Awwa Research Foundation

Microbial/Disinfection By-Products Research Council

Information Collection Rule Data Analysis

Subject Area:
Efficient and Customer-Responsive Organization

Information Collection Rule Data Analysis

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Information Collection Rule Data Analysis

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Sponsored by:
Microbial/Disinfection By-Products Research Council

Jointly funded by:
Awwa Research Foundation
6666 West Quincy Avenue
Denver, CO 80235
and
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

Published by the
Awwa Research Foundation and
American Water Works Association

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This study was funded for the Microbial Disinfection By-Products Research Council (M/DBP) by the U.S. Environmental Protection Agency (USEPA) and the Awwa Research Foundation (AwwaRF) under Cooperative Agreement No. CR826288-01. The M/DBP Research Council, USEPA, and AwwaRF assume no responsibility for the content of the research studies 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 the M/DBP Research Council, USEPA, or AwwaRF. This report is presented solely for informational purposes.

Library of Congress Cataloging-in-Publication Data has been applied for.

Copyright © 2002
by
Awwa Research Foundation
and
American Water Works Association
Printed in the U.S.A.

ISBN 1-58321-273-6

Printed on recycled paper

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FOREWORD

The Awwa Research Foundation is a nonprofit corporation 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 working professionals. Under the umbrella of a Strategic Research Plan, the Research Advisory Council prioritizes the suggested projects based on 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 nonmember utilities and individuals.

Projects are managed closely from their inception to the final report by the foundation's 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 in providing 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.

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Utilities face increasingly stringent regulations and confront the challenge of managing information produced as a result of regulatory negotiations. This book captures the extensive analyses of Information Collection Rule (ICR) data conducted by members of the Technical Workgroup who supported the Microbial Disinfection By-products Federal Advisory Committee negotiations in 1999–2000. Each chapter of the book provides a stand-alone analysis of critical information generated by the ICR. The book is expected to form the basis from which researchers, utility personnel, regulatory officials, and others will extend future analyses of this singular water quality data resource. The foundation undertook this research project to assemble and analyze the vast amount data collected under the ICR.

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PREFACE

The Information Collection Rule (ICR) was created in response to the need for data to support regulatory decision-making with respect to controlling disinfection by-products (DBPs) and pathogens in drinking water. The Regulatory Negotiation Committee, convened in 1993 to recommend revisions to the Trihalomethane Rule and the Surface Water Treatment Rule, conceived the ICR to fill critical data gaps related to balancing health risks from waterborne pathogens and DBPs. Accordingly, the ICR was designed to assess national occurrence of DBPs and microbial pathogens and to characterize existing treatment practices.

The ICR established monitoring and data reporting requirements for large public water systems. Surface water and groundwater systems that served more than 100,000 people were required to monitor DBPs and DBP-related parameters and to report treatment information. Surface water systems also collected samples to be analyzed for pathogens in treatment plant influent. A total of 500 treatment plants (representing 296 public water systems) conducted ICR monitoring during the 18-month period from July 1997 through December 1998. The ICR data set provides a national description of: (1) influent water quality parameters; (2) primary and secondary disinfectant use; (3) occurrence of DBPs and DBP precursors in treatment plants, finished water supplies, and distributions systems; (4) occurrence of microbial pathogens in surface water plants; and (5) information on treatment plant design and monthly operation. A subset of ICR water systems conducted treatment studies using either granular activated carbon or membrane processes to evaluate DBP precursor removal and DBP control.

The ICR data provided a critical foundation for the Federal Advisory Committee Act (FACA) process that took place during 1999–2000 to revise the regulations for microbes and DBPs. A Technical Workgroup (TWG) was formed to implement the analyses and presentations of ICR data in support of the FACA negotiations. The TWG guided design of the ICR auxiliary databases to facilitate rapid data analysis in response to FACA committee needs and subsequently developed the Surface Water Analytical Tool, or SWAT, to model the outcome of various regulatory scenarios. Thus, the TWG played a critical role in informing the FACA Committee during the deliberations leading to its September 2000 Agreement in Principle.

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The idea to compile a book focused on the analysis of ICR data was conceived in October 1999, and the editors committed to undertake this project. The project was motivated by the desire to capture the enormous efforts of TWG members who for two years were involved in supporting the FACA effort, to make their work available to utilities and members of the scientific community, and to lay a foundation for other researchers faced with the daunting task of making sense of the ICR data. Funding in support of this work was sought and provided from the Microbial Disinfection By-products Research Council, which is jointly supported by the U.S. Environmental Protection Agency and the American Water Works Association Research Foundation.

Each of the 23 chapters in this book underwent a thorough peer-review process. Two anonymous experts reviewed each chapter. As noted in the Acknowledgments section, peer reviewers were recruited among the authors and coauthors of the chapters and among other professionals chosen to provide specific expertise. The editors also reviewed each chapter to ensure that they all meshed into a coordinated whole.

This book does not constitute the final word on the analysis of ICR data. The editors hope the book is not an end but the beginning of a long-term effort by researchers, students, utility professionals, and consultants to mine the wealth of information contained in the ICR data. We expect the material in this book to provide the foundation for future efforts that will fully describe the ICR data set.

Michael J. McGuire
Jennifer L. McLain
Alexa Obolensky

November 2002

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ACKNOWLEDGMENTS

Without the enormous amount of work contributed by the authors of each chapter, this book would not have been possible. The authors and coauthors are listed at the beginning of each chapter, and their affiliations are listed here. The editors are particularly grateful to the institutions that supported these authors as they prepared the chapters and during the review and editing process.

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Each chapter was peer-reviewed by at least two anonymous experts in the field. The pool of peer reviewers consisted of many of the authors and coauthors just listed, as well as other experts including Dr. Jennifer L. Clancy, Ms. Holly Shorney, Dr. David A. Reckhow, Dr. Philip C. Singer, and Dr. James M. Symons. We are very grateful to all the reviewers.

The editors owe a huge debt of gratitude to Nancy Zeilig, who provided detailed editing for each chapter and prepared the book for publication. An independent editor and writer based in Denver, Nancy Zeilig was editor of *Journal AWWA* for 19 years. Her skills and expertise were invaluable in the completion of this project.

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We also thank Marion Shorey for creating several important compilations of material for the book, including the list of abbreviations.

The editors are grateful to the Microbial Disinfection By-products Research Council, supported by the Awwa Research Foundation (AwwaRF) and the U.S. Environmental Protection Agency (USEPA), for the funding that supported a portion of this work. We are especially grateful to Traci Case, the project officer, and the other AwwaRF staff who guided us through the publishing process for the book.

Finally, the editors thank our families for their patience and support during the long hours required to complete this project.

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November 2002

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EXECUTIVE SUMMARY

The topics chosen for this book reflect the broad scope of the national Information Collection Rule (ICR) survey conducted during 1997–1998. An enormous data analysis effort lies behind the information presented in this book. Even so, these 23 chapters are merely an introduction to the wealth of information on drinking water quality, pathogen occurrence, and water treatment available in the ICR data set. This book is designed so that each chapter can, for the most part, stand alone. Subject and author indexes should help readers locate items of interest. For those who read the entire book, you have our admiration. For those of you looking for specific information, we hope the following highlights of key findings from each chapter will spark your interest and entice you to dive more deeply into the material.

After reading Chapters 1 and 2, readers should be convinced that implementation of the ICR was an outstanding effort representing extensive planning, careful sample collection, accurate and precise analytical methods, and a high level of water quality data validation. The degree of planning and economic commitment devoted to ICR implementation is unparalleled in drinking water data collection programs. As a result of these efforts and the ICR's systematic and well-documented quality assurance program, users can have a high degree of confidence in the ICR data.

Chapter 3 provides an inventory of ICR water systems and treatment plants. The geographic distribution and service population sizes of ICR systems are presented along with a summary of the types of source water and treatment processes used at all 500 ICR plants. Analyses of weather patterns during the ICR data collection period are discussed to give the data a broader historical context.

Chapter 4 indicates that nationwide occurrence of total trihalomethane (TTHM) concentrations decreased by 50–60% between 1975 and 1998. This decrease in TTHM concentrations was driven by existing regulations and by the desire of water utilities to prepare for more stringent regulations. The occurrence of extremely high TTHM values in individual distribution system samples resulted in the recommendation of a provision in the Stage 2 Disinfection By-products (DBP) Rule requiring that the maximum contaminant level (MCL) for TTHM be met at each sampling location on the basis of a locational running annual average

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concentration. Correlation analyses showed that TTHM was not well predicted by influent concentrations of total organic carbon (TOC) alone. TTHM concentrations increased slightly with increasing TOC concentrations. No clear relationship was observed between influent concentrations of bromide and TTHM.

Chapter 5 reports the overall mean ICR distribution system concentration of the sum of five haloacetic acids (HAA5) as 23.7 μg/L. The overall mean distribution system HAA9 concentration for the 143 plants reporting these data was 28.4 μg/L, compared with mean HAA5 and TTHM concentrations of 20.4 and 32.7 μg/L at the same plants. On average, TTHM concentrations were much closer to HAA9 concentrations than HAA5 concentrations. Notable differences between the subclasses of dihaloacetic and trihaloacetic acid species were observed with respect to speciation patterns and secondary disinfectant used. Trends related to precursor concentrations, pH, secondary disinfectant, and geographic region are presented.

Chapter 6 illustrates that understanding the bromine-substituted DBPs is especially important for plants with high influent concentrations of bromide. A shift in speciation to the more bromine-substituted DBPs occurred among TTHM, HAAs, and haloacetonitriles (HANs) as influent bromide concentrations increased. For all DBP classes, however, the range of speciation within each category of bromide concentrations was quite large.

Analyses presented in Chapter 7 show that variations in TTHM concentrations across individual distribution systems tended to be greater than corresponding variations in HAA5 concentrations. Distribution system DBP concentrations were frequently lower than associated finished water concentrations, especially among the non-THM DBPs. The simulated distribution system test provided fairly precise estimates of TTHM and HAA5 concentrations in chloramine systems (r^2 values of 0.77 and 0.80, respectively).

Chapter 8 tells us that, with calibration, the model used to predict current and future DBP and treatment distributions is a satisfactory tool for determining national trends. The calibrated model was incorporated into the Surface Water Analytical Tool, which supported the U.S. Environmental Protection Agency's (USEPA's) efforts to develop the Stage 2 DBP Rule and the Long Term 2 Enhanced Surface Water Treatment Rule. The model is not yet robust enough to accurately predict DBP concentrations at individual treatment plants.

Bromate occurrence data from ICR plants that used chlorine dioxide or ozone are presented in Chapter 9. Bromate was detected in 11% of the finished water samples collected by

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ICR plants using chlorine dioxide, with concentrations ranging from below the minimum reporting level of 0.2 μg/L up to 2.4 μg/L. This suggests that bromate is not an important by-product of chlorine dioxide disinfection. Finished water bromate concentrations at the 20 ICR plants using ozone ranged from below 0.2 μg/L up to 25.1 μg/L. Increases in influent bromide concentration and ozone dosage were each associated with increased bromate formation.

Chapter 10 shows good correlations between the concentrations of TTHM, HAA5, and other halogen-substituted ICR DBPs and total organic halogen (TOX), even though water quality, treatment practices, and disinfectant type varied from plant to plant, indicating that TOX can be used as a surrogate for DBPs. On average, TTHM and HAA5 made up 20–50% of the TOX. Other ICR DBPs (namely, bromochloroacetic acid, HAAs, chloral hydrate, chloropicrin, and the haloketones) accounted for another 5% of the TOX.

Chapter 11 presents occurrence data for the unregulated DBPs monitored under the ICR, demonstrating their low concentrations compared with TTHM and HAA5 concentrations. Median concentrations for all of these DBPs were typically a few micrograms per liter. Concentrations tended to be higher in distribution systems that relied on surface water sources compared with those that used groundwater sources. No other comprehensive, national data set on these nonregulated DBPs exists.

Chapter 12 shows that selection of primary and secondary disinfectants by ICR utilities reflected source water quality. Higher influent TOC and bromide concentrations were associated with plants that had implemented alternative primary and secondary disinfectants. Source water quality and disinfectant selection appeared to be related to utility efforts to meet the TTHM MCL. TOC and bromide concentrations varied widely across the United States and did not co-occur at very high concentrations in the influents of ICR treatment plants.

Chapter 13 demonstrates that average percentage removals of TOC during the ICR met the percentage removal requirements of the Disinfectants/Disinfection By-products (D/DBP) Rule. Within each cell of the D/DBP Rule's 3 × 3 matrix of source water TOC and alkalinity, there was a high degree of variability in percentage TOC removal.

Analyses presented in Chapter 14 indicate that bromate formed as a result of a treatment plant's meeting *Cryptosporidium* inactivation requirements may limit the feasibility of applying ozone under certain water quality and treatment conditions. The Surface Water Analytical Tool was used to estimate the percentage of plants that used ozone for *Cryptosporidium* control and

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that would exceed the current bromate MCL of 10 μg/L or a possible future MCL of 5 μg/L. With a requirement for 0.5-log inactivation of *Cryptosporidium*, 46% of the systems evaluated would be expected to exceed a bromate MCL of 5 μg/L, and 64% would be expected to exceed 4 μg/L (80% of the hypothetical MCL and the presumed design guideline). Requiring utilities to meet 1.0-log inactivation would dramatically decrease the feasibility of using ozone because under these conditions all systems would be expected to exceed an annual average bromate concentration of 4 μg/L at least once.

Disinfection practices and national distributions of log inactivation of pathogens in relation to different types of treatment are characterized in Chapter 15. The analytical results present a national picture of the extent to which large utilities were meeting the disinfection requirements of the Surface Water Treatment Rule during implementation of the ICR. Eighteen percent of the ICR surface water plants achieved <0.5-log inactivation of *Giardia*, and 12% achieved <2-log inactivation of viruses. A substantial number of plants (primarily those using chloramines) apparently did not consistently achieve the minimum inactivation levels recommended in USEPA's guidance manual for the Surface Water Treatment Rule.

Chapter 16 presents a microbial index for categorizing data on drinking water sources in a way that allows the effectiveness of potential microbial indicators for *Cryptosporidium* to be evaluated. Based on the ICR and Supplemental Survey data sets, a microbial index of 5 to 10 *Escherichia coli* per 100 mL was used to identify plants that used reservoir/lake sources and were vulnerable to *Cryptosporidium*, whereas 50 *E. coli* per 100 mL was used to identify vulnerable plants that used flowing stream sources.

Results of the analysis in Chapter 17 suggest that *Giardia* and *Cryptosporidium* occurrence and concentrations were strongly influenced by the hydrologic attributes of the source water system (i.e., reservoir/lake versus flowing stream) and the presence or absence of watershed control programs. Differences in *Giardia* and *Cryptosporidium* concentrations were most pronounced in relation to differences between reservoir/lake sources and flowing stream sources, regardless of whether the water was filtered or unfiltered. However, watershed control programs implemented by unfiltered systems appeared to prevent some source water contamination by *Cryptosporidium*.

Chapter 18 shows that viruses were detected in 24% of ICR samples of treatment plant influent (N = 3365). Of the 207 ICR plants that conducted source water monitoring, 80%

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detected viruses at least once during the 18-month sampling period. Viruses were detected in the effluent of seven of the 43 treatment plants that monitored finished water for viruses. The chapter illustrates that the risk of viral infection from treated water is of potential concern at some water treatment plants. These results emphasize the importance of the Interim Enhanced Surface Water Treatment Rule requirement that treatment plants not compromise disinfection to control DBPs.

Chapter 19 reports that national distributions of *Cryptosporidium* occurrence derived from the ICR and the two Supplemental Surveys had median concentrations near 0.02 oocysts/L. However, the ICR survey yielded a greater location-to-location variance and predicted the greatest number of water sources with very high (more than 1 oocyst/L) and very low (less than 0.001 oocyst/L) occurrence.

Chapter 20 describes the ICR Laboratory Spiking Program for protozoa. This program demonstrated mean analytical method recoveries of 12% for *Cryptosporidium* and 26% for *Giardia*. Recoveries between and within laboratories were highly variable.

Chapter 21 presents a substantial amount of information on a major component of the ICR—studies of DBP precursor removal by granular activated carbon (GAC) and membranes. An evaluation of 10- and 20-minute empty-bed contact times (EBCTs) during GAC treatment showed that greater normalized throughput was achievable at 20 minutes of EBCT. In studies of nanofiltration, influent and permeate blends aimed at achieving target MCLs were modeled to provide a water quality distribution for each MCL target across all studies. The chapter also presents three case studies that demonstrate the impact of membrane type on water quality. Overall, 67% of the plants that evaluated GAC were able to meet the target MCLs, and 84% of plants that evaluated nanofiltration were able to do so. A direct comparison between the technologies is difficult because the membrane studies treated water supplies with higher DBP precursor concentrations than did the GAC studies.

Chapter 22 illustrates that softening plants, for the most part, met the TOC removal requirements of the D/DBP Rule during the ICR. The authors also showed that contrary to impressions formed during the 1992–93 regulatory negotiations related to revising the Trihalomethane Rule and the Surface Water Treatment Rule, removal of TOC was independent of magnesium removal.

Chapter 23 rounds out the presentations by focusing on how utilities that participated in ICR monitoring can use the data to make regulatory compliance and operations decisions. A case

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study describes how one utility used its ICR experience as a model in designing an ongoing water quality monitoring program for internal use. Data gathered through this program led to a better understanding of water quality in the utility's distribution system, improved operation and maintenance of the system, and guidance for future planning efforts.

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CHAPTER 1

ICR IMPLEMENTATION AND DATA COLLECTION CHALLENGES

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ABSTRACT

Joining forces to overcome a number of challenges, the U.S. Environmental Protection Agency (USEPA) and the drinking water industry collected water quality and treatment data under the Information Collection Rule (ICR) to support the development of microbial and disinfection by-product (MDBP) regulations. The Technical Support Center of USEPA's Office of Ground Water and Drinking Water, in Cincinnati, Ohio, had direct responsibility for implementing the ICR. This chapter describes the development and implementation of processes and systems to assure that data collected under the ICR met the quality criteria deemed necessary for developing future MDBP regulations. Methods of validating the data are explained, and the auxiliary databases supporting ICR data analyses are described.

USEPA managed applicability determinations and sampling plans for 296 water systems that conducted the 18-month ICR monitoring program. In addition, the agency managed treatment study plans and reports for 99 plants performing ICR treatment studies, as well as reviews and approvals for more than 600 laboratories seeking authorization to analyze ICR samples. Complex data systems were developed to manage the sampling plans and monitoring data, the treatment study results, and the laboratory approvals. An automated data validation process was developed to perform quality control checks of the monitoring data. After being validated, the data were extracted into auxiliary databases to facilitate analyses by the Technical Workgroup that supported negotiations for the MDBP Federal Advisory Committee's Stage 2 Disinfection By-products Rule and Long Term 2 Enhanced Surface Water Treatment Rule.

INTRODUCTION

The 18-month monitoring program conducted under the Information Collection Rule (ICR) produced data that were analyzed and used as the foundation for developing future microbial and disinfection by-product (MDBP) regulations. This chapter discusses the implementation and data collection challenges that the U.S. Environmental Protection Agency (USEPA) and the drinking water industry joined forces to overcome. The chapter also reviews

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the ICR requirements, highlights USEPA-led implementation activities, explains the data validation process, and describes the auxiliary databases that supported analyses of the data.

The ICR data provided USEPA with a substantial database of occurrence and treatment information for water systems serving at least 100,000 people. The data also include the results of treatment studies undertaken by the water systems required to conduct them. These data were used in conjunction with other information such as health effects data, research results, cost analysis, and technical feasibility to evaluate the potential effects of options under consideration for the Stage 2 Disinfection By-products (DBP) Rule and the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR).

The 18-month monitoring program was designed to gather data on water quality parameters, microbial contaminants, DBPs, DBP precursors, treatment plant design, and operating parameters at 296 large public water systems affected by the ICR. USEPA managed implementation of the ICR, including validation and analysis of the data. Data validation and analysis were carried out to ensure that ICR data met the quality criteria defined in the final ICR (USEPA 1996a) and identified by USEPA and other stakeholders as necessary for developing future regulations.

ICR MONITORING REQUIREMENTS

The monitoring requirements of the ICR can generally be divided into monitoring for DBPs and related parameters, microbiological monitoring, collecting treatment plant design and operating information, and monitoring for treatment study applicability. Surface water systems serving ≥100,000 people were required to conduct all of the monitoring. Groundwater systems serving ≥100,000 people were required to monitor for DBPs and related parameters and for treatment study applicability. Groundwater systems serving at least 50,000 but fewer than 100,000 people were only required to monitor for treatment study applicability. Sampling requirements are discussed briefly in the following section and are detailed in the final rule (USEPA 1996a) and the *ICR Sampling Manual* (USEPA 1996j).

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The 18-Month Monitoring Program

The ICR monitoring requirements for microorganisms and for DBPs and related parameters are often referred to as the 18-month monitoring program. This program, conducted at 296 water systems, occurred from July 1997 through December 1998. DBPs and related parameters were monitored at surface water and groundwater systems, whereas microbes were monitored only at surface water systems. Table 1.1 lists the microbial parameters sampled. Water systems could apply for an exemption from monitoring for viruses by submitting historical coliform data to USEPA. Table 1.2 lists the DBPs and related parameters monitored at all systems. Several parameters listed in Table 1.2—total organic carbon (TOC), total organic halogen (TOX), and ultraviolet absorption at 254 nm (UV_{254})—are also referred to as surrogate parameters. Additional surrogate parameters for DBPs were monitored at systems using disinfectants other than free chlorine, such as chloramines, hypochlorite solution, ozone, or chlorine dioxide. These additional parameters are listed in Table 1.3 (USEPA 1996a, 1996j).

Sampling Locations

Generally, water samples were taken at the influent to the treatment plant, before each point of disinfection, after every unit process downstream from the addition of chlorine or chloramines, before and after filtration, at the finished water sampling location, and at distribution system sample locations. Microbial samples were taken at the influent sampling point and, if required, at the finished water sampling point. Finished water microbial samples were required if influent *Giardia* or *Cryptosporidium* concentrations exceeded 10 cysts or oocysts per liter or if total culturable virus concentrations in influent samples exceeded one MPN per liter during the first 12 months of the 18-month monitoring period. Water quality parameters and DBP precursors were measured in the influent and throughout the treatment plant and distribution system. DBPs were generally monitored after filtration, at the finished water sampling point, and in the distribution system (USEPA 1996a). Figure 1.1 illustrates sample locations on a simplified treatment plant schematic. Specific requirements for sampling throughout the treatment plant depended on individual process configurations.

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Table 1.1

Microbial parameters sampled

Cryptosporidium
Giardia
Total culturable viruses
Total coliforms
Fecal coliforms or *E. coli*

Table 1.2

DBPs and related parameters sampled at all ICR plants

Disinfectant residuals	Haloketones	Total organic halogen
Chlorine demand	Chloropicrin	UV_{254}
Trihalomethanes	Chloral hydrate	Water quality parameters—pH, alkalinity, calcium and total hardness, temperature, turbidity
Haloacetic acids	Ammonia	
Haloacetonitriles	Bromide	
	Total organic carbon	

Table 1.3

Additional DBP parameters sampled at plants using disinfectants other than chlorine

Cyanogen chloride	Bromate
Chlorite	Aldehydes
Chlorate	

Treatment Process Information

Each plant that conducted the 18-month monitoring program reported data on source water, treatment processes, and chemical feeds. Typical data reported on unit processes included water flows, volumes, contact times, and surface areas. Data on chemical feed doses and formulas, including information on disinfectants, was collected throughout the treatment plant. Design process data were reported in the Initial Sampling Plans (ISPs) and in the final sampling plan designs, whereas monthly operating process data were provided each sampling period. ISPs, which included treatment plant schematics as well as ICR sampling points, were approved by USEPA before monitoring began (USEPA 1996a, 1996k, 1996l). An example ISP is shown in Figure 1.1 (McGuire 1994a, 1996a; Chowdhury et al. 1997).

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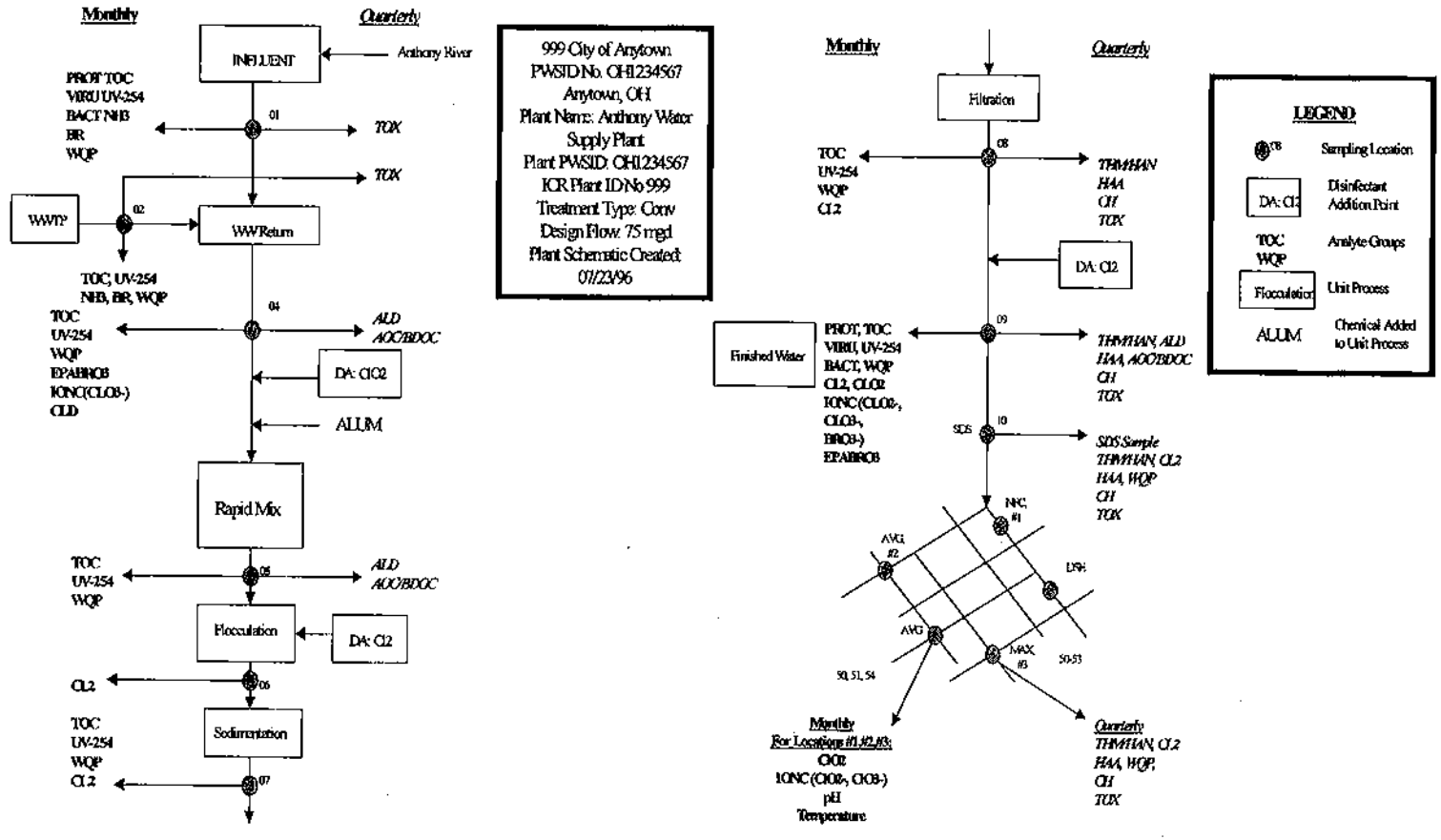

Figure 1.1 Schematic of an example ICR water treatment plant

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Monitoring Frequency

Microbial and water quality data were collected monthly during the 18-month monitoring period. Most DBPs were measured quarterly. Ozone and chlorine dioxide plants reported monthly bromate results, and chlorine dioxide plants reported monthly chlorite and chlorate results.

Monthly samples were supposed to reflect typical operating conditions at the plant. Each set of monthly samples was required to be collected within a 72-hour period. ICR sampling was not designed to follow a plug of water from the influent through the distribution system; for example, the influent and treatment plant samples could be collected on days one and two, and the distribution system samples could also be collected on day one. A minimum of 14 days was required between monthly sampling periods. A minimum of two months was required between quarterly sampling periods (USEPA 1996j).

Treatment Study Applicability Monitoring

All public water systems serving ≥100,000 people and groundwater systems serving ≥50,000 people were required to conduct monthly treatment study applicability monitoring from August 1996 through July 1997. Surface water systems were required to collect samples at the influent sampling point; groundwater systems were required to collect samples at the finished water sampling point. The results of treatment study applicability monitoring determined whether a water system was required to conduct a treatment study (USEPA 1996a, 1996g).

OVERVIEW OF IMPLEMENTATION ACTIVITIES

The ICR Implementation Team in the Technical Support Center (TSC) of USEPA's Office of Ground Water and Drinking Water (OGWDW) in Cincinnati, Ohio, managed implementation of the ICR, using a team-based approach under an implementation manager and an implementation coordinator. Teams were developed to support determinations of the rule's applicability to specific water systems, water utility coordination, chemistry laboratory approval,

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microbiology laboratory approval, database system development and implementation, sampling and analyses for alternative disinfectants, treatment studies, and technical assistance. Assistance from stakeholders supplemented USEPA's resources and supported the process. The team approach, both inside and outside USEPA, was critical to keeping implementation on schedule and to providing adequate assistance to water systems and laboratories.

Many new processes were implemented to ensure high-quality data. These new processes included ISP approvals, laboratory approvals in addition to the certification process, and electronic reporting and validation of data. ICR implementation had to begin concurrently with promulgation of the final rule so the data would be available for negotiations on the Stage 2 DBP Rule and the LT2ESWTR. Project and data management tools were used throughout implementation to coordinate all ICR activities and information.

TECHNICAL ASSISTANCE

All aspects of the ICR required technical assistance. The scale of the implementation challenges and assistance needs is indicated by the number of pages in the *Federal Register* notice of the final rule (USEPA 1996a) versus the number of pages in the rule's reference manuals. Table 1.4 lists the ICR reference manuals. The *Federal Register* notice consisted of 34 pages; altogether, the manuals comprise more than 1,600 pages. In addition, USEPA distributed 21 *ICR Updates* (USEPA 1999) throughout the 18-month monitoring period to support laboratories and water systems and to clarify requirements. The American Water Works Association (AWWA), the Association of Metropolitan Water Agencies (AMWA), and individual water systems and laboratories also developed training materials and conducted workshops to support ICR implementation. In addition to these printed materials, the videos listed in Table 1.5 were produced to help train individuals who used the ICR software and the sampling techniques and analytical methods for protozoa and viruses.

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Table 1.4

Information Collection Rule manuals

Manual title	Reference
ICR Sampling Manual	USEPA 1996j
DBP/ICR Analytical Methods Manual	USEPA 1996d
ICR Manual for Bench- and Pilot-Scale Treatment Studies	USEPA 1996g
ICR Microbial Laboratory Manual	USEPA 1996h
ICR Reference Manual: Understanding the ICR	USEPA 1996i
Reprints of EPA Methods for Chemical Analyses Under the Information Collection Rule	USEPA 1996m
ICR Water Utility Database System Users' Guide (manual and 6 disks) and *Release 1.1* (instructions and 3 disks)	USEPA 1996k, USEPA 1996l
ICR Laboratory Quality Control (QC) Users' Guide (manual and 5 disks) and *Release 1.1* (instructions and 2 disks)	USEPA 1996e, USEPA 1996f
Information Collection Requirements Rule—Protozoa and Enteric Virus Sample Collection Procedures (pocket guide)	USEPA 1995b
ICR Treatment Studies Data Collection Spreadsheets User's Guide (manual and 4 disks)	USEPA 1997

Table 1.5

Information Collection Rule videos

Video title	Reference
Protozoa and Enteric Virus Sample Collection Procedures	USEPA 1995c
Virus Monitoring Protocol for the Information Collection Requirements Rule	USEPA 1995d
ICR Protozoan Method	USEPA 1995a
An Introduction to the ICR Water Utility Database System	USEPA 1996c
An Introduction to the ICR Laboratory QC Database System	USEPA 1996b

The A-Team, a technical assistance team supported by AWWA, provided telephone and e-mail support to utilities during the early stages of ICR implementation (McGuire 1994b, 1996b). The A-Team consisted of consulting engineers, water utility engineers, and scientists. USEPA support teams assisted laboratories and water systems with ICR requirements, sampling,

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methods, and use of the data systems. Formal USEPA mechanisms—including the chemistry laboratory support hotline, data system hotline, TSC implementation team support, and Safe Drinking Water Hotline—were set up to manage questions that arose during ICR implementation. AWWA provided training on the development of ICR plant sampling schematics, the development of ISPs, and use of the ICR data entry systems. Each water system and laboratory usually assigned one person to take lead responsibility for managing the organization's ICR activities.

All of these support mechanisms were required to manage implementation of the ICR. Written documents, video information, and training sessions were needed to disseminate ICR requirements. Personal assistance, including the timely feedback of electronic and telephone communications, was necessary to explain ICR requirements and to provide help with individual challenges.

LABORATORY REVIEWS AND APPROVALS

ICR approval was required for laboratories analyzing ICR samples for DBPs, DBP surrogates, water quality parameters, protozoa, viruses, or coliform bacteria. The ICR approval process ensured that laboratories were capable of providing the quality of data necessary to support future regulatory development. Initial and ongoing approvals were required for these laboratories. Details of the resulting data quality are discussed in Chapter 2 (Fair et al. 2002).

Approval of Chemistry Laboratories

During ICR implementation, more than 400 laboratories applied for approval to analyze ICR samples for DBPs, DBP surrogates, and water quality parameters. Of these, 380 received approval. These consisted of commercial, utility, and state laboratories, as well as other (university and federal) laboratories, as shown in Table 1.6. There were 20 chemical parameters for which approval could be granted, with 52 combinations of methods and analytes. A total of 4,452 laboratory approval decisions were reviewed, tracked, and maintained throughout the 18-month monitoring period.

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Table 1.6

Chemistry laboratories approved for ICR analyses as of December 1998

Laboratories	All parameters	Water quality parameters	DBPs/DBP surrogates/ DBP precursors
Utility	309	304	139
Commercial	57	51	41
State	14	13	13
Other*	2	1	1
Total	382	369	193

* University or federal

Initial approval for analyses of DBPs, DBP surrogates, and water quality parameters was based on criteria USEPA developed with the assistance of a panel of experts. Panel members, who had extensive experience in performing DBP analyses or evaluating laboratory capabilities, included representatives of utility laboratories, a commercial laboratory, state agencies, a university laboratory, a private certification organization, and USEPA. The approval procedures and criteria are outlined in the *DBP/ICR Analytical Methods Manual* (USEPA 1996d).

Approvals were granted on the basis of method and analyte (e.g., Method 502.2 for trihalomethanes [THMs]), and requirements for approval were parameter-dependent. For selected water quality parameters, the process could be as simple as submitting an application documenting state certification or state approval for the method and analyte. Approval for other methods and analyte groups—THMs, haloacetic acids (HAAs), haloacetonitriles (HANs), and other parameters—required laboratories to submit data demonstrating they could meet the ICR performance criteria of minimum reporting limit, precision, and bias, as well as satisfactory participation in a performance evaluation (PE) study. Other items reviewed were personnel and quality assurance information, including the table of contents from the laboratory's quality assurance (QA) plan. Laboratories also submitted information about analytical equipment and sample handling procedures.

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As the deadline for laboratory approval approached, it became apparent that a number of water utility laboratories had not applied for ICR approval. Although DBP samples could be shipped to a contract laboratory, samples for some water quality parameters (e.g., disinfectant residuals) had to be analyzed immediately on site. To accommodate these laboratories, ICR approval for selected analytes continued well into the ICR monitoring period.

An individual laboratory was allowed to exchange an ICR method approval if its analytical needs changed. The most frequently requested method exchange was for TOC analysis. Such cases usually involved the replacement of instrumentation—for example, if a laboratory purchased a new high-temperature combustion TOC instrument (SM-5310 B) to replace an ultraviolet (UV)–persulfate TOC instrument (SM-5310 C). The laboratory requesting a method exchange had to satisfactorily complete the same initial ICR approval process as for the earlier method; then the replacement method was approved, and approval for the old method was rescinded.

USEPA's TSC coordinated and analyzed aldehyde, cyanogen chloride, and low-level bromate samples for approximately 100 ICR plants each month. This decision was made for four reasons: (1) the in-house USEPA laboratory had expertise in all three of these analytical methods; (2) in 1996, the analytical method for low concentrations of bromate was not considered readily transferable to laboratories doing routine analyses; (3) USEPA was uncertain about whether a PE program for aldehydes and cyanogen chloride could be developed to meet the monitoring schedule; and (4) the standards for these samples called for short holding times. Therefore, USEPA assumed the costs for sampling kits, analyses, and overnight delivery of these samples to TSC (USEPA 1996a, 1996j).

Maintenance of ICR approval to analyze DBPs, DBP surrogates, and DBP precursors depended primarily on the laboratory's successful participation in six quarterly ICR PE studies. Approved laboratories that failed a PE study for a particular method and analyte group immediately had a second opportunity to pass. During monitoring, 12 to 29 laboratories per quarter lost approval for one or more method and analyte group by failing two consecutive ICR PEs (the original PE and the make-up PE). Table 1.7 lists the main reasons for such failures. Some laboratories sought to have ICR approval reinstated. Requirements for reinstatement depended on the reason for the consecutive PE failures. The requirements ranged from simply

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passing the next PE to submitting a new application with newly generated method performance data and successful participation in the next ICR PE study. In all, 16 laboratories regained approval for one to two methods.

Another means of assuring data quality for ICR chemistry laboratory approval was on-site laboratory audits. Thirty-five DBP laboratory audits were conducted during the 18-month monitoring period to ensure that ICR laboratory requirements were being followed. The laboratories selected for these audits represented more than 10% of those approved for DBP analyses. Selection for an on-site audit was based on one of the following reasons:

- Difficulty meeting initial approval criteria,
- Questionable laboratory performance based on PE studies or calls from clients,
- Analysis of a significant number of ICR samples, or
- Random selection.

Table 1.8 presents the evaluation protocols used for on-site audits and lists the five most commonly identified problems. Laboratories were required to correct identified problems. In a few instances, USEPA rejected some ICR data because of audit findings, and one laboratory lost ICR approval for one of its methods as a result of an on-site audit.

Another technique for monitoring laboratory performance was a completeness criterion—i.e., a percentage of ICR sampling results accepted into the ICR Federal Database System (ICR FED). Although USEPA had planned to use this criterion during the 18-month monitoring period, this plan was not possible because the extended process of developing the data validation software delayed the uploading of QC data from the laboratories and monitoring data from the water systems. The first opportunity to determine completeness of the first month's monitoring data (collected in July 1997) was October 1998, when the data were finalized. Because monitoring concluded two months later, USEPA could not hold laboratories accountable for meeting completeness criteria under the laboratory approval program.

A more immediate concern was that the delay in completing the validation system could result in significant losses of data, because laboratories might not become aware of mistakes until their first set of QC data had been processed on the ICR FED, well after the laboratories had completed their analyses. To help laboratories assess whether they were meeting ICR

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requirements, USEPA offered laboratories the opportunity for an informal review of their QC data during the latter part of 1997. Laboratories were instructed to send a copy of their ICR QC database to an ICR support contractor, who conducted a cursory review of the data to determine if ICR QC requirements were being followed. Laboratories were notified of the outcome of these reviews.

Table 1.7

Most common reasons for consecutive failures of ICR PE studies

Not reporting data for approved parameters	Analytical errors
Reporting an incorrect method number	Reporting late
Mathematical errors	

Table 1.8

On-site evaluations of ICR chemistry laboratories

Protocols	
	Tour facility
	Review QA information
	Examine ICR Quality Control (QC) data
	Interview each analyst
	Hold debriefing session with laboratory management
Problems identified	
	Wrong concentration of check standards or spikes
	Incorrect sample collection or preservation protocol
	Failure to use USEPA stock solutions
	Subcontracting to non–ICR-approved laboratories
	Incorrect or incomplete QA documentation

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Approximately 70 laboratories submitted copies of their ICR QC databases to an ICR support contractor for review. This process helped to identify laboratories that were not entering all of their QC data into the database or were not analyzing all of the required QC samples. In many cases, the laboratories were able to correct their databases and send USEPA substitution diskettes for uploading into the ICR FED. USEPA received 102 substitution diskettes from 54 laboratories as a result of the review process. Throughout the ICR effort, USEPA and its support contractor provided technical assistance to laboratories by means of articles in the *ICR Update* (USEPA 1999), responses to calls to the ICR chemistry hotline, periodic mailings, production of help guides, and review of laboratory and utility reports from the ICR validation process.

Approval of Microbiology Laboratories

As the ICR Rule was finalized, much concern was raised about method performance, laboratory capacity, and expertise at protozoan and virus analyses using ICR methods. Specific issues centered on low recoveries typically observed with the analytical method for protozoa. USEPA and AWWA conducted training on protozoan and virus analyses to educate analysts in the ICR procedures. Laboratory approval criteria were designed to ensure that the most qualified analysts were approved to conduct these ICR analyses.

Approval of laboratories for coliform analyses was based on verification of state or USEPA certification and use of required methods. ICR approval for virus and protozoan analyses was analyst- and laboratory-based, unlike the chemistry and coliform laboratory approvals, which were only laboratory-based. Initial and ongoing approvals for virus and protozoan analysts were based on successful completion of monthly PE studies, successful analysis of QC samples, and results of on-site laboratory audits (USEPA 1996h).

Ninety-five laboratories applied for ICR approval to analyze protozoa. Of these, 51 were eligible for on-site evaluations, and 29 were approved by the time ICR microbial monitoring began. Thirty-one laboratories applied for ICR approval to analyze viruses, 20 were evaluated on site, and 12 were approved by the beginning of the 18-month monitoring period. By the end of the monitoring period, 10 laboratories remained approved for virus analyses, 28 for protozoan

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analyses, and 310 for coliform analyses (Table 1.9). At these laboratories, 19 analysts were approved for virus analyses and 48 for protozoan analyses.

PE studies conducted during ICR implementation measured the ability of analysts to use the ICR protozoan and virus methods. PE samples were not spiked water samples but filters containing viruses or protozoa, which were analyzed according to ICR methods. Analysts were required to pass an initial PE round to gain ICR approval to analyze these samples. To maintain approval, they were required to meet a six-month rolling average for monthly PE samples. The PE results showed that the performance of analysts remained consistent throughout ICR implementation, and PE recoveries remained above the minimum set by USEPA.

For approved analysts, the median recoveries on valid PE samples, both initial and ongoing, were 47% for *Giardia*, 40% for *Cryptosporidium*, and 42% for viruses. However, these percentages do not reflect overall method recoveries, because the organisms were spiked directly onto the PE filters and were not filtered from a water sample. Typical recoveries from water samples analyzed according to the complete ICR methods are expected to be much lower. Figures 1.2 and 1.3 present the frequency distributions of the results from all valid PE samples. Two thirds of all recoveries fell between 25% and 70% for *Giardia*, 19% and 64% for *Cryptosporidium*, and 24% and 85% for viruses.

As part of the ongoing process of laboratory approval, 26 protozoan and 11 virus laboratories were audited from May through November 1998. These audits were conducted to ensure that the quality of the analyses and the quality of the data were consistent with findings from the initial on-site evaluations. In general, the laboratories were in compliance with ICR method requirements, and laboratory personnel met the qualifications for ICR analysts. Most of the problems identified during the audits involved the failure of analysts to record detailed information about the analyses. Table 1.10 outlines the protocol for on-site evaluations and lists some problems identified by on-site evaluators.

An important, yet often overlooked, function of microbiology laboratory approval was the technical assistance provided through the process. Initially, approval requirements and ICR methods were clarified. During monitoring, procedural techniques were addressed because of the ongoing contact between the laboratory approval coordinator at USEPA's TSC and the analysts who were reporting monthly QC and PE data. The laboratory approval coordinator often

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addressed questions that arose during validation of the ICR microbiology data. The ICR approval criteria for microbiology laboratories, along with the exchange of information between USEPA and the analysts, improved the quality of the ICR microbiology data.

Table 1.9

Microbiology laboratories approved for ICR analyses as of December 1998

Parameter	Laboratory	Analyst
Protozoa	28	48
Viruses	10	19
Coliforms	310	Not applicable

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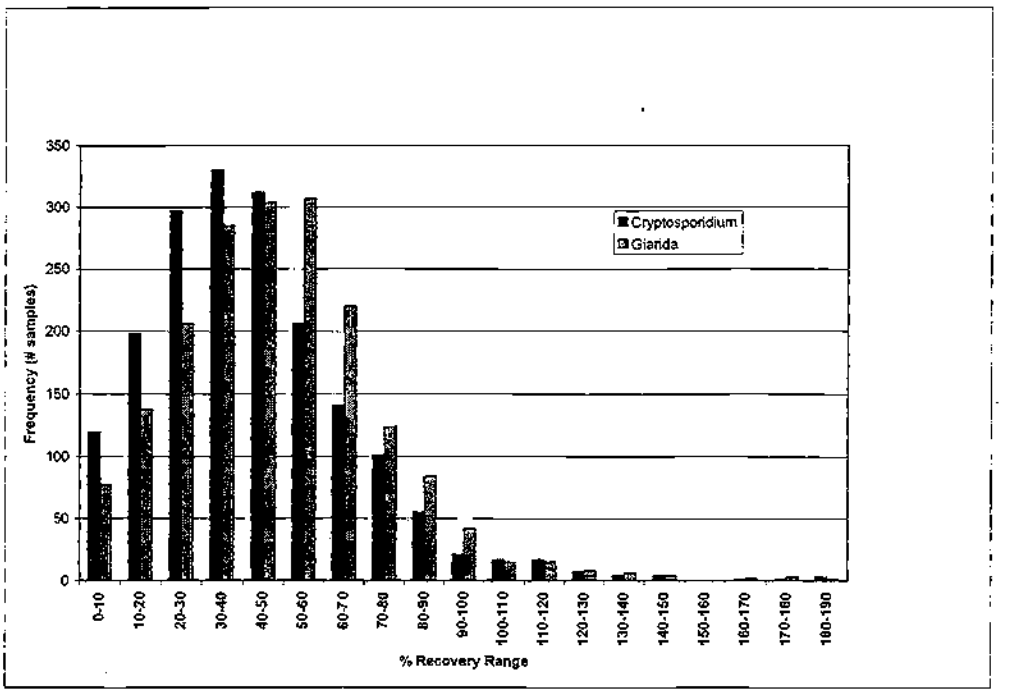

Figure 1.2 Distribution of percentage recoveries for valid protozoan PE samples

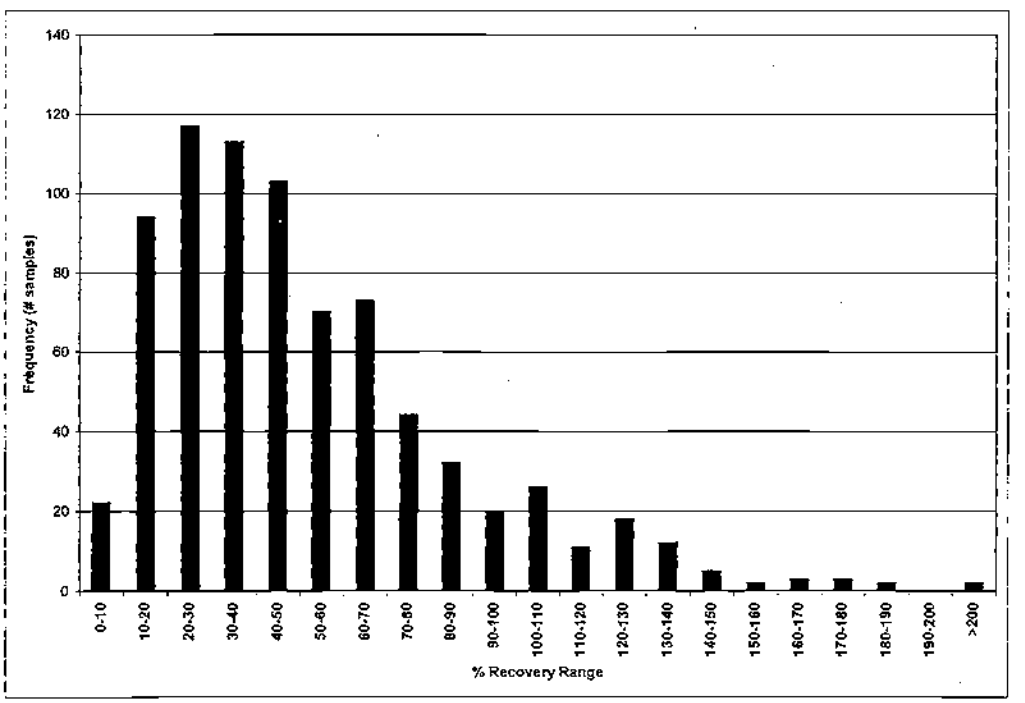

Figure 1.3 Distribution of percentage recoveries for valid virus PE samples

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Table 1.10

On-site evaluations of ICR protozoan and virus laboratories

Protocols	
	Examine standard operating procedures, including tour of facility
	Review personnel qualifications
	Evaluate laboratory's and analyst's ICR analytical procedures
	Evaluate QA and record-keeping procedures
	Provide immediate feedback on deviations from ICR analytical methods
Problems identified	
	Failure to record detailed information for each step of sample analysis
	Incomplete documentation of ICR QC requirements
	Deviations from ICR method performance
	Use of non–ICR-approved personnel for parts of analyses
	Incorrect or incomplete QA documentation

UTILITY APPLICABILITY AND SAMPLING PLANS

USEPA's TSC conducted detailed reviews of water utilities' supply, treatment, and distribution systems to determine the applicability of the ICR requirements to each system.

ICR Applicability

Many large water systems operate more than one treatment plant, and some have multiple water sources, including both surface and groundwater supplies. Some public water systems only redisinfect purchased water (in which case the system could be considered a treatment plant under the ICR), whereas other water systems supplement their treated water with purchased water. During ICR applicability reviews, the ICR treatment categories listed in Tables 1 and 2 of the rule were assigned to each treatment plant (USEPA 1996a). Altogether, 296 water systems encompassing 500 treatment plants were required to participate in the 18-month monitoring

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program. A detailed inventory of these systems and plants is presented in Chapter 3 (Roberson 2002) of this book.

Unique ICR public water system (PWS) and treatment plant identification numbers were assigned during the applicability review. Although most states assign a single PWS identification number to all plants in one community water system, a few states assign separate PWS identification numbers to each plant in a community water system. Some water systems that do not treat water before wholesaling it to other systems did not have PWS identification numbers at the time of ICR implementation. Therefore, unique ICR PWS and treatment plant identification numbers were established for each ICR system and plant.

Initial Sampling Plans

USEPA required submission and approval of ISPs to ensure that ICR requirements were appropriately applied to the water systems participating in the 18-month monitoring program. AWWA's A-team was instrumental in training and providing technical assistance to these water systems during preparation of the ISPs (McGuire 1994b, 1996b). AWWA worked with the water systems to develop ICR Initial Sampling Schematics (ISSs), which the water systems could then use along with the ICR Water Utility Database (USEPA 1996k, 1996l) to develop ISPs. Figure 1.1, which illustrates a sample ISS, was part of an ISP and was used to determine sampling requirements. USEPA's TSC conducted thorough reviews of each ISP for the following reasons:

- To consistently apply the ICR requirements to each unique treatment plant configuration affected by the rule,
- To collect accurate process design information from each treatment plant, and
- To assist in the selection of appropriate ICR sampling locations and parameters.

The ISP review and approval process proved extremely valuable because nearly 80% of the ISPs required modification after an initial review. Modifications included, but were not limited to, correcting chemical additions and sampling locations, defining influent sampling points for influents common to two treatment plants, proper sequencing of unit processes and associated sampling points, and correcting chemical feed formulas. More than 90% of the ISPs

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were approved after a second review. Many utilities misinterpreted the requirements explained in the ICR guidance materials, and USEPA's TSC implementation team was able to clarify these requirements during the ISP review process.

TREATMENT STUDY APPLICABILITY AND REVIEW

Treatment study applicability monitoring affected 493 water treatment plants, of which 482 conducted monthly monitoring for TOC. Water systems could avoid conducting a treatment study by meeting one of the following criteria:

- Meeting the TOC avoidance criteria or the distribution system DBP avoidance criteria (Table 1.11),
- Operating a full-scale granular activated carbon (GAC) or membrane treatment system, or
- Contributing to a USEPA–American Water Works Association Research Foundation (AwwaRF) research fund.

Plants could also grandfather data from previous studies in lieu of conducting a new study if the grandfathered data met certain minimal requirements (Allgeier, Shukairy, and Westrick 1998; USEPA 1996a, 1996g).

Table 1.11

Criteria for avoiding treatment studies

Plant types	Average TOC concentration	Average distribution system THM4*†	Average distribution system HAA5†
Surface water plants	Influent ≤4.0 mg/L		
Groundwater plants	Finished ≤2.0 mg/L		
Surface or groundwater plants		<40 μg/L	<30 μg/L

* The sum of four THM species

† The distribution system DBP avoidance criteria applied only to plants that used free chlorine in the distribution system.

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Affected utilities were required to submit TOC results, along with an application to avoid the treatment study requirement, or a study plan by November 1997. USEPA's TSC reviewed these applications along with the TOC monitoring results to determine ICR treatment study applicability for each plant. Based on the results of this monitoring, 385 plants (78%) met the criteria to avoid the treatment study requirement. Four plants (1%) contributed to the MDBP research fund in lieu of conducting studies. The remaining 104 plants (21%) conducted individual studies, submitted grandfathered data from previous studies, or conducted studies in collaboration with other plants. These 104 plants submitted results from 99 studies, including 63 GAC studies and 36 nanofiltration studies. Figure 1.4 illustrates the distribution of studies by treatment technology (Allgeier, Shukairy, and Westrick 1998). The results and analyses of these studies are captured in the ICR Treatment Study Database and are discussed in Chapter 21 (Hooper and Allgeier 2002) of this book. The ICR Treatment Study Database was developed in the Microsoft® Access™ environment and is available on CD-ROM (USEPA 2000a).

USEPA's TSC reviewed the final treatment study reports for completeness and accuracy. Data- reporting requirements were detailed in the manuals for ICR treatment studies (USEPA 1996g, 1997). The use of standard data-reporting spreadsheets streamlined data submission and enabled USEPA to develop a highly automated data review process that allowed the engineering team to review as much as 90% of the data from each study. The final reports for each of the 99 studies required some degree of follow-up with the utilities to clarify data and information. Common problems included missing information, data entry errors, incorrectly reported units of measure, and incorrect chlorination procedures. The use of sophisticated review spreadsheets—along with the reviewers' knowledge of GAC, nanofiltration, and DBP formation—allowed USEPA to recognize erroneous or missing information and to work with utilities to develop complete, accurate data.

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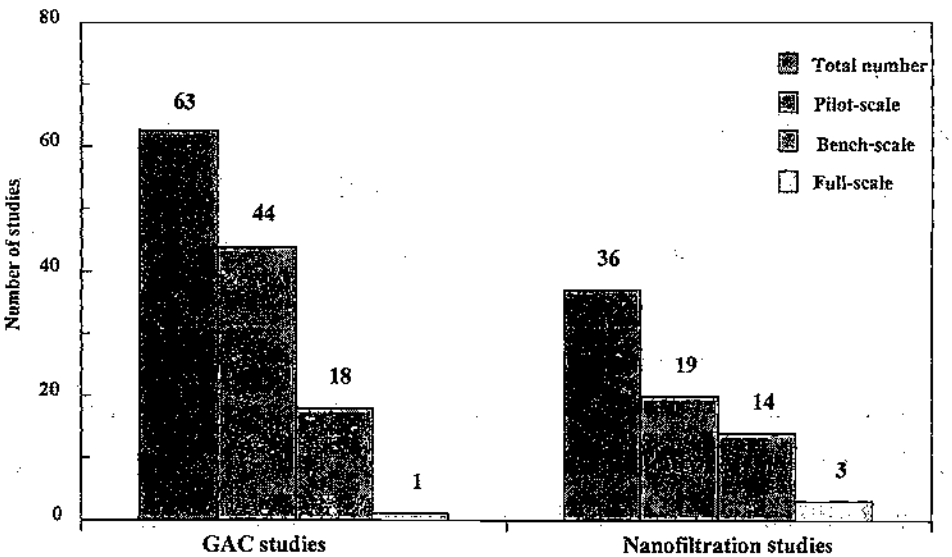

Figure 1.4 ICR treatment studies

ICR DATA MANAGEMENT SYSTEM

The ICR data management system was developed to plan, manage, and report results of the 18-month monitoring program. The ICR data management system (Figure 1.5) consists of the ICR Water Utility Database System (USEPA 1996k, 1996l), the ICR Laboratory Quality Control (QC) Database System (USEPA 1996e, 1996f), and the ICR FED. The Water Utility and the Laboratory QC systems are PC-based applications used to collect and report treatment process, sampling, and QC information required by the ICR. Utilities and laboratories reported data to USEPA via diskettes generated from the Water Utility and the Laboratory QC database systems. Once validated, the data were stored in the ICR FED to be used for data analyses. The ICR FED, an Oracle™ database, is available to the public. Databases for laboratory approval, ICR applicability, and treatment studies were developed and maintained separately from ICR FED.

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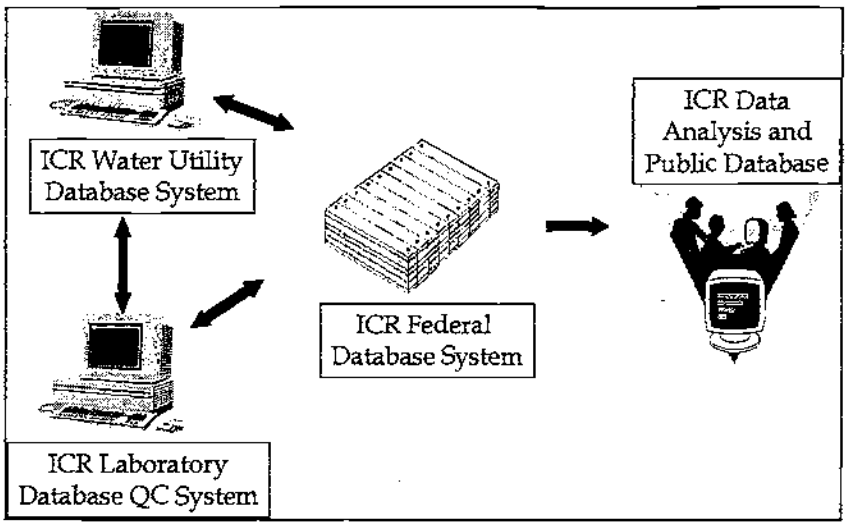

Figure 1.5 ICR data management system

The ICR data system was designed and tested with a joint applications design process and included input from laboratory and water industry representatives (McGuire and Rosen 1995; McGuire 1995, 1996c). Communicating knowledge of analytical methods and water treatment practices from water industry or laboratory experts to computer system developers was a challenge. Furthermore, USEPA was still defining some ICR regulatory requirements as data system requirements were being deliberated. Delays in the development of ICR FED validation software led to significant data management challenges, as discussed in the following sections.

Data Reporting

Each month ICR utilities submitted unit process data for each of their ICR plants, plus collection information and analytical results for each ICR sample along with some QC information. The ICR schematics and sample collection information were unique for each utility. Water systems reported the design and operating parameters listed in Table 6 of the ICR (USEPA 1996a) using the Water Utility Database System. Treatment plant and unit process parameters included type of process train, water flow rates, contact times, filter run times, chemical feeds, and volumes. These treatment data were updated monthly for each of the 500

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ICR treatment plants. Using the Water Utility Database System, treatment plant design information was collected prior to July 1997, as discussed earlier, and final design information was collected after ICR monitoring was complete in December 1998.

Chemistry, protozoan, and virus laboratories reported monthly ICR QC data using the Laboratory QC Database System. Examples of reported QC data include analytical batch information, plus results for shipping blanks, calibration check standards, and method blanks (Fair et al. 2002). Coliform laboratories reported QC data to the water systems for submission along with the system's monthly sampling results. The specific QC requirements of the ICR are detailed in the *DBP/ICR Analytical Methods Manual* (USEPA 1996d) and the *ICR Microbial Laboratory Manual* (USEPA 1996h).

Data Processing and Validation

All of the data from laboratories and utilities participating in the 18-month monitoring program were processed on the ICR FED, a central data system at USEPA. The flow diagram in Figure 1.6 shows the progression of the data upload and validation process. Once samples were collected and analyzed, utilities and laboratories entered data into the corresponding database system. Data were reported to USEPA on diskettes on a monthly basis. After the diskettes were inventoried and the data uploaded to the computer system, USEPA processed the data using validation algorithms on ICR FED. Validation reports (VL and VA reports) containing the results of samples that failed validation by not meeting ICR criteria (USEPA 1996d, 1996h) were generated by ICR FED. Validation failures occurred for a variety of reasons—for example, if sample holding times were exceeded, if the laboratory was not approved for the method, or if the calibration standard failed. Reports containing monthly results for each utility (VU, VL, and VA reports) were also generated. These reports were distributed to laboratories and utilities for review and correction of any errors. When USEPA received diskettes with corrected data sets, the inventory, upload, and validation steps were repeated. At that point, final reports were generated, and the data were available for extraction from ICR FED for analysis. A full processing cycle, including one data resubmission step, took six months to complete.

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Figure 1.7 illustrates the volume of diskette submissions USEPA managed throughout the 18-month monitoring period. USEPA finished validating data for the first quarter of the 18-month monitoring period by May 1999 and for the final quarter by December 1999. All data corrections were completed by April 2000.

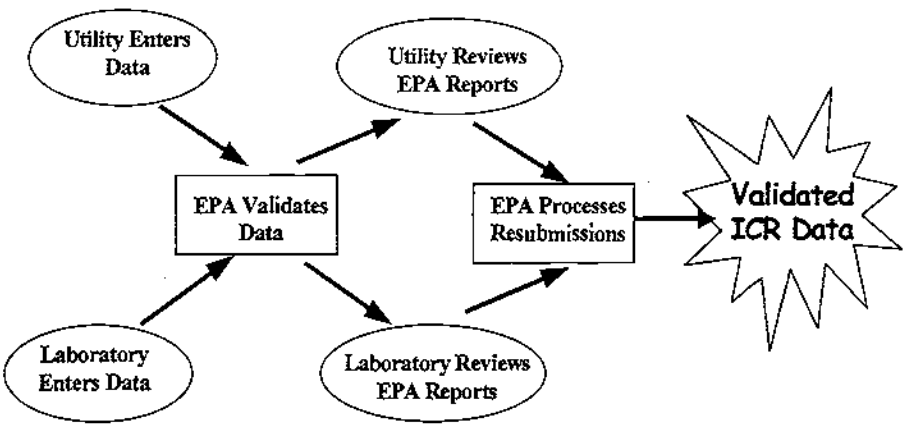

Figure 1.6 ICR data reporting process

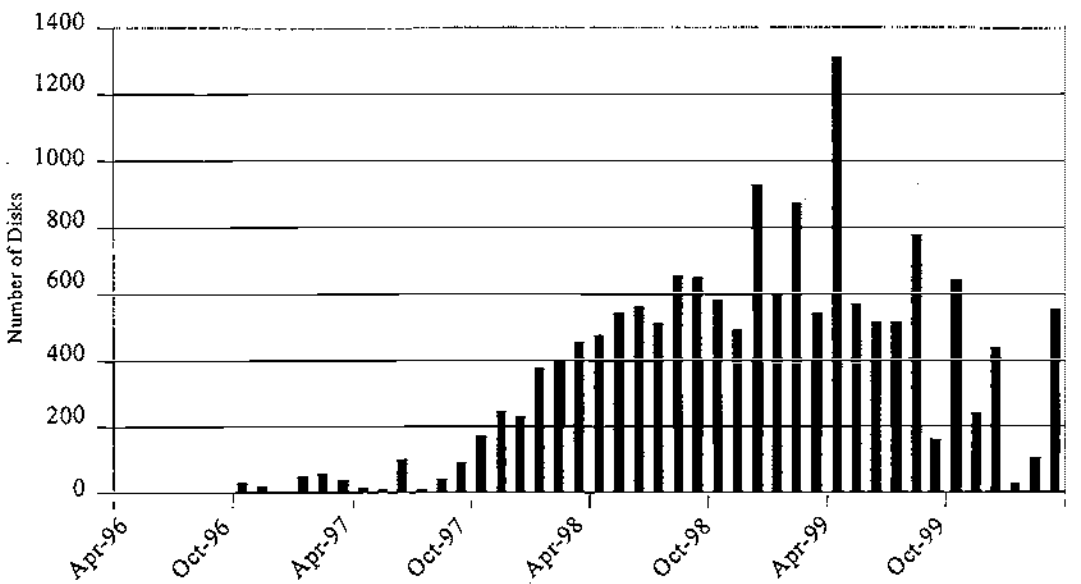

Figure 1.7 Diskettes USEPA received each month

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Laboratory QC data reported by laboratories or utilities, and laboratory approval information maintained by USEPA, were used to validate monthly monitoring results after the data were uploaded to ICR FED. If monitoring results did not meet ICR criteria, as discussed in Chapter 2 (Fair et al. 2002), the results were nullified by ICR FED and given a USEPA QA code of "R" (for "reject"). In addition, utilities assigned QA codes to each analytical result at the time the data were entered into the ICR Water Utility Database System. This procedure allowed utilities to identify and report sampling or laboratory problems that might not be identified by validation criteria. The utility QA codes were "A" (for "acceptable"), "Q" (for "questionable"), or "R" (for "reject"). ICR FED validation algorithms nullified analytical results that had been assigned the utility QA code "R." Information about treatment plant unit processes and chemical applications was not validated using ICR FED algorithms. Utilities verified this information by reviewing data within the Water Utility Database System or printed reports.

Data Management Challenges

USEPA originally intended to complete ICR FED by the summer of 1997 in order to begin validating laboratory and utility data when they were first reported in the fall of 1997. Unfortunately, significant delays in the final development and testing of the validation system postponed start-up of ICR FED operation until the spring of 1998, and the system was not fully functional until the fall of 1998. This delay presented one of the most significant data collection challenges encountered during ICR implementation, primarily because USEPA was unable to give water systems and laboratories timely feedback on the validity of data submitted during the early months of ICR monitoring.

Water systems and laboratories assisted USEPA with final debugging of the validation algorithms by reporting individual problems that arose in connection with their initial validation reports. USEPA had to optimize the data validation process to manage the backlog of monitoring data that had accumulated because of the delayed start-up of ICR FED. Final validation of the 18-month monitoring data was successful because of the dedication and cooperation of the ICR water systems and laboratories and the ICR data team at USEPA.

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ICR DATA ANALYSIS

Various approaches were possible for analyzing the validated data that resided in the Oracle™ database ICR FED. The selected approach depended on the questions that needed to be answered. To characterize DBP precursor concentrations in source water, or DBP distribution system occurrence data, a vertical analysis was used. This approach allowed aggregation of the data based on geographic or hydrologic distributions at a particular sampling location. For example, TOC occurrence could be evaluated by using a cumulative probability distribution at the influent sampling points of all surface water treatment plants. Another approach involved a horizontal analysis that considered changes in parameters through the treatment plant. An example of such an analysis was the use of 18 sets of monthly data to validate the Water Treatment Plant Model predicting DBP formation (Swanson et al. 2002).

A schematic of vertical and horizontal analyses is shown in Figure 1.8. Consideration of scenarios permitted by vertical and horizontal analyses led to the development of auxiliary ICR databases, each designed for specific data analysis objectives. The auxiliary databases, unlike ICR FED, were developed in Microsoft® Access™.

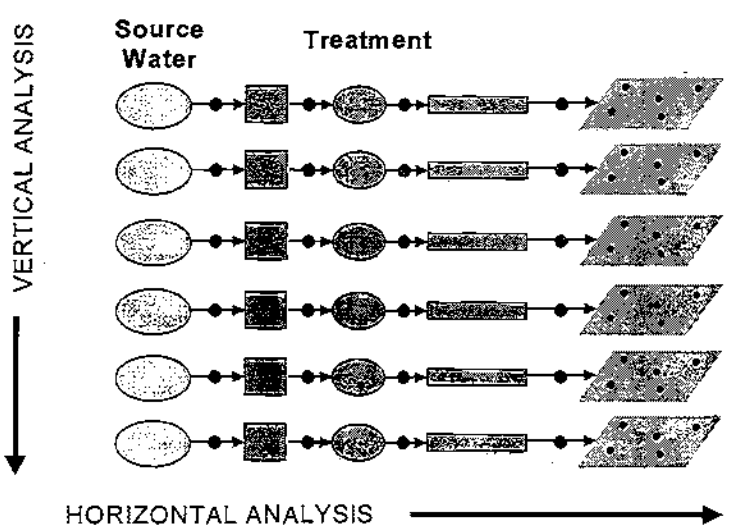

Figure 1.8 The ICR data analysis process

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Principal Auxiliary Database

The technical work group (TWG) that supported the MDBP Federal Advisory Committee negotiations for the Stage 2 DBP Rule determined that the ICR data could be more readily analyzed in a format other than ICR FED. This determination led to the design of a principal auxiliary database, the ICR Auxiliary Database Version 5 and the Query Tool Version 2 (AUX1), which houses a significant portion of the validated ICR data (USEPA 2000b). AUX1 contains utility and treatment plant information, treatment operations data, ISPs, final sampling plan designs, and sampling results. Except for identifying laboratories and analysts approved to analyze protozoan and virus samples, AUX1 does not contain any QC data.

AUX1 is a Microsoft® Access™ relational database. Its data and structure were selected to allow analyses that would support rule development. The structure of AUX1 lends itself to vertical analyses and is not ideal for horizontal or through-plant analyses; the database was designed to facilitate examining a single variable across all plants and for specific aggregates—e.g., the concentration of total THMs (TTHM) at the finished water sampling point in plants using chlorination. A query tool for use with AUX1 was developed to serve database users without relational database skills. Because examining a single variable through a single plant was difficult, though not impossible, with AUX1 (e.g., changes in TOC concentration through a plant practicing enhanced coagulation), secondary auxiliary databases were developed.

Secondary Auxiliary Databases

Several secondary auxiliary databases (AUX2–AUX6), also constructed in Microsoft® Access™, focused on horizontally linked data. Whereas the primary auxiliary database (AUX1) was derived from ICR FED, the secondary auxiliary databases (AUX2–AUX6) were derived from AUX1. A schematic of the auxiliary databases is shown in Figure 1.9.

Auxiliary Database 2 (AUX2) is a CT (concentration × time) and disinfectant decay database. One of the main objectives of ICR data analysis was to characterize baseline treatment under existing regulations. AUX2 facilitated analysis of through-plant log inactivation of *Giardia* and viruses and analysis of disinfectant decay in the distribution system.

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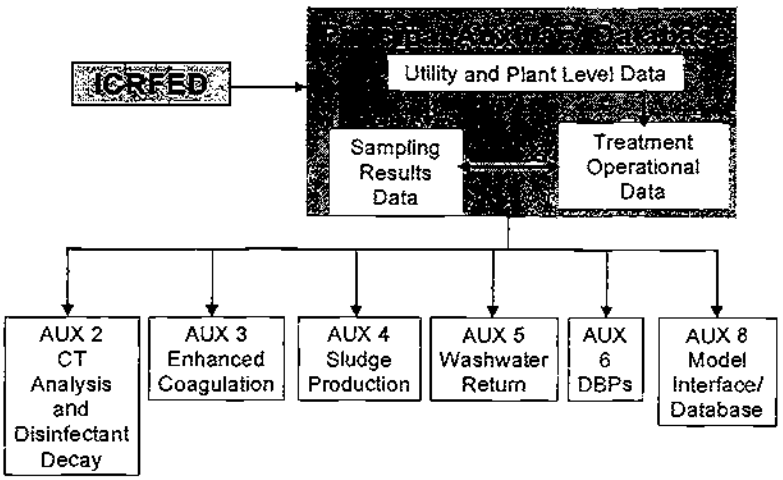

Figure 1.9 ICR auxiliary databases

The purpose of Auxiliary Database 5 (AUX5), the washwater return database, was to examine the effects of washwater return on water quality in the plant. Using data from AUX5, water quality parameters from upstream of the washwater return were compared with water quality parameters in the washwater return.

To assess exposure, it is important to know how specific DBPs increase or decrease between the finished water sampling point and the ICR sampling point reflecting maximum detention time in the distribution system. Auxiliary Database 6 (AUX6) was designed to analyze DBP occurrence through a specific plant's distribution system. AUX6 also houses corresponding precursor concentrations, disinfectant dosages, and disinfection reaction conditions such as pH, temperature, and contact time. (AUX7, created to assess source water quality issues, was not developed because it was not expected to provide useful information beyond that furnished by the other databases.)

Auxiliary Database 8 (AUX8) was created to house input and output files generated by the Water Treatment Plant Model and the Surface Water Analytical Tool, as discussed in Chapter 8 (Swanson et al. 2002). AUX8 also has an interface with AUX1 to extract input parameters and is able to document the model runs for each set of model conditions.

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Data Transformation in Auxiliary Databases

As the necessary data were extracted for incorporation into AUX1, additional fields were added and some data manipulation steps were taken to allow the data to be presented in a more user-friendly format. Data transformation is described in detail in the dictionary and documentation within AUX1 (USEPA 2000b). Data for AUX2–AUX6 were extracted from AUX1 and, therefore, incorporated the same data manipulation criteria as AUX1.

Because some of the analyses would require data to be segregated based on the type of source water being treated or the type of disinfection being used at the plant and in the distribution system, this information was added to AUX1 based on an examination of the data in ICR FED. Each treatment plant's source water was categorized as surface water (SW), groundwater (GW), mixed (MIX), or purchased water (PUR) based on the percentage of water flows reported in ICR FED. Surface water sources were further subcategorized as reservoir or lake (RL), flowing stream (FS), groundwater under the direct influence of surface water (GWUDI), or mixed (MIX). The type of disinfectant used at each plant and in each distribution system was determined by using the information reported for chemical feeds. Disinfectants used in treatment plants were classified as chlorine (CL2), chloramines (CLM), chlorine dioxide (CLX), ozone (O3), various combinations of disinfectants, or null. Disinfectants used in distribution systems were designated as either chlorine (CL2) or chloramines (CLM).

ICR utilities reported the chemical formula and applied dose for each chemical used at the treatment plant. When these data were transferred to AUX1, the chemical feed dosages were normalized to common units in order to ensure consistent comparisons during data analysis. The normalization step required expert intervention by the MDBP TWG. Other fields that were created for AUX1 and were not in ICR FED reflected categories for population served, the quarter in which sampling occurred, USEPA region, calculations of TOX relative percent difference (TOXRPD), hydrologic unit codes (HUC), and calculations of chlorine demand (CLD).

All concentrations reported as less than the minimum reporting level (<MRL) were converted to "-999" in AUX1 to maintain numerical values in the concentration fields of the database. These "-999" values were related to a table (within AUX1) that summarized the MRL

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concentrations by analyte, as defined in the ICR (USEPA, 1996d). If the concentration for an analyte was missing in ICR FED, AUX1 maintained the missing value as null.

The ICR FED did not contain data reflecting aggregate DBP concentrations for TTHM, HANs, HAA5, the sum of six HAAs (HAA6), or the sum of nine HAAs (HAA9). Because some of the data analyses would require sum concentrations for these classes of compounds, these sums were calculated and added to AUX1 for convenience. If the concentration of one of the analytes in a compound class was missing, the sum concentration was shown as null in AUX1. If the concentration of a DBP analyte was <MRL, a zero was substituted for that analyte's concentration in the summation calculation.

Analyses for TOC, TOX, and UV_{254} absorbance were required to be performed in duplicate; as a result, ICR FED contains two concentrations per sample for each of these analytes. When these data were extracted to AUX1, all duplicate results were averaged, so AUX1 contains only one TOC, TOX, and UV_{254} concentration for each sample. When the duplicate concentrations for TOC, TOX, and UV_{254} were averaged, <MRL values were replaced with the appropriate MRL; then, if the average concentration equaled the MRL, the average was replaced with "–999." In cases in which a TOX sample was not reported as analyzed in duplicate in ICR FED, the individual concentration was extracted to AUX1. In cases in which a TOC or UV_{254} sample was not reported as analyzed in duplicate, the data failed USEPA's QA requirement and thus the concentration was shown as null in ICR FED; the null concentration was maintained in AUX1.

Another modification that was made to ICR FED data during extraction to AUX1 involved disinfectant residual and ammonia concentrations. Because of a limitation in the data-reporting software, utilities were not able to report concentrations <0.1 mg/L for disinfectant residuals or ammonia. In order to capture this information, the utilities were instructed to flag the data with a QA code of "Q" and to place the actual concentration value in a comment field. All comment fields associated with these parameters were examined, and when the comment provided the actual concentration, it was substituted into AUX1. Ammonia and chlorine residuals that were reported as 0.1 mg/L were changed to "–333" when a comment indicated that the actual residual was <0.1 mg/L. If the ammonia and chlorine residual values were shown as

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zero in ICR FED, the zero was maintained in AUX1. An expert group from the MDBP TWG conducted this data transformation process.

Access to ICR Data

The ICR data that were reported to ICR FED and extracted to AUX1 led to the rich analyses presented in subsequent chapters of this book. Most of the authors relied on the auxiliary databases for their respective analyses; the majority used AUX1.

The ICR data are available in easily accessible formats. A CD-ROM contains the Microsoft ®Access™ database called ICR Auxiliary 1 Database Version 5.0 and the Query Tool Version 2 (USEPA 2000b). This CD can be obtained from USEPA's National Service Center for Environmental Publications (telephone: 1-800-490-9198). The Envirofacts Data Warehouse on USEPA's Internet site contains summary data about microorganisms and disinfection by-products from the ICR Auxiliary 1 Database Version 5.0 (USEPA 2000c) and includes simple query capabilities. Graphic and tabulated ICR data are also available on the Internet (Cadmus 2001).

SUMMARY

More than 600 laboratories and a total of 296 large water systems representing 500 treatment plants collected and reported data for the 18-month ICR monitoring program. Each water system was required to enter monthly data into the ICR Water Utility Database, which was designed to accept monitoring and engineering data. Approved laboratories were required to enter quality control data into the ICR Laboratory QC Database System. Data were then uploaded into the ICR FED, validated, and reported back to utilities and laboratories for verification and, when necessary, resubmission prior to final validation. Data in the ICR FED were subsequently extracted into auxiliary databases to facilitate data analyses. Results from 99 ICR treatment studies were reported using standard data-reporting spreadsheets and were reviewed by USEPA. Findings from analyses of the ICR data are presented in subsequent chapters of this book.

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Challenges that had to be overcome during ICR implementation included centralized USEPA approvals of laboratories and public water system sampling plans, timely dissemination of information and training, use of new electronic data-reporting systems, and development and implementation of data validation processes. Utilities and laboratories incorporated the added burden of the ICR requirements into their operations throughout data collection and validation. Delays in development of the data validation software led to delayed review of validated data by laboratories and utilities. Technical assistance teams were staffed despite limited resources. Data in the Oracle™ ICR FED database were restructured into Microsoft ®Access™ auxiliary databases to enable water treatment plant professionals and regulators to analyze the data with relative ease. Schedule pressures were a continual challenge from 1993, when the Regulatory Negotiating Committee agreed to an ICR, through data collection and validation, to completion of the data analyses conducted to support development of the Stage 2 DBP Rule and the LT2ESWTR.

When the drinking water industry joined with USEPA to undertake ICR implementation, the expertise and perseverance of all of the participants resulted in the most comprehensive database created to date—a database containing data on disinfectants, disinfection by-products and precursors, microorganisms, water quality parameters, and engineering treatment processes for systems serving ≥100,000 people. Presentation and analyses of these data were a critical part of the MDBP Federal Advisory Committee negotiations for the Stage 2 DBP Rule and the LT2ESWTR. It is anticipated that the data will be used by industry, government agencies, and academia for years to come.

ACKNOWLEDGMENTS

USEPA staff members who worked on the ICR Implementation teams often do not get recognized outside the OGWDW's Technical Support Center. Individuals, other than this chapter's co-authors, at USEPA, Cincinnati, Ohio, deserving recognition for excellence and perseverance in implementing the ICR are listed here alphabetically: Eric Bissonette, Phyllis Branson, Cindy Bultman, Edward Cottrill, Daniel Williams, Charles Feldmann, Shay Fout, Christopher Frebis, Christy Frietch, Edward Glick, Alison Gusses, Susan Hagedorn, Stephanie

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Harris, Daniel Hautman, Lillian Holmes, Donald Klosterman, Norman Kowal, Richard Lieberman, Cynthia McCauley, Caroline Madding, Daniel Mossburger, David Munch, Kent Neathery, Bonita Newport, Jane Pleiman, Frank Schaefer, Katrina Schneider, Lois Shadix, James Sinclair, Glen Shaul, Thomas Sorg, Alan Stevens, Timothy Straub, Larry Weiner, and James Westrick. Organizations that supported the ICR included: SAIC-EHSG, SAIC-SDC, ICF Kaiser, the Centers for Disease Control and Prevention, AWWA, AMWA, TPMC, McGuire Environmental Consultants, ICR water systems and consultants, and ICR laboratories.

Members of the Data Analysis Technical Workgroup, including some of the authors, who were responsible for development of the ICR auxiliary databases included Stig Regli, Jennifer McLain, Jimmy Chen, Daniel Schmelling, and Michael J. Messner from USEPA, as well as many other stakeholders.

This research was supported in part by appointments to the OGWDW's internship program administered by the Oak Ridge Institute for Science and Education through an interagency agreement between USEPA and the U.S. Department of Energy.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The scientific views expressed are solely those of the authors and do not necessarily reflect those of USEPA.

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CHAPTER 2

QUALITY OF ICR MONITORING DATA

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ABSTRACT

All parties involved in planning the Information Collection Rule (ICR) were concerned that the data collected during the 18-month monitoring effort be of satisfactory quality for use in developing future regulations. Laboratories and utilities were required to report specific quality control (QC) data to the U.S. Environmental Protection Agency along with the monitoring data. An automated data validation process was used to determine if the QC criteria were met for each parameter measured in a sample. If the QC criteria were not met for a parameter, the concentration reported for that parameter was removed from the federal database. Overall, 92 percent of the analytical data met the ICR QC requirements.

QC requirements for positive and negative control samples were placed on ICR laboratories and analysts performing protozoa and virus analyses. The most stringent QC checks were performed on data from the analyses of disinfection by-products (DBPs) and DBP surrogates. Duplicate and fortified samples were also analyzed, so that precision and accuracy estimates could be determined for the data on DBPs and DBP surrogates.

Evaluations of the QC data for DBPs and DBP surrogates indicate the national databases (the ICR Federal Database System and Auxiliary Databases 1–6) contain high-quality data suitable to support regulation development. The median accuracy for individual analytes ranged from 96% to 116% (expressed as percent recovery). For the parameters of greatest concern from a regulatory development perspective—total trihalomethane (TTHM), the sum of six haloacetic acids (HAA6), chlorite, bromate, bromide, and total organic carbon (TOC)—accuracy of the data from the tenth to the ninetieth percentile (which represents 80% of the data) ranged between 67% and 122%. Median precision for individual analytes ranged from 0 to 8.8% (expressed as relative percent difference [RPD]). For the parameters of regulatory concern, the ninetieth percentile of the RPD data (which represents 90% of the data) was less than 31%.

BACKGROUND

One of the major issues discussed during development of the Information Collection Rule (ICR) concerned the quality of the analytical data to be generated during the 18-month monitoring period. The ICR Advisory Committee recognized that the data must meet specific accuracy and precision targets in order to achieve the regulation's objectives. Because the data

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were to be generated by many laboratories, strict quality controls were essential to maintain the comparability of data among laboratories.

In August 1993, the U.S. Environmental Protection Agency (USEPA) sponsored two workshops to help the agency establish quality control (QC) criteria. One workshop, which included experts in protozoan and virus analyses, focused on standardizing the methods for analyzing *Giardia*, *Cryptosporidium*, and viruses. The other workshop, which involved experts in laboratory evaluations and disinfection by-product (DBP) analyses, examined procedures to ensure the comparability of data generated by the chemical analyses. Workshop participants included representatives from academia, the drinking water industry, commercial laboratories, and federal, state, and local governments. Recommendations from these meetings formed the basis of the ICR methods, QC requirements, and laboratory approval processes proposed February 10, 1994 (USEPA 1994).

Public comments on the proposed rule and additional workshops with the experts helped the agency revise and refine the criteria to those delineated in the final rule promulgated May 14, 1996 (USEPA 1996a). The QC requirements established by the ICR were more extensive than those included in the analytical methods (USEPA 1996b, 1996c, 1996d). Laboratories and utilities were required to report most of the QC data to USEPA along with the monitoring data. The additional QC requirements and the reporting of QC data were both novel approaches in the collection of monitoring data under the federal regulatory program for drinking water. As a result, the development of new systems for collecting, reporting, and evaluating the data were necessary (Wysock et al. 2002).

This chapter discusses what is known about the quality of the data collected during ICR monitoring. All monitoring data were validated upon receipt into the federal database, and a brief overview of this validation process is presented. The data that met the minimum QC requirements were retained in the federal database, and a subset of that data was used in the data analyses described in subsequent chapters of this book.

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VALIDATION OF ICR MONITORING DATA

Data on treatment plant design and operations, the 18-month monitoring data, and the associated QC data from laboratories were assembled in an Oracle™ database called the ICR Federal Database System (ICR FED). This database was designed to associate the occurrence and QC data reported by water utilities with QC data from the laboratories and to automatically verify that the specified QC criteria were met for each data point (Wysock et al. 2002). The database included validation algorithms that checked the QC data against the requirements in order to confirm that proper protocols had been followed when the ICR samples were analyzed. The QC checks performed by the validation algorithms are listed in Table 2.1 along with a list of the QC data used to perform the checks.

The concentrations reported for monitoring data that did not meet the QC criteria were removed from ICR FED. Some laboratory analyses generated data for more than one compound or parameter—e.g., a trihalomethane (THM) analysis measured chloroform ($CHCl_3$), bromodichloromethane, dibromochloromethane, and bromoform ($CHBr_3$). If the analytical results for one of the compounds failed to meet minimum QC requirements, the concentration reported for that compound was removed from ICR FED, and the concentrations reported for the other compounds were retained in ICR FED. The automated validation process ensured that the final data used to support development of future regulations met the minimum QC requirements specified in the ICR.

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Table 2.1

QC data used to validate ICR monitoring data

Validation checks on all monitoring data:

Was the laboratory approved to perform this analysis?

Was the sample analyzed with an approved method?

Was the sample analyzed within an appropriate time period after collection? (Bacterial samples excluded)

Validation checks on some monitoring data:

Was the analyst approved to perform this protozoan or virus analysis?

Was the sample properly preserved?

Was the sample contaminated during the analysis?

Was the extraction process working properly?

Were the calibration curves accurate?

Was the analysis sensitive enough to meet reporting requirements?

Was the analysis precise enough? (Applied only to data on TOC and ultraviolet absorption at 254 nm)

QC data reported by utility

Laboratory identification number

Sample collection date

Volume of sample collected for protozoan and virus analyses

Internal standard recovery for each applicable sample

Surrogate standard recovery for each applicable sample

pH of preserved samples for each applicable method

Dechlorinating agent used for selected sample types

Duplicate results for analyses that were always performed in duplicate (results for total organic halogen were not used in validation process)

QC data reported by laboratory

Laboratory identification number

Analyst identification number for protozoan and virus analyses

Sample extraction date

Sample analysis date

Method blank analytical results

Calibration check standard analytical results

Positive and negative control analytical results for protozoan and virus samples

Laboratory fortified sample analytical results (not used in validation process)

Duplicate sample analytical results—excluding samples that were always analyzed in duplicate (not used in validation process)

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Establishing QC criteria and rejecting data that didn't meet these criteria were new to the federal regulatory program for drinking water. Even though the QC criteria had been developed with input from the laboratory community, data users were concerned that the criteria were unrealistic. Specifically, they were concerned that laboratories would not be able to meet the requirements and that as a result the ICR FED would not contain enough data for use in developing future regulations. This risk was addressed in two ways. First, the validation software was designed with tables containing the criteria, so that the criteria could be adjusted without modifying the programming code. Second, after each validation cycle, USEPA evaluated the percentage of data rejected because of QC failures and the reasons for the failures. If large quantities of data were being lost because of unachievable QC requirements, USEPA had the capability to adjust the validation process to accept lower-quality data or to work with utilities and laboratories to fix the problems.

Determining the percentage of data that met QC criteria was complicated by several factors. First, during early validation cycles, the validation software used in ICR FED contained glitches that caused some data to be rejected even though they actually met the QC requirements. This resulted in underestimates of the rate of data acceptance. Although these glitches were eventually corrected so that they did not influence the final data, they played a confounding role early on when USEPA was trying to determine if the QC criteria were too stringent. Second, it was difficult to determine how many samples were actually collected each month. Because the data-reporting software allowed utilities to copy their sampling points from month to month, samples were automatically identified in the database based on the data reported for the previous month. In some cases, this meant samples that were never collected were artificially created in the data-reporting phase. There was no way to distinguish these "nonexistent" samples from samples that were lost prior to analysis or samples that were rejected by the utility. (In theory, the reporting software provided a way to mark samples as "lost," "not analyzed," or "rejected," but unfortunately samples were not designated in a consistent manner.) Therefore, the total number of samples used to calculate the percentage of data meeting QC requirements was always an overestimate, which meant the rate of data acceptance was underestimated. The third complicating factor was data entry errors. After each validation cycle, utilities and laboratories were given the opportunity to correct data entry errors. Often, these errors were mistakes in the

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reported sample collection date, sample analysis date, or other supporting QC data. Many data entry errors were corrected, allowing the data to pass validation during the next cycle. However, some utilities and laboratories did not attempt to correct data entry mistakes. This caused the rejection of data that might otherwise have been acceptable.

Despite these problems with determining the percentage of data that met the QC requirements, it became clear after the first few validation cycles that the QC criteria for all the microbial and chemical parameters were reasonable and that most of the ICR laboratories were able to perform at the expected minimum level. Early estimates of acceptable data were lower than the final numbers because of the factors just discussed. For example, after data for the first three months of ICR monitoring were validated, it was estimated that 80% of the cyanogen chloride (CNCl) data generated during the first quarter met all the QC requirements. This number changed to a 95% acceptance rate for the first quarter of CNCl data in the final database.

USEPA determined that at least 80% of the data for each parameter measured was acceptable (i.e., met minimum QC criteria). Actual percentages varied from month to month and from compound to compound. A summary of the percentages of acceptable data contained in the final ICR FED is presented in Table 2.2.

QUALITY OF DATA ON WATER QUALITY PARAMETERS

The quality of the monitoring data maintained in ICR FED and available for extraction into the auxiliary databases can be described on several levels. The laboratories that generated the data had undergone review and approval, which ensured at least a minimal level of competence. Specific analytical methods with known performance characteristics were used. In addition, all analyses were performed within a specified time frame, ensuring that concentrations measured in the laboratory reflected actual concentrations at the time the samples were collected.

The minimum QC checks just described were the only validation performed on the data for water quality parameters and disinfectant residuals. It was believed that these analyses were so commonly performed that as long as they were conducted by experienced laboratories and with acceptable methods, the data for water quality parameters would be of sufficient quality to meet ICR objectives.

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Table 2.2

Quarterly summaries of data passing final ICR FED validation with a USEPA quality assurance code of "A" (Accepted)

Analyte	Total		Quarter 1		Quarter 2		Quarter 3		Quarter 4		Quarter 5		Quarter 6	
	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass
Trihalomethanes														
Chloroform	16158	87%	2683	85%	2697	88%	2649	87%	2800	88%	2701	87%	2628	87%
Bromodichloromethane	16297	88%	2688	85%	2697	88%	2671	87%	2814	89%	2781	89%	2646	88%
Dibromochloromethane	16257	87%	2688	85%	2688	88%	2661	87%	2804	89%	2755	88%	2661	88%
Bromoform	16257	87%	2688	85%	2690	88%	2649	87%	2814	89%	2792	89%	2624	87%
Haloacetic acids														
Monochloroacetic acid	15626	84%	2497	79%	2468	80%	2634	86%	2713	86%	2710	86%	2604	87%
Dichloroacetic acid	16374	88%	2694	85%	2644	86%	2765	90%	2850	90%	2795	89%	2626	87%
Trichloroacetic acid	16280	87%	2698	85%	2635	86%	2735	89%	2800	88%	2783	89%	2629	87%
Monobromoacetic acid	16320	88%	2675	84%	2629	86%	2746	89%	2850	90%	2798	89%	2622	87%
Dibromoacetic acid	16419	88%	2693	85%	2651	86%	2776	90%	2843	90%	2819	90%	2637	88%
Bromochloroacetic acid	16367	88%	2660	84%	2655	86%	2775	90%	2827	89%	2814	90%	2636	88%
Bromodichloroacetic acid	5120	88%	890	86%	798	85%	851	94%	907	92%	883	91%	791	82%
Chlorodibromoacetic acid	4712	83%	890	85%	621	70%	829	92%	862	88%	750	82%	760	80%
Tribromoacetic acid	3554	67%	656	66%	341	41%	637	77%	637	72%	644	72%	639	71%
Inorganic DBPs														
Chlorite	2155	93%	372	91%	349	97%	361	93%	385	92%	367	90%	321	94%
Chlorate	3554	93%	585	90%	583	97%	586	92%	629	94%	629	93%	542	92%
Bromate	1769	83%	287	76%	279	85%	259	81%	324	84%	321	85%	299	87%
Low bromate concentrations*	1941	96%	349	100%	281	88%	302	99%	329	95%	353	96%	327	97%
Haloacetonitriles														
Trichloroacetonitrile	15092	81%	2421	77%	2444	80%	2544	84%	2645	84%	2598	84%	2440	81%
Dichloroacetonitrile	15257	82%	2411	77%	2461	80%	2537	83%	2665	84%	2648	85%	2535	82%
Bromochloroacetonitrile	15262	82%	2446	78%	2472	81%	2529	83%	2670	84%	2610	84%	2535	84%
Dibromoacetonitrile	15143	82%	2449	78%	2448	80%	2515	83%	2654	84%	2603	84%	2474	82%
Other halogen-substituted DBPs														
1,1-Dichloropropanone	15378	83%	2463	79%	2461	80%	2595	85%	2683	85%	2642	85%	2534	84%
1,1,1-Trichloropropanone	15279	83%	2436	78%	2456	80%	2565	84%	2664	84%	2648	85%	2510	83%
Chloral hydrate	14812	80%	2289	73%	2370	77%	2519	82%	2582	81%	2444	79%	2608	86%
Chloropicrin	14853	80%	2325	74%	2372	77%	2502	82%	2617	83%	2571	83%	2466	82%
Cyanogen chloride	1769	97%	268	95%	290	99%	304	99%	311	95%	308	97%	288	94%
Total organic halogen	20513	92%	3316	89%	3281	89%	3389	92%	3560	94%	3478	92%	3489	95%
Aldehydes														
Aldehydes†	761	96%	130	97%	121	100%	120	98%	127	91%	140	95%	123	95%

(continued)

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Table 2.2 (Continued)

Analyte	Total		Quarter 1		Quarter 2		Quarter 3		Quarter 4		Quarter 5		Quarter 6	
	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass	Total pass	% Pass
DBP Precursors														
Bromide	12079	94%	2053	94%	1988	94%	2004	95%	2018	94%	2067	94%	1949	93%
Total organic carbon	36163	88%	5682	82%	5873	86%	6044	90%	6384	93%	6296	91%	5884	88%
Ultraviolet absorption at 254 nm	36192	88%	5702	82%	5951	88%	5987	89%	6238	91%	6262	90%	6052	90%
Microbiological parameters														
Cryptosporidium	7023	97%	1172	96%	1174	98%	1162	99%	1187	97%	1181	96%	1147	96%
Giardia	7023	97%	1172	96%	1174	98%	1162	99%	1187	97%	1181	96%	1147	96%
E. coli	9692	99%	1649	100%	1620	99%	1584	99%	1606	99%	1614	99%	1619	99%
Fecal coliforms	9712	99%	1654	100%	1627	99%	1587	99%	1611	99%	1614	99%	1619	99%
Total coliforms	9719	99%	1663	100%	1627	99%	1587	99%	1611	99%	1613	99%	1618	99%
Viruses	4241	97%	706	97%	709	99%	697	98%	709	97%	724	98%	696	96%
Water quality parameters														
Alkalinity	55480	99%	9418	99%	9196	99%	9117	99%	9314	99%	9408	99%	9027	99%
Calcium hardness	54124	97%	9252	97%	8980	97%	8822	96%	9117	97%	9228	97%	8725	96%
Total hardness	54408	97%	9183	97%	8929	96%	8977	98%	9231	98%	9296	98%	8792	97%
Turbidity	55101	98%	9383	99%	9131	98%	9006	98%	9293	99%	9359	99%	8929	98%
pH	63087	97%	10728	97%	10475	97%	10322	97%	10640	98%	10706	97%	10216	97%
Temperature	63465	98%	10790	98%	10554	98%	10401	98%	10673	98%	10751	98%	10296	98%
Disinfectant residuals														
Chlorine dioxide	1796	95%	324	96%	287	97%	295	93%	317	97%	312	96%	261	92%
Chlorine	7379	88%	1233	87%	1226	88%	1206	88%	1243	88%	1257	88%	1214	90%
Free chlorine	45488	99%	7744	99%	7587	99%	7436	98%	7655	99%	7675	98%	7391	98%
Total chlorine	46192	99%	7812	99%	7707	100%	7543	99%	7774	99%	7833	99%	7523	99%
Ozone	1471	90%	248	90%	233	91%	199	88%	237	89%	298	93%	256	88%
Ammonia	13102	98%	2244	99%	2175	98%	2135	97%	2181	97%	2227	98%	2140	98%

* Low bromate concentrations refer to analyses performed by USEPA's laboratory using a more sensitive method than that available to other laboratories (Wysock et al. 2002).
† All aldehydes had the same percent passing rates for all quarters with the exception of formaldehyde (Quarter 1, 115 samples [85%] passed; Quarter 2, 107 samples [94%] passed) and methyl glyoxal (Quarter 4, 124 samples [89%] passed)

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QUALITY CONTROL FOR MICROBIOLOGICAL DATA

A number of steps were taken to help ensure the quality of the ICR data for microorganisms. To be approved to analyze bacterial samples (for total coliforms, *Escherichia coli*, or fecal coliforms), a laboratory had to be certified for these analyses under the Drinking Water Laboratory Certification Program. Of 9,783 total coliform analyses, 9,719 (99%) passed validation. Sixty-two analyses were rejected because the laboratory was not approved, and two were rejected because the data reported contained a typographical error.

Because no certification program existed for viruses or protozoa, laboratories had to be approved to perform these analyses. The approval process included submitting an application, undergoing an on-site evaluation, and analyzing initial performance evaluation (PE) samples. Laboratories maintained approval by successfully analyzing monthly PE samples and weekly QC samples, as well as undergoing an on-site evaluation and data audit.

On-site evaluations were performed by USEPA and contract personnel and included a review of laboratory procedures, personnel qualifications, and PE and sample data. PE samples, which consisted of filters containing viruses or protozoa, were analyzed according to the ICR methods. Laboratories were required to pass both the on-site evaluation and an initial round of PE sample analyses to be approved to analyze samples for viruses or protozoa. To remain approved throughout ICR implementation, laboratories were required to pass a six-month rolling average of monthly PE samples.

Of the 95 laboratories that applied for approval to analyze protozoa, 51 were eligible for on-site evaluation and 29 were approved. Of the 31 laboratories that applied to analyze viruses, 20 were evaluated on site and 12 were approved. At the end of the ICR monitoring period, 27 protozoan laboratories and 10 virus laboratories remained approved.

In order for protozoan and virus samples to pass validation, both the laboratory and the analyst had to be approved, the batch positive and negative control samples had to meet the acceptance criteria, and all holding times had to be met. For protozoa, positive control samples consisted of *Giardia lamblia* and *Cryptosporidium parvum* that were received monthly from the contractor who supported USEPA, added to 40 liters of purified water, and carried through the

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entire analytical procedure. Similarly, the positive virus QC samples consisted of titered polio viruses that were received from the contractor, added to 40 liters of purified water, and carried through the entire analytical procedure. The negative control samples for both analyses consisted of blank filters that were carried through the entire analytical procedure. A positive QC sample and a negative QC sample were analyzed each week that samples were analyzed.

Of 7,246 protozoan analyses, 7,023 (97%) passed validation. Four samples failed because the analyst was not approved, 87 failed because holding times were exceeded, 18 failed QC, and 85 failed because of missing QC data. Additional sample results were not included in ICR FED because the laboratory or utility rejected the sample or analytical result. (Utilities could reject data that were suspect, even if the data successfully passed the validation process.) Some samples failed validation for multiple reasons, so the number of failures attributed to the stated reasons exceeds the number of failed samples.

Of 4,354 virus analyses, 4,241 (97%) passed validation. Thirteen samples failed the batch positive QC sample, 25 samples exceeded holding times, and 60 were missing batch QC data. Additional sample results were rejected because the laboratory or utility rejected the sample or analytical result. These data are summarized in Table 2.3.

Table 2.3

Completeness of ICR microbiological data

Parameter	Total coliforms	Protozoa	Viruses
Number of samples	9817	7246	4354
Samples failed because laboratory or analyst was not approved	62	4	0
Samples failed because holding times were exceeded	NA*	87	25
Samples failed because of QC failures	2	18	13
Samples failed because of missing QC data	NA	85	60
Data anomalies	54	438	218
Data anomalies resubmitted	46%	78%	78%

* NA = not applicable

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During ICR implementation, ICR utilities and laboratories received technical support to address questions about sampling, methodology, and data entry. Nevertheless, when USEPA began to review the ICR data, a number of data anomalies were discovered. For example, there were instances in which the number reported for total coliforms was much smaller than the result for fecal coliforms or *E.*coli. Analytical volumes were sometimes inconsistent with reported detection limits. Approximately 6% of the samples had anomalies with protozoan data and 5% with virus data. Utilities received reports identifying these anomalies and asking them to check with the laboratories and to resubmit corrected results, if appropriate. Utilities submitted corrected data for 46% of the anomalies related to total coliforms and for 78% of the anomalies related to protozoa and viruses.

Because of the expense of the analytical methods and the difficulty of preparing accurately dosed samples, efforts were not made to acquire data to estimate accuracy (from matrix spike analyses) and precision (from duplicate analyses) for the microbiological parameters measured under the ICR. For total coliforms, the use of certified laboratories provided some assurance that these results would be similar to those produced during monitoring under the Total Coliform Rule. For protozoa and viruses, analyzing duplicate samples was not acceptable because of analytical costs, and matrix spike samples were impractical because of the inability to spike large-volume samples in the field. Therefore, precision and accuracy data are not available for the ICR microbial parameters. Consequently, USEPA tried to assure the quality of the data by relying on laboratory approval, QC samples, and PE studies (USEPA 1999a and 1999b). Detection sensitivity depends on sample volume and on recovery. Although recovery was unknown for individual ICR samples or matrices, it was estimated at a mean of 12% for *Cryptosporidium* and 26% for *Giardia* for the entire sampling period, based on data from the ICR Laboratory Spiking Program (Messner and Wolpert 2002, Scheller et al. 2002).

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QUALITY OF DATA ON DBPS AND DBP SURROGATES

Background

With the exception of THM analyses, analyzing DBPs and DBP surrogate parameters was relatively new to drinking water laboratories. Unlike the analyses for protozoa and viruses, it was feasible to collect much of the QC data generated when the analyses for DBPs and DBP surrogates were performed, so that extensive data checks could be incorporated into the ICR validation process. Results from each analysis were verified to meet the ICR QC specifications listed in Table 2.1. In addition, precision and accuracy data were gathered, so that the quality (precision and accuracy) of the data accepted into ICR FED could be determined.

The ICR required laboratories to perform duplicate analyses of all samples of total organic carbon (TOC), ultraviolet absorption at 254 nm (UV_{254}), and total organic halogen (TOX). Data from duplicate analyses of TOC and UV_{254} that did not meet the ICR precision requirements were removed from ICR FED (USEPA 1996b). The ICR also required that a minimum of 5% of the DBP and bromide samples be analyzed in duplicate. These were laboratory duplicates because the replicates were taken from the same sample bottle. The actual number of reported duplicates was greater than 5% of the samples in all cases, in part because a duplicate was required with each batch of samples being analyzed. In addition, some laboratories performed extra duplicate analyses. Excluding TOC, UV_{254}, and TOX, for which all of the samples were analyzed in duplicate, the overall percentage of samples analyzed in duplicate was 9.6%; the percentage of duplicate analyses for individual analytes ranged between 6% and 25%.

To ensure that the occurrence data were of known quality at the low end of the range of concentrations measured and to provide consistency in the ICR databases, minimum reporting levels (MRLs) were established for each analyte. ICR laboratories were required to demonstrate that they could accurately measure at these concentrations each time a set of samples was analyzed. Based on the recommendations of the technical experts who advised USEPA on the ICR QC requirements, the MRLs were established with two expectations:

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- Most samples were expected to contain concentrations greater than the respective MRLs, and concentrations less than the MRL were not expected to be of health significance.
- Most laboratories were expected to be able to meet the precision and accuracy criteria at the MRLs under normal operating conditions.

The MRLs are shown in Table 2.4.

A minimum of 5% of the TOC, TOX, bromide, and DBP samples were fortified with known amounts of the analytes of interest so the bias of the measurements could be determined. The overall percentage of fortified samples was 9.8%; the percentage fortified with individual analytes ranged from 7% to 26%.

Laboratories were instructed to use specific concentrations when fortifying samples. They were to alternate between specified low, medium, and high concentrations, so that bias data could be obtained across the expected range of concentrations. However, laboratories tended to favor spiking with medium concentrations. Spike concentrations are summarized in Table 2.4.

Data from the duplicate and fortified samples were used to determine the overall precision and accuracy of the data stored in ICR FED. Prior to any statistical analyses of these data, several clean-up steps were taken: (1) In two cases, utilities incorrectly reported low concentrations of bromate as <5μg/L instead of the actual result given to them by USEPA's laboratory. (The results from USEPA's laboratory were substituted.) (2) A few obvious data entry errors were excluded from the data set. (3) Protocols were established for handling concentrations that were less than the MRL. These exclusions are summarized in Table 2.5. Not calculating precision when both of the concentrations in a duplicate pair were reported as less than the MRL was the only clean-up procedure that resulted in exclusion of significant amounts of data. The number of results excluded for this reason is presented with the precision data in Table 2.6.

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Table 2.4

Minimum reporting levels and number of ICR samples fortified in each concentration range

Analyte	MRL	Low		Medium		High	
		Spike concentration	Number of fortified samples	Spike concentration	Number of fortified samples	Spike concentration	Number of fortified samples
Trihalomethanes (μg/L)							
TTHM			78		808		243
Chloroform	1.0	≤5	71	(5, 30)	683	≥30	238
Bromodichloromethane	1.0	≤5	91	(5, 30)	854	≥30	262
Dibromochloromethane	1.0	≤5	130	(5, 30)	848	≥30	263
Bromoform	1.0	≤5	176	(5, 30)	854	≥30	265
Haloacetic acids (μg/L)							
HAA5			179		834		237
Monochloroacetic acid	2.0	≤5	335	(5, 30)	866	≥30	249
Dichloroacetic acid	1.0	≤5	122	(5, 30)	886	≥30	256
Trichloroacetic acid	1.0	≤5	150	(5, 30)	872	≥30	246
Monobromoacetic acid	1.0	≤5	332	(5, 30)	918	≥30	258
Dibromoacetic acid	1.0	≤5	285	(5, 30)	928	≥30	257
HAA6			175		832		235
Bromochloroacetic acid	1.0	≤5	208	(5, 30)	922	≥30	253
HAA9			65		97		90
Bromodichloroacetic acid	1.0	≤5	70	(5, 30)	149	≥30	132
Chlorodibromoacetic acid	2.0	≤5	115	(5, 30)	138	≥30	118
Tribromoacetic acid	4.0	≤5	93	(5, 30)	98	≥30	92
Inorganic DBPs (μg/L)							
Chlorite	20.	≤50	36	(50, 400)	152	≥400	74
Chlorate	20.	≤50	74	(50, 400)	293	≥400	91
Bromate	5.0	≤7	56	(7, 20)	156	≥20	114
Low bromate concentrations	0.20	≤0.5	27	(0.5, 2.5)	38	≥2.5	50
Haloacetonitriles (μg/L)							
HAN			133		700		239
Trichloroacetonitrile	0.50	≤2	187	(2, 15)	723	≥15	243
Dichloroacetonitrile	0.50	≤2	109	(2, 15)	725	≥15	246
Bromochloroacetonitrile	0.50	≤2	129	(2, 15)	735	≥15	244
Dibromoacetonitrile	0.50	≤2	125	(2, 15)	724	≥15	245
Other halogen-sutstituted DBPs (μg/L)							
1,1-Dichloropropanone	0.50	≤2	167	(2, 15)	738	≥15	245
1,1,1-Trichloropropanone	0.50	≤2	144	(2, 15)	735	≥15	244
Chloral hydrate	0.50	≤2	69	(2, 15)	683	≥15	220
Chloropicrin	0.50	≤2	177	(2, 15)	653	≥15	237
Cyanogen chloride	0.50	≤1	15	(1, 10)	147	≥10	66
Total organic halogen (μg Cl^-/L)	50.	≤100	253	(100, 300)	655	≥300	201
Aldehydes (μg/L)							
Formaldehyde	5.0	≤7.5	31	(7.5, 30)	40	≥30	45
Acetaldehyde	5.0	≤7.5	46	(7.5, 30)	46	≥30	45
Glyoxal	5.0	≤7.5	43	(7.5, 30)	46	≥30	45
Methyl glyoxal	5.0	≤7.5	46	(7.5, 30)	46	≥30	45
Other aldehydes*	5.0	≤7.5	47	(7.5, 30)	46	≥30	45
Precursors							
Bromide (mg/L)	0.020	≤0.05	233	(0.05, 0.15)	1243	≥0.15	428
Total organic carbon (mg/L)	0.70	≤2	351	(2, 6)	2783	≥6	397
Ultraviolet absorbance at 254 nm (cm^{-1})	0.009	NA†	NA	NA	NA	NA	NA

* Other aldehydes include propanal, butanal, pentanal, hexanal, heptanal, benzaldehyde, octanal, nonanal, and decanal.

† Spiked samples were not analyzed for UV_{254}.

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Table 2.5
Data excluded from precision and accuracy calculations

Obvious data entry errors:

- Samples associated with a duplicate or fortified sample that was analyzed months after the sample collection date (these samples were assumed to have been incorrectly associated during data entry)
- Samples for which the utility and laboratory data were reported in different units (e.g., milligrams per liter versus micrograms per liter)
- Fortified samples for which a zero or negative concentration was reported
- Fortified samples for which zero was reported as the amount added to create the fortified sample

Samples associated with more than one duplicate or fortified sample:

- When more than one pair of duplicates existed for the same sample, the duplicates analyzed in a batch other than that containing the original sample were excluded. For duplicates within the same batch, only the first duplicate pair for the sample was used; all other duplicates for that sample were excluded.
- Only one fortified sample per ICR sample was used in the bias calculation. Fortified samples analyzed in a batch other than that containing the original sample were excluded when more than one pair existed. When more than one fortified sample was contained in the same batch, only the first fortified sample was used; all others were excluded.

Precision calculations were not performed for an analyte in a sample if:

- The concentration of the analyte was missing
- One or both of the analyte concentrations in a duplicate pair were reported as less than the minimum reporting level (<MRL)

Accuracy calculations were not performed for an analyte in a sample if:

- The concentration of the analyte was missing
- The fortified amount was less than half the background concentration
- The concentration reported for the fortified sample was less than the background concentration

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The ICR FED does not contain summed data for THMs, haloacetonitriles (HANs), or haloacetic acids (HAAs). Therefore, sums of the analytes in these DBP classes were calculated to determine the precision and accuracy of the data on these aggregate parameters. If the concentration of one of the analytes in a DBP class was missing, a sum was not calculated for the sample—e.g., a value for total THMs (TTHM) was not calculated if the $CHBr_3$ value for the sample was missing. If an analyte concentration was <MRL, a zero was substituted in the summation for that analyte. This is the same protocol that was followed in generating the aggregate measures in the auxiliary databases used to synthesize and analyze the ICR data (USEPA 2000, Wysock et al. 2002).

Precision of data on DBPs and DBP surrogates

Precision of the data on DBPs and DBP surrogates was estimated by calculating the relative percent difference (RPD) for each duplicate pair using the following formula:

$$\text{RPD} = \frac{|(X_1 - X_2)|}{(X_1 + X_2)/2} \times 100\%$$

in which X_1 = the concentration measured in the regular ICR sample (and reported by the utility) and X_2 = the concentration measured in the duplicate sample.

A correlation analysis was performed on the precision data for each analyte to determine if RPD was dependent on the analyte's concentration in the sample. Of the 47 analytes examined, only 10 showed a statistically significant correlation. Of those 10, one (TTHM) was marginally significant, and three (TOX, TOC, and UV_{254}) had such large sample sizes (>13,000) that even very small correlations were deemed statistically significant. For the remaining six analytes, the significant correlation was due to the influence of a few samples with extremely large RPDs. Based on this assessment of the data, it was decided to aggregate all the RPD data for each analyte rather than segregating it into concentration ranges.

Because the precision data for each of the DBPs and DBP surrogates do not follow a normal distribution (as determined using either the Shapiro-Wilk or Kolmogorov distributional test), the data are presented using nonparametric statistics. The 10th, 25th, median, 75th, and

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90th percentiles for each analyte's RPD are presented in Table 2.6. The number of data points available for calculating the RPDs was smaller for analytes that were not frequently detected above the MRL. For example, 1,040 duplicate pairs for $CHBr_3$ were not used in the RPD calculations because the concentrations reported in both samples were <MRL. Only 186 duplicate pairs for $CHCl_3$ could not be used for this reason.

All but three of the analytes—monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), and bromate—have a median RPD of less than 5%, and all but five—MCAA, MBAA, bromate, trichloroacetonitrile, and dibromoacetonitrile—have a 75th percentile RPD of less than 10%. This suggests very good overall precision of the DBP and DBP surrogate data in ICR FED. No attempt was made to remove duplicate pairs for which high RPDs were determined, even though it is likely that some of them were due to data entry errors that occurred at the utility or laboratory. RPDs of 189% and 166% were observed for TTHM and HAA6 samples, respectively, but the 90th percentiles were 14% and 20%, respectively.

A number of factors that might not influence the data set of an individual utility contribute to the variability of the data in ICR FED. Multiple laboratories generated the data using more than one method for some of the parameters. In addition, the analyses were performed over a 19-month time period. All of these factors would tend to decrease precision. The precision achieved by most laboratories individually should be better than that indicated for the aggregate data in ICR FED.

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Table 2.6

Precision of ICR data as demonstrated by relative percent difference (RPD) determinations from duplicate samples

Analyte	Number excluded—both samples <MRL	MRL*	N	10th percentile	25th percentile	Median	75th percentile	90th percentile	Median sample concentration*
Trihalomethanes									
TTHM	129		1218	0.26	1.1	3.2	6.9	14.	33.
Chloroform	186	1.0	1178	0.0	1.1	3.2	6.9	14.	20.
Bromodichloromethane	218	1.0	1149	0.0	1.0	3.2	6.8	12.	7.7
Dibromochloromethane	520	1.0	826	0.0	0.74	3.2	6.8	13.	3.4
Bromoform	1040	1.0	298	0.0	0.50	4.4	8.7	17.	2.6
Haloacetic acids									
HAA5	158		1211	0.12	1.2	4.0	9.3	21.	21.
Monochloroacetic acid	1004	2.0	315	0.0	2.2	6.7	16.	32.	3.2
Dichloroacetic acid	220	1.0	1236	0.0	0.82	3.6	8.5	16.	11.
Trichloroacetic acid	312	1.0	1132	0.0	0.85	3.6	8.7	18.	9.9
Monobromoacetic acid	1290	1.0	148	0.0	1.1	7.9	16.	36.	1.5
Dibromoacetic acid	969	1.0	458	0.0	1.2	4.3	8.7	19.	2.4
HAA6	156		1207	0.22	1.2	3.8	8.7	20.	25.
Bromochloroacetic acid	380	1.0	1057	0.0	1.1	3.8	8.5	16.	3.3
HAA9	46		233	0.31	1.2	2.7	5.7	11.	25.
Bromodichloroacetic acid	98	1.0	304	0.0	0.0	2.7	6.5	11.	3.0
Chlorodibromoacetic acid	254	2.0	118	0.0	0.0	3.2	5.1	11.	3.1
Tribromoacetic acid	272	4.0	8	0.0	1.8	2.7	4.0	5.7	5.0
Inorganic DBPs									
Chlorite	141	20.	212	0.0	0.15	1.2	3.3	6.4	430
Chlorate	185	20.	302	0.0	0.77	2.2	5.0	8.9	110
Bromate	309	5.0	27	0.0	2.0	8.8	16.	24.	7.0
Low bromate concentrations	51	0.20	58	0.70	1.7	3.7	9.3	31.	1.2

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Table 2.6 (continued)

Analyte	Number excluded—both samples <MRL	MRL*	N	10th percentile	25th percentile	Median	75th percentile	90th percentile	Median sample concentration*
Haloacetonitriles									
HAN	194	0.5	943	0.0	1.3	3.8	8.8	21.	3.6
Trichloroacetonitrile	1162	0.5	25	0.0	0.18	1.3	11.	25.	1.2
Dichloroacetonitrile	318	0.5	851	0.0	0.78	3.6	7.9	13.	2.2
Bromochloroacetonitrile	434	0.5	720	0.0	0.06	3.2	7.5	15.	1.3
Dibromoacetonitrile	646	0.5	505	0.0	1.0	4.5	11.	19.	1.2
Other halogen-substituted DBPs									
1,1-Dichloropropanone	596	0.5	556	0.0	0.03	4.8	9.9	18.	0.97
1,1,1-Trichloropropanone	482	0.5	691	0.0	0.28	3.3	7.0	13.	1.8
Chloral hydrate	256	0.5	836	0.0	1.5	4.1	8.3	15.	4.0
Chloropicrin	838	0.5	263	0.0	0.32	4.0	9.6	17.	0.81
Cyanogen chloride	51	0.5	203	0.57	1.9	4.4	8.3	14.	2.6
Total organic halogen	6003	50.	13911	0.0	1.2	3.8	7.6	14.	140
Aldehydes									
Formaldehyde	66	5.0	65	0.25	0.93	1.9	3.5	6.5	9.4
Acetaldehyde	121	5.0	23	0.14	1.1	1.9	2.2	3.0	7.0
Glyoxal	119	5.0	24	1.9	2.4	4.0	6.5	9.6	9.5
Propanal	141	5.0	3	0.98	0.98	2.8	3.8	3.8	7.2
Methyl glyoxal	135	5.0	10	0.66	1.9	4.2	4.9	9.3	8.3
Other aldehydes†	145	5.0	0						
Precursors									
Bromide	470	0.020	1341	0.0	0.45	2.5	5.9	12.	0.060
Total organic carbon	3555	0.70	32455	0.0	0.0	0.0	3.9	6.5	2.3
Ultraviolet absorption at 254 nm	2744	0.009	33306	0.0	0.0	0.0	2.2	4.9	0.040

* All concentrations are in μg/L except TOX (μg Cl⁻/L), bromide (mg/L), TOC (mg/L) and UV_{254} (cm^{-1}).

† Other aldehydes include: butanal, pentanal, hexanal, heptanal, benzaldehyde, octanal, nonanal, and decanal.

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Accuracy of data on DBPs and DBP surrogates

Accuracy of the data on DBPs and DBP surrogates was estimated by calculating the percent recovery for each fortified sample using the following formula:

$$\% \text{ Recovery} = \frac{(X_2 - X_1)}{Y} \times 100\%$$

in which X_1 = the background concentration measured in the ICR sample (reported by the utility), X_2 = the concentration measured in the fortified sample (reported by the laboratory), and Y = the concentration added to X_1 to produce the fortified sample. There was no requirement for spiked samples for UV_{254}, so no estimate of accuracy was determined.

The percent recovery data for each analyte were analyzed. The percent recovery was higher for samples with low spike concentrations than for samples with medium and high spike concentrations. It was speculated that some of this positive bias might be due to the protocol used to calculate the percent recovery for cases in which the background concentration in the sample was <MRL. These <MRL values were replaced by a zero for the percent recovery calculation. If the background concentration was slightly below the MRL, then the percent recovery could appear to be almost 200% because of the use of a zero.

To test this theory, the percent recovery data were recalculated by substituting the MRL values for analytes with background concentrations <MRL. As expected, the percent recovery was lower for samples with low spike concentrations than for samples with medium and high spike concentrations. These results support the theory that calculation of recoveries in samples with low spike concentrations are overly influenced by the values used as the background concentrations in the calculation when the concentrations were reported as <MRL.

One solution to this problem would have been to calculate percent recoveries only for analytes with background concentrations above the MRL. This option was evaluated, but it would have significantly reduced the number of samples for many analytes. For example, 177 $CHBr_3$ samples had been fortified at the low spike concentration. Excluding samples with background concentrations <MRL reduced the number to 18. Overall, if samples having background concentrations <MRL and receiving low spike concentrations had been excluded

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from the analysis, 11% of the entire data set would have been lost; for some analytes (e.g., many of the aldehydes), as much as 34% of the data would have been lost. If all <MRL data (not just that from samples with low spike concentrations) had been eliminated from the accuracy determination, the loss would have increased to 44% of the data set and 100% of the data for some analytes.

Excluding samples with background concentrations <MRL was not a viable solution because of the large loss of data. In addition, when the data were aggregated rather than being examined by spike concentration, the low spike concentrations did not significantly influence the overall data. The aggregate median percent recoveries did not change more than 3% when the data on low spike concentrations were combined with the data on medium and high spike concentrations. Therefore, it was decided to present the data as an aggregate rather than by spike concentration. Because the data did not follow a normal distribution (as determined by either the Shapiro-Wilk or Kolmogorov distributional test), nonparametric statistics were used for the presentation. The 10th, 25th, median, 75th, and 90th percentiles for each analyte's percent recovery are listed in Table 2.7.

With the exception of two analytes—chlorodibromoacetic acid and tribromoacetic acid (TBAA)—the median percent recovery was between 96% and 111%; the majority of individual analytes had a median percent recovery slightly greater than 100%. The 10th and 90th percentiles for TTHM (both individually and as a sum) range between 79% and 120%, whereas the range is 81–135% for HAA6 analytes—MCAA, dichloroacetic acid, trichloroacetic acid, MBAA, dibromoacetic acid, and bromochloroacetic acid. Because these percent recoveries are so close to 100%, they suggest a high degree of accuracy in the TTHM and HAA6 data in ICR FED. Similar conclusions can be drawn for bromate, chlorite, bromide, and TOC.

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Table 2.7

Accuracy of ICR data as demonstrated by percent recoveries from fortified samples

Analyte	Number of samples	10th percentile	25th percentile	Median	75th percentile	90th percentile	Median background concentration*
Trihalomethanes							
TTHM	1129	87	94	100	106	114	28.
Chloroform	992	79	89	98	108	120	12.
Bromodichloromethane	1207	80	92	100	108	118	5.8
Dibromochloromethane	1241	88	94	100	109	119	1.4
Bromoform	1295	86	93	100	108	120	<1.0
Haloacetic acids							
HAA5	1250	89	97	103	109	120	16.
Monochloroacetic acid	1450	81	94	104	115	135	<2.0
Dichloroacetic acid	1264	86	94	100	109	120	7.5
Trichloroacetic acid	1268	84	95	102	110	124	5.2
Monobromoacetic acid	1508	86	96	103	111	131	<1.0
Dibromoacetic acid	1470	89	97	104	115	130	<1.0
HAA6	1242	89	97	103	109	120	19.
Bromochloroacetic acid	1383	86	96	102	110	124	1.9
HAA9	252	99	103	107	112	125	17.
Bromodichloroacetic acid	351	99	105	110	120	138	1.5
Chlorodibromoacetic acid	371	97	106	115	125	150	<2.0
Tribromoacetic acid	283	88	105	116	125	140	<4.0
Inorganic DBPs							
Chlorite	262	77	89	98	104	109	27.
Chlorate	458	84	94	99	104	113	22.
Bromate	326	67	82	97	110	120	<5.0
Low bromate concentrations	115	75	84	96	105	122	<0.20
Haloacetonitriles							
HAN	1072	90	97	105	116	128	2.7
Trichloroacetonitrile	1153	86	96	106	119	134	<0.50
Dichloroacetonitrile	1080	81	92	100	110	126	1.3
Bromochloroacetonitrile	1108	88	98	106	118	134	0.70
Dibromoacetonitrile	1094	88	98	109	120	140	<0.50

(continued)

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Table 2.7 (continued)

Analyte	Number of samples	10th percentile	25th percentile	Median	75th percentile	90th percentile	Median background concentration*
Other halogen-substituted DBPs							
1,1-Dichloropropanone	1150	84	93	101	112	125	<0.50
1,1,1-Trichloropropanone	1123	85	93	100	110	124	0.70
Chloral hydrate	972	74	85	97	109	120	2.1
Chloropicrin	1067	86	96	105	118	136	<0.50
Cyanogen chloride	228	84	93	101	111	118	1.7
Total organic halogen	1109	82	93	100	108	126	75.
Aldehydes							
Formaldehyde	116	92	99	108	137	161	<5.0
Acetaldehyde	137	95	102	111	129	145	<5.0
Glyoxal	134	92	100	111	123	136	<5.0
Propanal	138	97	100	105	112	127	<5.0
Methyl glyoxal	137	89	97	104	116	138	<5.0
Butanal	138	94	99	104	109	120	<5.0
Pentanal	138	95	101	106	114	123	<5.0
Hexanal	138	94	99	105	112	123	<5.0
Heptanal	138	95	99	106	116	132	<5.0
Benzaldehyde	138	91	96	102	108	115	<5.0
Octanal	138	93	98	104	113	122	<5.0
Nonanal	138	92	99	107	118	129	<5.0
Decanal	138	87	97	104	113	121	<5.0
Precursors							
Bromide	1904	85	95	101	109	120	0.034
Total organic carbon	3531	88	95	100	105	111	2.0

* All concentrations are in μg/L except TOX (μg Cl⁻/L), bromide (mg/L), and TOC (mg/L).

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CONCLUSIONS

During development of the ICR, one of the objectives was to establish QC requirements that balanced the need for high-quality data with the need for a complete data set. It was believed that if at least 80% of the data met the QC acceptance criteria, this should be enough for the analyses necessary to support development of future regulations. With the exception of TBAA data (of which only 67% met QC requirements), all analytical data met this goal. Half of the parameters measured successfully completed USEPA's validation process with a 90% or greater pass rate. Overall, 92% of the analytical data (1,024,210 of the total 1,114,657 values reported) passed the validation process. This indicates that the data quality standards set by USEPA and based on advice from expert panels were reasonable and achievable.

Evaluations of the QC data for chemical parameters indicate that the national databases (ICR FED and Auxiliary Databases1–6) created from ICR monitoring results contain high-quality data suitable to support development of future regulations. Median accuracy of the data on individual analytes ranged from 96% to 116% (expressed as percent recovery). For the parameters of most concern from a regulatory development perspective (i.e., TTHM, HAA6, chlorite, bromate, bromide, and TOC), accuracy data from the tenth to the ninetieth percentile (which represents 80% of the data) ranged between 67% and 122%. Median precision of the data on individual analytes ranged from 0 to 8.8% (expressed as RPD). For the parameters of regulatory concern, the ninetieth percentile of the RPD data (which represents 90% of the data) was less than 31%.

The precision and accuracy of the ICR data may be better than the estimates derived from the QC data and presented in this chapter because no effort was made to remove outliers from the ICR FED QC data sets, even though some data pairs were so different from the norm that they appeared to be data entry errors. Because these data were not detected until after the final validation process had been completed, it was too late to contact the laboratories for potential corrections. One factor that could have contributed to these probable errors was the data-reporting process. The ICR laboratories reported the data for duplicate and fortified samples, but the ICR utilities reported analytical results for the regular ICR samples. The laboratories did not

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have an opportunity to review the data their client utilities reported to ICR FED, so they had no way to catch data entry errors. Likewise, the utilities did not have an opportunity to review the QC data their laboratories reported to ICR FED. Because neither saw the QC data side-by-side with the ICR data, possible data-reporting errors went undetected. In retrospect, a QC report showing the RPD and percent recovery calculations should have been generated each validation cycle. This would have enabled both the laboratories and the utilities to review the data more thoroughly.

Another approach that might have eliminated some potential data entry problems would have been to allow laboratories to report analytical data after utility review and approval. Under the ICR, laboratories reported monitoring data to the utilities and the utilities reported their analytical data directly to ICR FED. This created an extra step in the data-reporting process that might have led to data entry errors. The downside of this approach is that laboratory analysts are less likely to fully understand the context of water quality data than utility staff. The ICR approach was chosen to allow utilities to delete data that appeared to be incorrect based on staff knowledge of the spatial or temporal context of the samples (information that may not have been available to the laboratories).

The utilities also reported some of the QC data (e.g., data on dechlorinating agents, internal standard percent recoveries, and surrogate standard percent recoveries). Data entry errors in these QC data were especially difficult to track down and correct because the laboratory was removed from the reporting process. This problem lowered the percentage of data that passed the validation process, even though some of it likely met ICR QC requirements.

An additional factor that might have contributed to an underestimate of the quality of ICR data was the use of MRLs. MRLs were used to help ensure that occurrence data at the lowest end of the range of concentrations were of known quality. However, this procedure complicated analysis of the QC data because it eliminated the availability of concentration information for precision and accuracy calculations. For the estimates discussed in this chapter, values <MRL were eliminated in the precision calculations, but this was not a viable option for the accuracy determinations. If this type of project is undertaken again, a mechanism for collecting data on concentrations between the detection level and the MRL should be considered for the samples

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used for QC analyses. These data would provide background concentrations for determining percent recoveries for spiked samples and RPD calculations for duplicates. This procedure is routinely used in laboratories. Handling of the <MRL data for the QC samples would need to be carefully considered in order to avoid confusion between data used for QC calculations and data used to determine occurrence.

Precision and accuracy data were not collected for the microbiological analyses because of the difficulty of preparing accurate spike doses. However, ICR laboratories had to be USEPA-approved for coliform, protozoan, and virus analyses. Laboratories were also required to use specified methods. The certification and approval processes included on-site laboratory evaluations and PE samples. Laboratories approved to analyze protozoa and viruses were required to submit monthly PE samples and weekly QC samples. Although these requirements did not provide precision and accuracy data, they probably resulted in the production of better quality data than would have been the case without these measures. The ICR constituted the first attempt to standardize methods for analyzing protozoa and viruses. It also marked the first use of PE and QC samples for these analyses.

The ICR FED is unusual compared with other national databases because it contains QC data that can be used to document the quality of the data. Each piece of analytical data is also associated with the laboratory's identification and the analytical method used. In addition, analytical results had to meet minimum QC requirements in order to be maintained in ICR FED and exported to Auxiliary Databases 1–6.

The ICR QC data set is one measure that can be used to evaluate laboratory analytical performance. For most samples, individual laboratories should be able to achieve better precision and less bias than demonstrated by the data in ICR FED because the number of methods, analysts, and instruments would be minimized. However, some drinking water matrices are subject to interference during analysis and thus would be expected to cause increased bias, poorer precision, or both. Experience under the ICR indicates that the majority of laboratories and utilities are conscientious about meeting specific and achievable QC requirements. If other national data collection and database creation efforts included the extensive QC criteria used in the ICR survey, they would engender as much confidence as the ICR data.

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ACKNOWLEDGMENT

This research was supported in part by appointments to the USEPA Office of Ground Water and Drinking Water's internship program administered by the Oak Ridge Institute for Science and Education through an interagency agreement between USEPA and the U.S. Department of Energy.

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CHAPTER 3

AN INVENTORY OF ICR SYSTEMS, TREATMENT PLANTS, AND SOURCE WATER SUPPLIES

J. Alan Roberson

ABSTRACT

This chapter inventories the number of water systems affected by the Information Collection Rule (ICR), the geographic distribution of ICR systems, and the population served by ICR systems. ICR treatment plants are discussed according to the type of source water and the type of treatment used at the plant. To consider ICR data within a larger context, precipitation during the ICR monitoring period is compared with historical national climatic data.

INTRODUCTION

The Information Collection Rule (ICR) focused primarily on surface water and groundwater systems serving 100,000 people or more (USEPA 1996a). These systems conducted an intensive 18-month sampling program to monitor water quality parameters, microorganisms, disinfection by-products (DBPs), and treatment plant conditions (USEPA 1996b, 1996c). Groundwater systems serving at least 50,000 but fewer than 100,000 people were affected to a much lesser extent; these systems collected 12 months of data on total organic carbon (TOC) to determine if they had to conduct ICR treatment studies (Hooper and Allgeier 2002). This chapter discusses the ICR systems serving 100,000 people or more, the treatment plants and source water supplies of these systems, and the representativeness of ICR data compared with historical national climatic data.

ICR SYSTEMS

Based on the ICR requirements, 296 water systems serving ≥100,000 people conducted 18 months of intensive sampling. An ICR Public Water System Identification (ICRPWSID) number was used to track each water system during ICR implementation. When possible, each system's ICRPWSID number was the same as its Public Water System Identification (PWSID)

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number in the Safe Drinking Water Information System (SDWIS), the U.S. Environmental Protection Agency's (USEPA's) database for tracking regulatory compliance. One California system met the requirements to conduct ICR monitoring but did not have a SDWIS PWSID number; in this case USEPA assigned the system an independent ICR system (ICRPWSID) number.

Data for the summary information presented in this chapter were extracted from ICR Auxiliary Database 1 (AUX1) version 5.0, which contained data from 296 utilities with water quality information from 500 water treatment plants. AUX1 classified water systems into four categories based on their source of supply: surface water (SW), groundwater (GW), a mixture of both (MIX), or distributor/wholesaler (DIS/WH). A utility whose treatment plants produced more than 80% of the system's finished water from surface sources was classified as a surface water system. Groundwater systems were defined similarly. In a mixed system, neither surface water nor groundwater alone made up more than 80% of the system's production. An overwhelming majority of the systems (211 out of 296, or 71.3%) were classified as surface water systems throughout ICR monitoring. Groundwater systems accounted for 63 (21.3%) of the ICR systems, and mixed systems accounted for 20 (6.8%). Two systems (0.7%) were classified as distributor/wholesaler.

Source water supplies for surface water systems were further subdivided into reservoir/lake (RL), flowing stream (FS), a mixture of both (MIX), or groundwater under the direct influence of surface water (GWUDI). A majority of the surface water sources (121 out of 211, or 57.3%) were classified as reservoir/lake at the beginning of ICR monitoring. Flowing stream sources accounted for 66 (31.3%) of the surface water systems, and mixed systems accounted for 24 (11.4%). Three systems (1.4%) were classified as groundwater under the direct influence of surface water.

By the end of the ICR sampling period, the total number of systems had decreased by one or two. Sampling period 15 (September 1998) included 294 systems, whereas sampling periods 17 and 18 (November and December 1998) included 295 systems. This change in the number of systems was likely the result of diskettes not being uploaded to the data management system or systems not reporting data for a given sampling period. Out of a possible total of 5,328 values, 5,324 were reported, indicating that the data were more than 99.9% complete.

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Variations in the number of systems within each classification were slightly larger, but changes in source water supply can be expected to occur at some systems over time. The number of surface water systems varied from 210 to 215; the number of groundwater systems varied from 63 to 67; and the number of mixed systems varied from 15 to 20. The number of distributor/wholesaler systems remained fixed at 2.

GEOGRAPHIC DISTRIBUTION

Because most ICR monitoring was conducted by systems serving ≥100,000 people, ICR systems were concentrated in five states with large populations. California led the nation with 44 ICR systems. Florida followed with 25 systems, and Texas was not far behind with 21. After the top three states, New York and Pennsylvania followed with 16 and 14 systems, respectively. Systems in these five states accounted for 119 (40.2%) of the 296 ICR systems. Both distributor/wholesaler systems were in New York. Eight states had only one ICR system each, and three states had no ICR systems. Puerto Rico had six ICR systems, and the District of Columbia had one. The geographic distribution of the 296 ICR utilities is shown in Figure 3.1.

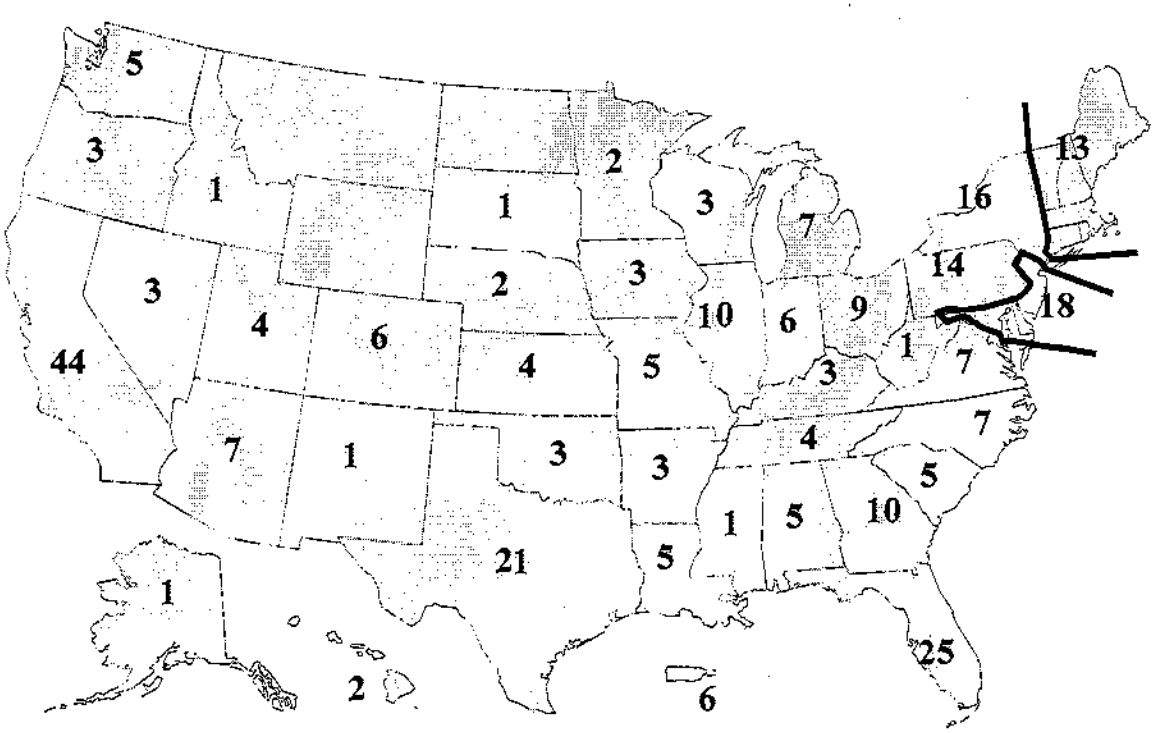

Figure 3.1 Geographic distribution of ICR utilities

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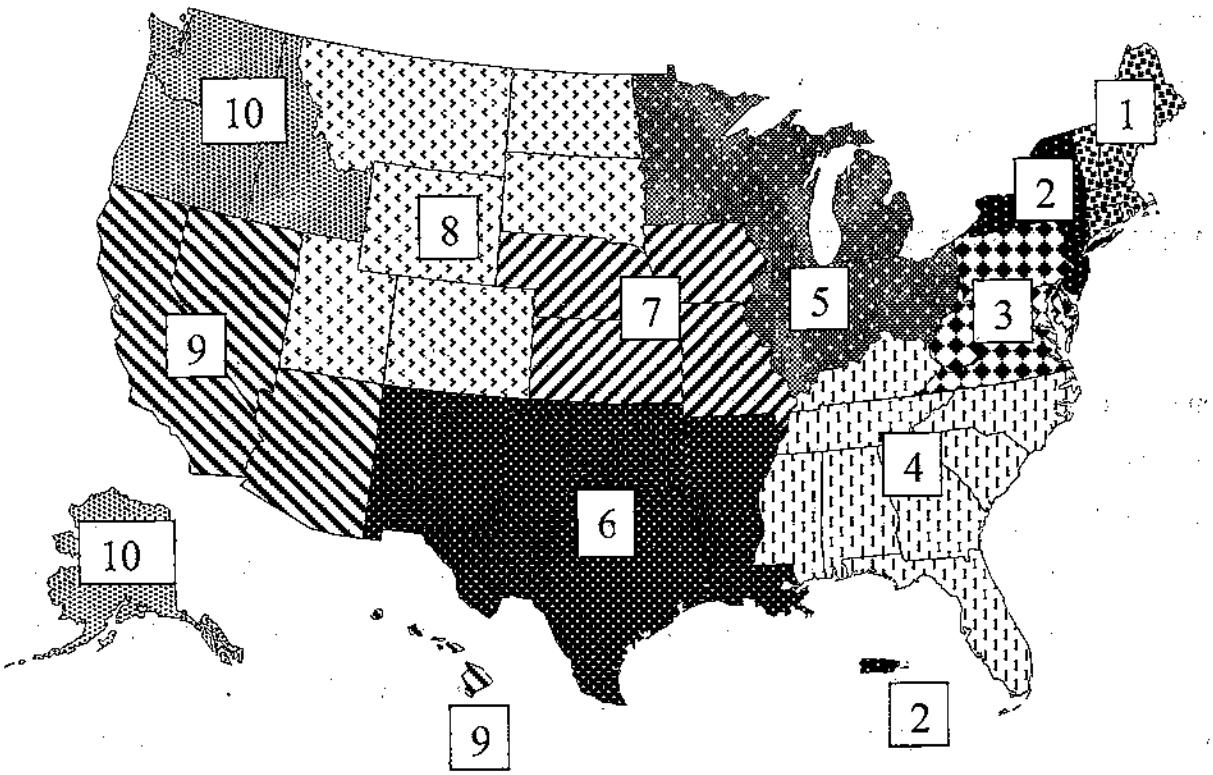

Figure 3.2 USEPA regions

Throughout this book, the ten USEPA regions (Figure 3.2) are used for regional comparisons of ICR systems and treatment plants. Surface water systems dominated in three of the five states with the highest number of ICR systems. Pennsylvania had 14 surface water systems (100%) out of 14 ICR systems overall; Texas had 17 surface water systems (81%) out of 21 systems overall; and New York had 11 surface water systems (69%) out of 16. On the other hand, Florida had the highest percentage of groundwater systems (22 out of 25 ICR systems, or 88%). California had 16 groundwater systems (37%) out of 43 ICR systems.

Because the overwhelming majority of Florida's ICR systems were groundwater systems, and because the state ranked second in the number of ICR systems per state, the moniker "The Florida Effect" was used to describe this state's impact on the analysis of the ICR data on groundwater systems. Initial analysis of the data on TOC concentrations in source water showed a similar national distribution in surface water and groundwater systems. This result was

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counterintuitive, because groundwater sources typically have lower TOC concentrations than surface water sources. When the Florida groundwater sources were analyzed separately, the distribution of surface water TOC concentrations was appropriately higher than that of groundwater TOC values (McGuire and Hotaling 2002).

Combinations of TOC and bromide concentrations were also a factor when ICR results from Florida were combined with results from California and Texas (the first and third ranked states for number of ICR systems). These three states dominated ICR results in general, containing 90 (30.4%) of the 296 ICR systems. Nevertheless, the large number of systems concentrated in these three states does not skew the analysis of ICR data from the perspective of their use in developing future water quality regulations. National compliance costs and associated benefits have to be estimated for every federal drinking water regulation under consideration. Water utilities must pay for capital costs and for operation and maintenance costs associated with treatment changes required for compliance with whatever regulation is eventually promulgated. From a national perspective, if a number of systems from these three states have to make treatment changes to comply with a national drinking water regulation, then a correspondingly large number of people will receive the benefits from these changes. The reduced risk of exposure to DBPs, for example, that would result from a given regulation would benefit the customers of all systems making these changes in treatment technology, regardless of their location.

POPULATION SERVED

Because of the size of the ICR systems, approximately half of the U.S. population served by community water systems was represented by ICR data. At the beginning of ICR implementation, the 296 ICR systems served 131.8 million (52.7%) out of approximately 250 million people served by community water systems. During the 18 months of ICR monitoring, the total population served, as reported in ICR data, varied between 127.6 million (December 1997) and 140.5 million (May 1998). This variation was due to changes in wholesale purchases during the course of ICR monitoring—smaller systems that were not ICR participants varied their purchases of treated water from ICR systems.

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At the outset of ICR monitoring, the 211 surface water systems served 109.5 million people (83.1% of the population served by ICR systems), and the 63 groundwater systems served 16.7 million people (12.7%). The 20 systems with mixed sources of supply served 5.3 million people (4.0%), and the 2 distributor/wholesaler systems served 0.3 million people (0.2%). The population served by the systems in each category varied slightly during each month of ICR monitoring.

The population served by surface water systems varied between 103.9 million and 117.5 million. The population served by groundwater systems varied between 16.7 million and 20.1 million. The population served by systems with mixes sources varied between 4.1 million and 5.2 million. The population served by the distributor/wholesaler systems showed no variation.

Based on system classifications, surface water systems served a larger percentage of the population compared with the percentage of ICR systems using surface water as a source of supply (Table 3.1).

Table 3.2 shows the percentages of the population served by retail and wholesale ICR systems categorized by source water type. ICR systems served a total of 131.8 million people.

Table 3.1

Population served by ICR systems categorized by source water type

	SW (%)	GW (%)	MIX (%)	DIS/WH (%)
Water systems	71.3	21.3	6.8	0.7
Population served	83.1	12.7	4.0	0.2

Table 3.2

Population served by retail and wholesale ICR systems

	SW (million people)	GW (million people)	MIX (million people)	DIS/WH (million people)
Retail systems	72.1	14.9	4.9	0.3
Wholesale systems	37.4	1.8	0.4	0.002

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ICR TREATMENT PLANTS

Data from the treatment plant level had to be analyzed to understand DBP formation throughout a treatment plant. McGuire Environmental Consultants developed initial treatment plant schematics to help utilities generate detailed treatment plant and distribution system schematics (McGuire 1994). Detailed engineering data on each ICR treatment plant were entered into the ICR Water Utility Data System (USEPA 1996c).

At the onset of monitoring, ICR samples were collected from 500 treatment plants within the 296 ICR systems. Data from these 500 plants were stored in the TUXPLTDES Microsoft Access table created for sampling period 0. Although SDWIS identifies individual water systems by number, it generally does not identify individual treatment plants by a unique number; therefore, ICR water treatment plant identification (ICRWTPID) numbers had to be assigned for each ICR plant. The ICRWTPID numbers made plant-level analysis of ICR data possible. For system-level analyses, each PWSID had to account for one or more treatment plants and one or more sources of supply. For example, the Columbus, Ohio, water system had one PWSID but three ICRWTPIDs—one each for the Hoover Reservoir, the Scioto River, and the South Wellfield.

Similar to its classification for water systems, AUX1 classified treatment plants as surface water (SW), groundwater (GW), a mixture of both types of sources (MIX), or purchaser/distributor/wholesaler (DIS/WH). A majority of the plants used only surface water sources, with 395 (71.7%) of the ICR plants classified as surface water plants at the start of ICR monitoring. Groundwater plants accounted for 130 (25.9%) of the ICR plants, and mixed plants accounted for 4 (0.8%). Eight (1.6%) plants were classified as purchaser/distributor/wholesaler.

Like the ICR systems, ICR treatment plants were concentrated in states with large populations. California led the nation with 78 ICR plants. Texas followed with 41 plants, and Florida was not far behind with 37. After the top three states, New York and Pennsylvania followed with 26 and 23 plants, respectively. Plants in these five states accounted for 205 (40.9%) of ICR plants overall. These five states had both the highest number of ICR systems and the highest number of ICR plants, and the percentage of ICR plants in the five states was essentially the same as the percentage of ICR systems. Four states—Maine, New Hampshire, South Dakota, and West Virginia—had only one ICR treatment plant.

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The majority of the population served by ICR plants received finished water from surface water plants using a reservoir/lake source. At the start of ICR sampling, reservoir/lake plants served 69.7 million people (63.7%), flowing stream plants served 27.2 million (24.8%), mixed plants served 11.6 million (10.6%), and plants using groundwater under the direct influence of surface water served 1 million (0.9%). As with ICR systems, the total population served by plants in each category varied slightly each month during ICR monitoring. Reservoir/lake plants served 64.5 to 73.4 million people; flowing stream plants served 22.7 to 34.9 million; and mixed plants served 11.6 to 18.0 million. The population served by plants using groundwater under the direct influence of surface water showed little variation (1.0 to 1.3 million people).

Although ICR treatment plants were categorized by the type of treatment used at the plant, categorization turned out to be a more difficult task than anticipated because of the number of unique treatment configurations, particularly those associated with softening plants. Five treatment plant categories for softening plants were defined to address the numerous softening configurations. Table 3.3 presents the treatment plant categories defined for the ICR and the number of plants in each category.

Conventional treatment plants dominated the ICR results, accounting for 272 (54.4%) of the 500 ICR plants. Groundwater that was only disinfected followed with 66 (13.2%) plants.

REPRESENTATIVENESS OF THE ICR DATA

How representative are the ICR data (collected during the second half of 1997 and all of 1998) compared with other data? This question could be answered from two standpoints—climate and source water quality. The first approach would compare rainfall and other weather patterns that occurred during the ICR with historical weather patterns; the second approach would compare source water quality parameters during the ICR with historical source water quality parameters.

From a national perspective, data from the National Weather Service provide a historical context for the temperatures and rainfall that occurred during ICR monitoring. Because most of the analyses presented in this book relied on data from the last 12 months of ICR monitoring (January 1998 to December 1998), the weather patterns of 1998 are discussed in this chapter. The calendar year 1998 was unusual in that it was the warmest and fifth wettest year on record in

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the United States since 1895 (National Climatic Data Center, 1999). Approximately 75% of the country was much warmer than normal during 1998, whereas less than 1% had annual temperatures much cooler than normal. Eight states, primarily in the Northeast, set records for warmest average temperature during calendar year 1998.

Table 3.3

ICR plants categorized by type of treatment

ICR abbreviation for treatment plant type	*N**	Type of treatment plant	Description of treatment
CONV	273	Conventional	Restricted to surface water plants and consisting of rapid mix, flocculation, sedimentation, filtration, and disinfection
DF	23	Direct filtration	Restricted to surface water plants and consisting of rapid mix, flocculation, filtration, and disinfection
ILF	6	In-line filtration	Restricted to surface water plants and consisting of rapid mix, filtration, and disinfection
SOFT	61	Softening	A summary category for softening plants consisting of single-stage (SOFT), two-stage (TS/SOFT), split-treatment (ST/SOFT), coagulation–sedimentation and softening (CS/SOFT), and complex parallel treatment (CPT/SOFT) systems; plants served by both surface water and groundwater could be in this category.
SSF	2	Slow sand filtration	Restricted to surface water plants; low-velocity filtration plus disinfection
MEMBRANE	2	Membrane filtration	Primarily microfiltration and ultrafiltration of surface water supplies
UNFILT/SW	16	Unfiltered surface water	Surface water that is only disinfected and receives no type of filtration
DIS/GW	66	Disinfected groundwater	Disinfection is the only treatment step for Groundwater
OTHER/GW	37	Other groundwater	A variety of other groundwater treatment systems including aeration, granular activated carbon, and iron and manganese removal
DIS/WH	7	Disinfected wholesale water	Water purchased from a wholesaler and disinfected; source can be surface water or groundwater.
OTHER	7	Other treatment	Plants that did not fit any of the other categories listed in this table
Total	500		

* *N*=number of plants

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Rainfall records are more critical, because rainfall is more likely to affect concentrations of DBP precursors, such as TOC or bromide, and pathogen loading, such as *Cryptosporidium* or *Giardia* concentrations. National annual average precipitation during the calendar years 1961 through 1990 was 27.16 inches, compared with a national annual average of 32.61 inches during January–November 1998. Approximately 22% of the country was much wetter than normal in 1998, whereas only about 2% was much drier than normal. Figure 3.3 shows that most states, particularly those in the West, received above-average precipitation in 1998. In this figure, a numerical value greater than 52 is above average, based on the scale used by the National Climatic Data Center. The West led the country in increased rainfall, with 25.70 inches for January–November 1998 compared with the 1961–1990 average of 14.18 inches (an increase of 81%). The central United States recorded 45.09 inches of precipitation during 1998 compared with 39.61 inches during 1961–1900 (an increase of 14%). The South, Southwest, and Northwest received only small increases in precipitation in 1998.

Because of regional variations in temperature and rainfall within the United States, it is difficult to generalize about the representativeness of ICR data from a national perspective. Although the country as a whole had the fifth wettest calendar year on record, localized droughts occurred during 1998. The region from the central Atlantic Coast to New York experienced the second driest July–November on record, and local water restrictions were implemented in some areas. In addition, it is not clear that temperatures correlate with DBP precursor concentrations or with pathogen loading.

From a regional perspective, additional analysis would be needed to evaluate the representativeness of ICR data. The higher-than-normal average temperatures might have increased outdoor water use, which could have affected groundwater quality as pumping was increased. The increased precipitation in the West would have had a significant impact on DBP precursors such as TOC and bromide by diluting the naturally occurring material.

From a local perspective, a surface water utility could collect historical rainfall data within its watershed. In a small watershed, this would likely involve a few National Weather Service monitoring stations. In a large watershed, this could involve several hundred weather stations and a substantial data collection and management effort. In a study of the Delaware River at Trenton, New Jersey, increased concentrations of *Giardia* and *Cryptosporidium* were associated with rainfall (Atherholt et al. 1998).

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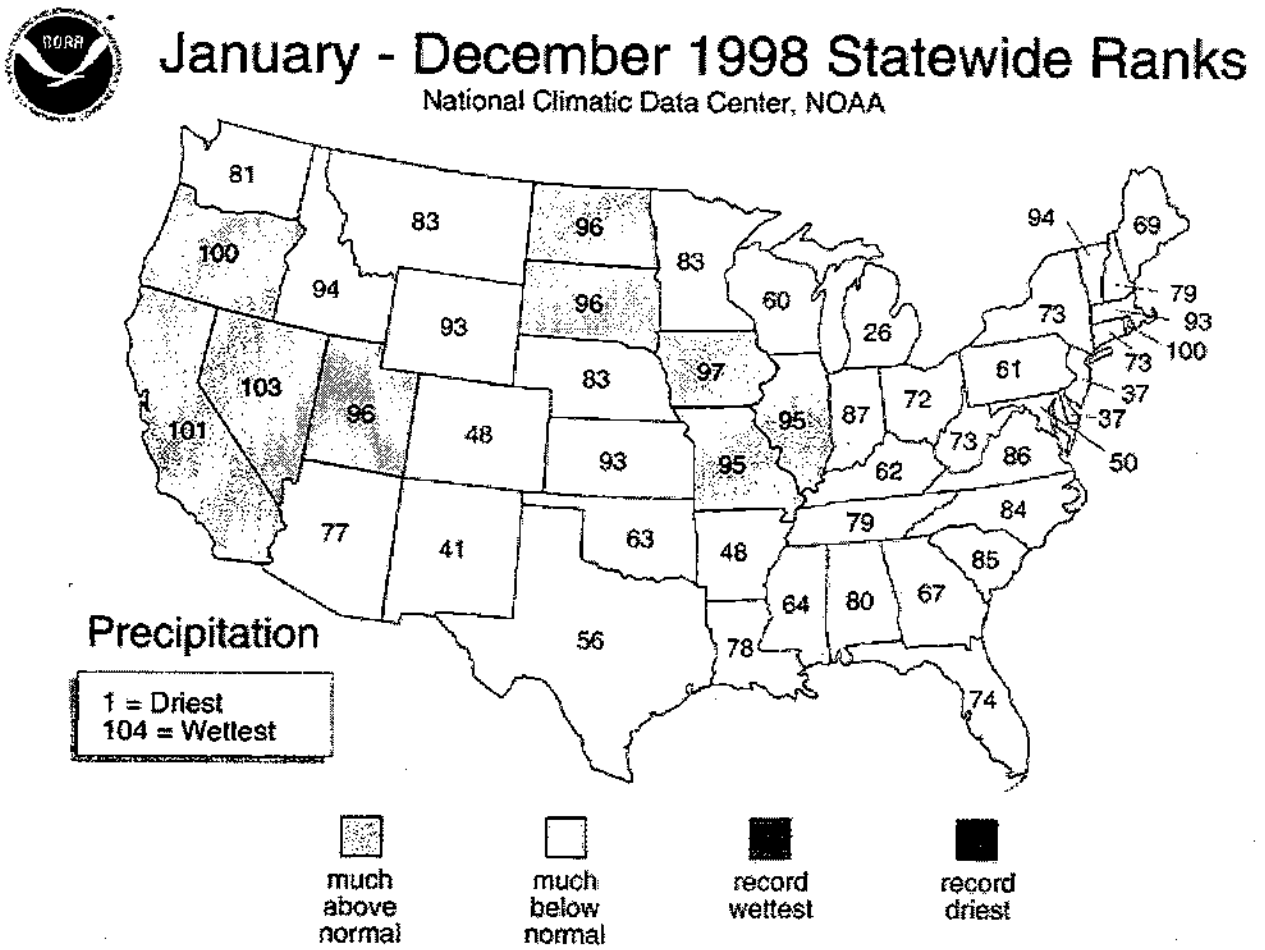

Source: http://lwf.ncdc.noaa.gov/img/climate/research/1998/ann/j-dpranks_pg.gif.

Figure 3.3 National precipitation map

Because precipitation generally correlates with stream flows and runoff, another approach would be to look at utility records of reservoir levels or historical stream flow data from U.S. Geological Survey gauging stations. However, comparisons of stream flow data with rainfall data should be carefully interpreted. For example, two rainstorms, each yielding one inch of rain, two days apart would have a different effect on source water quality than two rainstorms, each yielding one inch of rain, on two consecutive days or than one storm yielding two inches of rain. The storm interval can also affect source water quality. A storm yielding one inch of rain and lasting 24 hours would have a different impact than a storm yielding the same amount of rain

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but lasting only 2 hours. The shape of the hydrograph of the storm is critical to the storm's impact on source water quality.

Increased stream flow may or may not correlate with increased pathogen loading. A study at ten sites in the United Kingdom did not show a relationship between stream flow and *Giardia* and *Cryptosporidium* concentrations (Carrington and Miller 1993). However, a study of two rivers in Washington found lower *Cryptosporidium* concentrations during low stream flows (Hansen and Ongerth 1991). The "first flush" from a storm sewer outfall can be a source of high pathogen concentrations, and extremely high concentrations of *Giardia* and *Cryptosporidium* have been found in the first flush of stormwater in California (Stewart et al. 1997). Again, it is not clear that reservoir levels or stream flows necessarily correlate with DBP precursor concentrations or pathogen loading.

At the local level, a more robust analysis of the representativeness of ICR data should compare historical source water quality data with ICR source water quality data. If a utility has water quality records for a few years prior to ICR monitoring, a graphic analysis could allow an examination of how average ICR concentrations of TOC or bromide compare with historical concentrations. A historical analysis of actual DBP concentrations would also be useful. Chapter 23 of this book discusses how ICR data can be used to improve water quality and to comply with future regulations.

CONCLUSIONS

During the 18-month ICR monitoring period, 296 water systems collected detailed data from 500 treatment plants. Five states with large populations dominated the ICR results because 40% of ICR systems were located in these states. Surface water systems, comprising more than 70% of ICR systems, also dominated the ICR data collection effort. Most of the population served by ICR plants received finished water from surface water plants using a reservoir/lake source. More than half of the ICR plants were conventional filtration plants.

Although a large number of ICR systems were located in a handful of states, the ICR data represent the treatment costs and associated reductions in exposure that would result from a national drinking water regulation based on these data. From a national perspective, it is difficult to draw conclusions about the representativeness of ICR data versus historical data without a

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more detailed analysis of climate and weather patterns than this volume permits. From a regional perspective, conclusions about the impact of the increased precipitation that occurred in certain regions of the United States during ICR monitoring would require careful analysis. From a local perspective, comparing historical data with ICR data would be useful in improving water quality and complying with future regulations.

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CHAPTER 4

TRIHALOMETHANES IN U.S. DRINKING WATER—NORS TO ICR

Michael J. McGuire and Nicole Graziano

ABSTRACT

The National Organics Reconnaissance Survey (NORS) and the National Organics Monitoring Survey (NOMS), both conducted in the mid- to late-1970s, led to promulgation of the total trihalomethane (TTHM) regulation in 1979. In 1987, the American Water Works Research Foundation (AwwaRF) supported a survey in which more than 727 utilities submitted quarterly TTHM averages over a three-year period (1984–86). Detailed TTHM data were also collected as part of the Information Collection Rule (ICR) implemented from July 1997 through December 1998. This chapter presents a thorough analysis of TTHM occurrence in ICR systems and compares that occurrence with the findings from previous surveys.

