acids were removed by the GAC to a greater degree than were trihaloacetic acids. However, both groups were removed, in contrast to the annular reactor study and other distribution system and controlled laboratory studies, which showed that the trihalogenated acetic acids are not biodegradable. The fact that the HAAs are degraded but the THMs are not is a significant factor influencing the relative concentrations of these two classes of DBP species in finished drinking water.

These findings confirm that the THMs and the three classes of HAA species (mono-, di-, and trihalogenated species) have different formation mechanisms and, to some degree, different precursors. Additionally, once formed, many of them behave differently. However, the compounds within each class of DBPs (i.e., the different trihalogenated HAA species, dihalogenated HAA species, and trihalogenated methanes), tend to be formed through similar chemical pathways and behave similarly in aqueous solution.

Because of the ability to reliably measure all nine bromine- and chlorine-containing HAA species and to predict HAA3 concentrations when only HAA6 data are available, this research has shown that, for the more than 5,000 samples examined from the first 12 months of the ICR Auxiliary 1 database, overall HAA concentrations (i.e., HAA9) in finished drinking water are approximately equal to overall THM (THM4) concentrations. By comparison, the HAA5 species were found to comprise only about 60 percent of the corresponding THM4 concentrations. HAA5 measurements significantly underestimate overall HAA occurrence. The results of this project show that including these other HAA species can contribute significantly to overall HAA occurrence, even for waters with relatively low bromide concentrations. Total HAA occurrence in
U.S. drinking waters is not well represented by considering only HAA5, and the current MCL, which applies only to HAA5, is not sufficiently protective of public health if HAAs are indeed a public health concern.

The frequency distribution analyses performed in this study were helpful in evaluating the status of finished drinking water with respect to current and future THM and HAA regulations. The findings, especially those involving HAA9, should be strongly considered in future regulatory activities.

**RECOMMENDATIONS**

Water utilities should monitor THM and HAA concentrations more intensively throughout their treatment plant(s) and water distribution systems. More rigorous monitoring will lead to a better understanding of the extent of formation of these two principal classes of DBPs and of factors that influence the relative behavior of THMs and HAAs in their water systems.

Utilities monitoring for THMs and HAAs should extend their monitoring activities to include all nine of the bromine- and chlorine-containing HAA species. Analytical methodologies now exist to allow all nine species to be measured precisely. At the very least, the model presented in this project should be employed to predict the formation of HAA3 so that total HAA occurrence (HAA9) can be determined.

In addition, future regulatory activity should be directed at all nine HAAs. Regulation of only five of the nine HAAs underestimates overall HAA occurrence, and does not make sense from either a chemical or regulatory point of view.

Future regulations should also consider separate MCLs for each class of HAA species, (i.e., the mono-, di-, and trihalogenated HAAs). Each class behaves differently in terms of their mechanisms of formation, their chemical and biological stability, and their overall behavior in aquatic systems.
CHAPTER 1
INTRODUCTION

OBJECTIVES

The objectives of this project were to investigate the relative occurrence of haloacetic acids (HAAs) and trihalomethanes (THMs) in treated drinking waters and to determine water quality, treatment, and distribution system conditions that influence their relative concentrations.

BACKGROUND

Public health concern about the disinfection process was first raised more than 25 years ago with the identification of chloroform and other THMs in chlorinated drinking water (Rook 1974; Bellar, Lichtenberg, and Kroner 1974). Since then, more than 100 chemical by-products of the disinfection process (called DBPs) have been found in treated drinking water (U.S. Environmental Protection Agency [USEPA] 1997). Based on several studies (e.g., Quimby et al. 1980; Christman et al. 1983; Krasner, Sclimenti, and Hwang 1989; Stevens et al. 1989), the most prevalent chlorination by-products by weight are the THMs, followed by the HAAs, chloral hydrate, haloacetonitriles, haloketones, and chloropicrin. Between 20 and 60 percent of the halogenated materials resulting from chlorination are accounted for by these compound classes, of which the concentrations of the THMs and HAAs likely comprise more than 50 percent on a weight basis (USEPA 1997).

THMs in finished drinking water have been regulated since 1979 (USEPA 1979). When this project began, the USEPA was planning to tighten the regulations on THMs and to also regulate HAAs (USEPA 1994a). Since then, the USEPA has promulgated Stage 1 of the Disinfectants/Disinfection By-Products (D/DBP) Rule (USEPA 1998), which establishes maximum contaminant levels (MCLs) of 0.080 mg/L (80 µg/L) for total THMs (TTHMs) and 0.060 mg/L (60 µg/L) for five of the haloacetic acids (HAA5). The five HAAs are monochloroacetic acid (ClAA), monobromoacetic acid (BrAA), dichloroacetic acid (Cl₂AA), trichloroacetic acid (Cl₃AA), and dibromoacetic acid (Br₂AA). The second stage of the D/DBP Rule, expected to be promulgated in May 2002, listed 0.040 mg/L (40 µg/L) and 0.030 mg/L
(30 μg/L) as placeholders for the THM and HAA MCLs, respectively. Roberson et al. (1995) discuss the rationale underlying these proposed levels.

Regulation of only five of the nine bromine- and chlorine-containing HAAs is based on occurrence data (e.g., Krasner, Sclimenti, and Hwang 1989), although research findings by Cowman and Singer (1996) suggest that some of the bromine-containing HAAs may be present at appreciable concentrations, even in waters with low bromide concentrations. The Information Collection Rule (ICR; USEPA 1994b), which became effective in July 1997, called for the collection of a large array of water quality and treatment data, including THM and HAA concentrations within water treatment plants and in water distribution systems. Although systems were encouraged to collect data for all nine bromine- and chlorine-containing HAAs, only the collection of data for six HAAs (the regulated HAA5 and bromochloroacetic acid, BrClAA) was required.

THM levels have been shown to exceed HAA levels in some water systems (see, for example, Krasner, Sclimenti, and Hwang 1989; Gramith et al. 1993; Roberson et al. 1995; Arora, LeChevallier, and Dixon 1997). In others, the reverse is true (Singer, Obolenski, and Greiner 1995; Williams, Williams, and Gordon 1996; Arora, LeChevallier, and Dixon 1997). THM formation has been studied extensively, and THMs tend to be stable in water distribution systems. HAAs are less well studied, and their kinetics of formation and stability are not as well characterized. They tend to be formed faster than THMs (Reckhow and Singer 1984), some of the species are known to decompose at elevated pH values (Reckhow and Singer 1985; Krasner, Sclimenti, and Hwang 1989), and some of the species are known to biodegrade in the absence of a chlorine residual (e.g., Williams, Williams, and Gordon 1996; Baribeau, Prévost, and LaFrance 1994). Additionally, bromine incorporation into HAAs parallels that of bromine incorporation into THMs (Pourmaghaddas et al. 1993, Cowman and Singer 1996), but this has not been demonstrated to a significant degree in actual distribution systems.

Factors that are expected to influence the relative distribution of HAAs and THMs are

- pH of chlorination and distribution
- Temperature
- Bromide concentration
• Chemical characteristics of natural organic material (NOM) in the water (e.g., specific ultraviolet absorbance of the water [SUVA], hydrophilic versus hydrophobic dissolved organic carbon [DOC])
• Contact time
• Type of disinfection scenario (chlorination only, chlorination/chloramination, or ozonation/chlorination)
• Potential for biodegradation of HAAs

To understand the underlying causes of the relative differences in THM and HAA formation in different waters, controlled studies need to be conducted in which the various factors contributing to these differences are investigated.

APPROACH

All four bromine- and chlorine-containing THM species (THM4, equivalent to what is typically referred to as TTHMs) and all nine bromine- and chlorine-containing HAAs (referred to herein as HAA9) were measured as part of this investigation. Studies were conducted both on a bench scale and in the field at actual full-scale treatment plants, including their respective distribution systems. ICR data were also analyzed as part of this investigation. The study had five major components:

1. A laboratory phase of controlled investigations to assess the stability of the different HAA species under a variety of solution conditions. Before this phase of the study was conducted, existing methods for the analysis of HAA9 were investigated and a modified derivatization method for HAA9 analysis was developed and validated.
2. A bench-scale, controlled, laboratory chlorination study in which six waters with differing NOM characteristics from different U.S. regions were chlorinated under a variety of solution conditions. The bench-scale studies also included chlorination before and after optimal coagulation of the waters, and hydrophobic/hydrophilic fractionation of the NOM and chlorination of these fractions.
3. Analysis of ICR data to examine the relative occurrence of HAA and THM concentrations in finished water, and an evaluation of the factors that influence the relative dominance of these two principal classes of DBPs. As part of this analysis, a theoretical model was developed and validated. The model allows for the prediction of bromodichloroacetic acid (BrCl₂AA), dibromochloroacetic acid (Br₂ClAA), and tribromoacetic acid (Br₃AA) concentrations, the three missing HAAs (HAA3) for which mandatory monitoring was not conducted as part of the ICR.

4. A full-scale plant study to assess the distribution and speciation of THMs and HAAs in a variety of different waters from geographically diverse regions, with differing water quality, treatment, and distribution system characteristics. In this phase of the study, samples of treated water were collected at various locations in the treatment plant and distribution system of 10 U.S. utilities. An attempt was made to pair the utilities so that the two treatment plants drew water from the same water source but used different treatment scenarios.

5. Two controlled biostability studies in which annular reactors and biologically active filters were used to evaluate the biodegradability of different HAA species under different treatment and distribution conditions. The annular reactor study was conducted at the Weymouth Treatment Plant of the Metropolitan Water District (MWD) of Southern California. The biological filtration study was conducted at one of Illinois American Water Company’s facilities in East St. Louis, Ill.

In all phases of this study, all four bromine- and chlorine-containing THMs and all nine bromine- and chlorine-containing HAAs were measured.

**ORGANIZATION OF REPORT**

This report consists of seven chapters in addition to this introductory chapter. **Chapter 2** contains the results of the studies directed at the measurement and stability of all nine HAAs. Investigations of the impact of water quality and treatment characteristics on HAA and THM formation under controlled laboratory chlorination conditions are presented in **chapter 3**. The analysis of ICR data on THM and HAA occurrence, including development and validation of a
conceptual model for the missing HAA3 species, comprises chapter 4. Chapter 5 presents the study of the impact of water quality and treatment characteristics on HAA and THM concentrations in several full-scale water treatment systems. Chapter 6 describes the study that evaluated biodegradation and biostability of HAAs in a simulated distribution system using annular reactors. Results of the case study investigating the control of HAA concentrations through biological filtration are presented in chapter 7.

Each chapter constitutes a separate research effort directed at the overall objectives of this project, and contains a unique and specific set of objectives, describes the procedures employed to meet those objectives, and presents and discusses the results and conclusions related to those objectives. Chapter 8 presents a summary of the findings of the individual research efforts and the conclusions as they apply to the overall project objectives.
CHAPTER 2
MEASUREMENT AND STABILITY OF HALOACETIC ACIDS IN DRINKING WATER

INTRODUCTION

HAAs are highly water-soluble DBPs that exist as ions at ambient pH. As part of their analysis, they must first be converted to their protonated forms before extraction from water with organic solvent, and then subsequently derivatized to form more volatile methyl esters that can be analyzed by gas chromatography (GC).

In November 1998, the USEPA established the MCL for five of the nine bromine- and chlorine-containing haloacetic acids (monochloro-, monobromo-, dichloro-, dibromo-, and trichloroacetic acid), termed HAA5, at 60 µg/L (USEPA 1998). The four unregulated species (bromochloro-, bromodichloro-, dibromochloro-, and tribromoacetic acid) are more highly brominated than HAA5 and may be just as toxic as HAA5. Nevertheless, the four remaining HAAs cannot be regulated until an analytical method that can accurately and reproducibly quantify these species is put in place. Additionally, overall HAA occurrence and factors influencing HAA behavior cannot be fully evaluated until a method is available for their analysis as well.

Routinely practiced methodologies, USEPA Method 552 (USEPA 1990a) and method 6251B from Standard Methods (APHA, AWWA, and WEF 1995) work well in quantifying six of the nine bromine- and chlorine-containing HAAs, which include bromochloroacetic acid along with the HAA5 and are collectively referred to as HAA6. Problems arise, however, when an effort is made to extend these methodologies to the HAA3 species (bromodichloro-, dibromochloro-, and tribromoacetic acid). Inefficiencies in the extraction or derivatization processes, or both, preclude accurate quantitation of HAA3 using either method as written. Before the HAA3 species can be investigated or regulated, a reproducible method for HAA3 analysis must exist. Because both the USEPA and Standard Methods procedures work well for HAA6, the ability to extend these methodologies for use with all nine HAA species is necessary. Without this capability, it is not possible to monitor these species for regulatory compliance.
STUDY DESIGN AND OBJECTIVE

The goal of this part of the project was to adapt either method 6251B (Standard Methods) or USEPA Method 552.2 (USEPA 1995a) to establish an accurate, sensitive, and reproducible method for HAA9 analysis. The efficiencies of the current methodologies in converting the HAA3 species to their corresponding esters were assessed. Both methods involve acidifying water samples, then extracting the acids from salt-containing water into methyl tertiary butyl ether (MTBE). Following extraction, the acids are converted to their methyl esters using acidic methanol (USEPA Method 552.2) or diazomethane (CH$_2$N$_2$; method 6251B [Standard Methods]), and analyzed using gas chromatography with electron capture detection (GC-ECD). These established methods were assessed for their effectiveness in derivatizing the HAA3 species, and an adapted methodology that could accurately quantify all nine HAAs was developed.

Once the methodology for HAA9 analysis was in place, a series of experiments examining the stability of HAAs in water under various pH and temperature conditions was performed. Little research to this point has been published about the stability of HAAs in water. These experiments helped to establish the conditions under which HAAs will decompose.

CURRENT ANALYTICAL METHODS

Nine bromine- and chlorine-containing haloacetic acids are produced from the chlorination of NOM (Table 2.1). Several different methods have been published for analyzing HAAs, the most popular involving extraction from water, derivatization, and analysis using GC-ECD. Because HAAs are nonvolatile, they cannot be measured by direct GC analysis. As the acids are halogenated, however, they are very sensitive to electron capture detection. If GC-ECD is to be used for HAA analysis, it is necessary to extract the acids from water into an organic solvent, then derivatize them to convert the acids to their more volatile methyl esters (which are more amenable to GC analysis). Because HAAs are present almost entirely in their ionized forms at ambient pH, it is also necessary to acidify each water sample before extraction to protonate the HAAs so that they will partition preferentially into the extraction solvent.
<table>
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<tr>
<th>Acid acronym</th>
<th>Molecular weight (g/mol)</th>
<th>Structure</th>
<th>Boiling point (°C)</th>
<th>Boiling point of ester (°C)</th>
<th>pKa *</th>
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<td>129.5</td>
<td>2.85</td>
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<tr>
<td>BrAA</td>
<td>138.95</td>
<td><img src="image" alt="Structure" /></td>
<td>208</td>
<td>132</td>
<td>2.69</td>
</tr>
<tr>
<td>Cl₂AA</td>
<td>128.94</td>
<td><img src="image" alt="Structure" /></td>
<td>194</td>
<td>142.9</td>
<td>1.48</td>
</tr>
<tr>
<td>Cl₃AA</td>
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<td>167.5</td>
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<tr>
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<td>128–130</td>
<td>N/A †</td>
<td>1.48</td>
</tr>
<tr>
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<td>173.39</td>
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<td>225</td>
<td>0.72</td>
</tr>
</tbody>
</table>

* pKa: negative logarithm of the acidity constant.
† N/A: not analyzed.
A major shortcoming of the published GC-ECD methods is that the methods, as written, give inconsistent results for the HAA3 species. The methylating agents used (diazomethane or acidic methanol) are unable to convert the HAA3 species completely to their corresponding ester. In addition, the conversion efficiencies of the two derivatizing agents appear to fluctuate from run to run.

This would seem to dictate that the only way to assess, with any certainty, the recovery and derivatization efficiencies for HAA3 in field samples (and to compare them to the recovery and derivatization efficiencies for the calibration curve used to quantify the unknown samples) would be to spike every sample with known concentrations of HAA standards, then calculate the spike recovery. If the spike recoveries for the calibration curves and field samples are significantly different, the analyte concentrations calculated for the field samples would most likely be inaccurate. Even if the conversion efficiencies for the calibration curve and unknown samples were shown to be similar, the fact that percent conversion is low for HAA3 means that the limit of detection (LOD) would not be particularly low for these species. Some of the less commonly used HAA analytical methods eliminate the need for extraction, acidification, and derivatization, or all three, before analysis. Regardless of these apparent advantages over the GC-ECD methods, none of the alternative methods has been shown to quantify the HAA3 species accurately and consistently. Furthermore, when the same sample is analyzed using different methods, the results obtained using each method are often significantly different. These shortcomings illustrate the need for a consistent, sensitive analytical method for the HAA3 species. None of the current published methods can quantify HAA3 in a reproducible manner.

**Liquid-Liquid Extraction (LLE) With Derivatization**

The most widely used methods for HAA analysis are method 6251B (*Standard Methods*) and USEPA Method 552 (and its subsequent updates). Both of these methods involve extraction of the acids from water into MTBE followed by esterification to convert the acids to their methyl ester derivatives. The methylated acids are then quantified using GC-ECD. Method 6251B (*Standard Methods*) and USEPA Method 552 use diazomethane as the derivatizing agent, and USEPA Method 552.2 (USEPA 1995a) uses acidic methanol. The use of diazomethane has been somewhat discouraged in the literature because of the toxic, carcinogenic, and explosive nature of
the derivatizing agent. USEPA Method 552.2 was developed to present a safer alternative to diazomethane. However, USEPA Method 552.2 takes longer and involves even more handling steps than the already laborious esterification using diazomethane. USEPA Method 552.2 was also designed to quantify all nine HAA species, although it does not necessarily do so. In fact, acidic methanol is known to decarboxylate tribromoacetic acid (Br₃AA). It is apparent, then, that the USEPA method exhibits serious limitations in quantifying at least Br₃AA. Method 6251B (Standard Methods) was developed to quantify only the HAA6 species and has not previously been demonstrated, as written, to be effective for measuring all nine HAA species. Therefore, it was essential to first evolve a reliable method that could accurately measure all nine HAA species with a high degree of sensitivity, accuracy, and reproducibility.

**Haloacetic Acid Stability Issues**

Often, before water samples can be analyzed for HAAs, they must be transported from the water utility where they were collected to a laboratory for analysis. Thus, it is important to develop a sampling protocol to ensure that the analyte concentrations are preserved during transport. The analytes are preserved by adding a chlorine-quenching agent to the samples to prevent continued reaction of the chlorine with DOC during transport. USEPA Method 552.2 and method 6251B (Standard Methods) use ammonium chloride as the quenching agent. Alternatives include ammonium sulfate, sodium sulfite, sodium thiosulfate, and sodium arsenite. Croué and Reckhow (1989) showed that some DBPs such as chloropicrin, trichloroacetonitrile, and dibromoacetonitrile are rapidly destroyed in the presence of sulfite. This finding illustrates the importance of evaluating the effects of different quenching agents on the species to be analyzed before sample collection begins. Research has also shown that HAAs may be biodegradable (e.g., Williams and Williams 1998). For this reason, it may be necessary to use a biocide to preserve samples during transport. Before a biocide is added to the sampling protocol, the effects of different biocides on HAA stability must be examined.
MATERIALS AND METHODS

Glassware and Reagents

HAA standards and haloester standards were obtained from Supelco, Inc. (Bellefonte, Pa.). Six of the HAAs (monochloro-, monobromo-, dichloro-, dibromo-, trichloro-, and bromochloroacetic acid) were purchased as a mixture containing 2 mg/mL of each component dissolved in MTBE. The three remaining bromine- and chlorine-containing HAAs (bromodichloro-, dibromochloro-, and tribromoacetic acid) were purchased as neat standards. Single-component stock solutions were prepared for each of the HAA3 by dissolving a weighed amount of each component in a known volume of UltraResi-Analyzed MTBE (J.T. Baker, Phillipsburg, N.J.) to obtain concentrations of between 2 and 5 mg/mL. As with the acid standards, six of the haloesters were purchased in a mixture containing 1 mg/mL of each methyl ester (ClAA, BrAA, Cl2AA, Br2AA, Cl3AA, and BrClAA) dissolved in MTBE, and the other three bromine- and chlorine-containing haloesters (BrCl2AA, Br2ClAA, and Br3AA) were purchased as neat standards. Stock solutions for the haloesters for HAA3 were prepared in the same manner as the HAA3 standard stock solutions. HAA3 stock solutions were prepared as single-component solutions because the HAA3 species, particularly Br3AA, are subject to degradation. By preparing separate stock solutions for each of these standards, the standards could be easily monitored and replaced upon degradation, preventing contamination of the HAA6 stock solution. All stock solutions were stored in a freezer at –11°C in 5-mL amber glass vials with screw-top caps and polytetrafluoroethylene (PTFE)-lined septa. New stock solutions were prepared every 3 months, or upon degradation.

1,2,3-Trichloropropane (Aldrich Chemical Co., Milwaukee, Wis.) was used as the internal standard during analysis of HAAs. Stock solutions of the internal standard were prepared by dissolving a weighed amount of the standard in MTBE. Internal standard stock solutions were prepared at a concentration of 5 ± 1 mg/mL. 2,3-Dibromopropionic acid, the surrogate recovery standard, was purchased from Supelco as a single-component stock solution (1 mg/mL) in MTBE. The surrogate recovery methyl ester was also purchased from Supelco as a single-component stock solution (1 mg/mL) dissolved in MTBE. The internal standard and surrogate stock solutions
were stored at –11°C in 5-mL amber glass vials with screw-top caps and PTFE-lined septa. Stock solutions of the internal standard and surrogate were replaced every 3 months, or as needed.

Stock solutions were prepared at much higher concentrations than could be used during analysis. For this reason, it was necessary to prepare dilutions of the HAA standards, methyl ester standards, and the surrogate recovery standard before analysis. Primary and secondary dilutions were prepared containing all nine HAA species at concentrations of 100 µg/mL and 10 µg/mL, respectively. Microliter volumes for dilutions of all standards were measured using either a 10–60 µL or 50–250 µL SMI Micro/Pettor (Fisher Scientific, Pittsburgh, Pa.). The dilutions were prepared in MTBE and stored at –11°C in 5-mL amber glass vials. The primary and secondary dilutions of HAA9 were prepared no longer than 1 week before use. A primary dilution containing the methyl esters of all nine HAA species was prepared in the same manner as the acid dilutions at a concentration of 100 µg/mL. A primary dilution of the surrogate recovery standard was prepared in MTBE at a concentration of 20 µg/mL. Surrogate recovery dilutions were also stored at –11°C in 5-mL amber glass vials. The surrogate dilution was replaced as needed, or upon contamination.

UltraResi-Analyzed MTBE (J.T. Baker) was used as the extraction solvent, as well as to prepare stock solutions of standards. Granular, analytical grade anhydrous sodium sulfate (Mallinckrodt Baker, Inc., Paris, Ky.) and certified American Chemical Society (ACS) PLUS grade sulfuric acid (Fisher Scientific) were used during the extraction process. The sodium sulfate was baked at 400°C for at least 24 hours in a Lindbergh muffle furnace (Watertown, Wis.), then cooled to room temperature before use. Sodium sulfate was baked to remove impurities and to ensure that the salt was completely anhydrous. The sulfuric acid was dispensed from an amber glass reagent bottle equipped with a Lab Industries Repipet II dispenser (Fisher Scientific) capable of dispensing 0.0–5.0 mL of acid. All samples were extracted by vortexing with a Thermolyne Type 16700 Mixer (Fisher Scientific). Magnesium sulfate (Aldrich Chemical Co.) was used to remove dissolved water from the MTBE before derivatization.

Both diazomethane and acidic methanol were used to derivatize HAAs as part of the analytical procedure. Diazomethane was generated using Di(ethylene glycol) ethyl ether (Carbitol) and N-methyl-N-nitroso-p-toluenesulfonamide (Diazald). Both reagents were purchased from Aldrich Chemical Co. The reaction was catalyzed using a 45 percent w/w aqueous solution of potassium hydroxide (J.T. Baker). Excess diazomethane was quenched using Baker-Analyzed
silicic acid (n-hydrate, powder), purchased from J.T. Baker. Acidic methanol was prepared using UltraResi-Analyzed methanol (J.T. Baker) and Certified ACS PLUS-grade sulfuric acid (Fisher Scientific). After derivatization, the acid solution was neutralized with a saturated sodium bicarbonate (Fisher Scientific) solution. The solution was prepared by adding approximately 150 mL of deionized organic-free water (DOFW) to a beaker. DOFW was prepared by purifying tap water using a Dracor Water Systems purifying system (Dracor, Inc., Durham, N.C.). The purifying system was equipped with two mix-bed resins, a carbon tank, and a macrodeionizer. Sodium bicarbonate was added gradually, with stirring, until the solution became saturated (i.e., the sodium bicarbonate began to settle to the bottom of the beaker rather than dissolving). The saturated solution was filtered under vacuum to remove the solid sodium bicarbonate and stored at room temperature in a 250-mL amber glass reagent bottle until use.

At the time of collection, it was necessary to stabilize aqueous samples through the addition of both a biocide and a chlorine-quenching agent. Several reagents were evaluated for this purpose. Sodium azide and mercuric chloride (both from Aldrich Chemical Co.) were evaluated as biocides. The chlorine-quenching agents that were tested included ammonium chloride (Mallinckrodt), ammonium sulfate (Mallinckrodt), sodium sulfite (Fisher Scientific), sodium thiosulfate (Mallinckrodt), and sodium meta-arsenite (Aldrich Chemical Co.).

Many experiments performed as part of the study required pH adjustment and buffering. Solutions were adjusted to varying pH values using either a 0.1M phosphate or 0.25M borate buffer, and 0.1M sodium hydroxide or 0.1M hydrochloric acid. The phosphate buffer was prepared using either monobasic sodium phosphate (Fisher Scientific) or monobasic potassium phosphate (Mallinckrodt). Borate buffer solutions were prepared using ACS-grade sodium borate (Fisher Scientific). Sodium hydroxide pellets (Mallinckrodt) were used to prepare 0.1N sodium hydroxide solutions, and certified ACS PLUS-grade hydrochloric acid (Fisher Scientific) was used to prepare 0.1M hydrochloric acid solutions. Each buffer was prepared as directed by the CRC Handbook of Chemistry and Physics (Lide 1995). Table 2.2 lists the volumes of buffer and sodium hydroxide (NaOH) or hydrochloric acid (HCl) that were combined to prepare each pH solution. A Fisher Scientific pH meter was used to measure the pH of the resulting buffers, and NaOH or HCl was added as needed to achieve round pH values of 6, 7, 7.5, 8, 8.5, 9, 9.5, and 10. Because free chlorine is very unstable in aqueous solutions, it was necessary to standardize
chlorine stock solutions to determine their exact concentrations on each day that samples were to be chlorinated. The stock solutions were standardized according to method 408A (*Standard Methods*), the Iodometric Method (APHA, AWWA, and WEF 1995). First, 4.904 g anhydrous potassium dichromate (Mallinckrodt) was added to 1 L DOFW to make a 0.1 N solution. Twenty-five grams of sodium thiosulfate were added to 1 L DOFW to make a 0.1 N solution. The thiosulfate solution was standardized by titrating it with the potassium dichromate. The chlorine stock solution was then standardized by titrating the solution against the sodium thiosulfate.

Samples were collected in clear 40-mL EnviroWare Borosilicate USEPA vials with screw-top caps and PTFE-lined septa (Fisher Scientific). Either 20-mL clear glass vials with screw-top caps and PTFE-lined septa or 2-mL volumetric flasks with screw-top caps and PTFE-lined septa (VWR Scientific Products, Suwanee, Ga.) were used for the derivatization step of the analytical procedure. Buffer solutions were stored in amber glass reagent bottles with screw-top caps and PTFE-lined septa. Clear borosilicate autosampler vials (Fisher Scientific) were used for GC analysis. The vials were sealed using aluminum crimp-caps lined with Teflon-faced rubber septa (Fisher Scientific). All glassware was scrupulously cleaned before use. First, the glassware was soaked overnight in a solution of Alconox (Alconox Inc., White Plains, N.Y.) soap and tap water. It was then rinsed thoroughly with tap water, and soaked for at least 24 hours in an acid bath.

### Table 2.2
Buffer solutions giving round values of pH at 25°C

<table>
<thead>
<tr>
<th>pH</th>
<th>Buffer used(^a)</th>
<th>Volume 0.1(M) NaOH added (mL)</th>
<th>Volume 0.1(M) HCl added (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.1(M) dihydrogen phosphate</td>
<td>5.6</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>0.1(M) dihydrogen phosphate</td>
<td>29.1</td>
<td>N/A</td>
</tr>
<tr>
<td>7.5</td>
<td>0.1(M) dihydrogen phosphate</td>
<td>40.9</td>
<td>N/A</td>
</tr>
<tr>
<td>8</td>
<td>0.1(M) dihydrogen phosphate</td>
<td>46.1</td>
<td>N/A</td>
</tr>
<tr>
<td>8.5</td>
<td>0.025(M) borate</td>
<td>N/A</td>
<td>15.2</td>
</tr>
<tr>
<td>9</td>
<td>0.025(M) borate</td>
<td>N/A</td>
<td>4.6</td>
</tr>
<tr>
<td>9.5</td>
<td>0.025(M) borate</td>
<td>8.8</td>
<td>N/A</td>
</tr>
<tr>
<td>10</td>
<td>0.025(M) borate</td>
<td>18.3</td>
<td>N/A</td>
</tr>
</tbody>
</table>

\(^a\) 50 mL of phosphate or borate buffer was used for all pH values.

N/A: not added.
containing a 10 percent aqueous solution of concentrated ACS PLUS-grade nitric acid (Fisher Scientific). Following the acid wash, glassware was rinsed three times with tap water, then three times with DOFW. The treated water was then filtered through a 1-\( \mu \)m prefilter and a capsule filter to remove bacteria. After rinsing with DOFW, nonvolumetric glassware was dried overnight at 180°C. Volumetric glassware was rinsed three times with Baker Analyzed high-performance liquid chromatography (HPLC)-grade methanol (J.T. Baker) and dried overnight in a ventilation hood and inverted onto dioxin-free paper. Caps and PTFE-lined septa were washed according to the same procedure, then dried overnight at 80°C. This entire cleaning procedure was performed after every experiment, except for soaking overnight in the soap solution. The soap and water wash was performed every 3 months. For routine cleaning between analyses, the glassware was rinsed with tap water before soaking in the acid bath, rather than soaking overnight in the Alconox soap solution.

Diazomethane was generated using an MNNG (1-methyl-3-nitro-1-nitrosoguanidine) diazomethane-generation apparatus (Aldrich Chemical Co.). Before use, the generators were cleaned according to the procedure outlined in the preceding paragraph. Immediately after use, the generators were soaked in a 5\( \text{N} \) sodium hydroxide bath for at least 30 min to destroy any unreacted Diazald. The generators were then rinsed thoroughly with tap water, and soaked for at least 24 hours in the 10 percent nitric acid bath. Following the acid bath, the generators were rinsed three times with tap water, then three times with DOFW, then dried overnight at 180°C.

**Current Analytical Methods**

*Liquid-Liquid Extraction With Derivatization*

To quantify HAAs using GC, the acids must be extracted from water into an organic solvent, and esterified to convert each halogenated carboxylic acid into its more volatile methyl ester derivative. Method 6251B (*Standard Methods*) was developed to quantify the HAA6 species: ClAA, BrAA, Cl\(_2\)AA, Br\(_2\)AA, Cl\(_3\)AA, and BrClAA. The procedure involves a microextraction of the acids from water into MTBE followed by methylation of the acids using diazomethane. USEPA Method 552.2 involves a similar microextraction step, but acidic methanol is used as the derivatizing agent instead of diazomethane. Method 6251B (*Standard Methods*) was
designed to analyze the HAA6 species; USEPA Method 552.2 was designed to quantify all nine HAA species.

HAA levels in field samples were quantified using multilevel calibration curves, which were prepared with DOFW fortified with HAA9 standards. Calibration solutions were prepared, in duplicate, spanning six concentration levels, including a blank. Five 100-mL volumetric flasks were filled to the neck with DOFW. Each flask was then spiked with an appropriate volume of the primary or secondary standard dilution using a 10–60 µL SMI Micro/Pettor, to obtain concentrations of 1, 5, 10, 25, and 50 µg/L. The flasks were topped to the line with DOFW, capped, and inverted three times to mix. The calibration standards were extracted and derivatized at the same time as the field samples to be quantified. A fresh calibration curve was generated for each batch of samples analyzed.

Before extraction, MTBE was spiked with approximately 200 µg/L of the internal standard, 1,2,3-trichloropropane. The solution was prepared by filling a 500-mL volumetric flask to the neck with MTBE. An appropriate amount of internal standard stock solution was added to the solvent using a 10–60 µL SMI Micro/Pettor. The volumetric flask was filled to the line with MTBE, capped, and inverted three times to mix. After preparation, the MTBE with internal standard solution was transferred to a 1-L amber reagent bottle equipped with a Lab Industries L/I Repipet II dispenser (Fisher Scientific) capable of dispensing 1–10 mL of solvent. One-inch-wide Teflon tape was wrapped around the seal between the dispenser and the reagent bottle in an effort to prevent contamination of the solvent. The bottle was stored in a ventilation hood until use. The day before samples were to be analyzed, more extraction solvent was prepared (if necessary). An aliquot of the MTBE with internal standard solution was analyzed on the GC to ensure that the solvent solution had not been contaminated since the previous experiment. If the solvent was found to be contaminated, a new solution was prepared and the solvent bottle was washed several times with the new solution before filling to wash out any traces of the contaminated solvent. Upon sample analysis, the same batch of MTBE with internal standard was used to extract both the calibration standards and the unknown samples.

When samples were collected in the field, the sample bottles were stored in the refrigerator at 4°C until the day of analysis (no longer than 2 weeks). Before sample extraction began, the sample bottles were allowed to sit on the lab bench for approximately 1 hour until they had warmed to room temperature.
As a quality control measure, all samples and calibration solutions were analyzed in duplicate. Twenty milliliters of each sample or calibration standard was measured using a 25-mL graduated cylinder and transferred into a clear glass 40-mL vial with a screw-top cap and a TFE-lined septum. The calibration standards were transferred to the 40-mL vials in order of increasing concentration, starting with blank DOFW and finishing with the 50 µg/L calibration point. The same 25-mL graduated cylinder was used for all calibration points and unknown samples; however, the cylinder was rinsed twice with approximately 5-mL aliquots of the appropriate sample or calibration solution before each 20-mL aliquot was measured. The graduated cylinder was not rinsed between measurements of duplicate samples.

The samples and calibration standards were taken to a ventilation hood and 20 µL of the surrogate primary dilution was added to each sample vial using a 10–60 µL SMI Micro/Pettor, giving a final concentration of 20 µg/L of surrogate in each sample. After the surrogate was added, the samples or calibration standards were acidified with 1.5 mL of concentrated sulfuric acid to obtain a pH of 0.5 or lower. Each bottle was capped and inverted once to mix after the acid addition. Because this step generates heat, the samples were placed in an ice bath for a few minutes to return them to room temperature. The acidification step converted the HAAs almost entirely to their protonated forms, which are more readily extractable into MTBE. After acidification, approximately 10 g of anhydrous sodium sulfate, previously baked at 400°C for 24 hours, was added to each sample, followed by 4 mL of MTBE containing internal standard. Each vial was vortexed for 60 sec to extract the acids from the aqueous phase into the organic phase. Following extraction, the vials were allowed to sit for at least 5 min so that the water and ether layers could separate completely.

*Derivatization With Acidic Methanol*

The methanol for this procedure was acidified using concentrated sulfuric acid. A 50-mL volumetric flask was placed in an ice bath, and 20–30 mL of methanol was added to the flask. Five milliliters of concentrated sulfuric acid was added drop-wise to the methanol. The volumetric flask was filled to the mark with methanol, capped, and inverted three times to mix. The solution was stored at room temperature in a 100-mL amber glass reagent bottle until use, for no longer than 1 week. Using a 2-mL glass bulb pipette, 2 mL of the upper ether layer of each extracted
sample was transferred to a 20-mL clear glass vial with a screw-top cap and a TFE-lined septum. One milliliter of acidic methanol was added to each vial using a 1-mL glass bulb pipette. The vials were capped, inverted once to mix, and placed in an incubator at 50°C for 2 hours. Acid-catalyzed derivatization of the analytes occurred via the Fischer esterification reaction, shown in Equation 2.1:

\[
\begin{align*}
H_2SO_4 & \\
CX_3COOH + CH_3OH & \rightarrow CX_3COOCH_3 + H_2O \\
\text{Haloacetic Acid} & \text{Methyl Ester Derivative} \\
X = \text{Cl, Br, or H}
\end{align*}
\]

After derivatization, the vials were removed from the incubator and allowed to cool to room temperature before removing the caps.

A volume of 4 mL of saturated sodium bicarbonate solution was added to each vial, in 1-mL increments, to neutralize the acid in each extract. Each vial was shaken for two minutes, with frequent venting to allow carbon dioxide (CO\(_2\)) gas to escape. The addition of carbonate to the acidified methanol neutralizes the excess H\(^+\) ions present in the extract through the formation of carbonic acid. CO\(_2\) gas is released as a result of the back extraction of H\(^+\) ions into the aqueous phase and the formation of carbonic acid. CO\(_2\) is released until the distribution of carbonate in the aqueous solution reaches equilibrium. Once equilibrium was reached (i.e., no more gas was being released), the organic and aqueous phases were allowed to separate. Then approximately 1 mL of the upper ether layer of each vial was transferred into an autosampler vial and sealed with a crimp cap.

*Derivatization With Diazomethane*

Diazomethane is formed by the reaction of Carbitol and Diazald. The reaction is catalyzed by the addition of strong base. Because diazomethane is toxic, carcinogenic, and explosive, extreme care was taken during its preparation. The diazomethane solution was kept cold at all times, and was not stored in the freezer for longer than 1 week before use or destruction.

Diazald and Carbitol were chosen as the diazomethane precursors rather than MNNG because MNNG is a known potent mutagen. It has been reported in the literature that Diazald can
be used in place of MNNG in the MNNG-diazomethane generation apparatus (Ngan and Toofan 1991). Two models of generators, both composed of low-extractable borosilicate glass, were used (see Figure 2.1). One model was assembled with Clear-Seal (Wheaton Science Products) grease-free joints (unground), and the other used an O-ring with a pinch clamp instead of Clear-Seal joints. The latter model was found to be more effective in producing a strong diazomethane solution, as the O-ring seal prevented the escape of diazomethane at the joint between the inner and outer jackets of the generator. Both types of generators consist of an inner tube equipped with a vapor release hole at the top, fitted into an outer collection jacket. As gaseous diazomethane is formed in the inner tube, the product escapes via the vapor release hole and collects in the outer jacket of the generator.

The entire process of diazomethane production was carried out with the generators resting in an ice bath placed far to the rear of a ventilation hood. The diazomethane solution must be kept cold to prevent explosion. In addition, because Carbitol is both carcinogenic and teratogenic, and Diazald is a severe irritant, exposure to diazomethane and its precursors must be prevented.

Each diazomethane generator produced 3 mL of diazomethane solution. To derivatize each sample, 225 µL of diazomethane is needed. Therefore, each time diazomethane was generated, it was necessary to calculate how many generators would be needed to produce enough diazomethane for all the samples. Diazomethane was generated according to the procedure described below.

First, 3 mL of MTBE was added to the outer tube of the generator. The two parts of the generator were then assembled and clamped using a pinch-clamp. Care was taken to ensure that the escape hole at the top of the inner tube of the generator was facing up. This prevented any of

![Figure 2.1 Millimole MNNG diazomethane-generation apparatus](image-url)
the reactants from spilling into the collection tube when the contents of the generator were mixed. Next, 1 mL of Carbitol and approximately 250 mg of Diazald were added to the inner tube of the generator, along with 1 mL of MTBE. To avoid excess handling of the Diazald, the reagent was not weighed each time diazomethane was prepared. Two hundred and fifty milligrams of Diazald was initially weighed by placing a balance in a ventilation hood. It was then determined that nine small, flattened spatulas of Diazald equaled approximately 250 mg of Diazald. This was used as a rough measure for Diazald in future preparations. After adding the reactants, each generator was capped with a screw-top cap with a PTFE-lined septum, and the contents of the tube were mixed gently (taking care that the contents of the inner jacket did not escape into the outer tube) so the reactants could dissolve in the MTBE.

The diazomethane reaction was catalyzed by adding 1.5 mL of 45 percent w/w potassium hydroxide solution to the Diazald solution. The base was added by piercing the septum of the cap and adding the solution drop-wise using a 5-mL gas-tight syringe equipped with an 18-gauge syringe needle. It was essential to add the potassium hydroxide slowly, to prevent pressure buildup in the inner tube of the generator. The diazomethane was allowed to form for 30 to 45 min while mixing gently every 5 to 10 min. Diazomethane is a yellow gas. As the gas was formed, the diazomethane dissolved in the MTBE in the outer tube of the generator as an ethereal solution.

After the reaction was complete, the generators were removed one by one from the ice bath, and the diazomethane from all of the generators was collected together in a 40-mL clear glass vial with a screw-top cap and a TFE-lined septum. First, the outer tube was wiped thoroughly to remove condensation from the outside of the generator. Water destroys diazomethane by reacting with it to form nitrogen gas and possibly methanol. The screw-top cap was removed from the generator, the generator was unclamped, and the inner tube was removed and placed in a 5N sodium hydroxide bath. The 40-mL vial was then uncapped, the contents of the outer tube were poured into the vial, and the 40-mL vial was recapped. The outer tube of the generator was also placed into a 5N sodium hydroxide bath. This process was repeated for all generators. The 40-mL collection vial was then placed inside a 250-mL beaker for protection, and the solution was stored in an explosion-proof freezer until immediately before use.

The diazomethane generators were allowed to soak in the 5N sodium hydroxide bath for at least 30 min, to destroy any unreacted Diazald. The generators were then cleaned according to the procedure described for glassware.
Using a disposable glass Pasteur pipette, 2 mL of the upper ether layer of each sample or calibration standard was transferred to a 2-mL volumetric flask with a screw-top cap and a TFE-lined septum. The MTBE–diazomethane solution was removed from the freezer and taken to a ventilation hood. Next, 250 µL of cold diazomethane solution was added to each sample vial using a 50–250 µL SMI Micro/Pettor. Samples were capped and inverted once to mix after the derivatizing agent was added. Caution was taken to avoid exposure to the toxic diazomethane by keeping both the extract and the vial containing the diazomethane solution well to the back of the ventilation hood during this step. After the diazomethane was added, all samples were placed in an explosion-proof refrigerator for 15 min, then placed in the hood for 15 min to allow them to return to room temperature. Each extract was examined to make sure that a persistent, if faint, yellow color remained. It is important that excess derivatizing agent is added to each sample, so that the esterification reaction will go to completion for all nine HAA species.

After the 30-min reaction time, excess diazomethane was quenched in each sample with approximately 100 mg of silicic acid. One small, flattened spatula of silicic acid was found to equal approximately 100 mg. After adding quenching agent, each extract was capped, inverted to mix, and left in the ventilation hood for approximately 15 min to allow excess silicic acid to settle to the bottom of the flask.

Approximately 1 mL of the upper layer of each sample extract was transferred to a clear glass borosilicate autosampler vial using a disposable glass Pasteur pipette. The autosampler vials were sealed using crimp-top aluminum caps lined with Teflon-faced rubber septa. Samples were either analyzed immediately on the GC or stored in the freezer at −11°C for no longer than 2 weeks. If stored in the freezer, the samples were allowed to warm to room temperature before GC analysis.

Gas Chromatography

Samples were analyzed on a Hewlett-Packard (HP) model 5890 Series II GC equipped with a ⁶³Ni electron capture detector, an HP 6890 Series autosampler, and fused silica capillary columns. Helium (99.999 percent pure) was used as the carrier gas, and nitrogen (99.999 percent pure) was used as the make-up gas. The carrier gas was further purified with both a high-capacity carrier gas purifier (Supelco) and an R&D oxygen trap (J&W Scientific, Inc., Folsom, Calif.) before entering the GC. Table 2.3 lists the GC conditions.
Before use, the column was conditioned by installing one end of the column into the injector, but leaving the detector end of the column unattached. A plug was attached to the inlet to the detector to prevent contamination of the detector during column conditioning. The carrier gas was allowed to flow through the column, the oven temperature was raised to 250°C, and the column was baked overnight. After conditioning, the oven and the detector were brought back to room temperature, and the column was attached to the detector. Once the baseline of the detector stabilized, the samples were loaded onto the GC. If sample extracts had been stored in the freezer before analysis, the extracts were allowed to return to room temperature before the sample sequence was run. Before running the calibration curve or unknown samples, a sample vial containing only MTBE was injected onto the column to condition the GC column and to ascertain that analytical interferences were absent. Following injection of the solvent blank, a vial containing MTBE with internal standard was injected into the column. The calibration curve was then run following the MTBE with internal standard, starting with the lowest calibration point (0 µg/L) sequentially up to the highest calibration point (50 µg/L). After the calibration curve was run, the vial containing MTBE with internal standard was injected again before analyzing the

<table>
<thead>
<tr>
<th>Table 2.3 — GC conditions for HAA analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column</strong></td>
</tr>
<tr>
<td>Length: 30 m</td>
</tr>
<tr>
<td>ID: 0.25 mm</td>
</tr>
<tr>
<td>Film thickness: 1 µm</td>
</tr>
<tr>
<td><strong>Temperature program</strong></td>
</tr>
<tr>
<td>Ramp to 75°C at 5°C/min. Hold for 15 min. Ramp to 100°C at 5°C/min. Hold for 5 min. Ramp to 135°C at 5°C/min. Hold for 10 min.</td>
</tr>
<tr>
<td><strong>Injector</strong></td>
</tr>
<tr>
<td>Temperature: 180°C</td>
</tr>
<tr>
<td>Split valve opened at 0.5 min.</td>
</tr>
<tr>
<td><strong>Detector</strong></td>
</tr>
<tr>
<td>Temperature: 280°C–300°C</td>
</tr>
<tr>
<td><strong>Gas flow</strong></td>
</tr>
<tr>
<td>Nitrogen: 40–60 mL/min</td>
</tr>
</tbody>
</table>
unknown samples. Calibration check standards were run after every tenth sample. The calibration check standard consisted of a calibration point within the expected range of analyte concentrations (usually 10 µg/L). The check standard was run to ensure that the detector response did not change during the sample run. The relative peak areas (analyte peak area divided by internal standard peak area) of the analytes in the calibration check standard were compared to the relative peak areas for each species of the equivalent calibration point. If the relative standard deviation (RSD) between the check standard response and the calibration curve response was greater than 10 percent, the check standard and the samples following the check standard were rerun. If the RSD was still greater than 10 percent, the data obtained for the samples following this point were treated as suspect.

Data Analysis

HAA levels in the samples were quantified using a response factor calculated from the calibration curve data. The calibration curve was drawn using the results obtained for the calibration standards prepared as described earlier. The relative peak area (RPA), defined as the ratio of component peak area to internal standard peak area, was used instead of the absolute peak area to account for any changes in detector response during the sample run. The RPA for each calibration point was plotted versus the concentration for that point. A linear trend line was drawn through the points to create the calibration curve. The concentration of the unknown sample was calculated using the slope and the y-intercept of the trend line, along with the RPAs for the analytes in each sample.

Analytical results were quality assured by comparing the detector responses of the internal standard and the surrogate recovery standard for each sample or calibration point. If the peak response of the internal standard for a particular sample or calibration point was more than 10 percent different from the average peak response across the batch of samples, the sample or calibration point was rerun. If the internal standard response was still out of line, the data obtained for that sample or calibration point were disregarded. Deviations in internal standard response usually denote a problem with the instrumental analysis and can be corrected by rerunning the sample. Experimental error during the extraction or derivatization process was detected by examining the peak response of the surrogate recovery standard for each sample or calibration point.
point. If the peak response of the surrogate recovery standard for a particular sample or calibration point was more than 10 percent different from the average peak response for the surrogate across the batch of samples, the data obtained for that sample or calibration point were disregarded. The RSD between duplicate samples was examined for all samples and calibration solutions. If the RSD was greater than 10 percent for calibration point duplicates, the data for the duplicate most out of line from the linear trend line were disregarded. If the RSD for sample duplicates was greater than 10 percent, the results for that particular sample were treated as suspect.

**METHOD DEVELOPMENT**

**Extraction and Analysis**

*Liquid-Liquid Extraction With Derivatization*

As discussed earlier, published HAA analytical methods can quantify the HAA6 species accurately and reproducibly. Problems arise, however, in attempting to extend these methodologies to incorporate the HAA3 species. The first step in developing an analytical method that could be used to quantify all nine bromine- and chlorine-containing HAA species was to assess the current methodologies and determine their efficiencies in quantifying the HAA3 species. The GC-ECD methods are most commonly used and are approved for USEPA work. Therefore, USEPA Method 552.2 (acidic methanol derivatization) and method 6251B (*Standard Methods*) (diazomethane derivatization) were chosen as the focus of this effort. The degree of sensitivity that can be achieved using either of these methods is a function of the extraction and derivatization efficiencies of the methods. The goal is to achieve near 100 percent reproducible extraction and derivatization efficiencies to maximize the detector response at a given concentration for each analyte. Both GC-ECD methods use similar extraction procedures but different derivatizing agents. Hence, the first step in assessing the two methods was to determine which derivatizing agent was most effective in methylating all nine HAA species.

The first assessment experiment compared the derivatization efficiencies of acidic methanol and diazomethane in methylating each of the HAA3 species. For this experiment, acid standards were prepared in DOFW at four different concentrations, including a blank. Each
sample solution was then extracted in duplicate according to the procedure described earlier. The acid standards were then methylated using diazomethane, and the percent conversion of acid to corresponding ester was calculated for each species. Next, the experiment was repeated using acidic methanol as the derivatizing agent, and the results of the two experiments were compared. This comparison was used to decide which method to pursue in terms of derivatization optimization for the HAA3 species. Once the optimal derivatizing agent was determined, the chosen method would be adapted to achieve maximum recovery of the HAA3 species without sacrificing sensitivity in quantifying the HAA6 species.

The derivatization efficiencies of diazomethane and acidic methanol in converting each HAA species to its corresponding ester were determined by comparing calibration curves for the derivatized acid standards to calibration curves that were prepared using methyl ester HAA standards. To do this, it was necessary to calculate the theoretical ester concentration of each acid species if 100 percent extraction and derivatization efficiencies were achieved. Using this calculation, the calibration curve for each species was drawn by plotting the theoretical ester concentration for a given concentration of acid standard in MTBE versus the relative peak area (peak area of analyte divided by peak area of internal standard) obtained for that particular concentration.

