Final

OCCURRENCE ASSESSMENT FOR DISINFECTANTS AND DISINFECTION BYPRODUCTS IN PUBLIC DRINKING WATER SUPPLIES

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Occurrence Assessment for D/DBP in Public Drinking Water Supplies

Errata Sheet

1. Chapter 2, page 2-16
   - Delete "Inc." from "Demers, Renner, Inc., 1992"

2. Chapter 4, page 4-54
   - Replace (Gages, 1997) with (Gates, 1998)
   - Sentence 3: Delete "Like the chlorite ion".

3. Chapter 4, page 4-56, para 2
   - Replace "modified EPA method 300.0b", with "EPA method 300.0" here and in a few other places in the text.

4. Chapter 7, page 7-7, section 7.5.2 chlorite.
   - Replace "the 1994 proposed MCLG for chlorite was 0.08 mg/L", with "the 1998 final MCLG for chlorite is 0.8 mg/L."

5. Appendix B, page B-4, para 1, SM 45000.ClO2E
   - Replace "pH adjusted to 12" to "pH adjusted to 7".

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TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS iii

ACRONYM AND ABBREVIATION LIST ix

EXECUTIVE SUMMARY ES-1

1. INTRODUCTION 1-1

1.1 OVERVIEW OF THE REGULATORY BACKGROUND 1-1
1.2 PURPOSE OF THE DOCUMENT 1-4
1.3 DOCUMENT ORGANIZATION 1-7

2. USE OF DISINFECTANTS IN THE UNITED STATES 2-1

2.1 CHLORINE 2-3
2.1.1 Description of Chemistry 2-6
2.1.2 Use and Distribution 2-6
2.1.3 Advantages/Disadvantages 2-7
2.1.4 Dose Ranges 2-8
2.1.5 Byproducts 2-8
2.2 CHLORAMINES 2-9
2.2.1 Description of Chemistry 2-10
2.2.2 Use and Distribution 2-10
2.2.3 Advantages/Disadvantages 2-10
2.2.4 Dose Ranges 2-11
2.2.5 Byproducts 2-12
2.3 CHLORINE DIOXIDE 2-12
2.3.1 Description of Chemistry 2-13
2.3.2 Use and Distribution 2-15
2.3.3 Advantages/Disadvantages 2-15
2.3.4 Dose Ranges 2-16
2.3.5 Byproducts 2-17
2.4 OZONATION 2-18
2.4.1 Description of Chemistry 2-18
2.4.2 Use and Distribution 2-19
2.4.3 Advantages/Disadvantages 2-20
2.4.4 Dose Ranges 2-20
2.4.5 Byproducts 2-21

3. OCCURRENCE OF DBP PRECURSORS AND DISINFECTANTS 3-1

3.1 SUMMARY OF PRECURSOR OCCURRENCE DATA: TOTAL ORGANIC CARBON AND BROMIDE ION 3-1
3.1.1 Total Organic Carbon Occurrence 3-1
3.1.2 Bromide Ion Occurrence 3-8
3.2 DISINFECTANTS 3-11
3.2.1 Chlorine 3-11
3.2.2 Chloramine 3-13
3.2.3 Chlorine Dioxide 3-14

4. OCCURRENCE OF DISINFECTION BYPRODUCTS 4-1

4.1 SOURCES OF 1994 DISINFECTION BYPRODUCT OCCURRENCE DATA 4-1
4.1.1 National Organics Reconnaissance Survey 4-2
4.1.2 National Organics Monitoring Survey 4-2
4.1.3 Rural Water Survey 4-2
4.1.4 Community Water Supply Survey 4-3
4.1.5 AWWARF National Trihalomethanes Survey 4-3
4.1.6 EPA/AMWA/CDHS Study (35 Utility Study) 4-3
4.1.7 EPA Disinfection Byproduct Field Studies 4-3
4.1.8 Water Industry Data Base (1991) 4-4
4.1.9 AWWA 1991 Disinfection Survey 4-4
4.2 SOURCES OF POST-1994 DISINFECTION BYPRODUCT OCCURRENCE DATA 4-4
4.2.1 WaterStats 4-4
4.2.2 American Water Works Service Company Monitoring Data 4-5
4.2.3 State Compliance and Other Monitoring 4-5
4.2.4 Literature Search 4-5
4.3 DBP OCCURRENCE DATA 4-6
4.3.1 Chloroform 4-6
4.3.2 Bromodichloromethane 4-23
4.3.3 Dibromochloromethane 4-26
4.3.4 Bromoform 4-29
4.3.5 Total Trihalomethanes 4-31
4.3.6 Monochloroacetic Acid 4-38
4.3.7 Dichloroacetic Acid 4-39
4.3.8 Trichloroacetic Acid 4-40
4.3.9 Monobromoacetic Acid 4-42
4.3.10 Dibromoacetic Acid 4-43
4.3.11 Haloacetic Acids 5 4-43
4.3.12 Chloral Hydrate 4-47
4.3.13 Bromate Ion 4-49
4.3.14 Chlorite Ion 4-51
4.3.15 Chlorate Ion 4-54

5. NATIONAL OCCURRENCE 5-1

5.1 DATA SOURCES 5-1
5.1.1 AWWA WaterStats 5-2
5.1.2 AWWSCo Monitoring Data 5-3
5.1.3 State Compliance Monitoring Data 5-3
5.2 TTHM DATA 5-3
5.3 HAA5 DATA 5-6
5.4 CHLORITE AND BROMATE IONS 5-7
5.4.1 Bromate Ion 5-7
5.4.2 Chlorite Ion 5-7

6. SUMMARY OF EXPOSURE DATA FROM SOURCES OTHER THAN DRINKING WATER . 6-1

6.1 DISINFECTANTS 6-1
6.1.1 Chlorine, Hypochlorite Ion, and Hypochlorous Acid 6-1
6.1.2 Chloramines 6-2
6.1.3 Chlorine Dioxide 6-3

6.2 DISINFECTION BYPRODUCTS 6-3
6.2.1 Chloroform 6-3
6.2.2 Bromodichloromethane 6-16
6.2.3 Dibromochloromethane 6-20
6.2.4 Bromoform 6-23
6.2.5 Total Trihalomethanes 6-25
6.2.6 Monochloroacetic Acid 6-26
6.2.7 Dichloroacetic Acid 6-26
6.2.8 Trichloroacetic Acid 6-26
6.2.9 Monobromoacetic Acid 6-27
6.2.10 Dibromoacetic Acid 6-27
6.2.11 Haloacetic Acids 5 6-28
6.2.12 Chloral Hydrate 6-28
6.2.13 Bromate 6-29
6.2.14 Chlorate and Chlorite 6-29

7. RELATIVE SOURCE CONTRIBUTION EVALUATION 7-1

7.1 OVERVIEW OF THE RELATIVE SOURCE CONTRIBUTION APPROACH 7-1
7.2 CHOICE OF THE POPULATION OF CONCERN 7-3
7.3 ESTIMATION OF EXPOSURE FROM DRINKING WATER 7-3
7.4 ESTIMATION OF EXPOSURE FROM SOURCES OTHER THAN DRINKING WATER 7-4
7.5 RELATIVE SOURCE CONTRIBUTION VALUES CHOSEN FOR INDIVIDUAL DISINFECTANTS AND DBPS 7-5
7.5.1 Disinfectants 7-5
7.5.2 Disinfection Byproducts 7-6

APPENDIX A SUMMARY OF SURVEYS AND STUDIES A-1

APPENDIX B ANALYTICAL METHODS B-1

REFERENCES R-1

LIST OF EXHIBITS

Exhibit 1-1. Disinfectants and Compounds Regulated by the Stage 1 D/DBP Rule 1-4

Exhibit 2-1. Number of Community Water Systems by Primary Water Source and Service Population 2-2
Exhibit 2-2. Percent of Plants Applying Specific Disinfection Treatment for Primarily Surface Water Systems 2-4
Exhibit 2-3. Percent of Plants Applying Specific Disinfection for Primarily Groundwater Systems . 2-5
Exhibit 2-4. Chlorine Dose Ranges 2-8
Exhibit 2-5. Disinfection Byproducts of Chlorine 2-9
Exhibit 2-6. Suggested Doses of Ammonia 2-11
Exhibit 2-7. Observed Chlorine Dioxide Doses 2-17
Exhibit 2-8. Suggested Doses for Ozone 2-21

Exhibit 3-1. Disinfection Byproduct Precursor and Disinfectant Occurrence 3-2
Exhibit 3-3. Groundwater TOC Levels from the GWSS Reported in the 1994 Proposed Rule 3-5
Exhibit 3-2. TOC Occurrence Data from the WIDB in the 1994 Proposed Rule 3-5
Exhibit 3-5. Comparison of AWWA Survey TOC Data with WIDB Data 3-6
Exhibit 3-7. Pre-ICR Data from the State of Utah (1994–1996) 3-8
Exhibit 3-8. Bromide Ion Occurrence by Source: 101 Utility Nationwide Study 3-9
Exhibit 3-9. Bromide Ion and TOC Occurrence in Source Water for Ozone Plants 3-10
Exhibit 3-10. Chlorine Dioxide Concentrations in Distribution Systems 3-15
Exhibit 3-11. Chlorine Dioxide Concentrations at Charleston Plant and Customer Houses 3-16

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary 4-7
Exhibit 4-2. Chloroform Concentration in Utah Plant Effluents (June 1990) 4-22
Exhibit 4-3. Bromodichloromethane Concentration in Thirty-Five Utah Plant Effluents 4-25
Exhibit 4-4. Dibromochloromethane Concentration in Utah Plant Effluents (June 1990) 4-28
Exhibit 4-5. Summary of Total Trihalomethane Concentrations from Public Water Systems in Massachusetts (1994–1996) 4-33
Exhibit 4-6. Summary of Total Trihalomethane Concentrations from Public Water Systems in Missouri (1996 – June 1997) 4-33
Exhibit 4-7. Summary of Total Trihalomethane Concentrations from New Jersey Public Water Systems (1994–1997) 4-34
Exhibit 4-8. Total Trihalomethane Concentrations from Public Water Systems in Oregon Serving More Than 10,000 Persons (1994–1996) 4-34
Exhibit 4-9. Pennsylvania Compliance Monitoring Data for Total Trihalomethanes 4-35
Exhibit 4-10. Texas Compliance Monitoring Data for Total Trihalomethanes 4-36
Exhibit 4-11. Trihalomethane Concentration in Utah Water Treatment Plants Using Surface Water (June 1990) 4-37
Exhibit 4-12. Seasonal Total Trihalomethane Variation in Utah Plant Effluents 4-37
Exhibit 4-13. Dichloroacetic Acid Concentrations from Six North Carolina Surface Water Systems 4-40
Exhibit 4-14. Trichloroacetic Acid Concentrations from Six North Carolina Surface Water Systems 4-42
Exhibit 4-15. Haloacetic Acids 5 Concentrations in Missouri Water Treatment Plants (1/97–6/97) . 4-44
Exhibit 4-16. Haloacetic Acids Concentrations from Eight North Carolina Surface Water Plants . . 4-45
Exhibit 4-17. Haloacetic Acids 5 Concentration from Thirty-Five Utah Surface Water Systems . . . 4-46
Exhibit 4-18. Seasonal Analysis of Haloacetic Acids 5 Concentrations from Thirty-Five Utah Surface Water Systems' Plant Effluents 4-46

Exhibit 4-19 Chlorite Ion Concentrations at Charleston Plant and Customer Houses 4-51
Exhibit 4-20 Occurrence of Chlorite Ion in Utilities Using Chlorine Dioxide 4-51
Exhibit 4-21 Chlorate Ion and Chlorite Ion Concentrations at Sixty-Five Utilities Using Chlorine Dioxide 4-53
Exhibit 4-22. Chlorate Ion Concentrations at Charleston Plant and Customer Houses 4-53
Exhibit 4-23. Occurrence of Chlorate Ion in Waters from Utilities Using Chlorine Dioxide 4-55
Exhibit 4-24 Occurrence of Chlorate Ion in Fifteen Utilities Using Hypochlorite Solution for Disinfection 4-55

Exhibit 5-1. Stage I D/DBP Rule MCLs 5-1
Exhibit 5-2. Summary Statistics on TTHM Based on WaterStats and AWWSCo 5-4
Exhibit 5-3. TTHM Compliance Monitoring Data (1994–1996): Surface and Groundwater Systems Serving Greater Than 10,000 People 5-5
Exhibit 5-4. Comparison of State TTHM Data for Systems Servings Fewer Than 10,000 People . . 5-5
Exhibit 5-5. Comparison of HAA5 Data for Systems Serving Greater Than 10,000 People 5-6
Exhibit 5-6. Available Data on Bromate Ion Occurrence in Drinking Water Supplies 5-6
Exhibit 5-7. Available Chlorite Ion Occurrence in Drinking Water Supplies 5-7

Exhibit 6-1. Chloroform Levels in Foods 6-5
Exhibit 6-2. Mean Chloroform Concentrations in Samples Designated for Further Analysis 6-5
Exhibit 6-3. Chloroform Levels in Food 6-7
Exhibit 6-4. Chloroform Levels in Food 6-7
Exhibit 6-5. Chloroform Concentrations in Food and Beverages 6-7
Exhibit 6-6. Summary Statistics of Chloroform in Ambient Air of New Jersey and North Carolina Subjects 6-9
Exhibit 6-7. Summary Statistics of Chloroform in Breath of New Jersey and North Carolina Subjects 6-9
Exhibit 6-8. Chloroform in Personal Air Samples from the EPA TEAM Study 6-10
Exhibit 6-9. Chloroform in Outdoor Air Samples from the EPA TEAM Study 6-10
Exhibit 6-10. Exposure Levels of Chloroform Monitored in Air 6-12
Exhibit 6-11. Chloroform Exposure from Outdoor Air 6-12
Exhibit 6-12. Chloroform Concentration in Indoor Air 6-13
Exhibit 6-13. Bromodichloromethane Levels in Food 6-17
Exhibit 6-14. Bromodichloromethane Concentrations in Food and Beverages 6-18
Exhibit 6-15. Summary Statistics of Bromodichloromethane in Ambient Air of New Jersey and North Carolina Subjects 6-19
Exhibit 6-16. Summary Statistics of Bromodichloromethane in Breath of New Jersey and North Carolina Subjects 6-19
Exhibit 6-17. Bromodichloromethane Occurrence and Exposure from Outdoor Air 6-20
Exhibit 6-18. Bromodichloromethane Occurrence and Exposure from Indoor Air 6-20
Exhibit 6-19. Dibromochloromethane Levels Found in Food 6-21
Exhibit 6-20. Dibromochloromethane Concentrations in Food and Beverages 6-21
Exhibit 6-21. Dibromochloromethane Occurrence from Outdoor Air 6-23
Exhibit 6-22. Dibromochloromethane Occurrence and Exposure from Indoor Air 6-23
Exhibit 6-23. Bromoform Levels Found in Food 6-23
Exhibit 6-24. Bromoform Occurrence and Exposure in Outdoor Air 6-25
Exhibit 6-25. Bromoform Occurrence and Exposure in Indoor Air 6-25
Exhibit 6-26. Total Trihalomethanes Levels in Food 6-25

Exhibit 7-1 Relative Source Contribution for Disinfectants and Disinfection Byproducts 7-8

ACRONYM AND ABBREVIATION LIST

35 Utility Study	EPA/AMWA/CDHS Study
AOC	Assimilable Organic Carbon
ASTM	American Society for Testing and Materials
AWWA	American Water Works Association
AWWARF	American Water Works Association Research Foundation
AWWSCo	American Water Works System Company
BDL	Below Detection Limit
Cl^-	Chloride
Cl_3	Trichloride
ClO_2	Chlorine Dioxide
ClO_2^-	Chlorite
ClO_3	Chlorate
CDSs	Concentrations in Distribution Systems
CWSS	Community Water Supply Survey
D/DBP	Disinfectant/Disinfection Byproducts
DBP	Disinfection Byproducts
DBPRAM	Disinfection Byproduct Regulatory Assessment Model
DPD	N,N-Diethyl-P-Phenylenediamine
DSS	Distribution System Samples
EPA	U.S. Environmental Protection Agency
ESWTR	Enhanced Surface Water Treatment Rule
FACA	Federal Advisory Committee Act
FACTS	Free (Available) Chlorine Test, Syringaldazine
FDA	U.S. Food and Drug Administration
FR	Federal Register
GAC	Granular Activated Carbon
GC	Gas Chromatograph
GC/ECD	Gas Chromatography/Electron Capture Detection
GC/MS	Gas Chromatography/Mass Spectrometry
GWSS	Groundwater Supply Service
HAA	Haloacetic Acid
HAA5	Haloacetic Acid-Five
HCl	Hydrochloric Acid
ICR	Information Collection Rule
KG	Kilogram
L	Liter
LOAEL	Lowest Observed Adverse Effect Level
M-DBP	Microbial Disinfection Byproducts
MCLG	Maximum Contaminant Level Goals
MCL	Maximum Contaminant Level
MDL	Method Detection Limit
MG	Milligram
MRDL	Maximum Residual Disinfectant Level
MRDLG	Maximum Residual Disinfectant Level Goal
MRL	Minimum Reporting Level
MTBE	Methyl-Tert-Butyl Ether
N	Nitrogen
Na	Sodium

NAS	National Academy of Sciences
NCI	National Cancer Institute
ND	Not Detected
NH_2Cl	Monochloramine
$NHCl_2$	Dichloramine
NOAEL	No Observed Adverse Effect Level
NOM	Natural Organic Matter
NOMS	National Organic Monitoring Survey
NORS	National Organics Reconnaissance Survey
O_2	Oxygen
$O_{3(aq)}$	Aqueous Ozone
OGWDW	Office of Ground Water and Drinking Water
PAC	Powdered Activated Carbon
PPB	parts per billion
PPM	parts per million
PWS	Public Water Systems
RfD	Reference Dose
RSC	Relative Source Contribution
RWS	Rural Water Survey
SDS	Simulated Distribution System
SDWA	1974 Safe Drinking Water Act
SM	Standard Method
SMWA	Association of Metropolitan Water Agencies
SWTR	Surface Water Treatment Rule
SPW	State Project Water
SUVA	Specific Ultraviolet Absorbance
TEAM	Total Exposure Assessment Methodology
THM	Trihalomethanes
TOC	Total Organic Carbon
TOX	Total Organic Halides
TSD	Technical Support Division
TTHM	Total Trihalomethane
UNC	University of North Carolina
UV	Ultraviolet
VOC	Volatile Organic Compound
WIDB	Water Industry Data Base
μg	Microgram

EXECUTIVE SUMMARY

The occurrence of disinfectants and DBPs in water intended for drinking has been documented in a range of different disinfection treatments and for different source water, finished water, and ground water. This document presents information from surveillance reports regarding occurrence of disinfectants and DBPs. To develop this document literature searches were conducted using several research databases. EPA notes that the occurrence data compiled in this document and the current national estimate of disinfectants and DBP occurrence reflects existing data. Substantial additional information that will be used to strengthen an estimate of national occurrence of disinfectants and DBP is currently being collected under the Information Collection Rule (ICR). However, EPA believes that the information in this document is sufficient to conclude that disinfectants and DBPs can and do occur in public water supplies at levels which may pose a risk to human health.

The 1996 Amendments to the Safe Drinking Water Act require EPA to promulgate the Interim Enhanced Surface Water Treatment Rule (IESWTR) and the Stage 1 Disinfectants and Disinfection Byproducts Rule (DBPR) by November 1998 (Section 1412 (b)(2)(C)). EPA proposed these two regulations, IESWTR (59 FR 38832) and Stage 1 DBPR (59 FR 38668), on July 29, 1994. The IESWTR was developed to provide additional microbial protection beyond that which is prescribed in the Surface Water Treatment Rule (54 FR 27486; June 29, 1989) and to control for *Cryptosporidium*. The Stage 1 DBPR was developed to limit the levels of several disinfectants and disinfection byproducts resulting from their use. EPA believes that the two rules need to be promulgated simultaneously to assure concurrent compliance and a balanced risk-based implementation. The Stage 1 DBPR applies to community water systems and non-transient non-community water systems that treat their water with a chemical disinfectant for either primary or residual treatment the IESWTR pertains to public water systems serving 10,000 people or greater.

The Agency has requested public comment regarding these rules on three occasions and has engaged in several stakeholder meetings to discuss and share information pertaining to rule development. In February 1997, EPA established the Microbial and D/DBP Advisory Committee under the Federal Advisory Committee Act (FACA) to collect, share and analyze new information and data, as well as to build a consensus relating to the regulatory implications of this new information. As a result of these negotiations, the Agency published Notice of Data Availability (NODA) for the IESWTR (59 FR 59486) and the Stage 1 DBPR (62 FR 59388) in November 1997. An additional NODA for the Stage 1 DBPR was published in

March 1998 which included new information and analyses that become available after the 1997 NODA (63 *FR* 15674).

The following document, "*Occurrence Assessment for Disinfectants/Disinfection Byproducts in Public Drinking Water*", was developed to support the Stage 1 DBPR. The intent of this document is to provide available information on the occurrence of disinfectants, disinfection byproducts, and source water precursors to DBPs in surface and ground water as well as finished water supplies. The document provides information on: drinking water treatment disinfection practices; occurrence of disinfect residuals and disinfection byproducts in distribution systems, exposure to disinfectants and disinfection byproducts, analytical methodologies utilized to measure the contaminants, and populations potentially exposed to the contaminants. The document emphasizes the occurrence of the regulated disinfectants and DBPs because a large number of people are exposed to DBPs and because of the different potential risks(e.g. cancer and adverse reproductive and developmental effects) that may result from exposure to DBPs.

The occurrence of disinfectants and DBPs in water intended for drinking has been documented in a range of different disinfection treatments and for different source water, finished water, and ground water. This document presents information from surveillance reports regarding occurrence of disinfectants and DBPs. To develop this document literature searches were conducted using several research databases. EPA notes that the occurrence data compiled in this document and the current national estimate of disinfectants and DBP occurrence reflects existing data. Substantial additional information that will be used to strengthen an estimate of national occurrence of disinfectants and DBP is currently being collected under the Information Collection Rule (ICR). However, EPA believes that the information in this document is sufficient to conclude that disinfectants and DBPs can and do occur in public water supplies at levels which may pose a risk to human health.

1. INTRODUCTION

The U.S. Environmental Protection Agency's (EPA) Office of Ground Water and Drinking Water (OGWDW) is developing a set of interrelated drinking water regulations to control disinfectants and disinfection byproducts (D/DBPs) and to refine control of microbiological pathogens in public water systems (PWSs). Conventional drinking water treatment practices involve the addition of disinfectant chemicals to the water that, while effective in controlling many harmful microorganisms, combine with organic matter in the water to form compounds known as disinfection byproducts (DBPs). EPA has determined that a number of organic DBPs, including some trihalomethanes (THMs) and some haloacetic acids (HAAs), cause cancer in laboratory animals and may be possible human carcinogens. One of the most complex questions facing water supply professionals is how to minimize the risks from these DBPs and still control microbial contaminants. In order to address these complex issues, EPA proposed the National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts rule on July 29, 1994. This rule proposed the first stage of a two-stage process for regulating D/DBPs.

This occurrence assessment document was prepared to support the Stage 1 D/DBPR. This section presents an overview of the regulatory background and approach for these regulations, describes the purpose and contents of this document, including the methodology used for developing data, and delineates the organization of the document.