Many groundwater and surface water TTHM samples collected under the ICR contained far higher TTHM concentrations than the 0.10 mg/L maximum contaminant level (MCL) in effect at the time. Apparently, the number of TTHM values exceeding the standard was so high because the MCL was based on running annual averages, in which high values can be averaged with lower concentrations to achieve compliance with the MCL.

The AwwaRF survey clearly showed a decrease in TTHM concentrations in water systems compared with the NORS and NOMS results, reflecting the implementation of TTHM control strategies by utilities. However, ICR results for 469 treatment plants and 10 blended distribution systems showed only a slight reduction in national TTHM occurrence since 1984–86. Although some utilities had installed advanced treatment processes in the 1990s in anticipation of promulgation of the Disinfectants/Disinfection By-products Rule, it appears that these process upgrades did not dramatically affect national TTHM concentrations at the time the ICR data were collected.

Nevertheless, a comparison of national TTHM occurrence surveys conducted from 1975 to 1998 illustrates a significant decline in TTHM concentrations during that period. Four descriptive statistics for NORS and ICR finished water data indicate that TTHM concentrations have been reduced by 50–60% over the 24-year period.

INTRODUCTION

In 1974, trihalomethanes (THMs) were discovered in treated drinking water around the world (Bellar, Lichtenberg, and Kroner 1974; Rook 1974; Rook 1976). To determine the national distribution of total THMs (TTHM) in the United States, the National Organics Reconnaissance Survey (NORS) was conducted in early 1975 (Symons et al. 1975) and was quickly followed by

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the National Organics Monitoring Survey (NOMS), which confirmed the findings of NORS (Munch, Feige, and Brass 1977; Brass et al. 1977). On the basis of these two national surveys, the health effects data available at the time, and limited cost information, the U.S. Environmental Protection Agency (USEPA) in 1979 established the TTHM maximum contaminant level (MCL) at 0.10 mg/L (USEPA 1979).

Subsequently, one minor and two major national TTHM surveys were conducted to determine the distribution of TTHM in U.S. drinking water. The most comprehensive survey of TTHM data occurred as part of the Information Collection Rule (ICR), which gathered data in 1997 and 1998 (USEPA 1996).

This chapter summarizes and analyzes the TTHM data collected as part of the ICR and compares them with TTHM data collected as part of several other national surveys.

NATIONAL SURVEYS TO ESTIMATE TTHM OCCURRENCE

Several estimates of TTHM occurrence in U.S. drinking water were made over the 24-year period 1975–1998. NORS was designed to identify national TTHM occurrence. Samples were collected from finished water locations at individual plants of the subject utilities and shipped back to the USEPA laboratory in Cincinnati for analysis. After each sample was collected and prior to shipping, a dechlorinating agent was added to the sample bottle to stop further THM production, and the sample was iced to preserve TTHM concentrations.

As a follow-up to the initial USEPA survey, a second survey, called NOMS, was designed to increase understanding of THM formation kinetics and to determine the best method of preserving samples collected as part of a survey. NOMS was actually a series of three surveys in which sample bottles were sent to 113 U.S. cities in 1975–76 (Munch, Feige, and Brass 1977; Brass et al. 1977). Samples collected under Phase 1 of NOMS were dechlorinated upon collection, making these results most comparable to the NORS data. All samples were sent to the USEPA laboratory in Cincinnati for analysis.

On January 14, 1987, 1,255 survey questionnaires were sent to water utilities serving more than 10,000 people as part of an investigation supported by the American Water Works Association Research Foundation (AwwaRF survey). The questionnaires asked each utility to compile quarterly average TTHM data over the period 1984–1986 and send them to a central

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database. The survey population consisted of all utilities serving more than 50,000 people and a sampling of utilities serving 10,000 to 50,000 people. A significant number of utilities (727 out of 1,255) submitted TTHM data (McGuire and Meadow 1988).

Four quarters of data on disinfection by-products (DBPs) were collected from 35 utilities (mostly large and very large utilities) from spring 1988 to winter 1989 (35-city survey). Samples for this survey were collected from clearwell effluents and were dechlorinated before being shipped to a central laboratory at 4°C. These data do not represent the maximum DBP concentrations that can occur in a distribution system (Krasner et al. 1989). Results from the 35-city and AwwaRF surveys were used in regulatory negotiations in 1992–93 and in the Federal Advisory Committee Act (FACA) negotiating process in 1997; they were instrumental in the development of the Disinfectants/DBP Rule, which was promulgated December 16, 1998, and became effective January 1, 2002 (Roberson et al. 1985, USEPA 1998).

As part of the ICR monitoring program, six quarters of DBP data were collected from the distribution systems of 296 utilities (500 treatment plants) during the period July 1997 to December 1998 (USEPA 1996). All U.S. utilities serving populations in excess of 100,000 people participated in ICR monitoring. Thus, the TTHM data from the ICR survey represents a census of TTHM data from very large utilities. The ICR was the most complex and expensive data-gathering effort from drinking water utilities ever attempted in the United States. ICR samples produced DBP data from five sampling points within each participating utility: the finished water (FIN) sampling point, a distribution system equivalent (DSE) location (a distribution site with well-characterized detention time), two locations representing average distribution system detention times (AVG1 and AVG2), and the location representing maximum distribution system detention time (MAX). USEPA-approved laboratories analyzed all ICR DBP samples.

METHODS

For the analyses presented in this chapter, ICR TTHM data were extracted from the ICR Auxiliary 1 database, version 5.0, which contains data from 296 utilities and DBP information from 500 water treatment plants. TTHM values that were below minimum reporting levels were replaced with zero values before further calculation or graphing. Although the ICR database

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contains analytical results from many sampling locations, this chapter focuses on results from the finished water sampling location and the four distribution system sampling points.

In several cases, the number of data points from which statistics are derived is different because of missing data. For example, if data from one of the four THMs was missing, no TTHM value was calculated. Null TTHM values were not included in any averages or graphed on any figures. Also, because water wholesalers did not collect samples from any distribution system, their treated water TTHM data are found only in the statistics on FIN locations. In addition, ICR sampling included 10 utilities that distributed blended water, and the distribution system data for these utilities are not directly related to a single treatment plant.

The descriptive statistics summarized in the tables in this chapter are consistent with common usage. Mean refers to the arithmetic average of all data. Median represents the 50th percentile of the data, with half the data points above the median and half below. P75 and P90 refer to the 75th and 90th percentile values that describe the TTHM concentrations for which 75% and 90% of the data are less than the listed numbers.

ANALYSIS OF ICR TTHM DATA

The characteristics of THM formation have been studied ever since the discovery of these DBPs in 1974. Factors influencing the amount and species of THM produced have been evaluated in numerous laboratory studies, including studies on the amount and type of organic precursors (Stevens et al. 1976) and studies on the influence of bromide concentration, water temperature, and amount and type of disinfectant (Symons et al. 1982). Using ICR TTHM data, this section examines these factors and others on a nationwide basis.

Table 4.1 summarizes all ICR TTHM data collected from all utilities that reported this information (including blended distribution systems). A total of 30,291 TTHM data points were used to construct this table.

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Table 4.1

Summary of ICR TTHM results

TTHM parameter	Measure	Finished water	Distribution system sampling sites				
			DSE	AVG1	AVG2	MAX	All distribution system sites
$CHCl_3$	Count	2,121	1,873	1,858	1,851	1,935	7,517
	Mean†	16.7	21.7	22.9	23.3	25.8	23.5
	Median†	12.0	16.0	17.9	17.3	19.3	17.7
	P90†	39.6	50.9	50.0	51.9	59.9	53.0
BDCM	Count	2,139	1,891	1,879	1,873	1,960	7,603
	Mean	6.7	8.1	8.4	8.4	8.9	8.4
	Median	5.0	6.5	6.8	6.7	7.3	6.8
	P90	16.0	18.0	19.0	19.0	19.2	19.0
DBCM	Count	2,136	1,887	1,877	1,871	1,953	7,588
	Mean	3.4	4.0	4.3	4.2	4.5	4.3
	Median	1.4	1.9	2.0	2.0	2.2	2.0
	P90	10.0	11.0	12.0	11.5	12.3	12.0
$CHBr_3$	Count	2,135	1,887	1,873	1,868	1,955	7,583
	Mean	1.0	1.2	1.4	1.4	1.5	1.4
	Median	0.0	0.0	0.0	0.0	0.0	0.0
	P90	2.9	3.4	3.9	3.7	4.3	3.8
TTHM	Count	2,108	1,865	1,852	1,843	1,921	7,481
	Mean	28.0	35.0	37.0	37.3	40.8	37.6
	Median	23.3	30.4	32.5	33.2	35.8	33.0
	P90	60.2	73.8	75.1	77.5	84.7	78.3

* Statistics include TTHM data for blended distribution systems.
† All mean, median, and P90 values are in μ/L.

As other studies have noted, chloroform ($CHCl_3$) dominated the three other THM species and was found at the highest mean concentration, 23 μg/L. Mean concentrations of bromodichloromethane (BDCM) at 8 μg/L and dibromochloromethane (DBCM) at 4 μg/L were far lower than the mean concentration of $CHCl_3$, and the overall mean concentration of bromoform ($CHBr_3$) was 1 μg/L. Overall mean and median values for the entire ICR TTHM data set were 38 and 33 μg/L, respectively.

Figure 4.1 presents box-and-whisker plots of the concentrations of the TTHM component species listed in Table 4.1. Figure 4.1 was constructed with all six quarters of TTHM data using the graphing program Statistica. As indicated in the figure legend, this box-and-whisker plot describes the 10%–90% range of concentrations, designated by the whiskers, and the interquartile range (25%–75%), illustrated by the boxes. Data points that differ substantially

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from the central tendency of these data sets are identified as outliers and extremes. In this chapter, outliers are defined as values greater than 1.5 times the interquartile range; extremes are defined as values more than 3.0 times the interquartile range. Plots for the bromine-substituted THM species (BDCM, DBCM and $CHBr_3$) indicate significant distributions of outliers and extremes, but these are nothing compared with the wide range of outliers and extremes shown above the box-and-whisker plot for $CHCl_3$.

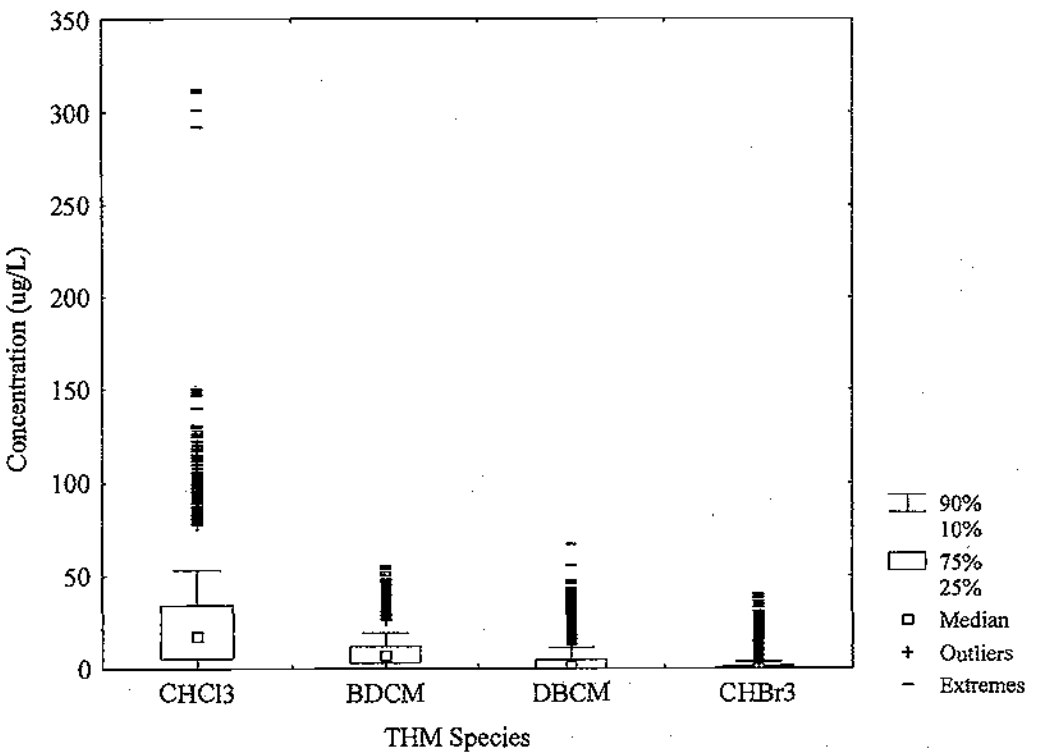

Figure 4.1 Comparison of ICR results for individual TTHM species, showing outlier and extreme values, over six quarters (TTHM concentrations in purchased and mixed supplies were included; those in finished water were excluded)

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TTHM Variability by Source of Supply

Chapter 1 of this book describes how the influents of ICR treatment plants were characterized with respect to the predominant source of supply (Wysock et al. 2002). The influent of most plants consisted of surface water or groundwater supplies. Figure 4.2 compares TTHM data from the distribution systems of all ICR utilities with TTHM data from the distribution systems of ICR utilities treating surface water or groundwater. In Figure 4.2, the four TTHM values above 300 µg/L were from the distribution system of a surface water utility in Mississippi. In Figure 4.1, these extreme values were shown to be composed primarily of $CHCl_3$. Figure 4.2 also shows that the total number of TTHM samples from all six ICR quarters is 760 more than the sum of all TTHM samples from plants treating surface water and ground water. The differential is due to the inclusion of TTHM data from blended distribution systems in the "ALL" category.

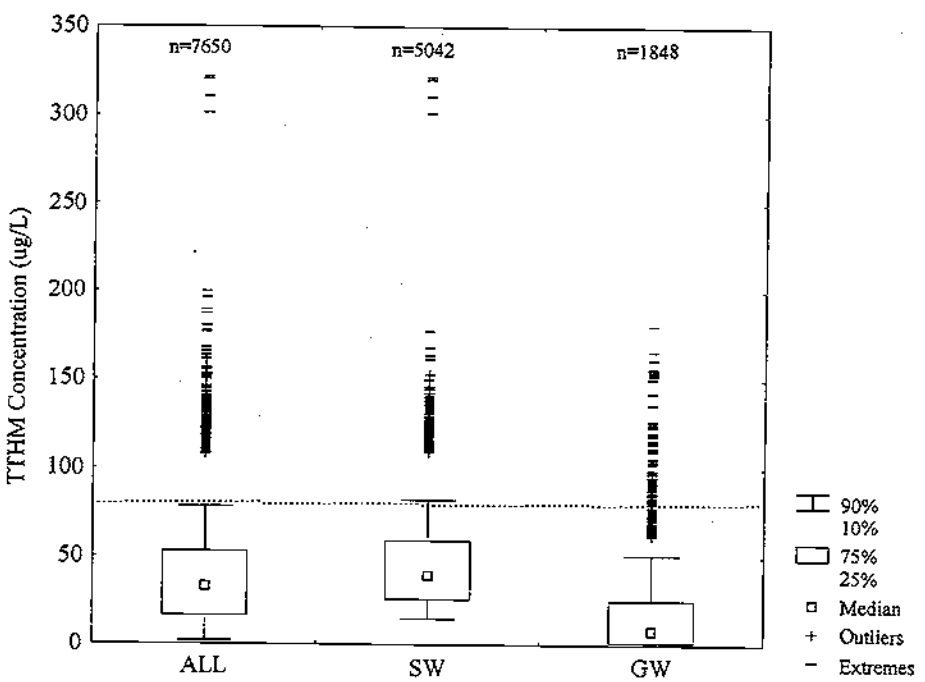

Figure 4.2 Comparison of TTHM results from the distribution systems of ICR surface water (SW) and groundwater (GW) utilities with TTHM results from all ICR distribution system data, showing outlier and extreme values, over six quarters

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The distribution system TTHM data from plants using groundwater as a source of supply show a pattern similar to that of the data from plants using surface water (Figure 4.2). The median TTHM concentration in samples from groundwater systems is far lower (7.8 μg/L) than the median concentration in samples from surface water systems (39.3 μg/L). In general, the distribution systems of U.S. utilities that produce disinfected groundwater have very low TTHM concentrations, primarily as a result of very low concentrations of organic precursors in groundwater supplies. However, the TTHM data for ICR groundwater systems include outliers and extremes at significantly high concentrations.

Figure 4.2 shows that there are many exceptions to the low TTHM concentrations usually found in groundwater. Groundwater supplies in the southeastern United States are generally high in total organic carbon (TOC) (see Chapter 12, McGuire and Hotaling 2002). During presentations of these data to the FACA committee as part of regulatory negotiations, these outlier values for groundwater DBPs were called the "Florida effect." The data shown in Figure 4.2 confirm this effect. Of the 116 outlier and extreme values shown on the groundwater box-and-whisker plot, 68 were from groundwater utilities in Florida. The next most frequently listed state contributing high TTHM values from groundwater was New Jersey, which accounted for only 10 of the 116 outliers and extremes.

TTHM Variations Over Time

Figure 4.3, one of the graphs presented to the FACA committee in late 1999, shows quarterly median TTHM data for groundwater and surface water plants by distribution system sampling location. Plots of the surface water data show progressively higher median concentrations of TTHM as samples were collected from the finished water, DSE, average, and maximum sampling locations. Quarters 1 and 5, which comprised the summer months (July–September) during which ICR samples were collected, showed the highest median values for all sampling locations from surface water systems. Quarter 3, which represented the only winter months of ICR monitoring, showed the lowest median values. Median values for Quarters 2 and 6 (fall quarters) were virtually indistinguishable from one another. Median values for the spring quarter (Quarter 4) were only slightly lower than those for the summer quarters and were higher than those for the winter and fall quarters, possibly reflecting the impact of increased runoff of

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organic precursors on TTHM production. Data for the groundwater systems show that none of the six quarterly median TTHM values changed during the 18-month ICR monitoring period because of the consistency (and low concentrations) of organic precursors in groundwater sources.

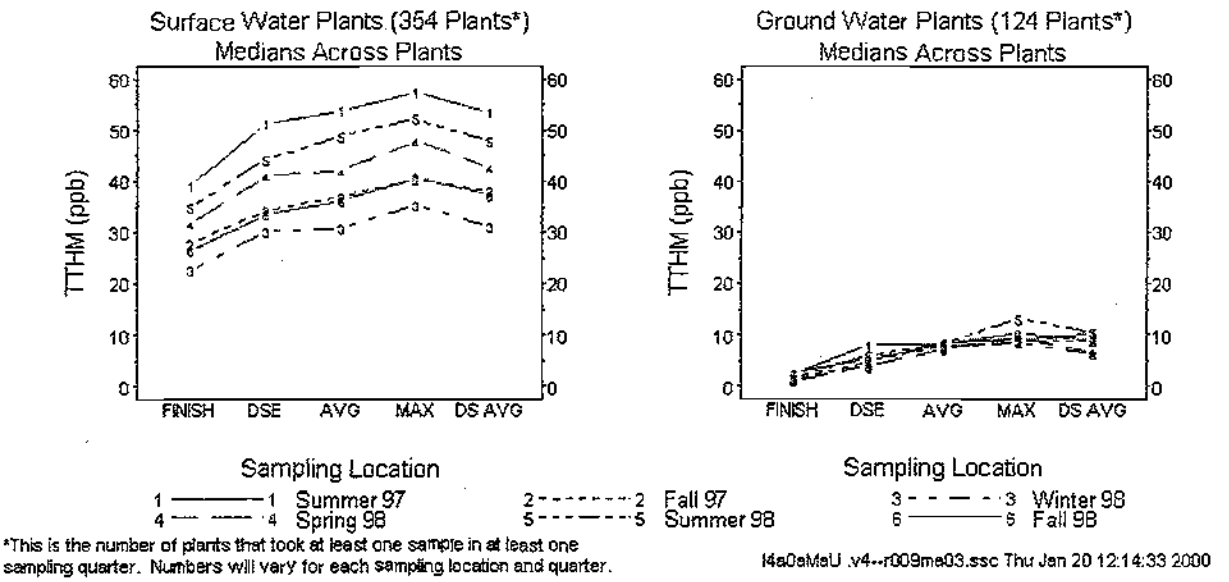

Figure 4.3 ICR TTHM data collected over six quarters and presented to the FACA Committee (*Source:* Cadmus 2001)

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Geographic Variability in TTHM Occurrence

Table 4.2 lists descriptive statistics for TTHM data associated with the 10 USEPA regions (Figure 3.2, Roberson 2002). TTHM data are not shown by state because the counts of plants and blended distribution systems by state are too low to allow meaningful statistical comparisons using quarterly TTHM data. The data in Table 4.2 indicate large differences in TTHM occurrence among USEPA regions. Mean TTHM concentrations ranged from 15 µg/L in the Pacific Northwest and Alaska (Region 10) to 47 µg/L in the Mid-Atlantic states of Virginia to Pennsylvania (Region 3). Median and P90 values showed the same trends—lowest to highest TTHM concentrations by region. Somewhat surprisingly, Region 3 had higher TTHM concentrations than Region 4, which includes southeastern states (including Florida) known to have the highest concentrations of organic precursors in their sources of supply. It is believed that utilities in Region 4 have already had to install treatment systems to reduce TTHM production in order to comply with the 1979 TTHM MCL of 0.10 mg/L.

Figures 4.4 and 4.5 plot the mean and P90 values from Table 4.2 on maps of the United States. Not surprisingly, Regions 3 and 4 show up in the highest category of mean TTHM concentrations (43–47 µg/L). Region 2 (New York, New Jersey, and Puerto Rico) has a high mean and a very high P90 TTHM value because of high organic precursor concentrations in the source water of the six ICR utilities located in Puerto Rico.

Table 4.2

ICR TTHM statistics* for 10 USEPA regions

USEPA region	Number of ICR plants	Mean (µg/L)	Median (µg/L)	P90 (µg/L)	Count
1	16	44.2	42.0	74.3	298
2	50	39.9	34.1	86.0	694
3	39	47.1	42.4	86.7	624
4	97	42.8	37.1	79.9	1,538
5	59	29.1	21.2	67.5	962
6	55	39.7	34.5	79.7	963
7	19	34.1	29.8	70.0	446
8	18	32.6	29.1	52.9	317
9	104	35.6	33.2	79.9	1,541
10	14	15.2	10.5	36.7	254
	Total: 471				

* Statistics exclude finished water concentrations but include values from blended systems.

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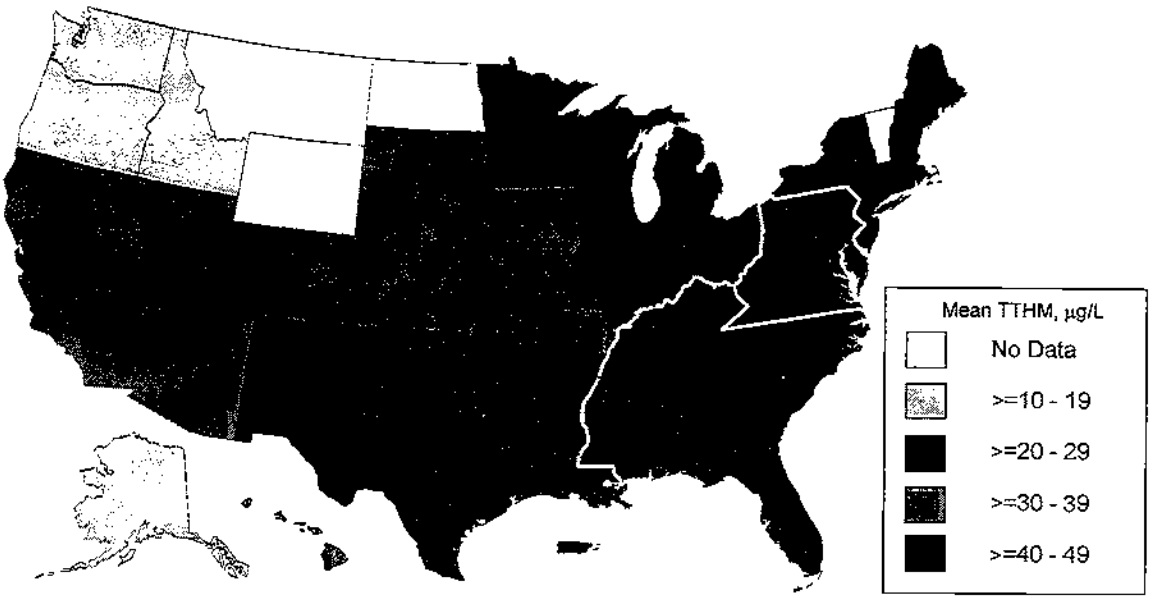

Figure 4.4 Mean TTHM concentrations by USEPA region—running annual averages for six quarters

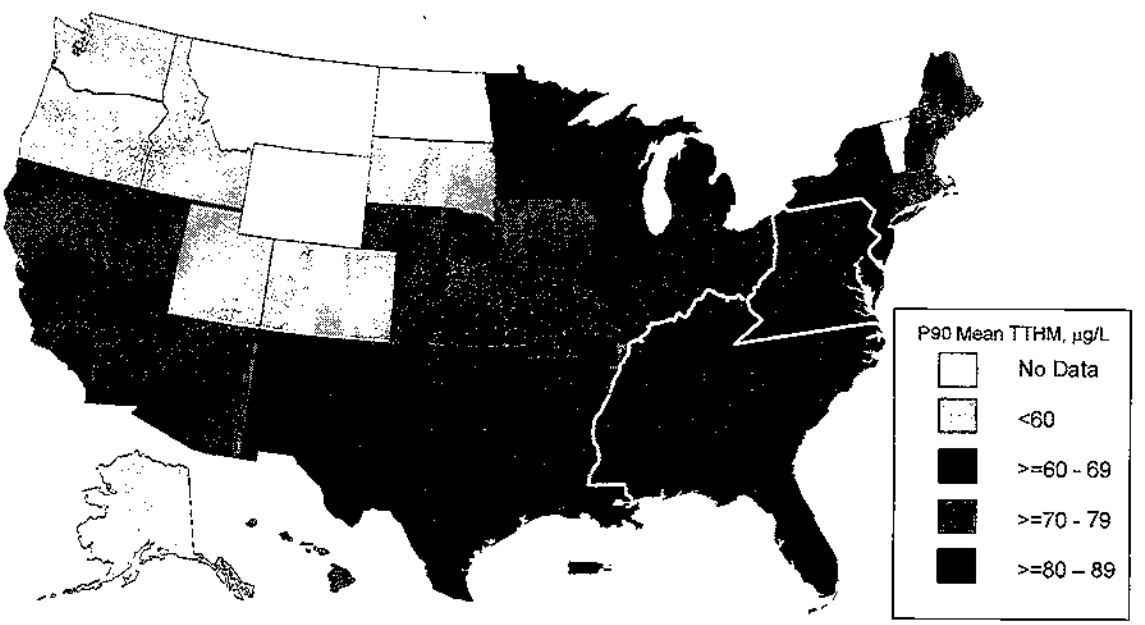

Figure 4.5 Ninetieth percentile mean TTHM concentrations by USEPA region—running annual averages for six quarters

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It is somewhat surprising to see Region 1 (New England) in the category with the highest mean TTHM occurrence, given the long winters and cold water temperatures in this region. Inspection of the information on source water quality, TTHM concentrations, and treatment at the ICR utilities in this region shows that source water quality does not explain the high TTHM concentrations in the New England states. Instead, the explanation is that 15 out of 16 plants used free chlorine as both the primary and secondary disinfectant, a practice that can be expected to produce significant TTHM concentrations. (The exception is Portland, Maine, the only ICR utility in the region that used ozone and chloramines.)

Comparing Figures 4.4 and 4.5 shows that the highest categories of mean and P90 values stretch from Region 6 (Texas, Louisiana, Arkansas, Oklahoma, and New Mexico) to the regions dominated by East Coast states. High TTHM concentrations in these regions stem from a combination of high source water precursor concentrations, high temperatures, and, for many utilities, continued reliance on free chlorine for primary and secondary disinfection. The Great Lakes states (Region 5) have the next highest TTHM concentrations, followed by the western and midwestern states, which have moderate TTHM concentrations. The Pacific Northwest and Alaska (Region 10) enjoy the lowest TTHM concentrations in the country.

TTHM Variation Within Distribution System Locations

Figure 4.6 presents box-and-whisker plots for the first four quarters of ICR TTHM data from finished water, DSE, average, and maximum sampling locations plus the distribution system average (DS AVG) for each quarterly set of values from each plant. The data are presented separately for plants using surface water and groundwater supplies. There are clear differences between the data sets of surface water and groundwater systems, but within each data set, there are few differences in mean and median values from the various sampling locations.

The ICR TTHM data were based on treatment plants, not on distribution systems. For example, a utility might have three treatment plants serving its distribution system. Two of these plants might produce high TTHM concentrations, and one might use a groundwater source that forms low TTHM concentrations. Under the 1979 TTHM regulation, quarterly averages for such a utility are calculated not by averaging data from individual plants but by averaging all of the

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data from all of the distribution system sampling locations over one quarter and then compiling a running annual average (RAA) of that data over four quarters.

Figures 4.3 and 4.6 are published on a Web site created by a company called SAIC and maintained for USEPA by the Cadmus Corporation (Cadmus 2001). For surface water supplies, the graphed data in Figure 4.6 show that overall TTHM average and median values for all the sampling points were less than 50 µg/L. All of the plants and utilities represented by the data in Figure 4.6 complied with the TTHM regulation. However, many individual data points and quarterly averages exceeded the 0.10 mg/L TTHM MCL in effect at the time of ICR sampling. A number of TTHM data points exceeded 200 µg/L, and four were well in excess of 300 µg/L.

On October 27, 1999, Figure 4.6 was presented to the FACA regulatory negotiation committee as part of a summary of ICR DBP data. Because of the high concentrations of the outliers and extremes shown on its plots, this figure had a greater impact on the committee than any other of the several hundred DBP graphs and tables presented over a nine-month period.

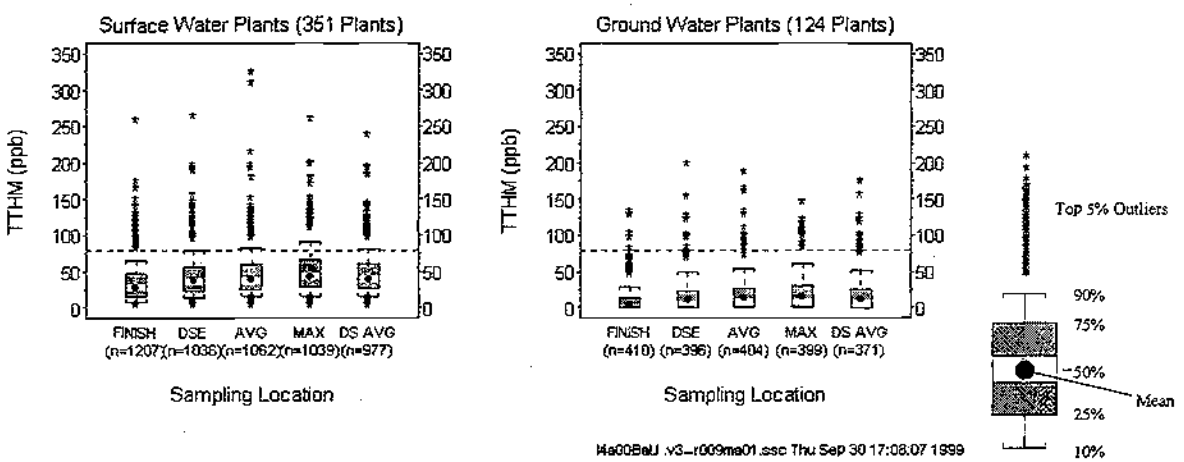

Figure 4.6 TTHM concentrations in the distribution systems of plants treating surface water and groundwater supplies (*Source:* Cadmus 2001)

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FACA committee members were surprised and concerned that systemwide averaging under the 1979 TTHM regulation allowed what appeared to be significant TTHM concentrations in systems complying with the MCL. In an attempt to reduce the high concentrations of TTHM and other DBPs served to water utility customers, the FACA committee recommended that the USEPA incorporate the concept of locational running annual averages (LRAAs) in the Stage 2 DBP Rule to ensure compliance with the MCLs for TTHM and HAA5 (the sum of five haloacetic acids) (USEPA 2000). An LRAA is calculated by averaging TTHM values for each distribution system sampling location over four quarters. Use of an LRAA for compliance purposes eliminates the possibility of averaging high and low TTHM values throughout a distribution system over the same quarter.

Table 4.3 compares descriptive statistics for LRAA data with those for RAA data collected over all six quarters of ICR sampling. LRAA statistics show increasing TTHM concentrations as sampling progressed from finished water to MAX locations. The last two columns of Table 4.3 compare the highest LRAA mean, median, and P90 values for all of the locations with the highest mean, median, and P90 values for the RAA data points collected during ICR monitoring. The highest LRAA values were greater than the highest RAA values.

The last two columns in Table 4.3 suggest that meeting a TTHM MCL based on LRAA calculations would be more difficult than meeting an MCL based on RAA calculations. This finding is further strengthened by the fact that ICR RAA data were based on average values from only one treatment plant, whereas RAA calculations for MCL compliance have been based on averages of many distribution system samples possibly representing different sources of supply.

Table 4.3

Highest TTHM LRAA and RAA concentrations

	Highest LRAA values by sampling site†					Highest	Highest
TTHM	FIN	DSE	AVG1	AVG2	MAX	LRAA	RAA
Count	481	434	433	433	441	496	448
Mean*	29.7	38.4	40.8	40.5	44.8	47.2	40.7
Median*	26.3	35.6	37.0	38.0	42.2	44.8	38.4
P90*	60.6	72.2	75.5	75.5	85.9	87.4	74.0

* All mean, median, and P90 values are in µg/L.

† Values for blended systems are included. LRAA values shown for each sampling location are those reported as the highest from the three annual periods comprising the 18-month IRC monitoring period.

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The Impact of Treatment on TTHM Formation

It is useful to examine TTHM concentrations in the distribution systems of a variety of treatment plants to see if the type of treatment has a major effect on DBP production. Figure 4.7 presents a box-and-whisker plot of TTHM occurrence data based on treatment plant type, as defined in Chapter 3 of this book (Roberson 2002). Median values for all treatment plant categories shown on the graph were very close, except for those in the two groundwater treatment categories—DIS/GW and OTHER/GW—whose median values were lower than the others. The outliers and extremes in the groundwater treatment categories are interesting because most Florida plants were classified as softening plants. A number of the groundwater treatment facilities treating sources high in organic precursors were located outside the state of Florida.

Except in the groundwater treatment categories, the interquartile ranges in all of the treatment categories overlap, indicating little difference among them.

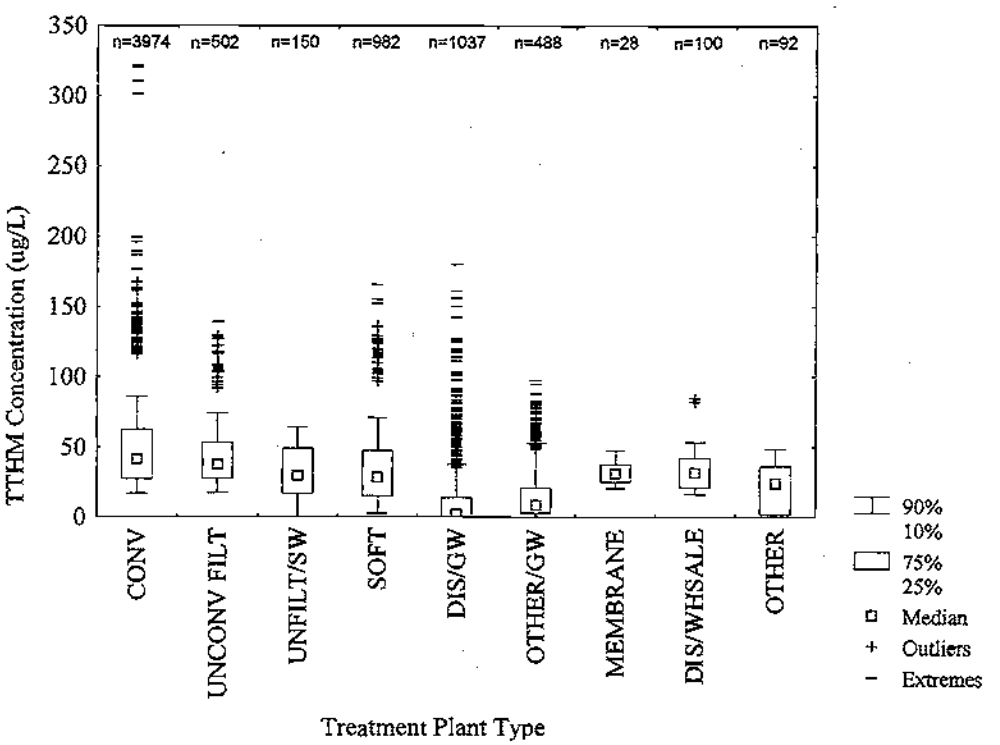

Figure 4.7 Comparison of TTHM concentrations in distribution systems as a function of treatment plant type (finished water samples were excluded; direct filtration, in-line filtration, and slow sand filtration plants were combined into the category for unconventional filtration; five types of softening plants were combined to form the category for softening plants)

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The influence of disinfectant type is examined in Figures 4.8 and 4.9. All the data in Figure 4.8 are separated according to categories designating the primary disinfectant used at the plant: free chlorine at CL2 plants, some form of chloramine at CLM plants, free chlorine followed by chloramine at CL2_CLM plants, chlorine dioxide at CLX plants, and ozone at O3 plants. There is not much difference among the box-and-whisker plots for all of the disinfectant categories. Outliers and extremes appear to dominate the CL2, CLX, and O3 categories, but these data must be interpreted with care. First, the number of plants in the three categories varied widely; several dozen plants used chlorine dioxide and ozone, whereas hundreds used free chlorine. Also, plants that had experienced problems with high TTHM concentrations in the past and that had source water supplies with high concentrations of organic precursors had already changed to alternative disinfectants such as chlorine dioxide or ozone before ICR monitoring began. Even with the alternative disinfectants, however, outliers and extremes were produced. The four extreme TTHM concentrations from the plant in Mississippi were produced with two different disinfectants.

Figure 4.9 indicates that the type of disinfectant used in the distribution system is not likely to predict distribution system TTHM concentrations. For example, given equal source water TOC concentrations, using chloramine as the distribution system disinfectant would be expected to result in lower TTHM concentrations overall. However, plants using chloramine had most likely changed to this disinfectant because high organic precursor concentrations in their source water had made it difficult for them to meet the 1979 TTHM MCL. In other words, the TTHM concentrations had already been "adjusted" as a result of regulatory compliance efforts. Both free chlorine and chloramine systems had a number of outliers and extremes. Surprisingly, the four extremely high TTHM values (greater than 300 μg/L) occurred in a chloraminated distribution system, illustrating that converting to an alternative disinfectant is not a panacea.

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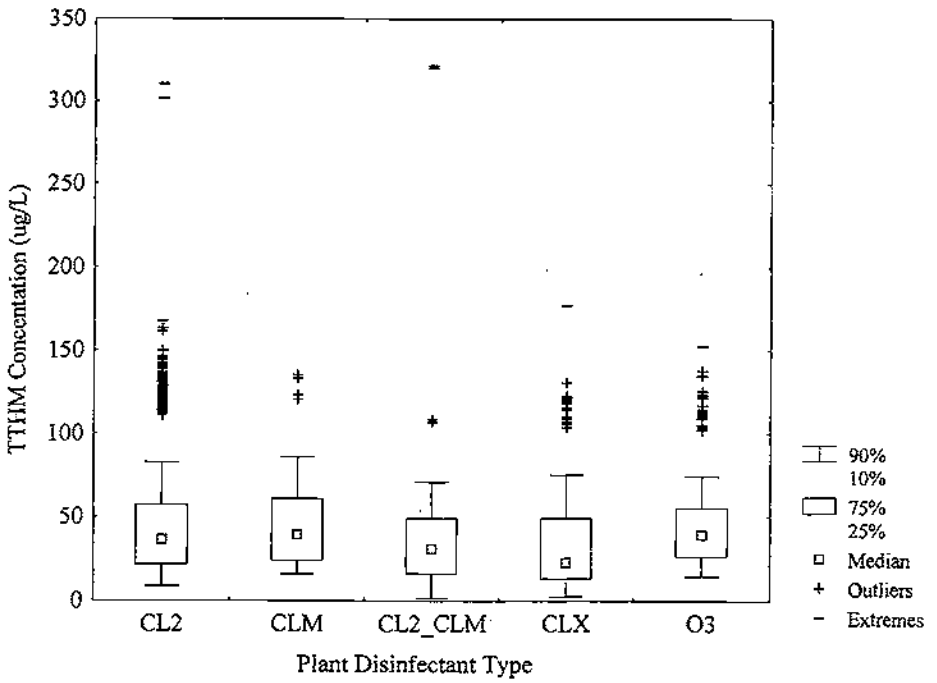

Figure 4.8 Comparison of distribution system TTHM concentrations as a function of type of disinfectant used in the treatment plant

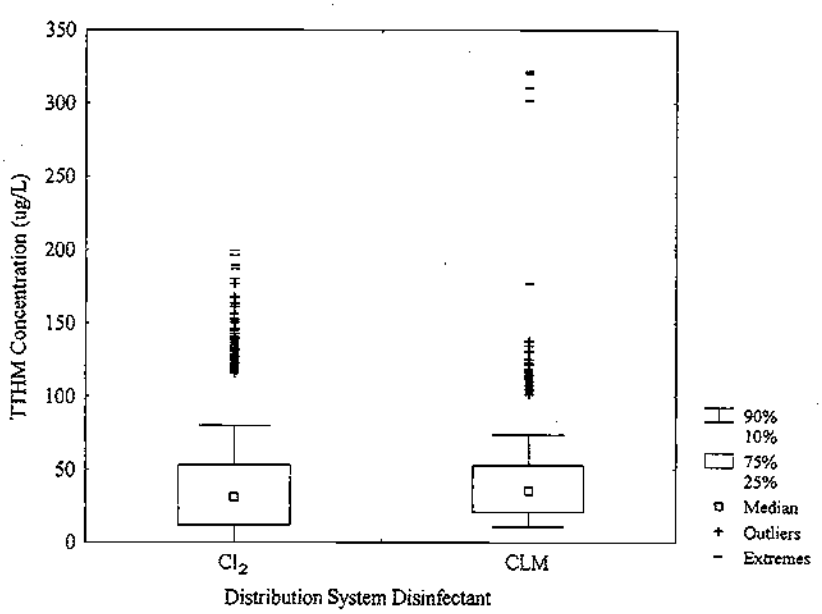

Figure 4.9 Comparison of TTHM concentrations as a function of type of disinfectant used in the distribution system

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Influence of Source Water Quality on TTHM Formation

Figure 4.10 shows that TOC concentration in treatment plant influent is a poor predictor of TTHM concentration in the distribution system. TTHM values increase slightly with increasing TOC concentrations, but the data vary substantially. Median and P90 values both show a slight increase across the five categories of TOC concentrations (<1mg/L to >4 mg/L), but the box-and-whisker plots overlap in all five TOC ranges. Figure 4.11 illustrates the poor correlation between paired data sets of influent TOC and finished water TTHM concentrations. The coefficient of determination (r^2) value of 0.1336 confirms that there is virtually no relationship between these two parameters in these paired data sets.

Many laboratory studies have demonstrated the influence of TOC concentration on the amount of TTHM formed. An important graph (based on NORS data) in a USEPA publication summarizing TTHM control (their Figure 1) showed, roughly, that increasing TOC concentrations in source water resulted in higher TTHM concentrations in the effluents of NORS treatment plants (Symons et al. 1982). It is not surprising that a relationship between TOC and TTHM existed in 1975 because, at that time, utilities had not yet reduced chlorine dosages or installed TTHM control technologies. But the ICR data set clearly shows that influent TOC alone is a poor predictor of TTHM occurrence in a wide range of U.S. treatment plants. In individual treatment plants and in narrow ranges of influent water quality conditions, higher influent TOC concentrations can certainly cause higher TTHM concentrations in treated water. In fact, a variety of water treatment parameters and environmental conditions affect TTHM formation, and these factors are discussed in detail in Chapter 8 of this book (Swanson et al. 2002). TOC was not a good overall predictor of TTHM formation in the ICR data set because by the time these data were collected, utilities had adjusted their treatment processes and disinfectants to achieve lower TTHM concentrations in order to meet current and future regulations.

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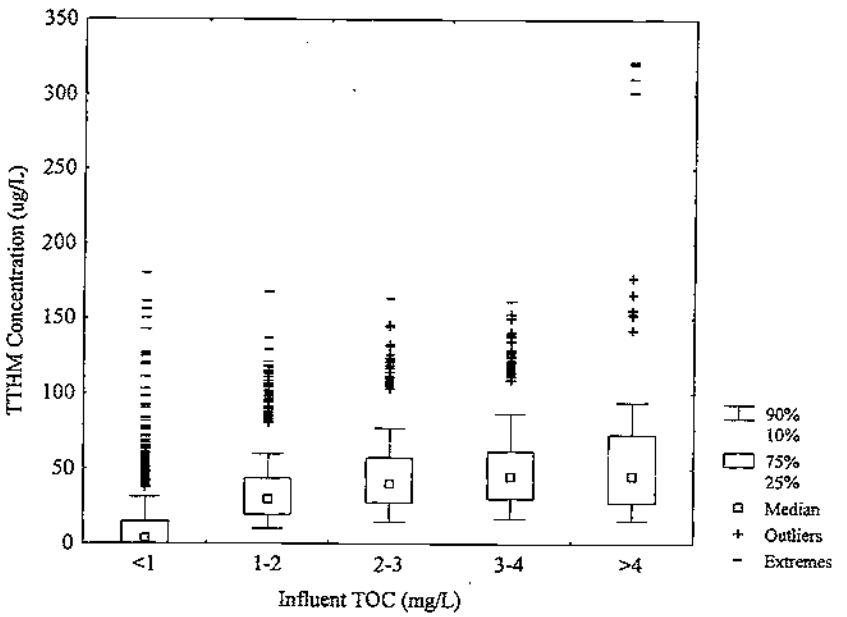

Figure 4.10 Comparison of mean distribution system TTHM concentration as a function of influent TOC concentration

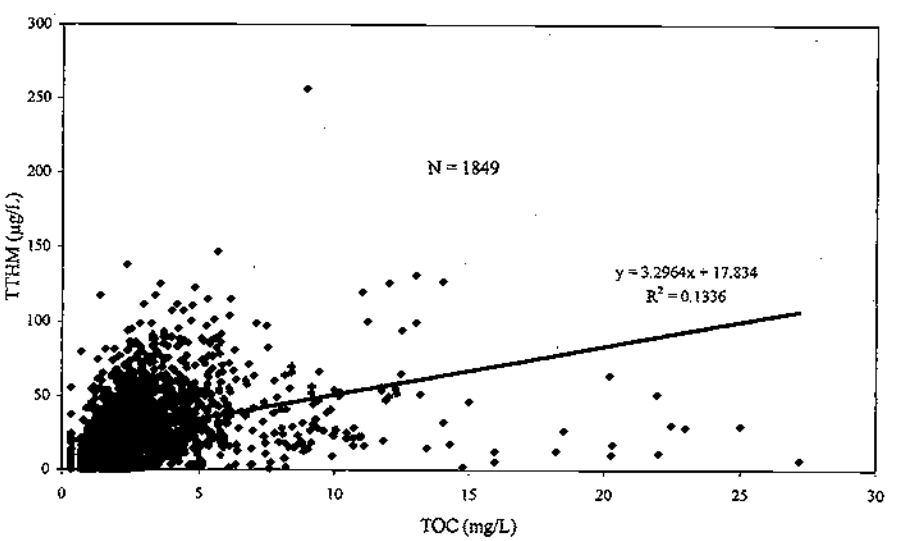

Figure 4.11 Influent TOC concentrations versus finished water TTHM concentrations in ICR plants

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In laboratory studies, bromide ion concentrations have been shown to affect TTHM production. However, the bromide data summarized in Figure 4.12 show that TTHM concentrations in the distribution systems of ICR utilities were not well predicted solely by bromide ion concentrations in plant influent. For this data set, on a microgram-per-liter basis, increasingly high bromide concentrations appeared not to affect the TTHM values produced. Utilities with very high concentrations of bromine-substituted THMs had probably taken action to control DBPs by the time these data were collected, and such control strategies undoubtedly confounded the relationship between these two parameters. Chapter 6 (McLain, Obolensky, and Shukairy 2002) demonstrates that higher bromide ion concentrations led to a higher degree of bromine substitution in bromine-substituted DBPs measured under the ICR.

Figure 4.13 presents a three dimensional picture of the relationships between TOC and bromide concentrations in plant influent and mean TTHM concentrations in distribution systems. By factoring out the influence of bromide, Figure 4.13 shows a clearer relationship between TOC concentrations in plant influent and TTHM production. When bromide concentrations in plant influent were low or moderate, mean TTHM concentrations increased with increasing TOC concentrations in the source water. At the highest bromide concentration, TTHM appears to increase and then decrease with increasing TOC. Once again, it appears that plants whose source water poses the greatest water quality challenges (TOC >4 mg/L, bromide >100 μ/L, $N = 372$) have taken steps to control TTHM concentrations (see Chapter 12, McGuire and Hotaling 2002).

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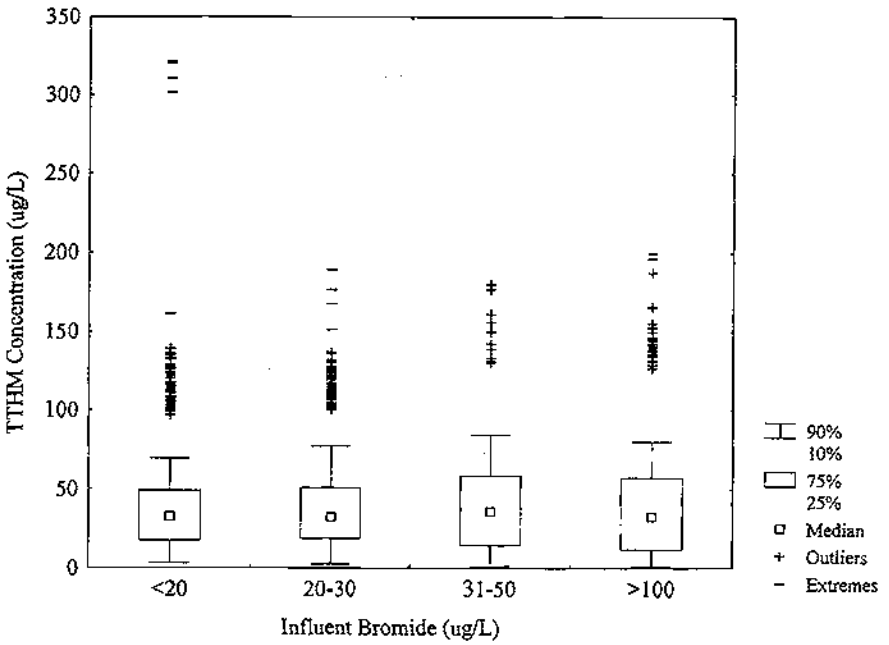

Figure 4.12 Comparison of mean distribution system TTHM concentrations as a function of influent bromide concentrations

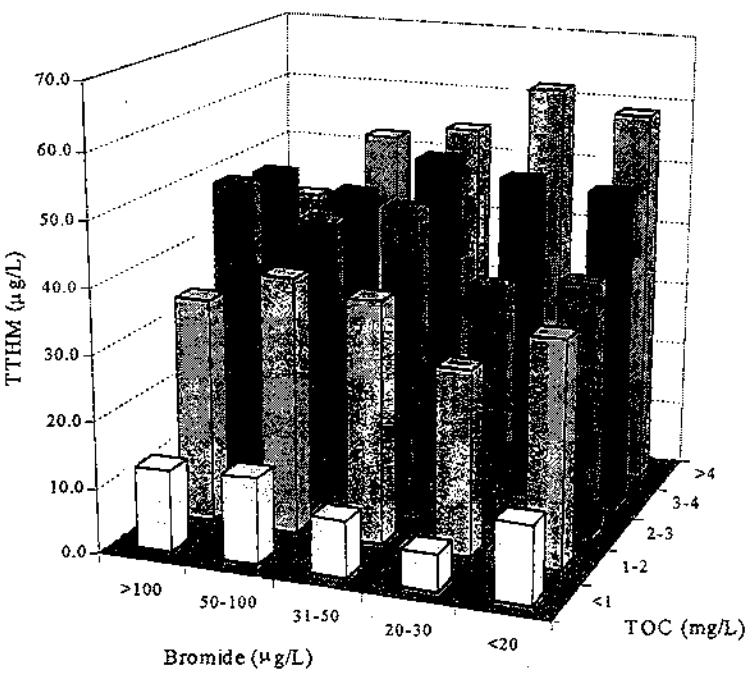

Figure 4.13 Mean distribution system TTHM concentrations plotted by influent TOC and bromide concentrations over six ICR quarters (*N* values were typically 150–300 for all bars)

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COMPARISON OF PREVIOUS TTHM SURVEY RESULTS WITH ICR DATA

Figure 4.14 presents cumulative frequency distribution graphs for the four national TTHM surveys. Each of these surveys produced the best estimate of TTHM occurrence in U.S. drinking water at the time it was conducted. However, these four surveys took place over a 24-year period and used completely different methods of data collection. Table 4.4 summarizes the characteristics of the four national surveys, plus the limited 35-city survey of DBP occurrence. Table 4.4 shows that NORS and NOMS measured only finished water TTHM concentrations. The AwwaRF survey collected no samples and performed no independent trace chemical analyses; instead, it collected utility TTHM compliance data. The ICR TTHM data set, of course, was produced by utilities collecting samples, having them analyzed for TTHM, and then reporting the results to a central database. The ICR TTHM data that are compared with data from the other surveys described in this section consist of averages from treatment plant distribution systems and from 10 blended distribution systems.

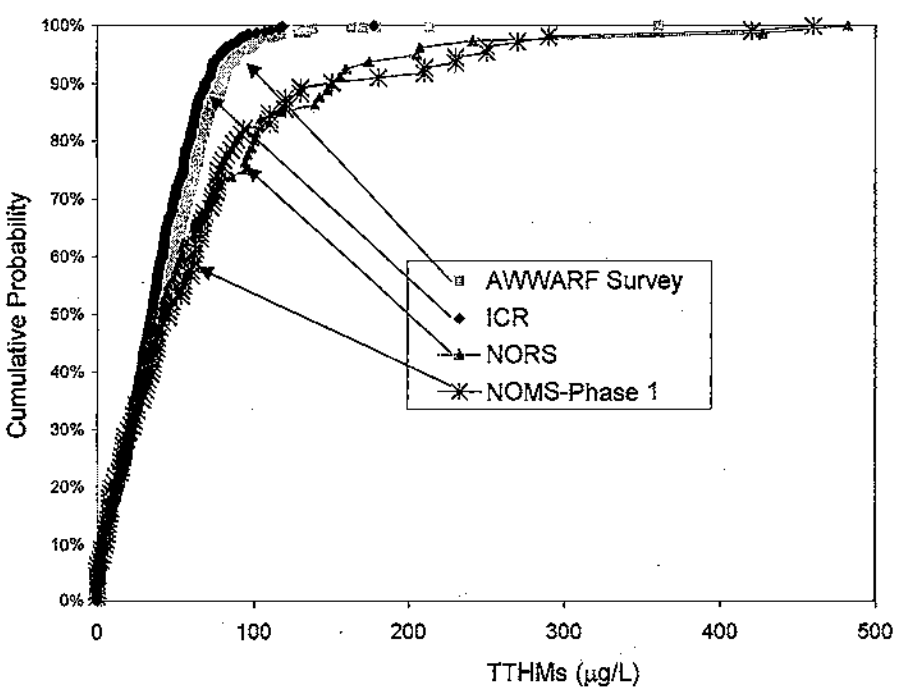

Figure 4.14 Comparison of cumulative frequency distributions from national TTHM surveys

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Table 4.4
Characteristics of national TTHM surveys compared in this analysis

Characteristics	National TTHM surveys				
	NORS	NOMS Phase 1	AwwaRF	35-city	ICR
Number of data points	80	111	727	35	479
Sampling period	1975	1975–76	1984–86	1988–89	1997–98
Sampling location	Plant finished water	Plant finished water	Utility distribution system (DS)	Plant finished water	469 treatment plant DSs; 10 blended DSs
Type of data	Single samples	Single samples	12 quarterly DS averages, averaged for each utility	Single samples averaged over four quarters	DS averages over six quarters
Data collection	Samples collected and shipped to USEPA lab for analysis	Samples collected and shipped to USEPA lab for analysis	Survey—samples collected by utilities and analyzed by certified labs	Samples collected and shipped to one lab for analysis	Samples collected by utility and analyzed by approved labs

Because the results of the four national TTHM surveys constitute the best estimates of national TTHM occurrence at the time they were conducted, it is possible to track changes in national TTHM concentrations over time. In Figure 4.14, the cumulative frequency distributions for NORS and NOMS data indicate much higher TTHM concentrations above a cumulative probability of about 40% compared with AwwaRF and ICR data. Below 40% cumulative probability, the data are indistinguishable from one another, because they consist of values from groundwater or surface water systems whose source water organic precursor concentrations were as low in 1997–98 as they had been in the mid-1970s.

Above 40% cumulative probability, NORS and NOMS data are similar to each other but quite different from the data collected in the AwwaRF and ICR surveys. The difference between data from NORS and NOMS on the one hand and data from the AwwaRF and ICR surveys on the other appears to be caused by utilities modifying their treatment process and disinfection practices in order to comply with the 1979 TTHM MCL. Table 4.5 lists some descriptive statistics for three national TTHM surveys and compares this information with ICR TTHM data. Data from the 35-city survey are also listed and show remarkable consistency with AwwaRF and ICR data. Table 4.5 indicates that median TTHM values for the five surveys are similar but that P75 and P90 values for the five data sets fall into two distinct groups—NORS and NOMS Phase 1 in one group and AwwaRF and ICR averages in the other.

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Table 4.5

Descriptive statistics from national TTHM surveys

Survey	Number of utilities/plants	Mean (µg/L)	Median (µg/L)	P75 (µg/L)	P90 (µg/L)	Maximum (µg/L)
NORS	80	67	41	94	150	482
NOMS Phase 1	111	68	45	78	150	460
AwwaRF	727	42	39	61	79	360
ICR averages	479	36	35	54	68	177
35-city	35	45	39	52	84	185
ICR finished water	2,108*	28	23	41	60	256

* Data points

Close inspection of Figure 4.14 and Table 4.5 suggests that the 1997–98 ICR data set had slightly lower overall TTHM concentrations than the AwwaRF TTHM survey data collected during 1984–86. If there is any difference between the TTHM distributions of the two data sets, it is mainly in the area at P90 and above. If this difference is real, it suggests that reductions in national TTHM occurrence continued over the 12-year period between the two surveys, possibly in anticipation of a more stringent TTHM MCL, which was under discussion during that period. Any differences between the results of the two surveys are likely to be small and could be overwhelmed by significant differences in the manner of data collection (see Table 4.4).

As indicated in Table 4.4, the four national data sets compare finished water values with average values from distribution system sampling locations. Figure 4.15 compares the cumulative frequency distributions for ICR finished water values with the ICR averages plotted in Figure 4.14. There is a difference of 10–15 µg/L among the frequency plots for most of the probability range (excluding the very beginnings and ends of the two curves).

DISCUSSION

Because NORS and NOMS data were collected before promulgation of the TTHM rule in 1979, these data reflect only finished water values during a period when there were no limitations on the amount of chlorine added for disinfection or oxidation. The AwwaRF and ICR data sets reflect TTHM occurrence in U.S. drinking water after widespread compliance with the TTHM MCL of 0.10 mg/L (based on RAAs of TTHM data). The high end of the TTHM concentrations at the utilities represented in the AwwaRF and ICR studies is certainly lower than

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the high end of the TTHM concentrations in the NORS and NOMS data sets. However, as illustrated in Figure 4.6, even the ICR survey showed very high TTHM concentrations in parts of some distribution systems.

Table 4.6 summarizes the percent reductions in finished water TTHM concentrations that occurred between NORS data and ICR data on finished water. Considering all the statistics and the relative shapes of the cumulative frequency distribution curves, a 50%–60% decrease in TTHM concentrations appears to have occurred over the 24-year period spanning NORS and the ICR.

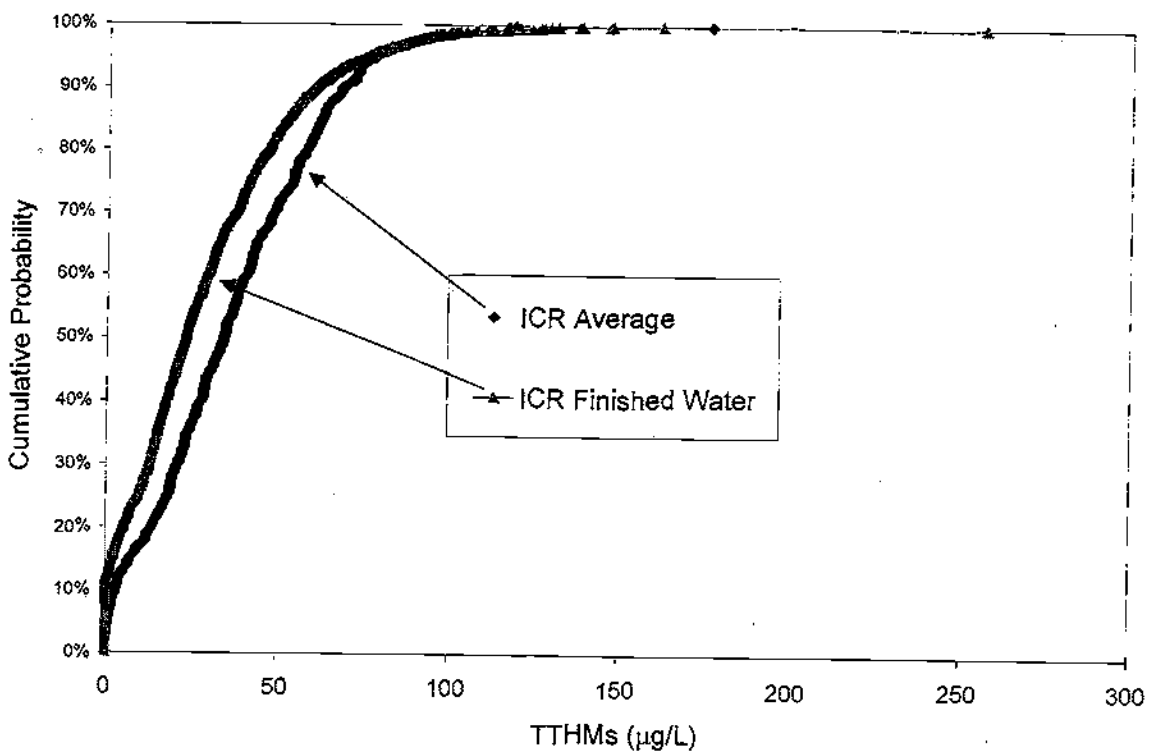

Figure 4.15 Comparison of ICR TTHM data from finished water locations and distribution system averages

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Table 4.6

Percent reductions in finished water TTHM—NORS to ICR

Statistics	Percent reduction between NORS and ICR
Mean	58%
Median	44%
P75	56%
P90	60%

In 2000, the FACA committee recognized the need to reduce the high TTHM concentrations in a number of distribution systems by recommending Stage 2 DBP Rule provisions that utilities meet a TTHM MCL of 80 µg/L on average at all distribution system locations (calculated as the LRAA). If TTHM occurrence in U.S. drinking water is assessed in 2012 after full implementation of the Stage 2 DBP Rule, it would not be surprising to see a noticeable reduction in the median values, a significant reduction in the mean values, and a truly substantial reduction in the P75 and P90 values shown for ICR averages in Table 4.5. A box-and-whisker plot of this 2012 TTHM data, calculated using the LRAA concept, would very likely show no outliers or extremes above the 80 µg/L MCL.

SUMMARY AND CONCLUSIONS

Based on the data presented in this chapter, the following conclusions can be drawn:

- Four major national surveys were conducted to assess TTHM occurrence in U.S. drinking water over the period 1975 to 1998.
- In the ICR data, outlier and extreme TTHM values in distribution system samples from treatment plants using surface water or groundwater supplies indicated that a large number of TTHM values exceeded the 1979 TTHM MCL of 0.10 mg/L. These outliers and extremes significantly affected FACA negotiators, resulting in the recommendation of a Stage 2 DBP Rule provision eliminating MCL compliance through the use of RAAs.
- TTHM concentrations in ICR groundwater systems were typically far lower than TTHM values in ICR systems served by surface water. Because the majority of the outliers and extreme data points were from the distribution system samples of Florida utilities, these high groundwater TTHM values are referred to as the "Florida effect."

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- Chloroform is by far the dominant TTHM species found in drinking water samples. Four extreme values for chloroform samples collected under the ICR were near or above 300 μg/L.
- The geographic distribution of ICR TTHM data shows that the East Coast, including the southeastern states, tended to have the highest TTHM concentrations in the United States. The lowest TTHM concentrations were found in USEPA Region 10, which is composed of Oregon, Washington, Idaho, and Alaska.
- LRAAs calculated with ICR TTHM data were higher than RAAs from the same data set. Utilities will find it more difficult to comply with an 80 μg/L LRAA MCL than with an 80 μg/L RAA MCL.
- Organizing TTHM data from ICR distribution systems by type of treatment did not indicate any obvious trend except for the lower concentrations in groundwater systems. Likewise, comparing TTHM concentrations on the basis of primary or secondary disinfectant did not show tremendous differences among disinfectant categories. The four highest TTHM concentrations were from a distribution system in Mississippi that used chloramine as the secondary disinfectant.
- Correlation analyses showed that TTHM concentrations in distribution system samples were not well predicted by influent TOC concentrations alone; TTHM increased slightly with increasing TOC concentrations. High bromide concentrations in plant influent appeared to have little or no effect on distribution system TTHM concentrations. A three-dimensional plot of TOC and bromide more clearly illustrated the dependence of TTHM on TOC.
- The limited relationship between disinfectant type, source water quality, and TTHM production was primarily the result of utility efforts to aggressively treat water with high concentrations of organic and inorganic precursors in order to ensure lower TTHM concentrations and compliance with the existing MCL.
- A comparison of national TTHM occurrence surveys from 1975 to 1998 illustrated a significant decline in TTHM concentrations during this period. Four descriptive statistics for NORS and ICR finished water data indicated that TTHM concentrations have been reduced by 50%–60% over the past 24 years.

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CHAPTER 5

OCCURRENCE OF HALOACETIC ACIDS IN ICR FINISHED WATER AND DISTRIBUTION SYSTEMS

Alexa Obolensky, Hiba Shukairy, and Valerie Blank

ABSTRACT

The Information Collection Rule (ICR) was the first comprehensive national data collection effort to address the occurrence of haloacetic acids (HAAs) in U.S. drinking water. ICR data provide a snapshot of HAA occurrence at large utilities during the 1997–1998 monitoring period. From regulatory and public health perspectives, the data describe public exposure, enable assessment of the impact of the Disinfectants/Disinfection By-products (D/DBP) Rule's maximum contaminant level for the sum of five HAA species (HAA5), and support development of the Stage 2 DBP Rule and other future regulations. From a research perspective, the data constitute a rich source for investigating relationships between HAA formation, source water quality, and treatment practices across a broad spectrum of conditions.

All ICR plants reported concentrations of six HAA species (HAA6). Approximately 30% of plants also reported concentrations of three additional HAA species that, along with HAA6, make up the sum of nine species (HAA9) and complete the picture of bromine- and chlorine-containing HAAs. This chapter provides an overview of ICR HAA occurrence data with respect to spatial, temporal, and geographic distribution, DBP precursor concentrations, and treatment and disinfection practices. Results for individual HAA species and for the sums of the HAA classes (HAA5, HAA6, HAA9) are discussed. In addition, the dihaloacetic and trihaloacetic acid subclasses are considered, and HAA and trihalomethane concentrations are compared.

BACKGROUND

It is now recognized that all oxidative chemical disinfection practices produce by-products from reactions with natural organic and inorganic constituents in source water. These by-products include halogen-substituted and non–halogen-substituted organic and inorganic compounds (Richardson 1998, Symons 1999). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the major halogen-substituted organic disinfection by-products (DBPs) in chlorinated drinking water, together comprising up to 50% of total organic halogen (TOX) concentrations. Results of the THM and TOX data collected under the Information Collection Rule (ICR) are reviewed in Chapter 4 (McGuire and Graziano 2002) and Chapter 10 (Shukairy, Blank, and McLain 2002) of this volume. Because THMs were the first class of DBPs to be

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discovered, and until recently were the only regulated DBPs, more research has been conducted on THMs than on HAAs. However, the pace of HAA research has increased over the past decade with the recognition of their importance and the development of regulations to address their occurrence in the United States. This chapter presents an analysis of ICR HAA results, summarizing occurrence trends and major findings with respect to water quality and treatment.

The HAA Class

The HAAs include nine bromine- and chlorine-containing chemical species having one, two, or three halogen atoms (chlorine or bromine or a combination of both chlorine and bromine) and are classified accordingly as mono-, di-, or trihaloacetic acids (MHAAs, DHAAs, THAAs). Concentrations of individual HAA species are usually added together and reported as HAA5, HAA6, or HAA9, depending on the species measured (see Table 5.1). Because chemical standards and commercial analytical services have only recently become available for measuring all nine HAAs, research and regulatory development to date have focused on HAA5 and HAA6. The Disinfectants/Disinfection By-products Rule (D/DBP Rule) limits running annual average (RAA) HAA5 concentrations to 60 μg/L (U.S. Environmental Protection Agency [USEPA] 1998).

Table 5. 1

Haloacetic acid species

HAA subclass	Species	Chemical abbreviation	Common abbreviation	In HAA5	In HAA6	In HAA9
MHAA	Monochloroacetic acid	$CH_2ClCOOH$	MCAA	✓	✓	✓
	Monobromoacetic acid	$CH_2BrCOOH$	MBAA	✓	✓	✓
DHAA	Dichloroacetic acid	$CHCl_2COOH$	DCAA	✓	✓	✓
	Dibromoacetic acid	$CHBr_2COOH$	DBAA	✓	✓	✓
	Bromochloroacetic acid	$CHBrClCOOH$	BCAA		✓	✓
THAA	Trichloroacetic acid	CCl_3COOH	TCAA	✓	✓	✓
	Bromodichloroacetic acid	$CBrCl_2COOH$	BDCAA			✓
	Dibromochloroacetic acid	$CBr_2ClCOOH$	DBCAA			✓
	Tribromoacetic acid	CBr_3COOH	TBAA			✓

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An important difference between HAAs and THMs is the fact that THMs consist of a single homologous series of compounds, each having three halogen atoms, whereas HAAs include species with one (MHAAs), two (DHAAs), or three (THAAs) halogen atoms. All four bromine- and chlorine-substituted THM species are captured in the total trihalomethane (TTHM) measurement, regardless of how their relative concentrations may shift with variations in water quality and treatment. In contrast, the commonly reported class sum measurements for HAA5 and HAA6 neglect several bromine-substituted HAA species, providing a measure of "total HAAs" that is biased towards chlorine-substituted species (see Table 5.1). Under conditions in which bromine-substituted species comprise a substantial fraction of HAAs, HAA5 and HAA6 sums may significantly under-represent total HAA concentrations and confound comparisons of HAA results across different water quality and treatment conditions. Relative bromide concentrations are an important determinant of HAA speciation patterns (Symons et al. 1995, Krasner et al. 1995). In Chapter 6 of this book, McLain, Obolensky, and Shukairy (2002) discuss relationships between source water bromide concentrations and observed ICR DBP speciation patterns. Because of unresolved concerns about the chemical stability and variable recovery rates of the bromine-substituted THAA species, even HAA9 may be problematic as an indicator of total HAA concentrations (Munch et al. 2000; Weinberg, Singer, and Brophy 2000).

Considering the HAA subclasses separately is important in understanding HAA occurrence and formation. Researchers have shown DHAAs and THAAs to have distinct relationships with water quality and treatment conditions (Baribeau et al. 2000; Cowman and Singer 1996; Reckhow and Singer 1985; Williams, Williams, and Gordon 1996; Liang and Singer 2001).

NOTES ON ICR DATA

All data under discussion were extracted from the ICR Auxiliary Database 1, version 5.0, referred to as AUX1 (USEPA 2000a). In Chapter 1 Wysock et al. (2002) provide a review of ICR database development, and in Chapter 2 Fair et al. (2002) discuss data quality assurance measures employed for the ICR. Specific data handling methods used for the analyses presented in this chapter are described in the text where appropriate. Included in the analyses presented here are results from ICR quarterly samples collected from treatment plant finished water and

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distribution system sites. The abbreviations FIN, DSE, AVG, and MAX describe types of ICR sampling sites: FIN refers to finished water; DSE refers to distribution system equivalent sites (distribution system locations with relatively well-characterized detention time); AVG refers to distribution system sites with average detention time (ICR sites AVG1 and AVG2); and MAX refers to ICR sites with relatively long detention times. All 500 ICR treatment plants reported HAA5 and HAA6 results, and a subset of 143 plants (138 distribution systems) reported HAA9 results. Plants in the latter category will be referred to in this chapter as the HAA9 plants. Findings for the HAA9 plants cannot necessarily be extrapolated to the entire ICR treatment plant population. Source water quality characteristics and treatment parameters for the HAA9 plants differed in some respects from those of ICR plants as a whole, so that DBP concentrations tended to be lower at HAA9 plants. When ICR HAA9 results are compared with other ICR DBP data, the other data are restricted to results from the HAA9 plants for consistency.

HAA data are not available for all 500 ICR treatment plants. Wholesale plants (27) reported only finished water DBPs; 20 blending plants served 11 combined distribution systems; and many discrete HAA results were invalidated by quality assurance violations. A total of 479 finished water supplies and 451 distribution systems are represented by the HAA5 data in AUX1, but the number of data points included in various analyses may differ. For example, when source water quality information was missing for a sampling period, HAA results for that sampling period were dropped when relationships with source water quality were examined. Methods of handling missing data are described where appropriate. Class sum concentrations (HAA5, HAA6, HAA9, TTHM) for discrete samples were not computed without valid results for all relevant species. Unless otherwise indicated, analyses encompass the results of all treated water field samples collected from FIN, DSE, AVG, and MAX locations during the six-quarter ICR monitoring period.

SUMMARY OF ICR HAA RESULTS

HAA5, HAA6, and HAA9 Results

Figure 5.1 summarizes ICR HAA results, showing associated TTHM results for comparison. Overall ICR median and mean HAA5 concentrations were 18 and 23 μg/L,

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respectively. Corresponding median and mean HAA6 concentrations were 21 and 26 µg/L, indicating that, at the central tendency of the data, inclusion of bromochloroacetic acid (BCAA) increased HAA5 concentrations by about 15%. The median TTHM concentration for the same samples was 31 µg/L. McGuire and Graziano (2002) provide a detailed review of ICR THM results. Although 90% of ICR HAA5 sample concentrations were below 50 µg/L, they ranged as high as 280 µg/L. Nevertheless, the upper 10% of HAA5 results were attributable to only 4% of the associated treatment plants, suggesting that, for the large systems represented, elevated HAA5 and HAA6 concentrations in the United States are limited to a small fraction of utilities. In Figure 5.1 and subsequent figures, outliers are data exceeding the 75th percentile plus 1.5 times the interquartile range (the difference between the 25th and 75th percentiles); extreme values are data exceeding the 75th percentile plus 3 times the interquartile range.

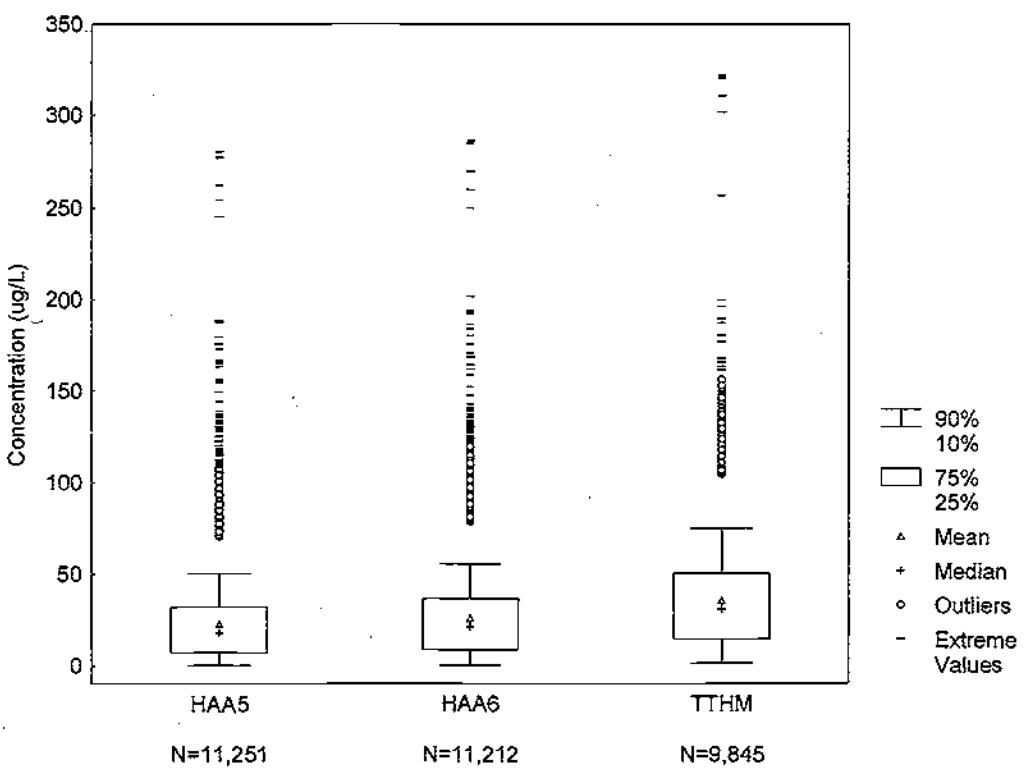

Figure 5.1 Distributions of HAA5, HAA6, and TTHM concentrations (all finished water and distribution system samples for six quarters)

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Figure 5.2 shows the distribution of available HAA9 results, alongside corresponding distributions of available HAA5, HAA6, and TTHM results for the same sampling events. The HAA5, HAA6, and TTHM data shown in Figure 5.2 (from HAA9 plants only) are subsets of those shown in Figure 5.1 (for all ICR plants), with distinct mean and median values. Median, mean, and 90th percentile HAA9 concentrations were 23, 27, and 60 µg/L, respectively, 30–53% higher than associated HAA5 concentrations (median, mean, and 90th percentile concentrations of 15, 20, and 46 µg/L, respectively). Overall, HAA9 concentrations were much closer to TTHM concentrations than HAA5 or HAA6 concentrations were. Median HAA5, HAA6, HAA9, and TTHM concentrations from the HAA9 plants were 15, 19, 23, and 26 µg/L, respectively. These data demonstrate the difference between HAA5 and HAA9 concentrations, at a national level, and the importance of considering HAA9 when describing "total" HAA concentrations (Cowman and Singer 1996; Roberts, Singer, and Obolensky 2002).

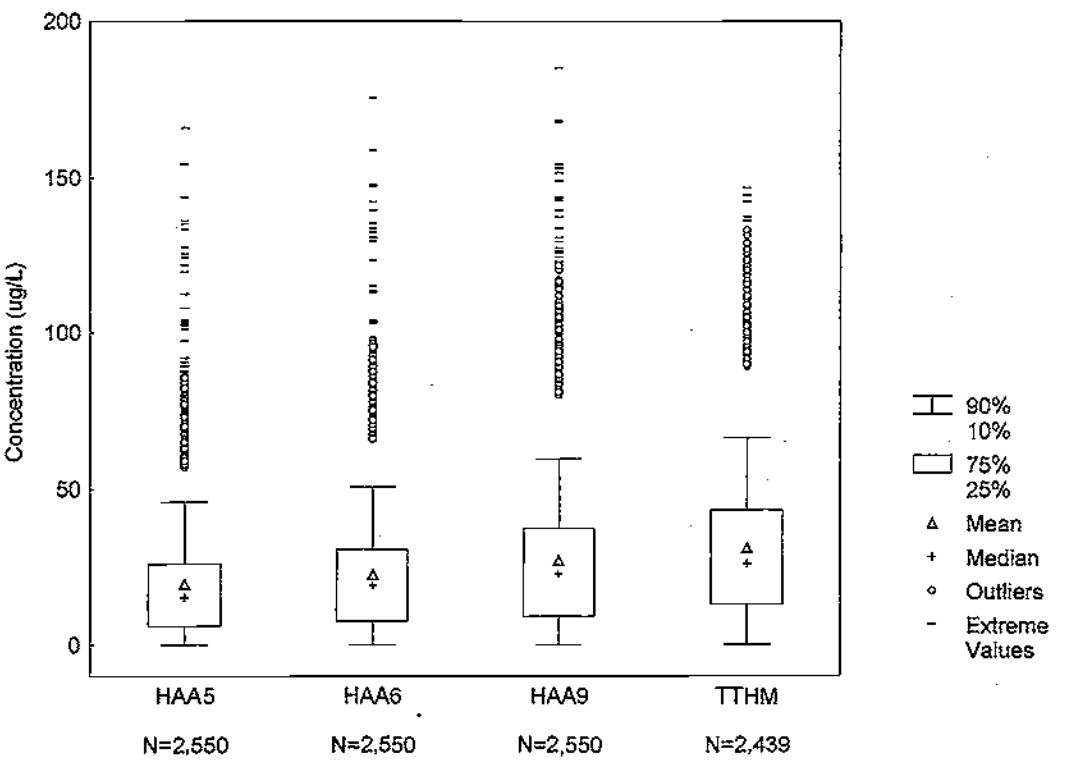

Figure 5.2 Distributions of HAA5, HAA6, HAA9, and TTHM concentrations at HAA9 plants (all finished water and distribution system samples for six quarters)

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A comparison of Figures 5.1 and 5.2 shows that DBP concentrations at the HAA9 plants tended to be slightly lower than those at ICR plants as a whole. Overall ICR median HAA5, HAA6, and TTHM concentrations were 18, 21, and 31 μg/L, respectively, compared with corresponding concentrations of 15, 19, and 26 μg/L at the HAA9 plants. Similarly, 90th percentile HAA5, HAA6, and TTHM concentrations were 50, 55, and 75 μg/L, respectively, for ICR plants overall, compared with corresponding values of 46, 51, and 66 μg/L for the HAA9 plants. The finding that DBP (HAA5 and TTHM) concentrations at the HAA9 plants were about 15% lower than those at ICR plants as a whole suggests that results from the subset of ICR plants that elected to monitor HAA9 may provide a somewhat low estimate of national HAA9 occurrence, compared with that which would be derived from a data set including all ICR plants. Nevertheless, the ICR represents the largest survey of HAA9 occurrence conducted to date, far larger even than any previous survey of HAA5 occurrence.

In an attempt to account for the lower DBP concentrations observed at the HAA9 plants, source water characteristics and treatment conditions at these plants were compared with those at ICR plants as a whole. Influent temperature and total organic carbon (TOC) concentrations and finished water pH tended to be slightly higher at HAA9 plants than at ICR plants overall (data not shown). However, influent bromide concentrations were significantly higher at the HAA9 plants, with a mean of 100 μg/L compared with a mean of 70 μg/L for ICR plants overall (mean of average influent concentrations). The proportion of softening plants was somewhat higher among the HAA9 plants compared with all ICR plants (17.3% versus 11.6%), a plausible explanation for the slightly higher average finished water pH at the HAA9 plants (8.1 versus 7.9). Otherwise, the distributions of treatment plant types and in-plant disinfection practices for the HAA9 plants were very similar to those for all ICR plants. The rate of chloramine use for secondary disinfection was slightly higher at HAA9 plants than at ICR plants overall (37.4% versus 33.1% of plant sampling periods).

Water quality and treatment factors do not provide a straightforward explanation for the lower DBP concentrations at HAA9 plants. Although elevated bromide concentrations can help explain lower HAA5 and HAA6 concentrations, these conditions might be expected to lead to higher TTHM concentrations, which was not the case. McGuire and Graziano (2002) show that ICR TTHM concentrations overall did not increase with bromide. Similarly, though the lower HAA5 and HAA6 concentrations can be partially attributed to higher pH conditions during

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treatment, this difference would also be expected to lead to higher TTHM concentrations at the HAA9 plants. The greater rate of chloramine use at the HAA9 plants may partially account for the lower TTHM concentrations observed at these plants compared with ICR plants overall.

HAA6 and HAA9 Species

Dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the dominant HAA6 species (see Figure 5.3). DCAA concentrations were slightly higher than TCAA concentrations at median (8.5 versus 6.2 µg/L) and mean (10.8 versus 9.8 µg/L) values but equivalent at the 90th percentile (24 µg/L). The 90th percentile concentration of BCAA was 7 µg/L, whereas corresponding 90th percentile concentrations of the remaining HAA6 species were all below 5 µg/L. TCAA exhibited the most extreme high concentrations. Although no DCAA concentrations exceeded 100 µg/L, individual TCAA concentrations ranged as high as 170 µg/L.

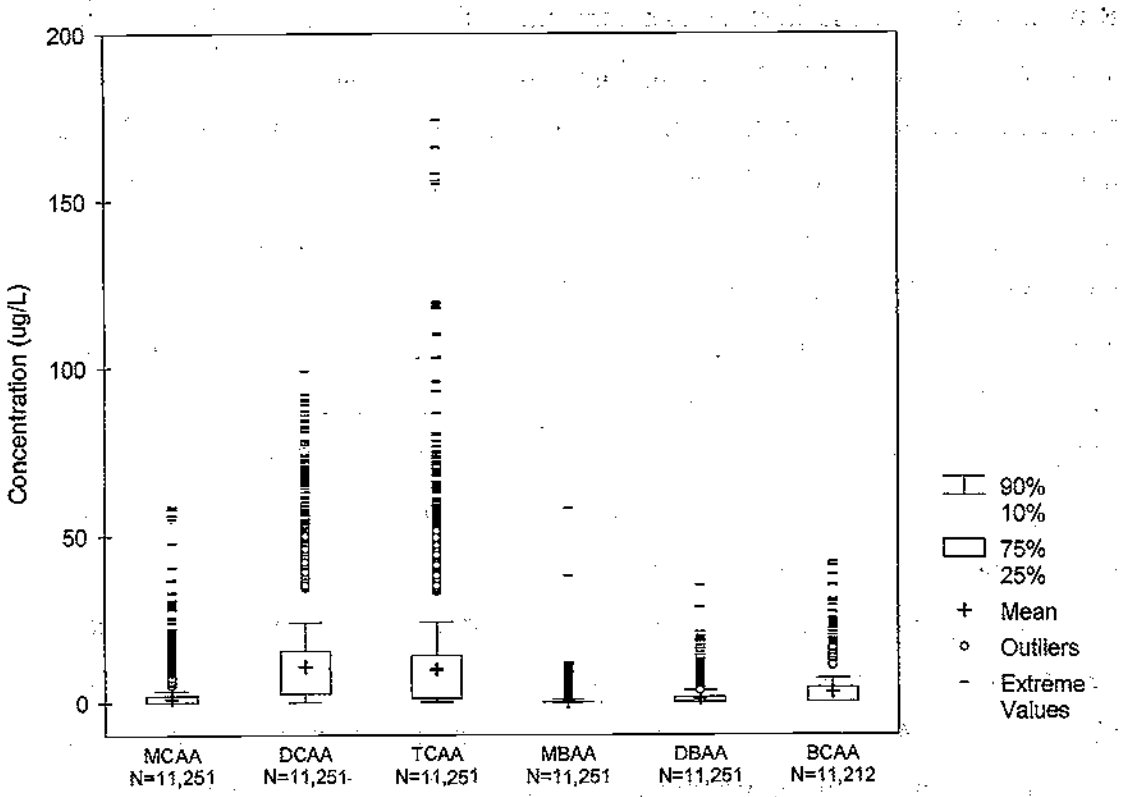

Figure 5.3 Distributions of HAA6 species concentrations (all finished water and distribution system samples for six quarters)

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Based on research and previous survey findings, monochloroacetic acid (MCAA) and monobromoacetic acid (MBAA) are expected to occur only at very low concentrations (typically below 5 μg/L). However, Figure 5.3 shows that numerous unexpectedly high MCAA results, and some unusually high MBAA results, were reported during ICR monitoring. Examination of the data showed that many samples with MCAA concentrations above 20 μg/L had low or undetectable concentrations of other DBPs, rendering these very high MCAA concentrations questionable. Such results may be partially attributable to analytical error, as MCAA generates a broad chromatographic peak that is subject to interference and is difficult to integrate. Although these suspect MCAA results represent a small fraction of all ICR DBP samples (only 5% of MCAA values exceeded 5 μg/L), they could skew analyses involving small subsets of HAA data and should be considered accordingly.

Figure 5.4 shows that TCAA and DCAA remained the dominant HAA species when HAA9 was measured. As observed for HAA6 data from ICR plants overall, DCAA concentrations at the HAA9 plants exceeded TCAA concentrations slightly at the mean and median levels. However, extremely high TCAA concentrations were not observed for these plants, as they were for ICR plants overall. Occurrence distributions for bromodichloroacetic acid (BDCAA) and BCAA were similar (mean concentrations of 3.1 and 3.3 μg/L, respectively), with mean concentrations of less than half those observed for DCAA and TCAA (mean concentrations of 9.5 and 7.7 μg/L). Occurrence distributions for dibromoacetic acid (DBAA) and dibromochloroacetic acid (DBCAA) were also similar (mean concentrations of 1.4 and 1.1 μg/L, respectively), with mean concentrations roughly half again those observed for BCAA and BDCAA. The somewhat lower DCAA and TCAA concentrations at HAA9 plants, compared with those at ICR plants overall, account for the proportionately lower HAA5 and HAA6 concentrations at HAA9 plants. BCAA concentrations at the HAA9 plants were slightly higher than BCAA concentrations at ICR plants overall, a result that is consistent with the higher source water bromide concentrations at HAA9 plants.

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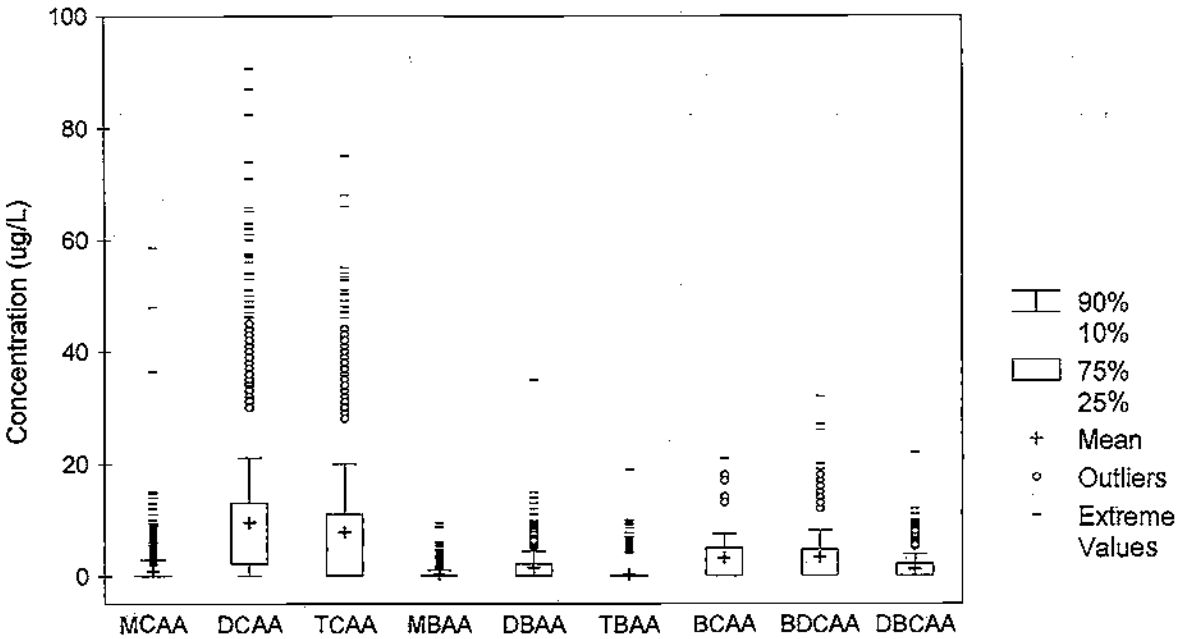

Figure 5.4 Distributions of HAA9 species concentrations (N = 2,550) at plants monitoring HAA9 (all finished water and distribution system samples for six quarters)

Sampling Location

Table 5.2 summarizes DCAA, TCAA, BCAA, DBAA, HAA5, and HAA9 results by sampling location. The overall median distribution system HAA5 concentration (18.5 µg/L) was 16% greater than the median finished water HAA5 concentration (15.9 µg/L). Similarly, the median distribution system HAA9 concentration (23.9 µg/L) was 20% greater than the median finished water HAA9 concentration (19.9 µg/L). These differences were substantially smaller than the corresponding 42% difference observed for TTHM data from the HAA9 plants (TTHM data from HAA9 plants are shown in Table 5.2). TCAA exhibited a much larger overall relative difference between distribution system and finished water concentrations than DCAA (34% versus 10%, based on median values for all plants). Based on overall median values, there was little distinction among the various ICR distribution system sampling locations with respect to HAA species or class sum concentrations.

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Table 5.2

Summary of ICR HAA results

HAA parameter	Measure‡	Finished water	All distribution system sites	Difference§	Distribution system sites		
					DSE	AVG**	MAX
DCAA*	Mean	9.6	11.1	16%	10.8	11.2	11.1
	Median	7.9	8.7	10%	8.8	8.9	8.2
	P90	21.1	24.1	14%	24.0	24.3	25.0
TCAA*	Mean	8.1	10.2	26%	9.8	10.3	10.6
	Median	5.0	6.7	34%	6.2	6.8	7.0
	P90	19.3	25.0	30%	24.0	24.9	26.0
BCAA*	Mean	2.7	3.0	11%	3.0	3.0	2.9
	Median	2.0	2.3	15%	2.3	2.3	2.2
	P90	6.8	7.1	4%	6.9	7.1	7.2
DBAA*	Mean	1.0	1.1	10%	1.0	1.1	1.1
	Median	0.0	0.0	0%	0.0	0.0	0.0
	P90	3.5	3.5	0%	3.4	3.5	3.5
HAA5*	Mean	19.8	23.7	20%	23.1	23.8	24.0
	Median	15.9	18.5	16%	18.2	18.7	18.0
	P90	43.5	51.7	19%	51.1	51.1	53.4
HAA5†	Mean	16.7	20.4	22%	19.8	20.4	21.1
	Median	13.4	15.7	17%	15.1	15.9	16.0
	P90	36.4	47.5	30%	48.1	46.7	48.7
HAA9†	Mean	23.2	28.4	22%	27.6	28.4	29.3
	Median	19.9	23.9	20%	22.7	24.3	24.3
	P90	48.5	60.9	26%	62.1	59.9	63.2
TTHM†	Mean	25.8	32.7	27%	30.6	32.3	35.5
	Median	19.7	28.0	42%	25.6	27.8	32.1
	P90	60.3	68.2	13%	66.2	67.6	74.1
	N *	2,406			2,140	4,479	2,226
	N †	550			481	1017	502

* Data for all ICR plants
† Data for HAA9 plants only
‡ All mean, median, and P90 (90th percentile) values in µg/L
§ (Statistic for distribution system sites minus statistic for finished water sites)/(statistic for finished water sites)
** All ICR sites designated as AVG1, AVG2, or AVG (AVG used for blended systems)

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These comparisons only address the data's central tendencies; they do not consider paired data or capture site-specific changes. Individual changes in ICR DBP concentrations from finished water to distribution system sampling locations varied widely with temperature, type and concentration of residual disinfectant, and other chemical and physical conditions in the distribution system, including sampling site. In Chapter 7, Obolensky and Frey (2002) discuss distribution system changes in ICR DBP concentrations using results of paired data analyses.

Median TTHM and HAA5 finished water concentrations for the final 12-month ICR sampling period were 22.1 and 16.1 μg/L (data not shown). These values can be directly compared with the corresponding results of 39 and 19 μg/L from a 1989 survey conducted by the Metropolitan Water District of Southern California (MWD) and encompassing four quarters of finished water monitoring (Krasner et al. 1989). The median finished water HAA5 concentration from ICR monitoring was slightly lower than that from the 1989 survey, whereas the median finished water TTHM concentration during the ICR was approximately half that of the earlier survey. Consequently, the ratio of median HAA5 to median TTHM concentrations for ICR finished water samples (0.73) was substantially higher than that for finished water samples in the 1989 study (0.49). The lower TTHM concentrations found during ICR monitoring can be partially attributed to lower source water TOC concentrations in ICR samples (median influent concentration of 2.4 mg/L), compared with those in the MWD survey (seasonal median influent TOC concentrations ranging from 2.9 to 3.2 mg/L). However, lower ICR TTHM concentrations may also stem from treatment changes implemented to meet regulations. McGuire and Graziano (2002) discuss ICR THM results in a historical context. The higher relative HAA5 concentrations in the ICR data, compared with data from the MWD survey, can be attributed in part to much lower source water bromide concentrations in ICR samples (median influent bromide concentration of 35 μg/L) compared with those in the MWD survey (seasonal median influent bromide concentrations ranging from 70 to 100 μg/L).

Spatial and Temporal Averages

The method used to average occurrence data affects reported concentration values significantly. For example, the D/DBP Rule sets a maximum contaminant level (MCL) based on the RAA of distribution system HAA5 concentrations, whereas the Stage 2 DBP Rule (USEPA

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2000b) is expected to change the basis for determining compliance to a locational running annual average (LRAA). For a fixed set of occurrence data, LRAA values will generally be higher than RAA values, making the Stage 2 requirement a more stringent standard. However, both RAA and LRAA approaches use annual average concentrations and do not capture seasonal fluctuations. In the following section, ICR data are summarized in terms of quarterly distribution system average concentrations, quarterly distribution system peak concentrations, annual average distribution system mean concentrations (RAA), and annual average location-specific concentrations (LRAA).

Quarterly Average and Peak Distribution System Concentrations

For each ICR distribution system, average and maximum (peak) HAA5 and HAA9 concentrations were determined for each sampling quarter in which two or more valid distribution system results had been reported. Tables 5.3 and 5.4 provide statistics describing these results. Because six quarters of HAA data were collected during ICR monitoring, the third and fourth calendar quarters were sampled twice, explaining the differences in sample counts shown in Tables 5.3 and 5.4. For both HAA5 and HAA9, quarterly distribution system average and peak concentrations tended to be lowest in the first and fourth calendar quarters and highest in the second and third quarters These patterns were more pronounced for peak concentrations than for average concentrations. For both HAA5 and HAA9, quarterly peak concentrations were approximately 10 μg/L higher than corresponding quarterly average concentrations at the 90th percentile. For example, the 90th percentile of quarterly average HAA5 concentrations for the first calendar quarter was 49.6 μg/L, compared with 58.6 μg/L for quarterly peak concentrations. Overall seasonal differences were larger for HAA9 than for HAA5. For example, the 90th percentiles of quarterly peak HAA5 concentrations ranged from 55.0 (fourth quarter) to 70.0 μg/L (third quarter); corresponding values for HAA9 ranged from 56.7 (first quarter) to 81.7 μg/L (second quarter). The stronger seasonal pattern for HAA9 may be related to bromide fluctuations; surface water bromide concentrations tend to increase during hotter, drier weather, exerting a downward influence on HAA5 concentrations relative to HAA9 concentrations.

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Table 5.3

Spatial and temporal average HAA5 concentrations

Concentration	*N*‡	Mean (µg/L)	Median (µg/L)	P75§ (µg/L)	P90§ (µg/L)	P95§ (µg/L)	P99§ (µg/L)
Q1 Average	368	23.1	17.9	31.1	49.6	66.7	118.1
Q2 Average	381	26.8	21.9	37.0	54.7	69.3	115.0
Q3 Average	715	25.4	19.8	36.1	55.7	70.7	105.1
Q4 Average	713	21.3	18.0	30.0	46.6	56.8	75.2
Q1 Peak	368	28.8	21.5	36.4	58.6	81.7	167.3
Q2 Peak	381	32.8	27.0	45.9	65.0	85.9	135.2
Q3 Peak	715	31.4	24.7	43.6	70.0	88.0	124.8
Q4 Peak	713	26.3	21.6	37.0	55.0	72.4	97.2
RAA*	329	23.5	19.9	33.2	49.2	58.1	93.8
LRAA†	332	27.6	23.9	38.5	54.7	67.3	106.9

* RAA computed only for distribution system results
† LRAA computed for all distribution system and finished water sampling locations
‡ For quarterly values, number of plant-quarters; for RAA and LRAA, number of plants
§ P75=75th percentile; P90=90th percentile; P95=95th percentile; P99=99th percentile

Table 5.4

Spatial and temporal average HAA9 concentrations

Concentration	*N*‡	Mean (µg/L)	Median (µg/L)	P75§ (µg/L)	P90§ (µg/L)	P95§ (µg/L)	P99§ (µg/L)
Q1 Average	88	24.3	24.0	30.8	46.8	59.9	112.9
Q2 Average	88	34.6	30.1	52.6	67.4	93.5	133.6
Q3 Average	172	30.3	24.8	45.2	66.9	77.9	124.0
Q4 Average	142	26.5	22.4	37.7	57.2	62.4	92.0
Q1 Peak	88	30.6	28.5	37.7	56.7	67.9	185.1
Q2 Peak	88	43.5	38.6	63.3	81.7	114.2	168.5
Q3 Peak	172	36.4	28.6	54.7	77.3	95.0	143.6
Q4 Peak	142	31.5	26.8	42.8	64.1	81.8	109.2
RAA*	50	24.5	21.8	40.8	60.5	71.1	89.8
LRAA†	50	33.0	28.7	44.7	69.8	83.4	110.1

* RAA computed only for distribution system results
† LRAA computed for all distribution system and finished water sampling locations
‡ For quarterly values, number of plant-quarters; for RAA and LRAA, number of plants
§ P75=75th percentile; P90=90th percentile; P95=95th percentile; P99=99th percentile

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RAA and LRAA Concentrations

RAA HAA5 and HAA9 concentrations for each ICR distribution system were calculated for each of the three consecutive annual periods encompassed by ICR monitoring (ICR quarters 1–4, 2–5, and 3–6). RAA values were computed as the average of four consecutive quarterly distribution system mean concentrations. At least two distribution system results were required to derive a quarterly mean, and an RAA was computed only when four such quarterly means were available. For each ICR distribution system, the highest RAA (out of the three potential values) was identified and included in the analyses discussed here. Thus, one HAA5 and one HAA9 RAA value were generated for each ICR distribution system having adequate data. Statistics describing these HAA5 and HAA9 RAA values are shown in Tables 5.3 and 5.4, respectively.

In a similar fashion, HAA5 and HAA9 LRAA concentrations were computed for each distinct DBP sampling location (including finished water) at each ICR treatment plant for each of the three consecutive annual periods encompassed by ICR monitoring (ICR quarters 1–4, 2–5, and 3–6). LRAA values were computed only when four relevant quarterly results were available for the specific sampling location. LRAA values were also determined for finished water because sampling points near the plant effluent could represent a compliance site for some utilities under the Stage 2 DBP rule. After HAA5 and HAA9 LRAA concentrations had been tabulated for the various plants, sampling locations, and annual periods, the highest HAA5 LRAA value and the highest HAA9 LRAA value associated with each ICR plant were identified and included in the analyses discussed here. Statistics describing these HAA5 and HAA9 LRAA values are shown in Tables 5.3 and 5.4, respectively.

Table 5.3 shows that the D/DBP Rule's MCL of 60 μg/L nearly coincides with the 95th percentile ICR HAA5 RAA concentration; 5% of ICR plants had an HAA5 RAA above 58 μg/L. Approximately 7% of plants had HAA5 LRAA concentrations above 60 μg/L, the MCL anticipated in the Stage 2 DBP Rule. The median HAA5 LRAA concentration of 23.9 μg/L was 20% higher than the corresponding median RAA concentration of 19.9 μg/L, reflecting the change in averaging approach. For HAA9, the same comparison showed an even larger relative difference of 32% (a median LRAA of 28.7 μg/L versus a median RAA of 21.8 μg/L). A separate analysis of paired HAA5 and TTHM data indicated that the set of ICR plants with

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HAA5 RAA (or LRAA) values above 60 μg/L was largely distinct from the set of plants having TTHM RAA (or LRAA) values above 80 μg/L.

This analysis was intended to illustrate the impact of averaging methods on occurrence estimates and to provide alternative summaries of ICR HAA data, not to provide accurate estimates of compliance rates. The ICR data represent only large systems during 1997–1998. They do not necessarily reflect changes implemented to meet the D/DBP Rule, although some systems had already implemented such changes at the time of ICR sampling (Cromwell et al. 2000). ICR RAA calculations were based on individual plants, whereas many utilities (especially large ones) use a systemwide approach to RAA compliance. System-based compliance rates (assuming multiple plants) are expected to be higher than plant-based compliance rates, as a result of averaging across systems. ICR monitoring resembled the D/DBP Rule RAA approach to compliance monitoring, with 25% of sampling sites representing long detention times. However, modified sampling plans under the Stage 2 Rule might lead to higher DBP results than those obtained at existing compliance-monitoring sites, other factors being equal.

TREATMENT, DISINFECTION PRACTICE, AND GEOGRAPHIC REGION

Distributions of HAA5 results by type of ICR treatment plant are shown in Figure 5.5. Conventional plants, representing the largest fraction of ICR plants reporting HAA5 data (55%), and unfiltered surface water plants, representing about 3% of plants, had the highest median (both 25 μg/L) and 90th percentile (57 and 60 μg/L, respectively) HAA5 concentrations. Disinfected groundwater plants, representing about 13% of plants, had the lowest median (below the minimum reporting level) and 90th percentile (13 μg/L) HAA5 concentrations. Lower average source water TOC concentrations (1.9 mg/L versus 3.2 mg/L) and higher average source water bromide concentrations (101 μg/L versus 60 μg/L) at ICR groundwater plants help account for the generally lower HAA5 concentrations at these plants compared with surface water plants. However, a small fraction of groundwater plants had uncharacteristically high HAA5 concentrations, indicated by extremely long tails in the data distribution shown in Figure 5.6; the 99th percentile HAA5 concentration (66 μg/L) for disinfected groundwater plants exceeded the 90th percentile concentration (13 μg/L) by almost sevenfold. Long tails were also evident in the distributions of HAA5 results for conventional, softening, and other groundwater plants.

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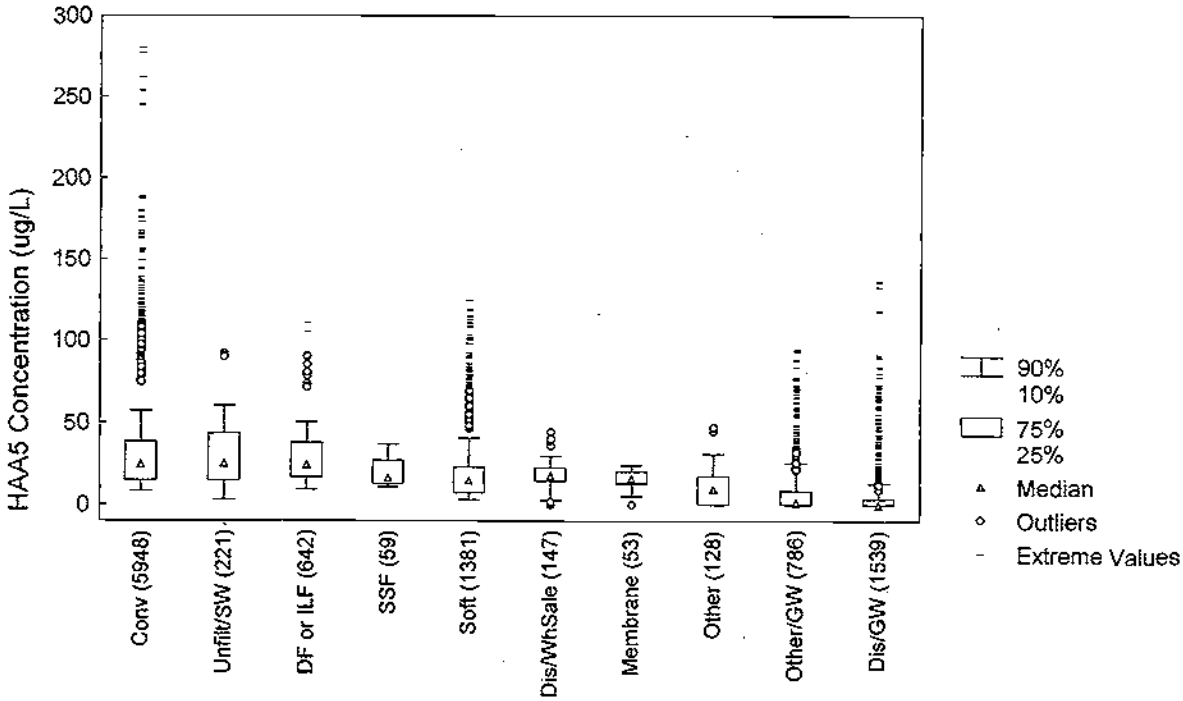

Figure 5.5 Distributions of HAA5 concentrations as a function of type of ICR treatment plant (all finished water and distribution system samples for six quarters; number of results from each type of plant shown in parentheses)

In AUX1, each ICR plant was characterized for each sampling period by the type of disinfectant applied within the plant and the type of residual disinfectant maintained in the distribution system (Chen and Regli 2002). AUX1 includes five classifications of treatment plant disinfectants: free chlorine only (CL2), free chlorine with chloramine (CL2_CLM), chloramine only (CLM), chlorine dioxide with free chlorine or chloramine (CLX), and ozone with free chlorine or chloramine (O3). If the utility applied any ozone for disinfection credit in the plant, the plant was classified as O3. If the utility applied any chlorine dioxide for disinfection credit in the plant, the plant was classified as CLX (unless it was already classified as O3). Distribution system residual disinfectants were classified as either CL2 or CLM.

Table 5.5 summarizes finished water HAA5 and HAA9 results by AUX1 treatment plant disinfectant categories. Finished water HAA5 and HAA9 concentrations tended to be highest at CL2_CLM plants and lowest at O3 plants, with 90th percentile HAA5 concentrations of 54.8 and

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28.6 µg/L, respectively. Corresponding 90th percentile HAA9 concentrations were 90.7 and 25.0 µg/L. Although HAA5 concentrations were similar at CL2, CLX, and CLM plants, HAA9 concentrations at CLX plants were markedly higher than at CL2 and CLM plants. However, few HAA9 data were available for categories other than CL2_CLM and CL2. Systems applying chloramines in the treatment plant had higher HAA concentrations than expected, based on disinfection practices alone, particularly in the CL2_CLM category. This is probably because plants with high DBP precursor concentrations tended to apply chloramines for THM control in order to comply with the interim 1979 TTHM rule (McGuire and Hotaling 2002, Singer 1993). Furthermore, at many of the ICR plants designated as CL2_CLM, most of the disinfectant contact time in the plant was with free chlorine; ammonia was added after filtration or after clearwell storage, immediately before finished water entered the distribution system. Many of the ICR plants designated as CLX used chlorine dioxide as a preoxidant only, achieving primary disinfection with free chlorine. Therefore these data are not a good indication of the benefit of chlorine dioxide for HAA control.

Table 5.5

Summary of finished water HAA5 and HAA6 results

by AUX1 primary disinfectant category

	Primary disinfectant category	*N**	Mean (µg/L)	Median (µg/L)	P90† (µg/L)
HAA5	CL2_CLM	441	29.1	22.5	54.8
	CL2	1181	21.6	17.4	45.3
	CLX	122	20.4	16.7	35.2
	CLM	126	20.4	16.3	38.9
	O3	88	11.8	7.9	28.6
HAA9	CL2_CLM	96	39.6	27.9	90.7
	CL2	267	24.5	22.0	47.7
	CLX	27	31.3	27.4	73.3
	CLM	31	21.4	20.3	41.1
	O3	16	12.7	10.9	25.0

* Number of HAA5 or HAA9 results for disinfectant category
† P90=90th percentile

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The effects of residual disinfectants on ICR HAA concentrations are largely confounded by differences in source water quality and treatment practices among plants using free chlorine or chloramines in the distribution system (McGuire and Hotaling 2002). Overall HAA5 results based on secondary disinfectant alone were indistinguishable. One notable trend in the HAA data was observed with respect to secondary disinfectant use. Figure 5.6 shows that overall DHAA and THAA concentrations were very similar in CL2 systems (median total DHAA and total THAA were 8.7 and 10.5 µg/L, respectively). However, the median total DHAA concentration was almost double the median total THAA concentration in CLM distribution systems (17.6 versus 9.6 µg/L).

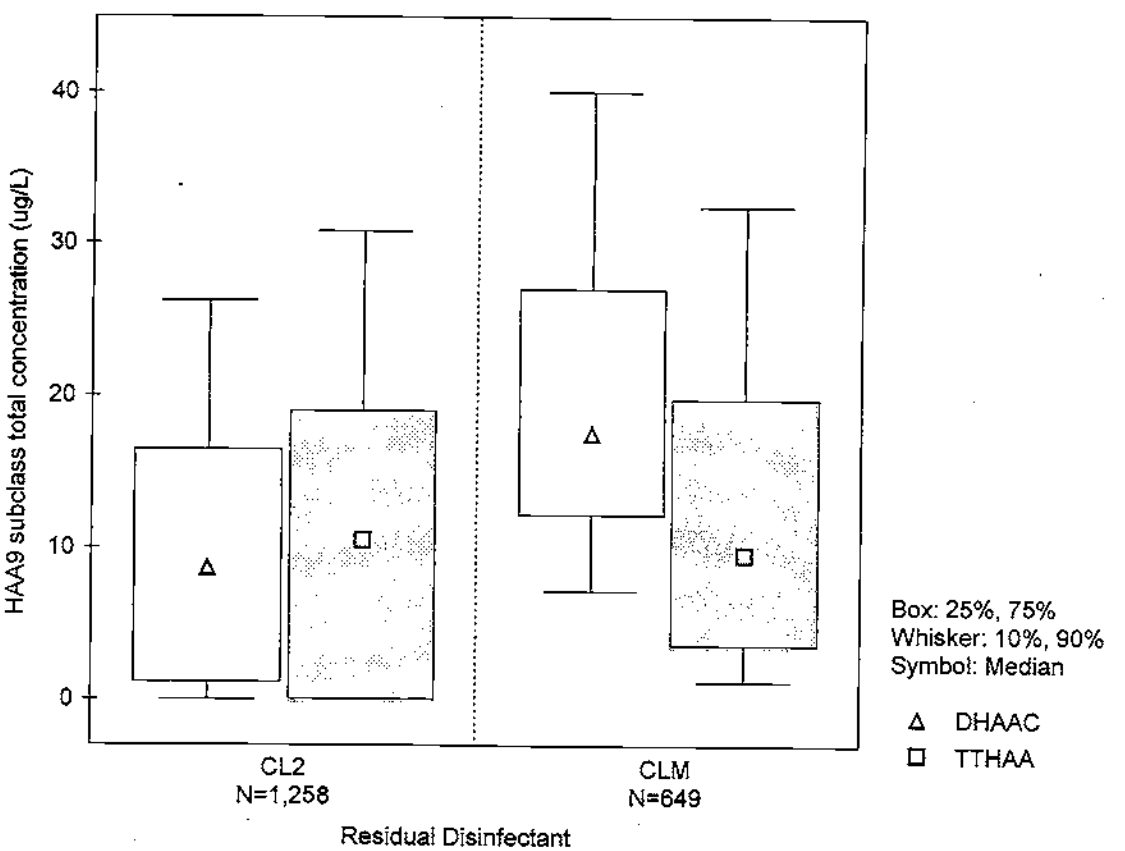

Figure 5.6 Distributions of total DHAA and total THAA concentrations as a function of type of secondary disinfectant (distribution system results for HAA9 plants over six quarters)

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HAA5 summary statistics by USEPA Region are presented in Table 5.6 (see Chapter 3 for a map of the United States showing USEPA regions). Though USEPA regions did not contain a uniform number of ICR plants, each region was represented by at least 10 plants, and the data provide a good geographic representation of national HAA5 occurrence. HAA5 concentrations were generally higher in USEPA regions east of the Mississippi River compared with western regions. ICR HAA9 plants were not well distributed geographically (almost 40% of the HAA9 plants were located in Region 9), and therefore the HAA9 data do not provide a regionally balanced picture of national HAA9 occurrence.

Table 5.6

HAA statistics for 10 USEPA regions

USEPA Region	Number of plants*	Percent of ICR plants in region*	Number of HAA9 plants†	HAA5‡ (µg/L)				
				Mean	Median	P75§	P90§	P95§
1	19	4%	4	28.9	26.0	39	55	64
2	50	11%	4	26.6	21.0	40	61	72
3	39	8%	5	33.6	30.4	48	70	86
4	95	20%	26	31.3	26.4	41	61	80
5	59	13%	14	17.3	9.1	20	43	68
6	57	12%	24	19.2	16.3	27	39	49
7	17	4%	7	19.4	16.2	25	39	50
8	17	4%	1	24.6	22.0	33	42	47
9	102	22%	52	15.3	12.9	23	36	47
10	12	3%	6	14.5	9.1	21	36	50
total	467		143					

* Water treatment plants having valid finished water HAA5 results
† Water treatment plants having valid finished water HAA9 results
‡ Data from all finished water and distribution system samples from all ICR plants
§ P75=75th percentile; P90=90th percentile; P95=95th percentile

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WATER QUALITY FACTORS

ICR HAA results were analyzed with respect to influent TOC and bromide concentrations for the relevant sampling period, as well as DBP sample temperature and pH levels. Though TOC and pH can change substantially during treatment, temperature does not change significantly, and bromide is generally conservative prior to oxidant addition (Summers et al. 1993). During ICR monitoring, many filtration plants were using enhanced coagulation, but applying significant disinfectant dosages at the head of the treatment train was still common practice (Cromwell et al. 2000, Chen and Regli 2002). Thus, for the ICR data set, use of source water TOC values should be satisfactory for identifying dominant trends with respect to HAA formation and organic precursor concentrations.

Figure 5.7 illustrates the general dependence of HAA5 on source water TOC. Mean HAA5 concentrations for successively higher TOC ranges were 4.5, 22.5, 32.8, and 39.2 µg/L, respectively. The fully chlorinated HAA6 species (DCAA and TCAA) increased most strongly with TOC (data not shown). Similar patterns were observed for HAA9 (data not shown).

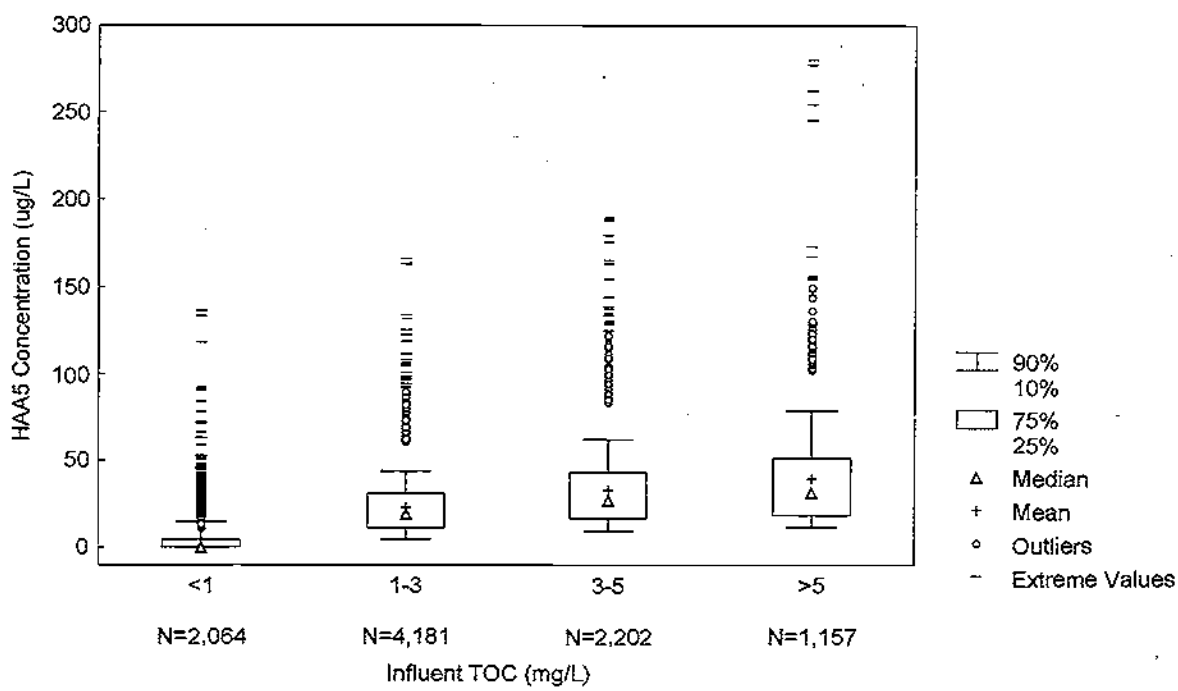

Figure 5.7 Distributions of HAA5 concentrations as a function of influent TOC concentration (all finished water and distribution system samples for six quarters)

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Mean concentrations of HAA5, HAA6, DCAA, TCAA, BCAA, and DBAA for different ranges of influent bromide concentration are shown in Figure 5.8. Concentrations of the bromine-substituted HAA6 species (BCAA and DBAA) increased with source water bromide values, whereas concentrations of the chlorine-substituted species (DCAA and TCAA) decreased. The overall mean HAA5 concentration for samples associated with high-bromide (>100 μg/L) source water was approximately 30% lower than that for samples associated with low-bromide (<20 μg/L) source water (16.9 versus 27.5 μg/L). Figure 5.9 shows the mean concentrations of HAA9 species within each range of bromide concentrations (data for HAA9 plants only). Although DCAA and TCAA declined, DBCAA and DBAA appeared to increase, with successively higher bromide values. Mean BDCAA and BCAA concentrations peaked and leveled off in the bromide range of 50–100 μg/L, followed by the range of >100 μg/L. These findings are consistent with the experimental results of Cowman and Singer (1996) and Pourmoghaddas et al. (1993).

HAA9 did not display a clear association with bromide (data not shown). Mean HAA9 concentrations for the four bromide ranges varied from 24.7 to 29.8 μg/L, peaking at an intermediate bromide range (50–100 μg/L). Based on the higher molecular weight of bromine relative to chlorine, it was surprising that the weight-based HAA9 concentrations did not increase with bromide. Instability of TBAA, poor recovery of BDCAA and DBCAA, or both might depress HAA9 concentrations, or bromine-substituted HAAs may not be formed to the same extent as chlorine-substituted HAAs because of competition with other reactions for bromide. The relationship between influent bromide level and DHAA species concentrations is compared with that for THAA species concentrations in Figure 5.10. Median total DHAA concentrations increased moderately with bromide, whereas median total THAA concentrations decreased substantially with higher bromide ranges. Increases in bromine-substituted DHAA species (BCAA and DBAA) more than offset the slight decreases in DCAA with higher bromide ranges. However, increases in bromine-substituted THAA species (BDCAA, DBCAA, and TBAA) did not compensate for the sharp drop in TCAA with increasing bromide ranges. Tribromoacetic acid (TBAA) concentrations for all bromide ranges shown in Figure 5.10 were below the reporting limit in more than 90% of all samples. These results focus attention on the question of whether differences in formation patterns, chemical instability, or poor recovery rates affect reported concentrations of bromine-substituted THAA species and thus of HAA9.

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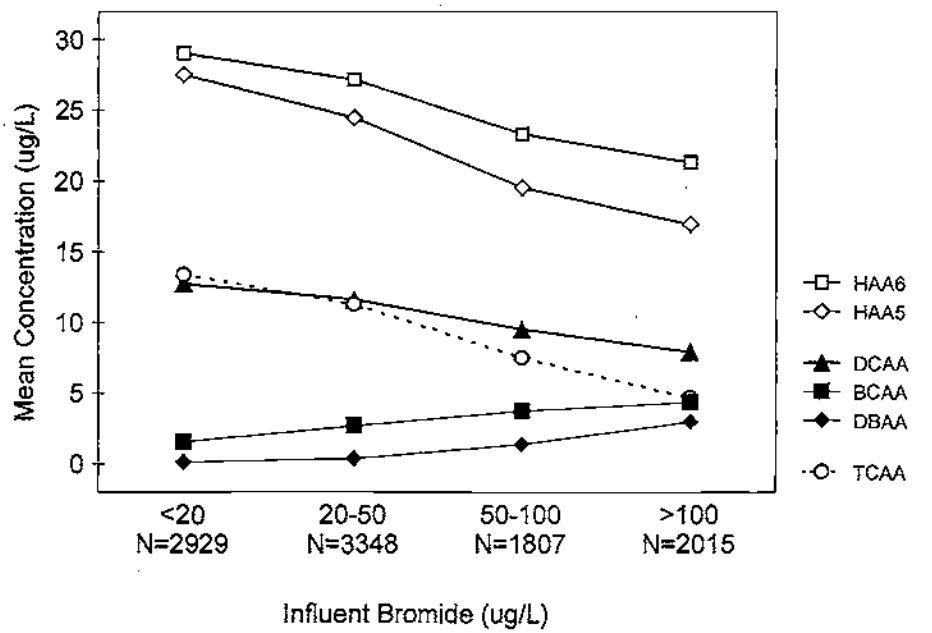

Figure 5.8 Mean concentrations of HAA6, HAA5, and HAA species as a function of influent bromide concentration (all finished water and distribution system samples for six quarters)

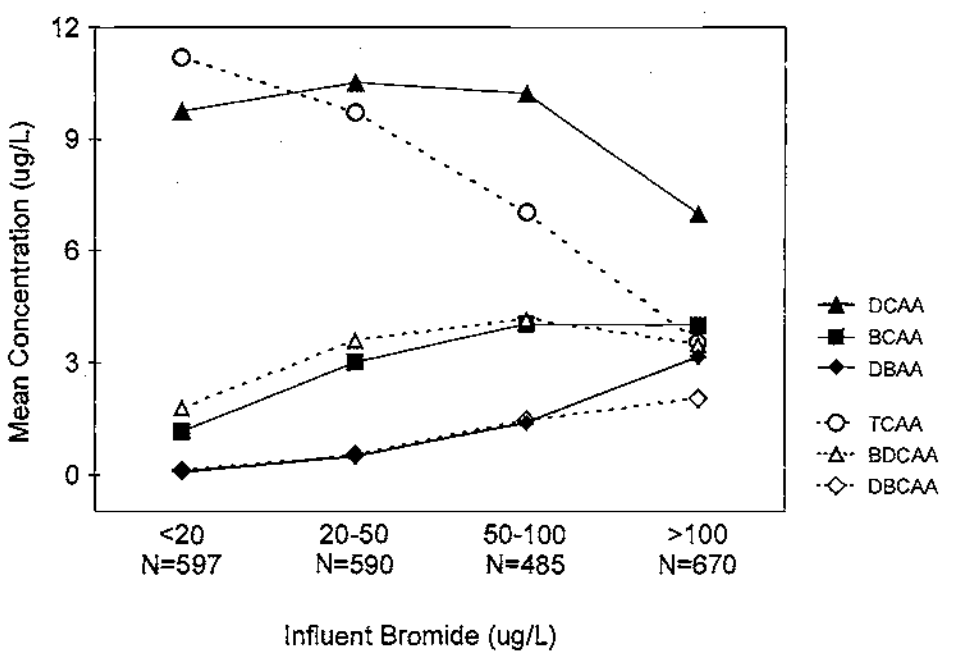

Figure 5.9 Mean concentrations of HAA9 species as a function of influent bromide concentration (finished water and distribution system samples from HAA9 plants over six quarters)

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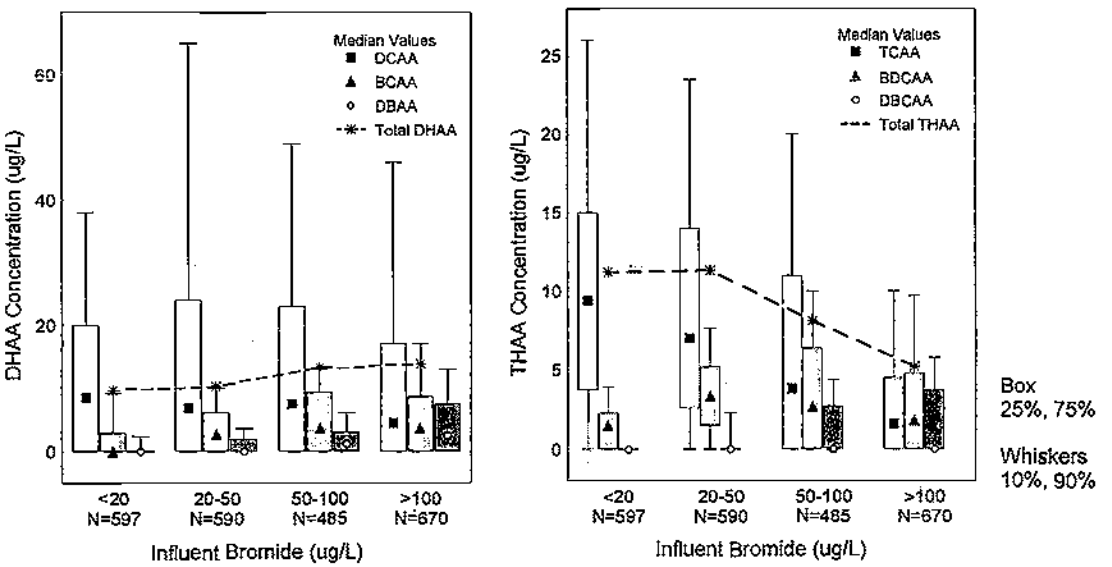

Figure 5.10 Total and species concentrations of DHAA and THAA as a function of influent bromide concentration (finished water and distribution system samples from HAA9 plants for six quarters)

With the exception of TCAA, the HAA species tended to increase moderately with temperature (data not shown). Mean HAA5 and HAA9 concentrations for samples at temperatures above 25°C were 27 and 34 µg/L, respectively, compared with 21 and 25 µg/L for those with temperatures below 15°C. Figure 5.11 shows the overall trends in HAA species concentrations as a function of sample pH in free chlorine and chloramine systems. On average, TCAA dropped sharply with increasing pH, regardless of the type of secondary disinfectant used. DCAA concentrations also tended to decrease with increasing pH in free chlorine systems but were not strongly associated with pH in chloramine systems. Concentrations of the bromine-substituted HAA species (BCAA and DBAA) tended to be highest at intermediate pH levels in chloramine systems, although mean concentrations of these species were low in all pH ranges.

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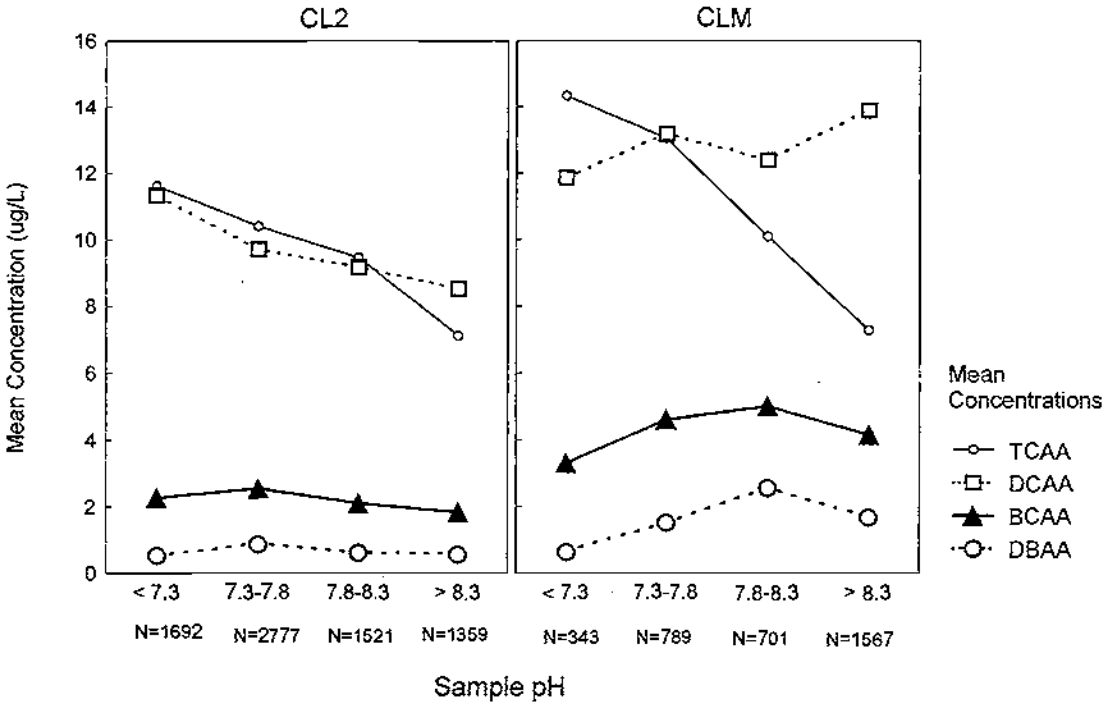

Figure 5.11 Mean concentrations of HAA6 species as a function of residual disinfectant type (left plot CL2, right plot CLM) (all finished water and distribution system samples for six quarters)

SUMMARY

Overall mean HAA5 concentrations in ICR finished water and distribution system samples were 19.8 and 23.7 μg/L, respectively. Corresponding 90th percentile concentrations were 43.5 and 51.7 μg/L, with observed concentrations as high as 280 μg/L. About one third of ICR plants reported HAA9 data. Overall mean concentrations of HAA9 in finished water and distribution system samples were 23.2 and 28.4 μg/L, respectively. However, TTHM and HAA5 concentrations at ICR HAA9 plants were approximately 15% lower than corresponding concentrations at ICR plants as a whole.

Mean HAA9 concentrations in finished water and distribution system samples were 39% higher than corresponding HAA5 concentrations for the same plants. On a sample-by-sample

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basis, HAA9 concentrations were generally much closer to TTHM concentrations than HAA5 concentrations were. TCAA and DCAA were the dominant species for both HAA5 and HAA9, comprising, on average, about 80% of HAA5 concentrations and 63% of HAA9 concentrations. Including BCAA in order to measure HAA6 added about 15% to HAA5 concentrations.

Overall, HAA5 and HAA9 concentrations were highest in the second and third calendar quarters and lowest in the first and fourth quarters; warmer water temperatures were associated with higher HAA5 and HAA9 values. A comparison of RAA and LRAA HAA5 concentrations showed that, on average, LRAA concentrations were about 20% higher than RAA concentrations when the highest, or compliance-controlling value, for each plant was considered.

HAA concentrations appeared to be related to influent TOC concentrations, although results ranged widely for all but the lowest TOC values. Disinfecting groundwater plants, with their generally lower TOC and higher bromide concentrations, had the lowest HAA5 concentrations of all treatment plant types. On a regional basis, HAA concentrations tended to be higher east of the Mississippi River, corresponding to regional differences in source water quality. ICR plants using ozone were distinguished by consistently low finished water HAA5 and HAA9 concentrations, whereas plants using both free and combined chlorine prior to distribution had the highest finished water HAA5 and HAA9 concentrations. Influent water quality conditions favoring high levels of DBP formation were most likely driving chloramine use at these plants. Because of a high degree of confounding related to source water quality, little overall difference was detected among HAA5 concentrations based on a simple distinction between the application of free or combined chlorine in the distribution system. However, DHAA concentrations tended to be substantially higher than THAA concentrations in chloramine systems, whereas DHAA and THAA concentrations were similar in free chlorine systems.

As expected, concentrations of bromine-substituted HAA species increased with increasing source water bromide concentrations. Total DHAA concentrations also increased with bromide. However, increases in the bromine-substituted THAA species did not compensate for dramatic decreases in TCAA at high bromide concentrations. This finding points to the need for further investigation into factors affecting THAA stability and measurement.

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CHAPTER 6
DISINFECTION BY-PRODUCT SPECIATION

Jennifer L. McLain, Alexa Obolensky, and Hiba M. Shukairy

ABSTRACT

This chapter evaluates factors affecting speciation of disinfection by-products (DBPs) and discusses the extent of bromine incorporation in trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) measured during implementation of the Information Collection Rule (ICR). ICR distribution system DBP data and influent bromide data representing a wide range of treatment plant types, disinfection practices, and source water quality characteristics were analyzed to examine DBP speciation shifts nationally. Speciation was determined as the molar percentage of fully chlorine-substituted, bromochloro-substituted, or fully bromine-substituted species in each ICR sample. Based on averaged results within specified bromide bins, a shift in speciation to the more bromine-substituted DBPs occurred as average influent bromide concentrations increased. For all three classes of DBPs studied, however, the range of speciation within each bromide bin was quite large. Differences in the relative amount of bromine-substituted species were observed among the three DBP classes. The proportion of bromine-substituted species increased in the following order: HANs > THMs > HAAs.

INTRODUCTION

Bromine-substituted disinfection by-products (DBPs) are a greater concern than the analogous chlorine-substituted DBPs, both because of their higher molecular weight, which results in a greater total mass of DBPs produced, and their apparent higher toxicity. Thus, the degree of speciation within DBP classes is of interest. This chapter evaluates the factors affecting DBP speciation and discusses the extent of bromine incorporation in trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) measured under the Information Collection Rule (ICR) (U.S. Environmental Protection Agency [USEPA] 1996).

The concentration of bromide in treatment plant influent is an important determinant of the type and mass quantity of DBPs formed during chemical disinfection of drinking water. Bromide is oxidized by chlorine or ozone to hypobromous acid (HOBr), which reacts with natural organic matter (NOM) in a manner similar to that of hypochlorous acid (HOCl). Moreover, the reaction kinetics of HOBr are faster than those of HOCl, so bromine-substituted

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by-products are preferentially formed so long as bromide is present (Rook et al. 1978, Oliver 1980, Symons et al. 1993, Cowman and Singer 1996). The kinetics of halogen incorporation are such that the ratio of the rate of bromination to the rate of chlorination increases with the extent of bromine substitution (Nokes, Fenton, and Randall 1999). Several researchers have reported that THM speciation shifted to the bromine-substituted THMs as a function of bromide concentration when all other parameters were held constant (Minear and Bird 1980; Oliver 1980; Amy, Tan, and Marshall 1991; Shukairy, Miltner, and Summers 1995); this was true even in the presence of excess chlorine (Luong, Peter, and Perry 1982). This speciation shift as a consequence of increased bromide concentrations has also been noted for HAAs (Pourmoghaddas et al. 1993, Cowman and Singer 1996). When the reaction was NOM-limited, higher concentrations of bromine-substituted DBPs were formed (Symons et al. 1993; Shukairy, Miltner, and Summers 1994). Removal of DBP precursors, though effective at controlling the total amount of DBPs formed, caused a shift in DBP speciation to the more bromine-substituted species (Hartman et al. 1991; Amy, Tan, and Marshall 1991; Krasner et al. 1992; Summers et al. 1993; Allgeier and Summers 1995). Similar shifts occurred when precursors were treated with low or medium doses of ozone prior to chlorination (Miltner, Shukairy, and Summers 1992; Symons et al. 1994; Shukairy, Miltner, and Summers 1994; Shukairy, Miltner, and Summers 1995). Under conditions of high NOM and low bromide concentrations, chlorine-substituted by-products predominated, especially during longer reaction times as the original bromide was consumed. In general, DBP speciation shifts were affected by the ratio of bromide to total organic carbon (TOC), the ratio of bromide to chlorine, NOM structure, and contact time (Symons et al. 1993; Shukairy, Miltner, and Summers 1994; Symons et al. 1994).

ICR distribution system DBP and influent bromide data representing a wide range of treatment plant types, disinfection practices, and source water quality characteristics were analyzed to examine DBP speciation shifts as a national trend.

METHOD OF ANALYSIS

The full 18-month set of ICR data—from July 1997 to December 1998—was used for this analysis. DBP data collected quarterly by each plant at four distribution system sampling points (a distribution system equivalent point, two points of average residence time, and one

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point of maximum residence time) were compared with bromide data collected at the plant influent during the month of DBP sampling. All null sample results were excluded from the analysis. If the value of one or more individual DBPs within a class was reported as null, the sum of the class was not calculated. The number of data points used for the DBP class analyses is indicated on select graphs within this chapter. All DBP results reported as less than the minimum reporting level (MRL) were recorded as zero. An analysis of the first 12 months of ICR data showed no difference in average DBP speciation among distribution system sampling points. Therefore, all distribution system data were included in this analysis with no differentiation among sampling locations. In addition, segmenting the data set according to the type of disinfectant used in the distribution system (chlorine versus chloramines) had no impact on speciation trends when 12 months of data were evaluated on a national level. An analysis of speciation by disinfectant type is thus not included in this chapter.

DBP speciation was determined on a molar basis. For each DBP family (THMs, HAAs, and HANs), the percentage of fully chlorine-substituted DBPs, mixed or bromochloro-substituted DBPs, and fully bromine-substituted DBPs was determined. For example, a sample containing 65 µg THM/L composed of 30 µg/L (0.25 µmol) chloroform, 20 µg/L (0.12 µmol) bromodichloromethane (BDCM), 10 µg/L (0.05 µmol) dibromochloromethane (DBCM), and 5 µg/L (0.02 µmol) bromoform ($CHBr_3$) had 0.44 µmol THMs, of which 57% was fully chlorine-substituted, 38% was mixed, and 5% was fully bromine-substituted.

Because the 18-month ICR data set is so large, quarterly sample results from each plant were binned according to rough quintiles for each parameter (Table 6.1), and all sample results within each bin were averaged.

Table 6.1

Bromide and DBP bins

Bin	Bromide (µg/L)	THMs (µg/L)	HAAs (µg/L)	HANs (µg/L)
Bin 1	<20 (MRL)	<10	<5	<1
Bin 2	20–30	10–25	5–15	1–2
Bin 3	30–50	25–40	15–25	2–4
Bin 4	50–100	40–60	25–40	4–6
Bin 5	>100	>60	>40	>6

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RESULTS AND DISCUSSION

THM Speciation

As expected, the average percentage of bromine-substituted THMs increased as influent bromide concentrations increased (Figure 6.1). Even with bromide concentrations below the MRL (<20 μg/L), a small percentage (1%) of $CHBr_3$ and 17% of mixed halogen-substituted THMs (BDCM and DBCM) were produced. At plants with the highest concentrations of bromide (>100 μg/L), more than half of the THMs were bromine-substituted. Although the trend of increasing bromine substitution among THMs is apparent on average across the bromide bins, THM speciation varied widely within each bin, as evidenced by the broad range encompassed by the 10th and 90th percentiles (Table 6.2). Several researchers have reported that as bromide increased, while all other parameters were held constant, the concentration of $CHBr_3$ increased, and the concentrations of both BDCM and DBCM passed through a maximum, then decreased (Minear and Bird 1980; Oliver 1980; Siddiqui and Amy 1993; Nokes, Fenton, and Randall 1999). When the ICR data were averaged over the selected bins, this trend was not observed. As bromide concentrations increased, the concentrations of $CHBr_3$ and mixed halogen-substituted THMs continued to increase. This observation may be due to a number of factors: ICR bromide concentrations were lower than those reported for laboratory studies and perhaps not high enough for maximum formation of mixed halogen-substituted THMs; ICR plant data were averaged over the selected bins so trends were dampened; and unlike under controlled laboratory conditions, other parameters that affect THM formation (e.g., chlorine concentration) were not constant within each bin.

When the ICR plants were categorized by type of source water, the percentage of bromine-substituted THMs produced by groundwater plants was significant—40% or greater—across all bromide bins (Figure 6.2). Presumably, this trend is due to the low TOC concentrations, and consequently high bromide-to-TOC ratios, typically found in groundwater supplies (the median TOC concentration for ICR groundwater supplies was less than the MRL of 0.7 mg C/L). Others have shown that when the ratio of bromide to TOC increased, there was a shift toward bromine-substituted DBPs (Amy, Tan, and Marshall 1991; Krasner et al. 1992). When available organic matter limits the reaction, greater concentrations of bromine-substituted

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DBPs are formed than chlorine-substituted DBPs because the reaction kinetics for bromine are faster than those for chlorine.

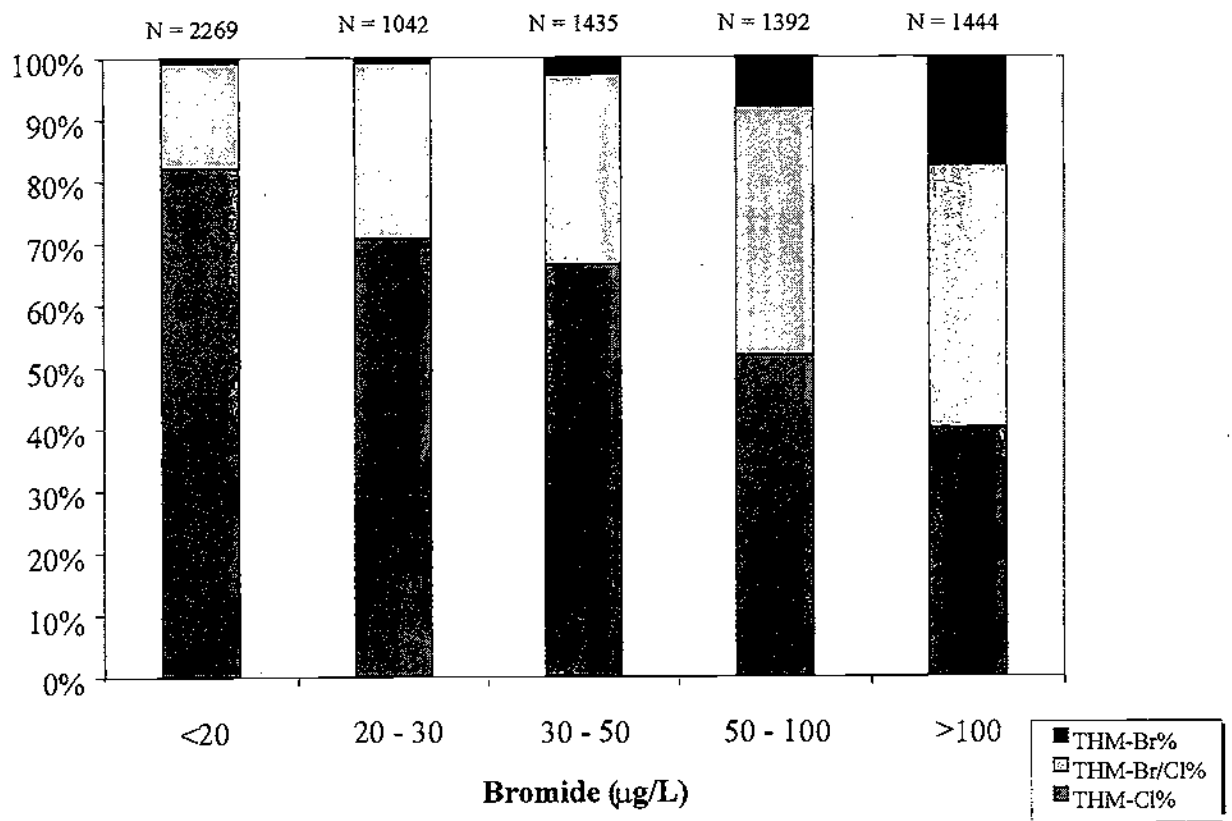

Figure 6.1 Averaged ICR THM data (18 months) binned according to rough quintiles of influent bromide concentrations—percent of fully chlorine-substituted THMs (chloroform), bromochloro-substituted THMs (BDCM and DBCM), and fully bromine-substituted THMs (bromoform) calculated on a molar basis

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Table 6.2

Molar percent of fully chlorine-substituted (chloroform), bromochloro-substituted (BDCM and DBCM), and fully bromine-substituted (bromoform) THMs in each bromide bin

Bromide bin	THM speciation	Average (%)	Median (%)	10th percentile (%)	90th percentile (%)
<20 µg/L	Chloro	82	87	64	96
	Bromochloro	17	13	4	35
	Bromo	1	0	0	0
20–30 µg/L	Chloro	71	76	47	88
	Bromochloro	28	24	12	52
	Bromo	1	0	0	0
30–50 µg/L	Chloro	67	74	35	85
	Bromochloro	31	26	14	56
	Bromo	3	0	0	4
50–100 µg/L	Chloro	52	59	0	80
	Bromochloro	40	39	19	62
	Bromo	8	1	0	27
>100 µg/L	Chloro	40	40	0	79
	Bromochloro	42	47	12	65
	Bromo	18	5	0	55

Comparing DBP formation and speciation using influent bromide concentrations is possible because bromide is generally conserved throughout most drinking water treatment processes. However, because of the variety of precursor removal strategies employed by plants that participated in ICR monitoring, comparing distribution system DBP concentrations with influent TOC concentrations would be meaningless. As a surrogate, the concentration of DBPs was used as an indicator of the amount of reactive organic material available at the point of disinfectant addition. Plants that produced low concentrations of THMs had the largest percentage of bromine-substituted THMs (BDCM, DBCM and $CHBr_3$), regardless of bromide bin (Figure 6.3). Bromine incorporation decreased in plants with low THM concentrations compared with plants with high THM concentrations, presumably because of a decrease in the ratios of bromide to TOC. The trend of increasing bromine incorporation as bromide concentrations increase is apparent for each of the THM bins.

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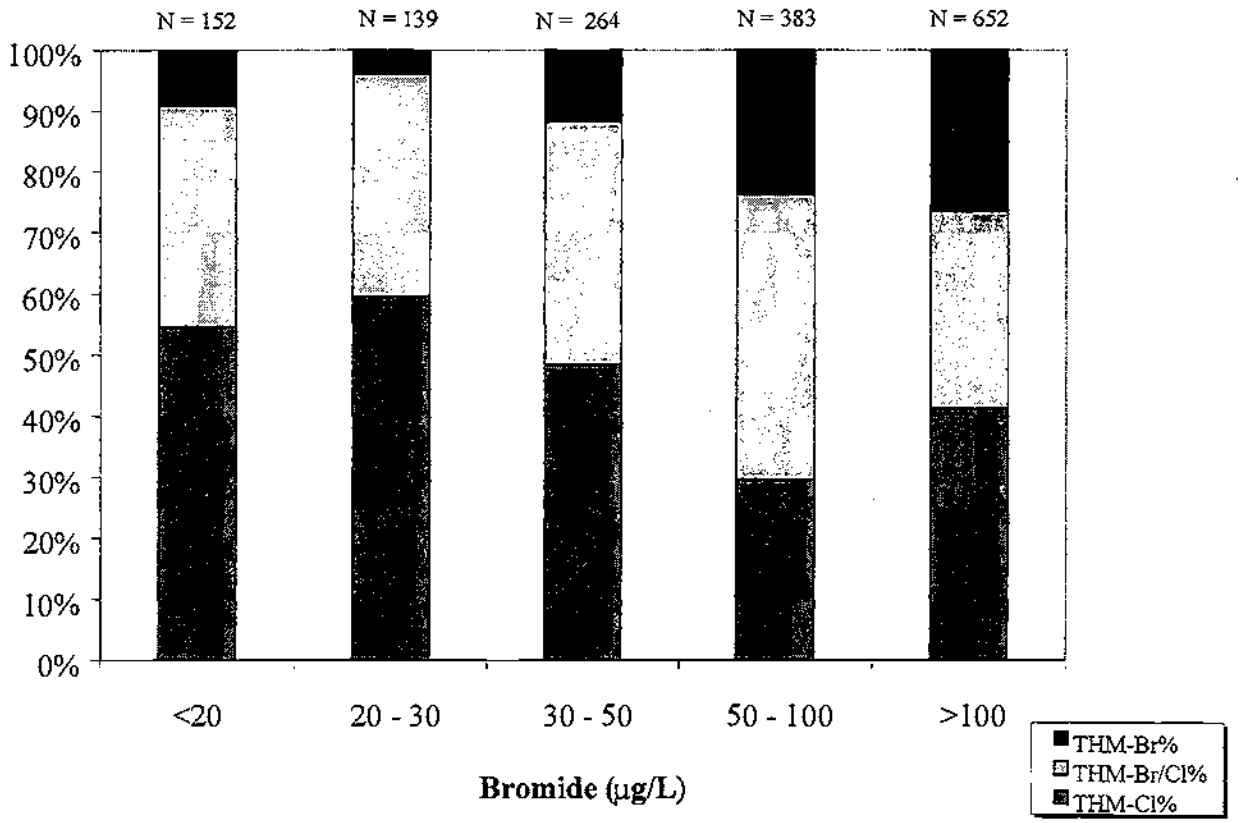

Figure 6.2 Averaged ICR THM data (18 months) from groundwater plants, binned according to rough quintiles of influent bromide concentrations—percent of fully chlorine-substituted THMs (chloroform), bromochloro-substituted THMs (BDCM and DBCM), and fully bromine-substituted THMs (bromoform) calculated on a molar basis

The shift in THM speciation is often measured by an incorporation factor (n), which is the ratio of THM-associated bromine to THMs, as described by Equation 6.1 (Gould, Fitchorn, and Urheim 1983):

$$n = \text{THM-Br } (\mu\text{mol})/\text{THM } (\mu\text{mol}) \qquad (6.1)$$

Thus, n is at a minimum if chloroform is the only THM formed ($n = 0$) and at a maximum if only bromoform is formed ($n = 3$). For a constant concentration of organic precursors, the bromine incorporation factor increases as the bromide concentration increases; for a constant bromide concentration, n decreases as the organic matter increases (Rathburn 1996). Average ICR n

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values calculated for each bromide bin ranged from 0.23 to 1.15 as the composition of the THMs ranged from predominantly chloroform (>30 µg chloroform/L versus <5 µg/L each of BDCM, DBCM, and bromoform) to a mixture containing near equivalent amounts (5–15 µg/L) of each of the THMs (Figure 6.4). Although bromine-substituted molecules are heavier than analogous chlorine-substituted molecules, chloroform was still the most abundant THM, on average by weight (micrograms per liter), in each bromide bin.

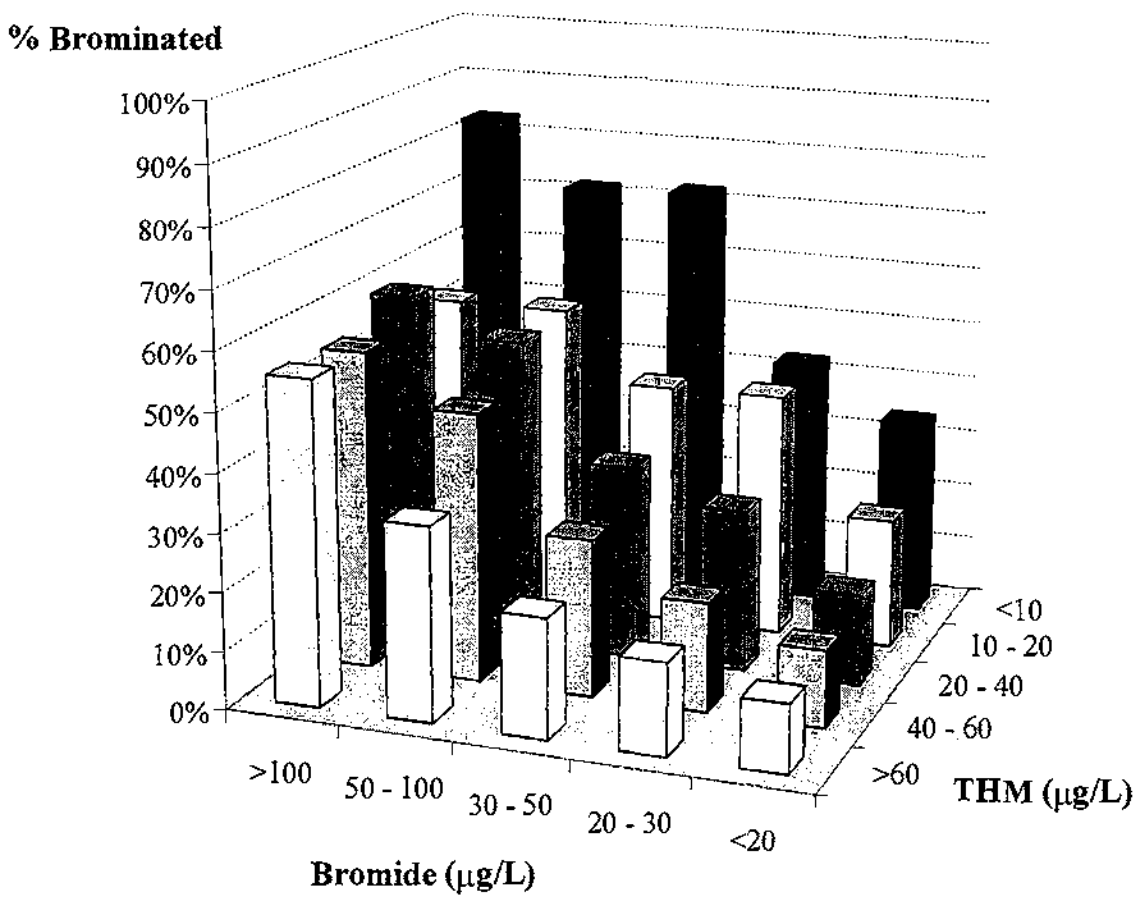

Figure 6.3 Averaged ICR THM data (18 months) binned according to rough quintiles of both influent bromide and average THM concentrations—total percent of bromochloro-substituted THMs (BDCM and DBCM) and fully bromine-substituted THMs (bromoform) calculated on a molar basis

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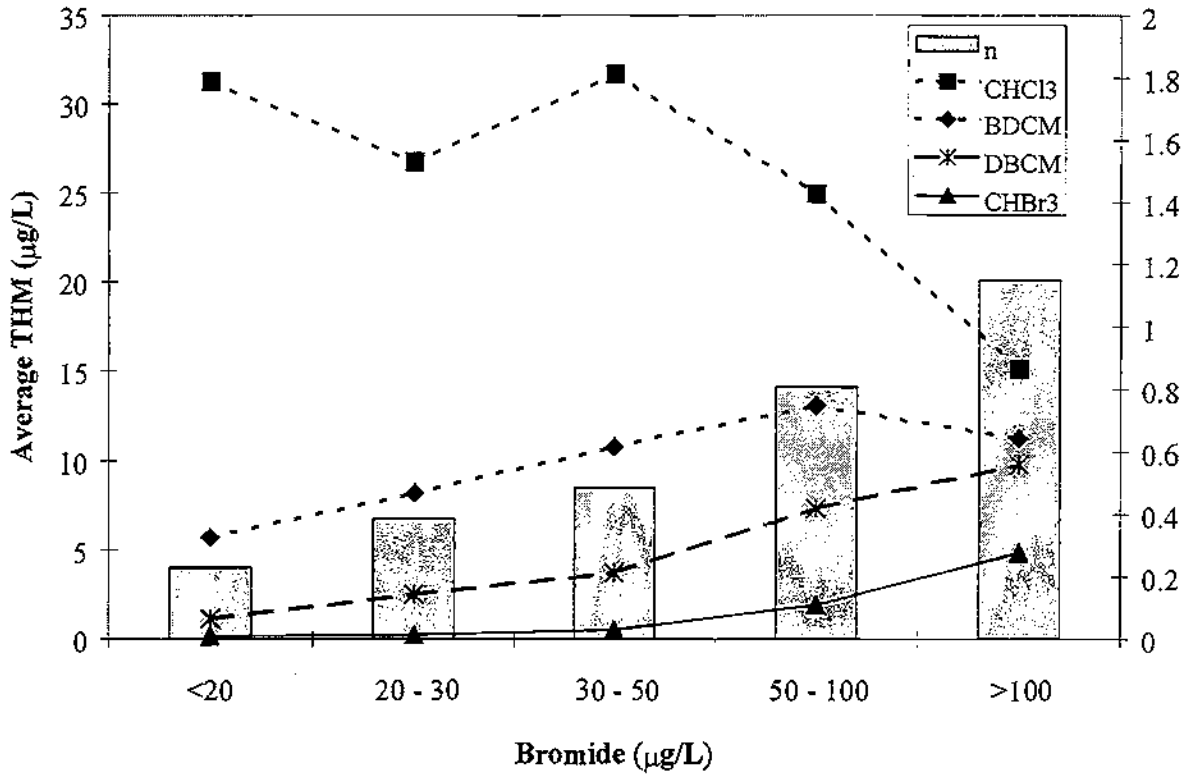

Figure 6.4 Averaged ICR THM data (18 months) binned according to rough quintiles of influent bromide concentrations—average bromine incorporation factor (*n*) for each bromide bin

HAA Speciation

The presence of bromide in chlorinated drinking water causes a shift in the distribution of HAAs to more bromine-substituted species (Pourmoghaddas et al. 1993). Analyzing speciation for HAAs is more problematic than for THMs because most ICR plants analyzed for only six of the nine possible bromochloro-substituted acetic acids—monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and bromochloroacetic acid (BCAA)—collectively termed HAA6. About 20% of the HAA samples collected were analyzed for all nine HAAs—the six previously listed plus bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromoacetic acid (TBAA). Analysis of the HAA6 data thus omitted important bromine-

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substituted HAAs and skewed the picture of speciation toward the fully chlorine-substituted HAAs. Even so, analyzing the HAA data as a class is worthwhile, given the current regulatory structure. An alternative approach would be to analyze the speciation of monohalo-, dihalo-, and trihaloacetic acids separately. A discussion of the ICR HAA data grouped in this manner appears in Chapter 5 (Obolensky, Shukairy, and Blank 2002).