The efficiency of each derivatizing agent in converting the acids to esters was determined by comparing the derivatized acid calibration curves to the methyl ester standard calibration curves. Because the acid standards were extracted in water, less than 100 percent recovery of each species following derivatization could be due in part to an extraction efficiency of less than 100 percent. As the same procedure was used to extract both the acidic methanol and diazomethane samples, however, differences between the two calibration curves could be attributed to differences between the derivatization efficiencies of the two methylating agents.

Figures 2.2 through 2.7 present the results for the derivatization assessment experiments for each of the HAA3 species. As can be seen, both acidic methanol and diazomethane are less than 100 percent efficient in converting dibromochloracetic acid (Br₂ClAA) and tribromoacetic acid (Br₃AA) into their corresponding esters. In addition, the acidic methanol derivatization took substantially longer than the already lengthy diazomethane derivatization, with the most laborious step involving neutralization of the acidic methanol following derivatization. When sodium
Figure 2.2 Derivatization efficiency of acidic methanol in esterifying BrCl₂AA

Figure 2.3 Derivatization efficiency of diazomethane in esterifying BrCl₂AA
Figure 2.4 Derivatization efficiency of acidic methanol in esterifying Br₂ClIAA

Figure 2.5 Derivatization efficiency of diazomethane in esterifying Br₂ClIAA

Figure 2.6 Derivatization efficiency of acidic methanol in esterifying Br₃AA
bicarbonate (NaHCO₃) is added to neutralize the derivatizing agent, CO₂ gas is generated at a furious rate. Each sample vial must be constantly vented during the neutralization process to avoid pressure buildup. Also, if the NaHCO₃ is added too quickly, the analytes may be sparged from the sample when CO₂ is released. These shortcomings in the USEPA method suggest that diazomethane derivatization, although more hazardous, is preferable to using acidic methanol for HAA9 analysis. It is clear, however, that both the USEPA method and the Standard Methods method would need to be adapted in some way for use in accurately quantifying the HAA3 species.

The decision was made to try to optimize the diazomethane method so that it could be used to reliably quantify the HAA3 species. Diazomethane was chosen rather than acidic methanol for two reasons. The first reason related to the laborious nature of USEPA Method 552.2 as described above, and because the diazomethane approach takes less time than the acidic methanol approach, this method might be preferable if it can be adapted to work for all nine HAA species. Second, methylation using acidic methanol is known to result in the partial decarboxylation of tribromoacetic acid to form bromoform (Peters et al. 1991). For this reason, values obtained for Br₃AA using the acidic methanol method must always be treated as suspect. Because the extent of decarboxylation may be different in different matrixes, it would not be known whether values obtained for Br₃AA in a sample matrix would be accurate if determined using a calibration curve prepared in laboratory-grade water. Finally, it has been reported that the sensitivity and accuracy of USEPA Method 552.2 in quantifying all nine HAA species appears to fluctuate (La Guardia 1996). La Guardia attributed this variation to loss of HAAs as CO₂ evolves when NaHCO₃ is added to neutralize the acidic methanol.

Figure 2.7 Derivatization efficiency of diazomethane in esterifying Br₃AA
It was concluded, then, that USEPA Method 552.2 exhibits serious limitations in regards to providing a reproducible method for HAA9 analysis. When considering method 6251B (Standard Methods) for HAA analysis, concern has been raised about the toxic, flammable, and explosive properties of diazomethane. If the appropriate precautions are taken during the preparation and use of diazomethane, however, these hazards should not present a problem.

If the diazomethane method is to be optimized so that it can be used for the HAA3 species, the likely causes of less-than-complete recovery from water or from conversion to methyl ester, or both, for HAA3 must be determined. Method 6251B (Standard Methods) includes a drying step in the procedure before derivatization with diazomethane, suggesting that the presence of water in the ether extracts may negatively affect the derivatization process. A test in our laboratory showed that diazomethane is in fact destroyed by water. When tap water (ambient pH) was dripped into a solution containing diazomethane, destruction of the derivatizing agent could be seen from the loss of yellow color and the generation of gas. The reaction for the hydrolysis of diazomethane (McGarrity and Smyth 1980) is shown in Equation 2.2:

\[
\text{CH}_2\text{N}_2 + \text{H}_3\text{O}^+ \xrightarrow{k_1} \text{CH}_3\text{N}_2^+ + \text{H}_2\text{O} \xrightarrow{k_2} \text{CH}_3\text{OH}_2^+ + \text{N}_2
\]  

(2.2)

where \( k_1 = 4 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \)

\( k_1 \ll k_2 \)

\( k_2 = 2.1 \text{ s}^{-1} \)

Water dissolves to a small degree in MTBE. The mole fraction of MTBE that is saturated with water is 0.942 (Riddick and Bunger 1970). Thus, a 2-mL aliquot of water-saturated MTBE will contain 5.8 percent (0.116 mL) water before derivatization. This dissolved water will exhibit a certain demand on the diazomethane. For the HAA6 species, it appears that the kinetics of methylation are fast enough that the esterification reaction can go to completion before the diazomethane is depleted by the dissolved water. Because the HAA3 species are the heaviest of the HAAs, it is possible that the esterification reaction occurs more slowly for BrCl\(_2\)AA, Br\(_2\)ClAA, and Br\(_3\)AA. For this reason, the diazomethane may become depleted by dissolved water to the extent that methylation of the HAA3 species is kinetically hindered. A literature
review showed an apparent lack of kinetic data that would support this hypothesis. If the reaction rate constants for the methylation of HAA9 by diazomethane were known, it could be established more definitively whether the inability of diazomethane to completely esterify the HAA3 species using method 6251B (*Standard Methods*) is related to the kinetics of esterification.

To determine if the presence of water was hindering the esterification reaction for HAA3, the effect of dewatering the MTBE extracts before derivatization on HAA3 esterification was examined. The drying step described in method 6251B (*Standard Methods*) involves filtering the MTBE extracts through sodium sulfate (Na$_2$SO$_4$) that had been oven-dried overnight at 400°C. The process requires fitting a small plug of acid-washed glass wool into a disposable pipette and adding 1 g of acidified Na$_2$SO$_4$ on top of the glass wool. Exactly 2 mL of sample extract is passed through the salt. Then the glass wool is rinsed with two 250-µL aliquots of MTBE. Each extract is then blown down to approximately 1.7 mL before derivatization. A simplified version of this process was attempted in our laboratory. Anhydrous magnesium sulfate (MgSO$_4$) was chosen as the drying agent instead of Na$_2$SO$_4$ because it can be used as obtained without first oven-drying it. It is important, however, to ensure that the MgSO$_4$ is free from contamination, which could interfere with HAA analysis. The purity of the MgSO$_4$ was assessed by adding diazomethane to MTBE alone and to MTBE with approximately 50 mg of MgSO$_4$ added. The samples were then analyzed on the GC to determine whether any quenched by-products resulted from the use of MgSO$_4$. One chromatographic peak was observed (which will be discussed later), but otherwise the MgSO$_4$ appeared to be free of contaminants that would interfere with quantifying HAAs.

Several disposable pipettes were fitted with glass wool, and approximately 1 g of anhydrous MgSO$_4$ was added on top of the glass wool. The sample extracts were passed through the MgSO$_4$, collecting exactly 2 mL of each extract for derivatization. A second method of drying the extracts was also attempted as a comparison to the filtration method. Approximately 100 mg of solid MgSO$_4$ was added to each reaction flask containing the MTBE extracts immediately before adding the diazomethane. After addition of the salt, each flask was capped and inverted once to mix. The excess MgSO$_4$ was allowed to settle to the bottom of the flask before the diazomethane was added. This drying step is much easier and quicker than the drying step described in *Standard Methods*. It also requires less sample handling, which reduces the possibility of sample loss.

Comparisons of the ester recoveries using both of these methods of drying are shown in Figures 2.8 through 2.13.
It is evident from these results that a portion of the analytes was lost during filtration through the MgSO₄. The loss is probably due to adsorption of the HAA species to the surface of the glass wool. Standard Methods suggests acidifying the glass wool to minimize adsorption of the analytes during filtration. Nevertheless, filtering each sample as described in Standard Methods and blowing down the samples with nitrogen before adding the diazomethane is very time-consuming. On the other hand, adding MgSO₄ to the MTBE extracts before derivatization is simple and effective. Drying the extracts in this manner results in near 100 percent conversion of

Figure 2.8 Derivatization efficiency of diazomethane for BrCl₂AA when extract is filtered through MgSO₄

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Figure 2.9 Derivatization efficiency of diazomethane for BrCl₂AA when MgSO₄ is added to extract

It is evident from these results that a portion of the analytes was lost during filtration through the MgSO₄. The loss is probably due to adsorption of the HAA species to the surface of the glass wool. Standard Methods suggests acidifying the glass wool to minimize adsorption of the analytes during filtration. Nevertheless, filtering each sample as described in Standard Methods and blowing down the samples with nitrogen before adding the diazomethane is very time-consuming. On the other hand, adding MgSO₄ to the MTBE extracts before derivatization is simple and effective. Drying the extracts in this manner results in near 100 percent conversion of
the HAA3 species to their corresponding esters. The addition of this drying step allows all nine HAA species to be quantified, providing that recovery of the HAA6 species is unaffected by the change. The effect of the drying step on recovery of the HAA6 species is shown in Figures 2.14 through 2.19. As these figures show, the recoveries from water and conversions to methyl esters for the HAA6 species are not compromised by adding the drying step.

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Figure 2.10 Derivatization efficiency of diazomethane for Br₂ClAA when extract is filtered through MgSO₄

Figure 2.11 Derivatization efficiency of diazomethane for Br₂ClAA when MgSO₄ is added to extract
Figure 2.12 Derivatization efficiency of diazomethane for Br$_3$AA when extract is filtered through MgSO$_4$

Figure 2.13 Derivatization efficiency of diazomethane for Br$_3$AA when MgSO$_4$ is added to extract
Figure 2.14 Recovery and esterification efficiency for ClIAA using the adapted method

Figure 2.15 Recovery and esterification efficiency for BrAA using the adapted method

Figure 2.16 Recovery and esterification efficiency for Cl₂AA using the adapted method
Figure 2.17 Recovery and esterification efficiency for BrClAA using the adapted method

Figure 2.18 Recovery and esterification efficiency for Cl₃AA using the adapted method

Figure 2.19 Recovery and esterification efficiency for Br₂AA using the adapted method
Gas Chromatography

One problem with adding MgSO₄ to the extracts before diazomethane is that sulfate reacts with the derivatizing agent to create a product (dimethyl sulfide) that elicits a detector response upon GC-ECD analysis. In evaluating the recovery of all nine HAA species using the modified procedure, it was noted that this peak co-eluted with bromochloroacetic acid when a DB-1701 column was used (see Figure 2.20). This made it difficult to quantify BrClAA below 5 µg/L. In an effort to rectify this problem, several different GC columns were evaluated, to see if the use of an alternate column would allow resolution of all nine HAA species from each other and from the surrogate and internal standards. It was found that the use of a DB-1 column would allow resolution of all peaks of interest (Figure 2.21).

Detection Limits

The adapted method with the drying step and the DB-1 column were used to analyze for HAA9 in all subsequent laboratory work described in this report. Appendix A contains a copy of the revised procedure. Practical quantitation limits (PQLs) were established at 1 µg/L for all nine HAA species. The term PQL refers to the minimum concentration for which a consistent, linear response for the analyte can be obtained using the method, or that generates a detector response that is four times higher than the background noise. In practice, this is the lowest point on the calibration curve that can be practically obtained and is linearly related to higher concentrations on the curve. The method detection limit (MDL) for each species is a statistical measurement.

The MDL is defined as the lowest concentration reported for which it can be stated with 99 percent confidence that the concentration is greater than zero (Government Printing Office 1998). The MDL is obtained by multiplying the standard deviation (SD) for the mean concentration of seven replicates by the student-t value at 99 percent confidence and n-1 degrees of freedom. For seven replicates, the student-t value is 3.143. Tables 2.4 and 2.5 list the MDLs for HAA9. HAA9 standards were added to DOFW and evaluated on seven replicate analyses of each species at their PQLs and at 3 µg/L. At the PQL, values obtained by the established methods are exhibited alongside the experimental MDL calculated using the adapted method (Table 2.4).
Figure 2.20 GC of HAA6 at 10 µg/L of each species using DB-1701 column; BrClAA co-elutes with interfering peak

Figure 2.21 GC of HAA9 at 10 µg/L of each species using DB-1 column; all nine HAA peaks resolved
Table 2.4
Method detection limits for HAA9 established at their PQL

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Standard concentration added (µg/L)</th>
<th>Mean measured concentration (µg/L)</th>
<th>SD (µg/L)</th>
<th>RSD (%)</th>
<th>Experimental MDL (µg/L)</th>
<th>USEPA MDL (µg/L)</th>
<th>Method 6251B (Standard Methods) MDL (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClAA</td>
<td>1.00</td>
<td>1.00</td>
<td>0.081</td>
<td>8</td>
<td>0.255</td>
<td>0.273</td>
<td>0.082</td>
</tr>
<tr>
<td>BrAA</td>
<td>1.00</td>
<td>0.923</td>
<td>0.036</td>
<td>4</td>
<td>0.113</td>
<td>0.204</td>
<td>0.087</td>
</tr>
<tr>
<td>Cl₂AA</td>
<td>1.00</td>
<td>0.932</td>
<td>0.046</td>
<td>5</td>
<td>0.146</td>
<td>0.242</td>
<td>0.054</td>
</tr>
<tr>
<td>BrClAA</td>
<td>1.00</td>
<td>0.929</td>
<td>0.031</td>
<td>3</td>
<td>0.096</td>
<td>0.251</td>
<td>0.04</td>
</tr>
<tr>
<td>Cl₃AA</td>
<td>1.00</td>
<td>1.048</td>
<td>0.107</td>
<td>10</td>
<td>0.337</td>
<td>0.079</td>
<td>0.054</td>
</tr>
<tr>
<td>Br₂AA</td>
<td>1.00</td>
<td>1.01</td>
<td>0.080</td>
<td>8</td>
<td>0.252</td>
<td>0.066</td>
<td>0.065</td>
</tr>
<tr>
<td>BrCl₂AA</td>
<td>1.07</td>
<td>1.56</td>
<td>0.110</td>
<td>7</td>
<td>0.344</td>
<td>0.091</td>
<td>N/A</td>
</tr>
<tr>
<td>Br₂ClAA</td>
<td>1.04</td>
<td>1.08</td>
<td>0.095</td>
<td>9</td>
<td>0.300</td>
<td>0.468</td>
<td>N/A</td>
</tr>
<tr>
<td>Br₃AA</td>
<td>0.945</td>
<td>0.958</td>
<td>0.061</td>
<td>6</td>
<td>0.191</td>
<td>0.820</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A: not analyzed.

Table 2.5
Method detection limits for HAA9 established for analyte concentration = 3 µg/L

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Spiked concentration (µg/L)</th>
<th>Mean measured concentration (µg/L)</th>
<th>SD (µg/L)</th>
<th>Relative SD (%)</th>
<th>MDL (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClAA</td>
<td>3.00</td>
<td>2.77</td>
<td>0.120</td>
<td>4</td>
<td>0.409</td>
</tr>
<tr>
<td>BrAA</td>
<td>3.00</td>
<td>2.88</td>
<td>0.093</td>
<td>3</td>
<td>0.316</td>
</tr>
<tr>
<td>Cl₂AA</td>
<td>3.00</td>
<td>2.91</td>
<td>0.067</td>
<td>2</td>
<td>0.228</td>
</tr>
<tr>
<td>BrClAA</td>
<td>3.00</td>
<td>2.79</td>
<td>0.040</td>
<td>1</td>
<td>0.136</td>
</tr>
<tr>
<td>Cl₃AA</td>
<td>3.00</td>
<td>3.07</td>
<td>0.106</td>
<td>3</td>
<td>0.361</td>
</tr>
<tr>
<td>Br₂AA</td>
<td>3.00</td>
<td>2.67</td>
<td>0.046</td>
<td>2</td>
<td>0.156</td>
</tr>
<tr>
<td>BrCl₂AA</td>
<td>3.22</td>
<td>2.95</td>
<td>0.129</td>
<td>4</td>
<td>0.440</td>
</tr>
<tr>
<td>Br₂ClAA</td>
<td>3.12</td>
<td>2.78</td>
<td>0.073</td>
<td>3</td>
<td>0.248</td>
</tr>
<tr>
<td>Br₃AA</td>
<td>2.84</td>
<td>2.26</td>
<td>0.053</td>
<td>2</td>
<td>0.181</td>
</tr>
</tbody>
</table>
The levels of standard concentrations added for HAA3 are not round numbers because the stock solutions for these species were prepared from neat standards in our laboratory, rather than purchased as stock solutions. It should be noted that the RSD decreases as the concentration of standard added increases. This is to be expected as the degree of difference between the detector response and the background noise of the instrument increases with increasing analyte concentration (i.e., random error inherent in the instrument becomes less significant at higher analyte concentrations). Even at the PQL (1 µg/L), however, the relative SD between the seven replicates is 10 percent or lower. This degree of variation between replicates is acceptable, particularly at low analyte concentrations.

*Spike Recoveries in Matrix*

During method development, all experiments were performed using HAA standards in DOFW. Before the adapted method could be used to analyze field samples, it was necessary to determine whether the method could transfer effectively to a matrix other than DOFW. This was done by analyzing spike recoveries of the HAA9 species in finished water samples from the Illinois American Water Company treatment plant in East St. Louis, Ill. Forty-milliliter samples of finished water were collected in triplicate from the East St. Louis plant. Duplicate samples were analyzed for HAA9, and the third sample was spiked with a cocktail containing 10 µg/L of each HAA species before analysis. The spike recovery was calculated using Equation 2.3.

\[
\text{Spike recovery} = \frac{M}{S + B} \times 100\%
\]  

(2.3)

where \( M \) = measured concentration with spike (µg/L)  
\( S \) = concentration of spike added (fortified concentration; [µg/L])  
\( B \) = background concentration (µg/L)

Spike recoveries for HAA9 are given in Table 2.6. The acceptable range for spike recoveries is within 80 to 120 percent. As the recoveries for HAA9 were all well within this range, the method was applied for subsequent sample analysis for the remainder of this project.
Interlaboratory HAA9 Analysis

As a measure of quality assurance for the method, a set of sample solutions prepared in our laboratory was analyzed for HAA9 by the University of North Carolina (UNC), as well as by two other laboratories with USEPA-ICR certification for HAA9 analysis. In our laboratory, we used the adapted method described in appendix A for HAA9 analysis. Laboratory #1 used USEPA Method 552.2; laboratory #2 used method 6251B (*Standard Methods*) without the drying step of the adapted method. The purpose of this study was to compare the results obtained by the three different laboratories for HAA9 analysis of the same samples. This comparison would help to establish the validity of the results obtained using the method developed during this research.

Three samples were prepared for the split sampling analysis. Settled water was collected from the Orange Water and Sewer Authority (OWASA) in Carrboro, N.C., and spiked with 301 µg/L NaBr as Br. Next, 6.98 mg/L chlorine as Cl₂ was added. The water was incubated headspace-free at 25°C for 24 hours. After chlorination, residual chlorine was quenched with 21.8 mg/L ammonium sulfate as NH₄⁺ as N, and 10 mg/L sodium azide was added as a bactericide (see below). Duplicate 20-mL samples were extracted and analyzed for HAA9 immediately (sample A). Additional identical split samples were prepared and shipped overnight to the participating laboratories. An

---

Table 2.6

Spike recoveries for HAA9 in East St. Louis finished water

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Background concentration (µg/L)</th>
<th>Fortified concentration (µg/L)</th>
<th>Mean measured concentration (µg/L)</th>
<th>Mean recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClAA</td>
<td>&lt;1.0</td>
<td>10.0</td>
<td>10.1</td>
<td>101</td>
</tr>
<tr>
<td>BrAA</td>
<td>&lt;1.0</td>
<td>10.0</td>
<td>11.3</td>
<td>113</td>
</tr>
<tr>
<td>Cl₂AA</td>
<td>18.0</td>
<td>10.0</td>
<td>26.3</td>
<td>94</td>
</tr>
<tr>
<td>BrClAA</td>
<td>1.66</td>
<td>10.0</td>
<td>12.6</td>
<td>108</td>
</tr>
<tr>
<td>Cl₃AA</td>
<td>10.6</td>
<td>10.0</td>
<td>21.2</td>
<td>103</td>
</tr>
<tr>
<td>Br₂AA</td>
<td>&lt;1.0</td>
<td>10.0</td>
<td>10.6</td>
<td>106</td>
</tr>
<tr>
<td>BrCl₂AA</td>
<td>1.35</td>
<td>10.7</td>
<td>12.9</td>
<td>107</td>
</tr>
<tr>
<td>Br₂ClAA</td>
<td>2.53</td>
<td>10.4</td>
<td>12.8</td>
<td>99</td>
</tr>
<tr>
<td>Br₃AA</td>
<td>&lt;1.0</td>
<td>10.4</td>
<td>11.4</td>
<td>109</td>
</tr>
</tbody>
</table>
An aliquot of sample A was adjusted to pH 6 (phosphate buffer) and spiked with a cocktail of HAA9 standards (sample B). The following concentrations of HAA9 were added:

- HAA6 = 10.0 µg/L (of each species)
- BrCl2AA = 10.3 µg/L
- Br2ClAA = 9.75 µg/L
- Br3AA = 10.9 µg/L

Samples were distributed for analysis as described for sample A. An additional aliquot of sample A was adjusted to pH 10 (borate buffer) and spiked with the same HAA9 cocktail as described for sample B (sample C). Samples were distributed for analysis as described for sample A. Table 2.7 shows the results of the interlaboratory comparison.

Considering the relative complexity of the methods employed and the previously documented inadequate quality control (QC) displayed for the HAA3 species by various laboratories attempting these analyses, the three sets of results showed relatively good agreement. The greatest disparity between data occurred for sample A, likely because sample A contained lower levels of each HAA species than samples B and C. For all three samples, laboratory #1 reported significantly different results for ClAA compared to the other two laboratories. This finding indicates that USEPA Method 552.2 (acidic methanol) may exhibit some problems with accurately quantifying ClAA.

Because sample A was chlorinated in the presence of a bromide spike, the levels of HAA3 species that were generated in the solution were relatively high. If a low-bromide water were chlorinated under similar conditions, one would expect much lower concentrations of HAA3, particularly Br2ClAA and Br3AA. As discussed in the previous section, the main shortfall of both USEPA Method 552.2 and method 6251B (Standard Methods) is the inability of both acidic methanol and diazomethane to completely convert the HAA3 species to their corresponding esters. This incomplete esterification of HAA3 results in higher PQLs for these three species. Because the samples generated for this interlaboratory analysis contained relatively high levels of HAA3, the inadequacies of the two methods in quantifying HAA3 were not completely demonstrated by this exercise. Both participating laboratories reported PQLs of 2.0 and 4.0 µg/L for Br2ClAA and Br3AA, respectively, compared to UNC’s 1 µg/L with the adapted method. If
lower levels of HAA3 were present in the samples used for the interlaboratory analysis, the problems associated with the two published methods would most likely have been more evident.

### Stability of Haloacetic Acids

Little is known about the stability of HAA9 in aquatic matrixes. USEPA Method 552.2 states that the acids are stable for up to 2 weeks at 4°C in drinking water in which residual chlorine has been quenched with ammonium chloride. The method does not present details of the

<table>
<thead>
<tr>
<th>Sample</th>
<th>ClAA</th>
<th>BrAA</th>
<th>Cl₂AA</th>
<th>BrClAA</th>
<th>Cl₃AA</th>
<th>Br₂AA</th>
<th>BrCl₂AA</th>
<th>Br₂ClAA</th>
<th>Br₃AA</th>
</tr>
</thead>
<tbody>
<tr>
<td>A—UNC</td>
<td>2.01</td>
<td>BDL</td>
<td>3.4</td>
<td>6.79</td>
<td>3.18</td>
<td>6.09</td>
<td>10.9</td>
<td>11.7</td>
<td>4.7</td>
</tr>
<tr>
<td>A—lab #1</td>
<td>5.5</td>
<td>1.7</td>
<td>5.9</td>
<td>9.1</td>
<td>3.7</td>
<td>9.1</td>
<td>11.4</td>
<td>10.0</td>
<td>3.2</td>
</tr>
<tr>
<td>A—lab #2</td>
<td>BDL</td>
<td>2.2</td>
<td>4.9</td>
<td>9.0</td>
<td>4.6</td>
<td>10</td>
<td>15</td>
<td>12</td>
<td>4.7</td>
</tr>
<tr>
<td>Average</td>
<td>3.76</td>
<td>1.95</td>
<td>4.73</td>
<td>8.30</td>
<td>3.83</td>
<td>8.40</td>
<td>12.4</td>
<td>11.2</td>
<td>4.20</td>
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<tr>
<td>SD</td>
<td>2.47</td>
<td>0.35</td>
<td>1.26</td>
<td>1.31</td>
<td>0.72</td>
<td>2.05</td>
<td>2.24</td>
<td>1.08</td>
<td>0.87</td>
</tr>
<tr>
<td>% RSD</td>
<td>66.0</td>
<td>18.0</td>
<td>27.0</td>
<td>16.0</td>
<td>19.0</td>
<td>24.0</td>
<td>18.0</td>
<td>10.0</td>
<td>21.0</td>
</tr>
</tbody>
</table>

| B—UNC  | 11.2 | 12.1 | 14.2  | 17.7   | 14.1  | 16.7  | 21.7    | 21.1    | 16.9  |
| B—lab #1 | 12.0 | 12.6 | 17.2  | 19.8   | 15.2  | 18.4  | 22.3    | 19.4    | 16.6  |
| B—lab #2 | 11.0 | 13.0 | 15.0  | 20.0   | 16.0  | 21.0  | 27.0    | 23.0    | 19.0  |
| Average | 11.4 | 12.6 | 15.5  | 19.2   | 15.1  | 18.7  | 23.7    | 21.2    | 17.5  |
| SD     | 0.53 | 0.45 | 1.55  | 1.27   | 0.95  | 2.17  | 2.90    | 1.80    | 1.31  |
| % RSD  | 5.0  | 4.0  | 10.0  | 7.0    | 6.0   | 12.0  | 12.0    | 9.0     | 7.0   |

| C—UNC  | 12.4 | 11.7 | 14.0  | 17.4   | 13.7  | 16.3  | 21.3    | 20.7    | 16.5  |
| C—lab #1 | 8.9  | 12.9 | 18.5  | 20.3   | 15.6  | 18.6  | 22.5    | 19.5    | 16.6  |
| C—lab #2 | 12.0 | 12.0 | 16.0  | 20.0   | 16.0  | 19.0  | 27.0    | 24.0    | 19.0  |
| Average | 11.1 | 12.2 | 16.2  | 19.2   | 15.1  | 18.0  | 23.6    | 21.4    | 17.4  |
| SD     | 1.92 | 0.62 | 2.25  | 1.59   | 1.23  | 1.46  | 3.00    | 2.33    | 1.42  |
| % RSD  | 17.0 | 5.0  | 14.0  | 8.0    | 8.0   | 8.0   | 13.0    | 11.0    | 8.0   |


* Below detection limit of 1.0 µg/L.
† Below detection limit of 2.0 µg/L.
holding studies that led to this conclusion, however, and it is unclear how the studies were conducted. Because of the lack of information in the literature on HAA stability, we performed a series of control studies that examined the stability of HAAs in water under varying pH and temperature conditions, as well as in the presence of several preservatives. The results of the studies were used to develop a sampling protocol that would be followed when collecting field samples for HAA9 analysis. Establishing this protocol ensured that the HAAs would remain stable from the time of collection until they were analyzed.

Impact of Biodegradation on Haloacetic Acid Stability

A study was performed to determine whether HAAs are stable in water at 25°C in the absence of a chlorine residual. Under ideal conditions, samples for HAA analysis would be kept cool from the time they were quenched of chlorine until they were analyzed. However, because samples must often be shipped from the collection site to an analytical laboratory, it must be determined whether exposure to ambient temperatures would have an impact on HAA stability in case of delay during shipment.

To test the stability of HAAs in water, HAA standards were prepared at nominal concentrations in DOFW at pH 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, and 10. A 0.1M phosphate solution was used to prepare the buffers for pH values 7.0, 7.5, and 8.0, and a 0.025M borate solution was used to prepare pH values 8.5, 9.0, 9.5, and 10.0. Five milliliters of the appropriate buffer was added to each sample solution to prepare the solutions at the varying pH values. Each solution was then adjusted to the desired pH using 0.1M sodium hydroxide or 0.1M hydrochloric acid, if necessary. HAA6 samples were prepared and studied separately from HAA3 so that degradation of HAA3 into any of the HAA6 species could be easily identified. Aliquots of the samples were analyzed in duplicate immediately after preparation, and the remainder of each sample solution was allocated headspace-free into several 40-mL vials and incubated in a Fisher Scientific Low Temperature Incubator at 25°C for analysis, in duplicate, after 7 and 14 days.

The results of these experiments for pH 7 and pH 10 are shown in Figures 2.22 and 2.23. Appendix B provides the complete results for all pH values. The error bars on each graph represent the SD between duplicate samples. The absence of a bar at a specific time point on any
of the graphs indicates total loss of the analyte. As can be seen, HAA6 species showed instability in the neutral pH region, even after just 7 days. In contrast, HAA6 species were fairly stable at the higher pH value. In examining the results across the entire pH range used in this study, a trend showing increasing stability with increasing pH is evident for the HAA6 species.

This trend is apparent for ClAA up to pH 9.5, with the acid remaining stable at pH 10.0 over 2 weeks. A similar trend was observed for BrAA, although this species remained stable at both pH 9.5 and pH 10.0. For the dihalogenated HAAs, a trend showing increasing stability with
increasing pH is apparent at pH values 7.0, 7.5, and 8.0. Above pH 8, the dihalogenated HAAs remained stable during the 2-week time period used for this study. Cl$_3$AA degraded at pH 7.0 and pH 7.5, but remained stable above pH 7.5.

The results of this study suggest that HAA6 could be subject to biological degradation, particularly in the neutral pH region at elevated temperatures. Little work on the bacterial degradation of HAAs has been published. The findings of Ploeg, Hall, and Janssen (1991), Meusel and Rehm (1993), and Williams and Williams (1998), however, help to lend validity to this hypothesis. Meusel and Rehm found that a gram-negative bacterium, *Xanthobacter autotrophicus*, was capable of degrading Cl$_2$AA. These authors also found that a haloacid dehalogenase enzyme was responsible for this bacterial degradation, and that the enzyme was induced within the bacterium when exposed to Cl$_2$AA. Ploeg and colleagues observed induction of this enzyme upon bacterial exposure to Cl$_2$AA, as well as Cl$_3$AA, Br$_2$AA, and Br$_3$AA. Williams and Williams (1998) were able to isolate *X. autotrophicus* in water samples obtained from the Newport News (Va.) Waterworks, and demonstrated its ability to use Cl$_2$AA as its sole carbon and energy source. It is possible that *X. autotrophicus*, or a different bacterium that has similar degradative abilities, was present in the water samples prepared for the experiment described in this report. Although the sample solutions were prepared in DOFW, not drinking water, we made no effort to sterilize either the DOFW or the glassware used for sample preparation and storage. Biodegradation of the HAAs is considered further in chapters 6 and 7 of this report.

Although HAA6 species appear to be biodegradable, the HAA3 species do not seem to follow the same trend. BrCl$_2$AA remained stable at all pH values, whereas Br$_2$Cl$_3$AA and Br$_3$AA showed uniform degradation across the entire range of pH values studied. The HAA3 species are bulkier and heavier than the HAA6 species, so it may be more difficult for bacteria to degrade HAA3. No research has been published to date about the impact of biodegradation on the stability of the HAA3 species. As the degradation of BrCl$_2$AA and Br$_3$AA appeared to be independent of pH, however, it is likely that the instability of these species cannot be attributed to biological degradation alone. It is well known that most species of bacteria are most active within the neutral pH region and become inactive at high or at low pH. For the HAA6 species, the largest degree of degradation occurred within the neutral pH region. Because the stability of HAA3 was not related to pH, a mechanism other than biodegradation may be partly responsible for the instability of Br$_2$Cl$_3$AA and Br$_3$AA. Research has shown that Br$_3$AA is susceptible to thermal decarboxylation.
in aquatic matrixes at ambient temperatures (Heller-Grossman et al. 1993). Thus, the decompo-
sition of Br$_2$ClAA and Br$_3$AA observed in this experiment could be partially caused by
decarboxylation of the acids rather than bacterial degradation. If this is the case, the need to keep
water samples collected for HAA9 analysis cool during shipment and storage before analysis
becomes critical.

**Impact of Chlorination on Haloacetic Acid Stability**

A second study was performed to examine the impact of chlorine on the stability of HAA9
in water. The sample solutions for this experiment were prepared as described in the previous
experiment, except that 2 mg/L of free chlorine as Cl$_2$ was added to each buffered solution. After
Cl$_2$ was added, the pH of each solution was measured to ensure that the target pH was maintained.
Aliquots of each solution were quenched with (NH$_4$)$_2$SO$_4$ and analyzed for HAA9 immediately,
in duplicate, on Day 0. The remainder of each solution was allocated headspace-free into 40-mL
vials and incubated at 25°C. Each solution was then analyzed, in duplicate, after 7 and 14 days.
Figures 2.24 and 2.25 illustrate the results of the experiment for pH 7 and pH 10. The complete
results at all pH values are given in appendix C. As can be seen, all nine HAAs appeared to be
stable at 25°C in the presence of chlorine. For many of the analytes, the Day 7 and 14 concentrations
appear to be higher than the Day 0 concentrations. Because the occurrence is fairly uniform for all
pH values, this observation might result from interaction with the trace organics present in the
DOFW matrix. In these solutions, the acids did not appear to degrade, even though decomposition
was apparent for the samples prepared and stored under similar conditions in the absence of
chlorine. This observation lends additional credence to the hypothesis that HAAs are
biodegradable at ambient pH and temperature in the absence of a biocide. For the solutions in this
experiment, free chlorine acts as a biocide that prevents biological degradation of HAA6 in the
samples. Again, this is assessed further in chapters 6 and 7. It should be noted that the addition of
Cl$_2$ to the sample solutions might lead to the formation of additional HAAs if any organic carbon
were present in the DOFW. If this were the case, losses of the analytes over the 2-week period
could be offset by the continued formation of HAAs. Thus, the appearance of stability of the acids
could actually result from continuous degradation and reformation of the analytes. It is thought,
however, that this effect did not occur to any significant extent in the solutions prepared for this experiment. Although the total organic carbon (TOC) of the DOFW was not measured when the solutions were prepared, the Dracor water purification system used to prepare the DOFW is equipped with macroreticular resins designed to remove organic matter from the water. Because of the findings of the experiments described above, it was decided that a biocide must be added to sample bottles before sample collection to maintain stability of the HAA9 species during shipment and storage before analysis.

The experiments described in this section were performed at 25°C to simulate worst-case temperature conditions to which the samples might be exposed. Although it is unlikely that the samples would be exposed to temperatures as high as 25°C during shipment, adding the biocide assures HAA stability in the event that temperatures become elevated during transport.
Impact of Biocide on Haloacetic Acid Stability

Before selecting a biocide to be used during sample collection, the impact of the biocide itself on HAA stability must be examined. Two biocides, mercuric chloride (HgCl₂) and sodium azide (NaN₃), were chosen for evaluation. These preservatives were chosen because they have been demonstrated as effective in other USEPA methods for DBP analysis (USEPA 1989). Formaldehyde was excluded from evaluation because it is a known volatile carcinogen. Although HgCl₂ and NaN₃ are also health hazards, they are not volatile and thus do not pose the risk of exposure via inhalation, as does formaldehyde. For this experiment, two 2-L solutions were prepared containing 10 µg/L of each HAA6 species, and 2.5 µg/L of each HAA3 species in DOFW. One of the solutions was adjusted to pH 7 (phosphate buffer) and the other to pH 10 (borate buffer). Aliquots of each sample were then apportioned, headspace-free, into 40-mL vials, in duplicate. The 40-mL vials contained either 10 mg/L HgCl₂ or 10 mg/L NaN₃. This concentration of each biocide should be sufficient to inhibit biological activity in the samples over the 2-week time course of the experiment. A control was prepared for each pH value, into which no biocide was added. The samples were stored in an incubator at 15°C for 24 hours. After 24 hours, the samples were moved to a refrigerator and stored at 4°C. These temperature conditions were designed to simulate conditions to which the samples would be exposed after sample collection during shipment to UNC and storage before analysis. Day 0 was specified as the time after 24 hours of incubation. The samples were analyzed on Days 0, 7, and 14. Figures 2.26 through 2.31 show the results of this experiment for each pH value. Because of problems with the Day 0 analysis, these data are not represented on the graphs. The bars shown for Day 0 represent the standard concentrations that were added to DOFW on the day the sample solutions were prepared. The effect of each biocide was evaluated based on its similarity in behavior to that of the control. In other words, only instability of HAAs as caused by each particular preservative was examined in this experiment. The conditions used in this experiment minimized the chance for biodegradation to occur in any of the samples, including the control. The solutions were stored at 4°C during most of the experiment, whereas the sample solutions in the experiments described previously were stored at 25°C.

Because of the colder temperature conditions, microbial activity was inhibited in this experiment. This allowed an evaluation of the biocides themselves to see if they affected the
Figure 2.26 Stability of HAA9 at pH 7 in the control (no biocide); 24 hours at 15°C, and up to 2 weeks at 4°C

Figure 2.27 Stability of HAA9 at pH 7 in the presence of NaN₃; 24 hours at 15°C, and up to 2 weeks at 4°C

Figure 2.28 Stability of HAA9 at pH 7 in the presence of HgCl₂; 24 hours at 15°C, up to 2 weeks at 4°C
Figure 2.29 Stability of HAA9 at pH 10 in the control (no biocide); 24 hours at 15°C, up to 2 weeks at 4°C

Figure 2.30 Stability of HAA9 at pH 10 in the presence of NaN₃; 24 hours at 15°C, up to 2 weeks at 4°C

Figure 2.31 Stability of HAA9 at pH 10 in the presence of HgCl₂; 24 hours at 15°C, up to 2 weeks at 4°C
stability of the HAAs in any way. The samples to which no biocide was added were used as controls against which the effects of each biocide on HAA9 were measured.

The results in Figures 2.23 through 2.28 indicate that neither NaN₃ nor HgCl₂ seriously affected HAA stability at either pH value. HgCl₂, however, did appear to have a slight negative impact on some of the HAAs (e.g., ClAA, particularly at pH 10). Although this impact was fairly minor, NaN₃ appeared to maintain the stability of the HAA9 species and did not interact with them. If sample handling conditions could be assured and prolonged exposure at elevated temperatures avoided, using biocides might be unnecessary. However, given the indications for potential biodegradation and the otherwise innocuous nature of sodium azide on HAA9 recovery and analysis, it was decided to incorporate sodium azide addition into the sample handling procedure.

**Impact of a Chlorine-Quenching Agent on Haloacetic Acids**

Along with selecting an appropriate biocide, it was necessary to choose a chlorine-quenching agent that would not degrade any of the HAA species. Five different chlorine-quenching agents were evaluated to assess their impact on HAA stability. The following quenching agents were chosen for evaluation:

- Ammonium chloride (NH₄Cl)
- Ammonium sulfate ((NH₄)₂SO₄)
- Sodium sulfite (Na₂SO₃)
- Sodium thiosulfate (Na₂S₂O₃)
- Sodium meta-arsenite (NaAsO₂)

The impact of each quenching agent on HAA stability was evaluated under the same temperature and pH conditions used in the experiment that examined the impacts of NaN₃ and HgCl₂ on HAA stability. The sample solutions were prepared at pH 7 and pH 10 with 10 µg/L of each HAA6 species and 2.5 µg/L of each HAA3 in DOFW. The quenching agents were added in solid form, in excess. The preservatives were added imprecisely to reflect the manner in which chlorine would be quenched when collecting field samples. Table 2.8 lists the amount of each quenching agent needed to quench 10 mg/L of Cl₂ in a 40-mL vial.
As shown in the table, the approximate amounts added were much higher than the required amounts. Thus, this experiment evaluated in part whether it was necessary to add a stoichiometric amount of a particular chlorine-quenching agent to preserve HAA9 stability. For each quenching agent, a few crystals of preservative were added to duplicate 40-mL vials. The sample solutions were then allocated headspace-free into these 40-mL vials. Several controls were also prepared, into which no quenching agent was added. The sample bottles were incubated at 15°C for 24 hours, then refrigerated for analysis on Days 0, 7, and 14.

Figures 2.32 and 2.33 illustrate the stability of HAA9 species in the presence of each quenching agent as compared to HAA9 stability in the absence of quenching agent (control). Appendix D contains the complete results, which show the effects of each quenching agent on the stability of the individual HAA species at both pH values. Figures 2.32 and 2.33 demonstrate the impact of each quenching agent on HAA9 as a whole. It is clear from these graphs that Na₂SO₃ and Na₂S₂O₃ have an adverse effect on the stability of one or more of the HAA species. In examining the data for the effects of NH₄Cl, (NH₄)₂SO₄, and NaAsO₂ on the individual species at pH 7 and pH 10, the first two reagents gave similar results. However, previous studies (Glaze and Weinberg 1993) have suggested that bromide contamination in analytical grade ammonium chloride, which is absent in ammonium sulfate, can contribute to artifactual formation of brominated organics when the reagent is added to free chlorine. Hence, (NH₄)₂SO₄ was selected as the most appropriate chlorine-quenching agent for HAA analysis. Figures 2.34 and 2.35 illustrate the impact of (NH₄)₂SO₄ on the stability of all nine HAA species. It is evident that the stability of HAA9 in the presence of (NH₄)₂SO₄ is similar to HAA stability in the absence of the quenching agent (control).

<table>
<thead>
<tr>
<th>Quenching agent</th>
<th>Required mass (mg)</th>
<th>Approximate mass added (mg)</th>
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<tbody>
<tr>
<td>NH₄Cl</td>
<td>0.31</td>
<td>25</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.38</td>
<td>25</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.74</td>
<td>25</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>1.44</td>
<td>25</td>
</tr>
<tr>
<td>NaAsO₂</td>
<td>0.75</td>
<td>25</td>
</tr>
</tbody>
</table>

As shown in the table, the approximate amounts added were much higher than the required amounts. Thus, this experiment evaluated in part whether it was necessary to add a stoichiometric amount of a particular chlorine-quenching agent to preserve HAA9 stability. For each quenching agent, a few crystals of preservative were added to duplicate 40-mL vials. The sample solutions were then allocated headspace-free into these 40-mL vials. Several controls were also prepared, into which no quenching agent was added. The sample bottles were incubated at 15°C for 24 hours, then refrigerated for analysis on Days 0, 7, and 14.

Figures 2.32 and 2.33 illustrate the stability of HAA9 species in the presence of each quenching agent as compared to HAA9 stability in the absence of quenching agent (control). Appendix D contains the complete results, which show the effects of each quenching agent on the stability of the individual HAA species at both pH values. Figures 2.32 and 2.33 demonstrate the impact of each quenching agent on HAA9 as a whole. It is clear from these graphs that Na₂SO₃ and Na₂S₂O₃ have an adverse effect on the stability of one or more of the HAA species. In examining the data for the effects of NH₄Cl, (NH₄)₂SO₄, and NaAsO₂ on the individual species at pH 7 and pH 10, the first two reagents gave similar results. However, previous studies (Glaze and Weinberg 1993) have suggested that bromide contamination in analytical grade ammonium chloride, which is absent in ammonium sulfate, can contribute to artifactual formation of brominated organics when the reagent is added to free chlorine. Hence, (NH₄)₂SO₄ was selected as the most appropriate chlorine-quenching agent for HAA analysis. Figures 2.34 and 2.35 illustrate the impact of (NH₄)₂SO₄ on the stability of all nine HAA species. It is evident that the stability of HAA9 in the presence of (NH₄)₂SO₄ is similar to HAA stability in the absence of the quenching agent (control).
Sample Stabilization

The findings of the experiments summarized above were used to establish a sampling protocol that would be used for collecting field samples from water treatment plants in subsequent phases of this project. Before using the established protocol for collecting samples in the field, it was necessary to determine whether the chosen preservatives would affect HAA stability in a matrix other than laboratory-grade water. To examine this issue, settled water was collected from the OWASA surface water treatment plant (Carrboro, N.C.). The TOC concentration of the water...
was not measured for the study. However, the average TOC content of settled water from this
source is approximately 3 mg/L. Two liters of the settled water were spiked with 300 µg/L of
sodium bromide as Br⁻ and chlorinated in the laboratory with 7 mg/L free chlorine as Cl₂. The
bromide spike was added to the water before chlorination to promote brominated HAA formation
because OWASA water is generally low in bromide content. After addition of chlorine, the settled
water was incubated headspace-free in the dark at 25°C for 24 hours. Duplicate 40-mL aliquots of
the solution were quenched of residual chlorine with approximately 25 mg of \((\text{NH}_4)\text{SO}_4\), and
10 mg/L of \(\text{NaN}_3\) (40 µL of a 10 mg/mL aqueous solution into each 40-mL vial) was added as a
biocide. The aliquots were analyzed immediately for HAA9. The remainder of the chlorinated
solution was split into two 500-mL volumetric flasks. Forty milligrams of \((\text{NH}_4)\text{SO}_4\)
(crystalline) was added to each flask to quench residual chlorine, and 10 mg/L of \(\text{NaN}_3\) (500 µL

Figure 2.34 Stability of HAA9 in the presence of \((\text{NH}_4)\text{SO}_4\) at pH 7

Figure 2.35 Stability of HAA9 in the presence of \((\text{NH}_4)\text{SO}_4\) at pH 10
of a 10 mg/mL aqueous solution) was added to inhibit microbial activity in the solutions. The contents of one of the volumetric flasks were adjusted to pH 6 (phosphate buffer) and the other to pH 10 (borate buffer) by addition of 5 mL of the appropriate buffer. These pH values represent extremes of the pH range likely to be found in drinking water. A spike containing 10 µg/L of each HAA species was added to both solutions. The spike was added so that degradation of each species could be easily identified even if the naturally occurring concentration of a particular species was low. Aliquots of the two sample solutions were analyzed immediately for HAA9. Aliquots of the pH-adjusted solutions were not measured for HAA9 before the spike was added. It was assumed, however, that the HAA9 concentrations would not have changed significantly as a result of the pH adjustment. For this reason, HAA9 concentrations in the pH-adjusted solutions before spike addition would be equivalent to HAA9 concentrations in the duplicate samples of the chlorinated water that were analyzed before pH adjustment. After measuring duplicate 20-mL aliquots of each pH-adjusted solution for HAA9 analysis, the remainder of each solution was transferred headspace-free into several 40-mL vials and stored in the dark at 4°C for analysis after 7 and 14 days.

Figures 2.36 and 2.37 illustrate the results of this experiment.

Based on these findings, it appears that the HAA6 species are not affected by the presence of (NH₄)₂SO₄ and NaN₃. The HAA3 species are more problematic, particularly at pH 6. At pH 6, HAA3 concentrations decreased by approximately 15 to 20 percent over the course of 1 week. Br₃AA degraded in a roughly linear fashion over the course of 2 weeks. BrCl₂AA and Br₂CIAA degraded somewhat during the first week of storage, then remained stable during the second week of storage. At pH 10, the HAA3 species remained fairly stable over the 2-week time course of the experiment. In examining the data for Br₃AA, the concentration of this species appeared to increase after 1 week, then return to the Day 0 concentration on Day 14. This observation is most likely an anomaly for the Day 7 data, rather than a true fluctuation in the Br₃AA concentration over 2 weeks. These observations suggest that HAA samples that are likely to contain the HAA3 species may need to be adjusted to higher pH values when collected so that the analytes will remain stable until analysis. Alternatively, samples that are expected to contain Br₃AA (i.e., waters with moderate to high levels of bromide) may need to be analyzed within a few days of collection. This experiment indicates, however, that samples collected from low-bromide waters
that are not expected to contain high levels of the brominated HAA species can be stored at 4°C for up to 2 weeks before analysis.

The samples described above were analyzed for HAA9 at three different time points: 0, 7, and 14 days. It was decided to perform a similar experiment to gain more information about the kinetics of HAA3 degradation. For this second experiment, HAA9 standards were prepared at a concentration of approximately 10 µg/L of each species in 2 L of DOFW. Next, 2 mg/L of chlorine as Cl₂ was added to the water to simulate a typical chlorine residual within the distribution system. After addition of chlorine, the solution was capped and inverted three times to
mix, then the chlorine was quenched by adding 14.7 mg of (NH₄)₂SO₄ to the 2-L solution. Then, 20.8 mg of solid NaN₃ was added to arrive at a final biocide concentration of 10.4 mg/L. The solution was mixed to dissolve the biocide and quenching agent, then split between two 1-L volumetric flasks, filling the flasks to the neck with sample solution. One solution was adjusted to pH 6 and the other to pH 10 by adding 5 mL of the appropriate buffer, then the flasks were filled to the line and inverted three times to mix. Each pH-adjusted solution was apportioned headspace-free into 16 40-mL vials. Duplicate vials for each pH value were analyzed immediately for HAA9. The rest of the vials were refrigerated at 4°C for analysis after 0.5, 1, 2, 3, 7, and 14 days.

The results of this experiment are shown in Figures 2.38 and 2.39.

Figure 2.38 Stability of the HAA9 standards in DOFW at pH 6 and 4°C over 14 days

Figure 2.39 Stability of the HAA9 standards in DOFW at pH 10 and 4°C over 14 days
Because of the expanded scale of the y-axis, HAA9 concentrations appear to fluctuate dramatically from day to day. The relative SD (SD ÷ average) between all data points at each pH value, however, is less than 10 percent. Thus, all HAA9 species appeared to be stable over the 2-week time course of the experiment at both pH 6 and pH 10.

The solutions used in this experiment were synthetic solutions (i.e., HAA standards were added to DOFW), as compared to the stability experiment in which HAAs were generated by chlorinating settled OWASA water. In the synthetic water, the HAA3 species did not show the same instability at pH 6 as they did in the OWASA water. This observation implies that constituents of a real water matrix may somehow have an impact on HAA3 stability. As the OWASA samples were pH-adjusted after chlorination and quenching of residual, it is puzzling as to why HAA3 were somewhat unstable at pH 6 but not at pH 10. As mentioned earlier, Br3AA is known to thermally decompose at ambient temperatures. This effect is more pronounced at alkaline pH, however, whereas HAA3 in the OWASA samples were less stable at pH 6 than pH 10. In addition, the samples were stored at 4°C, not ambient temperature, so thermal decarboxylation of HAA3 would be expected to be minimal. The conflicting results of these two experiments indicate that the stability of HAA9 in water may vary depending on the chemical characteristics of the matrix.