1.1 OVERVIEW OF THE REGULATORY BACKGROUND

The following list provides a brief chronology of EPA's rulemaking activities on disinfectants and DBPs:

- 1979—Promulgation of an interim maximum contaminant level (MCL) of 0.10 mg/L for total trihalomethanes
- 1992—Initiation of a negotiated rulemaking for the D/DBP rule
- 1994—Proposal of three rules: Stage 1 D/DBP rule, the Interim Enhanced Surface Water Treatment Rule (IESWTR), and the Information Collection Rule (ICR)
- 1996—Promulgation of the ICR
- 1997—Establishment of the Microbial and D/DBP Federal Advisory Committee.
- 1997—Stage 1 D/DBP Rule Notice of Data Availability (NODA)
- 1998—Stage 1 D/DBP Rule NODA

In November 1979, EPA promulgated an interim MCL for total trihalomethanes (TTHMs) of 0.10 mg/L as an annual average (44 FR 68624). This standard was based on the need to balance the requirement for continued disinfection of water to lessen exposure to pathogenic microorganisms while simultaneously lowering exposure to disinfection byproducts, which might be carcinogenic to humans. The interim TTHM standard only applies to PWSs serving at least 10,000 people that add a disinfectant to drinking water during any part of the treatment process. At their discretion, states may extend coverage to smaller PWSs.

In 1992, EPA initiated a negotiated rulemaking to develop a DBP rule. The Negotiating Committee established for the proposed D/DBP rule included representatives of state and local health and regulatory agencies, public water systems, elected officials, consumer groups, and environmental groups. Early in the process, the negotiators agreed that large amounts of information necessary to understand how to optimize the use of disinfectants while minimizing microbial and D/DBP risk on a plant-specific basis were not available. Nevertheless, the Negotiating Committee agreed to propose a D/DBP rule to extend coverage to all community and nontransient noncommunity water systems that use disinfectants. This proposed D/DBP rule would reduce the current MCL for TTHMs, regulate additional disinfection byproducts, set limits for the use of disinfectants, and reduce the presence of organic compounds in source water that could react with disinfectants to form byproducts.

The Negotiating Committee agreed to the development of three sets of rules: a two-staged D/DBP rule, an ESWTR, and an ICR. EPA is currently developing the D/DBP rule and ESWTR in two stages. The Stage 1 D/DBP and interim ESWTR were proposed in July 1994. EPA established a deadline of November 1998, as enacted in the 1996 amendments to the Safe Drinking Water Act, for the final promulgation of both the Stage 1 D/DBP rule and interim ESWTR. The Stage 1 D/DBP rules apply to all systems, while the interim ESWTR would only apply to systems serving 10,000 people or more. The Negotiating Committee agreed that a long-term ESWTR would be needed for systems serving fewer than 10,000 people when the results of more research and water quality monitoring became available. The long-term ESWTR could also include additional refinements for larger systems.

The Negotiating Committee decided that additional field data were critical for developing a reasonable set of rules and for understanding more fully the limitations of the current Surface Water Treatment Rule (SWTR). EPA, therefore, promulgated the ICR on May 14, 1996 (61 FR 24354). The purpose of the ICR is to collect occurrence and treatment information to evaluate the need for (1) possible changes to the current SWTR and existing microbial treatment practices and (2) future regulation of disinfectants and DBPs. The ICR will provide information necessary to determine the national occurrence

of DBPs in drinking water. Engineering data on how PWSs currently control chemical and microbial contaminants will also be collected under the ICR. This information will be used to assess the potential health problems created by the presence of DBPs and pathogens in drinking water and to assess the extent and severity of risk to assist the regulatory and public health decisions. The ICR data will be used for developing the long-term ESWTR and the Stage 2 DBP rule.

EPA established the Microbial and D/DBP Advisory Committee under the Federal Advisory Committee Act (FACA) on February 12, 1997, to collect, share, and analyze new information and data since the 1994 proposed rule, as well as to build consensus on the regulatory implications of this new information for the final Stage 1 D/DBP rule. The FACA Committee consisted of 20 members representing EPA, state and local public health and regulatory agencies, local elected officials, drinking water suppliers, chemical and equipment manufacturers, and public interest groups.

The compounds of concern under the Stage 1 D/DBP rule are listed in Exhibit 1-1. In the proposed Stage 1 D/DBP rule, three Maximum Residual Disinfectant Levels (MRDLs) and four MCLs were proposed. The proposed MDRL for chlorine and chloramines is 4.0 mg/L as Cl_2 and 0.8 mg/L as ClO_2 for chlorine dioxide. Four MCLs were proposed for DBPs: TTHMs (0.08 mg/L), haloacetic acids-five (HAA5) (0.06 mg/L), chlorite (1.0 mg/L), and bromate (0.10 mg/L). TTHMs are the sum of the concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform. HAA5 are the sum of the concentrations of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids. Although there are nine HAAs, only five will be regulated under this rule based on occurrence data availability at this time. EPA did not set an MCL for chloral hydrate because it is believed that the TTHM and HAA5 MCLs and the treatment technique (i.e., enhanced coagulation) for disinfection byproduct precursor removal will control for chloral hydrate.

EPA will use information on drinking water plant design and operations obtained under the ICR, as well as data and information from other sources, to develop, analyze, and assess options for proceeding with the Stage II D/DBP rule and long-term ESWTR.

The future rulemaking activities will be:

- 2000—Promulgation of long-term 1 ESWTR in November
- 2002—Promulgation of final long-term 2 ESWTR in November
- 2002—Promulgation of Final Stage 2 D/DBP rule in May.

Exhibit 1-1. Disinfectants and Compounds Regulated by the Stage 1 D/DBP Rule

Type/Family	Compound
Disinfectants	Chloramine(s)[1] Chlorine dioxide[1] Chlorine[1]
Trihalomethanes	Chloroform Bromodichloromethane Dibromochloromethane Bromoform Total trihalomethanes[2,3]
Haloacetic acids	Monochloroacetic acid[3] Dichloroacetic acid Trichloroacetic acid Monobromoacetic acid[3] Dibromoacetic acid[3] Haloacetic acids 5[2,3]
Others (disinfection byproducts)	Chloral hydrate Bromate[2] Chlorite[2]

1. MRDLs for chlorine, chloramines, and chlorine dioxide were proposed under the Stage 1 D/DBP proposed rule.
2. MCLs for TTHMs, HAA5, chlorite, and bromate were proposed under the Stage 1 D/DBP proposed rule.
3. Compounds not addressed in *Occurrence Assessment for Disinfections and Disinfection By-Products (Phase 6a) in Public Drinking Water* (EPA, 1992).

1.2 PURPOSE OF THE DOCUMENT

This document presents information on the occurrence, distribution, and exposure to the compounds of concern under the proposed Stage 1 D/DBP rule. The data on occurrence and exposure support several aspects of the drinking water regulatory development process:

- DBP occurrence levels in PWSs of various source and size characteristics provide EPA with the basis for estimating the number of systems and the size of the affected populations currently experiencing contaminant levels exceeding the MCL alternatives under consideration.
- DBP occurrence levels in the distribution systems of PWSs of various source and size characteristics will be used in conducting the cost impact analyses of the regulatory alternatives.
- DBP occurrence levels will be used in identifying the best available technology necessary for setting the MCL.

- Occurrence estimates will be used to develop the exposure assessments and, subsequently, the contribution of drinking water, relative to other sources of exposure, to total intake for setting the maximum contaminant level goals (MCLG) for contaminants.

- Exposure information is used to estimate the baseline health impact assessment of current levels and to evaluate the health benefits of the regulatory alternatives.

For the 1994 proposed rule, EPA developed the Disinfection Byproduct Regulatory Assessment Model (DBPRAM) to provide simulated occurrence and DBP formation data for the D/DBP rule regulatory impact analysis (RIA) (59 FR 38668). The SWTR, proposed enhanced SWTR, Total Coliform Rule, and the Lead-Copper Rule were chosen for compliance standards for the DBPRAM simulation. These assumptions allowed EPA to predict what levels would occur with these new and proposed rules. To account for the disinfection requirements typical of surface water plants, the DBPRAM used total organic carbon (TOC), bromide ion, and other water quality data from national surface water surveys to model DBP formation in surface water systems that used filtration but did not soften. Actual water quality data were used to simulate the DBP formation in occurrence values based on DBP empirical formation and disinfectant decay equations.

The model predicted TTHM and HAA5 levels but not individual DBPs, because reliable equations to predict the individual DBPs in a wide range of waters (e.g., high- and low-bromide ion concentration waters) were not available. Empirical equations used in the model were based on numerous bench-, pilot- and full-scale studies. Because analytical standards for bromochloroacetic acid, BDCAA, DBCAA, TBAA were not available during development and validation of the predictive equations used in the model, they were not included in the D/DBP Stage 1 HAA class of compounds. Any error that could result from this omission is probably low, especially in low-bromide ion waters where the potential for forming bromochloroacetic acids is low, but could be significant in high-bromide ion waters (Pourmoghaddas et al., 1993 and Singer 1996).

In addition to TTHM and HAA5 concentrations, the DBPRAM also predicted the following water quality after individual treatment processes:

- TOC removal during alum coagulation, granular activated carbon (GAC) adsorption, and nanofiltration

- Changes in alkalinity and pH resulting from chemical addition

- Disinfectant decay and residual chlorine and chloramine in plants and distribution systems.

The D/DBP Technologies Work Group reviewed the DBPRAM output during the negotiated rulemaking process. The model was validated through comparison to real world data and engineering judgment. The validation showed tendencies for both underpredictions and overpredictions. For example, TTHM formation from source waters either low or high in bromide ion showed a 20 to 35 percent less than what the models predicted. Conversely, the central tendency of the model was 5 to 10 percent over the prediction of the TOC removal by alum coagulation. The D/DBP Technologies Work Group corrected the outputs of the model according to the validation results.

Because the DBPRAM only provided occurrence data for surface water systems that use filtration and do not soften, additional data were used to supplement the model. To develop values for the RIA for systems not predicted in the model, data were used from case studies on numerous systems that either do not filter or filter and soften their water. These data were reviewed for compliance and predicted water qualities. Water quality values for groundwater were derived from the Water Industry Database (WIDB) and the Groundwater Supply Survey (GWSS) data. The 1994 proposed rule used the revised DBPRAM to identify the potential percent lessening of TTHM and HAA5 concentrations from waters treated by enhanced coagulation for large systems that filter but do not soften.

At the February 1997 FACA meeting, new data were presented for comparison to the DBPRAM projections used in the 1994 proposed rule. The data presented were occurrence data from treatment facilities that pre-disinfected at various locations in the treatment process. The results indicated that DBP formation could be reduced by continuing to pre-disinfect source water, but not to the same extent that could be achieved by post-disinfection after DBP precursor removal. The complex equations needed to model the application of pre-disinfection practices were not available to revise the DBPRAM. The presentation noted that the DBPRAM did not provide data for all systems (i.e., systems that filter and do not soften), the model could only provide limited empirical predictions, required revision against real world data to accurately characterize DBP occurrence, and, most importantly, could not account for modified pre-disinfection practices. Therefore, on advisement of the D/DBP Technologies Work Group, the D/DBP Advisory Committee decided to rely on actual occurrence data to support the final rule rather than modifying the DBPRAM.

To support the above regulatory processes and review the actual occurrence data an effort to collect, review, and summarize occurrence and exposure data was undertaken by EPA. This document presents the results of that effort. This document includes data from the document entitled *Occurrence Assessment for Disinfectants and Disinfection By-Products (Phase 6a) in Public Drinking Water* (EPA, 1992a) and the

preamble to the 1994 proposed D/DBP rule (59 *FR* 38668). Exposure estimates from sources other than drinking water will be used to establish the relative source contribution (RSC) for DBPs from drinking water. The RSC will then be used to establish MCLGs or MRDL goals (MRDLGs).

1.3 DOCUMENT ORGANIZATION

The remainder of this document is organized into six sections and two Appendixes, highlighted in the following list:

- **Section 2 – Use of Disinfectants in the United States**: This section provides information on the four most commonly used disinfectants: free chlorine, chloramine (combined chlorine), chlorine dioxide, and ozone. The section briefly describes each disinfectant, including method of application, use and distribution, advantages and disadvantages, dosage requirements, and potential byproducts of disinfection. Special considerations for using the disinfectants in groundwater and surface water systems and by system size are noted. Disinfection by ultraviolet radiation is not discussed in this document.

- **Section 3 – Occurrence of DBP Precursors and Disinfectants**: This section summarizes occurrence data available for the 1994 proposed rule and new data for disinfectants and the DBP precursors: TOC and bromide ion. Two documents present the data available for the proposed rule: *Occurrence Assessment for Disinfectants and Disinfection By-Products (Phase 6a) in Public Drinking Water* (EPA, 1992) and the preamble to the 1994 proposed rule (59 *FR* 38668). The new data were obtained from national surveys, preliminary ICR data, and peer-reviewed journals.

- **Section 4 – Occurrence of Disinfection Byproducts**: This section summarizes occurrence data available for the 1994 proposed rule and new data for DBPs. Two documents provide the data available for the proposed rule: *Occurrence Assessment for Disinfectants and Disinfection By-Products (Phase 6a) in Public Drinking Water* (EPA, 1992) and the preamble to the 1994 proposed rule (59 *FR* 38668). The new data were obtained from national surveys, compliance monitoring data from six states, and peer-reviewed journals.

- **Section 5 – National Occurrence**: This section addresses national occurrence of THMs and HAA5. Unfortunately, national occurrence estimates of systems cannot be derived from the limited available information. However, this section characterizes national occurrence based on the available data and compares summary statistics.

- **Section 6 – Summary of Exposure from Sources other than Drinking Water**: This section provides information on the potential exposure to DBPs via routes other than drinking water (e.g., food and air). The majority of articles reviewed did not provide exposure data but rather occurrence data for disinfectants and DBPs in food and ambient air.

- **Section 7 – Relative Source Contribution Evaluation:** The characterization of national exposure to contaminants in drinking water involves assessing the population's intake from drinking water consumption and other routes of exposure. This section describes the exposure for persons consuming treated water and assesses exposure from other sources, such as food and air.

- **Appendix A — Summary of Surveys and Studies:** This appendix provides a summary of the surveys and studies cited Sections 3 and 4 of the document. The summaries are more detailed than those in the narrative of other sections and discuss the sampling, analytical methods, and the results of the surveys and summaries.

- **Appendix B – Analytical Methods**: This appendix briefly summarizes the approved analytical methods for the Stage 1 rule and discusses the nationwide capacity of laboratory services to perform these analytical methods. In addition, this appendix describes the approved analytical methods for disinfectants and DBPs. The number of laboratories approved by EPA for ICR analysis of drinking water monitoring is provided as an indicator of the laboratory capacity and availability of analytical services.

2. USE OF DISINFECTANTS IN THE UNITED STATES

The water treatment process removes and/or inactivates microorganisms in water, particularly pathogens that can cause waterborne diseases. This function is especially important for surface supply sources. In many cases, surface water supplies contain discharges from upstream wastewater treatment plants, industrial facilities, stormwater runoff, and animal feed lots. In the treatment plant, some of the treatment processes, such as sedimentation and filtration, will remove most, if not all, of the microorganisms that cause waterborne diseases. However, filtration supplemented by disinfection is very important in the treatment process for preventing waterborne diseases caused by pathogens.

The 1995 *Community Water Systems Survey* (EPA, 1997a) reports that in the United States, 99 percent of surface water systems provide some level of water treatment before distribution to customers, and 99 percent of these treatment systems include disinfection as part of the treatment process. Disinfection comprises specialized treatment for inactivating harmful organisms. Disinfection can be accomplished in several ways: the most common process is the addition of a disinfectant to the water, which inactivates the pathogenic microorganisms. The most commonly used disinfectants are chlorine and chloramines. Chloride dioxide and ozone are also used somewhat for drinking water disinfection.

In addition to disinfection, these chemicals perform as oxidants and are used to treat drinking water for the following additional purposes:

- To control Asiatic clams and zebra mussels
- To oxidize iron, manganese, and sulfides
- To prevent regrowth in the distribution system and maintain biological stability
- To remove taste and odors through chemical oxidation
- To improve coagulation and filtration efficiency
- To prevent algal growth in sedimentation basins and filters
- To oxidize organic micropollutants such as pesticides, volatile organic compounds, etc.

The majority of community groundwater and surface water systems disinfect drinking water supply. More than 50,000 publicly and privately owned community water systems exist in the United States, not including federal- or state-owned systems. Exhibit 2-1 categorizes the 50,288 community water systems by water source (surface water, groundwater, and purchased water) and by service

Exhibit 2-1. Number of Community Water Systems by Primary Water Source and Service Population

Primary Water Source	Service Population Category (Number of Systems)								Total Number of Systems	Percent of Systems
	100 or Less	101–500	501–1,000	1,001–3,300	3,301–10,000	10,001–50,000	50,001–100,000	Greater than 100,000		
Primarily* Groundwater	13,205	13,140	4,980	4,769	2,375	1,370	170	94	40,103	80
Primarily Surface Water	360	820	429	1,135	816	891	204	207	4,862	10
Primarily Purchased	230	1,463	1,100	1,090	933	318	111	78	5,323	10
Total number of Community Water Systems									**50,288**	**100**

*Primarily means system obtains all or highest percentage of water from stated source.
Source: EPA, 1997a; EPA 1997b

population category. Eighty percent of these community water systems provide water primarily from groundwater sources (i.e., more than 50 percent of the water volume is from groundwater sources), while 10 percent provide water primarily from surface water sources. Eighty-five percent of these community water systems serve populations of less than 3,300 persons, while only two percent of these systems serve populations greater than 50,000.

Exhibits 2-2 and 2-3 present the percentage of plants using a specific disinfection treatment method for primary and secondary disinfection. During primary disinfection, disinfectants are added to raw water as part of the treatment scheme. During secondary disinfection, disinfectants are added prior to the distribution system to provide residual disinfection. Exhibits 2-2 and 2-3 do not represent the total percentage of plants that disinfect because an overlap exists between plants that perform both primary and secondary disinfection.

This section provides general information on the four common disinfectants. For each disinfectant, the section describes the chemistry and method of application, use and distribution, advantages and disadvantages, typical dosages needed, and potential byproducts.

2.1 CHLORINE

Chlorine is currently the most commonly used disinfectant in the United States. Through filtration and chlorination, waterborne diseases, including typhoid and cholera, have been virtually eliminated in the U.S. For example, in Niagara Falls, New York, between 1911 and 1915, the number of typhoid cases dropped from 185 deaths out of 100,000 to nearly zero following introduction of filtration and chlorination (White, 1986). Today, 67.5 percent of all surface water treatment plants use chlorine as a residual disinfectant (EPA, 1997b).

Chlorine has four effects when added to water—oxidation, addition, substitution, and disinfection. Chlorine will oxidize soluble iron, manganese, and sulfides that are typically found in groundwater sources. The oxidized products are typically removed by clarification and filtration. When chlorine reacts with natural organic matter in the water, it typically replaces or substitutes for a covalently bound atom in the organic molecule and forms halogen-substituted organic byproducts (e.g., trihalomethanes, chlorophenols, etc.), some of which have been shown to be possible human carcinogens. For disinfection, chlorine hydrolyzes in water to form hypochlorous acid (HOCl) and hydrochloric acid (HCl). Hypochlorous acid contains the active form of chlorine that inactivates or kills pathogens of concern.

Exhibit 2-2. Percent of Plants Applying Specific Disinfection Treatment for Primarily Surface Water Systems

Treatment Type	Service Population Category								
	100 or Less	101–500	501–1,000	1,001–3,300	3,301–10,000	10,001–50,000	50,001–100,000	Greater than 100,000	Total
Primary Disinfection									
Chlorine	59%	73.9%	67.3%	66.3%	68.8%	58.6%	47.6%	57.1%	63.8%
Chlorine Dioxide	0	0	0	5	4.7	13.2	14.2	7.8	6.3
Chloramines	4.6	0	1.1	2.1	0	2.2	15.5	10.8	3.1
Ozone	0	0	0	0	0.3	0	5.4	5.8	0.9
Primary Disinfection combinations	0	0	2	2.9	0.6	9.2	5.1	4.3	3.5
Secondary Disinfection									
Chlorine	49.7%	51.6%	80.6%	62.8%	77.9%	71.1%	73.8%	61.6%	67.5%
Chlorine Dioxide	0	0	0	0	0.3	[illegible]	5.9	1.6	1.6
Chloramines	0	0	0	2.9	2.1	15.6	29.4	24.4	8.1
Secondary Disinfection Combinations	0	0	0	2.1	4	3.9	1.9	11.2	3

Percentages could exceed 100 percent because many plants utilize different disinfectants for the same objective.
Source: EPA, 1997a; EPA, 1997b.

Exhibit 2-3. Percent of Plants Applying Specific Disinfection for Primarily Groundwater Systems

Treatment Type	Service Population Category								
	100 or Less	101–500	501–1,000	1,001–3,300	3,301–10,000	10,001–50,000	50,001–100,000	Greater than 100,000	Total
Primary Disinfection									
Chlorine	64.2%	69.9%	56.7%	73.2%	60.6%	57.4%	36.2%	38.1%	63.9%
Chlorine Dioxide	1.3	0	0	0	0	0	3.1	0	0 3
Chloramines	0	0	0	0	0	0.6	1.4	0.7	0 1
Ozone	0	0	0	0	0	0	0	0.6	0
Primary Disinfection Combinations	0.3	0.5	0	0.7	1	2.6	0	0	0 7
Secondary Disinfection									
Chlorine	23%	23.4%	32.5%	28.3%	42.5%	41.9%	54.5%	65.8%	31.0%
Chlorine Dioxide	0	1	0	0	0	0.6	0	0	0 4
Chloramines	0	0	0	0	0.1	1.1	3.9	4.3	0 3
Secondary Disinfection Combinations	0	0	0	0	0 1	0.1	0	0	0

Percentages could exceed 100 percent because many plants utilize different disinfectants for the same objective.
Source: EPA, 1997a; EPA 1997b.

2.1.1 Description of Chemistry

Disinfection with chlorine is simple, economical, efficient, measurable, and practical. Several types of chlorine are available for use as a disinfectant—chlorine gas, sodium hypochlorite (liquid), and calcium hypochlorite (tablet, granular, or powdered). Chlorine gas is often referred to as elemental chlorine. Chlorine is produced, collected, purified, compressed, cooled, packaged, and shipped as a liquefied gas under pressure.

Sodium hypochlorite is produced by reacting chlorine with sodium hydroxide. Typically, sodium hypochlorite solutions are referred to as liquid bleach or Javelle water. Generally, the commercial or industrial grade solutions produced have hypochlorite strengths of 10 to 16 percent. The stability of sodium hypochlorite solution depends on the hypochlorite concentration, the storage temperature, the length of storage (time), the impurities of the solution, and exposure to light. Decomposition of hypochlorite solution over time can affect the feed rate and dosage, as well as produce undesirable byproducts such as chlorite or chlorate ions (Gordon, et. al., 1995). Because of the storage problems, many systems are investigating onsite generation of sodium hypochlorite in lieu of its purchase from a manufacturer or vendor. Low concentrations (i.e., 5.25 percent or less) are supplied as common household bleach.

To produce calcium hypochlorite, hypochlorous acid is made by adding chlorine monoxide to water and then neutralizing it with a lime slurry to create a solution of calcium hypochlorite. The water is removed from the solution, leaving granulated calcium hypochlorite. Generally, the final product contains up to 70 percent available chlorine and 4 to 6 percent lime. Storage of calcium hypochlorite is a major safety consideration. It should never be stored where it is subject to heat or allowed to contact any organic material of an easily oxidized nature.

2.1.2 Use and Distribution

For use in treatment, chlorine gas feeders can be either direct feed or solution feed. Direct gas feeders deliver the chlorine gas under pressure directly to the point of application. Because direct feeders are less safe than solution feed chlorinators, solution feed is typically used. Chlorine gas is metered under vacuum and mixed in an injector with water to produce a chlorine solution, which is injected at the appropriate application point(s). With this type of system, the flow of chlorine gas is automatically shut off on loss of vacuum, stoppage of the solution discharge line, or loss of operating solution water pressure.