The HAA6 data followed the same trend as the THM data. The percentage of bromine-substituted HAAs increased as bromide concentrations increased (Figure 6.5). The data seem skewed because the percentage of fully chlorine-substituted HAAs was significantly greater than the percentage of fully chlorine-substituted THMs observed across all bromide bins. For example, 93% of HAA6 measured in the bin with the lowest bromide concentrations (<20 μg/L) consisted of MCAA, DCAA, and TCAA, whereas chloroform constituted only 82% of the THMs in the same bin. The percentage of chloroform dropped to 40% in the bin with the highest bromide concentrations (>100 μg/L), but the percentage of fully chlorine-substituted HAA6 remained relatively high at 63%. The data on mixed HAA6 in Figure 6.5 represent only BCAA; the impact of the other two bromochloro-substituted HAAs on speciation is discussed in a subsequent paragraph about HAA9 analysis. Within each bromide bin, there was a wide range of HAA6 speciation (Table 6.3).

Although the overall percentage of bromine-substituted HAA6 was lower than that of THMs, a similar pattern was observed when the data were analyzed as a function of DBP concentrations (Figure 6.6). On average, plants that produced very low concentrations of HAA6 (<5 μg/L) had the highest levels of bromine incorporation per bromide bin. For these plants, across four bromide bins, the concentrations of bromine-substituted HAAs were almost twice those produced by plants in the next highest HAA6 bin (5–15 μg/L). This indication of rapid bromine incorporation in source water with low TOC concentrations was borne out by analysis of the data for groundwater plants. Like the data shown in Figure 6.2 for THMs, the percentage of bromine-substituted HAA6 produced by groundwater plants within each bromide bin was fairly constant (data not shown).

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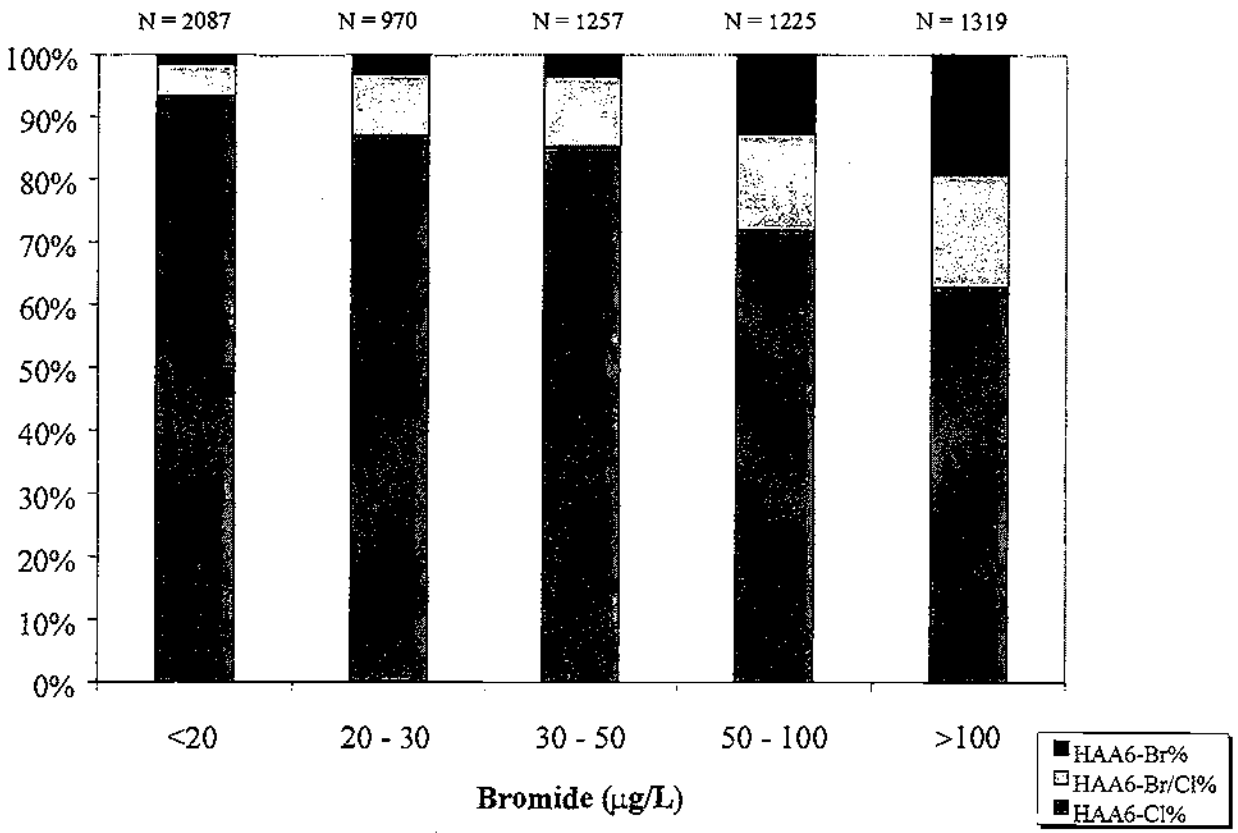

Figure 6.5 Averaged ICR HAA6 data (18 months) binned according to rough quintiles of influent bromide concentrations—percent of fully chlorine-substituted HAA6 (MCAA, DCAA, and TCAA), bromochloro-substituted HAA6 (BCAA), and fully bromine-substituted HAA6 (MBAA and DBAA) calculated on a molar basis

Analogous to the THM incorporation factor *n*, HAA speciation can be explained by an incorporation factor (*n'*), described by Equation 6.2 (Shukairy, Miltner, and Summers 1994; Symons et al. 1994):

$$n' = \text{HAA-Br } (\mu\text{mol}) / \text{HAA } (\mu\text{mol}) \qquad (6.2)$$

A true HAA incorporation factor cannot be calculated if the calculation is based only on HAA6 data. Because TBAA measurements are not included in HAA6, *n'* can only vary between 0 and 2. As noted, ICR HAA6 data predominantly reflected chlorine-substituted species; average ICR *n'* values ranged from 0.07 to 0.54 and did not come close to the theoretical *n'* maximum (Figure 6.7).

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Table 6.3

Molar percent of fully chlorine-substituted (MCAA, DCAA and TCAA), bromochloro-substituted (BCAA), and fully bromine-substituted (MBAA and DBAA) HAA6 in each bromide bin

Bromide bin	HAA6 speciation	Average (%)	Median (%)	10th percentile (%)	90th percentile (%)
<20 µg/L	Chloro	93	96	87	100
	Bromochloro	5	4	0	11
	Bromo	2	0	0	2
20–30 µg/L	Chloro	87	91	77	100
	Bromochloro	10	8	0	20
	Bromo	3	0	0	6
30–50 µg/L	Chloro	85	90	67	97
	Bromochloro	11	9	3	21
	Bromo	4	0	0	11
50–100 µg/L	Chloro	72	81	34	95
	Bromochloro	15	14	0	28
	Bromo	13	4	0	35
>100 µg/L	Chloro	63	68	24	93
	Bromochloro	18	19	0	29
	Bromo	19	11	0	50

Figure 6.7 also shows average microgram-per-liter concentrations for each of the HAA6 species within each bromide bin. The monohalogenated HAAs were minor contributors to HAA6 in any bromide bin. TCAA and DCAA were the most predominant HAA6 species on a weight basis. Shukairy, Miltner, and Summers (1995) reported that DCAA and TCAA were dominant when ratios of bromide to dissolved organic carbon were low. These authors found that at the highest bromide concentrations, BCAA and DBAA became dominant at the expense of the chlorine-substituted species. This dramatic shift to bromine-substituted DBPs was not as evident in the ICR data, however, because naturally occurring bromide concentrations are lower than those of the bromide-spiked water used in the study and because of the averaging of data within each bromide bin. BCAA had the third highest concentration of the HAA6 species in each bromide bin; thus, sampling for HAA5 under the Dinfectants/Disinfection By-products (D/DBP) Rule omits an important measure of HAA concentration, especially for water sources with high bromide concentrations.

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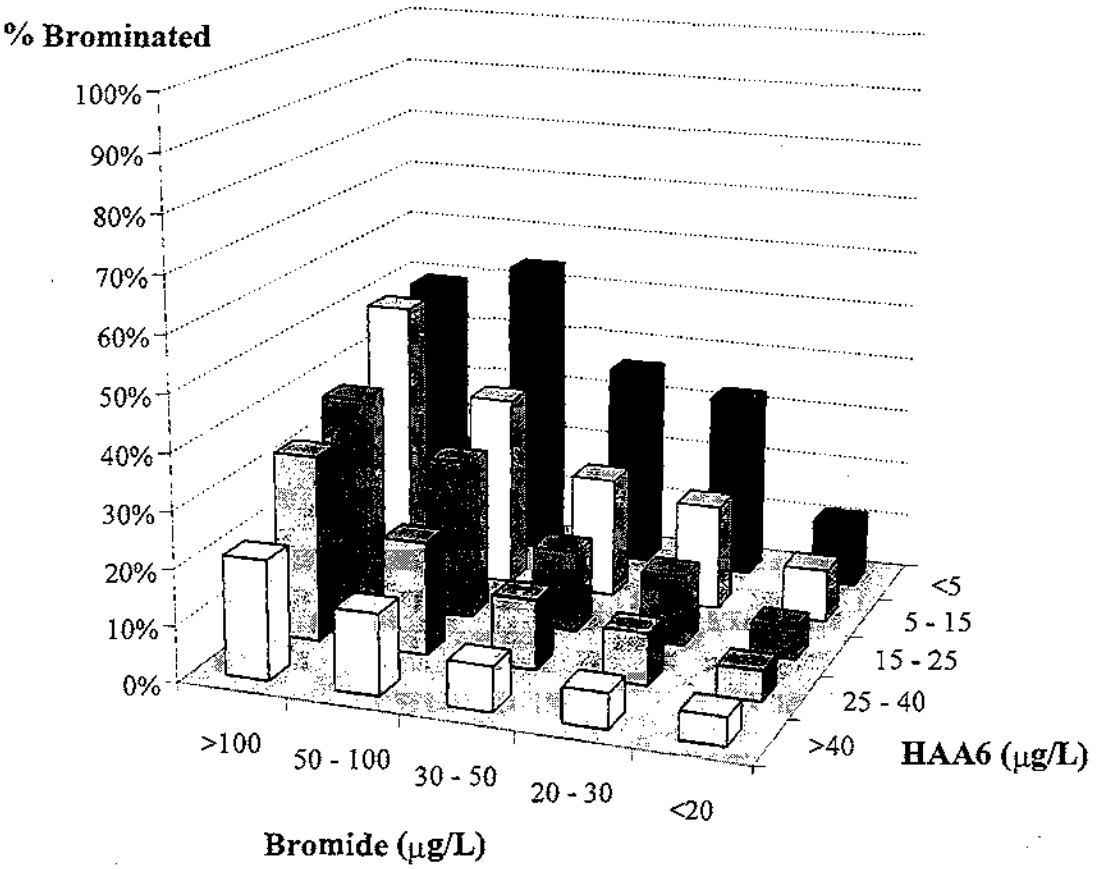

Figure 6.6 Averaged ICR HAA6 data (18 months) binned according to rough quintiles of both influent bromide and average HAA6 concentrations—total percent of mixed bromochloro HAA6 (BCAA) and fully bromine-substituted HAA6 (MBAA and DBAA) calculated on a molar basis

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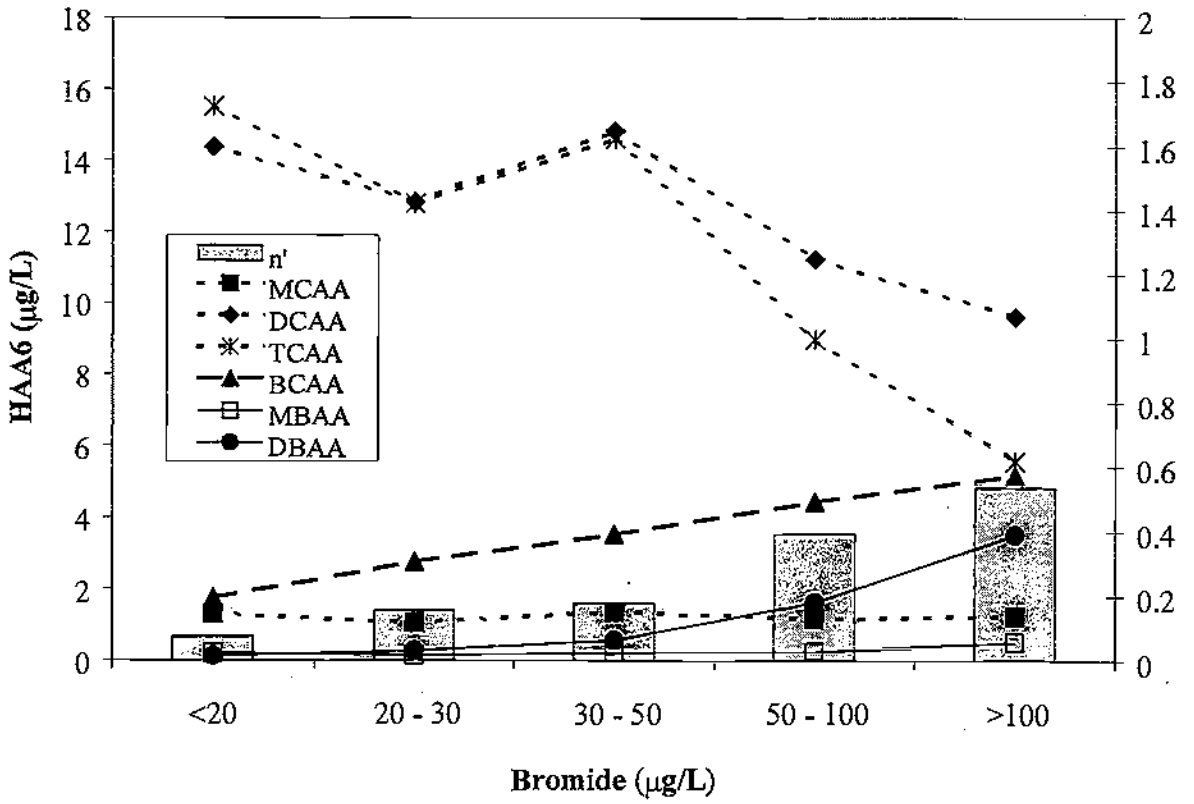

Figure 6.7 Averaged ICR HAA6 data (18 months) binned according to rough quintiles of influent bromide concentrations—average bromine incorporation factor (n') for each bromide bin (A true HAA incorporation factor cannot be calculated using the HAA6 subset of data on the HAA class of DBPs.)

The data subset on plants that measured all nine HAAs was analyzed to get a more representative picture of speciation in the HAA class. Plants that monitored for HAA9 had somewhat higher concentrations of bromide than ICR plants overall. HAA9 plants had bromide concentrations about 10 µg/L greater at the median (46 µg/L) than plants that monitored for only HAA6 and bromide concentrations 100 µg/L greater at the 90th percentile (260 µg/L). The higher influent concentrations of bromide at HAA9 plants translated into higher concentrations of bromine-substituted HAA6 species compared with plants that measured HAA6 only. The HAA9 data set had approximately 20% of the number of observations contained in the HAA6 data set. This number of observations was sufficient to segment the data by bromide bins but too

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low to further segment the data by source water type or HAA9 bins. Although the HAA9 plants had higher concentrations of bromine-substituted HAAs than the HAA6 plants, and the number of observations was smaller, the observed trends are still relevant at a national level.

Surprisingly, although influent bromide concentrations were higher at the plants with HAA9 data and the percentage of bromine-substituted HAAs increased with bromide to a greater extent than in the HAA6 data, the percentage of fully chlorine-substituted HAAs in the HAA9 data was still 4–10 % higher than in the THM data (Figure 6.8 compared with Figure 6.1). This difference may be due to the lower stability of trihaloacetic acids, especially TBAA, compared with the stability of trihalomethanes. Of course, the span of speciation within each bin was considerable (Table 6.4).

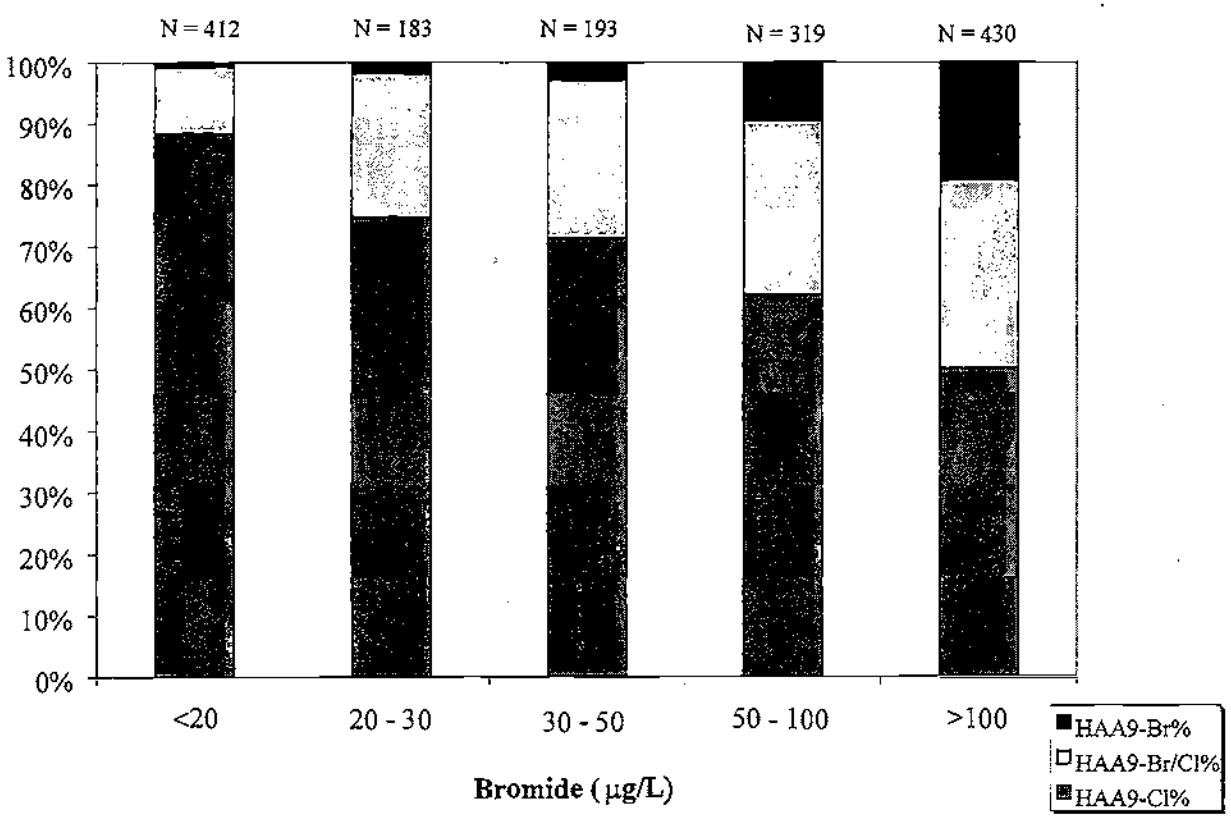

Figure 6.8 Averaged ICR HAA9 data (18 months) binned according to rough quintiles of influent bromide concentrations—percent of fully chlorine-substituted HAA9 (MCAA, DCAA, and TCAA), bromochloro-substituted HAA9 (BCAA, BDCAA, and DBCAA), and fully bromine-substituted HAA9 (MBAA, DBAA, and TBAA) calculated on a molar basis

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Table 6.4

Molar percent of fully chlorine-substituted (MCAA, DCAA, and TCAA), bromochloro-substituted (BCAA, BDCAA, and DBCAA), and fully bromine-substituted (MBAA, DBAA, and TBAA) HAA9 in each bromide bin

Bromide bin	HAA9 speciation	Average (%)	Median (%)	10th percentile (%)	90th percentile (%)
<20 µg/L	Chloro	84	89	67	100
	Bromochloro	15	11	0	31
	Bromo	1	0	0	0
20–30 µg/L	Chloro	74	78	54	88
	Bromochloro	24	22	10	40
	Bromo	2	0	0	8
30–50 µg/L	Chloro	59	62	16	91
	Bromochloro	30	31	5	49
	Bromo	11	5	0	27
50–100 µg/L	Chloro	53	51	12	88
	Bromochloro	28	27	8	48
	Bromo	19	11	0	46
>100 µg/L	Chloro	60	59	34	85
	Bromochloro	31	35	14	45
	Bromo	8	4	1	19

After chlorination of humic acids in the presence of high concentrations of bromide ion, Pourmoghaddas et al (1993) found that the bromine-substituted and mixed species predominated; however, the highest bromide concentration used in that study (450 µg/L) was much higher than the bromide concentrations reported in the ICR data.

A comparison of the HAA6 and HAA9 data (Figure 6.5 versus Figure 6.8) shows the importance of the bromochloro-substituted HAAs in understanding HAA production; the percentages approximately double. Other researchers have reported that the three bromochloro-substituted species constituted a significant fraction of total HAA concentrations (Cowman and Singer 1996) and that as bromide concentrations increased, the concentration of bromochloro-substituted HAAs decreased as the concentration of fully bromine-substituted HAAs increased (Pourmoghaddas et al. 1993, Cowman and Singer 1996). In the ICR data, even when bromide concentrations were below the MRL, the bromochloro-substituted species constituted 11% of the total HAA9 concentration. Analysis of the ICR data showed that concentrations of fully bromine-substituted HAAs increased but that the percentage of mixed HAAs remained fairly constant in the two bins with the highest bromide concentrations. The increase in the total

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fraction of bromine-substituted HAA species was reflected in average ICR *n'* values, which ranged from 0.12 to 0.74 (Figure 6.9).

Figure 6.9 also shows the average concentrations of each HAA9 species by bromide bin. In the bin containing low bromide concentrations, the concentration of each HAA9 species increased in the following order: TCAA > DCAA >> BDCAA > BCAA > MCAA > DBCAA > DBAA > MBAA = TBAA. For bromide concentrations in the midrange, the most significant change was that DCAA production exceeded TCAA production. In the bin containing the highest bromide concentrations, the order became: DCAA > BCAA > TCAA = BDCAA > DBAA > DBCAA > MCAA > TBAA > MBAA. This analysis of ICR HAA9 data indicates that just as BCAA is an important HAA that is not regulated under the D/DBP Rule, DBCAA and especially BDCAA are significant components of HAA formation and speciation.

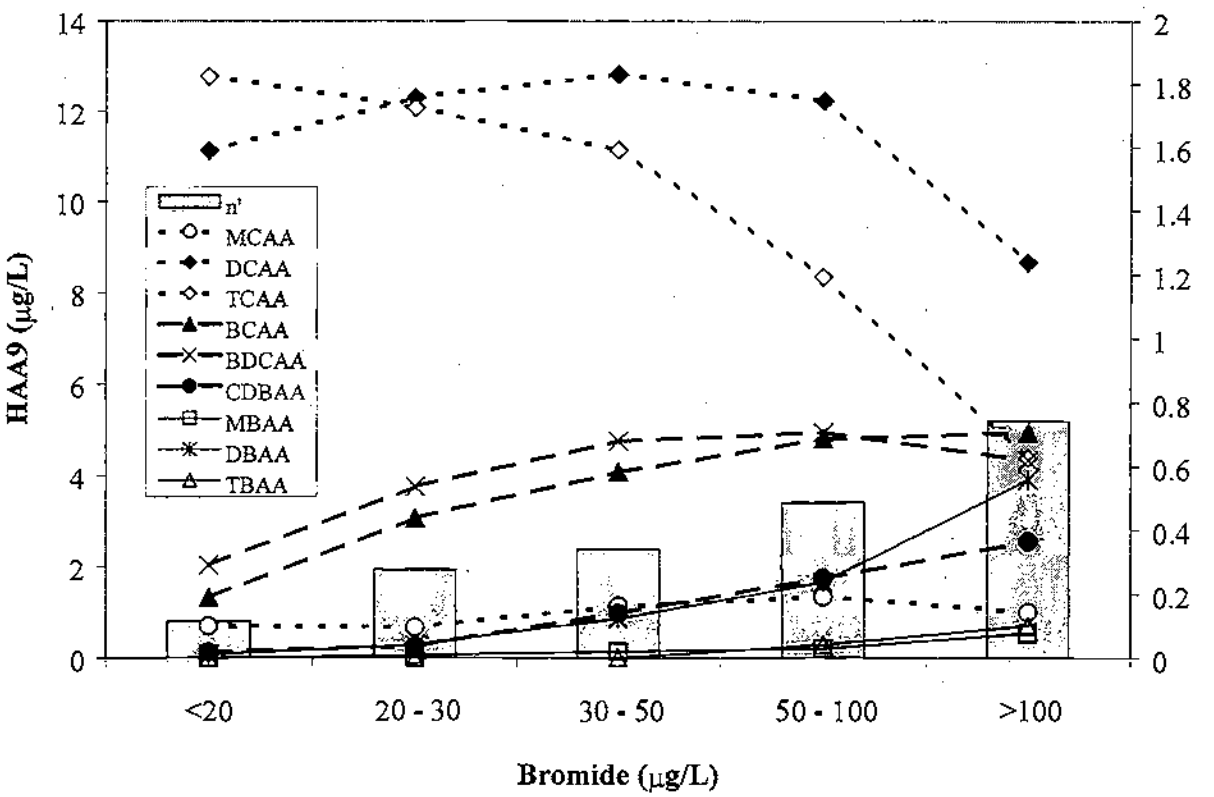

Figure 6.9 Averaged ICR HAA9 data (18 months) binned according to rough quintiles of influent bromide concentrations—average bromine incorporation factor (*n'*) for each bromide bin

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HAN Speciation

Haloacetonitriles form as a result of disinfection in the presence of amino acids (Trehy, Yost, and Miles 1986). Formation of bromine-substituted HANs thus depends on the nature of source water NOM and bromide concentrations, as well as other water quality parameters and disinfection conditions. The ICR HAN data set suffers from the same lack of comprehensiveness as the HAA6 data set. Although only four of the nine HANs were analyzed under the ICR—dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN)—analyzing the data set to study HAN speciation is appropriate for two primary reasons. First, all three dihaloacetonitriles were measured under the ICR. Second, trihaloacetonitriles are extremely unstable and difficult to detect; indeed, almost all reported TCAN values were below the MRL. The amount of bromine incorporation in the HAN class was dramatically greater than in either the THM or HAA class (Table 6.5, Figure 6.10). In the bin containing the highest bromide concentrations, the fully chlorine-substituted HANs (DCAN and TCAN) made up only 28% of total HANs produced, and the fully bromine-substituted DBAN comprised 43%. These numbers contrast with 40% chloroform and 18% bromoform in the same bromide bin. Bromine-substituted HANs totaled 60% of observed HANs in a study of Dutch water supplies (Peters, de Leer, and de Galan 1990). In a comparison of formation and speciation of HANs versus THMs, the percentage increase in HANs resulting from increased bromide concentrations was greater than that for THMs, and bromine-substituted HANs constituted more than 30% of total HANs produced (Via and Dietrich 1996).

When the bromide bin data were segmented across HAN bins, the results were similar to those for THMs and HAAs, except that in the bin containing the lowest bromide concentrations, the percentage of bromine-substituted HANs remained relatively constant across all HAN bins (Figure 6.11).

For ICR groundwater plants, the percentage of bromine incorporation was significant across all bromide bins. Even in the three bins containing the lowest bromide concentrations, more than 50% of HANs were bromine-substituted. In the two bins containing the highest bromide concentrations, bromine-substituted HANs constituted more than 70% of all HANs (data not shown).

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The average bromine incorporation factors for the ICR HAN data (n'') are shown in Figure 6.12 and described by Equation 6.3 (Allgeier and Summers 1995):

$$n'' = \text{HAN-Br } (\mu\text{mol}) / \text{HAN } (\mu\text{mol}) \tag{6.3}$$

The HAN4 n'' can range from 0 for TCAN or DCAN to 2 for DBAN. In the bin containing the highest bromide concentrations, the average n'' equals 1.15 and is the closest to the maximum theoretical bromine incorporation factor of any of the DBP classes studied under the ICR.

Although the proportion of bromine-substituted DBPs was greater for HANs than for either THMs or HAAs, DCAN was the predominant HAN on a weight basis for bromide bins 1 through 4. The concentration of DBAN dominated only in water sources with the highest bromide concentrations.

Table 6.5

Molar percent of fully chlorine-substituted (TCAN and DCAN), bromochloro-substituted (BCAN), and fully bromine-substituted (TBAN) HANs in each bromide bin

Bromide bin	HAN speciation	Average (%)	Median (%)	10th percentile (%)	90th percentile (%)
<20 µg/L	Chloro	81	87	50	100
	Bromochloro	13	10	0	30
	Bromo	7	0	0	19
20–30 µg/L	Chloro	68	73	44	100
	Bromochloro	22	22	0	35
	Bromo	10	0	0	22
30–50 µg/L	Chloro	59	66	0	88
	Bromochloro	26	25	0	44
	Bromo	14	7	0	45
50–100 µg/L	Chloro	41	43	0	76
	Bromochloro	30	31	0	48
	Bromo	29	20	0	66
>100 µg/L	Chloro	28	24	0	63
	Bromochloro	30	34	0	45
	Bromo	43	38	0	100

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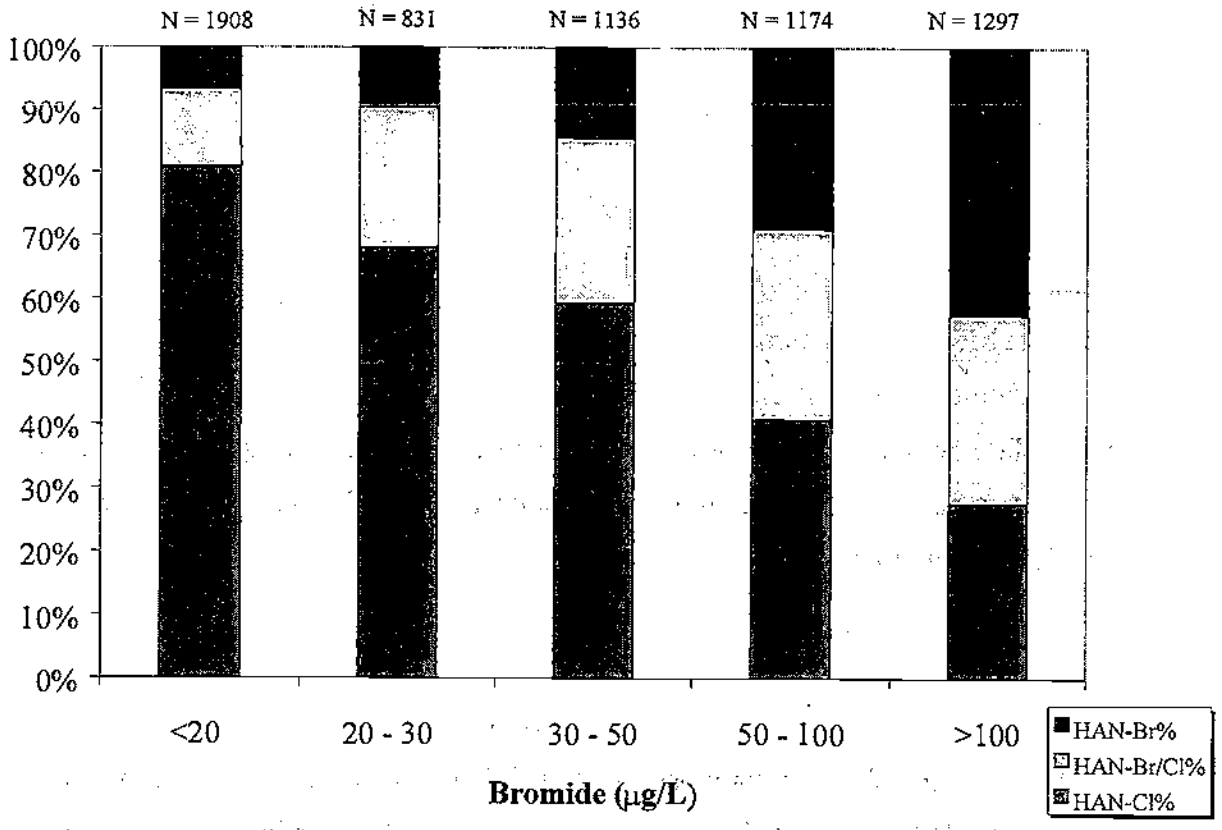

Figure 6.10 Averaged ICR HAN data (18 months) binned according to rough quintiles of influent bromide concentrations—percent of fully chlorine-substituted HANs (DCAN and TCAN), bromochloro-substituted HANs (BCAN), and fully bromine-substituted HANs (DBAN) calculated on a molar basis

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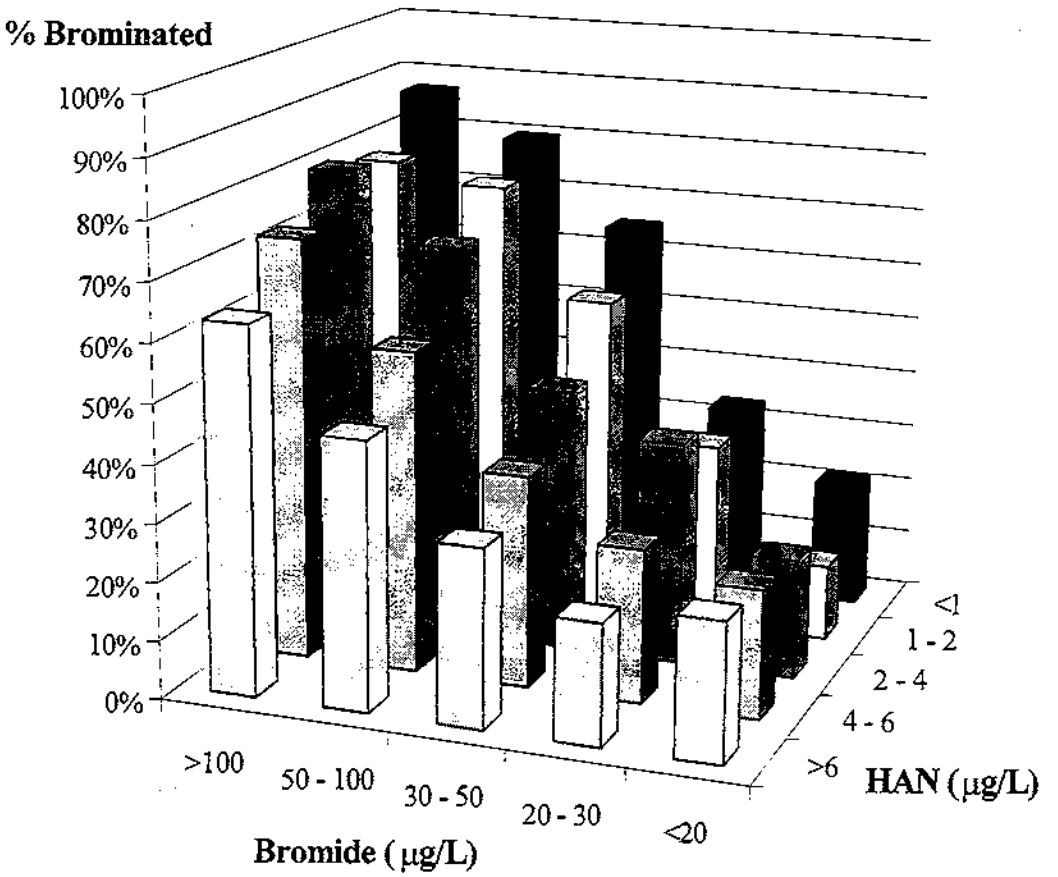

Figure 6.11 Averaged ICR HAN data (18 months) binned according to rough quintiles of both influent bromide and average HAN concentrations—total percent of bromochloro-substituted HANs (BCAN) and fully bromine-substituted HANs (DBAN) calculated on a molar basis

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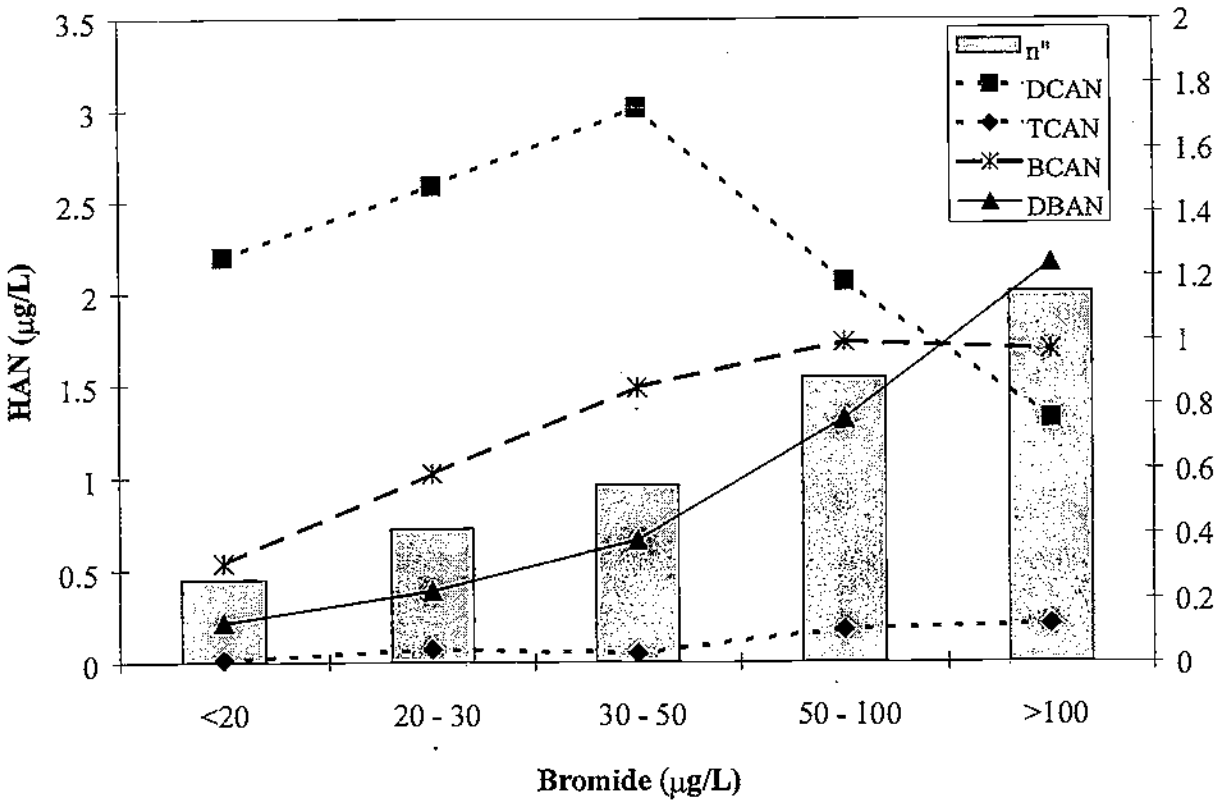

Figure 6.12 Averaged ICR HAN data (18 months) binned according to rough quintiles of influent bromide concentrations—average bromine incorporation factor (*n"*) for each bromide bin

Bromine Incorporation

Because bromide is generally conserved through most treatment processes, the concentration of influent bromide is reduced primarily by incorporation into DBPs. Many studies on bromine incorporation have been conducted using a limited number of water sources tested under controlled conditions (Amy, Tan, and Marshall 1991; Symons et al. 1993). Analysis of the ICR data on an average national level makes it difficult to fully assess factors that contribute to bromine incorporation. Although it is not possible to calculate the percentage of bromine incorporated into DBPs by comparing bromide concentrations before and after disinfection, as is done in laboratory studies, it is possible to approximate levels of bromine incorporation in each bromide bin.

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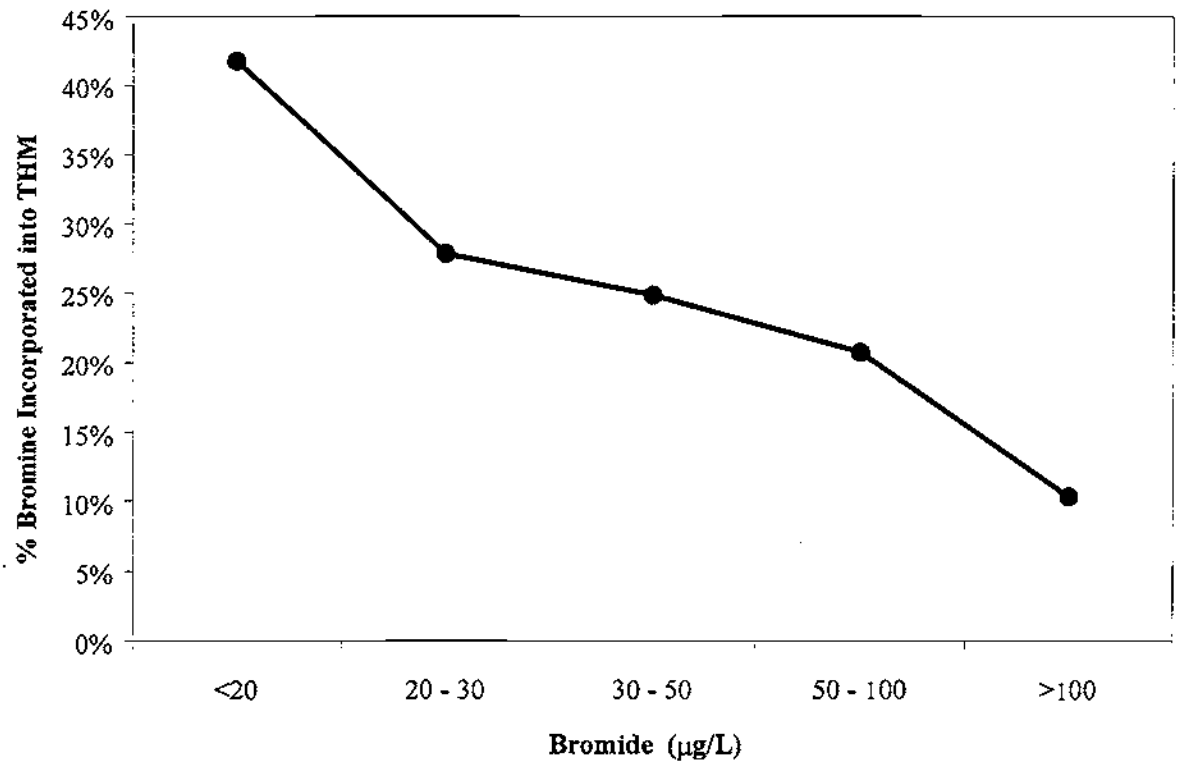

Figure 6.13 Molar percent of influent bromide incorporated as bromine into THM (samples collected at the point of distribution system maximum residence time)—percent incorporated is averaged and then binned according to rough quintiles of influent bromide concentration

The data set on the THM class is the most robust for analyzing bromine incorporation because of its high concentrations relative to most other DBP classes and because of the limitations of the HAA database. Moles of bromine incorporated into THMs at the point of distribution system maximum residence time were compared with moles of bromide present in the plant influent.

On average, for plants in the lowest bromide bin, 42% of influent bromine was incorporated into THMs; for plants in the highest bromide bin, 10% was incorporated (Figure 6.13). Symons et al. (1993) observed bromine incorporation rates of 11–31% in chlorinated water. Amy, Tan, and Marshall (1991) reported that about 25–60% of original bromide (at concentrations contained in the top two bromide bins of this study) was incorporated into THM

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species in ozonated water. Most likely, the trend of decreasing total bromide incorporation into THMs as bromide concentrations increase is due primarily to a relative decrease in available precursor sites (Symons et al. 1993). However, bromine incorporation is controlled by a number of other water quality and treatment factors that are not feasible to delineate on a national basis.

SUMMARY AND CONCLUSIONS

This examination of the ICR data revealed several DBP speciation trends at a national level. Speciation was determined as the molar percentage of fully chlorine-substituted, bromochloro-substituted, or fully bromine-substituted DBPs for each ICR sample. Based on averaged results within specified bromide bins, a shift in speciation to the more bromine-substituted DBPs among THMs, HAAs, and HANs was observed as average influent bromide concentrations increased. For all DBP classes, however, the range of speciation within each bromide bin was quite large, often including a minimum of 0% and a maximum of 100% for each of the three halogen categories.

Differences in the relative amount of bromine-substituted species were noted among the three DBP classes studied. The proportion of bromine-substituted species increased in the following order: HAN > THM > HAA. The average percentage of bromine-substituted HANs was 20% in the bin containing the lowest bromide concentrations and 73% in the bin containing the highest concentrations. For THMs, the respective percentages were 18% and 60%. In the bin with the lowest bromide concentrations, 7–12% of HAAs were bromine-substituted, depending on whether the HAA6 or HAA9 data set was used; in the bin with the highest bromide concentrations, these percentages increased to 47–50%, respectively.

The apparent ratio of bromide to TOC, as estimated by DBP concentrations and comparisons of data on groundwater and surface water, had a great impact on DBP speciation. Among all DBP classes, groundwater plants had a higher percentage of bromochloro-substituted or fully bromine-substituted species than surface water plants. This was true for all bromide bins. Even at low concentrations of influent bromide, the average percentage of bromine-substituted DBPs was significant for THMs, HAAs, and HANs. In addition, when plants were binned according to their ultimate DBP production, plants with low concentrations of THMs, HAAs, or

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HANs had higher percentages of bromine-substituted species than plants with low concentrations of these DBPs.

The D/DBP Rule requires water systems to sample for total THMs and HAA5. Data on the THM class give a good picture of the entire spectrum of DBP speciation because they contain a fully chlorine-substituted THM, a fully bromine-substituted THM, and two bromochloro-substituted species. Analysis of the ICR data on HAA6 and HAA9 shows the importance of assessing the bromochloro-substituted species, which are not included in HAA5, in understanding HAA occurrence and HAA speciation. Understanding the bromochloro-substituted species is especially important for plants with high influent bromide concentrations. Although HAN concentrations are typically much lower than THM and HAA concentrations, analysis of HAN data may give utilities insight into the extent of bromine incorporation that could occur in other DBP classes.

The D/DBP Rule also requires precursor (TOC) removal to limit DBP production. This analysis of the ICR data confirms that at lower levels of DBP formation, speciation in all DBP classes shifts to the bromine-substituted DBPs. Thus, the benefit of decreasing DBP production overall must be weighed against the possible increased risk of changing the relative proportions of DBP species.

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CHAPTER 7

DISTRIBUTION SYSTEM DBP RESULTS AND SDS PERFORMANCE

Alexa Obolensky and Michelle Frey

ABSTRACT

This chapter presents analyses of disinfection by-product (DBP) data collected under the Information Collection Rule (ICR). The analyses focus on differences between DBP concentrations in finished water and in distribution systems and on variations in DBP concentrations across individual distribution systems. Differences between DBP concentrations in the finished water of ICR plants and at specific distribution system monitoring sites were examined with respect to type of secondary disinfectant, type of source water, temperature, pH, and residual disinfectant concentration. Concentrations of the sum of five haloacetic acids (HAA5) varied less than concentrations of total trihalomethanes (TTHM) across individual distribution systems. This was true for both free chlorine and chloramine systems. Distribution system DBP concentrations were frequently lower than associated finished water concentrations, especially among the non-THM DBPs. The trihalogen-substituted HAA species and chloral hydrate tended to behave similarly to THMs in distribution systems, whereas the behavior of dihalogen-substituted HAAs was generally distinct from that of the trihalogen-substituted HAAs. The precision and accuracy of the simulated distribution system (SDS) test for modeling changes in DBP concentrations between plant effluent and distribution system locations was evaluated on a national basis. The SDS method provided fairly precise estimates of TTHM and HAA5 concentrations in chloramine systems (r^2 values of 0.77 and 0.80, respectively) and for HAA5 and the sum of nine haloacetic acids (HAA9) in free chlorine systems (r^2 values of 0.76 and 0.74, respectively). SDS predictions for TTHM in chloramine systems were somewhat less precise (r^2 = 0.69). The SDS method also showed a good degree of accuracy, with the exception of its predictions for dihalogen-substituted HAA species, which it tended to overestimate by about 15% in free chlorine systems.

INTRODUCTION

In order to assess consumer exposure to health risks from drinking water and to design appropriate regulatory programs, it is necessary to understand how disinfection by-product (DBP) concentrations vary across distribution systems and to obtain measurements representing both typical DBP concentrations and upper percentiles of DBP occurrence in individual systems. Recognizing that trihalomethanes (THMs) continue to form in the presence of residual chlorine, the 1979 Total Trihalomethanes (TTHM) Rule stipulated that at least 25% of a utility's compliance sampling locations represent maximum distribution system detention time (U.S.

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Environmental Protection Agency [USEPA] 1979). The Stage 1 Disinfectants/Disinfection By-products (D/DBP) Rule lowered the maximum contaminant level (MCL) for TTHM, added a new MCL for the sum of five haloacetic acids (HAA5), and maintained the monitoring framework established in 1979, which based compliance on annual average systemwide mean concentrations (USEPA 1998). The Stage 2 Disinfection By-products Rule will change DBP monitoring and compliance approaches. The Agreement in Principle for the Stage 2 Rule prescribes that TTHM and HAA5 MCLs be based on annual average concentrations at individual monitoring sites (USEPA 2000a). Because the intent of this approach is to ensure that consumers in all service areas of a distribution system are adequately protected from exposure to elevated DBP concentrations, Stage 2 monitoring will require sampling at locations where high TTHM and HAA5 concentrations are expected.

The common assumption that the highest TTHM concentrations are associated with the longest distribution system residence times does not necessarily hold for other DBPs. THMs tend to be stable in distribution systems and will continue to form where a free chlorine residual persists and organic precursors are available. The use of chloramines for secondary disinfection is a recognized and widely applied method for controlling continued THM formation in distribution systems. The formation kinetics and stability of haloacetic acids (HAAs) and other halogen-substituted organic DBPs are less well characterized. HAAs may form faster than THMs (Reckhow and Singer 1990); some of the HAA species may decompose at high pH values (Reckhow and Singer 1985, Krasner et al. 1989); and some of the species may be subject to biodegradation in the absence of a chlorine residual (Williams, Williams, and Gordon 1995; Baribeau et al. 2000). Haloacetonitriles (HANs), haloketones (HKs), and chloropicrin (CP) have also been shown to be chemically unstable, biologically unstable, or both (Koch et al. 1991, Levi et al. 1993).

Considering the potential for both formation and loss of DBPs in distribution systems, and the different formation kinetics of various DBP classes, peak concentrations of different DBPs are likely to occur at different sites within a given distribution system. Moreover, patterns of spatial variation in DBP concentrations across service areas are unlikely to be static across time. Changes in DBP concentrations during water distribution may depend on a variety of factors including prior treatment, type and concentration of residual disinfectant, water temperature and pH, detention time, pipe conditions, and biological activity. Hydraulic and water

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quality variations can be introduced by storage facilities, booster disinfection, and changes in valve and pumping configurations. Detention times for specific locations also vary as flow rates fluctuate with customer demand, which may vary on both diurnal and seasonal time scales.

Because of logistical difficulties with distribution system sampling and uncertainties about appropriate site selection, a surrogate for field sampling could offer utilities economic and scientific benefits. The simulated distribution system (SDS) method applies system-specific incubation conditions to finished water (time, temperature, pH, and secondary disinfectant concentration) to generate "simulated" distribution system samples (Koch et al.1991). Koch et al. (1991) showed that SDS results for jar-treated source water supplies provided good estimates of TTHM, HAA5, and chloral hydrate (CH) concentrations in the free chlorine distribution systems of three full-scale treatment plants but poor estimates of HAN and HK concentrations. SDS sampling was included in the ICR to examine DBP formation under controlled conditions and to determine if SDS samples could provide reliable estimates of DBP concentrations in distributed drinking water. For evaluation, ICR SDS samples can be compared with corresponding ICR field samples collected specifically for this purpose.

The analyses presented in this chapter characterize discrete differences between DBP concentrations in finished water and individual distribution system monitoring sites, spatial variation in DBP concentrations across distribution systems during individual monitoring periods, and the predictive capability of the SDS sampling method. Relationships between DBPs and secondary disinfectant type and concentration, source water type, temperature, and pH are considered. ICR occurrence data on TTHM, HAAs, and other organic DBPs monitored during ICR sampling are summarized by McGuire and Graziano (2002); Obolensky, Shukairy, and Blank (2002); and Blank, Shukairy, and McLain (2002), respectively.

ICR DATA

DBP parameters examined in this chapter include TTHM, HAA5, HAA9 (including bromochloroacetic acid, dichlorobromoacetic acid, dibromochloroacetic acid, and tribromoacetic acid, in addition to the HAA5 species,), HAN4 (the sum of four haloacetonitriles), and individual THM, HAA, HK, CH, and CP compounds. All six quarters of data were examined for each non-blending ICR plant. Data associated with blending plants were excluded because distribution

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system results for these systems cannot be associated with a discrete finished water supply. During each quarter of monitoring, non-blending ICR plants collected DBP samples at five locations per treatment plant (FIN, AVG1, AVG2, MAX, and DSE) and prepared one SDS sample per treatment plant. Each set of quarterly ICR samples from a specific plant was collected within the span of three days. ICR finished water samples (FIN) represented a point after which all treatment processes (including clearwell detention and the final point of chlorination) were complete. ICR MAX samples represented relatively long detention time in a plant's distribution system. ICR AVG1 and AVG2 samples represented average residence time in a plant's distribution system. The distribution system equivalent sample (DSE), taken from a distribution system location with well-characterized detention time, was collected specifically for comparison with the laboratory-incubated SDS sample for the same sampling quarter. DSE sampling locations were required to meet the following criteria: no additional disinfectant added between the finished water and the DSE sampling point; knowledge of approximate detention time at the DSE site; and no blending with water from other treatment plants (USEPA 1996a).

SDS samples were generated by incubating a volume of finished water under dark conditions at the plant effluent temperature for the estimated detention time of the corresponding DSE location. The general protocol for SDS sampling is described in Method 5710E of the 18th edition of *Standard Methods* (APHA, AWWA, and WEF 1992), and details of ICR SDS sampling are outlined in the *DBP/ICR Analytical Methods Manual* (USEPA 1996b). Water quality parameters (including temperature, pH, and chlorine residual) were measured at the end of the incubation period in the same manner as for DBP field samples.

METHODS USED FOR DATA ANALYSIS

Data were extracted from the ICR Auxiliary 1 Database, Version 5.0 (USEPA 2000b, Wysock et al. 2002). DBP concentrations below the minimum reporting level were replaced with zero values before further handling. For the purposes of this discussion, a plant-quarter describes one ICR sampling period for one treatment plant and its distribution system; data from each plant-quarter include DBP concentrations in up to five field samples and one SDS sample (as described previously). Plant-quarters were classified by type of source water (surface water or groundwater), type of secondary disinfectant (free chlorine or chloramines), or both.

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Analyses presented here use concentration range as a measure of the spatial variation in DBP concentrations across individual distribution systems (including finished water) for discrete plant-quarters. The range of TTHM concentrations was determined for each plant-quarter of data that included results for all five field samples, with the range defined as the difference between the highest and lowest observed concentrations. HAA5 concentration ranges for each plant-quarter were determined similarly.

Differences between DBP concentrations at finished water and distribution system sampling sites are presented in terms of "delta" DBP values. The appropriate finished water DBP concentration was subtracted from each distribution system sample DBP concentration to determine a delta DBP value for the sample (e.g., $\text{Delta}[CHCl_3]_{MAX} = [CHCl_3]_{MAX} - [CHCl_3]_{FIN}$). Delta DBP values were classified by type of secondary disinfectant (free chlorine or chloramines). Within the category for each disinfectant type, distributions of delta values were compiled for various other categories including sampling location, residual disinfectant concentration, pH, and temperature.

The evaluation of SDS performance involved assessing whether the SDS method adequately modeled observed DBP concentrations at distribution system DSE sites. Data from plant-quarters in which DBP concentrations were negligible (DSE samples with TTHM and HAA5 concentrations <10 µg/L) were excluded from this analysis based on the presumption that the SDS method is of less interest to systems that use source water containing very low DBP formation potential. This approach retained approximately 80% of the data on plant-quarters from free chlorine systems and 94% of the data on plant-quarters from chloramine systems. Results from pairs of SDS and DSE samples were classified by secondary disinfectant type and analyzed using linear regression.

RESULTS AND DISCUSSION

Figure 7.1 shows histograms, with corresponding cumulative frequency distributions, of the estimated detention times provided by ICR utilities for monitoring sites in non-blended distribution systems. Results for AVG1 and AVG2 locations were combined into "AVG" results for Figure 7.1 and subsequent discussions. The percentages of plants reporting associated detention times less than or equal to 12 hours, 24 hours, and 3 days are labeled on the cumulative

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frequency curves in Figure 7.1 for each type of sampling location. Though each type of site is represented by a wide range of detention times—from a few hours up to five days or more—median detention times increased in the order DSE (10h) < AVG (20h) < MAX (40h).

The need for reasonable confidence in the estimated detention times at DSE sites most likely led systems to select DSE sites relatively close to the plant. Reported DSE sampling location detention times had a bimodal distribution: approximately 30% had short detention times of 4 hours or less, and approximately 40% had detention times between 20 and 48 hours. Half as many AVG sites (16%) and only a small percentage of MAX sites (6%) had such short detention times (4 hours or less). The majority of MAX sites (67%) had detention times exceeding 24 hours, compared with 36% and 18% of AVG and DSE sites, respectively. Furthermore, almost a third (30%) of MAX sites had reported detention times of three days or more, compared with only 2% and 7% of DSE and AVG sites, respectively.

Based on these data, ICR results from DSE, AVG, and MAX locations can be interpreted as representing increasingly long detention times when the data are considered in aggregate. However the relative detention times of various DSE, AVG, and MAX sites should not be assumed to follow this order when individual systems are examined.

Spatial Variation in DBP Concentrations Within Distribution Systems

Figure 7.2 shows histograms of individual plant-quarter TTHM and HAA5 concentration ranges, grouped by type of source water and type of secondary disinfectant. The intervals indicated on the horizontal axes of these plots refer to the width of plant-quarter TTHM or HAA5 concentration ranges, without reference to absolute concentrations. For example, two hypothetical plant-quarters with TTHM concentrations spanning ranges of 100 to 115 μg/L and 20 to 35 μg/L, respectively, both have a TTHM range width of 15 μg/L and would both be counted in the interval (10, 20]. As mentioned, only plant-quarters with complete ICR records were included in this analysis (i.e., those with non-null DBP results for finished water and four distribution system sites).

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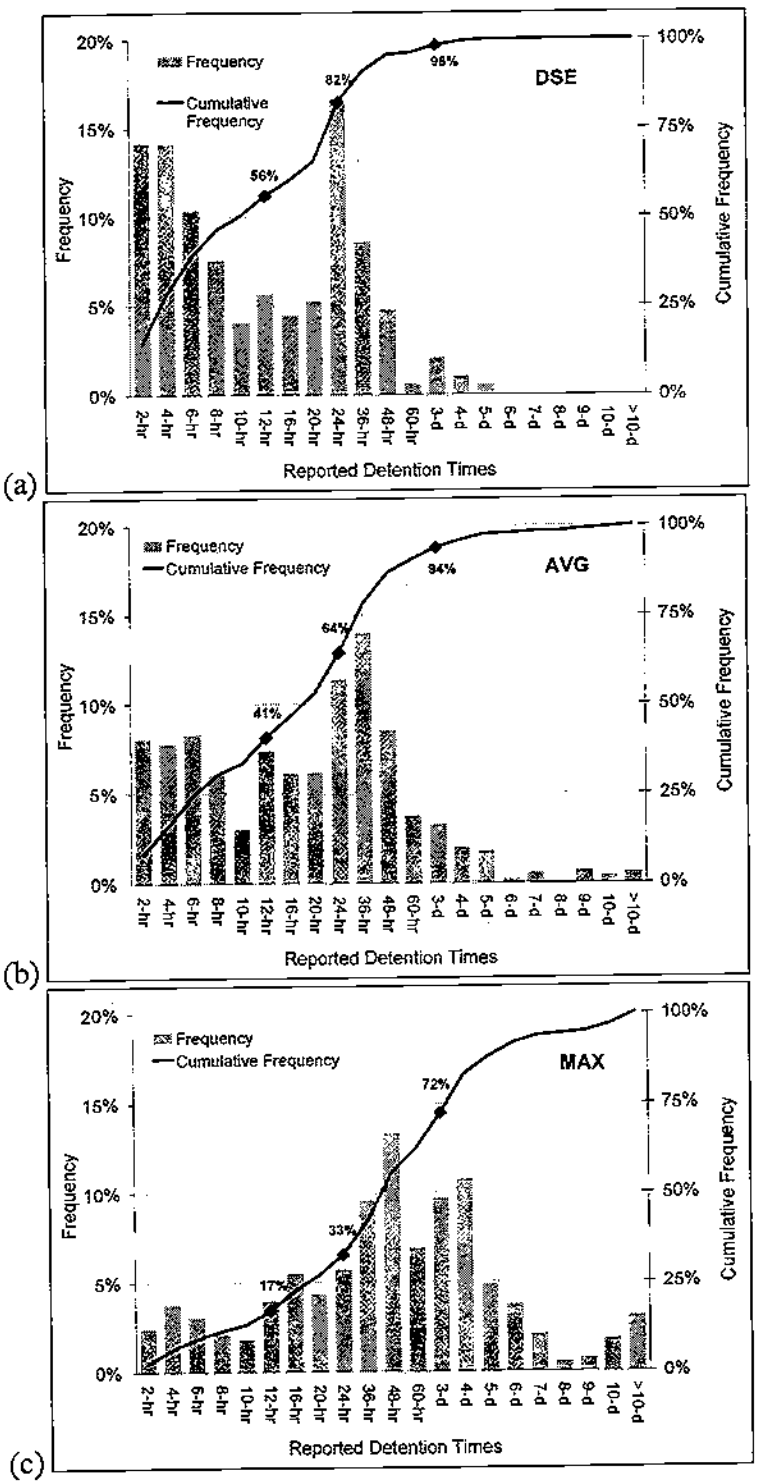

Figure 7.1 Reported detention times for types of ICR distribution system sampling locations: (a) DSE, (b) AVG (AVG1 and AVG2 combined), (c) MAX

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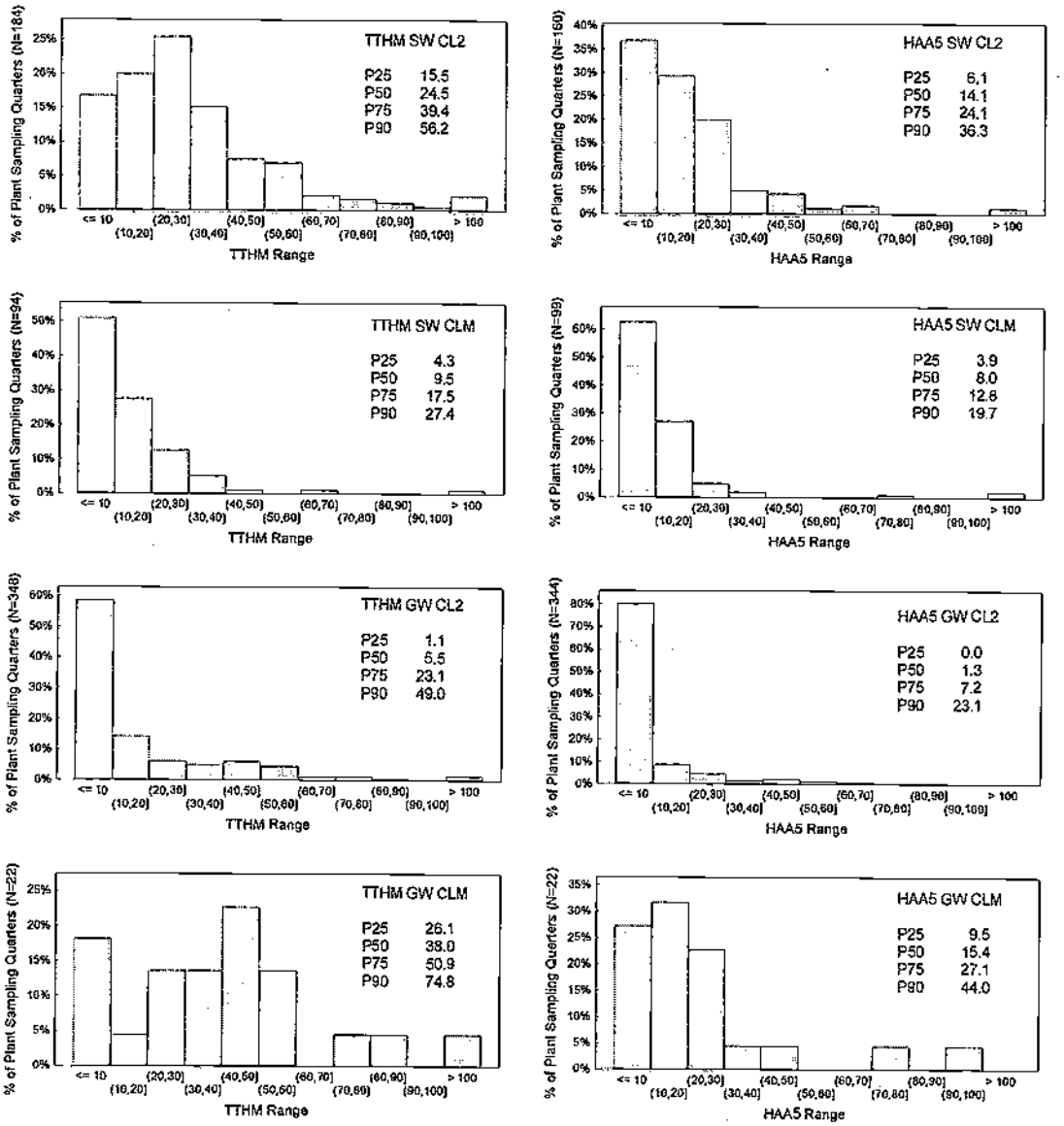

Figure 7.2 Distributions of ICR plant-quarter TTHM and HAA5 concentration ranges (the difference between the highest and lowest observed concentrations in each plant-quarter) grouped by type of source water (surface water [SW] or groundwater [GW]) and type of secondary disinfectant (chlorine [Cl2] or chloramines [CLM])—25th (P25), 50th (P50 = median), 75th (P75), and 90th (P90) percentile ranges indicated

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Variations in TTHM concentrations were generally greater than variations in HAA5 concentrations within individual ICR plant-quarters, regardless of source water or disinfectant category (compare the left and right columns of plots in Figure 7.2). For example, the median TTHM range for surface water systems using free chlorine was 24.5 μg/L, compared with 14.1 μg/L for HAA5. TTHM and HAA5 ranges were narrower, and more comparable, in surface water systems using chloramines, compared with those using free chlorine (compare first and second rows of plots in Figure 7.2). The median TTHM range in surface water systems using chloramine was 9.5 μg/L, less than half that in surface water systems using free chlorine (24.5 μg/L) and close to the median HAA5 range in the same systems (8.0 μg/L).

The opposite trend was observed with respect to type of secondary disinfectant in groundwater plants, where TTHM and HAA5 concentration ranges were much wider in chloramine systems than in free chlorine systems (compare third and fourth rows of plots in Figure 7.2). For example, the median TTHM range in groundwater systems using free chlorine was 5.5 μg/L, compared with 38.0 μg/L in groundwater systems using chloramine. These results probably do not reflect the effect of type of secondary disinfectant used at groundwater plants but rather stem from significant differences in source water quality and type of treatment between free chlorine plants and chloramine plants (McGuire and Hotaling, 2002). Most ICR groundwater plants using free chlorine had precursor-limited sources of supply, as indicated by negligible TTHM concentrations (never exceeding 5 μg/L in the data included in this analysis) and no detectable HAA5 in data from about half their plant-quarters. In contrast, TTHM concentrations in groundwater systems using chloramine exceeded 10 μg/L in all plant-quarters analyzed. Approximately half of the groundwater plants using chloramine used conventional or softening treatment, whereas the majority of groundwater plants using free chlorine treated water with disinfection only. Because such a small percentage of ICR groundwater plants used chloramines, only 22 plant-quarters of data were available for this analysis, compared with more than 300 plant-quarters of data from groundwater plants using free chlorine.

Unlike the data from ICR groundwater plants, data from ICR surface water plants represented relatively large numbers of plants using each type of secondary disinfectant, with comparable distributions of treatment plant types among free chlorine and chloramine systems. Thus, in the case of surface water plants, less variability in TTHM and HAA5 concentrations

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across distribution systems can be ascribed to the use of chloramines for secondary disinfection. However, the effect of chloramines on variability in DBP concentrations across the distribution systems of groundwater plants cannot be discerned from ICR data because of the small amount of data available on groundwater plants using chloramines and because of bias resulting from major differences in source water quality and treatment at these plants compared with groundwater plants using free chlorine.

Changes in DBP Concentrations From Finished Water Through Distribution

Differences between finished water and distribution system DBP concentrations were analyzed on the basis of paired samples. As explained previously, each distribution system DBP concentration was converted to its corresponding delta value by subtracting the appropriate finished water concentration. An individual delta value was negative when the distribution system DBP concentration was lower than the associated finished water concentration. Under an ideal sampling scenario, a negative delta value would reflect the net loss of DBP concentration in the distribution system. In reality, however, such results could also stem from diurnal fluctuations in finished water DBP concentrations, non–plug-flow behavior of distributed water, and analytical method imprecision. Nevertheless, the latter effects are expected to be more random than actual DBP loss (or formation) patterns, so real trends in the direction and magnitude of changes in DBP concentrations during distribution should be apparent when large data sets such as the ICR data are analyzed.

Overall delta DBP results are summarized in Figure 7.3, with box-and-whisker plots showing the median, interquartile range, and 10th and 90th percentiles of the distributions of delta values for each of the 17 ICR DBP species (the interquartile range spans the 25th to the 75th percentiles of data). In free chlorine distribution systems (left side of Figure 7.3), the largest differences in DBP concentrations relative to those in finished water were observed for chloroform ($CHCl_3$), with median and 90th percentile delta values of (+)4.8 and (+)27.0 μg/L. In free chlorine systems, bromodichloromethane (BDCM), trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), and CH also exhibited significant increases in concentration relative to those in finished water, with 90th percentile delta values of (+)7.2, (+)10.0, (+)8.5, and (+)6.1 μg/L, respectively. Substantial fractions of distribution system samples had negative

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delta values for many of the DBP species—19% of DCAA, bromochloroacetic acid (BCAA), and TCAA samples; 23% of bromochloroacetonitrile (BCAN) samples, 28% of dichloroacetonitrile (DCAN) samples, and 29% of trichloropropanone (TCP) samples. DCAA had the largest negative delta values in free chlorine systems; 10% of distribution system DCAA concentrations were more than 4 µg/L lower than corresponding finished water concentrations.

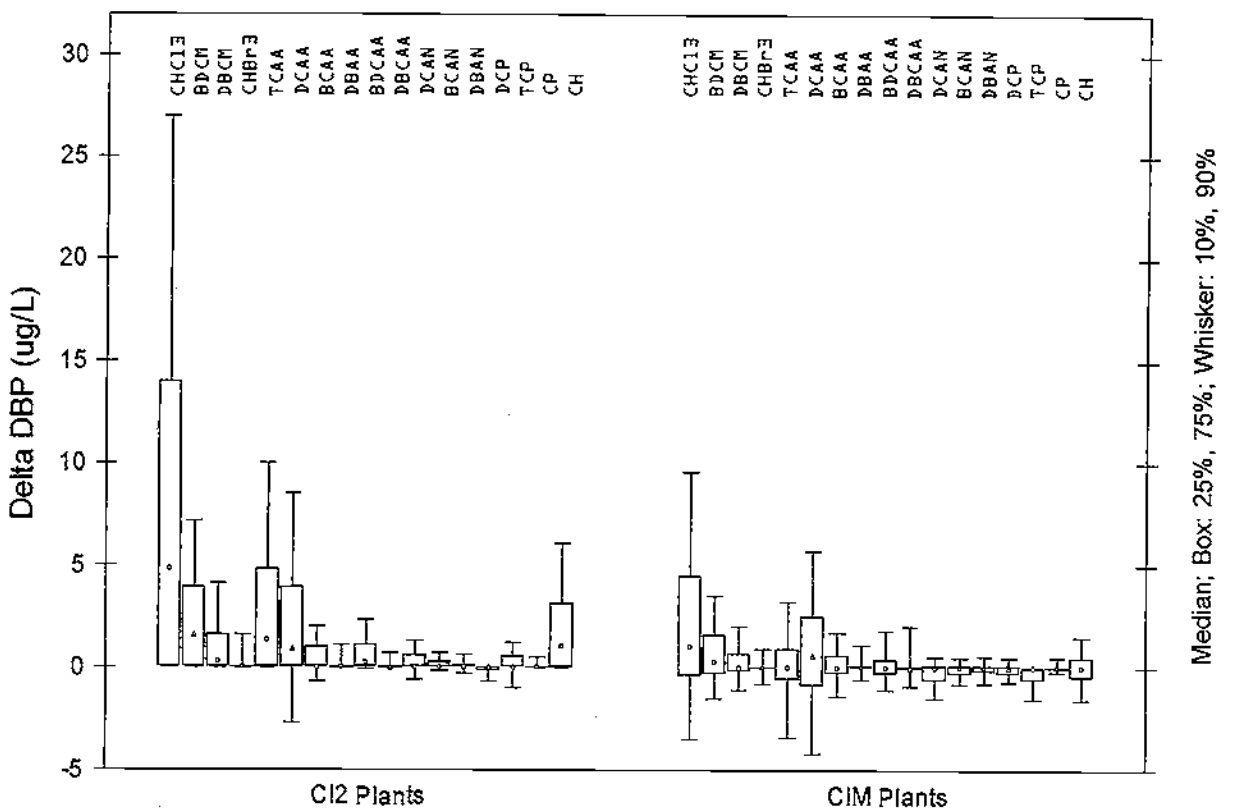

Figure 7.3 Distributions of delta DBP values, classified by type of secondary disinfectant, for all samples from non-blended distribution systems—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown; for free chlorine (Cl_2) plants N=5911 ($CHCl_3$), 6005 (BDCM), 6003 (DBCM), 5990 ($CHBr_3$), 5872 (TCAA), 5935 (DCAA), 5927 (BCAA), 5960 (DBAA), 1683 (BDCAA), 1545 (DBCAA), 5573 (DCAN), 5587 (BCAN), 5530 (DBAN), 5613 (DCP), 5571 (TCP), 5444 (CP), 5302 (CH); for chloramine (CLM) plants N=2697 ($CHCl_3$), 2712 (BDCM), 2712 (DBCM), 2704 ($CHBr_3$), 2701 (TCAA), 2706 (DCAA), 2711 (BCAA), 2717 (DBAA), 1014 (BDCAA), 903 (DBCAA), 2546 (DCAN), 2549 (BCAN), 2522 (DBAN), 2578 (DCP), 2550 (TCP), 2434 (CP), 2533 (CH)

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Distribution system increases in $CHCl_3$, TCAA, and CH concentrations were substantially smaller in chloramine systems than in free chlorine systems, whereas such differences with respect to type of secondary disinfectant were less evident for DCAA. The most striking observation among chloramine systems was the common pattern of negative delta values for all the measured DBP species. For species that had only small percentages of negative delta values in free chlorine systems, markedly higher fractions of distribution system samples had negative delta values in chloramine systems (27% of $CHCl_3$, 32% of BDCM, 30% of dibromochloromethane [DBCM], 42% of dichloropropanone [DCP], and 36% of CH samples). For species with appreciable percentages of negative delta values in free chlorine systems, these fractions were higher in chloramine systems (36% of BCAA, 33% of DCAA, 39% of TCAA, 48% of DCAN, 44% of BCAN, and 41% of TCP samples had negative delta values).

Relationships between delta DBP values and distribution system sampling location (as a surrogate for detention time) are shown in Figures 7.4 through 7.7; data for free chlorine and chloramine systems are shown separately in side-by-side plots. As previously discussed, ICR DSE, AVG, and MAX sites represent increasingly long distribution system detention times when considered in aggregate. Figure 7.4 shows that delta TTHM and delta HAA5 values increased steadily with detention time in free chlorine systems at the 75th and 90th percentiles but were relatively insensitive to detention time in chloramine systems. At the 90th percentile, delta TTHM values in free chlorine systems increased from 27.7 µg/L at DSE sites to 34.2 µg/L at AVG sites to 48 µg/L at MAX sites. At the 90th percentile, delta HAA5 values in free chlorine systems increased from 14.3 µg/L at DSE sites to 18.1 µg/L at AVG sites to 23.5 µg/L at MAX sites. Figure 7.4 shows that losses of HAA5 were most pronounced at MAX sites, regardless of secondary disinfectant type. Patterns with respect to detention time for delta TCAA and delta CH values were similar to those observed for delta TTHM values (see Figure 7.5). With respect to concentrations of individual THM species, increases with detention time were largest for $CHCl_3$, and decreased in the order $CHCl_3$ > BDCM > DBCM > bromoform ($CHBr_3$) at the central tendency (not shown).

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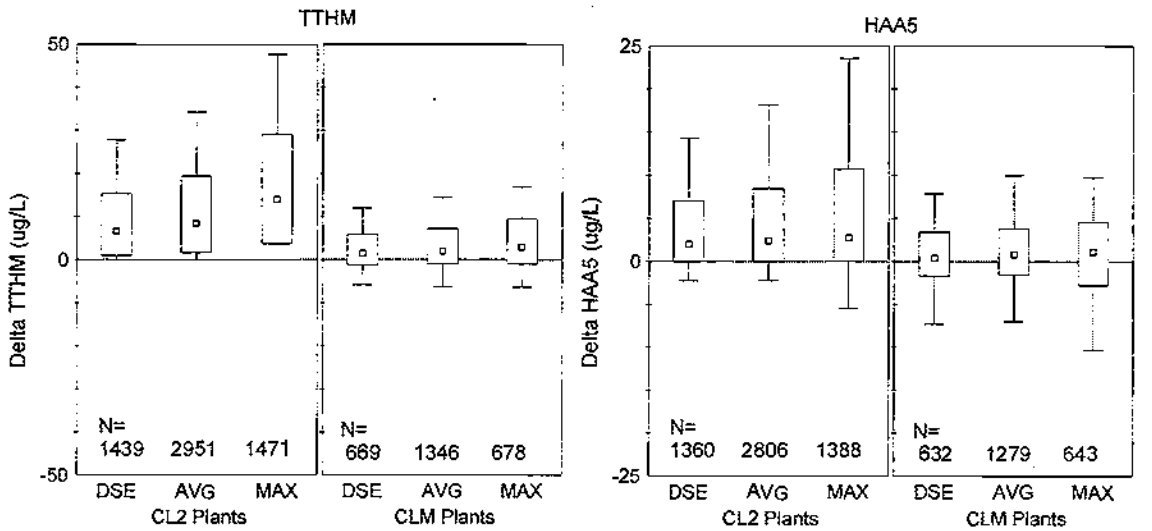

Figure 7.4 Distributions of delta TTHM and delta HAA5 values classified by type of ICR distribution system sampling site—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown

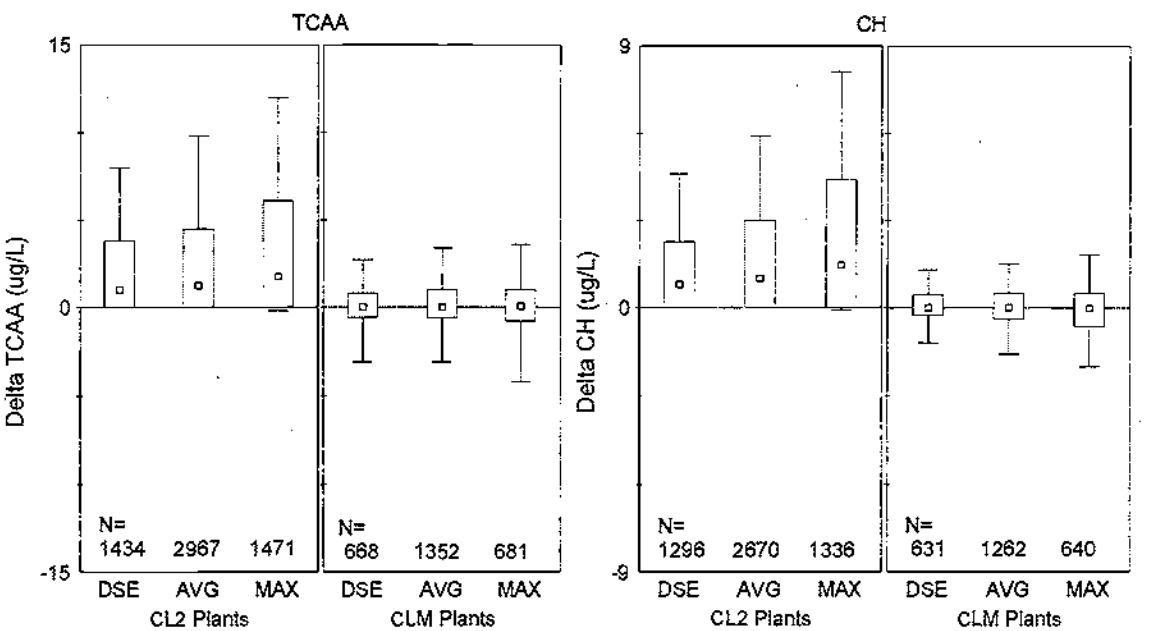

Figure 7.5 Distributions of delta TCAA and delta CH values classified by type of ICR distribution sampling location—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown

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In free chlorine systems, relationships between delta values and relative detention time differed significantly for the dihalogen-substituted HAA species and for TCAA. Results for DCAA and BCAA are shown in Figure 7.6 (compare with TCAA results shown in Figure 7.5). Similarly to TCAA, distribution system DCAA and BCAA concentrations generally increased with detention time in the upper half of the data distribution. However, unlike TCAA, substantial losses of DCAA and BCAA were observed in free chlorine systems, and losses tended to increase in magnitude with detention time. Losses of DCAA and BCAA also increased in magnitude with detention time in chloramine systems. Results for HAA5, shown in Figure 7.4, reflect the contributions of the major species TCAA, DCAA, and BCAA.

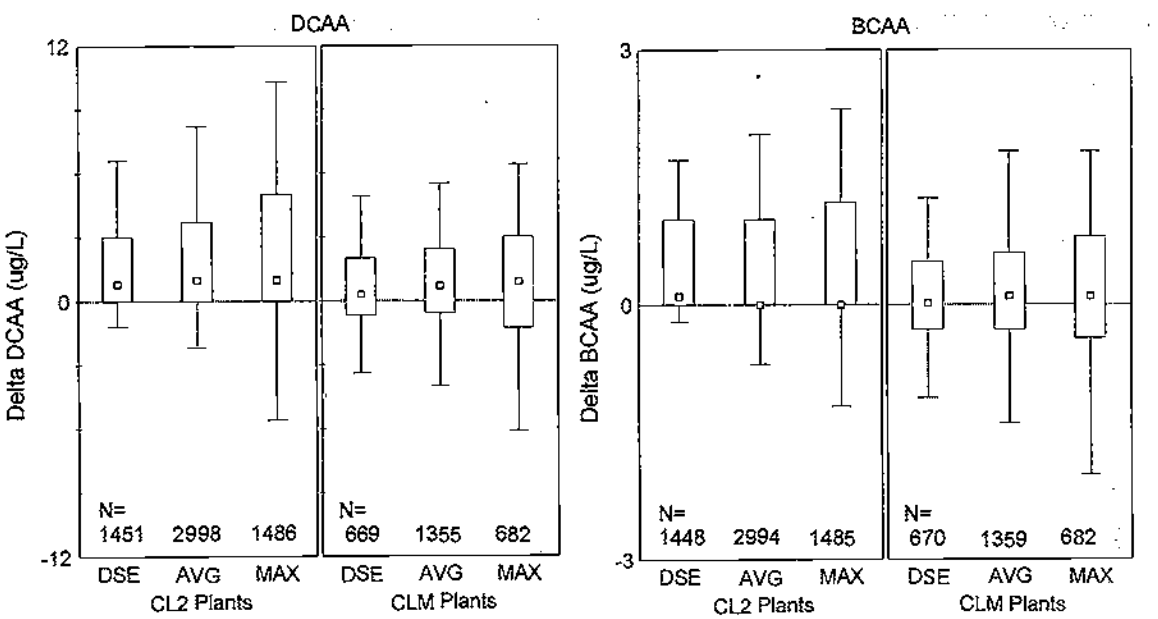

Figure 7.6 Distributions of delta DCAA and delta BCAA values classified by type of ICR distribution system sampling location—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown

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Figure 7.7 indicates that in distribution systems using free chlorine, DCP decayed in virtually all cases in which finished water concentrations were measurable. The same was true for TCP in chloramine systems. DCP was the only ICR DBP that was more prevalent in chloramine systems than in free chlorine systems, although decay was still the predominant direction of change in chloramine systems (see right plot in Figure 7.7). DCP and TCP losses were more pronounced at longer detention times, regardless of secondary disinfectant type. A plausible explanation for these patterns could include chlorination of DCP to yield TCP in free chlorine systems and higher rates of TCP hydrolysis in chloramine systems, where pH values were somewhat higher (overall mean of 8.3) than in free chlorine systems (overall mean of 7.7). Patterns of delta DCAN, BCAN, and dibromoacetonitrile (DBAN) values in free chlorine distribution systems suggested that these HAN species continued to form with increasing detention time. Losses of HAN species in chloramine systems were more pronounced at longer detention times (not shown). However, with the exception of CH, absolute concentrations of all the non-THM, non-HAA DBPs, and the magnitudes of their delta values, were generally low.

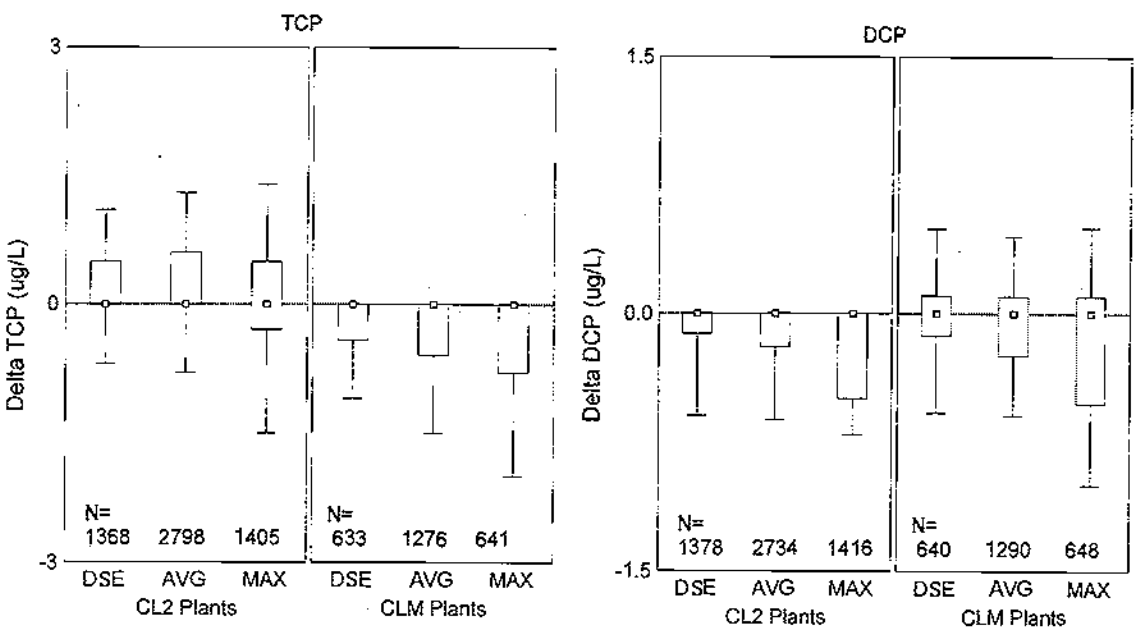

Figure 7.7 Distributions of delta DCP and delta TCP values classified by type of ICR distribution system sampling location—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown

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In free chlorine distribution systems, higher temperatures were associated with larger increases in THM and CH concentrations, whereas delta values for TCAA, DCAA, and HAN species were relatively insensitive to temperature except in the highest temperature range (above 25°C, not shown). In chloramine distribution systems, higher temperatures were generally associated with more pronounced DBP losses. This was evident for DCAA, CH, DCP, TCP, and, to the greatest relative extent, the HAN species (not shown).

Delta DBP values were strongly associated with finished water total chlorine residual concentrations in free chlorine systems. Delta values for TTHM, HAA5, TCAA, DCAA, CH, and HAN4 in free chlorine systems rose continuously with finished water total chlorine residual concentration (results for DCAA and TCAA shown in Figure 7.8). In the category for lowest finished water total chlorine residual (below 1.0 mg/L) the 90th percentile delta HAA5 value was 6.4 μg/L, compared with 34.7 μg/L in the highest category (above 2.5 mg/L). Corresponding 90th percentile delta TTHM values were 19.2 μg/L and 53.4 μg/L. In free chlorine distribution systems, higher finished water total chlorine residual concentrations were associated with greater magnitudes of both net TCP formation and net TCP loss, whereas higher residual concentrations in these systems were associated only with greater net losses of DCP (not shown).

Finished water total chlorine residual concentrations did not appear to be associated with changes in THM or CH concentrations in chloramine distribution systems. However, higher residual concentrations appeared to supress DCAA decay and, to a lesser extent, TCAA decay in these systems (see Figure 7.8). Higher residual concentrations also appeared to promote increased concentrations of DCAA in chloramine distribution systems, though to a much smaller extent than observed in free chlorine systems. Delta CP concentrations increased strongly with finished water total chlorine residual concentrations in chloramine distribution systems (data not shown). However, absolute CP concentrations were generally very low.

TTHM concentrations in free chlorine distribution systems increased moderately with sample pH. The median delta TTHM value for samples in the lowest pH range (<7.3) was 6.4, compared with 9.2 (pH 7.3–7.8), 10.0 (pH 7.8–8.3), and 12.3 μg/L (pH >8.3) for successively higher pH ranges (not shown). Median delta HAA5 values did not vary with pH, although the 90th percentile delta HAA5 value for samples above pH 8.3 (11.3 μg/L) was markedly lower than the 90th percentile delta HAA5 values (18.5–20.9 μg/L) for samples in the lower pH ranges (not shown). Delta DCAA, TCAA, and CH values were relatively insensitive to pH in free

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chlorine systems except at the highest pH range (pH >8.3), when distribution system increases in these DBP species were somewhat smaller than those at lower pH ranges (results for DCAA and TCAA shown in Figure 7.9). This effect was most pronounced for TCAA and CH. In chloramine systems, high pH appeared to suppress both DCAA and TCAA losses. However, though higher pH values appeared to promote continued DCAA formation in chloramine systems, they did not appear to promote continued TCAA formation in these systems (see Figure 7.9). Distribution system losses of TCP and HAN4 were enhanced at high pH in free chlorine distribution systems but were less clearly associated with pH in chloramine systems (see Figure 7.10).

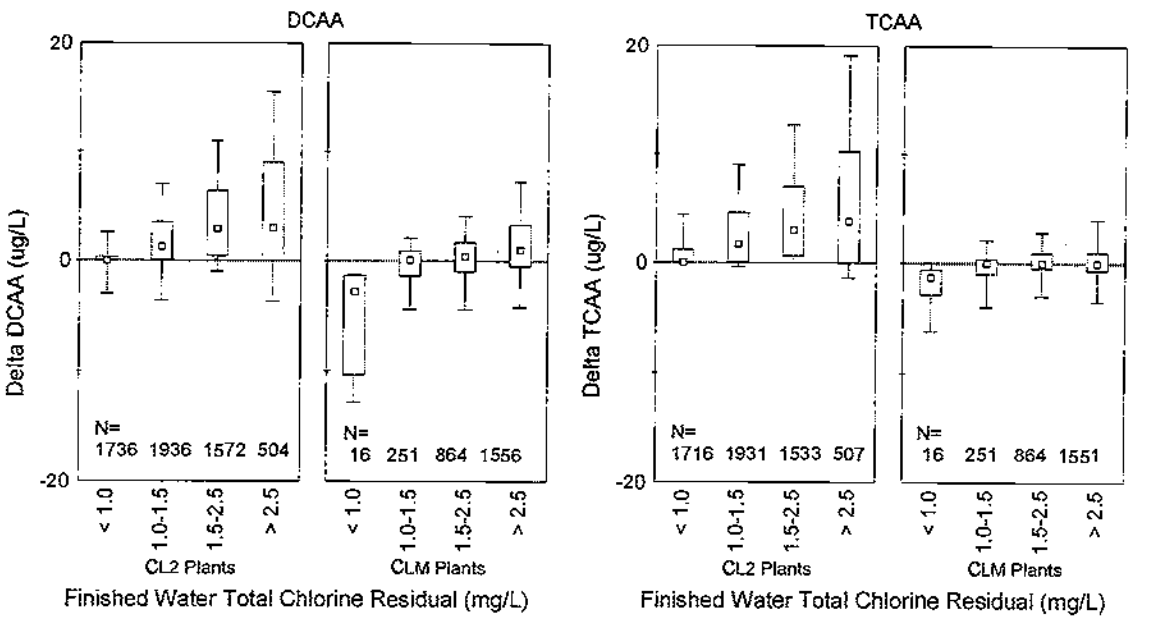

Figure 7.8 Distributions of delta DCAA and TCAA values as a function of finished water total chlorine residual concentration—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown

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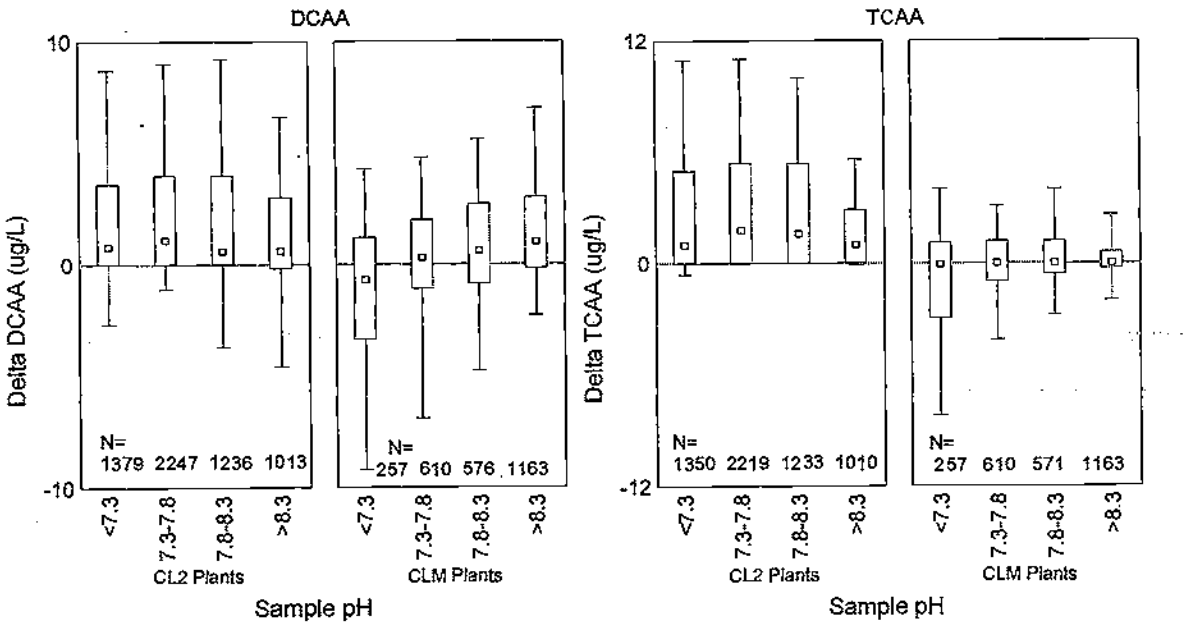

Figure 7.9 Distributions of delta DCAA and delta TCAA values as a function of sample pH—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown

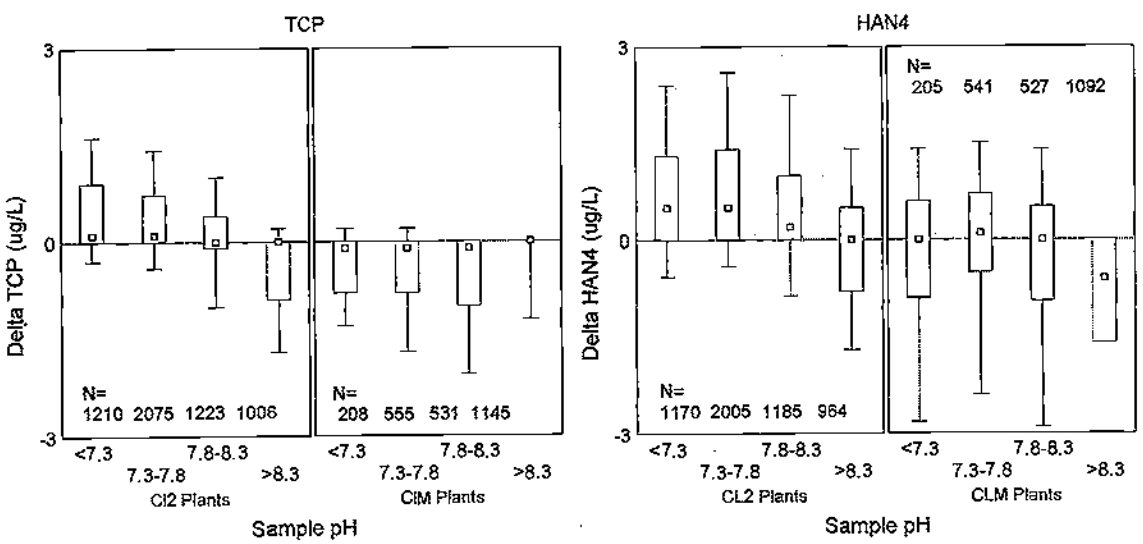

Figure 7.10 Distributions of delta TCP and delta HAN4 values as a function of sample pH—median (symbol), interquartile range (box), and 10th and 90th percentiles (whiskers) shown

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SDS Results

SDS performance was evaluated using results from a restricted set of ICR data in order to avoid biasing the evaluation with results from plant-quarters in which negligible DBP concentrations had been observed. Accordingly, linear regression was performed on sets of paired SDS and DSE results from plant-quarters whose DSE samples contained either TTHM or HAA5 concentrations of ≥10 μg/L. Data from free chlorine systems and chloramine systems were analyzed separately; a forced zero intercept was used in all cases to simplify interpretation of results ($[DBP_i]_{DSE}$ = *slope* * $[DBP_i]_{SDS}$). Therefore, this analysis describes the overall national performance of the SDS method for ICR plants, controlling for secondary disinfectant type but not considering the effects of water quality factors or type of treatment.

When the predictive capability of the SDS method is considered for any measurement target, a comparison of corresponding SDS and DSE sample results inherently incorporates analytical method imprecision. Corresponding SDS and DSE sample results cannot be expected to agree to a greater extent than the agreement observed for analytical method replicates (results for repeat analyses of identical samples). Fair et al. (2002) reported 90th percentile relative percent differences for ICR replicate TTHM and HAA5 measurements of 14% and 21%, respectively, indicating somewhat better analytical reproducibility for TTHM measurements than for HAA5 measurements No attempt was made here to account for background noise introduced by lack of absolute analytical reproducibility.

The slope of a best-fit line from regression of DSE results on SDS results, for a particular variable, represents how accurately SDS sample results modeled field sample results overall. A slope near 1.0 indicates accurate estimation, on average; a slope greater than 1.0 indicates a tendency for the SDS method to underestimate distribution system concentrations; and a slope less than 1.0 indicates a tendency for the SDS method to overestimate distribution system concentrations. As shown in Table 7.1, regression slopes were slightly below 1.0 for almost all ICR DBP variables, indicating that the SDS method tended to slightly overestimate distribution system concentrations for most DBPs—the smaller the slope, the larger the degree of overestimation. The r^2 values describe the precision of the relationships, or the degree of scatter, with a value of 1.0 representing exact agreement. The r^2 values for the SDS–DSE correlations ranged widely among the water quality and DBP variables and in many cases differed

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significantly by type of secondary disinfectant. From the standpoint of using the SDS method as a surrogate for distribution system sampling, the precision of the method (assessed by r^2) is more critical than its accuracy (assessed by the nearness of the slope to 1.0). Application of an adjustment factor (the regression slope) to the estimate (the SDS measurement) could easily compensate for a consistent, and therefore predictable, bias. However, imprecision implies a confidence interval on the estimate, with the potential that the estimate could be rendered useless if the interval is large enough.

Regression results are listed in Table 7.1 and illustrated in Figures 7.11–7.14. The highest level of precision observed in the SDS samples was for THM species in chloramine systems, with r^2 values of 0.85–0.89. SDS precision was consistently lower for the THM species in free chlorine systems, although still quite high, with r^2 values of 0.73–0.78. Lower SDS precision for TTHM compared with that for individual THM species (r^2 values of 0.80 and 0.69 for TTHM in chloramine and free chlorine systems, respectively) reflects accumulation of imprecision from the four THM species. Scatter plots of SDS and DSE results for THMs, showing regression lines, are provided in Figure 7.11 (for TTHM) and in Figure 7.12 (for individual THM species).

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Table 7.1

Slopes and r^2 values for regressions of DSE results on SDS results

	Secondary disinfectant					
	Free chlorine			Chloramine		
Variable	*N**	r^2	Slope	*N**	r^2	Slope
TTHM	1,146	0.6899	1.01	623	0.7969	0.99
HAA5	1,085	0.7556	0.93	584	0.7713	0.93
HAA9	211	0.7419	0.98	136	0.5705	0.94
HAN4	1,054	0.6178	0.90	584	0.6665	0.92
$CHCl_3$	1,156	0.7345	1.03	623	0.8472	0.99
BDCM	1,181	0.7312	0.97	627	0.8524	0.99
DBCM	1,180	0.7827	0.95	627	0.8882	0.98
$CHBr_3$	1,178	0.7631	0.92	627	0.8578	0.95
TCAA	1,158	0.7568	0.97	621	0.8372	0.95
BDCAA	314	0.8118	1.01	233	0.7124	0.95
DBCAA	282	0.7406	0.98	206	0.4623	0.94
DCAA	1,178	0.7000	0.86	622	0.6119	0.91
BCAA	1,173	0.5468	0.82	624	0.6736	0.94
DBAA	1,179	0.8246	0.87	626	0.8348	0.92
MCAA†	1,120	0.6333	0.96	590	0.4064	0.77
MBAA‡	1,163	0.4875	0.80	625	0.6417	0.88
DCAN	1,093	0.6421	0.86	597	0.6830	0.83
BCAN	1,090	0.8408	0.93	600	0.7923	0.91
DBAN	1,079	0.7776	0.91	595	0.4706	0.93
CH	1,053	0.7384	0.92	593	0.7130	0.90
CP	1,062	0.5607	0.92	569	0.6156	0.72
TCP	1,090	0.7076	0.90	598	0.6995	0.89
DCP	1,100	0.4968	0.86	605	0.5196	0.83
PH	1,354	0.6860	1.00	673	0.7951	1.00
Temperature	1,365	0.6895	1.02	700	0.7907	1.02
Total chlorine residual	1,329	0.4946	0.86	697	0.5271	0.91

* Number of SDS–DSE sample pairs; DSE samples with both TTHM and HAA5 values of <10 µg/L were excluded.
†.monochloroacetic acid
‡.monobromoacetic acid

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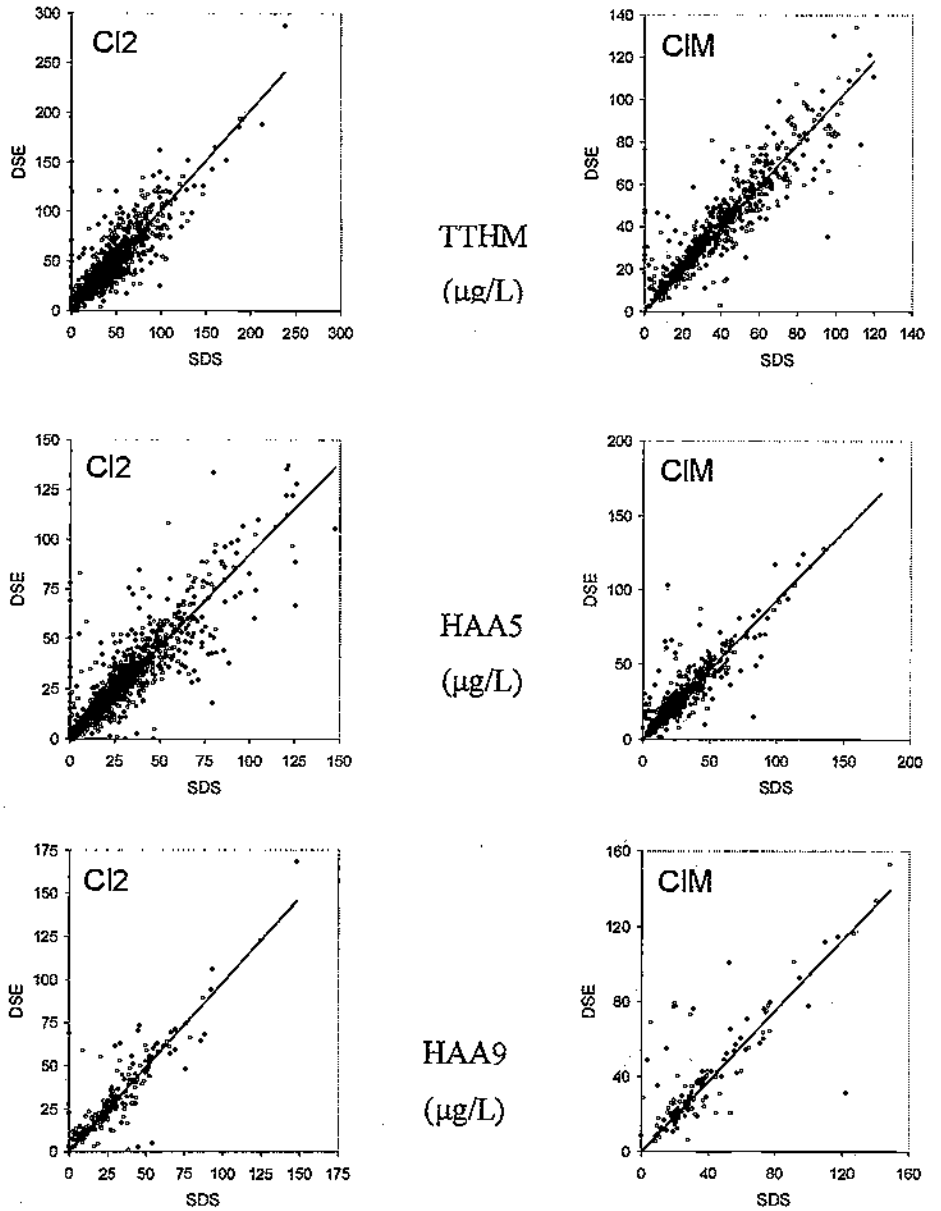

Figure 7.11 Correlations between SDS and DSE results for TTHM, HAA5, and HAA9

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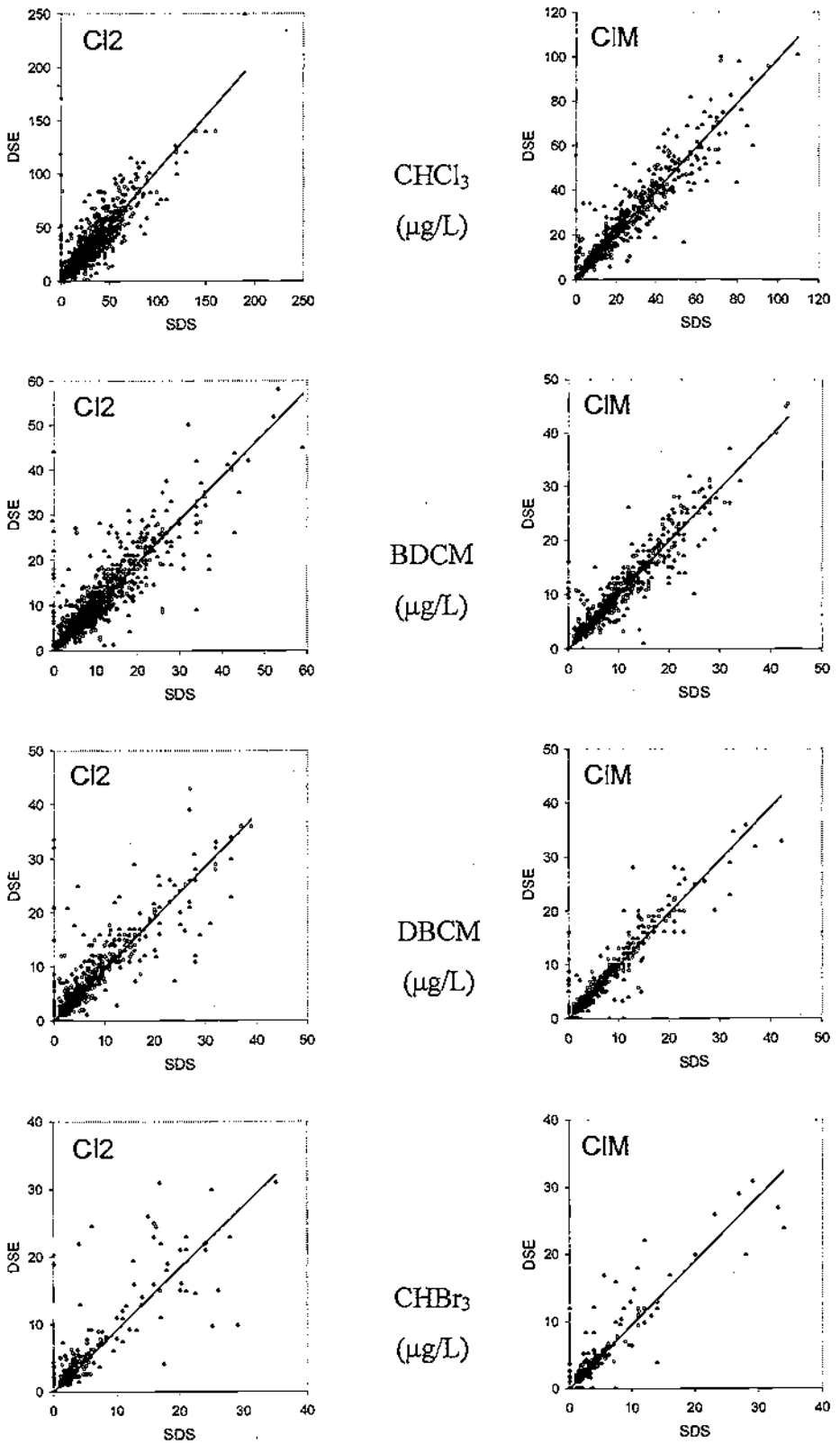

Figure 7.12 Correlations between SDS and DSE results for THM species

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SDS precision for the HAA species varied widely and did not exhibit a consistent pattern with respect to secondary disinfectant. In free chlorine systems, r^2 values for the trihalogen-substituted HAAs—TCAA, bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA)—were quite high, ranging from 0.74 to 0.81, and were comparable to those for the THM species (see Table 7.1 and Figure 7.13). In chloramine systems SDS precision for the trihalogen-substituted HAAs decreased with increasing bromine substitution; only TCAA had an r^2 value (0.84) comparable to the r^2 values observed for THM species in chloramine systems. The opposite pattern with respect to bromine substitution was observed for the dihalogen-substituted HAAs in chloramine systems: r^2 values for DCAA, BCAA, and dibromoacetic acid (DBAA) were 0.61, 0.67, and 0.83, respectively (see Table 7.1 and Figure 7.14). Of the dihalogen-substituted HAA species, DBAA had the highest r^2 value (0.82–0.83), regardless of secondary disinfectant type. The low and variable SDS precision observed for the monohalogen-substituted HAAs—MCAA and MBAA—is presumed to stem largely from the analytical imprecision associated with these analytes. Fair et al. (2002) reported these HAA species to have the lowest analytical precision of all the THM and HAA species. However the monohalogen-substituted HAA species generally occurred at low concentrations, contributing little to HAA5 concentrations and thus affecting SDS results for HAA5 minimally. Overall, SDS precision for HAA5 was similar in free chlorine (r^2 of 0.76) and chloramine systems (r^2 of 0.77) and was only slightly lower than SDS precision for TTHM in chloramine systems (r^2 of 0.80) (Table 7.1 and Figure 7.11). Overall SDS precision for HAA9 was similar to that for HAA5 in free chlorine systems (r^2 of 0.74) but was considerably lower in chloramine systems (r^2 of 0.57).

Regardless of secondary disinfectant type, the THM and trihalogen-substituted HAA species all had regression slopes between 0.92 and 1.03, indicating that the SDS method generally estimated DSE sample concentrations accurately. In free chlorine systems, SDS–DSE regression line slopes for the dihalogen-substituted HAA species (mean of 0.85) were somewhat lower than for the trihalogen-substituted HAA species (mean of 0.99). As a central tendency, the SDS method overestimated distribution system dihalogen-substituted HAA concentrations by about 15% in free chlorine systems but accurately estimated trihalogen-substituted HAAs. In chloramine systems, the SDS method overestimated the concentrations of dihalogen-substituted HAA species to a lesser degree (slopes ranged from 0.91 to 0.94).

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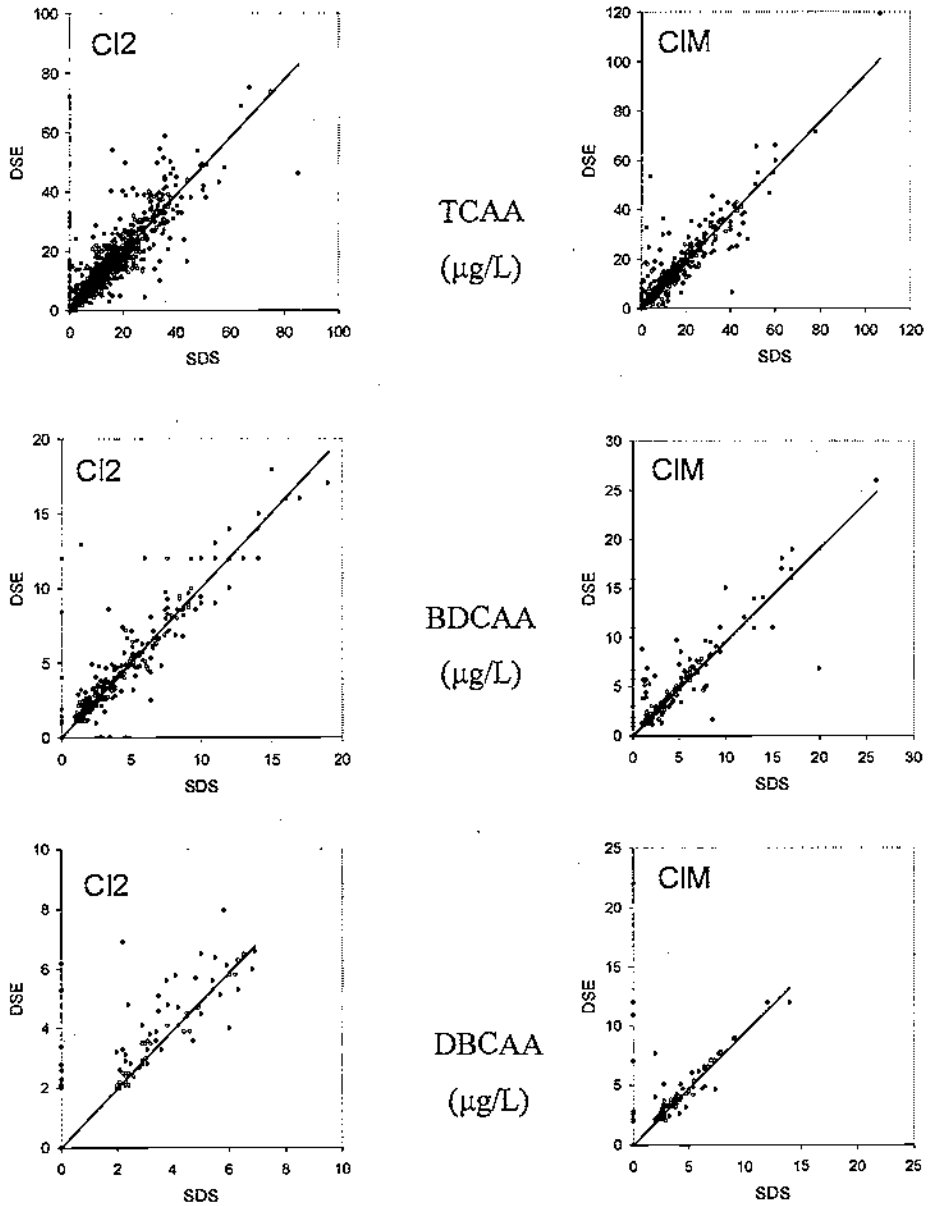

Figure 7.13 Correlations between SDS and DSE results for the trihalogen-substituted HAA species TCAA, BDCAA, and DBCAA

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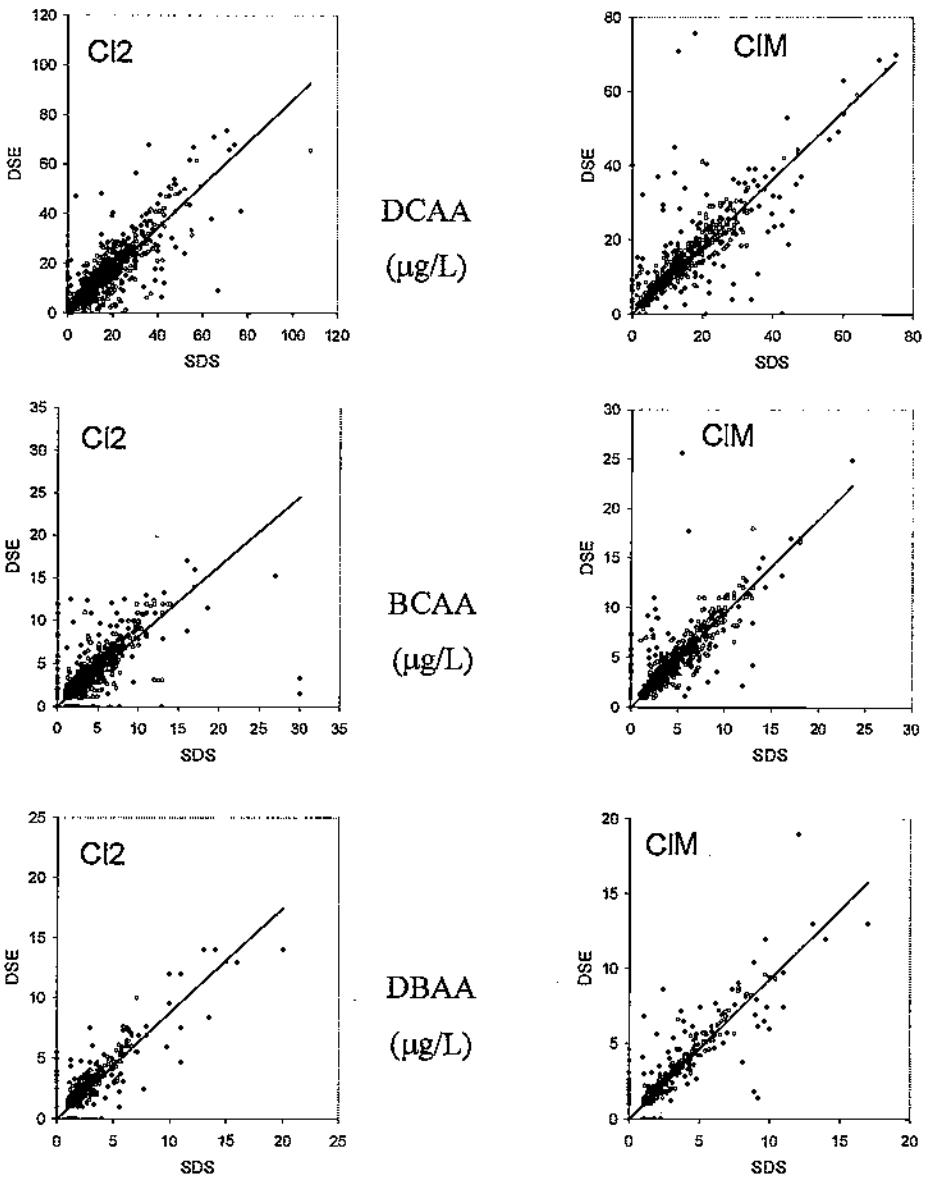

Figure 7.14 Correlations between SDS and DSE results for the dihalogen-substituted HAA species DCAA, BCAA, and DBAA

SUMMARY AND CONCLUSIONS

This analysis examined ICR DBP occurrence data in the context of distribution systems. The analysis included examination of spatial variability, patterns of differences in concentration

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relative to finished water, and the predictive capability of the SDS method at estimating distribution system DBP concentrations. On a national scale, variation in TTHM concentrations across individual distribution systems was significantly larger than variation in HAA5 concentrations in surface water systems using free chlorine. However, TTHM and HAA5 variability were comparable, and substantially smaller, in surface water systems using chloramine. The direction and magnitude of differences between DBP concentrations in finished water and at distribution system sampling locations varied for different by-products and in many cases were strongly related to secondary disinfectant type, distribution system detention time, temperature, pH, and total chlorine residual concentration in finished water. The data suggest that losses of DCAA, BCAA, BDCAA, DCP, and the HAN species were common in free chlorine systems. More surprising, the data suggest that all of the ICR DBP species, including THMs, commonly exhibited losses in distribution systems using chloramine.

In general, detention time, temperature, pH, and chlorine residual concentration had more impact on distribution system DBPs in free chlorine systems than in chloramine systems, and chlorine residual was typically the most important of these factors in relation to changes in DBP concentrations. In chloramine systems, high pH values appeared to play an important role in limiting DCAA and TCAA losses while promoting DCAA formation. In contrast, DCAA and TCAA increases appeared to be suppressed at high pH in free chlorine distribution systems.

SDS results were evaluated on a national basis to show dominant trends in this method's performance as a surrogate for field monitoring. For most DBPs, SDS sample concentrations slightly exceeded corresponding field sample concentrations. On average, the SDS method accurately estimated or only slightly overestimated THMs and the trihalogen-substituted HAAs, whereas it overestimated the dihalogen-substituted HAAs to a greater extent, especially in free chlorine systems. The degree of correlation between SDS and DSE results, a measure of the precision of SDS predictions, was similar for all the THM species and was quite high, especially in chloramine systems. The degree of correlation between SDS and DSE results varied widely among the HAA species, although the method's overall precision for HAA5 was comparable to that for TTHM in chloramine systems and stronger than that for TTHM in free chlorine systems. The degree of correlation between SDS and DSE results for HAA9 was quite strong for free chlorine systems but not as good for chloramine systems.

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A thorough evaluation of the SDS method's success at predicting distribution system DBP concentrations would need to consider the background noise introduced by analytical imprecision, which may represent a significant fraction of the imprecision observed in SDS results. It would also be appropriate to evaluate the predictive ability of the SDS method on a system-specific basis and to determine the types of conditions that favor and hinder acceptable precision of SDS predictions. Nevertheless, ICR data indicate that the SDS method provided reasonably precise and accurate estimates of distribution system TTHM, HAA5, and HAA9 concentrations in free chlorine systems and even better estimates of TTHM and HAA5 concentrations in chloramine systems. These results suggest that the SDS method holds great promise as a surrogate for distribution system field sampling for THMs and HAAs.

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CHAPTER 8

PREDICTING ICR SURFACE WATER PLANT BEHAVIOR WITH THE WATER TREATMENT PLANT MODEL

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ABSTRACT

This chapter describes the use of full-scale water quality and treatment information collected under the Information Collection Rule (ICR) to calibrate and evaluate the predictive algorithms of the Water Treatment Plant (WTP) Model. The WTP Model is a collection of empirical algorithms for predicting the quality of treated water, especially disinfection by-product (DBP) formation during water treatment. Most of the model's individual predictive algorithms were verified using independent data sets prior to this work. However, the ICR database provided a unique opportunity to test the model's ability to predict full-scale treatment plant performance with a large, diverse data set. Through this work, calibration factors were developed for several WTP Model algorithms to improve their ability to predict the central tendency of ICR data. These included algorithms for pH and total organic carbon (both for softening plants), the formation of total trihalomethanes (TTHM) under free chlorine conditions, and the formation of TTHM and five haloacetic acids under chloramine conditions. The calibrated model was incorporated into the Surface Water Analytical Tool, which supported the U.S. Environmental Protection Agency's efforts to develop the Stage 2 DBP Rule and the Long Term 2 Enhanced Surface Water Treatment Rule. A comparison of WTP Model output and observed data indicated good agreement. between model-predicted and observed distributions of treated water quality characteristics at ICR plants. However, predicted DBP distributions had longer upper tails than observed DBP distributions. Results indicated that this was likely due to the propagation of error through sequential predictive WTP Model algorithms. Furthermore, an evaluation of the agreement between predicted and observed water quality on a plant-by-plant basis showed significant deviations, indicating that the WTP Model may have significant limitations as a predictive tool for individual plants without site-specific calibration.

INTRODUCTION

Over the past two decades researchers have been working to develop numerical models to predict the formation of disinfection by-products (DBPs) in treated drinking water. More specifically, the challenge has been to predict trihalomethane (THM) and haloacetic acid (HAA) formation during treatment and delivery of chlorinated water. Formation of THMs and HAAs

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involves numerous factors, including multiple water quality and treatment variables. Furthermore, the specific chemical reactions involved in the formation of DBPs currently are not completely understood. As a result, empirical models have represented the state of the art in predicting DBP formation. These empirical models have been developed primarily through the statistical analysis of data generated by bench-scale tests. The value of bench-scale tests is that they allow the effects of many variables to be investigated systematically under controlled conditions, and a model generated from their results can be regarded with confidence. However, predicting DBP formation in full-scale systems is the ultimate goal. Because of practical limitations, less progress has been made in testing DBP models with full-scale data, especially across a broad range of water systems.

At the time this chapter was written, the U.S. Environmental Protection Agency (USEPA) was developing the Stage 2 DBP Rule and the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR). These rules are intended to simultaneously protect the public from DBPs and pathogenic organisms in drinking water. To prepare for this rulemaking effort, USEPA implemented the Information Collection Rule (ICR), which required large utilities to characterize raw, treated, and distributed water on a monthly basis over an 18-month period (July 1997 through December 1999) with a focus on disinfection and DBPs. USEPA compiled these data in a national ICR database, as described in Chapter 1 of this book (Wysock 2002). The work reported in this chapter represents the authors' effort to use these full-scale data to calibrate and evaluate the WTP Model's predictive algorithms. The resulting calibrated WTP Model was incorporated into the Surface Water Analytical Tool (SWAT), a compliance forecasting tool USEPA used during development of the Stage 2 DBP Rule and LT2ESWTR.

OBJECTIVES

This work compared WTP Model predictions with observations contained in the ICR database to accomplish two primary objectives:

- To calibrate the model, as needed, to better match the central tendency of ICR data, and
- To validate the model at two levels by characterizing the resulting agreement between predicted and observed data both on an overall (central tendency) and a paired basis.

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The overall goal was to improve the model's ability to predict the central tendency of observed full-scale DBP data and to increase its utility as a tool for forecasting national compliance with potential DBP provisions of the Stage 2 DBP Rule and the LT2ESWTR. In the process, an improved understanding of model and database limitations was pursued.

THE WTP MODEL

The WTP Model represents the collection of empirical models investigated in this work. USEPA initially funded development of the WTP Model to support the process of developing the Disinfectants/DBP Rule. First described by Harrington, Chowdhury, and Owen (1992), the WTP Model uses empirical equations to predict disinfection and DBP formation during water treatment. The model also predicts changes in pH, DBP precursors, and other parameters during water treatment. Because the WTP Model has an empirical basis, it is expected to generate reasonably accurate "central tendency" predictions, so it would likely predict reasonably well the DBP formation trends and the distribution of DBPs observed for a population of water treatment plants. Without site-specific calibration, however, the WTP Model would not likely predict DBP formation within a specific plant very well. Thus, the WTP Model is well suited for regulatory assessments that require predictions of DBP distributions, given distributions in raw water and under treatment conditions.

Figure 8.1 illustrates the general structure of the WTP Model. The WTP model represents a treatment plant as a series of unit processes, chemical addition points, and distribution system sampling locations. The model requires input data consisting of information on raw water quality, treatment train configuration, and individual treatment process design and operating criteria. Starting with raw water quality and the first treatment process in the plant, the WTP Model uses empirical equations to calculate water quality changes as the water passes from process to process. Stolarik et al. (2000) present DBP formation and other empirical algorithms for the version of the WTP Model used in this work. The effluent quality of one process is used as the influent quality of the next until the last process is reached.

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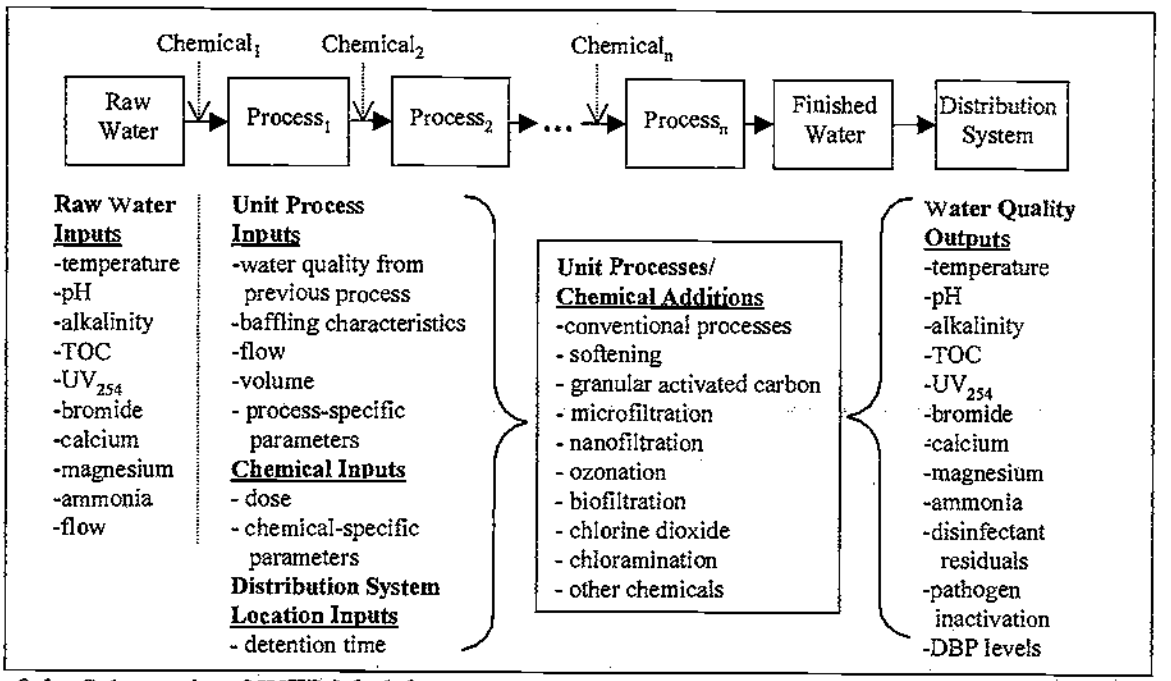

Figure 8.1 Schematic of WTP Model

METHODOLOGY

Model–Database System

Before the WTP Model could be analyzed using ICR data, a custom database had to be developed. This database—ICR Auxiliary Database 8 (AUX8)—was populated from ICR Auxiliary Database 1 (AUX1), which was extracted from the main comprehensive ICR database (ICR FED). AUX1 was the primary database used by the Stage 2 DBP Rule Technical Work Group (TWG), whereas AUX8 was designed specifically to support modeling. Thus, AUX8 contains ICR data that are properly formatted to serve as WTP Model input data. AUX8 also contains tables in which WTP Model outputs can be stored as they are generated during a model run. Finally, a program was developed to link the WTP Model and AUX8. This program, called the Surface Water Analytical Tool (SWAT), also contained a treatment technology decision tree. The main purpose of SWAT was to generate forecasting estimates that could predict the potential compliance of ICR surface water plants with various regulatory scenarios. For this work, SWAT was run in an operational mode that bypassed the decision tree and simply transferred observed inputs and predicted outputs between AUX8 and the WTP Model. Figure 8.2 schematically illustrates the system used for this analysis.

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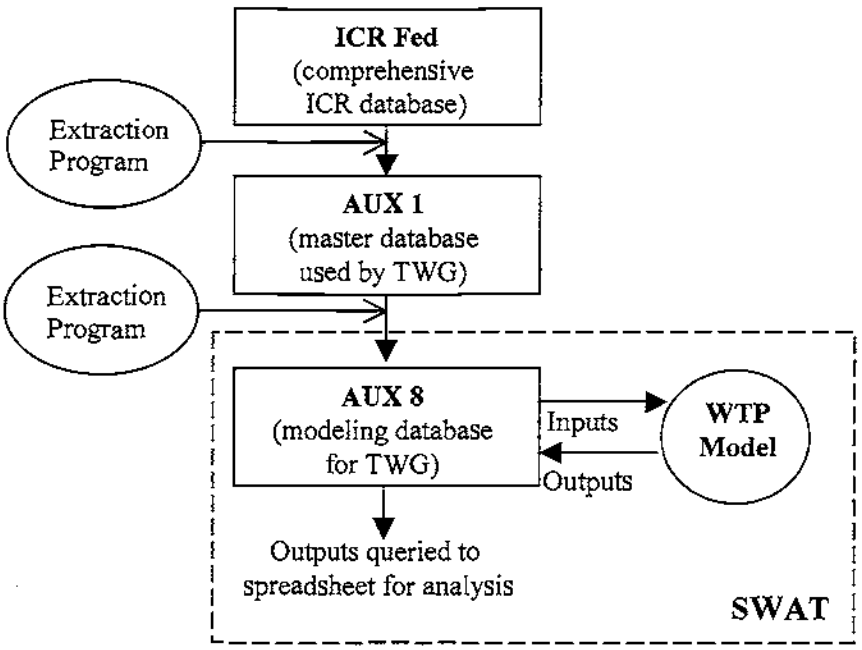

Figure 8.2 WTP Model–Database System

Data Set Used for Analysis

The ICR database contains monthly observations collected from 500 large surface water and groundwater treatment plants across the United States. However, not all of these plant-months (the data associated with a plant for a given month) were used in this analysis. The following points indicate how the AUX8 database was crafted to serve the project needs:

- The TWG for the Stage 2 DBP Rule used the WTP Model to analyze plants with surface water sources. Thus, AUX8 contained only data from plants treating surface water, groundwater under the direct influence of surface water, or both.
- Less than 5% of ICR plants were excluded from AUX8 and from this analysis because they included unit processes (such as air stripping) or process train configurations (such as those involving mid-stream blending) not supported by the WTP Model.
- Approximately 50% of plant-month records extracted from AUX1 into AUX8 were missing one or more raw water quality or treatment process parameter required for running the WTP Model. Data from these plants were not used in this work.

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- AUX8 contains data for the entire 18-month ICR period. However, the modeling analyses described here used only the last 12 months (January through December 1998) of data to avoid the introduction of seasonal bias. The TWG verified that no significant differences in raw or treated water quality distributions existed among any of the seven possible 12-month ICR data sets.
- The ICR required utilities to collect quarterly distribution system samples for DBPs at four locations, two of which represented average distribution system detention time and one of which indicated maximum detention time. For analyses using the WTP Model, these four locations were consolidated into two:
  - Distribution system average (DS_AVG)—The input for residence time and the observed DBP concentrations associated with this location for a given plant-month were set equal to the average of those observed at the four ICR sampling locations. Thus, predicted DS_AVG DBP values were calculated using an average detention time input (weighted to favor average detention time) and were compared with an average observed DBP concentration (also weighted in favor of concentrations associated with average detention time).
  - Distribution system maximum (DS_MAX)—The input for residence time and the observed DBP concentrations associated with this location in a given plant-month were set equal to those associated with the ICR sampling location representing maximum residence time.

Because ICR DBP samples were collected quarterly, there were significantly fewer data sets for observed DBP concentrations than for other parameters, such as pH, total organic carbon (TOC), chlorine residual, and chloramine residual, which were measured monthly.

A total of 2,158 plant-months were used in this analysis. Table 8.1 presents a statistical summary of raw water quality by plant-month. Figures 8.3a–8.3d show the distribution of treatment process types, source water types, distribution system disinfectants, and in-plant disinfectants by plant-month.

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Table 8.1

Distribution of raw water quality by plant-month*

Parameter	Units	Minimum	Percentiles 10th	25th	50th	75th	90th	Maximum	Mean
Temperature	Degrees Centigrade	0.6	7	11	16	22	26	43	16.3
pH	Standard units	5.2	6.7	7.2	7.7	8.1	8.3	14†	7.6
Alkalinity	mg/L as $CaCO_3$	1	12	24	80	121	168	459	82
TOC	mg/L	0.70	1.4	2.0	2.7	3.8	5.3	25	3.1
UV absorption at 254 nm	1/cm	0.009	0.027	0.042	0.072	0.116	0.177	1.10	0.096
Bromide	mg/L	0.020	0.020	0.020	0.027	0.054	0.119	28.0†	0.069
Hardness	mg/L as $CaCO_3$	1	8	20	62	113	168	486	75
Calcium	mg/L as $CaCO_3$	3	15	33	105	168	250	643	116
Ammonia	mg/L as N	0.0	0.0	0.0	0.1	0.1	0.3	2.3	0.13

* Total number of plant-months, $N = 2158$

† Though the AUX1 database was subjected to a validation process, questionable outlier data, such as those indicated, remained in the database and were transferred to AUX8; this is the primary reason that records containing the highest absolute residuals were eliminated from the calibration process, as described under the subheading "Approach."

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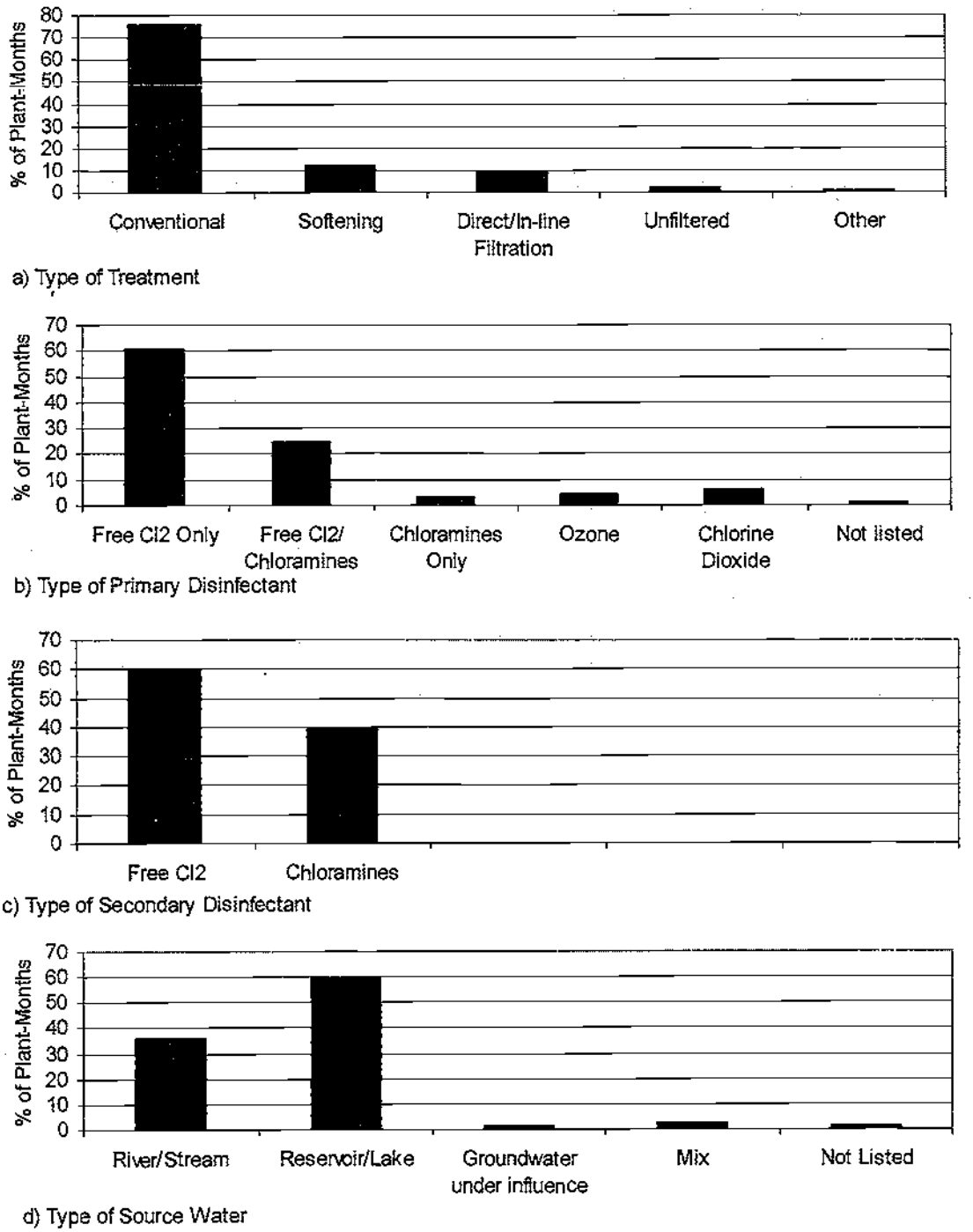

Figure 8.3 Characteristics of plant-months used in analysis of model

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Approach

The analysis described in this chapter represents a calibration of the WTP Model and an evaluation of its predictive capabilities. The model was calibrated by adjusting its predictions to better fit the central tendency of observed data. By evaluating the differences between observed values and the calibrated model's predicted values, the model was evaluated and its limitations were defined.

This analysis focused on several key algorithms within the WTP Model:

- pH adjustment
  - in non–softening plants
  - in lime softening plants
- TOC removal
  - in non–softening plants (alum or ferric coagulation)
  - in lime softening plants
- Free chlorine decay
- Chloramine decay
- THM and HAA formation with free chlorine
  - in the treatment plant
  - in the distribution system
- THM and HAA formation with chloramines

Because WTP Model algorithms at the end of this list use predicted values from algorithms at the top of the list as inputs, the calibration process warranted a step-wise approach. Thus, WTP Model algorithms were calibrated starting with pH and ending with DBPs. To accomplish this, the following general calibration approach was used for a given parameter:

1. A model run was performed to generate initial (uncalibrated) predictions, which were stored in AUX8 along with observed data.
2. To prevent plant-months with potentially misreported chemical dose or raw water quality data from biasing the analysis, any plant-months with a predicted alkalinity of <0 in finished water were eliminated from further consideration. This approach was implemented after detailed investigations showed that plant-months meeting this

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criterion often had questionable chemical doses or raw water quality parameters (i.e., pH, alkalinity, and hardness) that might have been reported incorrectly.

3. Predicted and observed data were queried from appropriate plant-months in AUX8. For example, if TOC removal during conventional coagulation was being evaluated, data would not be retrieved from softening plants.
4. Differences between observed and predicted data—i.e., absolute residuals—were calculated.
5. Observed and predicted data pairs with the highest 10% of absolute residuals for the parameter being calibrated were excluded from further consideration. This decision was made for the following reasons:
   a. It was recognized that ICR data contained extreme outliers (see Table 8.1),
   b. Closer inspection of the records for individual samples showed that many of these data might represent reporting errors,
   c. The large number of records with possibly misreported outliers precluded an investigation to determine whether to include or exclude them on an individual basis,
   d. Records with suspect data could often be identified by their tendency to result in high absolute residuals between predicted and observed values when subjected to WTP Model analysis, and
   e. The outlier data could significantly skew WTP Model calibration.
6. Scatter plots of predicted versus observed data for a given parameter were generated to identify appropriate calibration adjustments, if required. The first test to determine the need for calibration adjustment was to apply a line of best fit, forced through the origin, to the paired data. If the slope of this line was within 5% of unity, no calibration function or factor was applied. If this test failed for a given parameter, the scatter plots were used to determine which of two linear calibration adjustments to employ:
   a. Slope-based adjustment—This was the most common type of calibration adjustment made. In this case, the first step was to determine whether a line of best fit, not forced through the origin, applied to the paired data (predicted versus observed) had an intercept close to zero. If this was the case, the calibration was then made using a line of best fit forced through the origin. If the slope of this line differed from unity by more than 5%, a calibration factor equal to the inverse of this slope was

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employed. The WTP Model was then calibrated by incorporating this multiplicative factor into the appropriate algorithm.

b. Slope and intercept-based adjustment—In these cases, predicted and observed values were clearly related linearly, but a line of best fit applied to the paired data did not have an intercept close to zero. Instead, there was a clear trend of under-prediction at one end of the spectrum and over-prediction at the other end. In these cases, both the slope and intercept of the best-fit line were used to calibrate the appropriate WTP Model algorithm.

Once calibration adjustments were incorporated into the WTP Model algorithms, an evaluation of the model's performance proceeded as follows:

1. The WTP Model was re-run to generate a set of calibrated predictions,
2. Observed and (new) predicted data were queried from the database as described in calibration steps 2 and 3,
3. Distributions of observed and predicted data (without any data trimming as described in calibration step 5) were compared to assess the ability of the WTP Model to predict full-scale performance on a distribution-wide basis, and
4. Paired data were analyzed to investigate the WTP Model's ability to generate predictions matching site-specific ICR observations.

Thus, the WTP Model was calibrated using linear transformations of the original predictions to better match the central tendency of the observed ICR data. Because the form of the model's equations remained intact, evaluation results could then be used to verify the predictive power of the algorithm's equation form with the central tendency calibrated.

RESULTS

Results of the model calibration and evaluation are presented in this section. For clarity, a complete set of graphs is shown for the analyses of pH data and THM data. For brevity, summary data are presented for the other parameters.

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pH

The WTP Model calculates pH within the treatment plant and distribution system using basic equilibrium chemistry expressions and the assumption of a closed system (no air–water transfer of carbon dioxide). The model also assumes an activity coefficient of unity for all chemical constituents. Furthermore, in softening plants, the WTP Model uses equilibrium expressions to predict calcium carbonate and magnesium hydroxide precipitation. In non–softening plants, calcium and magnesium are assumed to remain in solution. Because of these different assumptions about precipitation and their effect on pH predictions, separate pH calibration analyses were conducted for softening and non–softening plants.

Figure 8.4 presents a scatter plot of observed and predicted pH in softening plants prior to model calibration. As with all calibration plots generated in this analysis, 10% of the paired data with the highest absolute residuals were excluded to minimize the influence of outliers and to facilitate a calibration matching the central tendency of observed data. The paired pH values in the plot consist primarily of data from samples of settled, filtered, and finished water. The uncalibrated algorithm under-predicted the observed values, and the under-prediction increased with increasing observed values. Regressing the paired data with a best-fit line indicated that a fair relationship existed between predicted and observed data ($r^2 = 0.33$) and that the algorithm would be calibrated best by using a linear transformation that accounted for both the slope and intercept (Figure 8.4 includes a best-fit line forced through the origin for comparative purposes). Thus, pH predictions in softening plants were calibrated as defined by Equation 8.1:

$$pH_{calibrated} = (pH_{uncalibrated} - 1.86) \div 0.71 \qquad (8.1)$$

in which $pH_{calibrated}$ is the pH after calibration and $pH_{uncalibrated}$ is the pH predicted by the uncalibrated model.

Figure 8.5 presents predicted and observed pH in softening plants after calibration. This plot was generated similarly to Figure 8.4 to check calibration results. A best-fit line, forced through the origin, shows the calibration was successful in achieving a slope that differed from unity by less than 5%. Thus, the model's central tendency was adjusted so that predicted and observed data pairs fell more symmetrically around a 1:1 line. The scatter about this line was described by an r^2 of 0.37.

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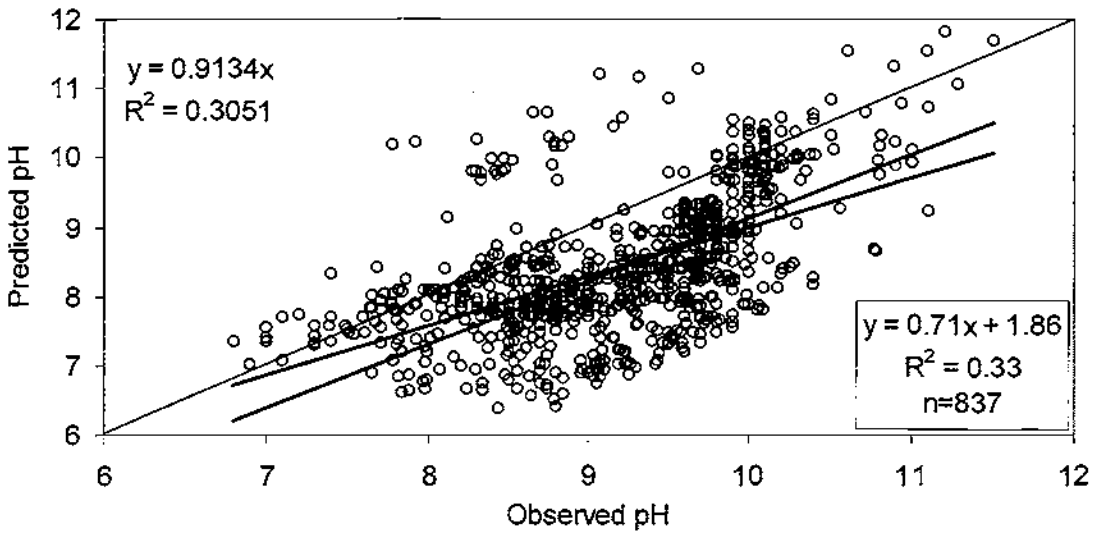

Figure 8.4 Predicted and observed pH in softening plants (before model calibration)

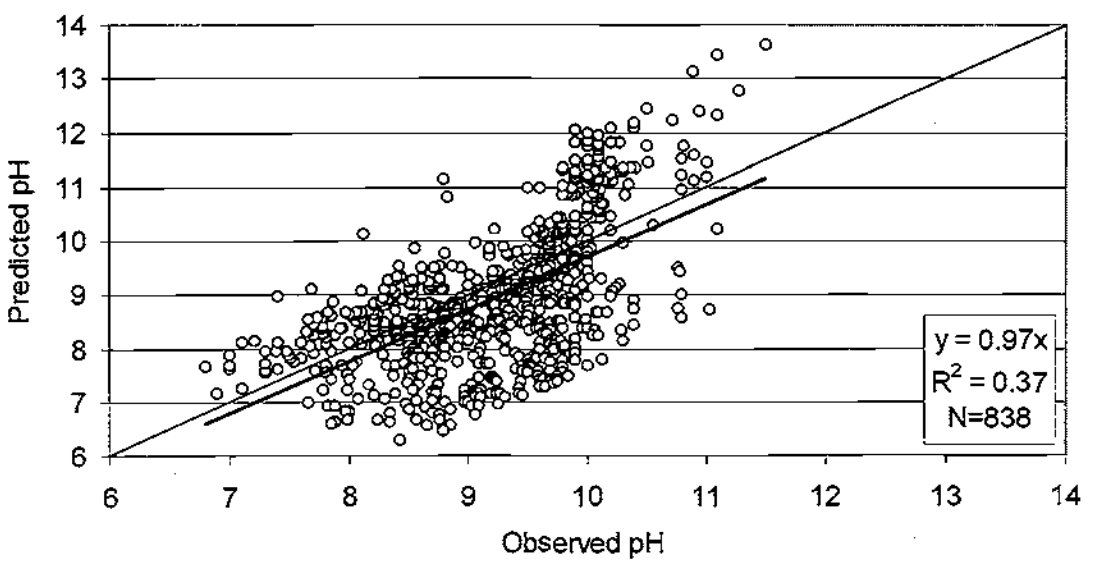

Figure 8.5 Predicted and observed pH in softening plants (after model calibration)

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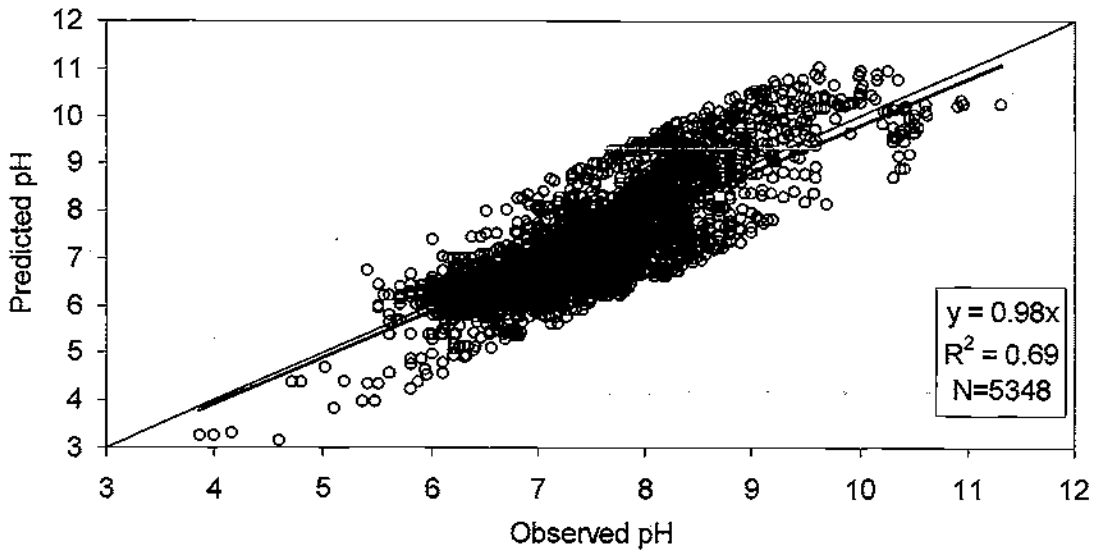

Figure 8.6 Predicted and observed pH in non–softening plants (no calibration needed)

Figure 8.6 shows the pre-calibration scatter plot for pH in non–softening plants. Because the paired data tended to fall around a line with a slope of 0.98, no calibration was deemed necessary. Table 8.2 summarizes calibration results for pH and other parameters.

With the pH algorithm calibrated, the overall agreement between ICR pH observations and WTP Model pH predictions could be assessed. Figure 8.7 compares the observed and predicted pH distributions using box-and-whisker plots. In the plots, the circles represent the 5th and 95th percentiles, the ends of the "whiskers" indicate the 10th and 90th percentiles, the ends of the box show the 25th and 75th percentiles, and the line within the box corresponds to the median. As with most model evaluation plots presented in this chapter, Figure 8.7 includes data for all types of plants and does not exclude data based on residuals of predicted and observed values. However, data for plant-months with negative predicted finished water alkalinity are excluded because of the high probability of incorrectly reported chemical doses. Figure 8.7 shows that the spread of predicted pH values was slightly greater than that of observed values, and differences in predicted and observed pH values at any given percentile were typically less than 0.3 pH units. Thus, the calibrated WTP Model represented the distribution of ICR pH values quite well.

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Table 8.2

Calibration results

Parameter	Sampling locations included in analysis	Treatment conditions	Calibration adjustment *	Result with calibration
PH	Any in-plant location but primarily settled, filtered, and finished water	Softening plants	$P_{cal} = (P_{orig}-1.86) \div 0.71$	Slope = 0.97; $r^2 = 0.37$; $N = 837$
		Non–softening plants	None	Slope = 0.98; $r^2 = 0.69$; $N = 5348$
TOC	Any in-plant location but primarily settled, filtered, and finished water	Softening plants	$P_{cal} = P_{orig} \div 0.87$	Slope = 0.95; $r^2 = 0.58$; $N = 799$
		Non–softening plants	None	Slope = 1.05; $r^2 = 0.84$; $N = 5285$
Free Chlorine	Any in-plant location but primarily settled, filtered, and finished water	Plants using free chlorine as the primary disinfectant	None	Slope = 0.95; $r^2 = 0.49$; $N = 4003$
Chloramine (as total Cl_2)	Any in-plant location but primarily settled, filtered, and finished water	Plants using chloramines within the plant	None	Slope = 0.87; $r^2 = 0.21$; $N = 919$
TTHM	Finished water	Plants with free Cl_2 only in plant and distribution system	$P_{cal} = P_{orig} \div 0.77$	Slope = 0.96; $r^2 = 0.50$; $N = 300$
	DS_AVG location	Plants with free Cl_2 only in plant and distribution system	$P_{cal} = P_{orig} \div 0.77$	Slope = 1.04; $r^2 = 0.52$; $N = 300$
	DS_AVG location	Plants with chloramines in distribution system	$P_{chloramines} = 0.3 \times P_{cal,freeCl2}$	Slope = 0.99; $r^2 = 0.27$; $N = 237$
HAA5	Finished water	Plants with free Cl_2 only in plant and distribution system	None	Slope = 0.98; $r^2 = 0.47$; $N = 292$
	DS_AVG location	Plants with free Cl_2 only in plant and distribution system	None	Slope = 1.00; $r^2 = 0.37$; $N = 290$
	DS_AVG location	Plants with chloramines in distribution system	$P_{chloramines} = 0.35 \times P_{cal,freeCl2}$	Slope = 1.02; $r^2 = 0.27$; $N = 233$

* P_{cal} = calibrated predicted value of parameter; P_{orig} = uncalibrated predicted value of parameter; $P_{chloramines}$ = calibrated value of predicted THM or HAA concentration with chloramines; $P_{cal,freeCl2}$ = calibrated value of predicted THM or HAA concentration with free chlorine

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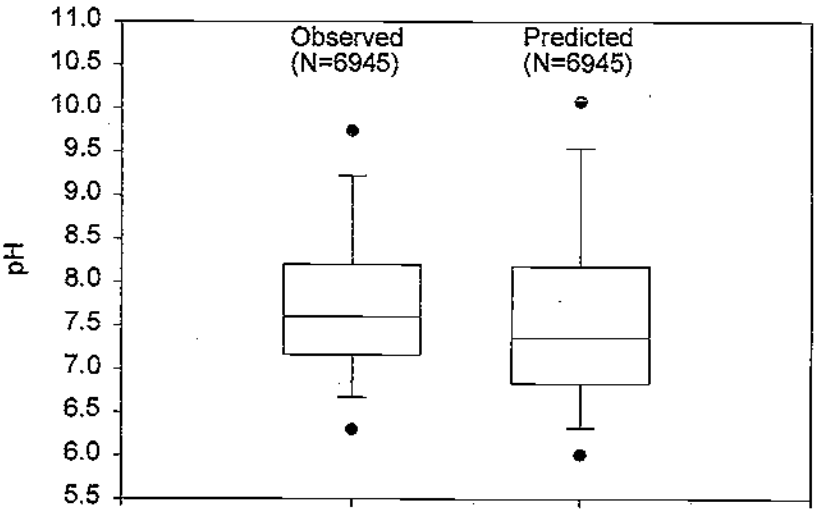

Figure 8.7 Distributions of observed and predicted pH values for all plants (after model calibration)

Table 8.3 presents a summary of paired data for evaluating pH and other parameters. To illustrate how paired predicted and observed data compared, the table shows 5th through 95th percentile values for three quantities:

- Residual (defined as the predicted value minus the observed value). The distribution of residuals illustrates the extent and frequency of both over- and under-prediction.
- Absolute residual (defined as the absolute value of the residual). The distribution of absolute residuals shows how often the absolute value of the residual was less than or equal to a given value.
- Relative residual (defined as the absolute residual divided by the average of the observed and predicted values times 100%). The distribution of relative residuals illustrates the extent of occurrence of absolute residuals on a normalized basis.