SUMMARY AND CONCLUSIONS

At the beginning of this project, an evaluation of the established methods for the analysis of HAA9 in drinking water revealed inconsistent and imprecise quantitation of some of the species, particularly for ClAA and for each of the HAA3 species. This was determined by calculating the recoveries of each of the species from aquatic matrixes by comparison of the chromatographic signal response for the derivatized acid (ester) with the response for the respective ester standard. In many cases, it appeared that HAA9 quantified by those techniques could be underestimating their true levels in finished waters. A thorough examination of the procedures was justified to ensure that true occurrence data for HAA9 were generated in the remainder of this project. A standard operating procedure was generated, which forms as appendix A to this report. This procedure incorporates the results of the evaluation of the analytical method described in this chapter and demonstrates the capability for measurement of
HAA9 in chlorine-quenched samples containing bactericide that are held for up to 14 days at 4°C in the absence of light before analysis. If sample-handling conditions could be assured and prolonged exposure at elevated temperatures avoided, biocide use might prove unnecessary. However, given the indications for potential biodegradation and the otherwise innocuous nature of sodium azide on HAA9 recovery and analysis, sodium azide is added to the empty sample bottles before sample collection. Subsequent evaluation of HAA9 stability in other drinking waters has confirmed that, in the presence of sodium azide and in the absence of a free chlorine residual using the specified quenching agent in this research, the method described in this report produces consistent and reproducible analysis of HAA9 in aqueous samples held up to 14 days.
CHAPTER 3
IMPACT OF WATER QUALITY AND TREATMENT CHARACTERISTICS ON HALOACETIC ACID AND TRIHALOMETHANE FORMATION UNDER CONTROLLED LABORATORY CHLORINATION CONDITIONS

INTRODUCTION

The primary objective of this portion of the study was to assess the impact of various water quality and treatment characteristics on HAA and THM formation and the relative distribution of these two classes of DBPs under controlled chlorination conditions in different types of waters. The studies were conducted on raw waters with different types of NOM, allowing for examination of the following variables:

- Chemical characteristics of NOM in the raw water, including SUVA and hydrophobic/hydrophilic organic carbon content
- pH of chlorination (pH 6 and 8)
- Bromide concentration (Br/TOC ratio)
- Chlorination contact time
- Impact of coagulation on HAA/THM distribution

In all cases, all nine bromine- and chlorine-containing HAA species were measured in addition to the four THM species. The analytical methods developed in chapter 2 were incorporated into this portion of the study.

MATERIALS AND METHODS

General Approach

All the experiments were conducted on raw waters (about 35 L) collected by operations personnel from six water utilities. The water was shipped by overnight carrier to the Drinking Water Research Center laboratories at UNC. The six utilities (listed in Table 3.1) were selected to provide waters with different SUVAs as well as geographical diversity.
Upon receipt, samples of the bulk raw water were taken for TOC, DOC, ultraviolet (UV) absorbance, bromide, pH, and alkalinity measurements. UV absorbance was measured at 254 nm (UV$_{254}$). As shown in Figure 3.1, a portion of the raw water (about 10 L) was acidified to pH 2.0, then passed through an XAD-8 resin column (Rohm and Haas, Philadelphia, Pa.) to determine the hydrophobic/hydrophilic distribution of the NOM and to isolate each fraction. Another portion of the raw water (about 15 L) was coagulated under “optimal” conditions, which were determined by preliminary jar tests, and then settled for collection of the supernatant. Alum was the only coagulant tested.

Once collected, all four water fractions derived from the original bulk water (i.e., raw water, coagulated water, hydrophobic fraction, and hydrophilic fraction), were chlorinated at pH 6.0 and pH 8.0, and HAA and THM concentrations were measured after storage periods of 1, 2, 4, 8, 24, and 72 hours in the dark, headspace-free, at 20°C (Figure 3.2). Before chlorination, all fractions were characterized by measuring TOC, DOC, UV$_{254}$, and bromide concentration. A portion of the hydrophobic fraction was diluted to the same TOC concentration as the hydrophilic fraction before characterization and chlorination, so that DBP production from the two fractions could be compared on an equal basis. If necessary, sodium bromide (NaBr) was spiked to some of the water fractions so that all the fractions had the same Br/TOC ratios. The limiting ratio tended to be either the hydrophilic fraction or the coagulated water. The chlorine dose was selected by preliminary chlorination experiments. Ultraviolet absorbance at 272 nanometers (UV$_{272}$) was measured along with free chlorine residuals and HAA and THM concentrations to determine if

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<thead>
<tr>
<th>Utility</th>
<th>Location</th>
<th>Source</th>
<th>Sample date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indianapolis Water Company</td>
<td>Indianapolis, Ind.</td>
<td>White River</td>
<td>Feb. 15, 1999</td>
</tr>
<tr>
<td>Manatee County Public Works Department</td>
<td>Bradenton, Fla.</td>
<td>Lake Manatee Reservoir</td>
<td>June 2, 1999</td>
</tr>
<tr>
<td>City of Groton Department of Utilities</td>
<td>Groton, Conn.</td>
<td>Poquonnock Reservoir</td>
<td>Nov. 23, 1999</td>
</tr>
</tbody>
</table>
any relationship existed between the decrease in UV absorbance at 272 nm (ΔUV272) and chlorine consumption, and ΔUV272 and DBP production. Coagulated water was fractionated with the XAD-8 resin using the same procedure used for the raw water fractionation to evaluate the relative removal of hydrophilic and hydrophobic organic carbon by coagulation.

It should be noted that Durham water was the first water sample examined in this study and preliminary experiments were conducted on this water to optimize the procedures. The results obtained from this water were tentative and are not included in this report.
Preparation of Glassware

Glassware for general laboratory use was soaked in detergent (Alconox) overnight, rinsed with tap water three times, rinsed with DOFW (Dracor) three times, immersed in a 10 percent nitric acid bath overnight, rinsed with tap water three times, rinsed with DOFW three times, and oven-dried at 180°C. Volumetric glassware was prepared in the same manner except that it was not oven-dried. Instead, it was rinsed with methanol (J.T. Baker) three times and air-dried in a hood. All plastic caps and septa were treated in the same manner as the general glassware, but they were oven-dried at 80°C rather than 180°C.

All the glassware used in the preliminary and final chlorination experiments, including pipets, volumetric flasks, amber and biochemical oxygen demand (BOD) bottles, ground-glass stoppers, caps, and septa, was rendered chlorine-demand-free. After being acid-washed and rinsed with tap water and DOFW, the glassware was soaked in a chlorine bath containing approximately 200 mg/L Cl₂ for at least 3 hours, rinsed with DOFW five times, then oven- or air-dried.

Glassware used for bromide analysis was cleaned in a dilute solution of Citranox Acid Cleaner and Detergent (Alconox), thoroughly rinsed with tap water and deionized water (Virginia Water Systems, Inc., Richmond, Va.), then air-dried before use.

Fractionation of Natural Organic Matter

Resin Preparation

Amberlite XAD-8 resin (Rohm and Haas) was used to fractionate the NOM in each of the source waters, in accordance with the method of Thurman and Malcolm (1981). The resin had previously been soxhlet-extracted for 24 hours each with the following sequence of solvents: methanol, acetonitrile, diethyl ether, and methanol, and had been soaked in 0.1N NaOH solution before being used in this study. The resin was packed to occupy an empty bed volume of 100 mL in a glass column (1 m long with a 3.5 cm diameter) that was filled with DOFW before resin addition. Air bubbles, if any, were driven off the resin bed.

The residual organic materials on the resin and possibly other organics released by resin bleed due to hydrolysis were eluted from the column in the reverse direction with 2 L of freshly
prepared 0.1\textit{N} NaOH at a flow rate of one bed volume per hour (1 bv/hr). The resin was then flushed in the normal direction at 2 bv/hr in sequential steps with 1 L of 0.1\textit{N} NaOH, 2 L of DOFW, 1 L of 0.1\textit{N} HCl, and 0.01\textit{N} HCl. All NaOH and HCl solutions were prepared from DOFW and reagent-grade materials (Fisher Scientific). Once these steps were complete, the column was ready to fractionate NOM from the source water.

\textit{Fractionation Protocol}

\textbf{Figure 3.3} is a schematic of the XAD-8 fractionation apparatus. There were two steps in the fractionation. The first was extraction of hydrophobic NOM onto the XAD resin. Concentrated sulfuric acid (Fisher Scientific) was added to about 10 L of raw water to adjust the pH down to 2.0, conditions under which the acidic functional groups on the NOM would be protonated, which enhanced sorption onto the XAD resin. HCl was avoided because of chloride interference in the subsequent bromide analysis using ion chromatography (IC). The acidified raw water was pumped through a small glass fiber plug, which removed any suspended solids in the raw water, then through the XAD column. The effluent flow rate was controlled at 2 bv/hr; the influent flow rate was a little higher to keep the column running continuously. The column was fitted with an overflow port and recycling apparatus for the feed water. The effluent (hydrophilic fraction) was collected in a glass container through tubing that was at a higher elevation than the

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fractionation_protocol}
\caption{Schematic of the XAD-8 fractionation protocol}
\end{figure}
top of the resin to prevent the water above the resin from draining out. The volume of raw water subjected to fractionation was determined by the amount of hydrophobic organic carbon needed for the subsequent experiments, based on an assumed 40 percent hydrophobic content of the raw water and a 30 percent carbon loss through elution and post-elution workup.

Once extraction was complete, the column was rinsed in the normal direction with 50 mL of DOFW to remove any residual raw water and sulfate ions. In the second step (elution), the hydrophobic NOM was eluted from the column in the reverse direction with 0.1\( N \) NaOH at a flow rate of 1 \( \text{bv/hr} \). The eluate was collected in 350- to 500-mL batches and neutralized with concentrated sulfuric acid to pH 6–7 to prevent base-catalyzed ester hydrolysis (Liao et al. 1982). The TOC concentration of each batch of the eluate was analyzed. Based on the measured TOC content of the raw water and the hydrophilic fraction, the percentage of hydrophobic carbon in the raw water was determined. One to three of the most concentrated batches of eluate were combined based on two criteria: (1) only the batches that were collected immediately after the concentration process were considered for combination; all the batches collected after the resin was left standing overnight in the 0.1\( N \) NaOH were discarded. This measure minimized contamination by resin bleed (Malcolm 1991); and (2) only the batches for which the cumulative recovery approached but did not exceed 100 percent were combined. Because an error of \( \pm 0.1 \text{ mg/L} \) from TOC measurement might cause as much as a \( \pm 5 \text{ percent} \) variation in recovery, \( \text{UV}_{254} \) was used as a supplementary tool to decide on the batches to be combined. After elution, the column was cleaned with 1 L each of 0.1\( N \) NaOH, DOFW, 0.1\( N \) HCl, and 0.01\( N \) HCl, sequentially as described above, to prepare it for future use.

**Coagulation Procedure**

*Preliminary Jar Tests*

Jar tests were performed to evaluate turbidity and NOM removal at several coagulant doses to determine the optimal conditions for subsequent bulk coagulation. Between 5 and 8 coagulant doses were tested for each raw water. The incremental coagulant doses between jars corresponded to 5.0 or 10.0 mg/L as alum \([\text{Al}_2(\text{SO}_4)_{13}(14–16)\text{H}_2\text{O}])\), as appropriate. The range of coagulant doses was based on data provided by the water utilities. Tests were conducted on
500-mL raw water samples using 600-mL glass beakers equipped with sampling ports. Before the jar test, the raw water was allowed to come to ambient temperature (20–25°C). To maintain the pH in every jar above 6.0 during the test, a preliminary experiment was conducted on a 500-mL raw water sample to determine the amount of sodium carbonate (Na₂CO₃) needed, if necessary, for each corresponding alum dose. The stock concentration of the alum and sodium carbonate solutions used in the jar tests was usually 5.0 g/L (0.5 g dissolved in 100 mL DOFW; Fisher Chemical Co., Fairlawn, N.J.) and 0.02N (0.212 g dissolved in 100 mL DOFW; Kanto Chemical Co., Inc., Tokyo, Japan), respectively.

After adding alum and sodium carbonate (if necessary), the six raw water samples were rapid-mixed for 1 min at 100 rpm using a Phipps and Bird (Richmond, Va.) six-place gang stirrer, and flocculated at 35 rpm for 20 min, then allowed to settle for 60 min before supernatant samples were withdrawn from the sampling port for TOC, UV₂₅₄, turbidity, and pH measurements. The optimal alum dose was chosen based on TOC, UV₂₅₄, and turbidity removal.

**Bulk Coagulation**

Bulk coagulation of the raw water was performed in six 2-L Phipps and Bird jars at the optimal alum dose and corresponding sodium carbonate addition. Raw water was rapid-mixed, flocculated, and settled in the same manner used in the preliminary jar tests, and the supernatants were collected and combined as the coagulated fraction for subsequent chlorination experiments.

**Hydrophobic/Hydrophilic Distribution of Organic Carbon in Coagulated Water**

The relative removal of hydrophobic versus hydrophilic materials by coagulation was evaluated by passing 1 L of coagulated water (acidified to pH 2.0 with concentrated H₂SO₄) through the XAD-8 column as described above. TOC, DOC, and UV₂₅₄ were measured for the influent and effluent and the percentages of hydrophilic and hydrophobic carbon in the coagulated water were calculated.
Chlorination Procedure

Preparation of Chlorine Solutions

Chlorine stock solution was prepared by diluting 25 mL of a 4 to 5 percent sodium hypochlorite solution (Aldrich Chemical Co.) into 500 mL of DOFW at a concentration of 2,000–3,000 mg/L as Cl$_2$. The stock solution was stored in the dark at 4°C in a bottle wrapped with aluminum foil. The actual concentration of the stock solution was determined on the day of use by sodium thiosulfate titration in accordance with method 4500-Cl B (*Standard Methods*) (APHA, AWWA, and WEF 1995). A volume of the standardized stock solution was diluted to prepare working solutions in the range of 100 to 500 mg/L as Cl$_2$, depending on the intended use.

Preliminary Chlorine Demand Experiments

A preliminary chlorination was performed on each water fraction to determine the chlorine demand for subsequent chlorination. Four 100-mL samples of each fraction were chlorinated in 125-mL amber Boston round bottles with Teflon-lined screw caps (Laboratory Supply Distributor Inc., Mt. Laurel, N.J.) with four chlorine doses ranging from 1.0 mg Cl$_2$/mg TOC to 2.0 mg Cl$_2$/mg TOC. A 100-mg/L chlorine working solution was prepared for this experiment. Before chlorination, the sample of the concentrated hydrophobic fraction was diluted to the same TOC concentration as the hydrophilic fraction. If the bromide concentration of the raw water (thus of the coagulated water and the hydrophilic fraction) was high (e.g., Manatee water), NaBr was also spiked into the hydrophobic fraction before chlorination. Before adding chlorine, the pH of all the samples was adjusted to pH 8.0 with Na$_2$HPO$_4$ (Mallinckrodt) and NaOH. The phosphate buffer had a concentration of 0.001M in the sample.

After the 24-hour holding period at 20°C in the dark, the free chlorine residual in each sample was determined using a chlorine residual pocket colorimeter (Hach Company, Loveland, Colo.). The samples were diluted with DOFW, as needed to ensure that the upper limit of the linear range of detection of the colorimeter (2.2 mg/L) was not exceeded. A calibration curve of free chlorine residual against chlorine dose was then constructed to determine a chlorine dose that
would produce a free chlorine residual of 1.0 mg/L after 24 hours. That dose was selected for subsequent final chlorination.

**Final Chlorination**

Each fraction of water was chlorinated in twelve 300-mL standard BOD bottles, six at pH 6.0 and six at pH 8.0. The pH adjustments were made with Na$_2$HPO$_4$ and H$_2$SO$_4$ (for pH 6) or NaOH (for pH 8) after the waters were brought to 20°C in an incubator. Again, the hydrophobic samples were diluted to the same TOC concentration as the hydrophilic samples. NaBr was spiked into each of the fractions, if necessary, to keep the same Br/TOC ratio for all the fractions of each water. This was usually dictated by the Br/TOC ratio of the coagulated water or the fractions of each hydrophilic fraction. An appropriate chlorine working solution was prepared so that 3.0 mL of this solution was added into each BOD bottle for the convenience of operation and calculation. The BOD bottles were filled three-quarters of the way with the sample, chlorine was added, and the remainder of the sample was added to fill the bottles. The bottles were sealed headspace-free and inverted three times, then placed in the dark in an incubator at 20°C.

One of the bottles at pH 6 and pH 8 was removed after the following storage times: 1, 2, 4, 8, 24, and 72 hours. Free chlorine residual was measured immediately using the Hach pocket colorimeter. Aliquots of the chlorinated samples were transferred to two 40-mL screw-cap vials with TFE-lined silicone septa (Laboratory Supply) for analysis of THM4 and HAA9. Both sets of vials contained sufficient (approximately 60 mg) ammonium sulfate (Mallinckrodt), which was used to quench residual chlorine. In the HAA9 vials, 20 µL of 10 mg/mL sodium azide (Aldrich Chemical Co.) was also added as a biocide if the samples were not analyzed within 24 hours. All the sample vials were stored headspace-free and refrigerated at 4°C until analysis. After sampling for THM and HAA analysis, the residual free chlorine in the remainder of the BOD bottles was quenched with ammonium sulfate, and the samples were saved for UV$_{272}$ measurements.
Analytical Methods

*Total Organic Carbon and Dissolved Organic Carbon Measurements*

TOC and DOC analysis was conducted using a Shimadzu 5000 Total Organic Carbon Analyzer equipped with an ASI 5000 autosampler (Shimadzu Corp., Columbia, Md.). All the operations were based on the procedures outlined in the Shimadzu instruction manual. The TOC concentration measured here is referred to as NPOC (nonpurgeable organic carbon, or nonvolatile organic carbon). NPOC measurement involved acidification of the samples with 2N HCl to pH 2–3 and sparging the samples with high-purity air (Holox Company, Norcross, Ga.) for 10 min to eliminate inorganic carbon before measuring the total carbon concentration. NPOC is identical to the TOC obtained by the acidic sparging process described in most standard methods.

A calibration curve of 0.0, 2.0, 4.0, and 8.0 mg C/L was prepared on the day of analysis from dilutions of a 1,000 mg/L organic carbon standard stock solution, which was made by dissolving 2.125 g reagent-grade anhydrous potassium hydrogen phthalate \([C_6H_4(COOK)(COOH)];\) Nacalai Tesque, Inc., Kyoto, Japan] in 1,000 mL of DOFW. Depending on the samples, the calibration curve ranged from 0.5 to 2.0 mg/L, or 2.0 to 10.0 mg/L, but always included a zero point. For samples with high alkalinity, the sparging time was longer to make sure CO₂ was eliminated, thereby preventing inorganic carbon from interfering with the organic carbon measurement. Replicate measurements were made on all samples until the coefficient of variation (CV) was less than 0.5 percent or the SD was less than 200 area units for three measurements. The reported TOC concentrations were taken as the mean of these three measurements.

DOC analysis was performed using the same procedure as for TOC except that the samples were first filtered through 0.45-μm Supor-450 membrane filters (Gelman Sciences, Ann Arbor, Mich.). The membrane filters were first rinsed with at least 150 mL of DOFW, then two 20-mL aliquots of the sample were filtered and discarded. Additional sample was then filtered and collected for DOC measurement. A fresh membrane filter was used for each sample.
Ultraviolet Absorbance Measurements

Both UV absorbance at 254 nm and at 272 nm were measured on samples previously filtered through pre-rinsed 0.45-µm Supor-450 membrane filters using a U-2000 UV-Visible spectrophotometer (Hitachi Instruments, Danbury, Conn.). DOFW was used to zero the instrument. Measurements were made using a 1-cm quartz cell, which was rinsed twice with sample before each measurement. No pH adjustment was made before measurement.

Alkalinity Measurements

Alkalinity was measured by the potentiometric titration method in Standard Methods (APHA, AWWA, and WEF 1995). For each measurement, a 200-mL sample (500 mL was used if the alkalinity was very low) was titrated to the equivalence point using a standardized 0.1N HCl solution (Fisher Scientific).

Turbidity Measurements

Turbidity was measured using a Hach Ratio Turbidimeter (Model 18900-69). The turbidimeter was calibrated with Hach Gelex Turbidity Standards.

Bromide Analysis

Analytical procedure. An IC system (Dionex, Sunnyvale, Calif.) was used for separation and analysis of bromide ion in the samples. The instrument was equipped with the following modules: AI-450 Version 3.32 and PeakNet Version 4.30 computer software with an RS232 Advanced Computer Interface, ASM-3 Automated Sampler, GPM-2 Gradient Pump, LCM-3 Conductivity Detector, and an Eluant DeGas Module.

Table 3.2 summarizes the IC operating conditions. A Dionex IonPac analytical column AS12 with an AG12 guard column was installed for bromide analysis. The guard column, which
contained the same resin material as the analytical column but was shorter, served to capture any impurities or particulates that might otherwise pass onto the analytical column and compromise the integrity of the methodology.

The mobile phase (or eluent) of 2.7 m\(M\) Na\(_2\)CO\(_3\)/0.3 m\(M\) NaHCO\(_3\) was pumped through the columns at a flow rate of 1.0 mL/min. To make the eluent, 0.5723 g Na\(_2\)CO\(_3\) (Certified ACS-grade, Fisher Scientific) and 0.0504 g NaHCO\(_3\) (“Baker Analyzed” grade, J.T. Baker) were dissolved and brought to a 2-L volume with DOFW (Virginia Water). Next, the mobile phase was filtered under vacuum through a Nylon-66 0.45-\(\mu\)m membrane filter (Alltech Associates, Inc., Deerfield, Ill.), and sparged with ultra-high-purity helium (Holox Company) for 20 min to remove any CO\(_2\) and air before first use. The chemical suppressor ASRS-II (Dionex) functioned to suppress the background conductivity of the eluent (i.e., CO\(_3^{2-}\) and HCO\(_3^{-}\)) while enhancing detection of the target analyte (Br\(^-\)). A regenerant of 25 m\(M\) H\(_2\)SO\(_4\), prepared by dissolving 5.6 mL of concentrated sulfuric acid in 4 L DOFW, was flowing at a higher rate (5–10 mL/min) through the suppressor in an opposite direction. The hydrogen ions in the regenerant were exchanged through the suppressor membranes with sodium ions in the eluent so that unionized H\(_2\)CO\(_3\) was formed in the eluent. This produced a very low background conductivity reading of around 15 \(\mu\)S.

The bromide standard stock solution (1 g/L) was prepared by dissolving 0.1288 g Certified ACS-grade NaBr (Fisher Scientific) in 100 mL DOFW. The stock solution was freshly prepared every 6 months and stored at 4°C in a glass amber bottle sealed with Teflon tape. A calibration curve of 0, 20, 50, 100, and 200 \(\mu\)g/L was prepared for the quantitative analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guard column</td>
<td>IonPac AG12</td>
</tr>
<tr>
<td>Analytical column</td>
<td>IonPac AS12</td>
</tr>
<tr>
<td>Analytical column capacity</td>
<td>52 (\mu)eq</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>2.7 m(M) Na(_2)CO(_3)/0.3 m(M) NaHCO(_3)</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1.0 mL/min</td>
</tr>
<tr>
<td>Suppressor</td>
<td>Chemical, ASRS-II</td>
</tr>
<tr>
<td>Regenerant and flow rate</td>
<td>25 m(M) H(_2)SO(_4), 5–10 mL/min</td>
</tr>
<tr>
<td>Sample loop size</td>
<td>150 (\mu)L</td>
</tr>
</tbody>
</table>

Table 3.2
IC parameters for Br analysis
Blanks, containing only DOFW, were analyzed right after the calibration curve and before the samples. All blanks, calibration standards, and samples were filtered before analysis using a pre-rinsed 0.45-μm Nalgene nylon syringe filter (Nalge Nunc International, Rochester, N.Y.). The analysis time for each calibration standard was 12 min, whereas all other blanks, standard additions, and samples required a 40-min run time to allow other ions in the samples to elute off the column and permit the column to equilibrate before the next analysis.

**Quality assurance.** Duplicate analyses were performed for all the blanks, calibration standards, and samples. Matrix spikes for raw water samples were prepared to evaluate method recovery for each specific matrix and to confirm the retention time for the analyte. Because all four fractions were derived from the same raw waters, spikes were done only to the raw water samples. To prepare a spiked sample, some sample was placed in the volumetric flask with an aliquot of the standard, then the flask was filled to the mark with more sample. The concentration of the spiked sample was theoretically about twice the concentration of the analyte that was expected in the sample. Thus the spiked sample was prepared after the raw water sample had been analyzed quantitatively. A recovery between 80 and 120 percent indicated a reliable analysis without significant matrix effects.

**Trihalomethane Analysis**

**Analytical procedure.** The LLE GC procedure for the analysis of THM4 (i.e., CHCl₃, CHBrCl₂, CHBr₂Cl, and CHBr₃) in the samples was modified after method 6232B (*Standard Methods*) (APHA, AWWA, and WEF 1995).

For each sample, a 20-mL aliquot was transferred to a 40-mL screw-cap vial with a TFE-lined silicone septum (Laboratory Supply) after warming up to room temperature. Four milliliters of THM-free Grade pentane (Burdick and Jackson, Muskegon, Mich.) containing approximately 40 μg/L of 1,2-dibromopropane (Sigma Chemical, Bellefonte, Pa.), which served as the internal standard (IS) that corrected for any deviation in the sample volume injected, was then added to the 20-mL sample. To enhance extraction efficiency, approximately 6 g of salting-out agent, anhydrous sodium sulfate (Certified ACS Grade; Mallinckrodt), which was previously baked at 400°C for 24 hours, was added to the sample vial. Next, the vial was vortex-mixed (Type 16700 Mixer-MaxiMixer I, Thermolyne, Dubuque, Iowa) for 1 min and a period of several minutes was
allowed for the aqueous and organic phases to separate. Where emulsions did not separate on standing, the vial was cooled below 4°C to promote separation. At least 1 mL of the upper pentane extract was transferred with a Pasteur pipette to a 1.8 mL autosampler vial and capped with an aluminum TFE-faced seal. To provide for reanalysis where necessary, the pentane extract was transferred to two autosampler vials. The extracts were stored in a freezer at −4°C until shortly before analysis.

A calibration curve of up to 9 points (e.g., 0, 1, 2, 5, 10, 25, 50, 100, and 200 µg/L) was prepared in DOFW, depending on the expected concentrations of the THM species. Because the THM standard stock solution (EPA Trihalomethanes Calibration Mix, Supelco) contained equal concentrations (2,000 µg/mL) of each of the 4 components, a calibration curve with many points (8–9) was prepared to encompass the full range of the possible concentrations in the water samples. Two intermediate standard dilutions of 10 µg/mL and 100 µg/mL were prepared in high-purity THM-free methanol (Burdick and Jackson) for use in preparing the calibration curve. The calibration solutions were extracted and stored in the same manner as the samples. This stock solution was prepared by weighing an appropriate amount of neat 1,2-dibromopropane and dissolving it in high-purity methanol. The stock solution was stored at −4°C and used for up to 6 months.

Sample extracts were analyzed on an HP model 5890A Series II GC-ECD. Table 3.3 summarizes the operating parameters. At the beginning of each analytical run, two pentane solvent blanks and two pentane + IS samples were injected to condition the GC and to verify that interferences were absent. Identification of the four THM species and the IS in the samples was based on comparison of retention times (RTs) of suspect peaks to the confidence limits for the RT of the authentic compounds in the standards. Another method was to compare the relative RT of suspect peaks (defined as the ratio of the RT of the THM species to the RT of the IS) in samples to the relative RT of the authentic compounds in standards. Additional evidence of compound identity was obtained from standard-spiked sample extracts (see below). Presence of separate peaks in the extract with the known addition confirmed that the suspect peak was not the compound of interest. Quantitative analysis was based on the relative peak area, (i.e., the ratio of the peak area of the THM species to the peak area of the IS).
Analytical quality control. The THM stock standard was stored at –4°C and used for up to 3 months. The two intermediate standards were kept only for up to 3 weeks and, if possible, were freshly prepared on the day of analysis. Chlorinated samples, once collected headspace-free, were analyzed within 14 days. No preservatives were added to the samples. Both standards and samples were brought to room temperature before analysis.

Before first use, the pentane and the high-purity methanol were analyzed on the GC using the same THM program to verify that they were free from interferences. A scaled-down quantity of IS pentane solution was also analyzed to ensure the absence of contamination in the IS stock before large volumes of the solution were prepared for extraction.

Duplicate samples and standards were collected and extracted. If the RSD for any analyte in the duplicate samples was greater than 10 percent, discretion was used in determining the validity of the result. If the RSD of the IS peak areas for a duplicate sample was greater than 10 percent, and the RSD for all the IS peak areas analyzed in the complete batch of calibration

### Table 3.3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column</strong></td>
<td>Type: DB-1 fused silica capillary (J&amp;W Scientific)</td>
</tr>
<tr>
<td></td>
<td>Length: 30 m</td>
</tr>
<tr>
<td></td>
<td>Internal diameter: 0.25 mm</td>
</tr>
<tr>
<td></td>
<td>Film thickness: 1 ( \mu \text{m} )</td>
</tr>
<tr>
<td><strong>Temperature program</strong></td>
<td>Initial temperature: 35°C, hold for 10 min</td>
</tr>
<tr>
<td></td>
<td>Ramp to 50°C at 5°C/min, hold for 1 min</td>
</tr>
<tr>
<td></td>
<td>Ramp to 250°C at 10°C/min, hold for 5 min</td>
</tr>
<tr>
<td></td>
<td>Run time: 39 min</td>
</tr>
<tr>
<td><strong>Injector</strong></td>
<td>Injection volume: 2 ( \mu \text{L} )</td>
</tr>
<tr>
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<td>Temperature: 180°C</td>
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<td><strong>Detector</strong></td>
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<td>Temperature: 280°C</td>
</tr>
<tr>
<td><strong>Carrier gas</strong></td>
<td>Helium (99.999+% purity; Holox)</td>
</tr>
<tr>
<td></td>
<td>Flow rate: 1.0 mL/min at 35°C</td>
</tr>
<tr>
<td><strong>Make-up gas</strong></td>
<td>Nitrogen (99.999+% purity; Holox)</td>
</tr>
<tr>
<td></td>
<td>Flow rate: 30 mL/min</td>
</tr>
</tbody>
</table>
and aqueous samples was also greater than 10 percent, the sample that contributed to this RSD was eliminated.

An aqueous QC check standard was prepared at a concentration approximating the mid-level calibration standard. This check standard was run after every tenth analysis to monitor the validity of the calibration. If the percent recovery for the QC check standard was out of the 80 to 100 percent range, analyses were repeated for any samples analyzed since the last QC check standard was done.

The raw water matrix was deemed representative of the matrixes of all four fractions. Thus standard additions (or matrix spikes) were prepared only for the raw water samples for each utility to evaluate matrix effects with the LLE method. The spiked samples were also used to confirm the identification of the THM species. To prepare a spiked sample, a 20-mL aliquot of the raw water sample was spiked with standards as appropriate so that the concentrations of THM species in the spiked sample were theoretically about twice the concentrations that were expected in the sample. Because a standard mix with equal concentrations for all the THM species was used, the spiking was conducted based on the estimated concentration of the dominant species, CHCl₃, in the raw water samples. Spiking was done on both pH 6 and pH 8 raw water samples. The spiked samples were extracted in the same manner used for all the other samples and calibration standards. A recovery between 80 and 120 percent indicated no significant matrix effects.

Haloacetic Acid Analysis

Analytical procedure. The nine HAA species were analyzed using the micro LLE GC method described in chapter 2 and detailed in appendix A.

Analytical quality control. The QC strategies for THM analysis were also applied to the HAA analyses. Two additional strategies were followed. If the surrogate peak area was absent or was very low compared to previous similar analyses, it was likely that there had been a derivatization problem (e.g., water in extract) or an extraction problem (e.g., water insufficiently acidified). If the SD for all the surrogate areas analyzed in the complete batch of calibration and aqueous samples exceeded 10 percent, the particular sample or samples that contributed to this high SD value were identified and eliminated from the results.
Direct ester standards were injected at the start of each set of analyses to verify the sensitivity, chromatography, and retention times on the GC. The ester standards were also run after every tenth analysis to monitor the variation in retention times and other chromatographic conditions.

RESULTS AND DISCUSSION

Fractionation of Natural Organic Matter in Raw Waters

Table 3.4 summarizes the XAD-8 fractionation recoveries and other relative information for all five waters. Consistent with the literature (Malcolm 1991), around 100 percent of the adsorbed (extracted) humic substances were desorbed (recovered) from the XAD-8 resin using 0.1N NaOH as the eluent. The recovery was calculated based on the sum of the TOC measurements for each of the individual eluent batches rather than on the TOC measurement of the final combined hydrophobic fraction.

As shown in Table 3.5, the SUVA values of the raw waters generally increase as the SUVA values and the percentages of the corresponding hydrophobic fractions increase. Some researchers (Reckhow, Singer, and Malcolm 1990; Chin, Aiken, and O’Loughlin 1994; Croué et al. 1999) have noted a strong correlation between SUVA and the aromatic-carbon content of NOM in natural waters. Because the hydrophobic fraction usually contains more aromatic carbon and higher-molecular-weight materials than the hydrophilic fraction, the SUVA of the hydrophobic fraction is consistently higher than that of the hydrophilic fraction.

Table 3.4
Summary of XAD-8 fractionation results

<table>
<thead>
<tr>
<th>Water sample</th>
<th>Raw water TOC (mg/L)</th>
<th>Hydrophilic TOC (mg/L)</th>
<th>Volume of raw water extracted (L)</th>
<th>Combined hydrophobic fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>No. of batches</td>
<td>Volume (L)</td>
</tr>
<tr>
<td>Indianapolis</td>
<td>3.4</td>
<td>1.8</td>
<td>8.97</td>
<td>1</td>
</tr>
<tr>
<td>Manatee</td>
<td>8.7</td>
<td>4.0</td>
<td>8.62</td>
<td>3</td>
</tr>
<tr>
<td>East St. Louis</td>
<td>5.1</td>
<td>2.9</td>
<td>9.17</td>
<td>2</td>
</tr>
<tr>
<td>Groton</td>
<td>3.6</td>
<td>2.0</td>
<td>10.22</td>
<td>2</td>
</tr>
<tr>
<td>Tolt</td>
<td>1.1</td>
<td>0.5</td>
<td>12.17</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 3.5
Characteristics of raw water, hydrophilic fraction, and hydrophobic fraction

<table>
<thead>
<tr>
<th>Fraction</th>
<th>TOC (mg/L)</th>
<th>DOC (mg/L)</th>
<th>UV$_{254}$ (L/cm)</th>
<th>SUVA (L/mg-m)</th>
<th>Hydrophobic fraction (%)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indianapolis water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw water</td>
<td>3.4</td>
<td>3.4</td>
<td>0.105</td>
<td>3.1</td>
<td>47</td>
</tr>
<tr>
<td>Hydrophilic fraction</td>
<td>1.8</td>
<td>1.8</td>
<td>0.042</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Combined hydrophobic$^+$</td>
<td>32.6</td>
<td>32.6</td>
<td>1.330</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Manatee water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw water</td>
<td>8.7</td>
<td>8.7</td>
<td>0.368</td>
<td>4.2</td>
<td>54</td>
</tr>
<tr>
<td>Hydrophilic fraction</td>
<td>4.0</td>
<td>4.0</td>
<td>0.110</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Combined hydrophobic$^+$</td>
<td>33.8</td>
<td>33.8</td>
<td>1.832</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>East St. Louis water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw water</td>
<td>5.1</td>
<td>5.0</td>
<td>0.163</td>
<td>3.3</td>
<td>43</td>
</tr>
<tr>
<td>Hydrophilic fraction</td>
<td>2.9</td>
<td>2.9</td>
<td>0.075</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Combined hydrophobic$^+$</td>
<td>26.1</td>
<td>26.1</td>
<td>0.955</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>Groton water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw water</td>
<td>3.6</td>
<td>3.6</td>
<td>0.125</td>
<td>3.5</td>
<td>44</td>
</tr>
<tr>
<td>Hydrophilic fraction</td>
<td>2.0</td>
<td>2.0</td>
<td>0.042</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Combined hydrophobic$^+$</td>
<td>19.8</td>
<td>19.8</td>
<td>0.754</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Tolte water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw water</td>
<td>1.1</td>
<td>1.0</td>
<td>0.049</td>
<td>4.8</td>
<td>56</td>
</tr>
<tr>
<td>Hydrophilic fraction</td>
<td>0.5</td>
<td>0.5</td>
<td>0.016</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Combined hydrophobic$^+$</td>
<td>17.2</td>
<td>17.2</td>
<td>0.916</td>
<td>5.3</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ Calculated by (1–TOC$_{\text{hydrophilic}}$/TOC$_{\text{raw}}$) × 100%.

$^+$ TOC, DOC, and UV$_{254}$ were measured values of the final combined hydrophobic fraction. The TOC values might be slightly different from those shown in Table 3.4, which were calculated based on the TOC of each of the individual eluent batches combined.
Coagulation of Raw Waters

Jar Test Results and Bulk Coagulation

Figures 3.4 and 3.5 show the jar test results for two representative waters. East St. Louis water has a medium initial TOC concentration and high alkalinity, where a relatively low percent removal of TOC was expected. Manatee water has a high TOC concentration and low alkalinity, where the best TOC removal was anticipated (Smith 1994, White et al. 1997). Table 3.6 summarizes the critical alum doses selected for bulk water coagulation and the resulting removals achieved by bulk coagulation for all five waters.

As indicated in Table 3.6, coagulation and sedimentation alone were not effective in removing turbidity and organic carbon from the Groton and Tolt low-turbidity raw waters. Instead, the unsettled floc in the supernatant elevated the turbidity of the water and contributed to poor TOC removal. Because these floc were removed when the water was filtered with a 0.45-µm membrane filter, the DOC and UV$_{254}$ removals were significantly higher than the apparent TOC removals for these two waters. No polymer was used to assist in solid-liquid separation. Subsequent chlorination was performed in the supernatant containing these unsettleable floc with their higher concentrations of DBP precursors.

Enhanced coagulation also requires the tests to be done under certain pH conditions depending on raw water alkalinity. In this study, the lowest pH values achieved during the jar tests without Na$_2$CO$_3$ addition were 7.5 for Indianapolis water and 7.2 for East St. Louis water. For the other three waters, all of which had low alkalinity, Na$_2$CO$_3$ was added to maintain the pH above 6.0. Because the alkalinity of Indianapolis and East St. Louis waters were relatively high, larger amounts of alum had to be applied to coagulate these waters. This explains why a higher alum dose was employed on the high-alkalinity East St. Louis water than on the low-alkalinity Manatee water, which had a higher TOC concentration.

Another noticeable finding is that the UV$_{254}$ reduction was greater than the corresponding TOC reduction for all the waters, thereby bringing about a reduction in SUVA from raw water to coagulated water. This is consistent with previous findings (White et al. 1997). Additionally, Table 3.6 suggests that both DOC removal and UV$_{254}$ removal increase as the SUVA of the raw
Figure 3.4 Jar test results of East St. Louis water

Figure 3.5 Jar test results of Manatee water
water increases. This is because high-SUVA hydrophobic NOM tends to be more susceptible to coagulation (Singer and Harrington 1993, Edzwald and Tobiason 1999).

Hydrophobic/Hydrophilic Distribution of Carbon in Coagulated Water

Table 3.7 shows that the percentage of the hydrophobic fraction of the organic carbon in raw waters consistently increased after coagulation, indicating that coagulation unexpectedly appeared to remove more hydrophilic NOM than hydrophobic NOM. Harrington (1997) compared the relative removal of hydrophobic and hydrophilic fractions from 13 waters reported in the literature. Those results did not show a consistent pattern with respect to preferential removal of hydrophobic NOM over hydrophilic NOM. This may result from the operational nature of determining hydrophobicity using the XAD-8 resin. Some substances that would not adsorb on the XAD-8 resin from an untreated water may do so if they remain in solution after coagulation. These organic materials may be complexed with aluminum and consequently exhibit different hydrophobicity (and molecular weight) from the parent substances. Thus, the operational definition based on XAD-8 resin adsorption may not truly reflect the hydrophobicity (and molecular weight) of organic matter in coagulated water. For this reason, no trend could be discerned in this study between the percentage of “hydrophobic” carbon and SUVA for the coagulated waters.

Table 3.6
Removals of TOC, UV$_{254}$, and turbidity by coagulation

<table>
<thead>
<tr>
<th>Water</th>
<th>Alum dose (mg/L)</th>
<th>Removal (%)</th>
<th>Initial alkalinity (mg/L)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOC</td>
<td>DOC*</td>
<td>UV$_{254}$*</td>
<td>Turbidity</td>
</tr>
<tr>
<td>Indianapolis</td>
<td>40</td>
<td>15</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td>Manatee</td>
<td>60</td>
<td>52</td>
<td>52</td>
<td>75</td>
</tr>
<tr>
<td>East St. Louis</td>
<td>70</td>
<td>25</td>
<td>24</td>
<td>31</td>
</tr>
<tr>
<td>Groton</td>
<td>30</td>
<td>38</td>
<td>48</td>
<td>71</td>
</tr>
<tr>
<td>Tolt</td>
<td>10</td>
<td>8</td>
<td>73</td>
<td>75</td>
</tr>
</tbody>
</table>

* After laboratory filtration.
† Turbidity increased after coagulation in these low-turbidity waters. The turbidity in Groton and Tolt raw waters were only 0.5 and 0.6 nephelometric turbidity unit (ntu), respectively. No polymer was used to assist solid-liquid separation.
As Table 3.7 also shows, SUVA values were decreased after coagulation, indicating that the UV-absorbing chromophores (i.e., aromatic and olefinic carbon) are preferentially removed by coagulation, as reported by other investigators (Collins, Amy, and Steelink 1986; Semmens and Staples 1986; Croué et al. 1993). This was also confirmed by Harrington (1997), who analyzed raw materials (humic substances) and aluminum-organic precipitates using $^{13}$C-NMR (nuclear magnetic resonance) spectroscopy. That study found that the aromatic carbon moieties were removed by alum coagulation to a greater degree than the aliphatic carbon moieties.

### Characteristics of Water Fractions Before Chlorination

Table 3.8 summarizes the characteristics of all four fractions of each water before chlorination. The concentrated hydrophobic fraction was diluted with DOFW to obtain the same TOC concentration as the hydrophilic fraction. The data in this table may be slightly different from those in Table 3.5 where the parameters were measured immediately after fractionation. Both Indianapolis and Manatee raw water were sampled twice by the water utilities over an interval of about 10 days, and two different raw water samples were sent to UNC. The raw water for fractionation came from the first sampling, while the raw water for coagulation and chlorination were the blended raw waters from the two samplings. As Table 3.8 shows, the five waters represent a wide range in quality and are from diverse geographic locations.

### Table 3.7

Percentage of hydrophobic carbon in raw and coagulated waters

<table>
<thead>
<tr>
<th>Water</th>
<th>Raw water</th>
<th>Coagulated water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% hydrophobic carbon</td>
<td>SUVA (L/mg-m)</td>
</tr>
<tr>
<td>Indianapolis</td>
<td>47</td>
<td>3.1</td>
</tr>
<tr>
<td>East St. Louis</td>
<td>43</td>
<td>3.3</td>
</tr>
<tr>
<td>Groton</td>
<td>44</td>
<td>3.6</td>
</tr>
<tr>
<td>Manatee</td>
<td>54</td>
<td>4.4</td>
</tr>
<tr>
<td>Tolt</td>
<td>56</td>
<td>4.7</td>
</tr>
</tbody>
</table>

* Not analyzed because of the low DOC content of the coagulated water.
Table 3.8
Characteristics of water fractions before chlorination

<table>
<thead>
<tr>
<th>Water and fraction</th>
<th>TOC (mg/L)</th>
<th>DOC (mg/L)</th>
<th>UV$_{254}$ (L/cm)</th>
<th>SUVA (L/mg-m)</th>
<th>Br$^-$ (µg/L)</th>
<th>Measured</th>
<th>Spiked*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indianapolis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>2.7</td>
<td>2.8</td>
<td>0.087</td>
<td>3.1</td>
<td>23</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>Coagulated</td>
<td>2.3</td>
<td>2.3</td>
<td>0.063</td>
<td>2.7</td>
<td>23</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>1.8</td>
<td>1.8</td>
<td>0.042</td>
<td>2.3</td>
<td>N/D†</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>1.8</td>
<td>1.8</td>
<td>0.076</td>
<td>4.2</td>
<td>N/M‡</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Manatee</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>8.1</td>
<td>8.2</td>
<td>0.359</td>
<td>4.4</td>
<td>173</td>
<td>173</td>
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<td>3.9</td>
<td>0.088</td>
<td>2.3</td>
<td>162</td>
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</tr>
<tr>
<td>Hydrophilic</td>
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<td>4.0</td>
<td>0.110</td>
<td>2.8</td>
<td>N/D†</td>
<td>173</td>
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</tr>
<tr>
<td>Hydrophobic</td>
<td>3.8</td>
<td>4.0</td>
<td>0.214</td>
<td>5.4</td>
<td>N/M‡</td>
<td>173</td>
<td></td>
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<tr>
<td>East St. Louis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>5.1</td>
<td>5.0</td>
<td>0.163</td>
<td>3.3</td>
<td>59</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>Coagulated</td>
<td>3.8</td>
<td>3.8</td>
<td>0.102</td>
<td>2.7</td>
<td>61</td>
<td>61</td>
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</tr>
<tr>
<td>Hydrophilic</td>
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<td>2.9</td>
<td>0.073</td>
<td>2.5</td>
<td>41</td>
<td>41</td>
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</tr>
<tr>
<td>Hydrophobic</td>
<td>2.8</td>
<td>2.8</td>
<td>0.101</td>
<td>3.6</td>
<td>N/D§</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>Groton</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>3.4</td>
<td>3.3</td>
<td>0.119</td>
<td>3.6</td>
<td>&lt;20**</td>
<td>&lt;20</td>
<td></td>
</tr>
<tr>
<td>Coagulated</td>
<td>2.1</td>
<td>1.7</td>
<td>0.035</td>
<td>2.1</td>
<td>&lt;20**</td>
<td>&lt;20</td>
<td></td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>1.9</td>
<td>1.8</td>
<td>0.042</td>
<td>2.3</td>
<td>&lt;20**</td>
<td>&lt;20</td>
<td></td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>1.9</td>
<td>1.9</td>
<td>0.075</td>
<td>3.9</td>
<td>N/D§</td>
<td>&lt;20</td>
<td></td>
</tr>
<tr>
<td>Tolt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw</td>
<td>1.2</td>
<td>1.1</td>
<td>0.052</td>
<td>4.7</td>
<td>N/M††</td>
<td>&lt;10‡‡</td>
<td></td>
</tr>
<tr>
<td>Coagulated</td>
<td>1.1</td>
<td>0.3</td>
<td>0.013</td>
<td>4.3</td>
<td>N/M††</td>
<td>&lt;10‡‡</td>
<td></td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>0.5</td>
<td>0.5</td>
<td>0.014</td>
<td>2.8</td>
<td>N/M††</td>
<td>&lt;10‡‡</td>
<td></td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>0.5</td>
<td>0.5</td>
<td>0.030</td>
<td>6.0</td>
<td>N/M††</td>
<td>&lt;10‡‡</td>
<td></td>
</tr>
</tbody>
</table>

* Br concentration after spiking not verified by IC measurement. Br added as necessary to obtain same target Br/TOC ratio as in hydrophilic fraction. No bromide added to Groton or Tolt water.

† Not detectable; chloride interference; assumed equal to Br concentration measured in raw water. HCl was used to adjust pH to 2.0 for fractionation of Indianapolis and Manatee raw water; H$_2$SO$_4$ was later used for the other three waters to avoid chloride interference.

‡ Not measured and assumed to be 0 for calculation of bromide spike.

§ Not detectable because of sulfate interference; assumed to be 0 for calculation of bromide spike. H$_2$SO$_4$ was added to neutralize hydrophobic fraction to pH 6–7 for storage.

** Below method detection limit: 20 µg/L.

†† Not measured; Tolt water utility database showed no more than 10 µg/L bromide present in raw water.

‡‡ No spike added; assumed to also be less than 10 µg/L.
Because the following parameters are used frequently throughout this section, they are defined here first.

- **DBP production**—measured concentration in chlorinated samples, µg/L or µmol/L
- **DBP formation potential (DBPFP) or DBP/TOC**—DBP production divided by TOC concentration, µg/mg C or µmol/mg C (TOC-normalized DBP production)
- **Relative distribution of HAA to THM, or HAA/THM ratio**—HAA production divided by THM production, µg/µg or µmol/µmol

Most of the discussion in this section is based on molar concentrations to control for the differences in bromide concentrations in different fractions and molecular weight differences among different HAA or THM species.

Because the MDL for HAAs and THMs is 1 µg/L, any HAA or THM species whose concentration was below this detection limit was not included in calculation of the concentration of HAA9 or THM4.

*Effect of Reaction Time*

Figures 3.6 through 3.21 illustrate the relationship between DBPFP and chlorination contact time for Indianapolis water and Manatee water. These two waters were selected for illustration as they represent a relatively low SUVA and a relatively high-SUVA water, respectively. As can be seen, at either pH 6 or pH 8, both HAA9 and THM4 were formed rapidly in the first few hours and then slowed to a generally steady rate of increase. By the end of the first 8 hours, around 55 to 70 percent of the 72-hour production had been achieved. As expected, as long as a free chlorine residual persisted, more HAAs and THMs continued to be formed. (The free chlorine residual at pH 8 after 72 hours in Manatee raw water was below 0.1 mg/L as Cl₂; for this reason the measured HAA or THM concentrations might be smaller than the actual formation potentials for this sample.)
Figure 3.6 Effect of chlorination contact time on HAA formation potential of Indianapolis water at pH 6: raw water versus coagulated water

Figure 3.7 Effect of chlorination contact time on HAA formation potential of Indianapolis water at pH 8: raw water versus coagulated water
Figure 3.8 Effect of chlorination contact time on HAA formation potential of Indianapolis water at pH 6: hydrophobic fraction versus hydrophilic fraction

Figure 3.9 Effect of chlorination contact time on HAA formation potential of Indianapolis water at pH 8: hydrophobic fraction versus hydrophilic fraction
Figure 3.10  Effect of chlorination contact time on THM formation potential of Indianapolis water at pH 6: raw water versus coagulated water.