Sodium hypochlorite, which is a dilute liquid chlorine solution, is normally fed directly with a motor-driven diaphragm and plunger-type chemical metering pump(s) to the appropriate application point(s). Although unusual, feeding sodium hypochlorite using a hydraulic injector or simple gravity flow is possible.

When calcium hypochlorite is used in a water treatment plant as a treatment process for continuous disinfection, it is mixed with water to form a dilute liquid chlorine solution and fed in the same manner as sodium hypochlorite. For spot disinfection, whether it be in a basin or pipe, calcium hypochlorite tablets are deposited in the appropriate location, water is added, and the tablets allowed to dissolve to form a liquid chlorine solution.

According to the 1995 *Community Water Systems Survey* (EPA, 1997a), most surface water and groundwater systems use chlorine for primary disinfection. Exhibit 2-2 provides the percentage of surface water systems that use chlorine. Exhibit 2-3 lists the percentage of groundwater systems that use chlorine. These exhibits also show that chlorine is the most widely used secondary disinfectant.

2.1.3 Advantages/Disadvantages

The following list presents selected advantages and disadvantages of using chlorine as a disinfection method for drinking water (Masschelein, 1992; Process Applications, Inc., 1992).

- Advantages of chlorination may include:
  - Chlorine oxidizes soluble iron, manganese, and sulfides.
  - Chlorine enhances color removal.
  - Chlorine controls taste and odor.
  - Chlorine may enhance coagulation and filtration of particulate contaminants.
  - Chlorine is an effective biocide.
  - The use of chlorine is the easiest and least expensive disinfection method, regardless of system size.
  - Chlorine is the most widely used disinfection method and, therefore, the most well known.
  - Chlorine is available as calcium and sodium hypochlorite that are more advantageous for smaller systems than chlorine gas because they are easier to use, are safer, and need less equipment compared to chlorine gas.
  - Chlorine provides a residual.

- Disadvantages of chlorination may include:
  - Chlorine may cause a deterioration in coagulation/filtration of dissolved organic substances.
  - Chlorine forms halogen-substituted byproducts.
  - Finished water could have taste and odor problems, depending on the water quality and dosage.

- Chlorine gas is a hazardous corrosive gas.
- Special leak containment and scrubber facilities could be required for chlorine gas.
- Typically, sodium and calcium hypochlorite are more expensive than chlorine gas.
- Sodium hypochlorite degrades over time and with exposure to light.
- Sodium hypochlorite is a corrosive chemical.
- Calcium hypochlorite must be stored in a cool, dry place because of its reaction with moisture and heat.
- A precipitate may form in a calcium hypochlorite solution because of impurities; therefore, an antiscalant chemical may be needed.
- Higher concentrations of hypochlorite solutions are unstable and will produce chlorate as a byproduct.
- Chlorine is less effective at high pH.
- Chlorine forms oxygenated byproducts that are biodegradable and which can enhance subsequent biological growth if a chlorine residual is not maintained.

Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

2.1.4 Dose Ranges

The guideline for a typical dose range for chlorine used by the U.S. Environmental Protection Agency (EPA) in review of the Public Water Systems' Initial Sampling Plans, which were required by the Information Collection Rule (ICR), was based on dosages provided in engineering design manuals and published articles. This range of doses, listed in Exhibit 2-4, includes both primary and secondary disinfection. Note that these ranges represent the extreme upper and lower dose values. Normal doses fall within these ranges.

Exhibit 2-4. Chlorine Dose Ranges

Chlorine Compound	Range of doses (mg/L)
Calcium hypochlorite	0.5 – 5
Sodium hypochlorite	0.2 – 2
Chlorine gas	1 – 16

Source: SAIC, 1996

2.1.5 Byproducts

Exhibit 2-5 lists identified disinfection byproducts associated with chlorine. Halogen-substituted organic byproducts are formed when natural organic matter (NOM) reacts with free chlorine or free bromine. Free chlorine is normally introduced into water directly as a primary or secondary disinfectant. Free bromine

results from the oxidation by chlorine of bromide ion in the water. Factors affecting the rate of formation and concentration of halogen-substituted disinfection byproducts (DBPs) include type and concentration of NOM, form of chlorine and dose, time, bromide ion concentration, pH, organic nitrogen concentration, and temperature. Organic nitrogen significantly influences the formation of nitrogen containing DBPs, including the haloacetonitriles, halopicrins, and cyanogen halides (Reckhow et al., 1990; Hoigne and Bader, 1988).

Exhibit 2-5. Disinfection Byproducts of Chlorine

Trihalomethanes	Chloroform	**Haloketones**	1,1-Dichloropropanone
	Bromodichloromethane		1,1,1-Trichloropropanone
	Dibromochloromethane	**Other Compounds**	Chlorophenols
	Bromoform		2-Chlorophenol
			2,4-Dichlorophenol
Haloacetic Acids	Monochloroacetic acid		2,4,6-Trichlorophenol
	Dichloroacetic acid		Chloropicrin
	Trichloroacetic acid		Chloral Hydrate
	Monobromoacetic acid		Cyanogen Chloride
	Dibromoacetic acid		N-Organochloramines
			MX*
Haloacetonitriles	Dichloroacetonitrile		
	Bromochloroacetonitrile		*3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
	Dibromoacetonitrile		
	Trichloroacetonitrile		
	Tribromoacetonitrile		

Source: Malcolm Pirnie, 1992; Richardson et al., in press

2.2 CHLORAMINES

Early researchers identified the disinfectant potential of chlorine-ammonia compounds (i.e., chloramines). The potential use of chloramines was considered after observing that when ammonia was present, although free available chlorine dissipated, disinfection still occurred. The subsequent disinfection was caused by inorganic chloramines.

Initially, chloramines were used for controlling taste and odor; however, chloramines were soon recognized as being more stable than free chlorine in the distribution system and, consequently, were found to be effective for controlling bacterial regrowth in the distribution system (Norton and LeChevallier, 1997). As a result, chloramines were used regularly during the 1930s and 1940s for disinfection. Because of an ammonia shortage during World War II, however, the popularity of chloramination declined. The recent concern over halogen-substituted organics (trihalomethane [THM] and haloacetic acid [HAA] formation) in water treatment and distribution systems increased interest in chloramines because they react differently

with humic and fenic acids than chlorine generally producing lower concentrations of DBPs (Symons et. al., 1998).

2.2.1 Description of Chemistry

Chloramines are formed by the reaction of ammonia with aqueous chlorine. In aqueous solutions, hypochlorous acid from the chlorine reacts with ammonia to form inorganic chloramines in a series of competing reactions. In these reactions, monochloramine (NH_2Cl), dichloramine ($NHCl_2$), or nitrogen trichloride (NCl_3) are formed. These competing reactions (and several others) are primarily dependent on pH and controlled to a large extent by the chlorine:ammonia nitrogen (Cl_2:N) ratio. Temperature and contact time also regulate this reaction. Monochloramine is predominately formed when the applied Cl_2:N ratio is less than 5:1 by weight. As the applied Cl_2:N ratio increases from 5:1 to 7.6:1, the breakpoint reaction occurs, thereby reducing the residual chloramine and ammonia nitrogen level to a minimum. Breakpoint chlorination results in the formation of nitrogen gas and nitrate. At Cl_2:N ratios above 7.6:1, free chlorine and nitrogen trichloride are present although being quite volatile the latter usually dissipates. To avoid breakpoint reactions, utilities normally maintain a Cl_2:N between 3:1 and 5:1 by weight. A ratio of 6:1 is actually optimum for disinfection because dichloramine predominates, but maintaining a stable operation at that point in the breakthrough curve is difficult. Therefore as mentioned above, a Cl_2:N ratio of 3:1 to 5:1 is typically accepted as optimal for chloramination.

2.2.2 Use and Distribution

Monochloramine can be formed by first adding ammonia and then chlorine, or concurrently adding both reactants. Ammonia is added first where the formation of objectionable taste and odor compounds caused by the reaction of chlorine and organic matter are a concern. Today, however, most drinking water systems add chlorine first and then ammonia, in conformance with the EPA Surface Water Treatment Rule disinfection requirements. Typically, the point of ammonia addition is selected to "quench" the free chlorine residual after a target contact time has been achieved based on optimizing disinfection versus minimizing DBP formation. Monochloramine is mainly used in water systems as a secondary disinfectant for maintaining a residual in the distribution system.

2.2.3 Advantages/Disadvantages

The following list highlights selected advantages and disadvantages of using chloramines as a disinfection method for drinking water (Masschelein, 1992).

- Advantages

  - Chloramines are not as reactive with organics as free chlorine in forming DBPs.
  - The monochloramine residual is more stable and longer lasting than free chlorine or chlorine dioxide, thereby providing better protection against bacterial regrowth in systems with large storage tanks and dead-end water mains.
  - Because chloramines do not tend to react with organic compounds, many systems will experience less incidence of taste and odor complaints when using chloramines.
  - Chloramines are inexpensive.
  - Chloramines are easy to make.

- Disadvantages

  - The disinfecting properties of chloramine are not as strong as other disinfectants, such as chlorine, ozone, and chlorine dioxide.
  - Chloramines cannot oxidize iron, manganese, and sulfides.
  - When using chloramine as the secondary disinfectant, it may be necessary to periodically convert to free chlorine for biofilm control in the water distribution system.
  - Excess ammonia in the distribution system may lead to nitrification problems, especially in dead ends and other locations with low disinfectant residual.
  - Monochloramine are less affective at high pH.
  - Dichloramines have treatment and operation problems.
  - Chloramines must be made on-site.

Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

2.2.4 Dose Ranges

The normal dose range for monochloramine is from 1.0 to 4.0 mg/L. The minimum dosage of monochloramine in the distribution system is typically 0.5 mg/L (Texas Natural Resource Conservation Commission, 1996). The range of ammonia doses, provided in Exhibit 2-6, includes doses for both primary and secondary disinfection.

Exhibit 2-6. Suggested Doses of Ammonia Compounds for Chloramines

Chemical	Dosage (mg/L)
Ammonium sulfate	0.1 – 3.0
Anhydrous ammonia	0.1 – 1.0
Ammonia hydroxide	0.1 – 3.0

Sources: Masschelein, 1992; SAIC, 1996

2.2.5 Byproducts

The effectiveness of chloramines in controlling DBP production depends upon a variety of factors, notably the chlorine to ammonia ratio, the point of addition of ammonia relative to that of chlorine, the extent of mixing, and pH.

Direct reactions between monochloramine and organic matter in water produce very few halogen substituted organic compounds, although some dichloroacetic acid can be formed, and cyanogen chloride formation is greater than with free chlorine (Jacangelo et al., 1989; Topodurti and Haas, 1991; Smith et al., 1993; Cowman and Singer, 1994; Symons et al., 1998). The inability to mix chlorine and ammonia instantaneously allows the free chlorine to react before the complete formation of chloramines. In addition, monochloramine slowly hydrolyzes to free chlorine in an aqueous solution. Therefore, halogen-substitution reactions occur even when pre-formed monochloramine is used (Rice and Gomez-Taylor, 1986). The closer the chlorine:ammonia ratio is to the breakpoint, the greater the formation of DBPs (Speed et al., 1987). As this chlorine:ammonia reaction takes place, the chloramination results in lower concentrations of numerous other halogen-substituted generated from free chlorine ((except in the cases of cyanogen chloride (Krasner et al., 1989; Jacangelo et al., 1989)). Increased concentrations of cyanogen chloride are observed when monochloramine is used as a secondary disinfectant instead of free chlorine.

The application of chloramines results in the formation of halogen-substituted organic material (i.e., TOX), although it occurs to a much lesser degree than from an equivalent dose of free chlorine. Little is known about the nature of these byproducts, except that they are more hydrophilic and larger in molecular size than the organic halides produced from free chlorine (Jensen et al., 1985; Singer 1992; Symons et al., 1998). Recent research has shown slow DBP formation when pre-formed chloramines were used in model compound experiments (Topudurti and Hass 1991; DeLaat et al., 1982).

2.3 CHLORINE DIOXIDE

Chlorine dioxide is a powerful oxidant originally used by industry as a bleaching agent and disinfectant. Chlorine dioxide was first used as a disinfectant for drinking water in 1944 at the Niagara Falls, New York, Water Treatment Plant. Currently, the major use of chlorine dioxide is as a pre-oxidant to control tastes and odors and to reduce THM formation in finished water (DeMers and Renner, 1992).

2.3.1 Description of Chemistry

Chlorine dioxide (ClO_2) is a neutral compound of chlorine in the +IV oxidation state. ClO_2 exists in a gaseous state at temperatures above 11–12°C. It is a relatively small, volatile and highly energetic molecule and is a free radical. It functions as a highly selective oxidant because of its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO_2^-) (Hoehn et al., 1996; Doerr, R.L. 1981). During drinking water treatment, chlorite is the predominant reaction byproduct, with 50–70 percent of the reacted chlorine dioxide being converted to chlorite and 30 percent to chlorate (ClO_3^-) or chloride (Cl^-) depending on secondary disinfectant.

Although chlorine dioxide can be produced from sodium chlorate ($NaClO_3$), most generators use sodium chlorite ($NaClO_2$) as the predecessor chemical. Efficiency, conversion, and yield are used to describe the generation of chlorine dioxide from sodium chlorite. These terms all relate to the purity of generated chlorine dioxide. The proportion of chlorine dioxide relative to other oxychlorine compounds, including chlorite, chlorate, or free chlorine, is important when chlorine dioxide is applied to the drinking water (Aieta and Berg, 1986). Although a significant amount of chlorite ion can appear in drinking water from application and subsequent reduction of chlorine dioxide, both unconverted precursor chlorite and over-oxidized chlorate ions can be constituent contaminants in generated solutions. EPA recommends that utilities limit the production of DBPs by maintaining high generator purity (i.e., more than 95-percent efficiency) and limiting excess chlorine to 5 percent of the applied dose of chlorine dioxide.

For most potable water applications, chlorine dioxide is generated from sodium chlorite. Two feed chemical combinations that generate chlorine dioxide yields in excess of 95 percent are (1) chlorine-sodium chlorite and (2) acid-sodium hypochlorite-sodium chlorite.

Chlorine Solution:Chlorite Solution. Chlorite ion (from dissolved sodium chlorite) will react in aqueous solution with chlorine or hypochlorous acid to form chlorine dioxide:

$$2ClO_2^- + HOCl + HCl \rightarrow 2ClO_{2(g)} + Cl^- + H_2O \qquad [1]$$

Thus, two moles of chlorite ions will theoretically react with one mole of chlorine (i.e., as hypochlorous acid) to produce two moles of chlorine dioxide. In order to fully utilize sodium chlorite solution, the more expensive of the two ingredients, excess chlorine is often used, which lowers the pH and drives the reaction further toward completion. The reaction is faster than the acid:chlorite solution method.

but much slower than the other commercial methods described in the following discussion. Chlorine dioxide production by this method is limited to about 1,000 pounds per day.

Acid:Chlorite Solution. Chlorine dioxide can be generated by acidification of sodium chlorite solution, and several stoichiometric reactions have been reported for such processes (Gordon et al., 1972). When chlorine dioxide is generated in this way, hydrochloric acid is generally preferred.

The stoichiometry expected for hydrochloric acid activation of sodium chlorite is:

$$5ClO_2^- + 4HCl \rightarrow 4ClO_2 + 5Cl^- + 2H_2O \qquad [2]$$

When catalyzed by the presence of chloride ion, acid activation of sodium chlorite has a maximum possible yield of 80 percent of the quantity of chlorine dioxide that could be produced from reaction of the same amount of sodium chlorite with chlorine (Pitochelli, 1995). The reaction is relatively slow, and production rates using this method are practically limited to about 25 to 30 pounds per day, due to the exothermic nature of the reactions.

Chlorine Gas:Chlorite Solution. Sodium chlorite solution can be "vaporized" and reacted under vacuum with molecular gaseous chlorine. This process uses concentrated reactants and is much more rapid than chlorine solution:chlorite solution methods (Pitochelli, 1995). If the chlorine and chlorite ion react stoichiometrically, the resulting pH is close to 7. Production rates are virtually unlimited, and some installed systems have reported producing more than 60,000 pounds per day.

$$2ClO_2^- + Cl_{2(g)} \rightarrow 2ClO_{2(g)} + 2Cl^- \qquad [3]$$

Chlorine Gas:Solid Chlorite. This method reacts dilute, humidified chlorine gas with specially processed solid sodium chlorite contained in sealed reactor cartridges:

$$2\ NaClO_{2(s)} + Cl_{2(g)} \rightarrow 2ClO_{2(g)} + 2NaCl_{(s)} \qquad [4]$$

The reaction is rapid and produces high-purity chlorine dioxide gas inherently free of chlorine and chlorate ions, because these ions will not carry into the gas phase. Use of multiple cartridges in series ensures an excess of the sodium chlorite; thus, all chlorine is reacted and the chlorine dioxide produced is chlorine free. Because the chlorine dioxide production rate is a function solely of the chlorine gas feed rate,

generators that use chlorine gas:solid chlorite technology are capable of effectively infinite turndown (i.e., the chlorine dioxide production rate can be adjusted without requiring recalibration between settings) (Pitochelli, 1995; Hoehn and Rosenblatt, 1996). The chlorine gas:chlorite solution method production capacities are limited to 2,000 pounds per day for practical reasons.

Besides the commercial processes discussed previously, other potential methods for generating chlorine dioxide include electrolysis of sodium chlorite solution (with or without the use of membranes to purify the chlorine dioxide product), irradiation of dilute sodium chlorite solution with UV light, and reduction of sodium chlorate with concentrated sulphuric acid and 50 percent hydrogen peroxide. (Sodium chlorate is neither an EPA nor Federal Insecticide, Fungicide, and Rodenticide Act-approved precursor for chlorine dioxide production for drinking water treatment.)

2.3.2 Use and Distribution

Chlorine dioxide is almost never used commercially as a gas because it cannot be safely compressed and shipped. For potable water treatment process, it is predominantly generated in aqueous solutions. Because of the volatile nature of the gas, chlorine dioxide works extremely well in plug flow reactors, such as pipe lines. It can be easily removed from dilute aqueous solution by aerated turbulence, such as in a rapid mix tank or aerated cascade. For post disinfection, chlorine dioxide can be added before clearwells or transfer pipelines.

Exhibit 2-2 shows that chlorine dioxide is most frequently used in surface water systems serving more than 10,000 persons. Today, an estimated 700 to 900 U.S. drinking water utilities use chlorine dioxide, largely to oxidize iron and manganese, control taste and odor, and lower THM levels (Hoehn, 1992). Some systems are looking to the higher disinfection efficacy of chlorine dioxide to assist in CT for *Cryptosporidium* control.

2.3.3 Advantages/Disadvantages

The following list highlights selected advantages and disadvantages of using chlorine dioxide as a disinfection method for drinking water (Masschelein, 1992; DeMers and Renner, Inc., 1992; Gallagher, et al., 1994).

- Advantages

  - Chlorine dioxide is more effective than chlorine and chloramines for inactivation of viruses, *Cryptosporidium*, and *Giardia*.
  - Chlorine dioxide oxidizes iron, manganese, and sulfides.
  - Chlorine dioxide may enhance the clarification process.
  - Taste and odors resulting from algae and decaying vegetation, as well as phenolic compounds, are controlled by chlorine dioxide.
  - Under proper generation conditions (i.e., no excess chlorine), halogen-substituted DBPs are not formed.
  - Chlorine dioxide is easy to generate.
  - Biocidal properties are not influenced by pH.
  - Chlorine dioxide provides residuals.

- Disadvantages

  - The chlorine dioxide process forms the specific byproducts chlorite and chlorate.
  - Generator inefficiency and optimization difficulty can cause excess chlorine to be fed at the application point, which can potentially form halogen-substituted DBPs.
  - Costs associated with training, sampling, and laboratory testing for chlorite and chlorate are high.
  - Equipment is typically rented, and the cost of the sodium chlorite is high.
  - Measuring a chlorine dioxide residual for determining disinfection credit is difficult.
  - Chlorine dioxide gas is explosive, so it must be generated onsite.
  - Chlorine dioxide decomposes in sunlight.
  - Chlorine dioxide must be made on-site.
  - Can lead to production of noxious odors in some systems.

Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

2.3.4 Dose Ranges

Before chlorine dioxide is selected for use as a primary disinfectant, an oxidant demand study must be completed. Ideally, this study should consider the seasonal variations in water quality, temperature, and application points. EPA recommends that the combined residuals of chlorine dioxide, chlorate, and chlorite not exceed 1.0 mg/L in finished water. This means that if the oxidant dosage is greater than about 1.4 mg/L, chlorine dioxide cannot be used as a disinfectant because the chlorite/chlorate ions byproduct would already be at the maximum level allowed. This range of doses, provided in Exhibit 2-7, includes both primary and secondary disinfection. Note that these ranges represent the extremes; normal doses fall within these ranges.

Exhibit 2-7. Observed Chlorine Dioxide Doses

Dose Range (mg/L)	Conditions	References
0.6 – 1.0	Finished water from lakes and streams	McGuire & Meadow, 1988
0.5 –1.5	Two utilities with odor complains	Hoehn, 1990
0.07 – 2.0	As reported: four utilities	Bolyard et al., 1993
0.5 – 2.0	Five utilities	Gallagher et al., 1994
2.0	Two treatment plants, ferrous chloride reduction study	Tarquin et al., 1995

Source: Masschelein 1992, SAIC 1996.

2.3.5 Byproducts

The application of chlorine dioxide to water results in oxidation/reduction reactions that form two inorganic DBPs in the treated drinking water: chlorite and chlorate (Rav Acha et al., 1984, Werdehoff and Singer, 1987). However, the application of chlorine-free chlorine dioxide does not form THMs and produces only a small amount of total organic halide (TOX) (Werdehoff and Singer, 1987) and other halogenated-substituted compounds at very low concentrations (Richardson et al., 1998). Chlorite and chlorate frequently are found as contaminants in chlorine dioxide feed streams, and chlorite is formed as a byproduct from disinfection with chlorine dioxide (Griese et al., 1991). However, chlorine dioxide does not generate bromine-substituted byproducts to the same extent as ozone in bromide-containing waters. Two principal sources of chlorite occurs in finished drinking water:

- Unreacted chlorite during the chlorine dioxide generation process
- Redux formation upon application of chlorine dioxide to water.

Incomplete reaction or non-stoichiometric addition of the sodium chlorite and chlorine reactants can result in unreacted chlorite or more likely chlorate in the chlorine dioxide feed stream. Upon application to water, chlorine dioxide is fairly unstable and rapidly dissociates into chlorite and chlorate at pH above 10. This dissociation is reversible with chlorite converting back to chlorine dioxide in the presence of free chlorine, but only to a limited extent where residuals are greater than one percent. Chlorite ion is generally the primary product of chlorine dioxide reduction. The distribution of chlorite and chlorate is influenced by pH and sunlight. The efficiency of the chlorine dioxide generator and the decay of chlorine dioxide and free available chlorine residual disinfectant concentrations also influence these distributions.

The quantity of chlorate produced during the chlorine dioxide generation process is greater with excess chlorine addition. Likewise, low pH can increase the quantity of chlorate during the chlorine dioxide generation process. The predominant source of chlorate ion in finished water: however, results from the oxidation of chlorite (from the applied chlorine dioxide) by free available chlorine used as a final distribution disinfectant (Gallagher et al., 1994). Consequently, the chlorate concentrations are expected to increase with increasing contact time in water containing chlorite and chlorine. Once formed, chlorate is stable in finished drinking water. Because chlorine dioxide does not hydrolyze in water, it exists as a dissolved gas as long as the pH of the water ranges from 2 through 10. In strongly alkaline solutions (pH greater than 9 or 10), however, formation rates of chlorite and chlorate increase with increasing concentrations of chlorine dioxide.