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Table 8.3

Evaluation results—analysis of paired data

Water quality parameter	Statistical parameter	Units	Percentile						
			5th	10th	25th	50th	75th	90th	95th
pH	Residual	pH units	−1.8	−1.2	−0.5	−0.2	0.2	0.9	1.6
(*N*=6945)	Absolute residual	pH units	0.0	0.1	0.2	0.4	0.9	1.7	2.3
	Relative residual	%	0.4	0.9	2.3	5.0	11	22	29
TOC	Residual	mg/L	−1.0	−0.5	−0.1	0.2	0.5	0.9	1.2
(*N*=6870)	Absolute residual	mg/L	0.0	0.0	0.1	0.3	0.7	1.2	1.7
	Relative residual	%	1.1	2.4	6.4	15	29	53	77
Free Cl_2	Residual	mg/L	−1.4	−1.0	−0.4	0.0	0.5	1.2	1.8
(*N*=4448)	Absolute residual	mg/L	0.0	0.0	0.2	0.4	0.9	1.5	2.1
	Relative residual	%	0.0	5.5	25	62	163	200	200
Chloramines	Residual	mg/L Cl_2	−2.9	−1.9	−0.7	0.1	0.9	1.6	3.0
(*N*=1022)	Absolute residual	mg/L Cl_2	0.1	0.2	0.4	0.8	1.4	3.0	3.4
	Relative residual	%	3.6	7.2	17	32	64	176	198
TTHM at	Residual	µg/L	−43	−30	−12	1.7	22	47	69
DS_AVG	Absolute residual	µg/L	1.6	2.9	7.9	17	34	56	78
(*N*=667)	Relative residual	%	4.2	8.8	21	47	81	121	153
TTHM at	Residual	µg/L	−58	−38	−19	−1.0	21	46	73
DS_MAX	Absolute residual	µg/L	2.1	3.3	8.9	20	37	63	85
(*N*=667)	Relative residual	%	4.5	8.8	23	45	81	119	151
HAA5 at	Residual	µg/L	−30	−20	−10	1.7	15	37	55
DS_AVG	Absolute residual	µg/L	0.9	1.8	5.5	12	24	43	61
(*N*=648)	Relative residual	%	6.5	11.5	26	51	76	91	96
HAA5 at	Residual	µg/L	−37	−27	−13	−0.1	13	37	54
DS_MAX	Absolute residual	µg/L	1.1	2.4	6.1	13	26	47	65
(*N*=648)	Relative residual	%	4.1	9.6	22	49	88	122	139

A comparison of Figure 8.7 and the pH data in Table 8.3 illustrates the differences in agreement between observed and predicted pH values on a distribution-wide basis and on a paired basis. Because the WTP Model is a central tendency model developed from empirical relationships, it was expected to predict distributions with reasonable accuracy (as shown in Figure 8.7). However, given the limitations of the model and the shortcomings of the ICR data, substantial differences (residuals) in paired predicted and observed data were also expected. Table 8.3 shows that the median pH residual was −0.2, indicating that predicted pH was frequently lower than observed pH. The table also indicates that the relative and absolute difference between predicted and observed pH values was less than 11% (or 0.9 pH units) 75% of the time.

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TOC

Because the WTP Model uses different algorithms to predict TOC removal in softening and non–softening plants, separate analyses were performed for TOC, just as they were for pH. Also similar to the pH analyses, the calibration process indicated that WTP Model predictions of TOC be adjusted in softening plants but not in non–softening plants. Table 8.2 shows that the algorithm for predicting TOC in softening plants required an upward adjustment by a factor of 1/0.87 (=1.14). The relationship between observed and predicted TOC data for non–softening plants was described by an r^2 value of 0.84, the highest for any parameter investigated.

Figure 8.8 (which includes data from softening and non–softening plants) presents a comparison of observed and predicted TOC distributions. In general, the distributions matched quite well; predicted values at the 75th percentile or below exceeded observed values by only 0.1–0.2 mg/L. Results of the evaluation of paired TOC data shown in Table 8.3 also indicate that model predictions typically were slightly higher than ICR observations. Furthermore, 75th percentile absolute and relative residuals were 0.7 mg/L and 29%, respectively, indicating that significant differences between observed and predicted TOC values were common.

Free Chlorine

Data from plants using only free chlorine as a primary disinfectant were selected for calibration of the WTP Model's free chlorine decay algorithm. As Table 8.2 indicates, no adjustment of free chlorine predictions was warranted because the slope of the best-fit line for the uncorrected predicted data and observed data was within 5% of unity. The calibration data set exhibited a reasonable correlation between predicted and observed values (r^2 = 0.49).

A distribution-wide evaluation of free chlorine predictions is shown in Figure 8.8. Compared with the distribution of observed values, the distribution of predicted values exhibited slightly more spread (0.2–0.3 mg/L) in the interquartile range (25th to 75th percentile) and a significantly longer upper tail (approximately 1 mg/L differences at the 90th and 95th percentiles). Evaluation of paired data showed that under-predictions and over-predictions were equally as common (median residual = 0.0). Although approximately 80% of the absolute residuals were less than 1 mg/L, 50% of the relative residuals were greater than 62%. Thus, significant differences existed between paired free chlorine predictions and observations.

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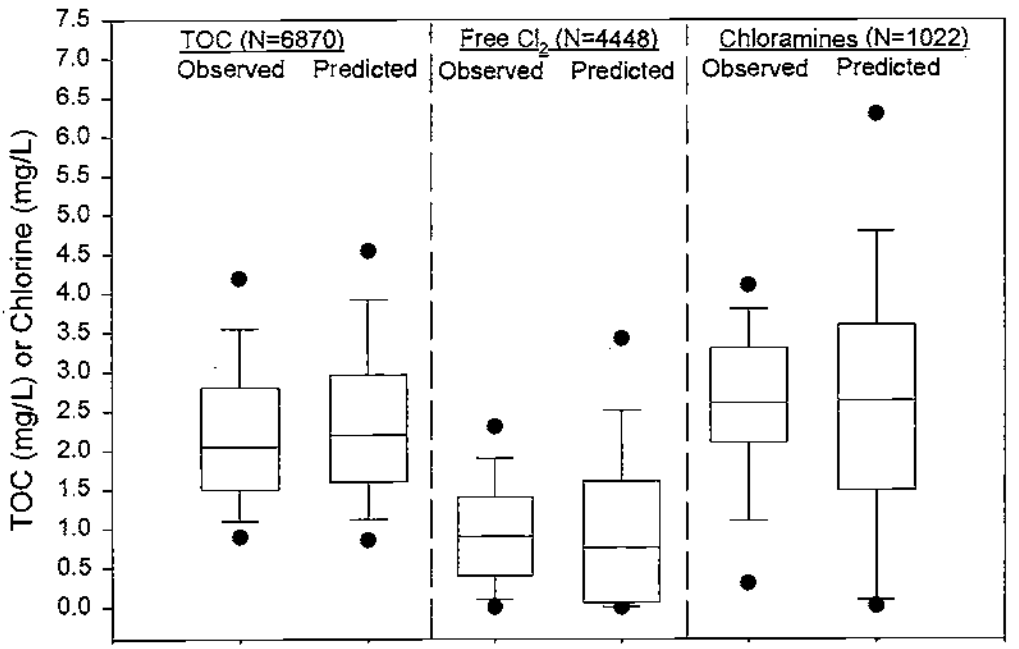

Figure 8.8 Distributions of observed and predicted TOC, free chlorine, and chloramines (as total chlorine)—all after model calibration

Chloramines

Although the slope of the best-fit line through predicted and observed calibration data for chloramines varied from unity by more than 5%, no calibration adjustment was made. This exception was made for chloramines for several reasons:

- The relationship between predicted and observed calibration data was weak enough (as evidenced by $r^2 = 0.21$) that multiple attempts at calibration failed to produce an improvement. This was primarily due to numerous predictions of a zero residual.
- Predicted chloramine residuals should be very sensitive to reported doses of both chlorine and ammonia because of breakpoint considerations. Thus, the combined effects of errors in reported dosages likely complicated the analysis for chloramines more than that for other parameters evaluated.
- Chloramine residual is not a critical parameter because it is rarely used to achieve disinfection credit. WTP Model predictions for DBP formation are driven by the total chlorine dose, not the chloramine residual.

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An evaluation of chloramine distributions (Figure 8.8) showed that median values matched quite well, but predicted values exhibited a much greater spread. An analysis of paired data (Table 8.3) showed that significant residuals existed between paired observations and predictions for chloramine residuals.

Disinfection By-Products

Calibration of WTP Model predictions for total trihalomethanes (TTHM) and the sum of five haloacetic acids (HAA5) was more involved than that for the previously discussed parameters. This was primarily due to the desire to develop calibration factors based on finished water DBPs, because reported detention times within the treatment plant were likely to be more accurate than those associated with distribution system sampling locations (DS_AVG or DS_MAX). However, because distribution system DBPs were of greater importance to the Stage 2 DBP rulemaking process, generating calibration plots at the DS_AVG location was desirable as a check. These steps were necessary to develop calibration factors for DBP formation under free chlorine conditions, and the calibration data sets were composed of values from plants using only free chlorine within the plant (for finished water analysis) and within the distribution system (for DS_AVG analysis). The WTP Model algorithms for DBP formation with chloramines also needed calibration. These original algorithms were defined as:

DBP formation with chloramines = 0.20 × DBP formation with free chlorine

After the portion of the algorithm dealing with DBP formation with free chlorine had been calibrated as described, calibrating the overall algorithm required only evaluation of the "0.20" factor. Because chloramines are used primarily within the distribution system, calibration data sets consisting of values from plants using chloramines as a secondary disinfectant were selected, and calibration plots were generated using data from the DS_AVG location. The "0.20" factor was then modified, the calibration plot regenerated, and the process repeated until a satisfactory calibration result was obtained.

Figure 8.9 contains the complete series of calibration plots generated for TTHM (for the chloramines condition, only the plot showing the results after calibration at the DS_AVG site is

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included). Table 8.2 shows that a calibration factor of 1/0.77 (=1.3) was developed based on the original calibration plot for finished water with free chlorine. Once this factor was incorporated into the model, satisfactory results were obtained for both the finished water (slope = 0.96, r^2=0.50) and DS_AVG (slope = 1.04, r^2 = 0.52) sampling locations. The calibration analysis for chloramine conditions indicated that TTHM formation with this disinfectant should be modeled with a factor of 0.30 (as opposed to the original 0.20 factor) applied to the result of the calibrated algorithm for formation under free chlorine conditions. Table 8.2 summarizes these results for TTHM and for HAA5. Although the relationship between observed and predicted values was weaker in the HAA5 calibration analysis than in that for TTHM (as evidenced by a comparison of r^2 values), no calibration adjustment was required for HAA5 formation with free chlorine because the slope of the best-fit line fell within 2% of unity at both the finished water and DS_AVG sampling locations. However, the analysis suggested that the ratio defining HAA5 formation with chloramines versus free chlorine should be changed from 0.20 to 0.35.

Figure 8.10 presents an evaluation of WTP Model TTHM predictions on a distribution-wide basis. As the figure shows, the middle 50% of observed and predicted distributions matched very well at both the DS_AVG and DS_MAX sampling locations. However, the distributions of predicted values at these two locations contained longer upper tails; 90th and 95th percentile values were 25–30 μg/L greater than those in the observed distributions. A comparison of Figure 8.10 with Figures 8.7 and 8.8 shows a progressively increasing disparity in the tails of predicted and observed distributions as one moves from pH, to TOC, to chlorine residual, to TTHM. Because the predictions of algorithms at the beginning of this list of parameters serve as inputs to the algorithms that appear later in the list, input errors and predictive errors propagate from the pH algorithm through the TTHM algorithm, and the probability of generating outlier predictions (data in the tails of the distributions) increases accordingly. This propagation of error, along with the fact that distribution system residence times are probably the least well-known inputs, is hypothesized as the primary reason that distribution system DBP predictions exhibit the greatest amount of spread (relative to corresponding observed distributions) of any of the parameters modeled.

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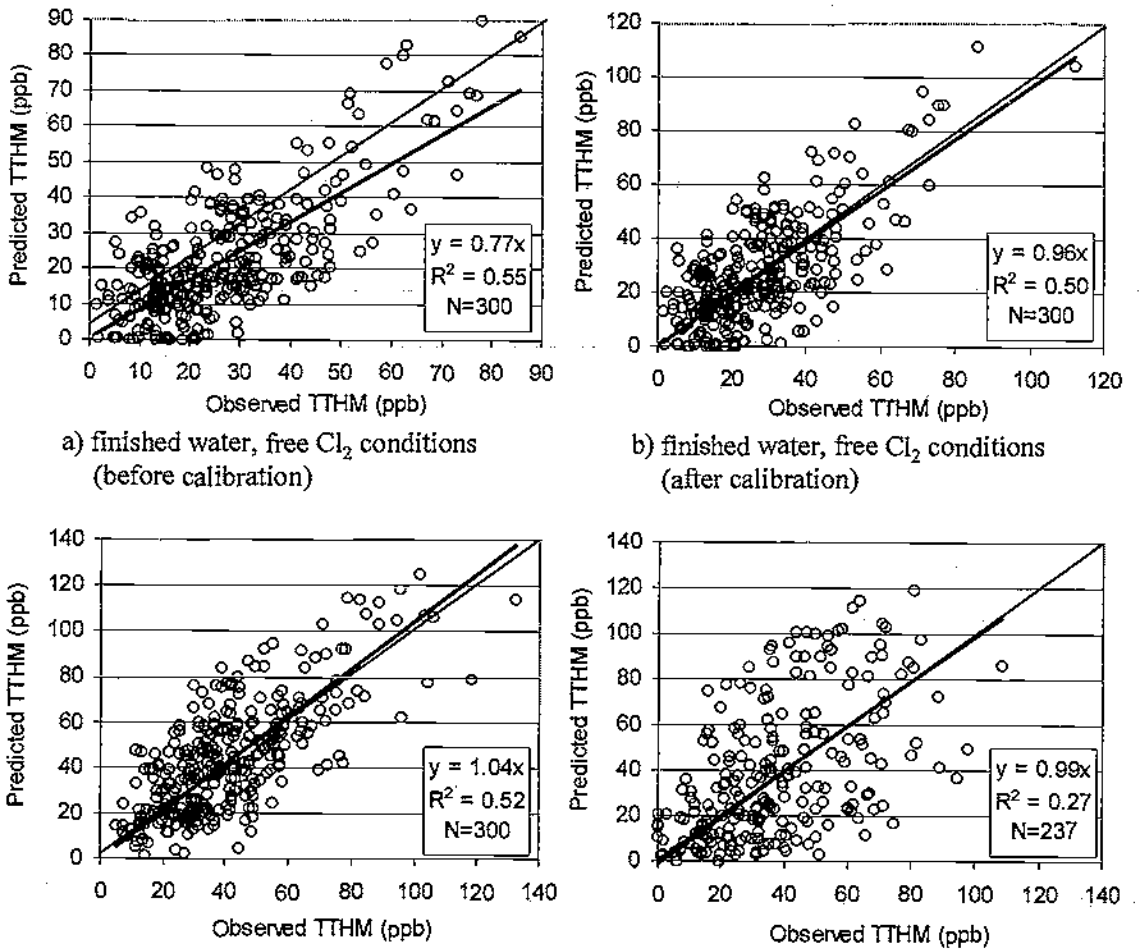

a) finished water, free Cl_2 conditions (before calibration)

b) finished water, free Cl_2 conditions (after calibration)

c) DS_AVG location, free Cl_2 conditions (after calibration)

b) DS_AVG location, chloramine conditions (after calibration)

Figure 8.9 Calibration plots for TTHM

Table 8.3 contains results of the evaluation of paired TTHM data at the DS_AVG and DS_MAX sampling locations. The table shows that for TTHM, negative residuals occurred with approximately the same frequency as positive residuals at both the DS_AVG (median residual = 1.7 μg/L) and DS_MAX locations (median residual = -1.0 μg/L). However, the magnitudes of positive residuals tended to be larger than those of the negative residuals. Furthermore, as the table indicates, relative residuals were substantial, with median values at the DS_AVG and DS_MAX locations of 47% and 45%, respectively.

Data presented in Figure 8.11 and Table 8.3 show that an evaluation of distribution-wide and paired HAA5 data yielded similar results to those obtained for TTHM.

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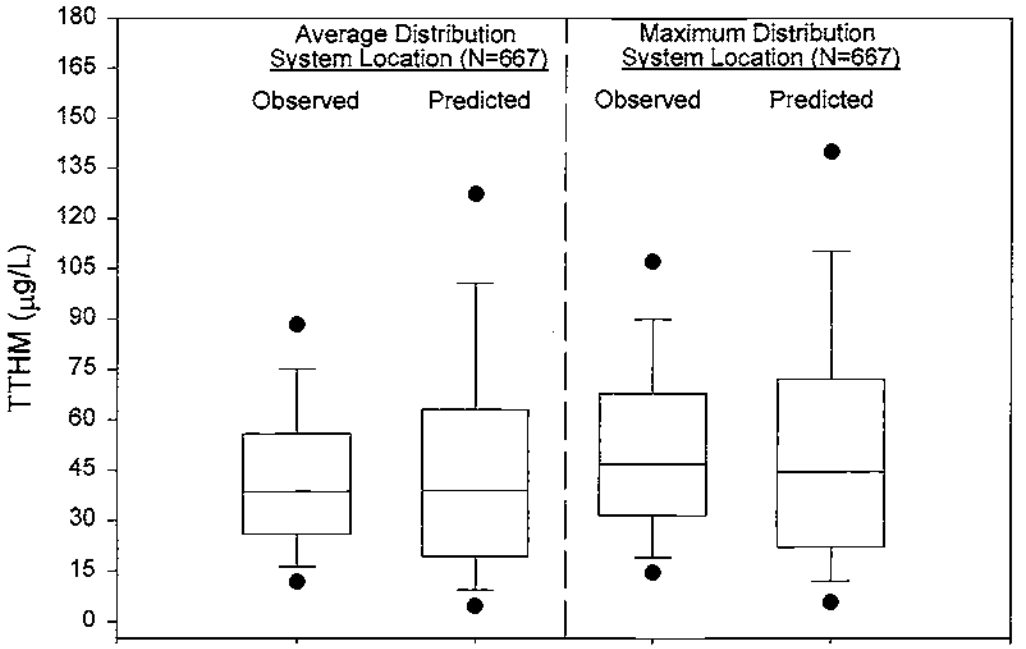

Figure 8.10 Distributions of observed and predicted TTHM values at distribution system locations with average and maximum detention times (after model calibration)

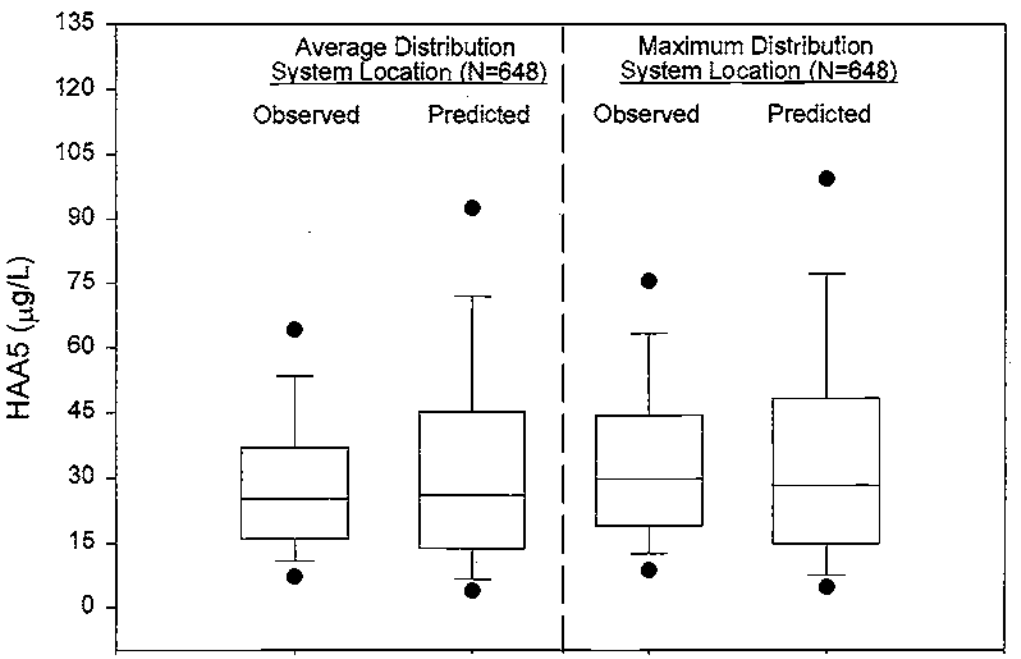

Figure 8.11 Distributions of observed and predicted HAA5 values at distribution system locations with average and maximum detention times (after model calibration)

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CONCLUSIONS

Several key WTP Model algorithms were calibrated and evaluated using full-scale data collected during the ICR. Full-scale data were used to calibrate a DBP model and to characterize its limitations. The calibration effort resulted in improvements to the following algorithms, enabling them to better match the central tendency of observed ICR data:

- pH in softening plants,
- TOC in softening plants,
- TTHM formation with free chlorine, and
- TTHM and HAA5 formation with chloramines.

The distribution-based evaluations indicated that, in general, the WTP Model could successfully translate distributions of raw water quality and treatment process inputs into predicted distributions of treated water quality that matched observed treated water quality distributions quite well. For most parameters, this assessment was most accurate for the lower 75% of a given distribution. Predicted distributions, especially for DBPs, tended to have longer upper tails, probably as a result of the propagation of input and predictive errors through the WTP Model's algorithms. This is not an insignificant finding from the standpoint of using the WTP Model within the SWAT program as a tool for forecasting national compliance with potential provisions of the Stage 2 DBP Rule. A degree of conservatism was likely introduced into the forecasting process because of the longer upper tails of the model-predicted DBP distributions.

Evaluation of paired data indicated significant differences between predicted and observed values for most parameters. Although some of the disagreement can be attributed to limitations of the ICR data, the magnitude of the differences indicates that the WTP Model may have significant limitations as a predictive tool for individual plant performance without site-specific calibration. The following sources of disagreement between predicted and observed data are hypothesized (presented in descending order of likely significance):

- Limitations in the WTP Model's ability to predict site-specific values because of its empirical basis,
- Reporting errors in ICR data (as model inputs and as observed values for comparison with model predictions),

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- Lack of correspondence between observed inputs and outputs (e.g., monthly ICR data on influent water quality, treatment conditions, and treated water quality were not necessarily collected on the same day),
- Simplifying assumptions or limitations in translating ICR treatment process information into WTP Model inputs, and
- Errors introduced during the translation of ICR data into WTP Model inputs.

In summary, this analysis showed that the WTP Model could capture trends in observed full-scale treated water quality for multiple parameters (as evidenced by the results obtained in final calibration plots) and could simulate the distributions of these parameters with reasonable accuracy. The analysis indicated that the WTP Model is a useful tool for predicting national distributions of treated water quality. The calibrated WTP Model from this work was used as the predictive engine within the SWAT to support national compliance forecasting efforts during development of the Stage 2 DBP Rule and the LT2ESWTR.

This analysis also reinforced the fact that the WTP Model was not designed to be a site-specific tool for predicting DBP formation and that more work needs to be done to develop site-specific water quality models suitable for analyzing full-scale systems.

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CHAPTER 9

BROMATE OCCURRENCE IN DISINFECTED WATER

Deborah M. Moll and Stuart W. Krasner

ABSTRACT

The 20 ozone plants and 28 chlorine dioxide plants that participated in Information Collection Rule (ICR) monitoring were required to report monthly concentrations of bromate before the point of disinfectant addition and in the finished water. Bromate was detected in only 11% of the finished water samples collected by ICR chlorine dioxide plants, and concentrations ranged from less than the minimum reporting level of 0.2 μg/L to 2.38 μg/L. This suggests that bromate is not an important by-product of chlorine dioxide disinfection. Finished water bromate concentrations at the 20 plants that used ozone during the ICR ranged from less than 0.2 μg/L to 25.1 μg/L. Increases in influent bromide concentration and ozone dosage were each associated with increased bromate formation. However, no nationwide association was found between bromate concentration and total organic carbon, pH, temperature, or ammonia concentration or between bromate concentration and ozone residual or ozone CT (the product of residual disinfectant concentration and time). An apparent association between increased alkalinity and increased bromate formation may have been related in part to other differences in water quality (bromide concentration and pH).

The six ICR plants that used hypochlorite for postdisinfection had, on average, 0.84 μg/L more bromate in the finished water than the amount formed during ozonation, whereas the 14 ozone plants that used chlorine gas averaged 0.2 μg/L less bromate in the finished water than in water sampled immediately after ozonation. No ICR plants had running annual average bromate concentrations that exceeded the bromate standard of 10 μg/L. However, bromate occurrence can vary over time at plants whose source water undergoes significant shifts in bromide loading.

The level of bromate formation shown in this nationwide dataset was consistent with other data indicating relatively low bromate formation when water was ozonated at dosages targeted to inactivate *Giardia* and viruses and to control taste- and odor-producing compounds. Although these plants did not exceed the bromate standard when using relatively low ozone dosages, much higher ozone dosages will be required to inactivate *Cryptosporidium*, and this will lead to increased bromate formation. In addition, the contribution of bromate from hypochlorite to the total concentration of bromate in finished water may cause compliance problems for some plants that use hypochlorite as a disinfectant if the maximum contaminant level for bromate is decreased to 5 μg/L. The ability of plants to use ozone for pathogen inactivation will depend on the amount of bromide in the water and on ozonation practices, which must be managed to allow plants to achieve inactivation while minimizing bromate formation.

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INTRODUCTION

As part of developing regulations to protect the public from adverse health effects of disinfection by-products (DBPs) and microbiological pathogens, the U.S. Environmental Protection Agency (USEPA) promulgated the Information Collection Rule (ICR) (USEPA 1996a). The primary objective of the ICR was to collect data that could be used in developing the Stage 2 Disinfection By-Products (DBP) Rule and the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR). USEPA had previously proposed that the LT2ESWTR might require inactivation of *Cryptosporidium* in addition to physical removal (USEPA 1994)..

Common water treatment disinfectants such as chlorine or chloramines are not effective at inactivating *Cryptosporidium*. Ozone is effective against *Cryptosporidium*, although the ozone dosages necessary for *Cryptosporidium* inactivation are much greater than those used to meet existing disinfection requirements (Oppenheimer et al. 1997a). However, ozonation forms bromate (sometimes abbreviated BrO_3^-) as a by-product in water sources in which bromide ion is present (Haag and Hoigné 1983). Limited data from plants using chlorine dioxide suggested that bromate can also be formed by sunlight-catalyzed reactions between chlorine dioxide and the bromide ion (USEPA 1996b). The Stage 1 Disinfectants/DBP Rule (USEPA 1998) established a maximum contaminant level (MCL) goal of zero for bromate, based on the results of several cancer studies (Kurokawa et al. 1986a, 1986b; DeAngelo et al. 1998), and set the MCL for bromate at 10 μg/L.

ICR ozone plants and chlorine dioxide plants used these disinfectants for a variety of purposes, including: (1) to meet the requirements of the Surface Water Treatment Rule (SWTR) for inactivation of *Giardia* and viruses (USEPA 1989); (2) for taste and odor control; (3) to control iron and manganese; and (4) to oxidize micropollutants, as described in publications by Ferguson, Gramith, and McGuire (1991) (for ozone) and by Aieta and Berg (1986) (for chlorine dioxide). The CT (the product of disinfectant residual concentration, C, and contact time, T) required for *Cryptosporidum* inactivation is 7.5 to 10 times that required for *Giardia* inactivation (Finch et al. 1994; Wickramanayake, Rubin, and Sproul 1985; Oppenheimer et al. 1997a, 1997b).

The 20 ICR plants that used ozone during one or more of the 18 months of data collection (July 1997 to December 1998) were required to monitor for bromate. Once a month, these plants

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reported bromate concentrations at the ozone-contactor influent and ozone-contactor effluent and in finished water. The 28 ICR plants that used chlorine dioxide were required to report monthly concentrations of bromate at a location before the first chlorine dioxide application and in finished water. Details of the ICR bromate monitoring requirements for ozone and chlorine dioxide plants are available in the *ICR Sampling Manual* (USEPA 1996b).

The Chemistry of Bromate Formation

Ozone reacts with bromide in water to form bromate (Haag and Hoigné 1983). Bromide present in source water may originate from dissolution of geologic formations, saltwater intrusion, saltwater aerosol deposition, connate water, oil field brines, or anthropogenic sources, or it may exist as an impurity in chlorinating solutions (Amy et al. 1994; Krasner, Sclimenti, and Means 1994). The formation of bromate during ozonation of water containing bromide involves a complex series of chemical reactions. Initially, ozone oxidizes bromide to hypobromous acid/hypobromite ion ($HOBr/OBr^-$). OBr^- can react with molecular ozone or with hydroxyl radicals to form bromite, which is then oxidized by molecular ozone to form bromate (Von Gunten and Oliveras 1998).

Ozone residual plays an important role in bromate formation (Krasner et al. 1993). Because the reaction of ozone with natural organic matter (NOM) is rapid, NOM typically exerts most of the initial ozone demand. The residual ozone then reacts with bromide to form bromate. Because CT also depends on ozone residual, treatment plants must balance the need to achieve a certain CT for inactivation credit with the need to minimize bromate formation.

Bromate formation is highly dependent on pH because pH governs the ratio of HOBr to OBr^-. At low pH values, HOBr, which does not react with ozone to form bromate, dominates. However, HOBr does react with NOM to form bromine-substituted organic by-products (Haag and Hoigné 1983). At high pH values, OBr^- is the dominant species and can be oxidized by ozone to form bromate. High pH also promotes the formation of hydroxyl radicals, leading to higher bromate formation. Thus, decreasing the pH can be an effective way to control bromate formation (Krasner et al. 1993, Coffey et al. 1998) but may lead to formation of bromine-substituted organic DBPs.

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Adding ammonia before ozonation reduces bromate formation because the ammonia acts as a sink for HOBr and OBr^-, which preferentially form bromamines in the presence of ammonia (Von Gunten and Hoigné 1992). However, when the amine group of bromamine is oxidized by ozone (a relatively slow reaction), bromide is released and may subsequently be oxidized to bromate.

Temperature affects the oxidation of bromide by changing the reaction rates, and alkalinity can have various effects on bromate formation. For example, intermediate steps in bromate formation can proceed through a radical-mediated mechanism with a secondary oxidant such as the carbonate radical (Von Gunten, Bruchet, and Costentin 1996).

Other Sources of Bromate in Drinking Water

Bromate has been found as a contaminant in hypochlorite (bleach) solutions (Bolyard, Fair, and Hautman 1992), and concern about bromate in hypochlorite solutions is increasing. More treatment plants are using hypochlorite for chlorination because of safety issues related to handling gaseous chlorine and the requirements of risk management plans. Bromate is formed when bromide-containing brine is oxidized during the manufacture of hypochlorite solutions. In a study of 14 U.S. drinking water systems using hypochlorination, bromate was detected in more than half of the hypochlorite stock solutions in concentrations ranging from 4 to 51 mg/L (Bolyard, Fair, and Hautman 1992). However, bromate was not detected in finished water chlorinated with these hypochlorite solutions (the minimum reporting level [MRL] was 10 μg/L). Alternatively, in a study of nine treatment works in the United Kingdom, bromate concentrations ranged from 50 to 1,150 mg/L in hypochlorite stock solutions and from 3 to 28 μg/L in the treated water supplies (Packham 1999).

ICR DATA

Sources of ICR Bromate Data

Because ICR ozone and chlorine dioxide plants were required to collect bromate data monthly, each of the 20 ozone plants and the 28 chlorine dioxide plants collected bromate data

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for at least one month of the 18 months of ICR monitoring. ICR bromate samples were analyzed by utility and commercial laboratories using USEPA Method 300.0. (USEPA 1993). The USEPA Technical Support Center laboratory also analyzed bromate samples using the Selective Anion Concentration and Chromatography (SAC) method (Hautman 1992), which can measure very low concentrations of bromate. For ICR reporting, the MRL for Method 300.0 was 5 μg/L; the MRL for the SAC method was 0.2 μg/L.

Table 9.1 summarizes the cumulative probability distributions of the 18 months of bromate data collected by chlorine dioxide and ozone plants; these data were reported by the utilities using EPA Method 300.0 (BRO3_UTIL) and by USEPA using the SAC method (BRO3_EPA). When USEPA Method 300.0 was used for the analyses, bromate was detected in only 1% of finished water samples from chlorine dioxide plants and 21% of finished water samples from ozone plants. In contrast, when the SAC method was used, bromate was detected in 11% and 89% of samples from chlorine dioxide and ozone plants, respectively.

With an MRL of 5 μg/L, USEPA Method 300.0 did not effectively quantify bromate at the lower concentrations needed to support development of the Stage 2 DBP Rule. Because USEPA Method 300.0 lacked the sensitivity to adequately characterize bromate in ICR samples, all further discussion of bromate data in this chapter will focus on data generated using the SAC method.

Bromate Occurrence in Plants Using Chlorine Dioxide

Bromate was detected in only 11% of the finished water samples collected at ICR chlorine dioxide plants; concentrations ranged from less than the MRL of 0.2 μg/L to 2.38 μg/L (Table 9.1). None of the 28 chlorine dioxide plants partipating in ICR monitoring used hypochlorite solutions in their disinfection schemes. These data suggest that bromate is not an important by-product of chlorine dioxide disinfection.

Bromate Occurrence in Plants Using Ozone

Finished water bromate concentrations at the 20 plants using ozone during at least one of the 18 months of ICR data collection ranged from less than the MRL of 0.2 μg/L to 25.1 μg/L

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(Table 9.1). The mean and median concentrations were 2.7 and 1.9 μg/L, respectively. When bromate was not detected (i.e., the concentration was <MRL), the <MRLs were set at zero for computing the mean concentration. Alternatively, when percentiles (including the median) were determined, <MRLs were counted and sorted with the values at or above the MRL.

In a recent American Water Works Association Research Foundation (AwwaRF) study of bromate in drinking water supplies with low and moderate concentrations of bromide, Douville and Amy (2000) surveyed 21 utilities in the United States and 3 utilities in France. The median and 90th percentile concentrations of bromide in these water supplies were 44 and 132 μg/L, respectively. Using a bromate method with an MRL of 0.4 μg/L, bromate was detected in most of the ozonated water supplies (the median and 90th percentile concentrations were 1.9 and 13 μg/L, respectively). The ICR and AwwaRF studies examined ozone plants with comparable concentrations of bromide (Table 9.2), and, in general, similar concentrations of bromate were produced.

Table 9.1

Distribution of finished water bromate concentrations

at ICR treatment plants using chlorine dioxide or ozone as the primary disinfectant*

	Primary disinfectant			
	Chlorine dioxide		Ozone	
Statistic	BRO3_EPA†	BRO3_UTIL‡	BRO3_EPA†	BRO3_UTIL‡
Percent less than MRL	89	99	18	79
Mean (μg/L)	0.05	N/A	2.7	N/A
Standard deviation	0.21	N/A	3.1	N/A
Minimum (μg/L)	<0.2	<5	<0.2	<5
5th percentile (μg/L)	<0.2	<5	<0.2	<5
10th percentile (μg/L)	<0.2	<5	<0.2	<5
25th percentile (μg/L)	<0.2	<5	0.43	<5
50th percentile (μg/L)	<0.2	<5	1.9	<5
75th percentile (μg/L)	<0.2	<5	3.5	<5
90th percentile (μg/L)	0.22	<5	7.3	7
95th percentile (μg/L)	1.00	<5	10.9	26.9
Maximum (μg/L)	2.38	8.0	25.1	50
Number of observations	362	304	302	277

*Based on the cumulative probability distributions of 18 months of data from ICR chlorine dioxide and ozone plants
†BRO3_EPA=analysis by the SAC method (MRL=0.2 μg/L)
‡BRO3_UTIL=analysis by USEPA Method 300.0 (MRL=5 μg/L)
N/A=not available

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Table 9.2

Distribution of water quality parameters at the point of ozonation (or plant influent) in ICR plants using ozone

Statistic	pH	Alkalinity (mg/L as $CaCO_3$)	Temperature (°C)	TOC (mg/L)	Bromide (µg/L)	NH_3-N* (mg/L)
Mean	7.89	90	17.1	4.0	90	0.13
Standard deviation	0.65	46	6.5	1.9	70	0.26
Minimum	6.07	2	1.0	<0.7	<20	<0.10
5th percentile	6.70	4	6.5	1.8	<20	<0.10
10th percentile	6.97	29	8.9	2.1	<20	<0.10
25th percentile	7.60	59	12.1	2.6	30	<0.10
50th percentile	7.91	88	17.0	3.6	60	0.10
75th percentile	8.20	120	22.2	4.7	140	0.10
90th percentile	8.44	146	25.7	7.0	200	0.22
95th percentile	9.22	161	27.0	7.6	230	0.90
Maximum	9.81	260	33.0	10.8	300	1.70
Number of observations	324	320	322	278	292	319

* NH_3-N = the concentration of ammonia expressed as nitrogen

In the early 1990s, an AwwaRF study of ozone treatment at 10 North American utilities was conducted at pilot- and full-scale (Glaze and Weinberg 1993). At the ozone dosages investigated, bromate was not detected in the effluent of four of the six utilities that had influent bromide concentrations of ≤60 µg/L. The analytical methods used to measure bromate during these studies had MRLs of 5 to 10 µg/L (Glaze and Weinberg 1993, Krasner et al. 1993). Bromate concentrations of 5 to 8 µg/L were occasionally reported for the two other utilities with low influent concentrations of bromide. At three of the four utilities in which influent bromide concentrations were 180 to330 µg/L, bromate was typically detected at concentrations of 9 to 18 µg/L in the finished water. No bromate was detected at the remaining utility with high-bromide source water, which was characterized by extremely high concentrations of total organic carbon (TOC) (26 mg/L) and hydrogen sulfide (Dunkelberger et al. 1992). The high concentrations of TOC and hydrogen sulfide may have produced a high initial ozone demand, thus decreasing the amount of ozone available to participate in the slower reactions leading to bromate formation.

One of the utilities with high-bromide source water that was part of the AwwaRF study conducted in the early 1990s (utility J) also participated in the ICR. During ICR monitoring, influent bromide concentrations at utility J (Table 9.3) were much lower than those reported in the early 1990s (Krasner et al. 1993), and, consequently, the finished water contained less

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bromate during the ICR (Table 9.3). Thus, bromate formation can vary over time at utilities whose source water undergoes significant shifts in bromide loading. Variations in other water quality parameters and in ozonation conditions also cause bromate formation to vary.

Water Quality Parameters at ICR Ozone Plants

During the 18-month monitoring period, all ICR treatment plants collected monthly samples at the plant intake to monitor several water quality parameters, including those that affect bromate formation: pH, temperature, alkalinity, TOC, bromide, and ammonia-nitrogen. Plants using ozone were also required to measure pH, temperature, alkalinity, and TOC at the first point of ozonation. For five ozone plants, the ICR Auxiliary Database 1 did not contain TOC concentrations at the point of ozonation for any of the 18 months of sample collection; therefore, influent TOC concentrations at these five plants were used for the ICR data analyses. Influent concentrations of bromide and ammonia-nitrogen were used for 18 of the 20 plants. The two remaining plants measured these constituents at the point of ozonation, and concentrations at the point of ozonation were used for the analyses. At utilities that preozonate, most water quality parameters would be the same at the point of ozonation and in the plant influent.

Table 9.3

Comparison of influent bromide concentrations at ICR ozone plants with historical bromide data from the same plants

Utility	Historical bromide concentrations (1988–92) (µg/L)			ICR bromide concentrations (1997–98) (µg/L)		
	Minimum	Median	Maximum	Minimum	Median	Maximum
Utility J*	320	395	500	24	75	223
Utility 18†	37	50	62	27	39	46
Utility A*	20	25	30	29	34	67
Utilities 19‡, 1§, and D*	40	130	280	<20	30	100
Utility I*	40	40	50	<20	<20	58
Utilities 6‡ and 7†	40	60	70	28	51	76
Utility 4§		320		200	240	300

* Krasner et al. 1993
† Amy et al. 1994
‡ Krasner et al. 1989
§ Jacangelo et al. 1989

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The distributions of water quality parameters at the point of ozonation (or plant influent) at ICR ozone plants (Table 9.2) fell within the normal ranges of these parameters in raw and partially treated water supplies at ICR plants as a whole. (See Chapter 3 [Roberson 2002] for a discussion of influent water quality data from all ICR treatment plants.) The relatively high pH values reported at the point of ozonation suggest that ICR utilities were not practicing low-pH ozonation to minimize bromate formation. Similarly, most of the ammonia concentrations were probably too low (<0.2 mg/L as NH_3-N) to control bromate formation (Coffey et al. 1999).

Bromide in ICR Source Water Supplies

At the 20 ICR plants using ozonation, bromide concentrations in plant influent over the 18-month sampling period ranged from less than the MRL of 20 µg/L to 300 µg/L (median and 90th percentile concentrations were 60 and 200 µg/L, respectively) (Table 9.2). When the distribution of influent bromide concentrations at all ICR plants was segmented by primary disinfectant, the data indicated that plants using alternative oxidants tended to treat water with higher bromide concentrations than plants using chlorine for primary disinfection.

Bromide data from the ICR ozone plants (1997–98) were compared with data from two historical nationwide studies, a nationwide bromide survey of 100 utilities (88 randomly selected, 12 targeted) conducted October 1991 through April 1993 (Amy et al. 1994), and a 35-utility nationwide DBP study conducted summer 1988 through winter 1989 (Krasner et al. 1989). The median bromide concentration in the nationwide bromide survey (56 µg/L) was similar to that in the ICR data (60 µg/L). However, the 90th percentile bromide concentration in the nationwide bromide survey (266 µg/L) was greater than the 95th percentile bromide concentration at ICR ozone plants (Table 9.2). In the 35-utility DBP study, the median and 90th percentile bromide concentrations of 110 and 548 µg/L, respectively, were higher than those at ICR ozone plants.

Bromide data from 7 of the 20 ICR ozone plants were included in one or more of several historical studies (Table 9.3). Utility J had much higher influent bromide concentrations during the late 1980s and early 1990s (historical median of 395 µg/L versus ICR median of 75 µg/L) because of a drought that had resulted in increased saltwater intrusion into the watershed (Krasner et al. 1993; Krasner, Sclimenti, and Means 1994). Utility D also had much higher

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influent bromide concentrations in the late 1980s and early 1990s (historical median of 130 μg/L versus ICR median of 30 μg/L) (Krasner et al. 1993) because during that period it had used a large percentage of an alternative water supply characterized by high bromide concentrations. Bromide concentrations at the remaining five ICR ozone plants for which historical bromide data were available did not differ significantly during these two time periods.

ICR Ozonation Conditions

Total plant ozone dosages, theoretical ozone CT values, and ozone residuals were reported by the utilities and compiled in the ICR database. The ozone dosage entered into the ICR database was the sum of all ozone doses for all ozone contactors reported by the utility. The reported ozone CT was the theoretical CT value calculated by the utility, based on the method of estimating ozone CT values set forth in the SWTR. Ozone residual concentrations were reported by the utilities and reviewed by experts for accuracy. The reviewed data (ICR Auxiliary Database 1, parameter EXO3RES) were used in these analyses. Over the 18-month monitoring period, ozone dosages for the 20 ozone plants ranged from 0.5 mg/L (5th percentile) to 12.0 mg/L, with a mean of 2.34 mg/L (Table 9.4). Utilities reported ozone CT values ranging from 0 to 60.0 mg/L-min (the mean and median were 2.40 mg/L-min and 0.48 mg/L-min, respectively). Ozone residuals ranged from less than the MRL of 0.1 mg/L to 0.5 mg/L (median = 0.1 mg/L).

Some ICR utilities set disinfection dosages to meet the *Giardia* and virus inactivation criteria established by the SWTR (USEPA 1989). The theoretical log inactivation of *Giardia* and viruses achieved by ozone at each plant during each month of ICR monitoring was reported by the utilities and compiled in the ICR database. Inactivation ranged from 0.1-log to 3.4-log (10th to 90th percentile) for *Giardia* (median = 0.5-log) and 0.0-log to 4.8-log for viruses (median = 2.0-log). The ICR utilities were not operated for *Cryptosporidium* inactivation, and many were not operated for *Giardia* and virus inactivation credit but rather for removal of taste and odor compounds. *Cryptosporidium* inactivation would require much higher ozone CT values—an estimated 5 to 20 times higher than those used for *Giardia* inactivation (Oppenheimer et al. 1997b).

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Table 9.4

Distribution of ozonation parameters and pathogen inactivation levels reported for ICR plants using ozone

Statistic	Ozone CT (mg/L-min)	Ozone dosage (mg/L)	Ozone residual (mg/L)	Log inactivation of *Giardia*	Log inactivation of viruses
Mean	2.40	2.34	0.08	1.3	2.1
Standard deviation	7.19	1.85	0.09	1.5	1.8
Minimum	0	N/A	<0.1	0	0
5th percentile	0.01	0.51	<0.1	0	0
10th percentile	0.10	0.65	<0.1	0.1	0
25th percentile	0.23	1.2	<0.1	0.5	0.8
50th percentile	0.48	1.8	0.1	0.5	2.0
75th percentile	1.81	2.9	0.1	1.7	2.8
90th percentile	2.31	5.0	0.2	3.4	4.8
95th percentile	15.0	6.0	0.2	3.7	5.8
Maximum	60.0	12.0	0.5	9.9	9.9
Number of observations	323	316	282	315	315

N/A=not available

Impact of Water Quality and Ozonation Conditions on Bromate Formation

The impact of water quality parameters and ozonation conditions on bromate formation was analyzed using the 18 months of ICR monitoring data. As mentioned, the water quality analytes included alkalinity, TOC, pH, and temperature (generally measured at the first point of ozonation) and bromide and ammonia-nitrogen (measured at the plant influent). Ozonation parameters reported by each utility included ozone dosage, ozone CT, and ozone residual. The ozone-to-TOC ratio was calculated using the reported ozone dosage and TOC values. Bromate data paired with missing data for other water quality parameters were not included in that particular analysis.

The bromate data were segmented into bins for each water quality and ozonation parameter, and cumulative probability distributions of bromate concentrations in finished water were calculated. For example, the distributions of bromate formation within quintiles of influent bromide concentration (each representing approximately 20% of the data) were compared in the analysis described in the following section. Binned data included values that were <MRL for bromate concentration and for water quality parameters. Bromate values reported as <MRL were designated as zeros for these analyses.

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Bromide

The formation of bromate is highly sensitive to influent bromide concentration (Najm and Krasner 1995, Coffey et al. 1998). Because bromate formation also depends on many other water quality and ozonation parameters, a simple plot of bromide versus bromate in any survey of a wide range of water supplies does not typically yield a good relationship. However, when bromate concentrations at the 20 ICR ozone plants were compared within quintiles of bromide concentrations, the overall effect of higher influent bromide concentrations was increased bromate formation (Figure 9.1). In the ICR dataset, the median bromate concentration in finished water increased from less than 0.2 μg/L in plants with influent bromide concentrations of <MRL of 20 μg/L to a bromate concentration of 3.4 μg/L in plants with influent bromide concentrations >100 μg/L. The maximum finished water bromate concentration in the lowest quintile of bromide concentrations was 2.7 μg/L, whereas more than 60% of the samples in the two highest quintiles (bromide >50 μg/L) had finished water bromate concentrations greater than this value.

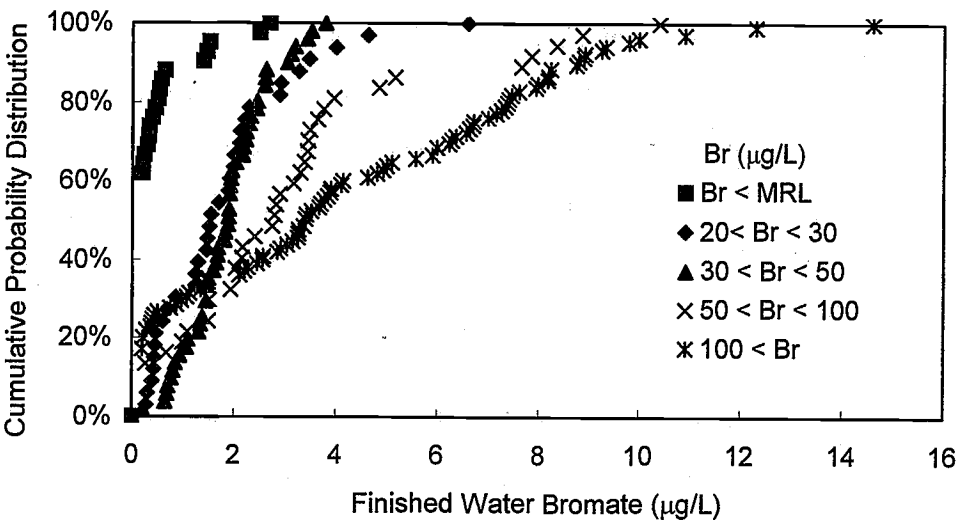

Figure 9.1 Effect of influent bromide concentration on bromate formation at ICR ozone plants

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In each quintile with a measurable amount of bromide, approximately 30% of the samples contained low concentrations of bromate (<2 μg/L). In these samples, higher bromide concentrations alone did not appear to result in increased bromate formation. This result is due to the impact of other water quality and ozonation parameters on bromate formation. However, in each quintile, most of the samples showed increased bromate formation with higher bromide concentrations. During periods when the source water of certain utilities may contain higher bromide concentrations (Table 9.3), more bromate formation than that observed during ICR monitoring can be expected. However, changes in other parameters, such as ozonation conditions, also affect bromate formation.

Ozonation conditions

To analyze the effect of ozone on bromate formation, finished water bromate concentrations were binned by quintiles of ozone dosage and ozone CT values and sextiles of ozone-to-TOC ratios. Utilities reported ozone residual concentrations ranging from 0 to 0.5 mg/L, and reported concentrations increased in 0.1 mg/L steps. Bromate concentrations were compared across the bins for each ozone parameter and at each of the reported ozone residual concentrations. Increasing the ozone dosage led to increased bromate formation at ozone doses <3 mg/L, but ozone doses ≥3 mg/L did not lead to greater bromate formation (Figure 9.2). The median bromate concentration in finished water increased from 0.6 μg/L in samples with ozone doses of <1 mg/L to 3.0 μg/L in samples with ozone doses of 1.5–2 mg/L, then remained relatively constant over the two bins with the highest ozone dosages. The 75th and 90th percentile bromate concentrations increased over the first four bins (up to ozone doses of 3 mg/L) from 1.3 μg/L to 6.7 μg/L and from 2.2 μg/L to 8.2 μg/L, respectively, before decreasing slightly in the bin of highest ozone dosages. Although ozone residual, ozone CT, and ozone-to-TOC ratio affect bromate formation at an individual plant level (Coffey et al. 1998), the ICR data did not appear to represent any overall trends for these parameters at the national level. More details on conditions in individual contactors at each ozone plant are available in ICR Auxiliary Database 2 (USEPA 2000).

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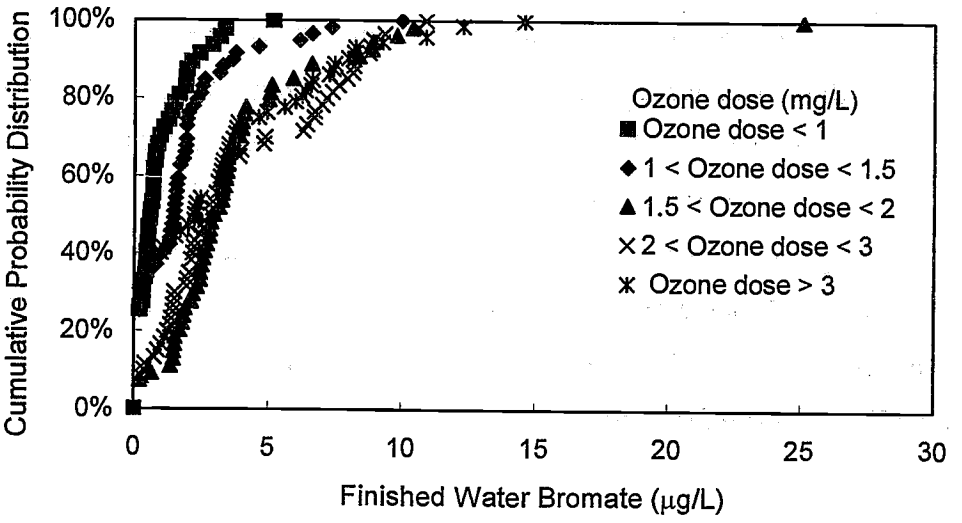

Figure 9.2 Effect of ozone dosage on bromate formation at ICR ozone plants

In bench-scale tests with ozone dosages designed to inactivate *Cryptosporidium*, Song et al (1997) found that water sources with bromide concentrations >100 μg/L consistently formed bromate concentrations >10 μg/L. Likewise, in demonstration-scale tests of water sources containing ~100 to 400 μg/L of bromide, ozonation designed to achieve ~1-log inactivation of *Cryptosporodium* at ambient pH (~8) resulted in the formation of 21 to 48 μg/L of bromate (Coffey et al. 1998). When water sources containing 100 to 110 μg/L of bromide were ozonated in demonstration-scale tests to achieve only ~2-log inactivation of *Giardia*, only 4 to 6 μg/L of bromate was formed (Coffey et al. 1998). The ICR ozone plants used relatively low ozone doses (median = 1.8 mg/L) compared with those used in these *Cryptosporidium* studies (e.g., ozone doses of 4.0 mg/L) (Coffey et al. 1998) because they targeted conditions to achieve inactivation of *Giardia* and viruses and oxidation of taste- and odor-producing compounds. Thus, bromate formation reported during ICR monitoring was lower than the bromate formation that would be expected if these plants operated under conditions designed for *Cryptosporidium* inactivation.

The use of ozone dosages sufficient to inactivate *Cryptosporidium* is expected to increase the percentage of bromide that is oxidized to bromate. In the ICR database, the conversion of bromide to bromate on a molar basis was <17%, with median and 75th percentile values of 2.2% and 3.4%, respectively. In the recent AwwaRF study on bromate, the median and

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75th percentile molar conversions were 2.1 and 4.9%, respectively (Douville and Amy 2000). In demonstration-scale tests over a wide range of ozone dosages at ambient pH, the molar conversion typically ranged from ~2 to 3% for ~2-log inactivation of *Giardia* to ~10 to 14% for ~1-log inactivation of *Cryptosporidium* (Coffey et al. 1998).

Alkalinity

When data from ICR ozone plants were pooled, bromate formation appeared to increase with increasing alkalinity (Figure 9.3). The bromate concentrations were segmented by quartiles of alkalinity measured at the point of ozonation. In the lowest quartile, for samples with alkalinity <60 mg $CaCO_3$/L, bromate concentrations in finished water were <8.4 μg/L, with a median concentration of 0.2 μg/L. Samples in the two middle quartiles, with alkalinity ranging from 60 to 90 and 90 to 120 mg $CaCO_3$/L, had similar distributions of bromate in finished water, with median concentrations of 2.2 μg/L. The median bromate concentration in samples with alkalinity >120 mg $CaCO_3$/L, 3.3 μg/L, was the highest in the alkalinity quartiles.

The apparent relation between alkalinity and bromate formation may have been affected by how influent bromide concentrations and pH values were segmented in this analysis. In the nationwide bromide survey (Amy et al. 1994), all of the water sources with high bromide concentrations had moderate to high alkalinity values. There is no reason that high-alkalinity water sources represented in the ICR database should have high bromide concentrations. Nevertheless, the high-alkalinity sources tended to have high bromide concentrations, which led to higher bromate formation than would be expected if high alkalinty and high bromide values had not occurred concurrently. Likewise, the low-alkalinity sources had low pH (less buffering capacity), which would be expected to result in less bromate formation. Thus, the effect of alkalinity on bromate formation at ICR ozone plants was, in part, related to other differences in water quality (i.e., bromide, pH).

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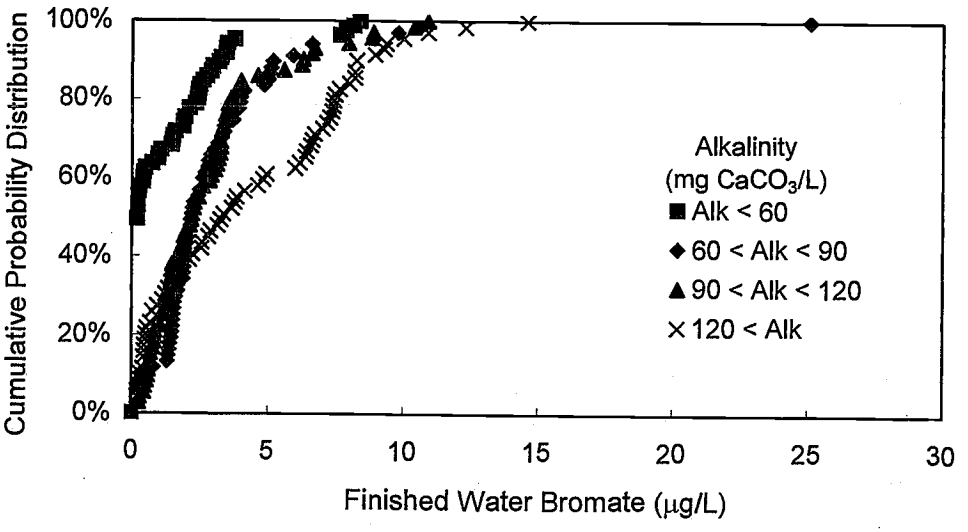

Figure 9.3 Apparent effect of alkalinity on bromate formation at ICR ozone plants

TOC

When ICR bromate concentrations were segmented into quartiles by TOC concentration (Figure 9.4), TOC did not appear to have any systematic effect on bromate formation at the point of ozonation. TOC competes with bromide for ozone and hydroxyl radicals and reacts with $HOBr/OBr^-$, the main intermediary in bromate formation. Thus, higher TOC concentrations may lead to decreased bromate formation (Westerhoff et al. 1998). However, when a constant CT value is targeted, an increase in TOC will increase ozone demand, and thus more ozone will be required. Najm and Krasner (1995) found that when a constant CT value was targeted, increases in TOC also resulted in increases in bromate formation. NOM characteristics can also be a factor. NOM with higher humic content reacts more with ozone than NOM with low humic content (Douville and Amy 2000), which tends to decrease bromate formation.

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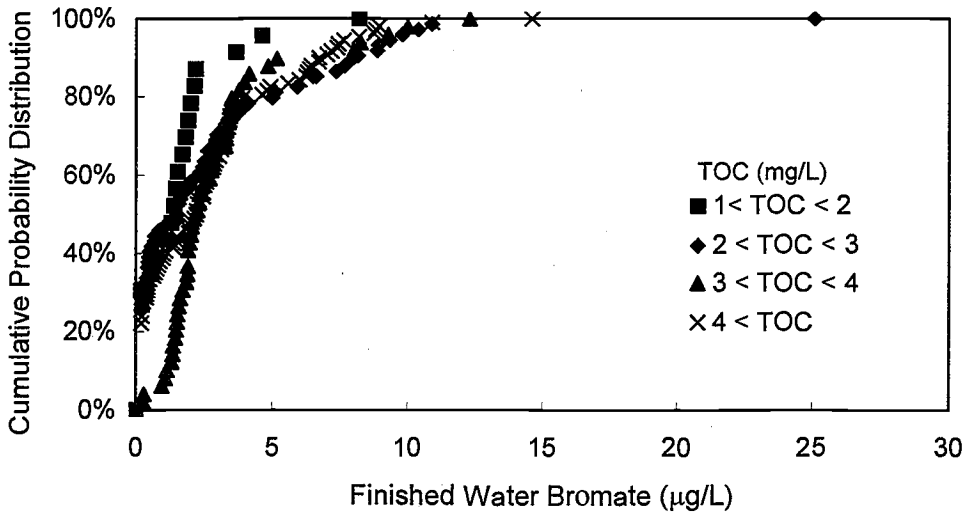

Figure 9.4 Effect of TOC on bromate formation at ICR ozone plants

Other Water Quality Parameters

Temperature, pH, and ammonia-nitrogen concentrations also showed no consistent effect on bromate formation when data from all ICR ozone plants were pooled. This result is not surprising, considering the relatively low ambient concentrations of ammonia and the relatively high pH at which ozonation occurred in ICR utilities (Table 9.2). Various researchers (Krasner et al. 1993; Allgeier, Summers, and Shukairy 1995; Coffey et al. 1998) have found that pH at the point of ozonation must be neutral or acidic to significantly reduce bromate formation. In the ICR database, 75% of the utilities ozonated at a pH of 7.6 or higher. When the addition of ammonia (0.2 to 2 mg/L as N) was evaluated at pilot- or demonstration-scale, bromate minimization was observed to varying degrees (Krasner et al. 1993, Coffey et al. 1999). However, 90% of the water sources in the ICR database had ammonia-nitrogen concentrations ≤0.2 mg/L, indicating that these utilities were not adding ammonia to minimize bromate formation.

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Hypochlorite's Contribution to Bromate Formation

When used for postdisinfection, hypochlorite solutions contaminated with bromate will contribute to bromate formation. The quality of hypochlorite stock solutions varies considerably, affecting the amount of bromate that is added as contamination (Bolyard, Fair, and Hautman 1992; Packham 1999) The six ICR ozone plants using hypochlorite for postdisinfection had, on average, 0.84 μg/L more bromate in the finished water than the amount formed during ozonation (Figure 9.5). The 90th percentile and maximum contributions from hypochlorite solutions were 2.1 and 4.7 μg/L, respectively. The 14 ozone plants that used chlorine gas averaged 0.2 μg/L less bromate in the finished water than in water sampled immediately following ozonation. Bromate concentrations in the ozone contactor effluent and the plant effluent were the same at these plants. Based on the current quality of commercial hypochlorite solutions, the contribution of hypochlorite to total bromate concentrations in finished water may cause compliance problems in many plants if the MCL for bromate is decreased to 5 μg/L.

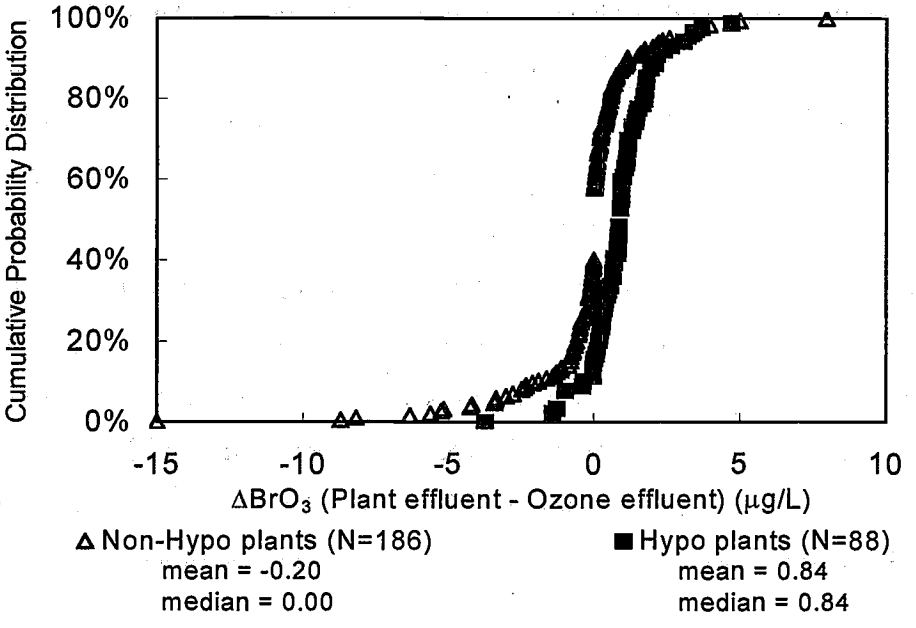

Figure 9.5 Contribution of hypochlorite solutions (Hypo) to bromate in the finished water of ICR ozone plants

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Compliance of ICR Plants With the Bromate MCL

Running annual averages (RAAs) of finished water bromate concentrations at each plant were calculated for the seven 12-month periods represented in the 18-month ICR data collection effort. RAAs were calculated only for 12-month periods for which at least eight data points were available. Figure 9.6 shows the maximum RAA (MRAA) for each plant during this period. The mean and median RAAs of all monthly bromate values from the 20 plants were 3.1 μg/L and 2.6 μg/L, respectively. No ICR plant had any RAA values that exceeded the 10 μg/L bromate standard for this time period, and only one plant had any RAA values >8 μg/L (the MCL minus a 20% safety factor).

Although these plants did not exceed recently promulgated compliance limits under conditions targeted at inactivating *Giardia* and viruses and controlling taste- and odor-producing compounds, much higher ozone dosages will be required for *Cryptosporidium* inactivation. In addition, the bromide concentrations measured at some ICR plants (e.g., utility J [Table 3]) represented a period of relatively low bromide concentrations.

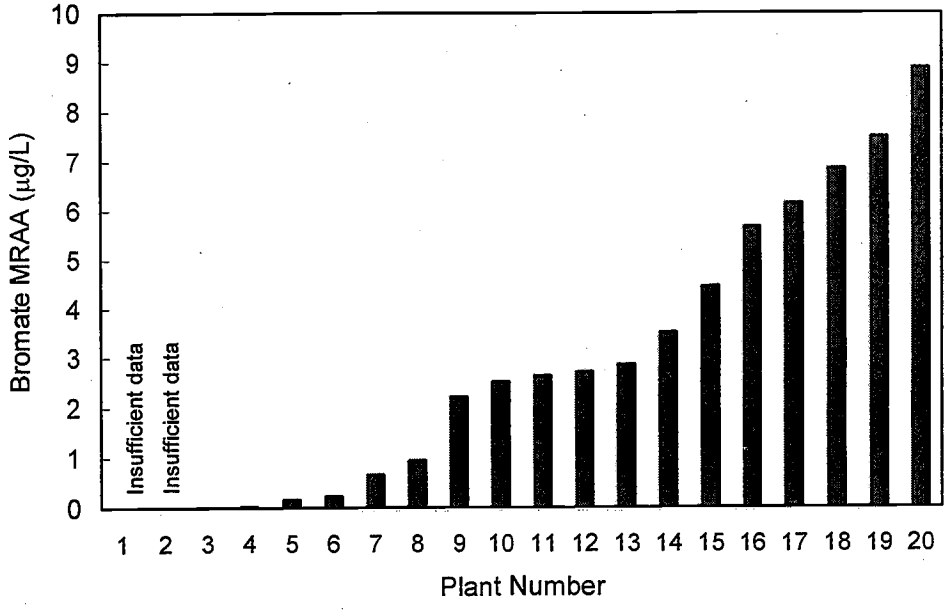

Figure 9.6 Maximum running annual average (MRAA) bromate concentrations for each ICR ozone plant during the 18-month monitoring period

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Some plants that will be required to inactivate *Cryptosporidium* under the LT2ESWTR may not be able to use ozone to achieve *Cryptosporidium* CT credit because the treatment process may cause bromate concentrations to exceed the MCL. Chapter 14 examines the simultaneous occurrence of bromide and *Cryptosporidum* in ICR water sources and models bromate formation at these plants when ozone is used under various *Crptosporidium* inactivation scenarios (Moll et al. 2002). The ability of plants to use ozone for *Cryptosporidium* inactivation will depend on the amount of bromide in the water and on ozonation practices.

For plants that are challenged by the presence of *Cryptosporidium* and high concentrations of bromide in the source water, several treatment options might allow the use of ozonation. If the alkalinity of the water is not too high, the utility could reduce the pH of the water before ozonation to minimize bromate formation (Coffey et al. 1998). Ammonia could be added to minimize bromate formation, but this strategy has been less consistently successful than pH control (Coffey et al. 1999). Alternatively, ozone could be used as part of an integrated disinfection strategy in water sources that are amenable to lower ozone dosages without exceeding the bromate MCL. Ozone could be used to meet *Giardia* and virus inactivation requirements, for taste and odor control, and for oxidation of micropollutants. Some plants might be able to use ultraviolet disinfection after filtration to inactivate *Cryptosporidium*. In such an integrated strategy, the plants would produce some bromate from ozonation but not as much as if they used ozone for all oxidation and disinfection needs.

SUMMARY AND CONCLUSIONS

The ICR data collection effort provided an opportunity to examine factors influencing bromate formation at a national level. Bromate was not an important by-product of disinfection with chlorine dioxide. Finished water bromate concentrations at the 20 plants using ozone during ICR monitoring were consistent with those in other studies that evaluated bromate formation under the relatively low ozone dosages used to inactivate *Giardia* and viruses and to control taste- and odor-producing compounds. Increases in influent bromide concentration and ozone dosage were each associated with increased bromate formation. However, no association was apparent between bromate formation and TOC, pH, temperature, or ammonia concentration or betweeen bromate formation and ozone residual or ozone CT. Increased alkalinity was

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apparently associated with increased bromate formation, an effect that may have been related in part to other differences in water quality (i.e., bromide and pH values). The lack of association between bromate formation and some of these parameters is not surprising, given the wide range of water sources and ozonation conditions represented in the ICR database. No ICR plant RAAs exceeded the bromate MCL of 10 μg/L during the data collection period, and only one plant had any RAA values >8 μg/L.

The level of bromate formation shown in this nationwide dataset was consistent with other data indicating relatively low bromate formation associated with low ozone dosages. Thus, the range of bromate concentrations reported during ICR monitoring was lower than the range that would be expected if these plants were operated under conditions designed to inactivate *Cryptosporidium*. Although these plants did not exceed compliance limits for bromate under conditions designed to inactivate *Giardia* and viruses and to control taste- and odor-producing compounds, much higher ozone dosages will be required to inactivate *Cryptosporidium*, and these dosages may lead to increased bromate formation depending on bromide concentrations and ozonation conditions. In addition, the contribution of hypochlorite to overall finished water bromate concentrations may cause compliance problems for many plants that use hypochlorite as a secondary disinfectant if the MCL for bromate is decreased to 5 μg/L in the future. Thus, the ability of plants to use ozone for *Cryptosporidium* inactivation will depend on the amount of bromide in the water and on ozonation practices, which must be carefully managed to allow plants to achieve the benefits of ozonation while minimizing bromate formation.

Some unanswered questions that are relevant to understanding future bromate formation in U.S. drinking water supplies include:

- How many plants will need to use advanced disinfectants for *Cryptosporidium* control?
- What ozone dosages will be necessary to control *Cryptosporidium* in U.S. drinking water supplies?
- How much bromate is likely to be formed under various *Cryptosporidium* inactivation scenarios (see Chapter 14 [Moll et al. 2002] for a discussion of this issue), and how will pH control affect bromate formation?
- What were the ranges of historical bromide concentrations in ICR plant influent? Can these ranges be used along with the ICR data to predict bromate formation under other water quality conditions (e.g., during a drought)?

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- How would hypochlorite's contribution to bromate concentrations be altered by changes in the manufacturing process and in utility use patterns?

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CHAPTER 10

TOX IN FINISHED WATER AND DISTRIBUTION SYSTEMS: RELATIONSHIPS WITH DBPS

Hiba M. Shukairy, Valerie Blank, and Jennifer McLain

ABSTRACT

The Information Collection Rule (ICR) constituted the nation's first large-scale effort to collect data on the occurrence of total organic halogen (TOX) in drinking water systems serving 100,000 people or more. This chapter presents influent, finished water, and distribution system TOX data collected during six quarters of ICR monitoring between July 1997 and December 1998. The chapter also examines the use of TOX as a surrogate measure for the disinfection by-products (DBPs) regulated under the Disinfectants/Disinfection By-products Rule—total trihalomethanes (TTHM) and the sum of five haloacetic acids (HAA5)—and for the other halogen-substituted DBPs monitored under the ICR. The results show good correlations between these DBPs and TOX, despite variability in water quality, water treatment practices, and type of disinfectant, indicating that TOX can be used as a DBP surrogate. On average, TTHM and HAA5 made up 20–50% of the TOX. Other DBPs monitored under the ICR—bromochloroacetic acid, haloacetonitriles, chloral hydrate, chloropicrin, and the haloketones—accounted for another 5% of the TOX. The chapter also discusses the impact of source water, disinfectant type, and bromide concentration on the correlation between DBPs and TOX and on the percentage of TOX accounted for by the DBPs measured.

BACKGROUND

Total organic halogen (TOX) is a summary parameter that quantitatively measures halogen-substituted disinfection by-products (DBPs). TOX is formed when a disinfectant, such as chlorine, chloramine, or chlorine dioxide, reacts with some of the natural organic matter in water.

As a water quality descriptor, TOX is a nonspecific parameter and is limited by recovery through adsorption of the halogen-substituted organics onto granular activated carbon used in the analytical technique. The adsorption step achieves greater than 80% recovery of most halogen-substituted compounds, but highly polar compounds such as monochloroacetic acids are poorly adsorbed (Takahashi, Moore, and Joyce 1981; Stevens et al. 1985). TOX is measured by microcoulometric titration of the organically bound halogen (as hydrogen halide or halogen)

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formed during combustion of the adsorbed organics, with no distinction made among chlorine, bromine or iodine. The reported measurement is based on the conversion of molar quantities of detected halogens to micrograms per liter as chlorine. In U.S. drinking water supplies, chlorine- and bromine-substituted DBPs are accounted for, whereas iodine-substituted by-products are not, probably because of their instability (Thomas, Weisner, and Brass 1980; Gould, Giabbai, and Kim 1985). In general, iodine-substituted by-products occur less frequently and in lower concentrations than the other trihalomethanes (Brass et al. 1977).

The DBPs that are typically measured and that make up a substantial fraction of TOX are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), chloral hydrate (CH), chloropicrin (CP), the sum of two haloketone species (HK2), and cyanogen chloride. These compounds are usually measured by established gas chromatography (GC) methods that can be performed routinely by qualified laboratories. To date, other halogen-substituted organics have been qualitatively identified in U.S. water supplies using GC/mass spectrometry (MS) or liquid chromatography/MS (Richardson 1998). Reported classes of compounds include halogen-substituted alkanes and alkenes, haloalcohols, halocarboxylic acids, haloamides, and halofuranones (Richardson 1998).

The commonly measured DBPs generally make up about 50% of the TOX. The remaining unidentified fraction comprises highly polar compounds that are difficult to remove from the water matrix or high-molecular-weight compounds that cannot be identified by typical GC methods. The unidentified fraction of TOX may also be tied up in labile compounds that decompose or dehalogenate upon analysis.

The interest in TOX stems from attempts to use it as a surrogate measure for halogen-substituted by-products that may pose a health concern. Although the health effects of unknown compounds cannot be directly evaluated, several researchers have shown TOX to be linearly correlated with mutagenicity (Meier, Lingg, and Bull 1983; Schenck and Lykins 1999). The concept of using TOX as a surrogate measure for other compounds is not new. Researchers have investigated the use of TOX as a DBP surrogate in specific water sources (U.S. Environmental Protection Agency [USEPA] 1982; Singer and Chang 1989, Reckhow and Singer 1990, Singer, Obolensky, and Greiner 1995).

The work described in this chapter had two primary objectives: (1) to investigate the usefulness of TOX as a surrogate parameter for the DBPs regulated under the

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Disinfectants/Disinfection By-Products (D/DBP) Rule, namely total THMs (TTHM) and the sum of five haloacetic acid species (HAA5), and (2) to assess the impact of source water, disinfectant type, and bromide concentration on the usefulness of this parameter as a surrogate for DBPs. This chapter also presents national distributions of six quarters of TOX data collected under the Information Collection Rule (ICR) and shows the national percentage of TOX accounted for by TTHM and HAA5 compared with that accounted for by the nonregulated DBPs monitored under the ICR. The chapter focuses on national trends and correlations and does not present individual plant evaluations.

MONITORING TOX UNDER THE ICR

Under the ICR, public water systems serving ≥100,000 people were required to monitor quarterly for DBPs. Requirements regarding the location of quarterly sampling for DBPs are presented in Table 5-2 of the *ICR Sampling Manual* (USEPA 1996a). TOX was measured in the plant influent, after filtration if a disinfectant was applied anywhere prior to filtration, in the finished water, at the entry point to the distribution system for plants that blended water before distributing it, and at four monitoring locations within the distribution system. The four distribution system locations were selected to represent two average residence times (AVG1 and AVG2), one maximum residence time (MAX), and one distribution system equivalent (DSE) sampling point (a distribution system site with well-characterized detention time). The DSE sample was used for comparison with a simulated distribution system (SDS) sample. Sampling requirements were designed to ensure that the SDS and DSE samples had similar DBP formation potentials so the usefulness of the SDS test for compliance monitoring could be assessed (Obolensky and Frey 2002). The SDS sample is not evaluated in this chapter.

The TOX measurements, based on Standard Method SM 5320B, were reported as duplicates for which a relative percent difference (RPD) was calculated. Unlike the duplicate measurements required for total organic carbon (TOC) and ultraviolet absorption at 254 nanometers (UV_{254} absorption), the TOX data were not subject to an RPD acceptance criterion during validation of the ICR data. However, TOX data were subject to all other quality control requirements. Chapter 2 (Fair et al. 2002) presents information on the ICR procedures for data validation and data quality assessment.

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METHODOLOGY USED FOR DATA ANALYSIS

The data used for the analyses discussed in this chapter are from Auxiliary Database 1 (AUX1), described by Wysock et al. (2002). Each DBP record in the database reflects a data point representing the treatment plant, the quarter during which the sample was collected, and the sampling location. Only data that passed validation were reported in AUX1; results that were not validated or were missing were reported as null. For the analyses described in this chapter, all null TOX values were excluded, and subsequently all related DBP data from the same plant, quarter, and location were also excluded. Similarly, if TTHM and HAA5 data were reported as null, the corresponding TOX data were also excluded. This screening procedure was used to compare paired data sets—i.e., TTHM, HAA5, and TOX data for the same plant, quarter, and location. DBP data that had utility codes of acceptable ("A") or questionable ("Q") were not differentiated except for the TOX data. Only data with a utility code of "A" (83% of total reported TOX concentrations) were used in the analyses. This decision was made because for some "Q" results, the preservation technique had been modified from the requirements (USEPA 1996b), rendering the data subset incomparable with the entire data set.

All DBP values, except for TOX concentrations that were less than the minimum reporting level (MRL) and were signified by a value of "–999" in AUX1, were replaced with a zero. This data manipulation is consistent with the way DBP data were handled in all other ICR data analyses. The TOX data were treated differently because of the nature of the calculations presented in this chapter. To avoid division by zero, the TOX values that were less than the MRL of 50 μg Cl^-/L were replaced by half the MRL (25 μg Cl^-/L). In addition, only TOX records that had RPDs ≤25% were selected.

Except for the six-quarter inventory of TOX distributions, the data presented in this chapter are restricted to those collected during the last 12 months of ICR monitoring—from month 7 (January 1998) through month 18 (December 1998). All ICR data analyses demonstrated that for any consecutive 12 months of ICR sampling, the trends in the data were almost indistinguishable (USEPA 2002). To validate the approach of analyzing only data from the last 12 months of monitoring, the TOX data from 18 months (six quarters) of ICR distribution system monitoring are shown in Figure 10.1. Cumulative frequency distributions (CFDs) for consecutive 12-month intervals—e.g., months 1 to 12 (interval 1) and months 5 to 16

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(interval 5)—were plotted, and the 25th, 50th, 75th, and 90th percentile ranks were calculated. Distributions of TOX data collected during any interval within the 12-month or four-quarter period were quite similar.

The choice to use only data from the last 12 months or four quarters (interval 7 on Figure 10.1) of ICR monitoring was based on the least number of "Q" data points for TOX. As utilities became more familiar with ICR monitoring and analytical procedures, fewer errors occurred, resulting in a higher number (91%) of acceptable records (interval 1, shown in Figure 10.1, has 5,081 records compared with 5,834 records in interval 7).

Data chosen for analysis in this work were from samples collected from plant influent, finished water, and distribution system MAX locations. CFDs for TOX concentrations from the four distribution system locations—AVG1, AVG2, MAX, and DSE—are shown in Figure 10.2. There were no distinct differences in the distributions of data from the four distribution system locations. Therefore, only data from the MAX locations were chosen to represent distribution systems for the detailed analyses.

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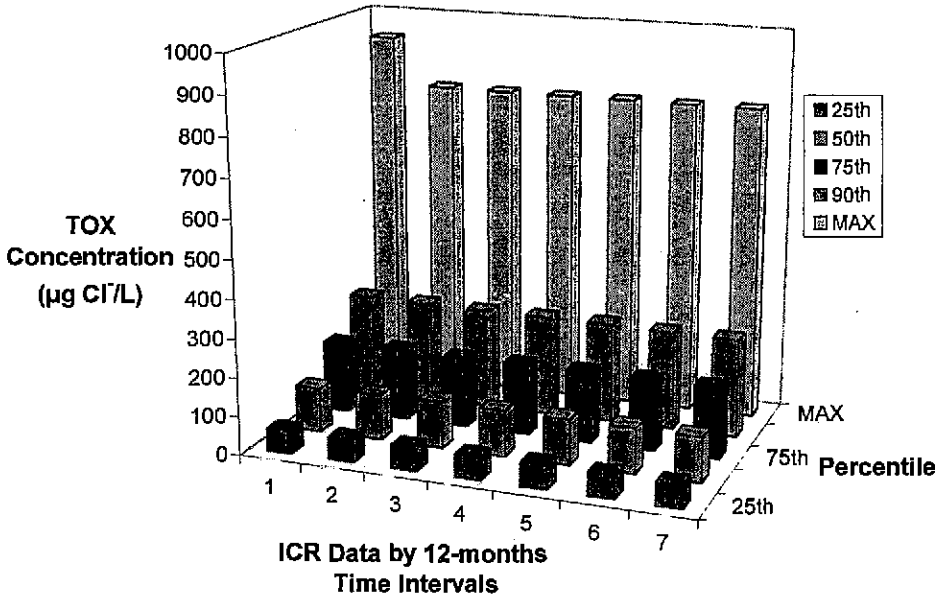

Figure 10.1 Cumulative frequency distributions of TOX concentrations from all distribution system sampling locations by 12-month intervals

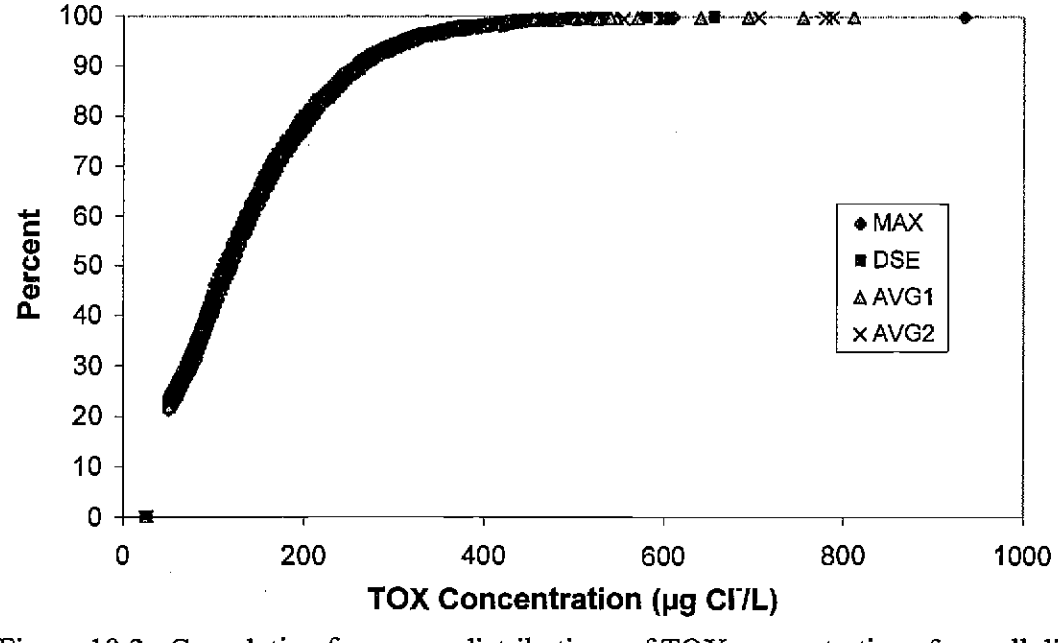

Figure 10.2 Cumulative frequency distributions of TOX concentrations from all distribution system sampling locations (AVG1, AVG2, MAX, and DSE)

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RESULTS AND DISCUSSION

Influent TOX Concentrations

Most of the influent TOX concentrations reported for the six quarters of ICR monitoring were below the MRL of 50 μg Cl^-/L. Only 5.6% of the TOX concentrations reported for influent surface water supplies were greater than the MRL (values ranged between 50 and 550 μg Cl^-/L). For influent groundwater supplies, 3.4% of the reported TOX concentrations were higher than the MRL (values ranged from 50 to 145 μg Cl^-/L). A 1981 USEPA survey conducted to evaluate the use of TOX as a surrogate for volatile organics indicated only background TOX concentrations in most source water supplies (USEPA 1981); ranges of <5 to 49 μg Cl^-/L and <5 to 85 μg Cl^-/L were reported for surface water and groundwater, respectively (Stevens et al. 1985). An MRL of 50 μg Cl^-/L was set for ICR TOX data to allow for variations in laboratory performance. A representative average ICR influent TOX concentration could not be calculated because of the limitations of this MRL, which was greater than 90% of the TOX concentrations found in ICR source water supplies.

Aggregate TOX Data

Changes in TOX concentrations within individual plants are not discussed in this chapter. The following section describes TOX concentrations observed in finished water and distribution system samples collected during all six quarters (18 months) of ICR monitoring. In AUX1, treatment plants and distribution systems are classified according to the type of disinfectant used at the time of sample collection. In the treatment plant, the disinfectant might be ozone, chlorine dioxide, chlorine, chloramine, or a combination of chlorine and chloramine. In the distribution system, the disinfectant would be either chlorine or chloramine.

TOX concentrations in finished water, aggregated by type of source water (surface water or groundwater) and type of disinfectant used in the treatment plant, are presented in Table 10.1.

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Table 10.1

TOX concentrations in ICR finished water samples for six quarters

Aggregate description	Number of plants	Number of samples	Range (μg Cl^-/L)	25th percentile (μg Cl^-/L)	50th percentile (μg Cl^-/L)	90th percentile (μg Cl^-/L)
All data	496	2,285	<50–1010	<50	102	242
Surface water						
All disinfectants	351	1,594	<50–1010	75	122	250
Chlorine*	208	880	<50–1010	77	116	247
Chloramine*	23	77	<50–718	69	120	290
Combined chlorine and chloramines*	84	393	<50–460	106	151	259
Ozone*	19	79	<50–310	<50	67	195
Chlorine dioxide*	28	101	<50–566	69	110	260
Groundwater						
All disinfectants	126	565	<50–605	<50	<50	145

* The primary disinfectant used in the treatment plant

The data in Table 10.1 show a wide range of reported TOX concentrations in finished water supplies monitored under the ICR (<50 to 1010 μg Cl^-/L). The distribution of TOX concentrations in finished water from groundwater supplies was much lower than that in finished water from surface water supplies; the 90th percentile value for groundwater was 58% less than that for surface water, and both the 50th and 25th percentile values for groundwater were less than the MRL of 50 μg Cl^-/L. The distribution of TOX concentrations in groundwater was skewed by the fact that more than half of the reported values were less than the MRL.

When the impact of using alternative disinfectants in surface water treatment plants was examined, two factors were evident: treatment plants using chloramine, with or without chlorine, had the highest 50th (and even 25th percentile) TOX concentrations, whereas ozone plants had the lowest. This result most likely occurred because plants that had already shifted to chloramine disinfection probably had high influent concentrations of TOC or bromide (McGuire and Hotaling 2002). These plants may have shifted to chloramines to meet the 1979 maximum contaminant level for TTHM. Plants that use ozone have lower concentrations of halogen-substituted DBPs because they generally do not apply chlorine or chloramines until just before the water enters the distribution system. TOX concentrations found in ozone plants that do not apply chlorine or chloramine prior to the distribution system entry point represent either bromine-substituted DBPs, such as bromoform, or TOX present in the plant influent.

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In the analyses presented in Table 10.1, purchased water and mixed water sources were included in the category for all data but excluded from the aggregate categories for surface water and groundwater supplies. A plant that changed disinfectants during the ICR was included in every aggregate category describing it because of the way the analysis was performed. Therefore, the sum of the plants in the surface water and groundwater categories may not equal the number of plants in the category for all data.

Because the CFDs of TOX concentrations from the four distribution system sampling locations are almost indistinguishable (Figure 10.2), the analyses presented in Table 10.2 include values from all four distribution system locations. The data were further aggregated by type of source water (surface water or groundwater) and type of disinfectant used in the distribution system (chlorine or chloramine). Aggregate data for surface water and groundwater include the categories designating the disinfectant used in the treatment plant.

Like the TOX results for finished water, nationally reported TOX concentrations in distribution systems covered a wide range (from <50 to 935 μg Cl^-/L). Groundwater distribution systems—especially those using chlorine—had lower TOX concentrations than surface water distribution systems. Among the groundwater plants, the 18 using chloramine as a secondary disinfectant had the highest 25th, 50th, and 90th percentiles, suggesting that these plants might have shifted to chloramine to decrease DBP concentrations. TOX distributions in surface water plants were similar, regardless of which secondary disinfectant was used.

Table 10.2

TOX concentrations in ICR distribution system samples for six quarters

Aggregate description	Number of plants	Number of samples	Range (μg Cl^-/L)	25th percentile (μg Cl^-/L)	50th percentile (μg Cl^-/L)	90th percentile (μg Cl^-/L)
All data	451	8,167	<50–935	59	116	263
Surface water						
Chlorine*	204	3,345	<50–935	92	137	265
Chloramine*	119	2,184	<50–811	82	132	254
Groundwater						
Chlorine*†	101	1,761	<50–640	<50	<50	168
Chloramine*	18	350	<50–788	82	117	287

* Disinfectant used in the distribution system

† 70th percentile <MRL

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TTHM and HAA5 concentrations, which account for a portion of the TOX, were also relatively higher in surface water plants. Median TTHM concentrations in surface water and groundwater distribution systems were 40 and 8.7 μg/L, respectively; median HAA5 concentrations in surface water and groundwater distribution systems were 24 and 2.5 μg/L, respectively (McGuire and Graziano 2002; Obolensky, Shukairy, and Blank 2002; USEPA 2002).

Use of TOX as a Surrogate for DBPs

The primary reason for correlating TOX concentrations with DBP concentrations is to investigate how well TOX predicts the formation of TTHM and HAA5, the halogen-substituted DBPs regulated under the D/DBP Rule. The analyses discussed in this chapter were based on the assumption that TOX recoveries for all the known DBPs were 100%. Although most identified TOX compounds have recoveries greater than 80%, some are poorly adsorbed (Takahashi, Moore, and Joyce 1981; Stevens et al. 1985). Figures 10.3 and 10.4 show the correlations between TOX and TTHM (on a mass basis) and between TOX and HAA5 (on a mass basis) during one year (months 7 through 18) of ICR monitoring. The coefficient of determination (r^2) for both plots was less than 0.6 for all finished water samples, regardless of source water type or type of disinfectant used in the plant.

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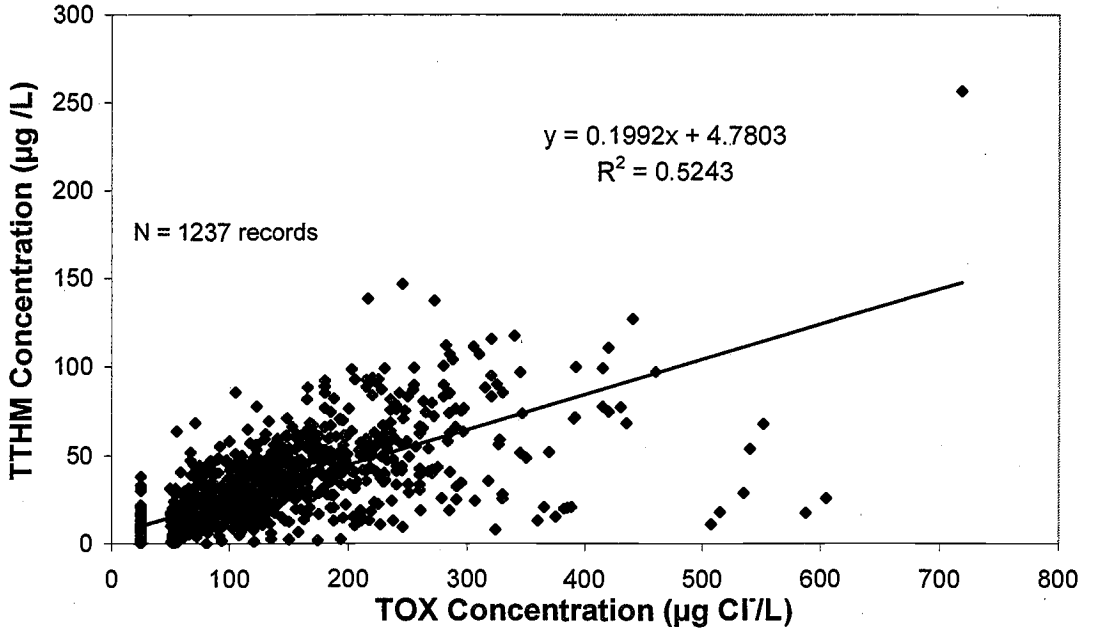

Figure 10.3 Correlation of TTHM with TOX in finished water

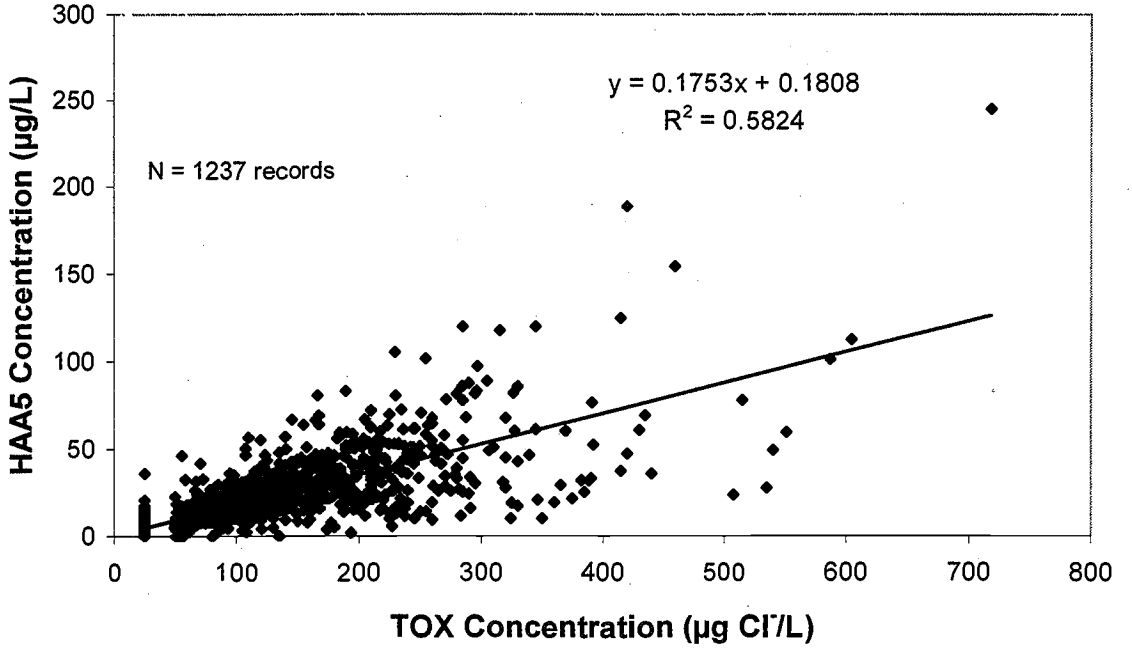

Figure 10.4 Correlation of HAA5 with TOX in finished water

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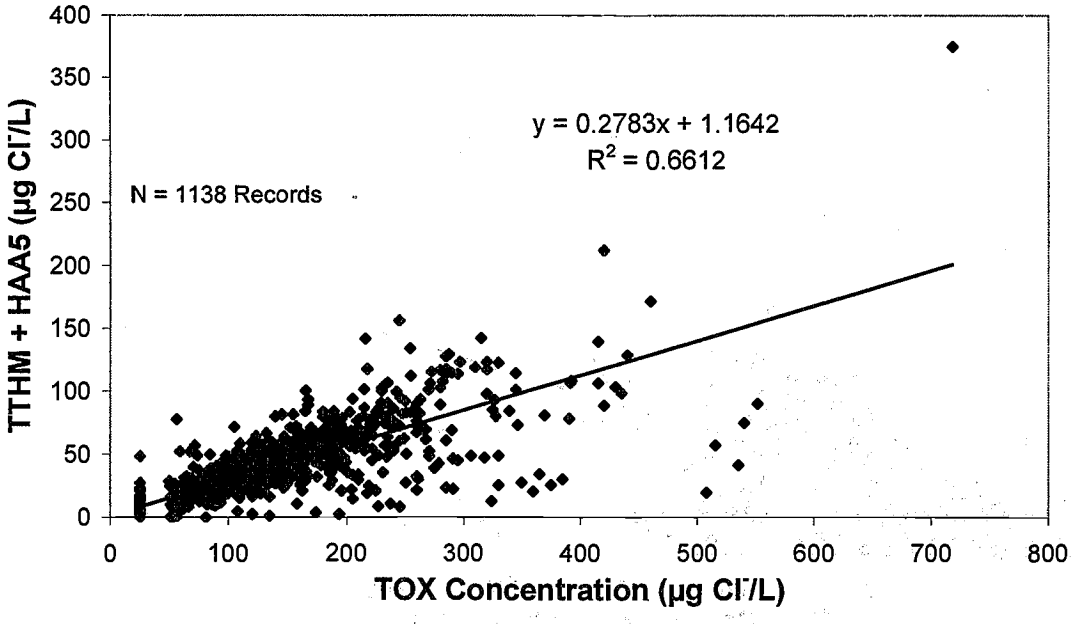

Figure 10.5 Correlation of TTHM and HAA5 (as halogen) with TOX in finished water

When TTHM and HAA5 were summed based on conversion to their chloride equivalents—i.e., to the same units of measure used for TOX—the correlation improved (Figure 10.5). This pattern was observed for all data aggregates. Therefore, to investigate how creating subsets of the data by sampling location or source water type and disinfectant type would affect the correlations, DBP concentrations were converted to chloride equivalents in TOX units (on a mass basis) and correlated with the corresponding TOX paired sample. An example of the calculation is presented in Table 10.3. All TTHM and HAA5 species were calculated as chloride equivalents, as shown in the example, and the sum was correlated with the TOX.

Table 10.4 presents r^2 values for correlations of TTHM and HAA5 (expressed as micrograms of chloride per liter) with TOX in various subsets of the data—surface water, groundwater, and type of disinfectant used in the plant.

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Table 10.3

Calculation of DBP concentrations as chloride equivalents

DBP	Reported concentration (μg/L)	Molecular weight	Number of halogens	Weight ratio as Cl	Multiplier	DBP (as μg Cl^-/L)
Chloroform (THM)	50	119.4	3	[3(35.45)/119.4]	0.891	44.6
Dibromoacetic acid (HAA5)	20	217.8	2	[2(35.45)/217.8]	0.326	6.52

Table 10.4

Correlation of TTHM and HAA5 (as halogen) with TOX in ICR finished water supplies

Source water type and plant disinfectant type	r^2	Number of samples†
Surface water		
All disinfectants	0.5911	835
Chlorine*	0.5867	470
All chloramines*	0.7160	242
Ozone*	0.4709	42
Chlorine dioxide*	0.2156	52
Groundwater		
All disinfectants	0.8226	273

* The primary disinfectant used in the treatment plant
† Based on finished water sampling location, plant, and quarter

Excluding all values that were less than the MRL did not improve the correlations. Singer, Obolensky, and Greiner (1995) investigated some DBP correlations (TOX correlated with TTHM, HAAs, and individual DBPs) for finished drinking water from six North Carolina utilities and obtained r^2 values between 0.8 and 0.9. Most of the plants in that study used surface water supplies, had similar treatment processes, and used chlorine for disinfection. The strong correlations observed among the DBP parameters were reported to be the result of similar treatment (alum coagulation) of surface water supplies with low alkalinity and low bromide concentrations, use of free chlorine for primary and secondary disinfection, and similar pH values for finished and distributed water.

Considering the variability of the ICR data on influent water quality, treatment practices, disinfectant types, and precursor concentrations, the general correlations presented in this chapter

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are quite good. As shown in Figures 10.5 and 10.6, the correlation between TOX and TTHM and HAA5 as chloride equivalents was better in samples collected at the distribution system MAX location than in finished water samples. Because contact time at the MAX location is appreciable compared with that at the finished water sampling point, MAX samples may better represent complete halogen-substituted by-product formation.

When all ICR-monitored DBPs (excluding cyanogen chloride, which was measured only at plants using chloramines) were converted to chloride equivalents and summed, the correlation improved slightly (see Figure 10.7 for data from the distribution system MAX location; data for finished water, not presented, had an r^2 of 0.6677). In addition to TTHM and HAA5, other DBPs monitored under the ICR were bromochloroacetic acid (BCAA), HANs, CH, CP, and HK2. Because only a small percentage of ICR plants elected to sample all nine HAA species, the other three HAA species were not included in this analysis.

The higher the r^2, the more the variability in TTHM and HAA5 concentrations can account for the variability in TOX concentrations and the better TOX can serve as a surrogate. Although using TOX as a surrogate may not be ideal in lieu of actually measuring TTHM, HAA5, and other DBPs, the relatively good correlations observed for such a wide range of water quality parameters and treatment and disinfection practices indicate that decreasing TTHM and HAA5 concentrations result in a simultaneous decrease in TOX values. The fact that TTHM and HAA5 comprise part of the TOX demonstrates an autocorrelation but still speaks for the use of TOX as a surrogate parameter for DBPs. When the unknown TOX concentration was calculated for the distribution system MAX location (measured TOX concentration minus the sum of the calculated TOX from the DBPs measured under the ICR) and correlated with TTHM and HAA5 individually or as a sum, the r^2 was in the range of 0.15 to 0.25. This shows that although TOX can be a reliable surrogate measure for DBPs, the good correlation with the regulated DBPs was dependent on the measured by-products. Decreasing TTHM and HAA5 concentrations may not necessarily decrease the unknown TOX concentration. Recovery of the unknown TOX may also be limited by the analytical method, or TOX may decompose or dehalogenate during analysis.

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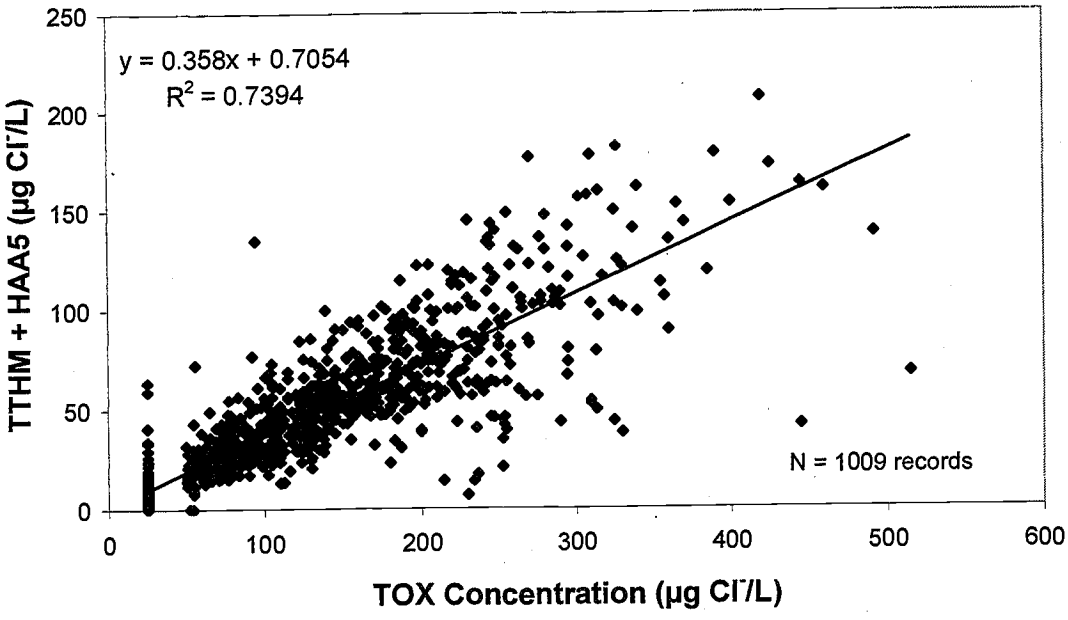

Figure 10.6 Correlation of TTHM and HAA5 (as halogen) with TOX at distribution system MAX locations

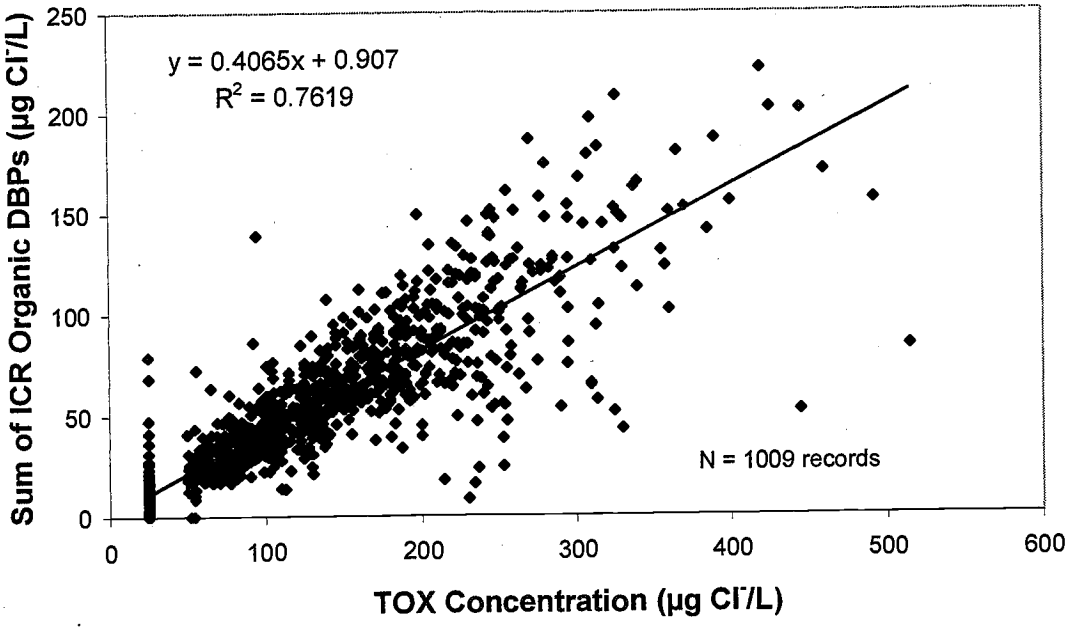

Figure 10.7 Correlation of the sum of TTHM, HAA5, BCAA, HANs, CP, CH and HK2 (as halogen) with TOX at distribution system MAX locations

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The correlations observed in ICR data indicate that the decreased TTHM and HAA5 concentrations expected to result from more stringent standards specified in the D/DBP Rule and the anticipated Stage 2 DBP Rule will generally control the sum of the halogen-substituted by-products represented by TOX. This is significant, given that TOX has been correlated with mutagenicity (Meier, Lingg, and Bull 1983; Schenck and Lykins 1999).

Identified Components of TOX

How much of TOX is accounted for by TTHM and HAA5? To answer this question, the measured concentrations of these parameters, and those of the other DBPs measured under the ICR, were converted to chloride equivalents (see Table 10.3) (bromine equivalents were calculated and then converted to chloride), and the total sum was calculated as a percent of the measured TOX. This calculation was performed for each record in AUX1. Figure 10.8 shows the CFDs of TTHM and HAA5 as a percent of TOX in finished water and distribution system MAX locations. The percent of TOX accounted for by TTHM and HAA5 varied widely; in some samples, TTHM and HAA5 made up almost 100% of the TOX. The 50th percentile ranged from 25 to 40%, which is more typical of the percentages reported in the literature (Singer, Obolensky, and Greiner 1995; Reckhow and Singer 1990).

When distributions in finished water were compared with those in MAX locations (Figure 10.8), the sum of TTHM and HAA5 as a percent of TOX increased slightly. This was expected because TTHM formation continues to increase with increasing contact time. In addition, some of the nonpurgeable fraction of TOX was lost (such losses occur because some of the metastable halogen-substituted organic compounds can lose a halogen, thus decreasing TOX). Finally, in the presence of chlorine, some TOX components (high-molecular-weight compounds) break up to form more of the smaller compounds such as TTHM (Miller and Uden 1983). All of these factors contribute to changes in the percent of TOX made up by identified components.

Figure 10.9 shows the impact of aggregating the data into subsets for surface water and groundwater and illustrates the effect of the groundwater data (median TOX value <MRL, Table 10.1) on distributions for the entire data set. Overall, TTHM and HAA5 appeared to account for a higher percent of TOX in surface water than in groundwater, but this is because the

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groundwater data include more <MRL values than the surface water data. In fact, distributions of groundwater and surface water data with values >MRL are similar (data not shown).

Impact of Bromide

Percent of TOX Accounted for by TTHM and HAA5

Figures 10.10 and 10.11 show the average percent of TOX accounted for by the DBPs regulated under the D/DBP Rule (TTHM and HAA5, shown by the bars on the left) and all other DBPs, excluding the three optional HAAs, monitored under the ICR (shown by the bars on the right) as a function of influent bromide concentration. The five bromide bins depicted in these figures (<MRL of 20 μg/L, 20–30 μg/L, 30–50 μg/L, 50–100 μg/L, and >100 μg/L) were created by dividing nationwide ICR bromide concentrations into quintiles based on all monthly influent bromide samples. See Chapter 12 (McGuire and Hotaling 2002) for a discussion of influent bromide concentrations in ICR plants.

On average, TTHM and HAA5 across all bromide bins accounted for 24–30% of the TOX in finished water (Figure 10.10). All the other monitored DBPs (BCAA, HANs, CH, CP, and HK2) made up less than 5% of the TOX in finished water samples. The latter DBPs, except for BCAA and two of the HAN species, are primarily chlorine-substituted. The percent of TOX accounted for by TTHM and HAA5 increased to about 40% in samples collected at the distribution system MAX location (Figure 10.11). As bromide concentrations increased, the percent of TOX accounted for by the DBPs measured under the ICR decreased slightly.

DBP speciation can be expected to shift to the more bromine-substituted DBPs with increasing bromide concentrations. ICR data on TTHM and HAA5 indicated a shift to the more bromine-substituted DBPs with increasing bromide concentrations (McLain, Obolensky, and Shukairy 2002). Such a shift can also be expected to occur in the unknown TOX. No trend relating TOX to increasing bromide concentrations was apparent, however, when the data were organized by bromide bin. The small impact of bromide concentration indicated in these figures occurred primarily because most of the DBPs monitored under the ICR were chlorine-substituted or mixed chlorine- and bromine-substituted species. Data on HAA5 do not reflect the true speciation shifts observed when the nine HAA species are taken into account (Obolensky, Shukairy, and Blank 2002).

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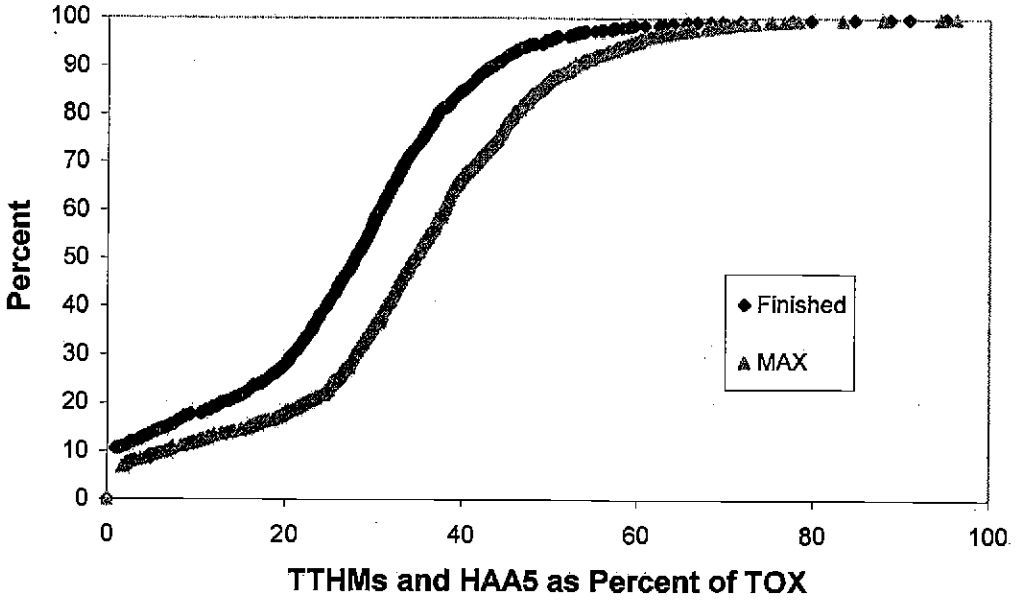

Figure 10.8 TTHM and HAA5 as a percent of TOX—CFDs for finished water and distribution system MAX locations

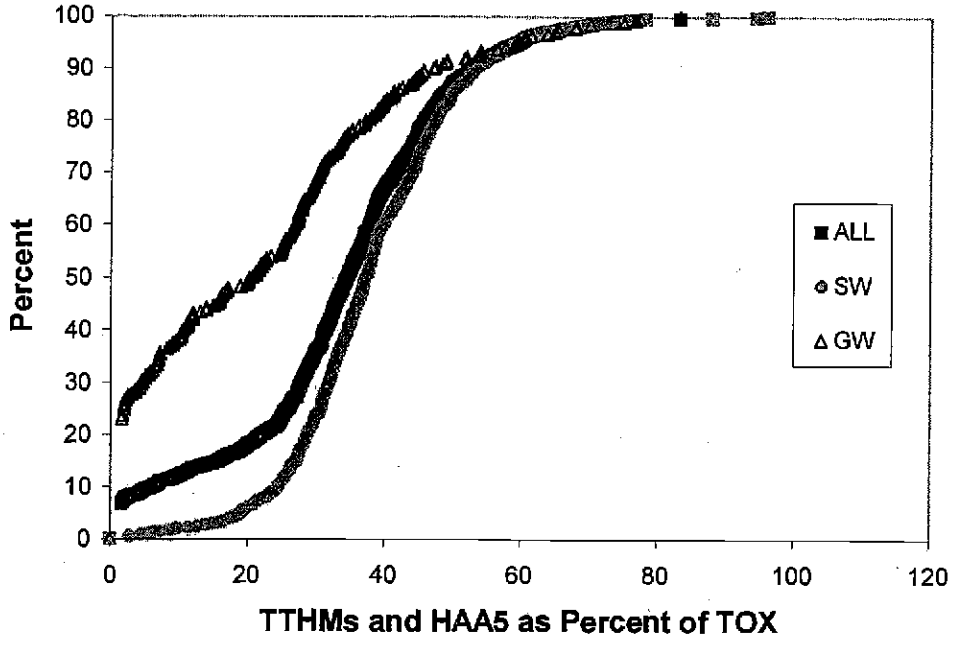

Figure 10.9 TTHM and HAA5 as a percent of TOX at distribution system MAX locations—CFDs by source water category (all sources, surface water [SW], and groundwater [GW])

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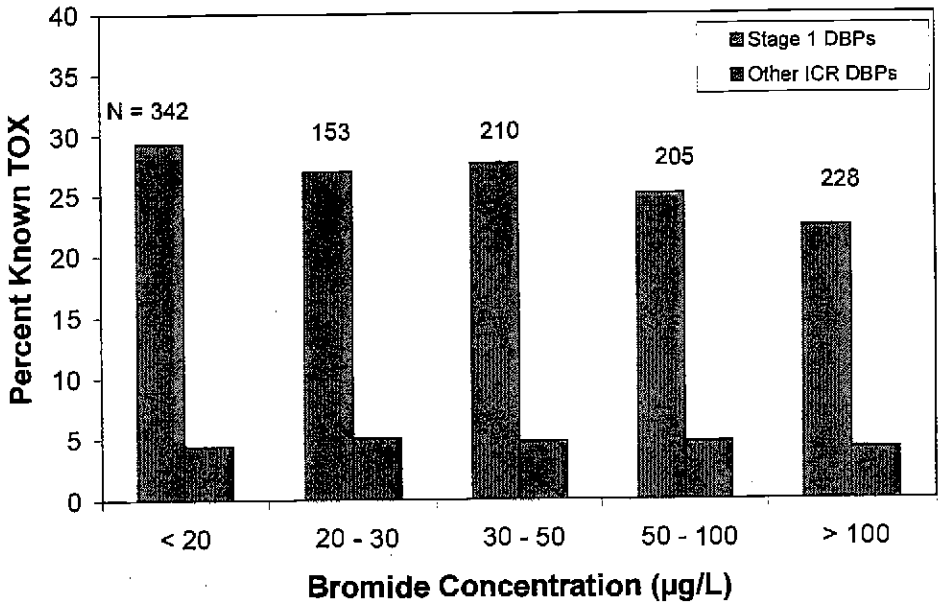

Figure 10.10 Identified DBPs as a percent of TOX in finished water

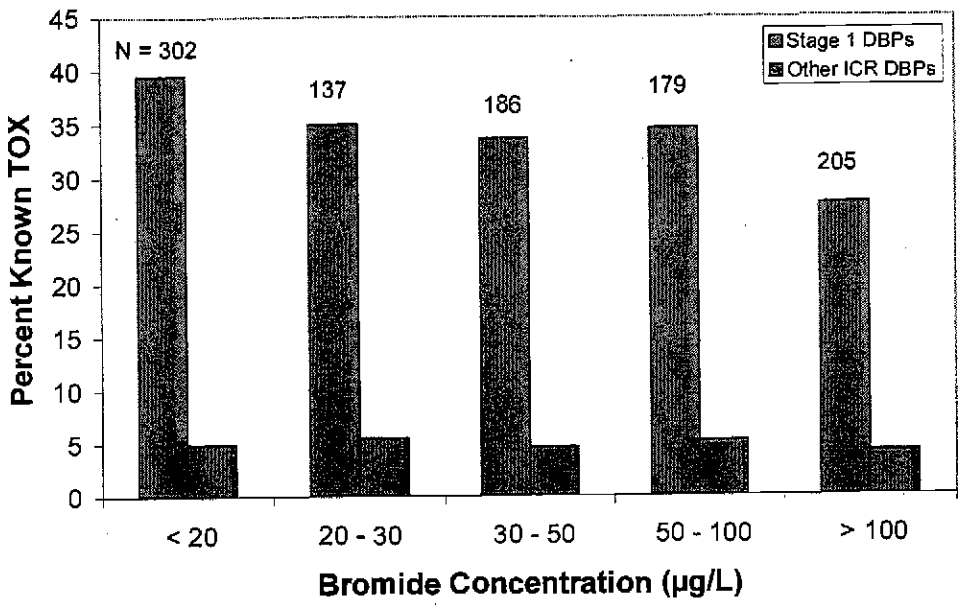

Figure 10.11 Identified DBPs as a percent of TOX at distribution system MAX locations

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On a mass basis, TOX values underestimate the mass of bromine incorporated into the organic molecules. As mentioned, TOX measurements are based on molar microcoulometric titration of the halogen with silver ions, followed by conversion of the molar value to mass as chlorine. The effect of bromide was also obscured when the TOX data were organized within bromide bins.

Correlation of TOX with Water Quality Parameters

Attempts to correlate TOX with other water quality parameters in a subset of the data on finished water did not yield good r^2 values. When TOX was correlated with finished water TOC and UV_{254} absorption at surface water plants using chlorine disinfection, the correlation was very poor (r^2 of 0.3066 and 0.3042 for TOC and UV_{254} absorption, respectively). Likewise, no correlation was found between TOX and pH in finished water. Singer, Obolensky, and Greiner (1995) found good correlations between TOX and consumed chlorine in water supplies that had similar pH values and that were subjected to similar treatment processes, including chlorine disinfection in both the plant and the distribution system. Using AUX1 data to assess such correlations, particularly those related to the distribution system, is difficult. The Auxiliary 6 Database, described by Wysock et al. (2002), is more useful for such detailed analyses.

SUMMARY

ICR data provided the means to evaluate the use of TOX as a surrogate measure for DBPs and to determine what percent of TOX is accounted for by the DBPs currently measured by known analytical methods. The impact of aggregating the data by source water type, disinfectant type, and bromide concentration on correlations between TOX and DBPs and on the percent of TOX made up by the measured DBPs was evaluated. The AUX1 database is the first national database of this magnitude to house data allowing the performance of such analyses and supporting the development of future water quality regulations.

- Although the TOX measurement is a nonspecific parameter, it is currently the only quantitative means of assessing unidentified halogen-substituted organic by-products that may pose some health concern in drinking water.

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- More than 90% of reported TOX concentrations in ICR treatment plant influent were below the MRL of 50 μg Cl^-/L.
- TOX concentrations reported for finished water and distribution system sampling locations during the 18 months (six quarters) of ICR monitoring ranged from <50 to 1000 μg Cl^-/L, depending on source water type and type of disinfectant used. The 50th percentile values ranged from <MRL to137 μg Cl^-/L. Groundwater plants had much lower TOX distributions than surface water plants. Plants using chloramine for disinfection had higher TOX concentrations than plants using chlorine, most likely because high source water precursor concentrations had prompted these plants to shift to chloramine to keep TTHM concentrations below 100 μg/L.
- As a surrogate parameter, TOX correlated well with TTHM and HAA5, particularly when the compounds were summed as chloride equivalents. Good correlations in the ICR data indicate that decreasing TTHM and HAA5 result in a general decrease in all of the halogen-substituted DBPs. These correlations hold in spite of variability in water quality, water treatment, and type of disinfectant used.
- On the basis of median concentrations in groundwater and surface water, 20–40% of the TOX was accounted for by TTHM and HAA5.
- Other DBPs monitored under the ICR (BCAA, HANs, CH, CP, and HK2) account for another 5% of the TOX.
- An examination of ICR distribution system data indicated that no nationwide impact on the percent of TOX accounted for by the measured DBPs could be attributed to source water type, disinfectant type, or bromide concentration.
- Overall TOX data for finished water do not correlate well with the corresponding data on TOC, UV_{254} absorption, or pH.

ACKNOWLEDGMENTS

The authors acknowledge the ICR treatment plants that collected the data used in these analyses and the ICR Implementation Team; the analyses described in this chapter were possible because of their hard work. The authors also acknowledge Alexa Obolensky, Philadelphia Water

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Department, for her input on the data analysis and Kent Sorrell, USEPA Technical Support Center, for his input and review of the manuscript.

DISCLAIMER

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CHAPTER 11
UNREGULATED ORGANIC DBPS IN ICR FINISHED WATER AND DISTRIBUTION SYSTEMS

Valerie Blank, Hiba M. Shukairy, and Jennifer McLain

ABSTRACT

This chapter presents cumulative frequency distributions for the following unregulated organic disinfection by-products (DBPs) monitored under the Information Collection Rule (ICR): trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, dibromoacetonitrile; 1,1-dichloropropanone; 1,1,1-trichloropropanone; chloral hydrate; cyanogen chloride; and chloropicrin. Concentrations of these DBPs were higher in surface water sources than in groundwater sources. In general, there were similarities between finished water data and distribution system data on each of these by-products. However, chloral hydrate concentrations were higher in distribution system samples (median = 2.8 μg/L; 90th percentile = 11.0 μg/L) than in finished water (median = 1.7 μg/L; 90th percentile = 7.4 μg/L). ICR finished water concentrations of aldehyde (formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal) are also presented. Overall, the range of concentrations for each DBP varied widely. Although median concentrations were fairly low compared with ICR concentrations of total trihalomethanes and the sum of five haloacetic acids, the data set is important because it constitutes the first comprehensive compilation of national occurrence data for unregulated organic DBPs.

INTRODUCTION

The Information Collection Rule (ICR) included monitoring requirements for both regulated and unregulated disinfection by-products (DBPs). The regulated DBPs included total trihalomethanes (TTHM), the sum of five haloacetic acids (HAA5), chlorite, and bromate. Monitoring for unregulated DBPs included sampling for additional HAAs, haloacetonitriles (HANs), haloketones (HKs), chloropicrin (CP), and chloral hydrate (CH). Cyanogen chloride (CNCl) was monitored by water systems using chloramines for disinfection; aldehydes were monitored by systems using ozone or chlorine dioxide (U.S. Environmental Protection Agency [USEPA] 1994).

The literature on DBP occurrence reflects a prevalence of research on the DBP classes associated with existing or pending regulations. This chapter focuses on occurrence data for the less frequently investigated organic DBPs monitored under the ICR: HANs, HKs, CP, CH,

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CNCl, and aldehydes. These DBPs were reported in occurrence studies conducted prior to promulgation of the ICR, but data collected under the ICR represent the first comprehensive data set to describe national occurrence of these DBPs.

BACKGROUND

When drinking water is disinfected, the organic material and bromide that are naturally present in the water react with the disinfectant to form DBPs. Because of complexities with the analytical method, only a small subset of these chemicals has been identified. Many of them are unstable and decompose during sampling or analytical processing. Others are highly polar and difficult to extract from water. Most of the common organic DBPs are measured by gas chromatography with electron capture detection, requiring analytical standards for quantification. Many other by-products have been identified by gas chromatography/mass spectrometry (GC/MS), but the methodology is semi-quantitative at best (Richardson 1998). Most of the DBPs that have been identified with available analytical methods are by-products of chlorination, oxidation, or both (Rook 1977, Krasner et al. 1989, Glaze and Weinberg 1993). At the time the ICR was proposed, limited information was available on the national occurrence of chlorination by-products, and even less was available on other measured DBPs. The ICR was designed to obtain national occurrence information for the regulated DBPs as well as the unregulated by-products discussed in this chapter.

This chapter presents cumulative frequency distributions of ICR occurrence data on the four HANs (HAN4)—trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN); on two haloketones (HK2)—1,1-dichloropropanone (DCP) and 1,1,1-trichloropropanone (TCP); and on CH, CNCl, and CP. Other researchers have documented the presence of these by-products in drinking water (Arora, LeChevallier, and Moser 1994; Arora, LeChevallier, and Dixon 1997; Krasner et al. 1989; LeLacheur, Singer, and Charles 1991; Richardson 1998; Singer, Obolensky, and Greiner 1995). The chapter also presents the distribution of aldehydes at ozone and chlorine dioxide plants, including formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal. Several researchers have reported the formation of these by-products as a result of oxidation processes (Glaze et al. 1991; Glaze and Weinberg 1993; LeLacheur, Singer, and Charles 1991; Richardson 1998).

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In addition, this chapter evaluates the impact of source water type and disinfectant type on the occurrence of these DBPs. Other by-products measured during ICR monitoring are reported elsewhere in this book. Only national distributions of ICR data are discussed; the data presented do not focus on individual treatment plants.

MONITORING UNDER THE ICR

The ICR required all surface water and groundwater systems serving 100,000 people or more to monitor influent, treated, and distributed water. Sampling requirements are described in the *ICR Sampling Manual* (USEPA 1996a). Water treatment plants collected monthly influent samples to be analyzed for the water quality parameters that influence DBP formation (McGuire and Hotaling 2002). In addition to quarterly monitoring for THMs (McGuire and Graziano 2002) and HAAs (Obolensky, Shukairy, and Blank 2002), utilities conducted quarterly sampling for the following disinfection by-products discussed in this chapter: TCAN, DCAN, BCAN, DBAN, DCP, TCP, CP, and CH. Samples were collected at the finished water sampling point and at four locations in the distribution system of each plant. The four distribution system locations included two sampling points intended to represent average residence time (AVG1 and AVG2), a point representing maximum detention time (MAX), and a distribution system equivalent (DSE) sampling point (a distribution system site with well-characterized detention time). The DSE sample was collected for comparison with a laboratory-incubated simulated distribution system sample (Obolensky and Frey 2002).

Plants using disinfectants other than chlorine had additional monitoring requirements (USEPA 1996a). Chloramine plants were required to sample for CNCl, a by-product associated with that disinfectant. Quarterly CNCl samples were collected at the finished water and distribution system MAX locations, and the results are reported in this chapter. The MAX sample was the only distribution system sample required because of the compound's lack of stability and the complexities of measuring it, factors that necessitated shipping samples to USEPA laboratories for analysis. Therefore, ICR data on CNCl and aldehydes (also analyzed by USEPA laboratories) are different from ICR data on other parameters in that no interlaboratory variability is associated with these data.

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Ozone and chlorine dioxide plants conducted additional monitoring for bromate and aldehydes. Plants using chlorine dioxide also monitored chlorite and chlorate. Moll and Krasner (2002) discuss the results of ICR bromate monitoring in Chapter 9 of this book. Results for aldehyde samples collected at the finished water sampling point are presented in this chapter.

The *DBP/ICR Analytical Methods Manual* (USEPA 1996b) describes the analytical methods used to analyze these compounds, their minimum reporting levels (MRLs), and their quality control requirements. The MRLs established for reporting ICR data were based on three factors: (1) the need for laboratories to meet precision and accuracy criteria at the MRL concentration without undue burden, (2) DBP occurrence information available at the time the ICR was promulgated, and (3) recommendations from a panel of experts. Fair et al. (2002) discuss the quality of ICR data in Chapter 2 of this volume.

METHODOLOGY USED FOR DATA ANALYSIS

All of the ICR data used in the analyses discussed in this chapter are from the Auxiliary Database 1 (AUX1) version 5.0. In Chapter 1, Wysock et al. (2002) discuss development of the ICR database systems. AUX1 includes only DBP results that met validation criteria. The data were collected during the six quarters of ICR monitoring (July 1997 through December 1998). Each data record provides results for a given plant at one sampling location during a particular sampling quarter. DBP concentrations that are below the MRL are reported in AUX1 as "–999." In the current analysis, each of these values was replaced with a zero.

Because the third and fourth quarters (i.e., fall and winter) were sampled twice during the six-quarter ICR monitoring period, the overall distribution of ICR data presented here may differ slightly from that of a data subset representing a single four-quarter period of ICR sampling.

RESULTS OF THE DATA ANALYSIS

Inventory of Results

The following sections describe the concentrations of compounds in samples of finished and distributed water collected during six quarters of ICR monitoring. Figures 11.1 and 11.2

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provide summary statistics (50th and 90th percentiles) for the data from finished water and distribution systems, respectively. Distribution system data for CNCl, however, is from the MAX location only because this was the only location monitored for that particular DBP. As shown in the figures, the 90th percentile concentrations of the unregulated organic DBPs monitored under the ICR rarely exceeded 10 μg/L.

Two sets of tables present the overall distribution of data from finished water and distribution systems (Tables 11.1–11.9). Each set includes a table aggregating the data by source water type and another grouping the data by disinfectant type (i.e., type of disinfectant used in the treatment plant for finished water results and type of disinfectant used in the distribution system for distribution system results). Aldehyde data are presented in a different format because these compounds were monitored only by a subset of ICR systems and only in finished water (USEPA 1996c).

Haloacetonitriles

The data in Table 11.1 show that total reported HAN4 concentrations in ICR finished water supplies ranged from less than the MRL of 0.5 μg/L up to 41.0 μg/L. The median HAN4 concentration in ICR finished water (2.7 μg/L) was within the range of median quarterly concentrations (2.5–4.0 μg/L) reported by Krasner et al. (1989). A comparison of HAN data by source water type showed that concentrations tended to be slightly higher at surface water plants (median = 3.1 μg/L, 90th percentile = 8.3 μg/L) than at groundwater plants (median = <0.5μg/L, 90th percentile = 7.2 μg/L). However, the highest overall HAN4 value of 41 μg/L was observed at a groundwater plant.

Analysis of the effect of type of disinfectant used in the treatment plant (Table 11.2) showed that surface water plants using chloramines (both with and without chlorine) had higher HAN4 values (at the 25th, 50th, and 90th percentiles) than plants using other disinfectants. These higher HAN4 concentrations may be due to the use of chloramine by plants that have high precursor concentrations in their source water (McGuire and Hotaling 2002).

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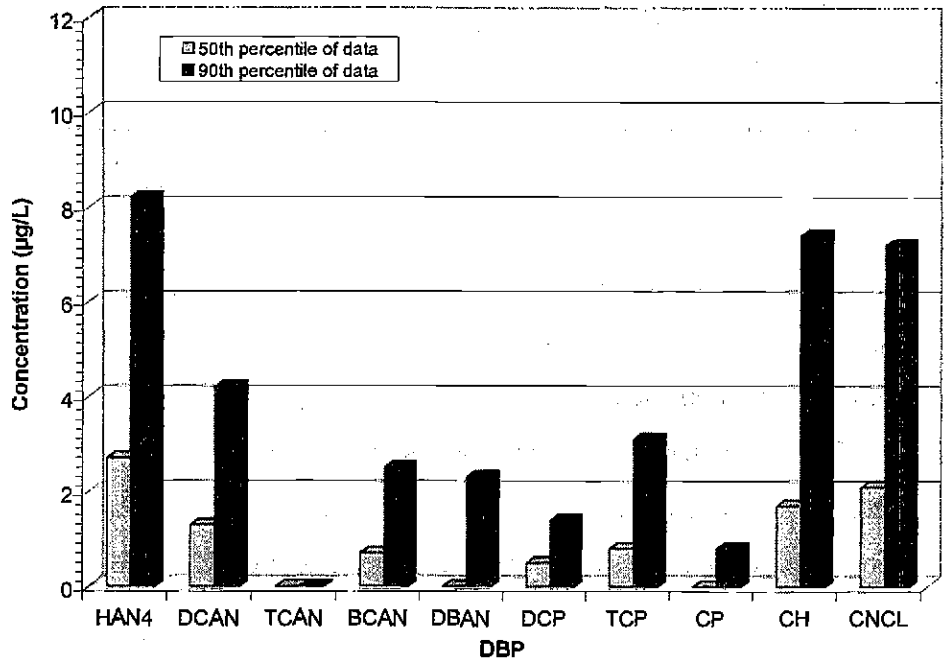

Figure 11.1 DBP concentrations in ICR finished water (all ICR plants, all finished water samples)

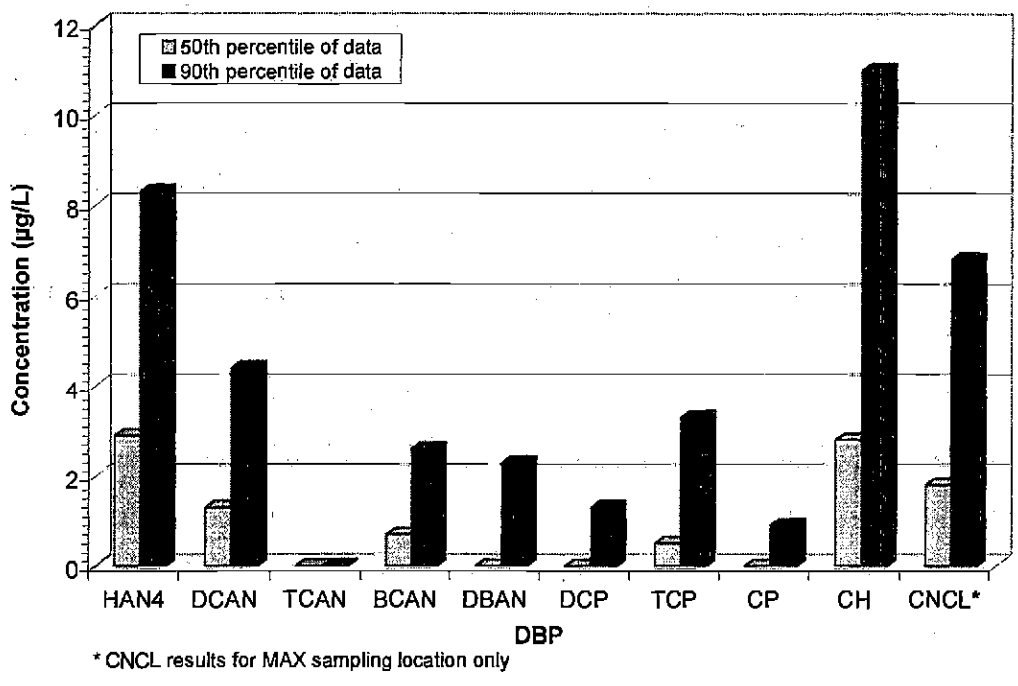

Figure 11.2 DBP concentrations in ICR distribution systems (all ICR plants, all samples from the four distribution system sampling locations)

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Table 11.1

Finished water haloacetonitriles

Plant category	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
All plants	DCAN	475	2,392	<0.5–20.6	<0.5	1.3	2.5	4.2
	TCAN	475	2,362	<0.5–36.7	<0.5	<0.5	<0.5	<0.5
	BCAN	474	2,392	<0.5–13.1	<0.5	0.7	1.5	2.5
	DBAN	474	2,371	<0.5–10.0	<0.5	<0.5	1.1	2.3
	HAN4	474	2,308	<0.5–41.0	0.8	2.7	5.2	8.2
Surface water	DCAN	342	1,699	<0.5–16.8	0.8	1.6	2.8	4.3
	TCAN	342	1,682	<0.5–12.0	<0.5	<0.5	<0.5	<0.5
	BCAN	342	1,702	<0.5–13.1	<0.5	0.8	1.5	2.5
	DBAN	342	1,682	<0.5–10.0	<0.5	<0.5	1.1	2.3
	HAN4	342	1,642	<0.5–19.0	1.6	3.1	5.4	8.3
Groundwater	DCAN	117	566	<0.5–20.6	<0.5	<0.5	0.7	2.4
	TCAN	117	555	<0.5–36.7	<0.5	<0.5	<0.5	<0.5
	BCAN	116	566	<0.5–6.6	<0.5	<0.5	0.8	2.0
	DBAN	116	563	<0.5–7.8	<0.5	<0.5	0.9	2.1
	HAN4	116	545	<0.5–41.0	<0.5	<0.5	2.0	7.2

Distribution system HAN4 concentrations (Table 11.3) (median = 2.9 µg/L, 90th percentile = 8.3 µg/L) were similar to concentrations in finished water (median = 2.7 µg/L, 90th percentile = 8.2 µg/L). As shown in Table 11.3, distribution system HAN4 concentrations ranged from below the MRL of 0.5 µg/L up to 51.6 µg/L. Concentrations in the distribution systems of these surface water plants (median = 3.2 µg/L, 90th percentile = 8.3 µg/L) were higher than those in the distribution systems of groundwater plants (median = 0.8 µg/L, 90th percentile = 7.0 µg/L), a finding consistent with HAN4 concentrations in finished water. Table 11.4 indicates that distribution system HAN concentrations were higher for plants practicing postchloramination (median = 3.6 µg/L, 90th percentile = 9.6 µg/L) than for plants using free chlorine (median = 3.1 µg/L, 90th percentile = 7.4 µg/L) as a secondary disinfectant. Observed differences in HAN4 distributions were small, as were actual concentrations. Because the comparisons were not controlled for precursor concentrations, making inferences about these differences is difficult.

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Table 11.2

Finished water haloacetonitriles—surface water plants

Plant disinfectant	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
Chlorine	DCAN	206	996	<0.5–15.2	1.0	1.7	2.8	4.2
	TCAN	206	992	<0.5–12.0	<0.5	<0.5	<0.5	<0.5
	BCAN	206	1,000	<0.5–13.1	<0.5	0.7	1.3	2.2
	DBAN	206	986	<0.5–10.0	<0.5	<0.5	0.7	1.4
	HAA4	206	966	<0.5–19.0	1.5	2.9	4.7	7.2
Chloramine	DCAN	20	82	<0.5–10.0	<0.5	1.6	3.1	4.4
	TCAN	20	80	<MRL	<0.5	<0.5	<0.5	<0.5
	BCAN	20	82	<0.5–5.5	0.6	1.1	2.2	3.9
	DBAN	20	81	<0.5–7.3	<0.5	1.1	2.5	3.4
	HAN4	20	79	<0.5–13.0	2.1	4.5	7.8	10.0
Chlorine/ chloramine	DCAN	83	367	<0.5–13.7	1.2	2.2	3.4	5.2
	TCAN	82	357	<0.5–2.6	<0.5	<0.5	<0.5	<0.5
	BCAN	83	366	<0.5–9.3	0.8	1.3	2.2	3.3
	DBAN	83	364	<0.5–8.9	<0.5	0.9	2.0	3.0
	HAN4	82	351	<0.5–17.5	2.9	5.1	7.8	10.9
Chlorine dioxide	DCAN	24	100	<0.5–16.8	<0.5	0.8	1.3	2.8
	TCAN	24	102	<0.5–3.3	<0.5	<0.5	<0.5	<0.5
	BCAN	23	101	<0.5–2.7	<0.5	0.6	1.4	2.0
	DBAN	23	101	<0.5–5.2	<0.5	0.9	2.2	2.9
	HAN4	23	99	<0.5–16.8	1.4	2.9	4.6	6.2
Ozone	DCAN	19	90	<0.5–7.8	<0.5	<0.5	1.1	2.0
	TCAN	19	88	<0.5–0.5	<0.5	<0.5	<0.5	<0.5
	BCAN	19	89	<0.5–5.2	<0.5	0.6	1.0	1.9
	DBAN	19	89	<0.5–3.5	<0.5	0.5	1.2	2.3
	HAN4	19	87	<0.5–14.6	0.7	1.7	3.5	5.2

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Table 11.3

Distribution system haloacetonitriles

Plant category	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
All plants	DCAN	429	8,518	<0.5–24.6	<0.5	1.3	2.7	4.4
	TCAN	429	8,430	<0.5–41.5	<0.5	<0.5	<0.5	<0.5
	BCAN	428	8,535	<0.5–13.4	<0.5	0.7	1.6	2.6
	DBAN	428	8,461	<0.5–24.0	<0.5	<0.5	1.2	2.3
	HAN4	428	8,256	<0.5–51.6	1.0	2.9	5.3	8.3
Surface water	DCAN	303	5,887	<0.5–24.6	0.8	1.7	3.0	4.5
	TCAN	303	5,850	<0.5–34.0	<0.5	<0.5	<0.5	<0.5
	BCAN	303	5,920	<0.5–13.4	<0.5	0.9	1.6	2.6
	DBAN	303	5,845	<0.5–24.0	<0.5	<0.5	1.0	2.3
	HAN4	303	5,724	<0.5–51.6	1.7	3.2	5.5	8.3
Groundwater	DCAN	110	2,187	<0.5–21.0	<0.5	<0.5	0.8	2.3
	TCAN	110	2,149	<0.5–41.5	<0.5	<0.5	<0.5	<0.5
	BCAN	109	2,182	<0.5–13.0	<0.5	<0.5	1.2	2.2
	DBAN	109	2,175	<0.5–10.0	<0.5	0.5	1.3	2.3
	HAN4	109	2,115	<0.5–44.4	<0.5	0.8	3.9	7.0

Table 11.4

Distribution system haloacetonitriles—surface water plants

Distribution system disinfectant	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
Chlorine	DCAN	199	3,678	<0.5–24.6	1.0	1.8	3.0	4.4
	TCAN	199	3,665	<0.5–34.0	<0.5	<0.5	<0.5	<0.5
	BCAN	199	3,703	<0.5–13.4	<0.5	0.8	1.4	2.5
	DBAN	199	3,647	<0.5–11.3	<0.5	<0.5	0.7	1.7
	HAN4	199	3,575	<0.5–51.6	1.6	3.1	5.1	7.4
Chloramine	DCAN	118	2,201	<0.5–19.8	<0.5	1.4	3.0	5.0
	TCAN	118	2,177	<0.5–20.5	<0.5	<0.5	<0.5	<0.5
	BCAN	118	2,209	<0.5–11.0	0.5	1.0	1.8	3.0
	DBAN	118	2,190	<0.5–24.0	<0.5	0.7	1.7	2.9
	HAN4	118	2,141	<0.5–26.3	1.8	3.6	6.5	9.6

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Haloketones

Concentrations of DCP in ICR finished water ranged from less than the MRL of 0.5 μg/L up to 6.1 μg/L (Table 11.5). The median finished water DCP concentration (0.5 μg/L) fell within the range of quarterly medians (0.46–0.55 μg/L) reported by Krasner et al. (1989). Finished water DCP concentrations at surface water plants were generally higher than those at groundwater plants, where 83% of finished water DCP concentrations were below the MRL of 0.5 μg/L. Finished water TCP concentrations were also higher at surface water plants than at groundwater plants, with reported groundwater TCP concentrations below the MRL of 0.5 μg/L in 90% of the data. The median finished water TCP concentration (0.8 μg/L) was consistent with the range of quarterly medians (0.35–0.8 μg/L) reported by Krasner and coworkers (1989).

Overall, DCP and TCP concentrations in distribution systems were similar to those in finished water (Table 11.7). A comparison of Tables 11.5 and 11.7 shows that distributions of DCP and TCP concentrations in finished water were not distinguishable from those in distribution systems.

Comparison of HK data aggregated by type of disinfectant used in the treatment plant at surface water systems (Table 11.6) shows that DCP concentrations at plants using chloramines alone or in combination with chlorine (medians = 1.1 μg/L and 0.9 μg/L, respectively) and at ozone plants (median = 0.7 μg/L) were somewhat higher than those at free chlorine or chlorine dioxide plants. Also, TCP values tended to be higher than DCP values at plants using free chlorine. Distribution system DCP concentrations were slightly higher at plants using chloramine as a secondary disinfectant than at plants carrying a chlorine residual in the distribution system (Table 11.8). In contrast, distribution system TCP data were slightly higher at plants carrying a chlorine residual than at plants practicing postchloramination.

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Table 11.5

Finished water haloketones, chloropicrin, and chloral hydrate

Plant category	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
All plants	DCP	475	2,410	<0.5–6.1	<0.5	0.5	0.9	1.4
	TCP	475	2,393	<0.5–12.8	<0.5	0.8	1.8	3.1
	CP	464	2,313	<0.5–9.1	<0.5	<0.5	<0.5	0.8
	CH	473	2,329	<0.5–46.0	<0.5	1.7	4.0	7.4
Surface water	DCP	342	1,714	<0.5–6.1	<0.5	0.6	1.0	1.5
	TCP	342	1,700	<0.5–12.8	<0.5	1.2	2.1	3.5
	CP	332	1,636	<0.5–4.3	<0.5	<0.5	0.5	1.0
	CH	340	1,655	<0.5–46.0	0.9	2.4	4.7	8.1
Groundwater	DCP	117	569	<0.5–3.5	<0.5	<0.5	<0.5	0.8
	TCP	117	568	<0.5–5.3	<0.5	<0.5	<0.5	0.5
	CP	116	555	<0.5–9.1	<0.5	<0.5	<0.5	<0.5
	CH	117	554	<0.5–20.0	<0.5	<0.5	<0.5	1.6

Table 11.6

Finished water haloketones, chloropicrin, and chloral hydrate—surface water plants

Plant disinfectant	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
Chlorine	DCP	206	1,006	<0.5–4.4	<0.5	0.5	0.8	1.2
	TCP	206	999	<0.5–9.8	0.7	1.4	2.4	3.6
	CP	203	974	<0.5–3.6	<0.5	<0.5	<0.5	0.8
	CH	204	943	<0.5–24.0	1.5	2.8	5.2	8.2
Chloramine	DCP	20	82	<0.5–3.6	0.6	1.1	1.5	2.0
	TCP	20	82	<0.5–6.8	<0.5	<0.5	1.0	2.4
	CP	20	80	<0.5–4.3	<0.5	<0.5	0.6	1.1
	CH	21	85	<0.5–36.0	<0.5	1.1	3.3	8.6
Chlorine/chloramine	DCP	83	370	<0.5–6.1	0.6	0.9	1.4	2.2
	TCP	83	365	<0.5–9.7	<0.5	1.0	2.0	3.3
	CP	76	335	<0.5–3.0	<0.5	<0.5	0.7	1.0
	CH	80	365	<0.5–40.5	0.7	2.3	4.8	8.2
Chlorine dioxide	DCP	24	102	<0.5–6.0	<0.5	0.5	0.9	1.3
	TCP	24	102	<0.5–5.1	<0.5	<0.5	1.5	2.7
	CP	24	98	<0.5–2.3	<0.5	<0.5	<0.5	0.6
	CH	26	104	<0.5–12.0	0.4	1.6	3.4	6.2
Ozone	DCP	19	90	<0.5–4.1	<0.5	0.7	1.7	2.4
	TCP	19	90	<0.5–7.3	<0.5	<0.5	1.4	2.2
	CP	19	88	<0.5–3.3	<0.5	<0.5	0.9	2.0
	CH	19	91	<0.5–32.6	<0.5	0.6	3.6	5.9

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Table 11.7

Distribution system haloketones, chloropicrin, and chloral hydrate

Plant category	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
All plants	DCP	429	8,586	<0.5–10.0	<0.5	<0.5	0.7	1.3
	TCP	429	8,527	<0.5–17.0	<0.5	0.5	1.8	3.3
	CP	419	8,283	<0.5–13.6	<0.5	<0.5	0.5	0.9
	CH	427	8,237	<0.5–92.2	<0.5	2.8	6.3	11.0
Surface water	DCP	303	5,946	<0.5–10.0	<0.5	<0.5	0.9	1.4
	TCP	303	5,899	<0.5–17.0	<0.5	1.0	2.2	3.7
	CP	294	5,725	<0.5–6.4	<0.5	<0.5	0.6	1.1
	CH	300	5,712	<0.5–92.2	1.5	4.0	7.5	12.0
Groundwater	DCP	110	2,196	<0.5–6.0	<0.5	<0.5	<0.5	0.7
	TCP	110	2,191	<0.5–5.3	<0.5	<0.5	<0.5	0.7
	CP	109	2,132	<0.5–13.6	<0.5	<0.5	<0.5	<0.5
	CH	111	2,099	<0.5–33.0	<0.5	<0.5	0.7	3.6

Table 11.8

Distribution system haloketones, chloropicrin and chloral hydrate—surface water plants

Distribution system disinfectant	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
Chlorine	DCP	199	3,705	<0.5–6.1	<0.5	<0.5	0.6	0.9
	TCP	199	3,678	<0.5–17.0	0.6	1.5	2.8	4.2
	CP	196	3,614	<0.5–6.4	<0.5	<0.5	0.6	0.9
	CH	196	3,519	<0.5–92.2	2.9	5.2	8.7	13.2
Chloramine	DCP	118	2,233	<0.5–10.0	<0.5	0.8	1.3	2.0
	TCP	118	2,213	<0.5–7.7	<0.5	<0.5	1.2	2.2
	CP	112	2,103	<0.5–5.0	<0.5	<0.5	0.8	1.2
	CH	115	2,185	<0.5–41.0	<0.5	1.9	4.7	8.7

Chloropicrin

CP concentrations in ICR finished water (Table 11.5) ranged from less than the MRL of 0.5 µg/L up to 9.1 µg/L, with 90% of the data at less than 0.8 µg/L (80% were below the MRL). Distribution system CP concentrations ranged from below the MRL of 0.5 µg/L to 13.6 µg/L, with 90% of the data at less than 0.9 µg/L (70% were below the MRL). Reported values above the MRL were mostly from surface water plants. Most of the CP data reported in the literature

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are below the MRL established for ICR reporting. For example, Singer, Obolensky, and Greiner (1995) found median concentrations of 0.28 μg/L in plant effluent and 0.43 μg/L in the distribution system. No difference in CP concentrations was discernible when the data were aggregated by disinfectant type (see Tables 11.6 and 11.8).

Chloral Hydrate

Table 11.5 shows that ICR finished water CH concentrations ranged from <MRL of 0.5 μg/L to 46 μg/L. Reported values above the MRL were generally from surface water plants (80% of reported groundwater values were below the MRL). Analysis of CH data aggregated by treatment plant disinfectant type shows no significant differences in finished water CH concentrations (Table 11.6). The median CH concentration in ICR finished water (1.7 μg/L) was similar to the values reported in other studies (Krasner et al. 1989—2.1 μg/L, USEPA 1992—2.5 μg/L), whereas the maximum reported CH concentration (46 μg/L) exceeded the highest values reported in these other studies (Krasner et al. 1989—22 μg/L, USEPA 1992—25 μg/L).

The data in Table 11.7 show that reported CH concentrations in distribution system samples ranged from <MRL of 0.5 μg/L up to 92 μg/L. A comparison of CH data aggregated by type of source water showed higher concentrations in surface water (median = 4.0 μg/L, 90th percentile = 12.0 μg/L) than in groundwater (median = <MRL of 0.5 μg/L, 90th percentile = 3.6 μg/L). CH concentrations in surface water were similar to those reported by Arora and coworkers (1994, 1997) (median = 4.4 μg/L, 90th percentile = 14.1 μg/L).

A comparison of the data in Tables 11.5 and 11.7 showed that CH concentrations observed in the distribution systems of ICR surface water plants (median = 4.0 μg/L, 90th percentile = 12.0 μg/L) were generally higher than those in the finished water of surface water plants (median = 2.4 μg/L, 90th percentile = 8.1 μg/L). Based on these results, CH concentrations appeared to increase somewhat across the distribution system. CH values were also slightly higher at plants using chlorine as a secondary disinfectant (median = 5.2 μg/L, 90th percentile = 13.2 μg/L) than at plants practicing postchloramination (median = 1.9 μg/L, 90th percentile = 8.7 μg/L). However, because the data represent varying source water and treatment conditions, other factors may have contributed to this difference.

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Cyanogen Chloride

Plants using chloramines were required to monitor CNCl in finished water and at the distribution system MAX location. The data in Table 11.9 show that CNCl concentrations in ICR finished water ranged from <MRL of 0.5 μg/L up to 21 μg/L, with values in surface water systems (median = 2.3μg/L) slightly higher than those in groundwater systems (median = 1.1 μg/L). CNCl concentrations in distribution system samples were also slightly higher in surface water systems (median = 2.1 μg/L) than in groundwater systems (median = 0.8 μg/L). Comparison of finished water and distribution system results did not suggest an increase in CNCl concentrations across the distribution system. The median CNCl concentration in ICR finished water (2.1 μg/L) was slightly higher than that reported by Krasner et al. (1989) for utilities delivering chloraminated water (median = 1.6 μg/L).

Aldehydes

Aldehyde concentrations were measured in the finished water of ICR plants using ozone or chlorine dioxide (Table 11.10). The four aldehydes discussed in this chapter are formaldehyde, acetaldehyde, glyoxal and methyl glyoxal. Other researchers have shown that these four aldehydes account for the majority of total aldheydes produced in ozone plants (Glaze et al. 1991; LeLacheur, Singer, and Charles 1991). Other aldehydes (propanal, pentanal, and butanal) were monitored under the ICR, but the most of the concentrations reported were <MRL of 5.0 μg/L. Some propanal and pentanal concentrations were around 10 μg/L, but these values were in the 95th percentile, or higher, of all observations. Most of the records used in this analysis were from surface water plants, although four records from one groundwater plant using ozone indicated the presence of aldehydes in finished water.

Comparison of results from ozone and chlorine dioxide plants showed that aldehydes were detected at higher concentrations in ozone plants than in chlorine dioxide plants (Figures 11.3 and 11.4). The chlorine dioxide data (Table 11.10) show that although formaldehyde was observed in more than 50% of the samples (mean = 5.3 μg/L, 90th percentile = 9.0 μg/L), the other aldehydes were reported as <MRL in 116 out of 117 samples (114 of 117 acetaldehyde

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samples had concentrations <MRL). The higher distributions observed in ozone plants is consistent with the increased aldehyde concentrations expected when a stronger oxidant is used.

Correlations and Analyses of Trends

Regression analyses were performed for each of the DBPs discussed in this chapter in an attempt to identify relationships in the reported data. These analyses compared the studied DBPs with regulated by-products (TTHM and HAA5) and with influent water quality parameters. The correlations were weak, as indicated by low coefficients of determination (r^2). For example, finished water HAN4 concentrations were not well correlated with TTHM or HAA5 concentrations in finished water. This finding did not match the HAN4 correlation with TTHM concentrations in clearwell effluent samples (r^2 = 0.90) reported by Krasner et al. (1989) in a study of 35 utilities. Although individual concentrations of each of these DBPs did not correlate well with TTHM, HAA5, or total organic halogen (TOX), Shukairy, Blank, and McLain (2002) performed summary comparisons of all ICR DBPs with TOX, and these comparisons produced good correlations.

Table 11.9

Distribution of cyanogen chloride concentrations aggregated by sampling location

Sampling location	Plant category	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
Finished water	All	174	914	<0.5–20.6	0.7	2.1	4.3	7.2
	SW*	140	730	<0.5–20.6	0.8	2.3	4.6	7.4
	GW†	28	145	<0.5–14.5	<0.5	1.1	2.9	6.1
Distribution system MAX	All	151	809	<0.5–18.3	<0.5	1.8	4.0	6.8
	SW*	114	593	<0.5–18.3	0.6	2.1	4.4	7.9
	GW†	26	134	<0.5–16.3	<0.5	0.8	2.2	4.2

* SW=surface water
† GW=groundwater

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Table 11.10

Finished water aldehyde concentrations

Plant category	DBP	Number of plants	Number of records	Range (µg/L)	25th percentile (µg/L)	50th percentile (µg/L)	75th percentile (µg/L)	90th percentile (µg/L)
All plants	Formaldehyde	41	227	<5.0–30.6	<5.0	5.3	8.2	13.7
	Acetaldehyde	41	236	<5.0–18.3	<5.0	<5.0	<5.0	5.4
	Glyoxal	41	236	<5.0–16.2	<5.0	<5.0	<5.0	5.4
	Methyl glyoxal	41	235	<5.0–6.4	<5.0	<5.0	<5.0	<5.0
Surface water/ozone	Formaldehyde	18	86	<5.0–30.6	<5.0	<5.0	9.6	21.8
	Acetaldehyde	18	90	<5.0–10.9	<5.0	<5.0	<5.0	8.2
	Glyoxal	18	90	<5.0–16.2	<5.0	<5.0	5.3	9.9
	Methyl glyoxal	18	90	<5.0–6.4	<5.0	<5.0	<5.0	<5.0
Surface water/chlorine dioxide	Formaldehyde	21	114	<5.0–23.6	<5.0	5.3	7.0	9.0
	Acetaldehyde	21	117	<5.0–5.4	<5.0	<5.0	<5.0	<5.0
	Glyoxal	21	117	<5.0–5.1	<5.0	<5.0	<5.0	<5.0
	Methyl glyoxal	21	116	<MRL	<5.0	<5.0	<5.0	<5.0

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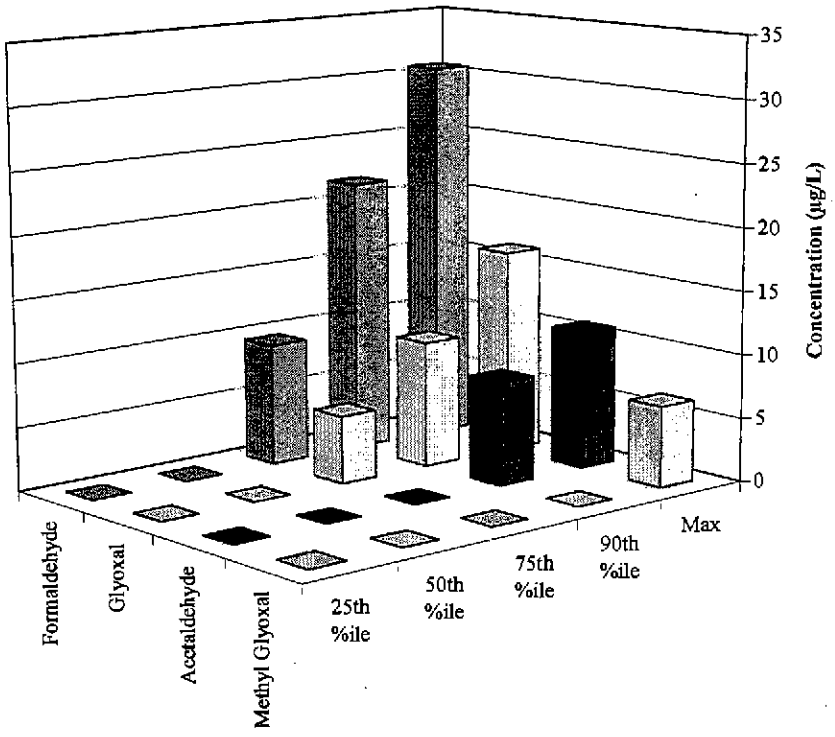

Figure 11.3 Aldehyde concentrations in finished water from surface water plants using ozone

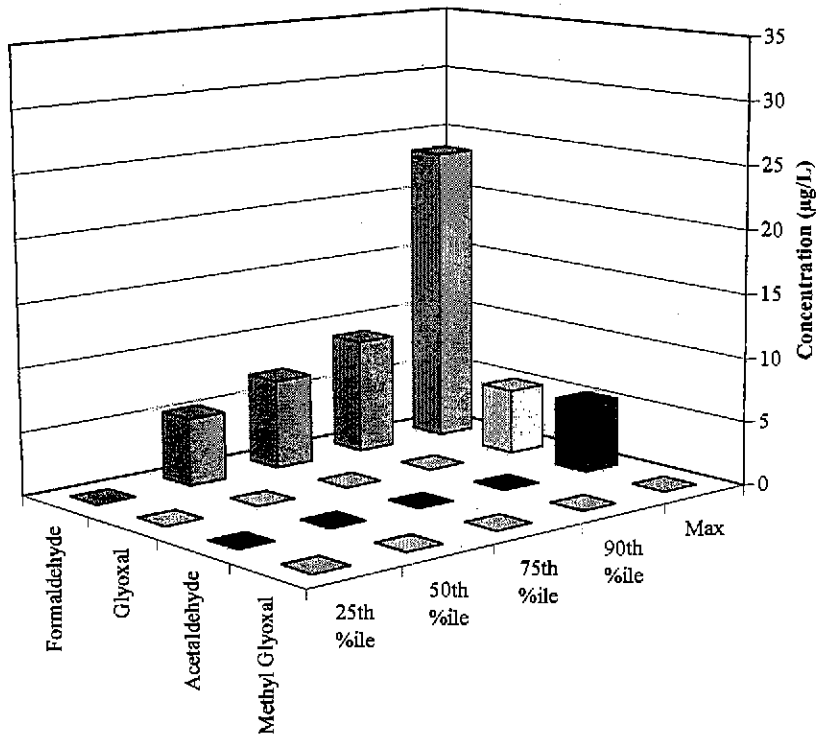

Figure 11.4 Aldehyde concentrations in finished water from surface water plants using chlorine dioxide

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SUMMARY

ICR monitoring results for HANs, HK2, CP, CH, CNCl, and aldehyde concentrations provide the first comprehensive data set on national occurrence of these DBPs in large public water systems.