Figure 3.11  Effect of chlorination contact time on THM formation potential of Indianapolis water at pH 8: raw water versus coagulated water.
Figure 3.12 Effect of chlorination contact time on THM formation potential of Indianapolis water at pH 6: hydrophobic fraction versus hydrophilic fraction.

Figure 3.13 Effect of chlorination contact time on THM formation potential of Indianapolis water at pH 8: hydrophobic fraction versus hydrophilic fraction.
Figure 3.14 Effect of chlorination contact time on HAA formation potential of Manatee water at pH 6: raw water versus coagulated water

Figure 3.15 Effect of chlorination contact time on HAA formation potential of Manatee water at pH 8: raw water versus coagulated water
Figure 3.16 Effect of chlorination contact time on HAA formation potential of Manatee water at pH 6: hydrophobic fraction versus hydrophilic fraction

Figure 3.17 Effect of chlorination contact time on HAA formation potential of Manatee water at pH 8: hydrophobic fraction versus hydrophilic fraction
Figure 3.18 Effect of chlorination contact time on THM formation potential of Manatee water at pH 6: raw water versus coagulated water

Figure 3.19 Effect of chlorination contact time on THM formation potential of Manatee water at pH 8: raw water versus coagulated water
Figure 3.20 Effect of chlorination contact time on THM formation potential of Manatee water at pH 6: hydrophobic fraction versus hydrophilic fraction

Figure 3.21 Effect of chlorination contact time on THM formation potential of Manatee water at pH 8: hydrophobic fraction versus hydrophilic fraction
These figures indicate that raw waters always had higher DBPFPs than the corresponding coagulated waters, and the hydrophobic fractions usually had higher DBPFPs than the corresponding hydrophilic fractions. These observations are consistent with the SUVA values of the different fractions.

Mass concentrations were used for these figures because an attempt was made to keep the Br/TOC ratio consistent for raw and coagulated water, as well as for the hydrophobic and hydrophilic fractions.

Comparisons of the time profiles for the formation of monohaloacetic acids (XAA), dihaloacetic acids (X_2AA), trihaloacetic acids (X_3AA), HAA9, and THM4 are illustrated in Figures 3.22 and 3.23. East St. Louis raw water is used here because these data were not shown in Figures 3.6 to 3.21. Among the three classes of HAA species, X_3AA gave the highest production throughout the reaction at pH 6. As pH increased from 6 to 8, the production of XAA and X_2AA were not affected, but X_3AA formation decreased significantly so that X_2AA production was comparable to that of X_3AA at pH 8. This decrease in X_3AA formation at pH 8, coupled with the increase in THM4 formation, led to more THM4 being formed than HAA9, whereas at pH 6, HAA9 formation was dominant over THM4 formation.

The distribution of HAA9 to THM4 as a function of time is illustrated in Figures 3.24 through 3.26. The HAA9/THM4 ratios after chlorination at pH 6 for 2, 4, 8, 24, and 72 hours did not exhibit much difference from the ratio after 1 hour of chlorination. The 45° line shown on this figure and on subsequent figures is the line of no effect. For all points that fall below the line, the value on the x-axis is greater than the corresponding value on the y-axis. The reverse is true for points that fall above the line of no effect. The HAA9/THM4 ratios after 24 and 72 hours of chlorination were also plotted against the HAA9/THM4 ratios after 4 and 8 hours of chlorination (not shown), with consistent results to those in Figures 3.25 and 3.26. Overall, as time increased, the ratio of HAA9/THM4 did not appear to change much.

Similar analyses for the X_3AA/X_2AA ratio for all water fractions show that the X_3AA/X_2AA ratio increased rapidly with increasing reaction time in the first 8 hours of chlorination, and then gradually plateaued (Figures 3.27 and 3.28). At pH 6, the formation of X_3AA was dominant over that of X_2AA after 8 hours (ratio > 1) but at pH 8, the relative dominance of these two HAA groups was largely dependent on the specific water fractions.
Figure 3.22 Effects of reaction time on the formation of HAA and THM species at pH 6 in East St. Louis raw water

Figure 3.23 Effects of reaction time on the formation of HAA and THM species at pH 8 in East St. Louis raw water
Figure 3.24 Effect of reaction time on the HAA9/THM4 ratio in all water fractions (first 8 hours of chlorination)

Figure 3.25 Effect of reaction time on the HAA9/THM4 ratio in all water fractions (24 hours versus 1 hour of chlorination)
Figure 3.26 Effect of reaction time on the HAA9/THM4 ratio in all water fractions (72 hours versus 1 hour of chlorination)

Figure 3.27 Distribution of $X_3$AA and $X_2$AA formation as a function of reaction time at pH 6 for all fractions of all waters
These figures indicate that the values of the HAA9/THM4 ratio and $X_{3AA}/X_{2AA}$ ratio varied widely among the different water fractions, which suggests that both the relative distribution of HAA9 and THM4 and the relative distribution of $X_{3AA}$ and $X_{2AA}$ are affected strongly by the characteristics of the specific waters.

**Effects of pH**

The distribution of HAA and THM species depends on the Br/TOC ratio or Br/Cl$_2$ ratio (e.g., Symons et al. 1993, Cowman and Singer 1996) and pH. Manatee coagulated water is used here to illustrate the effects of pH on the speciation of HAAs and THMs because it had the highest Br/TOC ratio of all the water fractions examined; therefore, all nine species of HAAs and all four species of THMs were observed upon chlorination.

As Figure 3.29 shows, increasing pH from 6 to 8 had very little effect on the formation of XAA and X$_2$AA, but significantly decreased the formation of all of the X$_3$AA species except Br$_3$AA, whose concentration was too low for any meaningful comparison. At both pH values, XAA species were formed least. The X$_3$AA species were dominant at pH 6, but yielded to X$_2$AA species at pH 8. All the compounds in each class of X$_i$AA ($i = 1,2,3$) behaved quite consistently,
which suggests that the formation mechanisms or the precursors, or both, are the same for the halogenated compounds in each class.

Figure 3.30 shows a comparison of the impact of pH on the speciation of the three HAA classes for all water fractions. This figure confirms the findings in Figure 3.29—for all fractions and all waters, $X_2$AA formation is the same at pH 6 and pH 8, and $X_3$AA formation is lower at pH 8 than at pH 6. XAA formation tends to be slightly higher at pH 8 than at pH 6, but the concentrations are so low that the trend may not be significant. A reasonable inference could be drawn from Figure 3.30 that the three classes of HAA species have distinct formation mechanisms (pathways) or different precursors.

In contrast to the HAAs, the formation of all four of the THM species showed a pronounced increase as the pH of chlorination increased from 6 to 8 (Figure 3.31). This finding is consistent with observations by previous researchers (e.g., Stevens et al. 1976; Morris and Baum 1978; Fleischacker and Randtke 1983; Reckhow and Singer 1985; Stevens, Moore, and Mittner 1989).

Figure 3.32 shows that for all of the water fractions, the formation of THM4 at pH 8 was always greater than at pH 6. The reverse was true for HAA9.

The speciation of HAAs and THMs at different pH values is determined by the formation mechanisms of the different species. Several reaction mechanisms have been proposed. The mechanism formulated by Reckhow and Singer (1985) is one of the most plausible. Based on this
Figure 3.30 Comparison of pH effects on the formation of XAA, X2AA, and X3AA for all water fractions

Figure 3.31 Effect of pH on the speciation of THMs in Manatee coagulated water
mechanism, THMs and X₃AA have a common precursor structure (R-CO-CX₃), and the relative formation of these species is determined by the nature of the R group and pH. Under alkaline conditions, base-catalyzed hydrolysis prevails, yielding more THMs. In acidic environments, on the other hand, X₃AA will be formed if the R group is a readily oxidizable functional group capable of easily donating an electron pair to the rest of the molecule. In the absence of such an oxidative cleavage (e.g., if the R group is not a readily oxidizable functional group), hydrolysis might still prevail, resulting in THMs. When the R group is a methyl group (e.g., CH₃-CO-CX₃, 1,1,1-trihaloacetone), THMs and X₂AA will be formed but not X₃AA. Reckhow and Singer’s work (1985) showed that the formation of Cl₂AA was roughly 60 percent of the formation of CHCl₃ at pH 7 via this pathway.

The conceptual model Reckhow and Singer (1985) proposed also showed that there might be more precursor structures and formation pathways for X₂AA than for X₃AA, which may make the formation of X₂AA exhibit more complex behavior with respect to pH. Therefore, it cannot be concluded that pH has no effect on X₂AA formation just because no difference in X₂AA formation was found between pH 6 and pH 8. In addition, this model did not explain the formation of XAA. A hypothesis would be that the activated carbon atom in the β-diketone moiety (R’-CO-CH₂-CO-R) is substituted only with one chlorine (R’-CO-CHCl-CO-R), but it is much harder for this structure to hydrolyze to CH₂Cl-CO-R than it is for R’-CO-CCl₂-CO-R to
hydrolyze to CHCl₂-CO-R, thus giving a very low yield of XAA (when R = OH). Hydroxide ions may catalyze this hydrolysis, resulting in slightly more XAA formation at pH 8 than at pH 6.

Figure 3.33 shows that more HAA9 were formed than THM4 at pH 6; the reverse was true at pH 8. However, at both pH 6 and pH 8, the formation of THMs was always dominant over the formation of X₃AA for any fraction of the five test waters (Figure 3.34). This finding is in contrast to Labouyrie-Rouillier’s work (1997). This would suggest that more of the R groups in the NOM of these fractions are not readily oxidizable functional groups (including the methyl group), or that pH 6 is not low enough to greatly inhibit the hydrolysis or to promote the oxidative cleavage reactions.

Effects of Organic Carbon Content and Characteristics: Total Organic Carbon, Ultraviolet Absorbance at 254 Nanometers, and Specific Ultraviolet Absorbance

**Specific ultraviolet absorbance.** Figure 3.35 illustrates the impact of SUVA on HAA formation potential at pH 6 for all five raw waters—the waters with higher SUVA values generally had higher haloacetic acid formation potentials (HAAFPs). As stated earlier, the organic carbon in high SUVA waters is relatively more hydrophobic, more aromatic, and of higher molecular weight; this kind of organic carbon is well recognized for its DBP formation potential. A similar pattern was observed for HAA formation at pH 8, and for THM4 formation as well (Figure 3.36).

Strong correlations have been established between SUVA and the total organic halide formation potential (TOXFP), trihalomethane formation potential (THMFP), and trichloroacetic acid formation potential (Cl₃AAFP) for isolated humic substances (Reckhow, Singer, and Malcolm 1990; Croué et al. 1999). In the results of this study, a modest correlation was obtained between SUVA and both HAA9 and THM4 formation potentials considering all of the water fractions (Figure 3.37 and 3.38). As the figures illustrate, the correlation between HAAFP and SUVA was slightly stronger than that between THMFP and SUVA, especially at pH 8. At pH 6, the HAAFP tended to increase more than THMFP as the SUVA of the water fractions increased. At pH 8, however, the two correlations essentially paralleled each other.

As demonstrated in Figure 3.39, when the four fractions were considered separately, the ratio of HAA9 to THM4 at pH 6 tended to increase as SUVA increased for raw waters, coagulated
Figure 3.33 Effect of pH on the distribution of HAA9 and THM4 for all water fractions

Figure 3.34 Comparison of the formation of THM4 and X₃AA for all water fractions
Figure 3.35 Comparison of HAAFP at pH 6 for all raw waters with different SUVA values

Figure 3.36 Comparison of THMFP at pH 8 for all raw waters with different SUVA values
Figure 3.37 Relationship between HAA9 and THM4 formation potential and SUVA at pH 6 for all water fractions

Figure 3.38 Relationship between HAA9 and THM4 formation potential and SUVA at pH 8 for all water fractions
waters, and hydrophobic fractions. However, no such pattern was observed at pH 8. For hydrophilic fractions, there was no apparent trend between the HAA9/THM4 ratio and SUVA, at either pH 6 or pH 8. When all the water fractions were considered together, no apparent correlation between SUVA and the relative formation of these two classes of DBPs was observed, although the HAA9/THM4 ratio appeared to show a slight increase with increasing SUVA at pH 6 (see Figure 3.37).

The HAA/THM ratio is dependent on the distribution of HAA and THM precursors in the water fractions, all other factors being equal. Like all other surrogate parameters, SUVA has its own limitations. As a substitute measure of the general hydrophobicity and aromaticity of the DOC in waters, SUVA is not able to completely differentiate between structures that contribute to HAA formation and those that contribute to THM formation. In addition, not all the aromatic structures that absorb UV radiation at 254 nm are “activated aromatic structures” that are able to react with chlorine to form DBPs. Thus SUVA can serve as a good indicator of overall DBPFP but provides little information about the relative distribution of HAA and THM precursors.

Figure 3.39 Relationship between the relative formation of HAA9 and THM4 and SUVA for all water fractions
Figure 3.39 shows again that pH is a very important factor that influences the distribution of HAAs and THMs. As pH increased from 6 to 8, the HAA9/THM4 ratio decreased (from greater than 1 to less than 1) for all the water fractions.

*Total organic carbon and ultraviolet absorbance at 254 nanometers.* TOC and UV$_{254}$ have also been widely used as surrogate parameters for monitoring DBP formation. As shown in Figures 3.40 and 3.41, good correlations were achieved between DBP production and both TOC and UV$_{254}$. In accordance with the findings of previous researchers (e.g., Edzwald, Becker, and Wattier 1985; Najm et al. 1994), UV$_{254}$ served as a slightly better predictor than TOC concentration. Similar correlations were observed at pH 8, although the equations of the lines of best fit were different than those at pH 6.

**Comparison of Hydrophobic and Hydrophilic Fractions**

Few studies have been devoted to a comparison of the reactivity of hydrophobic and hydrophilic NOM isolated from surface waters. More work has been done on comparisons between humic and fulvic acids, the major constituents of the hydrophobic NOM.

For Indianapolis water and Manatee water, it was shown above that both HAAFP and THMFP were higher in the hydrophobic fractions than in the corresponding hydrophilic fractions. This was true for all five waters (Figures 3.42 through 3.45). The nature and distribution of the hydrophobic and hydrophilic materials in different waters may differ, depending on the parent organic materials and the biogeochemical processes involved in carbon cycling within the specific watershed. However, hydrophobic and hydrophilic fractions derived from the same raw water may be similar in composition (nature or structure) but different in the relative amounts of each component.

As shown in Figures 3.42 through 3.45, all the hydrophobic fractions had higher SUVA values and gave higher DBPFPs than the corresponding hydrophilic fractions, except for East St. Louis water in which the DBPFPs of the two fractions were comparable. These results confirm the argument that hydrophobic carbon, which is rich in aromatic content, phenolic hydroxyl groups, and conjugated double bonds, is the major precursor of DBPs. Nonetheless, in waters where the proportion of hydrophobic NOM is relatively low, hydrophilic carbon may still play an
Figure 3.40 Relationship between HAA and THM production and TOC at pH 6 for all water fractions

Figure 3.41 Relationship between HAA and THM production and UV$_{254}$ at pH 6 for all water fractions
Figure 3.42 Comparison of HAA formation at pH 6 in hydrophobic and hydrophilic fractions (the numbers above the bars are the corresponding SUVA values)

Figure 3.43 Comparison of HAA formation at pH 8 in hydrophobic and hydrophilic fractions (the numbers above the bars are the corresponding SUVA values)
Figure 3.44 Comparison of THM formation at pH 6 in hydrophobic and hydrophilic fractions
(the numbers above the bars are the corresponding SUVA values)

Figure 3.45 Comparison of THM formation at pH 8 in hydrophobic and hydrophilic fractions
(the numbers above the bars are the corresponding SUVA values)
important role in DBP formation. It should be noted that transphilic carbon, as defined by Croué et al. (1999), which was reported to contain important DBP precursors such as aliphatic ketones and alcohols, was part of the hydrophilic fraction in this study because of the manner in which the fractionation was carried out (XAD-8 only).

No correlation could be established between SUVA and DBPFP among the different hydrophilic fractions because UV absorbance is a semiquantitative measure of the degree of conjugation, which is expected to be too low in the hydrophilic fractions to show good correlation. The low UV absorbance values may also be interfered with more strongly by the complicated matrix of the hydrophilic fractions. In contrast, the hydrophobic fractions with their correspondingly higher SUVA values usually had higher DBPFPs, except for Groton water, which had an unusually high DBPFP for its measured SUVA.

Figure 3.46 demonstrates that the hydrophobic fractions generally gave higher formation potentials of $X_2$AA, $X_3$AA, and THM4, regardless of the chlorination pH or origin and nature of the NOM. The opposite was observed, to a slight degree, for XAA. This may suggest that the structure and properties of the XAA precursors are different from those of $X_2$AA, $X_3$AA, and THM precursors, but this conjecture needs to be confirmed with more data, especially because the XAA concentrations tend to be very low.

No consistent trend was seen in the distribution of HAA9 and THM4 for the hydrophobic and hydrophilic fractions (Figure 3.47). At pH 8, the HAA9/THM4 ratio tended to be higher in the hydrophobic fraction than in the hydrophilic fraction, although the ratio was always less than 1 for both fractions. At pH 6, no significant difference in the ratio was observed between these two fractions. The pH effect suggests that there is no well-defined boundary between HAA and THM precursors; some structures may serve as common precursors of HAAs and THMs, as Reckhow and Singer suggested earlier (1985). The extent to which each are formed depends on reaction conditions, mainly pH. Sinha, Amy, and Sohn (1997) suggested that the hydrophobic fraction is more reactive than the hydrophilic fraction for THM formation, but that the two fractions are equally reactive in terms of HAA formation. It should be noted that their conclusions were drawn based on chlorination experiments at a single pH (pH 7), and thus might be limited. The smaller ratio of HAA9/THM4 for the hydrophilic fractions at pH 8 in this study might suggest that some NOM structures are more sensitive to pH than others. As pH increases, THM
Figure 3.46 Comparison of the formation of XAA, X₂AA, X₃AA, and THM4 at both pH values in hydrophobic and hydrophilic fractions

Figure 3.47 Comparison of the relative distribution of HAA9 and THM4 in hydrophobic and hydrophilic fractions for all waters and all contact times
formation from these structures may be improved (or HAA formation is suppressed, or both) to a larger extent than from other structures, giving a greater net decrease in the HAA9/THM4 ratio. Croué and colleagues (1999) suggested that hydrophilic fractions of NOM are more significant precursors of THMs than of HAAs, based on the fact that in finished drinking water (where hydrophilic fractions of NOM tend to be dominant), larger relative yields of THMs to HAAs are obtained than from chlorinated hydrophobic humic substances. Reckhow, Singer, and Malcolm (1990) also found that at pH 7, the THM4/X3AA ratio was always higher for fulvic acids than for humic acids. Their $^{13}$C-NMR data indicated that humic acids had a larger aromatic carbon content than fulvic acids, and that the majority of the fulvic carbon was aliphatic in nature. Based on this relationship, it may be concluded that aliphatic structures play a more important role in THM formation than in HAA formation. The higher proportion of such structures in the hydrophilic carbon makes the THM4/HAA9 ratio higher in the hydrophilic fractions than in the hydrophobic fractions.

**Effect of Bromide Concentration**

Because of the higher molecular weight of bromine (compared to chlorine), the incorporation of bromine into DBPs will increase the mass yields and make it more difficult to meet the DBP regulations if significant amounts of both bromide and precursor material are present in the source water. Additionally, previous research on THM formation has shown that although hypochlorous acid (HOCl) is a stronger oxidant than hypobromous acid (HOBr), HOBr is a stronger halogenating agent. This means that more organic material becomes reactive and more THM4 is produced, even on a molar basis (Symons et al. 1993). The effect of bromide is dependent on chlorine dose, reaction time, TOC concentration, and reaction temperature. Either the Br/TOC ratio (Trussell and Umphres 1978; Amy, Tan, and Davis 1991) or the Br/Cl (Br/Cl$^+$, Br/Cl$_2^+$) ratio (e.g., Heller-Grossman et al. 1993; Symons et al. 1993; Ichihashi, Teranishi, and Ichimura 1999) has been correlated with DBP speciation and production.

Two terms are used in this section to assess bromine substitution during HAA and THM formation. The first is the DBP-Br/DBP-Cl ratio, where DBP-X refers to the molar concentration ($\mu$mol/L) of the incorporated halide (X) in total HAA or total THM, which is equal to the summation of the molar concentrations of each individual HAA or THM species multiplied by the number of X atoms in its molecular formula. This term is consistent with the bromine
incorporation factor suggested by Gould, Fitchorn, and Urheim (1983). The second is percent bromine utilization, which is defined as \((\mu\text{mol DBP-Br}/\mu\text{mol initial Br}^-) \times 100\%\).

Figures 3.48 and 3.49 show the effect of Br/TOC and Br/Cl\(_2\) ratios on the speciation of HAA in coagulated waters. Coagulated water results are used here for illustration because the Br/TOC or Br/Cl\(_2\) ratio of coagulated waters were significantly different from each other, making the bromide effect more pronounced. Cl\(_2\) refers to the initial free chlorine molar concentration.

Figure 3.48 Effect of bromide on the speciation of HAA at pH 6 in coagulated waters

Figure 3.49 Effect of bromide on the speciation of HAA at pH 8 in coagulated waters
applied during chlorination. As expected, as the Br/TOC or Br/Cl₂ ratio increased, the mole fractions of the bromine-containing species increased significantly whereas the reverse occurred for the HAA species containing only chlorine. For the bromide concentrations explored in this study (see Table 3.9), the speciation was generally in this order: (Cl₃AA, Cl₂AA) > (BrCl₂AA, BrClAA) > ClAA > (Br₂ClAA, Br₂AA) > (Br₃AA, BrAA). The order of the two species within each group varies depending on pH or other conditions. For these bromide concentrations, the moles of bromine incorporated into monobromo-species are greater than those incorporated into dibromo- and tribromo-species. This is because the bromide concentration in the waters was relatively low and the chlorine concentration was much higher than the bromide concentration. As a result, HOBr (OBr⁻) was unable to compete over HOCl (OCl⁻) even though the former is a better halogenating species. It is expected that HAA speciation would keep shifting to the mixed bromochloro and brominated species at higher Br/TOC or Br/Cl₂ ratios, but the quantitative relationships among these species are complex (Pourmoghaddas et al. 1993, Cowman and Singer 1996). This suggests that the regulation of only five HAA species—ClAA, Cl₂AA, Cl₃AA, BrAA, and Br₂AA—may appreciably underestimate the overall occurrence of HAAs in finished drinking water (Cowman and Singer 1996). Because the formation mechanisms for the individual species within each of the XAA, X₂AA, and X₃AA groups are similar, no correlation was observed between Br/TOC or Br/Cl₂ ratio and the mole fractions of the individual XAA, X₂AA, and X₃AA species (not shown).

As stated earlier, the effect of bromide on the speciation of THMs has been well studied. Chlorination conditions (contact time, temperature, and pH) being equal, the distribution among the THM species shifted from chloroform to the more brominated forms as the initial Br/TOC ratio increased in the waters, as is demonstrated in Figures 3.50 and 3.51. For these waters, chloroform was still the most abundant species because the bromide concentration was relatively low. The mole fractions of all four THM species were almost independent of chlorination pH, which contrasts with what was observed for HAAs. This is probably because all four THM species are formed via the same, or at least similar, chemical pathways. For the HAAs, on the other hand, both the precursors and formation mechanisms for each class of HAA species are different and are functions of pH.
The fraction of brominated DBP species is determined by several factors, including chlorination conditions (initial chlorine dose, contact time, temperature, and pH), initial Br/Cl₂ ratio, Br/TOC ratio, and precursor characteristics (e.g., activated aromatic content versus aliphatic ketones). In this study, all these factors were kept essentially equal for the hydrophobic and hydrophilic fractions of each water except for the precursor characteristics. Thus Figure 3.52 can be used to compare the relative reactivity of the hydrophobic fraction and the hydrophilic fraction with respect to bromine incorporation. Figure 3.52 integrates all the data from both pH conditions and all contact times because no pH effect was observed (not shown). The plot shows that bromine was more reactive with the hydrophilic fraction than with the corresponding hydrophobic fraction in formation of HAAs and THMs, and chlorine was more reactive with the hydrophobic fraction than with the corresponding hydrophilic fraction. Because hydrophobic organic material

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* Initial ratio of bromide concentration to free chlorine dose (as Cl).
† Calculated as (HAA9-Br + THM4-Br)/(HAA9-Cl + THM4-Cl).
usually contains larger amounts of activated aromatic moieties, whereas hydrophilic organic material is rich in aliphatic structures such as aliphatic ketones and alcohols, it can be concluded that bromine is more reactive with aliphatic precursors than with aromatic precursors. The reverse is true for chlorine. This finding verifies the hypothesis proposed by Heller-Grossman and co-workers (1993) and is consistent with the results obtained by Huang and Yeh (1997), who worked with only one water.

Figure 3.50 Effect of bromide on the speciation of THM at pH 6 in coagulated waters

![Graph of THM speciation at pH 6](image)

Figure 3.51 Effect of bromide on the speciation of THM at pH 8 in coagulated waters

![Graph of THM speciation at pH 8](image)
Figure 3.53 gives the relative distribution of bromine and chlorine in HAA9 versus THM4 for all water fractions at all reaction times. Apparently, the brominated species comprised a higher molar proportion among the THMs than among the HAAs; pH and contact time had little impact on the distribution. Because bromine is more reactive with aliphatic precursors than with aromatic precursors (Figure 3.52), and bromine is more readily incorporated into THM species than into HAA species (Figure 3.53), we can deduce that THMs may be derived to a more significant degree from aliphatic structures than the HAAs, or that the hydrophilic fraction may contain relatively more THM precursors than the hydrophobic fraction. This is consistent with the hypothesis proposed above that aliphatic structures may play a relatively more important role in THM formation than in HAA formation.

Figures 3.54 and 3.55 confirm that bromine exhibits a faster rate in the substitution reaction than chlorine, especially in the waters with higher Br/TOC or Br/Cl₂ ratios (i.e., Manatee water), although chlorine plays a much more important role in the first oxidation step (Rook et al. 1978). For each water, the THM4-Br/THM4-Cl ratio was always higher than the corresponding HAA9-Br/HAA9-Cl ratio, consistent with Figure 3.53. The highest bromination rate was always observed at the beginning of the reaction because the concentrations of bromine and organic precursors (NOM) were highest at that time.
Figure 3.53 Comparison of the mole fraction of brominated species in HAA and THM

Figure 3.54 Comparison of the kinetics of bromination and chlorination in HAA and THM formation at pH 6 for coagulated waters
Bromine utilization was strongly dependent on the nature of the precursors, Br/Cl ratio and pH. As shown in Table 3.9, after 72 hours, the percentage of bromine that was incorporated into THMs and HAAs (ignoring other DBPs) was much higher than that of chlorine (see percent Br utilization and percent Cl utilization), and the molar ratio of incorporated bromine to incorporated chlorine was much greater than the initial Br/Cl ratio. These observations affirm that bromine is more reactive than chlorine in substitution and addition reactions that form HAAs and THMs. The very low chlorine utilization (2 to 4 percent) apparently suggests that much of the chlorine applied to the systems was not incorporated into organic molecules, but simply converted to chloride ion via oxidation reactions. Symons et al. (1993) found that for the same water, the percent bromine utilization tended to decrease as bromide concentration increased because the available sites in the precursors had been “saturated” by bromine and therefore the excess bromine could not react.

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Both the bromine and chlorine utilization percentage increased as pH increased from 6 to 8, but the incorporated bromine to chlorine ratio (DBP-Br/DBP-Cl) appeared to be relatively independent of pH. More bromine and less chlorine were utilized and incorporated into THMs and HAAs by the hydrophilic fraction than by the hydrophobic fraction, although both fractions had the same Br/TOC ratio; this is consistent with Figure 3.52. It should be noted that THMs and
HAAs account for only about 50 percent of the total DBPs formed from chlorination. Thus the overall bromine or chlorine utilization should be higher than the values given in the table.

As discussed above, it has been suggested that $X_3\text{AA}$ and the THMs may be derived from a common precursor (Reckhow and Singer 1985) and that all four species within each group may be formed via a common chemical pathway. Thus it might be hypothesized that the relative degree of bromine incorporation into the two groups of trihalo-species would be similar. If this is true, the molar ratio of $\text{BrCl}_2\text{AA}$ to $\text{Cl}_3\text{AA}$ should be equal to the molar ratio of $\text{CHBrCl}_2$ to $\text{CHCl}_3$. The same would be true for the $\text{Br}_2\text{Cl}_{3}\text{AA}/\text{Cl}_3\text{AA}$ ratio and the $\text{CHBr}_2\text{Cl}/\text{CHCl}_3$ ratio, as well as the $\text{Br}_3\text{AA}/\text{Cl}_3\text{AA}$ ratio and the $\text{CHBr}_3/\text{CHCl}_3$ ratio. This is of great practical importance because these relationships could be used to predict the formation of $\text{BrCl}_2\text{AA}$, $\text{Br}_2\text{Cl}_{3}\text{AA}$, and $\text{Br}_3\text{AA}$ from the available concentrations of $\text{Cl}_3\text{AA}$ and the THMs, given that the database for the former three species is quite limited but is well established for $\text{Cl}_3\text{AA}$ and the THMs.

Figures 3.56 and 3.57 illustrate the relationships between the molar ratios of $\text{BrCl}_2\text{AA}/\text{Cl}_3\text{AA}$ and $\text{CHBrCl}_2/\text{CHCl}_3$, and between $\text{Br}_2\text{Cl}_{3}\text{AA}/\text{Cl}_3\text{AA}$ and $\text{CHBr}_2\text{Cl}/\text{CHCl}_3$. Statistical t-tests were conducted for both regressions, indicating that the intercepts of both regression equations are significant ($P = 3.3 \times 10^{-8}$ for $\text{BrCl}_2$ and $P = 0.025$ for $\text{Br}_2\text{Cl}$) at the significance level of $\alpha = 0.05$; thus both intercepts were kept in the regression equations. Another t-test was performed to see if there was any significant difference between the mean of the ratios of $\text{BrCl}_2\text{AA}/\text{Cl}_3\text{AA}$ to $\text{CHBrCl}_2/\text{CHCl}_3$ and 1, and these turned out to be significant ($T = 9.35 \gg 1.96$ at $\alpha = 0.05$); the same was true for the dibromochloro species ($T = 44.96$). The correlation for the monobromo-substituted species has a lower correlation coefficient relative to that for the dibromo-substituted species ($R^2 = 0.90$ versus $R^2 = 0.95$), but less deviation from the theoretical model (slope of 0.77 versus 0.58). If it is true that aliphatic moieties play a more important role in THM formation than in HAA formation, bromine should be incorporated into THMs to a greater extent because aliphatic moieties (e.g., aliphatic ketones) are more “bromophilic” than aromatic moieties, as noted earlier (Figures 3.52 and 3.53).

Despite this apparent deviation of the molar ratios of these chlorinated samples from the theoretical value of 1.0 implied by the common precursor model of Reckhow and Singer (1985), a more comprehensive analysis of the distribution among the trihaloacetic acid species using the ICR database shows that the model does indeed appear to be valid. This is presented and discussed in depth in chapter 4.
Figure 3.56 Correlation between the BrCl$_2$/Cl$_3$AA ratio and the CHBrCl$_2$/CHCl$_3$ ratio

Figure 3.57 Correlation between the Br$_2$CIAA/Cl$_3$AA ratio and the CHBr$_2$Cl/CHCl$_3$ ratio
Coagulation has been reported to remove substantial amounts of DBP precursors (NOM), reducing the DBP formation potential of a water. Figure 3.58 illustrates the percentage reductions in TOC, UV\textsubscript{254}, HAA9 production (\textmu mol/L), THM4 production (\textmu mol/L), and HAA9 + THM4 production (\textmu mol/L) by alum coagulation and settling (chlorination at pH = 6 for 72 hours). The SUVA of the raw water increases from left to right on the X-axis. As SUVA increased, the percentage removals of TOC, UV\textsubscript{254}, HAA9, and THM all increased correspondingly, with the exception of Tolt water. (The results for the Tolt water are not representative of well-treated water because, as noted earlier in this chapter, the TOC [1.2 mg/L] and turbidity [0.6 ntu] of the Tolt raw water was very low, and coagulation with alum and subsequent settling were not effective in removing turbidity and TOC. Therefore, the precipitated NOM that was associated with the floc in the supernatant was not separated from the water and contributed to further DBP production.)

TOC was removed by coagulation to a lesser extent than UV\textsubscript{254} and the HAA and THM precursors, suggesting that coagulation preferentially removed UV-absorbing chromophores, and decreased the SUVA values and HAAFP and THMFP of the water. For the waters with relatively low SUVA values, such as Indianapolis and East St. Louis water, the DBPFP removals were slightly higher than UV\textsubscript{254} removal, and HAA9 and THM4 precursor removals were almost equal. For the high SUVA waters, the highest removal was observed for UV\textsubscript{254}, and more HAA9 precursors than THM4 precursors were removed. Because the hydrophobic content of the NOM is more susceptible to coagulation than the hydrophilic portion (Collins, Amy, and Steelink 1986; Semmens and Staples 1986; Singer and Harrington 1993), the relative reduction of HAA9 and THM4 suggests that the hydrophobic carbon may contain more HAA9 precursors than THM4 precursors; the reverse is true for the hydrophilic carbon. Low-SUVA waters usually have a lower fraction of hydrophobic carbon and are relatively less amenable to coagulation.

Figure 3.59 shows that coagulation tends to remove more X\textsubscript{3}AA precursors than THM precursors for the high-SUVA waters. As the SUVA of the raw water decreases, both X\textsubscript{3}AA and THM precursor removals decrease and become comparable to each other. X\textsubscript{2}AA precursor removal has a similar behavior to X\textsubscript{3}AA precursors, but is almost always lower than the latter. In
Figure 3.58 Removals of TOC, UV$_{254}$, and HAA and THM precursors by coagulation

Figure 3.59 Comparison of removals of $X_2$AA, $X_3$AA, and THM4 precursors by coagulation
the low SUVA waters, THM precursor removal is higher than X$_2$AA precursor removal. These findings suggest again that X$_2$AA and X$_3$AA precursors are relatively more hydrophobic than THM precursors, and are thus more susceptible to coagulation.

Harrington (1997) analyzed the untreated humic substances and the aluminum precipitates after treatment by coagulation using $^{13}$C-NMR. The results showed that the aromatic carbon moieties were removed by alum coagulation to a greater degree than the aliphatic carbon moieties, and that oxygen-substituted aliphatic carbon was removed more effectively than carbon-substituted and hydrogen-substituted aliphatic carbon. Coupled with the DBP removal results obtained in this study, it can be concluded that the majority of HAA precursors are aromatic in nature; THMs may have relatively more aliphatic moieties as their precursors in addition to aromatic structures. This confirms that hydrophilic carbon, which contains a larger portion of aliphatic moieties than hydrophobic carbon, has a higher fraction of THM precursors than hydrophobic carbon (see discussion above). It is important to note that the activated aromatic structures are still the main precursors for both HAAs and THMs, but the aliphatic structures may play a more important role in THM formation than in HAA formation.

Because coagulation removed more HAA9 precursors than THM precursors, the relative distribution of HAA9 and THM4 tended to shift toward THM4 in coagulated water (especially for waters with high SUVA values), as shown in Figure 3.60. This is consistent with the observations in real water treatment systems. Some examples of this are presented in chapter 5.

Coagulation is known to be ineffective for bromide removal; bromide behaves conservatively through the coagulation process (Amy 1993). Therefore, coagulation shifts the Br/TOC and Br/Cl$_2$ ratio by removing TOC, altering DBP speciation. As Figures 3.61 and 3.62 show for Manatee water, the mole fractions of the mixed bromochloro and brominated DBP species increased significantly after coagulation; in contrast, the mole fractions of the DBP species containing only chlorine decreased.

**Surrogate Parameters of Disinfection By-product Production**

As demonstrated above, HAA and THM formation are highly dependent on source water characteristics such as TOC (DOC), UV$_{254}$, SUVA, proportion and nature of hydrophobic NOM, and bromide concentration. Treatment processes that can change these (or part of these)
Figure 3.60 Effect of coagulation on the relative distribution of HAA9 and THM4 for all waters

Figure 3.61 Effect of coagulation on the speciation of HAA
parameters, such as coagulation, will alter DBP formation during the subsequent disinfection process. The conditions under which the disinfection process is performed also have significant impacts on DBP formation and species distribution. Contact time, pH, disinfectant type, temperature, disinfectant dose, and residual are some of these important factors. Because DBP formation is such a complex function of so many variables, it is useful to find surrogate parameters to estimate or monitor DBP production under a wide range of conditions. Chlorine consumption and change in UV absorbance (e.g., Korshin, Li, and Benjamin 1997) are two parameters that can be easily and quickly measured during chlorination. The following analysis addresses the effectiveness of these two surrogate parameters.

**Chlorine Consumption**

Chlorine consumption varies with contact time, chlorination pH, and water quality. As reaction time increases, more chlorine is consumed (not shown). A slightly higher chlorine consumption was observed at pH 8 than at pH 6 (Table 3.8), all other factors being equal. No apparent pattern was observed between TOC-normalized chlorine consumption and SUVA (Figure 3.63). A better trend was observed for the hydrophobic fractions than for the other fractions because the hydrophobic fraction has a relatively less complicated matrix, and chlorine
is consumed mainly by the NOM functional groups. In the other fractions, large amounts of other chlorine-consuming materials (reducing agents like ammonia, organic nitrogen, and ferrous iron, for example) might exist, but these have little to do with SUVA. The positive relationship between chlorine consumption and hydrophobic SUVA (see Figure 3.63) suggests that activated (defined as electron-rich) aromatics are the major components in NOM that have high chlorine reactivity.

As shown in Table 3.10, at either pH, raw water always had a higher chlorine demand than coagulated water, suggesting that coagulation preferentially removed chlorine-consuming organic carbon from the raw waters. The relative chlorine demand of the hydrophobic and hydrophilic fractions appears to be related to the raw water SUVA values. For the low-SUVA raw waters, the hydrophilic fraction is a greater chlorine consumer than the hydrophobic fraction; the opposite occurs for the high-SUVA raw waters. This again suggests that hydrophilic NOM plays a more important role in low-SUVA waters (waters with low humic content) than in high-SUVA waters with respect to reactivity with chlorine. This may also be related to the fact that hydrophilic NOM tends to have higher concentrations of nitrogen in its structure.

Figures 3.64 and 3.65 show the strong linear relationships between HAA9 and THM4 formation and chlorine consumption at pH 6 and pH 8 for all water fractions at all contact times. Obviously, pH influences the correlation equations, with a lesser effect for HAA9. The relationships for both HAA9 and THM4 appear independent of water quality characteristics and
reaction time. When the sum of HAA9 and THM4 concentrations is considered, the effect of pH is eliminated (see Figure 3.66). Figure 3.66 indicates that the prediction of the summed HAA9 + THM4 production by chlorine consumption is also not influenced by reaction time and water quality characteristics. No strong correlation could be established between HAA9 + THM4 formation potential ([HAA9 + THM4]/TOC), and chlorine demand (mg Cl₂ consumed/mg C). This agrees with the finding by Labouyrie-Rouillier (1997).

Table 3.10
Chlorine demand of all water fractions after 72 hours of chlorination

<table>
<thead>
<tr>
<th>Water</th>
<th>SUVARaw (L/mg-m)</th>
<th>Chlorine demand at pH 6 (mg Cl₂/mg C)</th>
<th>Chlorine demand at pH 8 (mg Cl₂/mg C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>Coagulated</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>Indianapolis</td>
<td>3.1</td>
<td>1.4</td>
<td>1.1</td>
</tr>
<tr>
<td>East St. Louis</td>
<td>3.3</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Groton</td>
<td>3.6</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>Manatee</td>
<td>4.4</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Tolt</td>
<td>4.7</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Figure 3.64 Correlation between HAA9 production and chlorine consumption for all water fractions and all contact times
Figure 3.65 Correlation between THM4 production and chlorine consumption for all water fractions and all contact times

Figure 3.66 Correlation between (HAA9 + THM4) production and chlorine consumption for all water fractions, both pH values and all contact times
In summary, chlorine consumption was found to serve as a very useful tool for monitoring and estimating the summed HAA9 + THM4 production, and the prediction is independent of water quality characteristics (e.g., NOM concentration and properties and bromide concentration) and chlorination conditions (e.g., chlorine dose, pH, and contact time). However, the prediction of HAA9 or THM4 production alone is pH-dependent and the quantitative relationships need to be established and used only at specific pH values.

Change in Ultraviolet Absorbance ($\Delta \text{UV}$)

Because UV absorbance is destroyed as the aromatic units of NOM react with chlorine to form DBPs, the correlation between DBP formation and the decrease in UV absorbance was explored. Strong linear relationships have been observed between TOX and chloroform formation and the decrease in UV_{272} (Korshin, Li, and Benjamin 1996, 1997; Li, Korshin, and Benjamin 1998, 2000). Figures 3.67 and 3.68 show that both the equation and the strength of the regression between THM4 formation and $\Delta \text{UV}_{272}$ are strongly pH-dependent, but pH does not have much of an effect on the correlation between HAA9 formation and $\Delta \text{UV}_{272}$. The correlation for THM4 is not as strong as those reported by Korshin and co-workers (1997) and Li and colleagues (1998), and the intercept of the regression equation is positive instead of negative as these authors reported. When the sum of HAA9 and THM4 production is considered, the correlation appears less dependent on pH (Figure 3.69).

Figure 3.70 illustrates that a strong correlation between HAA9 or THM4 formation and $\Delta \text{UV}_{272}$ was obtained at pH 6 for each of the hydrophobic fractions at different contact times, but that the hydrophobic fractions from different waters behave differently. Even for the different fractions derived from the same raw water, the correlations are also different (not shown). These findings suggest that the prediction of HAA9, THM4, and the summed HAA9 + THM4 production using $\Delta \text{UV}_{272}$ is somewhat influenced by the characteristics of NOM, reaction time, and pH.

The relationship between chlorine consumption and $\Delta \text{UV}_{272}$ (Figure 3.71) is quite similar to that between the summed HAA9 + THM4 production and $\Delta \text{UV}_{272}$ (Figure 3.69). A stronger correlation was obtained for the hydrophobic fractions than for the other fractions (not shown), probably because of the simpler matrix of the hydrophobic fractions.

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Figure 3.67  Correlation between HAA9 production and change in UV\textsubscript{272} for all water fractions and all contact times

Figure 3.68  Correlation between THM4 production and change in UV\textsubscript{272} for all water fractions and all contact times
Figure 3.69 Correlation between (HAA9 + THM4) production and change in UV$_{272}$ for all water fractions, both pH values and all contact times.

Figure 3.70 Correlation between HAA9 or THM4 production and change in UV$_{272}$ at pH 6 for different hydrophobic fractions at all contact times.
CONCLUSIONS

The primary goal of this part of the study was to evaluate the impact of various water quality and treatment characteristics on the formation and distribution of HAAs and THMs under controlled laboratory chlorination conditions. To reach this goal, waters with a wide range of TOC (1.2–8.1 mg/L), UV$_{254}$ (0.052–0.359 cm$^{-1}$), SUVA (3.1–4.7 L/mg-m), and bromide concentrations (<10–173 µg/L) were sampled from five different geographical locations, coagulated with alum, fractionated with XAD-8 resin, chlorinated at pH 6 and 8, and stored at 20°C in the dark for various contact times (up to 72 hours). The XAD-8 fractionation technique recovered almost 100 percent of the organic carbon adsorbed on the resin, which was defined as the hydrophobic fraction, accounting for 43 ~ 56 percent of the DOC in the raw waters.

The study results show that the formation of HAA and THM species increased as chlorination contact time increased, with the fastest rate occurring at the beginning of the reaction. By the end of the first 8 hours of chlorination, around 55 to 70 percent of the 72-hour production had been achieved for both the THMs and HAAs. The relative distribution of HAA9 and THM4 was reasonably consistent throughout the reaction period at both pH 6 and pH 8. The $X_3$AA/$X_2$AA
ratio, however, increased with increasing contact time at both pH values. This ratio increased particularly rapidly during the first 8 hours of chlorination, and remained essentially unchanged after 24 hours. Both the HAA9/THM4 ratio and the $X_3$AA/$X_2$AA ratio varied widely among the different waters and fractions, reflecting the strong impact of water quality characteristics.

SUVA, as a surrogate parameter for the hydrophobicity and aromaticity of NOM in water, was shown in this study to be moderately correlated with the HAA9 and THM4 formation potentials ($\mu$mol/mg C). The slightly stronger correlation observed between HAAFP and SUVA might suggest that the HAA precursors are more aromatic in nature than the THM precursors. The origin of the aquatic NOM also influenced the correlations; different DBPFPs were observed for similar SUVA values. SUVA is not capable of completely differentiating between the relative formation of HAAs and THMs because of its inherent nature as a nonspecific surrogate, although the HAA9/THM4 ratio tended to be slightly higher in the water fractions with higher SUVA values. TOC concentration and UV$_{254}$ showed strong correlations with both HAA and THM production; UV$_{254}$ exhibited a slightly stronger correlation.

Chlorination pH plays a very important role in determining the distribution of HAA and THM species. Increasing pH from 6 to 8 increased the production of all four THM species but decreased the production of $X_3$AA species, with little effect on the production of $X_2$AA species. The formation of XAA tended to be slightly higher at pH 8 than at pH 6. These findings also suggest that the THMs and the three classes of HAA species have distinct formation mechanisms or different precursors; the compounds within each class of DBPs, however, may be formed through the same or similar chemical pathways. The formation of THM4 was higher than the formation of HAA9 at pH 8, and the reverse was true at pH 6. However, THM4 formation was consistently greater than $X_3$AA formation regardless of pH. In addition, more chlorine was consumed at pH 8 than at pH 6.

The hydrophobic fractions from almost all waters gave higher formation potentials of $X_2$AA, $X_3$AA, and THM4 than the corresponding hydrophilic fractions, which is consistent with their relative SUVA values. XAA precursors, however, might be more hydrophilic. These results confirm earlier work indicating that hydrophobic carbon, which is rich in aromatic content and phenolic hydroxyl groups, is the main precursor of DBPs. The comparable DBPFPs between the East St. Louis hydrophobic and hydrophilic fractions suggest that, in waters where the proportion of hydrophobic NOM is relatively low, hydrophilic carbon may also play an important role in
DBP formation. This is also supported by the finding that the hydrophilic fraction had a greater chlorine demand than the corresponding hydrophobic fraction for the waters with relatively low SUVA values. A strong correlation was observed between DBPFP and SUVA for the hydrophobic fractions, but no apparent correlation was observed for the hydrophilic fractions.

The HAA9/THM4 ratio was higher in the hydrophobic fractions than in the hydrophilic fractions at pH 8, but no significant difference was observed at pH 6. It is speculated that the less hydrophobic (more aliphatic) precursors may play a more important role in THM formation than in HAA formation, as others have also hypothesized (Croué et al. 1999).

Considering the influence of bromide for the bromide concentrations tested, as the Br/TOC ratio increased, the mole fractions of bromine-containing species increased significantly. For the species containing only chlorine, the reverse was true. Because of the low Br/Cl ratio in this study, the number of moles of bromine incorporated into monobromo-species was greater than that incorporated into dibromo- and tribromo-species, and the species containing only chlorine were still predominant. The hydrophilic fractions exhibited consistently higher reactivity with bromine than the hydrophobic fractions, which supports the work by Huang and Yeh (1997) and Heller-Grossman and co-workers (1993) who thought that bromine was more readily incorporated into aliphatic precursors than into aromatic precursors (with the reverse being true for chlorine). This study also shows that the brominated species comprised a higher molar proportion among the THMs than among the HAAs; pH and reaction time had little impact on this distribution. Bromine was more reactive in substitution reactions and was incorporated into HAA and THM species faster than chlorine. Most of the chlorine was consumed in oxidation reactions. Increasing pH increased the utilization of both bromine and chlorine but did not change the incorporated bromine to chlorine ratio. Two models were constructed to predict the formation of bromine-containing X₃AA species (BrCl₂AA and Br₂Cl₃AA) from the concentrations of Cl₃AA and the THMs, and it was found that the relative degree of bromine incorporation into the THMs was greater than that into X₃AA at both pH 6 and pH 8, especially for dibromo-species. This finding suggests either that the formation kinetics of THM and X₃AA are different or that THM precursors are possibly more aliphatic (and thus more “bromophilic”) than X₃AA precursors.

Coagulation removed substantial amounts of DBP precursors and shifted the distribution of HAA and THM species. The effectiveness of coagulation is mainly dependent on the TOC and SUVA of the raw waters, although alkalinity strongly influences the alum dose. In general, waters
with higher SUVA values, which usually contained more hydrophobic and aromatic carbon, were more susceptible to coagulation. For all the waters studied, coagulation removed more UV$_{254}$ than TOC, thereby lowering the SUVA values and suggesting that coagulation preferentially removes UV-absorbing chromophores. For the waters with relatively low SUVA values, HAA9 and THM4 removals were comparable, and both removals were higher than UV$_{254}$ removals. For the high-SUVA waters, UV$_{254}$ was removed to the largest extent, and HAA9 precursors and even X$_3$AA precursors were removed to a greater degree than THM4 precursors. Coupled with Harrington’s findings (1997), these results suggest that HAA precursors are more hydrophobic and aromatic than THM precursors. Coagulation altered the Br/TOC ratio of the water and shifted the speciation of HAAs and THMs toward the bromochloro and brominated species.