2.4 OZONATION

Ozone was first used for drinking water treatment in 1893 in the Netherlands. While used frequently in Europe for disinfecting drinking water, ozonation was slow to transfer to the United States. In 1991, approximately 40 water treatment plants serving more than 10,000 people in the United States used ozone (Langlais et al., 1991). This number has grown to 201 in 1997 (Rice and Dimitrou, 1997). Most of these facilities are small: 90 plants treat below 1 mgd and only 6 exceed 100 mgd, as of May 1997.

Ozone is used in water treatment for disinfection and oxidation. Early application of ozone was primarily for non-disinfection purposes such as color removal or taste and odor control. Since implementation of the Surface Water Treatment Rule and in anticipation of the DBP and ESTWR rules, however, ozone usage for disinfection has increased. Ozone is a powerful oxidant, second only to the hydroxyl free radical among chemicals typically used in water treatment. Therefore, it is capable of oxidizing many organic and inorganic compounds in water.

2.4.1 Description of Chemistry

Ozone exists as a gas at room temperature. The gas is colorless with a pungent odor readily detectable at concentrations as low as 0.01 to 0.05 ppm, which is below concentrations that will cause the health problem. Ozone gas is highly corrosive and toxic.

Basic chemistry research (e.g., Hoigne and Bader, 1983a; Hoigne and Bader, 1983b; Glaze, 1987) has shown that ozone decomposes spontaneously in water treatment by a complex mechanism involving the generation of hydroxyl radicals. The hydroxyl radicals are among the most reactive oxidizing agents in water, with reaction rate constants for many compounds, as much as 10^9 times faster than that of ozone itself.

Ozone reacts in two modes in aqueous solution: (1) direct oxidation of compounds by aqueous ozone ($O_{3,aq}$) and (2) oxidation of compounds by hydroxyl radicals produced during the spontaneous decomposition of ozone (Hoigne and Bader, 1977).

2.4.2 Use and Distribution

Ozone is used in drinking water treatment for various purposes:

- Disinfection
- Inorganic pollutant oxidation, including iron, manganese, and sulfide
- Organic micropollutant oxidation, including taste and odor compounds, phenolic pollutants, and pesticides
- Organic macropollutant oxidation, including color removal, increasing the biodegradability of organic compounds, THM and TOX precursor control, and destruction of chlorine demand
- Improvement of coagulation and filtration.

Ozone is an unstable molecule; therefore, it must be generated at the point of application. It is generally formed by combining an oxygen atom with an oxygen molecule (O_2). This reaction is endothermic and requires a considerable input of energy. Ozone can be produced several ways, although one method, corona discharge, predominates in the water industry. Ozone can also be produced by irradiating an oxygen-containing gas with electrolytic reactions, ultraviolet light, or high-energy radiation. These are all processes that produce free oxygen radicals from electron or photon energy input.

Corona discharge, also known as silent electrical discharge, consists of passing an oxygen-containing gas through two electrodes separated by a dielectric and an air gap. A voltage is applied to the electrodes, causing an electron flow across the air gap. These electrons provide the energy to dissociate the oxygen molecules, leading to the formation of ozone.

For most applications, ozone is either fed to the source water or after some type of clarification and clarification process. Turbidity and ozone demand (the amount of ozone required for all oxidation requirements of the water) provide basic guidance on how to use ozone in the treatment process. By moving the ozonation process further downstream, the ozone demand and production of oxidation byproducts are reduced. The advantage of placing ozone ahead of filtration is that biodegradable organics produced during

ozonation can be removed in the filters if they are operated biologically. Biological filtration is often a necessity for waters with high levels of NOM.

2.4.3 Advantages/Disadvantages

The following list highlights selected advantages and disadvantages of using ozone as a disinfection method for drinking water (Masschelien, 1992).

- Advantages
  - Ozone is more effective than chlorine, chloramines, and chlorine dioxide for inactivation of viruses, *Cryptosporidium*, and *Giardia*.
  - Ozone oxidizes iron, manganese, and sulfides.
  - Ozone can sometimes enhance the clarification process and turbidity removal.
  - Ozone controls color, taste, and odors.
  - One of the most efficient chemical disinfectants, ozone requires a very short contact time.
  - In the absence of bromide, halogen-substituted DBPs are not formed.
  - Upon decomposition, the only residual is dissolved oxygen.
  - Biocidal actively not influenced by pH.
- Disadvantages
  - DBPs are formed, particularly bromate and bromine-substituted DBPs, in the presence of bromide, aldehydes, ketones, etc.
  - The initial cost of ozonation equipment is high.
  - The generation of ozone requires high energy and must be generated on-site.
  - Ozone is highly corrosive and toxic.
  - Biologically activated filters are needed for removing assimilable organic carbon and biodegradable DBPs.
  - Ozone decays rapidly at high pH and warm temperatures.
  - Ozone provides no residual.
  - Ozone requires higher level of maintenance and operator skill.

Because of the wide variation of system size, water quality, and dosages applied, some of these advantages and disadvantages may not apply to a particular system.

2.4.4 Dose Ranges

The typical dose range guideline for ozone that was used in EPA's review of the Public Water Systems' Initial Sampling Plans that were required by the ICR was based on dosages provided in engineering design manuals and published articles. This range of doses, provided in Exhibit 2-8, is for primary disinfection only. Note that these ranges represent extremes; and normal values are in between these values.

Exhibit 2-8. Suggested Doses for Ozone

Water Source	Dosage (mg/L)
Groundwater	1.0 to 3.0
Surface Water	1.0 to 5.0 (normal) 1.0 to 10.0 (extreme circumstances)

Sources: SAIC, 1996, Masschelein, 1992

2.4.5 Byproducts

A variety of organic and inorganic byproducts have been observed following ozonation of water. Ozone itself does not form halogen-substituted DBPs when participating in oxidation/reduction reactions with natural organic matter. If bromide is present in the source water, however, bromine-substituted DBPs can be formed. The primary factors affecting the speciation and concentrations of bromine-substituted byproducts are pH, and the ozone-to-bromide and total organic carbon-to-bromide ratios (Singer, 1992).

The principal benefit of using ozone for controlling THM formation is that ozone allows free chlorine to be applied later in the treatment process after some of the precursors have been removed and at lower doses, thereby reducing DBP formation potential. However, application of a secondary disinfectant following ozonation requires special consideration for potential interaction between disinfectants. For example, chloral hydrate formation has been observed to increase when using chlorine as a secondary disinfectant after ozone (McKnight and Reckhow, 1992; Logsdon et al., 1992). One byproduct of ozonation, acetaldehyde, is a known precursor for chloral hydrate, a byproduct of chlorination. Enhancement of chloral hydrate formation has not been observed when monochloramine is applied as the secondary disinfectant or if biologically active filtration is used following ozonation and prior to chlorination (Singer, 1992). Chloropicrin formation from free chlorine appears to be enhanced by pre-ozonation (Hoigne and Bader, 1988).

Oxidation byproducts, including aldehydes, ketones, aldo-acids, ketoacids, and AOC will be formed upon ozonation of water. The primary aldehydes that have been measured are formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal (Glaze et al., 1991). Total aldehyde concentration in drinking water disinfected with ozone ranges from less than 5 to 300 µg/L, depending on the TOC concentration and the applied ozone to organic carbon ratio (Van Hoof et al., 1985; Yamada and Somiya, 1989; Glaze et al., 1989a; Krasner et al., 1989; Glaze et al., 1991; LeLacheur et al., 1991). Aldehydes with higher molecular weights have also

been reported (Glaze et al., 1989b). Insufficient data exist to determine the health impacts associated with the ingestion of aldehydes in drinking water.

Ozonation of a source water containing bromide can produce hydrobromic acid and, thus, bromine-substituted byproducts, the brominated analogues of the chlorinated DBPs. These bromine-substituted byproducts include bromine-substituted, bromoform, the bromine-substituted acetic acids and acetonitriles, aldo-acids, bromopicrin, and cyanogen bromide. An ozone dose of 2 mg/L produced 53 µg/L of bromoform and 17 µg/L of dibromoacetic acid in a water containing 2 mg/L of bromide ion (McGuire et al., 1990). Ozonation of the same water spiked with 2 mg/L bromide ion showed cyanogen bromide formation of 10 µg/L (McGuire et al., 1990). Furthermore, ozone can react with the hypobromite ion to form bromate (Siddiqui and Amy, 1993; Krasner et al., 1993a; Amy et al., 1997). Bromate formation is affected by NOM, pH, bromide ion concentrations, inorganic carbon, and ozone dose. NOM exerts a high demand on ozone in competition with molecular ozone. This competition for molecular ozone is affected by the NOM composition as well as concentrations. Additionally, decreasing pH (8.5 – 6.5) generally decreased bromate formation. Higher bromide ion concentrations and high inorganic carbon concentrations were noted with increased bromate ion formations (Amy et al., 1997). The amount of bromide incorporated into the measured DBPs accounts for only one-third of the total source water bromide concentration. This indicates that other bromine-substituted DBPs exist that are not yet identified (McGuire et al., 1989; AWWARF, 1992).

3. OCCURRENCE OF DBP PRECURSORS AND DISINFECTANTS

3.1 SUMMARY OF PRECURSOR OCCURRENCE DATA: TOTAL ORGANIC CARBON AND BROMIDE ION

The 1994 DBP proposed rule provided data summarizing the occurrence of disinfectants, disinfection byproducts (DBPs), and DBP precursors. Most of this information came from the 1992 occurrence document. The 1992 occurrence document did not, however, address precursor occurrence data (EPA, 1992a). The 1994 proposed rule provided the only source of national occurrence data for total organic carbon (TOC) and bromide ion. Precursor information discussed in the preamble is summarized below and presented in Exhibit 3-1.

The majority of recent studies addressing DBP occurrence in the United States measured TOC and bromide. These precursor data are included below. Descriptions of the major studies are located in Section 4.1.

3.1.1 Total Organic Carbon Occurrence

The TOC level in source water is generally a good indication of the amount of DBP precursors in the water (Singer and Chang, 1989). In the Water Industry Database (WIDB), 157 utilities provided TOC data in 1991. Of the utilities reporting on groundwater systems, 57 of those facilities identified TOC values ranging from below the detection limit (BDL = 0.05 mg/L to 15 mg/L). For these 57 groundwater systems, the 50th and 75th percentiles were 0.84 and 1.9 mg/L.

TOC levels reported by 100 surface water systems ranged from BDL to 30 mg/L. For these waters, the 25th, 50th, and 75th percentiles were 2.6, 4.0, and 6.0 mg/L, respectively. The WIDB also identified the number of utilities that did not have TOC data at the time. For surface water, 897 utilities did not provide TOC values. Among the groundwater utilities, 854 did not provide TOC data. Exhibits 3-2 and 3-3 summarize the data presented in Tables VI-1 and VI-2 of the proposed rule (56 FR 38716, 38721, July 29, 1994).

The Groundwater Supply Survey (GWSS) reported groundwater TOC occurrence data, by EPA Region, for 945 utilities during 1980-1981. Sixty-nine percent of these utilities chlorinated their water, while 31 percent did not. When the TOC data were combined to present values for all groundwater systems, the 25th, 50th, and 75th percentiles were 0.3, 0.6, and 1.4 mg/L TOC, respectively. Tables VI-3 A, B, and C from the proposed rule presented these groundwater data, which are reproduced in Exhibit 3-3 (56 FR 38721, July 29, 1994).

Exhibit 3-1. Disinfection Byproduct Precursor and Disinfectant Occurrence

Survey (Year)	Location	Sample Information (Number of Systems)	Concentration of Precursors in Source Water (mg/L)			Notes
			Range[1]	Mean	Median	
Total Organic Carbon						
WIDB (1989–1990)	157 utilities nationwide	GW systems (57) SW systems (100)	BDL – 15 BDL – 30	0.84 4.0	– –	75th percentile = 1.9 90th percentile = 6.0
GWSS (1980–1981) Westrick et al. (1983)	945 GW systems	GW using Cl_2 (654) GW not using Cl_2 (291)	Max. 14 Max. 18	0.7 0.5	– –	75th percentile = 1.4[2] 90th percentile = 2.9
AWWA (1997)	198 ICR utilities, 50 states; Sept., Oct., Nov. 1996	SW > 100,000 (888 samples, 329 plants) GW > 50,000 (251 samples, 110 plants)	BDL – 22.7 BDL – 13.0	3.29 1.35	2.77 0.76	Std. Dev = 2.2 Std. Dev. = 2.3
AWWSCo (1991)	19 water utilities	Source water	0.44 – 8.7	4.4	3.9	75th percentile = 7.3
Arora et al. (1994)	2 sampling phases, 1991 20 water systems	Source Waters: River (8) Reservoir (12)	 1.3–8.7 0.4–7.8	 5.4 3.4	 – –	
Utah Pre-ICR Data (1996)	7 SW > 100,000, 1994–1996	Source water	0.37 – 13.0	2.16	1.93	75th percentile = 2.33 90th percentile = 3.10
Bromide Ion						
Glaze et al. (1993)	AWWA study – 7 full-scale water systems	9 Source water samples taken (10)	BDL – 0.28	–	–	DL = 0.01
EPA/AMMWA/CDHS (1988–1989) Krasner et al. (1989)	35 utilities nationwide	Groundwater/surface water	BDL – 3.0	–	0.1	
Amy et al. (1994) Westerhoff et al. (1994)	101 utilities nationwide, October 1991–April 1993	Source Waters: Lakes (34) Rivers (29) Groundwater (36)	 0.002 – 0.322 0.004 – 0.426 0.002 – 2.69	 0.038 0.101 0.168	 0.023 0.063 0.062	Std. Dev. 0.054 0.115 0.428
AWWSCo (1991)	19 water utilities, 10 states	Source water Winter 1991 Summer 1991	 BDL – 0.10 BDL – 0.37	 0.037 0.065	 0.03 0.04	
Utah Pre-ICR Data (1996)	7 SW utilities > 100,000; 1994–1996	Quarterly samples – source waters	BDL – 0.040	0.010	BDL	75th percentile = 0.020 90th percentile = 0.030

Exhibit 3-1. Disinfection Byproduct Precursor and Disinfectant Occurrence (Continued)

Survey (Year)	Location	Sample Information (Number of Systems)	Concentration of Precursors in Source Water (mg/L)			Notes
			Range[1]	Mean	Median	
Chlorine						
WIDB (1989–1990)	Large utilities nationwide	Residual chlorine at average customer 228 SW plants & 215 GW plants	BDL – 3.5 BDL – 5	0.94 0 88	0.80 0 33	
NORS (1975)	80 cities nationwide	Finished water at treatment plant SW (64), GW (16)	BDL – 2.8	–		Typical dosage 0.6 mg/L
AWWARF (1987) McGuire & Meadow (1988)	National survey	Finished water from: Lakes Flowing streams Groundwater Mixed-supplies	–	–	–	Dose range: 0.1–>20 mg/L 2.2[3] 2.3[3] 1 2[3] 1.0[3]
EPA (1992b) (1987-1989)	Disinfection byproducts field studies October 1987 – March 1989	Free chlorine sampled in distribution system (45)	BDL – 3.2	0.7	0.5	
AWWA Disinfection Survey (1991)	283 utilities nationwide	Finished water entering the distribution system	0.07 – 5.0	1.10		90th percentile = 2 8
EPA/AMMWA/CDHS (1988–1989) Krasner et al. (1989)	35 water utilities nationwide	Samples from clearwell effluent in four quarters (17)	0.3 – 5.2	1.5	1.0	
Chloramine						
WIDB (1989–1990)	140 utilities nationwide	Distribution system average chloramine	0.3 – 4.8	–	1.6	90th percentile = 3 0
AWWARF (1987) McGuire & Meadow (1988)	National survey	Finished water from: Lakes (~30) Flowing streams (34)	– –	– –	– –	Dosage: 1.5 mg/L. 2.7mg/L
EPA (1992b) (1987-1989)	Disinfection byproducts field studies	At the plant (11) Distribution system (8)	1.2 – 3 6 0.1 – 3.3	2.1 1 4	1 5 1 1	
EPA/AMMWA/CDHS (1988–1989) Krasner et al. (1989)	35 water utilities nationwide	Samples from clearwell effluent, four quarters (13)	0.9 – 5.5	2.3	1 8	

Exhibit 3-1. Disinfection Byproduct Precursor and Disinfectant Occurrence (Continued)

Survey (Year)	Location	Sample Information (Number of Systems)	Concentration of Precursors in Source Water (mg/L)			Notes
			Range[1]	Mean	Median	
Chlorine Dioxide						
AWWARF (1987) McGuire & Meadow (1988)	Nationwide plants using ClO_2	~20 surface plants > 25,000 (lakes & streams)	–	–	–	Typical ClO_2 dosage: 0.6 – 1.0 mg/L
Gallagher et al. (1994)						ClO_2 dosage:
	Charleston, WV	Aug. 12–14, 1990 (41)	0.02[4] – 0.78	0.03	BDL	2.0[5] mg/L
	New Castle, PA	July 25–28, 1990 (33)	0.11 – 0.37	0.22	0.20	–
	Gulf Coast Water Authority	(111)	–	0.21	0.15	0.5 – 2.0 mg/L
Hoehn et al. (1990)	Utility in Charleston, WV	Below filter at plant (2)	BDL – 0.01	0.01	–	ClO_2 dosage:
		Clearwell at plant (1)	0.12	0.12	–	2.0 mg/L
		Customer D (odor present)(2)	0.05 – 0.12	0.09	–	
		Customer E (no odor(1)	0.12	0.12	–	

[1] Overall mean range.
[2] Overall percentile for all systems.
[3] Dosage.
[4] Added only to half the plant, and the chlorine dioxide was monitored only in water from that treatment train.
[5] Below MDL.

Abbreviations

AMWA	Association of Metropolitan Water Agencies	GW	Ground Water
AWWA	American Water Works Association	GWSS	Ground Water Supply Survey
AWWARF	American Water Works Association Research Foundation	MDL	Method Detection Limit
AWWSCo	American Water Works Service Company	ND	Not Detected
BDL	Below Detection Limit	NORS	National Organics Reconnaissance Survey
CDHS	California Department of Health Services	SW	Surface Water
DL	Detection Limit	TSD	Technical Services Division
DS	Distribution System	WIDB	Water Industry Data Base

Exhibit 3-2. TOC Occurrence Data from the WIDB in the 1994 Proposed Rule

Source	Number of Utilities	Minimum (mg/L)	Maximum (mg/L)	Percentile (mg/L)		
				25th	50th	75th
Groundwater	57	BDL	15.0	BDL	0.84	1.88
Surface Water	100	BDL	30.0	2.55	4.0	5.95

Source: 59 FR 38716, July 29, 1994

Exhibit 3-3. Groundwater TOC Levels from the GWSS Reported in the 1994 Proposed Rule

Source	Number of Utilities	Maximum (mg/L)	Percentile (mg/L)			
			25th	50th	75th	90th
Groundwater – Chlorine	654	14	0.3	0.7	1.7	3.3
Groundwater – No Chlorine	291	18	0.3	0.5	1.1	2.2
All Utilities	945	18	0.3	0.6	1.4	2.9

Source: 59 FR 38721, July 29, 1994

In January 1997, a survey of 298 Information Collection Rule (ICR) utilities was conducted by McGuire Environmental Consultants for the American Water Works Association (AWWA) Survey. One of the objectives was to gather TOC data for use in the Microbial Disinfection Byproducts (M-DBP) stakeholder process to develop the final Stage 1 DBP rule. Data were requested from surface water systems serving more than 100,000 people and groundwater systems serving more than 50,000 people in 50 states. Two hundred seventy-five utilities provided three months of TOC data from September, October, and November 1996. Exhibit 3-4 presents results of the statistical analyses, grouped by groundwater (110 treatment plants) and surface water (329 treatment plants) sources (AWWA, 1997).

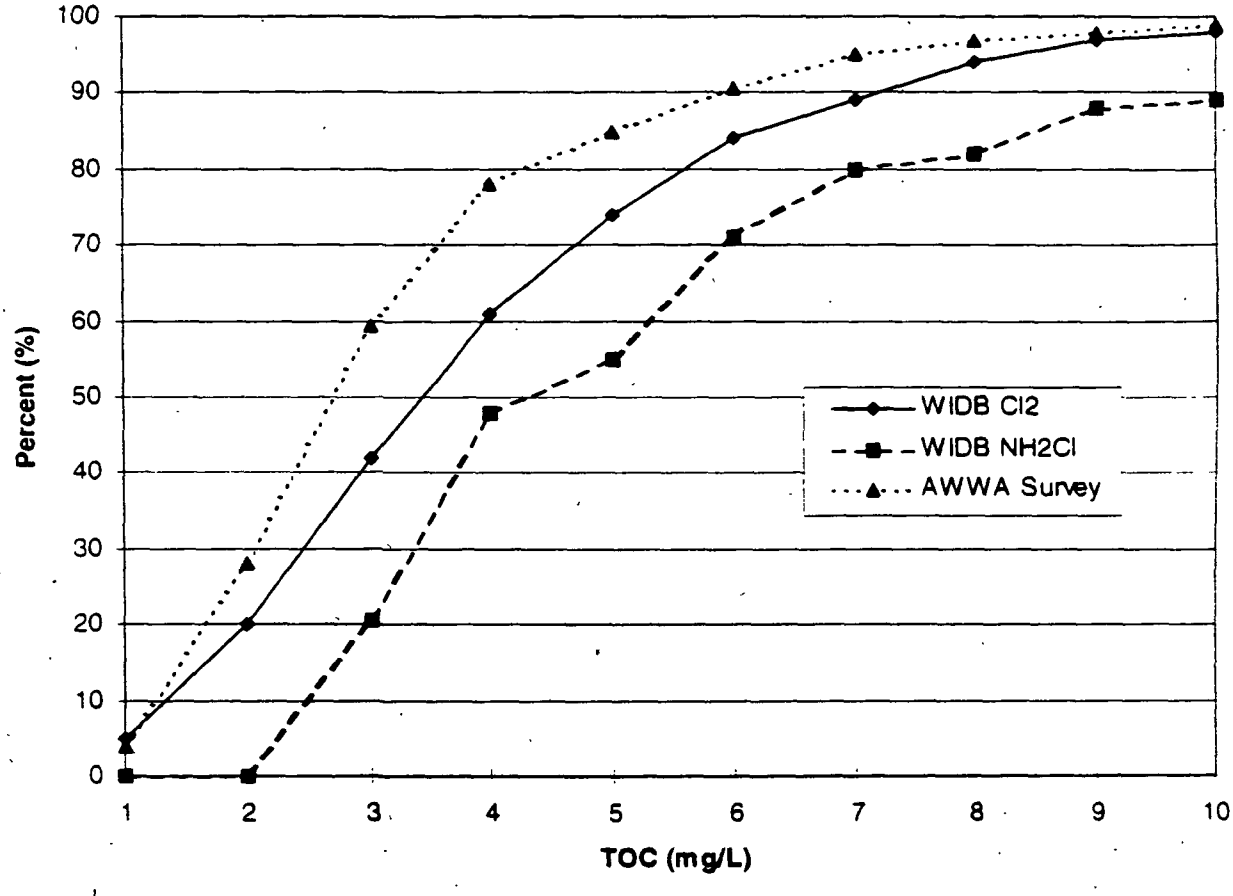
Exhibit 3-4. TOC in ICR Groundwater and Surface Water Plants: September–November 1996

Source Water	Number of Samples	Range (mg/L)	Mean (mg/L)	Median (mg/L)	Standard Deviation
Groundwater (110 plants)	251	0 – 12.9	1.35	0.76	2.312
Surface Water (329 plants)	888	0 – 22.7	3.29	2.77	2.197

Source: AWWA, 1997

Exhibits 3-5 and 3-6 compare the TOC data from the AWWA survey to data used in the Stage 1 DBP proposal (i.e., the WIDB and the GWSS). Groundwater TOC data from the AWWA survey are consistent with the GWSS. However, the TOC levels in surface waters are significantly lower than those in the 1992 WIDB data. The AWWA survey samples were collected in September, October, and November, while the WIDB samples were collected at different times over several years. A more accurate estimate of the national TOC occurrence will be available when one year of ICR data are collected.