- The 90th percentile concentrations of these DBPs rarely exceeded 10 μg/L.
- These by-products occurred in higher concentrations in surface water systems than in groundwater systems.
- CH concentrations were higher in distribution systems than in finished water, whereas concentrations of HANs, HKs, CP, and CNCl were similar in finished and distributed water.
- HAN4 concentrations were slightly higher in plants using chloramines than in plants using other disinfectants. This finding may be the result of a shift to chloramine disinfection because of higher source water precursor concentrations at these plants.
- Finished water DCP concentrations were similar at chloramine and ozone plants, and lower DCP concentrations were observed at plants using chlorine or chlorine dioxide. DCP values did not vary with the type of disinfectant used in the distribution system. TCP concentrations did not vary with the type of disinfectant used in either the finished water or the distribution system.
- CP and CH concentrations were similar, regardless of the type of disinfectant used in the plant.
- CH concentrations were higher in plants adding chlorine in the distribution system than in plants practicing postchloramination.
- Aldehyde concentrations were higher in ozone plants than in chlorine dioxide plants.
- These DBPs did not correlate well, individually or for the group sum of HAN4, with influent parameters (TOC, bromide, temperature) or with TTHM or HAA5 concentrations.

The range of reported concentrations for each of these DBPs varied widely. However, median ICR concentrations of these DBPs were fairly low compared with ICR concentrations of TTHM and HAA5. Because the concentrations were low and formation is influenced by many

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factors, it is difficult to discern relationships among the by-products and monitored water quality parameters that typically affect formation. However, the ICR data set on these by-products is important because it includes national occurrence data collected under a variety of source water and treatment conditions. The data also provide baseline national occurrence information that can be used to evaluate health risks associated with these DBPs.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The scientific views expressed are solely those of the authors and do not necessarily reflect those of USEPA.

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CHAPTER 12

RELATIONSHIPS BETWEEN SOURCE WATER QUALITY AND CHOICES OF PRIMARY AND SECONDARY DISINFECTANTS

Michael J. McGuire and Michael L. Hotaling

ABSTRACT

Influent water quality measurements collected during implementation of the Information Collection Rule (ICR) numbered in the tens of thousands of discrete values. Data on total organic carbon (TOC) and bromide varied widely across the United States, and very high concentrations of each parameter did not appear to occur concurrently in the influent of ICR treatment plants. Examination of the treatment techniques used by ICR plants did not show any overall trends related to influent concentrations of TOC and bromide until the data on primary and secondary disinfectants were "binned" with TOC and bromide data. This chapter explores the relationships between source water quality and the primary and secondary disinfectants used at ICR treatment plants.

Graphs of TOC, bromide, and TOC × bromide indicate that ICR utilities selected primary and secondary disinfectants on the basis of influent water quality. Higher concentrations of TOC and bromide in a plant's influent resulted in selection of alternative primary disinfectants such as ozone, chlorine dioxide, and chloramines and, more clearly, selection of an alternative secondary disinfectant—chloramines.

Even so, the data presented in this chapter indicate that many treatment plants whose water sources have relatively high TOC and bromide concentrations are still using free chlorine. These plants could significantly reduce their concentrations of total trihalomethane and the sum of five haloacetic acids by changing either or both of their primary and secondary disinfectants to something other than free chlorine.

INTRODUCTION

The Information Collection Rule (ICR) generated far more water quality data than just information on microorganisms and disinfection by-products (DBPs) (Wysock et al. 2002, Fair et al. 2002). To put the DBP data in context, it is important to examine the overall occurrence and variability of water quality constituents measured during the ICR.

During presentations of ICR water quality information to the Federal Advisory Committee (FACA) in 1999 and 2000, it was observed that DBP concentrations were not well correlated with influent water quality. Sorting out the relationships between source water quality,

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types of treatment, and DBPs was difficult because the Disinfectants/Disinfection By-Products (D/DBP) Rule was in final form during the ICR monitoring period, and there was speculation that utilities were making treatment changes to comply with this rule as ICR data were being collected. The only explanation that made sense at the time of the FACA meetings was that changes in treatment and disinfection practices might have obscured the impact of high concentrations of total organic carbon (TOC) and bromide on DBP concentrations.

This chapter presents summary statistics on influent water quality data collected under the ICR, describes general water treatment trends in ICR utilities, and examines the relationships between influent water quality and treatment methods, especially disinfection practices.

SOURCE WATER QUALITY DATA

Water quality data were extracted from the ICR Auxiliary 1 Database (AUX1) version 5.0, which contains data from 296 utilities and their 500 water treatment plants. ICR values below minimum reporting levels were replaced with zeros before further calculations were performed.

Tables 12.1 and 12.2 list a number of important water quality parameters measured in all ICR treatment plant influents. Unlike other chapters in this book, which describe separate investigations of data on surface water and groundwater plants, this chapter examines overall water quality variability and the resulting treatment technologies applied to meet DBP regulations. Table 12.1 shows statistics on water quality parameters that are of particular interest with respect to the production of DBPs after chlorination. High water temperatures and high pH levels are known to increase the formation of trihalomethanes (THMs). Ultraviolet absorbance at 254 nm (UV_{254}) is an integral part of the specific ultraviolet absorbance (SUVA) calculation—or in the case of ICR data, the TSUVA calculation (SUVA estimated using TOC instead of dissolved organic carbon)—that is used as a surrogate for the removable fraction of natural organic matter in water supplies. The AUX1 database contains a wide range of TOC, bromide, and UV_{254} data. The maximum TOC value of 27.5 mg/L is correct and represents very high source water TOC. The descriptive statistics for bromide listed in Table 12.1 are correct after one adjustment. (AUX1 contains six bromide values of 25 *milligrams* per liter or greater from one utility in Massachusetts. It is certain that these six bromide values are off by a factor of 1,000 and

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were entered into the ICR Federal Database incorrectly. The next highest bromide concentration reported in AUX1 is 2.2 mg/L.) The rest of the descriptive statistics describe reasonable and representative concentrations of DBP precursors and important DBP-production parameters in U.S. drinking water supplies.

Table 12.1

ICR influent water quality data related to DBP production

Statistic	TOC (mg/L)	Bromide (mg/L)	UV_{254} (/cm)	pH	Temperature (°C)
Mean	2.8	0.069	0.087	7.53	17.7
Median	2.4	0.036	0.06	7.6	18
Maximum	27.5	2.23	1.9	12.1	43.6
Minimum	<0.35	<0.01	<0.0045	3.7	0.1
90th percentile	5.3	0.16	0.174	8.27	26.7
10th percentile	<0.35	<0.01	<0.0045	6.7	8
Total number of values	7,504	7,959	7,508	8,554	8,563
Number of values below MRL*	1,186	2,173	887	NA†	NA†

* MRL = minimum reporting level
† NA = not applicable

Table 12.2

ICR influent water quality data—other parameters

Statistic	Alkalinity (mg/L as $CaCO_3$)	Turbidity (NTU)	Calcium hardness (mg/L as $CaCO_3$)	Total hardness (mg/L as $CaCO_3$)	Ammonia-nitrogen (mg/L)
Mean	103	11.8	92	139	0.14
Median	93	2.2	76	118	0.10
Maximum	500	3200	515	806	5.10
Minimum	1	0	1	1	0
90th percentile	210	24	200	289	0.30
10th percentile	13	0.12	10	18	0
Total number of values	8,539	8,379	8,258	8,238	8,212
Number of values below MRL*	NA†	NA†	NA†	NA†	NA†

* MRL = minimum reporting level
† NA = not applicable

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Table 12.2 lists a variety of other water quality parameters measured under the ICR. Alkalinity, calcium, and total hardness were measured as part of the input parameter matrix for the DBP production model. The revised version of this model, based on ICR data (including data on the DBP precursors listed in Table 12.1), is described in Chapter 8 (Swanson et al. 2002). The huge range of values for influent ammonia-nitrogen indicates a significant inorganic chlorine demand at some treatment plants. Destroying the ninetieth percentile concentration of ammonia-nitrogen (0.3 mg/L) would require the application of about ten times as much free chlorine (about 3 mg/L) as ammonia-nitrogen before a free chlorine residual would be created. The turbidity data show that ICR plants were influenced by rainfall-runoff events during a significant percentage of the 18-month monitoring period. In addition to controlling DBPs, the main function of treatment plants is to remove particles and pathogens. High influent turbidity (and, in some cases, very low influent turbidity) can challenge particle and pathogen removal efforts.

Figures 12.1 and 12.2 show national distributions of the same TOC and bromide data described in Table 12.1. Unlike the figures in Chapter 4 that depict quarterly distribution system data on total THM (TTHM) concentrations by U.S. Environmental Protection Agency region, Figures 12.1 and 12.2 present TOC and bromide data by state because three times as many data points are available for TOC and bromide on the basis of monthly sampling. The combined surface water and groundwater TOC data shown in Figure 12.1 indicate high TOC concentrations in Virginia, North Carolina, Florida, Texas, and the Midwest (with a scattering of high values in New England). In some states, high TOC concentrations occur in both groundwater and surface water, but in other states the TOC concentrations differ. Most of the data on TOC in groundwater supplies (not shown) indicate concentrations of less than 1 mg/L, except in Florida where very high TOC concentrations are found in groundwater. High TOC concentrations in the Southeast, the South, and the upper Midwest are found primarily in surface water sources.

The distribution of bromide across the United States is more complicated than TOC occurrence. Figure 12.2, which shows combined bromide values for groundwater and surface water sources, indicates the occurrence of high bromide concentrations in the Midwest and in Florida, Texas, New Mexico, Arizona, and California. High groundwater bromide concentrations (not shown) are confined to these same five states. Most of the other states either had no data on bromide concentrations in groundwater or had moderate concentrations.

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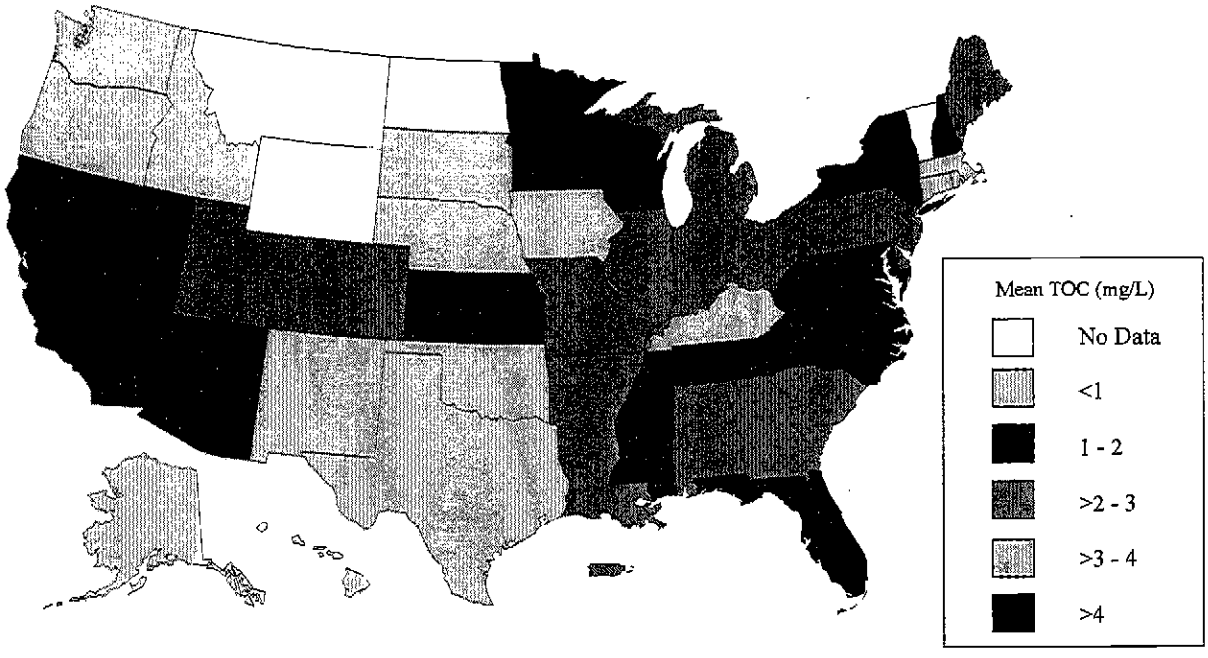

Figure 12.1 National distribution of TOC occurrence in surface water and groundwater

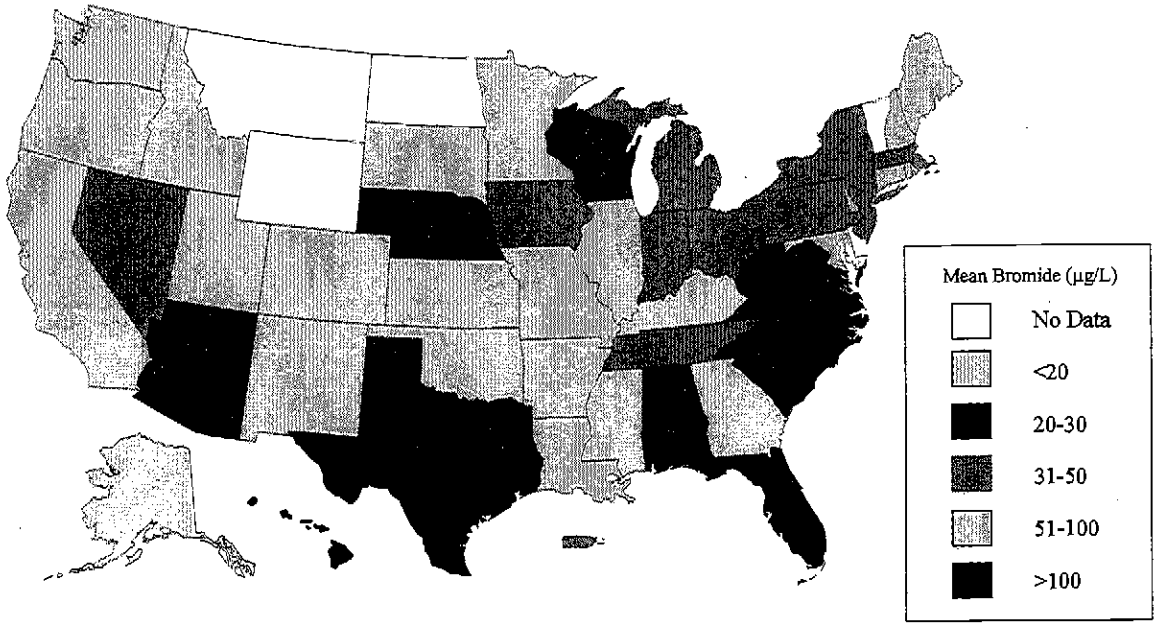

Figure 12.2 National distribution of bromide occurrence in surface water and groundwater

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A comparison of Figures 12.1 and 12.2 illustrates the co-occurrence of high bromide and high TOC concentrations in Florida, Texas, Oklahoma, Kansas, Nebraska, and South Dakota. The lowest bromide and TOC concentrations co-occurred in the Pacific Northwest and Alaska.

Figure 12.3 plots paired concentrations of bromide versus TOC in all ICR plant influents. Several patterns are immediately apparent. The very high TOC concentrations (>10 mg/L) do not co-occur with very high bromide concentrations (>0.50 mg/L), but dozens of ICR influent samples had either very high bromide (up to 2 mg/L) or very high TOC (27 mg/L) values. If very high TOC and bromide concentrations did co-occur in a plant's influent, it would be extremely difficult for that plant to use any free chlorine for any appreciable contact time and still meet the 1979 TTHM maximum contaminant level (MCL) of 0.10 mg/L. In most of the paired data shown in Figure 12.3, bromide concentrations ranged from less than the minimum reporting level (MRL) to 0.50 mg/L, and TOC concentrations ranged from <MRL to 10 mg/L (16% and 27%, respectively).

The broad ranges in water quality parameters measured under the ICR indicate the challenges confronting U.S. water utility managers, who must comply with the D/DBP Rule.

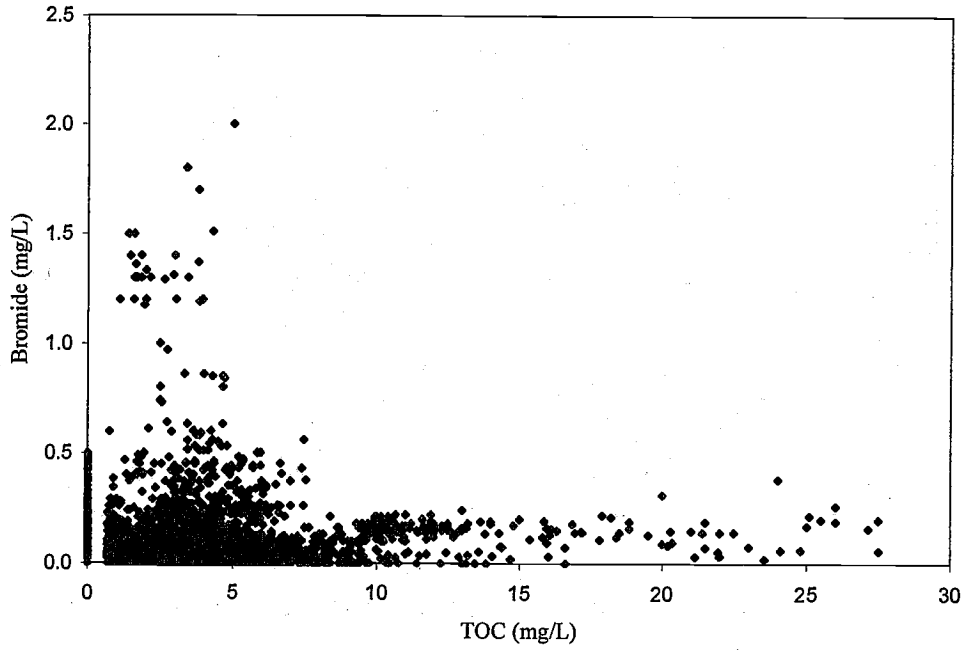

Figure 12.3 Relationship between TOC concentrations and bromide concentrations in the influent of ICR plants (based on plant-months)

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DISINFECTION AND TREATMENT TECHNOLOGIES

Figure 12.4 summarizes the water treatment technologies used by 431 of the 500 plants involved in ICR monitoring. Both groundwater and surface water plants are included in the data shown in Figure 12.4; ICR plants not included in this figure were classified in other treatment categories. Conventional treatment (CONV), generally characterized as coagulation–sedimentation–filtration, was by far the most common treatment technology used at ICR plants. A smaller percentage of plants used direct filtration and in-line filtration, described as unconventional treatment (UNCONV). Plants applying only disinfection to unfiltered surface water (UNFILT/SW) constituted a small portion of ICR plants. Disinfection only (DIS/GW) was the most common treatment used for groundwater supplies. The softening category (SOFT) represents a variety of simple, two-stage, split-treatment and other complex softening processes used to reduce hardness (see Chapter 22 [Clark, James, and Lawler 2002] for a detailed discussion of softening at ICR plants). Disinfection of wholesale supplies (DIS/WHSALE), membrane treatment (MEMBRANE), and other groundwater treatment techniques (OTHER/GW) account for the remaining treatment categories represented in Figure 12.4.

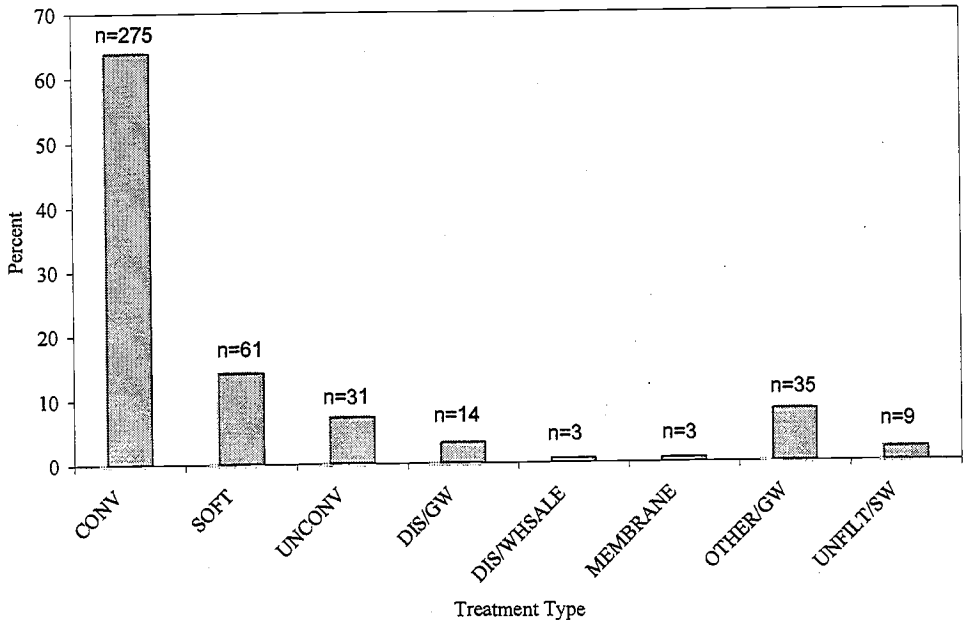

Figure 12.4 ICR plants classified by treatment technology

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Attempts were made to segment the treatment technologies shown in Figure 12.4 into "bins" of influent TOC and bromide concentrations (not shown). The purpose of this effort was to determine if these influent water quality parameters drove the selection of treatment processes. No relationship was found between influent TOC and bromide concentrations and treatment plant type, possibly because ICR utilities had chosen treatment technologies for a variety of reasons that were unrelated to TOC and bromide (e.g., the need to filter surface water, high hardness concentrations, high source water concentrations of pathogens, and treatment costs).

Primary and secondary disinfectants are of principal importance in the formation of DBPs, and the distribution of their use among ICR plants is described in Figures 12.5 and 12.6. Free chlorine was the most prevalent primary disinfectant used by ICR utilities. Alternative primary disinfectants such as ozone, chlorine dioxide, and chloramines were used in about 13% of plant-months (months of data collected by ICR treatment plants). Theoretically, ICR sampling could have produced a maximum of 9,000 plant-months of data (i.e., 500 plants times 18 months). Plant-months were calculated and graphed in Figures 12.5 and 12.6 because some treatment plants changed primary and secondary disinfectants from month to month over the 18-month monitoring period.

Figure 12.6 shows that 69% of ICR plants used free chlorine as a secondary disinfectant in their distribution systems. The number of utilities that changed their distribution system disinfectant to chloramines prior to ICR monitoring increased between 1979, when the TTHM MCL was promulgated, and 1987 (McGuire and Meadow 1988).

Although overall statistics on the types of treatment and disinfectants used at ICR plants are of general interest, it is more important to understand which plants with specific influent water qualities were using free chlorine or alternative disinfectants during ICR monitoring. The FACA negotiators in 1999–2000 were interested in understanding the effects of technology and the capacity for installing additional treatment at a relatively low cost in order to achieve better control of DBPs (for example, switching to alternative disinfectants).

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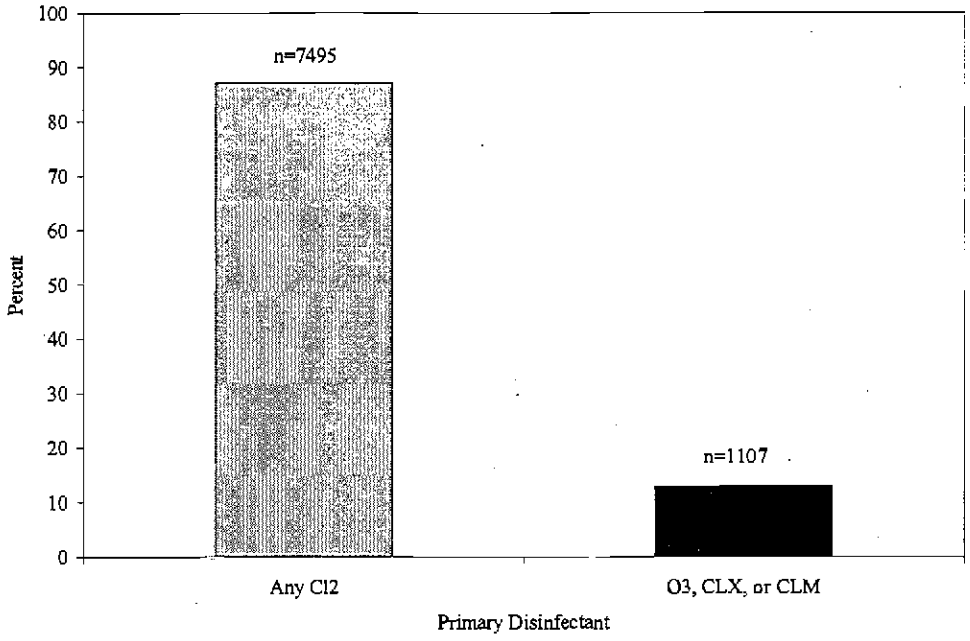

Figure 12.5 Primary disinfectants used by ICR treatment plants (based on plant-months)

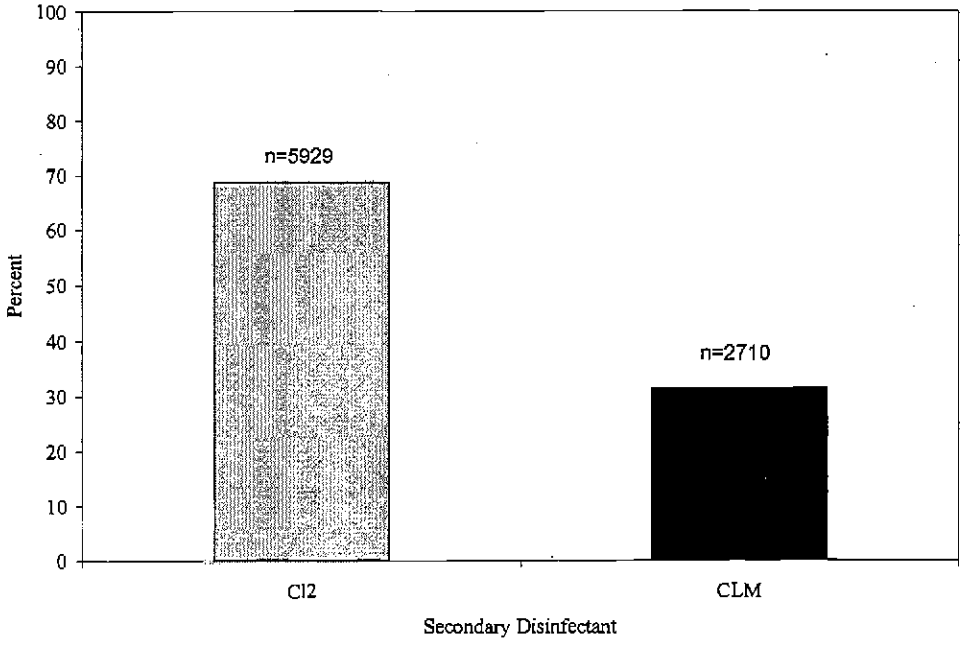

Figure 12.6 Secondary disinfectants used by ICR treatment plants (based on plant-months)

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DISINFECTION AND SOURCE WATER QUALITY RELATIONSHIPS

Primary Disinfectants

Figures 12.7, 12.8, and 12.9 synthesize ICR information on source water quality and choice of primary disinfectant. Each graph plots the percentage of plant-months in which ICR plants used free chlorine or an alternative disinfectant as the primary disinfectant. Plant-month percentages are organized into five bins of TOC values representing approximate quintiles, or ranges, each comprising 20% of the TOC values. For example, in the bin for TOC concentrations ranging from 0.9 to 1.95 mg/L, free chlorine was used as the primary disinfectant in 97% of the plant-months, and an alternative disinfectant (such as ozone, chlorine dioxide, or chloramines) was used as the primary disinfectant in 3% of the plant months.

Overall, Figure 12.7 shows that increasing concentrations of TOC in source water supplies required a higher percentage of ICR plants to change to a primary disinfectant other than free chlorine. In other words, if a treatment plant with high concentrations of natural organic matter in its source of supply used free chlorine, the utility would risk violating the existing TTHM MCL of 0.10 mg/L. Chapter 4 discusses the relationship between influent TOC concentrations and TTHM produced at ICR plants (McGuire and Graziano 2002).

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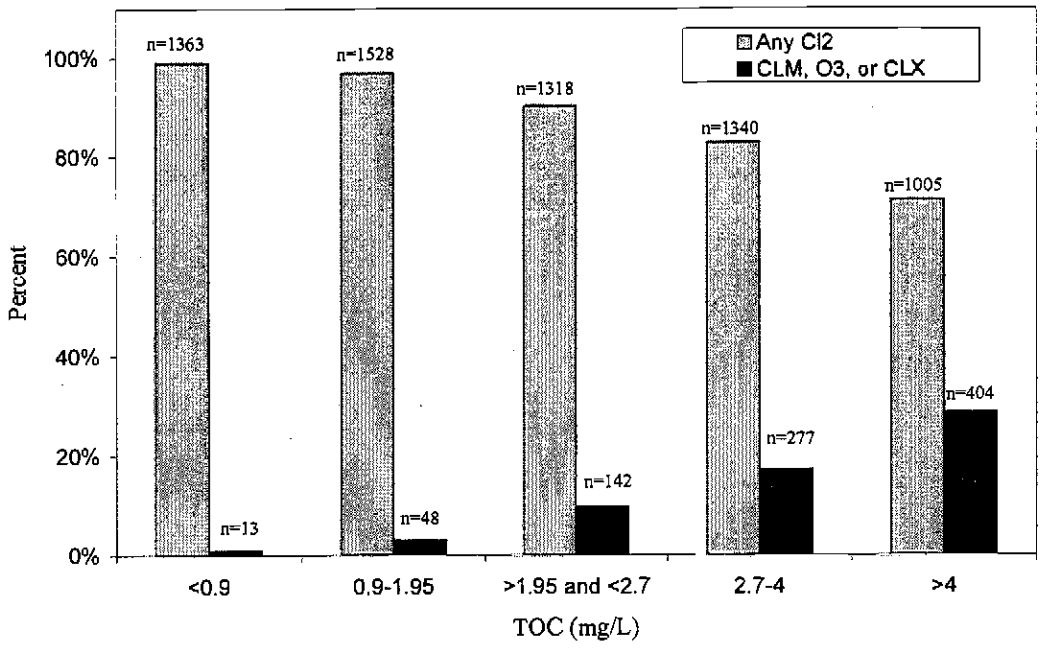

Figure 12.7 Primary disinfectants used by ICR treatment plants and binned according to influent TOC data (based on plant-months)

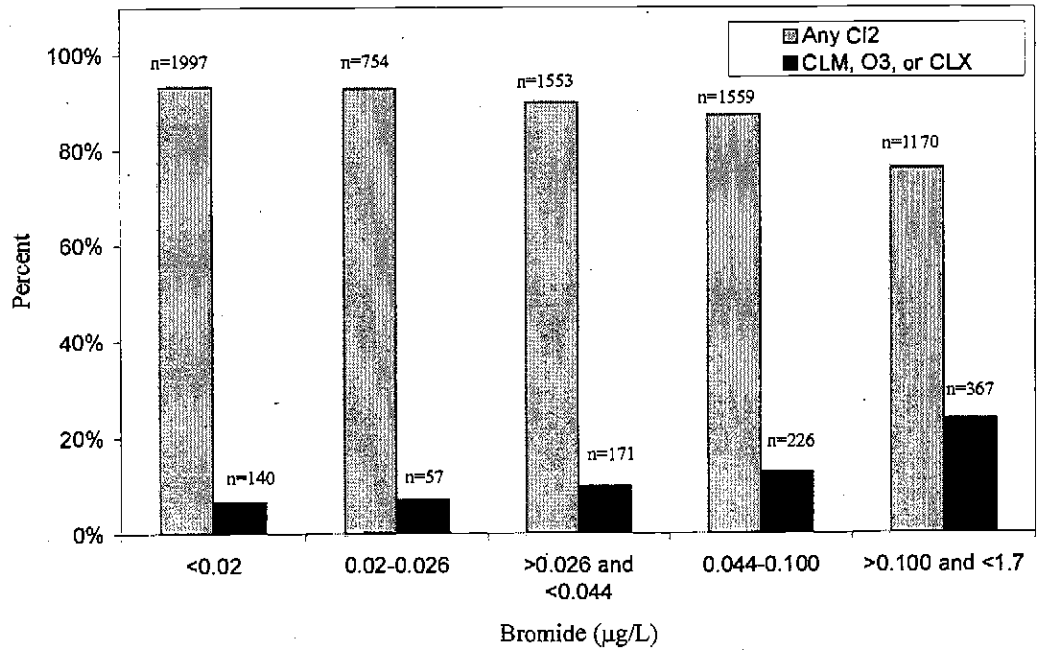

Figure 12.8 Primary disinfectants used by ICR treatment plants and binned according to influent bromide data (based on plant-months)

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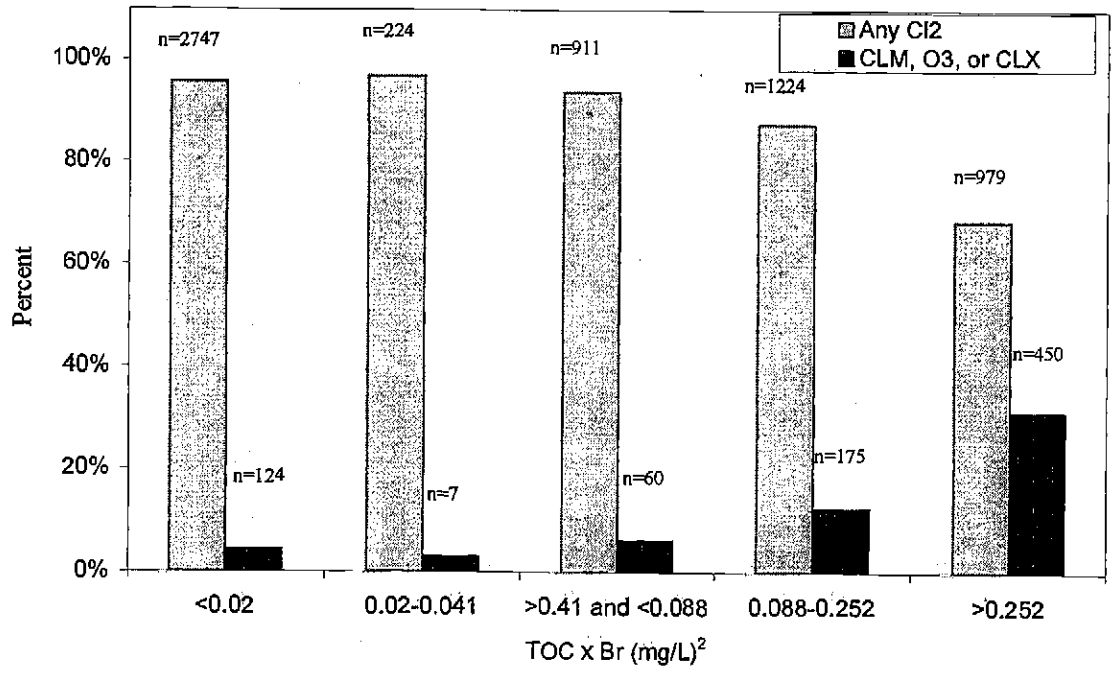

Figure 12.9 Primary disinfectants used by ICR treatment plants and binned according to the product of influent TOC × bromide (based on plant-months; units = milligrams per liter, squared)

Figure 12.8 shows that ICR treatment facilities also appear to have chosen primary disinfectants on the basis of influent bromide concentrations. This finding is somewhat surprising, because national distributions of bromide were not widely known before ICR sampling was conducted. Without data on bromide concentrations, utilities were probably choosing primary disinfectants on the basis of some other parameter that likely had some type of relationship with bromide in source water supplies. In the 1980s and 1990s, water utilities were modifying their primary disinfectant based on the occurrence of THMs in their distribution systems. Utilities that had high TTHM concentrations and were uncomfortably close to the 0.10 mg/L MCL probably switched to alternative primary disinfectants to avoid the effect of high bromide concentrations on THM formation. Under laboratory conditions, increasing bromide concentrations while maintaining constant concentrations of TOC and free chlorine produced higher concentrations of THMs (Pourmoghaddas et al. 1993, Symons et al. 1987).

Figure 12.9 plots the product of TOC and bromide concentrations (in units of milligrams per liter, squared) to illustrate the combined effects of these two DBP precursors on the choice of

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primary disinfectant. In the bin containing the highest concentrations of TOC × bromide (>0.252 $[mg/L]^2$), alternative primary disinfectants were used in 31% of plant-months, whereas in the bins containing the highest concentrations of TOC and bromide alone, alternative primary disinfectants were used in 29% and 24% of plant-months, respectively. Thus, when the two precursors were considered together, the highest TOC and bromide product in the influent seemed to influence almost one third of the plants in that category to change to an alternative primary disinfectant.

Secondary Disinfectants

Figures 12.10, 12.11, and 12.12 synthesize ICR information on source water quality and choice of secondary disinfectant. These figures show that poor source water quality resulted in more choices of alternative secondary disinfectants than alternative primary disinfectants. For example, in the bin containing the highest TOC concentrations (>4 mg/L) alternative primary disinfectants were used in 29% of plant-months, whereas alternative secondary disinfectants were used in 66% of plant-months. This is not surprising, because one of the first things utilities did upon realizing that they might have trouble meeting the 1979 TTHM MCL was to change their distribution system disinfectant from free chlorine to chloramines (McGuire and Meadow 1988, Kreft et al. 1985). Using chloramines in the distribution system was a lot less expensive for utilities than implementing an alternative primary disinfectant such as ozone or chlorine dioxide.

Figure 12.12 shows that the impact of considering both TOC and bromide in selecting a secondary disinfectant was greater than the impact of considering either precursor separately, as was the case with selection of a primary disinfectant. In the bin containing the highest concentrations of TOC × bromide (>0.252 $[mg/L]^2$), chloramines were used in 74% of plant-months, whereas in the bins containing the highest concentrations of TOC and bromide alone, chloramines were used in 66% and 57% of plant-months, respectively.

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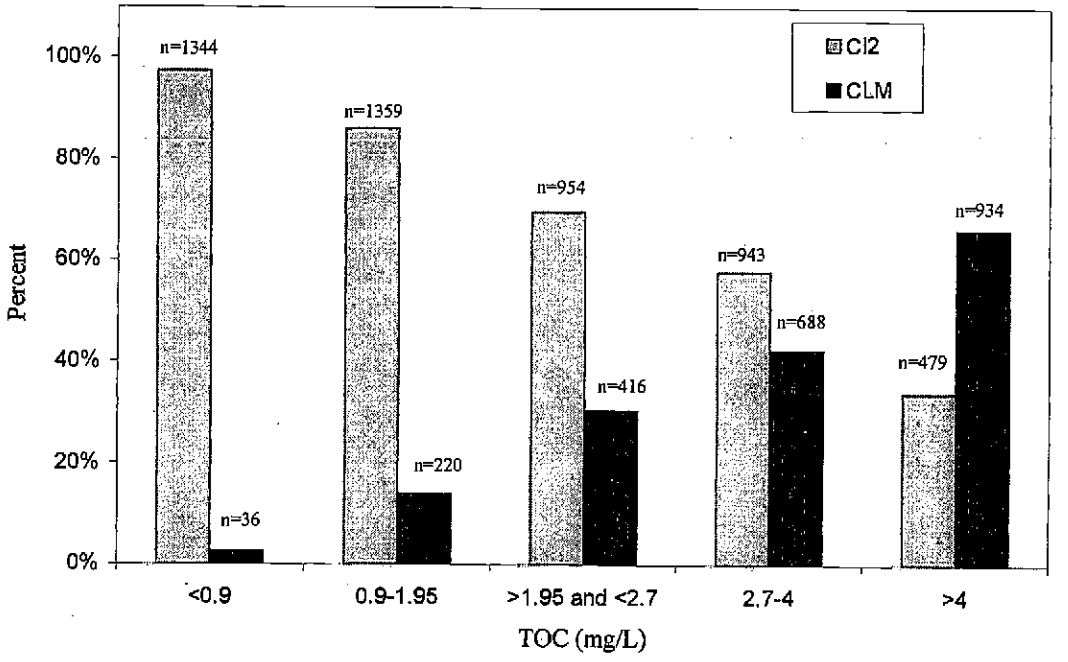

Figure 12.10 Secondary disinfectants used by ICR treatment plants and binned according to influent TOC data (based on plant-months)

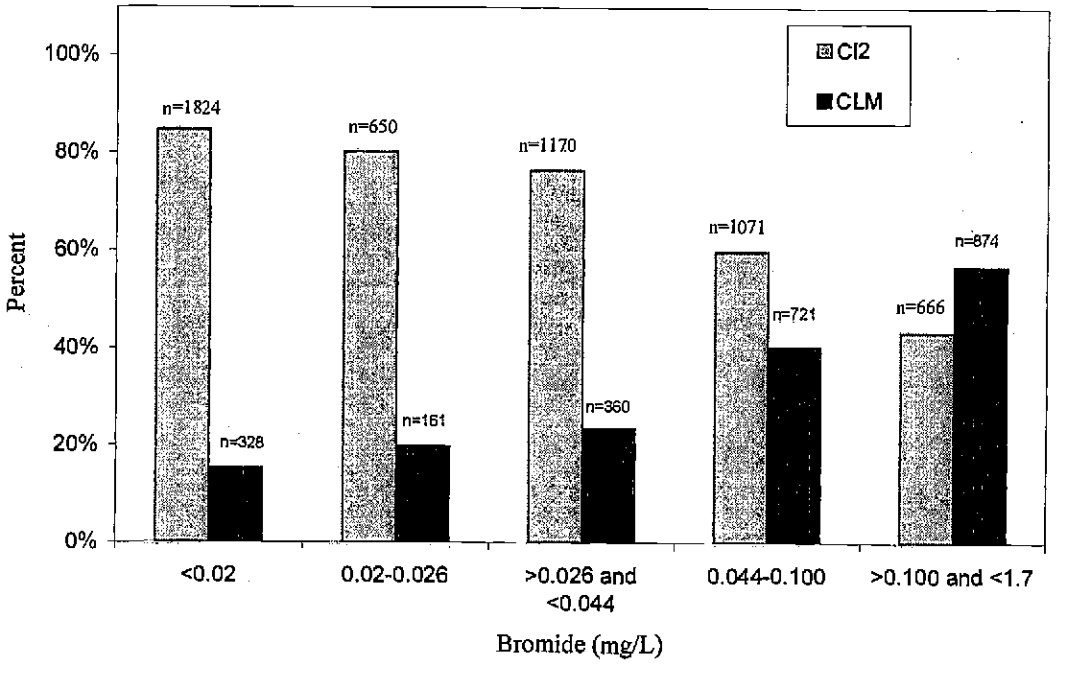

Figure 12.11 Secondary disinfectants used by ICR treatment plants and binned according to influent bromide data (based on plant-months)

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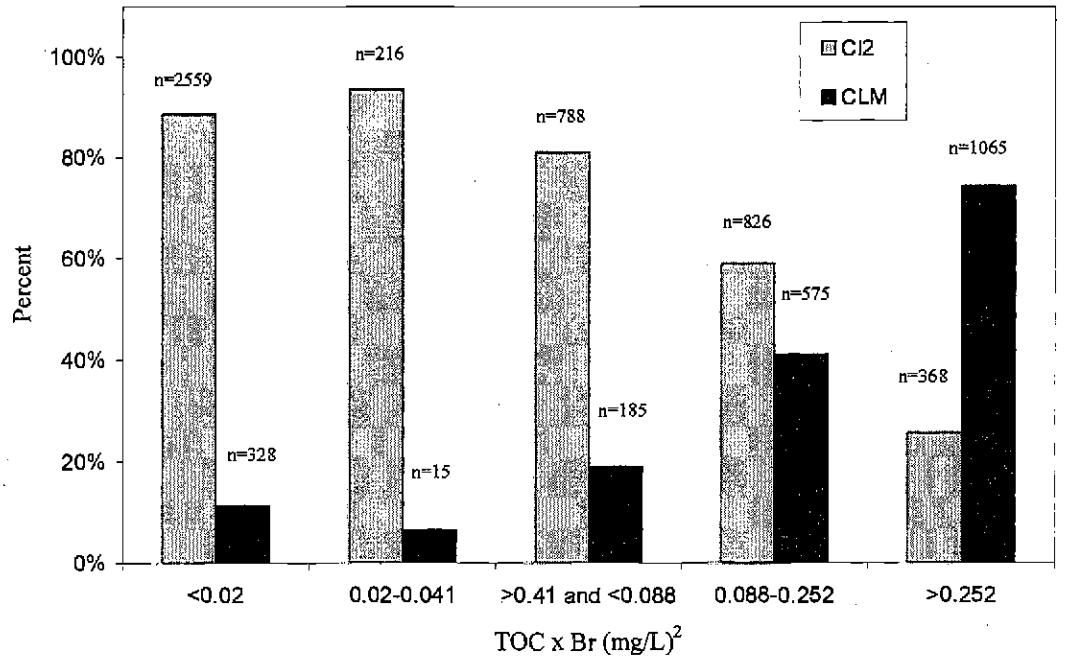

Figure 12.12 Secondary disinfectants used by ICR treatment plants and binned according to the product of influent TOC × bromide (based on plant-months; units = milligrams per liter, squared)

The data shown in Figures 12.7–12.12 indicate that many ICR plants with relatively high TOC and bromide concentrations have continued to use free chlorine. To achieve further reductions in DBP formation, the obvious choice for these plants would be to change either or both of their primary and secondary disinfectants to something other than free chlorine.

SUMMARY AND CONCLUSIONS

Influent inorganic and organic water quality at ICR treatment plants was highly variable. High TOC and bromide concentrations co-occurred in the influent of ICR plants in Florida, Texas, Oklahoma, Kansas, Nebraska, and South Dakota. Fortunately for ICR utilities, a scatter plot of TOC and bromide data pairs illustrated that very high levels of TOC (>10 mg/L) did not co-occur with very high bromide levels (>0.50 mg/L) in any treatment plant influent.

The results presented in this chapter show that ICR plants were more likely to apply primary and secondary disinfectants other than free chlorine if their influent contained high concentrations of TOC and bromide. This conclusion is in agreement with the findings presented

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in Chapter 4 (McGuire and Graziano 2002), which showed that source water TOC and bromide concentrations exerted an influence on TTHM concentrations in distribution system samples. As stated in Chapter 4, water treatment plants have adjusted their treatment schemes by modifying the single most important factor in THM production—contact with free chlorine used as either a primary or secondary disinfectant. The data in this chapter confirm that many treatment plants adjusted their primary and secondary disinfectants if their source water contained high concentrations of organic and inorganic precursors. By converting to the use of alternative disinfectants, ICR utilities have complied with the 1979 TTHM MCL. Utilities still using free chlorine will be faced with similar choices as they try to comply with the D/DBP and Stage 2 DBP rules.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Nicole Graziano, who verified the data extractions from AUX1 and helped prepare the figures.

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CHAPTER 13

TREATMENT PLANT PERFORMANCE FOR TOC REMOVAL

Michelle M. Frey, Chad Seidel, and Laurie Sullivan

ABSTRACT

The Information Collection Rule (ICR) required participating utilities to collect monthly water quality and treatment data over an 18-month period. This monitoring effort provided a baseline picture of treatment plant performance in removing total organic carbon (TOC) and of the relationship between TOC removal and disinfection by-products control. This chapter presents an integrated analysis of the ability of ICR surface water plants to meet treatment objectives for controlling organics through the use of coagulation, sedimentation, and filtration.

ICR data directly supported expected trends reflected in the design of the enhanced coagulation requirements of the Disinfectants/Disinfection By-products Rule (D/DBP) with respect to TOC reduction capabilities based on influent TOC and alkalinity. On average, ICR plants whose TOC removal efficiency was consistent with removals specified in the D/DBP Rule's 3 × 3 matrix of source water TOC and alkalinity were deemed able to meet the minimum TOC removal requirements. However, TOC removal efficiency varied substantially among ICR plants.

INTRODUCTION

The Disinfectants/Disinfection By-products (D/DBP) Rule requires all surface water plants using conventional treatment of surface water or groundwater under the direct influence of surface water to comply with a treatment technique for removing total organic carbon (TOC) (U.S. Environmental Protection Agency [USEPA] 1998). The D/DBP Rule also requires conventional and softening plants to enhance existing TOC removal processes. An analysis of the rule's enhanced softening provisions and treatment plant capabilities is discussed in Chapter 22 (Clark, James, and Lawler 2002). This chapter evaluates the ability of large conventional plants to achieve the rule's enhanced coagulation (EC) requirements and assesses the benefits that could be expected with respect to controlling DBPs.

The Information Collection Rule (ICR) required participating plants to collect water quality and treatment data on a monthly basis from July 1998 through December 1999 (USEPA 1996). Of the 363 surface water plants that participated in ICR monitoring, 271 were

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conventional plants (Table 13.1). Overall, water sources with the highest TOC concentrations were associated with lime softening plants, but conventional surface water plants also had substantial TOC concentrations in their sources of supply. The presence of background concentrations of TOC in source water leads to the formation of halogen-substituted DBPs when chlorine-based disinfectants are applied. The disinfection practices of ICR surface water plants were dominated by the use of free chlorine, either alone or in combination with ammonia (Table 13.2). In fact, 60% of ICR surface water plants using conventional treatment applied free chlorine as the sole disinfectant in the plant and in the distribution system.

Coagulation treatment is considered "enhanced" when the TOC removal is sufficient to meet the amount specified in the D/DBP Rule. The definition of compliance with the rule's EC requirements is complex, allowing treatment plants several pathways for compliance. Exhibit 13.1 provides a brief explanation of the evaluations performed in this analysis to determine the ability of ICR conventional plants to meet the EC requirements.

The EC requirements were intended to provide further protection against the formation of unidentified DBPs in addition to that afforded by compliance with the standards for total trihalomethane (TTHM) and the sum of five haloacetic acids (HAA5). Thus, plants that achieve the TOC removal mandated by the D/DBP Rule's EC requirements would be expected to produce lower overall DBP concentrations than plants treating source water of similar quality (i.e., source water with the same ranges of TOC and alkalinity, as defined by the matrix described in Exhibit 13.1) without meeting the EC requirements.

Because the D/DBP Rule had not been promulgated at the time of ICR monitoring, the ICR data represent an 18-month snapshot of TOC removal performance by surface water plants prior to implementation of the EC requirements. This chapter analyzes the ICR data on conventional surface water plants in order to assess the characteristics of such facilities with respect to the EC requirements and to determine whether enhanced levels of TOC control correspond to overall lower concentrations of halogen-substituted DBPs in drinking water supplies.

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Table 13.1

Characteristics of ICR surface water treatment plants

Type of plant	Number of plants	Average of annual average measurements categorized by type of plant				
		TOC (mg/L C)	Alkalinity (mg/L)	UV_{254} (/cm)	Bromide (mg/L)	pH
Conventional	271	3.2	77	0.1	0.1	7.6
Softening	39	13.6	168	0.13	0.11	8
In-line/direct filtration	29	2.2	68	0.06	0.03	7.5
Slow sand/other filtration plants	6	2	74	0.05	0.03	7.4
Membrane filtration	1	1.4	156	0.04	0.02	8
Unfiltered	17	1.6	33	0.04	0.01	7.2

Table 13.2

Disinfection practices used by ICR surface water treatment plants

Type of plant	Plant disinfectant type*					Distribution system disinfectant type†	
	CL2	CL2_CLM	CLM	O3	CLX	CL2	CLM
Conventional	161	62	11	13	7	161	94
Softening	11	15	4	4	3	9	28
In-line/direct filtration	19	1	0	0	5	19	7
Slow sand/other filtration plants	3	1	0	0	0	5	1
Membrane filtration	1	0	0	0	0	1	0
Unfiltered	5	0	0	0	1	13	3

* ICR plants were classified according to the disinfectant applied within the plant (CL2 = free chlorine only, CL2_CLM = free chlorine followed by chloramine, CLM=chloramine only, O3 = ozone applied at any point in the plant, and CLX = chlorine dioxide applied at any point in the plant). Because some water systems apply only a final disinfectant in the distribution system (indicated by the distribution system disinfectant type), the sum of the plants classified by type of disinfectant may not equal the total number of plants categorized by type of treatment.

† Indicates the final disinfectant applied in the distribution system (CL2 = free chlorine, CLM = chloramine)

ENHANCED COAGULATION PRACTICES AT CONVENTIONAL PLANTS

Data collected under the ICR provided the means to assess the ability of conventional surface water treatment plants to remove organics. The monitoring effort at these plants included measuring the organic content and general water quality parameters of the source of supply, the process water at key treatment points, and the filtered effluent (Figure 13.1). TOC was measured, at minimum, at the point where influent entered the plant, following sedimentation, and following filtration. The monitoring program's design permitted an evaluation of through-the-plant TOC removal as well as an assessment of the ability of ICR facilities to meet the EC requirements. In all of the analyses discussed in this chapter, measurements of TOC and

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ultraviolet absorbance at 254 nm (UV_{254}) that were below detection were set at half of the ICR reporting limit. For samples in which DBPs were below detection, DBP measurements were set at a value of zero.

Exhibit 13.1
Assessment of compliance with enhanced coagulation requirements

The Step 1 enhanced coagulation (EC) requirements for total organic carbon (TOC) removal, as defined in the Disinfectants/Disinfection By-products (D/DBP) Rule, were evaluated to determine the compliance ability of affected Information Collection Rule (ICR) surface water treatment plants. Compliance with the EC requirements is based on achieving the TOC removal efficiencies stipulated in a 3 × 3 matrix of source water TOC and alkalinity (shown below).

Source water TOC (mg/L C)	Source water alkalinity (mg/L $CaCO_3$)		
	≤60	60–120	>120
>2–4	35%	25%	15%
>4–8	45%	35%	25%
>8	50%	40%	30%

Plants are permitted to satisfy the EC requirements by meeting any one of six alternative compliance criteria identified in the D/DBP Rule. Only three of the alternative compliance criteria were included in this analysis:

- Source water TOC <2 mg/L C in any month or as an annual average,
- Treated water TOC <2 mg/L C in any month or as an annual average, and
- Source water TSUVA (specific ultraviolet absorbance, or the ratio of TOC to UV absorbance at 254 nm) ≤2.0 in any month or as an annual average when the treated water sampling location is located before the first point of chlorine addition.

Determining compliance involves calculating each plant's TOC removal "performance ratio" on a monthly basis and then assessing whether the annual average performance ratio exceeds a value of 1.00. Each plant's monthly performance ratio is calculated as the greater of the following values:

1. The ratio of *actual* TOC removal (%) to the *required* TOC removal (%) specified for the plant's 3 × 3 matrix category for that month, or
2. A value of 1.00 if any one of the alternative compliance criteria is met.

Each plant's annual performance ratio is calculated as the greater of the following values:

1. Arithmetic average of the monthly performance ratios, or
2. A value of 1.00 if any one of the annually based alternative compliance criteria is met.

A plant is considered to be in compliance with the D/DBP Rule's EC requirements when its annual performance ratio exceeds 1.00.

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TOC Removal at Conventional Surface Water Plants

The removal of TOC by coagulation, sedimentation, and filtration depends on the amount and nature of the TOC in the plant influent, the pH of the coagulation process, and the mass of coagulant added during treatment (Edwards 1997, Tseng and Edwards 1999). Water sources with low background concentrations of TOC can be expected to be more difficult to treat than sources with higher TOC concentrations. Sources with TOC concentrations of less than 2 mg/L are excluded from the Step 1 EC requirements because of the difficulty of further reducing the TOC and because such low concentrations should minimize potential DBP formation (Figure 13.2). The nature of a water supply's organic content is also important in determining its treatability (Amy et al. 1992; Edwards 1997; Mueller, Schmitt, and Frimmel 2000). Particulate-phase organic carbon is typically almost completely removed by the conventional water treatment process. Furthermore, a water supply's dissolved organic carbon (DOC) content can be described by the relative magnitude of its sorbable and nonsorbable fractions.

Measuring a water supply's ratio of UV_{254} to DOC, known as specific ultraviolet absorbance (SUVA), can indicate the partitioning of dissolved organic matter into sorbable and nonsorbable fractions (Edwards 1997). In water sources with low SUVA (<2 L/mg-cm), the nonsorbable fraction of the DOC can be expected to be dominant, and therefore these supplies are more difficult to treat by coagulation. Thus, water sources with higher SUVA can be expected to be more amenable to the reduction of DOC (and thus TOC) through coagulation. This is the rationale for the alternative compliance criterion for influent and treated water SUVA.

Removal of the sorbable fraction of DOC depends strongly on the coagulation pH achieved during treatment. As shown in Figure 13.2, the expectation that TOC removal will improve in water sources with lower alkalinity is due to the ability to reduce pH during coagulation. In addition, increased TOC removal can be expected in water supplies with higher TOC concentrations and SUVA measurements greater than 2.0 L/mg-cm.

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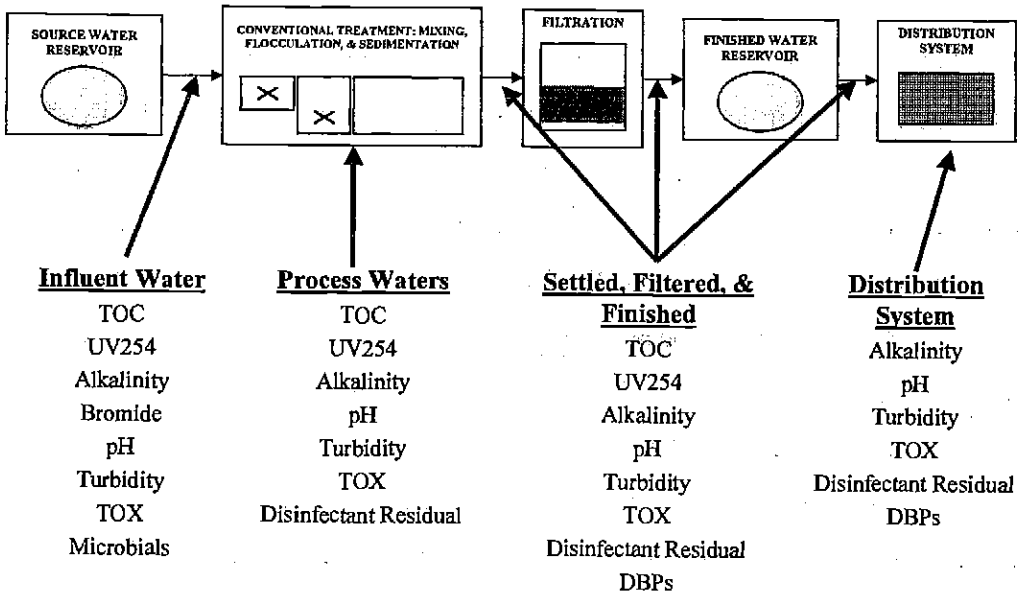

Figure 13.1 Monthly monitoring requirements under the ICR

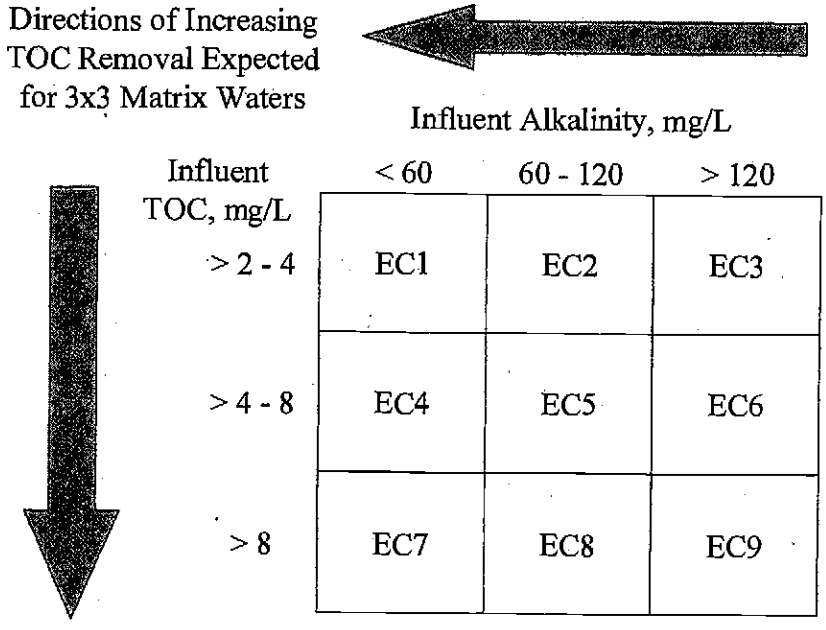

Figure 13.2 Influent classifications and trends in TOC removal categorized according to the D/DBP Rule's 3 × 3 matrix of source water TOC and alkalinity

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Expected trends in TOC removal based on background water quality were observed for ICR plants (Figure 13.3). Within each category of source water TOC concentrations, higher TOC removal occurred in sources with lower alkalinity. Substantially greater TOC reductions were achieved in influent containing higher TOC concentrations within the same alkalinity class. The analysis presented in Figure 13.3 shows the average TOC concentration removed (calculated as the influent TOC concentration minus the filtered effluent TOC concentration in milligrams per liter) by conventional surface water plants as a function of influent TOC and alkalinity conditions. This analysis used values from the ICR plant-months (months of data collected by ICR treatment plants) in which influent TOC and alkalinity could be characterized by the plant's location in the 3 ×3 matrix. Plant-month data were used because the EC requirements apply on a monthly basis and because paired samples of influent TOC and alkalinity determine the minimum TOC removal the facility is required to achieve. A total of 3,996 observations were theoretically available for this analysis (data from 222 surface water plants using conventional treatment with records from 18 months of sampling). However, because of data losses, the actual number of observations—or plant-months—available for this analysis was 3,292 or 82% of the maximum potential number.

Inferences About SUVA and TOC Removal

As shown in Figure 13.3, a substantial portion of the observations (38%) represented influent water conditions that would not be considered amenable to TOC reduction by coagulation. To determine which water sources were in this category (designated as EC0 in the 3 × 3 matrix), an approximation of SUVA was used. Known as "TSUVA," this approximation is based on the ratio of the UV_{254} measurement and the TOC concentration in the influent. (DOC was not measured as part of ICR monitoring.) The TSUVA was calculated only for plant-months in which influent turbidity was below 10 NTU, based on the assumption that at higher turbidities a significant fraction of influent TOC could be in particulate form (SUVA ≠ TSUVA). The EC0 category included data from 444 (35%) plant-months when influent TSUVA was below 2.0 L/mg-cm, 558 (45%) plant-months when influent TOC was below 2 mg/L, and 245 (20%) plant-months when both influent TOC and TSUVA were below 2 mg/L and 2.0 L/mg-cm, respectively. This result indicates that many conventional surface water treatment plants may use

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source water considered difficult to treat with respect to TOC. TOC removal from water sources in this category consistently ranged between 0 and 1 mg/L when TSUVA was greater than 2.0 L/mg-cm (Figure 13.4), indicating that substantial TOC reductions can be achieved even in water sources containing low TOC concentrations (median removal efficiency of 27%).

However, in sources in which TSUVA was less than 2.0 L/mg-cm, TOC removal varied considerably (Figure 13.4). In some cases, substantial TOC removal was observed in sources with low TSUVA, but these results were considered questionable. Poor TOC removal by coagulation is expected in sources with low SUVA. In addition, the possibility that some ICR plants measured influent UV_{254} after preoxidation cannot be ruled out, especially for plants that applied seasonal preoxidation at their intakes for water quality and operational purposes (e.g., mussel control or iron and manganese oxidation).

Influent TOC, mg/L	Influent Alkalinity, mg/L < 60	60 - 120	> 120
> 2 - 4	EC1 N = 547 (16%) Average = 1.13	EC2 N = 555 (17%) Average = 0.72	EC3 N = 327 (10%) Average = 0.60
> 4 - 8	EC4 N = 288 (9%) Average = 2.89	EC5 N = 192 (6%) Average = 1.57	EC6 N = 87 (3%) Average = 1.44
> 8	EC7 N = 49 (1%) Average = 9.07	EC8 Insufficient Data Available	EC9 Insufficient Data Available
	EC0 N = 1,247 (38%) Average = 0.56		

Figure 13.3 Average TOC removal (in mg/L C) at ICR surface water plants using conventional treatment (N = number of plant-months available in each category)

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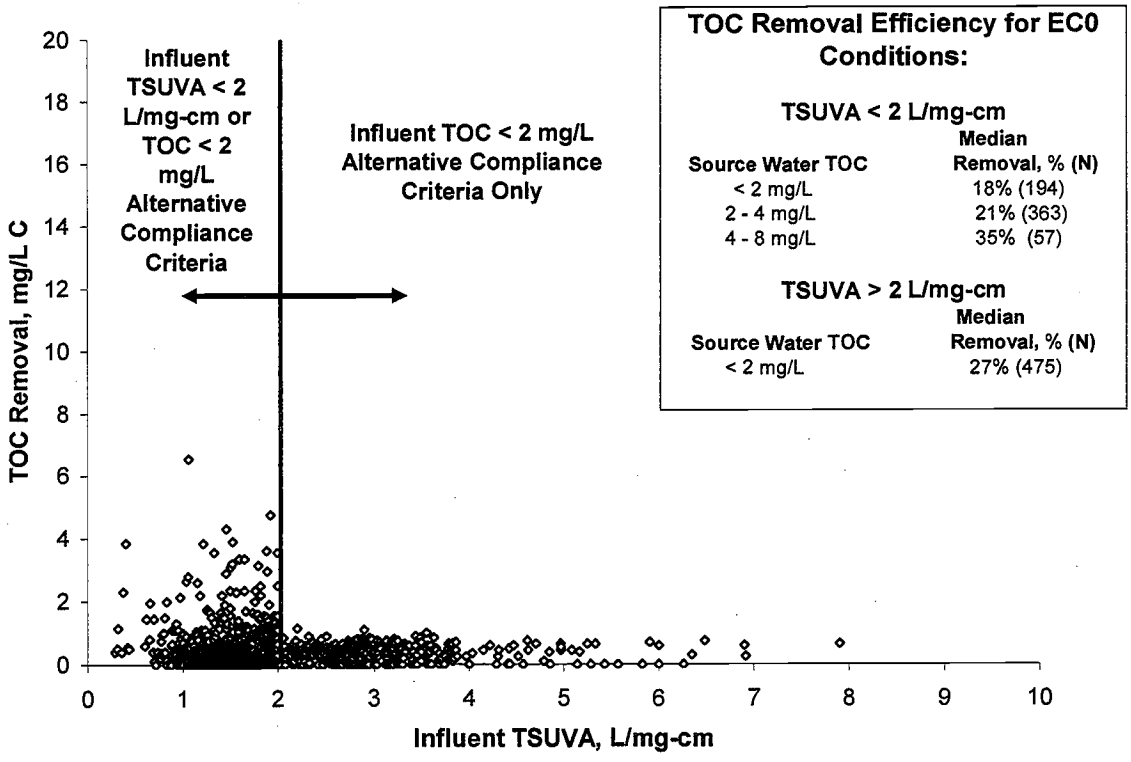

Figure 13.4 TOC removal by conventional treatment in plant-months when influent TOC concentrations were <2 mg/L C or influent TSUVA was ≤2.0 L/mg-cm

No increases in TOC removal were observed in water sources with increasingly higher TSUVA (Figure 13.5). However, a comparison of Figures 13.5a and 13.5b shows a trend of increased TOC removal with increasing influent TOC concentrations. In influent with TOC concentrations of 2–4 mg/L (matrix categories EC1–EC3), less than 2 mg/L of TOC was consistently removed, regardless of the source's TSUVA. In influent with TOC concentrations of 4–8 mg/L (categories EC4–EC6), TOC removals ranged from 2 to 4 mg/L C. In influent with TOC concentrations greater than 8 mg/L, TOC removal was substantially higher, ranging from 4 to 20 mg/L C. Thus, although increased TSUVA did not correlate with greater TOC removal, the mass of TOC removed by conventional treatment was clearly correlated with influent TOC concentrations.

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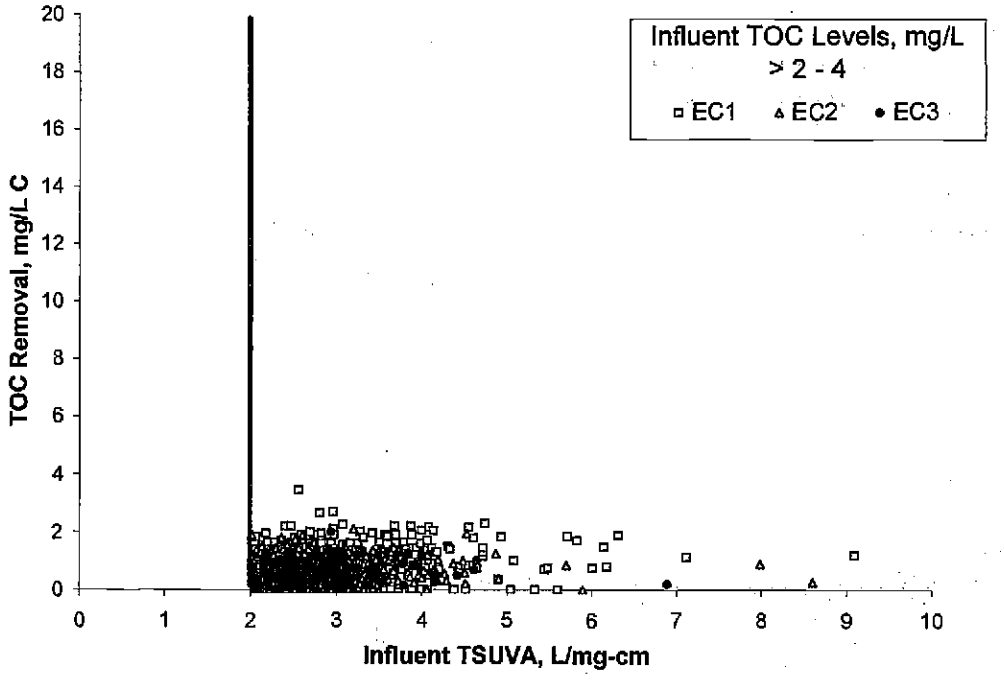
(a) TOC removal from influent in 3 × 3 matrix categories EC1–EC3



(b) TOC removal from influent in 3 × 3 matrix categories EC4–EC7

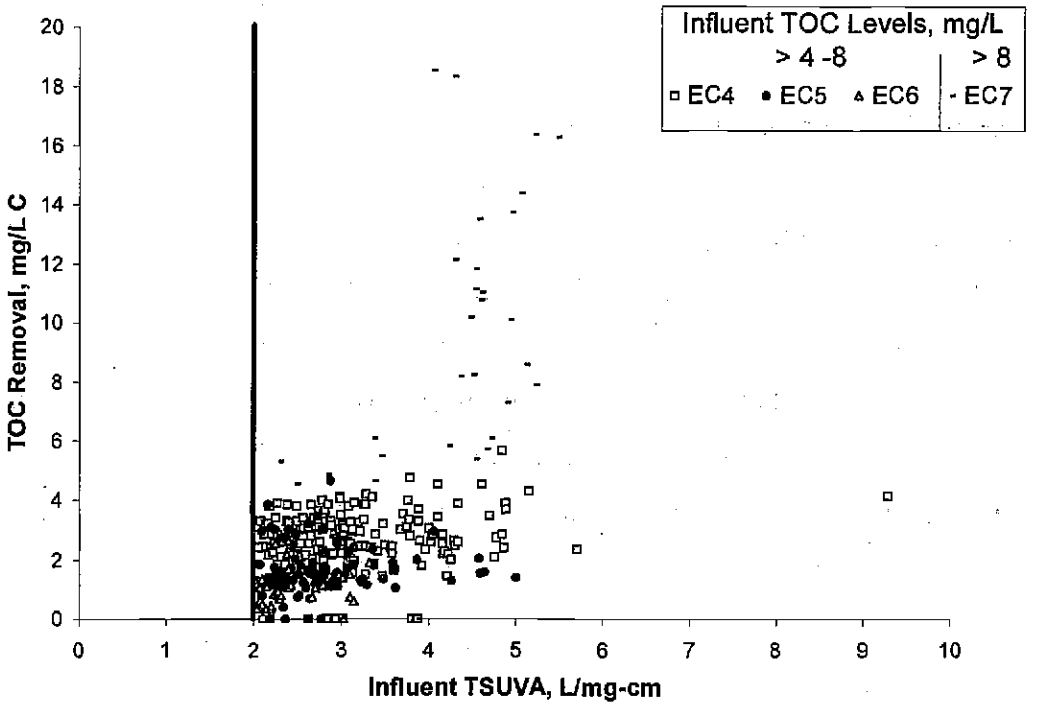


Figure 13.5 Trends in TOC removal by conventional treatment correlated with influent TSUVA

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TOC Removal Efficiency

The fraction of influent TOC removed by conventional treatment is shown in Table 13.3, which demonstrates the same trends in relative removal performance as those for actual mass removals on average. In fact, average removal efficiency through the filters was very near the minimum removal efficiency required in each of the 3 × 3 matrix categories for which data were available. Based on average values, TOC removal in filtered water was consistently greater than TOC removal achieved through settling alone; differences in removal ranged from 3% to 8% of influent TOC.

Although average conditions indicated this important difference between TOC removals in settled water and filtered water, data from individual plant-months indicated variable removal performance between settled and filtered effluents (Figure 13.6). Though 30% of the paired samples showed greater TOC removal through the filters, a fraction (<5%) showed higher removal efficiencies (beyond analytical error) in the sedimentation units. In addition, values from 67% of the paired samples fell within an analytical error band of ±0.25 mg/L C. This error band may appear small, but for water sources with TOC concentrations between 2 and 4 mg/L, the error band can represent 10% of the influent TOC concentration. Therefore, utilities may want to consider monitoring both settled and filtered water and using the lower TOC measurement to calculate TOC removal efficiency.

The variability in removal performance among ICR plants as well as seasonal variations in water quality are indicated by the standard deviation of TOC removal shown for each category in the 3 × 3 matrix. In most categories, the TOC removal achieved by affected plants varied substantially. Typically, the relative standard deviation (the ratio of the standard deviation to the average value) exceeded 50%, with the notable exception of filtered water from plants using influent in categories EC4 and EC7. Although 49 plant-months of data were available for influent in category EC7, these data represent the operation of approximately five plants and therefore may not constitute a large enough sample to support any broad conclusions about the variability of TOC removal in influent of this type. The low variability in TOC removal from influent in category EC4 shows that plants treating water supplies with moderately high TOC and low alkalinity consistently removed a substantial fraction of the TOC present in their influent. However, such consistency was not observed for water supplies of other quality. These

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observations suggest that consistent TOC removal may generally be easier to achieve at plants that use source water in the EC4 category.

Enhanced Coagulation Performance Ratios and Compliance Challenges

Compliance with the EC requirements can be determined by two generalized approaches: (1) determining a plant's annual average performance on the basis of its ability to meet the minimum requirements of the Step 1 provisions each month, or (2) determining annual average influent or treated water conditions that meet the alternative compliance criteria (see Exhibit 13.1). The two approaches converge when a plant collects sufficient information to use either approach in determining compliance and applies the one with the most beneficial outcome.

To assess the ability of ICR conventional surface water plants to comply with the EC requirements, the authors evaluated all available options for compliance and determined the "best case" for each plant. Because ICR plants collected data over an 18-month period, the data yielded up to seven annual periods for which compliance could be determined (months 1–12, 2–13, 3–14, etc.). Though the analysis determined each plant's best compliance scenario within each of the seven annual periods, the aggregate analysis of compliance challenges was based on any annual period in which a plant could not achieve compliance. In this way, the effects of seasonal variations in water quality and treatment performance could fully be explored.

Monthly performance ratios were calculated on the basis of the 3 × 3 matrix requirements for TOC removal efficiency, the TOC concentration and TSUVA of the plant's influent, and the TOC concentration of the plant's filtered water. The performance ratio for TOC removal was calculated as the ratio of actual TOC removal to the TOC removal required by the 3 × 3 matrix. If the plant met any of the alternative compliance criteria, a performance ratio of 1.00 was also assigned. The larger of the two values was selected as the plant's monthly performance ratio.

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Table 13.3

TOC removal efficiency* at ICR conventional surface water plants as a function of influent matrix category

Influent TOC (mg/L C)	Influent alkalinity (mg/L $CaCO_3$) <60 Settled water	<60 Filtered water	60–120 Settled water	60–120 Filtered water	>120 Settled water	>120 Filtered water
>2–4	*Required: 35%*		*Required: 25%*		*Required: 15%*	
	28% (16%)	37% (21%)	17% (15%)	24% (14%)	13% (13%)	17% (43%)
>4–8	*Required: 45%*		*Required: 35%*		*Required: 25%*	
	45% (18%)	52% (9%)	23% (16%)	31% (14%)	22% (15%)	29% (15%)
>8	*Required: 50%*		*Required: 40%*		*Required: 30%*	
	65% (12%)	69% (13%)	Insufficient data available		Insufficient data available	
TOC <2 mg/L or TSUVA ≤2.0 L/mg-cm			Settled water 13% (27%)		Filtered water 22% (22%)	

* Values shown represent average removal efficiency; standard deviations are shown in parentheses.

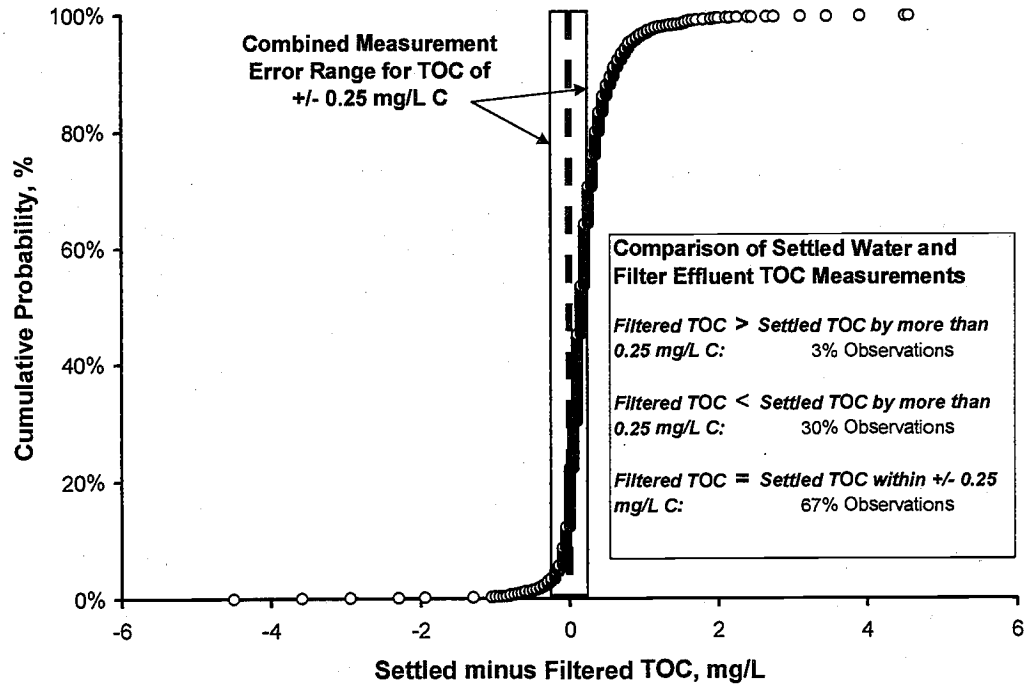

Figure 13.6 Differences in treated water TOC concentrations as a function of sampling location within ICR conventional surface water plants.

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For any month in which the plant met an alternative compliance criterion, the minimum performance ratio that could be assigned was 1.00. Therefore, for all months in which a plant's influent was in the EC0 category, the plant's performance ratio equaled 1.00. When a plant's influent was in other matrix categories, there was a distribution of monthly performance ratios (Figure 13.7). The frequency with which less than the required performance was achieved was greatest for water sources in the EC5 category (TOC concentration of 4–8 mg/L, alkalinity of 60–120 mg/L) and least for sources in the EC7 category (TOC concentration of >8 mg/L, alkalinity of <60 mg/L). The trend in performance ratios was similar to the trends in TOC mass removal and removal efficiency—better performance was observed in water sources with low alkalinity (EC1 = 17% and EC4 = 14% of plant-months with performance ratios <1), regardless of influent TOC concentration, than in sources with higher alkalinity (30% to 40% of plant-months with performance ratios <1).

Annual maximum performance ratios were calculated for each plant for each of the seven annual periods. A total of 225 plants had sufficient data available for all seven periods to be included in the analysis. Each plant was assigned a matrix category for each annual period, based on the annual average TOC concentration and alkalinity of its influent during that period. In addition, each plant was assigned an overall matrix category based on the mode among the seven annual periods.

The seven annual performance ratios of a given plant were often similar. To determine the significance of the annual periods, the relative change in performance ratio values across the seven annual periods was determined. The relative change was calculated as follows:

$$\text{Relative Change} = \frac{(\text{Maximum PR} - \text{Minimum PR})}{\text{Average PR}}$$

Performance ratios at 16% of the plants did not change across the seven annual periods, and ratios at an additional 51% showed a relative change of less than 10% (Figure 13.8). Thus, two thirds of the plants had performance ratios that remained consistent across all seven periods. Performance ratios at the remaining plants showed more substantial disparity; at some plants, the relative change in performance ratios was more than 50%. Substantial agreement was found between plant-month and annualized performance ratios (Table 13.4); plants in categories EC5 and EC7 were in the worst and best positions, respectively, with respect to being able to meet the

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EC requirements. Annual average performance ratios below 1.00 for the fraction of plants in each of the remaining categories agreed favorably with the performance ratios found in the monthly analyses. Overall, 57 of the 225 plants (25%) would have been unable to meet the EC requirements during at least one annual period.

DISINFECTION BY-PRODUCT RESPONSES TO ENHANCED COAGULATION PRACTICES

The EC requirements of the D/DBP Rule were specifically designed to improve the overall quality of drinking water treated with chlorine-based disinfectants because it was believed that reductions in TOC would correspond to reductions in the formation of total organic halogen (TOX) upon disinfection. A comprehensive analysis of TOX occurrence and formation is presented in Chapter 10 (Shukairy, Blank, and McLain 2002). This analysis focuses on the relationship between the concentrations of halogen-substituted organics and the enhanced coagulation practices of ICR plants. The formation of DBPs generally depends on the availability of precursors (e.g., TOC type and concentration) and the disinfection practices used at the treatment plant. The TOC content of filtered effluent from ICR conventional surface water plants demonstrated the expected trends reflected by the EC requirements (Table 13.5). The lowest filtered water TOC concentrations were found in plants whose influent met the exclusion conditions specified in the 3 × 3 matrix (category EC0). Increased TOC concentrations in filter effluent progressed from water sources with low alkalinity to sources with high alkalinity (horizontally through the 3 × 3 matrix) and from water sources with low TOC concentrations to sources with high TOC concentrations (vertically through the 3 × 3 matrix). If TOC alone controlled DBP formation, the progression of DBP concentrations would be expected to be the same as that observed for TOC concentrations; however, disinfection practices also influence DBP formation trends.

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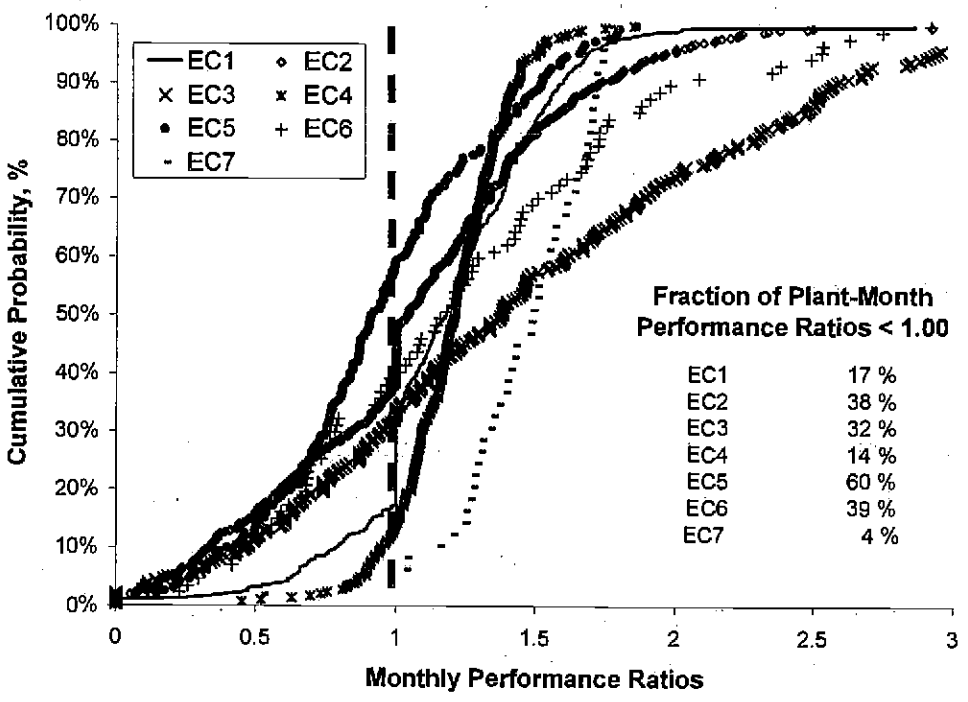

Figure 13.7 Cumulative frequency distribution of monthly performance ratios

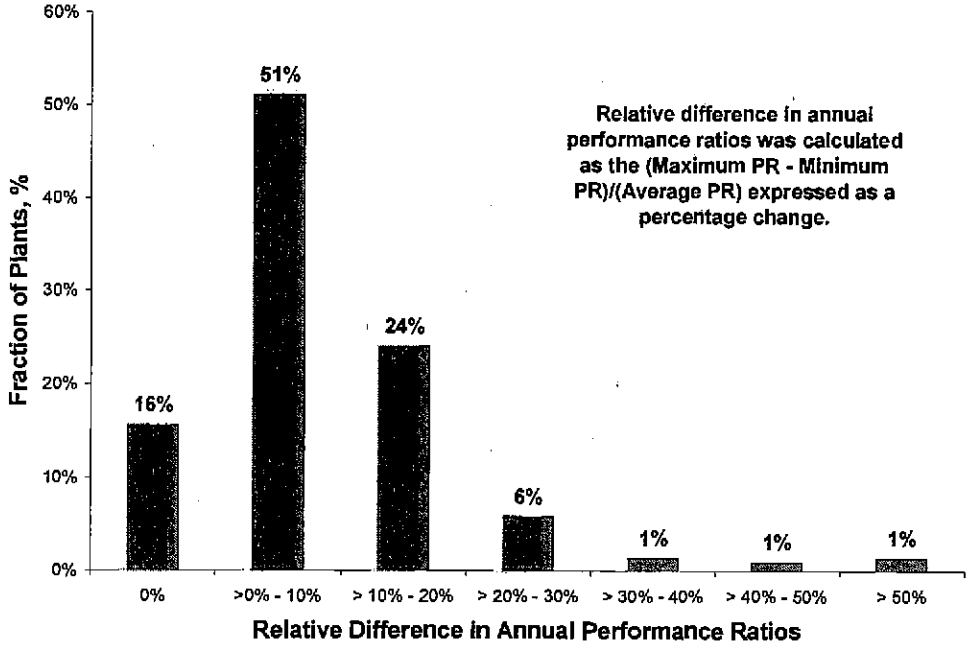

Figure 13.8 Discrete distribution of relative difference in the seven annual performance ratios of ICR conventional surface water plants

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Table 13.4

Annual performance ratios* of ICR conventional surface water plants as indicators of their ability to comply with enhanced coagulation requirements

Influent TOC† (mg/L C)	Influent alkalinity† (mg/L $CaCO_3$)		
	<60	60–120	>120
>2–4	*Required removal: 35%* *N* = 49 plants Fraction with PR <1: 16% Median PR: 1.08	*Required removal: 25%* *N* = 51 plants Fraction with PR <1: 41% Median PR: 1.04	*Required removal: 15%* *N* = 31 plants Fraction with PR <1: 39% Median PR: 1.02
>4–8	*Required removal: 45%* *N* = 21 plants Fraction with PR <1: 5% Median PR: 1.16	*Required removal: 35%* *N* = 15 plants Fraction with PR <1: 60% Median PR: 0.87	*Required removal: 25%* *N* = 8 plants Fraction with PR <1: 38% Median PR: 1.02
>8	*Required removal: 50%* *N* = 3 plants Fraction with PR <1: 0% Median PR: 1.43	*Required removal: 40%* Insufficient data available	*Required removal: 30%* Insufficient data available
TOC <2 mg/L or TSUVA ≤2.0 L/mg-cm‡		*N* = 47 plants Fraction with PR<1: 6% Median PR: 1.43	

* Performance ratio=PR (values shown are based on the minimum annual average PR for conventional plants)
† Plants were assigned to categories within the 3 × 3 matrix on the basis of their annual average influent TOC and alkalinity. Average conditions and respective 3 × 3 matrix locations were identified for each plant for all seven annual periods. Each plant's final matrix location was based on the mode among all seven annual periods.
‡ Results represent the monthly PRs of plants with annual conditions sufficient for them to be classified in the EC0 category. In any plant-month, these facilities might not be able to achieve a minimum PR value of 1.00.

The disinfection practices of plants that have to meet the EC requirements affect the potential benefits of reductions in DBP formation resulting from TOC control. Generally, free chlorine is more commonly applied at plants with lower influent TOC concentrations (Table 13.6), both within the plant and as the final distribution system disinfectant. At plants with higher influent TOC concentrations (e.g., plants in the matrix categories EC4 through EC7), the use of chloramines increases. The frequency with which advanced oxidants such as ozone and chlorine dioxide are used appears to be relatively independent of the plant's matrix category. But water treatment plants use advanced oxidants for multiple reasons, not just for controlling DBPs.

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Table 13.5

Filter effluent TOC concentrations (mg/L) as a function of influent TOC and alkalinity

Influent TOC (mg/L C)	Influent alkalinity (mg/L $CaCO_3$)		
	<60	60–120	>120
>2–4	N = 502 Average: 1.73 5th percentile: 1.10 95th percentile: 2.45	N = 528 Average: 2.12 5th percentile: 1.45 95th percentile: 3.05	N = 312 Average: 2.51 5th percentile: 1.50 95th percentile: 3.35
>4–8	N = 284 Average: 2.65 5th percentile: 1.81 95th percentile: 3.65	N = 186 Average: 3.36 5th percentile: 2.36 95th percentile: 13.49	N = 82 Average: 3.46 5th percentile: 2.21 95th percentile: 5.00
>8	N = 48 Average: 3.56 5th percentile: 2.52 95th percentile: 13.94	Insufficient data available	Insufficient data Available
TOC <2 mg/L or TSUVA ≤2.0 L/mg-cm		N = 1,129 Average: 1.60 5th percentile: 0.50 95th percentile: 3.10	

Table 13.6

ICR conventional surface water plants classified by disinfection practices and enhanced coagulation matrix categories

Plant classification	Plant disinfectant type*					Distribution system disinfectant type†	
	CL2	CL2_CLM	CLM	O3	CLX	CL2	CLM
EC0	34	5	0	0	0	31	8
EC1	29	8	0	0	5	34	8
EC2	22	12	1	2	0	19	18
EC3	11	7	2	1	2	13	10
EC4	14	2	1	0	1	12	6
EC5	4	5	1	0	1	3	8
EC6	3	4	0	1	0	2	6
EC7	0	1	1	0	0	0	2

* ICR plants were classified according to the disinfectant applied within the plant (CL2 = free chlorine only, CL2_CLM = free chlorine followed by chloramine, CLM=chloramine only, O3 = ozone applied at any point in the plant, and CLX = chlorine dioxide applied at any point in the plant). Because some water systems apply only a final disinfectant in the distribution system (indicated by the distribution system disinfectant type), the sum of the plants classified by type of disinfectant may not equal the total number of plants categorized by type of treatment.

† Indicates the final disinfectant applied in the distribution system (CL2 = free chlorine, CLM = chloramine)

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Most ICR plants met the D/DBP Rule's standards for TTHM (80 μg/L) and HAA5 (60 μg/L), measured as running annual averages (RAAs) (Figure 13.9). Although HAA5 compliance appears to be the greater challenge, all plants in categories EC3, EC4, and EC6 are susceptible to elevated DBP concentrations. When the Stage 2 DBP Rule standards for TTHM and HAA5 are considered—using the locational RAA (LRAA) method of determining compliance with the respective limits of 80 μg/L and 60 μg/L—substantially more plants will be affected (Figure 13.10).

Trends in TTHM and HAA5 formation are indicated by the formation of TOX (Figure 13.11). The fraction of TOX captured by TTHM and HAA5 ranged from 40% to 55% when calculated on the basis of RAA values but only 35% to 50% when calculated on the basis of LRAA values. Thus, although TTHM and HAA5 make up a substantial portion of the TOX formed, an equal amount of unidentified halogen-substituted by-products is also present.

The degree to which improved TOC control can further reduce such by-products is unclear. No statistical difference in TTHM, HAA5, or TOX concentrations was found in the analysis of ICR plants' ability to comply with the D/DBP Rule's EC requirements (Student's t-test for two populations of unequal variance at the 95% confidence level [Rohlf and Sokal 1981]). HAA5 values were statistically different when a 90% confidence interval was used; however, lower HAA5 concentrations were found at plants that did not meet the EC requirements than at plants that did (Figure 13.12).

The highest DBP concentrations were observed among ICR plants that most commonly met the EC requirements (Table 13.7). Nearly 95% of the plants in EC4 matrix category met the EC requirements, yet these same plants had the highest TTHM and HAA5 concentrations. Many of these plants (67%) commonly used free chlorine, whereas other plants with the same range of influent TOC concentrations typically applied chloramines as the distribution system disinfectant (73% of EC5 plants and 75% of EC6 plants). If a proportional conversion of disinfection practices—from free to combined chlorine—occurred at EC4 plants, DBP concentrations would likely be substantially reduced. This change would likely result in better congruence of the expected trends between EC compliance and DBP formation.

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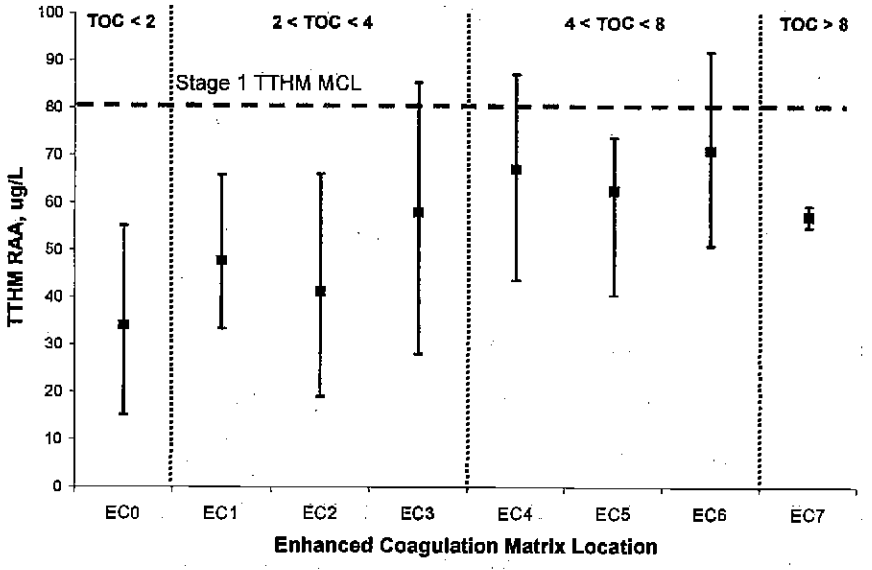
(a) Running annual average TTHM concentrations



(b) Running annual average HAA5 concentrations

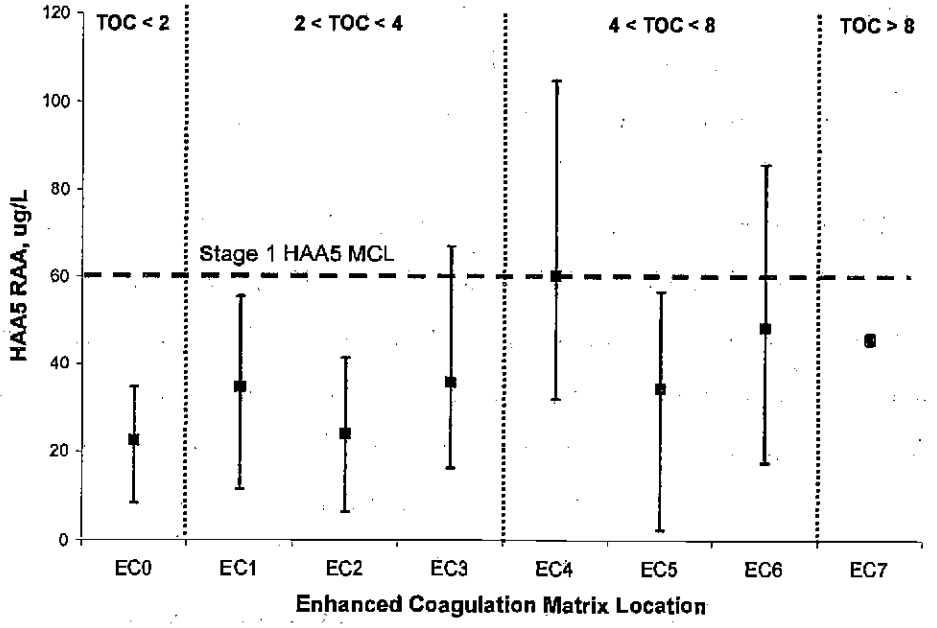


Figure 13.9 Running annual average (a) TTHM and (b) HAA5 concentrations at ICR conventional surface water plants classified by their location in the enhanced coagulation matrix (symbol indicates the average value; bars indicate 10th and 90th percentile values)

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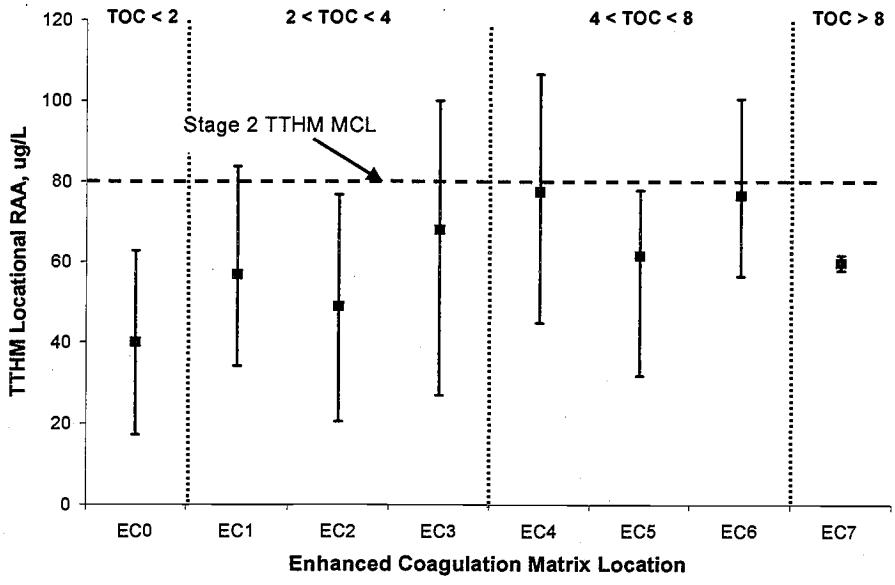
(a) Maximum locational running annual average TTHM concentrations



(b) Maximum locational running annual average HAA5 concentrations

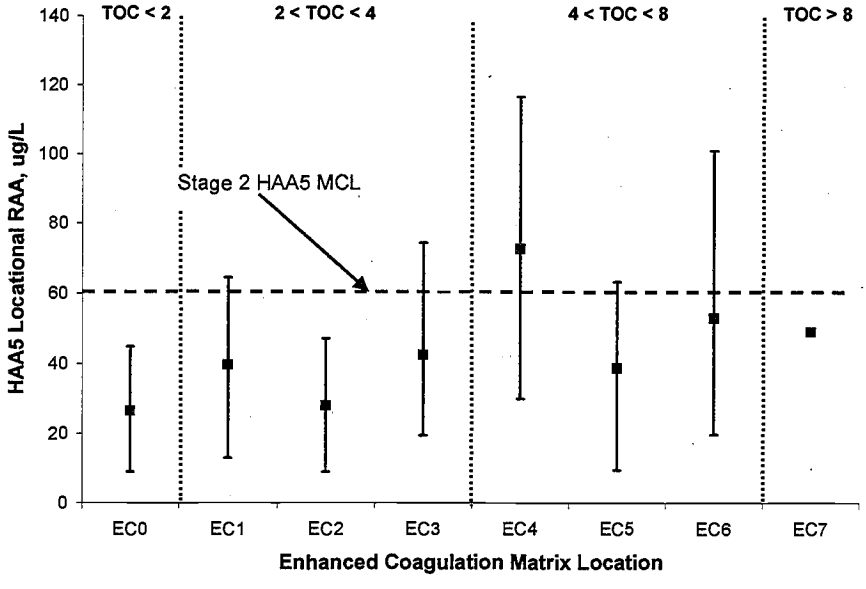


Figure 13.10 Maximum locational running annual average (a) TTHM and (b) HAA5 concentrations at ICR conventional surface water plants classified by their location in the enhanced coagulation matrix (symbol indicates the average value; bars indicate 10th and 90th percentile values)

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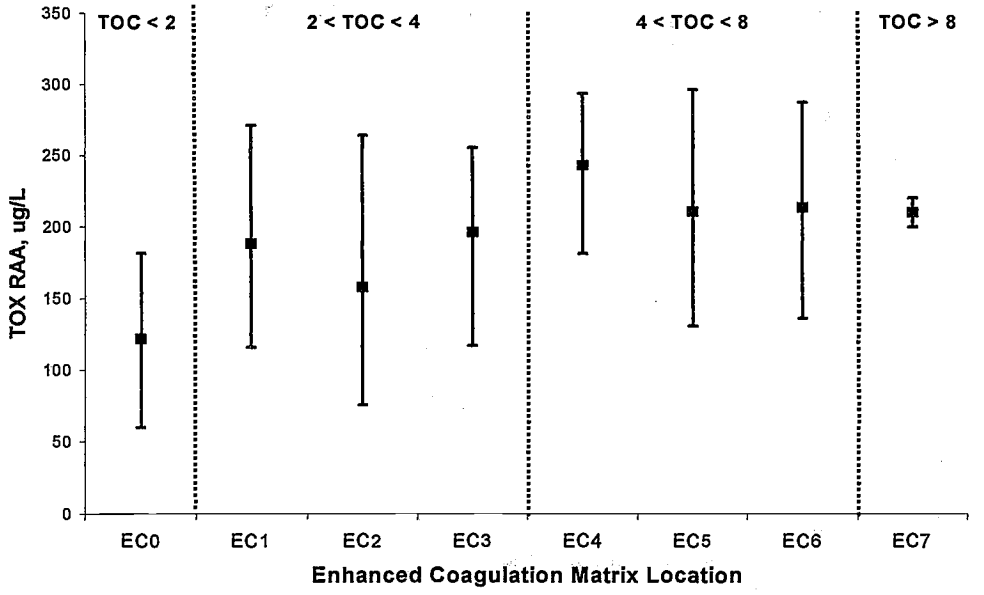
(a) Running annual average TOX concentrations



(b) Locational running annual average TOX concentrations

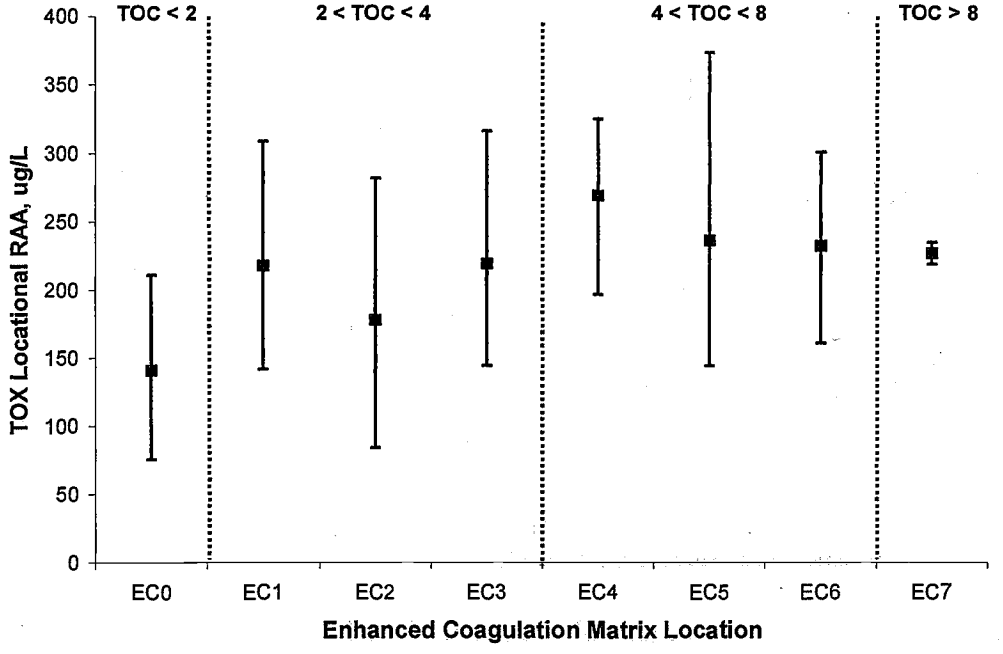


Figure 13.11 Maximum TOX concentrations at ICR conventional surface water plants classified by their location in the enhanced coagulation matrix (symbol indicates the average value; bars indicate 10th and 90th percentile values)

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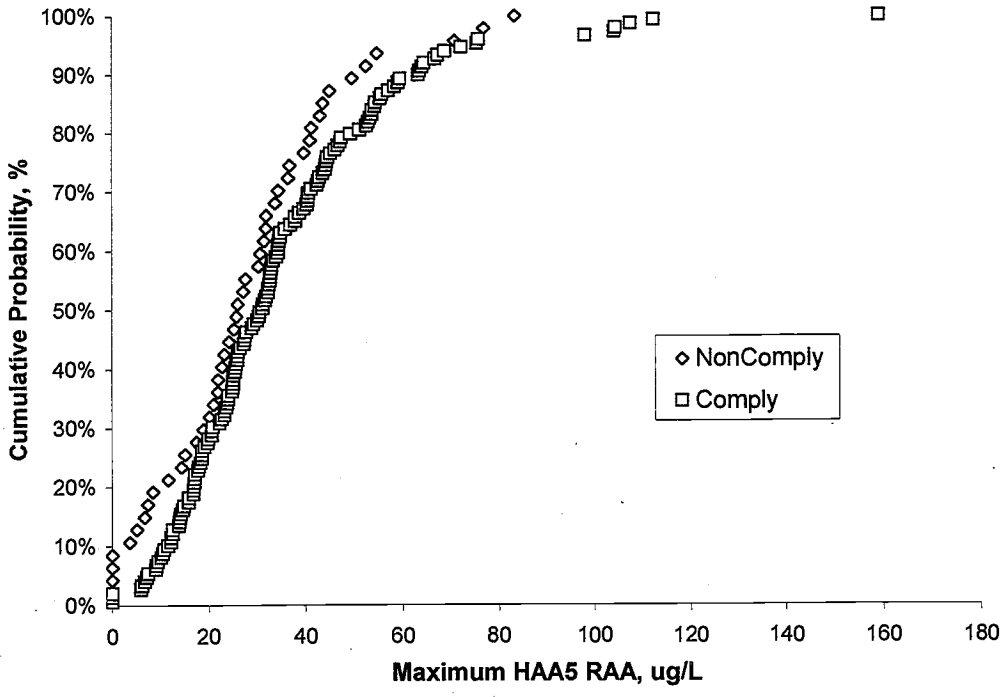

Figure 13.12 Cumulative distribution of HAA5 concentrations shown as a function of ICR conventional surface water plants' ability to comply with the enhanced coagulation requirements

Table 13.7

Effect of disinfection and enhanced coagulation practices on DBP formation

Influent TOC (mg/L)	Plant's matrix category	Percentage of plants using free chlorine	Percentage of plants with PR* <1.00	90th percentile LRAA values		
				TTHM (µg/L)	HAA5 (µg/L)	TOX (µg/L)
<2	EC0	79	3	63	414	211
>2–4	EC1	81	14	84	614	309
	EC2	51	43	77	47	282
	EC3	57	39	100	713	316
>4–8	EC4	67	6	107	117	325
	EC5	27	55	78	63	373
	EC6	25	38	101	101	300
>8	EC7	0	0	62	49	234

* PR = performance ratio

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Similarly, the degree of free chlorine use at EC1 plants (81%) compared with that at EC2 (51%) and EC3 (57%) plants contributes to the higher DBP concentrations found in EC1 plants, despite the greater ability of EC1 plants to comply with EC requirements. The premise that improving coagulation performance to reduce TOC concentrations will also produce lower DBP concentrations could not be directly determined from available ICR data. In fact, a positive correlation was found between EC performance ratios and DBP concentrations (significant at $\alpha = 0.05$). This inverse relationship is directly related to the use of free chlorine by plants in certain categories of the EC matrix.

CONCLUSIONS

The D/DBP Rule requires surface water plants using conventional treatment to enhance coagulation practices in order to improve the overall quality of drinking water, specifically by attempting to control DBP formation. The conventional surface water plants that participated in ICR monitoring exhibited a range of TOC reductions through their coagulation, sedimentation, and filtration processes. The ICR data directly supported expected trends reflected in the design of the EC requirements with respect to TOC reduction capabilities based on influent TOC and alkalinity. Plants treating water with similar influent TOC concentrations achieved lower TOC reductions with increasing alkalinity, and plants treating water with similar alkalinity levels achieved higher TOC reductions with higher influent TOC concentrations.

On average, ICR plants in each category of the EC matrix would have been able to meet the minimum Step 1 removal requirements for TOC, but TOC removal efficiency varied substantially among the plants. The relative standard deviations of TOC removal efficiencies were typically greater than 50%. At least half of the ICR plants in nearly all of the matrix locations could have met the minimum EC requirements when both the minimum removal efficiency and the alternative compliance criteria were considered. Overall, 25% of the ICR plants would not have been able to meet EC requirements during the ICR monitoring period.

Analysis of the ICR data does not provide strong evidence to support the use of enhanced coagulation to reduce either regulated or unregulated DBPs. In fact, a positive correlation was found between EC performance ratios and TTHM, HAA5, and TOX concentrations in distribution systems. Though removing TOC from influent certainly assists water systems in

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controlling DBPs, plants that face compliance challenges may have to consider alterations to their disinfection practices in addition to practicing enhanced coagulation in order to effectively lower DBP concentrations.

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CHAPTER 14

CO-OCCURRENCE OF *CRYPTOSPORIDIUM* AND BROMIDE IN THE INFLUENT OF ICR TREATMENT PLANTS

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ABSTRACT

Ozonation is an important disinfection technology for controlling *Cryptosporidium*, a protozoan pathogen that resists inactivation by conventional disinfectants. However, the ozonation process can cause the formation of bromate, a probable human carcinogen, in water supplies containing bromide ion. Bromate concentrations formed as a result of a treatment plant's meeting *Cryptosporidium* inactivation requirements may limit the feasibility of ozone applications under certain water quality and treatment conditions. Data reported during implementation of the Information Collection Rule (ICR) provided an opportunity to evaluate the co-occurrence of bromide and *Cryptosporidium* in the influent of ICR plants treating surface water and to predict the likelihood of plants exceeding bromate limits under the ozonation conditions specified in the negotiated Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) Agreement in Principle.

Data from the 18 months of ICR monitoring included measurements of both bromide and *Cryptosporidium* in 5,433 influent samples, representing 352 ICR surface water plants. Maximum running annual averages (MRAAs) of *Cryptosporidium* concentrations were calculated for 331 treatment plants. Calculated *Cryptosporidium* MRAAs for 260 (79%) of the plants were less than 0.075 oocysts/L, a value that would exempt these plants from further treatment requirements in addition to conventional treatment for *Cryptosporidium* control under the negotiated LT2ESWTR. The remaining 71 treatment plants (21%) exceeded the negotiated *Cryptosporidium* action level of 0.075 oocysts/L—62 plants had MRAAs ranging from 0.075 oocysts/L to less than 1 oocyst/L, and 9 plants had MRAAs ranging from 1 oocyst/L to less than 3 oocysts/L. Influent bromide concentrations at these plants covered a broad range. Based on a running annual average, none of the plants exceeded 3 oocysts/L. Plants with *Cryptosporidium* MRAAs above the 0.075-oocysts/L action level will need to evaluate the feasibility of using ozonation to meet the *Cryptosporidium* inactivation requirements of the LT2ESWTR. Increasing bromide concentrations increases the chance that plants will exceed the maximum contaminant level (MCL) for bromate when using ozone to meet *Cryptosporidium* inactivation requirements.

The use of simulation modeling offers a probabilistic approach to ozone feasibility assessments. A model called the Surface Water Analytical Tool was used to predict the likelihood that plants using ozone for *Cryptosporidium* control will exceed the current bromate MCL of 10 μg/L and a possible future MCL of 5 μg/L. If the regulatory limit was reduced to 5 μg/L and water utilities were required to achieve only 0.5-log inactivation of *Cryptosporidium*, 46% of the systems evaluated would be expected to violate the bromate MCL at least once per year and 64% would be expected to exceed 4 μg/L (a concentration representing 80% of the hypothetical 5 μg/L MCL). Requiring utilities to meet 1.0-log inactivation would dramatically

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decrease the feasibility of ozone use. If the regulatory limit was reduced to 4 μg/L, 84% of systems would be expected to have annual average bromate concentrations above the MCL at least once a year and all systems would be expected to exceed 4 μg/L at least once a year. These results demonstrate the decreasing feasibility of using ozone to inactivate *Cryptosporidium* with reduced bromate MCLs, especially when higher levels of inactivation are required.

INTRODUCTION

Ozonation is an important disinfection technology for controlling *Cryptosporidium*, a protozoan pathogen that resists inactivation by chlorine (Korich et al. 1990). However, when ozone is applied in water containing bromide ion, bromate is formed as a by-product (Haag and Hoigné 1983). Bromate is of concern because it is an animal carcinogen and has been classified by the U.S. Environmental Protection Agency (USEPA) as a probable human carcinogen (USEPA 1998). Knowledge of whether *Cryptosporidium* and bromide occur simultaneously (referred to as "co-occurrence" in this chapter) in source water is critical in determining whether ozone is a feasible alternative to chlorine as a primary disinfectant under the cluster of rules regulating microbes and disinfection by-products (DBPs).

The Information Collection Rule (ICR) required 500 drinking water treatment plants to report monthly water quality monitoring data and treatment parameters, including influent bromide concentration. Of these 500 plants, 71% treated surface water and were therefore also required to monitor for *Cryptosporidium* each month. The ICR data collection effort provided an opportunity to evaluate the co-occurrence of bromide and *Cryptosporidium* in the influent of ICR surface water plants.

Plants using source water with high concentrations of *Cryptosporidium* will face treatment decisions regarding *Cryptosporidium* control. Under the negotiated Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) Agreement in Principle (USEPA 2000a), utilities would be able to choose among various treatment options described in the "toolbox"[1] to achieve the *Cryptosporidium* control required for their facilities. Some utilities will require inactivation credit, depending on *Cryptosporidium* concentrations in the plant influent.

[1] Under the negotiated LT2ESWTR Agreement in Principle, utilities implementing the management practices or technologies in the technology toolbox receive *Cryptosporidium* removal/inactivation credit as follows: 0.15 NTU filter turbidity (95% of the time)—0.5-log removal credit, watershed control program—0.5-log removal credit, inactivation with ultraviolet light—0.5 to >2.5-log inactivation, ozone—0.5- to 2.0-log inactivation, membrane treatment—0.5 to >2.5-log removal, other (e.g., pretreatment)—to be determined.

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The use of ozone as the inactivation agent for *Cryptosporidium* could lead to formation of unacceptable concentrations of bromate. Chapter 9 discusses the occurrence of bromate in ICR ozone plants (Moll and Krasner 2002). In this chapter, the feasibility of using ozone for *Cryptosporidium* control is examined on the basis of (1) the trends in bromide and *Cryptosporidium* occurrence in ICR plants, and (2) the likelihood that such plants could exceed bromate limits.

OZONE—ITS BENEFITS AND RISKS

Ozone is a more effective disinfectant than the conventional disinfectants chlorine and chloramines (Korich et al. 1990). Thus, resistant pathogens such as *Cryptosporidium*, which are not effectively inactivated by these disinfectants, are vulnerable to inactivation by ozone (Korich et al. 1990). However, because protozoan cysts, and particularly *Cryptoporidium* oocysts, resist inactivation by ozone as well, relatively high doses of ozone are needed to inactivate *Cryptosporidium* oocysts. The use of high doses of ozone generally leads to formation of higher concentrations of ozonation DBPs, including bromate. The negotiated LT2ESWTR Agreement in Principle requires surface water systems that detect source water concentrations exceeding 0.075 oocysts/L to remove *Cryptosporidium* by means of physical barriers, advanced disinfection processes (i.e., ozonation, chlorine dioxide, or ultraviolet [UV] irradiation), or both (USEPA 2000a). These plants may therefore consider using ozone to meet additional treatment requirements mandated in the LT2ESWTR.

Ozone's initial reactions with natural organic matter (NOM) occur at electron-rich aromatic and unsaturated sites (Langlais, Reckhow, and Brink 1991). Because these same sites are targets of chlorine oxidation and addition reactions, the use of ozone as a primary disinfectant followed by chlorine as a secondary disinfectant usually results in less formation of halogen-substituted organic DBPs than when chlorine is used as the primary disinfectant. However, Reckhow and Singer (1984) showed that ozonation may not decrease the formation of some halogen-substituted DBPs such as dichloroacetic acid and may increase the formation of others (e.g., 1,1,1-trichloropropanone). The reaction of ozone with NOM also leads to greater formation of aldehydes and organic acids than the reaction of NOM with other disinfectants. Aldehydes and organic acids can act as precursors to the formation of halogen-substituted organic DBPs such as chloroacetaldehyde, chloral hydrate, and cyanogen chloride (McKnight and Reckhow

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1992, Pedersen et al. 1999). These by-products can also be used as an easily assimilable growth substrate for microorganisms in the distribution system (Van der Kooij, Hijnen, and Kruithof 1987). Removing these compounds by biological filtration before adding a secondary disinfectant and before releasing water to the distribution system leads to lower production of halogen-substituted organic DBPs and greater microbiological stability of distributed water (Bablon, Ventresque, and Aim 1988).

In water that contains bromide, ozone oxidizes bromide to hypobromous acid/hypobromite ion ($HOBr/OBr^-$); under conditions of high pH when OBr^- is present, OBr^- reacts with hydroxyl radicals to form bromite, which ozone further oxidizes to bromate. Under conditions of low pH, HOBr dominates the bromide oxidation chemistry. Because HOBr does not react with ozone to form bromate (Haag and Hoigné 1983), lowering pH minimizes bromate formation (Krasner et al. 1993).

Ozonation of water containing bromide and NOM can also produce bromine-substituted organic DBPs such as bromoform and bromine-substituted acetic acids (Doré et al. 1988). Some bromine-substituted DBPs may pose a greater health risk than certain nonbromine-substituted DBPs (Bull 1995, Pegram 1995). The reactions of ozone and NOM compete with the oxidation of bromide. In general, as the total organic carbon (TOC) concentration increases, bromate formation decreases (Westerhoff et al. 1998). However, when CT (the product of disinfectant residual concentration, C, and contact time, T) is held constant, increasing TOC concentrations will increase ozone demand, requiring a higher ozone dosage. Najm and Krasner (1995) found that when a constant CT was targeted, increases in TOC also resulted in increases in bromate formation. The co-occurrence of *Cryptosporidium*, bromide, and TOC in the influent of ICR treatment plants will be discussed in a subsequent section.

As part of the Stage 1 Disinfectants/Disinfection By-products (D/DBP) Rule, USEPA promulgated a maximum contaminant level (MCL) of 10 μg/L for bromate (USEPA 1998). Although the original placeholder for bromate during the Federal Advisory Committee discussions leading to the negotiated Stage 2 DBP Rule Agreement in Principle was 5 μg/L, the actual Stage 2 DBP Rule Agreement in Principle proposes to maintain the bromate MCL at 10 μg/L, in part because of concerns that a standard that was too low would limit the ability of utilities to apply ozone.

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CRYPTOSPORIDIUM AND BROMIDE OCCURRENCE IN ICR SURFACE WATER

ICR sample collection began in July 1997 and was completed in December 1998. The 500 drinking water treatment plants affected by the regulation were required to report monthly water quality monitoring data and treatment parameters, including influent bromide concentrations. Plants treating surface water were also required to report monthly data on influent concentrations of certain microorganisms, including *Cryptosporidium*. Records from the 18 months of ICR monitoring included both bromide and *Cryptosporidium* data from 5,433 influent samples, representing 352 ICR surface water plants.

Categories for treatment plant water sources were designated for all ICR samples. These source water categories were surface water (SW), groundwater (GW), purchased finished water (PUR), and mixed (MIX). Types of surface water were further characterized into reservoir or lake (RL), flowing stream (FS), mixed (MIX), and groundwater under the direct influence of surface water (GWUDI). If a certain type of source water made up more than 80% of total surface water flow at the plant, the surface water type was designated accordingly; otherwise the surface water type was designated as MIX. Within the ICR database, FS and RL sources were identified as the two major types of surface water, together representing 95% of the 5,433 influent samples.

Cryptosporidium Occurrence in the Influent of ICR Surface Water Plants

Identified potential sources of *Cryptosporidium* oocysts in water supplies include wastewater treatment plant discharges, combined sewer overflows, and wildlife and agricultural activity in a watershed (LeChevallier, Norton, and Lee 1991; States et al. 1997). This chapter discusses analyses of *Cryptosporidium* data reported as "Total *Cryptosporidium*" concentrations in Auxiliary Database 1 (AUX1) of the ICR Federal Database System. These values represented both empty *Cryptosporidium* oocysts and those with either presumed or confirmed internal structures.

Table 14.1 presents summary statistics of *Cryptosporidium* concentrations in influent samples collected concurrently with bromide samples. All nondetects (recorded as "–999 in AUX1) were treated as "0" for the analyses presented in this chapter. Data are presented for all samples as a whole and for all samples in each surface water category.

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Table 14.1

Distribution of total *Cryptosporidium* concentrations in influent at ICR surface water plants that also collected bromide samples

Statistic	All source water types	RL*	FS†	MIX‡	GWUDI§
Number of observations	5,433	3,232	1,972	145	84
Mean (oocysts/L)	7	2	15	8	0
Standard deviation	60	38	86	38	0
50th percentile (oocysts/L)	0	0	0	0	0
75th percentile (oocysts/L)	0	0	0	0	0
90th percentile (oocysts/L)	0	0	10	9	0
95th percentile (oocysts/L)	15	0	63	20	0
97th percentile (oocysts/L)	45	8	125	94	0
99th percentile (oocysts/L)	190	40	400	192	0
Maximum (oocysts/L)	2,000	1,923	2,000	357	0

*Reservoir or lake
†Flowing stream
‡Mixed water source
§Groundwater under the direct influence of surface water

Occurrence of Bromide in ICR Surface Water Plant Influent

Bromide ion in source and finished water supplies originates from dissolution of geologic formations, saltwater intrusion, saltwater aerosol deposition, and anthropogenic sources such as oil field brines; it may also be present as an impurity in chlorinating solutions (Amy et al. 1994). The highest average bromide concentrations in the influent of ICR surface water plants (>100 μg/L) were found in Texas and Florida (Figure 14.1). Statewide average bromide concentrations were generally higher in the Midwest and Southwest, whereas plants in the Northwest and Northeast had the lowest influent bromide concentrations.

Of the 5,433 influent samples for which both bromide and *Cryptosporidium* data were available in AUX1, 1,850 (34%) of the bromide concentrations were reported as below the minimum reporting level (MRL) of 20 μg/L. Influent bromide concentrations ranged from below the MRL (20 μg/L) to 2,230 μg/L, with a median concentration of 30 μg/L. The distribution of bromide concentrations in RL and FS systems did not vary significantly from the overall distribution (Table 14.2).

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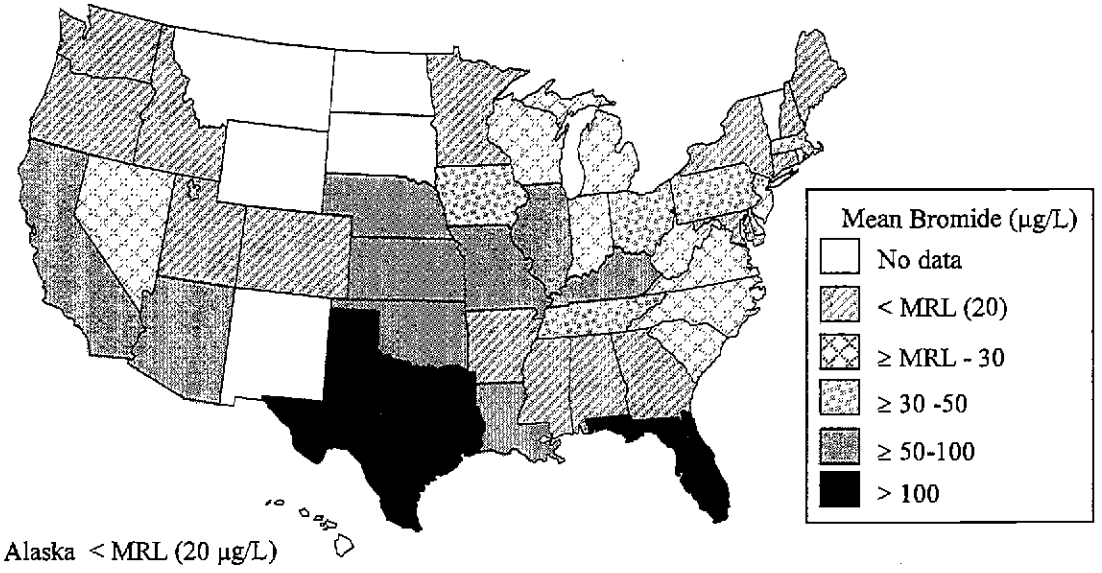

Figure 14.1 Mean influent bromide concentrations in 353 ICR surface water plants

Two other nationwide bromide surveys were conducted during the 10 years preceding monitoring. Amy and co-workers (1994) conducted a nationwide bromide survey for the American Water Works Association Research Foundation (AwwaRF) from October 1991 through April 1993; this survey included 88 randomly selected utilities (68 serving >50,000 people and 20 serving <50,000) and 12 targeted utilities (all serving >50,000) with known problems related to bromide. In addition, bromide data were collected in a 35-utility nationwide DBP study conducted by Metropolitan Water District of Southern California for USEPA from summer 1988 through winter 1989 (Krasner et al. 1989). The median bromide concentration at ICR surface water plants (30 µg/L) was lower than those observed in these other studies (56 µg/L and 110 µg/L, respectively).

Comparing bromide concentrations in the influent of ICR surface water plants with data collected during the AwwaRF survey from 68 randomly selected large utilities (serving >50,000) and summarized by USEPA Region indicated that the geographic areas with high and low bromide concentrations were consistent between the two surveys, although average bromide

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concentrations for each USEPA Region were generally slightly lower during ICR monitoring (differences ranged from –42 μg/L to +7 μg/L).

Co-Occurrence of *Cryptosporidium* and Bromide in ICR Surface Water Plant Influent

For this analysis, the 5,433 influent surface water samples for which both *Cryptosporidium* and bromide data were reported in AUX1 were segmented into quintiles (with each quintile "bin" representing approximately 20% of the data) based on bromide concentration and into four categories based on *Cryptosporidium* oocyst concentration. Table 14.3 shows the number of influent samples in which *Cryptosporidium* oocysts were not detected and indicates when they were detected at low (0.9 to <10 oocysts/100 L), medium (10 to <100 oocysts/100 L), and high (≥100 oocysts/100 L) concentrations in each quintile of bromide concentrations.

Table 14.2

Distribution of bromide concentrations in influent

at ICR surface water plants that also collected *Cryptosporidium* samples

Statistic	All surface water types	RL*	FS†	MIX‡	GWUDI§
Number of observations	5,433	3,232	1,972	145	84
Mean (μg/L)	56	57	55	38	59
Standard deviation	109	124	83	38	47
Minimum (μg/L)	0	0	0	0	0
5th percentile (μg/L)	0	0	0	0	0
10th percentile (μg/L)	0	0	0	0	22
25th percentile (μg/L)	0	0	0	0	36
50th percentile (μg/L)	30	28	31	35	46
75th percentile (μg/L)	64	63	68	62	63
90th percentile (μg/L)	130	134	130	92	135
95th percentile (μg/L)	207	220	200	100	152
Maximum (μg/L)	2,230	2,230	850	161	260

* Reservoir or lake
† Flowing stream
‡ Mixed water source
§ Groundwater under the direct influence of surface water

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Table 14.3

Co-occurrence of *Cryptosporidium* and bromide in ICR surface water influent

	Cryptosporidium (oocysts/100 L)				
Bromide (μg/L)	<0.9*	≥0.9–<10	≥10–<100	≥100	Total
<20 (MRL)	1,694	34	94	28	1,850
≥20–<30	781	12	33	11	837
≥30–<50	950	8	46	19	1,023
≥50–<100	849	13	30	19	911
≥100	778	4	18	12	812
Total	5,052	71	221	89	5,433

* Nondetects; 0.9 oocysts/100 L was the lowest value reported in influent samples.

Cryptosporidium was not detected in 5,052 (93%) of the samples, and nondetects were distributed over the range of bromide concentrations. *Cryptosporidium* was detected in the low, medium, and high categories in the remaining 381 (7%) of influent water samples. Of the samples that tested positive for *Cryptosporidium*, 156 (41%) had bromide concentrations below the MRL (20 μg/L), and 129 (34%) had low bromide concentrations (bromide values in bins 2 and 3, from ≥20 to <50 μg/L), whereas 96 (25%) of the samples had moderate to high bromide concentrations (bromide concentrations ≥50 μg/L). Thus, 93% of the influent samples tested in the ICR did not indicate a treatment challenge posed by the presence of *Cryptosporidium*. Approximately 5% of the samples indicated a challenge by *Cryptosporidium* but contained low concentrations of bromide. Two percent of the samples indicated a treatment challenge posed by both *Cryptosporidium* and moderate to high bromide concentrations.

Comparisons of influent *Cryptosporidium* concentrations and bromide concentrations in FS and RL sources indicated that *Cryptosporidium* and bromide (*Cryptosporidium* concentrations ≥0.9 oocysts/100 L and bromide concentrations ≥20 μg/L) co-occurred less frequently in RL sources (2% of samples) than in FS sources (6% of samples).

Meeting the Long Term 2 Enhanced Surface Water Treatment Rule

The negotiated LT2ESWTR Agreement in Principle (USEPA 2000a) classifies treatment plants for *Cryptosporidium* control based on influent *Cryptosporidium* concentrations. Treatment plants will be required to take additional action beyond conventional treatment if the maximum running annual average (MRAA) *Cryptosporidium* concentration in influent samples collected

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over a 24-month sampling period exceeds 0.075 oocysts/L. Plants will be segmented into four *Cryptosporidium* occurrence bins requiring increasing levels of treatment using one or more alternatives from the technology toolbox. Bin classifications and their corresponding treatment requirements include: (1) plants with MRAA *Cryptosporidium* concentrations of <0.075 oocysts/L (no additional treatment required), (2) plants with MRAAs ranging from 0.075 oocysts/L to <1 oocyst/L (1.0-log treatment), (3) plants with MRAAs ranging from 1 oocyst/L to <3 oocysts/L (2.0-log treatment with at least 1.0-log inactivation), and (4) plants with MRAAs exceeding 3 oocysts/L (2.5-log treatment with at least 1.0-log inactivation). For more details, see footnote 1 and the LT2ESWTR Agreement in Principle (USEPA 2000a).

The ICR data on *Cryptosporidium* and bromide were analyzed to determine whether ICR treatment plants exceeded the negotiated action level of 0.075 oocysts/L. This analysis was conducted to evaluate two considerations: (1) whether ICR plants are likely to be required to add further treatment under the negotiated LT2ESWTR Agreement in Principle, and (2) in what percentage of these plants will the use of ozone be feasible. The following criteria were used to assign surface water types to each treatment plant and to calculate MRAAs of total *Cryptosporidium* oocyst concentrations for each plant:

- Plant "Influent" samples with a source water type of "Surface Water" were selected.
- A treatment plant had to use a specific type of surface water (i.e., FS or RL) for at least 9 of the 12 sampling periods to be assigned to a surface water category.
- All nondetects in the database were converted to zeros before any calculations were performed.
- At least nine *Cryptosporidium* measurements were required for calculation of each annual average.
- Seven annual averages were calculated from the 18 months of data, and the maximum value was designated as the MRAA.
- Fifty percent or more of the annual averages calculated (a maximum of seven) were required to be in the same occurrence bin for the treatment plant to be classified in that category.

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Table 14.4

Distribution of maximum running annual average (MRAA) *Cryptosporidium* concentrations organized by source water type

MRAA (oocysts/L)	All source water types	RL†	FS‡	MIX§	GWUDI**
≤0.075	260*	175	70	4	4
>0.075–≤1	62	18	40	3	0
<1–≤3	9	1	8	0	0
>3	0	0	0	0	0

* Eight plants included in this total used more than one type of source water during the data collection period.
† Reservoir or lake
‡ Flowing stream
§ Mixed water source
** Groundwater under the direct influence of surface water

These criteria for completeness of data, classification of surface water type, and agreement of calculated RAAs within bin classifications were followed to decrease the effect of data variability on classification, thus reducing the potential for misclassification of treatment plants in surface water categories and in *Cryptosporidium* occurrence bins.

Cryptosporidium MRAAs were calculated for 331 water treatment plants including 118 plants with FS sources and 194 plants with RL sources. Because some of the plants changed source water supplies during the data collection period, not all of them could be unequivocally assigned to a surface water category. One surface water type was consistently used by 323 water treatment plants and met all six criteria described. The MRAAs of 71 of these plants exceeded 0.075 oocysts/L. Under the negotiated LT2ESWTR agreement, these plants would fall into the occurrence bins requiring additional treatment beyond conventional treatment (Table 14.4). Of the 71 plants exceeding the action level, 48 (68%) used FS sources and 19 (27%) used RL sources.

The number of surface water plants whose MRAA *Cryptosporidium* concentration fell into each *Cryptosporidium* occurrence bin requiring additional treatment was plotted against quintiles of mean RAA bromide concentrations (Figure 14.2). Plants with MRAA *Cryptosporidium* concentrations greater than the 0.075-oocysts/L action level may consider ozonation and other options to meet the more stringent treatment requirements. MRAA *Cryptosporidium* concentrations at 260 (79%) of the plants were <0.075 oocysts/L, which would exempt these plants from additional treatment requirements under the negotiated agreement for the LT2ESWTR. Of these 260 plants, 111 (43%) had mean RAA bromide concentrations less

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than the MRL of 20 μg/L. The remaining 149 plants with MRAA *Cryptosporidium* concentrations of less than 0.075 oocysts/L were relatively evenly distributed among the bromide bins. Mean RAA bromide concentrations at the 62 plants in the second *Cryptosporidium* bin (≥0.075 oocysts/L–<1 oocyst/L) and the 9 plants in the third *Cryptosporidium* bin (≥1 oocyst/L–<3 oocysts/L) were also evenly distributed among the bromide bins.

A treatment plant's chance of exceeding the bromate MCL while using ozone to meet *Cryptosporidium* CT requirements increases as bromide concentrations increase within each *Cryptosporidium* occurrence bin. Plants that use source water containing high TOC concentrations will have to apply higher ozone dosages to meet *Cryptosporidium* inactivation requirements and to overcome the additional ozone demand. Although high TOC concentrations generally decrease bromate formation (Westerhoff et al. 1998), Najm and Krasner (1995) found that when a constant CT was targeted, increases in TOC concentration resulted in increases in bromate formation. Thus, balancing the formation of bromate and halogen-substituted DBPs with achieving *Cryptosporidium* CT requirements will be challenging for utilities treating water with both high TOC concentrations and moderate to high bromide concentrations.

The 18 months of ICR monitoring encompassed a total of 1,278 monthly sampling events at the 71 plants whose MRAA *Cryptosporidium* concentrations exceeded the threshold action level. AUX1 contained monthly data on both bromide and TOC concentrations for 1,017 of these sampling events. Bromide and TOC concentrations were ≥50 μg/L and <4 mg/L, respectively, in 177 (17%) of the samples, representing one or more sampling events at 24 (34%) of the plants (Table 14.5). Thus, 34% of the 71 *Cryptosporidium*-challenged plants had both moderate to high bromide concentrations and high TOC concentrations at some point during the ICR monitoring program. These conditions may present a special treatment challenge to utilities wishing to use ozone for *Cryptosporidium* control because of the need to balance *Cryptosporidium* treatment requirements with the formation of bromate and halogen-substituted DBPs. The next section discusses the use of the Surface Water Assessment Tool (SWAT) model to predict the likelihood that plants will exceed significant bromate concentrations when using ozone to control *Cryptosporidium*.

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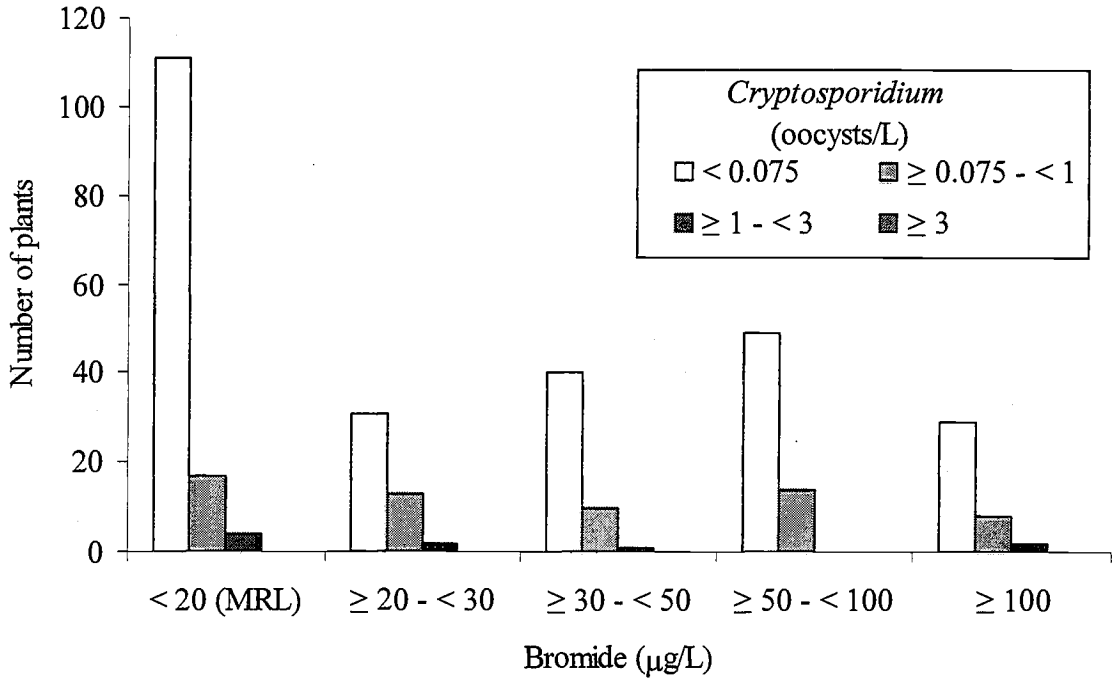

Figure 14.2 Maximum running annual average (MRAA) *Cryptosporidium* concentrations stratified by mean RAA bromide concentrations in ICR surface water plants

Table 14.5

Bin distributions of monthly bromide and TOC concentrations at the 71 plants with maximum running annual average *Cryptosporidium* concentrations ≥0.075 oocysts/L

	TOC (mg/L)					
Bromide (µg/L)	≤1	>1–≤2	>2–≤3	>3–≤4	>4	Total
<20 (MRL)	17	79	64	42	63	265
≥20–<30	3	44	41	25	45	158
≥30–<50	1	61	38	43	76	219
≥50–<100	1	15	52	47	74	189
≥100	1	10	26	46	103	186
Total	23	209	221	203	361	1,017

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FEASIBILITY OF OZONE APPLICATIONS AT ICR PLANTS WITH ELEVATED *CRYPTOSPORIDIUM* CONCENTRATIONS

Controlling *Cryptosporidium* at plants with elevated source water concentrations of this pathogen may require some degree of inactivation to be achieved by disinfection. The LT2ESWTR negotiations designated 0.5-log to 1.0-log minimum inactivation requirements based on *Cryptosporidium* concentrations in source water (USEPA 2000a). The ICR monitoring program identified 71 water treatment plants whose source water had annual average *Cryptosporidium* concentrations greater than 0.075 oocysts/L. These plants may need to install additional treatment for *Cryptosporidium* inactivation. The inactivation agents most likely to be used to meet such requirements are ozone, chlorine dioxide, and UV irradiation. The use of ozone for *Cryptosporidium* control can be considered feasible only if the plant is likely to produce low concentrations of bromate. Although the 10-μg/L bromate MCL established by the Stage 1 D/DBP Rule is expected to remain at 10 μg/L under the Stage 2 DBP Rule, the bromate MCL may be reduced in the future as a result of public health concerns and improved ability to measure bromate at low concentrations. Therefore, predicting the bromate concentrations expected to be formed as a result of meeting *Cryptosporidium* inactivation requirements can assess the true feasibility of future applications of ozone.

In this analysis, the feasibility of ozone applications at ICR treatment plants at risk for elevated *Cryptosporidium* concentrations was evaluated. The likelihood of plants producing elevated bromate concentrations was estimated using a series of modeling tools (described in Figure 14.3 and in more depth in the following sections). Results are described for bromate MCL options of 10 μg/L and 5 μg/L and take into account the range of compliance strategies plants might use to target maximum annual average bromate concentrations at 80% of the MCL values (a safety factor applied to ensure compliance).

Step 1: Predicted Bromate Formation From Ozone Use for *Cryptosporidium* Inactivation

The application of ozone at plants challenged by *Cryptosporidium* will produce bromate, but the concentration that will be produced is unknown. Therefore, expected bromate concentrations at these ICR plants had to be predicted. The SWAT model was used to predict

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bromate formation when 0.5-log and 1.0-log inactivation of *Cryptosporidium* were achieved at all ICR plants. Estimates of the *Cryptosporidium* inactivation performance of ozone used the relationship between CT (the product of ozone residual and contact time), defined by Anderson et al. (2001), and the percentage of *Cryptosporidium* inactivation. The SWAT model predictions are appropriate for the development of relationships and trends at a national level, but its plant-specific predictions are unreliable (USEPA 2000b). Therefore, although the *Cryptosporidium*-challenged plants identified through ICR data were likely to have been included in the SWAT predictions, using the SWAT model's predictions of bromate formation at these plants was considered unreliable. Instead, a probabilistic approach was applied. In this approach, the national trends identified through SWAT runs were used to determine the likelihood that the ability of *Cryptosporidium*-challenged plants to apply ozone would be limited because of their potential to produce bromate.

- **Step 1.** Predict Bromate Formation by Ozone use for Cryptosporidium Inactivation
  - Use SWAT model to predict bromate formation for all ICR surface water plants.
- **Step 2.** Identify Unique Strata of Bromide to TOC (Br:TOC) Ratios on the Basis of Bromate Formation
  - Determine distribution of predicted bromate levels within various ranges of Br:TOC ratios
- **Step 3.** For Cryptosporidium Challenged ICR Plants, Determine the Monthly Distribution of Br:TOC Ratios
  - Number of months within each unique strata of Br:TOC ratios for each plant.
- **Step 4.** Assign Twelve Months of Distributed Bromate Predictions for Each Cryptosporidium Challenged Plants by Br:TOC Strata
  - Parameterized distribution of bromate was input for twelve predicted months of bromate formation within the Monte Carlo simulation model for each plant.
- **Step 5.** Run Monte Carlo Simulation to Estimate the Distribution of Annual Average Bromate Levels for Cryptosporidium Challenged Plants
  - Randomly select bromate levels from defined distributions for each month was used to calculate an annual average bromate level in each iteration step of the Monte Carlo simulation. Each plant had 1,000 estimates of annual average bromate concentrations from which the chance of exceeding a bromate limit was determined.
- **Step 6.** Determine the Fraction of ICR Plants with Various Chances of Exceeding an Annual Average Bromate Limit
  - For all Cryptosporidium challenged plants, the fraction of plants with Any Chance, a 10% chance, a 25% chance, a 50% chance, a 75% chance, a 90% chance or to Always expect to exceed a bromate limit was determined.

Figure 14.3 Steps to determine the likelihood that bromate formation would limit the use of ozone by *Cryptosporidium*-challenged plants

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The SWAT model's prediction of bromate formation was based on the following model developed by Ozekin, Westerhoff, and Amy (1998):

$$BrO_3^- = 1.19*10^{-7}(UVA)^{-0.623}(pH)^{5.68}(O_3)^{1.31}(Br^-)^{0.96}(Alk)^{-0.201}(1.035)^{(T-20)}(time)^{0.336} \quad (14.1)$$

in which BrO_3^- is the bromate formed in micrograms per liter, time is the reaction time in minutes, pH is the pH of the ozonated water, O_3 is the transferred ozone dose, Br^- is the bromide concentration in micrograms per liter, Alk is the alkalinity of the ozonated supply in milligrams of equivalent calcium carbonate per liter, and UVA is the ultraviolet absorption of the water at 254 nm measured per cm^{-1}.

The distribution of bromate formation predicted by Equation 14.1 for 0.5-log and 1.0-log inactivation of *Cryptosporidium* is shown in Figure 14.4. Bromate formation at more than 90% of the ICR plants was predicted at below 10 μg/L. With regard to long-term bromate concerns, 10% to 20% of the ICR plants would potentially be affected by a lower bromate limit of 5 μg/L.

Bromate formation depends strongly on the pH of the ozonated water (Haag and Hoigné 1983). For SWAT model runs, the application of ozone was presumed to occur at the source water location so that the pH value used in the model was the influent pH, a measured value in lieu of a predicted value for this critical parameter. Under any given pH condition, the formation of bromate depends on the ratio of bromide and the UVA of the water. Because UVA and TOC are strongly related, the bromide to TOC (Br:TOC) ratio can provide a normalized measure by which the bromate formation potential at treatment plants operating under various water quality conditions can be compared. In this analysis, the Br:TOC ratio is expressed in units of milligrams per milligram.

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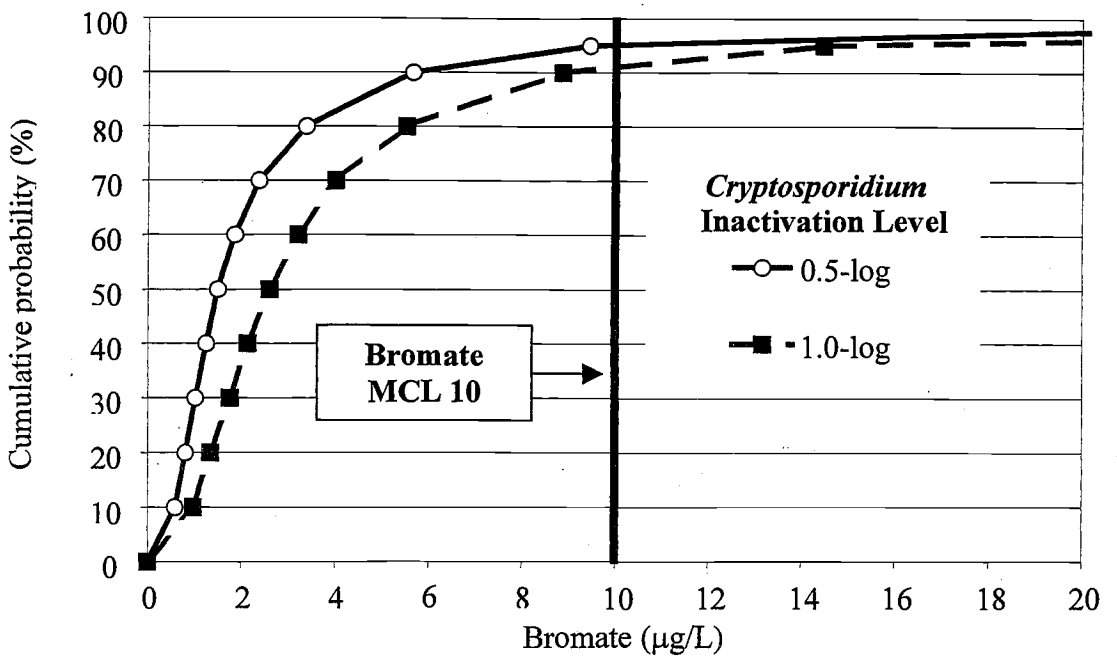

Figure 14.4 Distribution of predicted bromate concentrations expected at ICR surface water plants meeting requirements for 0.5-log and 1.0-log inactivation of *Cryptosporidium*

Step 2: Distributions and Stratification of Bromide-to-TOC Ratios

The distribution of Br:TOC ratios in the influent of ICR plants included in the SWAT model was determined, and the Br:TOC ratios were divided into decile ranges (Table 14.6). This procedure identified a substantial number of substrata in the expected ranges of bromate formation. When this stratification approach was used, a clear trend in source water quality variations was observed: (1) a linear relationship between bromide and TOC concentrations was exhibited in all deciles except the first group (Br:TOC ratio = <10%) and the last group (Br:TOC ratio = >90%) (Table 14.6), and (2) TOC concentrations progressively decreased and bromide concentrations progressively increased with increasing deciles of Br:TOC ratios (Table 14.6). The linearity of the relationship between bromide and TOC within the various Br:TOC decile groups results from the data segmentation and does not reflect general co-occurrence trends.

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Table 14.6

Decile ranges of bromide to total organic carbon (Br:TOC) ratios and relationships between bromide and total organic carbon concentrations for each decile

Decile (range)	Br:TOC ratio (mg/mg)	Concentration range (mg/L)		Linear relationship	
		TOC	Bromide	Coefficient*	r^2 †
1st (<10%)	<0.0054	3–20	<0.02–0.10	223	0.327
2nd (10–20%)	0.0054–0.0071	3–9	<0.02–0.05	158	0.909
3rd (20–30%)	0.0071–0.0087	2.3–7.5	<0.02–0.22	117	0.988
4th (30–40%)	0.0087–0.0105	2–12	<0.02–0.11	103	0.985
5th(40–50%)	0.0105–0.0127	1.6–8	<0.02–0.10	84	0.982
6th (50–60%)	0.0127–0.0154	1.3–6	<0.02–0.09	70	0.980
7th (60–70%)	0.0154–0.0188	1.1–8.5	<0.02–0.16	58	0.987
8th (70–80%)	0.0188–0.025	0.8–7.5	<0.02–0.16	44	0.972
9th (80–90%)	0.025–0.040	< 0.7–8.5	<0.02–0.26	28	0.894
10th (>90%)	>0.040	< 0.7–7.5	<0.02–1.4	—‡	0.524

* Coefficient for best-fit linear relationship of form: TOC = Coefficient × Bromide

† Correlation coefficient for the best-fit relationship between TOC and bromide

‡ The relationship between TOC and bromide in the final decile was nonlinear: TOC = 1.283 × Ln(Bromide) + 5.21.

The distribution of expected bromate formation was determined for each decile group of Br:TOC ratios. A statistical comparison of the ten distributions of expected bromate formation indicated five distinct ranges of Br:TOC ratios. These five ranges, or substrata, were used in the subsequent steps of this analysis. Differences in the distributions of expected bromate production among the five ranges of Br:TOC ratios are shown in Figure 14.5. Similar trends were found within the substrata for both levels of inactivation considered in this study (0.5-log and 1.0-log). These substrata showed increasingly higher bromate concentrations with increasing Br:TOC ratios. Approximately 35% of the records with Br:TOC ratios >0.040 resulted in expected bromate concentrations greater than 10 μg/L when 0.5-log inactivation was targeted. When the targeted level of inactivation was increased to 1.0-log, more than 50% of the records with ratios >0.040 resulted in expected bromate concentrations greater than 10 μg/L.

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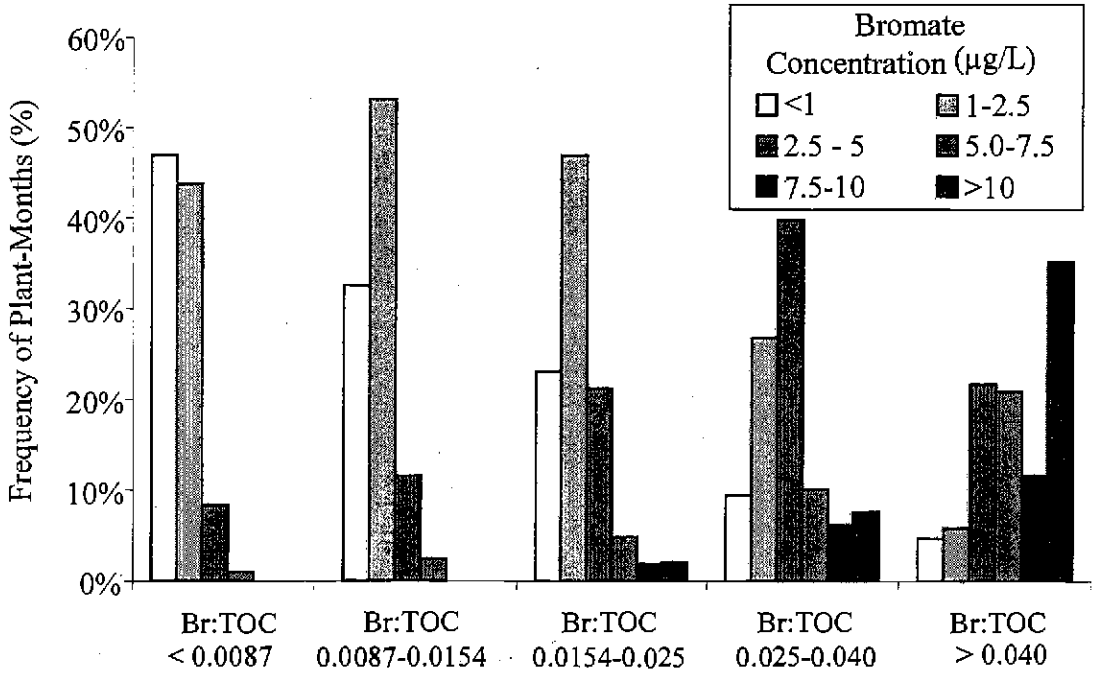
(a) *Cryptosporidium* Inactivation Level = 0.5-log



(b) *Cryptosporidium* Inactivation Level = 1.0-log

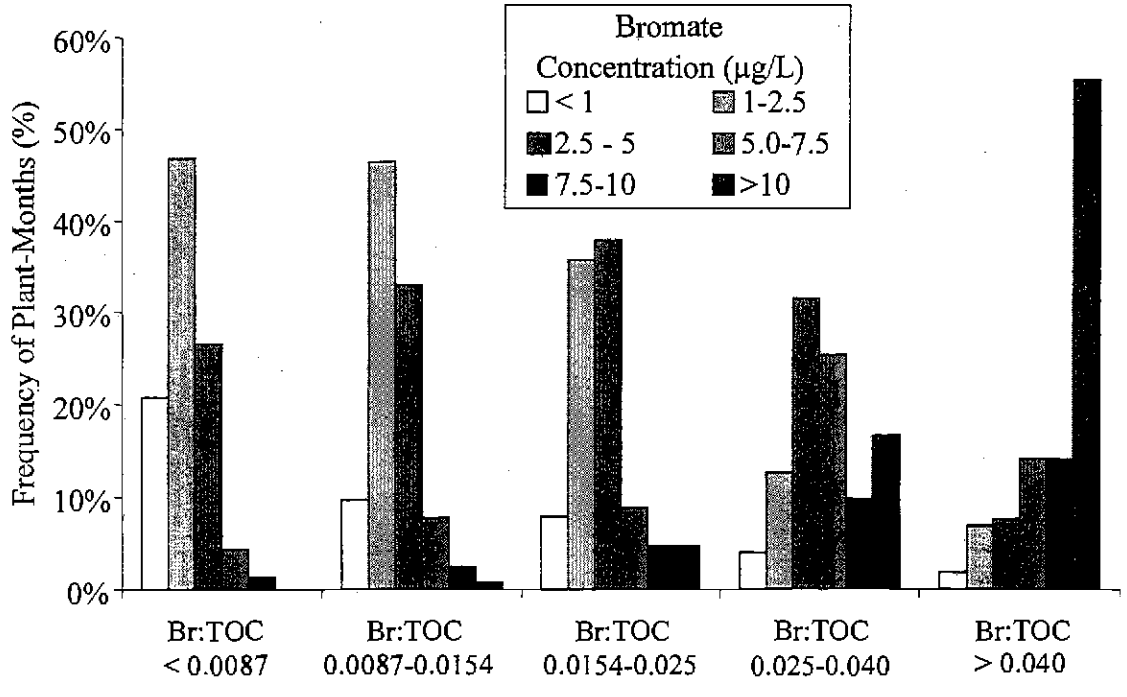


Figure 14.5 Frequency distribution of SWAT-predicted bromate concentrations in each substratum of bromide to TOC (Br:TOC) ratios for (a) 0.5-log inactivation of *Cryptosporidium* and (b) 1.0-log inactivation of *Cryptosporidium*

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Step 3: Br:TOC Ratios for *Cryptosporidium*-Challenged ICR Plants

Through the ICR monitoring program, 71 plants were identified as *Cryptosporidium*-challenged. Data from these specific plants were evaluated to determine each plant's Br:TOC ratios and the frequency with which monthly Br:TOC ratios fell within each of the defined classes shown in Figure 14.5. Forty-one percent of the monthly Br:TOC ratios at *Cryptosporidium*-challenged plants were in the lowest range; almost 50% were in the three intermediate classes; and 12% were in the highest range (Figure 14.6). Br:TOC ratios at only 13% of the *Cryptosporidium*-challenged plants remained in the same class during all months for which data were available. Temporal variability in Br:TOC ratios for each plant was so great that 31% of the plants experienced months in which the ratios fell across at least three concentration ranges; 24% had Br:TOC ratios in two ranges; 20% had Br:TOC ratios in four ranges; and 11% had Br:TOC ratios across all five concentration ranges. The variability in Br:TOC ratios at each plant was used directly in the Monte Carlo simulation model, the next step in this analysis, to ensure representation of potential bromate formation across monthly conditions.

Steps 4, 5, and 6: Monte Carlo Simulation Model and Likelihood of Exceeding Bromate Limits

A Monte Carlo simulation model was developed to predict the annual average bromate concentration at each *Cryptosporidium*-challenged plant represented in the ICR data (Figure 14.7). On the basis of the observed variability in source water Br:TOC ratios, each of the *Cryptosporidium*-challenged plants was assigned a number of months each year during which its Br:TOC ratio would be within a given range (one of the five ranges identified in the analyses discussed previously). A monthly bromate concentration was then assigned to each plant by random selection of a value within the defined distribution of bromate concentrations for the given Br:TOC class represented during that month. For example, if 100% of a plant's monthly Br:TOC ratios were below 0.0087 mg/mg (Class 1), 12 months of predicted bromate concentrations would be sampled from the distribution of SWAT-predicted Br:TOC ratios with similar values. Similarly, if 50% of a plant's monthly Br:TOC ratios were between 0.0154 mg/mg and 0.025 mg/mg and the remaining 50% were above 0.040 mg/mg, the Monte Carlo

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simulation model would select six months of bromate values from the distribution defined for Class 3 (Br:TOC range = 0.0154–0.025 mg/mg) and six months of bromate values from the distribution defined for Class 5 (Br:TOC range = >0.040 mg/mg).

The annual average bromate concentration for each *Cryptosporidium*-challenged facility was determined by averaging the monthly values. Thus, for each of the 71 plants, the Monte Carlo simulation model generated 12 months of predicted bromate concentrations for each iteration or step within the model. The Monte Carlo simulation model repeated this series of calculations 1,000 times. Therefore, 1,000 annual average bromate concentrations were predicted for each *Cryptosporidium*-challenged plant.