Chlorine consumption was found to be a good predictor ($R^2 \approx 0.93$) of the summed production of HAA9 + THM4 regardless of pH, water quality, and reaction time. However, the prediction of either HAA9 or THM4 production alone from chlorine consumption was affected by pH. The $\Delta$UV$_{272}$ was found to be another useful predictor of the production of HAA9, THM4, and summed HAA9 + THM4. However, $\Delta$UV$_{272}$ did not predict as well as chlorine consumption, and it also appeared to be related to pH, water quality, and reaction time. A strong correlation between chlorine consumption and $\Delta$UV$_{272}$ was observed for the hydrophobic fractions, but not for the other fractions.
CHAPTER 4
ANALYSIS OF INFORMATION COLLECTION RULE DATA FOR HALOACETIC
ACID AND TRIOHALOMETHANE OCCURRENCE

INTRODUCTION

The only regulated haloacetic acids at this time are HAA5 (ClAA, BrAA, Cl2AA, Cl3AA, and Br2AA; USEPA 1999a). Stage 1 of the D/DBP Rule regulates HAA5 at a running annual average of 60 µg/L. Although occurrence data for TTHMs and six of the nine bromine- and chlorine-containing HAAs (HAA5 plus BrClAA) are now available as a result of the ICR (USEPA 1999b), occurrence data on BrCl2AA, Br2ClAA, and Br3AA, collectively referred to as HAA3, are limited. Even though there are nine bromine- and chlorine-containing HAAs (HAA9), only five were regulated in the Stage 1 D/DBP Rule because HAA5 were the only HAAs for which occurrence data were available for consideration when Stage 1 was promulgated. Standards for BrClAA were developed later and the database for HAAs in general was limited. Cowman and Singer’s (1996) work on HAA speciation showed the importance of considering HAA9 when analyzing DBPs, even in low-bromide waters. It prompted HAA9 measurement standards to be introduced where before there were only standards for HAA5 and HAA6. Some water utilities then measured HAA9 for the ICR, but most did not because it was optional under the ICR (USEPA 1999b).

Auxiliary 1 (Aux 1), which is the primary database used to store ICR DBP data, was used for this study. The data were collected from 296 public water systems, each serving at least 100,000 people, from July 1997 to December 1998 (18 months). At the start of the research presented in this chapter, only data collected during the first 12 months of the ICR endeavor were available. Consequently, only data for this period were used in the analysis that follows. This new DBP information offers a much more comprehensive look at DBP data from water utilities across the country than previous studies (Krasner et al. 1989; Stevens et al. 1989; Reckhow and Singer 1990; Singer, Obolenski, and Griener 1995) because of its larger scale.
OBJECTIVES

Recognizing this advantage, the overall objective of this part of the project was to gain a better understanding of DBP occurrence, particularly the presence of the HAAs, in U.S. drinking waters, using available data in the ICR database. A more specific objective of this study was to analyze the ICR data to explore relationships between total THM (THM4) and total HAA (HAA9) occurrence on a national scale. Measuring only HAA6 concentrations as required by the ICR does not truly reflect overall HAA occurrence in treated drinking waters. For this reason, total HAA concentrations are likely to be underestimated if HAA5 occurrence is used as in Stage 1 of the D/DBP Rule. Therefore, a second objective of this study was to develop a model to predict HAA3 concentrations from the THM and HAA data already available. This proposed model was capable of converting HAA6 data in the ICR database into HAA9 data by predicting the unknown HAA3 concentrations. This information could then be used to develop a more complete and accurate record of overall HAA occurrence, and allow for a more appropriate comparison with overall THM occurrence. These comparisons have the potential to be used in future regulatory actions designed to establish MCLs for the HAAs. The final objective of this portion of the work was to reevaluate THM and HAA relationships in U.S. drinking water according to the predictions developed by the model, and to explore factors contributing to the relative dominance of THMs and HAAs in finished drinking water.

HAA3 PREDICTIVE MODEL

Using Krasner et al.’s (1989) and Cowman and Singer’s (1996) studies on brominated THM and HAA species, respectively, and Reckhow and Singer’s (1985) and Reckhow, Singer, and Malcolm’s (1990) research on NOM precursors of trihalogenated DBPs, it was hypothesized that each of the bromine-containing trihalogenated HAA3 species would form in the same proportion with respect to Cl3AA as their brominated THM counterparts form with respect to chloroform (CHCl3). Regression analysis was used to test this hypothesis as described below.

The model equations are

\[
\frac{[\text{BrCl}_2\text{AA}]}{[\text{Cl}_3\text{AA}]} = (\text{slope}) \times \frac{[\text{CHBrCl}_2]}{[\text{CHCl}_3]} \quad (4.1)
\]
\[
\frac{[\text{Br}_2\text{ClAA}]}{[\text{Cl}_3\text{AA}]} = (\text{slope}) \times \frac{[\text{CHBr}_2\text{Cl}]}{[\text{CHCl}_3]}
\] (4.2)

\[
\frac{[\text{Br}_3\text{AA}]}{[\text{Cl}_3\text{AA}]} = (\text{slope}) \times \frac{[\text{CHBr}_3]}{[\text{CHCl}_3]}
\] (4.3)

where “slope” is the slope of the regression line introduced by plotting the ratio on the left-hand side as the dependent variable and the ratio on the right-hand side as the independent variable. All concentrations are in micromolar (\(\mu\text{M}\)) units.

For the hypothesized model, based theoretically on Cowman and Singer (1996), Reckhow and Singer (1985), and Reckhow, Singer, and Malcolm (1990), the slope is assumed to be equal to 1. Actual slopes of the linear equations (Equations 4.1 to 4.3) were determined from the first 12 months of ICR data and compared to the theoretical value of 1. This theoretical value was also used to predict HAA3 concentrations simply by reworking Equations 4.1 to 4.3 and by setting “slope” equal to 1. Using the model’s predictions, overall expected HAA occurrence can be determined.

**PROCEDURES**

The Auxiliary 1 (Aux 1) Database, Version 3.0, issued on Sept. 23, 1999, was a Microsoft Access (Microsoft Corporation) file that included 38 tables and 10 queries, forms, reports, and macros. Of the 48 total entries, only three tables were needed to meet the objectives of this project: TUXDBP, TUXPLTMON, and TUXSAMPLE. TUXDBP included all available DBP concentrations in micrograms per liter (\(\mu\text{g/L}\)). Each DBP data point gathered from Aux 1 represented one DBP concentration, gathered from one water treatment plant, during one particular sampling event, from one point in the distribution system, including finished water (at the point of entry [POE] to the distribution system). TUXPLTMON contained disinfection information about each water treatment plant participating in the Aux 1 data collection and the nature of the source water for each sample, and TUXSAMPLE gave more detailed information about each water sample tested, including the sampling locations in the distribution system.
Relative Trihalomethane and Haloacetic Acid Concentrations

To examine known THM and HAA occurrence, HAA5 concentrations in micrograms per liter were sorted and matched with THM4 concentrations in micrograms per liter from the same treatment plant, sampling event, and distribution system sampling point. This was done by creating an appropriate query in Microsoft Access. Treatment plants with identification numbers less than 100 were neglected because they represented plants treating blended water from different sources. The data were sorted in the same way for HAA6 and HAA9 concentrations, where such data were available. Missing information for certain treatment plants or sampling periods (null values) were also neglected for this data sorting, including the many entries with missing HAA3 concentrations. The remaining concentrations were plotted, and Microsoft Excel (Microsoft Corporation) was used to perform regression analysis. Standard error and 95 percent confidence intervals were calculated in SPSS (SPSS, Inc.), a statistical application package.

For each treatment plant and sampling event, the THM and HAA concentrations were collected from two points of average residence times in the distribution system (labeled “avg1” and “avg2” in Aux 1); at the POE to the distribution system (labeled “finish” in Aux 1); from a laboratory simulated distribution system sample point (labeled “sds” in Aux 1); and from an actual location in the distribution system representing the residence time that corresponded to the simulated sampling point (labeled “dse” in Aux 1). These sampling points were chosen to examine THM and HAA relationships because they represent average DBP concentrations to which the public is exposed. The most distant points in the distribution system, the ones with the longest detention time (labeled “max” in Aux 1), were neglected in this analysis because some evidence suggests that HAA concentrations decrease at “max” points in the distribution system as a result of biodegradation at low chlorine residuals (e.g., Williams and Williams 1998). Including these data might have skewed the results. The HAA and THM comparisons were done for all source waters (e.g., surface waters and groundwaters) and all disinfectant types (e.g., free chlorine, combined chlorine, and chlorine dioxide) by setting certain criteria in the Microsoft Access queries. All waters, disinfectants, and event types except for “max” were used to inspect the DBP relationships as a broad, typically average representation of water samples from the 296 nationwide facilities. After the model was used to make HAA predictions, one final analysis was
performed in the same way to examine the relationship between THM4 concentrations and the newly predicted HAA9 occurrence.

Prediction of HAA3

To predict HAA3 concentrations, DBP concentrations in Aux 1 were recorded and displayed in parts per billion (ppb or µg/L) units as listed in the ICR database. For many of the DBPs, however, a better depiction of their relationships with other DBPs was best represented in molar concentrations because of the different halogen contents of the different HAA species and the different atomic weights of chlorine and bromine. Thus molar concentrations were used to create the ratios found in Equations 4.1 to 4.3. A Microsoft Access query was created to convert DBPs to micromoles per liter (µmol/L or µM). Because THM4, HAA3, HAA5, HAA6, and HAA9 are all cumulative measures of concentrations, µM values for these were calculated by summing the appropriate individual DBP concentrations after converting them to µM units. For this task, below detection limit (BDL) entries were included by setting them equal to zero. This was done to obtain enough non-null measurements of individual species to result in a cumulative total for the aforementioned collective DBP measures. By rearranging Equations 4.1 to 4.3 to arrive at Equations 4.4 to 4.6:

\[
[\text{BrCl}_2\text{AA}] = (\text{slope}) \times [\text{Cl}_3\text{AA}] \times [\text{CHBrCl}_2]/[\text{CHCl}_3] \tag{4.4}
\]

\[
[\text{Br}_2\text{ClAA}] = (\text{slope}) \times [\text{Cl}_3\text{AA}] \times [\text{CHBr}_2\text{Cl}]/[\text{CHCl}_3] \tag{4.5}
\]

\[
[\text{Br}_3\text{AA}] = (\text{slope}) \times [\text{Cl}_3\text{AA}] \times [\text{CHBr}_3]/[\text{CHCl}_3] \tag{4.6}
\]

In another Microsoft Access query, predicted values for the individual HAA3 species were calculated in micromolar units and summed (neglecting samples where null values still existed from lack of Cl₃AA or THM data) to obtain predicted HAA3 concentrations. The theoretical slope of 1 was used to develop these predictions.
To examine the reliability of the theoretical model, the predicted values for each HAA3 species were plotted against the actual BrCl₂AA, Br₂ClAA, and Br₃AA molar concentrations calculated previously for the available ICR data where such species were measured. A similar plot was created to collectively show the predicted HAA3 concentrations against observed HAA3 concentrations. Predicted HAA9 was calculated by adding known HAA₆ concentrations to the corresponding predicted HAA3 concentrations and these values were plotted against the observed HAA9 concentrations.

Cumulative Frequency Distributions

Cumulative frequency distributions for the THMs and HAAs were produced to compare their ICR-measured occurrence and their predicted occurrence as determined by the model. As mentioned previously, some water utilities measured all HAA9 species as part of the ICR data-gathering activity, but most did not because it was optional and because the last three trihaloacetic acids (HAA3) are more difficult to analyze. For these reasons, HAA9 predictions (which do not require actual HAA3 measurements in the proposed model) are useful from a regulatory standpoint, as is their use in assessing overall HAA occurrence.

To examine the distribution of predicted HAA9 concentrations, as well as observed concentrations of HAA9, HAA5, and THM4, cumulative frequency distribution plots were prepared using the data analysis histogram option in Microsoft Excel. Avg1, avg2, dse, sds, and finish sampling points were chosen to perform these analyses because they are representative of the average concentrations to which people are exposed. Median and ninetieth percentile concentrations were determined from these plots. In addition to observed THM4, HAA5, and HAA9 cumulative frequency plots, cumulative frequency distributions were also plotted for predicted HAA9 concentrations using the theoretical slope of 1. All distributions were prepared using microgram-per-liter concentration units to be consistent with practice and regulatory requirements. Predictions for HAA9 were made in micrograms per liter in the same way as they were for micromolar concentrations, again using the theoretical slope of 1 and Equations 4.4 to 4.6.

The same cumulative frequency distributions were created for “max” THM4, HAA5, and predicted HAA9 concentrations by resorting the data to examine any differences caused by using remote distribution system points.
RESULTS AND DISCUSSION

Relative Trihalomethane and Haloacetic Acid Concentrations in the Information Collection Rule Database

For each sample event for which there were paired values for THM4 and HAA5 concentrations, the ratio of the two was calculated (on a weight basis). Figure 4.1 is a diagram showing the frequency of occurrence of different HAA5/THM4 ratios (see bar graph on left side of figure), and a cumulative curve showing the percentage of values that were less than the indicated ratio. “N” is the number of paired concentrations available; N = 5,614 in this case). The ratios were calculated for all distribution system samples, including the finished water (POE value) and the simulated distribution system sample, but excluding the “max” location as explained above. The ratios are for all waters sampled in the ICR database, and for all disinfection scenarios. The mode of the frequency distribution is about 0.7, and the median or 50th percentile ratio (P50) is seen to be 0.63 µg/µg, indicating that HAA5 concentrations were 63 percent of the THM4 concentrations for half the waters sampled. These findings are consistent with those of Krasner et al. (1989), in which the median ratio of HAA5 to THM4 was reported to be 0.5 in a study of 35 U.S. treatment facilities.

Figure 4.1 Frequency distribution of observed HAA5/THM4 ratio for all waters and disinfection scenarios in first 12 months of ICR data (avg1, avg2, dse, sds, finish; N = 5,614)
Figure 4.2 shows a similar plot for the sampling events in which all HAA9 species were measured. Because fewer utilities measured all nine HAA species, fewer paired THM4 and HAA concentrations were available for this analysis (N = 1,243 in Figure 4.2 compared to N = 5,614 in Figure 4.1). As expected, the distribution of HAA/THM4 ratios shifts to higher values when all nine HAA species are considered. The mode of the distribution is closer to 0.9 and the median (50th percentile) ratio is 0.86 µg/µg, suggesting that total HAA concentrations are approximately equal to total THM concentrations in finished drinking water.

Prediction of HAA3

To extend this finding to all waters in the ICR database, even for those in which BrCl2AA, Br2ClAA, and Br3AA (collectively HAA3) were not measured, the model described above was tested using the subset of data from utilities in the ICR database that measured all nine HAAs. Figure 4.3 is a graph of the predicted BrCl2AA concentrations (in micromolar units), using Equation 4.4 and setting the slope equal to unity (y = x), against the measured BrCl2AA concentrations from the limited ICR database. The predicted values are seen to match the measured values very well, indicating that the model is relatively reliable for predicting BrCl2AA concentrations.

Figure 4.4 shows a similar plot for Br2ClAA concentrations. The predicted values were derived using Equation 4.5 and again setting the slope equal to unity. The predicted values do not match the observed values as well in this case; it appears that the model overpredicts Br2ClAA to some extent, and there is much more scatter among the points than in the case of BrCl2AA. This may result from the relatively low measured concentrations of Br2ClAA, which are closer to the limits of analytical detection than those of BrCl2AA.

A similar attempt was made to test the Br3AA model (Equation 4.6) against ICR data for Br3AA. However, too many of the Br3AA values were below analytical detection limits, so a valid assessment of the model could not be made. Nevertheless, the closeness of the match for the BrCl2AA model and the reasonable representation of the Br2ClAA data suggested that each of the missing HAA3 species could be modeled using Equations 4.4 to 4.6.
To demonstrate this, predicted HAA3 concentrations, obtained by summing the predicted BrCl2AA, Br2ClAA, and Br3AA values using Equations 4.4 to 4.6, are plotted against the corresponding observed HAA3 measurements from Aux 1 in Figure 4.5. The predictions match the measured HAA3 concentrations to a significant degree. To demonstrate the goodness of the fit, as represented by the y = x line of perfect agreement, a regression analysis was performed on the predicted and measured concentrations, and the slope of the regression line, correlation coefficient, SD, and confidence intervals were calculated. Although not shown on the plot, the slope was 1.08, the R^2 value was 0.74, the SD was 0.019, and the 95 percent confidence interval...
was between 1.0 and 1.1 for the regression line. The fact that the model gives predictions that are encompassed by the relatively tight confidence intervals of the calculated regression line indicates that the difference between the predicted and observed HAA3 concentrations shown in Figure 4.5 are not statistically significant. Accordingly, it is reasonable to state that the proposed model has value as a predictor of HAA3.

Figure 4.6 shows an especially good match between predicted and observed HAA9 concentrations. The predicted HAA9 concentration was determined by summing the observed

Figure 4.4 Comparison between predicted and observed Br₂Cl₄A concentrations for all waters and disinfection scenarios in first 12 months of ICR data (avg1, avg2, dse, sds, finish; N = 1,707)

Figure 4.5 Comparison between predicted and observed HAA3 concentrations for all waters and disinfection scenarios in first 12 months of ICR data (avg1, avg2, dse, sds, finish; N = 1,176)
HAA6 concentrations from the ICR database and the predicted HAA3 concentrations as determined by the theoretical model from Equations 4.4 to 4.6. Therefore, two-thirds of the nine HAA species are autocorrelated in this plot, thereby accounting for the very strong apparent correlation.

Comparison of Frequency Distributions and Application of the Model

Figure 4.7 is a frequency distribution plot for THM4 occurrence at average points in the distribution system, represented by the avg1, avg2, dse, sds, and finish sampling points for the first 12 months of ICR data. All source waters and all disinfection scenarios are included (N = 7,515). The cumulative plot shows that the median THM4 concentration (P50) is 29.7 µg/L, similar to the value reported by Krasner et al. (1989), and that 90 percent of the Aux 1 sampling sites had THM4 concentrations equal to or less than 73 µg/L (P90). About 93 percent of the points (see Table 4.1) fall below the Stage 1 D/DBP Rule MCL for THM4 (USEPA 1999a) of 80 µg/L (excluding the max stations; see below). However, if the MCL for THM4 is reduced to 40 µg/L (the placeholder for THM4 in the Stage 2 D/DBP Rule; USEPA 1999a), Figure 4.7 and Table 4.1 show that only about 64 percent of the waters would have a THM4 concentration less than 40 µg/L.

Figure 4.8 shows a parallel frequency distribution plot for HAA5 concentrations. The median HAA5 concentration was 17.9 µg/L, similar to the value reported by Krasner et al. (1989) and approximately 60 percent of the THM4 concentration, which is consistent with the results.
Figure 4.1 shows that 94 percent of HAA5 measurements fell at or below the Stage 1 MCL of 60 µg/L (USEPA 1999a) when the max samples were not included. The proposed Stage 2 D/DBP Rule has a placeholder MCL of 30 µg/L for HAA5. Figure 4.8 and Table 4.1 show that only 72 percent of the waters had HAA5 concentration below this value based on the first 12 months of ICR data.

Figure 4.7 Frequency distributions for observed THM4 concentrations for all waters and disinfection scenarios in first 12 months of ICR data (avg1, avg2, dse, sds, finish; N = 7,515)

Table 4.1
Comparisons of observed THM and observed and predicted HAA concentrations to Stage 1 and proposed Stage 2 MCLs

<table>
<thead>
<tr>
<th>DBPs</th>
<th>THM4</th>
<th>HAA5</th>
<th>Observed HAA9</th>
<th>Predicted HAA9</th>
<th>avg1, avg2, dse, sds, and finish</th>
<th>max</th>
</tr>
</thead>
<tbody>
<tr>
<td>D/DBP Rule MCLs (µg/L)</td>
<td>Stage 1</td>
<td>Stage 2 placeholder</td>
<td>Stage 1</td>
<td>Stage 2 placeholder</td>
<td>Stage 1</td>
<td>Stage 2 placeholder</td>
</tr>
<tr>
<td>THM4</td>
<td>80</td>
<td>40</td>
<td>29.7</td>
<td>73</td>
<td>7.2</td>
<td>35.8</td>
</tr>
<tr>
<td>HAA5</td>
<td>60</td>
<td>30</td>
<td>17.9</td>
<td>50.5</td>
<td>6.3</td>
<td>28.2</td>
</tr>
<tr>
<td>Observed HAA9</td>
<td>—</td>
<td>—</td>
<td>22.1</td>
<td>57.2</td>
<td>8.8</td>
<td>34.2</td>
</tr>
<tr>
<td>Predicted HAA9</td>
<td>—</td>
<td>—</td>
<td>31.1</td>
<td>70.1</td>
<td>15.7</td>
<td>51.8</td>
</tr>
</tbody>
</table>

Table 4.1 shows that the percentage of samples exceeding the Stage 1 MCL for HAA5 is 60 µg/L (USEPA 1999a), and the distribution shows that 94 percent of HAA5 measurements fell at or below that MCL when the max samples were not included. The proposed Stage 2 D/DBP Rule has a placeholder MCL of 30 µg/L for HAA5. Figure 4.8 and Table 4.1 show that only 72 percent of the waters had HAA5 concentration below this value based on the first 12 months of ICR data.
However, if all nine of the bromine- and chlorine-containing HAAs are included in the assessment of overall HAA occurrence, Figure 4.9 shows the corresponding frequency distribution for HAA9 based on the measured values of all nine HAA species.

Because all utilities were not required to analyze HAA9 as part of the ICR monitoring requirements, the database for HAA9 is much smaller (N = 1,549 for Figure 4.9 compared to N = 7,116 for Figure 4.8). Figure 4.9 shows that the median observed HAA9 concentration is 22.1 µg/L, approximately 23 percent higher than the median HAA5 concentration, and about 75 percent of the median THM4 concentration (compare to Figure 4.2).

To extend the database to make a similar comparison of HAA9 for all ICR database entries, HAA9 concentrations were developed for all the ICR entries using Equations 4.4 to 4.6, with the individual THM species concentrations and the concentrations of Cl$_3$AA as inputs to the model. Figure 4.10 is the resulting frequency distribution plot for HAA9 using the predicted HAA3 model to supplement the available HAA9 observations in the ICR database. Accordingly, for the N = 5,232 samples, the median HAA9 concentration is 31.1 µg/L, which is approximately equal to the median TTHM concentration. If the MCL for HAAs of 60 µg/L were to apply to all HAAs (HAA9 instead of HAA5), Figure 4.10 and Table 4.1 indicate that approximately 16 percent of the waters would exceed this value, compared to 6 percent that would exceed the MCL as it applies to HAA5 only (see Figure 4.8).
These findings suggest that total HAA occurrence in U.S. drinking waters is not well represented by considering only HAA5 and that the current MCL (which applies only to HAA5; USEPA 1999a) is not sufficiently protective of public health if HAAs are indeed a public health concern. Table 4.1 summarizes the median and the 90th percentile THM and HAA concentrations, the percentages of water samples exceeding the Stage 1 MCLs for THM4 or HAA5, or the equivalent if the MCL were to apply to HAA9, and the percentages of water samples that would exceed the proposed Stage 2 THM4 or HAA5 placeholders. As noted above, HAA9

Figure 4.9 Frequency distributions for observed HAA9 concentrations for all waters and disinfection scenarios in first 12 months of ICR data (avg1, avg2, dse, sds, finish; N = 1,549)

Figure 4.10 Frequency distributions for predicted HAA9 concentrations for all waters and disinfection scenarios in first 12 months of ICR data (avg1, avg2, dse, sds, finish; N = 5,232)
concentrations tend to be significantly higher than HAA5 concentrations, and HAA9 tends to be present in finished drinking water at concentrations similar to the THM4 concentrations. HAAs (as HAA5) are currently regulated under Stage 1 at MCLs that are 75 percent of those for THM4 (60 µg/L versus 80 µg/L, respectively; USEPA 1999a). The Stage 2 placeholder maintains this same percentage (30 µg/L versus 40 µg/L, respectively). As seen in Figures 4.7, 4.8, and 4.10, and summarized in Table 4.1, median HAA5 occurrence is only about 60 percent of THM4 concentrations, but the expected median overall HAA9 occurrence is approximately equal to the median THM4 concentration based on the theoretical model developed in this project. This suggests that the THM4 and total HAA concentrations are more similar than previously believed. Figure 4.11 is a frequency distribution plot, parallel to Figures 4.1 and 4.2, which was developed from the predicted HAA9 concentrations and shows HAA9/THM4 ratios for paired sample points. The distribution of the HAA9/THM4 ratios has a mode of about 1.1 and a median value of 0.94 µg/µg. The predictions from the model presented in this study indicate, therefore, that HAA9 occurrence is much greater than currently accounted for with respect to actual measurements and regulatory considerations.

This is illustrated further by Figures 4.12 through 4.14. Figure 4.12 is a side-by-side comparison of the frequency distributions of the HAA5/THM4 and HAA9/THM4 ratios for all locations examined. It is clear that the distribution shifts significantly to higher values when all HAA species are considered. Figure 4.13 shows a side-by-side comparison of the frequency distribution of HAA9 and THM4 concentrations, illustrating that the distribution of concentrations

![Figure 4.11 Frequency distributions of predicted HAA9/observed THM4 ratios for all waters and disinfection scenarios in first 12 months of ICR data (avg1, avg2, dse, sds, finish; N = 5,198)](image)
are quite similar. The mode in both cases is about 35 µg/L, and the distribution is skewed similarly toward higher concentrations. The cumulative frequency distribution in Figure 4.14 shows that the distribution of HAA concentrations approaches the distribution of THM4 concentrations when all HAA9 species are considered.

Because of growing concerns about DBP exposure in all parts of the distribution system, Figures 4.15 through 4.17 were developed to examine worst-case scenarios. These figures show the same types of frequency distributions for THM4, HAA5, and HAA9, respectively, applied to
the max ICR sampling stations. The results (summarized in Table 4.1) show a modest increase in
the median and 90th percentiles for max concentrations of THM4, but a smaller increase for
HAA5 and observed HAA9, as compared to the corresponding percentiles calculated based on
avg1, avg2, dse, sds, and finish values. There was essentially no change in the predicted HAA9
median and 90th percentile values. Accordingly, the relative relationship between HAA9 and
THM4 concentrations at the max location is approximately 77 µg/µg (for the median ratio) rather
than 1.05 µg/µg as was noted above for the other points in the distribution system.
Application of Model to Explore Factors Influencing Haloacetic Acid and Trihalomethane Distribution

Based on the results of the controlled laboratory investigations described in chapter 3, it was found that pH and the characteristics of the NOM, as reflected by the SUVA of the water, are significant factors that influence the relative dominance of HAAs and THMs in chlorinated water. Accordingly, the ICR database, with the predicted values of HAA9 based on the presentation and
discussion reported earlier in this chapter, was examined to see the extent to which specific factors influencing the distribution of HAA and THM concentrations could be identified. In the presentation that follows, all HAA and THM measurements are from the first 12 months of the ICR data collection. HAA5 and THM4 are measured quantities from the ICR database, and HAA9 is a predicted value, calculated from the measured HAA6 values and the predicted concentrations of BrCl₂AA, Br₂ClAA, and Br₃AA. For this analysis, only surface water treatment plants using free chlorine as primary and secondary disinfectants were examined, to avoid confounding factors introduced by different types of disinfection practices and to avoid the relatively low values encountered when dealing with groundwaters.

\[ pH \]

To examine the effects of pH on the HAA/THM ratio, the pH of the filtered water was used. It was assumed that the pH of the filtered water would capture the pH regime accompanying DBP formation within the treatment plant for utilities adding free chlorine to raw or settled water. Utilities were divided into two groups, those with filtered water pH values less than 7, and those with filtered water pH values greater than 8. These pH groupings were selected to emphasize any trends, to keep the number of samples in both groups relatively consistent, and to use integer pH values.

Figure 4.18 is a frequency distribution plot of the HAA5/THM4 ratio in filtered water from those facilities with filtered water pH values less than 7 (N = 80). Figure 4.19 is the corresponding plot for facilities with filtered water pH values greater than 8 (N = 123). For filtered water pH values less than 7, the median HAA5/THM4 ratio of the filtered water was 1.48 (see Figure 4.18). For pH values greater than 8, the distribution of HAA5 to THM4 tended to be lower, with a median ratio of 0.52 (see Figure 4.19). When all nine HAAs were considered, the HAA9/THM4 ratios for filtered water increased, with a median ratio of 1.72 for pH values less than 7 and 0.98 for pH values greater than 8 (see Figures 4.20 and 4.21, respectively). Figures 4.22 and 4.23 show the paired frequency distribution plots for the two different pH regimes for HAA5 and HAA9, respectively, and Figures 4.24 and 4.25 show the corresponding paired cumulative frequency distribution plots. For both sets of figures, it is evident that the distribution
shifts to higher HAA/THM4 ratios when chlorination is carried out at lower pH values, and when all nine HAAs are considered in place of HAA5.

Similar findings were observed for finished water. In this case, it was assumed that the relative distribution of THMs and HAAs in the finished water is still primarily influenced by the pH of coagulation, settling, and filtration, which is represented by the pH of the filtered water. In some facilities, the pH might be increased between filtration and the POE to the distribution system, but it is believed that most utilities using only free chlorine for disinfection would not

Figure 4.18 Frequency distribution of HAA5/THM4 ratio for surface waters disinfected with free chlorine; filtered pH < 7 (filtered, N = 80)

Figure 4.19 Frequency distribution of HAA5/THM4 ratio for surface waters disinfected with free chlorine; filtered pH > 8 (filtered, N = 123)
increase the pH until after the clearwell, thereby maximizing the effectiveness of chlorine for disinfection. Figures 4.26 and 4.27 show, respectively, for HAA5 and HAA9, that the distribution of HAA/THM ratios in finished water shifts to higher values for pH values less than 7 compared to pH values greater than 8. The cumulative frequency distribution plots in Figures 4.28 and 4.29 also reflect this shift; for HAA5, the median HAA/THM ratio is 0.58 at pH values greater than 8 compared to 0.98 for pH values less than 7. For HAA9, the median ratio for pH values greater than 8 is 0.74 compared to 1.20 for pH values less than 7.
Table 4.2 is a summary of the median HAA/THM4 ratios calculated for HAA5 and HAA9, for filtered, finished, average distribution system locations (avg1 and avg2), and maximum distribution system locations (max). Again, the data are grouped by filtered water pH values less than 7 and filtered water pH values greater than 8. Although we understand that filtered water pH values are not representative of the pH values in the distribution system (the latter are likely to be higher), it is still interesting to note that in all cases, the HAA9/THM4 ratios are significantly greater than the corresponding HAA5/THM4 ratios, and that the HAA9/THM4
ratios for pH values less than 7 still are greater than or approach 1.0 despite the fact that pH increases in the distribution system should favor formation of THMs over HAAs. The observation that the ratio decreases with increasing residence time in the distribution system could be attributable either to the faster rate of HAA formation in the treatment plant and the correspondingly slower rate of HAA formation in the distribution system, or to the expected increase in pH in the distribution system, which favors THM formation.

Figure 4.24 Cumulative percentage of HAA5/THM4 ratio for surface waters disinfected with free chlorine (filtered water)

Figure 4.25 Cumulative percentage of HAA9/THM4 ratio for surface water disinfected with free chlorine (filtered water)
To examine seasonal effects on the relative distribution of THMs and HAAs, a similar comparison of the HAA/THM ratio was made between DBP measurements for samples taken in the summer and winter quarter. The first summer quarter in the ICR database is noted as Quarter 1, corresponding to the period from July 1 to Sept. 30, 1997, while the winter quarter, designated as Quarter 3, corresponds to the period from Jan. 1 to Mar. 30, 1998. Canadian researchers (Williams,
LeBel, and Benoit 1996) found that HAA concentrations dominated significantly over THM concentrations during their winter sampling of 53 water systems. THMs, conversely, were dominant during their summer sampling period.

The ICR results are consistent with the Canadian observations, as illustrated in Figures 4.30 through 4.33. For the winter quarter (Quarter 3), the distribution of HAA/THM ratios shifts to higher values relative to the summer quarter (Quarter 1) for finished waters and for waters with average residence times in the distribution system, both for HAA9 and HAA5. Table 4.3 shows the median of the distributions. Again, it is apparent that the ratios decline between finished water

Figure 4.28 Cumulative percentage of HAA5/THM4 ratio for surface waters disinfected with free chlorine (finished water)

Figure 4.29 Cumulative percentage of HAA9/THM4 ratio for surface waters disinfected with free chlorine (finished water)
and water in the distribution systems, reflecting the faster rate of HAA formation in the treatment plant and the correspondingly slower rate of formation in the distribution system relative to that of the THMs.

**Temperature**

Temperature effects on the relative distribution of THMs and HAAs are shown in Figures 4.34 through 4.37. The temperature groupings were chosen to emphasize temperature effects and to keep the number of samples in each group relatively uniform. The figures show that the

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Table 4.2
Impact of pH of chlorination on median HAA/THM4 ratios for surface waters disinfected with free chlorine (pH values refer to pH of filtered water)

<table>
<thead>
<tr>
<th>Location</th>
<th>HAA5/THM4 (µg/µg)</th>
<th>HAA9/THM4 (µg/µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH &lt; 7</td>
<td>pH &gt; 8</td>
</tr>
<tr>
<td>Filtered water</td>
<td>1.48</td>
<td>0.52</td>
</tr>
<tr>
<td>Finished water</td>
<td>0.98</td>
<td>0.58</td>
</tr>
<tr>
<td>Average distribution system (DS)</td>
<td>0.85</td>
<td>0.52</td>
</tr>
<tr>
<td>Maximum DS</td>
<td>0.70</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Figure 4.30 Frequency distribution of HAA5/THM4 ratio for surface waters disinfected with free chlorine (finished water)

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distribution of HAA/THM ratios shifts toward higher values at the lower temperatures for finished water and for water at the average distribution system residence time when either HAA5 or HAA9 are considered. Again, this is consistent with the Canadian findings (Williams, LeBel, and Benoit 1996) and the findings noted above in which HAAs are favored over THMs in the winter quarter compared to the summer quarter. Table 4.4 shows the impact of temperature on the median HAA/THM4 ratio for the two sampling locations. As in the previous cases, the ratios are lower in the distribution system than in the finished water.

Figure 4.31 Frequency distribution of HAA9/THM4 ratio for surface waters disinfected with free chlorine (finished water)

Figure 4.32 Frequency distribution of HAA5/THM4 ratio for surface waters disinfected with free chlorine (avg1 and avg2 locations)
Because the addition of ammonia to chlorinated water is expected to stop the formation of both THMs and HAAs, the distribution of HAA/THM ratios for surface waters disinfected with free chlorine in the water treatment plant and chloramines in the distribution system was examined. Figures 4.38 through 4.41 demonstrate that the HAA/THM ratio in the distribution system is essentially the same as the ratio in the finished water, verifying that chloramination stops subsequent THM and HAA formation (or at least keeps the relative distribution the same) for this group of utilities.

**Chloramination**

Figure 4.33  Frequency distribution of HAA9/THM4 ratio for surface waters disinfected with free chlorine (avg1 and avg2 locations)

Table 4.3  
Impact of season on median HAA/THM4 ratios for surface waters disinfected with free chlorine

<table>
<thead>
<tr>
<th>Location</th>
<th>HAA5/THM4 (µg/µg)</th>
<th>HAA9/THM4 (µg/µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quarter 1 summer</td>
<td>Quarter 3 winter</td>
</tr>
<tr>
<td>Finished water</td>
<td>0.64</td>
<td>0.85</td>
</tr>
<tr>
<td>Average DS</td>
<td>0.51</td>
<td>0.76</td>
</tr>
</tbody>
</table>
SUMMARY AND CONCLUSIONS

In this study, HAA5 concentrations were found to be approximately 60 percent of the corresponding THM4 concentrations for the more than 5,000 samples examined from the first 12 months of the ICR Auxiliary 1 database. These findings are consistent with the results of the 35-utility study conducted by Krasner et al. (1989). However, HAA5 measurements do not account for
Although a complete set of concentrations of BrClAA is available in the ICR database, limited data are available for BrCl₂AA, Br₂ClAA, and Br₃AA. The results in this chapter show that inclusion of these other HAA species can contribute significantly to overall HAA occurrence, as has been suggested even for waters with relatively low bromide concentrations (Cowman and Singer 1996).

In the model presented in this chapter, it was proposed that the three trihalogenated HAA species that are missing, for the most part, in the ICR database (i.e., BrCl₂AA, Br₂ClAA, and
Table 4.4
Impact of temperature on median HAA/THM4 ratios for surface waters disinfected with free chlorine

<table>
<thead>
<tr>
<th>Location</th>
<th>HAA5/THM4 (µg/µg)</th>
<th>HAA9/THM4 (µg/µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature &lt;12°C</td>
<td>Temperature &gt;17°C</td>
</tr>
<tr>
<td>Finished water</td>
<td>0.86</td>
<td>0.65</td>
</tr>
<tr>
<td>Average DS</td>
<td>0.78</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Figure 4.38 Frequency distribution of HAA5/THM4 ratio for surface waters disinfected with free chlorine in the water treatment plant and chloramine in the distribution system

Figure 4.39 Frequency distribution of HAA9/THM4 ratio for surface waters disinfected with free chlorine in the water treatment plant and chloramine in the distribution system
Br$_3$AA) would be present in similar proportions to Cl$_3$AA, on a mole fraction basis, as CHBrCl$_2$, CHBr$_2$Cl, and CHBr$_3$, respectively, are present relative to CHCl$_3$ formation. Consequently, the model allows calculation of BrCl$_2$AA, Br$_2$ClAA, and Br$_3$AA concentrations (collectively HAA3) from knowledge of the concentrations of the individual THM species and Cl$_3$AA. The model was validated using the limited, but still significant, measured concentrations of HAA3 in the ICR database. For all types of source waters and all disinfection scenarios, the predicted HAA3 concentrations represented the concentrations actually measured as part of the ICR effort quite well.

Figure 4.40 Cumulative percentage of HAA5/THM4 ratio for surface waters disinfected with free chlorine in the water treatment plant and chloramine in the distribution system

![Figure 4.40](image1)

Figure 4.41 Cumulative percentage of HAA9/THM4 ratio for surface waters disinfected with free chlorine in the water treatment plant and chloramine in the distribution system

![Figure 4.41](image2)
Application of the model to the entire 12 months of ICR data showed that HAA9 concentrations were appreciably higher than HAA5 concentrations, and demonstrated that overall HAA concentrations (i.e., HAA9) in finished drinking water were approximately equal to overall THM (THM4) concentrations. Total HAA occurrence in U.S. drinking waters is not well represented by considering only HAA5 and the current MCL which applies only to HAA5 is not sufficiently protective of public health if HAAs are indeed a public health concern.

The frequency distribution analyses performed in this study were helpful in evaluating the status of finished drinking water with respect to current and future THM and HAA regulations. The findings, especially those involving HAA9, should be strongly considered in future regulatory activities.

Additionally, the results from analysis of the first 12 months of ICR data confirm the findings from the bench-scale controlled laboratory studies in chapter 3 which show that the ratio of total HAAs to total THMs increases with decreasing chlorination pH. The HAA to THM ratio was also found to increase with decreasing temperature, and HAA/THM ratios were found to be lowest in the winter than in the summer. Use of chloramines in the distribution system was found to maintain the same relative distribution of HAAs to THMs as in the finished water at the POE to the distribution system.
CHAPTER 5
IMPACT OF WATER QUALITY AND TREATMENT CHARACTERISTICS ON HALOACETIC ACID AND TRIHALOMETHANE CONCENTRATIONS IN SELECTED FULL-SCALE WATER TREATMENT SYSTEMS

INTRODUCTION

The objective of this phase of the project was to determine the relative distribution and speciation of THMs and HAAs in a variety of U.S. water treatment plants with differing raw water quality, treatment processes, and distribution system characteristics. To determine the influence of the treatment strategy on DBP formation, plants were selected that use free chlorine, free chlorine and chlorine dioxide, free chlorine and ozone, and free chlorine and chloramines as primary disinfectants, and free chlorine or chloramines as secondary disinfectants. An attempt was made to pair the facilities by selecting treatment plants that drew water from the same or similar sources but used different types of treatment schemes.

PROCEDURES

Table 5.1 describes each treatment plant briefly. Some of the plants were sampled on one occasion; others were sampled twice. Details on the points of disinfectant addition and dosages are given below.

To assess the influence of water quality on the formation and distribution of the HAAs and THMs, water was collected immediately before it reached the first point of chlorination and analyzed for TOC, DOC, UV$_{254}$, bromide, temperature, and pH. The SUVA was calculated as UV$_{254}$ $\times$ 100/DOC. Additionally, the water was fractionated using an XAD-8 resin column and the TOC and DOC of the hydrophilic fraction was measured. The TOC and DOC of the hydrophobic fraction were calculated as the difference between the organic carbon content of the influent water and the measured hydrophilic organic carbon content of the column effluent.

To determine the influence of the specific disinfection scenario, samples in the water treatment process train were taken after each point of disinfectant addition, at the POE to the...
distribution system, and at up to three locations in the distribution system. The samples were analyzed for free and total chlorine residual and pH at the time of sample collection, and after the disinfectant residual was quenched, the samples were analyzed for THMs and HAAs.

**Sampling Procedure**

Water utility personnel collected all the samples according to written instructions provided by UNC. The water collected before the first point of chlorination was stored in three 1-L amber glass bottles; no preservatives were added. This water was used for water quality characterization,
including the XAD-8 fractionation. All measurements were performed within 4 weeks of sample collection.

The samples for THM and HAA analysis within the treatment plant and in the distribution system were taken headspace-free in 40-mL glass vials (screw-top caps with TFE-lined septa). To stabilize the samples, a chlorine-quenching agent, ammonium sulfate (Mallinckrodt), was added to each THM and HAA sample vial. To prevent biodegradation of the HAAs, a biocide, sodium azide, was added to the HAA sample vials in accordance with the findings described in chapter 2. The concentration of sodium azide in each sample was 40 µg/L.

To ensure the quality of the analysis, each sample was taken in duplicate. Temperature, pH, and the free and total chlorine residual were measured and reported by the water utilities. The UNC laboratory used IC to analyze the bromide concentration.

To exclude the influence of any contamination during shipping, travel blanks were sent with the sample containers. These blanks consisted of 40-mL vials that contained the quenching agent and the biocide, filled headspace-free with DOFW. The water utilities sent the samples to UNC by overnight carrier in an ice chest. The samples were stored at 4°C on receipt. The extractions for the THMs and the HAAs took place within 2 weeks of sample collection.

**Laboratory Procedures**

Cleaning of glassware, preparation of reagents, and performance of the analytical procedures were the same as described in chapter 3.

**RESULTS AND DISCUSSION**

**Water Quality Characteristics**

Table 5.2 presents the water quality characteristics for each plant. SUVA ranged from a low of 1.1 L/mg-m for WSSC on Oct. 18, 1999, to a high of 3.5 L/mg-m for Palm Beach County’s Haverhill plant. Low SUVA values are often a result of coagulation and clarification before disinfectant addition. This can be seen for AVEK, Durham, and Raleigh, all of which chlorinate
Table 5.2
Characteristics of water sampled immediately before the first point of disinfectant addition

<table>
<thead>
<tr>
<th>Plant Location</th>
<th>Date of Sampling</th>
<th>Temp. (°C)</th>
<th>pH</th>
<th>TOC (mg/L)</th>
<th>Hydrophobic TOC (%)</th>
<th>DOC (mg/L)</th>
<th>Hydrophobic DOC (%)</th>
<th>UV$_{254}$ (cm$^{-1}$)</th>
<th>SUVA (L/mg-m)</th>
<th>Br$^-$ (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belvedere, Fla.</td>
<td>05/24/99</td>
<td>25.9</td>
<td>7.1</td>
<td>8.9</td>
<td>78.7</td>
<td>9.3</td>
<td>80.6</td>
<td>0.298</td>
<td>3.2</td>
<td>173</td>
</tr>
<tr>
<td>Haverhill, Fla.</td>
<td>05/24/99</td>
<td>26.4</td>
<td>7.1</td>
<td>10.0</td>
<td>82.0</td>
<td>10.0</td>
<td>83.0</td>
<td>0.347</td>
<td>3.5</td>
<td>152</td>
</tr>
<tr>
<td>FCWA, Va.</td>
<td>06/14/99</td>
<td>26</td>
<td>8.1</td>
<td>2.3</td>
<td>48.7</td>
<td>2.6</td>
<td>53.8</td>
<td>0.088</td>
<td>3.4</td>
<td>65.0</td>
</tr>
<tr>
<td></td>
<td>10/18/99</td>
<td>14.3</td>
<td>7.7</td>
<td>2.9</td>
<td>51.7</td>
<td>3.4</td>
<td>52.9</td>
<td>0.090</td>
<td>3.1</td>
<td>&lt;20</td>
</tr>
<tr>
<td>WSSC, Md.</td>
<td>06/14/99</td>
<td>26</td>
<td>7.8</td>
<td>1.6</td>
<td>50.0</td>
<td>1.8</td>
<td>50.0</td>
<td>0.044</td>
<td>2.4</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>10/18/99</td>
<td>17</td>
<td>7.6</td>
<td>2.2</td>
<td>36.4</td>
<td>2.7</td>
<td>44.4</td>
<td>0.031</td>
<td>1.1</td>
<td>&lt;20</td>
</tr>
<tr>
<td>AVEK, Calif.*</td>
<td>07/06/99</td>
<td>23</td>
<td>7.0</td>
<td>1.9</td>
<td>57.9</td>
<td>1.8</td>
<td>50.0</td>
<td>0.035</td>
<td>1.9*</td>
<td>173</td>
</tr>
<tr>
<td></td>
<td>11/15/99</td>
<td>16</td>
<td>7.0</td>
<td>1.9</td>
<td>52.8</td>
<td>2.1</td>
<td>57.1</td>
<td>0.035</td>
<td>1.7*</td>
<td>182</td>
</tr>
<tr>
<td>MWD, Calif.</td>
<td>07/06/99</td>
<td>22</td>
<td>7.9</td>
<td>2.0</td>
<td>52.6</td>
<td>1.9</td>
<td>52.6</td>
<td>0.063</td>
<td>3.3</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>11/15/99</td>
<td>20.1</td>
<td>7.9</td>
<td>3.3</td>
<td>63.6</td>
<td>3.0</td>
<td>73.3</td>
<td>0.062</td>
<td>2.1</td>
<td>105</td>
</tr>
<tr>
<td>Durham, N.C.*</td>
<td>09/07/99</td>
<td>25</td>
<td>6.9</td>
<td>3.4</td>
<td>52.9</td>
<td>2.6</td>
<td>42.3</td>
<td>0.046</td>
<td>2.3*</td>
<td>&lt;20</td>
</tr>
<tr>
<td></td>
<td>12/06/99</td>
<td>NA</td>
<td>3.1</td>
<td>74.2</td>
<td>2.9</td>
<td>72.4</td>
<td>0.066</td>
<td>2.3*</td>
<td>&lt;20</td>
<td></td>
</tr>
<tr>
<td>Raleigh, N.C.*</td>
<td>09/07/99</td>
<td>25.2</td>
<td>6.9</td>
<td>2.3</td>
<td>78.4</td>
<td>2.2</td>
<td>40.9</td>
<td>0.028</td>
<td>1.3*</td>
<td>40.4</td>
</tr>
<tr>
<td></td>
<td>12/06/99</td>
<td>NA</td>
<td>3.5</td>
<td>NA</td>
<td>3.3</td>
<td>NA</td>
<td>0.036</td>
<td>1.1*</td>
<td>&lt;20</td>
<td></td>
</tr>
<tr>
<td>GCWA, Texas</td>
<td>09/27/99</td>
<td>25.9</td>
<td>7.7</td>
<td>4.2</td>
<td>50.0</td>
<td>3.8</td>
<td>50.0</td>
<td>0.052</td>
<td>1.4</td>
<td>295</td>
</tr>
<tr>
<td>Houston, Texas†</td>
<td>09/27/99</td>
<td>27.8</td>
<td>NA</td>
<td>2.7</td>
<td>45.0</td>
<td>2.5</td>
<td>40.0</td>
<td>0.073</td>
<td>2.9</td>
<td>113</td>
</tr>
</tbody>
</table>

NA: not analyzed.

* Coagulated, settled water; not chlorinated.

† Coagulated, settled water after raw water chlorination.
after coagulation and settling. The other low SUVA values are a result of the relatively low humic (hydrophobic organic carbon) content of these waters. SUVA values can also be lowered appreciably by the application of oxidants and disinfectants, but in this study, all waters were collected before being subjected to oxidation or disinfection.

Most of the utilities drew water with a relatively low hydrophobic carbon content of around 50 percent, except for Palm Beach County and the Raleigh and Durham December samples. In those cases, the water had a high percentage of hydrophobic organic carbon.

The waters had a range of bromide concentrations, from a low of less than 20 µg/L to a high of 300 µg/L (GCWA).

**Plant-Scale Results**

*Palm Beach County Belvedere Plant (System #8) and Haverhill Plant (System #2)*

These two plants both use groundwater with a relatively high TOC concentration (around 10 mg/L; see Table 5.2). Approximately 80 percent of the organic carbon was hydrophobic in nature. Additionally, the bromide concentration was relatively high in these waters as well. On the day of sample collection, the bromide concentration was 152 µg/L for Haverhill and 173 µg/L for Belvedere (Figure 5.1). In addition, the raw water for both plants had a high hardness, a high ammonia content, and high sulfide levels.

Both treatment plant trains consisted of precipitative softening to reduce the hardness of the water, followed by filtration, and both systems used chlorine as a preoxidant and disinfectant. Belvedere chlorinated before softening and Haverhill after softening. In contrast to Belvedere, Haverhill added ammonia to the raw water to produce chloramines immediately upon the addition of chlorine. Both plants used chloramines as a postdisinfectant.

These plants were the only ones among the 10 water utilities investigated that used ozone; in both plants, ozone was used as an oxidant to remove color. The major difference between the two plants was the point of ozone addition and the ozone dosage. Belvedere added 3.2 mg/L of ozone before filtration and Haverhill added 8.7 mg/L of ozone after filtration.
Belvedere plant (System #8). Table 5.3 presents a summary of the Belvedere results. The following observations can be made. The sample after the first point of chlorine addition (see lime-softened water) had a very low chlorine residual and low levels of THMs and HAAs despite the fact that a high chlorine dosage of around 10 mg/L of free chlorine was applied to the raw water. The reason for this, according to water utility personnel, is that the raw water has a high level of ammonia (about 1.1 mg/L) and appreciable sulfide, both of which exert a significant chlorine demand.

The ozone application before filtration did not influence the DBP concentrations noticeably. After the application of additional chlorine and ammonia before filtration, the DBP concentrations in the filtered water increased, with HAAs increasing to a greater extent than THMs, despite the relatively high pH of the water (about pH 9). After that, the DBP concentrations remained relatively stable. Because a combined residual was present, essentially no additional THM or HAA formation took place in the distribution system.

In summary, despite the addition of 18 mg/L chlorine to this high-TOC water, only about 20 µg/L of THMs and 30–35 µg/L of HAAs were produced. This is attributed to the conversion of free chlorine to combined chlorine and the short time with which the water was in contact with free chlorine.