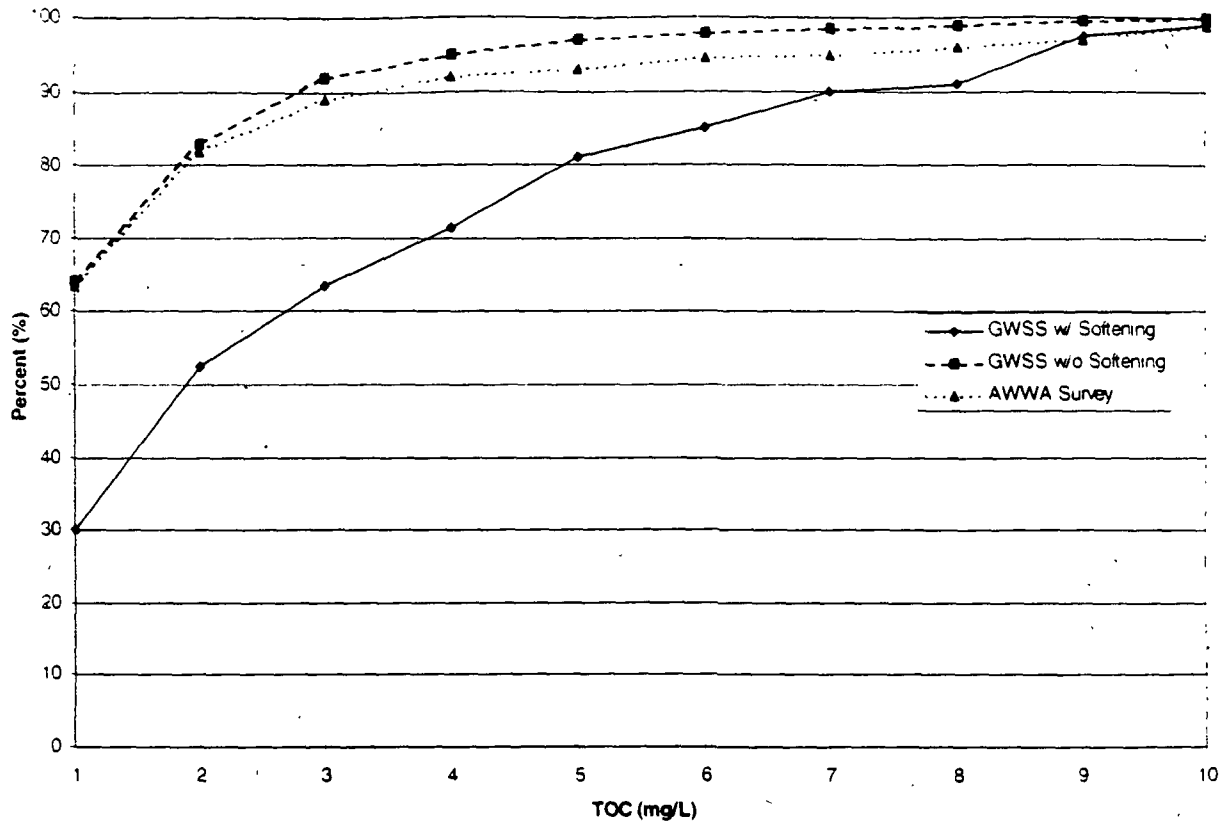
Exhibit 3-5. Comparison of AWWA Survey TOC Data with WIDB Data[1]



[1] Source Water Data

In 1989, the American Water Works Service Company (AWWSCo) initiated a project to evaluate precursor concentrations and the occurrence and formation of DBPs at approximately 20 of their 100 water systems, the majority of which have surface water treatment plants. The systems are located in 10 states, nine of which are located east of the Mississippi River. This project examined fewer systems in more detail than did the project described in section 4.1 that monitored 90 systems.

Exhibit 3-6. Comparison of AWWA Survey TOC Data with GWSS Data[1]



[1] Source Water Data

The data set used from the AWWSCo report was aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. The samples were collected in three phases: for Phase I during fall 1989 from 16 water treatment facilities, for Phase II during winter 1991 from 19 treatment facilities, and for Phase III from 21 facilities during summer 1991.

Samples from source waters (mostly surface waters), were analyzed for TOC concentrations in the fall of 1989, winter of 1991, and the summer of 1991 to observe seasonal differences. For the 19 source waters averaged over the winter and summer of 1991, the TOC concentrations ranged from 0.44 to 8.7 and averaged 4.4 mg/L TOC. The annual median was 3.9 and the 75th percentile was 7.3 mg/L TOC. Exhibit 3-1 summarizes these statistics (Arora et al., 1994).

State Data

Data provided from a Pre-ICR survey from the state of Utah were aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. Samples were taken from large

surface water systems (seven plants) serving more than 100,000 persons. Each of the seven treatment plants was sampled at four to six times between October 1994 and September 1996.

The TOC and bromide ion concentrations results from the source water samples were analyzed using all data points reported. Individual data points reporting less than the detection limit were converted to zeros and included in the analyses. Exhibit 3-7 combines the means, medians, and ranges and percentile concentrations of TOC and bromide ion.

Exhibit 3-7. Pre-ICR Data from the State of Utah (1994–1996)

Compound	Mean (mg/L)	Range (mg/L)	Percentile (mg/L)			
			25th	50th	75th	90th
TOC	2.16	0.27 – 13.0	1.30	1.93	2.33	3.10
Bromide ion	0.101	BDL – 0.04	BDL	BDL	0.03	0.03

Source: Pre-ICR data, 1996

3.1.2 Bromide Ion Occurrence

Bromide ion occurs in both groundwater and surface waters in the United States. It is a concern in both chlorinated and ozonated drinking water supplies because it affects the formation of DBPs in finished water. In ozonated water, bromate ion can be formed when waters containing sufficient levels of bromide ion are treated (Krasner et al., 1993a). Upon chlorination of waters containing bromide, bromide can substitute for chlorine and react with organic material to form such organic DBPs as bromine-substituted THMs or HAAs, depending on pH and other water quality characteristics (Glaze, et. al., 1993; Symons et al., 1993).

Krasner et. al. (1989) reported bromide ion levels in the 35 utility nationwide DBP study. Concentrations (groundwater and surface water) ranged from less than 0.1 to 3.0 mg/L bromide ion, with a median of 0.1 mg/L bromide ion. High levels may have been caused by saltwater intrusion or connate waters. Exhibit 3-1, presented previously, provides these results.

In a University of Colorado nationwide study of bromide ion occurrence, source water samples from 101 drinking water utilities across the United States were collected from October 1991 to April 1993 and

analyzed for bromide ion (Amy et al., 1994, Westerhoff et al., 1994). Except for 10 utilities known to have bromide ion-related problems, the utilities were randomly selected from the WIDB to obtain geographical and source type diversity. Exhibit 3-1, presented previously, provides these results.

The population-weighted averages for bromide ion concentrations for the randomly chosen large utilities and randomly chosen small utilities were 0.078 and 0.006 mg/L, respectively. Lake and reservoir sources were generally lower in concentration than rivers and groundwater. The 10th and 90th percentile distribution values were 0.0055 and 0.102 mg/L, respectively, for bromide ion. The authors of the University of Colorado Study suggested that connate seawater may occur ubiquitously and affect the distribution of bromide ion in drinking water sources.

Seasonal variations in bromide concentrations were minimal. The concentration range across the groundwater samples was higher, however, than across the samples from lakes and rivers, as shown in Exhibit 3-8. When the data included the targeted samples (average of 0.210 mg/L), the overall average increased to about 0.100 mg/L. Although the authors suggested that the values excluding the targeted facilities were probably more representative of random sampling these data were not available (Amy et al. 1994).

Exhibit 3-8. Bromide Ion Occurrence by Source: 101 Utility Nationwide Study

Statistical Parameter	Lakes	Rivers	Groundwater
Number of Samples	34	29	36
Average (mg/L)	0.038	0.101	0.168
Median (mg/L)	0.023	0.063	0.062
Range (mg/L)	0.002 – 0.322	0.004 – 0.426	0.002 – 2.690
Standard Deviation (mg/L)	0.054	0.115	0.428

Source. Amy et al., 1994; Westerhoff et al., 1994

The AWWSCo project also characterizes bromide ion occurrence as shown in Exhibit 3-1. This project examined fewer systems in more detail than did the project described in Section 4.1 which monitored 90 systems. Samples for bromide were collected from source waters (mostly surface waters) throughout the treatment train and in the distribution system to observe seasonal differences. These samples were collected during fall 1989, winter 1991, and summer 1991. For the 19 source waters sampled in both winter and summer 1991, the mean bromide concentrations were 0.037 and 0.065 mg/L, respectively. The winter samples ranged from BDL to 0.10 mg/L bromide, while the summer samples ranged from BDL to 0.37 mg/L

bromide. The median of the winter samples was 0.03 mg/L and the median of the summer samples was 0.04 mg/L.

Sample results for seven full-scale water systems across the country were discussed in an AWWA report examining drinking water ozonation treatment plants. Glaze et al., 1993 reported. A total of nine samples were taken from two plants sampled on two separate occasions. Samples of source water were collected and analyzed for bromide ion. The analytical method used was ion chromatography, which had a detection level of 0.01 mg/L bromide ion. Exhibit 3-9 presents the results of this effort.

Exhibit 3-9. Bromide Ion and TOC Occurrence in Source Water for Ozone Plants

Plant/Source	State/Province	Date Sampled	Bromide Ion (mg/L)	TOC (mg/L)
Rocky Mount/Tar River	North Carolina	5/26/90	0.04	5.76
Palm Beach Pilot Plant/GW	Florida	7/30/90	0.19	11.55
Belle Glade/Lake Okeechobee	Florida	7/31/90	0.24	25.9
Haworth/Oradall Reservoir	New Jersey	8/19/91	0.06	3.89
Sainte-Rose	Québec	2/19/91	BDL	6.11
N. Bay Regional/ N. Bay Aqueduct	California	10/2/91	0.05	2.94
Los Angeles/LA Aqueduct	California	7/23/90	0.28	2.56
Los Angeles/LA Aqueduct	California	9/10/91	0.22	3.2
El Sobrante/San Pablo Reservoir	California	10/15/91	0.02	2.82
Bull Run	Oregon	1/29/91	BDL	11.0

Source: Glaze et al., 1993

Data provided from a Pre-ICR survey from the state of Utah were aggregated by sample location to provide a range of statistics for precursors. Samples were taken from seven large surface water systems serving more than 100,000 persons. Each of the treatment plants was sampled at four to six times between October 1994 and September 1996.

The TOC and bromide ion concentration results from the source water samples were analyzed using all data points reported. Individual data points reporting less than the detection limit were converted to zero and included in the analyses. The means, medians, ranges, and percentile concentrations of TOC and bromide ion are shown in Exhibit 3-1, presented previously.

3.2 DISINFECTANTS

3.2.1 Chlorine

Chlorine hydrolyzes in water to form hypochlorite and hypochlorous acid. Chlorine and hypochlorites are used to disinfect drinking water, sewage and wastewater, and swimming pools. They have also been used for general sanitation and control of bacterial odors in the food industry. In addition, chlorine is used as a reagent in synthetic chemistry and in manufacturing chlorinated lime (a fabric bleach), detinning and dezincing iron, and producing synthetic rubber and plastics. Much of the available information comes from the addition and oxidation reactions with inorganic and organic compounds known to occur in aqueous solutions. Such factors as reactant concentrations, pH, temperature, salinity, and sunlight influence these reactions (Stevens and Symons, 1977; Merck Index, 1989; Johnson and Jensen, 1986; White, 1986).

In the disinfection treatment of drinking water, chlorine is added to water as chlorine gas (Cl_2) or as calcium or sodium hypochlorite. In water, the chlorine gas hydrolyzes to hypochlorous acid and hypochlorite ion and is measured as free chlorine residual. Maintenance of a free chlorine residual throughout the distribution system is important as an indicator for external contamination indicated by an absence of a residual and for continual bacteria kill. Currently, maximum chlorine dosage is limited by taste and odor constraints and, indirectly, by regulations on total trihalomethanes (TTHMs). Additionally, the implementation of the Surface Water Treatment Rule (SWTR) will increase the number of systems using chlorination and the degree of chlorine dosage due to contact time requirements.

The WIDB contains results from a survey conducted in 1989-90 of approximately 600 drinking water systems serving more than 50,000 people in the United States. Estimates, based on data from the WIDB, are that 51 percent of the surface water systems and 77 percent of the groundwater systems in the United States that serve more than 10,000 people currently use chlorine for disinfection. For those community water systems serving 25 to 10,000 people, 100 percent of the surface water systems and 50 percent of the ground water systems use chlorine. Fifteen percent of the noncommunity groundwater systems use chlorine. It is estimated that the population exposed to chlorine from the use of chlorination alone in community drinking water systems is 70.3 million from surface water plants and 36 million from groundwater plants serving more than 10,000 people and is 17.4 million and 16.1 million from surface water systems and groundwater plants serving between 25 and 10,000 people (WIDB, 1990).

National Surveys

The EPA's 1975 National Organic Reconnaissance Survey (NORS) sampled the drinking water of 80 U.S water supplies. Of these 80 supplies, 16 had groundwater sources and 64 had surface water sources. According to survey results, chlorine residuals reportedly ranged from BDL to 2.8 mg/L, with an approximate median concentration of 0.6 mg/L (Symons et al., 1975). Exhibit 3-1, presented previously, provides these results.

In 1987, the American Water Works Association Research Foundation (AWWARF) sponsored a national survey of trihalomethanes (THMs) conducted by the Metropolitan Water District of Southern California. As part of this survey, alternate treatment technologies were investigated that would lower THM levels. According to survey results, typical chlorine dosage in drinking water was 2.2, 2.3, 1.2, and 1.0 mg/L for systems using lakes, flowing streams, groundwater, and mixed-supplies, respectively, as their raw water sources. Overall, doses ranged from 0.1 to more than 20 mg/L (McGuire and Meadow, 1988). Exhibit 3-1, presented previously, provides these results.

EPA's Technical Support Division (TSD) has compiled a data base of its disinfection byproducts field studies. The studies included a chlorination byproducts survey, conducted from October 1987 to March 1989. In this survey, free chlorine was sampled in finished water at the treatment plant and in the distribution system. Among 71 finished water samples, concentrations ranged from 0.1 to 5.0 mg/L, with a mean of 1.7 mg/L and a median of 1.4 µg/L. In the distribution system, the concentrations from 45 samples ranged from 0 to 3.2 mg/L, with a mean and median of 0.7 and 0.5 mg/L, respectively (EPA, 1992b). Exhibit 3-1, presented previously, provides these statistics.

Chlorine residual in drinking water for the average customer was determined using WIDB data from 228 surface water plants and 215 groundwater plants. For surface water plants, the chlorine residual ranged from 0 to 3.5 mg/L, with a mean of 0.94 mg/L and a median of 0.80 mg/L. For groundwater plants, values ranged from 0 to 5 mg/L, with a mean of 0.88 mg/L and a median of 0.33 mg/L (WIDB, 1990). Exhibit 3-1, presented previously, provides these results.

Five national surveys reported residual levels for free chlorine in U.S. drinking water. The AWWA's 1991 disinfection survey collected data from 283 utilities. Each facility was asked to respond to questions involving disinfection and quality control. Survey results indicated that mean free chlorine residuals in drinking water entering distribution systems were found to range from 0.07 to 5.00 mg/L, with a median of

1.10 mg/L (AWWA, 1991). The 75th and 90th percentiles wre 1.9 and 2.8 mg/L, respectively. Residual chlorine concentrations 97.6 percent of survey respondents was less than or equal to 4.0 mg/L.

3.2.2 Chloramine

Chloramine is used to disinfect drinking water and is formed as a byproduct of chlorination when source waters contain ammonia. It is also used as a primary or secondary disinfectant, usually with chloramine being generated onsite by the addition of ammonia to water following treatment by chlorination. The use of chloramines has been shown to reduce the formation of certain byproducts, notably THMs, relative to chlorination alone. Chlorination byproduct formation can be minimized when the ammonia is added prior to or in combination with chlorine. Ammonia addition reduces the chlorine residual of the water being treated. In some plants, however, ammonia may be added some time after the addition of chlorine, allowing the chlorine residual to react with precursor chemicals (Bull and Kopfler, 1990; EPA, 1980; Cooper et al., 1985).

It has been estimated from the WIDB that 29 percent of community surface water systems and 11 percent of community groundwater systems in the United States that serve more than 10,000 people use chloramines for disinfection. Approximately 56.5 million people served by these surface water systems and 7.8 million people served by these groundwater systems are exposed to chloramines from disinfection (WIDB, 1990), with this number increasing as more utilities convert to chloramines for secondary disinfection in order to control DBP formation.

National Surveys

In 1987, AWWARF sponsored a national survey of THMs conducted by the Metropolitan Water District of Southern California. According to survey results, typical chloramine concentrations in drinking water were 1.5 mg/L for systems using lakes and 2.7 mg/L for systems using flowing streams as their raw water sources (McGuire and Meadow, 1988). These results are presented in Exhibit 3-1.

EPA's TSD has compiled a data base of its disinfection byproducts field studies conducted from October 1987 to March 1989. For the 11 samples collected at the plant, the data ranged from 1.2 to 3.6 mg/L for chloramine residuals. The mean and median concentrations were 2.1 and 1.5 mg/L, respectively. For the eight samples collected in the distribution system, the data ranged from 0.1 to 3.3 mg/L, while the mean and median concentrations were 1.4 and 1.1 mg/L respectively (EPA, 1992b). Exhibit 3-1, presented previously, provides these statistics.

For the EPA 35 Utility Study, 13 samples were collected on a quarterly basis from clearwell effluent. Chloramine residual concentrations ranged from 0.9 to 5.5 mg/L for the sampling events, while the mean and median concentrations were 2.3 and 1.8 mg/L, respectively (Krasner et al., 1989; EPA and AMWA, 1989). Exhibit 3-1, presented previously, provides these results.

3.2.3 Chlorine Dioxide

Chlorine dioxide is used by water treatment plants as a disinfectant and to combat taste, odor, and color problems in drinking water. THMs are not readily formed as a byproduct of treatment. Chlorine dioxide used to treat water is most commonly generated from the reaction of aqueous sodium chlorite ($NaClO_2$) with chlorine (Gordon and Bubnis, 1996).

National Surveys

WIDB information has been used to determine the percentages of surface water and groundwater plants in the United States that use chloride dioxide for disinfection. Of those systems serving more than 10,000 people, an estimated 10 percent of surface water plants and one percent of groundwater plants fit into this category. It is assumed that none of the plants serving fewer than 10,000 people uses chloride dioxide. WIDB data have also been used to determine the numbers of people exposed to chlorine dioxide used for disinfection by plants serving more than 10,000 people. Estimates are that 12.4 million people served by surface water plants and 0.2 million people served by groundwater plants fit into this category (WIDB, 1990).

In 1987, AWWARF sponsored a national survey of THMs conducted by the Metropolitan Water District of Southern California. According to survey results, typical chlorine dioxide dosage used in drinking water was 0.6 mg/L for systems using lakes and 1.0 mg/L for systems using flowing streams as their raw water sources (McGuire and Meadow, 1988). Exhibit 3-1, presented previously, provides these results.

Gallagher et al. (1994) evaluated chlorine dioxide generator operations at several water treatment facilities in the United States to determine if generator optimization reduces byproduct concentrations. The study also evaluated different analytical methods and sample preservation techniques. The resulting data, presented below, provided an indication of chlorine dioxide and its DBP concentrations in water treated with ClO_2.

Onsite analysis used amperometric titration from Standard Methods for analysis of ClO_2 and its byproduct concentrations in generator effluent. Reductive flow injection analysis with colorimetric detection is useful for the determination of chlorine dioxide and perhaps chlorite ion (ClO_2^-).

Most utilities that apply chlorine dioxide at dosages of 1 mg/L or slightly greater were able to meet the currently recommended level of 1 mg/L for the sum of chlorine dioxide, chlorite ion, and chlorate concentrations. Furthermore, most utilities were able to meet the maximum residual disinfectant level (MRDL) for ClO_2 of 0.8 mg/L, which is the level EPA proposed in 1994 for chlorine dioxide. Concentrations of ClO_2 in the range of 0.1 to 0.3 mg/L were not uncommon in systems where chlorine dioxide had been added to source water and the finished water was dosed with free chlorine. During the study, concentrations approaching 0.6 mg/L were observed in some clearwells after free chlorine had been added. Exhibit 3-10 identifies the concentrations of ClO_2 at three utilities.

Exhibit 3-10. Chlorine Dioxide Concentrations in Distribution Systems

Location	Number of Samples	ClO_2 Dose (mg/L)	Concentration in the DS (mg/L)		
			Range	Mean	Median
Charleston, WV (August 12–14, 1990)	41	2.0	BDL* – 0.78	0.03	BDL
New Castle, PA (July 25–28, 1990)	33	–	0.11 – 0.37	0.22	0.20
Gulf Coast Water Authority	111	0.5 – 2.0	–	0.21	0.15

*BDL = 0.1 mg/L.
Source: Gallagher et al., 1994

Local Studies

Hoehn et al. (1990) conducted a study to determine the contribution of drinking water disinfected with chlorine dioxide to household odors reported at houses in Lexington, Kentucky, and Charleston, West Virginia. Source waters at both plants were rivers, and samples were collected from the plants and from houses. The Lexington treatment adds chlorine dioxide to source water at doses of 1.0 mg/L; the treatment process in Charleston adds 2.0 mg/L of chlorine dioxide. Samples were analyzed using the amperometric method of Aieta et al. and the flow injection analysis of Gordon et al. Exhibit 3-11 shows chlorine dioxide concentrations in the Charleston treatment plant and distribution system. Results from sampling at Lexington were not given.

Exhibit 3-11. Chlorine Dioxide Concentrations at Charleston Plant and Customer Houses (mg/L)

Compound	Below Filter at Plant		Clearwell at Plant	Customer D (Odor Present)		Customer E (No Odors)
	11/3/88	11/4/88	11/3/88	11/3/88	11/4/88	11/3/88
ClO_2	BDL	0.01	0.12	0.05	0.12	0.12

Source: Hoehn et al., 1990

4. OCCURRENCE OF DISINFECTION BYPRODUCTS

4.1 SOURCES OF 1994 DISINFECTION BYPRODUCT OCCURRENCE DATA

A summary of the disinfection byproduct occurrence data available for the proposed Stage 1 disinfectant/disinfection byproducts rule (D/DBPR) is presented in *Occurrence Assessment for Disinfectants and Disinfection By-Products (Phase 6a) in Public Drinking Water* (EPA, 1992). This section of the document presents occurrence data for the 15 contaminants being considered for regulation under the proposed rule. The U.S. Environmental Protection Agency (EPA) received comments on the occurrence document and these comments were incorporated in this section. The sources of data will be described first followed by a discussion of the disinfection byproducts (DBPs) being considered in the D/DBPR.