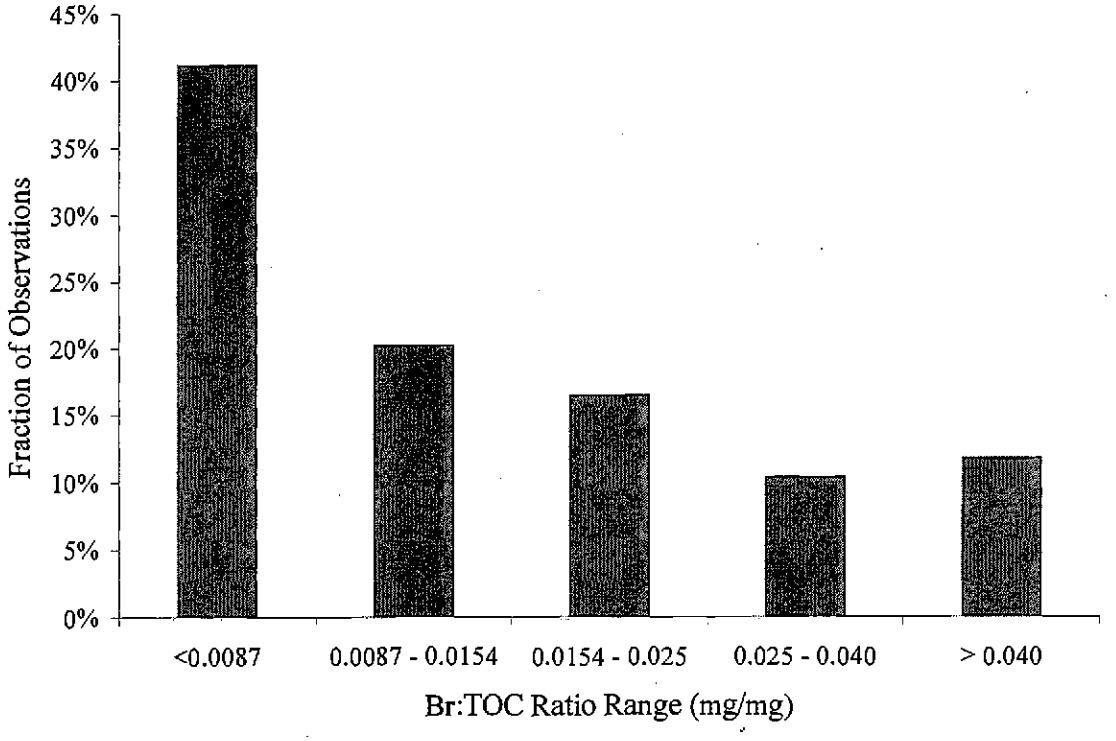

Figure 14.6 Frequency of monthly Br:TOC ratios (mg/mg) for *Cryptosporidium*-challenged surface water plants represented in ICR data

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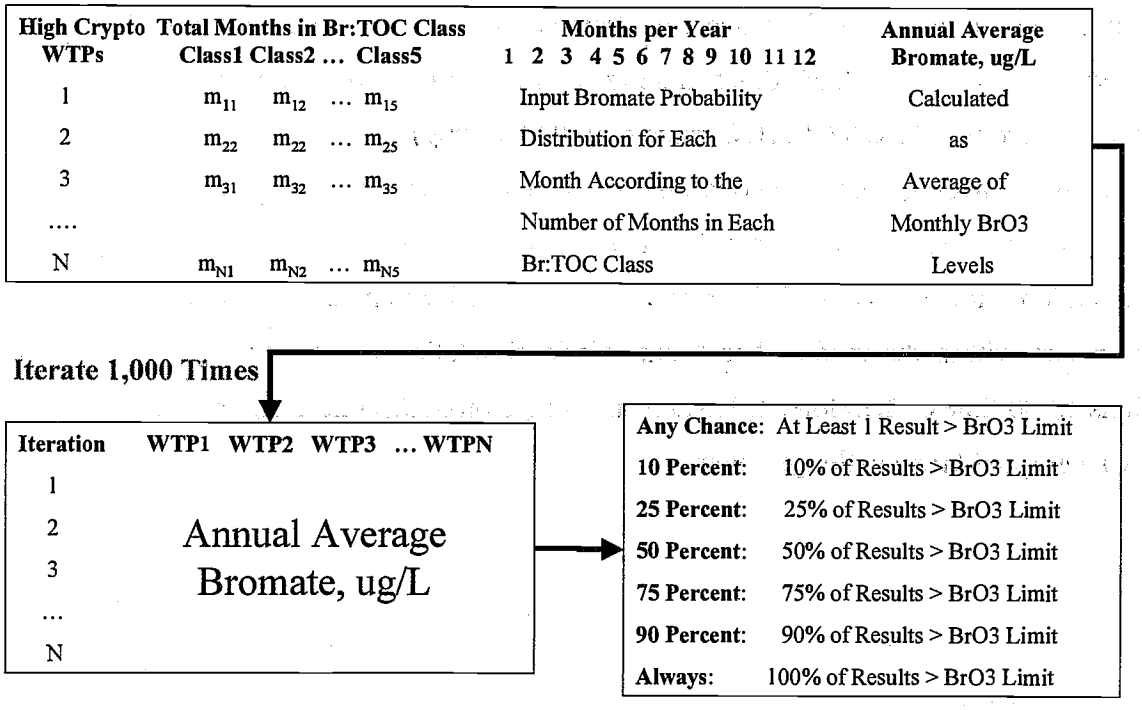

Figure 14.7 Algorithm used in the Monte Carlo simulation model for predicting bromate concentrations at *Cryptosporidium*-challenged surface water plants represented in ICR data

After 1,000 iterations, the distribution of annual average bromate concentrations for all 71 plants was determined and used to estimate the likelihood that plants would exceed a given bromate MCL. The bromate limits considered included the current 10-μg/L MCL and a potential MCL of 5 μg/L. The lower value was included so that the implications of establishing a lower bromate limit could be evaluated. These two conditions were considered with and without a safety factor of 80% of the MCL. The likelihood of such limits being exceeded was evaluated by determining each plant's probability of producing an annual bromate concentration above the MCL under consideration. Table 14.7 shows the fraction of *Cryptosporidium*-challenged plants expected to have a certain chance of exceeding a given bromate limit. For example, if all of the plants had to meet a 1.0-log inactivation criterion for *Cryptosporidium* control using ozone, 84% of those plants would have at least some chance of exceeding an annual average bromate concentration of 5 μg/L, 24% would have a 50% chance of exceeding 5 μg/L, 14% would have a 90% chance of exceeding 5 μg/L, and 6% would always exceed the 5 μg/L limit for bromate.

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Table 14.7

Likelihood of *Cryptosporidium*-challenged ICR surface water plants exceeding given limits on bromate ion (BrO_3^-)

	Bromate MCL of 5 μg/L		Bromate MCL of 10 μg/L	
Chance of exceeding BrO_3^- limit	BrO_3^- = >4 μg/L	BrO^- = >5 μg/L	BrO_3^- = >8 μg/L	BrO_3^- = >10 μg/L
0.5-log *Cryptosporidium* inactivation				
Any chance (>0%)	64%	46%	23%	10%
10%	24%	7%	0%	0%
25%	11%	0%	0%	0%
50%	4%	0%	0%	0%
75%	0%	0%	0%	0%
90%	0%	0%	0%	0%
100%	0%	0%	0%	0%
1.0-log *Cryptosporidium* inactivation				
Any chance (>0%)	100%	84%	50%	43%
10%	51%	41%	21%	19%
25%	44%	29%	17%	13%
50%	33%	24%	11%	9%
75%	26%	19%	9%	7%
90%	19%	14%	7%	6%
100%	7%	6%	0%	0%

The feasibility of ozone use depends on a utility's tolerance for the risk of producing bromate concentrations close to the regulatory limit. Presumably, continual compliance with an MCL would mean the utility considered any chance of exceeding the limit unacceptable. However, utilities might accept the risk of exceeding a targeted threshold at some value below the MCL, such as 80% of the MCL. On the basis of the Stage 1 D/DBP Rule's 10-μg/L MCL for bromate, only 10% of the *Cryptosporidium*-challenged ICR plants required to meet 0.5-log inactivation of *Cryptosporidium* would be expected to exceed the MCL itself, whereas 23% would be at some risk of exceeding 8 μg/L—a threshold representing 80% of the regulatory limit. Therefore, 13% of the plants would have to evaluate ozonation in terms of the trade-offs between their risk tolerance and treatment objectives, and an additional 10% would conclude that using ozone to inactivate *Cryptosporidium* was infeasible.

If the regulatory limit for bromate was reduced to 5 μg/L, 46% of the systems meeting 0.5-log inactivation of *Cryptosporidium* would be expected to violate the lowered MCL at some point, and 64% would be expected to exceed 4 μg/L, 80% of the lowered MCL. Requiring

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systems to meet 1.0-log inactivation dramatically decreases the feasibility of ozonation. With a targeted goal of 4 μg/L, all of the systems would be expected to have an annual average bromate concentration above the limit at some point.

These results demonstrate the decreasing feasibility of using ozone to inactivate *Cryptosporidium* if the bromate limit is lowered, especially if higher levels of inactivation are required. The question of ozone's suitability for use at a given utility can be addressed in part by testing techniques such as bench- and pilot-scale studies. However, these studies typically represent short-term water quality conditions and may not capture the full variability in water quality expected during decades of operation. Source water conditions that lead to substantial changes in both bromide and TOC concentrations (e.g., drought conditions) also need to be considered before the feasibility of ozonation can be determined.

The use of simulation modeling provides a probabilistic approach to determining the feasibility of using ozone for *Cryptosporidium* inactivation. Utilities likely to be challenged by *Cryptosporidium* should consider using such an approach to evaluate the suitability of ozone as a long-term measure for controlling this pathogen, especially if historical water quality information is available to demonstrate long-term trends. These modeling tools are readily available in user-friendly software. Their application can add substantial insight to utilities' decision-making processes in selecting appropriate treatment strategies to balance multiple water quality or performance objectives.

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CHAPTER 15

DISINFECTION PRACTICES AND PATHOGEN INACTIVATION IN ICR SURFACE WATER PLANTS

Jimmy Chen and Stig Regli

ABSTRACT

A baseline understanding of current nationwide drinking water treatment practices is necessary to evaluate the potential implications of options being considered for the Stage 2 Disinfection By-products (DBP) Rule and the Long Term 2 Enhanced Surface Water Treatment Rule. Characterizing disinfection practices and estimating the log inactivation of pathogens in treatment plants are critical components for understanding baseline treatment practices and conducting regulatory impact assessments. This chapter presents the results of comprehensive analyses of data collected under the Information Collection Rule (ICR) on disinfection and pathogen inactivation at surface water treatment plants.

Disinfection practices are characterized by national distributions of disinfectant types, dosages, and application points among various types of surface water plants. National distributions of disinfectant residual concentrations and log inactivation of pathogens are described in relation to different types of treatment. The analytical results present a national picture of the extent to which large utilities were meeting the disinfection requirements of the Surface Water Treatment Rule and the disinfectant residual limits of the Disinfectants/Disinfection By-products (D/DBP) Rule during implementation of the ICR.

INTRODUCTION

To help control the health risks posed by microorganisms in drinking water supplies, water systems use chemical disinfection instead of or in addition to the physical removal of microbes. However, introduction of chemical disinfectants imposes risks from the disinfectants and their by-products, and large surface water systems complying with both the Total Trihalomethane (TTHM) Rule (U.S. Environmental Protection Agency [USEPA] 1979) and the Surface Water Treatment Rule (SWTR) (USEPA 1989) must contend with this risk–risk tradeoff. The data collected under the Information Collection Rule (ICR) provide essential information for understanding how this risk–risk tradeoff has constrained disinfection practices in both water treatment plants and distribution systems. Furthermore, additional regulations—the Disinfectants/Disinfection By-products (D/DBP)

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Rule and Interim Enhanced Surface Water Treatment Rule (IESWTR) (USEPA 1998a, 1998b) and the forthcoming proposed Stage 2 DBP Rule and Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR)—have prompted, or will ultimately compel, water systems to modify disinfection practices in order to comply with more stringent limits. The baseline disinfection data collected under the ICR are useful for understanding the potential implications of new regulations related to controlling DBPs and pathogens.

This chapter characterizes disinfection practices and associated pathogen inactivation at ICR plants treating surface water. (Characterizing disinfection practices includes describing disinfectant types, dosages, and application points, as well as evaluating other factors that might affect these practices.) Disinfectant residual concentrations and pathogen inactivation levels are summarized in national distribution curves computed by means of various aggregation strategies. These data are analyzed to provide a national picture of the extent to which large utilities were meeting the disinfection requirements of the SWTR and to compare these practices with the disinfectant residual criteria specified in the D/DBP Rule, which was promulgated during ICR implementation. Log inactivation values for *Giardia* and viruses were computed from data in ICR Auxiliary Database 2 (AUX2); disinfection practices were characterized by using ICR Auxiliary Database 1 (AUX1). Because data (e.g., CT Tables—tables of C [disinfectant residual concentration] times T [contact time]) for calculating log inactivation of *Cryptosporidium* were not available when this chapter was written, estimates of *Cryptosporidium* inactivation are not included here. These estimates will be presented in a forthcoming USEPA guidance manual supporting the LT2ESWTR.

Disinfection practices can vary seasonally as a result of changes in source water quality (e.g., water temperature). ICR data were collected monthly during the 18-month period of July 1997 through December 1998. If all of the disinfection data from the entire 18-month monitoring period were used to characterize disinfection practices, the description would reflect a bias because the data would include both sets of values for the six-month periods of July through December. Therefore, the calculations presented in this chapter are based only on ICR data from the last 12 months of sampling (i.e., for a one-year cycle from January to December 1998). Calculations of plant averages include only data from plants with more than 9 months of records (out of the 12 months).

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ANALYTICAL RESULTS

Types of Disinfectants

In the AUX1database, disinfectants are classified based on their use within the plant and the distribution system. For the treatment plant, five classifications of disinfectants are defined:

- CL2—Free chlorine, when only chlorine (Cl_2) is used as a disinfectant;
- CL2_CLM—Free chlorine followed by chloramine, when ammonia (NH_3) is added after free chlorine has already been applied in one or more preceding unit processes;
- CLM—Chloramine, when Cl_2 and NH_3 are simultaneously added into a unit process and no chlorination has been applied earlier;
- CLX—Chlorine dioxide (ClO_2), if chlorine dioxide is used anywhere in the plant; and
- O3—Ozone (O_3), if ozone is used anywhere in the plant.

For the distribution system, two classifications of disinfectants—CL2 and CLM—are defined, based on the type of disinfectant applied at the last application point before the water enters the distribution system.

AUX1 includes data from 353 surface water plants reporting disinfection records for a total of 3,861 plant-months of data collected during the last 12 months of the ICR monitoring period. Figure 15.1 indicates the distribution of disinfectant types recorded in AUX1 for all surface water plants on a plant-month basis. Plants classified as having a disinfectant type of CL2/CL2 (Cl_2 at the plant/Cl_2 in the distribution system) predominated (53.7% of plant-months). The combination of Cl_2 and NH_3 was used 34.7% of the time (23.4% CL2_CLM/CLM, 6.3% CL2/CLM, 4.9% CLM/CLM, and 0.1% CL2_CLM/CL2). Advanced disinfectants were used 11.5% of the time (6.3% CLX and 5.2% O3). Almost 88% of plants (309 out of 353) used Cl_2-based disinfectants (CL2, CL2_CLM, or CLM), and 6.5% of these (20 out of 309) switched from Cl_2 to chloramine (or vice versa) for at least 1 month during the last 12 months of ICR monitoring. Similarly, about 7% of plants (25) changed the type of disinfectant used in the distribution system for at least 1 month during the last 12 months of monitoring; 18 of these 25 plants were identical to those switching between Cl_2 and chloramine in the plant. Ninety-one percent of plants using Cl_2 used gaseous Cl_2; 15% used hypochlorite; and 4.5% used both forms of Cl_2 during the last 12 months of monitoring.

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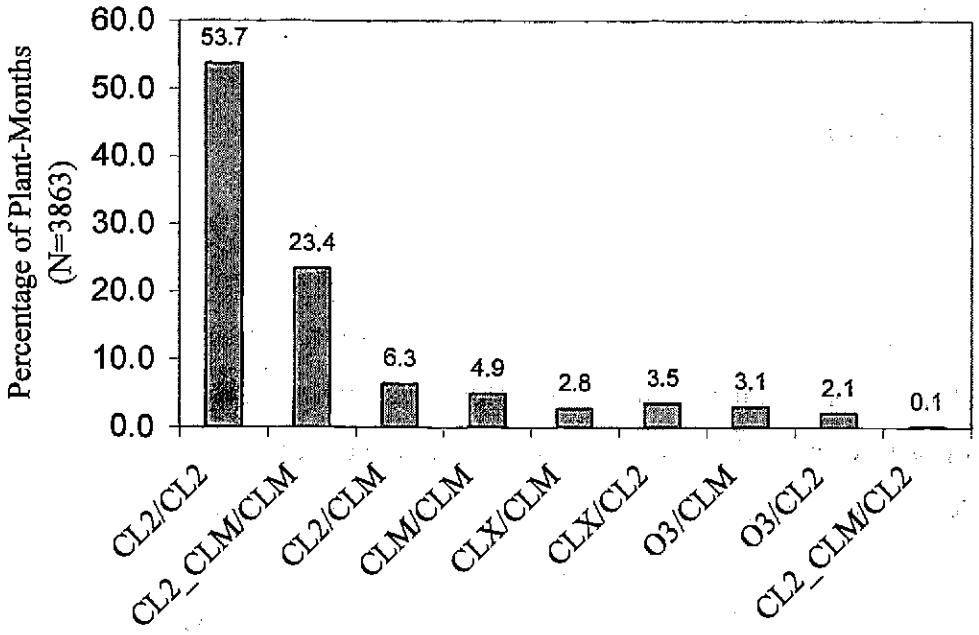

Figure 15.1 Classifications of disinfectants used in ICR surface water treatment plants and distribution systems (based on data collected during the last 12 months of ICR monitoring)

Table 15.1 summarizes the types of disinfectants used on a plant-month basis as a function of treatment plant type (defined under the ICR). Among conventional plants, the classification CL2/CL2 was the most common (57% of plant-months), followed by CL2_CLM/CLM (23% of plant-months). In contrast, the classification CL2_CLM/CLM was more prevalent than CL2/CL2 among softening plants (40% versus 18% of plant-months), probably because of high pH conditions and the difficulty of complying with the 100-μg/L maximum contaminant level (MCL) specified in the TTHM Rule with Cl_2 in the distribution system. Advanced disinfectants (ClO_2 or O_3) were also used to a greater extent in softening plants than in conventional plants (24% versus 11% of plant-months). Table 15.1 also shows that CL2/CL2 was the most common classification for direct filtration plants (66% of the time), unfiltered plants (65% of the time), and all other categories of plants combined (92% of the time), probably because relatively low DBP precursor concentrations in the source water allowed these water systems to meet the TTHM standard using free chlorine alone.

The extent to which conventional plants were classified as CL2/CL2 appeared to be largely a function of the concentration of organic DBP precursors in the source water. Table 15.2 shows the

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percentage of plant-months during which conventional plants used only free chlorine as a function of source water total organic carbon (TOC) and chlorine demand. The percentage of plant-months during which plants used only free chlorine was consistently higher for water sources with lower concentrations of TOC. This trend was not observed for chlorine demand, implying that chlorine demand might not have been a factor affecting the use of free chlorine versus other disinfectants.

Table 15.1

Distribution of disinfectant classifications as a function of treatment plant type*

	Type of plant				
Disinfectant classification (plant/distribution system)	Conventional (*N*=3011) %	Softening (*N*=417) %	Direct/in-line filtration (*N*=322) %	Unfiltered (*N*=69) %	Other† (*N*=39) %
CL2/CL2	56.7	17.7	65.5	65.2	92.3
CL2_CLM/CLM	23.4	39.6	7.1	0	7.3
CL2/CLM	5.6	5.8	12.1	17.4	0
CLM/CLM	4.6	13.0	0	0	0
CLX/CLM	1.8	12.7	0	0	0
CLX/CL2	4.2	2.9	0	0	0
O3/CLM	1.7	8.4	6.2	17.4	0
O3/CL2	1.8	0	9.0	0	0
CL2_CLM/CL2	0.1	0	0	0	0

* Expressed as a percentage of plant-months of data collected during the last 12 months of ICR monitoring
† Includes one membrane plant classified as CL2/CL2 for three months

Table 15.2

Percentage of conventional plants using only free chlorine, shown as a function of source water TOC and chlorine demand

		Range of TOC concentrations in source water* (mg C/L)		
		<2	2–4	≥4
Range of chlorine demand* (mg Cl_2/L)	<1	82% (*N*=411)	61% (*N*=773)	35% (*N*=214)
	1–2	87% (*N*=24)	50% (*N*=183)	36% (*N*=171)
	≥ 2	96% (*N*=24)	49% (*N*=86)	35% (*N*=98)

* Based on plant averages reported during the last 12 months of ICR monitoring

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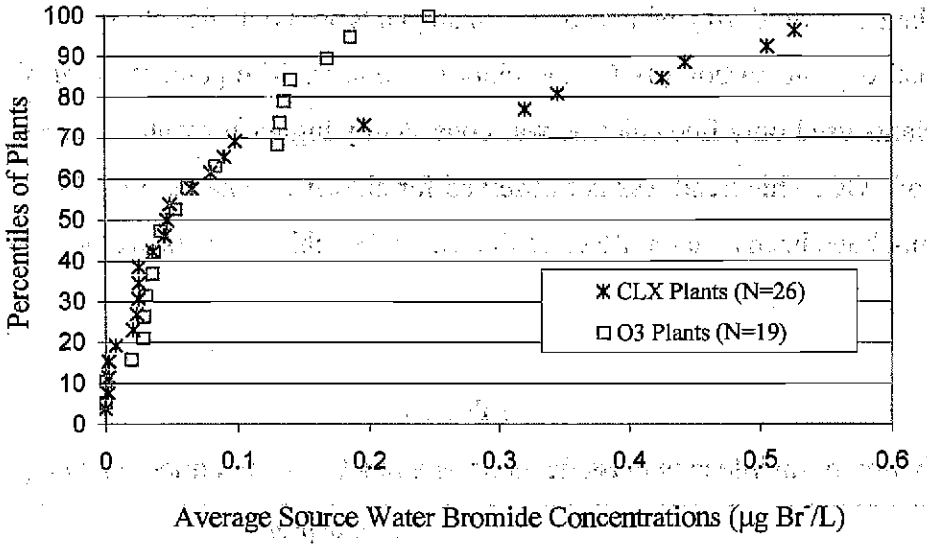

Figure 15.2 Use of O_3 versus ClO_2 as a function of source water bromide concentrations (based on data collected during the last 12 months of ICR monitoring)

Figure 15.2 shows the extent to which bromide (Br^-) occurred in the source water of plants using O_3 or ClO_2. No conventional plant used O_3 when source water Br^- concentrations were higher than 0.23 mg/L, suggesting that high Br^- concentrations in source water constrained O_3 use but not ClO_2 use, perhaps because of the bromate standard (10 µg BrO_3^-/L) proposed in 1994 (and finalized in 1998) under the D/DBP Rule (USEPA 1998a).

Disinfectant Application Point and Dosage

Two key operational parameters that affect pathogen control and DBP formation are the dosage of the disinfectant and the location where it is applied. These parameters influence the effective contact time and the disinfectant residual concentration that are available to inactivate microorganisms and to form DBPs in a water system. Because disinfectant application points and dosages vary widely among different types of treatment plants using different disinfectants, the following discussion describes disinfection practices at ICR plants using the most common disinfection scheme and classified as CL2/CL2.

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Table 15.3

Number of disinfectant application points in plants using only free chlorine, shown as a function of plant type*

Type of plant	Plant-months (%)			
	1 location	2 locations	3 locations	>3 locations
Conventional (*N*=1696)	37	53	10	0
Softening (*N*=74)	51	49	0	0
Direct/in-line filtration (*N*=206)	41	49	10	0
Unfiltered (*N*=45)	47	53	0	0
Other† (*N*=27)	100	0	0	0

* Based on data collected during the last 12 months of ICR monitoring
† Includes one membrane, one slow sand filtration, and two other plants

Table 15.3 indicates the number of disinfectant application points for various types of plants using only free chlorine. The data indicate that most plant types used one or two application points; "other" plant types used only one. Direct filtration and in-line filtration plants—and 10% of the conventional plants—used three Cl_2 application points. Plants with multiple application points were most likely using Cl_2 to address multiple treatment objectives (e.g., disinfection, preoxidation, taste and odor control, and prevention of microbial growth within unit processes).

Figure 15.3 shows that the three most common points of Cl_2 application occurred at the rapid stage, just prior to filtration, and at the clearwell. Plants using only one application point added chlorine at the rapid mix stage (36% of the time), just prior to filtration (28% of the time), or at the clearwell (27% of the time). Compared with plants using one application point, a slightly higher percentage of plants using two application points applied Cl_2 at the filter (32% versus 28% of the time); a higher percentage of plants using two application points rather than one applied Cl_2 at the rapid mix stage (53% versus 36%) and at the clearwell (80% versus 27%). For plants using three application points versus those using two, the percentage was even higher at the rapid mix stage (83% versus 53% of the time) and much higher at the filter (82% versus 32%) and at the clearwell (97% versus 80%). Overall, the ICR data suggest that many plants may have the opportunity to shift Cl_2 application points farther downstream in the treatment train (e.g., from before rapid mix to some point following rapid mix, such as before flocculation, sedimentation, or filtration) as they consider meeting the standards in the D/DBP Rule and the forthcoming Stage 2 DBP Rule. Such changes may

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or may not be appropriate, depending on source water quality, available preoxidation options, and pathogen control objectives. The data also indicate that in softening plants using only chlorination, Cl_2 was most often applied at the filter or clearwell. When ClO_2 was used, it was most often applied prior to the rapid mix stage (65% of the time), perhaps because the intensity of mixing enhances dissolution of the ClO_2 gas into the water phase. In some cases, ClO_2 was used as a preoxidant to control taste and odor rather than as a disinfectant.

The large number of permutations complicates characterization of NH_3 and Cl_2 application points in plants using chloramines for disinfection. Figures 15.4A and B indicate the distribution of NH_3 application points among CL2_CLM plants and CLM plants, respectively. Figure 15.4A indicates that CL2_CLM plants applying NH_3 at one location tended to do so at the clearwell (53% of the time). Plants applying NH_3 at two points tended to do so mostly at the rapid mix stage (69% of the time) and the clearwell (53%). Figure 15.4B indicates that CLM plants applying NH_3 at one location did so mostly at the rapid mix stage (72% of the time); plants applying NH_3 at two locations did so at the rapid mix stage 80% of time, at the flocculation basin 48% of the time, just prior to filtration 31% of the time, and at the clearwell 46% of the time. Overall, the prevalence of NH_3 application at the point of rapid mix in CLM plants suggests that the water sources treated at these plants contain high concentrations of organic DBP precursors and that chloramines are applied to provide some pathogen inactivation and to prevent formation of chlorinated DBPs. Moving the chloramination point in these plants is not likely to be effective at further reducing DBPs.

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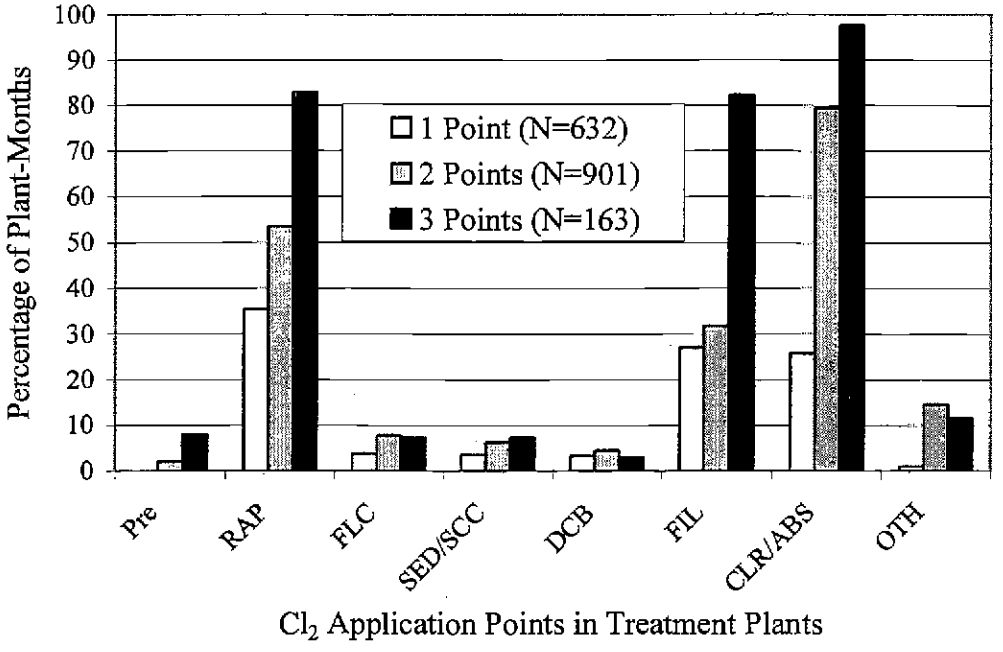

Figure 15.3 Cl_2 application locations in conventional plants using only free chlorine, as a function of the number of application points (based on data collected during the last 12 months of ICR monitoring)

Key: pre=pretreatment, RAP=rapid mix, FLC=flocculation, SED/SCC= sedimentation/clarifier, DCB=disinfection contact basin, FIL=filter, CLR=clearwell; OTH=other

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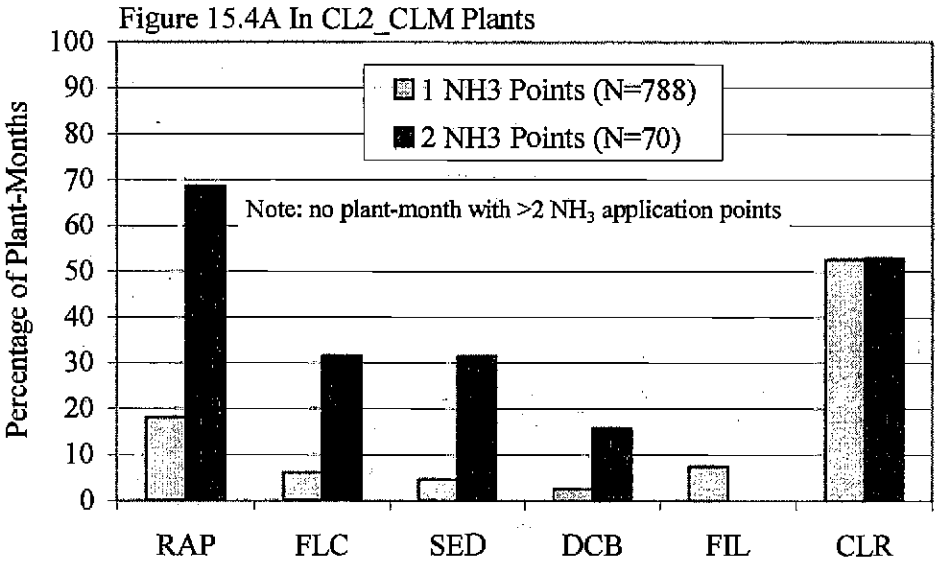

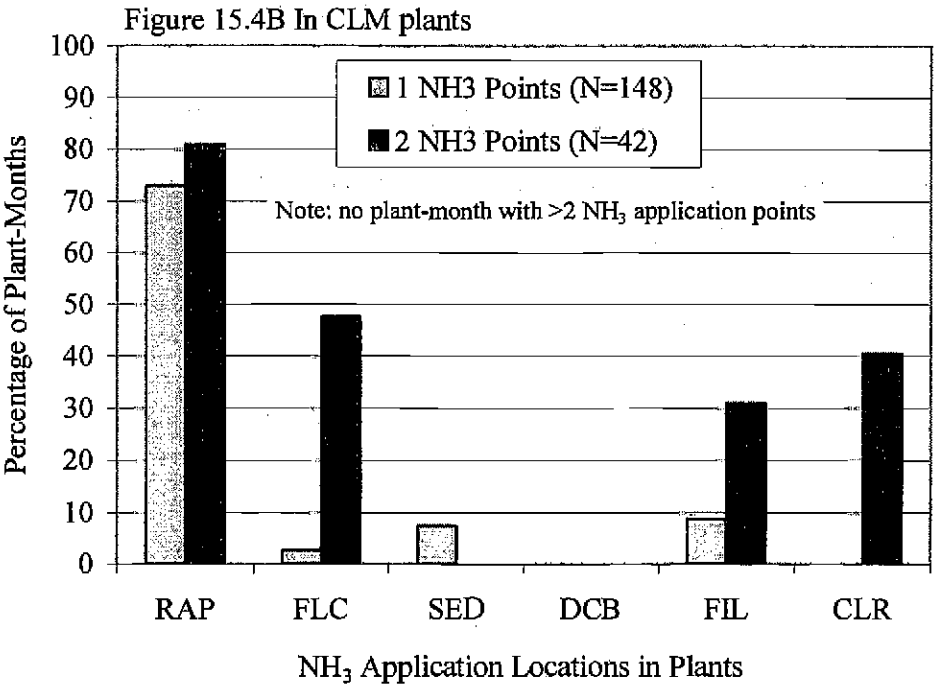

Figure 15.4 NH_3 application locations in CL2_CLM or CLM conventional and softening plants, as a function of number of application points (based on data collected during the last 12 months of ICR monitoring)

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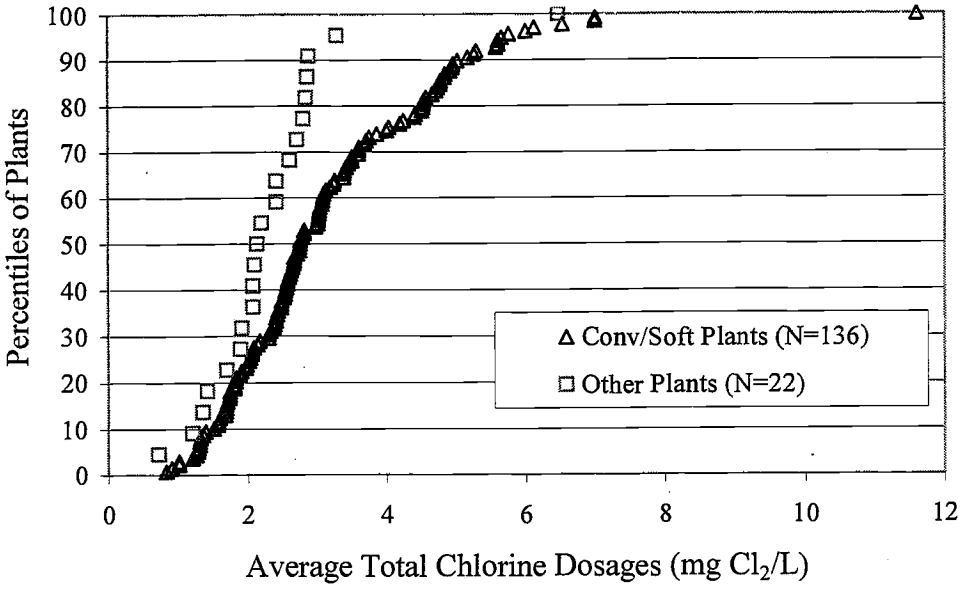

Figure 15.5 Total chlorine dosages in plants using only free chlorine (based on data collected during the last 12 months of ICR monitoring)

Figure 15.5 illustrates the distribution of average total chlorine dosages in conventional or softening plants using only Cl_2 as a disinfectant versus all other types of plants using only Cl_2. Average Cl_2 dosages in conventional and softening plants were substantially higher than those in other types of plants (a median of 2.8 mg Cl_2/L versus a median of 2.1 mg Cl_2/L); the difference is probably related to better source water quality in the latter types of plants. Table 15.4 shows that both chlorine demand and source water TOC concentrations were consistently higher in conventional and softening plants compared with other types of plants using only free chlorine. Table 15.5 shows that in conventional plants using only free chlorine, Cl_2 dosages generally increased with both source water TOC concentrations and chlorine demand. Figure 15.6 illustrates the difference in average total chlorine dosages in conventional and softening plants using only free chlorine versus those using chloramines (a median of 2.6 mg Cl_2/L versus a median of 5.0 mg Cl_2/L). The higher Cl_2 dosages applied in plants using chloramines are probably attributable to higher concentrations of organic material and higher chlorine demand; the higher Cl_2 dosages were probably needed to achieve adequate combined chlorine residuals for CT credits in the plants using chloramines.

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Table 15.4

Source water TOC and chlorine demand in plants using only free chlorine, shown as a function of plant type

Type of plant	Source water TOC* (mg C/L)			Chlorine demand* (mg Cl_2/L)		
	25th percentile	Median	95th percentile	25th percentile	Median	95th percentile
Conventional and softening	1.9 (*N*=178)	2.7 (*N*=178)	6.0 (*N*=178)	0.3 (*N*=158)	0.6 (*N*=158)	2.4 (*N*=158)
Other	1.4 (*N*=28)	1.8 (*N*=28)	3.3 (*N*=28)	0.2 (*N*=27)	0.3 (*N*=27)	1.1 (*N*=27)

* Based on the distribution of plant averages reported during the last 12 months of ICR monitoring

Table 15.5

Mean total chlorine dosages in conventional plants using only free chlorine, shown as a function of source water TOC and chlorine demand

		Range of source water TOC* (mg C/L)		
		<2	2–4	≥4
Range of chlorine demand* (mg Cl_2/L)	<1	2.6 mg/L (*N*=38)	3.1 mg/L (*N*=63)	4.8 mg/L (*N*=12)
	1–2	3.0 mg/L (*N*=2)	4.7 mg/L (*N*=13)	5.2 mg/L (*N*=11)
	≥ 2	3.3 mg/L (*N*=2)	4.7 mg/L (*N*=5)	7.0 mg/L (*N*=3)

* Based on plant means reported during the last 12 months of ICR monitoring

Plants using chloramines must control the ratio of free chlorine to ammonia-nitrogen (Cl_2:NH_3-N) to ensure adequate formation of chloramines. Excess NH_3 can lead to nitrification and thus can degrade water quality in the distribution system; excess Cl_2 can lead to a free chlorine residual and associated DBP formation. Figure 15.7 shows the distribution of Cl_2:NH_3-N weight ratios in plants using chloramines. The curve indicates that about 95% of the plants using chloramines had a plant average Cl_2:NH_3-N weight ratio above 2.5, the stoichiometric ratio for formation of monochloramine (NH_2Cl) in chlorine-demand–free water. About 50% of the plants had a weight ratio greater than 7.6, the stoichiometric ratio required to reach chlorination breakpoint in chlorine-demand–free water. The high Cl_2:N ratios relative to what might be prescribed for use with chlorine-demand–free water indicate high chlorine demand in the water sources treated at these

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plants. Also noteworthy is the variability in the Cl_2:N ratio at many of these plants during the last 12 months of ICR monitoring; this implies variability in chlorine demand or Cl_2 dosage. Variability in the Cl_2:N ratios may indicate the challenge some plants face in maintaining appropriate ratios in response to fluctuating source water quality. The extreme Cl_2:N ratios suggest that some plants might sometimes be overdosing Cl_2.

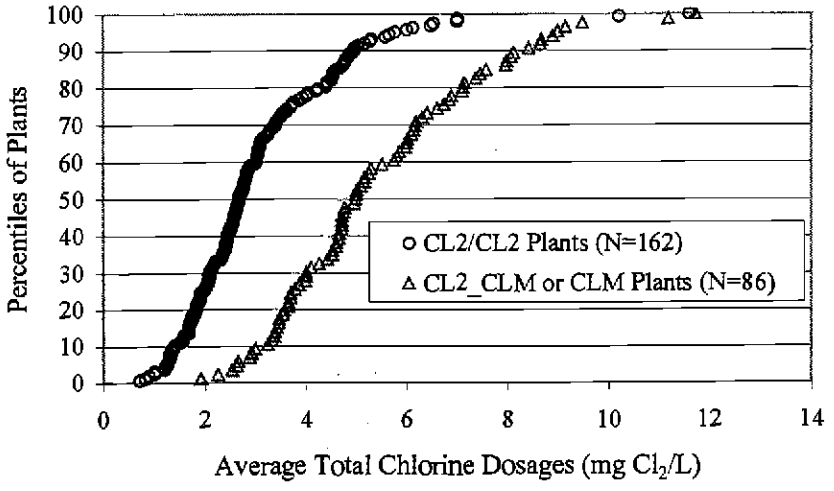

Figure 15.6 Total chlorine dosage as a function of type of disinfectant (based on data collected during the last 12 months of ICR monitoring)

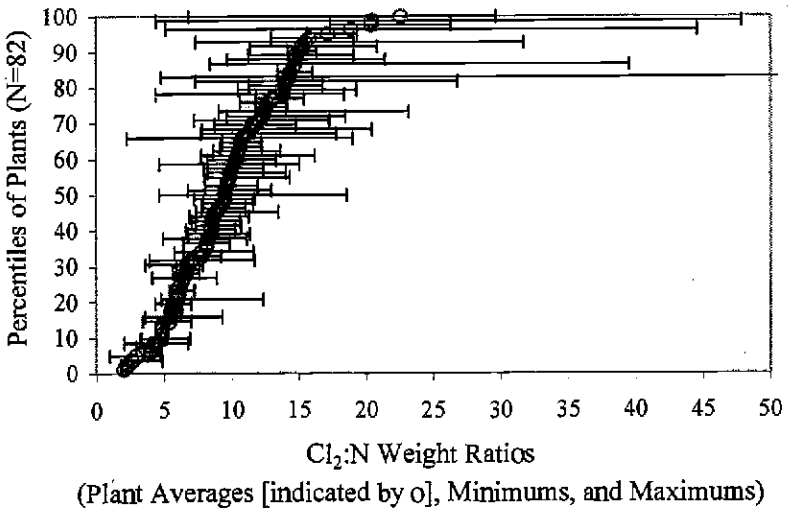

Figure 15.7 Cl_2:NH_3-N weight ratios in CL2_CLM and CLM plants (based on data collected during the last 12 months of ICR monitoring)

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Figures 15.8A and B indicate total ClO_2 and O_3 dosages (expressed as plant monthly averages, minimums, and maximums) in plants using these disinfectants. Eighty-five percent of CLX plants used an average ClO_2 dosage below 1.5 mg/L (Figure 15.8A), perhaps because of the chlorite (ClO_2^-) standard (1.0 mg ClO_2^-/L) specified in the D/DBP Rule. The variability in ClO_2 dosages suggests that some plants may need to tighten control of ClO_2 applications in order to consistently meet the D/DBP Rule's ClO_2 or ClO_2^- limits in finished water. About 90% of plants using O_3 used an average dosage below 2.5 mg O_3/L (Figure 15.8B). O_3 dosages in some plants varied widely from month to month.

Disinfectant Residuals

Controlling disinfectant residuals in finished and distributed water is essential for compliance with the SWTR and the D/DBP Rule. The SWTR requires that finished water have a residual disinfectant concentration of >0.2 mg/L at the entry point to the distribution system and that a detectable residual be maintained within the distribution system (no more than 5% of monthly samples can have residuals below the detection limit during any two consecutive months) (USEPA 1998b). The D/DBP Rule specifies maximum residual disinfectant levels (MRDLs) of 4.0 mg Cl_2/L for average residual concentrations of chlorine and chloramine in the distribution system (USEPA 1998a). The D/DBP Rule also specifies an MCL of 0.8 mg ClO_2/L, based on daily sampling at the entry point to the distribution system and, if the MCL is exceeded at the entry point, at subsequent distribution system locations on the next day. Furthermore, the SWTR requirements for pathogen inactivation are based on log inactivation as determined by a disinfectant residual concentration at the end of the disinfection process in the plant.

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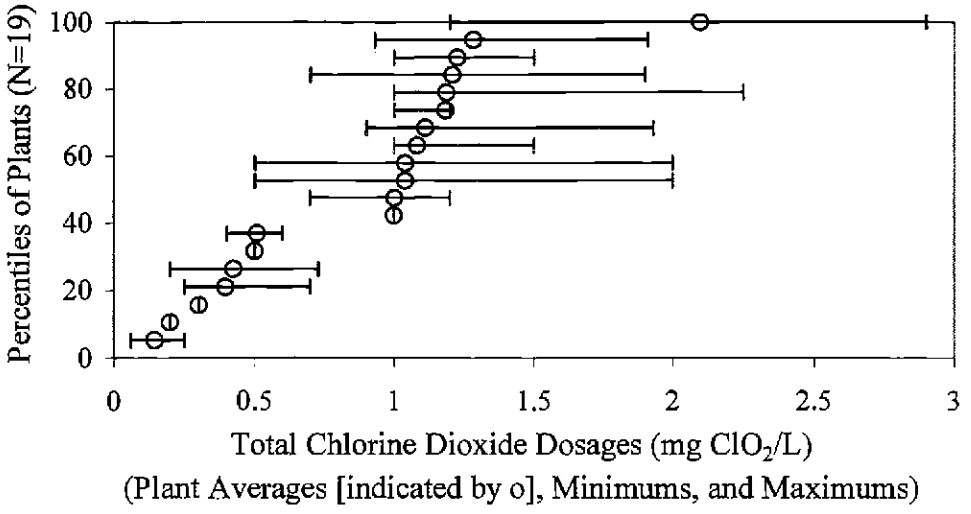

Figure 15.8A Total chlorine dioxide dosages in CLX plants (based on data collected during the last 12 months of ICR monitoring)

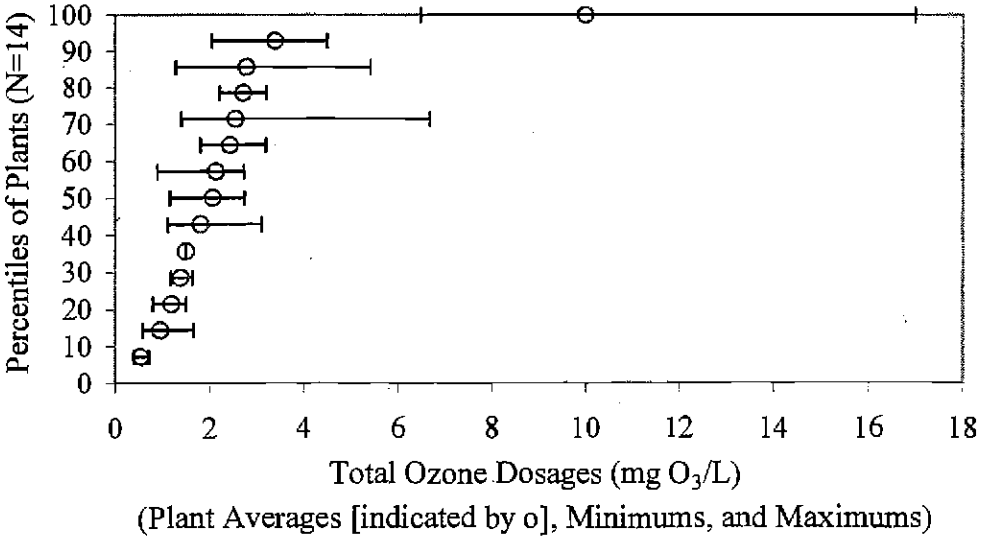

Figure 15.8B Total ozone dosages in O3 plants (based on data collected during the last 12 months of ICR monitoring)

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Figure 15.9 depicts the distribution of minimum and maximum concentrations of Cl_2 and total chlorine residuals in the finished water of all ICR unblended surface water plants. (For plants that do not blend water before distributing it, the finished water sampling point and the entry point to the distribution system are the same.) The data indicate that 2% of plants had total chlorine residuals of <0.2 mg Cl_2/L for at least 1 month during the last 12 months of ICR monitoring (Figure 15.9A). Carrying a total residual of <0.2 mg/L for more than a 4-hour period is a violation of the SWTR. The data also indicate that 34% of plants had minimum free chlorine residuals of <0.2 mg/L (Figure 15.9B). Figure 15.10 shows the distribution of Cl_2 residuals at the distribution system location believed to represent maximum residence time (the ICR max location). Ninety-five percent of plants maintained a detectable total chlorine residual at the ICR max location, whereas a few plants had total chlorine residuals of >4.0 mg/L for 1 or more months during the last 12 months of ICR monitoring (Figure 15.10A). Although these data are not definitive because of the small number of distribution system sampling points included in the ICR records, they suggest that most ICR systems were meeting the distribution system disinfectant residual requirements of the SWTR.

Figure 15.11A indicates that 4 out of 19 CLX plants (21%) consistently exceeded the 0.8 mg/L D/DBP MCL for ClO_2 at the entry point to the distribution system. Eight out of 19 plants (42%) exceeded the 0.8 mg/L MCL at least once during the last 12 months of the ICR sampling period. These data suggest that at least 40% of ICR plants using ClO_2 will need to adjust dosages to comply with the final Stage 1 DBP Rule.

For plants using O_3 as a disinfectant, the distribution of O_3 residual concentrations in the last O_3 contact chamber is shown in Figure 15.11B (under the ICR, O_3 residuals were monitored only in the contact chambers). Although average residual concentrations fell within a relatively narrow range (between 0.07 and 0.27 mg O_3/L), they varied significantly within plants from month to month, probably because of variations in O_3 dosages (as shown in Figure 15.8B) and fluctuations in source water quality (e.g., temperature and TOC concentrations).

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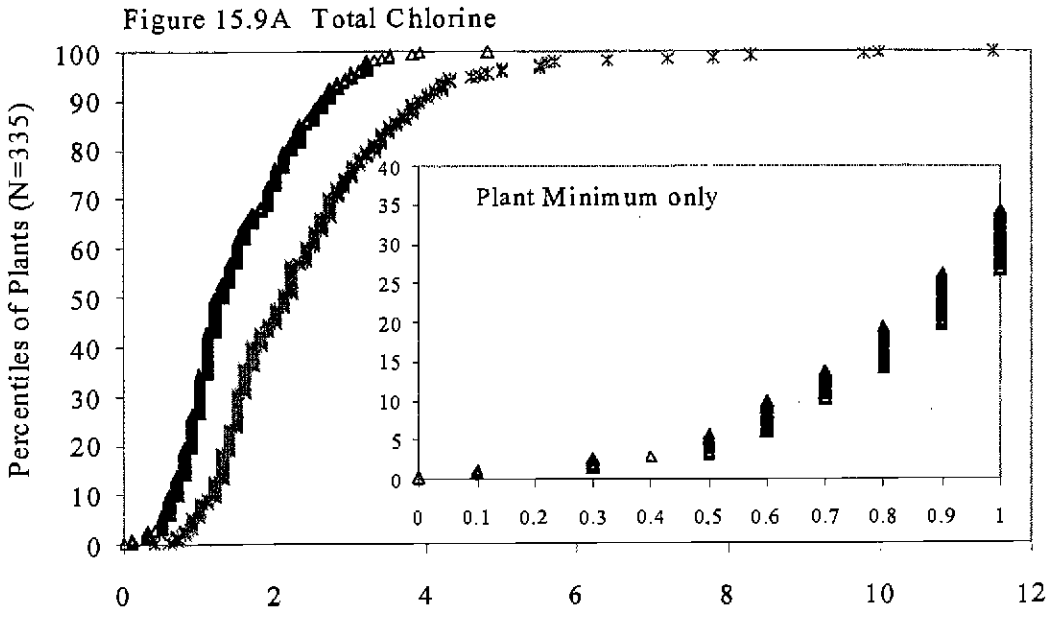

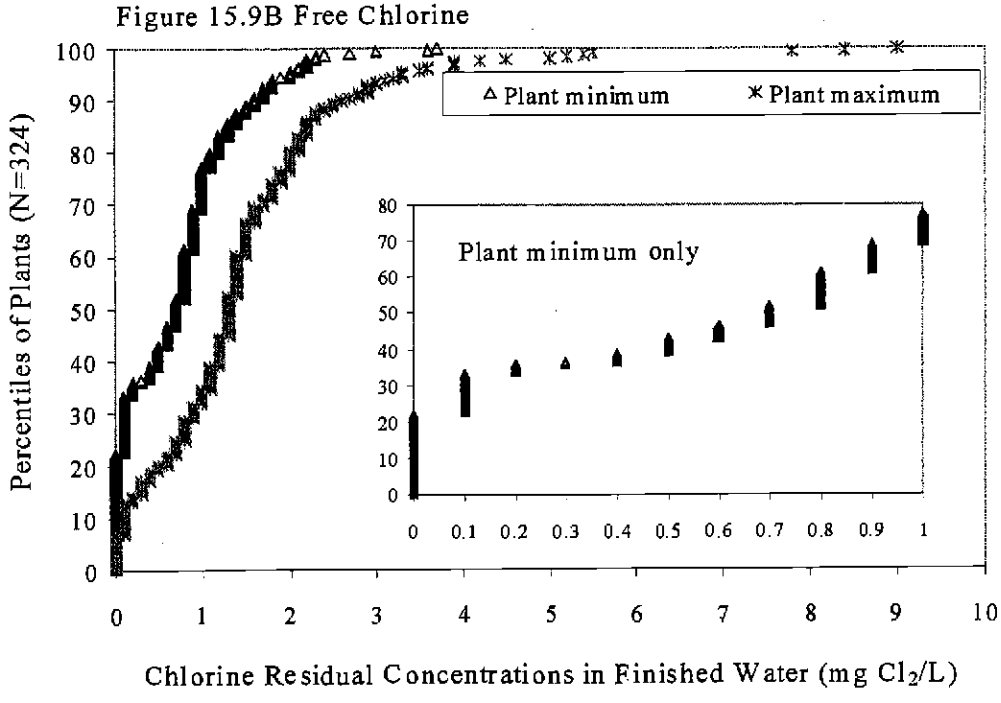

Figure 15.9 Chlorine residual concentrations in finished water at unblended surface water plants (based on data collected during the last 12 months of ICR monitoring)

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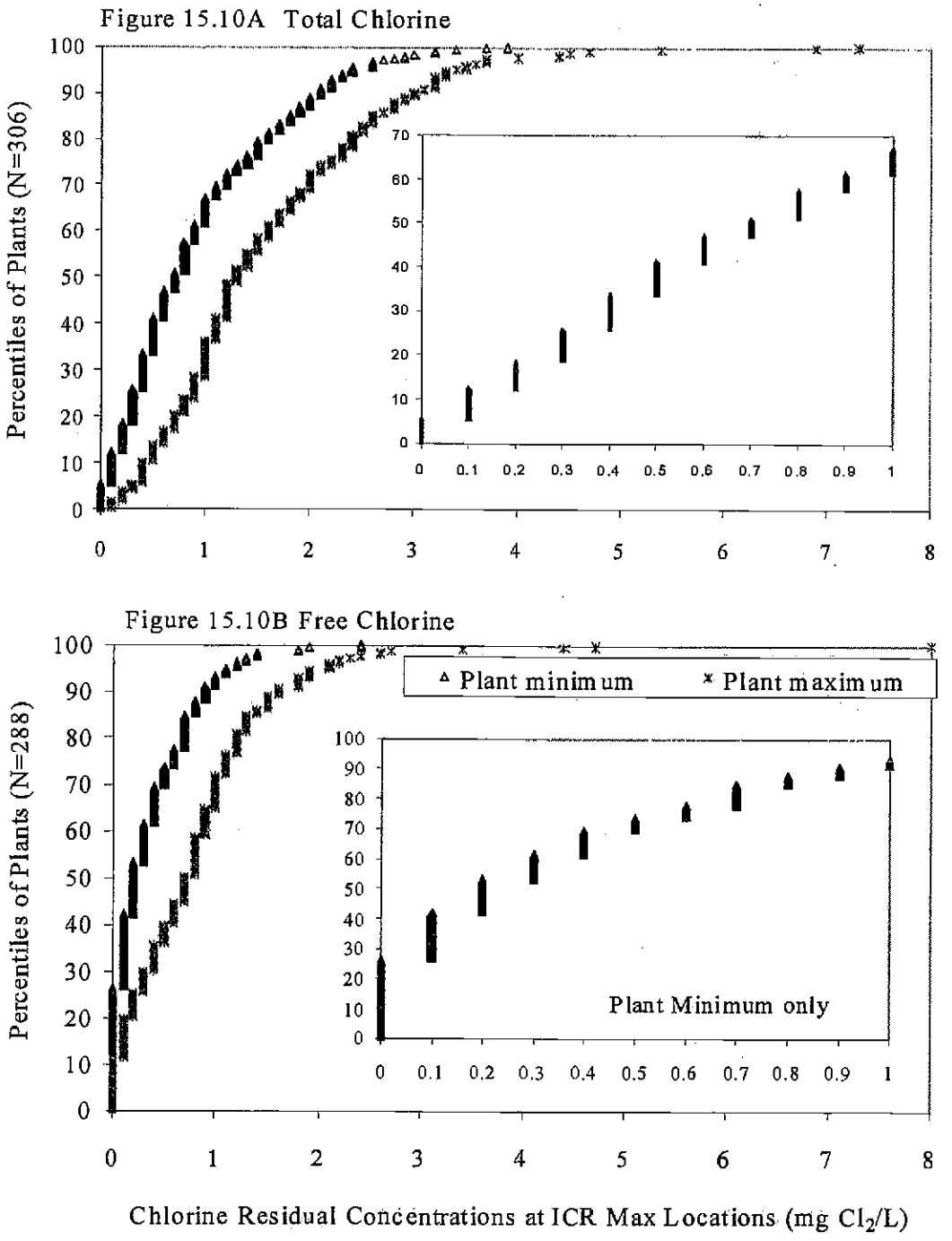

Figure15.10 Chlorine residual concentrations at ICR distribution system max locations (based on data collected during the last 12 months of ICR monitoring)

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Log Inactivation of Pathogens

Estimated log inactivation results are based on data from AUX2. Pathogen inactivation from ClO_2 disinfection is excluded because of insufficient information on ClO_2 residuals. Figure 15.12A indicates the minimum level of *Giardia* inactivation achieved by ICR surface water plants and calculated from CT values reported during the last 12 months of ICR monitoring. The median value for minimum *Giardia* inactivation was 1.6 logs. Eighteen percent of plants achieved less than 0.5-log inactivation of *Giardia* during 1 of the 12 monthly reporting periods. USEPA's guidance manual for complying with the SWTR recommends that plants using conventional treatment provide at least 0.5-log inactivation of *Giardia* throughout the year; plants using direct filtration are advised to provide at least 1-log *Giardia* inactivation (USEPA 1991). Thus, it appears that some ICR plants may not have been meeting minimum SWTR requirements for *Giardia*. Figure 15.12A also indicates the range of log inactivation of *Giardia* achieved by ICR surface water plants during the last 12 months of monitoring (the curve labeled the "Delta of Max & Min" indicates the difference between the highest level of inactivation and the lowest). Twenty-eight percent of the plants provided theoretical *Giardia* inactivation levels ranging across more than 10 logs during the last 12 months of sampling. These fluctuations were probably due to variations in water quality (e.g., temperature and chlorine demand) and changes in contact times or Cl_2 residual concentrations during disinfection.

Figure 15.12B provides the same type of inactivation information for viruses. The extremely high levels of virus inactivation indicated on the x-axis are based on linear extrapolations of inactivation levels suggested by CT values and are only gross estimates. The purpose of this graph is merely to indicate that very high theoretical levels of virus inactivation were being achieved in many ICR surface water plants (those using only Cl_2 and maintaining a Cl_2 residual with substantial contact time). Figure 15.12B shows that about 12% of the plants achieved less than 2-log inactivation of viruses for 1 or more months during the last 12 months of ICR monitoring. USEPA's guidance manual for the SWTR recommends that filtration plants achieve at least 2-log inactivation of viruses to comply with the SWTR. The SWTR requires unfiltered water systems to achieve at least 4-log inactivation of viruses (USEPA 1991). In Chapter 18, Shaw, Regli, and Chen (2002) describe health risk implications as a function of virus concentrations in source water and virus inactivation achieved during treatment.

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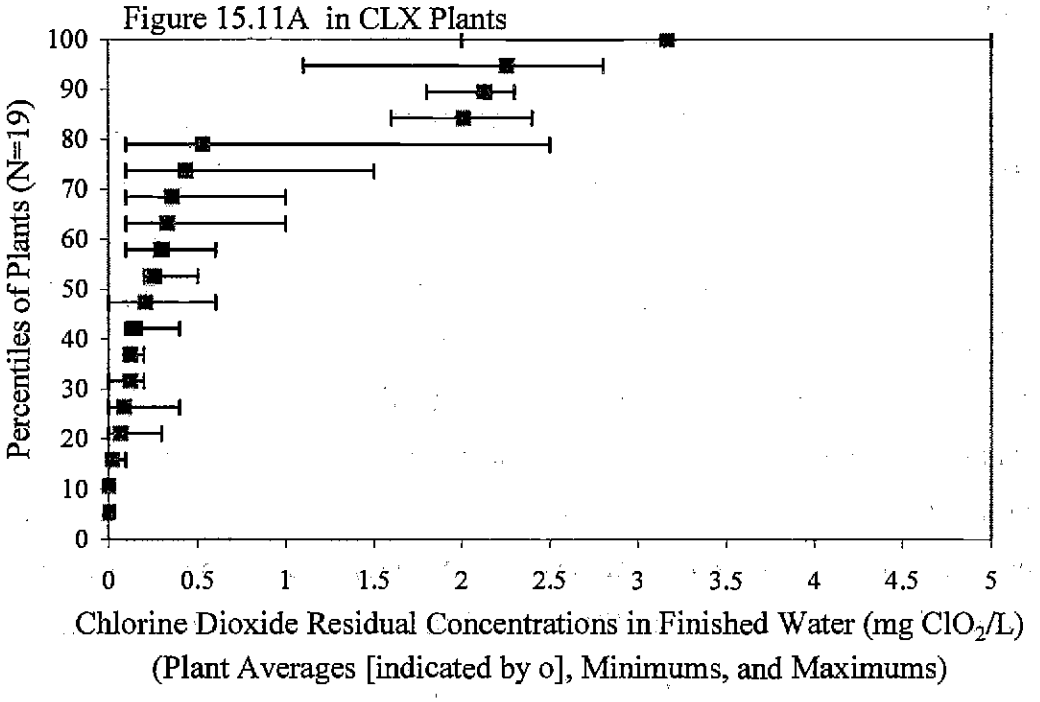

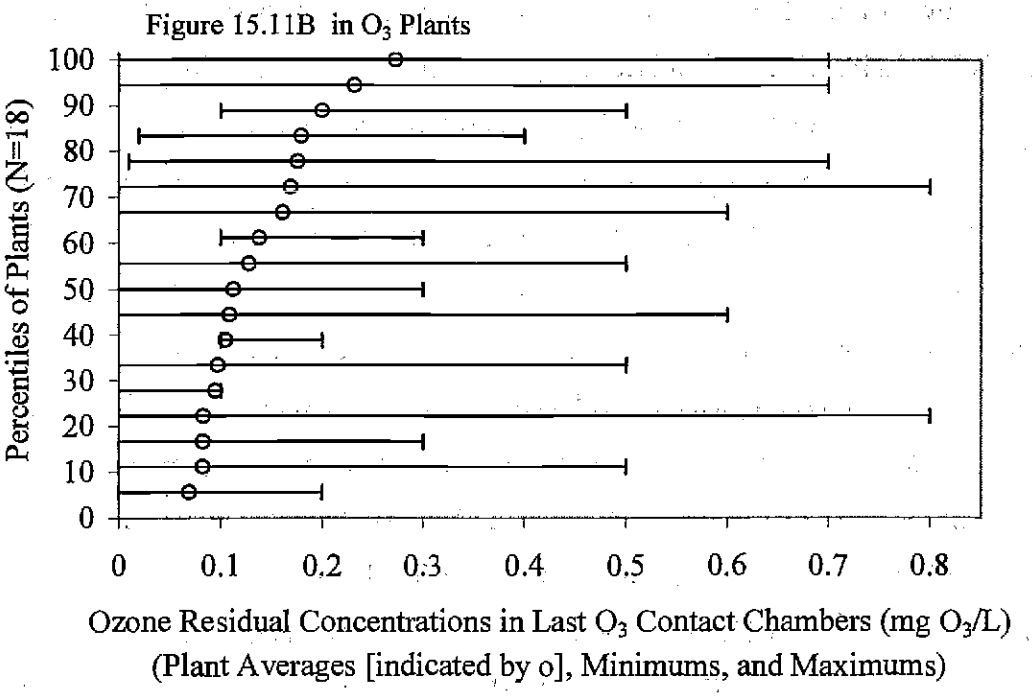

Figure 15.11 Chlorine dioxide and ozone residual concentrations in CLX and O3 plants (based on data collected during the last 12 months of ICR monitoring)

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Figure 15.12A Giardia Inactivation

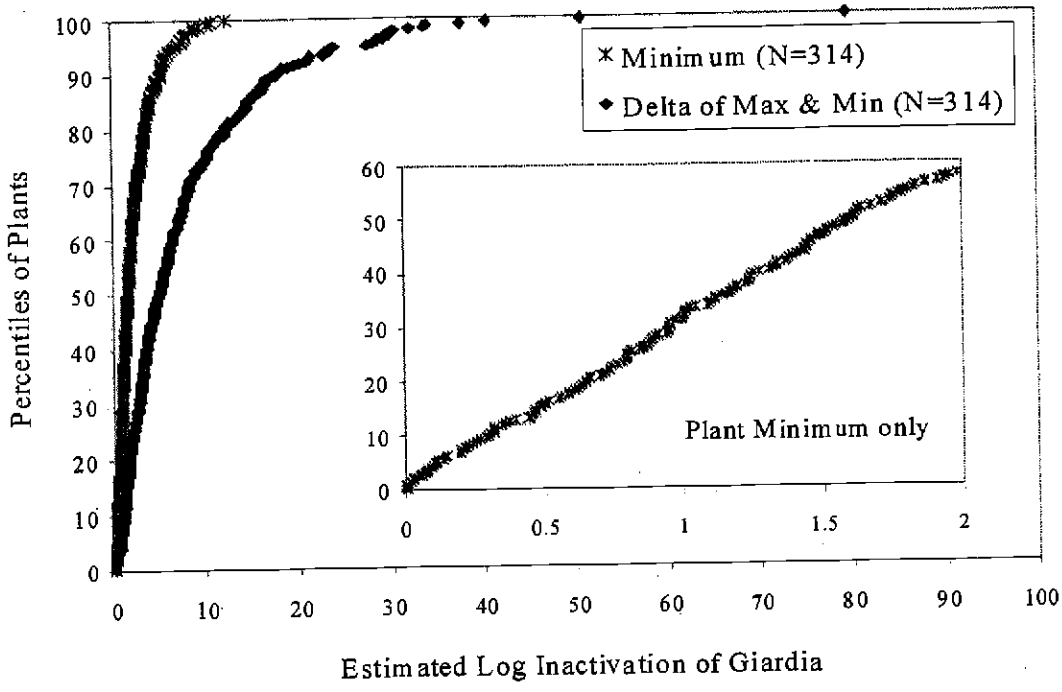

Figure 15.12B Virus Inactivation

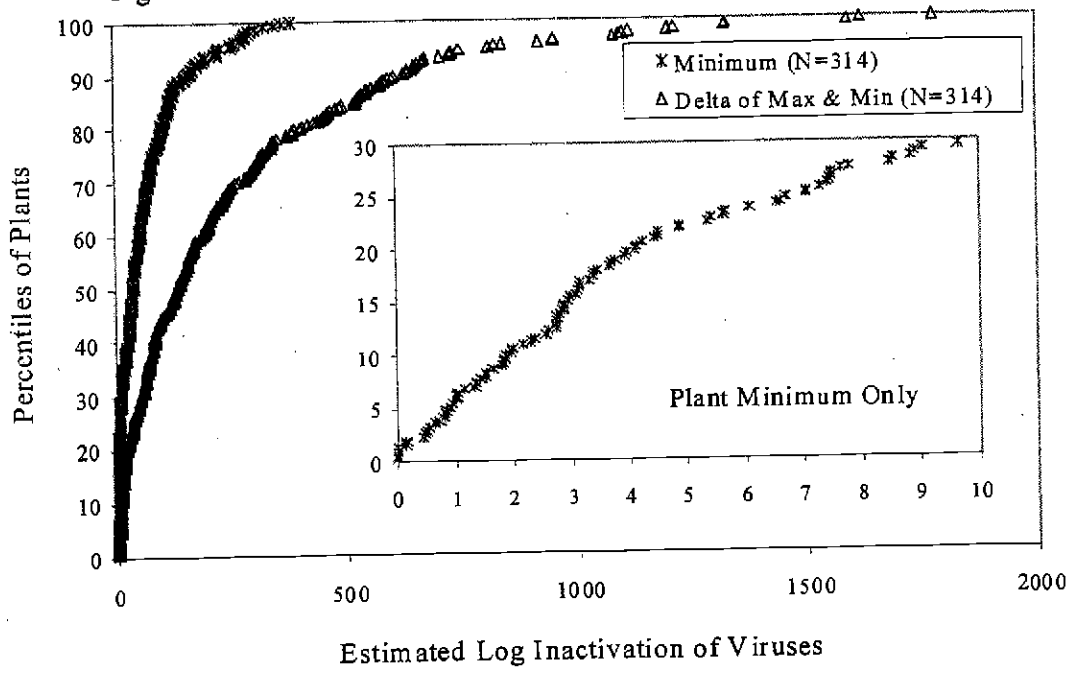

Figure 15.12 Estimated log inactivation of *Giardia* and viruses in surface water plants (based on the last 12 months of ICR monitoring)

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Figure 15.13 illustrates log inactivation as a function of ICR disinfectant type. Plants using only free chlorine generally achieved higher log inactivation of *Giardia* than plants using other types of disinfectants. There was little difference in *Giardia* log inactivation among plants classified as CL2_CLM, CLM, or O3. In contrast, Figure 15.13B shows significant differences in virus inactivation among plants using different disinfectant types. For instance, 3%, 16%, 22%, and 40% of plants classified as CL2, CL2_CLM, O3, and CLM, respectively, achieved a minimum virus inactivation of <2 logs. These percentages imply that surface water plants using O_3 or chloramines are more likely to be out of compliance with the 4-log virus inactivation requirement of the SWTR than plants using only Cl_2.

Figure 15.14 indicates that for conventional and softening plants, the distribution of *Giardia* log inactivation levels achieved by predisinfection (before filtration) and postdisinfection were similar. This finding suggests that pre- and postdisinfection played an equal role in *Giardia* inactivation in these plants during ICR implementation. Figure 15.14 also suggests that some plants might be able to move disinfection locations to achieve better control of DBPs and still maintain high levels of *Giardia* and virus inactivation.

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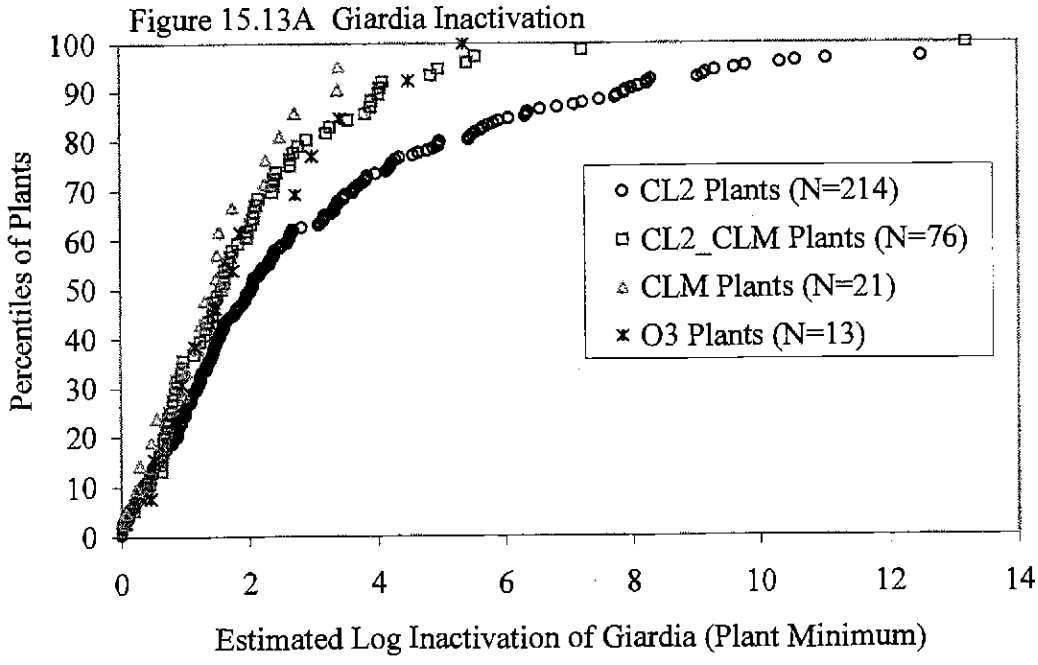

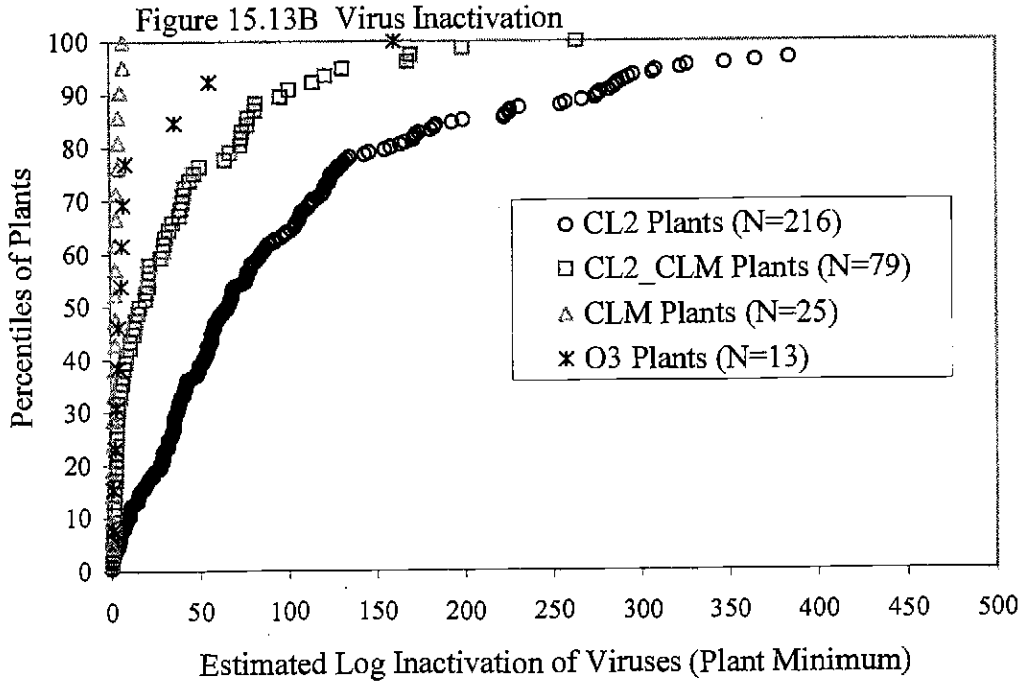

Figure 15.13 Log inactivation of Giardia and viruses as a function of type of disinfectant (based on data collected during the last 12 months of ICR monitoring)

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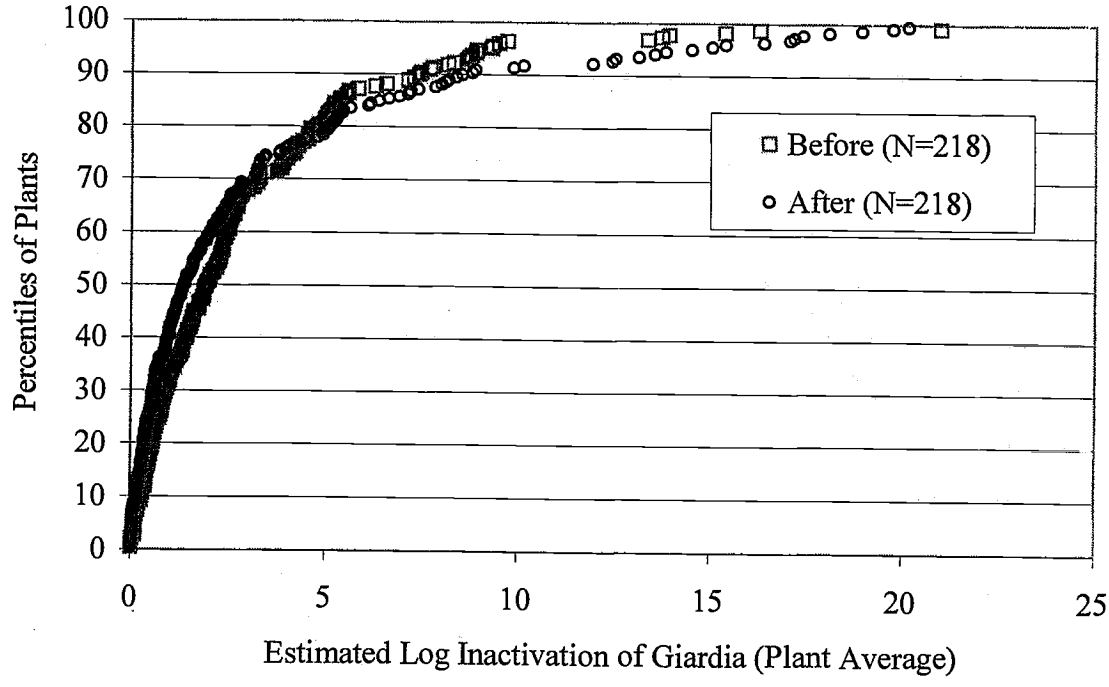

Figure 15.14 Log inactivation of Giardia before and after filtration in conventional and softening plants using chlorine, chloramines, or both (based on data collected during the last 12 months of ICR monitoring)

SUMMARY

ICR surface water plants that did not practice softening most commonly disinfected with free chlorine only. Most ICR softening plants used chloramines for at least one disinfection application. Though most conventional treatment plants used only free chlorine (57%), many used chloramines (37%) for at least one application within the treatment plant or in the distribution system. About 10% of ICR surface water plants used chlorine dioxide or ozone.

The type of disinfectant used appeared to be closely related to source water quality. Few plants used chlorine as the only disinfectant if source water TOC concentrations were high. Ozone was not used when average source water bromide concentrations exceeded 0.23 mg/L, whereas chlorine dioxide was used when bromide concentrations were as high as 1.0 mg/L.

Most conventional plants using only free chlorine had one or two disinfectant application points, generally at the rapid mix stage, just prior to filtration, or at the clearwell.

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Conventional and softening plants generally applied higher total chlorine dosages than other types of treatment plants. Conventional and softening plants also had higher concentrations of DBP precursors in their source water than other types of plants.

Plants using chloramines generally used higher disinfectant dosages than plants using only free chlorine. About half of the chloramine plants maintained chloramine dosages with a Cl_2:NH_3-N ratio greater than that required to reach the theoretical chlorination breakpoint.

Ten percent of plants using chlorine dioxide used average doses of >1.5 mg/L, and 42% of the plants exceeded the D/DBP Rule's residual limit of 0.8 mg ClO_2/L at least once during the ICR monitoring period. Perhaps more than a third of plants using chlorine dioxide will need to adjust treatment processes to comply with the MRDL specified in the D/DBP Rule.

Eighteen percent of the ICR surface water plants achieved <0.5-log inactivation of *Giardia*, and 12% achieved <2-log inactivation of viruses. A substantial number of plants (primarily those using chloramines) apparently did not consistently achieve the minimum inactivation levels recommended in USEPA's guidance manual for the SWTR. Depending on the pathogen removal credits given by states for physical treatment processes, some plants may not have been in compliance with SWTR requirements.

DISCLAIMER

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CHAPTER 16

USING *E. COLI* TO INDICATE SOURCE WATER SUSCEPTIBILITY TO HIGH CONCENTRATIONS OF *CRYPTOSPORIDIUM*

Misty L. Pope, Brian Ellis, Jeffrey S. Rosen, Kevin Connell, Jessica Pulz, Mark LeChevallier, Crystal Rodgers, Stig Regli, and Dan Schmelling

ABSTRACT

This chapter explores the use of *E. coli* as an indicator to identify drinking water sources that are susceptible to high concentrations of *Cryptosporidium*. Water treatment plants that use sources whose *E. coli* concentrations point to potentially high *Cryptosporidium* concentrations could then monitor for *Cryptosporidium*. The *E. coli* concentrations that were evaluated as indicators for high source water *Cryptosporidium* concentrations ranged from 5 *E. coli*/100 mL to 100 *E. coli*/100 mL. Water treatment plant data gathered under the Information Collection Rule (ICR) and its Supplemental Surveys (SS) were evaluated relative to two factors: (1) Did *E. coli* concentrations at the plant exceed the level that would trigger *Cryptosporidium* monitoring? and (2) Did the mean *Cryptosporidium* concentration at the plant exceed 0.075 oocysts/L (defined as the concentration of concern)? The sensitivity of the *E. coli* indicator (the percentage of plants that had high *Cryptosporidium* concentrations and also exceeded the *E. coli* trigger) was balanced with the number of plants that would be required to monitor for *Cryptosporidium*. The ICR and SS data sets show that a concentration of 10 *E. coli*/100 mL is the best trigger to identify reservoir/lake source water with high *Cryptosporidium* concentrations, whereas a concentration of 50 *E. coli* per 100 mL is the best trigger to identify flowing stream sources with high *Cryptosporidium* concentrations. These initial results must be verified with additional, larger *Cryptosporidium* and *E. coli* data sets.

BACKGROUND

During the Federal Advisory Committee's (FACA's) 1999 and 2000 discussions to help guide recommendations for the U.S. Environmental Protection Agency's (USEPA's) Long Term 2 Enhanced Surface Water Treatment Rule, the committee discussed the usefulness of *Cryptosporidium* monitoring in assessing a drinking water plant's vulnerability to high concentrations of this organism and whether alternatives to *Cryptosporidium* monitoring could yield the same assessment. A Technical Work Group (TWG) supported the FACA by providing technical support for evaluating data on the occurrence of microorganisms, including *Cryptosporidium, Giardia,* total coliforms, fecal coliforms, *E. coli,* and enteric viruses, as well as

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water quality parameters that are potentially related to the occurrence of these microbiological contaminants.

In an effort to target high-risk water systems, the FACA recommended that systems first monitor *Cryptosporidium* concentrations in their source water to determine the level of risk. Then, starting with a *Cryptosporidium* concentration of >0.075 oocysts/L, the FACA recommended requiring different levels of treatment on the basis of the risk found during monitoring. The FACA was concerned about the expense associated with *Cryptosporidium* monitoring, especially for small systems. Because no ideal indicator of the presence of *Cryptosporidium* was known, the TWG investigated the potential use of a screening parameter to assess a water source's vulnerability to high concentrations of *Cryptosporidium*. If such a parameter could be identified, small systems could first monitor for the screening parameter in lieu of monitoring for *Cryptosporidium*. Then, if concentrations of the screening parameter rose above a specified trigger level, the system would be required to monitor for *Cryptosporidium*. With this procedure, only high-risk small systems would incur the costs of *Cryptosporidium* monitoring. The screening parameter was not intended to demonstrate a strong correlation between *Cryptosporidium* occurrence and the indicator in specific samples but rather to identify watersheds that might have high concentrations of *Cryptosporidium*. An ideal screening parameter would be easy and inexpensive to analyze; it would produce unambiguous results; and it would have a long historical record that could be applied retroactively at many locations. This chapter presents results on the use of *E. coli* as a screening parameter to identify higher risk systems that should monitor for *Cryptosporidium*.

METHODOLOGY

Information Collection Rule and Supplemental Survey Data Sets

The use of *E. coli* as a screening parameter for *Cryptosporidium* occurrence was evaluated using two data sets—data gathered under the Information Collection Rule (ICR) and data from the ICR Supplemental Surveys (SS). During ICR monitoring, samples were collected once a month for 18 months (starting in July 1997 and ending in December 1998), resulting in 18 samples per plant. Samples were collected from approximately 350 large drinking water plants

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(each serving more than 100,000 people) and analyzed for a variety of water quality parameters and microbiological constituents. An immunofluorescence assay (IFA) was used to enumerate *Cryptosporidium* during the ICR (USEPA 1996).

During the SS, samples were collected twice a month for 12 months, resulting in 24 samples per plant. These samples were collected from a stratified random sample of 40 large ICR plants (each serving more than 100,000 people), the seven largest plants in the nation ("certainty" plants), a stratified random sample of 40 medium-size plants (serving 10,000 to 100,000 people), and a stratified random sample of 40 small plants (serving fewer than 10,000 people). Large and medium-size plants began collecting samples under the SS in March 1999 and continued through February 2000. During the SS, Methods 1622 (USEPA 1999a) and 1623 (USEPA 1999b) were used to analyze data on *Cryptosporidium* occurrence. Because small treatment plants did not analyze samples for *Cryptosporidium*, data from small plants were not used in developing the screening tool. Data from the seven certainty plants were also excluded from the screening tool analysis because they were not randomly selected. Messner and Wolpert (2002) discuss differences in protozoan analytical methods and results from the ICR and SS.

Nondetect Data for Protozoa

When nondetect *Cryptosporidium* results were reported in the ICR or SS databases, a value of zero oocysts/L was used. This procedure was recommended by a panel of expert statisticians assembled by USEPA in November 1998 to address this and other statistical issues associated with analyzing the ICR data (USEPA 1999c).

Censored Coliform Data

Detection limits for coliform data collected during ICR or SS sampling were based on the method of analysis and the volume of sample analyzed. The following approach to censored *E. coli* data ("greater than" or "less than" results) was applied to *E. coli* data:

Low censored data

- Results below the detection limit were replaced with zero if the detection limit was ≤10 (for example, a value of <9 *E. coli*/100 mL would be replaced by zero).

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- Results below the detection limit were not used if the detection limit was >10 (for example, a value of <100 *E. coli*/100 mL would not be used).

High censored data

- High censored results were replaced by the censor limit if the limit was >500 (for example, >1600 *E. coli*/100 mL would be replaced by 1600 *E. coli*/100 mL).
- High censored results were not used if the censor limit was ≤500 (for example, >350 *E. coli*/100 mL would not be used).

Treatment Plant Summary Data

Several approaches were considered for evaluating summary data for treatment plants, including a maximum rolling annual average, a maximum rolling six-month average, a plant maximum, and a simple mean. It was determined that plant data should not be summarized using plant maximum values because of concerns that a utility might be incorrectly classified as a result of an analytical error in a single sample. A maximum rolling average for a period of less than a year was not used in an effort to ensure that results were not affected by seasonal trends. Concern about seasonal effects also ruled out the simple mean approach for evaluating ICR *Cryptosporidium* concentrations.

For data on ICR plants, *Cryptosporidium* concentrations were summarized as maximum rolling annual averages and *E. coli* concentrations were summarized as simple means. The *Cryptosporidium* maximum rolling annual averages were calculated for each plant as follows: Step 1—the average value of 12 monthly samples was calculated for each of the seven 12-month periods within the 18-month ICR monitoring period; Step 2—the maximum value of the seven 12-month periods was considered the maximum rolling annual average. The analysis considered only plants that had at least nine *Cryptosporidium* records and nine *E. coli* records.

Because all SS samples were collected within a single year, simple plant means were calculated for SS plants. A minimum of six *E. coli* results was required.

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Source Water Designations

As the indicator system was being developed, it became apparent that plants would have to be evaluated on the basis of source water type because of a significantly different relationship between *E. coli* and *Cryptosporidium* in systems using reservoir/lake sources compared with systems using flowing stream sources. *E. coli* concentrations in reservoir/lake sources are much lower than those in flowing stream sources ($p = 0.0001$ for both the ICR and SS data sets). In the ICR data, the mean *E. coli* value was 411/100 mL for flowing streams and 184/100 mL for reservoir/lake sources. The SS data showed a similar trend of greater mean *E. coli* values in flowing streams than in reservoir/lake sources, with a mean *E. coli* value of 278/100 mL in flowing streams and 14/100 mL in reservoir/lake sources. In the ICR data, the median *E. coli* value was 119/100 mL for flowing streams and 3/100 mL for reservoir/lake sources. The SS data showed a similar trend of greater median *E. coli* values in flowing streams than in reservoir/lake sources, with a median *E. coli* value of 83/100 mL in flowing streams and 4/100 mL in reservoir/lake sources (Table 16.1).

Source water categories in the ICR database were somewhat ambiguous because of the use of multiple water sources and the complexity involved in defining the categories. Only samples that could be clearly associated with a single source water category were used in these analyses. In the SS database, each plant's source water type was designated as "flowing stream," "reservoir/lake" or "both." Plants using both flowing stream and reservoir/lake sources were not included in the screening parameter analysis.

Table 16.1

E. coli concentrations in systems using reservoir/lake sources versus systems using flowing stream sources

Type of source water	Mean number of *E. coli* per 100 mL	Median number of *E. coli* per 100 mL
ICR reservoir/lake	184	3
ICR flowing stream	411	119
SS reservoir/lake	14	4
SS flowing stream	278	83

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RESULTS

Several Parameters Evaluated as Possible Screening Tools

ICR and SS data were evaluated to determine parameters that could be used to assess a water source's susceptibility to *Cryptosporidium* occurrence. Initially, concentrations of fecal coliforms, total coliforms, *E. coli,* viruses, and turbidity were compared with concentrations of total *Cryptosporidium* oocysts and oocysts with internal structures. Although preliminary analyses indicated that total coliform, fecal coliform, and *E. coli* might be useful screening tools, analyses placed greater emphasis on *E. coli* and fecal coliforms because of the direct relationship between these parameters and fecal contamination. *E. coli* provided better performance as a *Cryptosporidium* indicator than fecal coliform. Although turbidity was considered in an effort to enhance the *E. coli* screening tool, turbidity did not improve the screening tool's accuracy.

Trigger Level Determined

Once *E. coli* was chosen as the screening parameter, an analysis was conducted to determine the specific *E. coli* concentration that should trigger *Cryptosporidium* monitoring. Potential trigger values ranging from 5 *E. coli*/100 mL to 100 *E. coli*/100 mL were evaluated. Assessing the efficacy of an *E. coli* concentration as a trigger for *Cryptosporidium* monitoring involved evaluating each water treatment plant in the data set relative to two factors: (1) Did the plant's *E. coli* concentration exceed the level that would trigger *Cryptosporidium* monitoring? and (2) Did the mean *Cryptosporidium* concentration at the plant exceed 0.075 oocysts/L (defined by FACA as the level of concern)? Accordingly, plants were sorted into four categories on the basis of their *Cryptosporidium* and *E. coli* concentrations:

- Plants with high *Cryptosporidium* concentrations (>0.075 oocysts/L) that exceeded the indicator trigger level (Table 16.2, category D);
- Plants with high *Cryptosporidium* concentrations (>0.075 oocysts/L) that did not exceed the indicator trigger level (Table 16.2, category C);
- Plants with low *Cryptosporidium* concentrations (<0.075 oocysts/L) that exceeded the indicator trigger level (Table 16.2, category B); and

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- Plants with low *Cryptosporidium* concentrations (<0.075 oocysts/L) that did not exceed the indicator trigger level (Table 16.2, category A).

Performance of Screening Parameter Assessed

The usefulness of the *E. coli* trigger level was evaluated on the basis on the following parameters, each of which is described in Table 16.2:

- False positives,
- False negatives,
- Plants protectively classified,
- Plants incorrectly classified,
- Plants saved from *Cryptosporidium* monitoring,
- Sensitivity,
- Specificity, and
- Plants required to monitor for *Cryptosporidium.*

The efficacy of a particular *E. coli* concentration as a trigger for *Cryptosporidium* monitoring was evaluated on the basis of sensitivity and the percentage of plants that would be required to monitor. Sensitivity was defined as the percentage of plants with high *Cryptosporidium* concentrations (>0.075 oocysts/L) that would appropriately be required to monitor on the basis of a specific *E. coli* trigger value. Sensitivity was considered critical because it characterizes the ability of the indicator to identify those plants that have high levels of pathogen contamination and should monitor for *Cryptosporidium*. Although lowering the *E. coli* trigger value would achieve greater sensitivity, this approach would cause more plants with low *Cryptosporidium* concentrations in their source water to exceed the trigger level and to incur unnecessary *Cryptosporidium* monitoring costs. Consequently, identifying an appropriate *E. coli* concentration to trigger monitoring requires balancing sensitivity with the number of plants that would be required to monitor.

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Table 16.2

Calculations considered in assessing indicator performance

Breakdown of plants into *Cryptosporidium* bin	Breakdown of plants using *E. coli* to trigger monitoring	
	Did not exceed *E. coli* trigger value	Exceeded *E. coli* trigger value
Low concentrations	A	B
High concentrations	C	D

	Description of calculation	Calculations used to assess indicator performance
1.	If a plant exceeds the *E. coli* trigger, what is the chance that the plant has a low *Cryptosporidium* concentration? (False positive)	B/(B+D)
2.	If a plant does not exceed the *E. coli* trigger, what is the chance that the plant has a high *Cryptosporidium* concentration? (False negative)	C/(A+C)
3.	What percentage of plants with high *Cryptosporidium* concentrations would exceed the *E. coli* trigger? (Sensitivity of indicator)	D/(C+D)
4.	What percentage of plants with low *Cryptosporidium* concentrations would not exceed the *E. coli* trigger? (Specificity of indicator)	A/(A+B)
5.	What percentage of all plants would be protectively classified either by exceeding the *E. coli* trigger or by exhibiting low *Cryptosporidium* concentrations?	(A+B+D)/(A+B+C+D)
6.	What percentage of all plants would be incorrectly classified by exhibiting high *Cryptosporidium* concentrations but failing to exceed the *E. coli* trigger?	C/(A+B+C+D)
7.	What percentage of all plants would be correctly saved from monitoring (the number of plants in the low *Cryptosporidium* bin that did not exceed a trigger value divided by the sum of all plants)?	A/(A+B+C+D)
8.	What percentage of plants would be required to monitor?	(B+D)/(A+B+C+D)

Trigger Concentrations for Reservoir/Lake Sources

Results of the analysis to determine an *E. coli* trigger for plants using reservoir/lake sources are shown in Table 16.3 and Figures 16.1 and 16.2. With both the ICR and SS data sets, *E. coli* trigger values of 50/100 mL and 100/100 mL showed unacceptably low sensitivity. With the ICR data, an *E. coli* concentration of 10/100 mL resulted in a sensitivity of 80% and would require 28% of plants to monitor for *Cryptosporidium*. A lower *E. coli* concentration, such as

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5/100 mL, increased the sensitivity to 90%, but the number of plants required to monitor increased to 43%. A greater difference in the sensitivity of potential trigger values was observed with the SS data set—sensitivities increased from 33% to 67% when *E. coli* concentrations of 10/100 mL and 5/100 mL, respectively, were used. Based on the SS data, the percentage of plants required to monitor increased from 21% to 45% when *E. coli* concentrations of 10/100 mL and 5/100 mL, respectively, were used. Although an *E. coli* trigger value of 5/100 mL would be more conservative for identifying water sources with high concentrations of *Cryptosporidium,* it would increase the number of reservoir/lake plants required to monitor for *Cryptosporidium* from approximately one quarter to one half. Thus, a trigger value of 10 *E. coli*/100 mL for plants using reservoir/lake sources balances sensitivity with the number of plants required to monitor.

Trigger Concentrations for Flowing Stream Sources

Results of the analysis to determine an *E. coli* trigger for plants using flowing stream sources are shown in Table 16.4 and Figures 16.3 and 16.4. *E. coli* trigger values of 5/100 mL, 10/100 mL, and 50/100 mL produced 100% sensitivity in both data sets. This means that in these data sets, all plants whose mean *Cryptosporidium* concentrations exceeded 0.075 oocysts/L also exceeded the 50/100-mL *E. coli* trigger value. However, these trigger values are not highly specific in targeting only plants with high *Cryptosporidium* concentrations. The data indicate that 73% of all ICR plants and 62% of all SS plants had mean *E. coli* concentrations exceeding 50/100 mL, even though only 36% and 19% of the ICR and SS plants, respectively, had mean *Cryptosporidium* concentrations exceeding 0.075 oocysts/L. At a higher *E. coli* trigger value, such as 100/100 mL, the sensitivity of the indicator dropped (to 50% with the SS data set), and the percentage of plants exceeding the trigger value was still relatively high (59% and 30% of ICR and SS plants, respectively). Thus, a high percentage of plants would be required to monitor for *Cryptosporidium* with *E. coli* trigger values of either 50/100 mL or 100/100 mL. However, to minimize false-negative results, a trigger concentration of 50 *E. coli*/100 mL is optimal for plants using flowing stream sources.

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Table 16.3

Use of various *E. coli* trigger values to indicate the need for *Cryptosporidium* monitoring at plants using reservoir/lake sources*

	E. coli trigger value															
	5/100 mL				10/100 mL				50/100 mL				100/100 mL			
	ICR		SS		ICR		SS		ICR		SS		ICR		SS	
Did plant exceed *E. coli* trigger value?	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes
Plants with ≤0.075 oocysts/L	70	44	17	13	87	27	24	6	107	7	28	2	108	6	29	1
Plants with >0.075 oocysts/L	1	9	1	2	2	8	2	1	8	2	3	0	9	1	3	0
What percentage of plants with high *Cryptosporidium* concentrations would exceed the *E. coli* trigger? (Sensitivity of indicator)	90%		67%		80%		33%		20%		0%		10%		0%	
What percentage of plants would be required to monitor for *Cryptosporidium*?	43%		45%		28%		21%		7%		6%		6%		3%	

* Based on ICR and SS data and using a *Cryptosporidium* concentration of 0.075 oocysts/L as the level of concern

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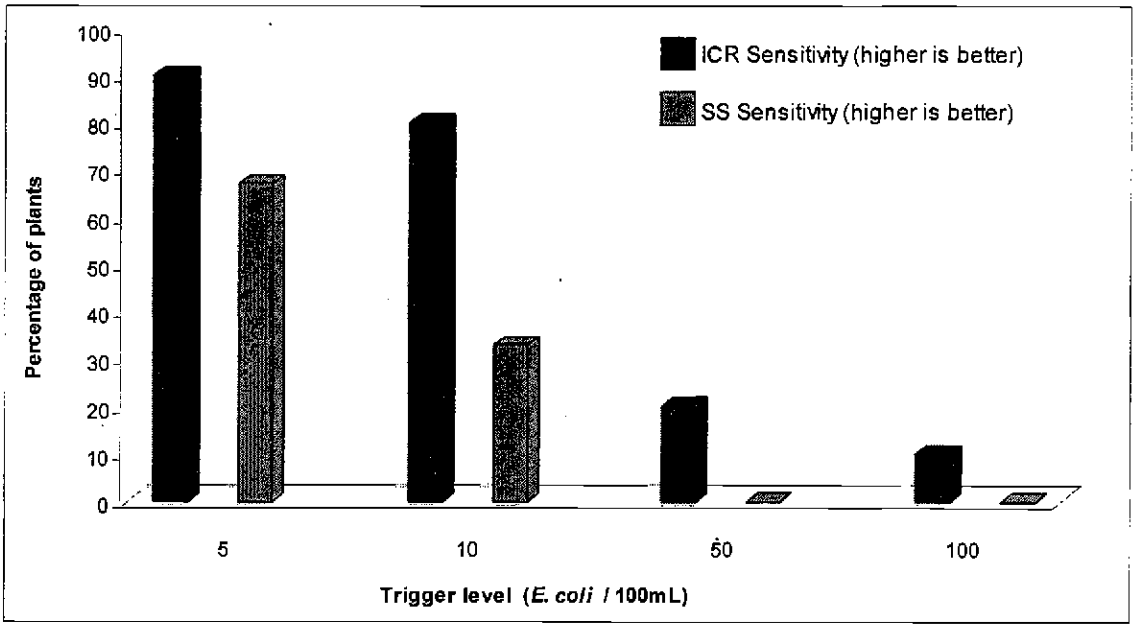

Figure 16.1. Effect of different *E. coli* trigger values on indicator sensitivity at a *Cryptosporidium* level of concern of 0.075 oocysts/L in reservoir/lake sources

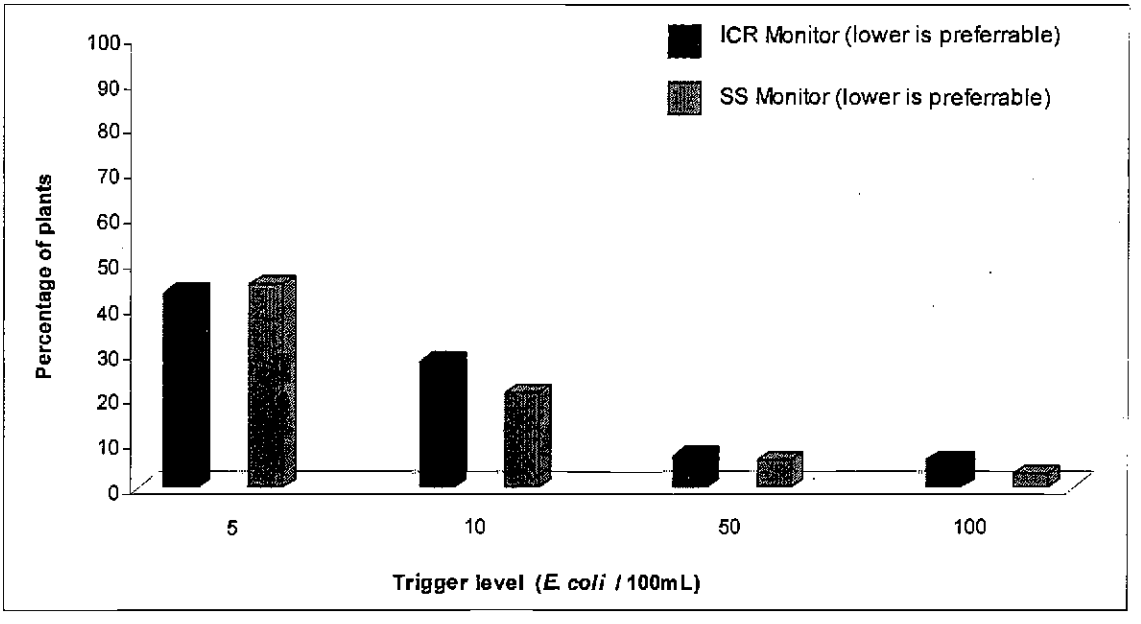

Figure 16.2. Effect of different *E. coli* trigger values on plant monitoring requirements at a *Cryptosporidium* level of concern of 0.075 oocysts/L in reservoir/lake sources

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Table 16.4

Use of various *E. coli* trigger values to indicate the need for *Cryptosporidium* monitoring at plants using flowing stream sources*

	E. coli trigger value															
	5/100 mL				10/100 mL				50/100 mL				100/100 mL			
	ICR		SS		ICR		SS		ICR		SS		ICR		SS	
Did plant exceed *E. coli* trigger value?	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes
Plants with ≤0.075 oocysts/L	6	36	2	15	7	35	5	12	18	24	8	9	24	18	11	6
Plants with >0.075 oocysts/L	0	24	0	4	0	24	0	4	0	24	0	4	3	21	2	2
What percentage of plants with high *Cryptosporidium* concentrations would exceed the *E. coli* trigger? (Sensitivity of indicator)	100%		100%		100%		100%		100%		100%		88%		50%	
What percentage of plants would be required to monitor for *Cryptosporidium*?	91%		90%		89%		76%		73%		62%		59%		38%	

* Based on ICR and SS data and using a *Cryptosporidium* concentration of 0.075 oocysts/L as the level of concern

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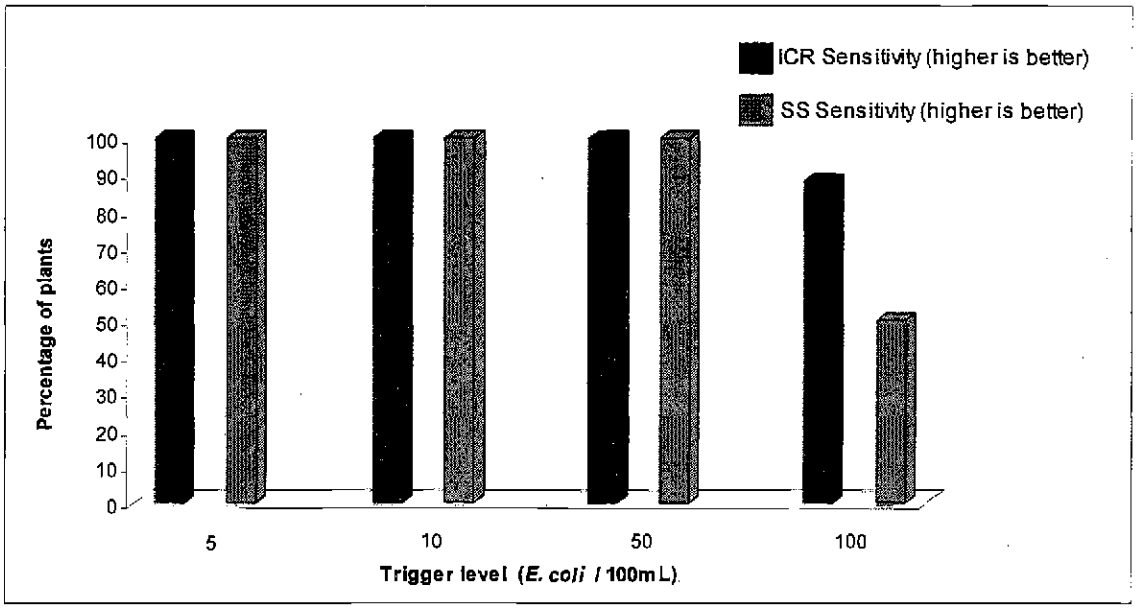

Figure 16.3. Effect of different *E. coli* trigger values on indicator sensitivity at a *Cryptosporidium* level of concern of 0.075 oocysts/L in flowing stream sources

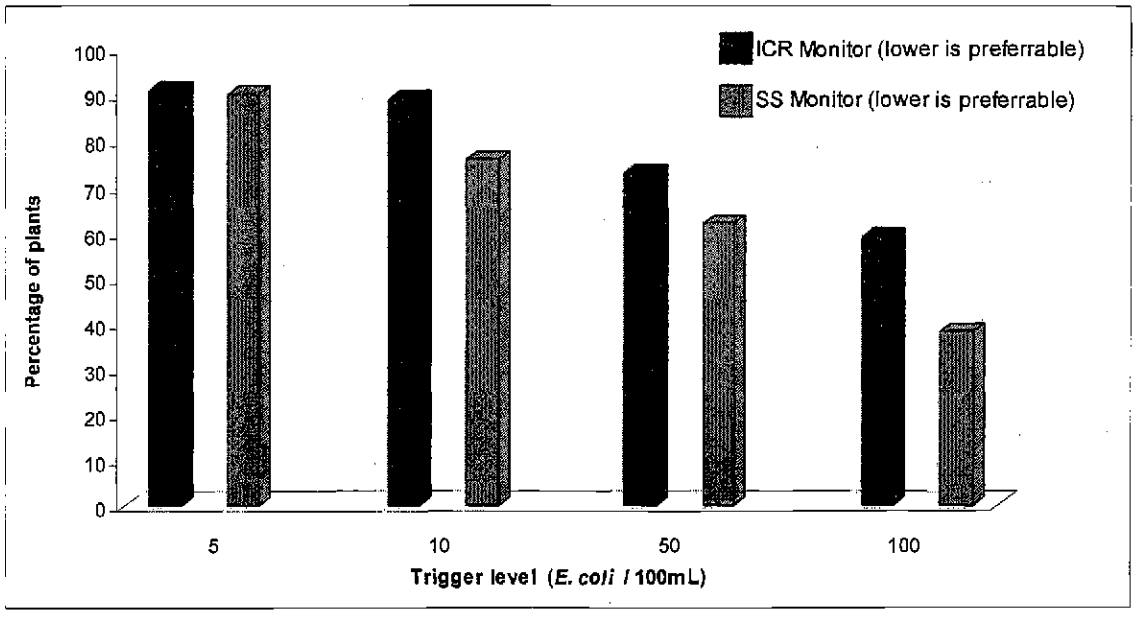

Figure 16.4. Effect of different *E. coli* trigger values on plant monitoring requirements at a *Cryptosporidium* level of concern of 0.075 oocysts/L in flowing stream sources

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Limitations and Differences in the ICR and SS Data Sets

The efficacy of *E. coli* as an indicator of source water susceptibility to high *Cryptosporidium* concentrations must be measured by the limitations and differences in the two data sets on which this analysis is based. These limitations and differences are discussed in the remainder of this section.

Sampling Frequency and Volume Analyzed

Both the ICR and SS data sets are limited in their ability to accurately characterize source water concentrations of *Cryptosporidium* oocysts and *E. coli.* Potential biases could be due to the infrequent sampling and the low sample volumes analyzed. *Cryptosporidium* oocysts occur in drinking water sources according to a Poisson distribution, resulting in infrequent detection, which is exacerbated by monthly sampling (under the ICR) or semimonthly sampling (in the SS) and analysis of average sample volumes of 10 L (in both studies) compared with watershed volumes of billions of gallons. Because of the relatively infrequent occurrence of oocysts in the environment and the small percentage of the watershed represented by each sample, the likelihood of oocysts being captured in the volume analyzed is low, even if oocysts are present in the water.

Number of Plants Represented

The SS included fewer plants than the ICR, and variations in this small data set were further magnified because flowing stream and reservoir/lake data were evaluated separately. In the reservoir/lake category, the ICR data set included 124 plants, and the SS included 33. In the flowing stream category, the ICR data set included 66 plants, and the SS included 21.

Analytical Methods

Although the analytical methods used in both studies were limited by imperfect recoveries and precision, Methods 1622 and 1623, used in the SS, were more accurate and precise than the IFA method used in the ICR. The ICR IFA method was characterized by 12% mean *Cryptosporidium* recoveries in 140 spiked source water samples, with a relative standard

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deviation (RSD) of 97% (Scheller et al. 2000). In contrast, Methods 1622 and 1623 were characterized by a mean *Cryptosporidium* recovery of 43% in 430 spiked source water samples, with an RSD of 47% (Connell et al. 2000).

Data Reporting

Protozoan measurements in the ICR data set were more prone to extrapolation errors than those in the SS data set. No sample volumes examined during the SS were less than 1 L, whereas 23% of the sample volumes examined during the ICR were less than 1 L. Moreover, SS sample volumes were reported to the nearest quarter of a liter, not rounded to the nearest whole liter, as in the ICR data set, and protozoan data from the SS were reported as the number of organisms counted per volume examined, instead of the number of organisms per 100 L, regardless of sample volume, reported in the ICR data set.

Likelihood of Cryptosporidium Detection

Cryptosporidium was detected in 79% of SS plants versus 44% of ICR plants. Moreover, when all the samples from each study were pooled, *Cryptosporidium* oocysts were detected in 14% of SS samples compared with 7% of ICR samples (USEPA 2000). This difference in detection rate was likely due to differences in the sample volumes examined in each study and differences in the sensitivities of the methods used. Under the SS, the mean and median sample volumes examined were 10 L, with a standard deviation of 1 L. Although the mean sample volume examined under the ICR also was 10 L, the standard deviation was 21 L, and the median was only 3 L. Methods 1622 and 1623 also may be more sensitive to low concentrations of *Cryptosporidium* oocysts than the IFA method used in the ICR. When challenged with spike concentrations of 50 to 100 oocysts/L, the ICR method exhibited a mean recovery of 12%; when challenged with lower spike concentrations of 8 to 20 oocysts/L, Methods 1622 and 1623 demonstrated a higher mean recovery of 43% (Scheller et al. 2000, Connell et al. 2000).

Potential False-Positive Results

Slides examined during the SS had less interfering debris than slides examined during the ICR because Methods 1622 and 1623 use an antibody-based immunomagnetic separation step to

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extract target organisms from the sample, and this step resulted in less background interference. The lower level of interference would likely reduce the possibility of false-positive results. Of all the *Cryptosporidium* oocysts identified in the two data sets, 38% of those reported in the ICR were empty compared with 16% of those reported in the SS. In addition, 37% of the oocysts reported in the SS had internal structures compared with 23% of those reported in the ICR. The ability to confirm presumptive oocysts by identifying internal structures increases confidence in the accuracy of these microscopic identifications.

CONCLUSIONS

A number of possible indicators of high *Cryptosporidium* occurrence were initially evaluated, including fecal coliforms, total coliforms, *E. coli,* viruses, and turbidity. *E. coli* provided the best performance as a *Cryptosporidium* indicator. Source water type affected the *E. coli* trigger level that best indicated high *Cryptosporidium* concentrations.

The sensitivity of the *E. coli* indicator (the percentage of plants that had high *Cryptosporidium* concentrations and also exceeded the *E. coli* trigger) was balanced with the number of plants that would be required to monitor for *Cryptosporidium*. The ICR and SS data sets show that 10 *E. coli*/100 mL is the best trigger to identify plants using reservoir/lake sources with high *Cryptosporidium* concentrations, whereas 50 *E. coli*/100 mL is the best trigger to identify plants using flowing stream sources with high *Cryptosporidium* concentrations.

Limitations of the ICR and SS data sets—including analytical methodology, limited *E. coli* data, variations in *E. coli* methods, number of plants represented, sample volumes analyzed, data reporting anomalies, and false-positive results—highlight the need for studies with additional, larger *Cryptosporidium* and *E. coli* data sets.

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CHAPTER 17

PROTOZOA OCCURRENCE IN THE SOURCE WATER OF FILTERED AND UNFILTERED ICR SYSTEMS: INFLUENCE OF HYDROLOGIC ATTRIBUTES AND WATERSHED PROTECTION PROGRAMS

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ABSTRACT

When the Surface Water Treatment Rule (SWTR) was promulgated in 1989, the U.S. Environmental Protection Agency recognized that some U.S. water supplies were of such high quality that the cost of filtering them could not be justified by the additional public health protection filtration might provide. Therefore, the SWTR allowed filtration waivers for public water systems that met certain conditions. These conditions included requirements for strict watershed control programs and source water quality criteria for coliforms and turbidity. This chapter compares Information Collection Rule data on *Giardia* and *Cryptosporidium* occurrence in the source water of filtered and unfiltered water systems to determine whether the source water protection requirements of the SWTR provided an effective barrier to pathogenic organisms. The first objective of this study was to determine if *Giardia* and *Cryptosporidium* concentrations and frequency of detection were substantially different in the source water of filtered and unfiltered systems. Comparisons of filtered and unfiltered systems were performed for each of the following source water categories: reservoir/lake, flowing stream, and all surface water types. A second objective of the study was to determine if the turbidity standard applied to unfiltered systems under the SWTR was a suitable surrogate for evaluating *Giardia* and *Cryptosporidium* penetration into source water supplies. To this end, correlation analyses were performed to evaluate the relationship between protozoan occurrence and source water turbidity in unfiltered plants.

The results of this analysis suggest that *Giardia* and *Cryptosporidium* occurrence and concentrations were strongly influenced by the hydrologic attributes of the source water system (e.g., reservoir/lake versus flowing stream) and the presence or absence of watershed control programs. Differences in *Giardia* and *Cryptosporidium* concentrations were most pronounced in relation to differences between reservoir/lake sources and flowing streams, regardless of whether the system was unfiltered or filtered. However, watershed control programs implemented by unfiltered systems appeared to prevent some source water contamination by *Cryptosporidium*, as evidenced by *Cryptosporidium* concentrations that were five to six times lower in ulfiltered systems than in filtered systems. *Giardia* concentrations in unfiltered systems were also lower than those in filtered systems when the upper range of the distribution was considered. There was no discernible association between protozoan concentrations and turbidity in any type of unfiltered source water. This lack of correlation suggests that the turbidity standard applied under the SWTR was not suitable for unfiltered systems that rely primarily on pristine water supplies and strict watershed protection programs to limit pathogen concentrations in finished water.

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INTRODUCTION

Recognizing that surface water supplies often contain high concentrations of fecal microorganisms originating from livestock wastes or septic systems, the U.S. Environmental Protection Agency (USEPA) promulgated the Surface Water Treatment Rule (SWTR) in June 1989 in an effort to prevent waterborne diseases caused by pathogens such as *Giardia lamblia.* Ingestion of *Giardia* is known to cause digestive problems such as diarrhea, cramps, and nausea. The SWTR requires surface water systems to filter and disinfect their water to provide a minimum of 99.9 percent combined removal and inactivation of *Giardia.* The adequacy of the filtration process is evaluated by measuring the turbidity of the treated water to determine if it meets USEPA's performance standard. The filtration performance standard under the SWTR requires the turbidity of combined filter effluent to be less than or equal to 0.5 nephelometric turbidity units (NTUs) in 95 percent of the measurements taken every month. In addition, the standard specifies that no measurement can exceed 5 NTU.

Some utilities with pristine water supplies, however, worked with USEPA to avoid the filtration requirement by asserting that the added cost of filtration was not always justified by the additional public health protection provided by filtration. As a result, the SWTR established conditions under which a utility may be granted a waiver from the filtration requirement. Included in these conditions was a requirement that unfiltered systems implement watershed control programs. SWTR guidelines for watershed control programs generally focus on minimizing the potential for source water contamination by *Giardia* and viruses. For example, watershed control programs must characterize watershed hydrology, land ownership, and activities that might have an adverse effect on source water quality and must minimize the potential for source water contamination by *Giardia lamblia* and viruses. The guidelines recommend that livestock grazing and sewage discharges not be permitted within the watershed of an unfiltered system but indicate that these activities may be permissible on a case-by-case basis when long detention times and high degrees of dilution occur between the point of activity and the water supply intake. The SWTR guidelines do not, however, require any specific watershed control practices.

In December 1998, USEPA promulgated the Interim Enhanced Surface Water Treatment Rule (IESWTR) with the goal of improving protection against pathogenic microorganisms. In

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particular, the IESWTR is aimed at reducing concentrations of *Cryptosporidium* in filtered drinking water supplies through strengthened turbidity performance standards and improved monitoring of filter performance. *Cryptosporidium*, when ingested, can cause cryptosporidiosis, which produces symptoms ranging from a mild stomach upset to life- threatening disease in people with severely compromised immune systems. For unfiltered systems, the IESWTR expands on the existing watershed control requirements of the SWTR to include control of *Cryptosporidium*. This component of the IESWTR was predicated on the assumption that unfiltered water systems in compliance with the source water requirements of the SWTR pose a cryptosporidiosis risk equivalent to that of a water system with a well-operated filter plant and a water source of average quality. (With promulgation of the Long Term 1 Enhanced Surface Treatment Rule in January 2002, unfiltered systems were required to update their watershed control programs to minimize the potential for contamination by *Cryptosporidium* oocysts.)

Several studies have provided evidence that watershed characteristics and watershed protection practices can significantly influence surface water concentrations of *Giardia* and *Cryptosporidium*. A study by LeChevallier, Norton, and Lee (1991) found progressive increases in *Giardia* concentrations in water supplies with decreasing watershed protection. Watershed protection in this study was defined in qualitative terms by categorizing data from source water with the following attributes: (1) protected watershed, (2) watershed with limited access, (3) recreational use, (4) agricultural use, (5) sewage discharges, (6) industrial–urban discharges. A less clear relationship between source water protection and oocyst concentrations was observed for *Cryptosporidium*. The authors hypothesized that watershed controls aimed at controlling point sources for pathogens (e.g., sewage effluent) would likely be effective at reducing *Giardia* concentrations. The same watershed controls, however, might be less effective in reducing *Cryptosporidium* concentrations if this pathogen was introduced into water supplies primarily through nonpoint sources. Hansen and Ongerth (1991) found that human and domestic animal activity in a watershed increased *Cryptosporidium* oocyst concentrations in surface water by as much as 10–15 times over those associated with a controlled public water supply watershed. Furthermore, the authors concluded that management practices limiting human activity in public water supply watersheds may reduce oocyst concentrations as much as fivefold.

In 1997, USEPA implemented the Information Collection Rule (ICR) as part of a nationwide research project to support development of national drinking water standards.

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Giardia and *Cryptosporidium* concentrations in source water were among the data collected through this monitoring effort.

OBJECTIVES

The study described in this chapter compared ICR data on *Giardia* and *Cryptosporidium* occurrence in the source water of filtered and unfiltered surface water treatment plants to determine whether the source water protection requirements of the SWTR provided an effective barrier to pathogenic organisms. A survey was conducted to characterize watershed protection practices at six of the largest unfiltered water systems in the United States. ICR data were analyzed to determine if source water *Giardia* and *Cryptosporidium* concentrations and detection frequencies were significantly different in these unfiltered systems relative to filtered systems. Separate comparisons of unfiltered and filtered systems were performed for each of the following source water categories: flowing stream, reservoir/lake, and all surface water types.

A second objective of this study was to determine if source water turbidity was a suitable surrogate for evaluating source water concentrations of *Giardia* and *Cryptosporidium* in unfiltered plants. Although SWTR turbidity requirements are an appropriate indicator of water treatment performance in filtered systems, they may not be relevant for unfiltered systems, which rely primarily on pristine water supplies and strict watershed protection programs to limit pathogen concentrations in finished water. Analyses were performed to evaluate the relationship between source water turbidity and *Giardia* and *Cryptosporidium* concentrations and detection frequencies in unfiltered plants.

APPROACH

Control Group of Unfiltered Systems

To facilitate comparisons of the source water characteristics of filtered and unfiltered systems, six large unfiltered water systems in the United States were selected to represent unfiltered systems as a whole. These six utilities had previously been organized into a workgroup

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that collectively addressed issues relating to the implementation of future surface water treatment regulations. Participating utilities included:

- Massachusetts Water Resources Authority (MWRA), Massachusetts,
- New York Department of Environmental Protection (NYDEP), New York,
- Portland Water Bureau (PWB), Oregon,
- Seattle Public Utilities (SPU), Washington,
- San Francisco Public Utilities Commission (SFPUC), California, and
- Tacoma Public Utilities (TPU), Washington.

Because two of these utilities (SPU and NYDEP) obtain water from multiple sources, a total of nine source water supplies were evaluated in this study. Seven of these were classified as reservoirs or lakes, and two were classified as rivers. Smaller unfiltered systems that were included in the ICR database but were not participants in the workgroup were excluded from this analysis because detailed information relating to their watershed protection programs was not readily available. Therefore, this study's conclusions regarding the benefits of watershed protection programs are generalized for larger utilities and may not necessarily apply to smaller unfiltered systems. For the most part, watershed protection practices employed by unfiltered systems have served to maintain the a-priori pristine nature of their source water. This study does not explicitly examine the potential benefits of these watershed protection practices when applied to nonpristine sources. Thus, in a broader sense, this study could also be construed to be an examination of protozoan occurrence in pristine sources relative to less pristine sources associated with unfiltered systems.

A survey questionnaire, distributed to representatives from each of the six utilities, requested specific information on the type and extent of their watershed protection practices. After compilation, these data provided a qualitative assessment of watershed protection practices used by unfiltered utilities. Subsequent comparisons of data on *Giardia* and *Cryptosporidium* concentrations in unfiltered and filtered systems were based on the assumption that the filtered systems in the ICR data set had not implemented similar watershed protection practices because of the lack of a regulatory requirement.

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Data Collection

Monthly ICR samples were collected from July 1997 to December 1998 by treatment plants associated with public water utilities serving at least 100,000 people. Data on *Giardia* and *Cryptosporidium* concentrations in source water were collected from treatment plants that use surface water (e.g., lakes or rivers) or groundwater under the direct influence of surface water. Additional water quality data (e.g., turbidity, alkalinity, hardness, pH) were collected concurrently with the data on pathogen concentrations. *Giardia* and *Cryptosporidium* concentrations were determined by a fluorescent antibody procedure. Sampling and testing for protozoa and water quality parameters were conducted in accordance with established protocols for the ICR (APHA, AWWA, and WEF 1995; USEPA 1995, 1996a, 1996b). USEPA compiled data from the ICR sampling program into a Microsoft Access™ database called ICR Auxiliary Database 1 (AUX1) to facilitate retrieval and analysis of the data. ICR implementation and database development are discussed in Chapter 1 (Wysock et al. 2002).

Data Handling and Analyses

Queries were executed to extract *Giardia*, *Cryptosporidium*, and turbidity data from AUX1 for water systems in two categories: (1) unfiltered systems in the control group, and (2) filtered systems using surface water as their source of supply (this category includes systems that mix surface water and groundwater supplies). Each category was further subdivided into surface water classifications of reservoir/lake or flowing stream. These data were then exported to Excel™ spreadsheets (Microsoft®, Redmond, Wash.) and the STATISTICA™ statistics/graphics software package (StatSoft Inc.®, Tulsa, Okla.) so that tabular and graphic data summaries could be generated and statistical analyses could be performed. For all data analyses, nondetectable concentrations of *Giardia* and *Cryptosporidium* were assigned a value of zero. Geometric means for *Giardia* and *Cryptosporidium* concentrations were calculated by using a value of +1 in place of zeros and then subtracting 1 from the calculated mean.

Associations between *Giardia* and *Cryptosporidium* concentrations and turbidity were investigated using Spearman's rank correlation coefficients. Use of the Spearman's rank correlation coefficient provided a measure of the monotonic association between protozoa

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concentrations and turbidity. Because this test is performed on the ranks of the data, the Spearman's rank correlation coefficient does not require the data to meet the assumption of normality. The significance of correlation coefficients was tested using a significance level of 0.05.

RESULTS AND DISCUSSION

Watershed Protection Practices in Unfiltered Systems

Table 17.1 provides a brief summary of watershed protection practices used by each utility in the control group of unfiltered systems. Based on information from the questionnaire distributed to these utilities, watershed protection practices were generally focused on reducing potential sources of pathogens in the watershed. For the most part, this goal was accomplished through strict limitations on all human activities that potentially contribute to source water contamination. In some cases, these restrictions were imposed through direct ownership and control of watershed land by the utilities. For example, SPU owns a large percentage of the watersheds of the two river systems it uses as source water. Both watersheds are closed to public access and are actively patrolled to detect and eliminate any potential threats to water quality. Most of the unfiltered systems were engaged in efforts to increase their ownership of land in their watersheds to attain direct control over activities that may influence water quality.

Restrictions on privately held watershed lands are also imposed by all these utilities through government regulations or cooperative agreements with landowners. For example, the Massachusetts Watershed Protection Act of 1992 limits certain activities in hydrologically sensitive areas of MWRA's watersheds to prevent water quality degradation. A 1997 Memorandum of Agreement between New York City and upstate watershed communities imposes numerous restrictions on land use, including: siting constraints on wastewater treatment plants, wastewater treatment plant technology requirements, and controls on stormwater, impervious surfaces, and hazardous substances and wastes. Because PWB's source water originates from a watershed within a national forest, federal legislation (the Bull Run Act, P.L. 95-200, 1997) requiring the U.S. Forest Service to develop and comply with ambient water quality standards was established to maintain high-quality source water for the city of Portland.

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Additional U.S. Forest Service regulations prohibit public access to the watershed from which PWB obtains source water. SFPUC and TPU have adopted cooperative written agreements that limit activities within their respective watersheds. Water quality benefits stemming from these land-use restrictions are generally complemented by the extensive use of best management practices such as buffer zones, erosion control measures, and diversion structures aimed at controlling adverse water quality effects from specific land uses (e.g., timber harvesting and road maintenance).

In addition to controlling human activities that contribute to source water degradation, most of the unfiltered systems included in the survey had taken actions to identify nuisance animals that might contribute to increased pathogen concentrations in the water supply. These actions included DNA typing (NYDEP and SPU) and wildlife and animal inventory programs (MWRA, PWB, and SFPUC). MWRA had also conducted water quality modeling and bacteria decay studies to assess the fate and transport of pathogens originating from bird feces. Measures implemented to reduce potential contamination from animal sources included direct animal trapping and removal and habitat modification designed to discourage animal use in a particular area. For example, MWRA had implemented an aggressive daily bird control program since 1991 to move gulls and other birds away from reservoir intakes. MWRA had also used landscaping modifications to discourage nesting geese and had established "no beaver zones" near reservoir intakes where animals were trapped and removed. NYDEP had implemented a waterfowl management program since 1993 to discourage bird roosting near reservoirs. PWB used stream modifications to discourage beaver and trapped and removed beaver and muskrat from the reservoir watershed. SPU enhanced habitat in nonsensitive areas to lure problem wildlife away from critical watershed areas.

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Table 17.1

Summary of watershed protection practices used by unfiltered systems in the control group

Utility	Watershed lands owned by utility (%)	Restrictions on non–utility owned watershed lands (yes/no)	Point source discharges allowed in watershed (yes/no)	Nuisance animal control program in place (yes/no)	Source water monitoring program in place (yes/no)	Terrestrial monitoring program in place** (yes/no)
MWRA	39	yes	no	yes	yes	yes
NYDEP	6	yes	yes‡	yes	yes	no
PWB	4	yes	no	yes	yes	yes
SFPUC	5	yes	no§	yes	yes	no
SPU	99.9*; 29†	yes	no§	yes	yes	yes
TPU	9	yes	no	no	yes	no

* SPU's Tolt River watershed

† SPU's Cedar River watershed

‡ All new and existing wastewater treatment plants are required to provide sand filtration, disinfection, phosphorus removal, and microfiltration or an approved equivalent.

§ No direct discharges are allowed; however, potential discharges could occur as a result of failures of nondischarging sewage and wastewater facilities.

** Defined as a formal terrestrial monitoring program to determine or protect forest health

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Source water monitoring programs in reservoirs, tributary streams, and treatment system intakes were also a key component of the watershed protection programs of unfiltered systems. This monitoring was used to establish baseline source water quality and to track long term changes. For some unfiltered systems (e.g., MWRA, NYDEP, and PWB), anomalous results from source water monitoring programs automatically triggered additional investigation to determine the cause. MWRA, PWB, and SPU had also implemented terrestrial monitoring programs on watershed lands to promote healthy forest conditions and to monitor disease and insect infestations.

Distribution of *Giardia* and *Cryptosporidium* in Unfiltered and Filtered Systems

In general, *Giardia* and *Cryptosporidium* occurred with low to moderate frequency in water samples collected during the ICR study. ICR protozoan results are reviewed in Chapter 19 (Messner and Wolpert 2002). *Giardia* was detected in 42 and 19 percent of the samples from unfiltered and filtered surface water systems, respectively (Table 17.2). *Cryptosporidium* was detected in 6 and 7 percent of the samples from unfiltered and filtered surface water systems, respectively (Table 17.2). These results differ from those of several other investigations in which *Cryptosporidium* detection frequencies exceeded *Giardia* detection frequencies (Rose, Gerba, and Jakubowski 1991; LeChavallier, Norton, and Lee 1991). However, direct comparisons of *Giardia* and *Cryptosporidium* occurrence are difficult to interpret because of potential differences in recovery efficiencies for these pathogens. For example, field and laboratory spiking studies conducted by USEPA suggest that mean recoveries achieved by the ICR analytical method are 26 precent for *Giardia* and only 12 percent for *Cryptosporidium* (Messner 1999).

Comparisons between source water types indicated that hydrologic attributes of the source water system (reservoir/lake or flowing stream) influenced *Giardia* and *Cryptosporidium* occurrence. For example, the percentage of samples with detectable concentrations of *Giardia* and *Cryptosporidium* was roughly 1.5 to 3 times higher in flowing stream sources than in reservoir/lake sources, regardless of whether the system was unfiltered or filtered.

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Table 17.2

Summary statistics for *Giardia* and *Cryptosporidium* by unfiltered and filtered system source water type

Source water type*	Number of samples	Percent of positive samples	Median† (cyst/100 L)	Arithmetic mean† (cysts/100 L)	Geometric mean† (cysts/100 L)	25th Percentile† (cysts/100 L)	75th Percentile† (cysts/100 L)	90th Percentile† (cysts/100 L)	Maximum† (cysts/100 L)
Giardia									
Unfiltered SW	159	42	0.0	3.0	0.74	0.0	3.0	8.3	50
Unfiltered RL	124	36	0.0	1.2	0.4	0.0	1.0	3.8	15
Unfiltered FS	35	63	5.0	9.5	3.2	0.0	9.8	37	50
Filtered SW‡	5,246	19	0.0	28	1.1	0.0	0.0	53	2,521
Filtered RL	3,129	10	0.0	5.5	0.38	0.0	0.0	1.0	544
Filtered FS	1,942	32	0.0	65	3.3	0.0	34	196	2,521
Crytosporidium									
Unfiltered SW	159	6	0.0	0.18	0.044	0.0	0.0	0.0	8.0
Unfiltered RL	124	6	0.0	0.10	0.022	0.0	0.0	0.0	3.8
Unfiltered FS	35	9	0.0	0.48	0.13	0.0	0.0	0.0	8.0
Filtered SW‡	5,246	7	0.0	7.0	0.29	0.0	0.0	0.0	1,923
Filtered RL	3,129	4	0.0	2.5	0.13	0.0	0.0	0.0	1,923
Filtered FS	1,942	12	0.0	15	0.59	0.0	0.0	12	1,887

* SW = surface water system; RL = reservoir/lake system; FS = flowing stream system

† Unit of measure for *Cryptosporidium* is oocysts/100 L.

‡ Includes systems that mix surface water and groundwater supplies

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When unfiltered and filtered systems were compared within the reservoir/lake and flowing stream source water categories, the percentage of samples with detectable concentrations of *Giardia* was roughly twice as high for the unfiltered systems in both categories. Unfiltered and filtered systems had roughly the same percentage of samples that were positive for *Cryptosporidium* in both source water categories. Interpretation of these trends, however, is complicated by some inconsistencies in the ICR protozoan laboratory method as it was applied to unfiltered and filtered systems. In the laboratory method, cyst and oocyst counts from a small "assayed sample volume" are normalized to a concentration based on a 100-liter volume (Atherholt and Korn 1999, USEPA 1996a, 1996b). The protocol for the laboratories performing ICR analyses did not require a constant assayed sample volume. Review of ICR data indicated that the median assayed volume of samples from unfiltered surface water sources was 63 L, whereas the median assayed volume of samples from filtered surface water sources was only 3 L. The larger assayed volumes of samples from unfiltered systems would presumably increase the frequency of *Giardia* and *Cryptosporidium* detection because a larger fraction of the samples would have been microscopically analyzed for these pathogens.

Like the frequencies of *Giardia* and *Cryptosporidium* occurrence, differences in the central tendencies of pathogen concentrations were greatest in relation to differences between reservoir/lake and flowing stream source water types (Table 17.2). For example, geometric means for *Giardia* concentrations in reservoir/lake systems were approximately eight times lower than those for flowing stream systems, regardless of whether the system was unfiltered or filtered. Similarly, geometric means for *Cryptosporidium* concentrations in reservoir/lake systems were approximately five to six times lower than those for flowing stream systems. Substantial differences between *Cryptosporidium* concentrations in unfiltered and filtered systems were also apparent when separate comparisons were made within the reservoir/lake and flowing stream source water categories. For example, the geometric mean for *Cryptosporidium* concentrations in unfiltered reservoir/lake systems was roughly six times lower than the geometric mean for filtered reservoir/lake systems. Likewise, the geometric mean for *Cryptosporidium* concentrations in unfiltered flowing stream systems was approximately five times lower than the geometric mean for filtered flowing stream systems. Unlike the geometric means for *Cryptosporidium* concentrations, however, the geometric means for *Giardia*

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concentrations in unfiltered and filtered systems were very similar when separate comparisons were made within the reservoir/lake and flowing stream source water categories.

Differences between the two surface water categories were generally more pronounced when *Giardia* and *Cryptosporidium* concentrations were evaluated over the entire distribution of data. Cumulative frequency distribution plots of individual *Giardia* and *Cryptosporidium* sample concentrations by source water category (Figures 17.1 through 17.4) generally show the data to be positively skewed, as evidenced by the shallow slope of the distributions for each source water category. The y-intercepts of these plots, representing the percentage of samples with undetected concentrations of *Giardia* or *Cryptosporidium*, illustrate the generally low rates of detection of these pathogens in ICR samples. Concentrations of *Giardia* and *Cryptosporidium* in the tails of the distributions (e.g., the 90th to 95th percentiles) were generally much lower for unfiltered systems than for filtered systems. However, some of these differences may relate to differences in the size of the assayed sample volumes for unfiltered and filtered systems. For example, many of the high protozoa concentrations recorded in filtered water systems were based on extrapolations of low concentrations detected in very small assayed sample volumes. These extrapolations may artificially inflate the difference between filtered and unfiltered source water *Giardia* and *Cryptosporidium* concentrations.

Overall, *Giardia* and *Cryptosporidium* occurrence and concentrations were strongly influenced by the hydrologic attributes of the source water system and the presence or absence of watershed control programs. The reservoir/lake systems most likely exhibit lower pathogen concentrations because longer residence times in these systems allow particles associated with *Giardia* cysts and *Cryptosporidium* oocysts to settle out of the water column before it reaches the treatment plant intake. Turbulent water flow in river systems, however, keeps *Giardia* cysts and *Cryptosporidium* oocysts in suspension and, during periods of extremely high flow, may actually resuspend cysts and oocysts deposited on river bottoms or in storm drain sediments (Atherholt et al. 1998). In many cases, river systems may also receive direct discharges of sewage and other industrial effluents and may be more susceptible to contamination from nonpoint sources because they have a greater amount of exposed shoreline than reservoir/lake systems. These factors increase the likelihood that high concentrations of pathogens will be present in flowing stream sources.

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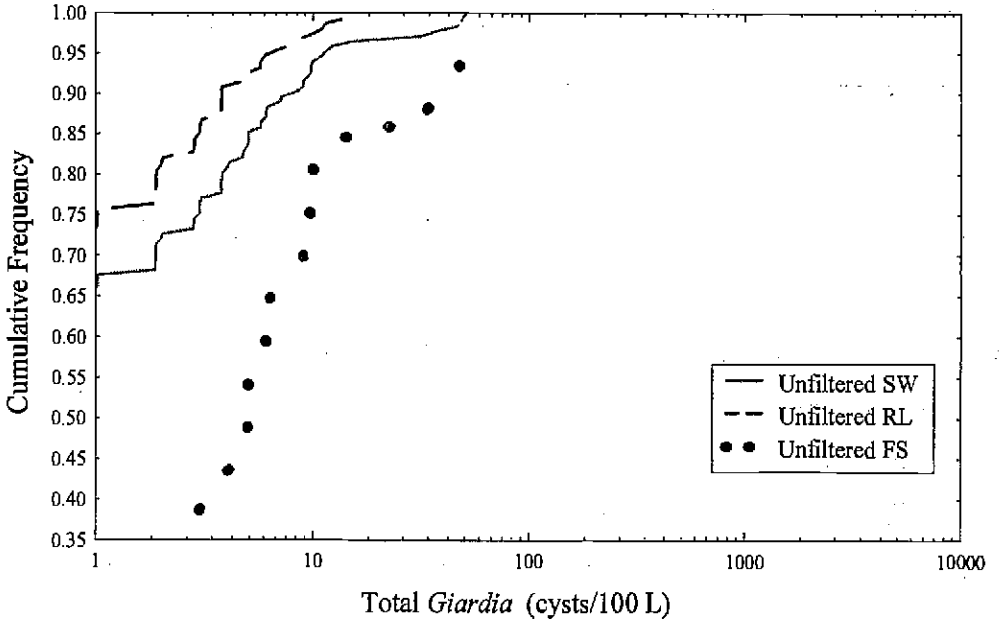

Figure 17.1 Cumulative frequency distributions of unfiltered system *Giardia* concentrations by source water category

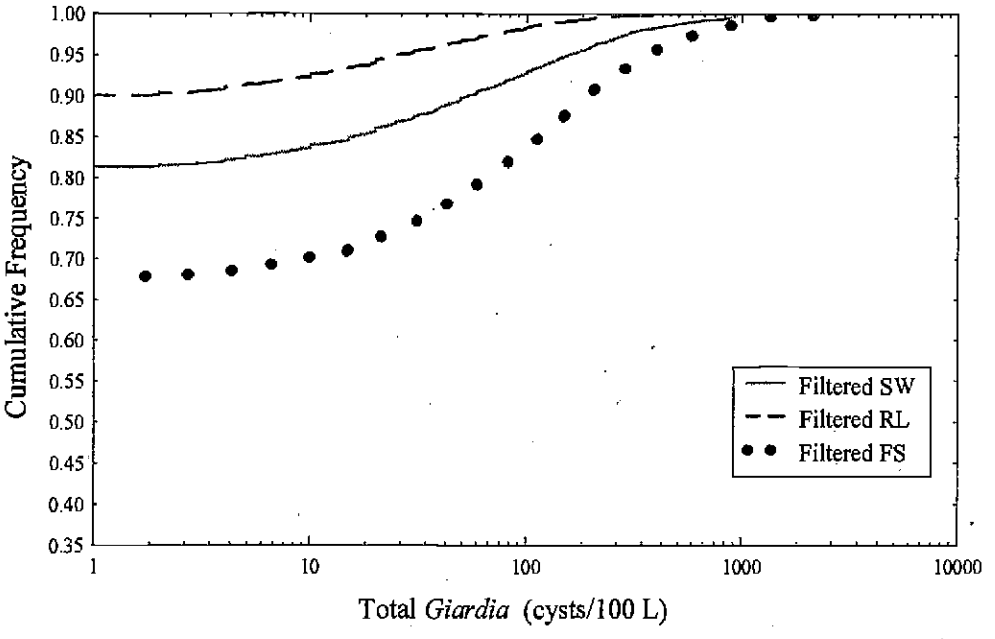

Figure 17.2 Cumulative frequency distributions of filtered system *Giardia* concentrations by source water category

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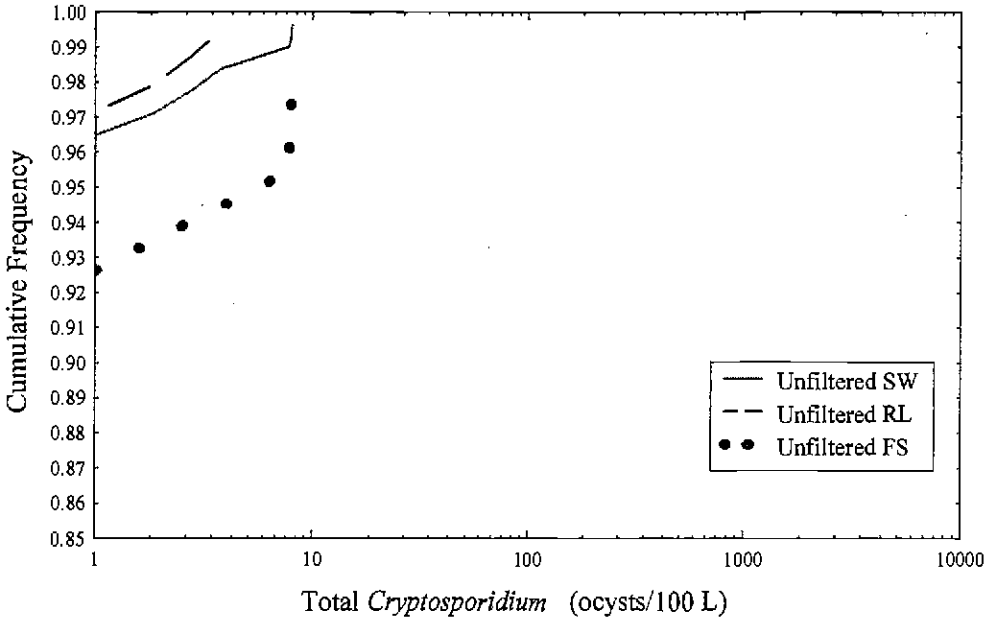

Figure 17.3 Cumulative frequency distributions of unfiltered system *Cryptosporidium* concentrations by source water category

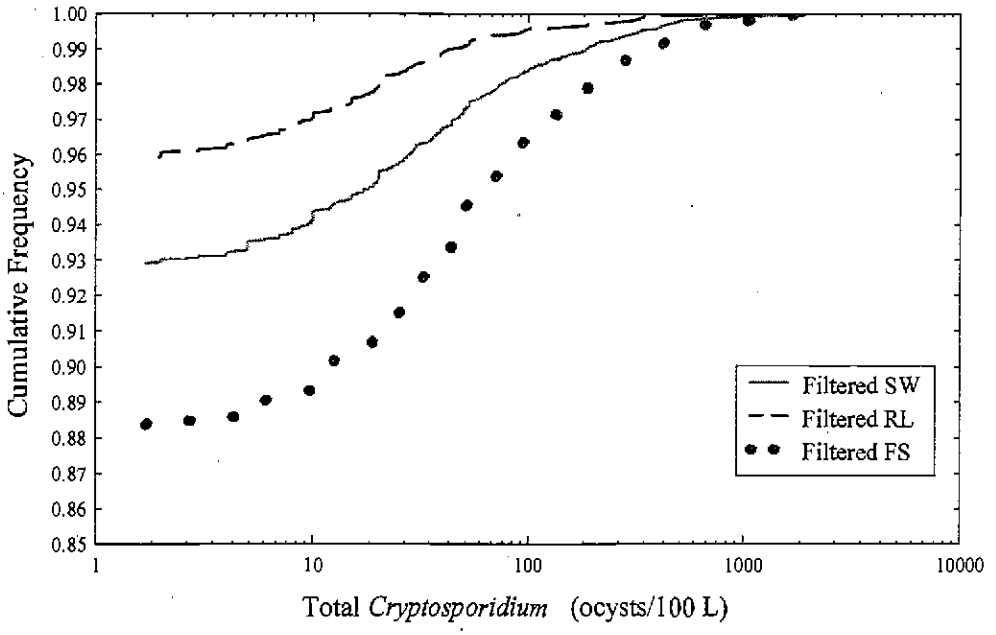

Figure 17.4 Cumulative frequency distributions of filtered system *Cryptosporidium* concentrations by source water category

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Watershed control programs implemented by unfiltered systems in response to SWTR and IESWTR regulatory requirements were generally aimed at reducing potential sources of *Giardia* and *Cryptosporidium* in the watershed. Lower *Cryptosporidium* concentrations measured in samples from unfiltered systems relative to samples from filtered systems suggest that these programs do prevent some source water contamination by this pathogen. *Giardia* concentrations were also lower in unfiltered systems relative to filtered systems when the upper range of the distribution was considered. Evaluating the relative effectiveness of watershed control practices in preventing *Giardia* and *Cryptosporidium* contamination is problematic due to the previously noted differences in recovery efficiencies for these pathogens. Because *Giardia* and *Cryptosporidium* originate from the same source (i.e., animal fecal material), watershed protection practices that are effective for one of these pathogens should be reasonably effective for the other. Some researchers, however, believe that elevated *Giardia* concentrations are more frequently associated with point sources of pollution whereas elevated *Cryptosporidium* concentrations may be more influenced by pollution from nonpoint sources (LeChevallier, Norton, and Lee 1991). Given these considerations, more research is needed to determine how watershed protection practices might differentially target these pathogens.

Giardia and *Cryptosporidium* Associations With Turbidity

Summary statistics for *Giardia* and *Cryptosporidium* concentrations are shown in Tables 17.3 and 17.4, respectively, in relation to unfiltered system source water types and turbidity levels. These data generally show no discernible associations between protozoan concentrations and turbidity. Spearman rank correlation coefficients computed from these same data (Table 17.5) also indicate that protozoan concentrations were not significantly correlated with turbidity in any type of unfiltered source water. These results differ from the findings of several other studies that have shown a significant correlation between *Giardia* and *Cryptosporidium* concentrations and turbidity (Atherholt et al. 1998; LeChavallier, Norton, and Lee 1991). The lack of correlation in the ICR data on unfiltered systems may indicate that the turbidity standard applied under the SWTR was not a suitable measure for evaluating *Giardia* and *Cryptosporidium* penetration into the source water supplies of unfiltered systems.

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Table 17.3

Summary statistics for *Giardia* by source water types and turbidity levels in unfiltered systems

Source water type*	Source water turbidity (NTU)	Number of samples	Percent of positive samples	Median (cysts/100 L)	Arithmetic Mean (cysts/100 L)	Geometric Mean (cysts/100 L)	25th Percentile (cysts/100 L)	75th Percentile (cysts/100 L)	90th Percentile (cysts/100 L)	Maximum (cysts/100 L)
SW	0–0.5	70	37	0.0	4.0	0.94	0.0	4.0	9.5	50
	0.5–1	55	47	0.0	1.4	0.40	0.0	1.9	3.8	15
	1–2	31	48	0.0	3.9	1.1	0.0	4.7	9.8	47
	2–3	2	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	>3	1	0	0.0	0.0	0.0	–	–	–	0.0
RL	0–0.5	53	23	0.0	1.0	0.31	0.0	0.0	3.8	12
	0.5–1	51	49	0.0	1.4	0.39	0.0	1.9	3.0	15
	1–2	19	42	0.0	1.2	0.43	0.0	1.9	4.7	5.7
	2–3	1	0	0.0	0.0	0.0	–	–	–	0.0
	>3	–	–	–	–	–	–	–	–	–
FS	0–0.5	17	82	6.0	13	5.7	4.0	10	49	50
	0.5–1	4	25	0.0	1.2	0.49	0.0	2.5	4.9	4.9
	1–2	12	58	5.1	8.2	2.9	0.0	9.8	12	47
	2–3	1	0	0.0	0.0	0.0	–	–	–	0.0
	>3	1	0	0.0	0.0	0.0	–	–	–	0.0

* SW=surface water system; RL=reservoir/lake system; FS=flowing stream system

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Table 17.4

Summary statistics for *Cryptosporidium* by source water types and turbidity levels in unfiltered systems

Source water type*	Source water turbidity (NTU)	Number of samples	Percent of positive samples	Median (ocysts/100 L)	Arithmetic mean (ocysts/100 L)	Geometric mean (ocysts/100 L)	25th Percentile (ocysts/100 L)	75th Percentile (ocysts/100 L)	90th Percentile (ocysts/100 L)	Maximum (ocysts/100 L)
SW	0–0.5	70	4	0.0	0.14	0.029	0.0	0.0	0.0	8.0
	0.5–1	55	9	0.0	0.15	0.034	0.0	0.0	0.0	3.8
	1–2	31	6	0.0	0.34	0.10	0.0	0.0	0.0	7.8
	2–3	2	0	0.0	0.0	0.00	0.0	0.0	0.0	0.0
	>3	1	0	0.0	0.0	0.00	–	–	–	0.0
RL	0–0.5	53	2	0.0	0.017	0.0	0.0	0.0	0.0	0.90
	0.5–1	51	10	0.0	0.17	0.036	0.0	0.0	0.0	3.8
	1–2	19	5	0.0	0.15	0.055	0.0	0.0	0.0	2.8
	2–3	1	0	0.0	0.0	0.0	–	–	–	0.0
	>3	–	–	–	–	–	–	–	–	–
FS	0–0.5	17	12	0.0	0.53	0.13	0.0	0.0	1.0	8.0
	0.5–1	4	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1–2	12	8	0.0	0.65	0.19	0.0	0.0	0.0	7.8
	2–3	1	0	0.0	0.0	0.0	–	–	–	0.0
	>3	1	0	0.0	0.0	0.0	–	–	–	0.0

* SW=surface water system; RL=reservoir/lake system; FS=flowing stream system

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Table 17.5

Correlation between *Giardia*, *Cryptosporidium*, and turbidity in unfiltered systems

Source water type*	Number of samples	Spearman's *r*	p-level†
Giardia			
SW	159	–0.0020	0.9799
RL	124	0.1358	0.1327
FS	35	–0.1984	0.2532
Cryptosporidium			
SW	159	0.0650	0.4157
RL	124	0.0687	0.4481
FS	35	0.0897	0.6083

* SW=surface water system; RL=reservoir/lake system; FS=flowing stream system

† p-levels denote the probability that the null hypothesis (i.e., $r = 0$) is true; the null hypothesis is rejected when the p-level is less than 0.05

These results assume that variations in assayed sample volumes did not preclude detection of a relationship between protozoa and turbidity. This could potentially have occurred if high-turbidity samples tended to have smaller sample assay volumes and thus lower frequencies of *Giardia* and *Cryptosporidium* detection. To examine this potential, data on unfiltered system turbidity and sample assay volumes were compiled and statistically evaluated for a significant negative correlation. A scatter plot of these data is presented in Figure 17.5. The Spearman rank correlation coefficient (r = 0.286) computed from these same data indicated no significant negative correlation between turbidity and sample assay volume. This result tends to support the conclusion that there is no association between *Giardia* and *Cryptosporidium* concentrations and turbidity in unfiltered systems.

Some researchers, however, have cautioned against drawing definitive conclusions on the basis of data collected in survey-type studies such as the ICR monitoring effort (Atherholt et al. 1998). Sampling plans of this type are generally not designed to answer specific questions about relationships between pathogens and water quality data and may miss the intrinsic variability in the data because they do not specifically track individual hydraulic events (LeChevallier et al. 1997). Given these considerations, this study's conclusions regarding potential relationships between protozoa concentrations and turbidity should be confirmed by a study with a plan specifically designed to evaluate this question.

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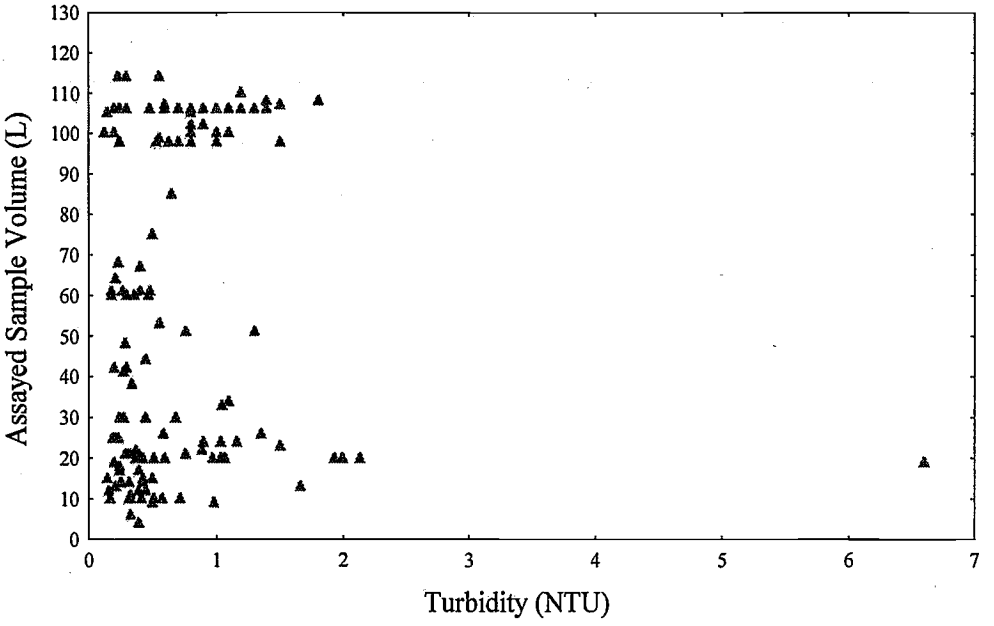

Figure 17.5 Scatter plot of turbidity measurements and assayed sample volumes from unfiltered systems

CONCLUSIONS

- The percentage of samples that were positive for *Giardia* was higher in unfiltered systems than in filtered systems. This trend, however, may relate to the substantially larger assayed volumes of *Giardia* and *Cryptosporidium* samples from unfiltered systems.
- *Giardia* and *Cryptosporidium* concentrations were strongly influenced by watershed characteristics and surface water type. Differences in *Giardia* and *Cryptosporidium* concentrations were most pronounced in relation to differences between reservoir/lake and flowing stream sources, regardless of whether the system was unfiltered or filtered.
- Watershed control programs implemented by unfiltered systems appeared to prevent some source water contamination by *Cryptosporidium*, as evidenced by *Cryptosporidium* concentrations that were five to six times lower in unfiltered systems than in filtered systems. *Giardia* concentrations in unfiltered systems were also lower than in filtered systems when the upper range of the distribution was considered.

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- *Giardia* and *Cryptosporidium* concentrations were not significantly correlated with turbidity in any type of unfiltered source water (i.e., all surface water types, reservoir/lake sources, and flowing stream sources). This lack of correlation suggests that the turbidity standard applied to unfiltered systems under the SWTR was not a suitable surrogate for evaluating *Giardia* and *Cryptosporidium* penetration into source water supplies. This inference, however, should be confirmed through further study specifically designed to evaluate relationships between turbidity and protozoa concentrations in the source water of unfiltered systems.

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CHAPTER 18

VIRUS OCCURRENCE AND HEALTH RISKS IN DRINKING WATER

Susan Shaw, Stig Regli, and Jimmy Chen

ABSTRACT

Results of monthly virus monitoring in source water and estimates of monthly virus reduction achieved by water treatment plants during implementation of the Information Collection Rule (ICR) were used to estimate monthly virus concentrations in finished water and the level of risk of viral infection associated with drinking water from these plants. During ICR implementation, 207 plants that relied strictly on surface water supplies monitored their source water for viruses; 80% of these plants detected viruses at least once during the 18-month monitoring period. Viruses were detected in the finished water of 7(16%) of the 43 plants that also monitored their finished water. In 95% of plant-months (months of data collected by ICR treatment plants), estimated treatment performance exceeded the 4-log removal–inactivation requirement of the Surface Water Treatment Rule (SWTR).

A virus risk analysis assessed the potential impact of reducing the levels of virus treatment from those in place at plants during ICR monitoring to those strictly required to meet SWTR directives. The analysis was based on ICR virus concentrations in source water and on the assumption that plants provide only 4-log virus reduction (2-log physical removal plus 2-log inactivation). Estimated risk from the hypothetical changes in treatment, as measured by the percentage of plants with mean finished water virus concentrations greater than 4.4×10^{-7} most probable number/L (the virus concentration associated with an estimated 10^{-4} annual risk of infection), increased by approximately one order of magnitude—from 5% of plants to 46%.

This analysis suggests that careful consideration of the adequacy of virus inactivation may be warranted for plants that operate near the minimum required level of virus inactivation and for plants considering changes in disinfection practices.

INTRODUCTION

Information Collection Rule (ICR) data on virus occurrence and water treatment can be used to evaluate the extent to which viruses are controlled by surface water treatment plants in the United States. These data can also be used to evaluate the adequacy of the minimum 4-log removal–inactivation requirement specified in the Surface Water Treatment Rule (SWTR). Although many water systems are currently achieving virus inactivation well in excess of the minimum requirement, there is a concern that some systems might weaken virus inactivation practices to comply with the

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Disinfectants/Disinfection By-products Rule (D/DBP Rule) and the forthcoming Stage 2 DBP Rule and thereby compromise virus protection in finished water.

The Interim Enhanced Surface Water Treatment Rule (IESWTR), which was promulgated in 1998, included disinfection benchmarking provisions. These provisions were intended to ensure that reductions in baseline inactivation levels implemented for compliance with maximum contaminant levels (MCLs) specified in the D/DBP Rule would not undermine protection against microbial pathogens. Similar benchmarking provisions or additional virus inactivation requirements may be needed under the forthcoming Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) to ensure that adequate virus protection is maintained. Specific virus control criteria may be particularly important for systems intending to control DBPs by using chloramine as the primary disinfectant because chloramination, unless preceded by the application of free chlorine with sufficient contact time, is virtually ineffective against viruses (Sobsey 1989). Virus control criteria may also be important for systems selecting ultraviolet (UV) light or microfiltration as a treatment strategy to control both DBPs and *Cryptosporidium*. Although UV light disinfection and microfiltration are very effective at reducing concentrations of protozoa in water, they are much less effective at reducing virus concentrations (Clancy et al. 1998, Sobsey 1989, Taylor and Wiesner 1999).

An analysis of the ICR data on virus occurrence and treatment addressed these issues and attempted to answer the following questions:

- What virus concentrations occurred in the surface water sources of ICR treatment plants?
- What levels of treatment for viruses (both physical removal and chemical inactivation) were in effect at ICR plants with different source water virus concentrations?
- What are estimated virus concentrations in finished water, and how do such estimates compare with data on actual virus occurrence in finished water?
- What do measured virus concentrations in finished water tell us about our assumptions regarding water treatment for viruses?
- Based on the ICR data, what potential risks to human health are associated with viruses, and to what extent do ICR data suggest the need for specific virus control criteria in the LT2ESWTR?

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METHODOLOGY

Virus Sampling and Analysis Under the ICR

ICR guidelines and requirements emphasized data quality in order to minimize variability caused by differences in sample collection and analytical procedures. Requirements included the use of a single approved analytical method for viruses, the use of ICR-approved laboratories to analyze virus samples, and the collection of samples according to ICR procedures (U.S. Environmental Protection Agency [USEPA] 1995).

The total culturable virus assay, the approved method for analyzing ICR samples for viruses, does not produce an exact count of the number of viruses detected in the sample. Rather, it produces a statistical estimate of the virus concentration, a most probable number (MPN) with upper and lower confidence bounds, based on the number of confirmed positive cultures and the number of cultures inoculated. Only the central estimates of virus concentration are discussed in this chapter.

The Buffalo Green monkey (BGM) cell culture assay approved for ICR virus analyses is specific for enteroviruses, e.g., poliovirus, coxsackievirus and echovirus. The method does not detect various other significant waterborne human pathogens such as Norwalk virus, the hepatitis A and E viruses, adenovirus, human astrovirus, and rotavirus.

Laboratories approved to analyze ICR virus samples had to meet specific performance standards, including successful analysis of initial and monthly spiked and blank performance evaluation (PE) samples. A memorandum from the ICR Microbiology Coordinator to participating laboratories described the virus PE program, preparation of the virus spiking solution by a laboratory at the Centers for Disease Control and Prevention (CDC), and the statistical analysis of the performance of all participating laboratories and analysts (Feige 1999). The spiked PE samples were prepared by injecting a "known" quantity of viruses onto a filter. CDC determined the virus spike concentrations using MPN methods and plaque assays on BGM cells. The relative standard deviation of the virus spike concentrations ranged from 7% to 49%; the median was 29%. The median percentage virus recovery from the PE samples analyzed by the 24 analysts participating in the program ranged from 22% to 80%; the corresponding relative standard deviation ranged from 34% to 95%. Feige (2002) reported one false positive PE sample result (or 0.7% of 153 blank PE samples analyzed); the corresponding number of false negative results from spiked samples was 8 (or 1.0%

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of 807 PE samples analyzed). Although results from the analysis of these PE samples provide information on the analyst's ability to perform the ICR method, they do not indicate the method's ability to recover viruses from laboratory or natural water samples. The ICR PE program did not measure method recovery, because the spiked viruses were injected onto the filter rather than being diluted in a large volume of water and drawn through the filter. The method's actual recoveries in the field are expected to be lower than recoveries from the spiked PE samples because virus recovery in the PE samples does not account for viruses not captured by the filter or for reduced virus counts caused by water matrix effects, e.g. turbidity.