Haverhill plant (System #2). Table 5.4 summarizes the Haverhill results. At the first sampling point (clarifier effluent), a high combined chlorine residual of 4.1 mg/L was measured.
### Table 5.3
Summary of DBP results for the Belvedere plant (System #8) utility, May 24, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime-softened water after applying 10.3 mg/L Cl₂ to raw water</td>
<td>9.7</td>
<td>ND</td>
<td>0.6</td>
<td>9.8</td>
<td>8.3</td>
</tr>
<tr>
<td>Filter influent, after adding 3.2 mg/L O₃ (before second chlorine addition)</td>
<td>9.4</td>
<td>0.1</td>
<td>0.6</td>
<td>9.7</td>
<td>12.6</td>
</tr>
<tr>
<td>Filtered water, after adding 7.7 mg/L Cl₂ and 0.8 mg/L NH₃ before filtration</td>
<td>8.9</td>
<td>0.6</td>
<td>5.0</td>
<td>15.4</td>
<td>32.5</td>
</tr>
<tr>
<td>Finished water at POE to distribution system</td>
<td>8.9</td>
<td>0.6</td>
<td>4.7</td>
<td>18.6</td>
<td>34.3</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>9.1</td>
<td>NA</td>
<td>3.7</td>
<td>15.4</td>
<td>28.8</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>8.6</td>
<td>NA</td>
<td>2.6</td>
<td>19.2</td>
<td>28.1</td>
</tr>
</tbody>
</table>

ND: not detected.
NA: not analyzed.

### Table 5.4
Summary of DBP results for the Haverhill plant (System #2) utility, May 24, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent after applying 1.1 mg/L NH₃ to raw water and 10.3 mg/L Cl₂ to lime-softened water</td>
<td>9.8</td>
<td>0.3</td>
<td>4.1</td>
<td>26.3</td>
<td>32.2</td>
</tr>
<tr>
<td>Filtered water before O₃ addition</td>
<td>9.7</td>
<td>0.5</td>
<td>3.8</td>
<td>32.9</td>
<td>33.8</td>
</tr>
<tr>
<td>Filtered water after adding 8.7 mg/L O₃ to filter effluent</td>
<td>9.0</td>
<td>0.4</td>
<td>4.5</td>
<td>30.7</td>
<td>42.1</td>
</tr>
<tr>
<td>Finished water at POE after adding 4.0 mg/L Cl₂</td>
<td>8.9</td>
<td>0.4</td>
<td>4.2</td>
<td>38.7</td>
<td>50.2</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>8.7</td>
<td>NA</td>
<td>2.8*</td>
<td>24.3*</td>
<td>30.7*</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>8.8</td>
<td>NA</td>
<td>3.3</td>
<td>37.7</td>
<td>40.2</td>
</tr>
</tbody>
</table>

NA: not analyzed.

* These values are not consistent with the others; this could be because of sampling problems or because the water at this location was blended with water from another plant.
which resulted from adding ammonia to the raw water and applying free chlorine after softening. Most of the THMs and HAAs were formed at this location, probably as a result of fast reactions of NOM with free chlorine before the free chlorine reacted with ammonia to produce chloramines (i.e., because of poor mixing). As in the case of the Belvedere plant, ozonation after filtration did not change the DBP concentrations or the chlorine residual. With the addition of more chlorine, the excess free ammonia converted it to chloramines and only a small amount of additional DBPs was formed. After this, no more THMs or HAAs were formed in the distribution system because of the presence of the combined residual.

In summary, 35–40 µg/L of THMs and 40–50 µg/L of HAAs were formed from the application of about 14 mg/L of chlorine to this high-TOC water.

A comparison between the results for both water plants shows that despite similar water quality characteristics, the Haverhill plant produced nearly twice as much THMs and more HAAs at the POE to the distribution system than the Belvedere plant (see Tables 5.3 and 5.4). Most of the DBPs for Haverhill were formed during the first chlorination; most of the DBPs for Belvedere were formed during the second chlorination. This is most likely due, in part, to the fact that Haverhill adds chlorine to lime-softened water at high pH (9.8), while Belvedere adds the chlorine to ambient raw water at pH 7.1 (before softening). It is well known that THM formation is accelerated at elevated pH values. Although the second addition of chlorine at Belvedere is at a high pH (8.9), it occurs after ozonation, which probably oxidizes a portion of the DBP precursors to make them less reactive with chlorine. Hence the point of chlorine addition and the pH at which it is applied plays a very important role in the extent of DBP production. In addition, when chloramines are used, the relative rates of reactions between chlorine with NOM and ammonia determine the extent of DBP production.

In terms of the distribution and relative dominance of the different DBPs, the Belvedere and Haverhill plants showed the same pattern. As expected, based on the findings in chapter 3 and those of Reckhow, Singer, and Malcolm (1990) and Croué et al. (1999), more HAAs than THMs were formed as a result of the high hydrophobic character of the organic carbon. Among the HAAs, the concentrations of the dihalogenated acids were larger than those of the trihalogenated species (see Figure 5.1). Dichloroacetic acids constituted 44 to 51 percent of the total HAA concentration. The dominance of the dihalogenated species is most likely a result of the high pH at which chlorination took place. Reckhow and Singer (1985) suggested that the THMs and the
trihalogenated acetic acid species are formed through similar chemical pathways and have the same precursors. Because THM formation is catalyzed by hydroxide, increasing the pH of chlorination above 8 results in a decrease in the trihalogenated acid species and an increase in the THM concentrations. Dihalogenated acetic acid formation is relatively insensitive to pH (Reckhow and Singer 1985; Singer, Shi, and Weinberg 1998).

The distribution of the THMs and HAAs showed that, despite the high bromide level in the raw water, the principal species formed were the chlorinated DBPs (see Figure 5.1). For both waters, the chloroform concentration was around 85 to 90 percent of the total THM concentration. An explanation for this could be that despite the high bromide concentration, the Br/TOC ratio is relatively low because of the correspondingly high TOC concentration in this water. Additionally, it could be a result of the reaction of bromine with NH3 rather than with NOM. The HOCl added oxidizes Br− to HOBr, but NH3 in the water can tie up the HOBr as NH2Br and NHBr2, making it less available to react with NOM. For this reason, NOM reacts primarily with HOCl to produce predominantly chlorinated DBPs. Cowman and Singer (1996) observed that bromine incorporation into HAAs was less during chloramination than during chlorination.

**Fairfax County Water Authority and Washington Suburban Sanitary Commission**

Both water utilities draw their water from the Potomac River within a short distance of each other. The SUVA values ranged from 1.1 L/mg-m to 2.3 L/mg-m and the bromide concentration ranged from below the detection limit (20 µg/L) to 65 µg/L. The hydrophobic fraction of the organic carbon was around 50 percent (see Table 5.2).

The water utilities used a treatment process with coagulation and sedimentation followed by filtration. For the sampling on June 14, 1999, both water utilities added free chlorine to the raw water and again after it was filtrated. FCWA, however, converted the free chlorine to monochloramine just before the POE to the distribution system to carry a combined chlorine residual in the distribution system. In contrast to June, both treatment plants skipped prechlorination of the raw water in October.

**Fairfax County Water Authority Corbalis plant.** In June (see Table 5.5), 2.8 mg/L chlorine was applied to raw water before coagulation, and a chlorine residual of only 0.2 mg/L was measured in the clarifier effluent. Most of the THMs and HAAs were formed as a result of this
Table 5.6 shows the results for the second sampling. In comparison to the first sampling, no free chlorine was added to the raw water. As a result, no chlorine residual was detected and nearly no DBPs were found after coagulation and sedimentation. The low DBP levels observed could have been a result of the return of filter backwash water. The first chlorine addition of 3.8 mg/L to the filter effluent led to the formation of most of the DBPs observed for the whole treatment process. The last application of 1.8 mg/L chlorine to the filter clearwell effluent increased the residual to 4.3 mg/L free chlorine and resulted in a small increase in the THM and HAA concentrations. The addition of 1.1 mg/L ammonia produced a combined residual, and the formation of additional DBPs in the distribution system was essentially stopped.
In comparing the levels of DBPs produced on the two sampling dates, it is clear that the THM and HAA concentrations are much lower on the second date. This could be a result of the lower temperature in October compared to June (see Table 5.2) or the fact that the chlorine was applied after coagulation, sedimentation, and filtration, which removed the more reactive precursors. The THM concentrations were greater than the HAA concentrations on both sampling dates; the relative distribution of both groups of DBPs was not influenced by the point of chlorine addition.

*Washington Suburban Sanitary Commission Potomac plant.* For the first day of sampling, the chlorine dose to the raw water was very low and only small amounts of DBPs were detected in the clarifier effluent (see Table 5.7). The main purpose for this chlorination, according to plant personnel, was to control algae growth in the flocculation and sedimentation basins. The addition of 4.2 mg/L chlorine after filtration produced most of the DBPs. DBP formation continued through the storage tank and into the distribution system as a result of the continuing presence of a free chlorine residual.

In comparison to the FCWA results (see Table 5.5) for the same day, the ultimate formation patterns of THMs and HAAs were similar. At FCWA, most of the DBPs were produced as a result of chlorine addition to the raw water, with no additional formation in the distribution system as a result of the presence of a combined chlorine residual. At WSSC, DBPs formed both

Table 5.6
Summary of DBP results for the FCWA Corbalis plant, Oct. 18, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM₄ (µg/L)</th>
<th>HAA₉ (µg/L)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent</td>
<td>7.6</td>
<td>ND</td>
<td>ND</td>
<td>&lt;1.0</td>
<td>8.8</td>
</tr>
<tr>
<td>Filtered water after adding 3.8 mg/L Cl₂ to filter effluent</td>
<td>7.2</td>
<td>3.1</td>
<td>3.2</td>
<td>33.8</td>
<td>21.8</td>
</tr>
<tr>
<td>Filtered water after adding 1.8 mg/L Cl₂ to filter clearwell effluent</td>
<td>7.7</td>
<td>4.3</td>
<td>4.4</td>
<td>43.1</td>
<td>29.4</td>
</tr>
<tr>
<td>Finished water at POE after adding 1.1 mg/L NH₃</td>
<td>7.7</td>
<td>0.3</td>
<td>4.3</td>
<td>42.8</td>
<td>29.0</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>7.7</td>
<td>0.2</td>
<td>2.7</td>
<td>42.9</td>
<td>29.9</td>
</tr>
<tr>
<td>Remote point in the distribution system</td>
<td>7.4</td>
<td>0.3</td>
<td>2.9</td>
<td>49.2</td>
<td>35.9</td>
</tr>
</tbody>
</table>

ND: not detected.

* The HAA values shown here are based on a calibration curve developed from the first sampling because of problems experienced with the standards.
in the filtered water and in the distribution system. No difference is apparent in the relative distribution of the THMs and HAAs for the two plants sampled on this same date.

In the October sampling (see Table 5.8), WSSC did not use any chlorine as a preoxidant before coagulation. As a result, no chlorine residual was detected after sedimentation and the DBP concentrations were negligible. DBPs formed after the addition of 4.7 mg/L chlorine following filtration. As in June, the free chlorine residual was carried into the distribution system and formation of DBPs continued through the treatment plant and in the distribution system.

In terms of the distribution of THMs and HAAs, both water utilities (FCWA and WSSC) show a similar pattern. Tables 5.5 through 5.8 show that more THMs were produced than HAAs. For FCWA, the shift in the point of chlorine addition on the two dates affected THM formation more than it did HAA formation. THM formation was reduced by nearly 70 percent for the second sampling date when chlorine was added after coagulation; the HAA concentrations were about the same. In accordance with the relatively low bromide levels, chloroform concentrations constituted 60 to 80 percent of the total THM concentrations. As a result of the decrease in the bromide concentration for the second day of sampling (see Table 5.2), higher percentages of chloroform were observed. For the HAAs, dichloroacetic and trichloroacetic acids were the dominant species. In June, more trichloroacetic acid was produced, and in October, more

---

Table 5.7
Summary of DBP results for the WSSC Potomac plant, June 14, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent after applying 0.5 mg/L Cl₂ to raw water</td>
<td>7.5</td>
<td>0.01</td>
<td>0.2</td>
<td>11.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Influent to storage tank after adding 4.2 mg/L Cl₂ to filter effluent</td>
<td>NA</td>
<td>NA</td>
<td>3.9</td>
<td>33.3</td>
<td>18.3</td>
</tr>
<tr>
<td>Finished water after storage before pumping</td>
<td>7.5</td>
<td>NA</td>
<td>3.9</td>
<td>66.6</td>
<td>42.3</td>
</tr>
<tr>
<td>Finished water at POE after mixing with water from West plant</td>
<td>7.7</td>
<td>3.6</td>
<td>3.9</td>
<td>59.0*</td>
<td>40.4</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>7.8</td>
<td>1.3</td>
<td>1.4</td>
<td>111.0</td>
<td>59.8</td>
</tr>
<tr>
<td>Remote point in the distribution system</td>
<td>7.6</td>
<td>1.9</td>
<td>2.0</td>
<td>143.0</td>
<td>66.3</td>
</tr>
</tbody>
</table>

NA: not analyzed.
* Values may have been influenced by blending of the finished water from the two plants (East and West).

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dichloroacetic acid was produced for FCWA. For WSSC, the reverse was true. No explanation is readily available for these observations.

Antelope Valley East Kern Water District and Metropolitan Water District of Southern California

The water for these paired systems is drawn from an aqueduct (SPW) that is fed by water from the San Francisco Bay delta region in northern California. AVEK takes water from about the middle of the pipeline and MWD gets water near the end of the aqueduct in Los Angeles. The water has a relatively low TOC concentration, and around 50 percent of the TOC is hydrophobic carbon. In addition, a relatively high bromide concentration was present on the dates of sampling (see Table 5.2).

AVEK chlorinates after coagulation and clarification, but MWD chlorinates raw water. Both treatment plants chlorinate after filtration. Free chlorine is used in the AVEK distribution system; MWD uses combined chlorine as a secondary disinfectant.

Antelope Valley East Kern Water District. Table 5.9 presents the results for the AVEK sampling in July. At the filter effluent sampling point, following the addition of chlorine after
clarification, more than half of the ultimate THMs and HAAs were formed. The DBP concentrations increased with the second chlorine addition in the plant and throughout the distribution system.

Table 5.10 shows the results for the sampling in November. The same pattern as observed in July is apparent. Significant levels of DBPs were formed as a result of adding 1.8 mg/L chlorine after sedimentation. The postdisinfection step resulted in additional THM and HAA production. The free chlorine residual was carried into the distribution system and decreased from 1.1 mg/L at the POE to 0.7 mg/L for the remote point, leading to continuing formation of THMs and HAAs. It should be noted that, for both sampling dates, THM and HAA formation are relatively similar following the addition of chlorine to the clarified water, but THM formation continues thereafter to a much greater degree. This is especially true for the remote station in the distribution system and is consistent with the analysis of ICR data presented in chapter 4.

Metropolitan Water District of Southern California. Table 5.11 shows that a free chlorine residual of 0.5 mg/L was measured in the clarifier effluent after the addition of 2.0 mg/L chlorine to the raw water. Nearly 85 percent of the DBPs were formed as a result of this first chlorine addition. Thereafter, little additional formation of DBPs was observed in the plant because of the addition of ammonia after filtration to convert the free chlorine to combined chlorine. Despite the lack of a free chlorine residual, THM and HAA levels appeared to increase at the second midpoint and at the remote location in the distribution system. Perhaps these sample locations were influenced by water from another of MWD’s treatment plants.
### Table 5.10
Summary of DBP results for AVEK, Nov. 15, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂</th>
<th>Total Cl₂</th>
<th>THM₄</th>
<th>HAA₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent after adding 1.8 mg/L Cl₂</td>
<td>7.0</td>
<td>0.9</td>
<td>1.3</td>
<td>22.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Filter effluent after adding 1.3 mg/L Cl₂</td>
<td>7.0</td>
<td>1.9</td>
<td>2.1</td>
<td>48.0</td>
<td>30.8</td>
</tr>
<tr>
<td>Finished water at POE</td>
<td>7.1</td>
<td>1.4</td>
<td>1.6</td>
<td>59.8</td>
<td>38.4</td>
</tr>
<tr>
<td>Midpoint location in the distribution system, HRT = 12.9 hours</td>
<td>7.1</td>
<td>1.1</td>
<td>1.3</td>
<td>65.5</td>
<td>41.0</td>
</tr>
<tr>
<td>Midpoint location in the distribution system, HRT = 12.2 hours</td>
<td>7.2</td>
<td>1.2</td>
<td>1.3</td>
<td>63.0</td>
<td>38.9</td>
</tr>
<tr>
<td>Remote point in the distribution system, HRT = 61.9 hours</td>
<td>7.2</td>
<td>0.7</td>
<td>0.8</td>
<td>94.7</td>
<td>40.8</td>
</tr>
</tbody>
</table>

HRT: hydraulic retention time (estimated).

### Table 5.11
Summary of DBP results for MWD, July 6, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂</th>
<th>Total Cl₂</th>
<th>THM₄</th>
<th>HAA₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent after adding 2.0 mg/L Cl₂ before coagulation</td>
<td>7.7</td>
<td>0.5</td>
<td>0.5</td>
<td>48.5</td>
<td>34.6</td>
</tr>
<tr>
<td>Filter effluent after adding 1.7 mg/L Cl₂ before filtration and 0.6 mg/L Cl₂ and 0.6 mg/L NH₃ after filtration</td>
<td>8.5</td>
<td>ND</td>
<td>1.9</td>
<td>54.1</td>
<td>39.0</td>
</tr>
<tr>
<td>Finished water at the POE after adding 0.4 mg/L Cl₂</td>
<td>8.3</td>
<td>ND</td>
<td>2.6</td>
<td>56.6</td>
<td>41.1</td>
</tr>
<tr>
<td>Midpoint location in the distribution system, HRT = 3.8 hours</td>
<td>8.2</td>
<td>ND</td>
<td>2.5</td>
<td>56.2</td>
<td>41.1</td>
</tr>
<tr>
<td>Midpoint location in the distribution system, HRT = 16.5 hours</td>
<td>8.1</td>
<td>ND</td>
<td>2.4</td>
<td>64.5</td>
<td>62.4</td>
</tr>
<tr>
<td>Remote point in the distribution system, HRT = 27.4 hours</td>
<td>8.2</td>
<td>ND</td>
<td>2.3</td>
<td>67.0</td>
<td>48.0</td>
</tr>
</tbody>
</table>

HRT: hydraulic retention time (estimated).
ND: not detected.
The results for the sampling in November, shown in Table 5.12, reflect the same pattern as the results from July. Chlorination of the raw water produced most of the DBPs. After applying additional chlorine before filtration and chlorine and ammonia after filtration, the DBP concentrations increased and remained relatively uniform thereafter.

Although the overall THM and HAA levels are similar for AVEK and MWD, distinct differences can be seen in their patterns of formation. For MWD, THM formation dominates over HAA formation during raw water chlorination. Because most of the DBPs are formed at this point, THMs dominate over HAAs at all sample locations. This most likely results from the alkaline pH of chlorination at MWD (pH 7.7–7.9). At AVEK, the initial levels of THMs and HAAs are more similar because of the slightly acidic pH of chlorination (6.8–7.0) in the coagulated water, which tends to favor HAA formation. The continuing formation of THMs over HAAs in AVEK water is most likely a result of the relatively low SUVA (1.7–1.9) of the coagulated AVEK water.

Additionally, the distribution of the individual THM and HAA species is quite different in the two waters, both of which have relatively high bromide concentrations. At AVEK, because of the lower TOC concentration after coagulation, the Br/TOC ratio at the point of chlorination is

**Table 5.12**

Summary of DBP results for MWD, Nov. 15, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent after applying 1.9 mg/L Cl₂ before coagulation</td>
<td>7.9</td>
<td>0.6</td>
<td>0.6</td>
<td>57.0</td>
<td>26.9</td>
</tr>
<tr>
<td>Filter effluent after adding 1.8 mg/L Cl₂ before filtration and 2.7 mg/L Cl₂ and 0.5 mg/L NH₃ after filtration</td>
<td>7.6</td>
<td>ND</td>
<td>1.8</td>
<td>67.9</td>
<td>39.8</td>
</tr>
<tr>
<td>Finished water at the POE after adding 0.4 mg/L Cl₂</td>
<td>8.2</td>
<td>ND</td>
<td>2.5</td>
<td>69.7</td>
<td>39.4</td>
</tr>
<tr>
<td>Midpoint location in the distribution system, HRT = 4.8 hours</td>
<td>8.2</td>
<td>ND</td>
<td>2.3</td>
<td>72.1</td>
<td>39.8</td>
</tr>
<tr>
<td>Midpoint location in the distribution system, HRT = 18.1 hours</td>
<td>8.3</td>
<td>ND</td>
<td>2.3</td>
<td>82.4</td>
<td>47.5</td>
</tr>
<tr>
<td>Remote point in the distribution system, HRT = 27.1 hours</td>
<td>8.1</td>
<td>ND</td>
<td>2.1</td>
<td>77.3</td>
<td>42.5</td>
</tr>
</tbody>
</table>

HRT: hydraulic retention time (estimated).
ND: not detected.
higher, which favors formation of the brominated DBP species (see Figures 5.2 and 5.3). For MWD, where chlorine is added to the raw water with a higher TOC concentration and a lower Br/TOC ratio, formation of the chlorinated DBP species is dominant.

Durham Brown Plant and Raleigh Johnson Plant

Both Raleigh and Durham draw their water from surface impoundments in the central Piedmont region of North Carolina within 30 miles of each other. Although these paired systems have different water sources, they have similar organic carbon and SUVA values and relatively low bromide concentrations (see Table 5.2.)

The treatment trains at both plants include chlorination after coagulation and settling. Raleigh also chlorinated after filtration. Durham used a free chlorine residual in the distribution system whereas Raleigh converted the free chlorine to combined chlorine before the POE to the distribution system.

Because of contamination problems with the drying agent, magnesium sulfate, in the HAA extraction procedure, the HAA samples for September were stored for more than 5 weeks instead of the recommended period of 2 weeks. Accordingly, much lower concentrations of HAAs were measured than expected and the results are highly questionable.

Durham Brown plant. In September, the first sample taken was after coagulation and settling but before chlorination; consequently, nearly no DBPs were detected at the first sample point (see Table 5.13). DBP formation took place during and after filtration, as shown by the data for the filter effluent. Because of the use of free chlorine, DBP formation continued in the treatment plant and in the distribution system. The chlorine residual decreased from 3.0 mg/L at the POE to the distribution system to 1.7 mg/L for the first location in the distribution system; the THMs grew from 86 µg/L at the POE to 131 µg/L for the remote location. As noted above, the HAA concentrations shown are questionable because the storage time after collection exceeded recommended analytical requirements. Because of this, the HAA results for September will not be discussed in this report.

In December (see Table 5.14) the first sample was taken after coagulation and sedimentation and shortly after the addition of 5.6 mg/L chlorine. Most of the THMs and HAAs
Figure 5.2 HAA distribution at the POE for AVEK and MWD, Nov. 15, 1999

Figure 5.3 THM distribution at the POE for AVEK and MWD, Nov. 15, 1999
were formed during and after filtration. In the distribution system, the free chlorine residual decreased from 2.0 mg/L at the POE to the distribution system to 0.9 mg/L for the remote station, resulting in additional formation of THMs and HAAs. The THM concentration went from 54.9 µg/L to 84.6 µg/L in the distribution system and the HAA level from 80.7 µg/L to 104 µg/L.

In December, the only sampling date for which there were valid HAA data, Table 5.14 shows that HAA formation was dominant over THM formation. This is most likely a result of the relatively low pH (5.9–6.2) of chlorination, conditions that tend to favor HAA formation (as shown in chapters 3 and 4), and to the relatively high percentage of hydrophobic carbon, which also favors HAA formation (Reckhow, Singer, and Malcolm 1990; Croué et al. 1999).
**Raleigh Johnson Plant.** Table 5.15 presents the results for the Raleigh sampling in September. The formation of THMs and HAAs started with the addition of 2.0 mg/L chlorine before filtration. For the filter effluent, a free chlorine residual of 1.1 mg/L was measured. Up to that point, 12.0 µg/L of THMs were formed. The chlorine residual and the DBP concentrations were increased substantially by the second chlorine addition of 5.1 mg/L after filtration. In the clearwell effluent, a residual of 5.5 mg/L free chlorine was detected. With the application of 1.1 mg/L ammonia at the POE to the distribution system, the free chlorine residual was converted to a combined residual of 4.5 mg/L, which inhibited subsequent THM formation in the distribution system. As noted above, the HAA values shown are unreliable.

Table 5.16 gives the results for December. The addition of a total chlorine dosage of 5.7 mg/L before and after filtration led to a free chlorine residual of 3.6 mg/L and to the formation of 28.6 µg/L THMs and 40.6 µg/L HAAs. A combined residual of 2.9 mg/L was produced with the application of 0.9 mg/L ammonia at the POE to the distribution system. This residual stayed relatively stable in the distribution system and prevented any further increases in DBP concentrations.

In December, as in the case of Durham, HAA concentrations exceeded THM concentrations. Again, this is most likely a result of the acidic pH of chlorination after coagulation. The dominance of HAAs over THMs for these facilities has been reported previously (Singer, Obolenski, and Greiner 1995).

**Houston and Gulf Coast Water Authority**

These paired systems are located in southeast Texas and draw surface water within 30 miles of each other as their raw water. The waters had an organic carbon content that was approximately 50 percent hydrophobic in nature. Houston had a relatively high bromide concentration of 113 µg/L. GCWA, with a bromide concentration of 295 µg/L, was the water utility with the highest bromide level among the 10 utilities examined (see Table 5.2).

The two water utilities employed conventional treatment with coagulation and sedimentation followed by filtration. GCWA added chlorine and chlorine dioxide after filtration, and ammonia was added before the finished water storage tank and the POE to the distribution system. Houston added free chlorine and ammonia to its raw water to make monochloramine; no further disinfectant addition was made in the subsequent treatment process.
Table 5.17 presents the results for the GCWA sampling in September. Because of contaminated MTBE, the results for the HAAs are unreliable and will not be discussed here.

Because the chlorine and chlorine dioxide were applied after filtration, no chlorine was detected and the THM concentrations were negligible in the filtered water. After the disinfectant addition, a free chlorine residual of 3.7 mg/L was measured after filtration and most of the THMs

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent</td>
<td>4.7</td>
<td>NA</td>
<td>NA</td>
<td>ND</td>
<td>3.4</td>
</tr>
<tr>
<td>Filter effluent after adding 2.0 mg/L Cl₂ before filtration</td>
<td>6.9</td>
<td>1.1</td>
<td>NA</td>
<td>12.0</td>
<td>9.1</td>
</tr>
<tr>
<td>Clearwell effluent after adding 5.1 mg/L Cl₂ after filtration</td>
<td>7.9</td>
<td>5.5</td>
<td>NA</td>
<td>36.8</td>
<td>10.5</td>
</tr>
<tr>
<td>Finished water at the POE after adding 1.1 mg/L NH₃</td>
<td>8.5</td>
<td>NA</td>
<td>4.5</td>
<td>57.2</td>
<td>16.1</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>NA</td>
<td>NA</td>
<td>2.7</td>
<td>60.7</td>
<td>20.0</td>
</tr>
<tr>
<td>Remote location in the distribution system</td>
<td>NA</td>
<td>NA</td>
<td>2.5</td>
<td>63.4</td>
<td>18.4</td>
</tr>
</tbody>
</table>

NA: not analyzed.

ND: not detected.

* Questionable values; samples stored more than 5 weeks.

Table 5.16 Summary of DBP results for Raleigh, Dec. 7, 1999

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clarifier effluent</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Filter effluent after adding 1.7 mg/L Cl₂ before filtration</td>
<td>NA</td>
<td>0.4</td>
<td>0.8</td>
<td>22.0</td>
<td>33.8</td>
</tr>
<tr>
<td>Clearwell effluent after adding 4.0 mg/L Cl₂ after filtration</td>
<td>NA</td>
<td>3.6</td>
<td>3.4</td>
<td>28.6</td>
<td>40.6</td>
</tr>
<tr>
<td>Finished water at the POE after adding 0.9 mg/L NH₃</td>
<td>NA</td>
<td>3.0</td>
<td>2.9</td>
<td>42.2</td>
<td>NA</td>
</tr>
<tr>
<td>Midpoint location in the distribution system</td>
<td>NA</td>
<td>NA</td>
<td>3.0</td>
<td>43.1</td>
<td>NA</td>
</tr>
<tr>
<td>Remote location in the distribution system</td>
<td>NA</td>
<td>NA</td>
<td>3.3</td>
<td>48.0</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA: not analyzed.

Gulf Coast Water Authority. Table 5.17 presents the results for the GCWA sampling in September. Because of contaminated MTBE, the results for the HAAs are unreliable and will not be discussed here.

Because the chlorine and chlorine dioxide were applied after filtration, no chlorine was detected and the THM concentrations were negligible in the filtered water. After the disinfectant addition, a free chlorine residual of 3.7 mg/L was measured after filtration and most of the THMs
were formed at this point. Before the POE to the distribution system, ammonia was used to convert the free chlorine residual to a combined residual of 2.8 mg/L. By tying up the free chlorine with ammonia, DBP formation was essentially stopped; the THM concentrations in the distribution system were the same as those in the finished water.

For the THMs, bromoform was the largest THM species measured (around 45 percent of the total THM concentration); less than 1 µg/L of chloroform was measured. These observations are consistent with the high bromide concentration in this water.

For the Houston samples, the same MTBE contamination problem occurred as with the GCWA samples. Accordingly, the HAA results for Houston are unreliable and will not be discussed here. Table 5.18 shows that a combined chlorine residual of 3.8 mg/L was measured and up to 28.7 µg/L THMs were produced at the effluent of the rapid-mix basin. The addition of 1.2 mg/L ammonia took place before coagulant addition, 1 min after chlorine addition. The significantly high THM levels shown for the first sample point are not believed to be representative because the first sample was taken directly after the application of 5.7 mg/L chlorine. It is likely that this was not a well-mixed sample. No further formation of DBPs was observed after the

<table>
<thead>
<tr>
<th>Sample description</th>
<th>pH</th>
<th>Free Cl₂ (mg/L)</th>
<th>Total Cl₂ (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtered water</td>
<td>7.7</td>
<td>ND</td>
<td>ND</td>
<td>0.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Filter effluent after adding 4.2 mg/L Cl₂ and 0.7 mg/L ClO₂ to filter effluent</td>
<td>7.8</td>
<td>3.7</td>
<td>3.7</td>
<td>57.7</td>
<td>33.2</td>
</tr>
<tr>
<td>Finished water at the POE after adding 1.4 mg/L NH₃</td>
<td>7.8</td>
<td>ND</td>
<td>2.8</td>
<td>67.6</td>
<td>34.0</td>
</tr>
<tr>
<td>Midpoint location 1 in the distribution system</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>66.2</td>
<td>31.3</td>
</tr>
<tr>
<td>Midpoint location 2 in the distribution system</td>
<td>7.9</td>
<td>ND</td>
<td>2.0</td>
<td>54.7</td>
<td>34.1</td>
</tr>
<tr>
<td>Remote point location in the distribution system</td>
<td>7.9</td>
<td>ND</td>
<td>2.2</td>
<td>64.9</td>
<td>34.3</td>
</tr>
</tbody>
</table>

ND: not detected.
NA: not analyzed.
* Because of contamination of the MTBE, these values are questionable.
rapid-mix basin. It is likely that the lower THM levels measured in the distribution system are the result of mixing with finished water from Houston’s two other treatment plants.

Despite the relatively high bromide concentrations, less bromide than expected was incorporated into the DBPs and chloroform was the dominant THM species. This is probably a result of ammonia tying up the free bromine generated from the oxidation of bromide by free chlorine.

**Additional Observations**

*Influence of Water Quality Characteristics on Trihalomethane and Haloacetic Acid Formation*

In previous studies (e.g., Croué et al. 1999), including those described in chapter 3, it has been observed that because the precursors for the THMs and HAAs have a high proportion of aromatic carbon, the SUVA value is a good surrogate parameter for DBPFP. It has been shown that the higher the SUVA value, the higher the THM and HAA formation potentials.
To determine whether the results from this plant-scale study were consistent with the literature findings and with those reported in chapter 3, Figure 5.4 was constructed to illustrate the impact of the SUVA value of the water sampled immediately before the first point of disinfectant addition on the THM and HAA concentrations produced at the POE to the distribution system. In contrast to the literature, Figure 5.4 shows no obvious trend. This is most likely a result of the different pH values, temperatures, contact times, and the use of ammonia and other disinfectants/oxidants, all of which influence the extent of THM and HAA formation. The relationships in the literature and those in chapter 3 relate to DBPFPs (i.e., the formation of DBPs under uniform conditions of chlorination).

Croué and co-workers (1999) and Reckhow, Singer, and Malcolm (1990) found that the hydrophobic fraction tends to produce more HAAs than THMs. This was also shown in chapter 3 for the controlled laboratory chlorinations. That means for water with a high hydrophobic fraction, the HAAs should dominate over the THMs. In Figure 5.5, the THM results at the POE to the distribution system are plotted against the corresponding HAA results. The line shown represents a THM to HAA ratio of one. For all points above the line, more THMs than HAAs were produced, and for points below the line, the opposite is true.

All the points below the line represent the results for Haverhill, Belvedere, Raleigh, and the second sampling for Durham, all of which had a relatively high hydrophobic fraction (>60 percent). These full-scale plant studies confirm the laboratory studies from Croué and colleagues (1999) and Reckhow, Singer, and Malcolm (1990), as well as those described in chapter 3.

As for bromine incorporation into the THMs and HAAs, it was expected, based on the analysis of ICR results presented in chapter 4, that the molar ratios of bromodichloroacetic acid to trichloroacetic acid would be the same as the molar ratios of bromodichloromethane to chloroform, and that a similar relationship would hold for the ratio of the dibromochloro species. The expected relationships should be linear, pass through the origin, and have a slope of one. Figures 5.6 and 5.7 show that the plant-scale results tend to be consistent with this pattern.
Figure 5.4 Impact of SUVA value of the water sampled immediately before the first point of disinfectant addition on THM and HAA concentrations at the POE to the distribution system

Figure 5.5 THM and HAA concentrations at the POE to the distribution system
SUMMARY AND CONCLUSIONS

Samples were taken from 10 different water treatment plants across the country and their water distribution systems and analyzed for THMs, HAAs, and chlorine residual. To determine the influence of the treatment strategy on DBP formation, plants were selected that used free chlorine, chlorine dioxide, ozone or chloramines as oxidants and primary disinfectants, and free chlorine or chloramines as secondary disinfectants. To examine the influence of treatment

Figure 5.6 Comparison between the molar ratio of Cl₂BrAA/Cl₃AA and the molar ratio of CHBrCl₂/CHCl₃ for all sample points and all water plants

Figure 5.7 Comparison between the molar ratio of ClBr₂AA/Cl₃AA and the molar ratio of CHBr₂Cl/CHCl₃ for all sample points and all water plants
strategy, paired utilities taking water from the same or similar water sources were investigated in parallel.

The results show that the quantity of hydrophobic carbon can be a decisive factor in determining the distribution among the DBPs. For waters with hydrophobic carbon comprising more than 60 percent of the TOC concentration, the HAAs were dominant over the THMs, whereas for waters with hydrophobic organic carbon percentages of around 50 percent or less, the THM concentrations were larger than the HAA concentrations.

As expected, the higher the bromide concentration, the more brominated species were produced. Bromochloroacetic acid, bromodichloroacetic acid, and dibromochloroacetic acid were present at significant concentrations in these waters, attesting to the importance of measuring all nine HAA species. For waters with high bromide concentrations, the results indicate that using chloramines instead of free chlorine can decrease the formation of brominated DBP species and thereby lower the extent of bromine incorporation into the DBPs.

The distribution among the four trihalogenated HAA species was consistent with the model presented in chapter 4, suggesting that concentrations of BrCl₂AA, Br₂ClAA, and Br₃AA can be predicted from knowledge of the concentrations of the four THM species and Cl₃AA.
CHAPTER 6
EVALUATION OF THE BIODEGRADATION/BIOSTABILITY OF HALOACETIC ACIDS AND TRIHALOMETHANES IN A SIMULATED DISTRIBUTION SYSTEM

INTRODUCTION

A number of HAAs are known to be biodegraded under aerobic conditions (Singer et al. 1993; Williams, Williams, and Rindfleisch 1995; Baribeau et al. 2000b). Williams, Williams and Gordon (1996) studied the biodegradation of HAAs. These researchers set up enrichment cultures containing Cl₂AA and others containing Cl₃AA. The flask containing Cl₂AA showed visible turbidity, whereas the Cl₃AA flask had no visible turbidity after 6 weeks. Meusel and Rehm (1993) had found that X. autotrophicus was able to effectively degrade Cl₂AA. In addition, van der Ploeg and colleagues (1991) had demonstrated that the enzyme from X. autotrophicus could degrade ClAA, Cl₂AA, BrAA, and Br₂AA, but not Cl₃AA.

In this project, the biostability of the nine HAAs and the four THMs was investigated using a simulated distribution system. The effect of DBP contact with biofilm formed inside bench-scale reactors—in the absence of corrosion by-products, with and without a chlorine or chloramine residual—was addressed in both cold and warm waters. In addition, the bacteria known to be responsible for the biodegradation of some HAA species (X. autotrophicus GJ10) was monitored. At the end of the experiments, X. autotrophicus was spiked into the dechlor(am)inated reactors to investigate the potential enhancement of HAA removal by this organism, as well as its potential for biofilm colonization.

APPROACH

Annular reactors (ARs) were selected to simulate the distribution system. Because they permit liquid mixing and biofilm formation, they simulate the distribution system more accurately than batch incubation in bottles. They also give the unique advantage of allowing for the collection of both liquid and biofilm samples. Their small size (1,150 mL) and operational flexibility permit a better understanding of distribution-system phenomena by allowing spiking of different compounds without concern about downstream consumers.
Four reactors (Figure 6.1) were placed at the effluent of the MWD’s F.E. Weymouth Filtration Plant, located in La Verne, Calif. Because chlorine and ammonia are not added at the same point at the plant, both chlorinated and chloraminated waters were accessible. Therefore, two parallel trains of reactors were used (Figure 6.2): one received treated water with free chlorine and the other received treated water with chloramines. Because it has been shown that most DBP degradation in distribution systems occurs at high residence times—where the disinfectant concentration was low (Williams, Williams, and Rindfleisch 1995; Baribeau, Prévost, and LaFrance 1994)—each train was composed of two reactors: the upstream reactor received a positive disinfectant residual and the downstream reactor received dechlor(am)inated water. Therefore, the experimental plan simulated sample collection at three locations in the distribution systems: the treatment plant effluent (upstream reactor influent), a central location (between both reactors), and at the end of the distribution system (downstream reactor effluent).

During each sampling, laboratory batch incubations were also performed to distinguish the influence of the residence time (in the reactors and batch incubations) from any potential effect of the biofilm (in the reactors only). Parallel samples were collected at the upstream or downstream reactor influent, or both, and held in the dark, in sealed flasks, headspace-free at the


Figure 6.1 Schematic of an annular reactor
same temperature as the reactors. These batch samples were analyzed for all parameters after an incubation period as close as possible to the reactor residence time (12 hours in the reactors; 13.1 hours to 15.5 hours [an average of 14.4 hours] in the batch incubations).

From the liquid samples collected at the reactor influent and effluent, and the batch incubations, several parameters were analyzed: free and total chlorine residuals, all nine HAAs, all four THMs, and suspended heterotrophic plate count (HPC) bacteria. The ARs were monitored continuously for temperature and pH of the water feeding the reactors. The biofilm samples were analyzed for fixed biomass by HPC. Selected samples of suspended and fixed biomass were also screened for the presence of \( X. \ autotrophicus \).

**MATERIALS AND METHODS**

**Weymouth Plant**

MWD’s Weymouth plant—where the ARs were located—received either of two different source waters: Colorado River water (CRW) or California SPW or any blend of the two. The source water blend used at the Weymouth plant during the study is detailed in Table 6.1. The
The chemical matrix of these two waters is significantly different: CRW is higher in mineral content, whereas SPW is typically higher in organic content and bromide. During the course of this study, CRW had TOC typically from 2.5 to 3.0 mg/L and bromide from 0.06 to 0.07 mg/L, whereas SPW typically had 2.6 to 3.7 mg/L of TOC and 0.09 to 0.17 mg/L of bromide.

The treatment processes at the Weymouth plant included predisinfection with chlorine at a dose of 2.5–3.0 mg Cl₂/L (to yield a residual of 0.6–1.9 mg/L after sedimentation), coagulation (4.0–6.0 mg/L alum, 1.5–3.0 mg/L of cationic polymer), sedimentation, filtration, and postchloramination.

Table 6.1
Source water blend used at the Weymouth plant during AR study

<table>
<thead>
<tr>
<th>Date</th>
<th>CRW (%)</th>
<th>SPW (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12/98</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>01/01–15/99</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>01/16/99</td>
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<tr>
<td>01/19/99</td>
<td>0–17</td>
<td>83–100</td>
</tr>
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<td>01/20/99</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>01/21/99</td>
<td>0–26</td>
<td>74–100</td>
</tr>
<tr>
<td>01/22/99</td>
<td>26–52</td>
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</tr>
<tr>
<td>01/23/99</td>
<td>52–100</td>
<td>0–48</td>
</tr>
<tr>
<td>01/24–31/99</td>
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</tr>
<tr>
<td>09/01–10/99</td>
<td>73–75</td>
<td>25–27</td>
</tr>
</tbody>
</table>
Before dual-media (anthracite/sand) filtration, more chlorine was added to yield a residual of 2.5–2.7 mg/L of total chlorine at the clearwell effluent. At the filter effluent (before the clearwell), ammonia was added to achieve a ratio of 5 mg Cl₂ per mg NH₃-N, and enough caustic soda was applied to result in a pH of 7.9–8.2 at the clearwell effluent.

Annular Reactors

ARs were developed by BioSurface Technologies Corp. (Bozeman, Mont.) in collaboration with the Center for Biofilm Engineering (Montana State University, Bozeman, Mont.). The ARs consist of a rotor turning inside a stationary outer cylinder (Figure 6.1). Hydraulic conditions inside the reactor (such as shear stress and water velocity) depend on the rotational speed of the rotor. A rotational speed of 60 rpm was used, which simulated a hydraulic velocity of 1 ft/sec in a 4-in.-diameter pipe. Four draft tubes inside the inner cylinder enhance liquid mixing. The polycarbonate material permits biofilm development without the presence of corrosion or corrosion by-products. Removable wall segments (slides) on the outside wall of the inner cylinder were used to study the biofilm. The influent flow (1.6 mL/min) determined the water residence time inside the reactor (12 hours), simulating the residence time in the distribution system.

Before being placed in service, the reactors and the slides were scrubbed in detergent and water, and thoroughly rinsed, first with tap and then with deionized (DI) water. To eliminate any potential chlorine demand from the reactor materials, the reactors and slides were soaked overnight in DI water containing at least 100 mg Cl₂/L. The reactors and slides were thoroughly rinsed with DI water and air-dried. The slides were sterilized by autoclaving.

Annual Reactor Dechlor(am)ination

Bench-scale experiments were conducted to determine the dechlor(am)inating agent to be used between the upstream and downstream reactors that would quench both free chlorine and chloramine residuals, not degrade THMs or HAAs, and not inactivate microorganisms or inhibit biofilm development. Although ammonium sulfate [(NH₄)₂SO₄] was selected to quench chlorine residuals in HAA samples in Phase I of this study, this reagent does not destroy chloramine
residuals; the goal of this phase of the study was to eliminate any disinfectant residual in either of the downstream reactors.

Because the most common dechlor(amine)ating agent used before microbial analyses is sodium thiosulfate (Na$_2$S$_2$O$_3$), in-house experiments were conducted to evaluate the effect of this reagent on HAA concentrations. Although sulfur-reducing agents are commonly used to quench chlorine residuals for THM samples, these agents (especially when used in excess) destroy certain non-THM DBPs (Croué and Reckhow 1989, Krasner et al. 1989). At the same time, sodium sulfite (Na$_2$SO$_3$) and ammonium chloride (NH$_4$Cl), two other commonly used quenching agents, were also investigated. (NH$_4$Cl was evaluated in this test, as that was the quenching reagent used at Metropolitan for HAA samples [Krasner et al. 1989]. Both NH$_4$Cl and (NH$_4$)$_2$SO$_4$ convert free chlorine residuals to chloramine residuals; neither reagent is able to destroy a chloramine residual.) Concentrations of 18 mg/L of Na$_2$S$_2$O$_3$ or Na$_2$SO$_3$—which represents a stoichiometric amount for dechlorination with a small excess—or 100 mg/L of NH$_4$Cl were applied to the same water as that supplying the reactors (chlorinated and chloraminated waters from the Weymouth plant) at ambient pH (~8). Samples were incubated at 25°C for 0, 0.5, 1, 3, 10, and 17 days. These conditions represented a worst-case scenario considering that, in reality, the water residence time in the downstream dechlor(amine)inated reactors was only 12 hours, after which the collected samples were stored at 4°C before analysis.

Figure 6.3 presents the results for Cl$_2$AA. As expected, HAA formation continued to occur in the chlorinated water without a dechlorination/quenching agent. Results showed that the low amounts of sulfur-reducing agents tested did not produce any apparent (or significant) degradation of Cl$_2$AA (or the other seven HAAs that were present; Br$_3$AA was not detected). Although some of the 0.5- (or 1-) day incubation results appeared to have slightly higher HAA concentrations, the 3- and 17-day results are closer to the initial concentrations.

Based on these results, Na$_2$S$_2$O$_3$ was selected as the dechlor(amine)ination agent before the downstream reactors. The Na$_2$S$_2$O$_3$ concentration used was determined by stoichiometric calculations assuming that 2 moles of Na$_2$S$_2$O$_3$ dechlorinate 1 mole of Cl$_2$. A safety factor of 100 percent was added. A sterile solution of Na$_2$S$_2$O$_3$ at a concentration of 468 mg/L was continuously fed in the influent line of the downstream reactor at a flow rate of approximately 0.08 mL/min, which represented 5 percent of the total influent flow to the reactor. The appropriate Na$_2$S$_2$O$_3$ solution
concentration and flow rate were carefully selected to avoid dilution of the downstream reactor influent water. The Na$_2$S$_2$O$_3$ solution was freshly prepared each week and sterilized by autoclaving. Excess Na$_2$S$_2$O$_3$ may have reduced a portion of the dissolved oxygen (DO) in the downstream reactors. However, the DO concentration in the Weymouth plant effluent was relatively high. Thus, it is unlikely that the excess Na$_2$S$_2$O$_3$ would have consumed a significant portion of the DO.

**Bacterial Spiking Experiment**

At the end of the warm-water experiments, a bacteria known to be responsible for Cl$_2$AA biodegradation—*X. autotrophicus* GJ10 (Janssen et al. 1985)—was spiked between the upstream and downstream reactors, immediately following dechlor(am)ination. *X. autotrophicus* was purchased from American Type Culture Collection (ATCC #43050), and was grown in nutrient broth for 48 hours at 28°C under agitation (120 rpm). Water was collected at each upstream reactor (AR1-Cl$_2$ and AR1-NH$_2$Cl) influent and filter-sterilized through a 0.22-µm membrane.

![Figure 6.3](image_url)  
**Figure 6.3** Effect of dechlorination/quenching agents on the stability of Cl$_2$AA in chlorinated Weymouth plant filter effluent.
X. autotrophicus bacterial culture was washed twice by centrifugation/resuspension in the wash water buffer described in Standard Methods (APHA, AWWA, and WEF 1998) and resuspended into 250 mL of filter-sterilized AR1-Cl$_2$ and AR1-NH$_2$Cl influent water. The concentration of these suspensions was determined, and the rest was spiked into each downstream reactor (AR2-Cl$_2$ and AR2-NH$_2$Cl) at a rate of 0.16 mL/min, which corresponded to about 10 percent of the reactor influent flow. Because of seeding difficulties, the spiking period was slightly different in both reactors, which lasted 24 hours and 20 min in the chlorinated train and 21 hours in the chloraminated train. Total concentrations of $2.74 \times 10^9$ colony-forming units (CFU) and $1.79 \times 10^9$ CFU were spiked in AR2-Cl$_2$ and AR2-NH$_2$Cl, respectively.

**Analytical Parameters**

The analytical parameters monitored included all nine HAAs and the four THMs at each reactor influent and effluent and in batch samples, as well as basic physical–chemical parameters following the procedures described hereunder. Suspended biomass samples were collected in 15-mL sterile centrifuge tubes containing 0.01 percent Na$_2$S$_2$O$_3$. For the molecular techniques, liquid samples were collected in 1-L Wheaton bottles containing 0.01 percent Na$_2$S$_2$O$_3$. Biofilm samples (slides) were pulled from the reactors using a sterile hook and placed in a sterile 100-mL graduated cylinder containing filter-sterilized water collected at the influent of each chlorinated and chloraminated train. Each slide was collected only once during the study. Therefore, the period of colonization of each biofilm sample corresponds to the number of operating days of the reactors.

**Trihalomethanes**

THMs were measured utilizing a salted LLE with GC-ECD analysis (Munch and Hautman 1995).

**Haloacetic Acids**

HAAs were measuring utilizing an acidic and salted LLE, derivatization with acidic methanol, and analysis with a GC-ECD (Munch, Munch, and Pawlecki 1995).
**Chlorine Residuals**

The Hach pocket colorimeter chlorine test kit was used to measure the free and total chlorine residuals following a method adapted from *Standard Methods* (APHA, AWWA, and WEF 1998). A 2.5-cm sample cell was used, and appropriate dilutions were made to measure chlorine concentrations in the range of 0 to 2.0 mg Cl₂/L.

**Heterotrophic Plate Count Bacteria**

The total culturable biomass was measured for HPC bacteria using membrane filtration and incubation on R2A media for 7 days at 28°C (APHA, AWWA, and WEF 1998; Method 9215 D). Samples were run in triplicate. The biofilm concentration was determined by scraping the biofilm from the reactor slides using a sterile Teflon rod and resuspending the biomass in sterile water (water was collected from each upstream reactor influent and filter sterilized through a 0.22-μm membrane). The biofilm suspensions were homogenized for 1 min at 50 percent using a tissue homogenizer (VirTishear; VirTis Company, Gardiner, N.Y.) before membrane filtration. HPC enumeration was performed on the biofilm suspension.