This section briefly describes 10 pertinent data bases cited in the 1992 document and Exhibit 4-1 reports the corresponding results from analyses of the data bases. This exhibit is an extension of Exhibit 2-1 from the 1992 occurrence document and reflects corrections and clarifications in response to comments received from the D/DBP Technologies Work Group of the Regulatory Negotiating Committee. Additional regional and local studies were summarized in the 1992 document to further characterize the occurrence of the Stage I D/DBPs; however, they are not addressed in this document. The most recent data identified in literature searches, provided by commenters to the proposed rule (*FR* 59, 38668) and the Notices of Data Availability (*FR* 62, 59388; *FR* 63, 156743) and by peer reviewers have been included in this section.

This section presents the occurrence data on the DBPs for the Stage 1 D/DBP rule. Although a number of sources were available to characterize occurrence of DBPs, not all the sources were robust enough to characterize a national occurrence. For the most recent national occurrence data on total trihalomethanes (TTHMs) and haloacetic acids 5 (HAA5), a number of sources were available. These sources are summarized in Section 5 of this document, the American Waterworks Association (AWWA) WaterStats and the American Water Works Service Company (AWWSCo) datasets were selected for the *Regulatory Impact Analysis for the Disinfectants/Disinfection Byproduct Rule* because they are national in scope, contain recent data, and have a large sample size with sufficient accuracy. Additionally, state compliance monitoring data are included in this section and in Section 5 to provide a sense of regional variability throughout the nation for TTHMs and HAA5.

Prior to promulgation of a maximum contaminant level (MCL) of 100 µg/L total trihalomethanes (TTHMs) in 1979, EPA performed two surveys to obtain information on the occurrence of trihalomethanes

(THMs) and other organic compounds: the National Organics Reconnaissance Survey (NORS) (Symons et al., 1975) and the National Organic Monitoring Survey (NOMS) (EPA, 1978). These studies were used to develop the 1979 trihalomethane (THM) regulation. These studies no longer represent current occurrence of THMs in water systems serving more than 10,000 people because of changes in disinfection practices required in the Surface Water Treatment Rule, which became effective in 1993. However, data from these studies could be indicative of THM occurrence in small systems.

4.1.1 National Organics Reconnaissance Survey

NORS was conducted, by the EPA in early 1975, to characterize the presence and extent of TTHMs in the United States. Eighty water supplies, representing a wide variety of water sources and treatment technologies, were chosen for the study. The water supplies were geographically distributed throughout 80 different cities to characterize national occurrence. Eighty percent of these supplies used groundwater sources, while the remaining 20 percent used surface water sources. The survey sampled for several organics, including THMs.

4.1.2 National Organics Monitoring Survey

EPA conducted NOMS from March 1976 through January 1977 to identify sources and frequency of occurrence of organics and inorganics in drinking water supplies. NOMS was conducted in three phases: Phase I – March to April 1976, Phase II – May to July 1976, and Phase III – November 1976 to January 1977. NOMS involved sampling and analyzing finished water from 113 public water supplies across the United States. Ninety-two of these systems used surface water sources, while 21 of these systems used groundwater sources.

4.1.3 Rural Water Survey

The Rural Water Survey (RWS), conducted by EPA between 1977 and 1980, assessed the occurrence of organic compounds in public water supplies serving less than 10,000 people. It was conducted in order to evaluate the quality of drinking water in rural America. Samples from more than 2,000 households, representing more than 600 rural water supply systems, were examined. Most systems (i.e., 494) sampled for TTHMs used groundwater as their source water, and 154 used surface water. Of the 2,655 samples obtained, 800 were analyzed for purgeable halocarbons, including the four THMs. It should be noted that some samples were up to 27 months old prior to analysis.

4.1.4 Community Water Supply Survey

EPA conducted the Community Water Supply Survey (CWSS) in 1978. The survey examined 1100 drinking water samples provided by 452 systems, including 388 utilities serving populations of less than 10,000. These samples were collected at the treatment plants and in the distribution systems. The survey included analyses for chloroform, bromoform, bromodichloromethane, and dibromochloromethane. It should be noted the samples were one to two years old prior to analysis.

4.1.5 AWWARF National Trihalomethanes Survey

In 1987, the American Water Works Association Research Foundation (AWWARF) partially funded a grant awarded to the Metropolitan Water District of Southern California (MWD), to perform a national survey of THMs. The purpose of the THM survey was to determine the extent and costs of compliance with the THM MCL. Questionnaires were completed by 910 utilities, each serving greater than 10,000 people. Seven hundred and twenty-seven utilities reported THM data for one or more quarters for the years 1984 through 1986. Data on source water, treatment chemicals used, and populations served were also provided. The survey involved data collected from more than 67 percent of the population represented by water utilities serving greater than 10,000 customers.

4.1.6 EPA/AMWA/CDHS Study (35 Utility Study)

In 1987, EPA funded a cooperative agreement with the Association of Metropolitan Water Agencies (AMWA) to study the formation and control of DBPs in drinking water systems. Thirty-five utilities nationwide participated in the study performed by the MWD and James M. Montgomery Consulting Engineers, Inc. (JMM). The California Department of Health Services (CDHS) also contracted with the MWD to include 10 California utilities in the baseline phase of the study. The study provided data for seven groundwater systems, six that served greater than 50,000, and 28 surface water systems, 19 served greater than 50,000. Samples of plant influent and clearwell effluent were collected from each utility on a quarterly basis during 1988-89. The clearwell effluent samples were analyzed for chlorine residuals, surrogate parameters, and several chlorination DBPs, including: THMs, chloral hydrate, dichloroacetic acid, and trichloroacetic acid. Appropriate dechlorinating agents were added to all samples at the time of collection.

4.1.7 EPA Disinfection Byproduct Field Studies

The Technical Support Division (TSD) of the Office of Groundwater and Drinking Water has conducted several DBP field studies. A study of chlorination byproducts was performed from October 1987

to March 1989. Samples of source water, plant effluent, and water from a far point in the distribution system were collected from 21 community water supplies. Disinfection processes and concentrations of the four individual THMs, chloral hydrate, dichloroacetic acid, and trichloroacetic acid were characterized.

4.1.8 Water Industry Data Base (1991)

The Water Industry Data Base (WIDB) was developed through a joint effort by the American Water Works Association (AWWA) and the AWWARF. The study, conducted between 1989 and 1990, surveyed approximately 1,300 drinking water systems serving more than 10,000 people in the United States. A wide spectrum of information was covered in the survey, including utility characteristics and finances, surface and groundwater treatments, water quality monitoring, and water distribution characteristics. The WIDB provides a large data set of annual average TTHM data, free chlorine, and combined chlorine residuals. Estimates of these levels, based on the professional judgment of utility personnel, were compiled. Because of the comprehensive nature of the WIDB, the Regulatory Negotiating Committee used this data set in their regulatory impact analysis.

4.1.9 AWWA 1991 Disinfection Survey

The Disinfection Committee of AWWA's Water Quality Division conducted the AWWA 1991 Disinfection Survey. A total of 283 utilities participated in this study, responding to questions pertaining to disinfection and quality control, including: control methodology, chlorine demand, filtration, chlorine dose, contact times, and TTHM levels.

4.2 SOURCES OF POST-1994 DISINFECTION BYPRODUCT OCCURRENCE DATA

Section 4.2 describes occurrence data reviewed by EPA since the 1994 proposed rule. This section provides data from national surveys, five states' compliance monitoring data, and summarized articles from current scientific literature.

4.2.1 WaterStats

The WIDB was replaced by the WaterStats data base in 1996 and is currently maintained by the AWWA. WaterStats was developed to support the regulatory and legislative efforts of AWWA, assist AWWA in focusing research activities, and support educational endeavors of AWWA and interested parties. The 1996 study surveyed 3,162 public drinking water systems in the United States. Of the 956 respondents, 460 systems reported annual TTHM estimates, and 146 systems reported haloacetic acid (HAA) estimates.

These systems were in the United States and also reported the size of the population served. The survey covered a wide spectrum of information, including utility characteristics and finances, surface and groundwater treatments, water quality monitoring, and water distribution characteristics. Data from WaterStats form the basis of the regulatory impact analysis because they are considered the most representative, comprehensive data on DBPs and precursors.

4.2.2 American Water Works Service Company Monitoring Data

The AWWSCo, the largest investor-owned water utility in the United States, owns and operates more than 100 water systems. The systems are located in 10 states, 9 of which are east of the Mississippi River. AWWSCo collected information on the occurrence of DBPs in their distribution systems (Arora et al., 1994, 1997). AWWSCo provided EPA with a summary of TTHM and haloacetic acids 5 (HAA5) data for approximately 52 systems for 1991 and 1992. Information on source water and population served was also provided.

4.2.3 State Compliance and Other Monitoring

EPA requested all available TTHM compliance monitoring data and HAA data from nine state agencies. These agencies were selected to provide comparisons to the national estimates of occurrence generated from WaterStats. Five agencies submitted TTHM data on systems serving less than 10,000 people in addition to their data for systems serving 10,000 or more people. Data from the states of Massachusetts, Missouri, New Jersey, Oregon, Pennsylvania, and Texas were analyzed and presented. The state of Utah submitted "pre-Information Collection Rule (ICR) Data," which consisted of monitoring results consistent with ICR requirements, beginning in October 1994.

More detailed summaries of the national and state data are provided in the following sections on each of the disinfectants, DBPs, and DBP precursors. More detailed summaries on the surveys and summaries are provided in Appendix A. Exhibit 4-1, presented previously, summarizes the occurrence data from these sources. Additional sources of occurrence data were identified during a review of the scientific literature. Information from these sources are summarized in the following sections.

4.2.4 Literature Search

During a literature search, appropriate articles and studies were identified using keywords, including drinking water, contaminant names, or the Chemical Abstract Service Registry Number for specific disinfectants and DBPs. The literature searches were performed on several bibliographic services to ensure

identification of the most available data. In order to focus on the most recent data, only articles published since 1985, and not previously summarized in the documents supporting the proposed rule, were reviewed.

A total of 113 articles were identified from these searches. Studies conducted in the United States that best represent national occurrence of a contaminant were selected for this document. If national studies or monitoring projects were not available for a contaminant, then regional or local studies were cited.

The following information was extracted and summarized from each article: the type of public water system (e.g., size, source water, and disinfection process); the analytical methods used and any modifications to standard methods; occurrence information for disinfectants and DBPs, including range of detections and means, medians, and percentile rankings of detections; and any conclusions presented in the articles. Some authors provided additional data from their studies for inclusion in this document.

4.3 DBP OCCURRENCE DATA

4.3.1 Chloroform

Chloroform, the most prevalent THM in drinking water, occurs in public water systems as a result of drinking water chlorination and source water contamination. Chloroform is a byproduct of the chlorination of naturally occurring organic matter in raw water. Several water quality factors such as total organic carbon (TOC), pH, and temperature affect the formation of chloroform. Surface water systems have higher frequencies of occurrence and higher concentrations of chloroform than groundwater systems because humic and fulvic acids are found primarily in surface water sources and since groundwater is a relatively protected source. Since residual chlorine levels are maintained in water distribution systems for disinfection purposes, the formation of chloroform continues throughout the distribution system (Stevens and Symons, 1977; EPA, 1980).

Different treatment practices also affect the formation of chloroform. Chloroform levels can be reduced, although not eliminated, when chloramines are used to disinfect. The reduction is less, however, when chloramination involves a pre-chlorination step in which a free chlorine residual is maintained through a portion of the water treatment process prior to the addition of ammonia. Pre-ozonation followed by chloramination substantially reduces the formation of chloroform. In addition, the use of chlorine dioxide, rather than chlorine, produces lower levels of chloroform than chlorine (EPA, 1980, Singer, et al., 1989).

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Chloroform						
NORS (1975) Symons et al. (1975)	80 cities nationwide 80% SW, 20% GW	Finished water at treatment plant	Max. 311	–	23	(Pre-THM rule)
NOMS (1976–1977) Bull & Kopfler (1990)	113 community water supplies 92 SW, 21 GW	Finished water at treatment plants[g]	Max. 540	–	22 – 54.5[h]	Pos detections: 92%-100%[i]
CWSS (1978) Brass et al. (1981)	450 water supply systems	Finished water (1,100): Surface water Groundwater	 – –	 90[j] 8.9[j]	 60 BDL	Pos detections. 97%[i] SW 34%[i] GW
RWS (1978–1980)	>600 rural systems (>2,000 households)	Drinking water from: Surface water (154) Groundwater (494)	 – –	 84[j] 8.9[j]	 57 BDL	Pos. detections: 82%[i] SW 17%[i] GW
EPA/AMWA/CDHS (1988–1989) Krasner et al. (1989)	35 Water utilities nationwide (10 located in California)	Samples from clearwell effluent for 4 quarters	Max. 130	–	9 6–15[k] 14 (overall)	75% of data was below 33
EPA (1992b) (1987-1989)	Disinfection byproducts field studies	Distribution Systems (56): SW≥ 10,000 (39) SW <10,000 (11) GW< 10,000 (5)	BDL – 340 – – –	57 58.7 77.2 3.6	42	Pos. detections: 98% 90th percentile 141.0 110.0 9.4
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii:winter 1991 (19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 111.0	38.52	27.70	75th percentile=54 78 90th percentile=94 90
Niemenski et al. (1993)	Finished surface water from 35 Utah treatment utilities	Plant effluent from: 14 utilities >10,000 (SDS Samples) 21 utilities <10,000 (DS Samples)	10.22 – 39.52 0.51 – 91.10	 22.24 27.47	 17.24 19 70	 Std. Dev =21 $CHCL_3$/TTHM=0 79
Pre-ICR data (1996)	State of Utah, 1994-1996 7 SW utilities >100,000	Average distribution system samples	2.70 – 69.80	23.0	22.40	75th percentile= 31 93 90th percentile= 37 18

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Chloroform (cont'd)						
Singer et al. (1995)	Finished surface water from 8 North Carolina treatment plants	Distribution system samples (42) (June 1991- February 1992)	8 – 91	41	38	$CHCl_3$/TTHM 0 79
Bromodichloromethane						
NORS (1975) Symons et al. (1975)	80 Cities nationwide 80% SW, 20% GW	Finished water at treatment plant	Max. 100	–	2	Pos. detections: 90%
NOMS (1976–1977) Bull & Kopfler (1990)	113 community water supplies (92 SW, 21 GW)	Finished water at treatment plants[g]	Max. 183	–	5.9 – 14[h]	Pos. detections: 90%
CWSS (1978) Brass et al. (1981)	450 water supply systems	Finished water (1,100): Surface water Groundwater	– –	12[i] 5 8[i]	6.8 BDL	Pos. detections: 94%[i] SW 33%[i] GW
RWS (1978-1980)	>600 rural systems (>2,000 households)	Drinking water from: Surface water (154) Groundwater (494)	– –	17[i] 7.7[i]	11 BDL	Pos. detections: 76%[i] SW 13%[i] GW
EPA/AMWA/CDHS (1988–1989) Krasner et al. (1989)	35 Water utilities nationwide (10 located in California) (Spring 1988-winter 1989)	Samples from clearwell Effluent for 4 quarters	Max. 82	–	6.6 (overall) 4.1 – 10[k]	75% of data was below 14
EPA (1992b) (1987–1989)	Disinfection byproducts field studies October 1987 – March 1989	Distribution Systems (56)	BDL – 100	17	15	Positive detects 96%[i] SW & 98%[i] GW
		SW> 10,000 (39)	–	17.4	–	90th percentile
		SW <10,000 (11)	–	24.8	–	35.3
		GW< 10,000 (5)	–	2.2	–	51.0
						2.6 & 5.4
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991 (19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 36.00	11.94	9.25	75th percentile=16.00 90th percentile=24.80
Niemenski et al.(1993)	Finished surface water from 35 Utah treatment plants	Plant effluent from: 14 plants >10,000 (SDS Samples) 21 plants <10,000 (DS Samples)	1.03 – 14.0 0.10 – 20 0	5.08 5.01	4.25 4.73	

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Bromodichloromethane (cont'd)						
Singer et al. (1995)	Finished surface water from 8 North Carolina treatment plants	Distribution system samples (42)	3 – 21	8.8	8.1	BDCM/TTHM=0 19 Mean TOC=5 25 mg/L
Pre-ICR data (1996)	State of Utah, 1994-1996 7 SW utilities >100,000	Average distribution system samples	1.30 – 60	6.73	6.70	75th percentile=9 15 90th percentile=10 91
Dibromochloromethane						
NORS (1975) Symons et al. (1975)	80 cities nationwide 80% SW, 20% GW	Finished water at treatment plant	Max. 100	–	2	Pos. detections. 90%[i]
NOMS (1976-1977) Bull & Kopfler (1990)	113 community water supplies 92 SW, 21 GW	Finished water at treatment plants[g]	Max. 280	–	BDL - 3[h]	Pos. detections: 73%[i]
CWSS (1978) Brass et al. (1981)	450 water supply systems	Finished water (1,100): Surface water Groundwater	–	 5.0[j] 6.6[j]	 1.5 BDL	Pos detections. 67%[i] 34%[i]
RWS (1978-1980)	>600 rural systems (>2,000 households)	Drinking water from: Surface water (154) Groundwater (494)	–	 8.5[j] 9.9[j]	 0.8 BDL	Pos detections: 56%[i] 13%[i]
EPA/AMWA/CDHS (1988–1989) Krasner et al., 1989	35 water utilities nationwide	Samples from clearwell effluent for 4 quarters (Spring 1988-winter 1989)	Max. 63	–	3.6 (overall) 2.6-4.5[k]	75% of data was below 9.1
EPA (1992b) (1987-1989)	Disinfection byproducts field studies	Distribution Systems (56): SW≥ 10,000 (39) SW <10,000 (11) GW< 10,000 (5)	BDL – 41	6.6 6.3 10.4 1.8	3.4	Pos. detections.92% & 93% 90th percentile 17.3 35 0 3.6
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991 (19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 26.0	3.04	1.60	75th percentile= 3 15 90th percentile= 6 00

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L) Range	Mean	Median	Notes
Dibromochloromethane (cont'd)						
Niemenski et al. (1993)	Finished surface water from 35 Utah treatment plants	Plant effluent from: 14 plants >10,000 (SDS samples) 21 plants <10,000 (DS samples)	 0.49 – 10.0 0.20 – 16.0	 2.03 0.99	 0.82 0.83	DBCM/TTHM: 0.04
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	BDL – 5.90	1.5	1.30	75th percentile= 2.70 90th percentile= 3.60
Singer et al. (1995)	Finished surface water from 8 North Carolina treatment plants	Distribution system samples (42)	–	–	–	DBCM/TTHM<0.02
Bromoform						
NORS (1975) Symons et al. (1975)	80 cities nationwide 80% SW,20% GW	Finished water at treatment plant	Max. 92	–	BDL	
NOMS (1976–1977) Bull & Kopfler (1990)	113 community water supplies 92 SW (DS samples), 21 GW	Finished water at treatment plants[g]	Max. 280	–	BDL(all 3 phases)	DL=0.3
CWSS (1978) Brass et al. (1981)	450 water supply systems	Finished water (1,100): Surface water Groundwater	 –	 2.1[i] 11[i]	 BDL BDL	Pos. detections. 13%[i] SW 26%[g] GW
RWS (1978–1980)	>600 rural systems (>2,000 households)	Drinking water from: Surface water (154) Groundwater (494)	 –	 8.7[i] 12[i]	 BDL BDL	Pos. detections: 18%[i] SW 12%[g] GW
EPA/AMWA/CDHS (1988-1989) Krasner et al. (1989)	35 water utilities nationwide (10 located in California)	Samples from clearwell effluent for 4 quarters Spring 1988 – winter 1989	Max. 72	–	0.33–0.88[k] 0.57 (overall)	75% of data was below 2.8
EPA (1992b) (1987–1989)	Disinfection byproducts field studies	Distribution systems (56): SW≥ 10,000 (39) SW <10,000 (11) GW< 10,000 (5)	BDL – 10	1.0 0.8 1.4 2.3	BDL	Pos. detections.45% & 48% 90th percentile 3.1 5.1 –

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Bromoform (cont'd)						
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991 (19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 17.0	0.75	0.00	75th percentile= BDL 90th percentile= 0 90
Niemenski et al. (1993)	Finished surface water from 35 Utah treatment plants	Plant effluent from: 14 plants >10,000 (SDS samples) 21 plants <10,000 (DS samples)	Max. 0.38	–	–	– No detects for <10,000
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	BDL – 1.20	0.03	0.00	75th percentile= BDL 90th percentile= BDL
Singer et al. (1995)	Finished surface water from 8 North Carolina treatment plants	Distribution system samples (42) June 1991–February 1992	–	–	–	$CHBr_3$/TTHM = BDL
Total Trihalomethanes						
NORS (1975) Symons et al. (1975)	80 cities nationwide 80% SW, 20% GW	Finished water at treatment plant	Max. 482	68	41	90th percentile=120
NOMS (1976–1977) Bull & Kopfler (1990)	113 community water supplies 92 SW, 21 GW	Finished water at treatment plant[g]	Max. 784	84	55	90th percentile=60
RWS (1978–1980) Brass (1980)	677 cities nationwide <10,000 pop. 154 SW, 494 GW	Finished water samples (800)	Max. 313	36	18	90th percentile=95
AWWARF (1987) McGuire & Meadow (1988)	727 cities nationwide that serve >10,000 people	Quarterly mean of finished water 73% SW, 27% GW	Max. 360	42	39	
USEPA/AMWA/CDHS (1988–1989) Krasner et al. (1989)	35 utilities nationwide (10 located in California)	Samples from clearwell effluent for 4 quarters Spring 1988– winter 1989	–	–	36 (overall) 30–44[k]	
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 142	55.14	43.0	75th percentile=86 00 90th percentile=119 00
AWWA (1996)	460 water utilities	Distribution system samples	BDL – 96.0	43.2	44.0	

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Total Trihalomethanes (cont'd)						
Massachusetts compliance monitoring data (1994–1996)	Statewide					90th percentile
		SW < 10,000 (3)	15 – 75	41	37	71
		SW ≥ 10,000 (21)	2 – 502	54	50	90
		GW > 10,000 (8)	BDL – 207	46	44	89
		Mixed < 10,000 (2)	2 – 104	28	12	83
		Mixed > 10,000 (19)	BDL – 524	50	45	90
Missouri compliance monitoring data (1996–1997)	111 systems reporting					90th percentile
		SW < 10,000 (81)	BDL – 541	118	102	206
		SW > 10,000 (11)	0.7 – 165	44.5	37.3	82.5
		GW < 10,000 (1)	–	–	–	Single result 48.7 µg/L
		GW > 10,000 (14)	0.6 – 134	14.5	2.8	45.6
New Jersey compliance monitoring data (1994–1996)	Statewide					90th percentile
		SW < 10,000 (5)	21.86 – 88.97	48.0	27.3	83.6
		SW > 10,000 (23)	2.31 – 87.44	41.8	38.5	70.6
		GW < 10,000 (37)		6.84	2.59	16 9
		GW > 10,000 (86)	BDL – 47.98 BDL – 70.37	8.93	2.73	31.3
Oregon compliance monitoring data (1994–1996)	Statewide					90th percentile
		SW > 10,000 (27)	7 – 76	29	–	42
		GW > 10,000 (7)	5 – 31	16	–	28