Source water virus samples of 200 L to 300 L were collected at the treatment plant intake prior to any water treatment. Plants that monitored viruses in finished water collected a 1,500-L to 1,800-L sample after completion of all treatment processes, including the clearwell and the final point of disinfection, and before the distribution system entry point (USEPA 1996). Laboratories assayed the required 100-L equivalent volume of source water and 1,000-L equivalent volume of finished water, achieving theoretical detection levels of 10^{-2} MPN/L and 10^{-3} MPN/L, respectively.

Estimates of Treatment Efficiency and Finished Water Virus Concentrations

Log inactivation of viruses was calculated for each month of virus data reported by the 207 surface water plants. Calculations were based on the CT model equations for estimating log inactivation of viruses presented in Table 18.1. Input data for calculations of virus inactivation included water temperature and CT—i.e., the monthly product of the residual disinfectant concentration in the contact chamber effluent (C) and contact time (T_{10}) the time required for 10% of the water to pass through the contact chamber. A virus inactivation level was calculated for each month based on the sum of the inactivation level achieved in each unit process from the first point of disinfection in the treatment plant to the distribution system entry point. The model equations were developed for the Surface Water Analytical Tool (SWAT) to approximate the disinfection requirements published in the CT tables of the SWTR guidance manual (USEPA 1991) for chlorine (Cl_2), ozone (O_3) and chloramine. Chlorine dioxide (ClO_2) is not included in Table 18.1 because ICR data on ClO_2 residuals were insufficient to estimate inactivation. Therefore, no estimates of virus concentrations in finished water are provided for months in which ClO_2 was the primary disinfectant at a plant.

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For estimated CT values that exceeded the range of values included in the SWTR CT tables, the model assumes first-order kinetics in extrapolating the inactivation level. However, because the CT values for viruses are based on studies that did not evaluate inactivation greater than 4-log (USEPA 1991), the results of this approach to extrapolation from the CT tables should be interpreted with caution. Particularly with regard to the higher ranges of estimated inactivation, these results should be considered no more than an indicator of the degree of "excess" inactivation capacity. Although calculations based on the equations shown in Table 18.1 resulted in estimates of more than 10-log inactivation of viruses in 80% of plant-months (months of data collected by ICR treatment plants), only estimates of up to 10-log inactivation are presented in the figures in this chapter. However, when virus concentrations that might occur in finished water were estimated, inactivation levels were not truncated at 10-log inactivation.

In estimating a plant's total monthly reduction of viruses—all reductions achieved between the source water intake and the entry point to the distribution system—it was assumed that the filtration process achieves 2-log physical removal of viruses. The assumed 2-log physical removal was then added to the calculated level of inactivation, according to the SWTR guidance manual (USEPA 1991).

Table 18.1

CT model equations for estimating log inactivation of viruses

Disinfectant	Temperature	CT equation*
Free chlorine (applied at pH ≤9.5)	≤5°C	$(-\text{Log } I)=0.35 \times \text{temp}^{0.18} \times (CT)$
	>5°C	$(-\text{Log } I)=0.36 \times (1.07)^{\text{temp}} \times (CT)$
Free chlorine (applied at pH >9.5)	≤5°C	$(-\text{Log } I)=0.051 \times \text{temp}^{0.18} \times (CT)$
	>5°C	$(-\text{Log } I)=0.048 \times (1.07)^{\text{temp}} \times (CT)$
Chloramine	≤5°C	$(-\text{Log } I)=0.0014 \times \text{temp}^{0.25} \times (CT)$
	>5°C	$(-\text{Log } I)=0.0015 \times (1.07)^{\text{temp}} \times (CT)$
Ozone	≤5°C	$(-\text{Log } I)=2.20 \times \text{temp}^{0.26} \times (CT)$
	>5°C	$(-\text{Log } I)=2.25 \times (1.07)^{\text{temp}} \times (CT)$

* In these equations, (–log I)=log inactivation; C=the residual disinfectant concentration (in milligrams per liter); and T=the contact time (in minutes), defined as T_{10} in the SWTR guidance manual.

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In the ICR database, disinfectants and treatment plants were classified according to codes identifying the disinfectant in use at the plant during the month of sample collection. Plants using free chlorine as the primary disinfectant were classified as CL2 plants. Plants using either O_3 alone or a combination of O_3 and a chlorine-based disinfectant were designated O3 plants. A similar rule was applied to plants using ClO_2; they were classified as CLO2 plants. The classification CL2_CLM was used for plants in which ammonia was added after free chlorine had already been applied in at least one preceding unit process.

Finished water virus concentrations were calculated for each plant-month by multiplying the measured source water virus concentration for that month by the corresponding level of virus inactivation for that month.

Estimates of Risk

The risk of infection caused by viruses in drinking water was estimated based on a beta-Poisson dose–response model for rotavirus (Regli et al. 1991). Using the beta-Poisson dose–response model, the daily risk of infection from drinking a volume of water containing infectious organisms is described in Equation 18.1.

$$P_{i,d} = 1-(1+\mu V/\alpha)^{-\beta} \tag{18.1}$$

in which $P_{i,d}$ = daily probability of an infection (i) on a single day (d), V = daily volume of water ingested (L), μ = arithmetic mean virus concentration in water (MPN/L), and α and β = dose–response parameters. For rotavirus, the value of α is 0.42; the value of β is 0.26.

A daily risk of infection from viruses (assumed to have the same infectivity as rotavirus) was calculated using Equation 18.1 for each ICR plant for which estimates of finished water virus concentrations or actual finished water virus measurements were available. In calculating the arithmetic mean concentration of viruses for each plant (μ), all monthly values for viruses in finished water were summed for each plant, then divided by the corresponding total sample assay volume. Nondetects were counted as zeros and included in the calculation of the plant's mean concentration of viruses. The daily volume of water ingested (V) was assumed to be 1L.

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Equation 18.2 describes the probability of at least one infection in a year, $P_{i,y}$. Assumptions for this equation were that each day of the year constitutes a separate and statistically independent exposure to an identical volume of water with an identical distribution of viruses (μ). $P_{i,y}$, the probability of at least one infection in 365 days, is calculated using the daily probability $P_{i,d}$ from Equation 18.1 and inserting that value into Equation 18.2.

$$P_{i,y} = 1-(1-P_{i,d})^{365} \tag{18.2}$$

Using these assumptions and solving the two equations indirectly for the concentration, e.g. by trial and error, allows the determination of the mean virus concentration corresponding to $P_{i,y} = 10^{-4}$, the 10^{-4} annual risk of infection. This calculation suggests that if viruses with infectivity similar to that of rotavirus occur at a mean concentration of 4.44×10^{-7} MPN/L in finished water, a 10^{-4}, or 1 in 10,000, annual risk of at least one infection could be expected as a result of drinking 1 L of this water per day.

This model probably overestimates the risk posed by viruses in drinking water because rotavirus has the lowest infectious dose of all viruses for which published data are available. However, because dose–response data are all derived from healthy adults with no underlying health conditions that might make them more susceptible to infection, it is reasonable to use this model to estimate the upper bound of risk of viral infection.

ANALYSIS OF ICR VIRUS AND DISINFECTION DATA

Analytical results regarding virus concentrations in source water and finished water were based on data from ICR plants using strictly surface water as their source of supply. Data from ICR plants using mixed sources, i.e. a combination of surface water and ground water, were not included in any of the analyses presented in this chapter. All monthly virus data were used in calculating surface water plant statistics such as mean, median, and 90th percentile virus concentrations. Virus inactivation levels were also calculated for all plant-months for which adequate water quality and treatment data were reported.

Of the 344 ICR surface water treatment plants that monitored *Giardia* and *Cryptosporidium*, 207 (60%) also monitored monthly virus concentrations in their source water, according to the

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requirements of the ICR. A total of 3,365 values were reported for source water virus concentrations, with a mean of 16.3 values reported per plant. ICR surface water plants that did not monitor viruses in their source water had received a waiver based on historical monitoring data indicating low levels of microbial contamination from total coliforms, fecal coliforms, or *E. coli*. A plant was eligible to receive a waiver if 90% of its samples for one of these indicator bacteria, collected at a minimum frequency of five days per week over a recent six-month period, did not exceed the respective concentration of 100 total coliforms/100 ml, 20 fecal coliforms/100 ml, or 20 *E. coli*/100 ml.

Of the 207 plants monitoring their source water for viruses, 43 (20%) also monitored and reported virus concentrations in their finished water. (The ICR only required plants whose source water virus concentrations exceeded 10 MPN/L to monitor viruses in finished water.) At the time these 43 plants began monitoring finished water, none of their source water samples had exceeded the threshold that triggered the requirement to monitor viruses in finished water during subsequent ICR sampling months. By the end of the ICR monitoring period, only two plants had exceeded this trigger level. Virus concentrations were reported for 552 finished water samples; the mean number of samples reported per plant was 12.8, and the range was 3 to 18.

Occurrence of Viruses in Source Water

Figures 18.1a and 18.1b summarize the occurrence of viruses in ICR source water supplies. Figure 18.1a shows the cumulative distribution of virus concentrations in all 3,365 monthly source water samples and indicates that viruses were not detected in 76% of these samples. Among the 24% of source water samples in which viruses were detected, concentrations ranged from 1 to 1,974 MPN/100 L. Although only 24% of source water samples were positive for viruses, the maximum virus concentrations presented in Figure 18.1b illustrate that more than 80% of the plants had at least one source water sample that was positive. Mean source water virus concentrations ranged up to 112 MPN/100 L. Median and 90th percentile mean source water virus concentrations were 0.4 MPN/100 L and 5 MPN/100 L, respectively. Median and 90th percentile maximum virus concentrations were 3 and 40 MPN/100 L, respectively.

The following analysis was conducted to determine the extent to which plants using disinfectants associated with lower rates of virus inactivation, i.e., those classified as O3 or CLM plants, had less contaminated source water than those classified as CL2 or CL2_CLM plants. Virus

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data were classified according to the disinfectant used at the plant during the month in which the sample was collected. Figures 18.2a and 18.2b show the cumulative distributions of mean and maximum virus concentrations as a function of the type of disinfectant used during all or part of the 18-month ICR sampling period. Of the 207 plants monitoring for viruses, 32 used two disinfectants and one plant used three disinfectants during the ICR sampling period; these plants are represented by more than one data point in Figures 18.2a and 18.2b. Both figures indicate that the source water of CLM and O3 plants contained lower virus concentrations. A comparison of the maximum virus concentrations in Figure 18.2b shows that 68% of CLM plants and 58% of O3 plants had maximum virus concentrations of 1 MPN/100 L or less. The highest observed virus concentration in source water from these plants was only 12 MPN/100 L. By contrast, maximum source water virus concentrations exceeded 100 MPN/100 L in 5.6% of CL2 plants and 5% of CL2_CLM plants.

Estimates of Virus Inactivation

To estimate the occurrence of viruses in finished water, estimated inactivation levels (calculated according to the equations in Table 18.1) for each plant-month (for which adequate data were available to calculate log inactivation) were applied to the measured source water virus concentration for the corresponding plant-month. Estimated virus inactivation, as illustrated in Figures 18.3a, 18.3b, 18.4a, and 18.4b, varied extensively among plants, from month to month within the same plant, and by disinfectant type. Figure 18.3a illustrates the cumulative distribution of estimated log inactivation for the 20% of plant-months when less than 10-log inactivation was achieved. Estimates for more than 90% of plant-months exceeded 4-log inactivation. Figure 18.3b illustrates the cumulative distribution of estimated minimum, mean, and maximum log inactivation (up to a 10-log maximum). Estimates indicate that 90% of the plants achieved at least a 6-log mean inactivation and at least a 1-log minimum inactivation. Given the high inactivation levels estimated for most plants, it is interesting that 13.3% of the plants had at least one monthly estimate of 2-log inactivation or less.

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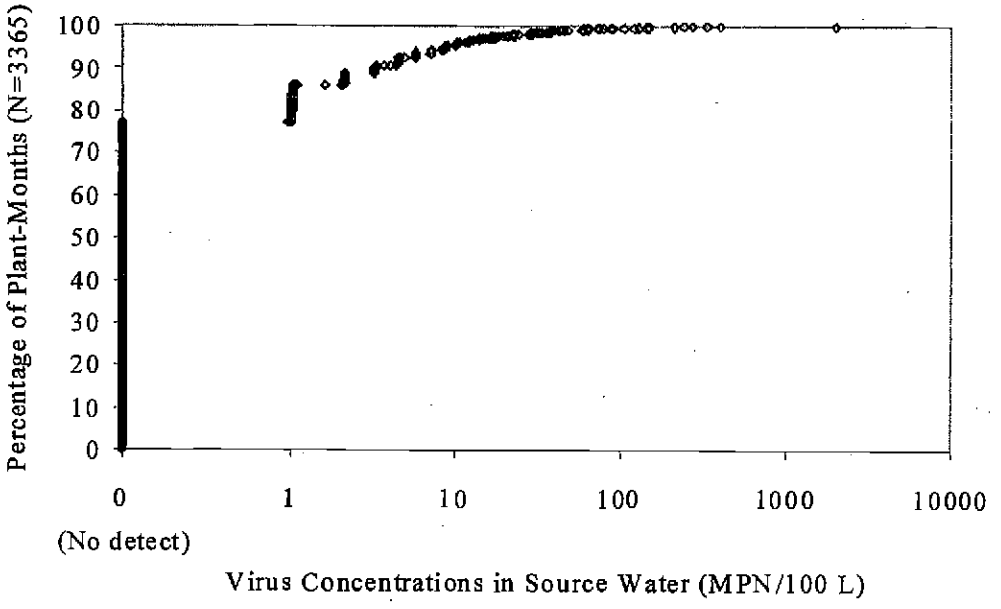

Figure 18.1a Cumulative distribution of virus concentrations in the source water of ICR surface water plants (by plant-month)

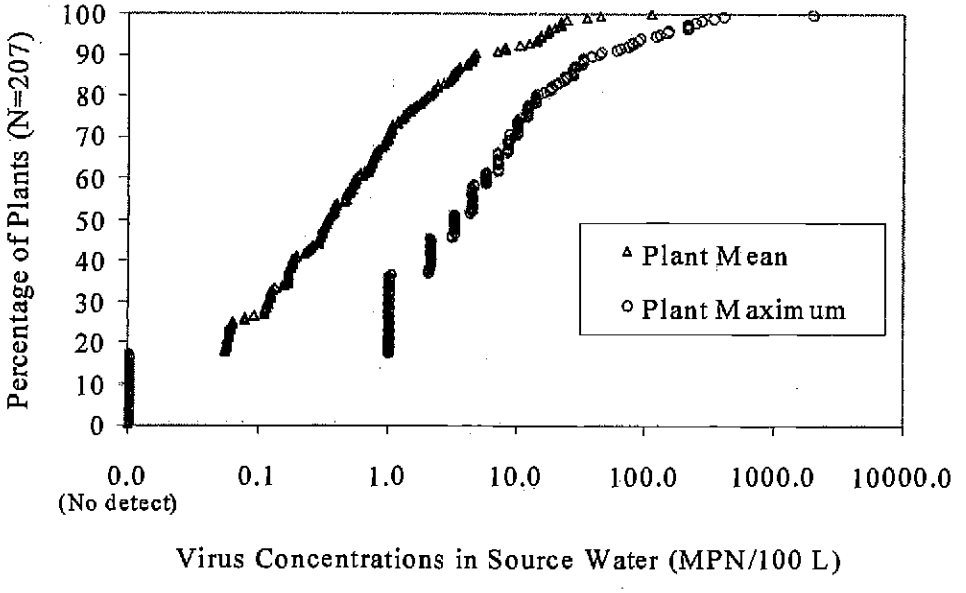

Figure 18.1b Cumulative distribution of mean and maximum virus concentrations in the source water of ICR surface water plants

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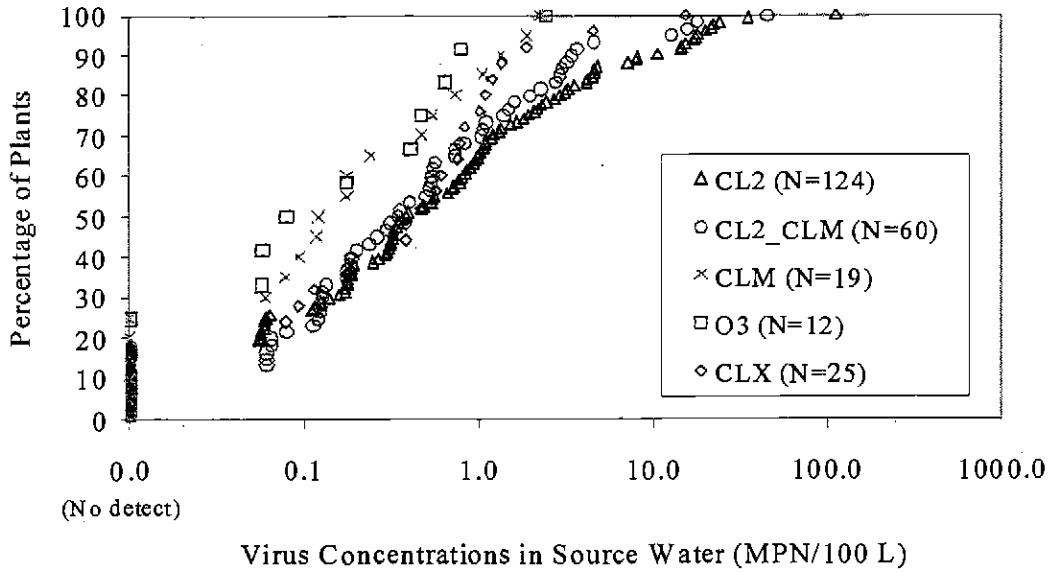

Figure 18.2a Cumulative distribution of mean virus concentrations in source water as a function of disinfectant types in use during ICR monitoring (33 of 207 plants are represented by more than one data point)

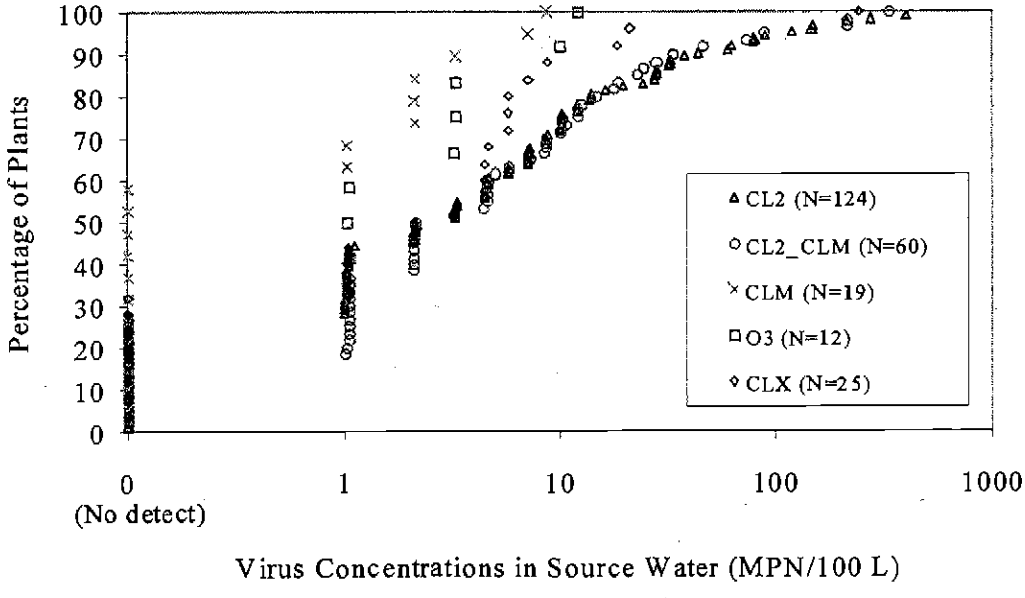

Figure 18.2b Cumulative distribution of maximum virus concentrations in source water as a function of disinfectant types in use during ICR monitoring (33 of 207 plants are represented by more than one data point)

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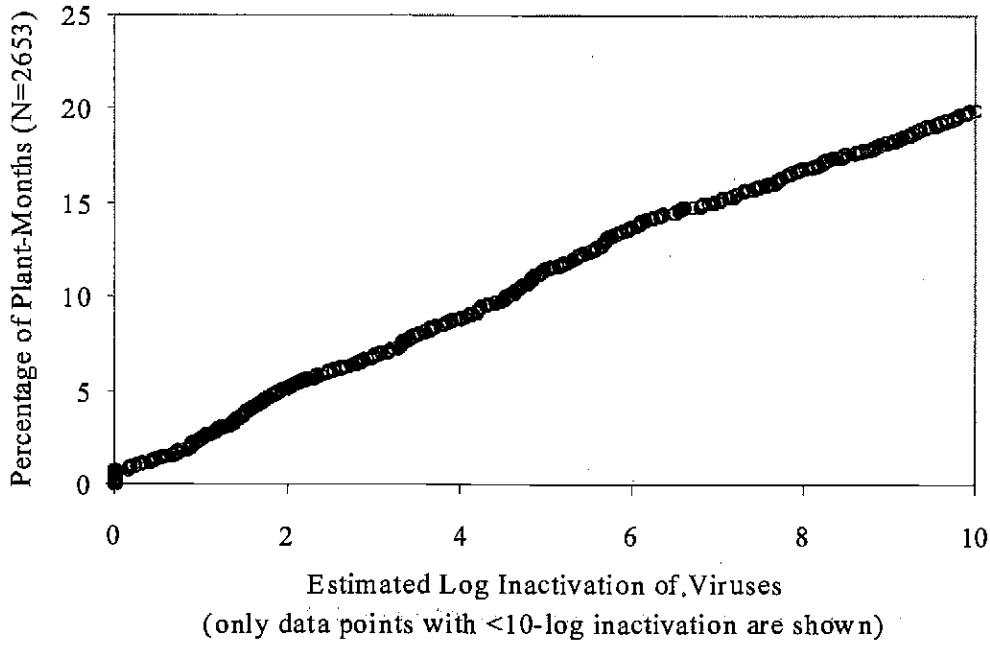

Figure 18.3a Cumulative distribution of estimated log inactivation of viruses (by plant-month)

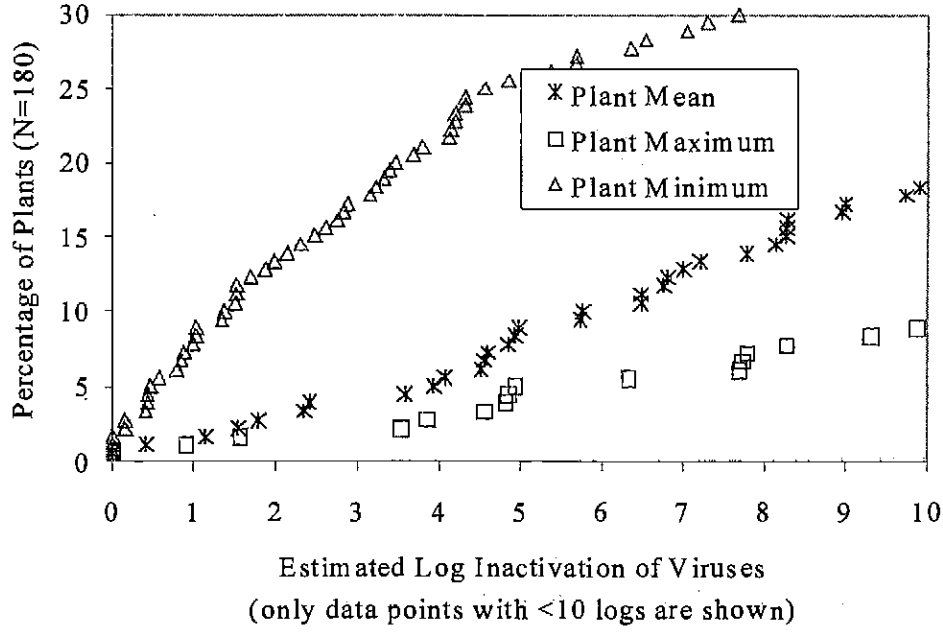

Figure 18.3b Cumulative distribution of estimated minimum, mean, and maximum log inactivation of viruses

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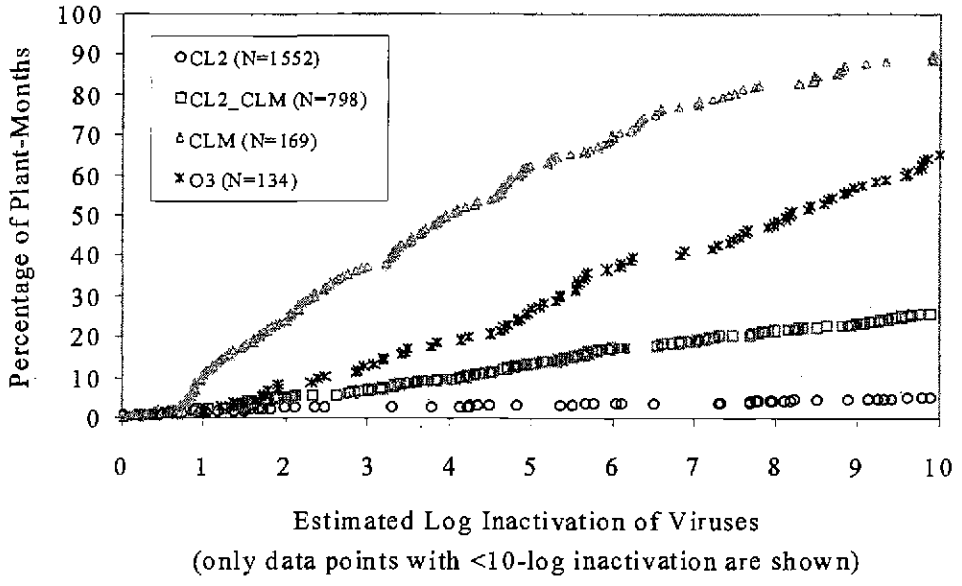

Figure 18.4a Cumulative distribution of estimated log inactivation of viruses (by plant-month) as a function of disinfectant types in use during ICR monitoring

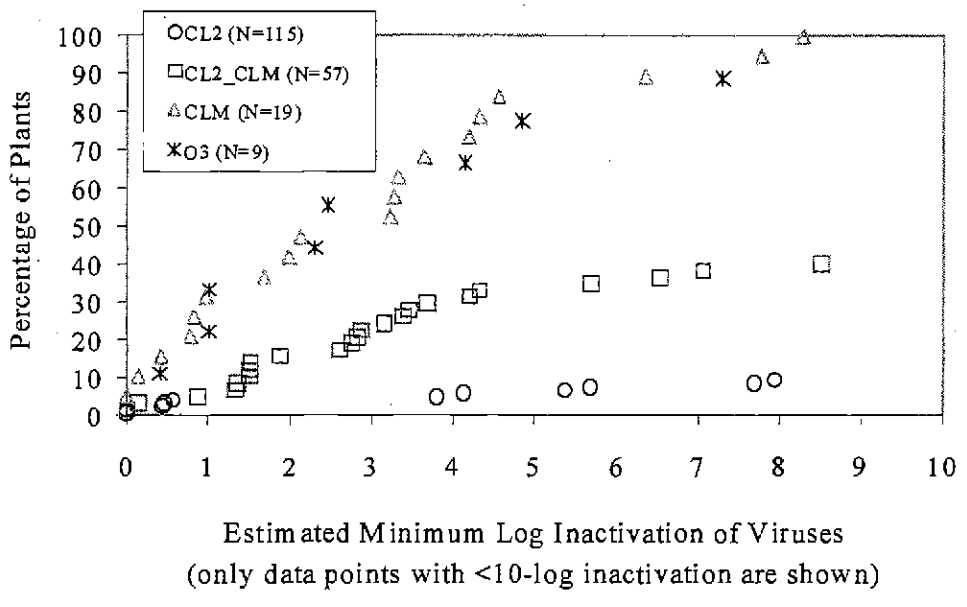

Figure 18.4b Cumulative distribution of estimated minimum log inactivation of viruses as a function of disinfectant types in use during ICR monitoring (20 of 180 plants are represented by more than one data point)

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As noted, the SWTR requires all plants to achieve at least 4-log combined removal and inactivation of viruses throughout the year. USEPA guidance for the SWTR (USEPA 1991) recommends that filtration plants use disinfection to achieve at least 2-log inactivation of viruses (on the assumption that filtration contributes the remaining 2-log removal). Thus, it appears that not all ICR systems consistently met the minimum treatment requirement for viruses.

Figure 18.4a shows the distribution of monthly virus inactivation by disinfectant type, and Figure 18.4b shows the distribution of minimum virus inactivation by disinfectant type. In Figure 18.4b, plants that used more than one type of disinfectant during the ICR monitoring period are represented by one data point corresponding to each disinfectant type. Both figures show that the lowest levels of virus inactivation were associated with periods when only chloramine was used. Somewhat higher levels of inactivation were associated with the use of O_3. The highest inactivation levels were associated with the use of Cl_2 alone. The data from CLM plants can be explained by the low effectiveness of chloramine as a viral disinfectant. The virus inactivation achieved by O_3, a highly effective disinfectant, tends to be limited by disinfection practices (comparatively lower residuals and shorter contact times).

As noted, 13.3 % of the plants achieved 2-log inactivation or less during at least one month. Figure 18.4a shows that these lower levels of inactivation were not all associated with chloramine or O_3 disinfection. In fact, 5.2% of CL2_CLM plant-months and 2.7% of CL2 plant-months are also represented in the category of 2-log inactivation or less. As shown in Figure 18.4b, the category of plants that achieved a minimum level of 2-log inactivation or less included more than 30% of CLM and O3 plants, 16% of CL2_CLM plants, and 4% of CL2 plants.

Estimates of Virus Concentrations in Finished Water

Given the monthly virus measurements in ICR source water and the corresponding monthly estimates of virus inactivation, monthly concentrations of viruses in finished water were calculated for each plant based on the monthly estimated inactivation level and an assumed 2-log physical removal by filtration. Figure 18.5a shows the cumulative distribution of these calculated finished water virus concentrations. In approximately 98% of all plant-months, estimated virus concentrations in finished water were less than or equal to 1.0×10^{-9} MPN/L, either because no viruses were

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detected in the source water or because of exceedingly high estimated inactivation levels. (To illustrate the cumulative distribution in a concise graph, finished water virus concentrations of zero and of less than 1.0×10^{-9} MPN/L were grouped into a category of finished water virus concentrations of 1.0×10^{-9} MPN/L or less.) The maximum calculated virus concentration in finished water was 2×10^{-4} MPN/L.

In Figure 18.5b, the cumulative distribution of estimated monthly virus concentrations in finished water was plotted by disinfectant category. Even though source water virus concentrations were generally lower at CLM and O3 plants (as illustrated in Figure 18.2b), the lower inactivation levels associated with chloramines and O_3 resulted in higher estimated finished water virus concentrations than estimated concentrations for CL2 and CL2_CLM plants.

Figure 18.6 shows the cumulative distribution of estimated mean concentrations of viruses in finished water and indicates that 88% of plants had estimated mean finished water virus concentrations at or below 1.0×10^{-9} MPN/L. The range of mean values extended up to 0.02 MPN/L. Approximately 5% of estimated mean concentrations were either at or above 4.4×10^{-7} MPN/L. The value of 4.4×10^{-7} MPN/L, the virus concentration associated with an estimated 10^{-4} annual risk of infection, is used only as a point of reference and does not imply an acceptable level of risk.

Measured Virus Concentrations in Finished Water

Forty-three (20%) of the 207 ICR surface water plants that monitored their source water for viruses also collected samples to determine virus concentrations in their finished water. This subgroup of plants collected a total of 552 finished water virus samples. Figure 18.7 shows the cumulative distribution of mean virus concentrations measured in the source water of this subgroup of plants, as a function of disinfectant type. The distributions in Figure 18.7 can be compared with those presented in Figure 18.2a for all 207 plants monitoring viruses in source water. Nine (1.6%) of the 552 finished water samples were positive for viruses. Viruses were detected in the finished water of 7 (16%) of the 43 plants monitoring finished water, with two plants reporting positive samples in two consecutive months. Data for the plant-months in which viruses were detected in finished water are shown in Table 18.2.

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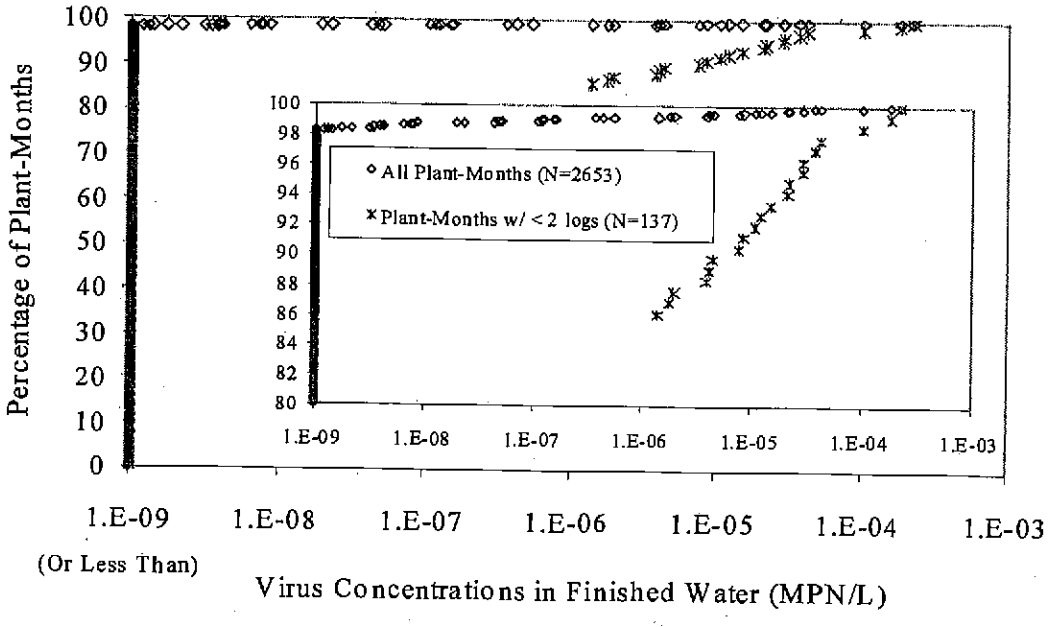

Figure 18.5a Cumulative distribution of estimated virus concentrations in finished water (based on source water virus concentrations and estimated log inactivation plus 2-log physical removal)

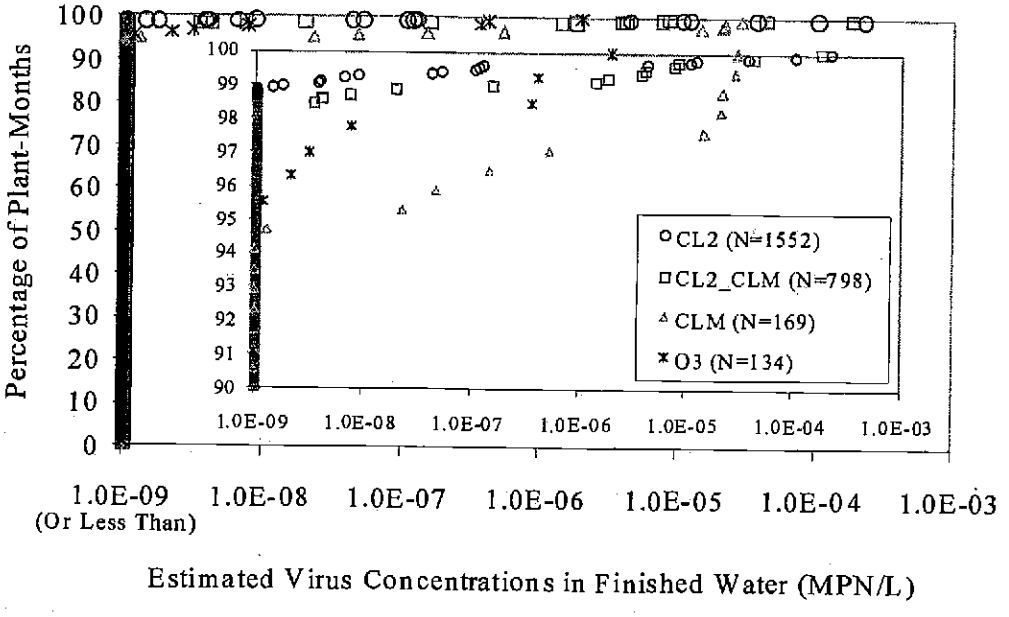

Figure 18.5b Cumulative distribution of estimated virus concentrations in finished water as a function of disinfectant types in use during ICR monitoring (based on source water virus concentrations and estimated log inactivation plus 2-log physical removal)

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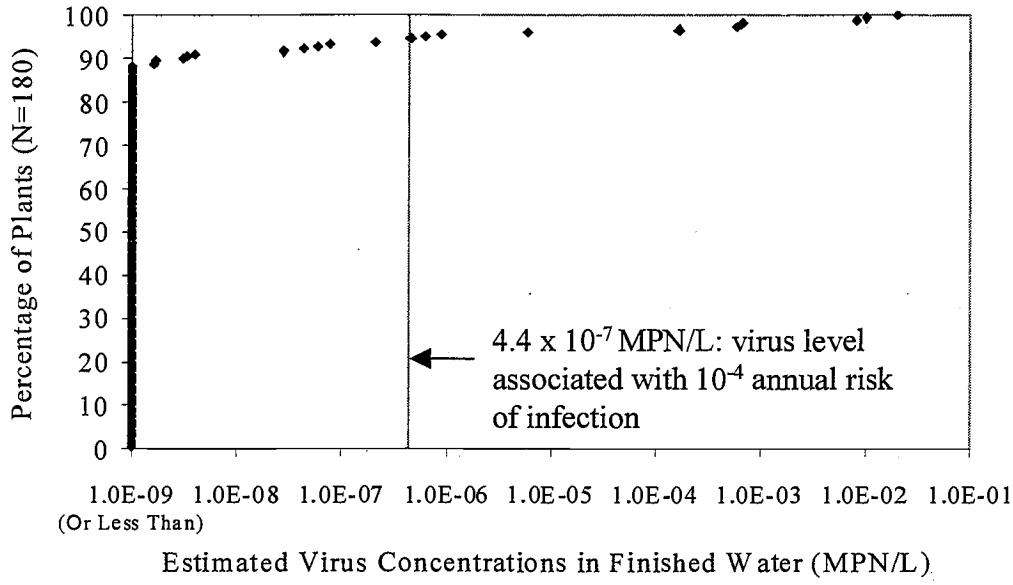

Figure 18.6 Cumulative distribution of estimated mean virus concentrations in finished water (based on source water virus concentrations and estimated log inactivation plus 2-log physical removal)

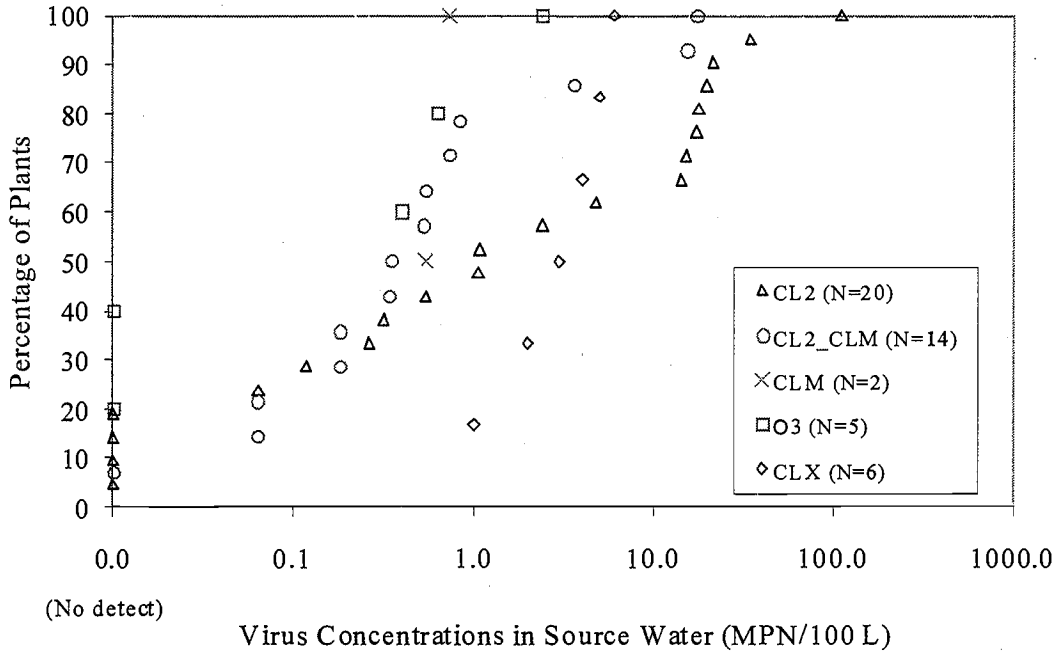

Figure 18.7 Cumulative distribution of mean virus concentrations in the source water of ICR plants monitoring viruses in finished water, shown as a function of disinfectant type (4 of 43 plants are represented by more than one data point)

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When data on residual disinfectant concentrations were reported for the corresponding plant-month, estimated inactivation ranged from 4.2-log to greater than 10-log, i.e., it exceeded the minimum 2-log disinfection requirement of the SWTR. Three of the seven plants that detected viruses in finished water used conventional treatment, three used lime softening, and one used direct filtration.

The detection of viruses in finished water was somewhat surprising, particularly because virus inactivation (when such data were available) was at least 4-log, i.e., a minimum of 6-log virus reduction was assumed to be occurring when these viruses were detected in finished water. This result raises questions regarding the accuracy of treatment estimates based on ICR data, at least for these particular plant-months, and, more importantly, whether the CT values specified in the guidance manual for the SWTR overestimate the level of inactivation that can be achieved.

One possible area for further investigation is the difference in inactivation achieved by disinfection when viruses are attached to particles versus when they are dispersed. The SWTR CT values (USEPA 1991) were based on disinfection studies using dispersed viruses. Research conducted by Sobsey, Fuji, and Hall (1991) suggests that current CT values may not adequately protect public health when viruses are cell-associated rather than dispersed. Given the importance of CT values in the regulatory framework, this area may deserve further scrutiny.

Table 18.3 presents measured mean concentrations of viruses in the source water of the seven plants that detected viruses in finished water (the plants listed in Table 18.2), along with two analyses of the annual risk of infection associated with drinking finished water from these plants. One risk analysis was based on the mean measured virus concentration in finished water, the other on the mean calculated virus concentration in finished water (based on monthly source water concentrations and corresponding monthly estimates of inactivation) from the same plants.

Mean virus concentrations in the source water of plants that detected viruses in their finished water spanned the same range of mean source water virus concentrations as all 207 plants, as shown in Figure 18.1b. Plants B, D, E, and F had mean source water virus concentrations on the same order of magnitude as the median mean concentration of 0.6 MPN/100 L. Plant C's mean virus concentration was two orders of magnitude higher, and the mean virus concentrations of plants A and G were at least an order of magnitude lower.

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Table 18.2

Measured virus concentrations and type of water treatment in place during plant-months in which viruses were detected in finished water

Plant ID	Sampling month	Plant disinfectant type	Log inactivation of viruses	Type of treatment†	Virus concentration in source water (MPN/100 L)	Virus concentration in finished water (MPN/100 L)
A	3	O3	NA*	DF	0	0.1
B	18	CL2	4.2	CONV	0	0.1
C	16	CL2	NA*	CONV	0	0.1
C	17	CL2	NA*	CONV	1	0.1
D	3	CL2	NA*	TS/SOFT	1	0.1
D	4	CL2	NA*	TS/SOFT	0	0.1
E	5	O3	8.1	TS/SOFT	1	0.2
F	6	CL2	>10	TS/SOFT	1	0.1
G	14	CL2	>10	CONV	0	0.1

* NA = no data available

† DF = direct filtration, CONV = conventional, TS/SOFT = two-stage lime softening

Table 18.3

Two estimates of the annual risk of infection from water produced by surface water plants that detected viruses in finished water

		Based on measured viruses in finished water		Based on estimated viruses in finished water	
Plant ID	Mean virus concentrations in source water* (MPN/100 L)	Mean virus concentrations in finished water* (MPN/L)	Estimated annual risk of infection†	Estimated mean virus concentrations in finished water‡ (MPN/L)	Estimated annual risk of infection**
A	0	5.5×10^{-5}	1.3×10^{-2}	§	
B	0.18	6.0×10^{-5}	1.3×10^{-2}	5.0×10^{-5}	1.1×10^{-2}
C	18.5	2.0×10^{-4}	4.4×10^{-2}	$<1.0 \times 10^{-9}$	$<1.0 \times 10^{-8}$
D	0.52	1.1×10^{-4}	2.5×10^{-2}	§	
E	0.40	1.1×10^{-4}	2.5×10^{-2}	4.0×10^{-8}	9.0×10^{-6}
F	0.72	5.6×10^{-5}	1.3×10^{-2}	$<1.0 \times 10^{-9}$	$<1.0 \times 10^{-8}$
G	0.06	1.3×10^{-4}	2.9×10^{-2}	$<1.0 \times 10^{-9}$	$<1.0 \times 10^{-8}$

* The sum of all monthly measured virus MPNs divided by the total sample volume assayed for source water and finished water, respectively

† Based on monthly measured mean virus MPNs in finished water, 1-L daily water consumption, and beta-Poisson model for rotavirus with alpha=0.26 and beta=0.42

‡ Based on measured source water virus concentrations and estimated log removal for corresponding month

§ Inadequate data to calculate inactivation levels for estimates of virus concentrations in finished water

** Based on monthly calculated mean concentrations of viruses in finished water, 1-L daily water consumption, and beta-Poisson model for rotavirus with alpha=0.26 and beta=0.42

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The estimated annual risk of infection, based on measured virus concentrations in finished water, did not vary substantially among the seven plants. However, with the exception of plant B, estimated risk based on mean measured concentrations of viruses in finished water was orders of magnitude higher than estimated risk based on mean estimated concentrations of viruses in finished water. Plant B's exceptional estimated risk can be explained by the high concentration of estimated finished water viruses that resulted from one plant-month when viruses were detected in the plant's source water and less than 2-log inactivation was achieved (data not shown).

DISCUSSION

The analysis of ICR data on virus occurrence in source water was partly characterized by the large percentage of samples in which viruses were not detected (nearly 80% of the 3,365 ICR virus samples were nondetects). Analysis of the virus data by type of treatment plant and type of disinfectant, as well as analysis of the estimated level of treatment associated with virus occurrence, provided a more complex characterization of virus distributions and of estimated health risks associated with drinking water.

Analysis of the ICR virus data by treatment plant showed that more than 80% of the 207 plants detected viruses in their source water at least once during the ICR monitoring period. The concentrations at which viruses were detected in source water were generally not very high, considering that some ICR plants drew source water from rivers subject to fecal contamination. The 90th percentile of maximum virus concentrations was 40 MPN/100 L, and only one sample exceeded 1,000 MPN/100 L. However, the ICR data on viruses in source water probably underestimates the true distribution of virus concentrations because of the method's expected incomplete recovery of viruses and the fact that the BGM cell assay of the ICR method detects only one group of enteric viruses, i.e., culturable enteroviruses. In research on archived ICR samples (Chapron et al. 2000), analysis of viruses provided evidence of the presence of other types of pathogenic viruses in ICR samples and suggested that the ICR cell assay may not be as sensitive as assumed. Results of this study should be interpreted with caution, however, because the non–ICR methods did not include a confirmation step to verify the identity of detected viruses. In this study, the researchers compared the number and type of viruses detected in 29 randomly selected archived ICR samples using both the ICR method and an integrated cell culture–polymerase chain reaction (ICC-RT-PCR) coupled

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with a nested PCR method. Whereas the ICR assay detected viruses in only 5 of the 29 samples, 27 of the 29 samples were positive for viruses using the ICC-RT-PCR–nested PCR method, and 19 samples were positive for an infectious virus. The ICC-RT-PCR–nested PCR method detected adenovirus types 40 and 41 in 14 of the 29 samples, astroviruses in 15, and enteroviruses in 17. The number of viruses found in the selected archived ICR samples might have been even higher if the analytical method was able to detect other waterborne pathogenic viruses, e.g., Norwalk virus, rotavirus, and the hepatitis A and E viruses.

Estimated virus inactivation, based on treatment performance data reported during the ICR, exceeded 10-log in nearly 80% of plant-months; however, the level of treatment provided varied extensively among and within plants. Of most concern are plants that achieved relatively low levels of virus inactivation, in particular the group of plants achieving less than 2-log inactivation at some time during ICR monitoring. Pressure to reduce DBPs in order to comply with the D/DBP Rule and the Stage 2 DBP Rule could lead to changes in disinfection practices that would weaken existing inactivation levels. Although treatment requirements for *Giardia* are currently more likely to govern disinfection practices than treatment requirements for viruses, this could change if more efficient treatment processes for the protozoan pathogens *Giardia* and *Cryptosporidium* (e.g., microfiltration or UV disinfection) are adopted. Because these technologies may be less effective at reducing viruses than technologies already in place (e.g., disinfection with chlorine), maintaining adequate virus inactivation will be particularly important if microfiltration or UV technologies are selected to meet treatment requirements for protozoa.

For many of the ICR plants, reducing disinfectant concentrations is unlikely to significantly increase the risk posed by viruses in finished water, particularly for plants with estimated inactivation greater than 10-log. Plants that currently achieve less than 4-log inactivation may be a concern, depending on the virus concentrations in their source water and the variability in treatment performance and disinfectant application. Figure 18.8 illustrates variability in the treatment performance achieved by the 38 plants in this category. Based on the estimates of treatment performance described earlier, 24 of these plants did not always achieve, or just barely achieved, the 2-log virus inactivation requirement of the SWTR. Moreover, treatment performance estimates indicate that two plants never achieved 2-log virus inactivation during the 18-month ICR monitoring period.

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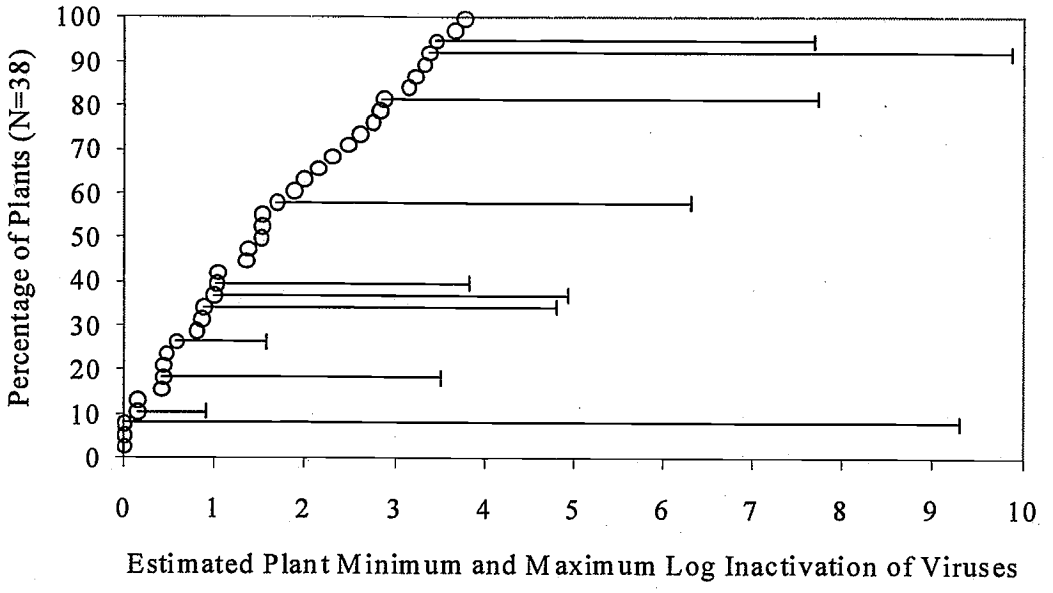

Figure 18.8 Variability of estimated log inactivation of viruses within plants (data are from plants with estimated minimum log inactivation <4; when the maximum inactivation is not shown, it is higher than 10-log)

Figure 18.9 illustrates the hypothetical distribution of estimated mean virus concentrations in finished water if treatment plants were to reduce disinfectant concentrations to just meet the minimum 4-log virus reduction requirement (e.g., by providing 2-log inactivation in addition to 2-log physical removal by filtration) and if source water virus concentrations were identical to those reported during ICR monitoring. According to this analysis, the finished water of approximately 46% of ICR surface water plants would have a mean virus concentration above 4.4×10^{-7} MPN/L. As noted, this concentration roughly corresponds to a 10^{-4} annual risk of viral infection from drinking an average of 1 L of water per day, assuming viruses with the same infectivity as rotavirus. Moreover, the finished water of 12% of plants with 5-log virus reduction and of 1% of plants with 6-log virus reduction would exceed the 10^{-4} risk level. These results make a case for caution and careful evaluation in decision-making about changes in disinfection practices, particularly for plants that do not provide high levels of virus inactivation. These results also indicate that the minimum level of protection required under the SWTR may not be adequate.

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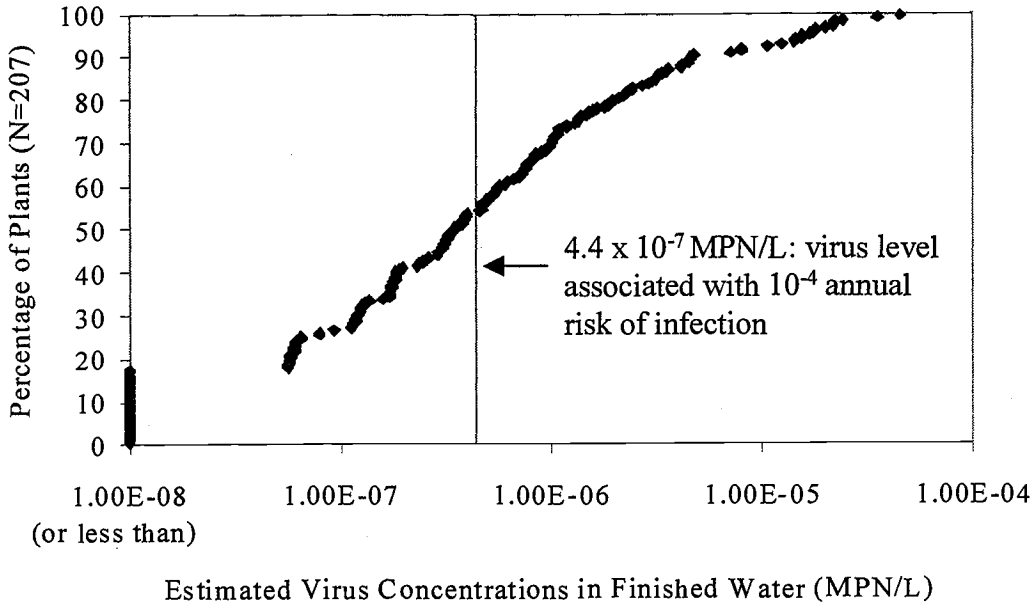

Figure 18.9 Cumulative distribution of estimated mean virus concentrations in finished water (based on 4-log inactivation and removal)

CONCLUSIONS

- Of the 207 ICR surface water plants that monitored their source water for viruses, more than 80% detected at least one virus among their monthly source water samples.
- The source water of 50% of the 207 plants had mean virus concentrations greater than 0.4 MPN/100 L. The source water of 10% of the plants had mean virus concentrations greater than 5 MPN/100 L. The highest mean concentration of viruses in source water was 112 MPN/100 L.
- Estimated virus inactivation for 90% of plant-months exceeded 4-log, indicating an overall 6-log reduction in viruses (assuming 2-log physical removal in addition to inactivation). The high percentage of plants achieving more than 4-log virus inactivation was mostly associated with the use of Cl_2 or a combination of Cl_2 and chloramine. Use of O_3 or only chloramine was typically associated with much lower virus inactivation estimates. Approximately 20% and 48% of O3 and CLM plant-months, respectively, had estimated

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virus inactivation of less than 4-log, compared with fewer than 10% of CL2 and CL2_CLM plant-months.

- Of the plants that monitored viruses in their source water, 43 (20%) also monitored their finished water for viruses. Seven (16%) of these plants detected viruses in their finished water. However, of the 552 finished water virus samples collected, only 9 (1.6%) were positive. Over the course of the 18-month monitoring period, measured mean concentrations of viruses in the finished water of these seven plants ranged from 5.5×10^{-5} MPN/L to 2.0×10^{-4} MPN/L, corresponding to annual risks of infection ranging from 1.3×10^{-2} to 4.4×10^{-2}. This risk estimate should be considered an upper bound because it is based on the assumption that the measured virus has the same infectivity as rotavirus, the virus with the lowest estimated dose response (of those for which such data are available). Mean measured concentrations of viruses in finished water were generally orders of magnitude higher than the mean estimated finished water concentrations calculated by applying estimated monthly treatment levels to corresponding monthly measured virus concentrations in source water.
- Lower mean and maximum virus concentrations in source water were associated with the use of chloramine or O_3 as a disinfectant compared with the use of Cl_2. Even though source water virus concentrations were generally lower at plants using chloramine or O_3, the lower levels of virus inactivation associated with these disinfectants resulted in higher calculated finished water virus concentrations compared with concentrations calculated for plants using only Cl_2 or a combination of Cl_2 and chloramine.
- Estimated inactivation for 24 (13.3 %) plants was barely 2-log or less at some time during ICR monitoring. (Under the SWTR, all treatment plants are required to maintain a minimum 4-log combined removal and inactivation of viruses. USEPA's guidance manual for the SWTR recommends that filtration plants achieve at least a 2-log reduction of viruses through disinfection, on the assumption that physical removal of viruses contributes a 2-log reduction.) Thus, it appears that not all ICR water systems consistently met the minimal treatment requirement for viruses.
- Estimated log inactivation associated with finished water samples in which viruses were detected ranged from 4.2-log to greater than 10-log; thus estimated treatment performance at these plants exceeded the minimum 2-log virus inactivation requirement of the SWTR.

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The extent to which viruses are present in finished water that has been subjected to treatment far exceeding the minimum requirement of the SWTR raises questions about the accuracy of treatment estimates based on the CT tables and about the adequacy of protection provided by compliance with minimum treatment requirements.

- The SWTR's minimum 4-log combined removal–inactivation requirement for viruses may not provide adequate protection against this group of waterborne pathogens. Although most plants currently achieve well in excess of the 4-log removal–inactivation requirement, concern remains that some systems may inappropriately change existing disinfection practices in order to minimally meet SWTR requirements, especially while they try to control DBPs under the forthcoming Stage 2 DBP rule.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The scientific views expressed are solely those of the authors and do not necessarily reflect those of USEPA.

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CHAPTER 19

CRYPTOSPORIDIUM AND *GIARDIA* OCCURRENCE IN ICR DRINKING WATER SOURCES—STATISTICAL ANALYSES OF ICR DATA

Michael J. Messner and Robert L. Wolpert

ABSTRACT

Because of low occurrence concentrations, small sample volumes, and low and variable recoveries associated with analytical methods, most measurements of *Cryptosporidium* and *Giardia* in water samples collected under the Information Collection Rule (ICR) were negative; many locations produced nothing but zero results over the duration of ICR monitoring. The greater median volumes analyzed and the higher recoveries achieved with the method used in the Supplemental Surveys (Method 1622) yielded fewer zeros, but some locations still showed no positive counts.

Bayesian statistical techniques were used to estimate national *Cryptosporidium* and *Giardia* occurrence distributions that were consistent with measured results. The statistical model accounted for the volumes analyzed and the low but variable recoveries. Median estimates were produced for the national distribution of mean concentrations of *Cryptosporidium* and *Giardia* in water treatment plant influent. Uncertainties in these estimates were represented by 90% credible bands. These same techniques were used with data sets from the Supplemental Surveys to estimate occurrence in large and medium-sized systems. Distributions of *Cryptosporidium* occurrence derived from the two Supplemental Surveys and the ICR had medians near 0.02 oocysts/L, but the ICR survey yielded a greater location-to-location variance and predicted the greatest number of water sources with very high (more than 1 oocyst/L) and very low (less than 0.001 oocyst/L) occurrence.

INTRODUCTION

The first thing one notices about the Information Collection Rule (ICR) data on protozoa is the prevalence of zeros. Of the 5,838 samples of treatment plant influent tested, only 7% were positive for *Cryptosporidium* and only 19% were positive for *Giardia*. Of the 350 drinking water sources represented, 196 showed all zeros for *Cryptosporidium* and 122 showed all zeros for *Giardia*. Although the zeros may accurately reflect what the microscopists identified in the small sample volumes analyzed (half the samples consisted of less than 3 liters), they may not accurately reflect the quality of the full influent volumes from which they were taken. The same can be said of the less frequently occurring positive values. When a rare protozoan is found in a

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small sample volume, the reported concentration tends to overstate the level of occurrence in that source water. The ability of measurements to accurately characterize source water occurrence is further hampered by the measurement system's low and variable recovery ability.

These data seem ill suited for the purpose of characterizing *Cryptosporidium* and *Giardia* occurrence in ICR drinking water sources. Yet because of their large number, and with supplemental information on method performance and a suitable statistical model, they can be used to paint a picture of national protozoa occurrence.

This chapter describes the ICR data on protozoa, furnishes empirical estimates of occurrence, presents a statistical model, explains the estimation approach, and provides model-based estimates of occurrence. Model-based occurrence estimates are displayed with uncertainty bounds and are compared with empirical distributions. Supplemental Survey data were analyzed under a similar model, and the resulting national estimates are also compared with empirical distributions.

ICR MONITORING DATA

Summary Statistics

The data set from 18 months of ICR monitoring contains the results of 5,838 protozoan assays of influent water samples. Each assay produced data on volume analyzed and counts for *Cryptosporidium* (total oocysts, empty oocysts, and oocysts with an amorphous structure or an internal structure) and *Giardia* (total cysts, empty cysts, and cysts with an amorphous structure, an internal structure, or more than one internal structure). Counts were converted to concentration values. These concentrations were entered in the ICR Auxiliary Database 1, along with detection limits derived as the reciprocal of volume analyzed. Reporting units used in the database were organisms per 100 liters. These units convey a false impression that the volumes assayed were 100 liters. To avoid giving this impression and to be consistent with conventions for reporting environmental data, this chapter adopts reporting units of organisms per liter.

Tables 19.1 and 19.2 provide summary statistics for the ICR protozoa data. Mean values were computed both as the mean of the reported individual concentration (ΣConc/N) and as the total count divided by the total volume (ΣCount/ΣVol). In every case, the former estimate was

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greater than the latter estimate. This is because of the relationship between occurrence, turbidity, and volume analyzed. Figure 19.1 shows that as turbidity increased, volumes analyzed tended to decrease (making the sample more difficult to filter, process, and examine) and concentrations tended to increase. Summing the counts and dividing by the sum of the volumes, sometimes called the "Poisson mean," under-represents the small-volume, high-concentration samples and causes this estimate of the mean to be biased low compared with the simple mean. The simple mean of the concentration estimates gives each sample the same weight, regardless of volume analyzed. When followed by an adjustment for method recovery, the simple mean is an unbiased estimate.

Table 19.1

Summary statistics for ICR protozoa data

	Cryptosporidium			*Giardia*			
Statistic	Total	Nonempty	Internal structure	Total	Nonempty	Internal structure	More than one internal structure
Number of samples	5,838	5,838	5,838	5,838	5,838	5,838	5,838
Total count	1,206	753	281	6,926	4,013	1,346	927
ΣConc/*N**	0.067	0.037	0.011	0.268	0.134	0.029	0.019
ΣCount/ΣVol	0.020	0.013	0.005	0.105	0.067	0.022	0.015

* Concentrations are shown as organisms per liter.

Table 19.2

Statistics by ICR source water type

		Total *Cryptosporidium*		Total *Giardia*	
Main source-water type	Number of observations	Number (and %) positive	Mean concentration (oocysts/L)	Number (and %) positive	Mean concentration (cysts/L)
Not specified	308	16 (5.1%)	0.063	42 (14%)	0.316
Flowing streams	1,942	226 (11%)	0.147	624 (32%)	0.652
Groundwater under the direct influence of surface water	68	0 (0%)	0	3 (4.4%)	0.188
Mixed	107	19 (18%)	0.053	42 (39%)	0.210
Reservoirs/lakes	3,129	128 (4.1%)	0.025	324 (10%)	0.055
Unfiltered	284	11 (3.9%)	0.001	70 (25%)	0.022
All main source-water types	5,838	400 (6.8%)	0.067	1,105 (19%)	0.268

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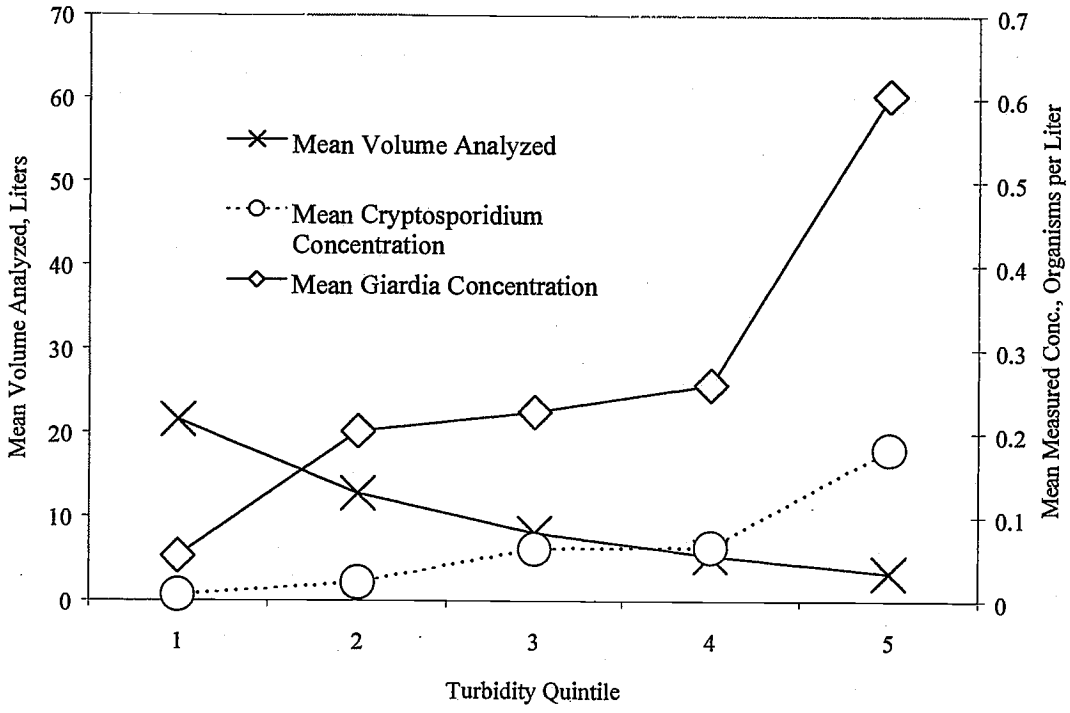

Figure 19.1 Protozoa concentrations increased and assayed volumes decreased as turbidity increased (mean turbidities for quintiles 1, 2, 3, 4, and 5 were 0.65, 1.8, 4.1, 9.4, and 59, respectively)

Performance of Analytical Method (Spiking Study)

In Chapter 20, Scheller et al. (2002) describe the design, implementation, and results of the U.S. Environmental Protection Agency's (USEPA's) 70-utility ICR Laboratory Spiking Program. This program was designed to provide information on how recoveries vary from lab to lab and from assay to assay. Recovery is often defined as the measured value of a spike divided by the spike's target value. In this analysis, recovery was defined differently—as the probability that an oocyst present in the sample would be identified and counted by the microscopist. If ICR protozoa recovery is modeled as a beta distribution with unknown parameters (α, β), the maximum likelihood values of these parameters (the values that provide the best agreement with the recovery data) are approximately 1.77 and 13.1 for total *Cryptosporidium* and 3.28 and 8.91 for *Giardia* (Messner 2000). Mean recovery associated with these parameter pairs is determined

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by dividing the first parameter by the sum of the two parameters, $\alpha/(\alpha+\beta)$. Based on this model, mean recoveries for *Cryptosporidium* and *Giardia* are therefore approximately 12% and 27%, respectively. Variance of recovery is represented by $\alpha\beta/((\alpha+\beta)^2(\alpha+\beta-2))$. Standard deviations of recovery for *Cryptosporidium* and *Giardia* are therefore approximately 9% and 14%. Coefficients of variation (standard deviation of recovery divided by mean recovery) are approximately 76% and 52%, respectively.

This information was used in two ways. First, for display purposes only, mean recoveries were used to adjust the mean concentrations observed in source water. Next, the parameterized *Crypotosporidium* and *Giardia* recovery distributions were incorporated into statistical models that were used in a Bayesian analysis to characterize national occurrence distributions and their uncertainties.

EMPIRICAL DISTRIBUTIONS

Figure 19.2 displays the observed distribution of mean concentrations of total *Cryptosporidium* and total *Giardia* found at ICR locations. The curves intersect the vertical axis at 0.56 and 0.38 because 196 of the 350 source waters produced all zeros for *Cryptosporidium* and 122 produced all zeros for *Giardia*. Because the empirical mean concentrations reflect considerable sampling and measurement errors, the (unknown) distribution of true source water mean concentrations should be less variable with fewer very high concentrations and fewer zeros. Estimating the occurrence distribution in a statistical framework requires a statistical model relating measurement result to occurrence and relating occurrence to location, time, source-water type, and turbidity.

STATISTICAL MODEL

Multilevel models are convenient tools to support inferences about the overall distribution of interesting quantities (like microbial concentrations) that are affected by global features (like seasonal and national trends), which may affect all sites, and local features (like water turbidity and watershed features), which may affect only a few.

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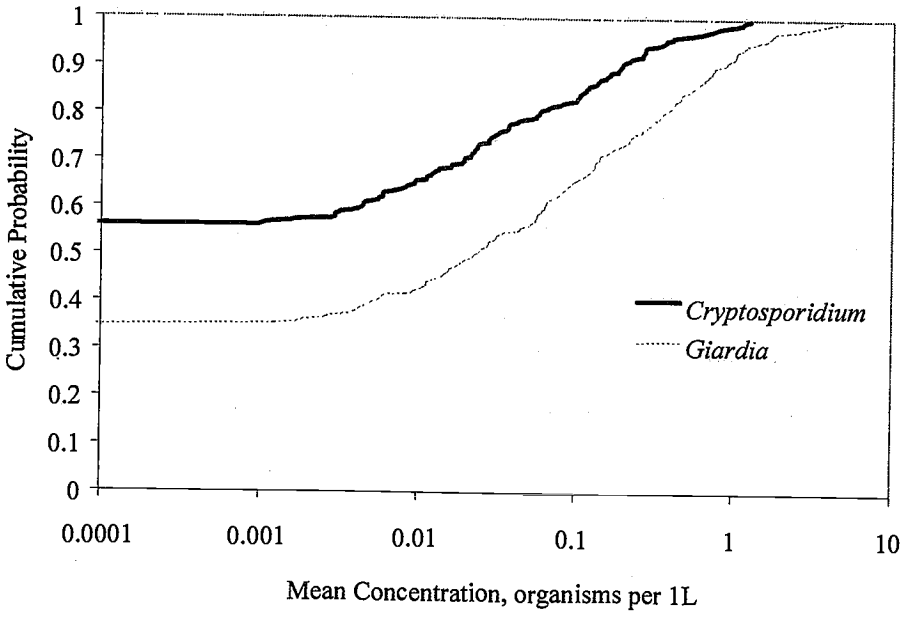

Figure 19.2 Observed (unadjusted) distribution of mean concentrations of *Giardia* and *Cryptosporidium* in water treatment plant influent

The model described in this chapter is constructed like an inverted tree with a single root, a number of branches, and many leaves. At the highest (root) level are the features that affect all locations and sampling times; these features are generally impossible to observe directly, but inferences can be made about them through their influence on observable features at lower levels of the model's hierarchy. At the middle (branch) level are features that are associated with individual locations or assay measurements but are not directly observable. At the lowest (leaf) level are observable features associated with each assay measurement, such as reported oocyst counts and sample volumes. The overall strategy for inference is to use information at each level to learn about unknown features in the higher levels.

The specific variables at the lowest (observed, assay-specific, "leaf") level include the 5,838 reported protozoan counts (Y_{ij}), each with a specified site (i, 1:350), sampling period (j, 1:18), volume assayed (V_{ij}, in liters), turbidity ($turb_{ij}$, in NTUs), and principal source-water type (MSW_{ij}, 1:5, representing flowing streams, reservoirs, and lakes, etc.).

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Limitations of the assay technique dictate that each protozoan in the sample has only an unknown chance of being reported; these recovery rates (r_{ij}) and the actual source-water protozoa concentrations (c_{ij}) are the variables at the middle (unobserved, location- or assay-specific, "branch") level of the model. At the top (root) level are parameters (a vector β of regression coefficients) needed to tie the lower two levels together, as described below.

In the model, reported oocyst counts (Y_{ij}) are treated as Poisson random variables with mean $\lambda_{ij} = V_{ij} * r_{ij} * c_{ij}$ given as a product of the sample volume (V_{ij}), the recovery rate (r_{ij}), and the source-water concentration (c_{ij}). A log-linear regression model describes concentration (c_{ij}) in functional form:

$$c_{ij} = \exp(\beta^0 + \beta^{tur} * \log(turb_{ij}) + \beta^{MSW}(MSW_{ij}) + \beta^{loc}{}_i + \beta^{mon}{}_j + \varepsilon_{ij})$$

The (top-level) vector β of regression coefficients includes an intercept term β^0 to reflect the overall average log concentration, a term $\beta^{tur} * \log(turb_{ij})$ proportional to the logarithm of turbidity, a term β^{MSW} that allows different source-water types to have different median concentrations, a term $\beta^{loc}{}_i$ that allows different locations to have different median concentrations, a term $\beta^{mon}{}_j$ that allows different months to have different median concentrations, and a residual term ε_{ij} embodying any remaining unmodeled variability.

To complete the model specification, probability distributions express the uncertainty about any unobserved quantities. The conditional distribution of these upper-level quantities is computed, given the observed values at the model's lowest level.

Independent data (ICR spiking and performance evaluation studies) suggest that the ICR protozoan method recovery rates (r_{ij}) vary randomly from one assay to another. For *Cryptosporidium*, these values average around 12% but vary greatly, for the most part falling between 1% and 30%. These recoveries are modeled as independent random variables with Beta probability distributions whose mean and geometric standard deviations match those from the spiking studies. Broad uncertainty about the regression coefficients (the βs) and the residuals (ε_{ij}), which in turn determine the concentrations (c_{ij}), is expressed using widely dispersed Student's *t* distributions.

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STATISTICAL ANALYSIS

The model just described includes a great many unobserved random variables: 375 regression coefficients (the β's), 5,838 residuals (ε_{ij}), and 5,838 recovery rates (r_{ij}). Conditional distributions of the unobserved variables are computed, conditional on the observed variables—counts (Y_{ij}), volumes (V_{ij}), and turbidities ($turb_{ij}$).

A simulation approach was used to evaluate these distributions and their means, making approximately 10,000 draws of the complete set of uncertain variables from their conditional probability distribution. Based on these draws, histograms were generated to represent the distributions, and averages were derived to estimate means. This technique is discussed by Casella and George (1992). BUGS software, used to conduct the simulation, is described by Gilks, Thomas, and Spiegelhalter (1994).

Analysis Plan

Numerous analytical runs were included in the statistical analysis plan to:

- provide separate estimates for different types of source water,
- provide estimates for nonempty cysts and oocysts,
- provide estimates for cysts and oocysts showing internal structure,
- test sensitivity to assumptions about the probability of false positives,
- test sensitivity to assumptions about the fraction of locations having true zero occurrence levels (source water that always has zero oocysts),
- do all of the above using Supplemental Survey data on large systems,
- do all of the above using Supplemental Survey data on medium-size systems, and
- challenge the model with artificial data (a quality-assurance check using known true distributions of mean concentrations in source water).

Table 19.3 lists a subset of the 140 analytical runs, showing what distinguishes each. The first six columns of the table describe the data set used and the type of source water and organism addressed. The seventh column, False Positive, is the model-assigned fraction of the count that is assumed to be algae or other objects mistakenly counted as protozoa. The eighth

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column, True Zero, is the portion of locations assumed to be oocyst-free all of the time. False Positive and True Zero are parameters that are set for each analytical run.

Experts do not agree on the appropriate concentrations for False Positive and True Zero. Results from the analysis of artificial-matrix blanks indicate the rate of false positive results may be in the range of 0 to 3% for total oocysts. To bracket the range of feasible false positive rates, analytical runs were conducted with false positive rates of zero, 1%, 2%, and 5%. Rates of 10%, 25%, and 50% were used only to assess the sensitivity of results to this parameter.

Some experts believe that protozoa are ubiquitous in surface water supplies and that no drinking water source is totally free of oocysts all of the time. Other experts suggest that some water sources contain protozoa concentrations below drinking water levels of concern and that such concentrations should be considered true zeros because they pose a negligible health risk. With this interpretation, some water sources may indeed have "practically zero" protozoa concentrations, producing positive results only when some other object is mistakenly counted as a protozoan (false positive). To cover the range of opinions, analytical runs were conducted with true zero rates of 0%, 0.1%, 1%, and 5%. To test the sensitivity of the results to this parameter, additional runs assumed true zero rates of 10%, 25%, and 50%.

Table 19.3

Selected runs from the data analysis plan

Run number	Data source	Data range (months)	Data subset	Source water	Pathogen	False positive (%)	True zero
3	ICR	18	All	All	Crypto	0	0%
4	ICR	18	All	All	Crypto	1	10^{-3}
4-prime	ICR	18	All, less 10	All	Crypto	1	10^{-3}
5	ICR	18	All	All	Crypto	1	10^{-3}
6	ICR	18	All	All	Crypto	1	10^{-3}
7	ICR	18	All	RS	Crypto	1	10^{-3}
10	ICR	18	All	RL	Crypto	1	10^{-3}
13	ICR	18	All	FS	Crypto	10	10^{-3}
27	ICR	18	All	All	*Giardia*	0	0
36a	Sup. Survey	12	40 systems	Large systems	Crypto	1	10^{-3}
36b	Sup. Survey	12	All	Medium systems	Crypto	1	10^{-3}
Sim1	Sim1	18	All	All	Crypto	0	0
Sim2	Sim2	18	All	All	Crypto	0	0

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Model-Based Estimates for *Cryptosporidium*

Each draw produced 350 × 18 = 6,300 concentration values, one for each monthly ICR sample of treatment plant influent. From these values, mean concentrations were computed for each location, producing a national distribution of mean concentrations of *Cryptosporidium* in source water. Ten thousand draws produced 10,000 national distributions. For 90% of these draws, the distribution of mean concentrations of *Cryptosporidium* fell within the credible bands displayed in Figure 19.3. The median distribution curve is shown between its 90% credible bands. For reference, this figure also includes the empirical distribution, adjusted upward for mean recovery by the analytical method. The empirical distribution indicates a slightly greater occurrence of high oocyst concentrations in source water (more than 1 oocyst/L) as well as a greater occurrence of mean concentrations less than 0.1 oocysts/L.

The predicted distributions are approximately lognormal in shape. Fitting lognormal distributions on the basis of the observed 25th and 75th percentiles, the parameters for the three curves are given in Table 19.4. Figure 19.4 shows that these probability density functions are bell-shaped when plotted on a log-scaled concentration axis.

Model-Based Estimates for *Giardia*

Eighteen-month mean concentrations of *Giardia* were computed for each ICR source water sampling location, and these mean concentrations were monitored as described for *Cryptosporidium*. For 90% of the simulation draws, the distribution of mean concentrations of *Giardia* fell within the credible bands displayed in Figure 19.5. The median distribution curve is shown between its 90% credible bands. As expected, the empirical distribution predicted a slightly greater occurrence of high concentrations (more than 100 cysts/100 L). Corresponding lognormal distribution parameters are given in Table 19.5, and probability density functions are shown in Figure 19.6.

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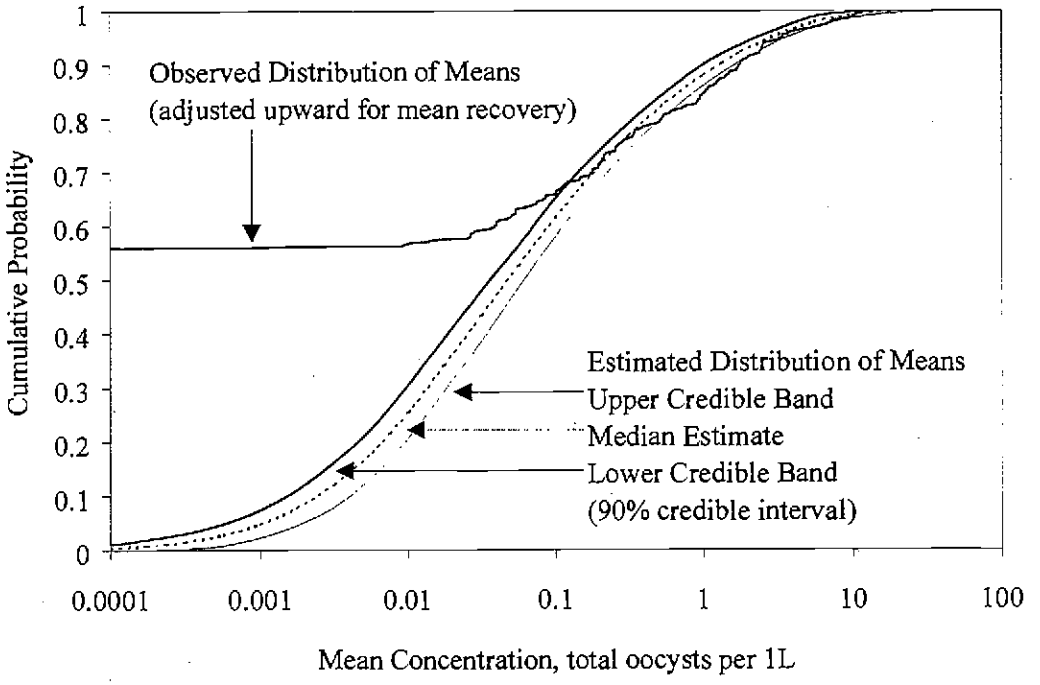

Figure 19.3 Estimated distribution of mean concentrations of *Cryptosporidium* in source water

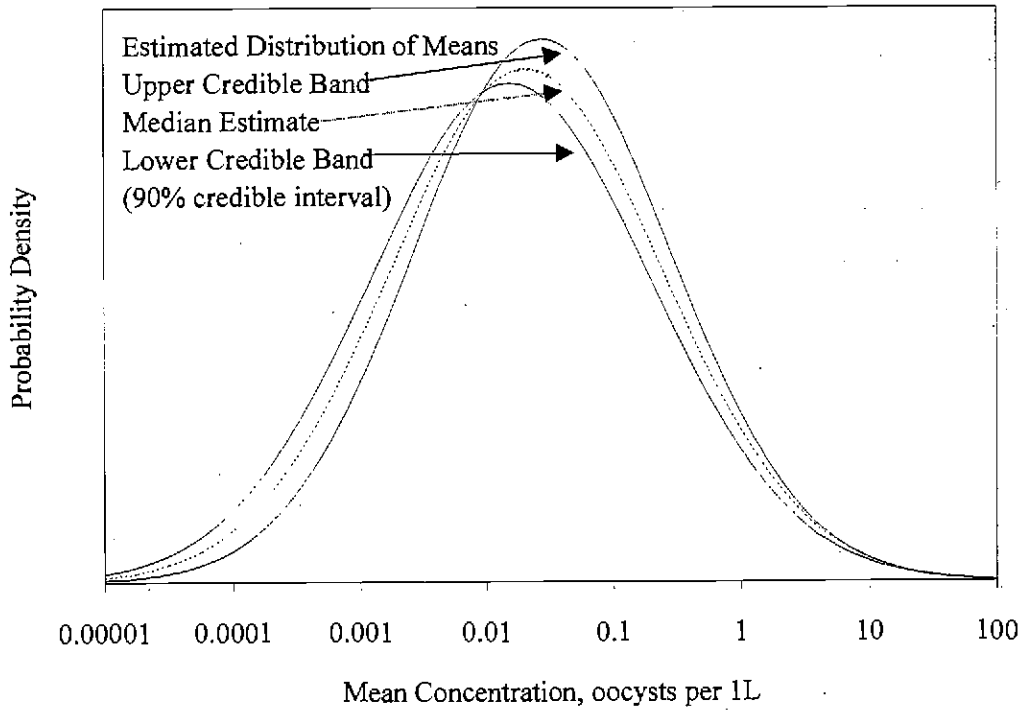

Figure 19.4 Estimated probability density function of mean concentrations of *Cryptosporidium* in ICR source water supplies

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Table 19.4

Parameters for lognormal distributions of mean concentrations of *Cryptosporidium*

Curve	1*n* (geometric mean)	1*n* (geometric standard deviation)
Median	–3.88	2.483
Lower band	–4.17	2.553
Upper band	–3.60	2.344

Table 19.5

Parameters for lognormal distributions of mean concentrations of *Giardia*

Curve	1*n* (geometric mean)	1*n* (geometric standard deviation)
Median	–3.24	3.027
Lower band	–3.49	3.197
Upper band	–3.10	2.889

Sensitivity Analyses

Many of the statistical analysis runs were planned to assess the sensitivity of results to changes in assumptions about false positive and true zero rates. A parameter was added to the model to account for false positive results. The value was set at 0%, 1%, 2%, 5%, 10%, 25%, and 50%. Estimated national distributions were found to be fairly insensitive to this parameter because large shifts in distribution accompanied only the largest false positive values.

A model parameter was added to allow some source water supplies to show exactly zero occurrence. Called the true zero, this rate was fixed at 0%, 1%, 5%, 10%, 25% and 50%. The impact of the true zero rate became obvious when the resulting national distribution estimates were viewed because the y intercept (the percentage of locations that had mean concentrations of less than 0.0001/liter) was nearly equal to the selected true zero rate. The upper half of the estimated distribution was affected very little by the true zero rate because most of these locations produced positive measurements, a result that would be highly unlikely if the concentration was always zero.

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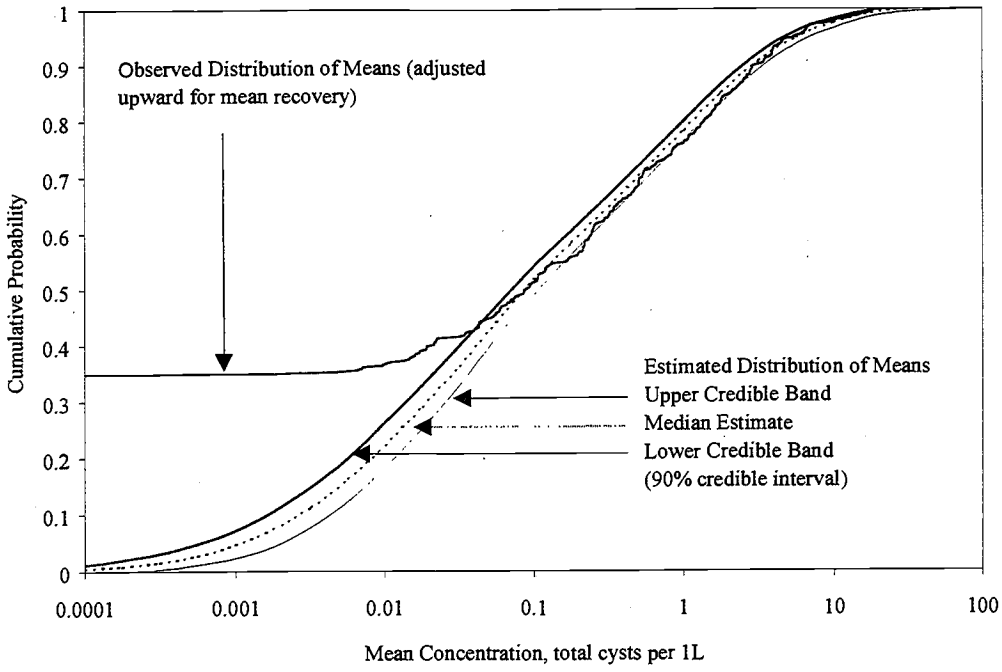

Figure 19.5 Estimated distribution of mean concentrations of *Giardia* in source water

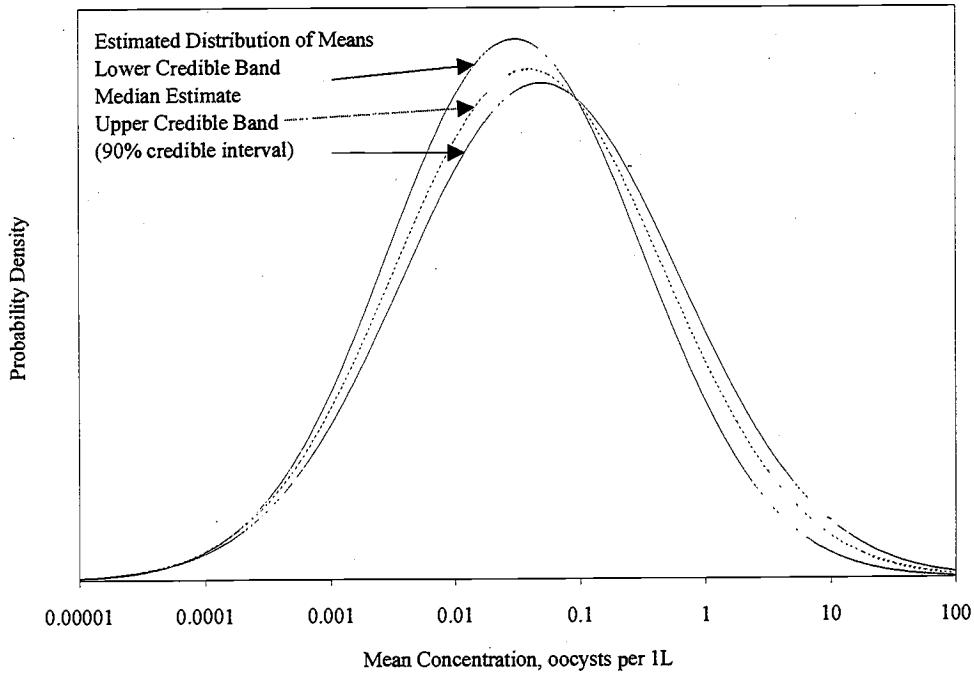

Figure 19.6 Estimated probability density functions of mean concentrations of *Giardia* in ICR source water supplies

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Quality Checks

Two artificial data sets were generated to challenge the data analysis program. The first set, Sim1, was generated using a statistical model that agreed very well with the model already described. Parameters β^0, β^{turb}, ϕ^{MSW}, ϕ^{loc}, ϕ^{month}, and ϕ^{resid} were selected at "reasonable" levels: $\beta^0 = \ln(0.03$ oocysts/L), $\beta^{turb} = 0$, $\phi^{MSW} = 2.04$, $\phi^{loc} = 1$, $\phi^{month} = 4$, and $\phi^{resid} = 1$. Other parameters and observed values were randomly selected, assuming normally distributed values for β^{MSW}, β^{loc}, β^{resid}, and εs. Volumes analyzed and turbidities were sampled from lognormal distributions having means and variances similar to those observed in the ICR data set. Recoveries were sampled from a beta distribution with paired parameters (1.77 and 13.1). Concentrations were derived and counts were simulated as Poisson random variables with parameters defined by the selected Vs, rs, and cs. The true distribution of source water mean concentrations was recorded but was not shared with the programmers. The only information revealed to the programmers was the simulated counts, volumes, turbidities, and main source-water types (1:4) identified by month (j = 1:18) and location (i = 1:400). Of the simulated counts, 95 % were zeros, and samples from 52% of the locations produced all zeros.

The statistical model provided a very reasonable estimate and credible bands for the distribution of source water mean concentrations. The true distribution curve fell entirely between the 90% credible bands. The analytical routine also produced reasonable estimates for the parameters. A set of estimates would have been judged unreasonable if an unusually large number of 90% credible intervals failed to include the true value or if any single true value fell very far outside its 90% credible interval.

The second artificial data set was generated with a true model that differed from the assumed model in an important aspect: the distribution of residuals (ε_{ij}) was gamma rather than normal. Figure 19.7 shows that the lognormal distribution having the same coefficient of variation as the chosen gamma has almost all of its probability mass above 0.01, whereas the gamma distribution has about 25% of its mass below 0.01. The effect of this is that the gamma density allows source water concentrations to be far below the mean much of the time, making nondetects (zeros) more common than with a lognormal distribution of occurrence.

Figure 19.8 shows that even with this deviation from the assumed model, the analytical program produced an accurate estimate of occurrence. The true and median distributions are

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almost indistinguishable in the figure. Estimates of monthly effects and other parameters were also reasonable. This ability to produce accurate estimates, even though the model is in some ways incorrect, is a good feature for any analytical model. Although no statistical model is perfect in describing an aspect of the environment, models that are robust against departures from underlying assumptions can produce useful, scientific estimates.

SUPPLEMENTAL SURVEY ESTIMATES

The Bayesian analytical method was applied to two Supplemental Survey data sets: one for large water systems and one for medium-size systems. Though smaller than the ICR data set, each Supplemental Survey data set produced distribution estimates comparable in quality (width of the 90% credible bands) to the distributions produced by ICR data.

Data from the Supplemental Survey of large systems predicted fewer occurrences of high and low concentrations of *Cryptosporidium* in source water (greater than 1 oocyst/L and less than 0.001 oocyst/L), revealing less location-to-location variability than indicated by the ICR data. Data from the Supplemental Survey of medium-size systems predicted slightly more frequent occurrences of high *Cryptosporidium* concentrations than data from the Supplemental Survey of large systems but fewer than the ICR data. Figure 19.9 shows that the Supplemental Surveys' estimated median concentrations of *Cryptosporidium* agree fairly well with the median concentration estimated from ICR data, approximately 0.02 oocysts/L. Although the curves agree very well in the center, they differ in the tails. This difference could be explained as a true difference in occurrence between different sampling years. It is possible, however, that some or all of the difference is due to the unknown number of false positives and false negatives included in the ICR data set. Other explanations are also possible. Until more information is available, analysts may want to consider all three estimates as potentially valid representations of the national distribution of *Cryptosporidium* occurrence.

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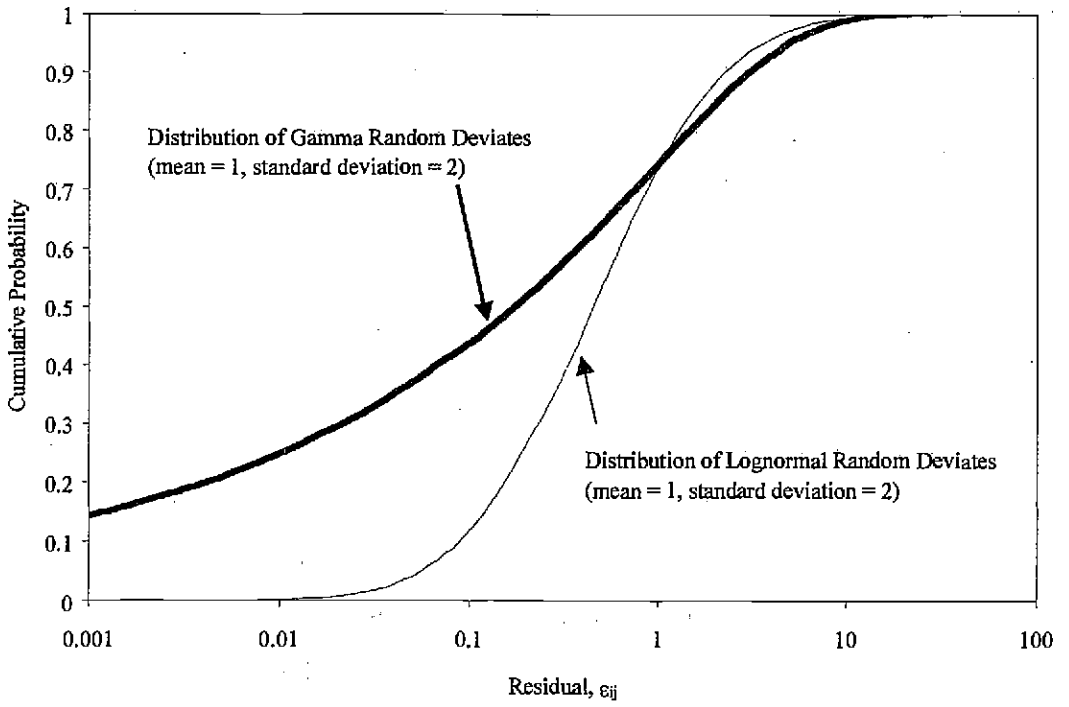

Figure 19.7 Lognormal and gamma distributions differ in shape

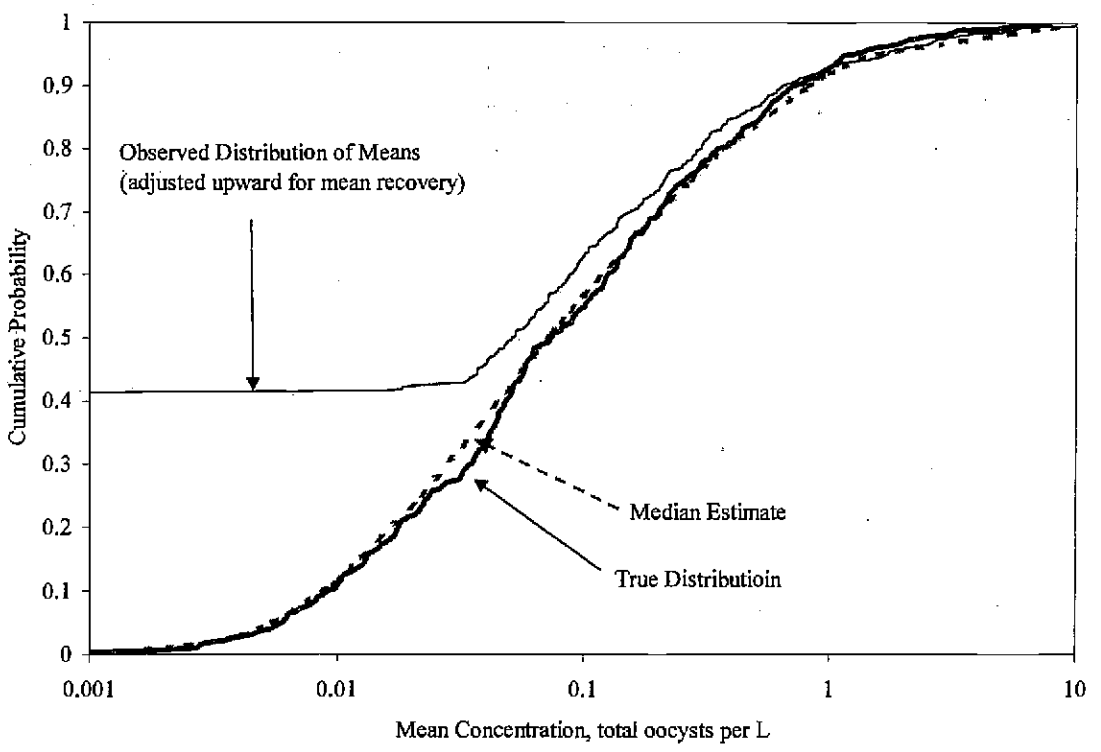

Figure 19.8 Estimated distribution matched the true distribution of the challenge data set

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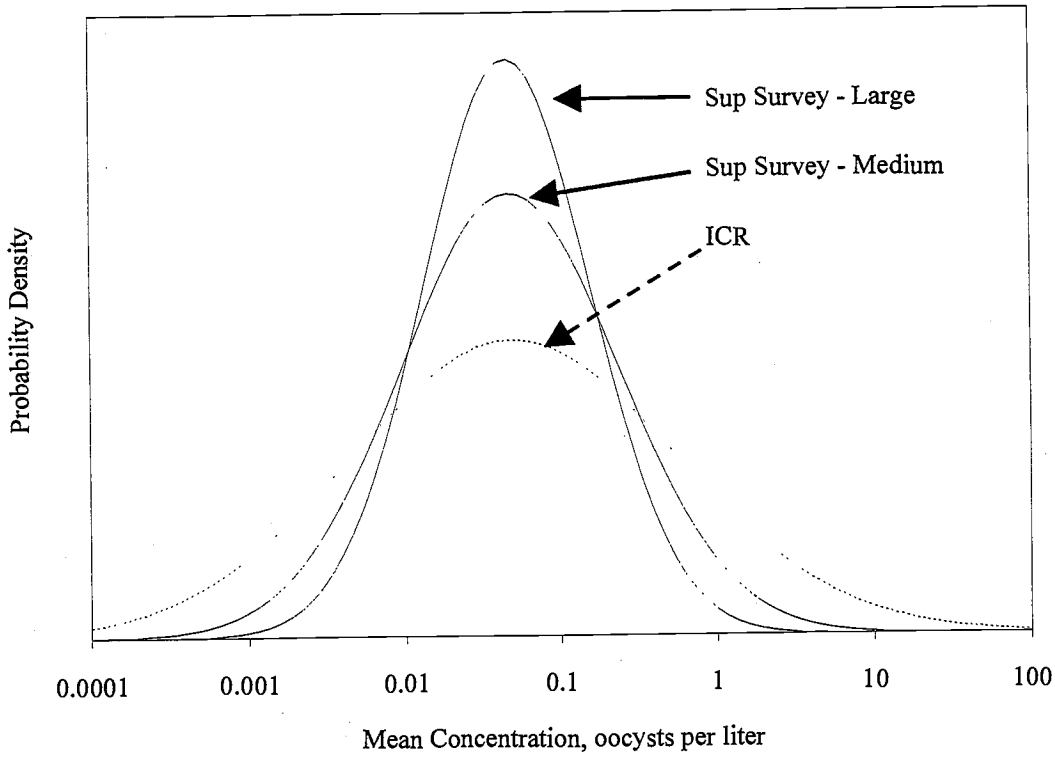

Figure 19.9 Distribution of national *Cryptosporidium* occurrence estimates derived from three surveys

CONCLUSIONS

Because of low occurrence concentrations, small sample volumes, and low and variable recoveries associated with the analytical methods, most ICR measurements of *Cryptosporidium* and *Giardia* were negative, and many locations produced nothing but zero results over the duration of ICR monitoring. The greater median volumes analyzed and the higher recoveries achieved with the method used in the Supplemental Surveys (Method 1622) yielded fewer zeros, but some locations still showed no positive counts.

Bayesian statistical techniques were used to estimate national protozoa occurrence distributions that were consistent with measured results. The statistical model accounted for volumes analyzed and the low but variable recoveries. Ninety percent credible bands were produced for the national distribution of mean concentrations of *Cryptosporidium* and *Giardia* in water treatment plant influent. These same techniques were used with data sets from the

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Supplemental Surveys to estimate occurrence in large and medium-size systems. Occurrence distributions derived from the two Supplemental Surveys and the ICR all had medians near 0.02 oocysts/L, but the ICR survey yielded a greater location-to-location variance and predicted the greatest number of water sources with very high (more than 1/liter) and very low (less than 0.001/liter) occurrence.

Although these analyses suggest that protozoa distributions in source water differ, they don't provide a statistical explanation for these differences. Credible bands overlap near the medians but do not overlap at the extremes. The extreme percentiles are not likely to differ because of chance alone. The statistically significant differences could be due to true differences in occurrence (i.e., national occurrence could have been more variable during the earlier time frame of the ICR survey). Another possible explanation involves fundamental differences in protozoan measurement methods whose recovery capabilities are not fully understood.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The scientific views expressed are solely those of the authors and do not necessarily reflect those of USEPA.

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CHAPTER 20

DESIGN, IMPLEMENTATION, AND RESULTS OF USEPA'S 70-UTILITY ICR LABORATORY SPIKING PROGRAM

Jennifer Scheller, Kevin Connell, Heather Shank-Givens, and Crystal Rodgers

ABSTRACT

The analytical method used to determine the occurrence of protozoa during implementation of the Information Collection Rule (ICR) was characterized by low and highly variable recoveries, particularly for *Cryptosporidium.* Consequently, protozoa counts from samples collected under the ICR are likely to be inaccurate estimates of actual *Cryptosporidium* and *Giardia* occurrence and concentrations. The U.S. Environmental Protection Agency's (USEPA's) Office of Ground Water and Drinking Water designed the ICR Laboratory Spiking Program to estimate average recoveries of *Cryptosporidium* and *Giardia* achieved under the ICR. On two sampling dates during the last eight months of ICR monitoring, 70 of the ICR water treatment plants collected an additional source water sample at the same time as their regular ICR source water sample. The 140 additional samples were spiked and analyzed along with the regular ICR samples, and the results were used to calculate average recoveries for *Cryptosporidium* and *Giardia.*

The Laboratory Spiking Program tested the ICR protozoan method using field samples that were spiked with 5,000–10,000 oocysts and cysts and processed in accordance with the protocol for the ICR protozoan method. Based on analytical results from the 140 spiked ICR samples, the mean recovery and standard deviation achieved for *Cryptosporidium* was 12%±11%, and the mean recovery and standard deviation for *Giardia* was 26%±17%.

Protozoa recoveries achieved in the Laboratory Spiking Program were highly variable. No statistically significant difference could be demonstrated for mean recoveries of *Cryptosporidium* or for variances in *Cryptosporidium* and *Giardia* recoveries among laboratories. However, significant differences in mean recoveries of *Giardia* occurred among laboratories. These differences may have been due to method variability, laboratory performance, matrix effects, or a combination of these factors.

INTRODUCTION

The Laboratory Spiking Program (LSP) was part of the Information Collection Rule's (ICR's) nationwide research effort to support development of future drinking water regulations. Because the analytical method used to determine the presence of protozoa in ICR samples exhibited low and highly variable recovery rates, particularly for *Cryptosporidium* (U.S. Environmental Protection Agency [USEPA] 1996a; Clancy, Gollnitz, and Tabib 1994; Clancy et al. 1999), there was

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concern that the ICR data could underestimate national distributions of protozoa occurrence. Given that these national estimates were intended to provide key inputs for development of the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR), there was also concern that they might lead to significant underestimates of the level of treatment required under various regulatory scenarios as well as underestimates of compliance costs.

In response to the low recovery rates of the ICR protozoan method and other data needs, USEPA developed and funded two studies to complement the ICR: (1) the ICR Supplemental Surveys and (2) the LSP. The Supplemental Surveys, conducted between March 1999 and April 2000, collected protozoan and water quality data from large, medium-size, and small water systems and attempted to address the ICR protozoan method's low recovery rates by estimating source water protozoan concentrations with improved analytical methods. The purpose of the LSP was to generate a statistically valid measure of the mean analytical recovery rates achieved during the last eight months of ICR protozoan monitoring. These data were then used as part of a Bayesian analysis conducted to model the occurrence of *Cryptosporidium* and *Giardia* in source water.

METHODS AND MATERIALS

Program Design

Under the ICR, 355 drinking water treatment plants filtered 100-L samples of source water at their influent point and sent the filters to approved ICR laboratories to be analyzed for protozoa. Under the LSP, a systematic random sample of 70 ICR plants collected an additional 100-L, bulk-volume sample at the same time as their ICR source water sample on two sampling dates during the last eight months of ICR monitoring.

The ICR sample was filtered in the field and shipped to the plant's routine protozoan laboratory for analysis; the additional, 100-L LSP sample was shipped in bulk to a central USEPA contract laboratory. The bulk sample was spiked with a suspension of viable *Cryptosporidium* oocysts and *Giardia* cysts that had been counted by means of a hemacytometer enumeration technique identical to that used to enumerate organisms for the ICR performance evaluation (PE) samples. The central laboratory filtered the spiked sample through a yarn-wound filter using the

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same filtration procedure and filter type used for the parallel ICR field sample. The spiked filter was shipped to the plant's routine protozoan laboratory for analysis alongside the corresponding unspiked ICR sample. The laboratory analyzed both samples using the ICR protozoan method.

The ICR protozoan laboratories submitted the LSP data to a central sample control center, operated by DynCorp under contract to USEPA, where the data were reviewed and validated prior to submission to USEPA. Figure 20.1 shows the flow of samples and data among the parties that participated in the LSP.

Selection of Plants and Laboratories

The 70 plants recruited to participate in the LSP were drawn from the 355 plants in the ICR Classification List. The sample design for plant selection was systematic with a random starting point: the 355 plants were sorted by laboratory used for protozoa analyses; a random starting point was set; and then a set of 70 plants was systematically selected. This selection was performed two additional times (the second and third draws served to replace plants that could not participate in the study). Plants selected in the previous draw(s) were excluded from subsequent draws. In addition to the sample design for randomly selecting plants, a second sample design was used to randomly select the two LSP sampling months to provide for a range of matrices over time. After the list of participating laboratories was compiled, a systematic design with a random start was used to ensure that the laboratories would not be overburdened by too many samples in a given month. Plants and laboratories that participated in the LSP are listed in Table 20.1.

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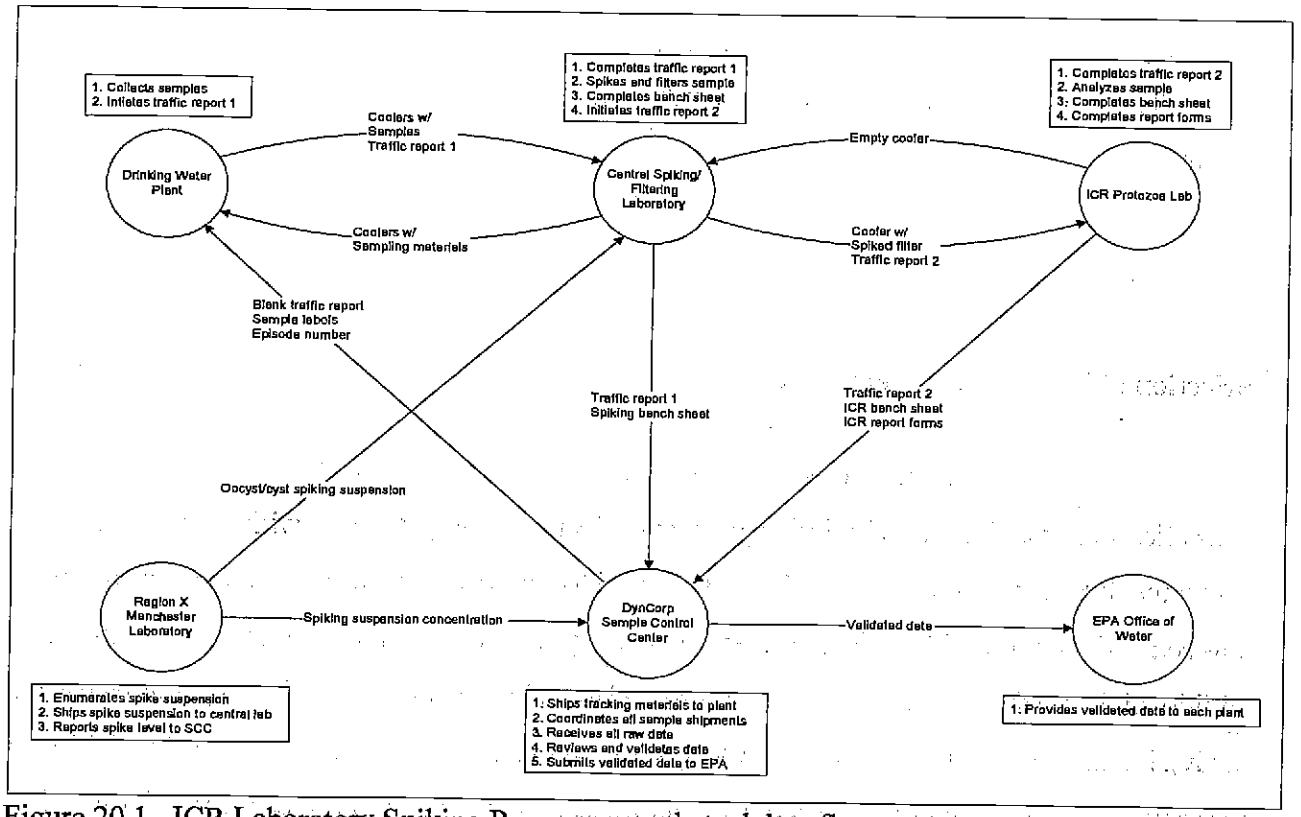

Figure 20.1 ICR Laboratory Spiking Program sample and data flow

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Table 20.1

Utilities and laboratories participating in the ICR Laboratory Spiking Program

Utility	Laboratory used for protozoa analyses
Illinois-American Water Co.—Peoria District	American Water Works Services Co., Inc
Kentucky-American Water Co.	American Water Works Services Co., Inc
Anchorage Water & Wastewater Utility	Analytical Services, Inc.
BHC Company	Analytical Services, Inc.
City of Austin	Analytical Services, Inc.
City of Fort Worth Water Department	Analytical Services, Inc.
City of Melbourne Water Production	Analytical Services, Inc.
Duke Power Company	Analytical Services, Inc.
Greenville Water System	Analytical Services, Inc.
Lincoln Water System	Analytical Services, Inc.
Little Rock Municipal Water Works	Analytical Services, Inc.
Metro Water Services	Analytical Services, Inc.
Mobile Area Water and Sewer System	Analytical Services, Inc.
North Jersey District Water Supply Commission	Analytical Services, Inc.
Sierra Pacific Power Company	Analytical Services, Inc.
Trenton Water Works	Analytical Services, Inc.
Winston-Salem/Forsyth County	Analytical Services, Inc.
Alameda County Water District	BioVir Laboratory
Birmingham Water Works	BioVir Laboratory
New Orleans Sewerage & Water Board	BioVir Laboratory
San Francisco Water Department	BioVir Laboratory
Tacoma Public Utilities	BioVir Laboratory
Washington Suburban Sanitary Commission	BioVir Laboratory
Zone 7 Water Agency	BioVir Laboratory
Brownsville Public Utilities Board	CH Diagnostic & Consulting Services, Inc.
City of Aurora, Utilities Department	CH Diagnostic & Consulting Services, Inc.
City of Scottsdale—Water Resources	CH Diagnostic & Consulting Services, Inc.
Cleveland Division of Water	CH Diagnostic & Consulting Services, Inc.
Cucamonga County Water District	CH Diagnostic & Consulting Services, Inc.
Helix Water District	CH Diagnostic & Consulting Services, Inc.
Providence Water Supply Board	CH Diagnostic & Consulting Services, Inc.
Saginaw Water Treatment Plant	CH Diagnostic & Consulting Services, Inc.
Salem Public Works Department	CH Diagnostic & Consulting Services, Inc.
Phoenix Municipal Water System	City of Phoenix
City of San Diego	City of San Diego
City of Baltimore Bureau of Water & Waste	Clancy Environmental Consultants, Inc
Dallas Water Utilities	Clancy Environmental Consultants, Inc
Philadelphia Water Department	Clancy Environmental Consultants, Inc
East Bay Municipal Utility District	East Bay Municipal Utility District
Ann Arbor Utilities Department	Environmental Associates Ltd.
City of Atlanta, Bureau of Water	Environmental Associates Ltd.
City of Brockton, DPW Utilities Department	Environmental Associates Ltd.
City of Columbus, DPU	Environmental Associates Ltd.
City of Detroit Water & Sewerage Department	Environmental Associates Ltd.
City of Jackson	Environmental Associates Ltd.
City of Los Angeles	Environmental Associates Ltd.
City Utilities of Springfield	Environmental Associates Ltd.

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Table 20.1 (continued)

Utility	Laboratory used for protozoa analyses
Macon Water Authority	Environmental Associates Ltd.
Metropolitan Lancaster Authority	Environmental Associates Ltd.
Ponce Urbano	Environmental Associates Ltd.
Regional Water Authority	Environmental Associates Ltd.
San Juan Metropolitan	Environmental Associates Ltd.
San Juan Water District	Environmental Associates Ltd.
Washington Aqueduct Division	Environmental Associates Ltd.
Massachusetts Water Resources Authority	Erie County Water Authority
Indianapolis Water Company	Indianapolis Water Company
Metropolitan Water District of Southern California	Metropolitan Water District of Southern California
Evanston Water Department	Milwaukee Health Department
Jefferson Parish Water Department	Milwaukee Health Department
City of New York DEP	New York City DEP
City of Wichita Falls	NSF International
Pennsylvania-American Water Company	Pennsylvania American Water Company
Southern Nevada Water System	Southern Nevada Water System
United Water New Jersey	United Water New Jersey
Akron Public Utilities Bureau	University Hygienic Laboratory
City of Abilene Water Utilities	University Hygienic Laboratory
City of Topeka Water Utilities Division	University Hygienic Laboratory
Lawton Water Treatment Plants	University Hygienic Laboratory
Upper Mohawk Valley Regional Water Board	Upper Mohawk Valley Regional Water Board
Salt Lake City Corporation, DPU	Utah Department of Health

Collection and Shipment of Source Water Samples

Participating plants used a Y-connector to collect the 100-L LSP source water sample and the plant's monthly ICR source water sample as split samples. The Y-connector allowed the 100-L grab sample to be collected while the ICR sample was being filtered. LSP sample collection began halfway through the process of filtering the ICR sample (approximately 10 minutes into the 20-minute filtering process). Temperature, turbidity, and pH were measured in the field and recorded along with the time, date, and location of sample collection on an LSP sample traffic report. The 100-L grab sample was collected in five 20-L cubitainers. Each cubitainer was packed into an individual, insulated cooler with two 8-lb. bags of ice. If the ICR plant was unable to ship the cubitainers immediately after sample collection, the cubitainers were stored in a refrigerator or in the coolers with ice, and the ice was replaced prior to shipment. The plant shipped the LSP sample to the Central Spiking/Filtering Laboratory via priority overnight service and shipped the routine ICR sample collected at the same time to the assigned protozoan laboratory.

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Central Laboratory Spiking, Filtering, and Shipping Procedures

To reduce variability in sample spiking, a single laboratory served as the Central Spiking/Filtering Laboratory for the LSP. Pacific Analytical Incorporated (PAI Inc.), a Carlsbad, Calif., laboratory under contract with the USEPA Office of Water's Engineering and Analysis Division, fulfilled this role. This laboratory was responsible for homogenizing, spiking, and filtering the bulk 100-L source water samples and for shipping the spiked, filtered samples to the appropriate ICR protozoan laboratories for analysis. PAI Inc. used a spiking and filtering system that had been bench-tested by USEPA Region 10's Manchester Environmental Laboratory in Port Orchard, Wash. (USEPA 1998).

The Central Spiking/Filtering Laboratory spiked and filtered each 100-L source water sample using the system shown in Figure 20.2. The 100-L sample contained in five 20-L cubitainers was combined in a 30-gal mixing tank. The sample was pumped through the filter at a rate of 4.0 L/min, according to the ICR protozoan sample collection protocol (USEPA 1995). The enumerated spiking suspension was diluted with 2 L of reagent water, and this solution was spiked into the line between the mixing tank and the filter at an approximate rate of 150 mL/min as the sample was being filtered. Once the 2-L diluted spiking suspension was almost gone, an additional 1 L of reagent water was pumped through the spiking line to ensure that the line was well rinsed. After sample spiking and filtering were complete, the filter was shipped overnight on ice to the designated protozoan laboratory to be analyzed alongside the unspiked sample.

The Central Spiking/Filtering Laboratory followed a decontamination protocol to mitigate carryover of protozoa from one sample to another; this protocol included discarding all tubing after each sample was processed. The central laboratory also processed positive and negative control samples once per week and sent these samples to USEPA Region 10's Manchester Environmental Laboratory for analysis to confirm that no organisms could be detected in negative samples and to compare ongoing system performance with initial system validation results. The central laboratory also conducted dye tests of the system to confirm proper flow patterns and mixing.

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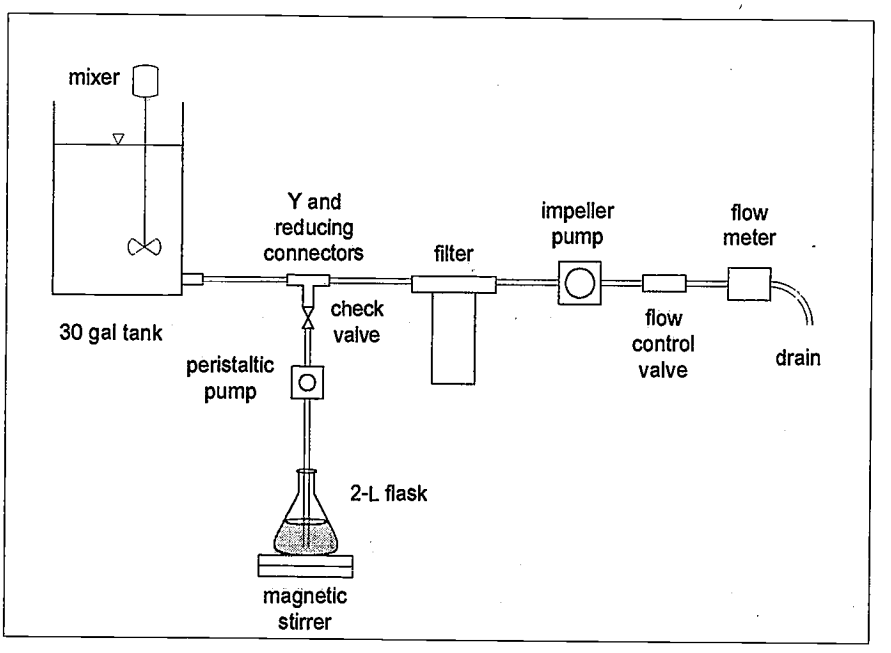

Figure 20.2 Design of spiking and filtering system

Sample Analysis

The ICR protozoan laboratories processed and analyzed each spiked, filtered sample according to the ICR Protozoan Method for Detecting *Giardia* Cysts and *Cryptosporidium* Oocysts in Water, a fluorescent antibody procedure described in the *ICR Microbial Laboratory Manual* (USEPA 1996b), except for the following additional requirements:

- Confirm the first 10 presumptive oocysts and cysts examined in each sample using differential interference contrast microscopy, and report the required characterization data. Count the remaining presumptive oocysts and cysts without confirmation and include them in the total number of cysts and oocysts reported.
- Begin analyzing samples within 96 hours of their being filtered at the central laboratory.
- Have the same analyst and principal analyst analyze both the spiked LSP sample and its corresponding ICR sample.

The ICR protozoan laboratories processed LSP samples and monthly ICR samples according to the same quality control procedures and the same analytical sequence, as defined in the *ICR*

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Microbial Laboratory Manual, including the analysis of positive and negative control samples and PE samples.

Preparation of Spiking Suspensions

The same procedures used to prepare PE samples for the ICR were used to prepare the spiking suspensions for the LSP (USEPA 1998). The spiking suspensions, which were enumerated using hemacytometer counts, were considered acceptable if the count did not deviate more than 50% from the expected number. After direct antibody staining, the stained cysts and oocysts in the suspension were counted, and these counts were compared with the original counts. If variability between the two counts was less than 20% (i.e., >80% staining), the protozoa suspension was considered acceptable.

Two target spike levels were used during the LSP. During the first four months, "low" spikes of approximately 5,000 organisms were used. During the last four months, "high" spikes of approximately 10,000 organisms were used. Enumeration data from the high- and low-spike periods are summarized in Table 20.2.

USEPA Region 10's Manchester Environmental Laboratory provided the enumeration results for each batch of spiking suspensions to the sample control center for use in calculating spiked sample recoveries. To reduce bias in the sample analyses, the analytical laboratories were blind to the concentration used by the Central Spiking/Filtering Laboratory to spike the filters.

Table 20.2

Summary of spike enumeration data from the ICR Laboratory Spiking Program

	Low-spike period				High-spike period			
	Cryptosporidium		*Giardia*		*Cryptosporidium*		*Giardia*	
	Mean recovery	Relative standard deviation	Mean recovery	Relative standard deviation	Mean recovery	Relative standard deviation	Mean recovery	Relative standard deviation
Average	5,273	14%	5,366	16%	10,354	15%	10,118	15%
Median	5,077	14%	5,023	13%	10,183	13%	9,998	13%
Minimum	4,473	10%	4,804	10%	9,997	11%	9,991	11%
Maximum	7,553	22%	6,426	30%	11,051	24%	10,484	23%

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Data Review

The Central Spiking/Filtering Laboratory and the ICR protozoan laboratories submitted their data to the DynCorp sample control center, where the data were reviewed for completeness using data review guidelines and checklists based on the requirements of the ICR protozoan method and on the Central Spiking/Filtering Laboratory's requirements. After review, the original data recorded by the laboratories were entered into a database designed for the LSP. After all information was transferred into the database, a report of the database entries was generated and used to verify that the data had been entered correctly. If data entry mistakes were found, the correct data were entered, and the data entry review process was repeated for those entries.

In addition to maintaining analytical results for data analysis, the LSP database ran the following automated checks:

- The database recalculated the protozoa concentrations reported by the analytical laboratory to confirm that the laboratory's results were correct.
- The database calculated the *Cryptosporidium* and *Giardia* recoveries for each sample based on the concentration reported by the analytical laboratory and the spiking suspension concentration reported by USEPA Region 10.

Data Analysis

LSP *Cryptosporidium* and *Giardia* recoveries were calculated by subtracting the concentration of cysts and oocysts per 100 L measured in the unspiked ICR sample from the concentration of the corresponding spiked LSP sample, then dividing the result by the number of cysts or oocysts spiked per 100 L.

Based on results from the 140 spiked samples, overall mean recoveries, and standard deviations, relative standard deviations (calculated as the standard deviation divided by the mean) were calculated for *Cryptosporidium* and *Giardia*. Mean recoveries and standard deviations were calculated for each plant and laboratory that participated in the LSP. Similar to earlier analyses conducted by Messner (1999), analysis of variance (ANOVA) tests were performed for *Giardia* and *Cryptosporidium* results to test whether different laboratories demonstrated different performance characteristics. An ANOVA overall F test ($\alpha = 0.01$) was conducted to determine if laboratories had

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achieved a common mean recovery for *Cryptosporidium* or *Giardia*. To identify which laboratories, if any, had significantly different mean recoveries, pairwise comparisons were run using the Tukey-Kramer method (α = 0.01) to compare mean recoveries for each laboratory pair. Tests for homogeneity of variance were also run for *Cryptosporidium* and *Giardia* results from each pair of labs using individual F-tests (α = 0.00005 to achieve an overall error rate of 0.01) for constant variance.

RESULTS AND DISCUSSION

Results of the Laboratory Spiking Program

The mean recovery of *Cryptosporidium* from the 140 spiked samples was 12%, with a standard deviation of 11%. Recovery of *Giardia* was generally higher, characterized by a mean recovery of 26% and a standard deviation of 17%. In addition to the variability across all samples, intra-utility and inter-utility variability were high, as indicated by the mean recoveries and standard deviations for the 70 plants participating in the LSP (Figure 20.3). Mean *Cryptosporidium* recoveries for the LSP plants ranged from 0% to 41%, and standard deviations ranged from 0% to 39%. Mean *Giardia* recoveries for the LSP plants ranged from 2% to 68%, and standard deviations ranged from 0.2% to 35%. Overall analytical results for the 140 LSP samples are summarized in Table 20.3.

Table 20.3

Summary of LSP analytical results

	Volume analyzed (L)	*Cryptosporidium* recovery (%)	*Giardia* recovery (%)	Turbidity (NTU)
Mean	8	12	26	21
Median	4	9	24	2.5
Minimum	0.02	0	0	0
Maximum	105	65	83	1,200
Standard deviation	15	11	17	107
Relative standard deviation	174%	96	65	513%

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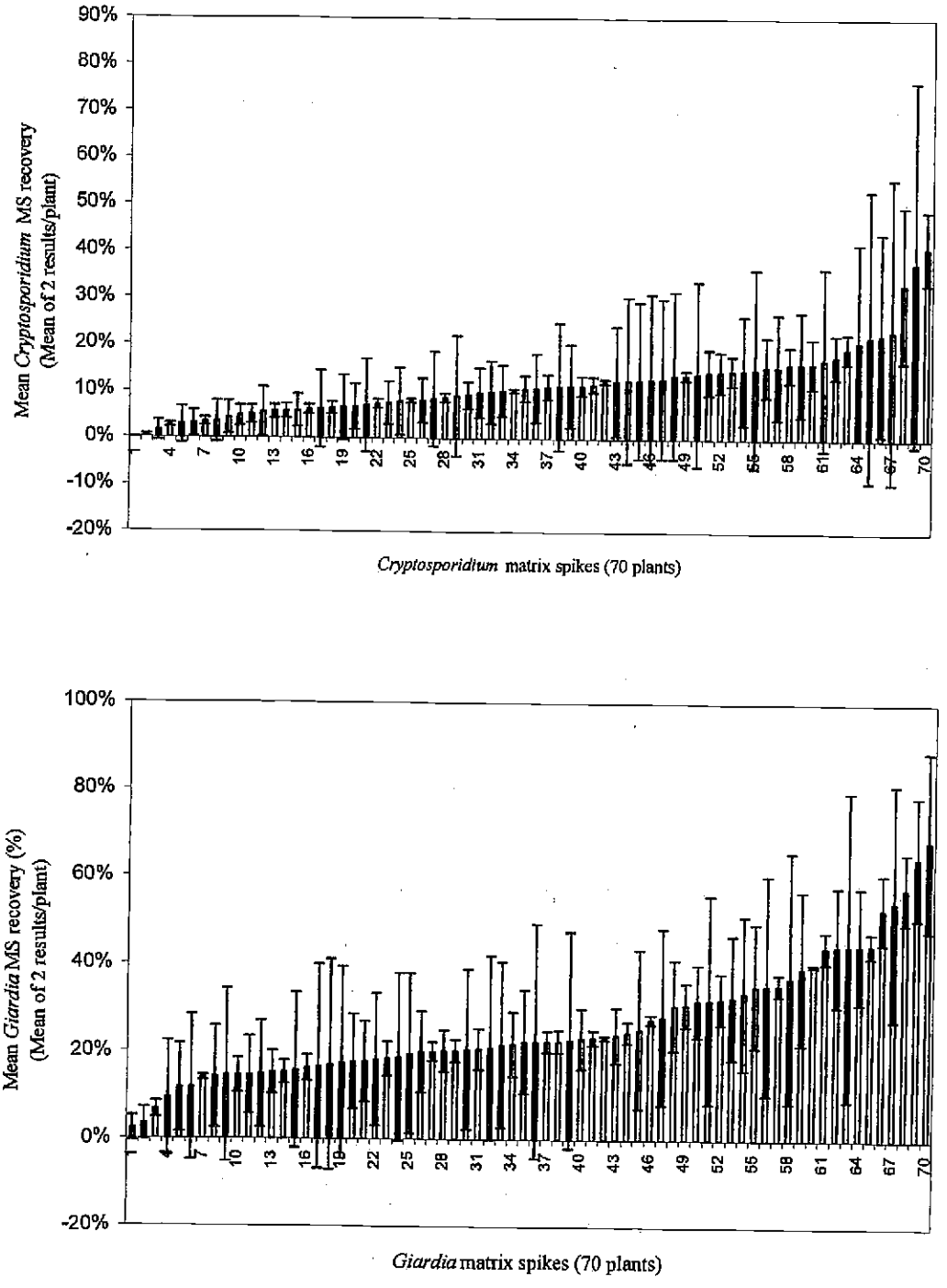

Figure 20.3 ICR Laboratory Spiking Program Plant Mean *Cryptosporidium* and *Giardia* matrix spike (MS) recoveries

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Evaluation of Intra- and Inter-Laboratory Variability

Twenty-one ICR protozoa laboratories analyzed the samples collected by the LSP plants. Table 20.4 provides mean volumes analyzed, mean recoveries, standard deviations, and relative standard deviations for each of these laboratories. Mean *Cryptosporidium* recoveries at the labs ranged from 6% to 19%, and the standard deviations ranged from 1% to 22%. Mean *Giardia* recoveries at the labs ranged from 7% to 68%, and the standard deviations ranged from 2% to 29%.

Table 20.4

Summary of LSP laboratory volumes analyzed and percent recoveries

			Cryptosporidium recovery			*Giardia* recovery		
Laboratory	Number of samples analyzed	Mean sample volume analyzed (L)	Mean (%)	SD* (%)	RSD† (%)	Mean (%)	SD* (%)	RSD† (%)
1	2	4.27	11	9	82	68	21	30
2	2	12.44	4	3	80	24	6	27
3	2	4.38	11	3	23	7	2	28
4	14	10.95	9	6	74	21	12	58
5	2	13.40	14	4	30	37	29	77
6	18	7.94	9	8	98	18	15	82
7	9	0.90	19	15	81	35	24	70
8	4	1.48	18	22	124	7	11	158
9	2	0.69	13	18	141	17	24	141
10	2	15.44	15	12	79	22	12	53
11	2	4.11	10	5	54	44	14	31
12	2	20.59	11	3	26	35	2	7
13	2	44.10	5	2	44	19	19	102
14	2	20.55	8	5	61	15	9	61
15	2	103.99	6	1	17	20	3	12
16	29	3.08	14	14	95	24	10	41
17	2	1.80	10	5	55	15	4	27
18	2	30.89	13	12	93	32	24	74
19	6	7.57	6	7	115	21	16	77
20	30	4.09	12	12	97	33	17	51
21	4	10.96	7	4	64	39	24	61

* SD = standard deviation
† RSD = relative standard deviation

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For *Cryptosporidium,* the hypothesis of a common mean recovery could not be rejected (based on the ANOVA overall F test at the 0.01 significance level). For *Giardia,* the hypothesis of a common mean recovery was rejected (based on the overall F test at the 0.01 significance level). The pairwise comparisons using the Tukey-Kramer method (at the overall 0.01 significance level) identified two laboratory pairs with significantly different mean recoveries of *Giardia*. The mean recovery of *Giardia* at Laboratory 1 was significantly higher than the mean recoveries of *Giardia* at Laboratories 6 and 8.

Tests for homogeneity of variance did not identify any laboratory pairs that were significantly different for *Giardia* or *Crytposporidium.*

Given the variability of recoveries achieved by the ICR protozoan method and the small number of samples analyzed by most of the laboratories participating in the LSP (many only analyzed two samples), it is difficult to determine whether any differences in laboratory performance occurred. The few differences in mean recoveries observed among the laboratories could be attributed to one or more of the following factors:

- Differences in laboratory performance,
- Inherent variability in the ICR protozoan method, and
- Matrix effects present in some samples but not in others.

Laboratories that analyzed more samples had a greater variety of matrix effects to deal with, whereas laboratories that analyzed samples from one utility only had to deal with temporal variability in the matrix.

Comparison of the ICR LSP and the ICR PE Program

The ICR LSP was designed to provide estimates of the recovery efficiency of the ICR protozoan method under conditions similar to actual ICR protozoa monitoring conditions (except that organisms were spiked into LSP samples at higher concentrations than would be expected in natural samples to minimize nondetects by the ICR method). The protozoa recovery values produced during the LSP were included in the Bayesian analysis used to develop a model for estimating the national occurrence of microbial pathogens. This model is described in Chapter 19 (Messner and Wolpert 2002).

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The ICR PE Program also generated recovery data on the ICR protozoan method. Mean recoveries of 41% for *Cryptosporidium* and 48% for *Giardia* were observed in the ICR PE Program. However, recovery data from the PE program were not used to estimate ICR method recovery. The ICR PE Program was designed to evaluate the performance of the ICR protozoan laboratories rather than the performance of the method. The LSP provides a better estimate of method performance during the ICR for several reasons:

- The ICR PE samples were prepared by spiking cysts and oocysts directly onto the filter, a procedure that failed to account for losses during filtration of the sample. The LSP samples were prepared by spiking the water samples prior to filtration.
- During the ICR PE Program, an artificial matrix was developed and used for all PE samples. In the LSP, sample matrices actually monitored during the ICR were spiked and analyzed to assess method performance.

Table 20.5 summarizes the differences between the ICR PE Program and the LSP.

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Table 20.5

Summary of the ICR LSP and the ICR PE Program

	ICR LSP	ICR PE Program
Program period	May 1998 to December 1998	January 1997 to December 1998
Program objective	Evaluate method performance	Evaluate laboratory performance
Method	ICR protozoan method	ICR protozoan method
Spiking method	Bulk, 100-L water sample spiked in line by central spiking laboratory, then filtered	Spiked directly onto filter (did not account for losses during filtration)
Mean volume analyzed	8 L	47 L
Spike dose	5,000–10,000	200–6,100
Mean *Cryptosporidium* recovery	12%	41%
Cryptosporidium spiking: relative standard deviation	Low-spike period: 10%–22% High-spike period: 11%–24%	7%–32%
Range of *Cryptosporidium* recoveries	0%–65%	0%–185%
Mean *Giardia* recovery	26%	48%
Range of *Giardia* recoveries	0%–83%	0%–189%
Giardia spiking: relative standard deviation	Low-spike period: 10%–30% High-spike period: 11%–23%	7%–25%

SUMMARY AND CONCLUSIONS

The ICR protozoan method is characterized by low recoveries and high variability. As a result, unadjusted ICR data may underestimate protozoa occurrence as well as the level of treatment required for protozoa removal and the costs of these treatment techniques. The LSP data fed the Bayesian analysis used to model probable distributions of *Cryptosporidium* and *Giardia* occurrence in source water. Analysis of the LSP data indicates the following conclusions:

- The ICR protozoan method achieved a mean *Cryptosporidium* recovery of 12% with a standard deviation of 11% and a mean *Giardia* recovery of 26% with a standard deviation of 17%, based on spike concentrations higher than those observed in natural ICR samples.
- Variability in *Cryptosporidium* and *Giardia* recoveries was high overall as well as between and within laboratories analyzing LSP samples.

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- Results from the LSP are more appropriate for estimating method recovery than results from the ICR PE Program because the LSP assessed recovery of the entire analytical system and used real-world matrices.
- No significant differences among laboratories could be demonstrated for mean recoveries of *Cryptosporidium*.
- Significant differences among laboratories were observed for mean recoveries of *Giardia*. These differences may be due to method variability, laboratory performance, matrix effects, or all of these factors.
- No significant differences among laboratories could be demonstrated to explain variances in *Cryptosporidium* and *Giardia* recoveries.
- Other significant differences among laboratories may not have been detected because of the small number of samples analyzed by most laboratories and the high variability of the results.

DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The scientific views expressed are solely those of the authors and do not necessarily reflect those of USEPA.

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CHAPTER 21

GAC AND MEMBRANE TREATMENT STUDIES

Stuart M. Hooper and Steven C. Allgeier

ABSTRACT

The treatment study requirement of the Information Collection Rule generated an unprecedented amount of data on the effectiveness of granular activated carbon (GAC) and nanofiltration at removing disinfection by-product (DBP) precursors. A total of 99 bench-, pilot-, and full-scale studies were conducted. Results of these studies are stored in the ICR Treatment Study Database.

This chapter summarizes the distribution of plants that conducted treatment studies, the types of studies performed, the conditions under which the technologies were evaluated, and the study results. The results were evaluated against the maximum contaminant levels (MCLs) specified in the Disinfectants/Disinfection By-products (D/DBP) Rule and against a more stringent combination of MCLs evaluated during regulatory negotiations for the Stage 2 DBP Rule.

GAC treatment studies generated single contactor breakthrough profiles; run times for blended effluent streams were modeled on the basis of estimates from single contactor data. An evaluation of 10- and 20-minute empty-bed contact times (EBCTs) showed that greater normalized throughput was achievable at 20 minutes of EBCT. Evaluation of the applicability of GAC should include optimization of EBCT to minimize total costs.

For nanofiltration studies, influent and permeate blends to achieve target MCLs were modeled to provide a water quality distribution for each MCL target across all studies. In addition, three cases studies demonstrated the impact of membrane type on water quality. The rejection characteristics of nanofiltration membranes, specifically for total organic carbon and bromide, can have important implications for meeting D/DBP Rule MCLs.

Overall, 67% of plants that evaluated GAC were able to meet the target MCLs; 84% of plants that evaluated nanofiltration were able to do so. However, a direct comparison of the two technologies cannot be made because the membrane studies treated water sources with higher median DBP precursor concentrations than the GAC studies did.

INTRODUCTION

The Information Collection Rule (ICR) required utilities that met certain criteria to conduct studies on the removal of disinfection by-product (DBP) precursors. These treatment studies were designed to evaluate the technical feasibility of using granular activated carbon (GAC) and membrane processes (specifically nanofiltration) to remove DBP precursors prior to the addition of chlorine-based disinfectants. Under the ICR treatment study requirement, results

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from a total of 99 studies were submitted to the United States Environmental Protection Agency (USEPA)—63 GAC studies and 36 membranes studies.

The submission of results from these studies led to an unprecedented effort on the part of USEPA and its contractors to develop a data analysis approach and a data management system. The goal of these efforts was to review, summarize, and consolidate the data as well as to facilitate their evaluation for use in developing the Stage 2 DBP Rule.

This chapter provides an overview of the ICR treatment study requirements and the base analytical approach used to review the quality of the data generated, extract key data elements, and reorganize the data into a format that could subsequently be used to evaluate the feasibility of using GAC treatment and nanofiltration to meet DBP targets considered during the Federal Advisory Committee's negotiations concerning the Stage 2 DBP Rule. The chapter also presents some basic analyses of the treatment study data.

BACKGROUND

During the 1992–93 regulatory negotiations to develop new rules for controlling microorganisms and DBPs, GAC and nanofiltration were identified as advanced technologies capable of removing DBP precursors to concentrations below those achievable with enhanced coagulation. The regulatory negotiation's technical workgroup determined that additional information was needed on the feasibility of using GAC and nanofiltration to remove DBP precursors prior to the addition of chlorine-based disinfectants (USEPA 1996a; Allgeier, Shukairy, and Westrick 1998). The principal goal of the ICR treatment studies requirement was to gather information that could be used to estimate the nationwide performance of these technologies and the cost of using them to comply with the placeholder maximum contaminant levels (MCLs) of the Stage 2 DBP Rule—40 μg/L for total trihalomethane (TTHM) and 30 μg/L for the sum of five haloacetic acids (HAA5), both calculated as running annual average concentrations (USEPA 1994).

Studies have shown that both GAC and membrane technologies are capable of reducing DBP precursors to low concentrations under certain conditions. GAC treatment is usually less expensive than membrane technology, although the cost of membrane technology has decreased in recent years (Bergman 1996; Chellam, Serra, and Wiesner 1998; Jacangelo et al. 1995). GAC

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treatment is flexible in its ability to produce finished water with different concentrations of DBP precursors because the effluents of multiple contactors can be blended. However, GAC is not usually cost-effective at treating influent with high DBP precursor concentrations, such as a total organic carbon (TOC) concentration greater than 6 mg/L, without pretreatment (USEPA 1996b). Membrane processes, specifically reverse osmosis or nanofiltration, can reduce DBP precursors to very low concentrations. Unlike GAC, these processes provide effective barriers to pathogens when split-stream treatment is not used and the membranes are free of leaks and defects. Even when treating water with high DBP precursor concentrations, membrane processes can yield excellent DBP precursor removal. Another advantage of membrane processes is their ability to remove inorganic contaminants, including the removal of hardness ions to provide softening. However, fouling can limit the application of membranes to surface water sources without advanced and potentially costly pretreatment. Finally, the concentrate, or waste stream, requires disposal and, in some cases, treatment prior to disposal (USEPA 1996b).

Utilities affected by the ICR treatment study requirement included surface water systems (including groundwater systems under the direct influence of surface water) that served a population greater than 100,000 and had an annual average source water TOC concentration above 4.0 mg/L based on 12 months of monitoring. Groundwater systems that served a population greater than 50,000 and had an annual average finished water TOC concentration above 2.0 mg/L were also required to perform treatment studies. Several criteria for avoiding the treatment study requirement were specified (USEPA 1996a; USEPA 1996b; Allgeier, Shukairy, and Westrick 1998). Treatment plants serving fewer than 500,000 people could conduct either bench- or pilot-scale studies, whereas those serving 500,000 people or more were required to conduct pilot-scale studies.

The choice of testing GAC or membrane processes was left to the utility's discretion, so long as the study plan was acceptable to USEPA. Bench-scale evaluation of GAC required use of the rapid small-scale column test (RSSCT), a cost-effective method for simulating GAC performance at pilot- or full-scale. The RSSCT uses GAC that is ground to a smaller size (usually by a factor of 5 to 15) and maintains similitude to the full-scale contactor by the application of scaling equations. These scaling equations are derived based on the assumption that the rate of diffusion of natural organic matter to adsorption sites within the GAC is proportional to the particle size (Summers et al. 1995). Bench-scale GAC studies were required

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to evaluate two empty-bed contact times (EBCTs) during each of four quarterly sessions to capture the impact of seasonal variations in water quality on GAC performance. Plants without significant seasonal variations in water quality evaluated other operational parameters, such additional EBCTs, type of GAC, influent pH, or pretreatment. EBCTs of 10 and 20 minutes were required, representing the range of EBCTs most likely to be considered in the design of a full-scale postfilter adsorber system.

Pilot-scale GAC studies were also required to evaluate EBCTs of 10 and 20 minutes. Only one pilot run was required for each EBCT, unless the 20-minute EBCT run ended in fewer than 4,000 hours, in which case a second pilot run was required. In both bench- and pilot-scale studies, each column was required to be operated until 70% TOC breakthrough was achieved or until other termination criteria, outlined in the ICR, were met (USEPA 1996a). More information on study design, length, and sampling requirements is available in the *ICR Manual for Bench- and Pilot-Scale Treatment Studies* (USEPA 1996b). This "rule-by-reference" document describes the treatment study requirements in detail and provides guidance on how to design and conduct the studies, as well as how to interpret study results.

Utilities that chose to assess membrane technology were required to evaluate either reverse osmosis or nanofiltration. Two bench-scale approaches for evaluating membrane technology were allowed—the rapid bench-scale membrane test (RBSMT) or the single-element bench-scale test (SEBST). Utilities that conducted the SEBST had two options—four quarterly studies or a single long term study—in order to capture the impact of seasonal variations in water quality on membrane performance. If seasonal variations were not significant, these plants evaluated other factors that affect membrane performance, such as pretreatment, recovery, and membrane type. RBSMTs and quarterly SEBSTs were required to evaluate two types of membranes, whereas long-term studies were required to evaluate only a single type.

Pilot-scale membrane studies were required to evaluate a single type of membrane. ICR pilot systems were designed similarly to full-scale arrays and were typically considered to provide data that were directly scalable to full-scale performance, whereas it was necessary to extrapolate full-scale performance from the bench-scale data. Details on the design, operation, and sampling requirements associated with each study protocol can be found in the *ICR Manual for Bench- and Pilot-Scale Treatment Studies* (USEPA 1996b).

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Treatment study sampling requirements were designed to assess GAC and membrane performance under a known set of influent conditions, as measured by water quality parameters and DBP formation assessed under simulated distribution system (SDS) conditions. Effluent from the GAC columns was sampled over time to determine the breakthrough profile of SDS DBPs as well as DBP precursors, measured as TOC and ultraviolet absorbance at 254 nm (UV_{254}). Similarly, influent, permeate, and concentrate samples obtained for membrane studies were chlorinated to assess the formation of SDS DBPs. The SDS parameters temperature, pH, and incubation time were selected to represent average distribution system conditions at the time of the particular study run. Thus, SDS chlorination conditions for most studies varied seasonally. Although individual plants used different disinfection practices, all treatment studies required an SDS test based on free chlorine residual. The use of a free chlorine residual in all studies facilitated the comparison of results across all studies and provided a conservative measure of DBP formation relative to plants using a combined residual. For quarterly bench-scale tests, the ICR mandated that all samples collected during a given quarter be chlorinated under the same target SDS conditions. For pilot-scale tests, in which conditions such as temperature can change over time, the SDS testing conditions reflected these seasonal variations. However, samples collected at the same time (influent and effluent for GAC studies or influent and permeate for membrane studies) were chlorinated under the same target SDS conditions.

Of the 99 treatment studies conducted, 63 evaluated GAC and 36 evaluated membrane processes. Sixty-nine studies were conducted with surface water sources, and 30 were conducted with groundwater sources. Of the 63 GAC studies, 44 were bench-scale studies, 18 were pilot-scale studies, and one was a full-scale study. Of the 36 membrane studies, 19 were bench-scale studies, 14 used the pilot-scale protocol, and three were conducted at full-scale facilities according to the pilot-study sampling protocol. Although most of the GAC studies used surface water sources (52 of 63 studies, or 83%), the membrane studies were more evenly split between surface water (44%) and groundwater sources (56%). These percentages reflect the general application of the two technologies—though membrane technology is more readily implemented for groundwater sources, GAC has traditionally been applied to surface water sources.

Four of the 63 GAC studies were excluded from the data analysis effort for quality control reasons. The remaining 59 studies were conducted by 58 plants, which were located in 22 states. Thirty-six percent of these plants were located in Texas (13 plants) and Florida (8 plants);

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no other state had more than four plants that conducted GAC studies. Thirty-one plants (53%) used conventional treatment, and 21 plants (36%) used a treatment train that included softening. Two plants (3%) used direct filtration, and four plants (7%) used aeration followed by primary disinfection with free chlorine.

Free chlorine was used as the primary disinfectant at 69% of the plants that conducted GAC studies. Chloramines, the most common residual disinfectant, were used at 66% of the plants. The median total population served by the plants that conducted GAC studies was 210,000, and the median total flow of water treated was 41 million gallons per day (mgd).

The 36 membrane studies were conducted at 32 plants, most of which (66%) were located in Florida; no other state had more than three plants that conducted membrane studies. Twenty-seven plants (84%) used conventional treatment or conventional treatment plus softening. Two plants used only aeration followed by chlorination, and the remaining three used nanofiltration.

As with the plants that conducted GAC studies, free chlorine was the most commonly used primary disinfectant (53%) at the plants conducting membrane studies, and a majority (69%) of these plants used chloramines as the residual disinfectant. The median total population served by the plants conducting membrane studies was 116,000, and the median total flow of water treated was 17 mgd.

DATA ANALYSIS APPROACH

All treatment study data that utilities submitted to USEPA were subjected to a base analysis, which included review, analysis, and reduction of the raw data from each study. The output from the base analysis is a standard set of data elements that are consistent across all studies and that provide more relevant and useful information than the raw data. The USEPA and key technical contractors developed the *ICR Treatment Study Database* (USEPA 2000a), a relational database designed to organize and manage the complex base analysis data sets. Results from the base analysis are managed in either the *GAC Data Module* or the *Membrane Data Module*, and the raw data from these studies are available through the *Treatment Study Data Library Module*. These modules are described in more detail in the *User's Guide* for the database (USEPA 2000b).

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The GAC and membrane data modules are powerful tools designed to support more sophisticated analyses by allowing users to sort and query the base analysis results in a variety of ways. These modules also perform calculations based on user-defined breakthrough criteria (for GAC studies) or user-defined blended water quality goals (for membrane studies).

Base Analysis of the GAC Treatment Studies

Over the course of a GAC study, a significant amount of data on influent and effluent water quality was collected. These data demonstrated the ability of GAC to remove DBP precursors as a function of operation time. In most cases, the data also provided a comparison of GAC performance at 10- and 20-minute EBCTs. In addition, plants investigated the effects of other variables—for example, seasonal variations in water quality and chlorination conditions, other EBCTs, additional pretreatment, GAC type, and influent pH—on GAC performance.

The base analysis of the GAC studies included an examination of influent water quality and effluent breakthrough data. Every water quality parameter measured during every GAC run yielded a breakthrough curve. To create a data set that could be easily queried on the basis of run time or treatment objective criteria, all breakthrough data were fit to the logistic function model. The basic form of this model is shown in Equation 21.1 (Chowdhury et al. 1996, Summers et al. 1998), and it was modified as described in *Base Analysis Document: GAC Studies* (USEPA 2000c).

$$C(t) = \frac{A_f}{1 + Be^{-Dt}} + A_0 \qquad (21.1)$$

in which A_0, A_f, B, and D = logistic function parameters; C = single contactor effluent concentration; and t = time.

The standard form of the logistic function model results in a relationship between concentration and run time, and the inverse form of the equation was developed to provide a direct calculation of run time as a function of concentration. To provide a higher rate of successful curve fits, and to limit the impact of deviant observations on model results, an outlier identification procedure was performed to statistically identify and remove data outliers (USEPA 2000c).

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In practice, GAC contactors can be operated more efficiently by blending the effluent streams from multiple contactors operated in parallel and by staggering the schedules for reactivating or replacing the GAC (Chowdhury et al. 1996, Summers et al. 1998, USEPA 1999). This mode of operation is termed "effluent blending" or "blended contactor operation." In this mode, each individual contactor continues to be operated as its effluent exceeds the treatment objective because the treatment objective must be maintained only in the blended effluent. Because the ICR GAC studies generated breakthrough curves representing single GAC contactors, a model was used to estimate the integral breakthrough curve, defined as a relationship between blended effluent water quality ($\overline{C}$) and the carbon reactivation or replacement interval for an individual contactor. The integral breakthrough curve, also referred to as the "blended contactor breakthrough curve," is derived by applying the average value function to the logistic function model (USEPA 1999):

$$\overline{C}(t) = A_0 + A_f + \frac{A_f}{Dt}\ln\left(\frac{1+Be^{-Dt}}{1+B}\right) \tag{21.2}$$

An important goal during base analysis was to model the integral breakthrough curve for every parameter analyzed during all GAC runs, and this was accomplished using the surrogate correlation approach. The surrogate correlation approach is based on deriving the integral breakthrough curve (using Equation 21.2) for TOC only. Then, data points on both the single contactor and integral breakthrough curves at a given TOC concentration are mapped, and all other water quality parameters associated with the single contactor effluent data set at that TOC concentration are applied to the blended effluent curve. Thus, the surrogate correlation approach simplifies the computations necessary for calculating water quality in blended effluent. Across all water quality parameters, the surrogate correlation approach was a more reliable predictor of blended effluent water quality data than the integral breakthrough curve (USEPA 1999). This was mainly due to the presence of a substantial number of breakthrough curves with increasing followed by decreasing concentrations (typically observed for bromine-substituted DBP compounds) for which the integral breakthrough curve was not a good predictor of blended effluent water quality. These results are discussed thoroughly elsewhere (USEPA 1999, USEPA 2000c).

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Base Analysis of Membrane Treatment Studies

The base analysis of the membrane studies included an evaluation of water quality and productivity data. The objective of this analysis was to assess the membrane's ability to produce water meeting specific treatment objectives at an acceptable rate and without excessive cleaning requirements. The base analysis of the membrane studies was designed to reduce the large amounts of raw data from each study to standard data elements that could be used to evaluate water quality and productivity across all membrane studies.

Over the course of a membrane study, a significant amount of data on influent, permeate, and concentrate water quality was collected. These data demonstrated the ability of nanofiltration to remove various contaminants as conditions—such as influent water quality, system operation, or pretreatment—changed during the study. However, the permeate and concentrate water quality data generated from the membrane studies were also affected by differences in study protocols such as concentrate recycling or operation at different recoveries.

During the base analysis, the effects of study protocol and operating conditions on permeate and concentrate water quality were accounted for through the application of the Differential Water Quality Model (USEPA 2000d). This model was used to normalize the permeate and concentrate water quality data from each study by calculating the equivalent water quality from a full-scale membrane array. Input to this model included a set of design assumptions for the full-scale array, influent water quality data from the study, and mass transfer coefficients for each water quality parameter (the mass transfer coefficients were derived from the experimental permeate water quality data). The model consists of a mathematical representation of the full-scale array, and this mathematical representation was solved through differential analysis. Details of this analysis and the Differential Water Quality Model are described in *Base Analysis Document: Membrane Studies* (USEPA 2000d).

The productivity analysis used the large amount of flow and pressure data collected over the course of a study to develop a few summary parameters that effectively describe membrane productivity. These productivity parameters include the rate of specific flux decline, the cleaning interval, cleaning efficiency, sustained flux, and sustained specific flux. Details of the productivity analysis are described elsewhere (USEPA 2000d).

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EVALUATING ADVANCED TREATMENT PROCESSES FOR DBP PRECURSOR REMOVAL

To demonstrate the applicability of GAC and nanofiltration as DBP precursor removal technologies, two treatment objectives were evaluated. The first was an annual average SDS TTHM concentration of 64 μg/L and an annual average SDS HAA5 concentration of 48 μg/L; this treatment objective is referred to as the 64/48 running annual average (RAA). The second treatment objective, a lower SDS TTHM target of 32 μg/L and an SDS HAA5 target of 24 μg/L, is referred to as the 32/24 RAA. The 64/48 RAA target was based on the MCLs specified in the Disinfectants/Disinfection By-products (D/DBP) Rule (an RAA of 80 μg/L for TTHM and 60 μg/L for HAA5) with a 20% factor of safety applied to each MCL. The 32/24 RAA target was based on one of the more stringent MCL combinations evaluated during the Stage 2 DBP Rule negotiations—40 μg/L for TTHM and 30 μg/L for HAA5, also with a 20% safety factor applied to each MCL. The treatment studies were designed to achieve the 32/24 RAA target (Allgeier, Shukairy, and Westrick 1998).

The SDS protocol followed during the ICR treatment studies required that the incubation time used during SDS testing be representative of average distribution system residence times (USEPA 1996b, 1997). This aspect of the SDS protocol was designed to match the compliance scenario of the D/DBP Rule, under which the concentration of DBPs occurring in the distribution system is calculated by averaging samples collected at all compliance locations. However, the Stage 2 DBP Rule will likely adopt MCLs based on locational RAAs (LRAAs)—utilities will need to comply with the MCLs, on the basis of RAAs, at each compliance location. Because all treatment study data are based on average distribution system residence times, the data cannot be directly compared with calculations reached by the LRAA approach. Plants will need to comply with the MCLs at longer-than-average residence times, and therefore DBP concentrations at the average distribution system residence time, for plants in compliance with the LRAA, will likely be lower than the MCL in most cases, particularly for TTHM.

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Removing DBP Precursors With GAC

Overview of ICR GAC Treatment Studies

Most of the 59 GAC treatment studies evaluated EBCTs of both 10 and 20 minutes, yielding a total of 351 individual GAC runs. Of these runs, 172 evaluated 10-minute EBCT contactors, and 161 evaluated 20-minute EBCT contactors. In the remaining 18 runs (5%), alternative EBCTs (5, 7.5, 8.5, 12.5, 15, 16.5, and 25 minutes) were evaluated in lieu of the requirement to investigate seasonal variations in water quality. Some studies also evaluated additional pretreatment steps, GAC types, or influent pH adjustment. A bituminous coal–based GAC was evaluated in 331 GAC runs (94%), and the remaining 20 runs (6%) evaluated lignite coal–based GACs. Five GAC manufacturers were represented by the GACs evaluated.

Forty-eight of the 59 GAC studies (81%) were conducted with surface water sources, and 11 studies (19%) were conducted with groundwater sources. All eight Florida plants that conducted treatment studies used a groundwater source; the three remaining groundwater sources were located in Nebraska.

Because GAC can be retrofitted for integration into a plant's existing treatment process, treatment study influent was usually sampled after being treated by existing full-scale processes and before the addition of chlorine-based oxidants. When a chlorine-based oxidant was added at a point that precluded sampling after existing full-scale processes, samples were collected prior to treatment (or after partial treatment) and remaining full-scale treatment processes were simulated by pilot- or bench-scale treatment.

Influent Water Quality and SDS Conditions in GAC Treatment Studies

A statistical summary of the distribution of SDS conditions in the GAC studies is given in Table 21.1. These statistics were based on the average value for each parameter in each study, an approach that parallels the method by which SDS DBP data were treated in this analysis. The median values for each parameter, calculated across all GAC studies, are similar to the proposed uniform formation conditions (UFC) test for assessing DBP formation (Summers et al. 1996). Incubation time and incubation temperature showed the largest variability; less variability was

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observed for pH and free chlorine residual. Although the average incubation temperature during each study is represented in the distribution summarized in Table 21.2, SDS temperatures varied widely during different seasonal runs in many studies.

Table 21.2 summarizes the distribution of influent water quality in the GAC studies. These data were compiled by calculating the average concentration of each parameter for each study and using these averages to develop statistical summaries across all studies. The median TOC concentration, 3.1 mg/L, and bromide concentration, 80 μ/L, were higher than median TOC and bromide concentrations in ICR plant influent, 2.4 mg/L and 36 μ/L, respectively (McGuire and Hotaling 2002). The median TOC and bromide concentrations in ICR plant influent were based on raw water sampling at all plants. The median SDS TTHM concentration in the influents used for GAC studies was 84 μ/L, higher than the 64/48 RAA. The data indicate that more than 90% of all ICR plants conducting GAC studies would exceed the 32/24 RAA without any additional treatment or change in treatment or disinfection practices. However, all treatment study SDS tests were conducted with free chlorine, whereas only 34% of plants conducting GAC studies reported using free chlorine as both the primary and residual disinfectant. Therefore, the mean SDS DBP concentrations observed in the treatment study influents were higher than the mean distribution system DBP concentrations at the plants conducting the studies.

Median SDS HAA5 concentrations were lower than SDS TTHM concentrations with respect to the RAA MCLs. The median SDS HAA5 concentration was 37 μg/L, 23% lower than the 48-μg/L HAA5 target, whereas that for SDS TTHM was 84 μg/L, 31% higher than the 64-μg/L TTHM target. Therefore, at most plants that conducted GAC studies, TTHM formation will control compliance with the 64/48 or 32/24 RAA MCLs.