**Xanthobacter autotrophicus GJ10**

*X. autotrophicus*. GJ10 was monitored by two techniques: sample plating on culture media and identification by molecular techniques targeting the genes specific to halogenated compound degradation. Although quantification is better achieved by the first technique, the second method is much more specific and allows recovery of the viable but nonculturable cells often encountered in disinfected waters. The molecular methods have made it possible to use a segment of nucleic acid for detecting and identifying microorganisms. Target nucleic acid amplification techniques like polymerase chain reaction (PCR) are often needed for detection of low copy numbers of bacterial DNA such as those observed in environmental samples. Amplification of DNA extracted directly from environmental samples has demonstrated the presence of many novel bacterial sequences that do not correspond to any cultured organisms (Devereux and Mundfrom 1994; Fuhrman, McCallum, and Davis 1993; Giovannoni et al. 1990; Rochelle et al. 1994; Schmidt,
Moreover, recovered DNA indicated the presence of a particular organism even though enrichment cultures specifically designed to isolate the organism failed to do so (Britschgi and Fallon 1994).

*Culturing technique.* An *X. autotrophicus* (ATCC #43050) pellet was reconstituted in sterile nutrient broth. Various media were evaluated for the recovery of *X. autotrophicus*: R2A, nutrient agar, nutrient agar supplemented with antibiotics (10 µg/mL of tetracycline, 50 µg/mL of ampicillin, and 50 µg/mL of kanamycin; van der Ploeg, van Hall, and Janssen 1991), as well as nutrient agar with tetracycline only (10 µg/mL). Incubations lasted 5 days at 28°C. Results showed that *X. autotrophicus* could not grow on nutrient agar supplemented with antibiotics, but colonies could grow and be enumerated on plain nutrient agar. The *X. autotrophicus* colonies were circular yellow, opaque, and entire in appearance, and were easily enumerated in pure-culture membrane filtration experiments. The colonies were more difficult to recognize in the presence of heterotrophic organisms. Difficulties in visually recognizing *X. autotrophicus* from other bacteria led to the necessity of using molecular techniques to confirm their presence in natural water.

Therefore, for each experiment, liquid samples and biofilm suspensions were filtered through a membrane and incubated on nutrient agar for 5–7 days at 28°C. Colonies suspected of being *X. autotrophicus* were enumerated, then picked, streaked on fresh nutrient agar plates, and incubated at 28°C for 24–72 hours. Samples that exhibited typical colonies were streaked a second time. From the second-streaked plates, colonies were picked and resuspended in 500–1,000 µL High tris-EDTA (HTE) buffer (50 mM tris, 20 mM ethylenediaminetetraacetic acid [EDTA], pH 7.5–8.0), and the DNA extracted by heating the isolates to 95°C for 10 min. These DNA extracts were screened by PCR amplification to confirm that the colonies from which they result were *X. autotrophicus*.

*Molecular techniques.* For each experiment, large volumes of each liquid sample (970–1,000 mL of reactor influent, 500–920 mL of reactor effluent, 820–950 mL of batch incubation sample, and all of the biofilm suspension) were also concentrated by membrane filtration. The DNA was extracted and amplified by a PCR technique that targeted the dehalogenase genes. The method is detailed below. Samples were filtered through sterile, 0.22-µm porosity, 45-mm diameter, polycarbonate membranes treated with polyvinyl pyrroldione. Sterile tris-EDTA buffer (10 mM tris, 1.0 mM EDTA, pH 7.5–8.0) was used to soak membranes before they were used and to rinse the filter manifolds before and after sample filtration. Membranes were aseptically folded in 1.7-mL
microtubes, immersed in HTE buffer, and stored at –20°C. DNA extraction involved addition of 0.75 mg/mL (final concentration) of proteinase K and 0.05 percent of lauryl sulfate, followed by incubation at 37°C for 30 min. Next, 0.65 percent of N-lauroysarcosine (sarkosyl) was added, followed by a 15-min incubation at 37°C. After addition of 1.1M of sodium chloride (NaCl), samples underwent a succession of three freeze/thaw cycles (–70°C for 10 min, +65°C for 5 min) before they were extracted with 0.5 percent hexadecyltrimethylammonium bromide (also known as CTAB)/NaCl and incubated at 65°C for 30 min. Microtubes were filled with phenol/chloroform/isoamyl alcohol (25:24:1 v/v/v) to extract the DNA and dissolve the membrane. An aliquot of the upper aqueous layer containing the DNA was transferred to a new microtube, and an equal volume of chloroform/isoamyl alcohol (24:1 v/v) was added. An aliquot of the upper aqueous layer was transferred to a new microtube, and 0.15 percent of glycogen was added. DNA was precipitated overnight in isopropanol (60 percent by volume isopropanol). DNA was pelleted by centrifugation, washed twice with 500 µL of 70 percent ice-cold ethanol, dried in a desiccator (AS160 Automatic SpeedVac; Savant Instruments, Holbrook, N.Y.), resuspended in 100 µL of sterile water, and stored at –20°C.

During each experiment, membrane filtration and extraction negative controls were processed. The membrane filtration control consisted of 500 mL of sterile tris-EDTA buffer filtered through a membrane, and the extraction negative control consisted of 300 µL of sterile HTE (without membrane). The DNA of these negative controls was extracted with the samples and amplified by PCR. These controls had to remain negative for an experiment to be considered valid. As a positive control for the molecular techniques, a 1.0-mL aliquot of a 48-hour culture of X. autotrophicus in tryptic soy broth was placed into a 1.5-mL microfuge tube to extract the total DNA. The culture suspension was pelleted at 10,000 × g for 3 min, resuspended in 500 µL of HTE buffer to wash, and recentrifuged. A fresh 5 percent Chelex-100 (Sigma Chemical) suspension was prepared in sterile Milli-Q water and kept stirring to ensure a homogenous suspension. The supernatant was removed and the pellet resuspended in 1.0 mL of Chelex-100, ensuring that the beads were evenly distributed. The sample was then incubated for 30 min at 60°C. Following incubation, the sample was vortexed vigorously for 20 sec, then incubated for 10 min at 95°C. The sample was again vortexed vigorously for 20 sec, and centrifuged for 3 min at 10,000 × g. The supernatant containing DNA was transferred to a fresh tube and stored at –20°C until use. Dilutions of DNA (1:50) were used as positive controls during PCR amplification.
The PCR primers targeting dehalogenase genes (*dhlA*, *dhlB*, and *dhlC*) specific to *X. autotrophicus* and proposed by Janssen et al. (1989); van der Ploeg, van Hall, and Janssen (1991); and van der Ploeg and Janssen (1995) were used. Amplification reactions were performed using PCR buffer containing 10 mM tris-HCl (pH 8.3), 50 mM potassium chloride (KCl), and 0.01 percent gelatin, along with 10 µg/mL of bovine serum albumin (BSA), 200 µM of each deoxynucleotide triphosphate (dNTP), 0.25 µM of each primer, and 1 unit (U) of AmpliTaq Gold polymerase enzyme (Perkin-Elmer Corp., Foster City, Calif.). Deoxyuracil triphosphate (dUTP) was substituted for deoxythymidine triphosphate (dTTP) in the amplification reaction so that uracil N-glycosylase (UNG, 1 U per reaction; Perkin-Elmer) could be included to prevent contamination by amplified products from previous PCR amplifications. PCR activity included UNG activation at 24°C for 10 min, and UNG denaturation and polymerase enzyme activation at 95°C for 10 min, followed by 35 cycles of denaturation at 94°C for 1 min, primer annealing for 1 min, and primer extension at 72°C for 2 min. The final extension was conducted at 72°C for 10 min. Each amplification included a positive control (*X. autotrophicus* DNA), and negative control (sterile molecular-biology-grade water). Amplicons were separated by agarose gel electrophoresis, stained in ethidium bromide, and photographed on a UV transilluminator (Sambrook, Fritsch, and Maniatis 1989). Optimum conditions for PCR amplification using each primer set were determined by comparison of band intensity of amplicons obtained from different MgCl₂ concentrations and annealing temperatures (Table 6.2). The primer specificity at the optimum conditions was determined for

<table>
<thead>
<tr>
<th>Gene</th>
<th>Primers *</th>
<th>Amplicon size (bp)†</th>
<th>Annealing temperature (°C)</th>
<th>MgCl₂ concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>dhlA</em></td>
<td>XADHALA-F XADHALA-R</td>
<td>475</td>
<td>62</td>
<td>2.5</td>
</tr>
<tr>
<td><em>dhlB</em></td>
<td>XADHALB-F XADHALB-R</td>
<td>324</td>
<td>65</td>
<td>1.5</td>
</tr>
<tr>
<td><em>dhlC</em></td>
<td>XADHALC-F XADHALC-R</td>
<td>238</td>
<td>62</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* XADHAL: *X. autotrophicus* dehalogenase; F: forward; R: reverse.
† bp: base pair.
PCR amplification using DNA from organisms exhibiting a different, but closely related DNA sequence: *Pseudomonas putida* (ATCC #12633), *P. phaseolicola* (ATCC #21781), *P. fluorescens* (ATCC #13525), and *Stenotrophomonas maltophila* (ATCC #13637).

**Sampling Dates**

In-house studies using ARs have shown that a preconditioning period of approximately 3 months is required for biofilm formation in water carrying a residual disinfectant. The reactors were started on Nov. 30, 1998, so that the initial tests could be conducted under cold-water conditions. Table 6.3 presents the experiments and the dates on which they were conducted.

Three times per week, the reactors were monitored for rotational speed (60 rpm), influent flow rate (1.6 mL/min), and free and total chlorine residual. In addition, the temperature and pH were analyzed three times per day at the chlorinated and chloraminated sample lines.

<table>
<thead>
<tr>
<th>Dates</th>
<th>Type of sampling</th>
<th>Days of reactor operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>02/24/99</td>
<td>Shake-down, cold water</td>
<td>86</td>
</tr>
<tr>
<td>03/17/99</td>
<td>Cold water (#1)</td>
<td>107</td>
</tr>
<tr>
<td>03/31/99</td>
<td>Cold water (#2)</td>
<td>121</td>
</tr>
<tr>
<td>04/06/99</td>
<td>Cold water (#3)</td>
<td>127</td>
</tr>
<tr>
<td>05/12/99</td>
<td>Split samples</td>
<td>163</td>
</tr>
<tr>
<td>06/16/99</td>
<td>Warm water (#1)</td>
<td>198</td>
</tr>
<tr>
<td>06/30/99</td>
<td>Warm water (#2)</td>
<td>212</td>
</tr>
<tr>
<td>07/14/99</td>
<td>Warm water (#3)</td>
<td>226</td>
</tr>
<tr>
<td>09/01/99</td>
<td>Spiking experiment</td>
<td>275</td>
</tr>
<tr>
<td>09/02/99</td>
<td>Post-spiking (24 hours)</td>
<td>276</td>
</tr>
<tr>
<td>09/09/99</td>
<td>Post-spiking (1 week)</td>
<td>283</td>
</tr>
</tbody>
</table>
RESULTS

Temperature and pH

The reactors were operated at the treated-water temperature and pH. Figure 6.4 shows the water temperature and the pH of the water fed to the reactors. The temperature varied from 10 to 25°C. On the cold- and warm-water sampling dates, the temperature was 13–14°C and 17–22°C, respectively. During the bacterial spiking experiment, the temperature was 25°C. The average pH values were 8.08 ± 0.07 and 8.10 ± 0.05 for the chlorinated and chloraminated train influents, respectively. As shown in Figure 6.4, the pH was relatively stable over the course of the study, except on days 214 and 224 where it decreased significantly (to 7.5–7.6) in the chlorinated train influent during brief periods of time for unknown reasons.

Because the liquid sample volume available during regular experiments was limited, it was not possible to measure the pH at each reactor influent, effluent, and batch incubation. Therefore, four special experiments were conducted in July and August 1999—before the spiking experiments—during which the pH was measured at each reactor influent and effluent. The average pH variation within each reactor (reactor-influent concentration minus reactor-effluent concentration) is shown in Table 6.4. The results indicate that the pH variation within each reactor was not significant.

Chlorine Residual

The free and total chlorine residuals at the influent of each train are presented in Figure 6.5, and the free and total chlorine demands across the upstream reactors are shown in Figure 6.6. The average free and total chlorine residuals at the influent of the upstream reactor of the chlorinated train (AR1-Cl2) were 2.47 ± 0.27 and 2.82 ± 0.26 mg Cl2/L, respectively, and the average total chlorine residual at the influent of AR1-NH2Cl was 2.56 ± 0.14 mg/L. As shown in Figure 6.6, the disinfectant residuals were relatively stable, except on day 196 where it dropped to 1.26 mg/L at the influent to AR1-Cl2 because of plant operational modifications. Some unexplained variability was also observed at the end of the study.
The free chlorine demand in AR1-Cl₂ was 0.86 ± 0.44 mg Cl₂/L, and the total chlorine demand in AR1-NH₂Cl was 0.62 ± 0.56 mg Cl₂/L. In AR1-Cl₂, these demands were slightly higher in warm water (0.90 mg/L) than in colder water (0.74 mg/L). Trends were similar in AR1-NH₂Cl with total chlorine demands of 0.25 and 0.71 mg/L in cold and warm waters, respectively. As Figure 6.6 illustrates, the chlorine demand increased significantly in AR1-Cl₂ on days 28 and 29. This reactor was accidentally disconnected from the supply water and was therefore partially emptied. The chlorine residual of the reactor effluent dropped to 0 mg/L and took a few days to recover. Other increases in chlorine demand occurred in the same reactor on different occasions (days 112 and 144) for no apparent reason. The total chlorine demand increased significantly in AR1-NH₂Cl after day 250 with almost a complete consumption of the chlorine. Such results

![Figure 6.4 Temperature and pH at the upstream-reactor influents](image)

**Table 6.4**

Average pH variation within each reactor

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Average pH variation *</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR1-Cl₂</td>
<td>+0.21</td>
<td>0.29</td>
</tr>
<tr>
<td>AR2-Cl₂</td>
<td>+0.03</td>
<td>0.17</td>
</tr>
<tr>
<td>AR1-NH₂Cl</td>
<td>+0.01</td>
<td>0.24</td>
</tr>
<tr>
<td>AR2-NH₂Cl</td>
<td>–0.06</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* Positive variations indicate an increase in pH; negative variations indicate a decrease in pH.

The free chlorine demand in AR1-Cl₂ was 0.86 ± 0.44 mg Cl₂/L, and the total chlorine demand in AR1-NH₂Cl was 0.62 ± 0.56 mg Cl₂/L. In AR1-Cl₂, these demands were slightly higher in warm water (0.90 mg/L) than in colder water (0.74 mg/L). Trends were similar in AR1-NH₂Cl with total chlorine demands of 0.25 and 0.71 mg/L in cold and warm waters, respectively. As Figure 6.6 illustrates, the chlorine demand increased significantly in AR1-Cl₂ on days 28 and 29. This reactor was accidentally disconnected from the supply water and was therefore partially emptied. The chlorine residual of the reactor effluent dropped to 0 mg/L and took a few days to recover. Other increases in chlorine demand occurred in the same reactor on different occasions (days 112 and 144) for no apparent reason. The total chlorine demand increased significantly in AR1-NH₂Cl after day 250 with almost a complete consumption of the chlorine. Such results
suggest nitrification within the chloraminated train reactors. Although no specific measurements—such as nitrite levels—were made to confirm it, previous studies conducted at MWD have shown that nitrification can easily develop in the reactors (Baribeau et al. 1999). Unfortunately, the bacterial spiking experiment was conducted during this period (see below).

The total chlorine residual measured at the influent and effluent of the downstream reactors was 0 mg/L, except on the occasions described below. After 28 days, the tube feeding the Na₂S₂O₃ solution in AR2-NH₂Cl was damaged and chloraminated water was fed into the reactor. On day 81, the Weymouth plant sample lines into which the reactors were tapped had to be chlorinated for maintenance purposes. This operation resulted in high chlorine residuals (>4.4 mg/L) in both reactors of the chlorinated train. The chloraminated train was also affected, but to a lesser extent (1.09 mg/L total chlorine at the effluent of AR2-NH₂Cl). Chloramines were also detected at the influent of AR2-NH₂Cl on days 98, 121, and 130 (1.49, 1.35, and 1.98 mg/L, respectively) because of Na₂S₂O₃ pumping problems. For all these events, as soon as the fact was noticed, Na₂S₂O₃ was added directly to the reactors to quench any excess residual and minimize the impact on the biofilm.

![Figure 6.5 Chlorine residual at the upstream-reactor influents (cold-water and warm-water sampling on days 86–127 and 198–283, respectively)](image-url)
Again because the liquid sample volume available was limited, the chlorine residual was not measured in the batch incubations during regular experiments. Therefore, three special experiments were conducted in July and August 1999, during which batch incubations were set up, and the free and total chlorine residuals measured before and after incubation. Results showed that the difference in chlorine consumption between the batch incubation and the reactor was generally insignificant (0.04–0.32 mg/L), except in the upstream chloraminated reactor (AR1-NH₂Cl). In this reactor, the total chlorine consumption was greater in the reactor than in the batch incubation, and the difference increased from one experiment to the next (difference of 0.24 mg/L—between the chlorine consumption in batch incubation and the chlorine consumption in the AR—to 1.06 mg/L), most likely because of nitrification within the ARs.

**Disinfection By-product Degradation**

**Haloacetic Acids**

*Effect of temperature.* Figures 6.7 and 6.8 show examples of the results of one of the cold-water sets of measurements (from Mar. 17, 1999; temperature ~13°C). The HAAs increased in concentration in the chlorinated upstream reactor (AR1-Cl₂), and most of the HAA species were
Figure 6.7 Formation and stability of HAAs in the AR study in cold, chlorinated water (Mar. 17, 1999; temperature = 13.5°C) (ClAA, BrAA, Br₃AA not detected)

Figure 6.8 Formation and stability of HAAs in the AR study in cold, chloraminated water (Mar. 17, 1999; temperature = 13.5°C) (ClAA, BrAA, Br₃AA not detected)
relatively stable in concentration in the dechlorinated downstream reactor (AR2-Cl$_2$; Figure 6.7). However, there was a significant increase in the concentrations of Cl$_3$AA and BrCl$_2$AA in the dechlorinated downstream reactor (AR2-Cl$_2$; this phenomenon was routinely observed on other dates as well). Because there was no chlorine residual present in the latter AR, the increase could have resulted from either (1) a breakdown of other DBPs to form the aforementioned HAAs or (2) analytical error. Research by Exner, Burk, and Kyriacou (1973) suggested that the alkaline degradation of haloacetonitriles produces haloacetamides and ultimately HAAs. Moreover, Croué and Reckhow (1989) demonstrated that the decomposition of certain DBPs can be accelerated in the presence of sulfite. The Na$_2$S$_2$O$_3$ added to the downstream reactors for dechlor(am)ination could have had a similar effect.

The HAAs (except perhaps Cl$_2$AA, which exhibited a very slight increase) were relatively stable in concentration in the chloraminated upstream reactor (AR1-NH$_2$Cl) and the concentrations remained constant (within analytical variability) in the dechloraminated downstream reactor (AR2-NH$_2$Cl; Figure 6.8).

For these experiments, the concentrations in the batch-chlorinated sample were higher than in the corresponding reactor effluent for the upstream reactor. The results of all the batch samples are discussed in detail below.

Figures 6.9 and 6.10 show examples of the results of one of the warm-water experiments (from June 30, 1999; temperature = 19.2°C). The HAAs increased in concentration in the chlorinated upstream reactor (AR1-Cl$_2$; Figure 6.9). The increase in the concentration of the HAAs in the warm-water experiments (e.g., a 95 percent increase for Cl$_2$AA; Figure 6.9) was much more than in the cold-water conditions (e.g., a 46 percent increase for Cl$_2$AA; Figure 6.7).

The dihalogenated HAAs (X$_2$AAs; i.e., Cl$_2$AA, BrClAA, and Br$_2$AA) degraded under the warm-water conditions in the absence of a chlorine residual and in the presence of a biofilm, whereas they were stable in the batch sample with no chlorine residual or biofilm (Figure 6.9). Alternatively, the concentrations of the trihalogenated HAAs (X$_3$AA; i.e., Cl$_3$AA, BrCl$_2$AA, and Br$_2$ClAA) remained essentially constant or increased slightly in the dechlorinated downstream reactor (AR2-Cl$_2$; Figure 6.9). Similar results were observed in the chloraminated upstream reactor (AR1-NH$_2$Cl) and dechloraminated downstream reactor (AR2-NH$_2$Cl; Figure 6.10).
Figure 6.9 Formation and stability of HAAs in AR study in warm, chlorinated water (June 30, 1999; temperature = 19.2°C) (ClAA ≤ 2 µg/L, BrAA ≤ 3 µg/L, Br₃AA not detected)

Figure 6.10 Formation and stability of HAAs in AR study in warm, chloraminated water (June 30, 1999; temperature = 19.2°C) (ClAA < 2 µg/L, BrAA < 2 µg/L, Br₃AA not detected)
Figures 6.11 and 6.12 summarize the reactor results for Cl$_2$AA in cold versus warm water. In either chlorinated or chloraminated water with a positive residual, Cl$_2$AA continued to form. When the residual was absent (because of the addition of a dechlorination agent), Cl$_2$AA was stable only in cold-water conditions, but was degraded under warm-water conditions. Figures 6.13 and 6.14 summarize the reactor results for Cl$_3$AA. This HAA continued to form in either cold- or warm-water conditions in the absence of a disinfectant residual. As noted above, bromine substitution in X$_2$AAs or X$_3$AAs resulted in similar trends for stability as the fully chlorinated species.

**Effect of bacterial spiking.** At the end of the warm-water experiments, *X. autotrophicus* GJ10 was spiked between the upstream and downstream reactors, immediately following dechlor(am)ination. These experiments were unfortunately conducted during the period when the chloraminated train exhibited high chlorine demand, most likely related to nitrification of that train.

Figures 6.15 and 6.16 show examples of the results for the HAAs for the experiment conducted 1 week after the bacterial spiking (from Sept. 9, 1999). The HAAs—in particular, Cl$_2$AA—increased in concentration in the chlorinated upstream reactor (AR1-Cl$_2$), whereas their concentration did not increase in the batch incubation (Figure 6.15). The X$_2$AAs degraded under warm-water conditions in the absence of a chlorine residual and in the presence of a biofilm. In addition, the X$_2$AAs degraded in the batch incubation with no chlorine residual or biofilm (Figure 6.15; see the section on *X. autotrophicus* below for a further discussion of this result). Alternatively, the concentrations of the X$_3$AAs were stable (or somewhat higher) in the dechlorinated downstream reactor (AR2-Cl$_2$) or batch incubation (Figure 6.15). Similar results were observed in the chloraminated upstream reactor (AR1-NH$_2$Cl) and dechloraminated downstream reactor (AR2-NH$_2$Cl; Figure 6.16).

Figures 6.17 and 6.18 summarize the reactor results for Cl$_2$AA with and without bacterial spiking (using the last warm-water experiment before the spiking as an example of the warm-water results without bacterial spiking). In either chlorinated or chloraminated water with a positive residual, Cl$_2$AA was stable or continued to form. When the residual was absent (because of the addition of a dechlorination agent), Cl$_2$AA was degraded under warm-water conditions. Figures 6.19 and 6.20 summarize the reactor results for Cl$_3$AA. This HAA continued to form or was not degraded in the absence of a disinfectant residual. As noted above, bromine substitution in X$_2$AAs
Figure 6.11 Formation and stability of Cl₂AA in the AR study in chlorinated water: cold (12–14°C) versus warm (17–22°C) water


Figure 6.12 Formation and stability of Cl₂AA in the AR study in chloraminated water: cold (12–14°C) versus warm (17–22°C) water

Figure 6.13 Formation and stability of Cl₃AA in the AR study in chlorinated water: cold (12–14°C) versus warm (17–22°C) water


Figure 6.14 Formation and stability of Cl₃AA in the AR study in chloraminated water: cold (12–14°C) versus warm (17–22°C) water

or X$_2$AAs resulted in similar trends for stability as the fully chlorinated species. The bacterial spiking did not change the amount of degradation of the X$_2$AAs or the rate of increase of the X$_3$AAs.

Other research in this project at East St. Louis has demonstrated that HAAs can be removed by granular activated carbon (GAC) filtration, presumably by biodegradation processes within the filter bed (Singer et al. 1999). The extent of removal depended on water temperature and the residual chlorine concentration. X$_2$AAs appeared to be removed to a greater degree than

Figure 6.15 Formation and stability of HAAs in the AR study in warm chlorinated water spiked with *X. autotrophicus* (Sept. 9, 1999; temperature = 24.5°C) (ClAA not detected, BrAA ≤1 µg/L, Br$_3$AA not detected)

Figure 6.16 Formation and stability of HAAs in the AR study in warm chloraminated water spiked with *X. autotrophicus* (Sept. 9, 1999; temperature = 24.5°C) (ClAA not detected, BrAA ≤2 µg/L, Br$_3$AA not detected)
X₃AAs, but both species appear to be biodegradable. The effect of temperature and residual chlorine in the full-scale GAC study was consistent with the findings in the AR study. In addition, both studies showed that the effect was very significant for X₂AAs. However, these studies had contradictory findings to some degree, where X₃AAs were found to be somewhat degraded across the GAC filters and yet were stable in the downstream ARs. The AR study—including the bacterial spiking experiment—is consistent with the research of van der Ploeg and colleagues.

![Figure 6.17](chart1.png)  
**Figure 6.17** Formation and stability of Cl₂AA in AR study in warm (21–25°C), chlorinated water with and without bacterial spiking

![Figure 6.18](chart2.png)  
**Figure 6.18** Formation and stability of Cl₂AA in AR study in warm (21–25°C), chloraminated water with and without bacterial spiking

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that demonstrated that the enzyme from *X. autotrophicus* could degrade Cl$_2$AA and Br$_2$AA, but not Cl$_3$AA. Williams, Williams, and Gordon (1996) also saw that Cl$_3$AA was not degraded in enrichment cultures.

**Effect of batch incubation.** The effect of batch incubation on the formation and stability of HAAs was not the same in the examples discussed above (compare Figures 6.9 and 6.15). Figures 6.21 and 6.22 compare the formation and stability of Cl$_2$AA in the reactors and batch

---

![Figure 6.19](image1.png)

**Figure 6.19** Formation and stability of Cl$_3$AA in the AR study in warm (21–25°C), chlorinated water with and without bacterial spiking

![Figure 6.20](image2.png)

**Figure 6.20** Formation and stability of Cl$_3$AA in the AR study in warm (21–25°C), chloraminated water with and without bacterial spiking

(1991) that demonstrated that the enzyme from *X. autotrophicus* could degrade Cl$_2$AA and Br$_2$AA, but not Cl$_3$AA. Williams, Williams, and Gordon (1996) also saw that Cl$_3$AA was not degraded in enrichment cultures.
Figure 6.21 Formation and stability of Cl₂AA in the AR study in chlorinated water: AR versus batch incubation


Figure 6.22 Formation and stability of Cl₂AA in the AR study in chloraminated water: AR versus batch incubation

incubations for the selected experiments in which batch samples were prepared. Except for one experiment (on Sept. 9, 1999), Cl₂AA formation was somewhat higher in the batch samples than in the upstream reactors (for chlorinated or chloraminated waters; see the section on X. autotrophicus for a further discussion of this result.) In the batch samples for the dechlorinated waters for the chlorinated train (Figure 6.21), there was no consistent pattern for the stability of Cl₂AA, whereas the trend (i.e., the effect of temperature) was clear for the downstream reactors (AR2-Cl₂) where Cl₂AA decreased across the reactor is the warm-water samples (Figures 6.11 and 6.17). There was a consistent trend in the dechloraminated reactor for the chloraminated train (AR2-NH₂Cl) with Cl₂AA decreasing across the reactor in the warm-water samples (Figure 6.22); there was no significant change between the influent and effluent of the batch incubations.

**Trihalomethanes**

In addition to evaluating the formation and stability of HAAs in the reactor study, the THM species were tested. Figures 6.23 and 6.24 show the THMs in warm, chlorinated and chloraminated water, respectively, before the bacterial spiking (June 30, 1999). THM formation increased in the upstream reactor (AR1-Cl₂) in the presence of chlorine, and their concentration was higher in the batch incubation (Figure 6.23), perhaps because of a lower available chlorine concentration as a result of the chlorine demand of the biofilm. This is similar to what was observed with the HAAs (Figure 6.9). The opposite was observed in the downstream reactor; the concentration of the THMs in the batch incubation was slightly lower than in the downstream reactor (Figure 6.23). The concentration of THMs was relatively stable in the presence of chloramines (Figure 6.24).

The concentrations of the THMs were somewhat lower in the influents to the downstream reactors (AR2-Cl₂ and AR2-NH₂Cl) than in the effluents of the respective upstream reactors (AR1-Cl₂ and AR1-NH₂Cl; Figures 6.23 and 6.24). The only action that took place in between the two ARs was the addition of a dechlorination agent, which should not be destroying THMs. Perhaps some of the observed loss was through volatilization during sampling (it took 20–25 min to fill the DBP bottles at the downstream reactor [AR2-Cl₂ and AR2-NH₂Cl] influent).
Figure 6.23 Formation and stability of THMs in the AR study in warm chlorinated water (June 30, 1999; temperature = 19.2°C)

Figure 6.24 Formation and stability of THMs in the AR study in warm chloraminated water (June 30, 1999; temperature = 19.2°C)
Nonetheless, the concentrations of THMs were relatively constant in the downstream reactor (AR2-NH₂Cl) in the absence of a chloramine residual (Figure 6.24), and they increased in the absence of a chlorine residual (Figure 6.23), just as the X₃AAs increased. The latter phenomenon could be caused by decomposition of intermediates, as suggested for X₃AAs. Unlike the X₂AAs, the THMs (as expected) did not undergo biodegradation.

Figures 6.25 and 6.26 summarize the reactor results for chloroform (CHCl₃) with and without bacterial spiking. In chlorinated water with a positive residual, CHCl₃ continued to form (Figure 6.25). When the chlorine residual was absent (because of the addition of a dechlorination agent), CHCl₃ was stable (Figure 6.25). In the chloraminated train—with or without a residual—CHCl₃ concentrations were stable or decreased somewhat (Figure 6.26). Again, this may have been caused (in part) by the method of sample collection, resulting in some volatilization of THMs. However, the decreases in the concentrations of CHCl₃ in the downstream reactor (AR2-NH₂Cl; Figure 6.26) were relatively small (9 to 20 percent) compared to those observed for Cl₂AA (69 to 77 percent; Figure 6.18). As noted above, bromine substitution in THMs resulted in similar trends for stability as the fully chlorinated species. The bacterial spiking did not change the stability of the THMs.

Suspended and Fixed Biomass

Heterotrophic Plate Count Bacteria

Suspended biomass. HPC-R2A data are presented in Figures 6.27 and 6.28 for liquid samples collected in the chlorinated and chloraminated trains, respectively. All results obtained during the four cold-water experiments (which include the shake-down experiment) were pooled together, as were the three warm-water experiments. The spiking and post-spiking experiments and the batch samples are plotted on separate curves. In general, the HPC concentrations measured during the spiking and post-spiking experiments were similar to those measured during the previous experiments for the upstream reactor of the chlorinated train. In the chloraminated train, however, HPC concentrations were higher in the upstream reactor during the spiking and post-spiking experiments, which can be explained by the suspected occurrence of nitrification in this reactor.
Figure 6.25 Formation and stability of CHCl$_3$ in the AR study in warm (21–25°C), chlorinated water with and without bacterial spiking.

Figure 6.26 Formation and stability of CHCl$_3$ in the AR study in warm (21–25°C), chloraminated water with and without bacterial spiking.
Suspended HPC concentrations increased during the dechlor(am)ination step from the upstream reactor (AR1-Cl₂ and AR1-NH₂Cl) effluent to the downstream reactor (AR2-Cl₂ and AR2-NH₂Cl) influent. In the chlorinated train, these increases were (on average) 2.86 and 3.78 log in cold and warm waters, respectively, and 2.32 and 1.91 log in cold and warm waters, respectively, in the chloraminated train. Between these two reactors, a sterile solution of Na₂S₂O₃ was fed and changed weekly, which should not have been responsible for the higher concentration of biomass measured at the downstream reactor influents. Before setting up the reactors, all of the tubings were also sterilized by autoclaving. The downstream reactor (AR2-Cl₂ and AR2-NH₂Cl) influent

![Figure 6.27](image1)

**Figure 6.27** Suspended biomass (HPC-R2A) in liquid samples collected in the chlorinated train (average values for each time period)

![Figure 6.28](image2)

**Figure 6.28** Suspended biomass (HPC-R2A) in liquid samples collected in the chloraminated train (average values for each time period)
sample—which showed unexplained high biomass levels—was collected after dechlor(am)ination, from the tubing connected to the reactor. It is possible that, considering the low flow of the water supplying the reactors (1.6 mL/min), microorganisms migrated from the reactors to the inside of the tube and colonized it. To eliminate this problem, all tubings would have needed to be changed on a regular basis, which was not done because of the difficulties encountered when placing these small tubes. The suspended HPC results were affected by this problem, whereas the DBPs should have been (and were) unaffected (e.g., Figures 6.11 and 6.12). The residence time in this tube was too short for the organisms to modify the water quality significantly compared to the 12-hour residence time of the reactor.

As discussed above, HPC concentrations were higher in the downstream reactors than in the upstream reactors. However, the increase in HPC concentration within each reactor (reactor effluent concentration minus reactor influent concentration) did not follow any specific trend (Table 6.5). HPC increases within the upstream reactor of the chlorinated train (AR1-Cl₂) were much lower (0.53 log on average) than in its chloraminated counterpart (AR1-NH₂Cl; 2.58 log on average). In the downstream reactor for the chlorinated train (AR2-Cl₂), HPC increases were 0.65 log (on average) before the spiking experiment and 1.92 log during the spiking experiment, most likely as a result of the additional organisms introduced. Such an increase was not observed in AR2-NH₂Cl, where the HPC increase remained stable at 0.24 log (on average). The high HPC concentration at AR2-NH₂Cl influent \(3.3 \times 10^5\) CFU/mL on average) may explain the low biomass increase in this reactor, as previous unpublished studies have shown that biomass concentrations seem to plateau in simulated and full-scale distribution systems.

### Table 6.5

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Chlorinated train</th>
<th>Chloraminated train</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cold water (log)</td>
<td>Warm water (log)</td>
</tr>
<tr>
<td>Increase in upstream reactor</td>
<td>0.78</td>
<td>0.49</td>
</tr>
<tr>
<td>Increase in downstream reactor</td>
<td>0.99</td>
<td>0.30</td>
</tr>
</tbody>
</table>

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HPC concentrations were higher in the chloraminated train than in the chlorinated train; average differences of 1.04 and 2.52 log were calculated between AR1-NH2Cl effluent and AR1-Cl2 effluent in cold and warm waters, respectively, and 0.15 and 0.31 log between AR2-NH2Cl effluent and AR2-Cl2 effluent in cold and warm waters, respectively. These results also show that the differences between both trains were more important in the upstream than in the downstream reactors. Suspended HPC concentrations tended to be higher in the warm water than in the cold water, whereas the increase in HPC bacteria within each reactor did not follow this trend.

In general, the HPC concentrations of the reactors were higher than that of the batch samples—0.47 or 0.23 log average difference between the batch samples and AR1-Cl2 or AR2-Cl2, respectively, and 3.00 log for AR1-NH2Cl—showing the effect of the biofilm on the suspended bacteria counts. However, results were different in the downstream reactor of the chloraminated train (AR2-NH2Cl), where the batch HPC concentrations were higher than in the reactor with an average difference of 0.43 log.

**Fixed biomass.** As for the biofilm results (Figure 6.29), higher HPC concentrations were measured in warm water than in cold water. These seasonal differences were more pronounced in the upstream reactors (1.52 log average difference between the cold and warm water samplings in AR1-Cl2 and 0.96 log in AR1-NH2Cl) than in the downstream reactors (1.05 log average difference between the cold- and warm-water samplings in AR2-Cl2 and 0.68 log in AR2-NH2Cl). These results also show that the seasonal differences were more important in the chlorinated train than in the chloraminated train.

In the chlorinated train (not including the spiking experiment), HPC–biofilm concentrations were 3.51 ± 0.82 logs higher (on average) in the downstream reactor than in the upstream reactor and 2.36 ± 0.54 logs higher (on average) in the downstream reactor than in the upstream reactor in the chloraminated train. In cold water, HPC–biofilm concentrations were 1.85 log higher (on average) in AR1-NH2Cl than in AR1-Cl2 (upstream reactors) and 0.90 log higher (on average) in warm water. Similarly, HPC concentrations were 0.38 and 0.18 log higher (on average) in AR2-NH2Cl than in AR2-Cl2 in cold and warm waters, respectively. As for the biofilm HPC bacteria, these results show that the difference between the chloraminated and chlorinated trains was more important in the upstream reactors.

These results are somewhat surprising considering that it is assumed that chloramines maintain lower levels of biomass because of its higher penetration capabilities. However, the
average level of chlorine in the chlorinated reactor was slightly higher (2.47 mg/L free chlorine and 2.82 mg/L total chlorine) than in the chloraminated reactor (2.56 mg/L total chlorine) (Figure 6.5).

**Relationship between degradation of the X₂AAs and the biomass.** The X₂AAs were degraded in the warm water in the downstream reactors (AR2-Cl₂ and AR2-NH₂Cl; Figures 6.11 and 6.12). In the chloraminated train, the X₂AAs were not degraded in warm water in the downstream batch incubations (AR2-NH₂Cl batch; Figure 6.22), whereas the X₂AAs were sometimes degraded in either cold or warm water in the downstream batch incubations in the chlorinated train (AR2-Cl₂ batch; Figure 6.21). The fixed biomass was consistently associated with biodegradation of the X₂AAs in the warm-water experiments. HPC–biofilm concentrations were highest in either train in the downstream reactors in the warm-water experiments (Figure 6.29). However, HPC–biofilm concentrations were relatively high in either train in the downstream reactors in the cold-water experiments. These results suggest that an increase in both biomass and temperature may be needed to biodegrade the X₂AAs. In cold water, we might see a decrease in X₂AAs, but at much higher residence time than 12 hours (lower metabolic activity of microorganisms at low temperature and lower degradation of X₂AAs).

**Xanthobacter autotrophicus**

During each sampling, sample aliquots were filtered through a membrane and incubated on nutrient agar for 5–7 days at 28°C to enumerate *X. autotrophicus*. Suspected colonies were
observed for some of the samples (Table 6.6). These colonies were counted, picked, and streaked twice on nutrient agar plates. Suspected colonies that were observed on the second-streaked plate (Table 6.7) were picked and resuspended in 500–1,000 μL HTE buffer, and the DNA was heat extracted (95°C for 10 min). These DNA extracts were screened by PCR amplification to confirm that the colonies from which they result were X. autotrophicus. Each sample collected was also filtered on membrane, and the DNA extracted directly from the membrane.

All the samples from the July 14, 1999, experiment were screened for the presence of X. autotrophicus by PCR amplification targeting all three dehalogenase genes (three primer sets). All samples from the Mar. 17 and June 16, 1999, experiments were screened for the presence of the dhlA gene, but only the downstream reactor samples were screening with the dhlB and dhlC primers. Because all of these samples were negative for X. autotrophicus, only selected samples (downstream reactors) were screened using all three genes for the other experiments. Results obtained from the regular samplings using the molecular methods demonstrated that none of the samples or suspected colonies were X. autotrophicus. X. autotrophicus was detected in some of the samples from the spike and post-spike experiments, which confirms the validity of the method.

Table 6.7 lists the samples that were analyzed by the culturing and molecular methods for the presence of X. autotrophicus. Results from the streaked plates show that X. autotrophicus was present in the downstream reactors immediately following the spiking experiment, except in the biofilm sample of the chlorinated train. The post-spike experiment indicated that X. autotrophicus was still detected at the effluent of the seeded reactors until at least a week after spiking. As observed immediately after spiking, X. autotrophicus was absent in the biofilm sample of the chlorinated train. After spiking, X. autotrophicus was present in the batch incubations collected at the reactor influent, which suggests that the spiked organism may have colonized the tubing feeding the downstream reactor during seeding. The presence of X. autotrophicus in the biofilm sample of AR1-Cl2 remains unexplained; however, the number of suspected colonies was very low (3 CFU; Table 6.6). The presence of X. autotrophicus in the membrane concentrates confirmed most of these results (Table 6.8).

As discussed above, X2AAs were degraded in warm water in the downstream batch incubation in the chlorinated train on Sept. 9, but not on June 30, 1999 (Figures 6.9, 6.15, and 6.21). This may have resulted from the presence of X. autotrophicus in the batch incubation sample collected on September 9 (Table 6.7).
Table 6.6
Potential X. autotrophicus colonies recovered on nutrient agar plates

<table>
<thead>
<tr>
<th>Sample locations</th>
<th>Cold-water samplings</th>
<th>Warm-water samplings</th>
<th>Spike experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>02/24/99</td>
<td>03/17/99</td>
<td>03/31/99</td>
</tr>
<tr>
<td>AR1-Cl₂</td>
<td>Influent</td>
<td>NA</td>
<td>NG*</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>NA</td>
<td>NTC</td>
</tr>
<tr>
<td></td>
<td>Biofilm</td>
<td>NA</td>
<td>NTC</td>
</tr>
<tr>
<td></td>
<td>Batch</td>
<td>NA</td>
<td>NG</td>
</tr>
<tr>
<td>AR2-Cl₂</td>
<td>Influent</td>
<td>NA</td>
<td>NTC</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>NA</td>
<td>NTC</td>
</tr>
<tr>
<td></td>
<td>Biofilm</td>
<td>2.90E+03</td>
<td>3.17E+03</td>
</tr>
<tr>
<td></td>
<td>Batch</td>
<td>3.00E+02</td>
<td>NA</td>
</tr>
<tr>
<td>AR1-NH₂Cl</td>
<td>Influent</td>
<td>NA</td>
<td>NTC</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>NA</td>
<td>NTC</td>
</tr>
<tr>
<td></td>
<td>Biofilm</td>
<td>NA</td>
<td>NTC</td>
</tr>
<tr>
<td></td>
<td>Batch</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>AR2-NH₂Cl</td>
<td>Influent</td>
<td>NA</td>
<td>TNTC</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>3.00E+03</td>
<td>4.67E+03</td>
</tr>
<tr>
<td></td>
<td>Biofilm</td>
<td>2.40E+03</td>
<td>2.03E+03</td>
</tr>
<tr>
<td></td>
<td>Batch</td>
<td>1.40E+04</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA: not analyzed.
* NG: No growth.
† NTC: No typical colonies.
‡ TNTC: Too numerous to count.
Table 6.7
Confirmed samples for the presence of *X. autotrophicus* (colonies streaked twice)

<table>
<thead>
<tr>
<th>Sample locations</th>
<th>Cold-water samplings</th>
<th>Warm-water samplings</th>
<th>Spike experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>02/24/99</td>
<td>03/17/99</td>
<td>03/31/99</td>
</tr>
<tr>
<td>AR1-Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Influent</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Effluent</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Biofilm</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Batch</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>AR2-Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Influent</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Effluent</td>
<td>NA</td>
<td>NA</td>
<td>–</td>
</tr>
<tr>
<td>Biofilm</td>
<td>NA</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Batch</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>AR1-NH&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>Influent</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Effluent</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Biofilm</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Batch</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>AR2-NH&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>Influent</td>
<td>NA</td>
<td>–</td>
</tr>
<tr>
<td>Effluent</td>
<td>NA</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Biofilm</td>
<td>NA</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Batch</td>
<td>NA</td>
<td>NA</td>
<td>–</td>
</tr>
</tbody>
</table>

NA: not analyzed.
* -: Absence of *X. autotrophicus* confirmed with all three genes targeted.
† +: Presence of *X. autotrophicus* confirmed with all three genes targeted.
‡ dhlA: Only the dhlA gene was present.
Table 6.8
Confirmed samples for the presence of *X. autotrophicus* (direct from membranes)

<table>
<thead>
<tr>
<th>Sample locations</th>
<th>Cold-water samplings</th>
<th>Warm-water samplings</th>
<th>Spike experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>02/24/99 03/17/99 03/31/99 04/06/99</td>
<td>06/16/99 06/30/99 07/14/99</td>
<td>09/02/99 09/09/99</td>
</tr>
<tr>
<td>AR1-Cl₂</td>
<td>Influent NA – * NA NA</td>
<td>– NA –</td>
<td>NA NA</td>
</tr>
<tr>
<td></td>
<td>Effluent NA – NA NA NA</td>
<td>– NA –</td>
<td>NA NA</td>
</tr>
<tr>
<td></td>
<td>Biofilm NA – NA NA NA</td>
<td>– NA –</td>
<td>NA NA</td>
</tr>
<tr>
<td></td>
<td>Batch NA – NA NA NA</td>
<td>NA NA NA</td>
<td>NA NA</td>
</tr>
<tr>
<td>AR2-Cl₂</td>
<td>Influent NA NA NA NA NA</td>
<td>NA NA NA</td>
<td>NA NA</td>
</tr>
<tr>
<td></td>
<td>Effluent – – – – –</td>
<td>– – –</td>
<td>+ † +</td>
</tr>
<tr>
<td></td>
<td>Biofilm – – – – –</td>
<td>– – –</td>
<td>+ +</td>
</tr>
<tr>
<td></td>
<td>Batch NA NA NA NA NA</td>
<td>NA NA NA</td>
<td>NA NA</td>
</tr>
<tr>
<td>AR1-NH₂Cl</td>
<td>Influent NA – NA NA NA</td>
<td>– NA –</td>
<td>NA NA</td>
</tr>
<tr>
<td></td>
<td>Effluent NA – NA NA NA</td>
<td>– NA –</td>
<td>NA NA</td>
</tr>
<tr>
<td></td>
<td>Biofilm NA – NA NA NA</td>
<td>– NA –</td>
<td>NA NA</td>
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<tr>
<td></td>
<td>Batch NA NA NA NA NA</td>
<td>NA NA –</td>
<td>NA NA</td>
</tr>
<tr>
<td>AR2-NH₂Cl</td>
<td>Influent NA NA NA NA NA</td>
<td>NA NA NA</td>
<td>NA NA</td>
</tr>
<tr>
<td></td>
<td>Effluent – – – – –</td>
<td>– – –</td>
<td>+ +</td>
</tr>
<tr>
<td></td>
<td>Biofilm – – – – –</td>
<td>– – –</td>
<td>+ +</td>
</tr>
<tr>
<td></td>
<td>Batch NA NA NA NA NA</td>
<td>– NA NA</td>
<td>NA NA</td>
</tr>
</tbody>
</table>

NA: not analyzed.

* * –: Absence of *X. autotrophicus* confirmed with all three genes targeted.

† +: Presence of *X. autotrophicus* confirmed with all three genes targeted.
CHAPTER 7
CONTROL OF HALOACETIC ACID CONCENTRATIONS BY BIOFILTRATION:
A CASE STUDY

INTRODUCTION

Recent evidence from the literature (e.g., Williams, Williams, and Rindfleisch 1995; Williams, Williams, and Gordon 1996; Williams and Williams 1998), along with the experimental findings discussed in chapter 6, indicate that the HAAs can be biodegraded in water distribution systems in the absence of a chlorine residual suggesting that biodegradation can be a mechanism for lowering HAA levels during drinking water treatment. This chapter presents the results of a plant-scale study examining the impact of biofiltration following chlorination for the control of HAA concentrations in finished drinking water.

PROCEDURES

This study was conducted at the Illinois American Water Company’s water treatment plant at East St. Louis, Ill. The source of water at East St. Louis is the Mississippi River. At the beginning of this study, the raw water was prechlorinated, coagulated, and settled before being filtered either through sand filters (Aldrich filters) or GAC/sand filters. A free chlorine residual was maintained across the sand filters, but the applied chlorine to the GAC filters dissipated across the filter bed. Early in the study, the East St. Louis facility switched to prechloramination of its raw water to control the extent of DBP production during pretreatment. Again, a chlorine residual (this time a combined residual) was maintained across the sand filters, but not always across the GAC bed. The filtered water from each set of filters was subsequently blended, then treated with additional chlorine and ammonia before being pumped into the distribution system. HAAs and THMs were formed as a result of prechlorination and were still formed, albeit to a lesser degree, as a result of prechloramination. Figure 7.1 is a flow sheet for the East St. Louis facility.

At the beginning of this study, one bank of GAC filters contained aged GAC that had been in place for more than 1 year; another bank of GAC filters contained virgin GAC that had been freshly placed in the filter bed. The aged GAC bed contained 0.432 m (17 in.) of GAC with an
effective size of 0.55–0.75 mm, over 0.305 m (12 in.) of sand with an effective size of 0.40–0.55 mm. The average hydraulic loading to the filter was 4.9 m/hr, providing an empty bed contact time of 9.0 min for the entire bed. The virgin GAC bed consisted of 0.381 m (15 in.) of carbon with an effective size of 0.55–0.75 mm, over 0.305 m (12 in.) of 0.40–0.55 mm sand; the average hydraulic loading was also 4.9 m/hr, with an empty bed contact time of 8.4 min for the entire bed. The sand filter contained 0.763 m (30 in.) of 0.40–0.55 mm sand. The average hydraulic loading to the sand filter was 2.9 m/hr, providing an empty bed contact time of 15.8 min. The aged GAC was presumed to be bioactive because of the lack of a chlorine residual in the filter effluent.

Samples were collected on approximately a monthly basis from November 1998 to August 1999 from various locations in the water treatment plant and distribution system for analysis of total THMs (THM4) and total HAAs (all nine bromine- and chlorine-containing HAAs [HAA9]). Following collection, the samples were shipped by overnight carrier to the respective analytical laboratories. THM analyses were performed by the American Water Works Services Company’s Water Quality and Research Laboratory in Belleville, Ill., using standard procedures in accordance with USEPA Method 502.2 (USEPA 1995b). HAA analyses were conducted by the University of North Carolina’s Drinking Water Research Center using a modified version of method 6251B Standard Methods (APHA, AWWA, and WEF 1995) and USEPA Method 552 (USEPA 1990a) developed by Brophy, Weinberg, and Singer (1999) and described in chapter 2 and appendix A.

Figure 7.1 Flow sheet for East St. Louis treatment plant
For the THM samples, the chlorine residual was quenched with sodium thiosulfate. The HAA samples were quenched with ammonium sulfate, and sodium azide was added as a preservative.

Free and total chlorine residuals were measured by plant personnel when the samples were collected. Other relevant water quality parameters were also measured (e.g., TOC, pH, and temperature) to assist in data analysis and interpretation.

RESULTS AND DISCUSSION

Table 7.1 summarizes the data collected for the sand (Aldrich) filters. THM and HAA concentrations, along with the corresponding chlorine residuals, are shown in Figures 7.2 and 7.3.