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Total Trihalomethanes (cont'd)						
Pennsylvania compliance monitoring data (1994–1996)	223 systems statewide (63 purchased SW)	Quarterly samples, distributions system samples				90th percentile
		SW < 10,000 (54 systems; 1,676 samples)	BDL – 162	46.0	44.5	83 7
		SW > 10,000 (119 systems; 7,345 samples)	0.64 – 113	40.0	42.0	63.8
		GW < 10,000 (25 systems; 306 samples)	BDL – 159	14.1	2.42	35.8
		GW > 10,000 (25 systems; 985 samples)	0.40 – 40.8	8.01	5.47	17.3
Texas compliance monitoring data (1994–1996)	227 systems statewide (48 purchased SW)	Quarterly samples				90th percentile
		SW > 10,000 (114 systems; 2,521 samples)	8.05 – 135.41	41.10	36.88	70.35
		GW >10,000 (102 systems; 1427 samples)	BDL – 121.02	23.72	14.59	60.33
		GW <10,000 (11 systems; 32 samples)	BDL – 120.58	26.21	18.85	52.00
Singer et al. (1995)	Finished water from Surface water *in 8 North Carolina utilities*	Distribution samples (42) *January 1991–February 1992*	39 – 82[n]	51	46	Avg. TTHM/TOX= 0 15
Niemenski et al. (1993)	Finished water from 35 surface water utilities in Utah	14 plants >10,000 (SDS samples)	28.8 – 81.6	50.7	51 8	
		21 plants <10,000 (dist. samples)	2.33 – 215	66.2	62.9	
		All plants	2.33 – 215	60.0	82 1	
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	5.20 – 87.4	31.3	32.1	75th percentile=40 4 90th percentile=46.8

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Monochloroacetic Acid						
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 3.98	1.38	1.19	90th percentile=2.65
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	BDL – 3.80	0.08	BDL	90th percentile=BDL
Dichloroacetic Acid						
EPA/AMWA/CDHS (1988–1989) Krasner et al. (1989)	35 water utilities nationwide (10 located in California)	Samples from clearwell effluent for 4 quarters Spring 1988–winter 1989	Max. 46	–	5.0–7.3[b] 6.4 (overall)	75% of data was below 12 DL=0.6
EPA (1992b) (1987–1989)	Disinfection byproducts field studies	Distribution systems (56): SW≥ 10,000 (39) SW <10,000 (11) GW< 10,000 (5)	BDL – 75	 22 28 1.9	–	Pcs. detections: 96% 90th percentile 48.0 41.0 4.7
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 45.2	17.3	17.0	75th percentile= 15.75 90th percentile= 35.6
Singer et al. (1995)	Finished Surface water from 8 North Carolina treatment plants	Distribution system samples (42)	9 – 60	30	28	
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Distribution system samples	BDL – 45.23	17.28	17.00	75th percentile=24 24 90th percentile=35.59
Trichloroacetic Acid						
EPA/AMWA/CDHS (1988–1989) Krasner et al. (1989)	35 water utilities nationwide (10 located in California)	Samples from clearwell effluent for 4 quarters	– –	– –	4.0–5.8[b] 5.5 (all)	75% of data was below 15.3 DL=0.6

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Trichloroacetic Acid (cont'd)						
EPA (1992b) (1987–1989)	Disinfection byproducts field studies	Finished water systems (69): SW > 10,000 (42) SW < 10,000 (20) GW < 10,000 (7) Distribution systems (55): SW ≥ 10,000 (39) SW < 10,000 (11) GW < 10,000 (5)	 BDL – 54 BDL – 77 	 14.4 14.8 1 9 17 16.6 1.1	 11 15 	90th percentile: 28 7 30.4 10.7 Pos. detections 90% & 91% 90th percentile 30 6 28.9 4.2
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 83.07	19.79	16.74	75th percentile=24 98 90th percentile=37 93
Singer et al. (1995)	Finished surface water from 8 North Carolina treatment plants	Distribution system samples (42)	12 – 79	36	37	
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	BDL – 32.20	14.18	14.50	75th percentile=[illegible] 90th percentile=25 30
Monobromoacetic Acid						
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 4.55	0.77	0.40	90th percentile=2 48
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	BDL – 2.40	0.10	BDL	90th percentile=BDL
Dibromoacetic Acid						
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 20.0	1.41	0.58	90th percentile=2.16
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	BDL – 4.70	0.71	BDL	90th percentile=2.55

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Haloacetic Acids(5) (HAA5)[15]						
EPA/AMWA/CDHS (1988–1989) Krasner et al. (1989)	35 water utilities nationwide (10 located in California)	Samples from clearwell effluent for 4 quarters	–	–	4.0 – 5.8[k] 5.5(overall)	75% of data was below 15.3 DL=0.6
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	4.69 – 134.3	41.35	37.04	75th percentile=52.27 90th percentile=72.35
Missouri compliance monitoring data (1997)	106 systems reporting January–June 1997					90th percentile
		SW < 10,000 (81)	0.1 – 284	88.0	80.4	165
		SW > 10,000 (11)	0.1 – 95.8	28.4	24.1	63.0
		GW > 10,000 (14)	0.1 – 43.2	6.8	3.2	17.1
		All systems (106)	0.1 – 284	69.2	56.3	150.4
Singer et al. (1995)	Finished surface water from 8 North Carolina treatment plants	Distribution system samples (42)	36 – 106	77	81	HAAs 4 High TOC, Low Br
Niemenski et al. (1993)	Finished water from 35 surface water utilities in Utah	Distribution samples (35)	1.00 – 89.8	30.0	20.1	
		>10,000 (14) (SDS samples)	8.06 – 51.5	19.0	17.7	
		<10,000 (21) (DS samples)	1.00 – 89.8	37.3	42.2	
Pre-ICR data (1996)	State of Utah, 1994–1996 7 SW utilities >100,000	Average distribution system samples	1.50 – 57.40	25.87	47.1	75th percentile=34.40 90th percentile=47.18
Chloral Hydrate						
EPA/AMWA/CDHS (1988–1989)[m] Krasner et al. (1989)	35 water utilities nationwide (10 located in California)	Samples from clearwell effluent for 4 quarters	Max. 22	–	1.7–3.0[k] 2.1(overall)	75% of data was below 4.1[12] DL= 0.02(1st quarter) & 0.01 (thereafter)
EPA (1992b) (1987–1989)	Disinfection byproducts field studies	Finished water:				Pos. detections:
		At the plant (67)	BDL – 25	5.0	2.5	90%
		Distribution systems (53)	BDL – 30	7.8	4.4	91%
Arora et al. (1994, 1997)	2 sampling phases 1991 20 water systems	Phase ii: winter 1991(19 facilities) Phase iii: summer 1991(21 facilities)	BDL – 27.33	6.27	4.35	75th percentile= 8.88 90th percentile= 14.08

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L)			Notes
			Range	Mean	Median	
Chloral Hydrate (cont'd)						
Niemenski et al. (1993)	Finished SW from 6 Utah treatment plants > 10,000	SDS samples in June 1990 (4)	0.7 – 3.76	–	–	
Pre-ICR data (1996)	State of Utah, 1994-1996 7 SW utilities >100,000	Average distribution system samples	BDL – 8.60	3.43	3.35	75th percentile= 5 33 90th percentile= 6.34
Bromate Ion						
Krasner et al. (1992)	North American pilot- and full-scale studies	10 utilities, pilot- and full-scale ozonation facilities	BDL – 20	–	–	O_3 dose=0.94 – 9 3 mg/L Br^- =BDL – 0 33 pH=5.6 – 9.9 MRL=5; 10 TOC=0 9 – 26 mg/L
Sorrell, Hautman (1992)	9 surface waters	Finished water plants using ozone (9)	BDL – 6.3	2.5	0.75	MDL=0.4 2 samples BDL
Grammith (1993)	MWD demonstration plant (5.5 MGD)	Ozonation sampled at contactor effluent	BDL – >10	–	–	O_3 dose=0.75 – 2 0 mg/L Br^- =0 17 – 0.5 mg/L pH=7.6 – 8 4 MRL=3
Chlorite Ion						
Hoehn et al. (1990)	2 houses (WV), November 3–4, 1988	Finished water Below filter at plant (2) Clearwell at plant (1) Customer D with odor problems (2) Customer E with no odor (1)	mg/L 1.67 – 1.04 0.71 0.90 – 0.31 0 93	mg/L 1.36 0.71 0.61 0.93	mg/L – – – –	ClO_2 Dose (mg/L) 2.0[b]
Bolyard et al. (1993)	4 sites using ClO_2	1 sample in 1990, 4 samples in 1991 (5)	mg/L 0.052 – 0.74	mg/L 0 31	mg/L 0 17	ClO_2 Dose (mg/L) 0.07 – 2.0

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Survey (Year)[a]	Location	Sample Information (No. of Samples)	Concentration in DS (µg/L) Range	Mean	Median	Notes
Chlorite Ion (cont'd)						
Gallagher et al. (1994)			mg/L	mg/L	mg/L	ClO_2 Dose (mg/L)
	Charleston, WV	August 12–14, 1990 (15)[c]	0.51 – 2.41	1.0	0.75	2.0[2]
	New Castle, PA	July 22–24, 1991 (54)	BDL – 0.1	0.03	0.03	0.75 – 1.1
	Gulf Coast Water Authority, TX	June 1989–April 1991 (40)	0.1 – 3.4	0.66	0.54	0.5 – 2.0
	Skagit, WA	September 24–25, 1990 (6)	0.36 – 0.38	0.37	0.37	0.7
	Columbus, GA	February 19–21, 1991 (4)	0.16–0.44	0.30	0.31	0.5, 1.0
		October 18, 1991 (9)	0.16–0.41	0.33	0.37	0.5, 1.0
CMA dataset (1997)	65 utilities nationwide using ClO_2	Monthly samples 1995–1997 (855)	mg/L 0.01 – 2.60[d]	mg/L 0.58	mg/L 0.52	75th percentile= 0.69 90th percentile=1.47
Chlorate Ion						
Hoehn, et al. (1990)	2 houses (WV), November 3-4	Finished water	mg/L	mg/L	mg/L	ClO_2 dose(mg/L)
		Below filter at plant (2)	0.14 – BDL[e]	0.14	–	2.0[b]
		Clearwell at plant (1)	BDL[e]	–	–	
		Customer D with odor problems (2)	0.28 – 0.22	0.25	–	
		Customer E with no odor (1)	0.28	0.28	–	
Bolyard et al. (1993)			mg/L	mg/L	mg/L	ClO_2 dose (mg/L)
	4 sites using ClO_2	1 sample in 1990, 4 in 1991(5)	0.02 – 0.33	0.18	0.14	0.07 – 2.0
	15 sites using hypochlorination	1991 (16)	0.01 – 0.66	0.16	0.08	NA
Gallagher et al. (1994)			mg/L	6mg/L	mg/L	ClO_2 dose (mg/L)
	Charleston, WV	August 12–14, 1990 (16)	0.08 – 1.52	0.24	0.14	2.0[b]
	New Castle, PA	July 22–24, 1991 (54)	0.30 – 0.58	0.39	0.39	0.75 – 1.1
	Gulf Coast Water Authority, TX	June 1989–April 1991 (40)	0.15 – 1.50	0.22	0.17	0.5 – 2.0
	Skagit, WA	September 24–25, 1990 (6)	0.09 – 0.10	0.10	0.10	0.7
	Columbus, GA	February 19–21, 1991 (4)	0.11–0.23	0.16	0.15	0.5, 1.0
		October 18, 1991 (9)	0.10–0.24	0.20	0.22	0.5, 1.0
CMA data set (1997)	65 utilities nationwide using ClO_2	Monthly samples 1995–1997 (855)	mg/L 0.01 – 2.40[f]	mg/L 0.40	mg/L 0.23	75th percentile= 0.38 90th percentile=1.20
Gordon et al. (1995)	111 systems using hypochlorination	1993–1995 (111)	mg/L BDL – 9.18	mg/L 0.49	mg/L 0.16	NA

Exhibit 4-1. Disinfection Byproduct Drinking Water Summary (Continued)

Footnotes:

a. Dates in parentheses indicate period of sample collection.
b. Chlorine dioxide is added to one of the two treatment trains in the plant with unequal blending of water.
c. One point in three days sampling was an outlier = 3.49 mg/L.
d. One point from 855 samples was 5.36 mg/L, which potentially has been a yield sample.
e. Sample interference during analysis – no valid data.
f. One point from 855 samples was 4.42 mg/L, which potentially has been a yield sample.
g. Sampled over three phases.
h. Median concentrations of the three phases.
i. Of systems sampled.
j. Mean of the positives.
k. Range of median for individual quarters.
l. Detection limit was 0.02 µg/L in the first quarter and 0.1 µg/L, thereafter.
m. In the 35 Utility Study, chloral hydrate had a good correlation with chloroform occurrence (r=0.85), while chloral hydrate had a poor correlation with bromoform levels ® = -0 24) In one water sample with a low level of bromide ions, chloral hydrate was detected in the distribution system up to 20 µg/L, but for another, bromide levels varied from 0.14 to 0.79 mg/L, resulting in chloral hydrate concentrations of 3.3 to 0.38 µg/L. Xie and Rechow (1992) identified brominated trihaloacetaldehydes in ozonated and chlorinated fluvic acid solutions containing inorganic bromide ion. However, the formation of these in chlorinated drinking water has not been investigated (Reference Xie, Y and Reckhow, 1992)
n. Range of plants' medians.
o. Includes DBAA, DCAA, MBAA, MCAA, and TCAA.

Abbreviations:

AMWA	Association of Metropolitan Water Agencies
AWWA	American Water Works Association
AWWARF	American Water Works Association Research Foundation
BDCM	Bromodichloromethane
BDL	Below Detection Limit
CDHS	California Department of Health Services
$CHBr_3$	Bromoform
$CHCl_3$	Chloroform
ClO_2	Chlorine dioxide
CMA	Chemical Manufacturer Association
CWSS	Community Water Supply Survey
DBCM	Dichlorobromomethane
DL	Detection Limit
DS	Distribution System
GW	Groundwater
GWSS	Groundwater Supply Survey
ICR	Information Collection Rule
JMM	James M. Montgomery Engineers, Inc.
MDL	Minimum Detection Limit
MGD	Million gallons per day
MRL	Minimum Reporting Limit
MWD	Metropolitan Water District of Southern California
NA	Not Applicable
ND	Not Detected
NOMS	National Organics Monitoring Survey
NORS	National Organics Reconnaissance Survey
O_3	Ozone
RWS	Rural Water Survey
SDS	Simulated Distribution System
SW	Surface Water
TOC	Total Organic Carbon
TOX	Total Organic Halide
TSD	Technical Services Division
WIDB	Water Industry Data Base

National Surveys

Eight surveys describing the national occurrence of chloroform in drinking water were presented in the 1992 occurrence document. Two of these, EPA's Groundwater Supply Survey and the Unregulated Contaminant Database, are not applicable to the occurrence of chloroform in distribution systems. The remaining six surveys are summarized in this section and the data are presented in Exhibit 4-1.

NORS reported a median concentration of 23 µg/L and a maximum detected level of 311 µg/L for chloroform. Since NORS was performed prior to the 1979 TTHM regulation which set the TTHM MCL at 100 µg/L, these results are expected to be higher than current levels for systems that disinfect and serve more than 10,000 people (Symons et al., 1975).

NOMS used two analytical methods to measure chloroform concentrations at the time of sampling and to measure the maximum chloroform formation due to the reaction of all the chlorine residual. During the three phases, chloroform was detected in 92 to 100 percent of the systems sampled. The median concentrations of the maximum chloroform formation in the three phases ranged from 22 to 54.5 µg/L. The maximum detected value was 540 µg/L. NOMS was conducted before the enactment of the 1979 TTHM regulation; therefore, these results are expected to be higher than current levels in systems that disinfect and serve populations of more than 10,000 people (Bull and Kopfler, 1990).

In the CWSS, 97 percent of the surface water supplies and 34 percent of the groundwater supplies detected chloroform. For the surface water supplies, the mean supplies detecting chlorform and the overall median were 90 and 60 µg/L, respectively. For the groundwater supplies, the mean samples detecting chlorform were 8.9 µg/L, and the overall median was below the minimum reporting limit (MRL) of 0.5 µg/L. The CWSS was conducted before the enactment of the 1979 TTHM regulation; therefore, these results may be higher than current levels in systems that disinfect and serve more than 10,000 people (Brass et al., 1981).

In the RWS, 82 percent of the surface water supplies and 17 percent of the groundwater supplies contained chloroform. For the surface water supplies, the mean of samples detecting chloroform and the overall median concentrations were 84 and 57 µg/L, respectively. For the groundwater supplies, the mean of the positives was 8.9 µg/L, and the overall median was below the MRL of 0.5 µg/L (Brass, 1981).

Clearwell effluent samples were analyzed for chloroform in the nationwide 35 Utility Study. The overall median for the quarterly sampling was 14 µg/L, with the medians of the individual quarters ranging

from 9.6 to 15 µg/L. The maximum detected value was 130 µg/L. Seventy-five percent of the data was below 33 µg/L for all four quarters (Krasner et al., 1989; EPA and AMWA, 1989). No samples were taken from the distribution system.

TSD compiled a data base using the results from its chlorination byproducts survey, which was conducted from October 1987 to March 1989 along with several other EPA DBP field studies. In the distribution system, the mean chloroform concentrations were 58.7 and 77.2 µg/L for plants serving above and below 10,000, respectively, with a 90th percentile concentration of 141.0 and 110.0 µg/L for 39 samples and 11 samples, respectively (EPA, 1992b). The groundwater systems serving less than 10,000 had a mean chloroform concentration of 3.6 µg/L for five observations, with a 90th percentile of 9.4 µg/L (EPA, 1992b).

Investigators collected samples in the fall 1989, winter 1991, and summer 1991 to observe seasonal differences for the AWWSCo project. THM analyses were conducted with EPA Method 501.1. Monitoring data from winter and summer 1991 were used to make statistical estimates. The mean and median chloroform concentrations in the distribution systems were 38.52 and 27.70 µg/L, respectively (Arora et al., 1994, 1997). Values ranged from BDL to 111.0 µg/L of chloroform. The 90th percentile concentration was 94.90 µg/L (Arora et al., 1994, 1997).

State Studies

Utah. Nieminski et al. (1993), from the Utah Department of Environmental Quality and the Utah Department of Health, studied DBPs in surface water treatment facilities in Utah. All plants used chlorine for primary and secondary disinfection. The study analyzed treated water for individual THMs, HAAs, and other halogenated DBPs. Samples were collected from 35 water utilities, including 14 serving more than 10,000 people and 21 serving fewer than 10,000 people. No significant differences in DBP occurrence were observed in large versus small utilities.

At the 14 larger systems, testing for DBPs was conducted quarterly to observe seasonal variations. These samples were collected at locations just prior to distribution and held for various periods to simulate conditions in the distribution system samples. At the small plants, samples were collected annually from the plant effluents and at the end of the distribution systems.

Samples were collected during three stages of DBP formation: immediately, after a period of time simulating distribution system detention time and after a seven-day holding time. The first set of samples

from each facility was preserved using 4.6 mg ammonium chloride to 40 mL water to quench the free chlorine. The second set of samples from 14 facilities was stored at a temperature and time simulating distribution system conditions to allow free chlorine to react with the precursors. At the end of this period, the chlorine residual was measured. The third set was held for seven days before quenching and was then analyzed. EPA Method 551 using a methyl-tert-butyl ether (MTBE) extraction was used rather than pentane to analyze individual THMs.

In a representative large plant, chloroform was the major THM compound detected, representing 77 percent THMs by weight. The authors provided EPA with analytical results of individual THM species from the plant effluents not published in the article. Exhibit 4-2 presents the mean, median, and range of plant effluent chloroform concentrations calculated from these data. It should be noted that concentrations in the distribution system were up to 40 percent greater than concentrations in the plant effluents.

Exhibit 4-2. Chloroform Concentration in Utah Plant Effluents (June 1990)

Population	Number of Systems	Chloroform (µg/L)		
		Range	Mean	Median
>10,000	14	10.2 – 39.5	22.2	17.2
<10,000	21	0.5 – 91.1	27.5	19.7

Source: Nieminski et al., 1993

Utah Pre-ICR Data. Data provided from a pre-ICR survey from the state of Utah were aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. Samples were taken from seven large surface water systems serving more than 100,000 persons. Water was collected from each treatment plant at several locations within the treatment process and in distribution system four to six times between October 1994 and September 1996.

The individual and total THM results from two average distribution system samples were analyzed. Monitoring results from all sampling events were used. Data points reporting below the detection limit (BDL) were converted to zeros and included in the analyses. The mean and median chloroform concentrations in the distribution systems were 23.0 and 22.4 µg/L, respectively. Values ranged from 2.7 to 69.8 µg/L of chloroform, and the 90th percentile concentration was 37.2 µg/L.

North Carolina. Drinking water from six North Carolina utilities was evaluated to assess the occurrence of DBPs in the state (Singer et al., 1995). Eight water treatment plants provide water for the six utilities. Because North Carolina has a relatively high TOC concentration in surface water sources of drinking water (average of 5 mg/L TOC in systems serving populations greater than 50,000), DBP levels were expected to be higher than levels reported in other studies. Source waters were characterized as relatively low in bromide ion levels. All plants used chlorine for disinfection; most plants applied chlorine to the settled water prior to filtration. Sample sets were collected three times from each utility between June 1991 and February 1992 to encompass high- and low-temperature periods. A total of 93 samples were collected from representative locations in the distribution systems and analyzed for four THMs, four HAAs, and other DBPs. The sampling locations were those used for THM compliance monitoring.

The average chloroform concentrations in the plant effluents and the distribution systems were 32 and 41 µg/L, respectively. The 42 distribution system samples had a median of 38 µg/L chloroform, with a range of 8 to 91 µg/L of chloroform. The average chloroform/TTHM ratio was 0.79, indicating that chloroform represented 79 percent of the TTHMs measured.

4.3.2 Bromodichloromethane

Bromodichloromethane occurs in public water systems that chlorinate water which contains humic and fulvic acids and bromide that can enter source waters through natural and anthropogenic means. Bromide enters source water from several water quality factors such as TOC, pH, and temperature affect the formation of bromodichloromethane. Surface water systems generally have higher frequencies of occurrence and higher concentrations of bromodichloromethane than groundwater systems since groundwater is a more protected source. Because residual chlorine is used in water distribution systems for disinfection purposes, the formation of bromodichloromethane continues throughout the distribution system (Stevens and Symons, 1977; Cooper et al., 1985; EPA, 1980).

Different treatment practices affect the formation of bromodichloromethane. The levels of bromodichloromethane can be lessened, but not eliminated, when chloramines are used to disinfect. The reduction is less, however, when chloramination involves a pre-chlorination step in which a free chlorine residual is maintained through a portion of the water treatment process prior to the addition of ammonia. Pre-ozonation followed by chloramination substantially controls the formation of bromodichloromethane, but ozonation prior to chlorination could increase the formation of bromodichloromethane. In addition, the use

of chlorine dioxide rather than chlorine has been shown to produce lower levels of bromodichloromethane (Cooper et al., 1985; EPA, 1980b).

National Surveys

Bromodichloromethane was detected in 98 percent of the systems sampled for NORS. The survey also reported a median concentration of 8 µg/L and a maximum detected value of 116 µg/L. NORS was performed prior to the 1979 TTHM regulation; therefore, these results are expected to be higher than current levels (Symons et al., 1975).

NOMS used two analytical methods to measure bromodichloromethane concentrations at the time of sampling and to measure the maximum bromodichloromethane concentrations due to the reaction of all the chlorine residual. Bromodichloromethane was detected during the three phases in more than 90 percent of the systems sampled. The median concentrations of the three phases ranged from 5.9 to 14 µg/L. The maximum detected value was 183 µg/L (Bull and Kopfler, 1990).

Ninety-four percent of the surface water samples collected for the CWSS detected bromodichloromethane. Bromodichloromethane was detected in thirty-three percent of the groundwater supplies . For the surface water supplies, the mean and the median were 12 and 6.8 µg/L, respectively. For the groundwater supplies, the mean was 5.8 µg/L, and the median was below the minimum reporting limit of 0.5 µg/L (Brass et al., 1981).