Table 21.1

Average SDS conditions in ICR GAC studies

SDS parameter	Median	25th–75th percentile range	10th–90th percentile range
Incubation time (hours)	24	17–45	7–58
Incubation temperature (°C)	20	16–23	14–26
Incubation pH	8.1	7.6–8.7	7.3–9.1
Free Cl_2 residual (mg/L as Cl_2)	0.9	0.8–1.0	0.6–1.3

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Table 21.2

Summary of influent water quality in ICR GAC studies

Parameter	Median	25th–75th percentile range	10th–90th percentile range
Alkalinity (mg/L $CaCO_3$)	60	34–116	11–151
Total hardness (mg/L $CaCO_3$)	114	88–167	27–226
Calcium hardness (mg/L $CaCO_3$)	86	44–118	18–180
Ammonia (mg N-NH_3/L)	0.06	0.04–0.15	0.00–0.26
Bromide (μ/L)	80	29–148	14–344
TOC (mg/L)	3.1	2.7–3.7	2.1–4.5
UV_{254} (1/cm)	0.059	0.047–0.079	0.039–0.101
TSUVA* (L/mg-m)	2.0	1.8–2.2	1.4–2.6
SDS Cl_2 demand (mg/L as Cl_2)	2.6	2.0–3.3	1.4–5.1
SDS TOX† (μg Cl^-/L)	234	168–283	132–385
SDS TTHM (μ/L)	84	49–108	33–192
SDS HAA5 (μ/L)	37	21–49	15–71
SDS HAA6 (μ/L)	42	28-58	19–76
SDS HAA9‡ (μ/L)	61	41–76	31–98
SDS BDCM§ (μ/L)	17	10–30	5–41

* TSUVA = ultraviolet absorbance at 254 nm divided by TOC concentration

† TOX = total organic halogen

‡ The number of reported values for HAA9 data is 54% of the number reported for HAA5 and HAA6 data; thus the HAA9 statistics are not directly comparable to the HAA5 or HAA6 statistics.

§ BDCM = bromodichloromethane

Controlling DBP Formation With GAC

The data collected for each parameter during all GAC runs yielded breakthrough profiles representing the relative performance of GAC for DBP precursor removal. All run times described in the following analysis were based on estimates of water quality during effluent blending from single contactor data. A lower bound of 90 days was placed on the GAC replacement cycle for purposes of evaluating the feasibility of GAC treatment, as it was for the compliance forecasts carried out during the D/DBP Rule regulatory negotiation. This limit not only provides a basis for evaluating the economic and practical feasibility of GAC treatment but also allows an evaluation of the need for 10 or 20 minutes of EBCT. Selection of EBCT can have significant implications for capital and operations and maintenance (O&M) costs.

For data analysis, the studies were separated into four categories:

- Compliance with the RAA after conventional treatment (GAC not required),
- Compliance with the RAA using GAC with a 10-minute EBCT and a minimum reactivation cycle of 90 days (GAC10),

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- Compliance with the RAA using GAC with a 20-minute EBCT and a minimum reactivation cycle of 90 days (GAC20), and
- Inability to achieve compliance with the RAA using either GAC10 or GAC20.

With regard to the fourth category, compliance may be possible using GAC10 or GAC20 and reactivation intervals shorter than 90 days. Some utilities may find it cost-effective to increase run times by implementing pretreatment, such as enhanced coagulation or pH adjustment. During the compliance forecast process conducted for the Stage 2 DBP Rule, plants that could not meet the RAA using GAC20 were assumed to need GAC10 or GAC20 with advanced oxidants and, if necessary, membrane treatment.

Compliance with the RAA was calculated by averaging the run times of multiple runs at the same EBCT in each study. Influent water quality was averaged across all runs in each study to determine if compliance with the RAA had been achieved with existing conventional treatment. In most cases, this average approximated a seasonal annual average because the studies were conducted quarterly, similar to the sampling requirements for the D/DBP Rule. If compliance with the RAA was achieved with existing conventional treatment, run time data from that study were not included in this analysis. In some studies, compliance with the RAA was not possible using GAC10 (run times were shorter than 90 days) but was possible using GAC20. In a number of studies, compliance was possible using GAC10 or GAC20 (with run times ≥90 days). In these cases, run times that were achievable with both GAC10 and GAC20 were included in the GAC run time analysis summarized in this section. This approach differs from the compliance forecast methodology, which stopped at the lowest-cost alternative for compliance. However, because many GAC studies were able to comply with the target RAAs using either GAC10 or GAC20, limiting the run time data summarized to the lowest-cost alternative for compliance would have reduced the number of runs included in the GAC20 data distribution. Including run times that were achievable with both GAC10 and GAC20 in the GAC20 data distribution allowed the data presented to more accurately represent the distribution of achievable run times. Plants that require GAC to comply with the MCLs specified in the D/DBP Rule should optimize contactor EBCT to minimize total costs, including both capital and O&M costs.

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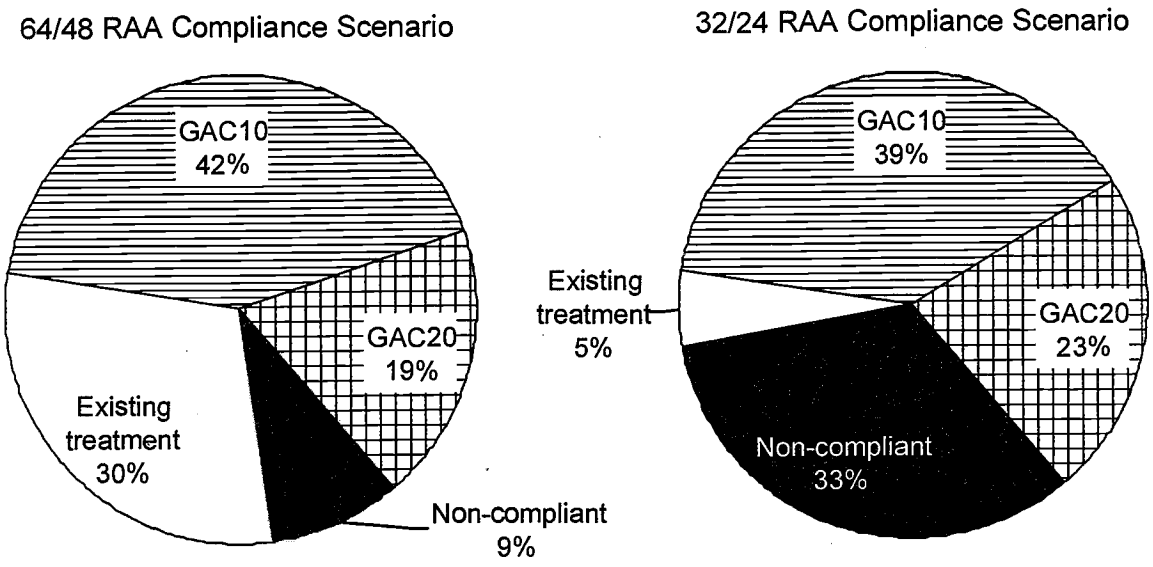

Figure 21.1 Distribution of GAC options for complying with the 64/48 and 32/24 RAAs

The distribution of compliance options using GAC is summarized in Figure 21.1. One study that only evaluated GAC at an EBCT of 15 minutes was eliminated from further analysis because this analysis is based on compliance options using GAC10 and GAC20; eliminating this study reduced the total number of plants to 58. Another study that evaluated a single EBCT of 20 minutes was omitted from the analysis summarized in Figure 21.1 because compliance using a 10-minute EBCT could not be determined; however, this study was included in subsequent run time analyses. As summarized in Figure 21.1, most studies (52, or 95%) showed that compliance with the 64/48 RAA was achieved with existing treatment or with existing treatment followed by GAC. When evaluated for compliance with the 32/24 RAA, however, 19 studies (33%) exceeded the RAA in less than 90 days, even with a 20-minute EBCT.

Figure 21.2 shows the distribution of blended contactor GAC run times to meet both regulatory targets and for both EBCTs. (In the data distributions shown in Figure 21.2 and subsequent figures in this chapter, the 25th and 75th percentiles are represented by the ends of the box, the 50th percentile is represented by the horizontal line within the box, and the 10th and 90th percentiles are represented by the whiskers. Individual data points represent values outside the range of the 10th to 90th percentiles.) The data summarized in Figure 21.2 include run times shorter than 90 days, though these data were excluded from the analysis shown in Figure 21.3.

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Figure 21.2 is provided so that the effect of EBCT and the regulatory target on blended contactor GAC run times can be observed without the effect of removing all run times of less than 90 days, which would skew the analysis. Figure 21.3 shows the distribution of compliance options for GAC treatment with a minimum run time of 90 days. The data in Figures 21.2 and 21.3 show that, as expected, longer run times were obtained with 20-minute EBCT contactors than with 10-minute EBCT contactors. However, Figure 21.3 does not show a large difference in median run times for GAC10 or GAC20 used to meet either RAA target. With GAC10, the median run time to the 64/48 RAA was 170 days; the median run time was reduced by 9%, to 154 days, for compliance with the 32/24 RAA. Similarly, the median GAC20 run time decreased from 272 days, for compliance with the 64/48 RAA, to 243 days, for compliance with the 32/24 RAA, an 11% decrease in median run time. The relatively small difference in median run time to achieve either RAA target is due in part to the effect on the data distribution of removing all run times of less than 90 days from the analysis. Two other reasons for the small difference are related to limitations inherent in the treatment study data set and the procedures followed in the data analysis.

First, the run time distributions summarized in Figures 21.2 and 21.3 are based on breakthrough profiles generated only by plants that exceeded the RAAs after existing conventional treatment: 40 plants for the 64/48 RAA and 54 plants for the 32/24 RAA. Therefore, the average quality of the water treated by GAC at the 54 plants summarized in the 32/24 RAA data distribution was better than that of the water treated by GAC at the 40 plants summarized in the 64/48 RAA data distribution. In fact, median GAC influent SDS TTHM and SDS HAA5 concentrations for the 32/24 RAA data distribution were 15% lower on average than those for the 64/48 RAA data distribution. The average TOC concentration was 8% lower. This difference in median GAC influent water quality makes a direct comparison of run times to the two RAA targets more difficult.

Second, 66% of the runs analyzed to generate the distributions summarized in Figure 21.3 did not exceed the RAA prior to the maximum blended contactor run time (RT_{BLmax}). Although single contactor breakthrough curves were not extrapolated, the upper bound of the blended contactor model run time, RT_{BLmax}, was set at 150% of the single contactor run length (USEPA 2000c). Because this value was based on the length of each run, it varied with each run. Therefore, the distribution of run times shown in Figure 21.3 was limited by the run time upper

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bound limit, RT_{Blmax}, and this analysis yielded a conservative distribution of GAC run times and water quality (in many cases, TTHM and HAA5 concentrations at the maximum run time were below the target). The distribution of GAC run times in this analysis is considered conservative because a majority of the runs could have been extended without causing the target RAAs to be exceeded.

The GAC run times summarized here represent the distribution of average run times achieved by each plant. From the perspective of full-scale treatment, seasonal changes in water temperature will result in seasonal variations in DBP formation at many plants. Higher DBP concentrations occur at many plants during the summer months, leading to more frequent GAC replacement during the summer. Conversely, DBP concentrations are generally lower during the winter months, resulting in longer GAC run times during that period. Utilities might choose to adjust reactivation frequencies throughout the year to achieve more consistent water quality in the distribution system. On the other hand, because utilities must maintain compliance with MCLs that are based on RAAs, a plant might choose to keep reactivation cycles constant throughout the year to simplify operation.

Figure 21.4 summarizes the distribution of concentrations of TOC, UV_{254}, SDS TTHM, SDS HAA5, SDS bromodichloromethane (BDCM), and SDS total organic halogen (TOX) when GAC10 and GAC20 were used to meet either regulatory compliance scenario. The water quality data for GAC10 and GAC20 represent only those studies that exceeded the 32/24 or 64/48 RAAs after existing treatment and were able to meet the RAAs using GAC10 or GAC20. For comparison, the distribution of water quality data prior to GAC treatment is also shown. The data summarized in Figure 21.4 demonstrate GAC's ability to reduce DBP precursor concentrations and other SDS DBP concentrations while achieving target SDS TTHM and SDS HAA5 concentrations. For example, the median SDS BDCM concentration while the 64/48 RAA was being met was 12 μg/L for GAC10 and 9 μg/L for GAC20. SDS BDCM concentrations dropped to 7 μg/L for GAC10 and 6 μg/L for GAC20 when GAC treatment was operated to meet the 32/24 RAA.

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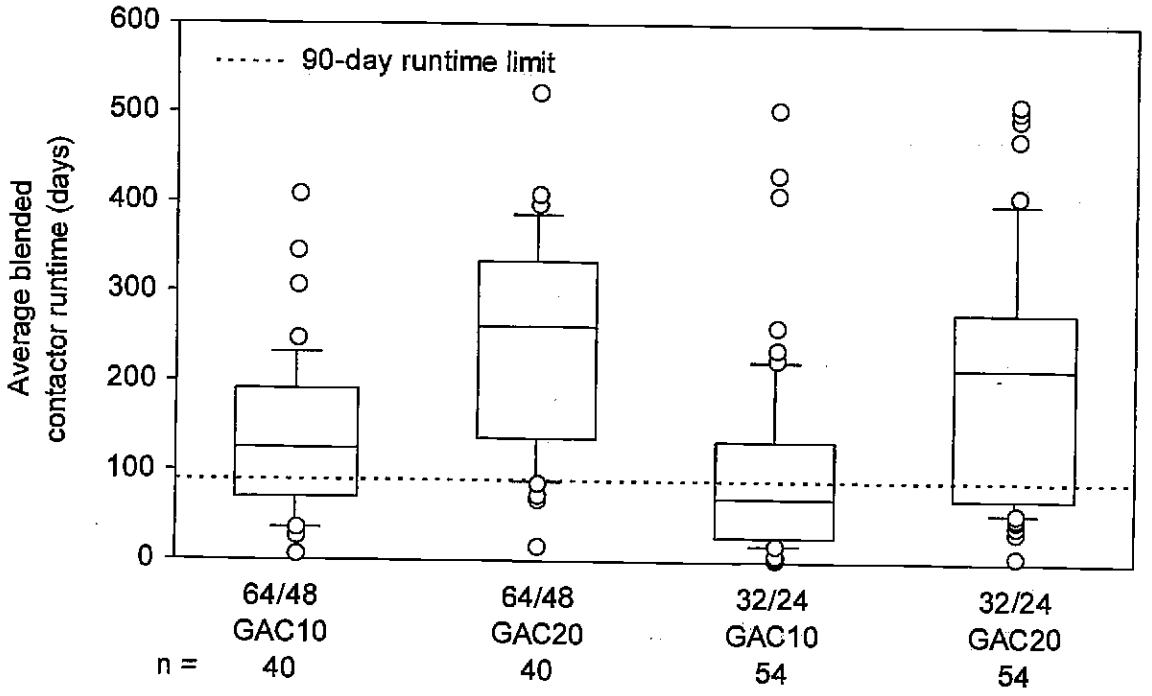

Figure 21.2 Distribution of average blended contactor run times for GAC10 and GAC20 used to meet the 32/24 and 64/48 RAA targets, including average run times of less than 90 days

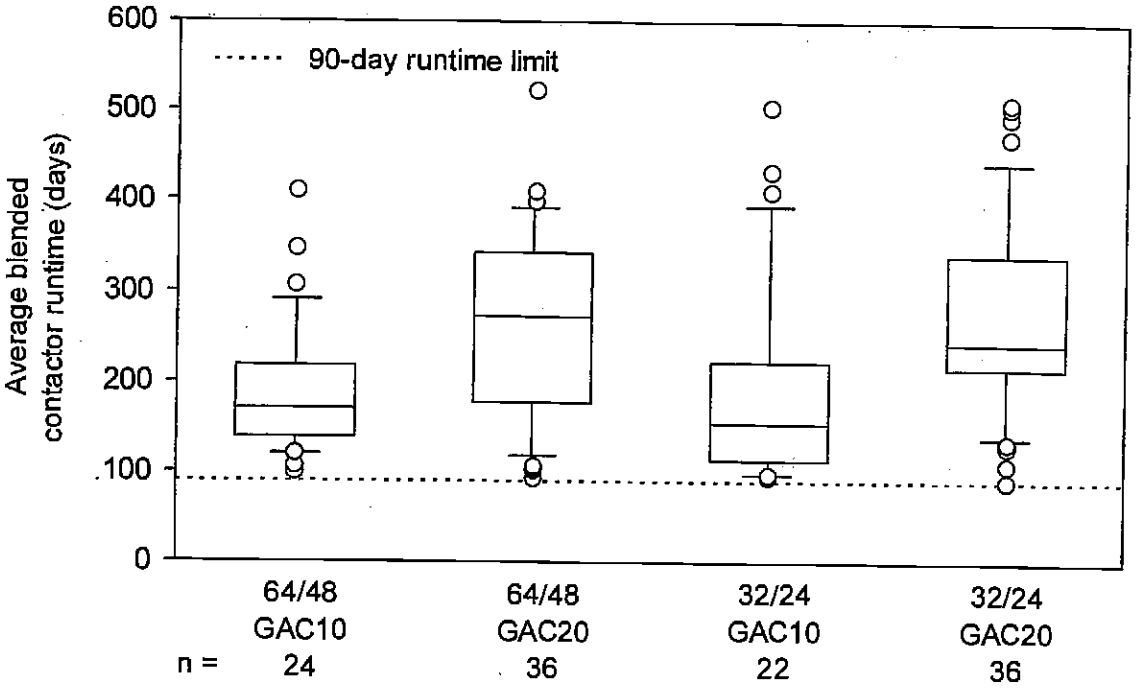

Figure 21.3 Distribution of average blended contactor run times for GAC10 and GAC20 used to meet the 32/24 and 64/48 RAA targets, excluding average run times of less than 90 days

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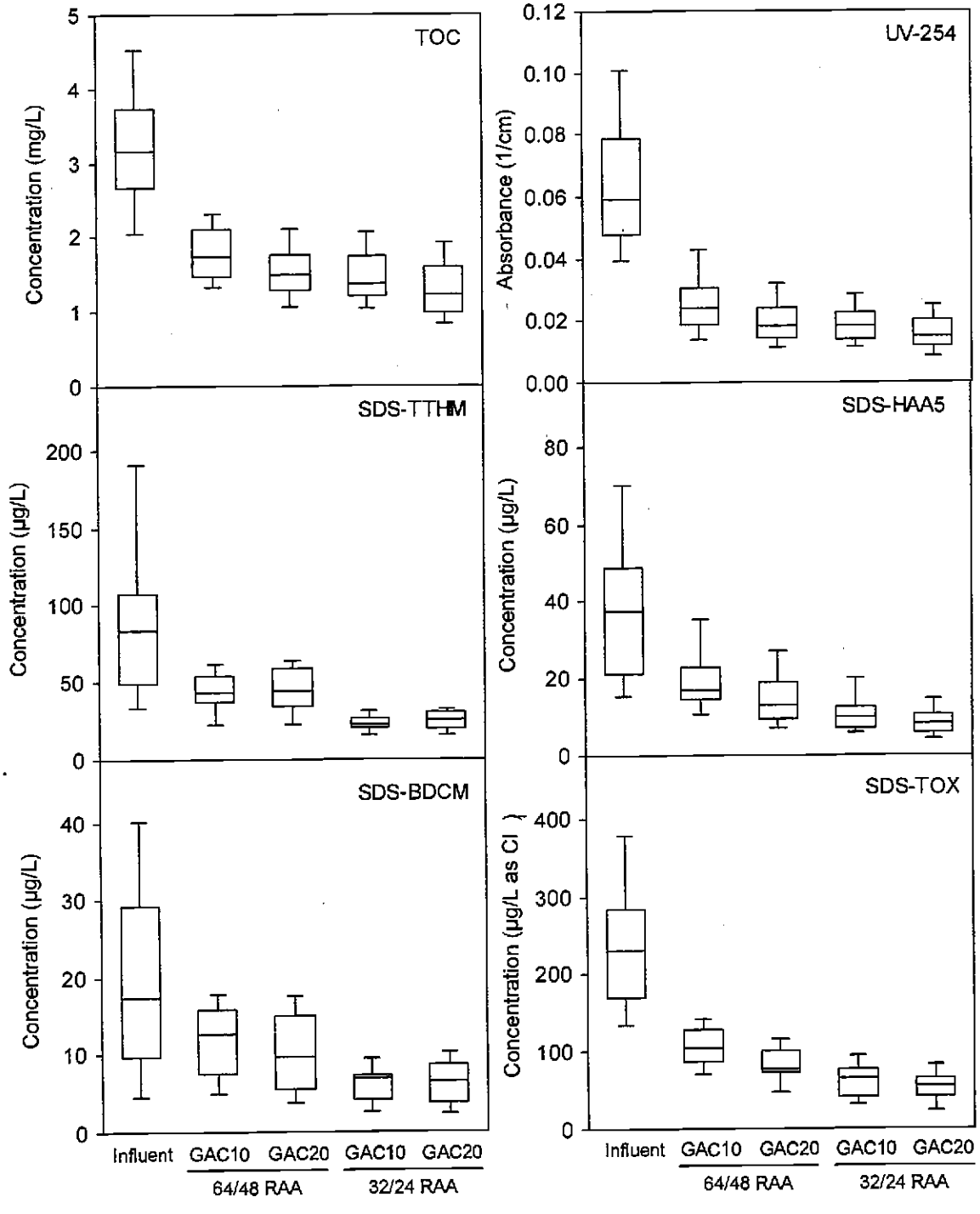

Figure 21.4 Distribution of water quality in GAC influent and blended effluent

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Effect of EBCT on GAC Throughput

EBCT is an important variable in evaluating the applicability of GAC treatment. In general, capital costs increase with greater EBCTs, but longer run times reduce operational costs. Implementation of GAC treatment should include an evaluation of optimal EBCT, and most GAC treatment studies conducted under the ICR evaluated EBCTs of 10 and 20 minutes. In an operating plant, however, EBCT is not a static parameter because actual EBCT varies with water production, assuming the number of contactors in service remains constant. A previous study showed that the carbon usage rate (the mass of carbon required to treat a given volume of water) for removing DBP precursors from four water supplies was not significantly affected by EBCTs between 10 and 20 minutes (Summers et al. 1998).

Only paired 10- and 20-minute EBCT contactors (those that received the same influent) were included in this analysis. Runs that did not exceed the 64/48 or 32/24 RAA prior to RT_{BLmax} were excluded; however, runs shorter than 90 days were included. Paired 10- and 20-minute EBCT columns were compared on the basis of throughput (bed volumes treated), which normalizes for the difference in EBCT. For both the 64/48 and 32/24 RAA targets, greater throughput was achieved with the 20-minute EBCT contactors. The distribution of the increase in throughput between 10- and 20-minute EBCT runs (GAC20–GAC10) is shown in Figure 21.5 for throughput based on compliance with both the 64/48 and 32/24 RAAs. The median increase at the 64/48 RAA was 1,400 bed volumes, whereas that at the 32/24 RAA was 1,200 bed volumes.

To provide a relative basis for comparison, Figure 21.5 also shows the distribution of percentage increase in throughput for each 20-minute EBCT run over its paired 10-minute EBCT run. For the 64/48 RAA, the median percentage increase in throughput was 25%, whereas that for the 32/24 RAA was 27%. A total of 45 comparisons (representing 19 water sources) were included in the analysis on the basis of the 64/48 RAA (27% of total possible comparisons). A total of 81 comparisons (representing 35 water sources) were included in the analysis on the basis of the 32/24 RAA (48% of total possible comparisons).

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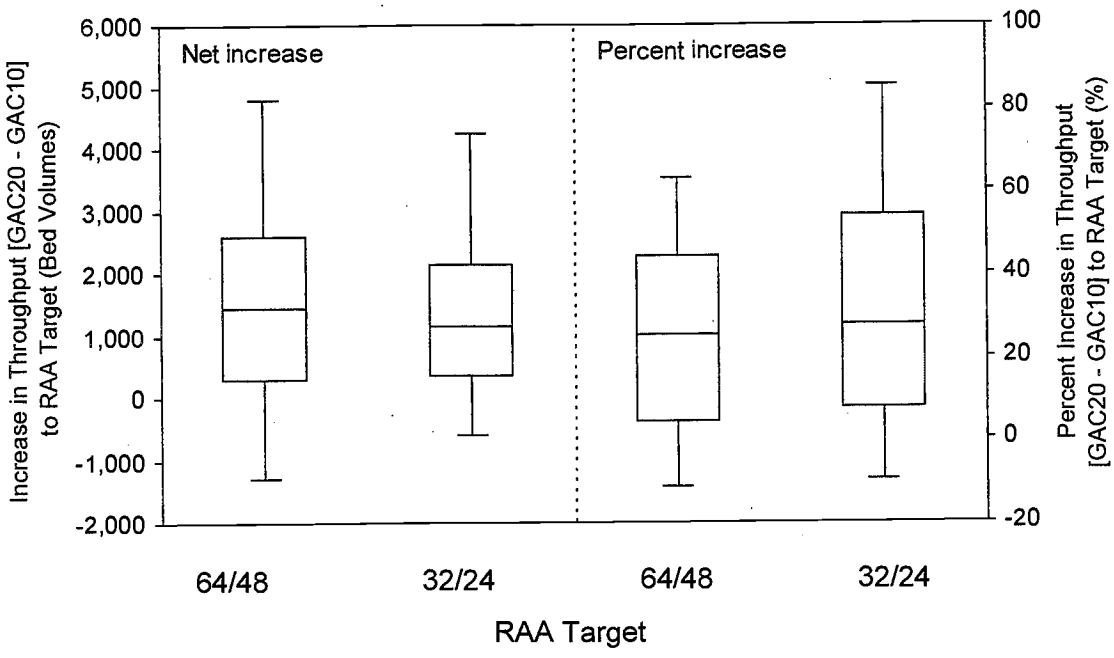

Figure 21.5 Distribution of net increase and percentage increase in GAC throughput to the 64/48 and 32/24 RAA targets

This analysis demonstrates the potential for an increase in throughput between EBCTs of 10 and 20 minutes. The gain may be due to more efficient adsorption or to more effective biological removal of DBP precursors in contactors with longer EBCTs. The wide range in the increase suggests that the effect of EBCT on throughput is site-specific; for some water supplies the difference was negligible, whereas for others it was large, as shown by the range of values for the 25th to 75th percentiles (Figure 21.5). Moreover, the impact of EBCT on throughput was substantially affected by seasonal variability in some water supplies. For these reasons, an evaluation of whether the potential increase in throughput with increasing EBCT will result in total cost savings (including both capital and O&M costs) should be performed on a case-by-case basis and seasonal effects should be considered. Because the median percentage increase in throughput was similar for both RAAs, these results should be applicable to GAC replacement cycles based on compliance with a target between the 64/48 and 32/24 RAAs.

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Removing DBP Precursors With Nanofiltration

Overview of ICR Membrane Treatment Studies

Of the 36 membrane studies conducted under the ICR, seven of the grandfathered membrane studies were conducted at only three sites. To avoid duplication during analysis, these seven studies were consolidated into three studies, resulting in the consideration of a total of 32 studies in the following analyses.

The ICR membrane studies were designed to evaluate a variety of conditions including different water supply sources, membranes, pretreatment processes, and operating conditions. These study conditions are summarized in the following section.

The 32 sites that evaluated membrane technology included 18 groundwater sites and 14 surface water sites (four lakes or reservoirs and ten rivers or streams). All of the groundwater studies were conducted in Florida, and ten of them used source water from the Biscayne Aquifer. The four plants that used reservoir or lake supplies are located in Florida (one site) and Virginia (three sites). The ten plants that used rivers or streams are located in Florida, Kansas, Missouri, Texas, New Jersey, and South Dakota. Although the distribution of these sources does not reflect the distribution of water supply sources across the United States, these sources contain high concentrations of DBP precursors. Furthermore, the large representation of Florida utilities reflects the fact that nanofiltration is an accepted technology in this state, where it can typically be applied to groundwater sources with minimal pretreatment.

Table 21.3 lists the membranes, grouped by manufacturer, used in the ICR treatment studies. Most of these membranes are constructed using a polyamide active layer. Exceptions are the PVD1, manufactured from a polyvinyl alcohol derivative; the NTR7450, manufactured from a polysulfone material; and the CALP, a cellulose acetate membrane. Except for the cellulose acetate membrane, all of the membranes carried a negative charge and were categorized as hydrophilic. The molecular weight cutoffs ranged from 100 to 1,000 Daltons, with a median value of 212 Daltons. On the basis of these characteristics, all of the membranes evaluated would be classified as nanofiltration membranes, but there are significant differences in their rejection characteristics. Both traditional softening membranes (those that reject more than 80% of

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hardness ions) and "loose" membranes (those that reject less than 80% of hardness ions) were evaluated. The impact of membrane type on rejection is discussed later in this section.

Utilities were typically required to evaluate GAC or nanofiltration after the use of existing processes that remove DBP precursors. Although this was usually the case for GAC studies, many membrane studies used pretreatment processes that differed from the existing full-scale treatment processes. This reflects the common design assumption that GAC is a potential retrofit technology that can be added after conventional filtration, whereas nanofiltration is not generally considered a retrofit technology for surface water plants because the pretreatment system must be designed and operated specifically to minimize membrane fouling.

Three categories of pretreatment technology were used during the ICR membrane studies: conventional membrane pretreatment, existing plant retrofit, and advanced membrane pretreatment. Fifty percent of the membrane studies used conventional membrane pretreatment, which consists of cartridge filtration to remove particulate matter and scale control, as necessary, to limit the precipitation of inorganic scale. This type of pretreatment is appropriate for groundwater supplies and was used exclusively on Florida groundwater sources during ICR membrane studies.

Nanofiltration of surface water typically requires pretreatment beyond cartridge filtration and scale control because of the high concentrations of particulate and organic matter in these sources, and this design practice was reflected in the membrane studies that evaluated surface water. Thirty-one percent of the ICR membrane studies used existing conventional filtration or lime softening processes as pretreatment, essentially using nanofiltration as a retrofit technology, and the majority of these studies (90%) used surface water sources.

Table 21.3

Membranes investigated during the ICR membrane studies

Manufacturer	Membranes	Percentage of all membranes tested
Desal	DS5-DK; DS5-DL	2
FilmTec	BW30; BW30LE; NF70; NF45; NF200B	41
Fluid Systems	TFC-HR; TFC-S; TFC-SR; TFC-ULP; CALP	28
Hydranautics	LFC1; ESNA1; NTR7450; PVD1	25
Osmonics	B22; MS	2
TriSep	TS80	2

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The remaining 29% of the ICR membrane studies used advanced pretreatment consisting of microfiltration of source water, chemical coagulation followed by microfiltration, or disinfection with chloramines or ultraviolet irradiation. Most studies (83%) that incorporated advanced pretreatment were conducted with surface water sources.

The key operating conditions applicable to nanofiltration are permeate recovery and flux. The median value of average permeate recovery in the ICR membrane studies was 64%, with a 10th to 90th percentile range of 55–80%. The median recovery was slightly lower than expected because the ICR required membrane systems to be operated at a recovery rate of 70% or higher. The reason for this deviation was often caused by operational difficulties encountered when single elements were operated or small pilot systems were operated at high recoveries with concentrate recycling. The high recoveries under this mode of operation often increased inorganic fouling, and in many cases the only solution to this problem was to lower recovery. During analysis of the water quality data generated by the ICR membrane studies, a mathematical model was used to normalize for the different recovery rates used (USEPA 2000d). The median flux was 13.2 gallons per day per square foot of membrane (gpd/sq ft), with a 10th to 90th percentile range of 8.9–16.4 gpd/sq ft. This is a reasonable range compared with the flux values typically used in the design of groundwater and surface water nanofiltration systems—10 and 15 gpd/sq ft, respectively.

Influent Water Quality and SDS Conditions for Membrane Treatment Studies

A statistical summary of average SDS chlorination conditions used during the ICR membrane studies is presented in Table 21.4. Incubation time showed the greatest variability across all membrane studies, with a 10th to 90th percentile range of 6 to 83 hours. This range in incubation times represents differences in the design and operation of the distribution systems of the plants conducting the studies. Average temperature, pH, and free chlorine residual showed much less variability across all membrane studies, but temperature varied substantially in many of the studies, especially those conducted at sites outside Florida.

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Table 21.4

Average SDS chlorination conditions used during ICR membrane studies

SDS parameter	Median	25th–75th percentile range	10th–90th percentile range
Incubation time (hours)	41	24–48	6–83
Incubation temperature (°C)	22	20–24	16–25
Incubation pH	8.0	7.5–8.2	7.4–8.2
Free Cl_2 residual (mg/L)	1.0	0.8–1.3	0.7–1.7

Table 21.5

Summary of average influent water quality during ICR membrane studies

Parameter	Median	25th–75th percentile range	10th–90th percentile range
Alkalinity (mg/L $CaCO_3$)	82	45–154	14–280
Total dissolved solids (mg/L)	305	241–459	113–533
Total hardness (mg/L $CaCO_3$)	223	169–273	63–305
Calcium hardness (mg/L $CaCO_3$)	199	139–240	45–253
Ammonia (mg N-NH_3/L)	0.18	0.07–0.58	0.03–0.74
Bromide (µg/L)	100	66–154	41–199
TOC (mg/L)	6.2	3.4–9.2	2.6–13.0
UV_{254} (1/cm)	0.182	0.082–0.342	0.053–0.441
TSUVA* (L/mg-m)	3.1	2.3–3.5	1.8–3.9
SDS Cl_2 demand (mg/L)	8.6	3.8–11.4	2.4–20.0
SDS TOX† (µg Cl^-/L)	544	308–992	168–1,400
SDS TTHM (µg/L)	201	82–238	54–371
SDS HAA5 (µg/L)	87	54–148	32–243
SDS HAA6 (µg/L)	94	59–150	38–254
SDS HAA9‡ (µg/L)	94	71–171	40–275
SDS BDCM§ (µg/L)	27	17–53	12–70

* TSUVA = ultraviolet absorbance at 254 nm divided by the TOC concentration

† TOX = total organic halogen

‡ The number of values reported for HAA9 data is 48% of the number reported for HAA5 and HAA6 data; thus the HAA9 statistics are not directly comparable to the HAA5 or HAA6 statistics.

§ BDCM = bromodichloromethane

The SDS chlorination conditions used during the membrane studies were similar to those used for the GAC studies, although the median value for incubation time during the membrane studies (41 hours) was higher that that during the GAC studies (24 hours). Still, the 25th to 75th percentile ranges for incubation time were similar.

Table 21.5 presents a statistical summary of influent water quality during the membrane studies. Both the median bromide concentration, 100 µg/L, and TOC concentration, 6.2 mg/L, were much higher in the influent used for the membrane studies than in the influent of the plants conducting the studies, 36 µg/L and 2.4 mg/L for bromide and TOC, respectively (McGuire and

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Hotaling 2002). This was to be expected, because the requirement to conduct ICR treatment studies was based on average TOC concentrations in the influent or finished water of the plant, as discussed earlier and in Chapter 1 (Wysock et al. 2002). Median DBP precursor and SDS DBP concentrations in the influents used for membrane studies were all higher than the median concentrations observed in the influents used for GAC studies.

Controlling DBP Formation With Nanofiltration

To assess the applicability of nanofiltration for removing DBP precursors, the 64/48 and 32/24 RAA targets were evaluated, as they were in the assessment of GAC's ability to control DBP formation. The basis for these targets was explained previously.

The influent water quality data presented in Table 21.5 and Figure 21.6 demonstrate that most plants that conducted membrane studies could not meet either the 64/48 or the 32/24 RAA target under the SDS conditions evaluated. Only 15% of the plants had average influent SDS TTHM concentrations below the 64-µg/L target, and only 23% had average influent SDS HAA5 concentrations below the 48-µg/L target. None of the plants had average influent SDS TTHM concentrations below the 32-µg/L target, and only 3% had average influent SDS HAA5 concentrations below the 24-µg/L target. Many of the plants that conducted membrane studies will likely need to take steps to minimize DBP formation to comply with the 64/48 RAA, and the majority of these plants would need to modify treatment to comply with the 32/24 RAA.

Permeate water quality data collected during the ICR membrane studies represents complete treatment by nanofiltration. However, many nanofiltration plants treat only a portion of the influent stream with nanofiltration and blend the bypassed influent with the permeate stream. Influent–permeate blending allows a nanofiltration facility to meet a treatment objective at a lower capital and operating cost compared with complete nanofiltration treatment. Figure 21.6 shows the distribution of the annual average concentrations of DBP precursors and SDS DBPs in the membrane influents, permeates, and influent–permeate blends designed to achieve the 64/48 and 32/24 RAA targets. In all cases, annual average SDS TTHM and SDS HAA5 concentrations in the permeates of the 32 membrane studies were at or below the 64/48 RAA. However, even with the application of nanofiltration, four of the plants (12%) were unable to achieve the 32-µg/L TTHM target of the 32/24 RAA. This inability was most likely due to the use of "loose"

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nanofiltration membranes that do not achieve high (≥90 percent) rejections of organic matter and do not reject bromide ion. Application of a tighter nanofiltration membrane to these same water supplies would likely result in SDS DBP concentrations below the 32/24 RAA.

The concentrations of other SDS DBPs and DBP precursors are important nonregulatory targets for many utilities. Nanofiltration reduced the median concentration of the precursors TOC and bromide by 94% and 56%, respectively. With respect to other SDS DBPs, nanofiltration reduced the concentrations of SDS TOX and SDS BDCM by 96% and 95%, respectively. The data presented in Figure 21.6 demonstrate the ability of nanofiltration to reduce the concentrations of DBP precursors and other SDS DBPs in addition to SDS TTHM and SDS HAA5.

To determine the relative proportions of flow that must be treated by nanofiltration and flow that can be bypassed, it is necessary to determine the blend ratio (the ratio of permeate to total flow) for the controlling treatment objective. The following analysis determined the range of blend ratios required to meet the 64/48 and 32/24 RAA targets in the membrane studies in which blending was an option and calculated the corresponding blended-water quality. A flow weighted average of influent and permeate water quality as described by USEPA (2000d) and verified by Gusses, Allgeier, and Shukairy (1999) was used to estimate blended-water quality.

Of the 32 plants that evaluated membrane technology under the ICR, four plants (13%) were able to meet the 64/48 RAA without additional treatment, whereas two plants (6%) could not meet this target even with nanofiltration. The remaining 26 plants (81%) were able to meet the 64/48 RAA with influent–permeate blending.

For each study in which blending was an option, the blend ratios for both the TTHM and HAA5 targets were calculated, and the greater value was designated as the controlling blend ratio. In 73% of cases, the 64-µg/L TTHM target controlled; the 48-µg/L HAA5 target controlled in the remaining 27% of cases. The median value of the blend ratios that achieved the 64/48 RAA was 0.75, but the blend ratios covered a wide range (the 10th to 90th percentile range was 0.24 to 0.89).

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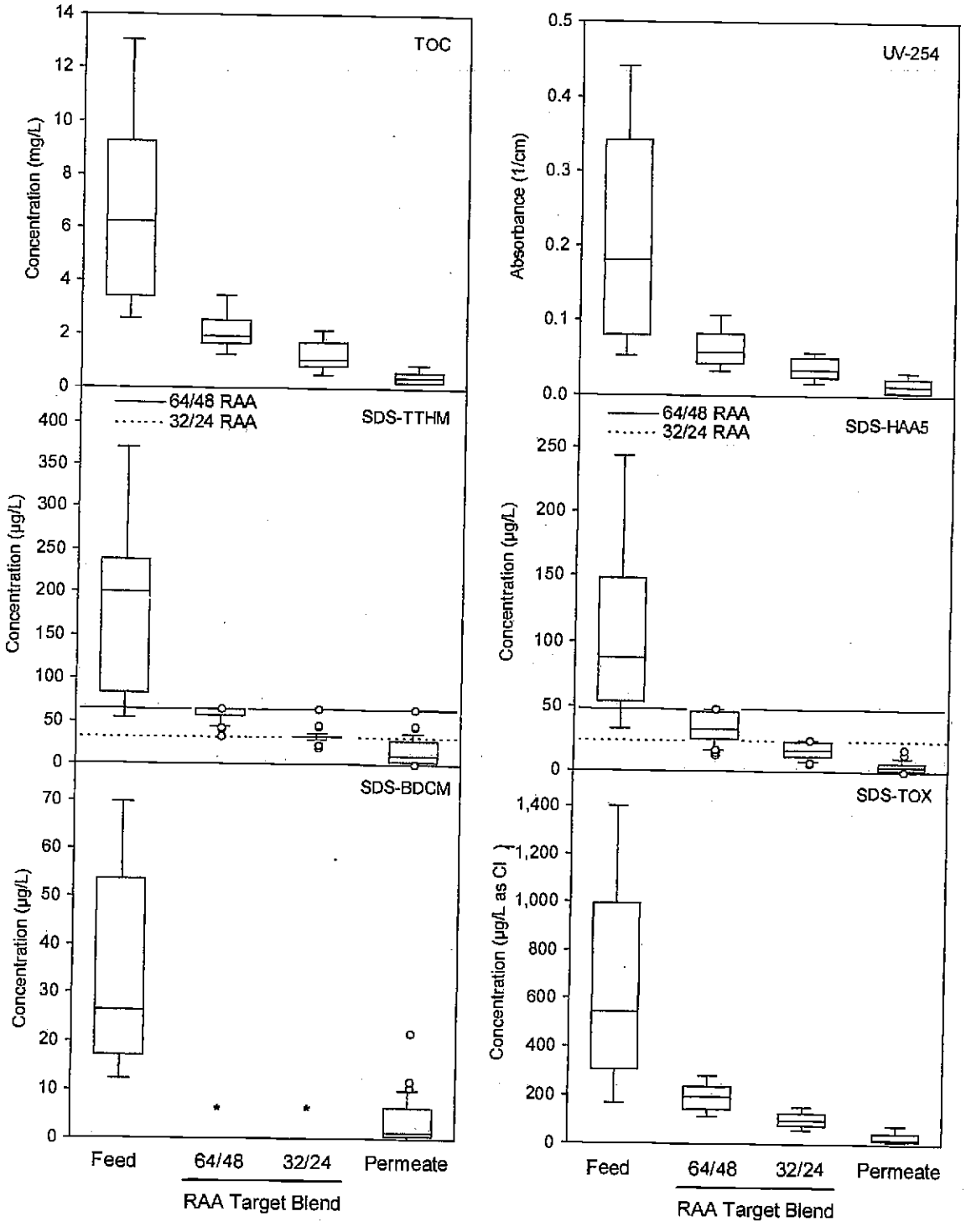

Figure 21.6 Distribution of average membrane feed, blended, and permeate water quality (concentrations of SDS BDCM could not be calculated because of model limitations)

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Figure 21.6 shows the distribution of SDS DBP and precursor concentrations corresponding to the influent–permeate blend that achieved the 64/48 RAA target in the 32 membrane studies. The incorporation of blending resulted in higher concentrations of precursors and SDS DBPs in the permeate, but these concentrations were still lower than those in the influent. The distribution of annual average SDS TTHM and SDS HAA5 data was based on the highest concentration among the influent, blended water, and permeate concentrations that met the 64/48 RAA in each study. The median SDS TTHM concentration was 64 μg/L, and the 10th to 90th percentile range was 44–64 μg/L. The median SDS HAA5 concentration was 33 μg/L, and the 10th to 90th percentile range was 16–48 μg/L. Under the scenario in which blending was considered an option, the distribution of both SDS TTHM and SDS HAA5 concentrations increased relative to permeate concentrations of these DBPs, but all of the values were at or below the 64/48 RAA target. Compared with influent concentrations, the median TOC and bromide concentrations were reduced by 68% and 24%, respectively, and the median SDS TOX concentration was reduced by 64%. Blended SDS BDCM concentrations could not be calculated because of limitations of the model used to predict the blended concentrations of individual DBP species (Gusses, Allgeier, and Shukairy 1999).

Under the conditions of the treatment studies, none of the 32 plants that evaluated membrane technology could meet the 32/24 RAA without additional treatment, and five plants (16%) could not meet this target even with nanofiltration. The remaining 27 plants (84%) were able to meet the 32/24 RAA by using influent–permeate blending. Although the percentage of plants that can use blending is similar for the 64/48 and 32/24 RAA targets, the number of plants that would need to modify treatment to meet the lower target was greater by 15%.

Blend ratios were calculated for both the TTHM and HAA5 targets, and the TTHM target controlled in 70% of the cases. The median value of the blend ratios for the 32/24 RAA was 0.88, but again the blend ratios covered a wide range (the 10th to 90th percentile range was 0.39 to 0.98). Blend ratios for the 32/24 RAA target were higher than those for the 64/48 RAA target, indicating a higher cost for nanofiltration to meet the 32/24 RAA.

The SDS DBP and precursor concentrations corresponding to the blend ratios that achieved the 32/24 RAA in the 32 membrane studies are also shown in Figure 21.6. In general, the blend ratios for the 32/24 RAA fell between those of the permeate and those for the 64/48 RAA target. The median SDS TTHM concentration was 32 μg/L, and the 10th to 90th percentile

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range was 29–37 μg/L (TTHM values above 32 μg/L represent plants that could not meet the target even with complete membrane treatment). The median SDS HAA5 concentration was 16 μg/L, and the 10th to 90th percentile range was 7–24 μg/L. Under the blending scenario for the 32/24 RAA option, the distribution of SDS TTHM values had a small range around the median; all values between the 28th and 88th percentiles are equivalent to the median value. The distribution of SDS HAA5 values showed slightly more variability, but all are at or below the 24-μg/L target.

Based on these results, 0 to 13% of all plants that conducted membrane studies could comply with a regulatory target between the 32/24 and 64/48 RAAs without implementing additional treatment. Between 6 and 16% of the plants that conducted membrane studies would not be able to comply with a regulatory target between the 64/48 and 32/24 RAAs using membrane treatment under the study conditions.

Impact of Membrane Type on Precursor Rejection

As discussed earlier, all of the RBSMT and quarterly SEBST studies evaluated at least two nanofiltration membranes, and several of the long-term studies also evaluated multiple membranes. These studies provide a direct comparison of different membranes treating the same water source.

Figure 21.7 shows the mean TOC and bromide rejections (and standard deviations, represented by the error bars) of all the membranes evaluated in at least two studies. The median TOC rejection for all membranes was 93%, ranging from 78% (for the NTR7450 membrane) to 99% (for the DS5-DL membrane). Bromide rejection showed much more variability across the membranes evaluated during the ICR. Figure 21.7 shows a substantial difference in bromide rejection by the loose membranes (NTR7450, NF200B, DS5-DL, NF45, TFC-SR, and TS80) compared with bromide rejection by the traditional softening membranes (CALP, ESNA1, NF70, LFC1, TFC-S, BW30LE, TFC-HR, and BW30). The median bromide rejection achieved by the loose membranes was 9% with a range of 5–15%, whereas the median bromide rejection achieved by the softening membranes was 74%, with a range of 66–89%. However, the median TOC rejections of the loose and softening membranes were the same, at 93%. The preferential rejection of TOC over bromide by the loose membranes resulted in substantial shifts in DBP

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speciation after treatment by these membranes. See Chapter 6 for a discussion of the effects of bromide and TOC concentrations on DBP speciation (McLain et al. 2002).

In several bench-scale studies, membranes with different rejection characteristics were evaluated under the same test conditions. In some cases, the permeate from these membranes was substantially different, with implications for meeting the 64/48 or 32/24 RAA targets. Three case studies demonstrate the impact of membrane type on finished water quality.

The bench-scale membrane study conducted for Lee County, Florida, evaluated the NTR7450 and TFC-SR membranes for treating this surface water using conventional filtration as pretreatment. Although both membranes could be considered loose with respect to rejection of inorganic solutes, the quality of the permeates was substantially different. The average permeate TOC concentration from the NTR7450 was 1.4 mg/L, higher than the average permeate TOC concentration from the TFC-SR membrane, 0.4 mg/L. This difference in TOC rejection resulted in average SDS TTHM and SDS HAA5 concentrations of 70 and 14 μg/L, respectively, in the NTR7450 permeate compared with 29 and 5 μg/L, respectively, in the TFC-SR permeate. The NTR7450 did not provide sufficient rejection of precursors to meet the 64/48 RAA, whereas the TFC-SR was able to meet the 32/24 RAA. For removing organic DBP precursors without removing inorganic constituents (and thus softening the water), a membrane with rejection characteristics like those of the TFC-SR may be ideal because it removes ≥90 percent of the organic matter but leaves sufficient alkalinity to produce stable (noncorrosive) finished water.

The city of Fort Lauderdale, Florida, evaluated the same two membranes for treating a groundwater source using cartridge filtration as pretreatment. The average TOC concentration in permeate from the NTR7450, 2.0 mg/L, was much higher than the average TOC concentration in permeate from the TFC-SR, 0.3 mg/L. Average SDS TTHM and SDS HAA5 concentrations in the NTR7450 permeate were 65 and 17 μg/L, respectively, and 12 and 2 μg/L, respectively, in the TFC-SR permeate. As with the results from Lee County, the NTR7450 was not able to meet the 64/48 RAA, whereas the TFC-SR produced higher quality permeate that met the 32/24 RAA.

In the third case study, Water District No. 1 of Johnson County, Kansas, evaluated a loose membrane, the NF200B, and a softening membrane, the BW30LE. This study was conducted with Missouri River water and used lime softening and scale control as pretreatment. Both membranes rejected TOC to concentrations below the ICR's minimum reporting level, but the BW30LE rejected more bromide than the NF200B. The average bromide concentration was

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22 μg/L in the BW30LE permeate and 111 μg/L in the NF200B permeate. This difference in permeate bromide concentrations resulted in higher SDS TTHM and SDS HAA5 concentrations in the NF200B permeate, 7 and 2 μg/L, respectively, compared with those in the BW30LE permeate, 2 and 0.3 μg/L, respectively. The higher bromide concentration in the NF200B permeate resulted in higher concentrations of bromine-substituted DBPs as well as higher concentrations of the sums of the DBP classes. Table 21.6 shows the average concentrations of bromine-substituted DBPs in the permeate streams from these two membranes.

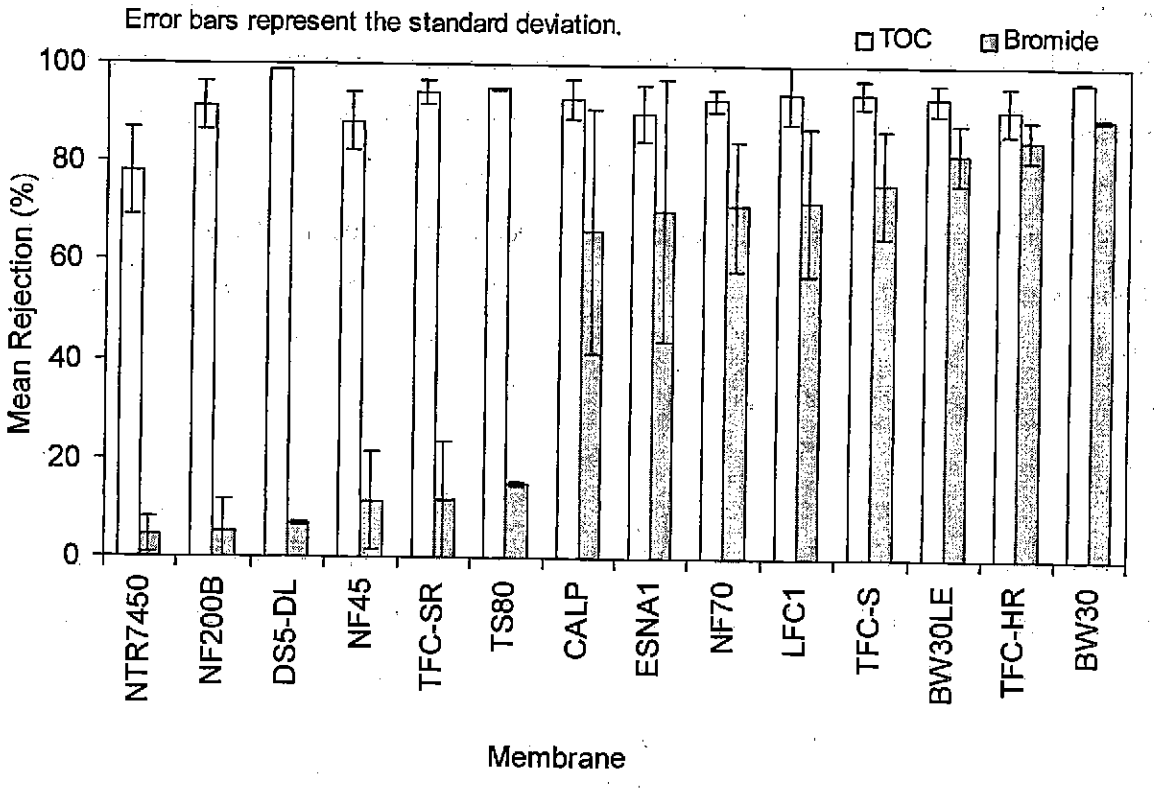

Figure 21.7 Average rejection of TOC and bromide by the membranes evaluated during ICR treatment studies

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Table 21.6

Average concentrations of bromine-substituted DBPs in the influent and permeate streams from the BW30LE and NF200 membranes evaluated in the Johnson County study

Parameter	Influent concentration (µg/L)	BW30LE permeate concentration (µg/L)	NF200B permeate concentration (µg/L)
Bromide	113	21.5	111
SDS BDCM*	23.5	0.4	1.1
SDS DBCM†	14.8	0.5	3.0
SDS $CHBr_3$‡	4.5	0.3	3.9
SDS DBAA§	4.6	0.1	1.1

* BDCM = bromodichloromethane
† DBCM = dibromochloromethane
‡ $CHBr_3$ = bromoform
§ DBAA = dibromoacetic acid

SUMMARY AND CONCLUSIONS

The GAC and membrane treatment studies were an important component of the ICR effort to gather water quality and treatability data from water systems nationwide. The impact of potential MCLs on the costs of advanced treatment can be significant, as the comparison of compliance with the 64/48 and 32/24 RAA targets shows.

Median GAC run times for compliance with the 64/48 RAA were 170 and 272 days for GAC10 and GAC20, respectively. Median GAC run times were shortened by an average of 10%—to 154 and 243 days for GAC10 and GAC20, respectively—when the GAC treatment was operated to comply with the 32/24 RAA target. Thirty percent of the plants that conducted GAC studies were able to meet the 64/48 RAA with existing conventional treatment, 42% were able to comply using GAC10, and 19% would require GAC20. Nine percent of the plants could not meet the 64/48 RAA with GAC20. Only 5% of the plants that conducted GAC studies met the 32/24 RAA with existing conventional treatment, 39% were able to comply using GAC10, and 23% would require GAC20. Thirty-three percent of the plants were unable to comply with the 32/24 RAA using GAC20.

In membranes studies in which blending was an option, the median influent–permeate blend for compliance with the 64/48 RAA was 0.75. This value increased by 17%, to 0.88, when a 32/24 RAA was the compliance target. Furthermore, 16% of the plants that conducted

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membrane studies could not comply with the 32/24 RAA target using complete treatment by nanofiltration, and 6% could not meet the 64/48 RAA target.

Data from the treatment studies provide useful information for the application of GAC and membranes. One important difference between implementing GAC and membrane technologies is that GAC can often be added as a retrofit technology, using the plant's existing processes as pretreatment, whereas pretreatment systems used prior to membrane processes must be designed and operated specifically to minimize membrane fouling. The influent used in many of the GAC studies was conventionally treated, whereas the membrane studies used a variety of pretreatment technologies, including microfiltration, scale control, and disinfection with chloramines or ultraviolet irradiation.

Most of the GAC treatment studies evaluated EBCTs of 10 and 20 minutes, providing an unprecedented database of information on GAC performance under these two conditions. Many membrane studies compared different types of membranes under the same influent water quality and operating conditions. The results of these comparisons demonstrate how certain design factors affect the ability of advanced treatment processes to meet specific water quality targets.

The results presented in this chapter represent a set of specific analyses focusing on two regulatory options that were discussed during the 1999–2000 negotiations for the Stage 2 DBP Rule. This analysis represents only a fraction of the information contained in the *ICR Treatment Study Database*. The database is a flexible platform that can be used to evaluate DBP precursor removal, DBP formation, process design information, and plant characteristics through user-defined queries. Furthermore, the methods used in the base analysis of the treatment study data represent an innovative way of managing the complex data sets generated during the ICR GAC and membrane studies. In this manner, the *ICR Treatment Study Database*, as well as the tools used to develop it, will serve as a valuable resource for analyzing and understanding GAC and membrane performance as DBP precursor removal technologies.

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CHAPTER 22

ENHANCED SOFTENING PERFORMANCE AND TOC REMOVAL

Sarah C. Clark, Felicia James, and Desmond F. Lawler

ABSTRACT

The Disinfectants/Disinfection By-products Rule designates enhanced softening as a performance criterion for softening plants to ensure the removal of specific amounts of total organic carbon (TOC). Evaluating data from softening plants that participated in Information Collection Rule (ICR) monitoring provided a means for better understanding the range of TOC removal at softening plants, the mechanisms by which TOC is removed during the softening process, and the systematic relationships between TOC removal and the removal of magnesium and alkalinity during softening. With few exceptions, ICR softening plants operated in the enhanced softening mode during the 18-month ICR monitoring period. No correlations between TOC removal and the removal of calcium or hardness were identified. The data demonstrated a weak correlation between TOC removal and magnesium removal. With the exception of results from a few samples, concentrations of disinfection by-products in softening plants were within the required maximum contaminant levels on a quarterly basis.

INTRODUCTION AND BACKGROUND

Treating drinking water by softening has long been recognized as an effective method of removing turbidity and producing generally high-quality finished water. Completion of sampling under the Information Collection Rule (ICR) and development of the ICR databases provided the opportunity to examine the performance of large softening plants.

The regulatory framework of the Disinfectant/Disinfection By-Products (D/DBP) Rule designates enhanced softening as a performance criterion by requiring softening plants to remove a certain amount of total organic carbon (TOC) in the treatment process (U.S. Environmental Protection Agency [USEPA] 1998). Softening plants are subject to the same TOC removal requirements as conventional plants. These requirements are stipulated in a 3 × 3 matrix of source water TOC and alkalinity, contained in the D/DBP Rule and presented in Chapter 13 (Frey, Seidel, and Sullivan 2002). Most softening plants are classified in the far right column of this matrix because the alkalinity of their source water is greater than 120 mg/L as $CaCO_3$, but a few fall into the classification for influent with alkalinity of 60–120 mg/L. In addition, the

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D/DBP Rule identified several alternative compliance criteria regarding magnesium removal and finished water alkalinity. Softening plants that cannot meet the removal requirements stipulated in the 3 × 3 matrix but that remove a minimum of 10 mg/L of magnesium as $CaCO_3$ are considered to be in compliance with enhanced softening criteria. Alternatively, softening plants that reduce their finished water alkalinity to 60 mg/L as $CaCO_3$ are in compliance with enhanced softening criteria.

In this analysis, the authors evaluated the ICR data from softening plants with three objectives: (1) to determine the range of TOC removal accomplished by softening, (2) to increase the understanding of TOC removal mechanisms, and (3) to look for systematic relationships between TOC removal and the removal of hardness and alkalinity through the softening process. Data were extracted from ICR Auxiliary Database 1, and all available data from the entire ICR monitoring period were used in the analysis. Because the ICR required sampling to be conducted at different intervals, some of the data used were monthly and some were quarterly sample results. When paired samples were required for analysis, all data sets containing both members of the pair were used.

Removal of Natural Organic Matter by Softening

Early studies of the use of softening to remove natural organic matter (NOM) from drinking water focused on color removal. Since the discovery of disinfection by-products (DBPs) in drinking water, the largest study on softening was conducted by Randtke and co-workers (Randtke et al. 1982; Liao and Randtke 1985, 1986). This study used synthetic water made by adding various inorganic salts and organic constituents to distilled water. Most of the NOM removal was attributed to coprecipitation, through which soluble organics adsorb onto the nuclei of the solids formed during softening or are incorporated into the precipitates as they form.

This study also demonstrated several attributes of NOM removal by softening. Liao and Randtke (1985) found that organic matter adsorbs onto $CaCO_3$ crystals during the earliest stages of the precipitation reaction. When magnesium hydroxide was precipitated with the calcium carbonate, surface adsorption was greatly enhanced—to the extent that surface adsorption accounted for much or all of the organics removal that occurred in the presence of magnesium (Randtke et al. 1982). Adding phosphate improved TOC removal somewhat, and so did adding

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soda ash five minutes after lime (allowing precipitation to be initiated twice). These investigators also found that high-molecular-weight organics were removed preferentially.

Qasim, Hashsham, and Ansari (1992) tested the effects of adding iron during lime softening of a high-turbidity (45 NTU) water source; they found that TOC reduction increased with increasing iron dosages over a range of 3 to 9.5 mg/L Fe. In a study of enhanced softening at six facilities, Shorney and Randtke (1994) found that TOC removal increased with magnesium hydroxide precipitation, but such precipitation increased the costs of chemicals and residuals disposal. In this study, low doses of iron improved TOC removal, but higher doses had no additional effect.

Thompson et al. (1997) studied three water sources from softening plants representing the three TOC ranges in the D/DBP Rule's matrix of source water TOC and alkalinity. These researchers conducted jar tests with varying dosages of lime (and lime plus soda ash). Organics removal during $CaCO_3$ precipitation was only modest, whereas magnesium hydroxide precipitation resulted in dramatic increases in the removal of dissolved organic carbon (DOC). These authors found specific ultraviolet absorbance, or SUVA, to be a good quantitative predictor of the effectiveness of softening at removing DOC.

Clark, Wiginton, and Musgrove (1994) conducted pilot tests and jar tests with source water taken directly from the reservoirs that feed the treatment plants of the city of Austin, Texas. Both pilot and jar tests indicated that the minimum TOC concentration achievable by enhanced softening was 1.7 to 2.0 mg/L. This study also showed that increasing ferric sulfate dosages produced little or no benefit with regard to removing TOC or reducing total trihalomethane (TTHM).

Ralls et al. (1999) and Kweon et al. (2000) reported on an ongoing study of enhanced softening. Using natural water supplies from Austin and St. Louis, these investigators found that softening could remove TOC to the concentrations required by current regulations but that this did not necessarily translate into lower DBP concentrations. In both water sources, the more highly bromine-substituted species of trihalomethanes (bromoform and dibromochloromethane) increased with increased softening (lime dosage), even though TOC concentrations decreased. In addition, magnesium hydroxide precipitation had only a marginal effect on TOC removal; the small amount of magnesium that coprecipitated with $CaCO_3$ at lime dosages and pH values

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below those required for magnesium hydroxide precipitation was apparently equally successful at removing TOC.

TREATMENT PLANTS INCLUDED IN THIS ANALYSIS

Like conventional plants, softening plants vary widely in design. Though it would be interesting to study ICR softening plants as a unified group in as large a database as possible, this analysis did not take that approach because the interest here was in examining the removal of TOC and the formation of DBPs during traditional softening processes (those including flocculation and sedimentation). This specific interest necessitated the elimination of some plants from the analysis.

Treatment plant information stored in the ICR database includes a description of each plant's design, and this evaluation began by extracting from the database all those plants with softening in the description. Next, the description of each of these plants was compared with the plant's ICR sampling schematic to determine whether the data elements in the database were comparable among plants. In addition, information from a Technical Workgroup survey of ICR softening plants was used as a reference for each plant's treatment scheme. As a result of this checking, some of the 63 plants initially extracted from the database were eliminated. Plants that used ozone or membrane filtration were excluded either because these processes directly affect TOC removal or because the location of these processes in the plants precluded the selection of sampling points that could demonstrate TOC removal by the softening process alone. Plants that used split treatment—water in one treatment train was softened and then blended with a stream that had not been softened—were also eliminated from the analysis. A total of 47 plants, as shown in Table 22.1, were included in the analysis presented here.

Softening plants are generally located in two areas of the United States. Most are located in an area stretching longitudinally through the middle of the country from Texas to the Dakotas and, at the northern end, east to Ohio. The second and smaller group of softening plants is in Florida. Locations of the plants included in this analysis are indicated on the map in Figure 22.1.

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Table 22.1

Softening plants whose ICR data were included in this analysis

ICR plant number	City	State	ICR plant number	City	State	ICR plant number	City	State
G-279	Gainesville	Fla.	M-382	Wichita	Kan.	G-529	Columbus	Ohio
G-282	Cocoa	Fla.	S-383	Topeka	Kan.	S-534	Toledo	Neb.
G-296	Ft. Lauderdale	Fla.	S-387	Louisville	Ky.	S-539	Youngstown	Ohio
G-297	Ft. Lauderdale	Fla.	S-388	Louisville	Ky.	S-546	Oklahoma City	Okla.
G-300	Miami–Dade	Fla.	G-421	Lansing	Mich.	M-604	Sioux Falls	S.D.
G-301	Miami–Dade	Fla.	G-422	Lansing	Mich.	S-639	Waco	Texas
G-302	Miami–Dade	Fla.	S-425	Minneapolis	Minn.	S-640	Waco	Texas
G-306	Boca Raton	Fla.	S-428	St. Paul	Minn.	S-653	Abilene	Texas
G-308	West Palm Beach	Fla.	G-429	Independence	Mo.	S-654	Austin	Texas
S-338	Cedar Rapids	Iowa	S-430	Kansas City	Mo.	S-655	Austin	Texas
S-340	Des Moines	Iowa	S-435	St. Louis	Mo.	S-656	Austin	Texas
G-345	Champaign	Ill.	S-436	St. Louis	Mo.	S-658	Wichita Falls	Texas
S-365	Springfield	Ill.	S-437	St. Louis	Mo.	S-659	Wichita Falls	Texas
S-368	Fort Wayne	Ind.	S-438	St. Louis	Mo.	M-709	Aurora	Ill.
S-379	Evansville	Ind.	S-527	Columbus	Ohio	G-734	Tampa	Fla.
			S-528	Columbus	Ohio	S-735	St. Louis	Mo.

G = groundwater plant; S = surface water plant; M = mixture of groundwater and surface water

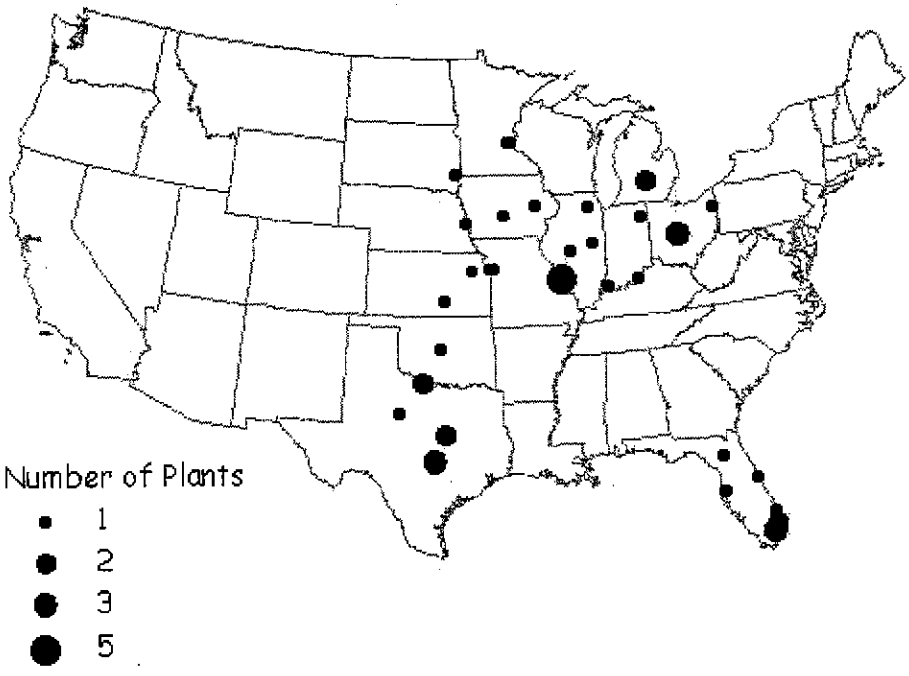

Figure 22.1 Locations of softening plants included in this analysis

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CHARACTERIZING INFLUENT AND FINISHED WATER

Although operators of softening plants are generally most concerned about the same finished water parameters that concern operators of conventional treatment plants, the softening process requires specific attention to pH, calcium hardness, magnesium hardness, and alkalinity. Evaluation of the data in this analysis included graphing water quality parameters on a monthly basis to ascertain the range of values (high, low, and typical) and their variation within individual plants. Some water quality parameters were common to specific geographic areas—particularly calcium hardness, magnesium hardness, total hardness, and TOC. Eighteen-month averages of water quality parameters at the 47 plants included in this analysis are presented in Table 22.2.

Influent pH at these softening plants ranged from approximately 7 to about 8.5. Influent pH values at most plants did not vary from month to month by more than ± 0.3 units; however, the pH at plant 604 in South Dakota varied by more than ± 0.5 units. Finished water pH values exhibited a wider spread, ranging from approximately 7 to about 10.5, with 83% of plants having a finished water pH above 8.5.

Influent calcium concentrations were nearly all less than 400 mg/L as $CaCO_3$. Typically, these values ranged between 200 and 400 mg/L as $CaCO_3$ in Florida water supplies and between 100 and 200 in non-Florida sources, with the exception of Kentucky and Ohio sources, which were typically below 100 mg/L as $CaCO_3$. The overwhelming majority of plants (88%) reported finished water calcium concentrations of less than 100 mg/L as $CaCO_3$. Finished water calcium concentrations at the Florida plants tended to be between 50 and 100 mg/L as $CaCO_3$, whereas those at the non-Florida plants were between 20 and 100. Finished water calcium concentrations at the remaining plants (12%) varied between 100 and 280 mg/L as $CaCO_3$.

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Table 22.2.
Water quality parameters at softening plants included in this analysis

ICR plant number	Average data from 18 months of monitoring					
	Influent			Finished water		
	TOC (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Total hardness (mg/L as $CaCO_3$)	TOC (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Total hardness (mg/L as $CaCO_3$)
G-279-FL	0.97	171.67	236.67	0.40	33.06	133.33
G-282-FL	5.54	208.22	326.22	3.78	38.83	114.22
G-296-FL	11.72	224.89	248.00	9.17	50.11	82.44
G-297-FL	9.91	214.50	251.22	7.16	31.33	77.78
G-300-FL	4.61	200.72	220.11	4.04	48.44	68.17
G-301-FL	15.39	213.61	222.39	12.00	62.39	81.33
G-302-FL	12.02	221.89	227.00	7.18	49.28	60.89
G-306-FL	12.53	217.67	249.44	10.01	51.22	90.83
G-308-FL	10.07	273.71	320.89	6.35	30.65	84.17
S-338-IA	2.22	266.06	270.50	1.36	74.72	118.89
S-340-IA	4.78	226.94	297.22	1.33	47.50	129.28
G-345-IL	2.13	327.28	254.00	1.57	150.72	79.67
S-365-IL	4.56	126.56	191.29	2.08	25.88	98.47
S-368-IN	7.70	212.11	257.00	3.14	36.28	105.28
S-379-IN	2.97	88.89	145.89	2.24	88.22	161.00
M-382-KS	3.24	188.33	206.94	2.42	82.00	108.71
S-383-KS	5.76	172.78	232.22	2.61	66.39	122.56
S-387-KY	2.74	87.61	160.17	2.16	80.61	168.11
S-388-KY	2.73	87.06	157.65	2.05	81.82	170.41
G-421-MI	2.50	322.78	431.50	1.49	36.83	99.89
G-422-MI	4.01	305.56	409.89	2.13	41.72	105.39
S-425-MN	8.72	160.33	181.94	4.35	39.28	76.89
S-428-MN	8.14	144.12	163.13	4.10	52.47	77.24
G-429-MO	2.21	194.00	274.78	1.56	48.56	119.56
S-430-MO	3.80	185.22	265.50	1.99	44.72	123.61
S-435-MO	3.64	152.67	219.06	2.73	50.83	124.94
S-436-MO	3.70	152.17	216.22	2.72	45.67	117.44
S-437-MO	2.38	155.22	173.50	1.55	69.33	102.11
S-438-MO	2.34	150.72	169.94	1.43	70.33	103.44
S-527-OH	5.53	108.78	161.67	2.63	25.67	114.50
S-528-OH	6.21	160.56	274.06	2.48	49.39	121.67
G-529-OH	1.50	281.94	427.22	0.97	41.06	117.83
S-534-OH	3.19	94.22	123.67	1.62	46.22	81.94
S-539-OH	5.24	75.11	132.33	3.19	33.94	90.83
S-546-OK	6.99	189.00	307.13	3.72	48.00	175.88
M-604-SD	4.87	293.82	485.83	3.09	46.06	281.67
S-639-TX	3.32	120.33	143.11	2.94	115.33	144.89
S-640-TX	2.90	120.56	143.11	2.87	114.12	144.06
S-653-TX	4.66	157.11	246.39	4.03	94.33	180.67
S-654-TX	3.72	163.89	206.61	2.45	56.39	99.89
S-655-TX	3.85	164.39	205.44	2.38	55.17	98.89
S-656-TX	3.24	183.47	225.29	1.85	53.24	99.59
S-658-TX	4.01	149.11	161.00	3.18	55.11	76.39
S-659-TX	4.63	147.14	156.86	3.15	54.93	71.14
M-709-IL	8.35	235.00	312.00	2.95	70.78	134.06
G-734-FL	2.68	235.63	251.13	2.60	229.75	255.63
S-735-MO	3.55	152.67	213.33	2.73	50.67	125.61

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Though magnesium hardness was not reported as part of ICR monitoring, calculating the difference between reported total hardness and reported calcium hardness, in accordance with Standard Method 3500B, produced approximate magnesium hardness values for each sampling event. Influent concentrations of magnesium hardness were generally less than 150 mg/L as $CaCO_3$, though a few values fell between 150 and 250. The data for plant 529 in Ohio stand out because this plant's influent magnesium hardness was calculated at 325 $\pm$ 25 mg/L as $CaCO_3$. Finished water magnesium concentrations at this plant and most of the other plants were just under 100 mg/L as $CaCO_3$. Both Kentucky plants, the South Dakota plant, and plant 709 in Illinois had finished water magnesium concentrations between 100 and 150 mg/L as $CaCO_3$.

Influent total hardness concentrations ranged between 100 and 600 mg/L as $CaCO_3$, with a few monthly data points below 100 mg/L. Although approximately 91% of the plants recorded influent total hardness concentrations between 100 and 350 mg/L as $CaCO_3$, Florida water sources occupied only the upper half of this range, whereas non-Florida sources were spread throughout the range. Plants with total hardness concentrations above this range—values between 350 and 600 mg/L as $CaCO_3$—were the South Dakota plant, plant 529 in Ohio, and both Missouri plants. Finished water total hardness concentrations typically ranged from 50 to less than 200 mg/L as $CaCO_3$; however, the South Dakota plant and plant 734 in Florida had finished water total hardness concentrations of 250 to more than 300 mg/L as $CaCO_3$.

Understanding the relative concentrations of calcium and magnesium in source water is useful in examining the results of softening. A higher calcium-to-magnesium (Ca:Mg) ratio indicates that more calcium is present for each unit of magnesium present; generally, a high value for this ratio reflects a low magnesium concentration rather than an extraordinarily high calcium concentration. Calculated influent Ca:Mg ratios for the plants in this analysis fell into two ranges. Although most of the plants had ratios of less than 5, several had ratios between 5 and 25, and the ratios at one Florida plant varied from 8 to 83. With the exception of a few monthly data points, all the plants with influent Ca:Mg ratios greater than 5 were located in Florida. Most of the Ca:Mg ratios calculated for finished water were less than 6, but four plants had ratios of up to at least 20 in some months.

As expected on the basis of assumptions reflected in the D/DBP Rule, most softening plants had source water in the highest alkalinity classification (>120 mg/L as $CaCO_3$) of the 3 $\times$ 3 matrix of source water TOC and alkalinity, though several plants had source water in the

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intermediate alkalinity range (60–120 mg/L as $CaCO_3$). The distribution of monthly plant data across the matrix is shown in Figure 22.2. Influent alkalinity concentrations varied greatly from a low concentration of approximately 50 mg/L as $CaCO_3$ to a high of nearly 350 mg/L as $CaCO_3$; plant 529 in Ohio reported one monthly value of 444 mg/L as $CaCO_3$. Though the data on influent alkalinity were generally uniformly distributed throughout this range of 50 to 350 mg/L as $CaCO_3$, values from the Florida plants appeared to be limited to approximately 200–300 mg/L as $CaCO_3$. Data from most plants showed finished water concentrations of less than 100 mg/L as $CaCO_3$ and greater than 25 mg/L as $CaCO_3$.

Shown in each rectangle in Figure 22.2 is the corresponding TOC removal percentage required by the matrix of source water TOC and alkalinity. The concentration of influent TOC varied from 0.9 to 20 mg/L across all plants. Most of the plants had influent TOC concentrations of less than 6 mg/L and exhibited little variance from month to month ($\pm$0.2). Plants with influent TOC concentrations greater than 6 mg/L tended to have a much larger degree of variance (+1.5 or more) and were located primarily in Florida, though both Minnesota plants were also in this group.

Evidence of basic geographic differences in water sources can be seen in Figure 22.3, where the Ca:Mg ratio is plotted as a function of influent TOC. The Florida water supplies are plotted with one symbol, and all the other plants are plotted with an alternative symbol. Not only did the Florida water sources have higher Ca:Mg ratios, but they also had higher influent TOC concentrations overall than the non-Florida sources. Two plants were exceptions to this pattern. Plant 279 in Florida had a relatively low Ca:Mg ratio and the lowest recorded influent TOC concentrations of all the plants (0.9—1.25 mg/L). Approximately one third of the Ca:Mg ratios for plant 639 in Texas were more than 5, though the plant's influent TOC concentrations were consistent with those of other non-Florida plants.

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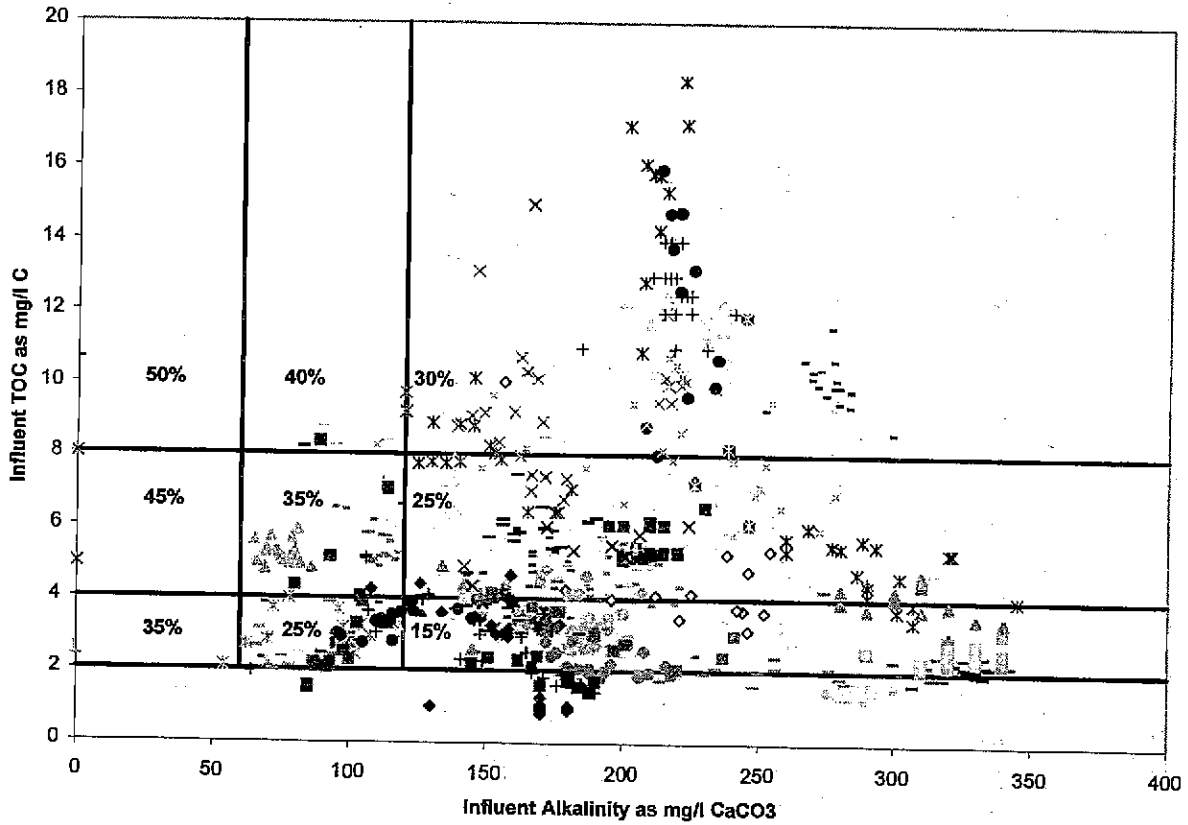

Figure 22.2 Distribution of monthly ICR softening plant data classified according to the D/DBP Rule's matrix of source water TOC and alkalinity

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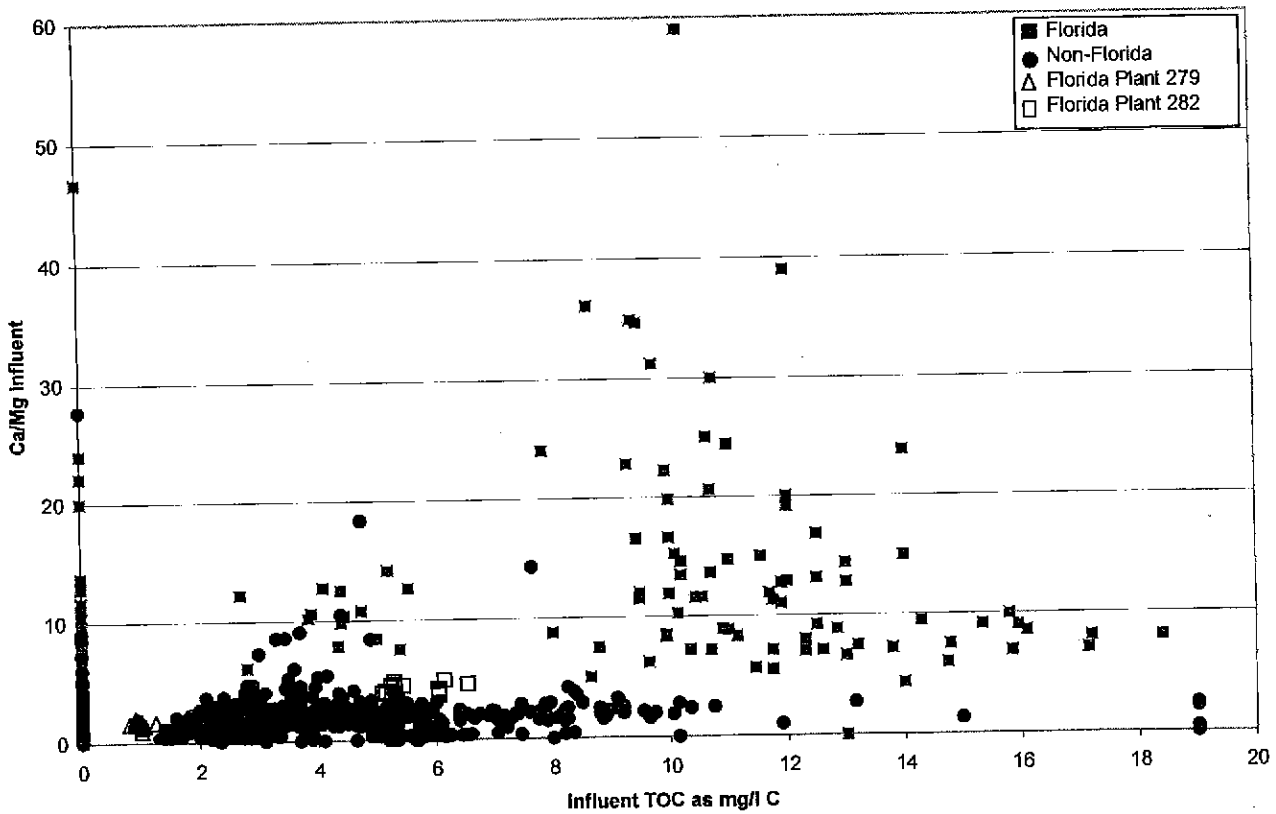

Figure 22.3 Geographic differences in source water characteristics

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SOFTENING TREATMENT

Hardness

Overall, the ICR data showed that individual softening plants produce finished water of fairly consistent quality. Nevertheless, a wide range of hardness removal was evident across all the plants. This variation is due to the fact that influent hardness varies across the country, and hardness removal goals apparently vary also. During ICR sampling, individual plants tended to operate with a constant or near constant lime dosage, as shown in Figure 22.4. All of the plants with very low (and sometimes negative) hardness removal concentrations used very low lime dosages, with data from some months showing no application of lime at all and some doses as low as 11–20 mg/L as $Ca(OH)_2$. Such plants probably add lime for purposes other than softening but were classified as softening plants under the ICR. Typical lime dosages in ICR softening plants ranged from 100 to 300 mg/L as $Ca(OH)_2$. Total hardness removal typically ranged from 20 to 80%.

The pH typically maintained during the softening process correlates with the lime dosages and the hardness removal percentages observed during ICR monitoring. Figure 22.5 shows monthly softening process pH values for the plants included in this analysis. Little or no hardness removal occurs at a process pH below 9. Above pH 9, calcium carbonate precipitation dominates until the pH reaches the range of 10.6 or above, at which point magnesium hydroxide precipitates if magnesium is present in the water. Given the range of pH at ICR softening plants, a range of hardness removal would be expected, and this is evident in the data.

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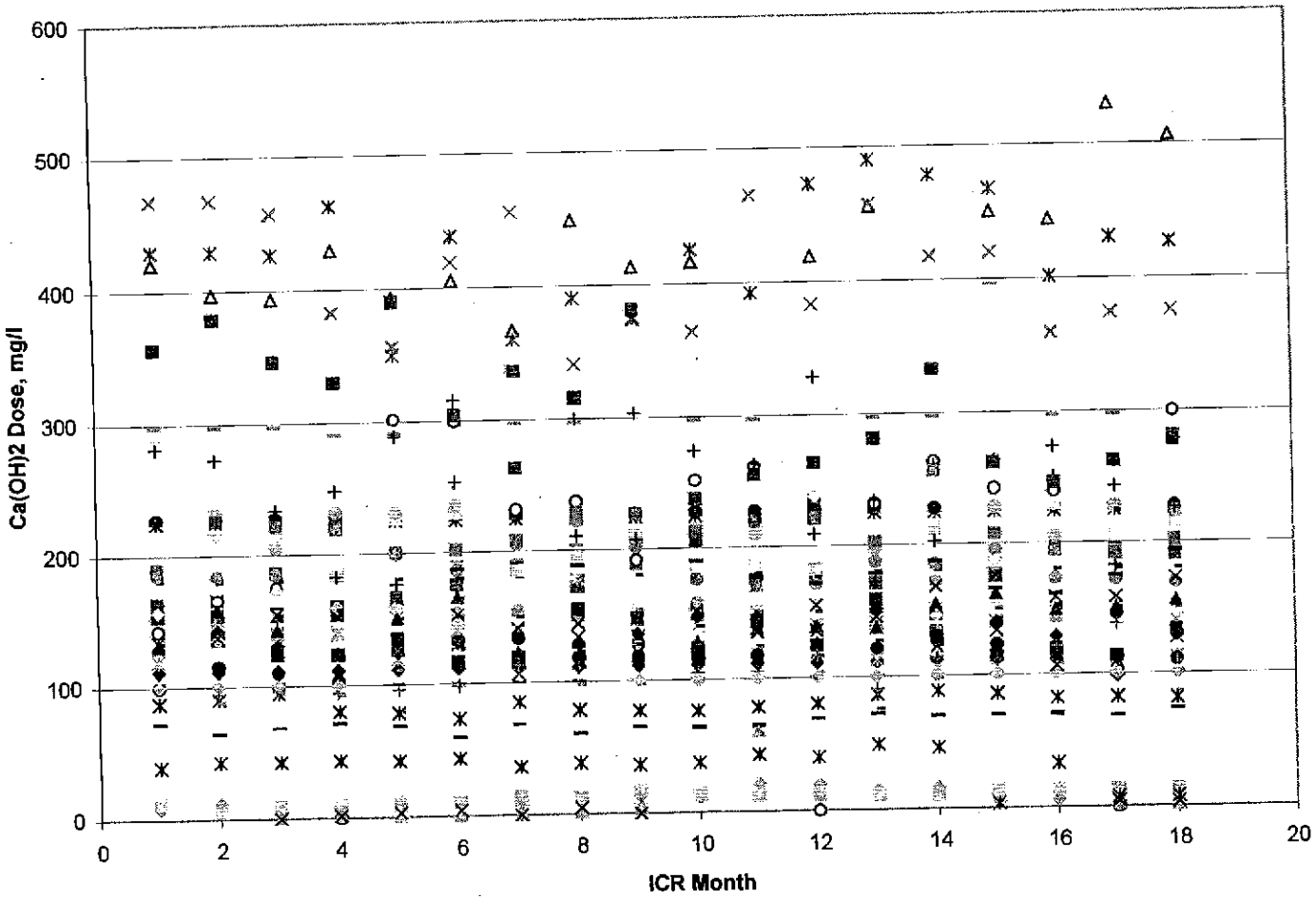

Figure 22.4 Lime dosages at individual softening plants were relatively constant during ICR monitoring

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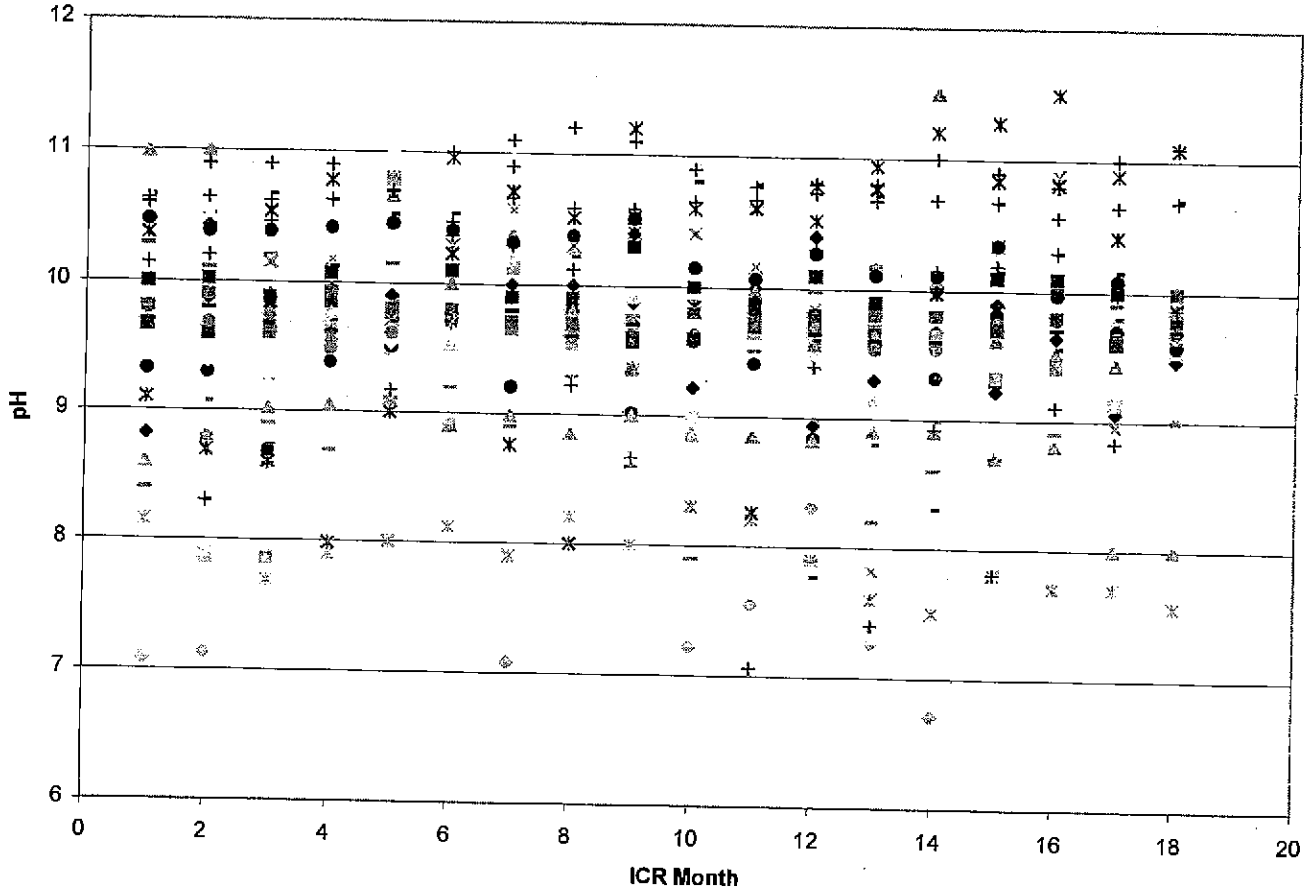

Figure 22.5 Softening process pH for plants included in this analysis

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Calculated percentages of calcium hardness removal showed that most plants achieved removals of 40 to 80%; the measured change in calcium hardness ranged from –25 to 350 mg/L as $CaCO_3$. The removal of TOC as a function of the change in calcium hardness is shown in Figure 22.6. Increases in calcium hardness occurred at some plants. The finished water in both Kentucky plants, for example, showed an increase in calcium hardness. These results indicate that although these plants add lime during their treatment processes, they are not primarily softening plants. TOC removal during softening does not correlate with changes in total hardness, total calcium hardness, or alkalinity across the treatment process. However, the data showed that softening effectively removed TOC (>20% removal).

Figure 22.7 shows monthly TOC removal percentages at all softening plants included in this analysis. More than 20% TOC removal was common among these plants, and many obtained removals in the range of 30 to 50%.

Finished water TOC concentrations were generally more consistent in plants with low influent TOC concentrations than in plants with high influent TOC concentrations (Figure 22.8). The upper diagonal line on Figure 22.8 is the line of 0 removal; the lower diagonal line is the line of 50% removal. Most plants achieved TOC removals between 0 and 50%, though a few monthly values were above 50%. Removal percentages did not seem to be related to influent TOC concentration because plants with high influent TOC concentrations achieved the same range of removal percentages as plants with low influent TOC concentrations. The data from individual plants fell into clusters, illustrating consistency in source water TOC concentration and TOC removal at each plant. Plants with data clustered in the range below the 50% line (greater than 50% TOC removal) most likely achieved high removal percentages because of the type of TOC in their influent, not because of differences in treatment (softening treatment generally does not differ from plant to plant). Figure 22.9, which compares influent TOC concentrations with TOC removal percentages, illustrates that an increase in influent TOC does not correspond to an increase in the percentage of TOC removal.

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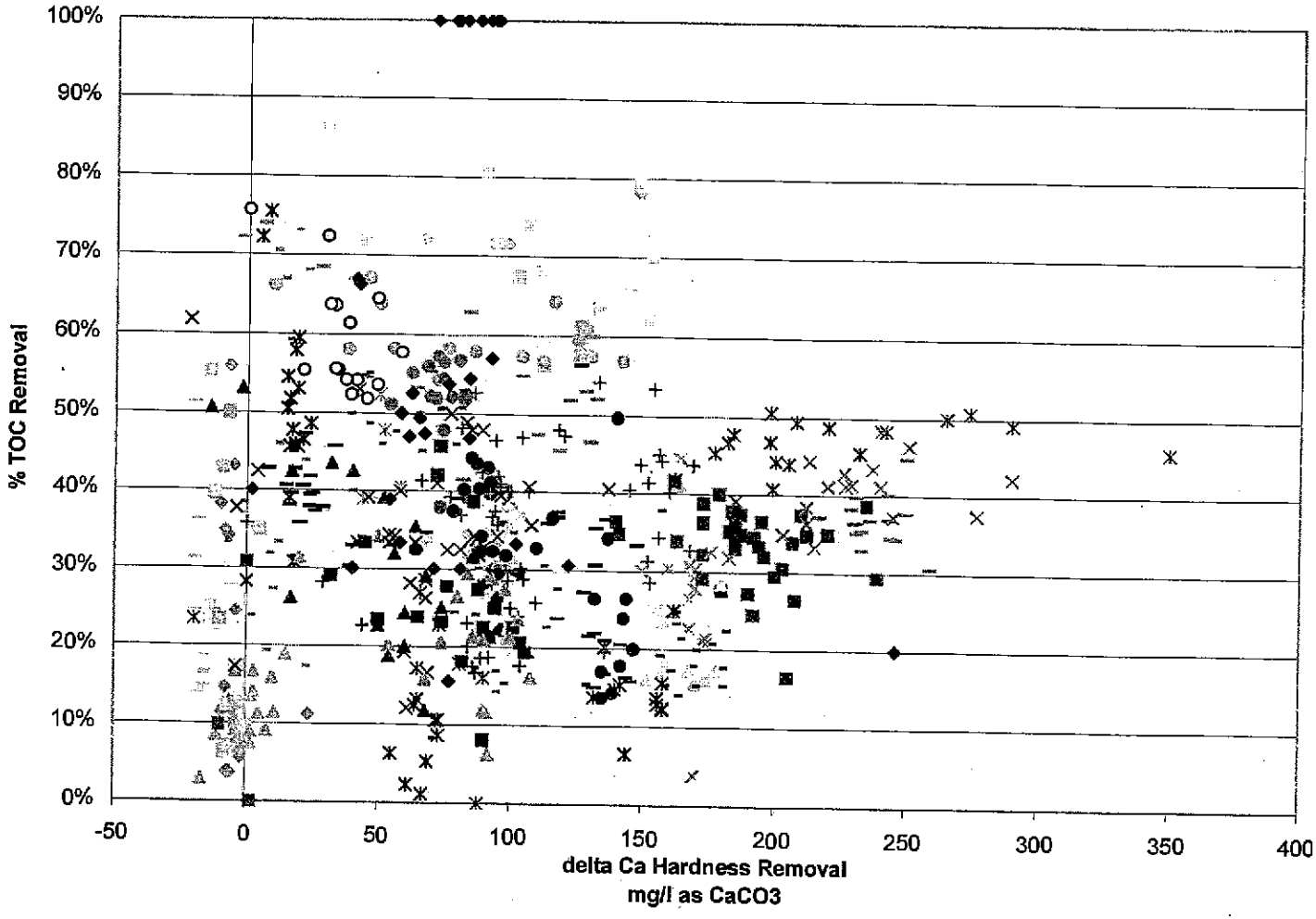

Figure 22.6 Calcium and TOC removal at softening plants included in this analysis

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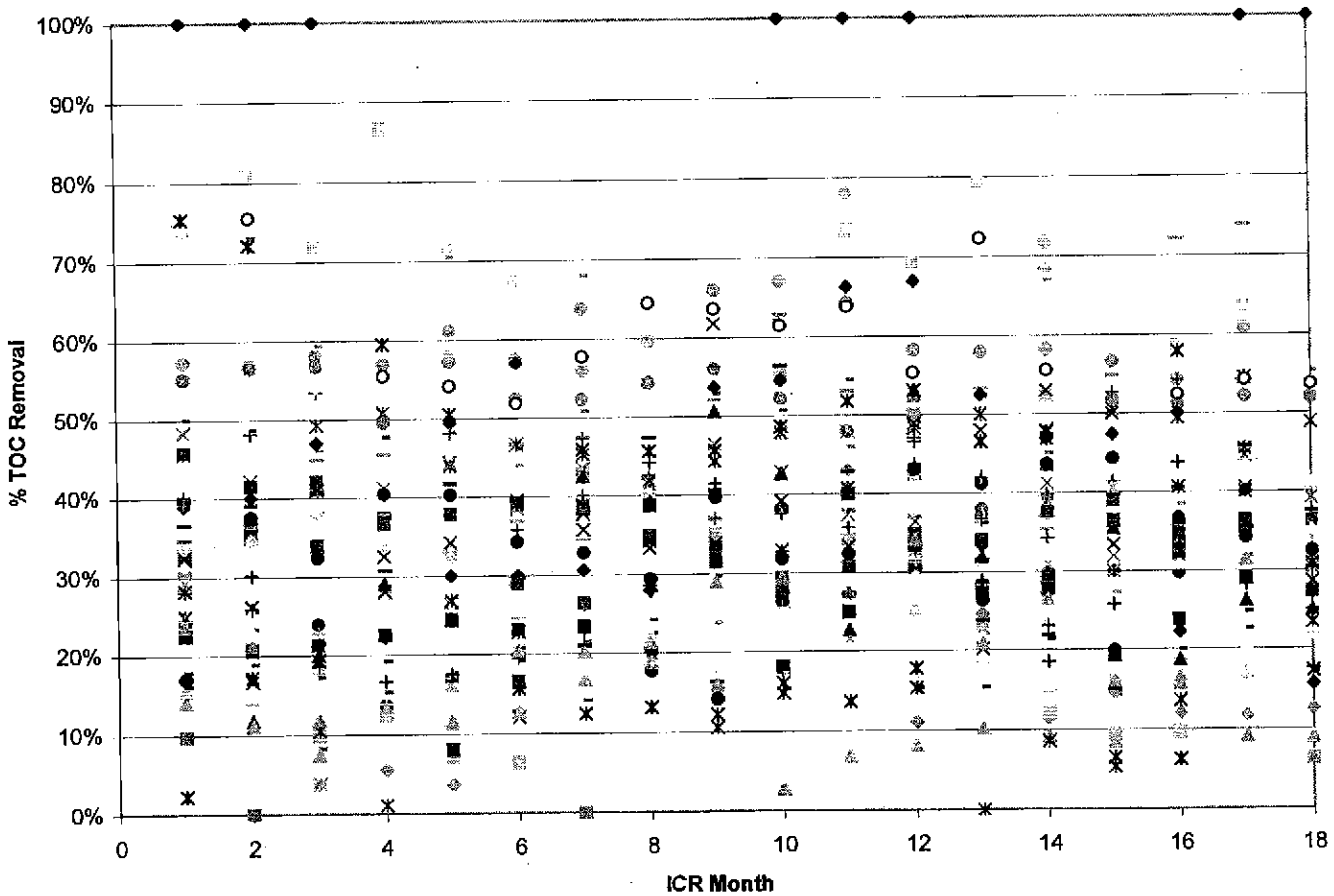

Figure 22.7 Monthly TOC removal percentages at softening plants included in this analysis

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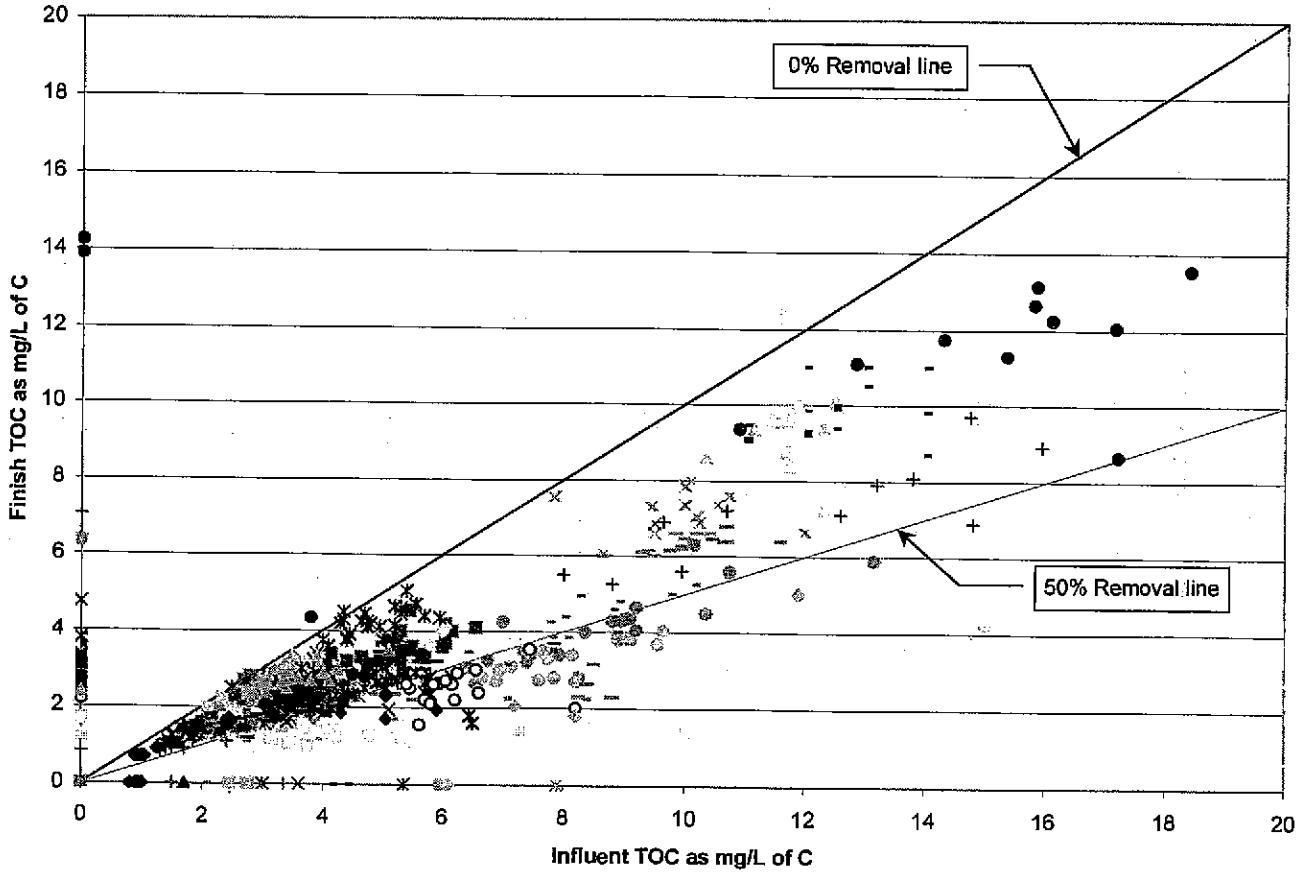

Figure 22.8 Finished water TOC concentrations were more consistent when influent TOC concentrations were low

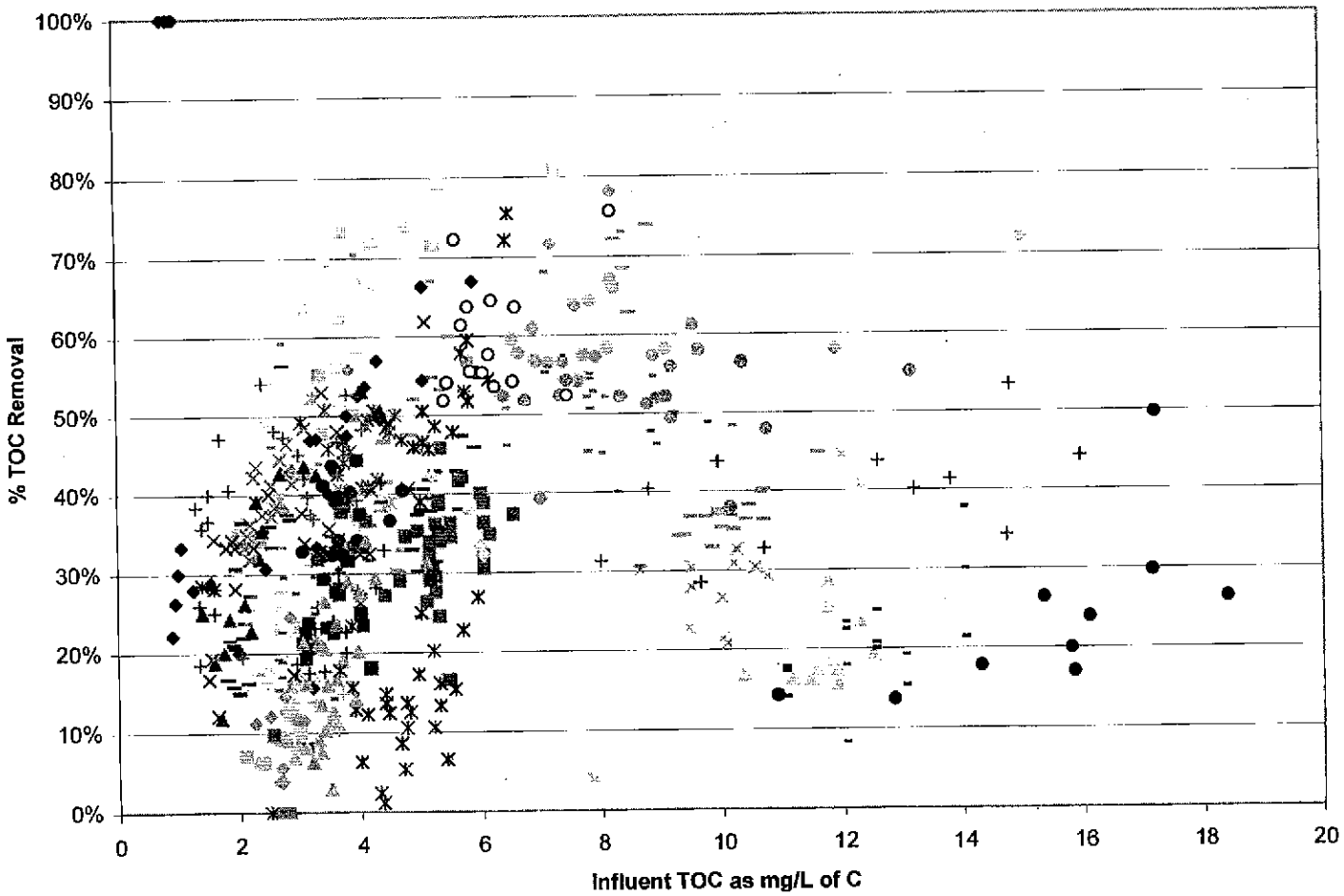

Figure 22.9 TOC removal percentages did not increase with influent TOC concentrations

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During development of the D/DBP Rule, it was assumed that a connection existed between magnesium removal and TOC removal. As a result, softening plants that cannot meet the TOC removal requirement specified in the 3 × 3 matrix are allowed to comply with enhanced softening requirements by meeting a specified minimum magnesium hardness removal of 10 mg/L as $CaCO_3$. Figure 22.10 illustrates TOC removal percentages as a function of changes in magnesium concentration. The data indicated a slight correlation between magnesium removal and TOC removal—as magnesium removal increased, the TOC removal percentage increased according to a trend that curves to the upper right on the graph. Monthly data points from all plants in this analysis indicated that ICR softening plants were removing more than 10 mg/L of magnesium as $CaCO_3$ at the time of most ICR sampling events. Thus, the assumption that sufficient TOC will be removed if 10 mg/L of magnesium is removed is accurate. Consequently, few softening plants would be expected to be out of compliance with TOC removal requirements. More notably, as shown by this figure, data from each plant tended to cluster, indicating a tendency for each plant to consistently produce finished water of a particular quality.

Another way of looking at the relationship between TOC and calcium and magnesium concentrations is to consider TOC removal as a function of the Ca:Mg ratio, as shown in Figure 22.11. As discussed previously, plants that have high Ca:Mg ratios generally have low magnesium concentrations, as is typical of water supplies in Florida. In this figure, square symbols indicate Florida plants, and round symbols indicate plants outside Florida. Plants with high Ca:Mg ratios can achieve good TOC removal; TOC removal in the Florida plants ranged from 10 to 45%. However, magnesium may influence removal, as indicated by the uppermost TOC removal values shown in this figure. Plants that are achieving TOC removal of greater than 50% generally have significant concentrations of magnesium as well as calcium, yielding low Ca:Mg ratios.

COMPLIANCE WITH THE D/DBP RULE

On the basis of the ICR data, the prospect of softening plants complying with the D/DBP Rule looks good. Although there was no requirement for compliance with TOC removal or magnesium removal criteria during the time frame of ICR sampling, most of the softening plants in this analysis could have met the TOC removal requirements stipulated by the 3 × 3 matrix, and

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only a few would have needed to further optimize treatment to comply with the rule. Figure 22.12 illustrates the ability of these plants to comply with the TOC removal requirements or one of the alternative compliance criteria (magnesium removal or finished water alkalinity). Because the database did not contain all 18 months of data for some plants, the compliance picture reflects only those months for which data were available. Only five plants could not have met the TOC provisions of the D/DBP Rule for any prolonged period. These five plants, and those that did not comply with the provisions of the rule for one or two months, are likely to be able to achieve compliance by adjusting their treatment practices through enhanced softening.

The data on TTHM and the sum of five haloacetic acids (HAA5) indicate that most softening plants complied with the maximum contaminant levels (MCLs) for these DBPs (80 μg/L for TTHM and 60 μg/L for HAA5) on a quarterly basis during ICR monitoring. Quarterly DBP data from ICR softening plants are shown in Figure 22.13. Although compliance will be based on running annual average DBP concentrations, Figure 22.13 indicates the general compliance picture, showing that quarterly DBP values from only two plants exceeded the MCLs—one for HAA5 only and the other for both TTHM and HAA5. These results imply that softening plants are removing enough TOC to minimize DBP formation or that they have modified disinfection practices sufficiently to keep DBP concentrations below regulated levels. Overall, few softening plants appear to have significant problems with being able to meet the MCLs specified in the D/DBP Rule.

Finished water alkalinity in softening plants appeared to be somewhat lower than expected by the Technical Workgroup prior to ICR monitoring. Regulatory requirements discourage plants from driving finished water alkalinity below 60 mg/L as $CaCO_3$ in order to ensure that corrosivity is not increased. Monthly values for finished water alkalinity were often less than 60 mg/L as $CaCO_3$, as shown by the data in Figure 22.14. These results imply that softening systems are using criteria other than or in addition to alkalinity to ensure that distributed water is not corrosive.

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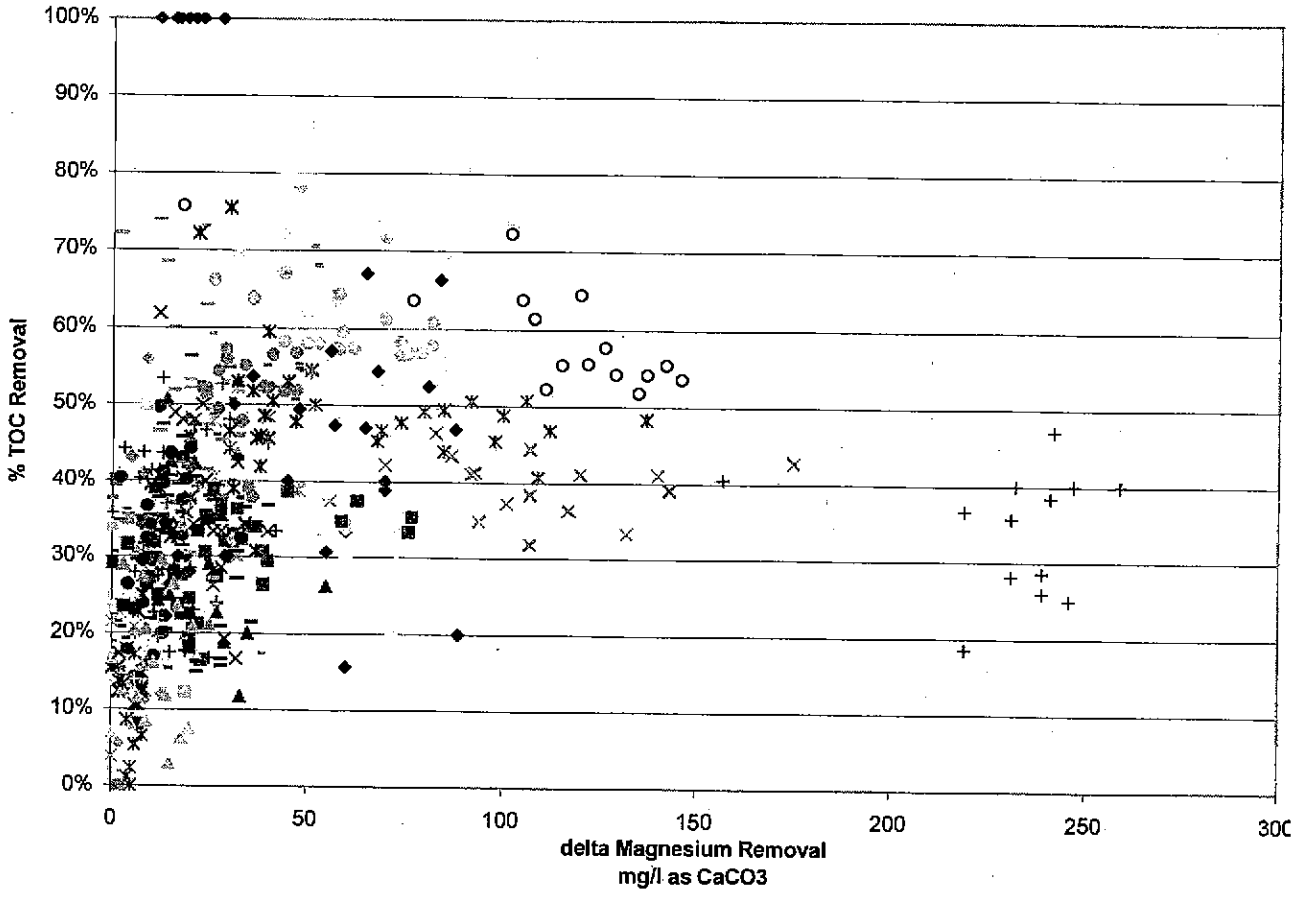

Figure 22.10 Correlation between magnesium removal and TOC removal by softening

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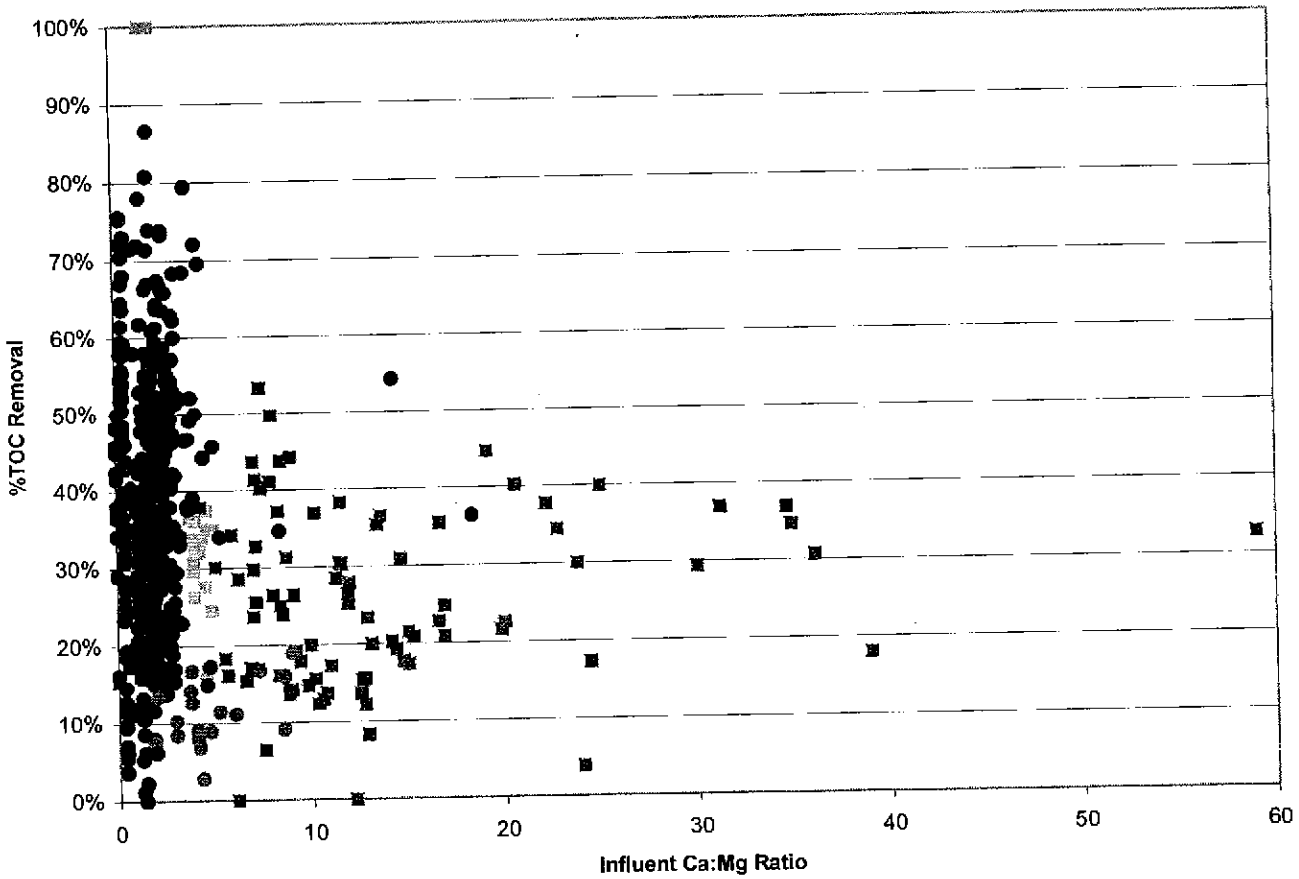

Figure 22.11 Relationship between TOC removal and source water Ca:Mg ratio

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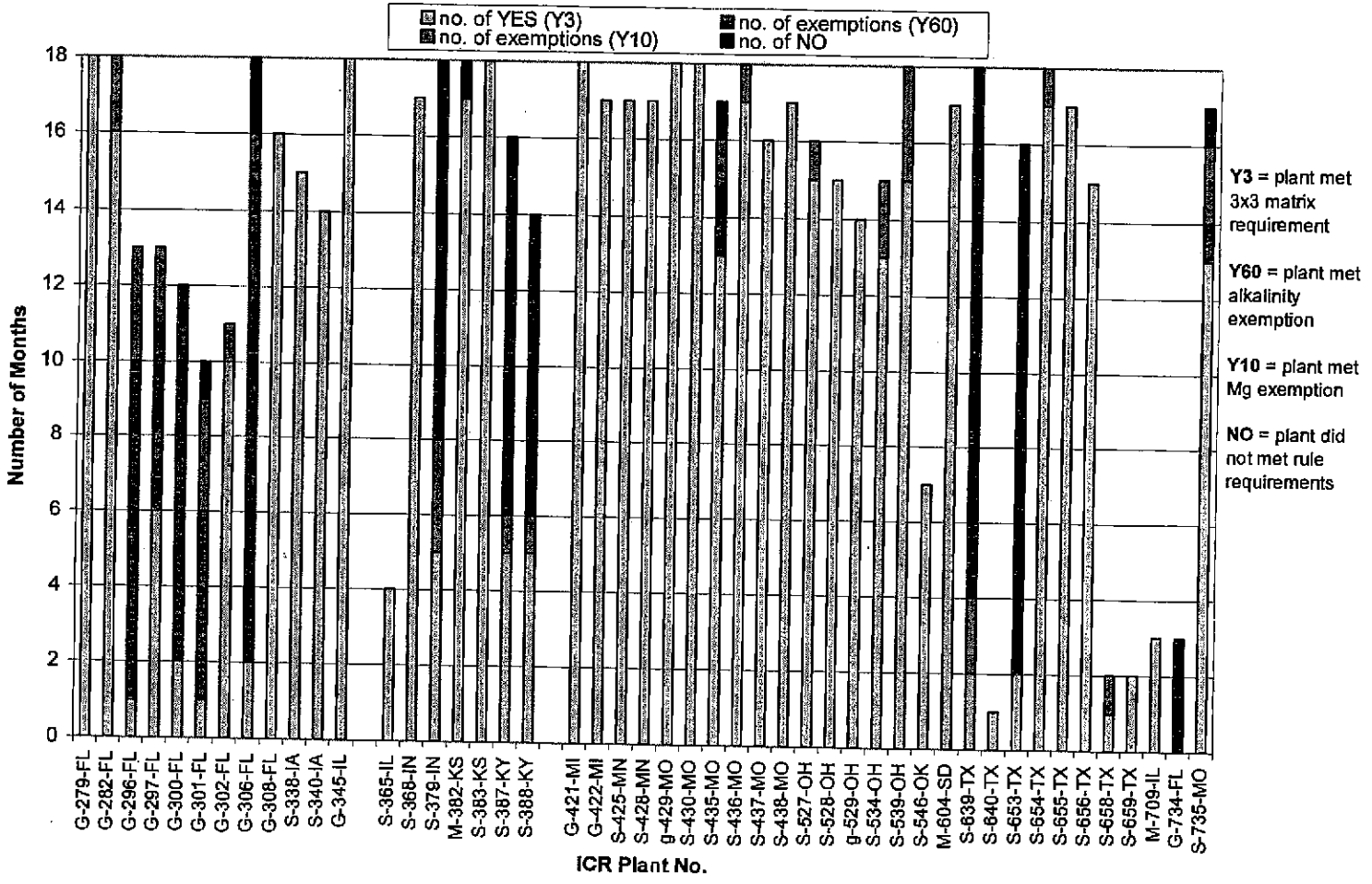

Figure 22.12 Number of months in which the softening plants in this analysis met TOC removal requirements

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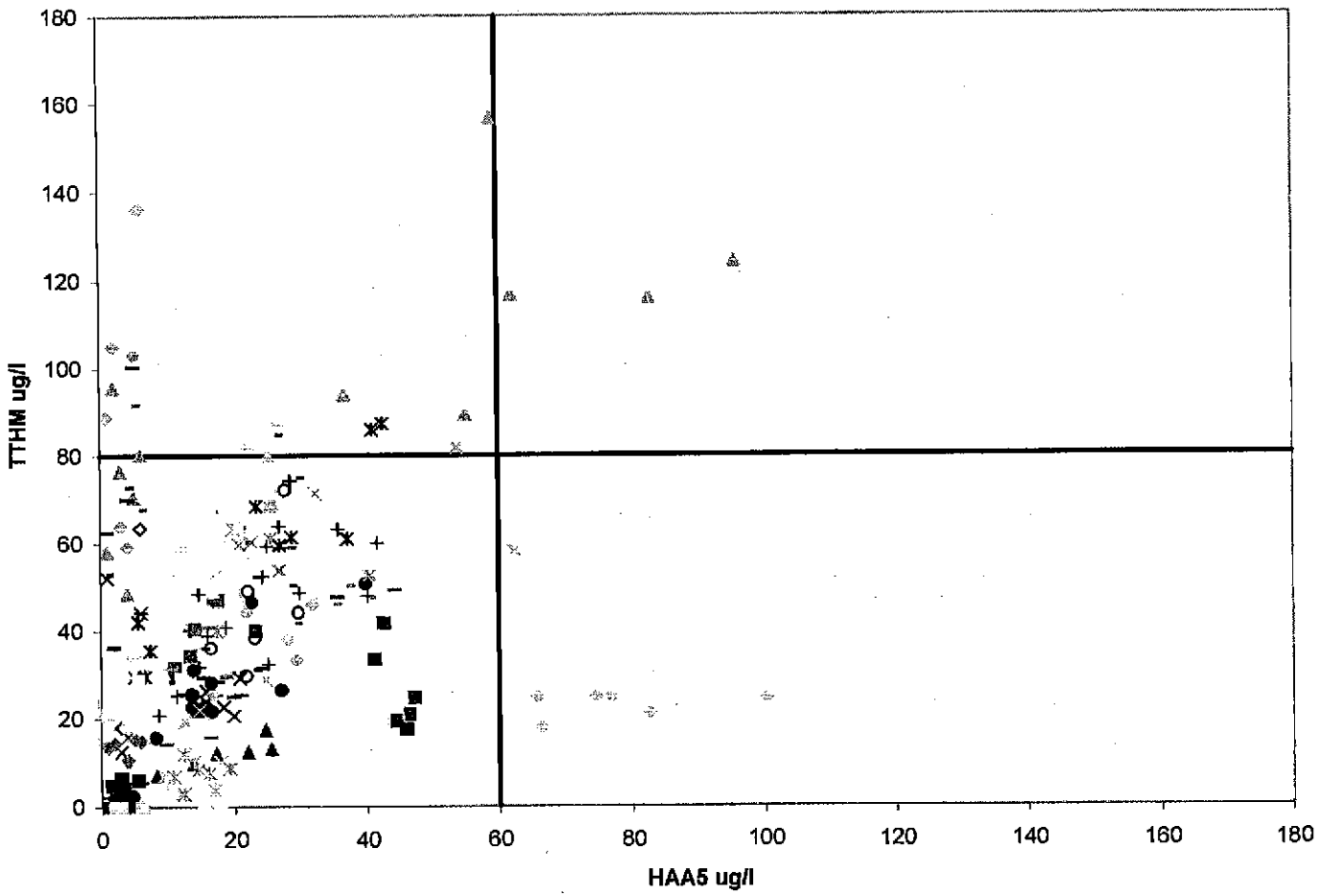

Figure 22.13 Quarterly average TTHM and HAA5 concentrations at softening plants included in this analysis

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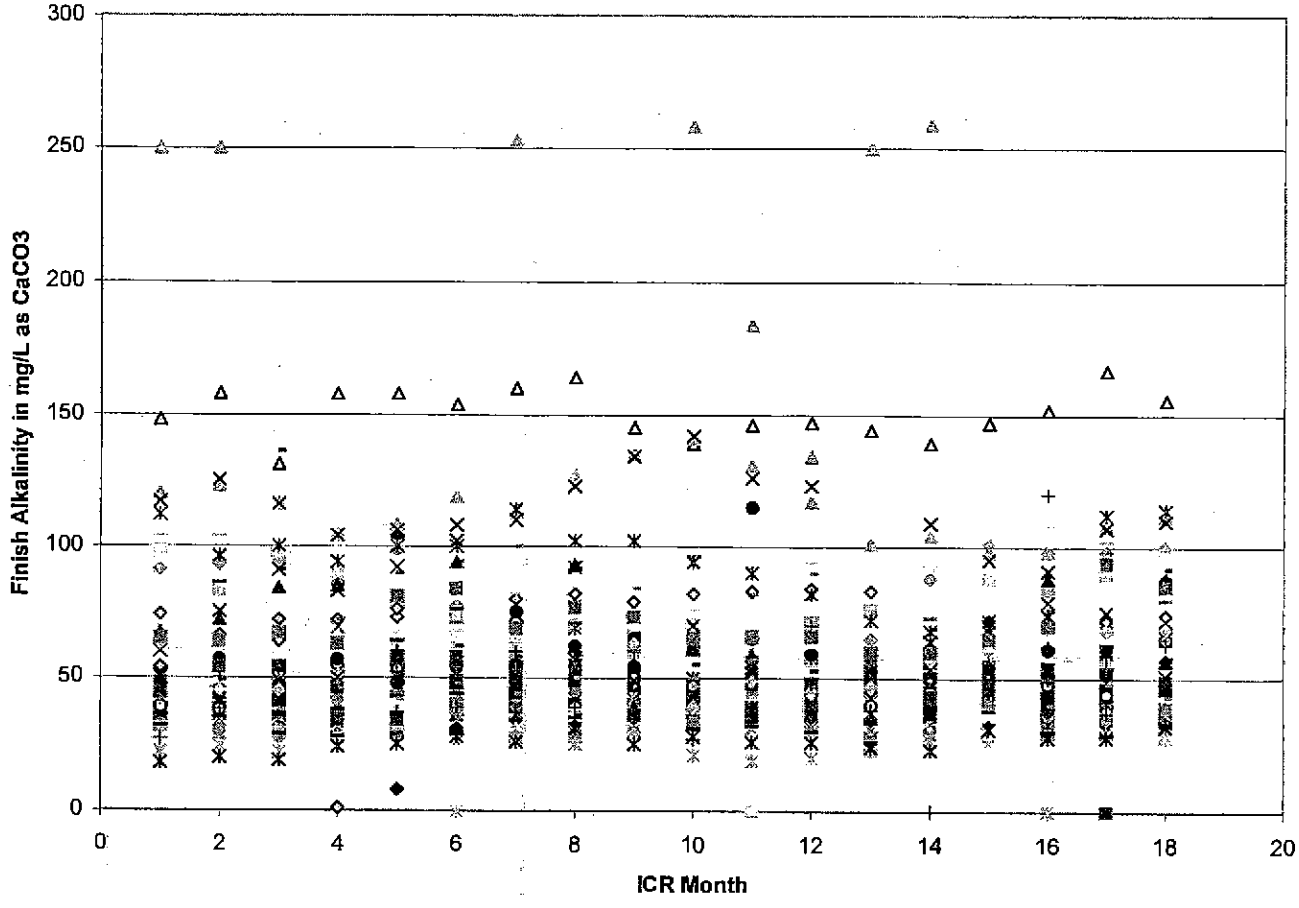

Figure 22.14 Monthly data on finished water alkalinity at softening plants included in this analysis

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CONCLUSIONS

The data set used in this analysis indicated few, if any, systematic trends to explain the mechanisms for either TOC removal or DBP formation in softening plants. Often, the data for a given parameter at an individual plant formed a cluster, indicating consistency of operation and consistency of effect. Although this result does not help explain the fundamentals of TOC removal or DBP formation, operators can take satisfaction in the fact that their plants appear to be producing finished water of consistent quality. Conversely, the lack of trends in the data causes some difficulty for operators who need to optimize treatment because no strong guiding principles are evident.

Because softening is a precipitation process that uses significant dosages of lime and generally moderate dosages of coagulant, it produces a lot of solids during the flocculation and sedimentation processes. These solids adsorb some fraction of influent NOM as a matter of course, making compliance with the TOC removal requirements and the DBP MCLs a natural result of the process. Because softening as practiced today is highly effective at removing TOC, there is little room to improve TOC removal by further enhancing the softening process. Driving the lime dosage upward changes the pH and increases magnesium removal when sufficient magnesium is present, but this data set did not show a strong correlation between magnesium removal and TOC removal.

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CHAPTER 23

HOW UTILITIES CAN USE ICR DATA TO IMPROVE WATER QUALITY AND MEET FUTURE REGULATIONS

Christine A. Owen and Robert M. Powell

ABSTRACT

The drinking water community spent a tremendous amount of time, money, and energy collecting, analyzing, and reporting data under the Information Collection Rule (ICR). Water quality and treatment data were gathered from 296 large water utilities across the United States and Puerto Rico during an 18-month monitoring period from July 1977 through December 1998. These data are now stored in a federal database that is accessible to water systems and consumers through the Internet.

This chapter describes the specific types of data that were collected under the ICR and outlines some ways in which utilities can use these data to improve the quality of the water they produce and distribute. The chapter also illustrates how using ICR data can help utilities predict their ability to comply with future water quality regulations.

A case study describes how one utility used its experience of collecting data under the ICR to design an ongoing water quality monitoring program for internal use. As a result, the utility learned more about the differences in its three sources of supply and identified specific distribution sites where water quality needs to be improved. These steps have helped the utility to formulate a plan for providing consistent water quality throughout the distribution system.

INTRODUCTION

Public water suppliers have had to modify their basic philosophy regarding water treatment over the past 20 years. No longer does providing an adequate supply constitute an adequate charge for water utilities. Water suppliers must consider both the quality and the quantity of the water they produce, and they must do so in a regulatory context that is complex and, in some cases, contradictory. For utilities interested in taking a long-term, broad-based perspective, a wealth of information is available in the data gathered under the Information Collection Rule (ICR). Utilities can use this information to evaluate many aspects of treatment plant and distribution system operations, as well as to support planning efforts. For the first time, a utility can answer questions such as "How well do we treat our source water compared with

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how other utilities treat similar sources?" and "How can we improve our treatment relative to that of other utilities across the country?"

WHAT WAS THE ICR?

The ICR represents the largest, most organized, and most carefully managed effort ever undertaken to gather water quality and treatment information. Data were collected from 296 public water systems from July 1997 to December 1998. These utilities, located across the United States and in Puerto Rico, served at least 100,000 people each and used groundwater, surface water, or a combination of both as sources of supply. The target utilities collectively spent more than $250 million dollars to collect samples, provide analyses, and compile the data for submission to the U.S. Environmental Protection Agency (USEPA). The data were reviewed extensively for quality purposes and reside in a database that is available to the public.

The water sources represented in the database are as diverse as the processes used to treat them. Detailed data on source water quality include information on the occurrence of microbial contaminants and disinfection by-product (DBP) precursor material. The quality of each treatment facility's source of supply is temporally related to finished water quality. Specifics about each treatment process are included in the results of monthly sampling at each plant. Finally, the database allows utilities to examine in a relatively systematic fashion the changes in water quality that occur in distribution systems.

The drinking water community spent a tremendous amount of time, energy, and money to comply with the ICR, and utilities should take advantage of the data generated. Although the ICR data come from large utilities, they are also applicable to midsize and smaller utilities.

WHAT TYPES OF DATA WERE GATHERED UNDER THE ICR?

The ICR was designed to give USEPA nationwide information characterizing source water quality, treatment practices, and the occurrence of waterborne pathogens and DBPs. The range of information collected under the ICR exceeded that of any previous study or survey. Specifically, the ICR data provide information on:

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- Source water quality,
- Operating parameters,
- Treatment train water quality,
- Filtered water quality,
- Finished water quality,
- Distribution system water quality, and
- Simulated distribution system samples.

Monthly or quarterly ICR data were collected from 500 water treatment facilities. Surface water plants were required to provide occurrence data on microorganisms including bacteria, protozoa, and viruses. All ICR treatment facilities collected data on source water total organic carbon (TOC), total organic halogen (TOX), bromide, and general water quality parameters such as calcium hardness, total hardness, temperature, alkalinity and pH. Information gathered on treatment processes included operating data such as flow rates, chemical dosages, recycle and return flows, and the water quality characteristics of recycle water. ICR water quality data on filtered and finished water are extensive, include TOC and DBP concentrations, and can be compared with both source water and distribution system water quality. ICR efforts also included the evaluation of simulated distribution system (SDS) samples, samples of treatment plant effluent that were collected and held under conditions roughly equivalent to distribution system conditions for 24 hours. Analytical results from the SDS samples may be useful to utilities using bench-scale laboratory studies to predict water quality changes in the distribution system. In addition, the ICR required some utilities to conduct pilot- or bench-scale studies to evaluate the effectiveness of using granular activated carbon (GAC) or membrane technology to remove DBP precursors. Results of these studies are discussed in Chapter 22 (Hooper and Allgeier 2002).

Because the ICR data were collected over an 18-month period, they provide insight into seasonal variations in water quality. The summer months, generally considered the most challenging for treating water and maintaining water quality, were represented in three of the six quarters of data gathered under the ICR. Seasonal variations were observed in source water quality and in water quality changes in the distribution system. In some regions of the country, seasonal changes in the quality of either source water or finished water may be the limiting factor

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when utilities evaluate compliance with drinking water regulations or implementation of new treatment technologies.

In considering the wealth of information collected under the ICR, utilities should also remember the limitations of these data. Designed as a research project, the ICR was intended to help predict compliance with various regulatory options under consideration for the cluster of rules being developed to control microorganisms and DBPs. Thus, the ICR data represent a snapshot of water treatment and water quality during the 18-month monitoring period. Comparisons of ICR data with historical water quality data indicate that long-term seasonal variations such as drought are not thoroughly described by the ICR data. Climatic variations may also contribute to the differences between historical data and ICR data, and the data set does not address natural disasters such as floods or hurricanes. These caveats aside, however, the data provide an overall picture of influent, effluent, and distribution system water quality associated with particular treatment facilities during a specific period of time.

HOW CAN UTILITIES USE ICR DATA?

First Steps

For utilities that want to make use of the ICR information, the initial step is to thoroughly review and describe the utility's treatment process. The ICR provides a useful, standardized data collection mechanism that allows the treatment process to be outlined. Each treatment facility is described by a series of process units, and the result is a flow diagram of the facility's treatment scheme. Although the ICR protocol was very structured, a utility's staff can conduct a similar exercise using their own operational knowledge and information. Creating a plant schematic and keeping it updated and accurate is invaluable—it is the starting point for evaluating existing treatment and proposed changes. The ability to consider the big picture of a utility's treatment process can help identify and reduce unintended negative consequences that could result from treatment modifications.

A current plant schematic for a facility that participated in the ICR must incorporate any changes that have occurred since the ICR effort. Since the conclusion of ICR monitoring, many

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utilities have installed treatment modifications or new technologies in order to comply with the Disinfectants/Disinfection By-products Rule or the Interim Enhanced Surface Water Treatment Rule. These modifications, and any others, should be included in the plant schematic.

In addition to creating a plant schematic, utilities will find it valuable to develop a picture of their distribution system. Distribution systems frequently vary more than treatment plants, and water quality is defined not only by what leaves the treatment facility but also by what is delivered to the customer's tap. Customer perceptions of water quality are generally determined entirely by what they see at the tap. Future regulations (as well as existing ones such as the Lead and Copper Rule) will continue to require that the water purveyor's responsibility extend from plant effluent to customer's tap.

Public water suppliers already collect a great deal of distribution system data. Sampling to determine compliance with DBP standards and with the Total Coliform Rule provides two sources of distribution system information, and utilities should include data from lead and copper sampling as well as bacteriological and DBP sampling when characterizing their distribution systems. Field data from customer complaints and routine chemistry analyses for parameters such as disinfectant residual can also be incorporated. These sources of information can identify distribution system dead ends and other areas of low use, as well as sites with unexpectedly high DBP concentrations. Distribution system descriptions can also include information on storage tanks and operating procedures and constraints.

The next step utilities will need to take in order to capitalize on the ICR information is to verify their own data. The staff of a utility that participated in the ICR would already be familiar with the arduous process of checking ICR data. Data entry mistakes still reside in the database, and although modifying the official ICR database is not possible at this point, utilities can make corrections for their own evaluations. Keeping in mind that the ICR data represent a snapshot in time, utilities should compile historical and post-ICR data in a database or spreadsheet to facilitate comparisons.

Some utilities have continued to collect samples and conduct analyses similar to those required under the ICR. Valuable insight into the intricacies of treatment can be gained from an internal monitoring program based on the components of the ICR. An internal program would not have to include the range of data collected under the ICR; it should be tailored to the utility's

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particular circumstances and needs. For example, a utility whose DBP concentrations are low in the filtered effluent but high in the distribution system may find that focused sampling in the distribution system suggests options for DBP control other than enhanced TOC removal in the treatment plant. The ICR sampling protocol can serve as a blueprint for developing such plans, and taking time to develop a utility database will facilitate use of the data in the future.

Utilities that did not participate in the ICR can also take a lesson from the ICR effort. If they are considering the implementation of new treatment options to meet a regulation, the ICR data may indicate treatment technologies that have proved to be reasonable, effective solutions for other utilities with similar source water quality. Basic characterization of source water is a cornerstone of understanding treatment, as is knowledge of the water quality changes that occur with each step in the treatment process. In addition, examining ICR data can help a utility that did not participate in the ICR gain insight into distribution system water quality as it relates to system configuration or treatment.

Next Steps

Utilities can begin to evaluate their treatment schemes with tools as simple as the Internet and the ICR Federal Database System (ICR FED) provided by USEPA or as complex as Microsoft Access software and the auxiliary databases extracted from ICR FED. ICR FED can provide utilities with broad information about national and state trends. All that is needed to use the ICR FED is Internet access to the Web site <http://www.epa.gov/enviro/html/icr/index.html>. Available on this site are the results of analyses of individual treatment facility source water and finished water quality. Looking at the data from this level could motivate a utility to expand the ability of its staff to mine ICR data more extensively by using the more complex Access tool.

Using ICR Data to Make Operations Decisions

A utility can use ICR data to:

- Make national, regional, and state comparisons,
- Review seasonal water quality variations,

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- Compare facilities with similar source water quality and treatment processes,
- Compare facilities with similar source water quality and different treatment processes,
- Compare finished water of similar quality,
- Anticipate the potential impact of additional treatment on finished water quality, and
- Consider how distribution system residence time can affect water quality.

The first view of ICR data that any utility can use is the national picture. For example, the ICR FED provides national and state distributions of microbial contaminants in source water and DBP concentrations in distribution systems. Individual utilities (or customers) can review how their water compares with water in the rest of their region or across the country. By examining data from a particular state or region, a utility might find some commonality with other facilities in terms of source water characteristics or the behavior of distribution system DBPs. An example is the so-called "Florida effect"(the fact that Florida groundwater supplies typically contain higher TOC concentrations than groundwater supplies in other parts of the country). This phenomenon, coupled with the state's warm climate and seasonal variations in water demand, can make the control of distribution system DBPs in Florida challenging. By examining the distribution system data of these utilities and the various treatment techniques they have used, another utility could evaluate the applicability of these treatment options in its own situation.

National, regional, and state comparisons can help a utility understand where it stands in relation to other utilities. By examining national ICR data on source water quality, a utility can reasonably evaluate how well it is treating its own water source. By examining the data from facilities that treat similar water with similar processes, a utility can find ways to improve the quality of its finished water. For example, enhanced TOC removal can be achieved through small, easily implemented changes in coagulant dosage, pH adjustment, or both. The ICR data include numerous examples of treatment plants that used enhanced coagulation, as well as monthly operations data from these facilities. Another utility could use these operating data to create a jar-testing plan that would help it optimize existing treatment processes to improve finished water quality. This kind of exercise can help utilities set realistic treatment goals.

Valuable comparisons can be made between facilities that have similar source water quality but use different treatment processes. By examining these data, a utility could conduct a paper evaluation of possible new treatment options and gain insight into what finished water

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quality could be achieved with specific source water characteristics and treatment processes. Although the use of ICR data for these types of evaluations cannot replace pilot testing, it can help a utility identify available options. The fact that the data are derived from actual full-scale treatment plants increases their credibility and usefulness.

Seasonal comparisons can provide insight into how water quality and treatment vary over the course of a year and how distribution system operations affect water quality. Even facilities that use different treatment schemes may find commonality in how they operate their distribution systems to control DBPs. In some cases, DBP control may be attainable only through additional precursor removal, whereas in other cases relatively simple operational changes in storage or demand management may suffice. Northern utilities looking for ways to control distribution system DBPs during the summer will find numerous warm weather distribution system DBP profiles from the South and Southwest.

Another type of valuable information a utility can glean from ICR data is local or regional utility contacts. Identifying other utilities that are confronting similar water quality challenges can provide contacts who can share experiences through phone calls or site visits. Utility staff members can benefit immensely from interacting with one another.

Using SDS Sample Results to Predict DBP Formation

After the SDS samples collected under the ICR had been held under conditions simulating those in the distribution system (similar temperature and pH; no light) for 24 hours, they were divided into smaller aliquots for general chemistry analyses and analysis of DBPs. Another set of ICR samples was collected from the distribution system at a location expected to represent similar residence time. Called distribution system equivalent (DSE) samples, these were actual distribution system samples. An important aspect of choosing the DSE sampling site was the utility's degree of confidence in the residence time of the water at that site; utilities were asked to estimate their confidence in this residence time as part of the ICR data collection and data entry tasks. A comparison of the analytical results from a utility's SDS and DSE samples can offer useful information about the dynamics of DBP formation in the utility's distribution system, changes in the water's chemistry, and the veracity of the utility's hydrodynamic models

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(if models were used to predict residence time at the DSE sampling site). For example, if a utility finds that SDS samples are a good predictor of what happens to DBPs in its distribution system, this would facilitate the modeling of DBP formation to predict regulatory compliance and might help with containing costs. Even more interesting would be circumstances in which DBP concentrations in the SDS and DSE samples varied significantly. In these cases, a utility might focus on the operation and maintenance of its distribution system as a means of controlling DBPs or other water quality changes. SDS samples indicate when the water chemistry is the controlling influence over water quality, whereas DSE samples indicate what happens to the chemistry once the water is inside the "organism" that water suppliers call the distribution system.

Using ICR Data to Predict Regulatory Compliance

By using all of the tools and information provided by the ICR, a utility can get an indication of what technologies might be appropriate for various water quality and regulatory challenges. By making the comparisons described in this chapter, a water utility can set the stage for evaluating future compliance given the quality and treatability of its source water. The format of the ICR database also provides an excellent model for organizing data to support utility planning efforts. Using ICR data may not allow a utility to predict compliance with a regulatory scenario with absolute confidence, but it can help the utility move in the right direction.

ONE UTILITY'S ICR EXPERIENCE

Some utilities have used ICR data to expand both their water quality knowledge and their operating programs. This section describes how one utility gathered information about its source water characteristics and distribution system conditions under the ICR and then used these data as the foundation for a more extensive, targeted monitoring program launched at the conclusion of ICR monitoring. The utility wholesales drinking water to five municipalities that serve approximately 600,000 retail customers. Using groundwater from the Florida Aquifer, the utility produces an average of 75 mgd from three well fields. The groundwater contains moderate concentrations of carbonate hardness, 1 to 2 mg/L of hydrogen sulfide, and 2 to 4 mg/L of TOC.

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Treatment includes aeration, addition of corrosion inhibitor, gas chlorination to achieve a free chlorine residual, and pH adjustment. The finished water consistently meets the requirements of the Safe Drinking Water Act and the Florida Department of Environmental Regulation.

Prior to implementation of the ICR, the utility conducted compliance monitoring for total trihalomethane (TTHM) concentrations as required. Additional noncompliance samples that were collected monthly provided more complete information on distribution system conditions. When the monitoring requirements of the ICR were defined, utility staff decided to use the ICR effort to expand their knowledge of distribution system conditions as much as possible. They located ICR sampling sites at historical THM monitoring sites whenever possible to maintain continuity of THM data from specific areas of the distribution system. In addition to TTHM concentrations, ICR distribution system samples were analyzed for TOX, haloacetonitriles, and the sum of five haloacetic acids (HAA5).

Results of ICR monitoring confirmed that the well field sources differed significantly, despite being drawn from the same aquifer. Two of the three groundwater supplies had similar TOC concentrations, whereas the third had significantly lower TOC concentrations. However, TTHM, HAA5, and TOX concentrations in plant effluent and in the distribution system were significantly different for all the groundwater sources. Concentrations of all the DBPs measured increased with distribution system residence time regardless of the source, as would be expected in a distribution system using free chlorine as a disinfectant. The ratio of TTHM to HAA5 was similar in all three sources and remained relatively constant throughout the distribution system. However, the ratio of HAA5 to HAA9 was different for the three sources, as was the ratio of bromine-substituted to non–bromine-substituted DBPs. After chlorination, the three groundwater supplies produced relatively similar concentrations of HAA5, but if the analyses of distribution system samples included measuring the more heavily bromine-substituted HAA9 species, differences in source water quality could be detected.

Monitoring results indicated that the utility could comply with DBP regulations permitting systemwide averaging of TTHM and HAA5 but that compliance with regulations requiring the computation of average TTHM and HAA5 concentrations at specific distribution system locations would be problematic. Water production at this utility takes place in the northern part of the county. Because the utility's consecutive distribution systems are long and

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almost linear, the effects of residence time are significant from north to south. The use of free chlorine under temperature conditions in Florida usually requires some boosting of the chlorine residual. Because of these factors, water that is distributed in the north end of the county has relatively low DBP concentrations, whereas water distributed in the south end of the county has significantly higher DBP concentrations. Locational running annual average concentrations of TTHM and HAA5 at sampling sites at the southern end of the distribution system would exceed maximum contaminant levels.

Because the ICR monitoring sites did not represent all areas of these distribution systems, the utility elected to expand the number of monitoring sites after ICR monitoring had concluded. Some sites were chosen to allow the evaluation of conditions where the longest residence times occurred. This network of sites forms the basis of an ongoing water quality assessment program, which helps the utility to identify areas of the consecutive distribution systems in which action is required to improve water quality. Such actions may include flushing, verifying the correct status of valves, or modifying chemical applications at the treatment plant or booster stations. Because of the data gathered through the water quality assessment program, the utility is able to operate on the basis of water quality considerations rather than pressure or quantity considerations to a much greater extent than in the past.

By collecting and evaluating ICR data and by continuing an expanded monitoring program after conclusion of the ICR effort, the utility has gained a much clearer picture of water quality differences in its consecutive distribution systems. The utility has learned that water sources that are apparently similar can exhibit significantly different characteristics in distribution systems. Though the utility has used the same water sources for decades, it will require new water sources of significantly different quality in the future. Lessons learned from the ICR effort and the continuing monitoring program indicate that providing consistent water quality throughout the distribution system will require treating and blending different sources of supply. Thus, this utility's experience under the ICR led to better understanding of water quality in the distribution system, improved operation and maintenance of the distribution system, and guidance for future planning efforts.

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SUMMARY

Utilities that want to improve the quality of the water they produce and distribute can make use of the comprehensive data collected under the ICR as they consider how to modify treatment processes or change distribution system management practices to improve water quality and meet regulatory standards. A utility can use ICR data to compare its water with other supplies in the region or across the country; to review seasonal variations in water quality; and to examine processes used to treat source water with similar characteristics.

Utilities that want to continue gathering water quality and treatment data for internal use will find the ICR sampling protocol to be a useful model for their own data collection programs. The format of the ICR database also provides an excellent tool for organizing data to support utility planning efforts.

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Hooper, S.M., and S.C. Allgeier. 2002. GAC and Membrane Treatment Studies. In *Information Collection Rule Data Analysis*, Edited by M.J. McGuire, J.L. McLain, and A. Obolensky. Denver, Colo.: AwwaRF.

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ABBREVIATIONS

ALD	Aldehyde
ALK	Alkalinity
AMWA	Association of Metropolitan Water Agencies
ANOVA	Analysis of variance
AUX1	Auxiliary 1 ICR Database
AUX2	Auxiliary 2 ICR Database
AUX3	Auxiliary 3 ICR Database
AUX4	Auxiliary 4 ICR Database
AUX5	Auxiliary 5 ICR Database
AUX6	Auxiliary 6 ICR Database
AUX7	Auxiliary 7 ICR Database
AUX8	Auxiliary 8 ICR Database
AVG1	First average detention time sampling point in ICR distribution systems
AVG2	Second average detention time sampling point in ICR distribution systems
AWWA	American Water Works Association
AwwaRF	Awwa Research Foundation
BCAA	Bromochloroacetic acid
BCAN	Bromochloroacetonitrile
BDCAA	Bromodichloroacetic acid
BDCM	Bromodichloromethane
BGM	Buffalo Green monkey
BrO_3^-	Bromate ion
Br:TOC	Bromide-to-TOC ratio
Ca:Mg	Calcium-to-magnesium ratio
CFD	Cumulative frequency distribution
CH	Chloral hydrate
CHBr3	Bromoform (tribromomethane)
CHCl3	Chloroform (trichloromethane)
Cl_2	Chlorine (the chemical)
CL2	Treatment plant disinfectant category: free chlorine, when only chlorine (Cl_2) is used
CL2	Distribution system disinfectant category: free chlorine, when only chlorine (Cl_2) is used
CL2_CLM	Treatment plant disinfectant category: free chlorine followed by chloramine, when ammonia (NH_3) is added after free chlorine has already been applied
CLD	Chlorine demand
CLM	Treatment plant disinfectant category: chloramine, when Cl_2 and NH_3 are simultaneously added into a unit process and no free chlorine has been applied earlier
CLM	Distribution system disinfectant category: chloramine, when only chloramine is used
ClO_2	Chlorine dioxide (the chemical)
ClO_2^-	Chlorite ion

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ClO_3^-	Chlorate ion
CLX	Treatment plant disinfectant category: chlorine dioxide, if chlorine dioxide (ClO_2) is used anywhere in the treatment plant
CNCl	Cyanogen chloride
CONV	Conventional treatment
CP	Chloropicrin
CPT/SOFT	Complex parallel treatment and softening treatment
CS/SOFT	Coagulation–sedimentation and softening treatment
CT	Disinfectant residual concentration (C in mg/L) × contact time (T in minutes)
D/DBP Rule	Disinfectants/Disinfection By-products Rule
DBAA	Dibromoacetic dcid
DBAN	Dibromoacetonitrile
DBCAA	Dibromochloroacetic acid
DBCM	Dibromochloromethane
DBP	Disinfection by-products
DCAA	Dichloroacetic acid
DCAN	Dichloroacetonitrile
DCP	Dichloropropanone
DHAA	Dihaloacetic acid
DIS/GW	Treatment of groundwater with disinfection only
DIS/WH	Disinfection/wholesale treatment category
DOC	Dissolved organic carbon
DS_AVG	Distribution system average (used in SWAT)
DSE	Distribution system equivalent sampling point in ICR distribution systems
DS_MAX	Distribution system maximum (used in SWAT)
EBCT	Empty-bed contact time
EC	Enhanced coagulation
EPDS	Entry point to distribution system
FACA	Federal Advisory Committee Act
FBR	Filter Backwash Rule
FIN	Finished water
FS	Flowing stream
GAC	Granular activated carbon
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
GW	Groundwater
GWR	Ground Water Rule
GWUDI	Groundwater under the direct influence of surface water
HAA	Haloacetic acid
HAA5	Haloacetic acid 5 (sum of five HAA species: MCAA, MBAA, DCAA, DBAA, TCAA)
HAA6	Haloacetic acid 6 (sum of six HAA species: MCAA, MBAA, DCAA, DBAA, BCAA, TCAA)
HAA9	Haloacetic acid 9 (sum of nine HAA species: MCAA, MBAA, DCAA, DBAA, BCAA, TCAA, TBAA, BDCAA, DBCAA)
HAN	Haloacetonitrile

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HAN4	Haloacetonitrile 4 (sum of four haloacetonitrile species: DCAN, DBAN, BCAN, TCAN)
HOBr	Hypobromous acid
HOBr/OBr^-	Hypobromous acid/hypobromite ion
HK	Haloketone
HK2	Haloketone 2 (sum of 2 haloketone species: DCP, TCP)
HOCl	Hypochlorous acid
HUC	Hydrologic unit code
ICR	Information Collection Rule
ICR FED	ICR Federal Database System
ICRPWSID	ICR public water system identification number
ICRWTPID	ICR water treatment plant identification number
IESWTR	Interim Enhanced Surface Water Treatment Rule
IFA	Immunofluorescence assay
ISP	Initial sampling plan
ISS	Initial sampling schematic
LCR	Lead and Copper Rule
LRAA	Locational running annual average
LSP	Laboratory Spiking Program
LT1ESWTR	Long Term 1 Enhanced Surface Water Treatment Rule
LT2ESWTR	Long Term 2 Enhanced Surface Water Treatment Rule
MAX	Maximum detention time sampling point in ICR distribution systems
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MCL	Maximum contaminant level
M/DBP	Microbial/Disinfection By-product
MHAA	Monohaloacetic acid
MIX	Mixed groundwater, surface water, and purchased water systems
MPN	Most probable number
MRAA	Maximum running annual average
MRDL	Maximum residual disinfectant level
MRL	Minimum reporting level
MS	Mass spectrometer
NH_3	Ammonia (the chemical)
NOM	Natural organic matter
NOMS	National Organics Monitoring Survey
NORS	National Organics Reconnaissance Survey
NTU	Nephelometric turbidity units
O_3	Ozone (the chemical)
O3	Treatment plant disinfectant category: ozone, if ozone (O_3) is used anywhere in the plant
OGWDW	Office of Ground Water and Drinking Water (USEPA)
PAC	Powdered activated carbon
PE	Performance evaluation
POX	Purgeable organic halides
PWSID	Public water system identification number

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PUR	Purchased finished water
PWS	Public water system
QA	Quality assurance
QC	Quality control
RAA	Running annual average
RBSMT	Rapid bench-scale membrane test
RSSCT	Rapid small-scale column test
RL	Reservoir/lake
RPD	Relative percent difference
RSD	Relative standard deviation
SDS	Simulated distribution system
SDWIS	Safe Drinking Water Information System
SEBST	Single-element bench-scale test
SAC	Selective anion concentration and selective anion chromatography
SOFT	Single-stage softening treatment
SS	Supplemental Surveys
Stage 2 DBP Rule	Stage 2 Disinfection By-products Rule
ST/SOFT	Split-treatment softening treatment
SUVA	Specific ultraviolet absorbance
SW	Surface water
SWAT	Surface Water Analytical Tool
SWTR	Surface Water Treatment Rule
T10	Time for 10% of volume to flow through a treatment process
T50	Time for 50% of volume to flow through a treatment process
TAW	Technical Advisory Workgroup (AWWA)
TBAA	Tribromoacetic acid
TCAA	Trichloroacetic acid
TCAN	Trichloroacetonitrile
TCP	Trichloropropanone
TCR	Total Coliform Rule
THAA	Trihaloacetic acid
THM	Trihalomethane
TOC	Total organic carbon
TOX	Total organic halogen
TOXRPD	TOX relative percent difference
TSC	Technical Support Center (USEPA, Cincinnati)
TSS	Total suspended solids
TS/SOFT	Two-stage softening treatment
TSUVA	Specific ultraviolet absorbance as estimated using TOC instead of DOC
TT	Treatment technique
TTHM	Total trihalomethane (sum of four THM species: $CHCl_3$, $CHBr_3$, BDCM, DBCM)—the abbreviation THM4 can be used instead of TTHM
TTHM-Br	Total trihalomethane bromine-substituted fraction
TTHM-Cl	Total trihalomethane chlorine-substituted fraction
TWG	Technical Work Group (under FACA Committee)

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UCMR	Unregulated Contaminant Monitoring Rule
UFC	Uniform formation conditions
UNFILT/SW	Unfiltered surface water
UNCONV	Unconventional treatment
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
UV_{254}	Ultraviolet absorbance at 254 nm
WTP	Water treatment plant

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6666 W. Quincy Avenue, Denver, CO 80235
(303) 347-6100

ISBN 1-58321-273-6

9 781583 212738

1P-6C-90947-03/03-JP