Table 7.1
Summary of data for sand filter influent and effluent

<table>
<thead>
<tr>
<th>Date</th>
<th>Location</th>
<th>Temperature (°C)</th>
<th>Cl2 residual* (mg/L)</th>
<th>TOC (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/23/98</td>
<td>Influent</td>
<td>NA</td>
<td>2.0</td>
<td>3.19</td>
<td>80.7</td>
<td>81.8</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>NA</td>
<td>NA</td>
<td>3.04</td>
<td>84.9</td>
<td>79.7</td>
</tr>
<tr>
<td>12/14/98</td>
<td>Influent</td>
<td>11.7</td>
<td>1.8</td>
<td>3.77</td>
<td>61.2</td>
<td>81.0</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>11.1</td>
<td>1.4</td>
<td>3.77</td>
<td>80.5</td>
<td>84.9</td>
</tr>
<tr>
<td>01/26/99</td>
<td>Influent</td>
<td>6.4</td>
<td>4.3</td>
<td>3.95</td>
<td>9.9</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>5.9</td>
<td>3.7</td>
<td>3.66</td>
<td>9.9</td>
<td>20.6</td>
</tr>
<tr>
<td>02/09/99</td>
<td>Influent</td>
<td>9.3</td>
<td>4.0</td>
<td>3.78</td>
<td>15.6</td>
<td>29.3</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>7.8</td>
<td>3.9</td>
<td>3.2</td>
<td>15.3</td>
<td>27.3</td>
</tr>
<tr>
<td>03/09/99</td>
<td>Influent</td>
<td>9.5</td>
<td>4.4</td>
<td>3.03</td>
<td>17.8</td>
<td>21.1</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>7.5</td>
<td>3.9</td>
<td>2.91</td>
<td>17.0</td>
<td>21.0</td>
</tr>
<tr>
<td>04/20/99</td>
<td>Influent</td>
<td>16.7</td>
<td>4.0</td>
<td>3.91</td>
<td>14.3</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>14.4</td>
<td>3.8</td>
<td>3.72</td>
<td>13.3</td>
<td>25.1</td>
</tr>
<tr>
<td>05/11/99</td>
<td>Influent</td>
<td>21.2</td>
<td>4.4</td>
<td>3.74</td>
<td>29.7</td>
<td>38.7</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>20.3</td>
<td>4.2</td>
<td>3.69</td>
<td>31.8</td>
<td>41.0</td>
</tr>
<tr>
<td>06/08/99</td>
<td>Influent</td>
<td>26.8</td>
<td>4.0</td>
<td>4.66</td>
<td>24.7</td>
<td>32.0</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>25.9</td>
<td>3.9</td>
<td>4.57</td>
<td>28.3</td>
<td>38.2</td>
</tr>
<tr>
<td>08/10/99</td>
<td>Influent</td>
<td>29.1</td>
<td>1.8</td>
<td>4.59</td>
<td>85.8</td>
<td>63.3</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>28.8</td>
<td>1.2</td>
<td>4.57</td>
<td>77.1</td>
<td>52.5</td>
</tr>
</tbody>
</table>

NA: not analyzed
* Raw water chlorination switched from free chlorine to combined chlorine in January 1999. All residuals reported after that time are total chlorine residuals. It is not clear why the residuals dropped again in August 1999.
It should be noted that the East St. Louis facility switched from prechlorination to prechloramination in January 1999. This accounts for the large increase in chlorine residual in the filter influent beginning in January (although it is not clear what happened in August 1999), and the fact that the chlorine residual shifted from free chlorine to combined chlorine (not shown). Note also that the THM4 and HAA9 concentrations in the filter influent decreased markedly from November and December to January when the utility switched from prechlorination to prechloramination, although part of this decrease may also be attributed to the slower reaction kinetics associated with the winter temperatures.

Figure 7.2 THM and residual chlorine concentrations for sand filter influent and effluent

Figure 7.3 HAA and residual chlorine concentrations for sand filter influent and effluent
As the temperature increased again from April to August, the THM and HAA concentrations in the filter influent also increased. The results in Table 7.1 and Figures 7.2 and 7.3 show that THM and HAA concentrations remain essentially unchanged as the water passes through the sand filter. Additionally, the THM and HAA concentrations in the filter influent are similar to each other (see Figures 7.4) and remain similar to each other in the filter effluent (see Figure 7.5).

In contrast, the results for the aged GAC filter illustrated in Table 7.2 and Figure 7.6 show a significant reduction in the HAA9 concentration across the GAC filter. HAA9 concentrations decreased from 16 to 58 percent, with the greatest decreases occurring during the warmer months.
when the residual chlorine concentration in the filter effluent was zero or approaching zero. There was no corresponding decrease in THM4 (see Figure 7.7) or TOC concentrations (Table 7.2), suggesting that the reduction in HAA concentrations was not attributable to adsorption on the GAC. Instead, it is believed that the reduction in HAA concentrations resulted from biological degradation of the HAAs, a phenomenon that has been reported previously in the literature (e.g., Singer et al. 1993; Williams, Williams, and Rindfleisch 1995; Williams, Williams, and Gordon 1996; Williams and Williams 1998) and that was demonstrated in chapter 6.

As a result of this removal of HAAs across the GAC bed, there is a noticeable difference in the relative concentrations of THMs and HAAs in the GAC filter influent and effluent (compare

<table>
<thead>
<tr>
<th>Date</th>
<th>Location</th>
<th>Temperature (°C)</th>
<th>Cl₂ residual* (mg/L)</th>
<th>TOC (mg/L)</th>
<th>THM4 (µg/L)</th>
<th>HAA9 (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/23/98</td>
<td>Influent</td>
<td>NA</td>
<td>1.8</td>
<td>2.88</td>
<td>78.7</td>
<td>69.0</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>NA</td>
<td>NA</td>
<td>2.72</td>
<td>68.5</td>
<td>35.5</td>
</tr>
<tr>
<td>12/14/98</td>
<td>Influent</td>
<td>11.1</td>
<td>2.4</td>
<td>3.41</td>
<td>66.9</td>
<td>89.7</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>8.9</td>
<td>0.2</td>
<td>3.41</td>
<td>58.2</td>
<td>40.3</td>
</tr>
<tr>
<td>01/26/99</td>
<td>Influent</td>
<td>7.0</td>
<td>5.1</td>
<td>3.42</td>
<td>12.7</td>
<td>29.1</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.7</td>
<td>1.3</td>
<td>3.52</td>
<td>13.8</td>
<td>24.5</td>
</tr>
<tr>
<td>02/09/99</td>
<td>Influent</td>
<td>3.9</td>
<td>5.1</td>
<td>3.32</td>
<td>17.9</td>
<td>33.1</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>4.8</td>
<td>1.1</td>
<td>3.15</td>
<td>21.8</td>
<td>25.6</td>
</tr>
<tr>
<td>03/09/99</td>
<td>Influent</td>
<td>8.2</td>
<td>5.3</td>
<td>3.27</td>
<td>18.2</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>4.1</td>
<td>1.3</td>
<td>2.81</td>
<td>19.8</td>
<td>20.9</td>
</tr>
<tr>
<td>04/20/99</td>
<td>Influent</td>
<td>12.6</td>
<td>4.8</td>
<td>4.02</td>
<td>17.7</td>
<td>32.7</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>10.9</td>
<td>0.6</td>
<td>3.72</td>
<td>20.8</td>
<td>24.8</td>
</tr>
<tr>
<td>05/11/99</td>
<td>Influent</td>
<td>18.9</td>
<td>6.1</td>
<td>3.68</td>
<td>37.2</td>
<td>48.0</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>18.5</td>
<td>0.7</td>
<td>3.59</td>
<td>41.2</td>
<td>33.2</td>
</tr>
<tr>
<td>06/08/99</td>
<td>Influent</td>
<td>25.1</td>
<td>4.5</td>
<td>4.56</td>
<td>50.8</td>
<td>49.3</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>24.4</td>
<td>0.4</td>
<td>4.26</td>
<td>52.2</td>
<td>23.7</td>
</tr>
<tr>
<td>08/10/99</td>
<td>Influent</td>
<td>27.5</td>
<td>2.6</td>
<td>4.32</td>
<td>40.4</td>
<td>53.1</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>27.4</td>
<td>0.1</td>
<td>4.26</td>
<td>49.3</td>
<td>5.9</td>
</tr>
</tbody>
</table>

NA: not analyzed.

* Raw water chlorination switched from free chlorine to combined chlorine in January 1999. All residuals reported after that time are total chlorine residuals.
Figures 7.8 and 7.9). The results are most striking in the warmer months of the year, when the chlorine residuals are lowest and the temperature is elevated. Under these conditions, biological activity is expected to be greatest.

Results for the virgin GAC bed (not shown), which was placed into operation on Nov. 11, 1998, were similar to those for the aged GAC bed after about 2 months. Initially, significant reductions in TOC and THM4 concentrations accompanied the HAA9 reductions, suggesting removal by adsorption. However, after 2 months, there was little change in the TOC and THM4 concentrations across the virgin GAC bed, but reductions in HAA9 continued. Because the HAA species have very low acidity constants, they tend not to be adsorbed very effectively by GAC under ambient pH conditions.
Although Mississippi River water does contain some bromide, dichloroacetic acid was the principal dihaloacetic acid species and trichloroacetic acid was the dominant trihaloacetic acid species. Table 7.3 and Figures 7.10 and 7.11 show that dichloroacetic acid concentrations were lowered to a greater extent than trichloroacetic acid concentrations across the aged GAC filters. Correspondingly, Tables 7.4 and 7.5 show that the overall dihaloacetic acid concentration was reduced to a greater degree than the trihaloacetic acid species, on both a weight and a molar basis.

Figure 7.8 Comparison of HAA and THM concentrations for aged GAC filter effluent

Figure 7.9 Comparison of HAA and THM concentrations for aged GAC filter influent
This is consistent with previously published reports (Williams and Williams 1998) and the results of the AR studies described in chapter 6, although in both of those studies, no biodegradation of trihaloacetic acids was observed. Perhaps the activated carbon facilitates or catalyzes the removal of the trihaloacetic acid species but, as noted above, this is most likely not attributable to adsorption on the GAC because of the low acidity constants of the trihaloacetic acid species.

Table 7.3
Behavior of dichloroacetic acid and trichloroacetic acid across GAC filters

<table>
<thead>
<tr>
<th>Date</th>
<th>Cl₂AA (µg/L) GAC influent</th>
<th>Cl₂AA (µg/L) GAC effluent</th>
<th>Cl₃AA (µg/L) GAC influent</th>
<th>Cl₃AA (µg/L) GAC effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/23/98</td>
<td>20.7</td>
<td>4.3</td>
<td>37.0</td>
<td>24.4</td>
</tr>
<tr>
<td>12/14/98</td>
<td>26.6</td>
<td>4.5</td>
<td>47.6</td>
<td>31.1</td>
</tr>
<tr>
<td>01/26/99</td>
<td>13.3</td>
<td>11.4</td>
<td>7.6</td>
<td>6.5</td>
</tr>
<tr>
<td>02/09/99</td>
<td>20.6</td>
<td>14.7</td>
<td>8.0</td>
<td>7.2</td>
</tr>
<tr>
<td>03/09/99</td>
<td>12.5</td>
<td>9.9</td>
<td>8.0</td>
<td>7.2</td>
</tr>
<tr>
<td>04/20/99</td>
<td>19.0</td>
<td>14.0</td>
<td>8.6</td>
<td>6.7</td>
</tr>
<tr>
<td>05/11/99</td>
<td>24.8</td>
<td>16.1</td>
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<td>9.7</td>
</tr>
<tr>
<td>06/08/99</td>
<td>25.3</td>
<td>8.3</td>
<td>16.9</td>
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<td>08/10/99</td>
<td>25.6</td>
<td>1.1</td>
<td>13.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Figure 7.10 Comparison between trichloroacetic acid concentrations in aged GAC filter influent and effluent
Table 7.6 presents the HAA results in terms of the distribution of bromine-containing and chlorine-containing HAA species. “Cl-incorporated” refers to the sum of the chlorine-containing species times the number of chlorine atoms in each species, calculated on a weight basis as chlorine. “Br-incorporated” is calculated in the same manner for the amount of bromine incorporated into the HAA species, and is calculated as bromine. Table 7.7 presents the same

<table>
<thead>
<tr>
<th>Date</th>
<th>Sum dihaloacetic acids (µg/L)</th>
<th>Sum trihaloacetic acids (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GAC influent</td>
<td>GAC effluent</td>
</tr>
<tr>
<td>12/14/98</td>
<td>29.7</td>
<td>8.6</td>
</tr>
<tr>
<td>01/26/99</td>
<td>16.5</td>
<td>11.5</td>
</tr>
<tr>
<td>02/09/99</td>
<td>22.8</td>
<td>16.4</td>
</tr>
<tr>
<td>03/09/99</td>
<td>14.7</td>
<td>12.4</td>
</tr>
<tr>
<td>04/20/99</td>
<td>21.6</td>
<td>16.9</td>
</tr>
<tr>
<td>05/11/99</td>
<td>28.5</td>
<td>19.1</td>
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<td>1.3</td>
</tr>
<tr>
<td>08/10/99</td>
<td>30.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 7.11 Comparison between dichloroacetic acid concentrations in aged GAC filter influent and effluent
information on a molar basis, (i.e., the sum of all HAA species times the number of chlorine or bromine atoms in each species times the molecular weight of each species). Tables 7.6 and 7.7 show that the chlorinated species dominated the overall HAA9 concentration, and that the reduction in HAA9 concentrations across the GAC filters was appreciable for both the chlorine- and the bromine-containing species.

Table 7.5
Behavior of dihaloacetic acids and trihaloacetic acids across GAC filters; molar basis

<table>
<thead>
<tr>
<th>Date</th>
<th>Sum dihaloacetic acids (µM/L)</th>
<th>Sum trihaloacetic acids (µM/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GAC influent</td>
<td>GAC effluent</td>
</tr>
<tr>
<td>12/14/98</td>
<td>0.224</td>
<td>0.066</td>
</tr>
<tr>
<td>01/26/99</td>
<td>0.120</td>
<td>0.086</td>
</tr>
<tr>
<td>02/09/99</td>
<td>0.172</td>
<td>0.124</td>
</tr>
<tr>
<td>03/09/99</td>
<td>0.109</td>
<td>0.093</td>
</tr>
<tr>
<td>04/20/99</td>
<td>0.162</td>
<td>0.128</td>
</tr>
<tr>
<td>05/11/99</td>
<td>0.214</td>
<td>0.145</td>
</tr>
<tr>
<td>06/08/99</td>
<td>0.222</td>
<td>0.010</td>
</tr>
<tr>
<td>08/10/99</td>
<td>0.250</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Table 7.6
Behavior of chlorine-containing and bromine-containing HAAs across GAC filters; weight basis

<table>
<thead>
<tr>
<th>Date</th>
<th>Sum Cl-incorporated HAAs (µg/L as Cl)</th>
<th>Sum Br-incorporated HAAs (µg/L as Br)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GAC influent</td>
<td>GAC effluent</td>
</tr>
<tr>
<td>12/14/98</td>
<td>219</td>
<td>131</td>
</tr>
<tr>
<td>01/26/99</td>
<td>59.3</td>
<td>50.6</td>
</tr>
<tr>
<td>02/09/99</td>
<td>71.1</td>
<td>65.0</td>
</tr>
<tr>
<td>03/09/99</td>
<td>57.2</td>
<td>52.6</td>
</tr>
<tr>
<td>04/20/99</td>
<td>71.5</td>
<td>57.4</td>
</tr>
<tr>
<td>05/11/99</td>
<td>98.6</td>
<td>81.3</td>
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<td>06/08/99</td>
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<td>19.6</td>
</tr>
<tr>
<td>08/10/99</td>
<td>104</td>
<td>9.3</td>
</tr>
</tbody>
</table>
With respect to the overall objectives of this project, some additional observations about the relative HAA9 and THM4 concentrations at East St. Louis are apparent. Tables 7.1 and 7.2, Figures 7.4 and 7.5, and Figures 7.8 and 7.9 indicate that, for the sand filter, in most cases, HAAs were dominant over the THMs in both the influent and the effluent, regardless of whether free chlorine or combined chlorine was used for pretreatment. However, because of the presumed biodegradation of HAAs within the GAC filters, THMs were the dominant DBP species in the effluent of the GAC filters, whereas HAAs were dominant in the filter influent.

### CONCLUSIONS

The research reported in this chapter has demonstrated that HAAs can be removed by GAC filtration, presumably by biodegradation processes within the filter bed. The extent of removal depends on water temperature and the residual chlorine concentration. Removal of HAAs was greatest when water temperatures were high and residual chlorine concentrations were low. Dihaloacetic acids appear to be removed to a greater degree than trihaloacetic acids, but both groups were removed. The fact that the HAAs are degraded but the THMs are not is a significant factor that influences the relative concentrations of these two classes of DBP species in finished drinking water. Hence, water treatment facilities may produce HAAs within the plant and still be able to remove them before distribution.

### Table 7.7

Behavior of chlorine-containing and bromine-containing HAAs across GAC filters; molar basis

<table>
<thead>
<tr>
<th>Date</th>
<th>Sum Cl-incorporated HAAs (µM/L)</th>
<th>Sum Br-incorporated HAAs (µM/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GAC influent</td>
<td>GAC effluent</td>
</tr>
<tr>
<td>12/14/98</td>
<td>1.42</td>
<td>0.82</td>
</tr>
<tr>
<td>01/26/99</td>
<td>0.39</td>
<td>0.33</td>
</tr>
<tr>
<td>02/09/99</td>
<td>0.50</td>
<td>0.44</td>
</tr>
<tr>
<td>03/09/99</td>
<td>0.38</td>
<td>0.35</td>
</tr>
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<td>04/20/99</td>
<td>0.49</td>
<td>0.41</td>
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<td>05/11/99</td>
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<td>0.55</td>
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<td>06/08/99</td>
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<td>0.12</td>
</tr>
<tr>
<td>08/10/99</td>
<td>0.78</td>
<td>0.06</td>
</tr>
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</table>
CHAPTER 8
CONCLUSIONS

This project has shown that several significant water quality and treatment factors influence the relative distribution of HAAs and THMs in treated drinking water, as well as the relative distribution of species within each of these major DBP groups. These conclusions are based on experimental results from: chlorination of a variety of different waters under controlled laboratory conditions; measurements made in selected full-scale water treatment systems (within the treatment plant as well as in the distribution system); and a comprehensive analysis of the first 12 months of ICR data. Issues of the stability of the different DBP species, especially their biodegradability, were also evaluated in this project.

All nine bromine- and chlorine-containing HAAs were studied in this project to obtain a complete assessment of overall HAA occurrence and HAA9 behavior relative to the four bromine- and chlorine-containing THMs. The study of all nine HAA species was made possible only after the existing HAA6 analytical methodology was modified to allow for more precise and more robust analysis of the remaining HAA3 species. A standard operating procedure for HAA9 was developed and is included in this report.

The sections that follow outline the conclusions that can be drawn from the results of the different component studies that comprised this project.

pH

pH was shown to be one of the principal factors controlling the distribution of HAAs and THMs and, therefore, the relative dominance of HAAs and THMs in finished drinking water. HAA9 concentrations tend to decrease with increasing pH whereas THM4 concentrations tend to increase with increasing pH. However, among the HAA species, the formation of the trihalogenated acetic acid species decreases with increasing pH whereas the formation of the dihalogenated acetic acid species is relatively independent of pH. The bromine-containing species in each class of HAAs behave in the same manner with respect to pH as their chlorine-containing counterparts.
In the controlled laboratory chlorination studies, increasing the pH from 6 to 8 increased the production of all four THM species, decreased the production of the trihalogenated acetic acid species, and had little effect on the production of the dihalogenated acetic acid species. The formation of monohalogenated acetic acid species tended to be slightly higher at pH 8 than at pH 6. The formation of THM4 was higher than the formation of HAA9 at pH 8, and the reverse was true at pH 6.

The results from analysis of the first 12 months of ICR data also showed that the ratio of total HAAs to total THMs increased with decreasing chlorination pH. Chlorinated surface water systems that had filtered water pH values less than 7 (and were therefore presumed to be chlorinated at pH values less than 7) were found to have higher HAA9/THM4 ratios than systems with filtered water pH values greater than 8. This was observed for filtered water, finished water at the POE to the distribution system, and water from average distribution system locations.

The results from sampling at the full-scale water treatment plants showed that HAA concentrations exceeded THM concentrations only when chlorination was practiced after coagulation at pH values less than 6.5–7.0, or for chlorination of raw waters with high concentrations of hydrophobic NOM (i.e., high SUVA values; see below). For all other cases, THM concentrations exceeded HAA concentrations.

**NATURAL ORGANIC MATTER**

The characteristics of the NOM in the water being chlorinated have a major impact on the relative distribution of THMs and HAAs. In general, waters with high hydrophobic organic carbon concentrations and high SUVA values tend to produce more HAAs relative to THMs than waters having low SUVA values, which are dominated by hydrophilic organic carbon.

In the controlled laboratory chlorination experiments, the waters with higher SUVA values produced slightly higher HAA9/THM4 ratios. SUVA, as a surrogate parameter for the hydrophobicity and aromaticity of NOM in water, was shown to be moderately correlated with the HAA9 and THM4 formation potential. The slightly stronger correlation observed between HAAFP and SUVA suggests that the HAA precursors are more aromatic in nature than the THM precursors. The hydrophobic fractions from almost all waters gave higher formation potentials for X2AA, X3AA, and THM4 than the corresponding hydrophilic fractions from the same water,
which is consistent with the SUVA findings. XAA precursors, however, appeared to be more hydrophilic. These results confirm earlier work indicating that hydrophobic carbon, which is rich in aromatic content and phenolic hydroxyl groups, is the main precursor of DBPs. The HAA9/THM4 ratio was higher in the hydrophobic fractions than in the hydrophilic fractions at pH 8, but no significant difference was observed at pH 6. The results suggest that aliphatic carbon may play a more important role in THM formation than in HAA formation.

Along these same lines, in the controlled laboratory experiments, coagulation removed substantial amounts of DBP precursors and shifted the distribution of HAA and THM species. In general, the waters with higher SUVA values, which usually contained more hydrophobic and aromatic carbon, were more amenable to coagulation. For all of the controlled laboratory experiments, coagulation removed more UV$_{254}$ than TOC, which lowered the SUVA values. For the high-SUVA waters, HAA9 precursors were removed to a greater degree than THM4 precursors. These results are consistent with the belief that HAA precursors are more hydrophobic and aromatic than THM precursors.

Similar findings were observed for the full-scale water treatment facilities in that HAA9 concentrations were found to exceed THM concentrations only for waters with high hydrophobic organic carbon concentrations or for waters that were chlorinated after coagulation.

Also, both the controlled laboratory study and the field study showed that, by removing only organic carbon and having no impact on the concentration of bromide, coagulation altered the Br/TOC ratio of the waters and shifted the subsequent formation of HAAs and THMs toward the bromochloro and brominated species.

**TEMPERATURE**

Temperature has a significant impact on the relative dominance of HAAs and THMs. Analysis of the ICR data indicated that, for surface water treatment plants using only free chlorine, the HAA9/THM4 ratio increased with decreasing temperature and, consistent with that finding, HAA9/THM4 ratios were found to be lowest in the winter months (January–March) and highest in the summer months (July–September).
BROMIDE

The concentration of bromide in water, particularly the Br/TOC ratio, has a marked impact on the distribution of bromine-containing HAAs and THMs. As the Br/TOC ratio increases, the mole fractions of bromine-containing species increase significantly, whereas the reverse occurs for the species containing only chlorine. This occurs for both HAAs as well as THMs.

The controlled laboratory chlorination studies found that the hydrophilic fractions exhibited consistently higher reactivity with bromine than the hydrophobic fractions. Bromine was found to be more reactive in substitution reactions and was incorporated into HAA and THM species faster than chlorine. Increasing pH increased the incorporation of both bromine and chlorine into THM and HAA species but did not change the relative distribution of bromine to chlorine within those species.

As part of this study, a model was developed to predict the formation of the three trihalogenated bromine-containing species that are not part of the regulated HAA5 species and for which limited data are available in the ICR database, notably BrCl₂AA, Br₂ClAA, and Br₃AA. The model indicates that BrCl₂AA, Br₂ClAA, and Br₃AA are present in similar proportions to Cl₃AA, on a mole fraction basis, as CHBrCl₂, CHBr₂Cl, and CHBr₃, respectively, are present relative to CHCl₃ formation. Consequently, the model allows calculation of BrCl₂AA, Br₂ClAA, and Br₃AA (collectively HAA3) concentrations from knowledge of the concentrations of the individual THM species and Cl₃AA. The model was verified using the limited HAA9 data from the ICR database, and was shown to represent data from the selected full-scale water systems examined in this study reasonably well.

REACTION TIME

Although HAAs have been reported in the literature to form more rapidly than THMs, the controlled laboratory chlorination results showed that the relative distribution of HAA9 and THM4 was reasonably consistent throughout the 72-hour reaction period at both pH 6 and pH 8. The results did show, however, that among the HAA species, the X₃AA/X₂AA ratio increased with increasing contact time at both pH values. This ratio increased particularly rapidly during the first 8 hours of chlorination, and remained essentially unchanged after 24 hours.
Analysis of the ICR data for surface water treatment systems using only free chlorine showed that the HAA9/THM4 ratio was highest in the filtered water, lower in the finished water, and even lower in the distribution system at average HRTs. This may reflect a more rapid rate of HAA formation relative to THM formation within the treatment plant because of the presence of more reactive precursors (presence of more hydrophobic carbon that favors formation of HAAs over THMs; see above); or a general shift toward higher pH values in finished water and in the distribution system relative to filtered water (higher pH values favor greater THM formation relative to HAA formation; see above). Use of chloramines in the distribution system was found to maintain the same relative distribution of HAAs to THMs as in the finished water at the POE to the distribution system. Essentially, chloramination of finished water stops subsequent THM and HAA formation.

BIODEGRADATION

The fact that HAA species are biodegradable and THM species are not may also have a significant impact on the relative distribution of THMs and HAAs. The AR studies, conducted in the presence and absence of a free chlorine or combined chlorine residual, showed clearly that when the residual was absent, the dihalogenated acetic acids were biodegraded under warm water conditions. The trihalogenated acetic acid species, however, were not biodegraded under similar conditions, nor were the THMs. In cold water, the X2AAs were stable because of slower reaction kinetics, but may also be biodegraded if longer HRTs are provided. In the presence of a free chlorine residual, both classes of HAA species and the THMs continued to form.

It was also found, in an in-depth full-scale plant evaluation, that HAAs can be removed by GAC filtration, presumably by biodegradation processes within the GAC bed. The extent of removal depends on water temperature and the residual chlorine concentration. Removal of HAAs was greatest when water temperatures were high and residual chlorine concentrations were low. Dihaloacetic acids were removed by the GAC to a greater degree than trihaloacetic acids, but both groups were removed, in contrast to the AR study and other distribution system and controlled laboratory studies, which showed that the trihalogenated acetic acids are not biodegradable.

The fact that the HAAs are degraded but the THMs are not is a significant factor influencing the relative concentrations of these two classes of DBP species in finished drinking water.
SUMMARY OF CONCLUSIONS

These findings confirm that the THMs and the three classes of HAA species (mono-, di-, and trihalogenated species) have different formation mechanisms and, to some degree, different precursors. Additionally, once formed, many of them behave differently. However, the compounds within each class of DBPs (i.e., the different trihalogenated HAA species, the dihalogenated HAA species, and the trihalogenated methanes), tend to form through similar chemical pathways and behave similarly in aqueous solution.

As a result of the ability to reliably measure all nine bromine- and chlorine-containing HAA species and to predict HAA3 concentrations when only HAA6 data are available, this research has shown, for the more than 5,000 samples examined from the first 12 months of the ICR Auxiliary 1 database, that overall HAA concentrations (i.e., HAA9) in finished drinking water are approximately equal to overall THM (THM4) concentrations. By comparison, HAA5 were found to comprise approximately only 60 percent of the corresponding THM4 concentrations. HAA5 measurements significantly underestimate overall HAA occurrence. The results from this project show that including these other HAA species can contribute significantly to overall HAA occurrence, even for waters with relatively low bromide concentrations. Total HAA occurrence in U.S. drinking waters is not well represented by considering only HAA5, and the current MCL, which applies only to HAA5, is not sufficiently protective of public health if HAAs are indeed a public health concern.

The frequency distribution analyses performed in this study were helpful in evaluating the status of finished drinking water with respect to current and future THM and HAA regulations. The findings, especially those involving HAA9, should be strongly considered in future regulatory activities.
APPENDIX A
PROCEDURE FOR HAA9 ANALYSIS

1. Apparatus

a) Sample containers and extraction vials: 40-mL screw-cap vials with TFE-lined silicone septa. Clean vials by washing with Alconox powder detergent, then soaking in a 10 percent ACS-Grade HNO₃ bath overnight. Rinse thoroughly with tap water, then rinse thoroughly (at least three times) with DOFW. Dry glassware in an 180°C oven for at least 24 hours. Repeat same procedure for caps and septa. For the caps and septa, set the oven temperature at 80°C.
b) Microsyringes: 5, 10, 25 µL
c) Micropipettors: 10–60 µL, 50–250 µL
d) Syringe: 5-mL glass, gas-tight syringe with 18-gauge stainless-steel needle
e) Volumetric flasks: 2, 5, 10, 100 mL. Clean flasks by washing with detergent, then soaking in a 10 percent HNO₃ bath overnight. Rinse thoroughly with tap water, then rinse thoroughly (at least three times) with DOFW. Finally, rinse three times with HPLC-grade methanol, then invert to air-dry on dioxin-free paper in a ventilation hood.
f) Vortex mixer: Thermolyne Type 16700 Mixer—MaxiMix I, or equivalent
g) Standard storage vials: 5-mL, amber glass with TFE-faced silicone septa. See part 1a for cleaning procedures
h) Transfer pipettes: 14.6- and 23-cm disposable glass Pasteur pipettes
i) Gas chromatograph: HP-5890 Series II
   1) Column: Type: DB-1 fused silica capillary (J&W Scientific)
      Length: 30 m
      Internal diameter: 0.25 mm
      Film thickness: 1 µm
   2) Temperature program: Initial temperature: 37°C. Hold for 21 min.
      Ramp to 136°C at 5°C/min. Hold for 3 min.
      Ramp to 250°C at 20°C/min. Hold for 3 min.
      Run time: 52.5 min.
3) Injector: Injection volume: 2 µL
   Temperature: 180°C
   Split valve opened at 0.5 min

4) Detector: Type: electron capture
   Temperature: 280–300°C

5) Carrier gas: Helium (99.999+ percent purity)
   Flow Rate: 1.0–1.5 mL/min at 37°C

6) Makeup gas: Nitrogen (99.999+ percent purity)
   Flow rate: 40–60 mL/min.

j) Salt scoop, small glass funnel, and 15-mL beaker: Stainless-steel spatula for scooping sodium sulfate; funnel and beaker for measurement and transfer of salt.

k) Pipetting dispensers: Adjustable 5- and 2-mL sizes with TFE transfer lines that can be mounted onto suppliers’ reagent bottles. These are to be used for dispensing MTBE and H₂SO₄, respectively.

l) Diazomethane generator: Use millimole-size generator with O-ring joint (Aldrich or equivalent). See part 1a for initial cleaning procedures. Immediately after use, soak entire apparatus in 5N NaOH for at least 30 min, to quench any unreacted Diazald. Rinse thoroughly with tap water, then soak in 10 percent HNO₃ bath overnight. Rinse thoroughly with tap water, then rinse thoroughly (at least three times) with DOFW. Dry glassware in an 180°C oven for at least 24 hours.

m) Volumetric and graduated pipettes: Two 1-mL volumetric pipettes, and one 5-mL graduated pipette. See part 1e for cleaning procedures.

n) Graduated cylinder: 25-mL. See part 1e for cleaning procedure.

o) Teflon tape: ½-in. and 1-in.

2. Reagents

   a) Extraction solvent: 99+ percent MTBE. UltraResi-Analyzed (J.T. Baker) or equivalent.


   c) Methanol (for rinsing glassware): HPLC grade or equivalent.
d) Reagents for diazomethane generation:
   1) Sodium hydroxide bath, 5N: Dissolve 200 g of ACS low-carbonate-grade pellets in 1 L tap water.
   2) Di(ethylene glycol) ethyl ether (Carbitol; Aldrich)
   3) N-methyl-n-nitroso-p-toluene sulfonamide (Diazald; Aldrich)
   4) Potassium hydroxide, KOH: 45 percent (w/w) solution (Aldrich)

e) Silicic acid: n-Hydrate powder (Baker)

f) Sulfuric acid, H₂SO₄: Concentrated, ACS grade

g) Drying agent: 99+ percent purity magnesium sulfate, MgSO₄. Anhydrous powder (Aldrich)

h) Haloacetic acid standard stock solutions (Supelco): MCAA, MBAA, DCAA, TCAA, BCAA, and DBAA were purchased in a multicomponent stock solution with a concentration of 2 mg/mL of each component in MTBE. BDCAA, CDBAA, and TBAA were purchased as neat standards, from which stock solutions were prepared in MTBE. Stock solutions can be stored in the freezer in amber vials, sealed with Teflon tape, for up to 3 months.

i) Multicomponent haloacetic acid additive solutions: Prepare a primary and a secondary dilution from the haloacetic acid stock solutions. When preparing these dilutions, choose concentrations that will allow 20–50 µL or less of each stock solution to be added to 100 mL of reagent water when preparing the calibration standards. Additive solutions should be prepared on the day of analysis.

j) Haloester standard stock solutions (Supelco): MCAA, MBAA, DCAA, TCAA, BCAA, and DBAA methyl esters were purchased in a multicomponent stock solution with a concentration of 1 mg/mL of each component in MTBE. BDCAA, CDBAA, and TBAA methyl esters were purchased as neat standards, from which stock solutions were prepared in MTBE. Stock solutions can be stored in the freezer in amber vials from 1 g, sealed with Teflon tape, for up to 3 months.

k) Multicomponent haloester additive solution: Prepare a primary dilution using the methyl esters stock solutions. This solution will be used to prepare one sample containing ester standards, to be run on the GC along with samples.

l) Internal standard (Aldrich): 1,2,3-trichloropropane, 99+ percent purity
m) Internal standard stock solution: Weigh 25 mg of standard in 5-mL MTBE. This will yield a stock solution with a concentration of 5 mg/mL. This stock solution can be stored in the refrigerator at 4°C and used for up to 6 months.

n) Surrogate (Supelco): 2,3-dibromopropionic acid, 99+ percent purity. Stock solution purchased at a concentration of 1 mg/mL in MTBE.

o) Surrogate additive solution: Prepare a solution by filling a 5-mL volumetric flask to the neck with MTBE. Add 100 µL of surrogate stock solution, then top to the line with MTBE. Cap and invert to mix. This will yield a surrogate additive solution with a concentration of 20 µg/mL.

p) Surrogate ester stock solution: Methyl-2,3-dibromopropionate, 98+ percent purity. Stock solution purchased at a concentration of 1 mg/mL in MTBE.

q) Surrogate ester additive solution: Prepare a solution by filling a 5-mL volumetric flask to the neck with MTBE. Add 100 µL of surrogate ester stock solution, then top to the line with MTBE. Cap and invert to mix. This will yield a surrogate additive solution with a concentration of 20 µg/mL.

r) Reagent water: DOFW.

3. Procedure

a) Preparation of diazomethane

   Process should be carried out in a ventilation hood.

   Set up diazomethane generation apparatus on ice. Add 3 mL of MTBE to the outside tube of the generator. Assemble to parts of generator together, with O-ring seal, and clamp. Make sure that the vapor outlet hole of the inner tube is facing up, so the reactants will not leak into the outside tube of the generator. Check for leaks in generator before adding reagents to inner tube of generator.

   Add 1 mL of MTBE, then 1 mL of Carbitol to the inside tube of generator. Add approximately 200 mg of Diazald to the inside tube of the generator. Close the screw-cap with TFE-lined septum and mix the contents of the inner tube gently. Make sure that none of the contents of the inner tube leaks out into the outer tube of the generator. Place reactor in an ice bath for 10 min.
Keeping reactor in ice bath, add 1.5 mL of 45 percent KOH drop-wise to the inner tube of the generator with a gas-tight syringe through the septum. Be careful not to allow pressure build-up in the inner tube.

Allow diazomethane to form on ice for 30–45 min. Every 5 min, mix contents of apparatus gently.

Remove reactor from ice bath. Wipe off any excess water from outside of generator. Remove inner jacket of the reactor and place it in a 5N NaOH bath. Transfer diazomethane from the outer tube of generator to a 40-mL vial with TFE-lined septum. Store diazomethane in an explosion-proof freezer until ready to be used. For safety reasons, this solution should be used within 24 hours.

Soak all glassware used to generate diazomethane in a 5N NaOH bath for at least 30 min, to destroy any unreacted Diazald.

b) Preparation of calibration standards

Prepare standards in 100 mL of DOFW.

Prepare aqueous calibration standards by injecting measured amounts of the appropriate multicomponent haloacetic acid additive solution into reagent water. Fill 100-mL volumetric flasks to the neck with reagent water. Add the appropriate amount of haloacetic acid additive solution, then fill to the line with reagent water. Prepare five different concentrations ranging from 1 µg/L to 50 µg/L, along with a sample of blank reagent water. Apportion 20-mL aliquots, using a graduated cylinder, of each calibration standard, in duplicate, into 40-mL glass, screw-top vials with TFE-lined silicone septa. Extract and derivatize these standards along with samples, according to the procedure outlined below.

If many samples are being analyzed, prepare a calibration point to be run after every 10 samples. Choose a concentration that is expected to be within the range of unknown samples.

Prepare one sample using the multicomponent, methyl ester additive solution. This standard should be prepared directly in MTBE, at a concentration within the range of expected concentrations for samples being analyzed.
c) Microextraction

Extraction and derivatization process should be carried out in a ventilation hood.

Remove samples from storage and allow them to equilibrate to room temperature. Transfer 20 mL from each sample container into a 40-mL glass, screw-top vial a with TFE-lined silicone septum.

Add 20 µL of the surrogate additive solution to each sample and mix contents gently. If adding spikes of known haloacetic acid concentrations to samples, do so at this time.

Add 2.0 mL of concentrated H₂SO₄ to each vial. Cool in an ice bath, then allow samples to return to room temperature. Add 10 g baked Na₂SO₄, then 4.0 mL MTBE. Immediately cap vial and shake briefly to break up any salt clumps.

Vortex each vial for 1 min, then stand vials upright and allow the two phases to separate for at least 3 min.

d) Derivatization and quenching

Transfer 2 mL of the top ether layer of each sample to a 2-mL volumetric flask. Add approximately 100 mg of anhydrous, powdered MgSO₄ to each sample. Cap and invert once to mix. Allow excess MgSO₄ to settle to bottom of flask.

Add 225 µL of cold diazomethane/MTBE solution to each sample. Cap sample and invert once to mix. Hold samples in an explosion-proof refrigerator at 4°C for 15 min, then place extracts in hood for another 15 min, until they reach room temperature. A persistent, if faint, yellow color should remain in each extract. This indicates that enough diazomethane was present in the extract to drive the esterification reaction.

Add approximately 0.1 g of silicic acid to each sample, to quench excess diazomethane. Let excess silicic acid settle to bottom of flask.

Transfer each extract to an autosampler vial for GC analysis. Be sure not to transfer any silicic acid to autosampler vials; silicic acid could clog the needle of the autosampler syringe. Store samples in freezer at −15°C until shortly before analysis. Allow extracts to warm to room temperature before analyzing on the GC.
APPENDIX B
DATA FOR HAA9 STABILITY IN WATER

Samples were incubated in the dark at 25°C for up to 2 weeks.

Figure B.1 Stability of ClAA in water at 25°C for up to 2 weeks

Figure B.2 Stability of BrAA in water at 25°C for up to 2 weeks
Figure B.3  Stability of Cl₂AA in water at 25°C for up to 2 weeks

Figure B.4  Stability of Cl₃AA in water at 25°C for up to 2 weeks

Figure B.5  Stability of BrClAA in water at 25°C for up to 2 weeks
Figure B.6 Stability of Br$_2$AA in water at 25°C for up to 2 weeks

Figure B.7 Stability of BrCl$_2$AA in water at 25°C for up to 2 weeks

Figure B.8 Stability of Br$_2$ClAA in water at 25°C for up to 2 weeks
Figure B.9 Stability of Br$_3$AA in water at 25°C for up to 2 weeks
APPENDIX C
DATA FOR STABILITY OF HAA9 IN PRESENCE OF FREE CHLORINE

Samples prepared in water in presence of 2 mg/L Cl₂ and incubated in the dark at 25°C for up to 2 weeks.

Figure C.1 Stability of ClAA in the presence of free chlorine

Figure C.2 Stability of BrAA in the presence of free chlorine
Figure C.3  Stability of Cl$_2$AA in the presence of free chlorine

Figure C.4  Stability of BrClAA in the presence of free chlorine

Figure C.5  Stability of Cl$_3$AA in the presence of free chlorine
Figure C.6  Stability of Br₂AA in the presence of free chlorine

Figure C.7  Stability of BrCl₂AA in the presence of Cl₂

Figure C.8  Stability of Br₂ClAA in the presence of Cl₂
Figure C.9 Stability of Br₃AA in the presence of Cl₂
APPENDIX D
DATA FOR HAA9 STABILITY IN PRESENCE OF QUENCHING AGENTS

Samples prepared in water and incubated in the dark at 15°C for 24 hours, then stored in a refrigerator at 4°C for up to 2 weeks.

![Figure D.1 Stability of ClAA in presence of quenching agent at pH 7](image1)

![Figure D.2 Stability of ClAA in presence of quenching agent at pH 10](image2)
Figure D.3  Stability of BrAA in presence of quenching agent at pH 7

Figure D.4  Stability of BrAA in presence of quenching agent at pH 10
Figure D.5  Stability of Cl$_2$AA in presence of quenching agent at pH 7

Figure D.6  Stability of Cl$_2$AA in presence of quenching agent at pH 10
Figure D.7 Stability of BrClAA in presence of quenching agent at pH 7

Figure D.8 Stability of BrClAA in presence of quenching agent at pH 10
Figure D.9  Stability of Cl₃AA in presence of quenching agent at pH 7

Figure D.10  Stability of Cl₃AA in presence of quenching agent at pH 10
Figure D.11 Stability of Br₂AA in presence of quenching agent at pH 7

Figure D.12 Stability of Br₂AA in presence of quenching agent at pH 10
Figure D.13  Stability of BrCl$_2$AA in presence of quenching agent at pH 7

Figure D.14  Stability of BrCl$_2$AA in presence of quenching agent at pH 10
Figure D.15 Stability of Br₂Cl₅AA in presence of quenching agent at pH 7

Figure D.16 Stability of Br₂Cl₅AA in presence of quenching agent at pH 10
Figure D.17  Stability of Br$_3$AA in presence of quenching agent at pH 7

Figure D.18  Stability of Br$_3$AA in presence of quenching agent at pH 10
REFERENCES


USEPA. 1997. 600-R-97-122. Research Plan for Microbial Pathogens and Disinfection By-Products in Drinking Water.


# ABBREVIATIONS

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<tr>
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<th>Description</th>
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<tr>
<td>ACS</td>
<td>American Chemical Society</td>
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<tr>
<td>[Al₂(SO₄)₃(14-16)H₂O]</td>
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<td>bromine incorporated into HAA9 species</td>
</tr>
<tr>
<td>HAA9-Cl</td>
<td>chlorine incorporated into HAA9 species</td>
</tr>
<tr>
<td>HAA9+THM4</td>
<td>summed quantity of HAA9 and THM4 concentrations</td>
</tr>
<tr>
<td>HAAFP</td>
<td>haloacetic acid formation potential</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrogen chloride</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>mercuric chloride</td>
</tr>
<tr>
<td>HOBr</td>
<td>hypobromous acid</td>
</tr>
<tr>
<td>HOCl</td>
<td>hypochlorous acid</td>
</tr>
<tr>
<td>HP</td>
<td>Hewlett Packard</td>
</tr>
<tr>
<td>HPC</td>
<td>heterotrophic plate count</td>
</tr>
<tr>
<td>HPC-R2A</td>
<td>heterotrophic plate count on R2A agar</td>
</tr>
<tr>
<td>HPLC</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>HRT</td>
<td>hydraulic residence time</td>
</tr>
<tr>
<td>HTE</td>
<td>high tris-EDTA</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>IC</td>
<td>ion chromatograph(y)</td>
</tr>
<tr>
<td>ICR</td>
<td>Information Collection Rule</td>
</tr>
<tr>
<td>IS</td>
<td>internal standard</td>
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<tr>
<td>KCl</td>
<td>potassium chloride</td>
</tr>
<tr>
<td>LLE</td>
<td>liquid-liquid extraction</td>
</tr>
<tr>
<td>M/DBP</td>
<td>Microbial/Disinfection By-Products Research Council</td>
</tr>
<tr>
<td>MBAA</td>
<td>monobromoacetic acid</td>
</tr>
<tr>
<td>MCAA</td>
<td>monochloroacetic acid</td>
</tr>
<tr>
<td>MCL</td>
<td>maximum contaminant level</td>
</tr>
<tr>
<td>MDL</td>
<td>method detection limit</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>magnesium sulfate</td>
</tr>
<tr>
<td>MNNG</td>
<td>1-methyl-3-nitro-1-nitrosoguanidine</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl-tertiary-butyl-ether</td>
</tr>
<tr>
<td>MWD</td>
<td>Metropolitan Water District of Southern California</td>
</tr>
<tr>
<td>N/A</td>
<td>not added or not available</td>
</tr>
<tr>
<td>N/D</td>
<td>not detectable or not detected</td>
</tr>
<tr>
<td>N/M</td>
<td>not measured</td>
</tr>
<tr>
<td>NA</td>
<td>not analyzed</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>sodium carbonate</td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>sodium thiosulfate</td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>sodium sulfite</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>sodium sulfate</td>
</tr>
<tr>
<td>NaAsO₂</td>
<td>sodium meta-arsenite</td>
</tr>
<tr>
<td>NaBr</td>
<td>sodium bromide</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>sodium bicarbonate</td>
</tr>
<tr>
<td>NaN₃</td>
<td>sodium azide</td>
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<td>NaOH</td>
<td>sodium hydroxide</td>
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<tr>
<td>ND</td>
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<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>NG</td>
<td>no growth</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>ammonium chloride</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>ammonium sulfate</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOM</td>
<td>natural organic material</td>
</tr>
<tr>
<td>NPOC</td>
<td>nonpurgeable organic carbon</td>
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<tr>
<td>ntu</td>
<td>nephelometric turbidity unit</td>
</tr>
<tr>
<td>OWASA</td>
<td>Orange Water and Sewer Authority (N.C.)</td>
</tr>
<tr>
<td>PCR</td>
<td>polymerase chain reaction</td>
</tr>
<tr>
<td>pKa</td>
<td>negative logarithm of the acidity constant</td>
</tr>
<tr>
<td>POE</td>
<td>point of entry</td>
</tr>
<tr>
<td>PQL</td>
<td>practical quantitation limit</td>
</tr>
<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
</tr>
<tr>
<td>QC</td>
<td>quality control</td>
</tr>
<tr>
<td>RPA</td>
<td>relative peak area</td>
</tr>
<tr>
<td>RSD</td>
<td>relative standard deviation</td>
</tr>
<tr>
<td>RT</td>
<td>retention time, residence time</td>
</tr>
<tr>
<td>SD</td>
<td>standard deviation</td>
</tr>
<tr>
<td>sds</td>
<td>simulated distribution system</td>
</tr>
<tr>
<td>SPW</td>
<td>State Project Water</td>
</tr>
<tr>
<td>SUVA</td>
<td>specific ultraviolet absorbance</td>
</tr>
<tr>
<td>TBAA</td>
<td>tribromoacetic acid</td>
</tr>
<tr>
<td>TCAA</td>
<td>trichloroacetic acid</td>
</tr>
<tr>
<td>TFE</td>
<td>tetrafluoroethylene</td>
</tr>
<tr>
<td>THM</td>
<td>trihalomethane</td>
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<tr>
<td>THM4</td>
<td>four trihalomethanes (CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃)</td>
</tr>
<tr>
<td>THM4-Br</td>
<td>bromine incorporated into THM4</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>------------</td>
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<tr>
<td>THM4-Cl</td>
<td>chlorine incorporated into THM4</td>
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<tr>
<td>THMFP</td>
<td>trihalomethane formation potential</td>
</tr>
<tr>
<td>TNTC</td>
<td>too numerous to count</td>
</tr>
<tr>
<td>TOC</td>
<td>total organic carbon</td>
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<tr>
<td>TTHM</td>
<td>total trihalomethane (CHCl₃, CHBrCl₂, CHBr₂Cl, CHBr₃)</td>
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<tr>
<td>TUXDBP</td>
<td>table of DBP concentrations in Aux 1 of ICR database</td>
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<td>TUXPLTMN</td>
<td>table of water plant information in Aux 1 of ICR database</td>
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<td>TUXSAMPLE</td>
<td>table of sampling locations in Aux 1 of ICR database</td>
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<tr>
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<td>unit</td>
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<tr>
<td>UNC</td>
<td>University of North Carolina</td>
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<tr>
<td>UNG</td>
<td>uracil N-glycosylase</td>
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<tr>
<td>USEPA</td>
<td>U.S. Environmental Protection Agency</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>UV₂₅₄</td>
<td>ultraviolet absorbance at 254 nm</td>
</tr>
<tr>
<td>UV₂₇₂</td>
<td>ultraviolet absorbance at 272 nm</td>
</tr>
<tr>
<td>∆UV</td>
<td>change in ultraviolet absorbance</td>
</tr>
<tr>
<td>∆UV₂₅₄</td>
<td>change in ultraviolet absorbance at 254 nm</td>
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<tr>
<td>∆UV₂₇₂</td>
<td>change in ultraviolet absorbance at 272 nm</td>
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<tr>
<td>WEF</td>
<td>Water Environment Federation</td>
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<td>WSSC</td>
<td>Washington Suburban Sanitary Commission (Md.)</td>
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<tr>
<td>WTP</td>
<td>water treatment plant</td>
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<tr>
<td>XAA</td>
<td>monohalogenated acetic acids</td>
</tr>
<tr>
<td>X₂AA</td>
<td>dihalogenated acetic acids</td>
</tr>
<tr>
<td>X₃AA</td>
<td>trihalogenated acetic acids</td>
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