RWS detected bromodichloromethane in 76 percent of the surface water supplies and in 13 percent of the groundwater supplies. For these surface water supplies, the mean and the median concentrations were 17 and 11 µg/L, respectively. For the groundwater supplies detecting bromodichloromethane, the mean was 7.7 µg/L, and the overall median was below the minimum reporting limit of 0.5 µg/L (Brass, 1981).

In the nationwide 35 Utility Study, clearwell effluent samples were analyzed for bromodichloromethane. The overall median for all four quarters was 6.6 µg/L, with the medians of the individual quarters ranging from 4.1 to 10 µg/L. The maximum detected value was 82 µg/L. For all four quarters, 75 percent of the data was below 14 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

The TSD has compiled a data base from the results of its disinfection byproducts field studies. The studies included a chlorination byproducts survey, which was conducted from October 1987 to March 1989.

In the distribution system, the mean was 17.4 and 24.8 µg/L for plants serving above and below 10,000, respectively, with 90th percentile bromodichloromethane concentrations of 35.3 and 51.0 µg/L for 39 and 11 samples, respectively. The groundwater systems serving less than 10,000 had a mean bromodichloromethane concentration in distribution system samples of 2.2 µg/L for five observations, with a 90th percentile of 5.4 µg/L. For a single sample from groundwater systems serving more than 10,000, the concentrations at the plant and in the distribution system, were 0.2 and 0.4 µg/L, respectively (EPA, 1992b).

Investigators collected samples in fall 1989, winter 1991, and summer 1991 to observe seasonal differences for the AWWSCo study. The mean and median bromodichloromethane concentrations in the distribution systems were 11.9 and 9.25 µg/L, respectively (Arora et al., 1994, 1997). Concentrations ranged from BDL to 36.0 µg/L of bromodichloromethane, and the 90th percentile concentration was 24.8 µg/L (Arora et al., 1994, 1997). Exhibit 4-1, presented previously, summarizes these statistics.

State Studies

Utah. Nieminski et al. (1993) evaluated bromodichloromethane for the Utah Department of Environmental Quality and the Department of Health. Sampling procedures and analytical methods are the same as those discussed in Section 4.3.1. Bromodichloromethane was the second most prevalent THM, with 19 percent by weight in a single representative large plant. The authors provided analytical results of individual THM species from the plant effluent not published in the article. Exhibit 4-3 presents the mean, median, and range of plant effluent bromodichloromethane concentrations calculated from these data. It should be noted that concentrations in the distribution system were up to 40 percent greater than in the plant effluents.

Exhibit 4-3. Bromodichloromethane Concentration in Thirty-Five Utah Plant Effluents (June 1990)

Population	Number of Systems	Bromodichloromethane (µg/L)		
		Range	Mean	Median
>10,000	14	1.0 – 14.1	5.1	4.3
<10,000	21	0.1 – 20.0	5.0	4.7

Source: Nieminski et al., 1993

Utah Pre-ICR Data. Data provided from a pre-ICR survey from the state of Utah were aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. Samples were

taken from seven large surface water systems serving more than 100,000 persons. Each treatment plant was sampled at several locations in the treatment process and distribution system four to six times between October 1994 and September 1996.

The individual and total THM results from two average distribution system samples were analyzed. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median bromodichloromethane concentrations in the distribution systems were 6.7 and 6.7 µg/L, respectively. Values ranged from 1.3 to 16 µg/L, and the 90th percentile concentration was 10.9 µg/L.

North Carolina. Drinking water from six North Carolina utilities was evaluated to assess the occurrence of DBPs in the state (Singer et al., 1995). All plants used chlorine for disinfection. Sampling procedures and analytical methods are the same as those discussed in Section 4.3.1. The average bromodichloromethane concentrations in the plant effluents and the distribution systems were 7.2 and 8.8 µg/L, respectively. The 42 distribution system samples had a median of 8.1 µg/L, with a range of 3 to 21 µg/L of bromodichloromethane.

4.3.3 Dibromochloromethane

Dibromochloromethane occurs in public water systems that chlorinate water containing humic and fulvic acids and bromide that can enter source waters through natural and anthropogenic means. Water quality factors such as TOC, pH, and temperature affect the formation of dibromochloromethane. Surface water systems have higher frequencies of occurrence and higher concentrations of dibromochloromethane than groundwater systems because humic and fulvic material are contained primarily in surface water sources. Since chlorine is used as a residual in water distribution systems for disinfection purposes, the formation of dibromochloromethane continues throughout the distribution systems (Stevens and Symons, 1977; EPA, 1980; Cooper et al., 1985).

Different treatment practices affect the formation of dibromochloromethane in drinking water. The levels of dibromochloromethane can be lessened, although not eliminated, when chloramines are used to disinfect. The reduction is less, however, when chloramination involves a pre-chlorination step in which a free chlorine residual is maintained through a portion of the water treatment process prior to the addition of ammonia. Pre-ozonation followed by chloramination substantially controls the formation of dibromochloromethane, but ozonation prior to chlorination could increase the formation of

dibromochloromethane. In addition, the use of chlorine dioxide rather than chlorine is expected to produce lower levels of dibromochloromethane (EPA, 1980; Cooper et al., 1985).

National Surveys

Dibromochloromethane was detected in 90 percent of the systems sampled for the NORS study. This study also reported a median concentration of 2 µg/L and a maximum level of 100 µg/L for dibromochloromethane. NORS was performed prior to the 1979 TTHM regulation; therefore, these results could be higher than current levels (Symons et al., 1975).

NOMS used two analytical methods to measure dibromochloromethane concentrations at the time of sampling and to measure the maximum dibromochloromethane concentrations due to the reaction of all the chlorine residual. Dibromochloromethane was detected during all three phases in 73 percent of the systems sampled. The median concentrations of the three phases ranged from BDL to 3 µg/L. The maximum detected value was 280 µg/L (Bull and Kopfler, 1990).

In the CWSS, 67 percent of the surface water supplies and 34 percent of the groundwater supplies contained dibromochloromethane. For the surface water supplies, the mean supplies that detected dibromochloromethane and the overall median were 5.0 and 1.5 µg/L, respectively. For the groundwater supplies, the mean of the positives was 6.6 µg/L, and the overall median was below the minimum reporting limit of 0.5 µg/L (Brass et al., 1981).

In the RWS, 56 percent of the surface water supplies and 13 percent of the groundwater supplies detecting dibromochloromethane. For the surface water supplies containing dibromochloromethane, the mean of the positives and the overall median concentrations were 8.5 and 0.8 µg/L, respectively. For the groundwater supplies, the mean of the positives was 9.9 µg/L, and the overall median was below the minimum reporting limit of 0.5 µg/L (Brass, 1981)

In the nationwide 35 Utility Study, clearwell effluent samples were analyzed for dibromochloromethane. The median concentration for all four quarters was 3.6 µg/L, with the medians of the individual quarters ranging from 2.6 to 4.5 µg/L. The maximum value detected was 63 µg/L. For all four quarters, 75 percent of the data was below 9.1 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

Dibromochloromethane was sampled for finished water at the treatment plant and in the distribution system for the TSD survey. For surface water systems, the distribution system mean was 6.3 and 10.4 µg/L for plants serving more and less than 10,000 people, respectively, with the 90th percentile concentration of 17.3 and 35.0 µg/L for 39 samples and 11 samples, respectively. Groundwater systems serving less than 10,000 people had a mean dibromochloromethane concentration of 1.8 µg/L for five observations, with a 90th percentile of 3.6 µg/L. For groundwater systems serving more than 10,000 people, dibromochloromethane was not detected in single samples, based on a detection limit of 0.2 µg/L (EPA, 1992b).

Investigators collected samples in fall 1989, winter 1991, and summer 1991 to observe seasonal differences for the AWWSCo project. THM analyses were conducted with EPA Method 501.1. The mean and median dibromochloromethane concentrations detected in the distribution systems were 3.0 and 1.6 µg/L, respectively. The data ranged from BDL to 26.0 µg/L, while the 90th percentile concentration was 6.0 µg/L (Arora et al., 1994, 1997). Exhibit 4-1, presented previously, summarizes these statistics.

State Studies

Utah. Nieminski et al. (1993) evaluated dibromochloromethane concentrations for the Utah Department of Environmental Quality and the Department of Health. The authors also noted that dibromochloromethane comprised four percent by weight of all THMs detected in a representative large plant from Utah's 35 water utility study. Exhibit 4-4 provides the mean, median, and range of plant effluent dibromochloromethane concentrations calculated from these data. It should be noted that concentrations in the distribution system were approximately 40 percent greater than concentrations in the plant effluents.

Exhibit 4-4. Dibromochloromethane Concentration in Utah Plant Effluents (June 1990)

Population	Number of Systems	Dibromochloromethane (µg/L)		
		Range	Mean	Median
>10,000	14	0.5 – 10.0	2.0	0.8
<10,000	21	0.2 – 16.0	1.0	0.8

Source: Nieminski et al., 1993

Utah Pre-ICR Data. The individual and total THM results from two average distribution system samples were analyzed for the pre-ICR survey. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median dibromochloromethane concentrations in the distribution systems were 1.5 and 1.3 µg/L,

respectively. The data ranged from BDL to 5.9 µg/L of dibromochloromethane, and the 90th percentile concentration was 3.6 µg/L. Exhibit 4-1 presented previously, summarizes these statistics.

North Carolina. Distribution system samples collected between June 1991 and February 1992 were analyzed for dibromochloromethane and had very small quantities (i.e., less than two percent) of TTHMs (Singer et al., 1995). The authors attributed these low levels to the relatively low bromide ion concentrations in the source waters.

4.3.4 Bromoform

Bromoform occurs in public water supplies that chlorinate drinking water containing humic and fulvic acids and bromide that can enter source waters through natural and anthropogenic means. Bromide ion enters source water from geological formations and from saltwater intrusion. In addition, bromide ion enters the environment from the agricultural use of methyl bromide and the presence of ethylene dibromide in leaded gasoline. Several water quality factors including TOC, pH, and temperature affect the formation of bromoform. Surface water systems are expected to have higher frequencies of occurrence and higher concentrations of THMs than groundwater systems due to the presence of organic material; however, the levels of bromoform in groundwater supplies may be the same or higher than the levels in surface water supplies due to the potentially higher occurrence of bromide ion in certain groundwater sources. Because free chlorine is used as a residual disinfectant in water distribution systems for disinfection purposes, the formation of bromoform continues throughout the distribution system (Stevens and Symons, 1977; Cooper et al., 1985).

Different treatment practices affect the formation of bromoform in drinking water. The levels of bromoform can be lessened, although not eliminated, when chloramines are used to disinfect. The reduction is less, however, when chloramination involves a pre-chlorination step in which a free chlorine residual is maintained through a portion of the water treatment process prior to the addition of ammonia. Pre-ozonation followed by chloramines substantially controls the formation of bromoform, but ozonation prior to chlorination could increase the formation of bromoform. In addition, the use of chlorine dioxide is expected to produce lower levels of bromoform than chlorine (Cooper et al., 1985).

National Surveys

NORS reported a median concentration of BDL for bromoform. The maximum detected value was 92 µg/L. NORS was performed prior to the 1979 TTHM regulation; therefore, these results are likely to be higher than current levels (Symons et al., 1975).

In NOMS, the median concentrations of the three phases all ranged BDL of 0.3 µg/L. The maximum detected value was 280 µg/L. NOMS was conducted before the enactment of the 1979 TTHM regulation; therefore, these results could be higher than current levels (Bull and Kopfler, 1990).

In the CWSS, 13 percent of the surface water supplies and 26 percent of the groundwater supplies contained bromoform. For surface water supplies, the mean of supplies detecting bromoform and the overall median were 2.1 µg/L and less than 1.0 µg/L, respectively, in the distribution systems. For the groundwater supplies, the mean of the positives was 11 µg/L, and the overall median was below the minimum reporting limit of 0.5 µg/L (Brass et al., 1981).

In the RWS, 18 percent of the surface water supplies and 12 percent of the groundwater supplies detected bromoform. For distribution system samples from surface water supplies, the mean of the supplies that detected bromoform and the overall median concentrations were 8.7 µg/L and less than 0.5 µg/L, respectively. For distribution system samples from groundwater supplies, the mean of the positives was 12 µg/L, and the overall median was below the minimum reporting limit of 0.5 µg/L (Brass, 1981).

In the nationwide 35 Utility Study, clearwell effluent samples were analyzed for bromoform. Samples were taken for four quarters (spring, summer, and fall 1988 and winter 1989). The median for all four quarters was 0.6 µg/L, with the medians of the individual quarters ranging from 0.3 to 0.9 µg/L. The maximum value detected was 72 µg/L. Seventy-five percent of the data collected for the quarterly samples was below 2.8 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

The TSD reported that in the distribution system, the mean bromoform concentration was 0.8 and 1.4 µg/L for plants serving above and below 10,000, respectively, with the 90th percentile concentration of 3.1 and 5.1 µg/L for 39 samples and 11 samples, respectively. The groundwater systems serving less than 10,000 had a mean bromoform concentration of 2.3 µg/L for five observations (EPA, 1992b).

Investigators collected samples in fall 1989, winter 1991, and summer 1991 to observe seasonal differences in bromoform concentration for the AWWSCo study. THM analyses were conducted with EPA Method 501.1. Monitoring data from winter and summer 1991 were used to make statistical estimates. The mean and median bromoform concentrations in the distribution systems were 0.8 µg/L and BDL, respectively (Arora et al., 1994, 1997). The data ranged was from BDL to 17µg/L bromoform, and the 90th percentile concentration was BDL.

State Studies

Utah. Niemiński et al. (1993) reported limited data for bromoform. The sample procedures and analytical methods are the same as those described in Section 4.3.1. Bromoform was only detected in the systems serving more than 10,000 people. According to the authors, bromoform was only detected in trace levels, with a maximum detected value of 0.38 µg/L. This comprised one percent of the total THMs detected at a single representative plant.

Utah Pre-ICR Data. The individual and total THM results from two average distribution system samples were analyzed. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median bromoform concentrations in the distribution systems were 0.03 µg/L and BDL, respectively. The range was BDL to 1.20 µg/L of bromoform, and the 90th percentile concentration was BDL.

North Carolina. Distribution system samples collected between June 1991 and February 1992 were analyzed for bromoform and had very small quantities (i.e., less than two percent) of TTHMs (Singer et al., 1995). The authors attributed these low levels to the relatively low bromide ion concentrations in the source waters.

4.3.5 Total Trihalomethanes

National Surveys

NORS reported a mean and median TTHM concentration of 68 and 41 µg/L, respectively. The maximum detected value was 482 µg/L. NORS was performed prior to the 1979 TTHM regulation; therefore, these results are likely to be higher than current levels for systems that disinfect and serve more than 10,000 (Symons et al., 1975).

NOMS reported mean and median TTHM concentrations of 84 and 55 µg/L, respectively. The maximum detected value was 784 µg/L. NOMS was conducted before the enactment of the 1979 TTHM regulation, therefore, these results are likely to be higher than current levels in systems that disinfect and serve more than 10,000 (Bull and Kopfler, 1990).

The RWS reported mean and median TTHM concentrations of 36 and 18 µg/L, respectively. The maximum detected value was 313 µg/L. The RWS was conducted before the enactment of the 1979 TTHM regulation; therefore, these results are expected to be higher than current levels in systems that disinfect and serve more than 10,000 (Brass, 1981).

In the AWWARF National THMs Survey (McGuire and Meadows, 1988), 727 utilities serving more than 10,000 people reported TTHM data for one or more quarters for the years 1984 through 1986. Twenty-seven percent of the utilities used groundwater as their source of drinking water; the remaining 73 percent used surface water sources. The survey reflected that greater than 67 percent of the population was represented by water utilities serving more than 10,000 customers. The overall mean and median TTHM levels were 42 and 39 µg/L, respectively, with a maximum detected value of 360 µg/L.

In the nationwide 35 Utility Study, clearwell effluent samples were analyzed for the four THMs. The overall median TTHM for all four quarters was 36 µg/L, with the medians of the individual quarters ranging from 30 to 44 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

The AWWSCo study reported that the mean and median TTHM concentrations in the distribution systems were 55.1 and 43.0 µg/L, respectively (Arora et al., 1994, 1997). The data ranged from BDL to 142 µg/L of TTHM, and the 90th percentile concentration was 119 µg/L. Exhibit 4-1, presented previously, summarizes these statistics.

The most recent version of Water Stats (AWWA, 1997) provided TTHM data for 460 systems. The mean value was 43 µg/L. The median and 90th percentile were 44 and 72 µg/L, respectively.

State Compliance Monitoring

Community water systems that serve populations of 10,000 or more and use disinfectants are required to monitor their drinking water distribution system for TTHMs. The four individual THM species

are measured individually, added together, and reported to the state. Many states only track the total of the four for compliance purposes.

In surface water systems, samples are collected quarterly from one or more points in the distribution system. Groundwater systems, that serve populations of more than 10,000 and use a disinfectant, initially collect four quarterly samples, however, these systems could be permitted to reduce sampling to one sample per year if the measured sample is less than the maximum TTHM potential. EPA requested information about the results of their TTHM monitoring data for the period between January 1, 1994, and December 31, 1996, from nine state agencies. EPA also asked these state agencies to provide available data on concentrations of individual THMs (i.e., chloroform, bromodichloromethane, dibromochloromethane, and bromoform), disinfectant residuals, total and individual HAAs, TOC in raw and finished water, and bromide ion in raw water. These data were not readily available. However, five states submitted TTHM data for systems that serve fewer than 10,000 and that disinfect. Non-detect values were calculated as zero for the averages, which is consistent with the method of determining compliance with the MCL.

Massachusetts. The state of Massachusetts compiled quarterly TTHM data from groundwater and surface water systems for the period between January 1994 and December 1996. Average TTHM concentrations and median values were calculated for systems serving populations of less than and greater than 10,000 persons. Exhibit 4-5 presents the concentrations.

Exhibit 4-5. Summary of Total Trihalomethane Concentrations from Public Water Systems in Massachusetts (Jan. 1994–Dec. 1996)

Population Served	Number of Systems	Number of Samples	TTHM (µg/L)		
			Mean	Median	Range
Surface Water					
≥10,000	21		54	50	1–502
<10,000	3		41	37	1–75
Groundwater (no systems serving <10,000)					
>10,000	8		46	44	BDL–207
Surface Water and Groundwater (mixed)					
>10,000	19		50	45	BDL–524
<10,000	2		28	12	1–104

Source: Massachusetts compliance data

Missouri. The State of Missouri compiled quarterly TTHM data from groundwater and surface water systems for 1996 and 1997. Exhibit 4-6 provides average TTHM concentrations and median values calculated for systems serving populations of less than and greater than 10,000 persons. Data from four systems that purchase water were provided but were not included in this summary.

Exhibit 4-6. Summary of Total Trihalomethane Concentrations from Public Water Systems in Missouri (1996–1997)

Population Served	Number of Systems	TTHM (µg/L)		
		Mean	Median	Range
Surface Water				
>10,000	11	44	37	1–165
<10,000	81	118	102	BDL–541
Groundwater				
>10,000	14	15	3	1–134
<10,000	1	49	–	–

Source: Missouri compliance data

New Jersey. The New Jersey Department of Environmental Protection provided compliance monitoring data for average TTHM concentrations at public water systems for 1994–1996. Exhibit 4-7 presents the average and median concentrations.

Exhibit 4-7. Summary of Total Trihalomethane Concentrations from New Jersey Public Water Systems (1994–1996)

Population Served	Number of Systems	TTHM (µg/L)		
		Mean	Median	Range
Surface Water				
>10,000	23	42	39	1–87
<10,000	5	48	27	1–89
Groundwater				
>10,000	86	9	3	BDL–70
<10,000	37	7	3	BDL–48

Source: New Jersey compliance data

Oregon. TTHM data for Oregon's public water systems include only systems serving more than 10,000 persons. Quarterly average TTHM concentrations for each water system were provided for a three-year period (1994–1996). Exhibit 4-8 presents the range of average values reported for each system and the overall average TTHM value that was calculated for groundwater and surface water systems.

Exhibit 4-8. Total Trihalomethane Concentrations from Public Water Systems in Oregon Serving More Than 10,000 Persons (1994–1996)

Source Water	Number of Systems	TTHM (µg/L)		
		Mean	Median	Range
Surface Water	27	29	26	7 – 76
Groundwater	7	16	16	5 – 31

Source: Oregon compliance data

Pennsylvania. The state of Pennsylvania provided compliance monitoring data characterizing TTHM concentrations in 223 surface water, purchased water, and groundwater treatment systems between 1994 and 1996. Samples were collected quarterly. The data set was limited to samples collected in the distribution system. Data were aggregated by source and the population being served by the public water supply. Data from systems using purchased water were included with surface water systems and aggregated by population served. Exhibit 4-9 presents the mean, median, and ranges of TTHM by water source for systems serving more than and less than 10,000 persons.

Exhibit 4-9. Pennsylvania Compliance Monitoring Data for Total Trihalomethanes

Population Served	Number of Systems	Number of Samples	TTHM (µg/L)		
			Mean	Median	Range
Surface Water					
>10,000[a]	119	7,345	40	42	1 – 113
<10,000[b]	54	1,676	46	45	BDL – 162
Groundwater					
>10,000	25	985	8	5	BDL – 41
<10,000	25	306	14	2	BDL – 159

Source: Pennsylvania compliance data

[a] 24 systems using purchased surface water are included.
[b] 39 systems using purchased surface water are included.

Texas. The state of Texas provided compliance monitoring data characterizing TTHM concentrations in 227 surface water, purchased water, and groundwater treatment systems between the years 1994 and 1996. Samples were collected quarterly. Data were aggregated by source and the population being served by the public water supply. In the analysis, 47 systems using purchased water were considered surface water systems. Systems using groundwater reported data for actual TTHM or potential TTHM values. Exhibit 4-10 provides the mean, median, and range by water source for systems serving more than and less than 10,000 persons.

Exhibit 4-10. Texas Compliance Monitoring Data for Total Trihalomethanes

Population Served	Number of Systems	Number of Samples	TTHM (µg/L)		
			Mean	Median	Range
Surface Water					
>10,000[a]	114	2,521	41	37	8 – 135
Groundwater[a]					
>10,000[b]	102	1,427	24	15	BDL – 121
<10,000[c]	11	32	26	19	BDL – 120

Source: Texas compliance data

a. This class includes 48 systems using purchased surface water.
b. Forty-six systems reported formation potentials.
c. Seven systems reported formation potentials.

State Studies

North Carolina. The TTHM samples were quenched with ammonium chloride at collection and analyzed by liquid-liquid or pentane extraction and capillary column gas chromatography/electron capture detection (GC/ECD) (Singer et al., 1995). The DBP analytes (i.e., THMs, haloacetonitriles, haloketones, and chloropicrin) were extracted into pentane after saturation with sodium sulfate. THM data resulted in a mean of 40 µg/L and a median of 35 µg/L for plant effluent. The distribution system mean and median were 51 and 46 µg/L, respectively. TTHMs in these six utilities constituted an average of 15 percent of the total organic halides (TOX) concentration, the same percentage as HAA5. The mean TTHM concentration in North Carolina utilities serving more than 10,000 from 1987 through 1989 was reported as 64 µg/L (Haws and Singer, 1989).

Utah. The sampling and analytical methods used were the same as those discussed in Section 4.3.1 (Nieminski et al., 1993). Exhibit 4-11 provides the ranges, means, and medians of plant effluent and distribution system TTHM concentrations for samples collected in June 1990.

Exhibit 4-11. Trihalomethane Concentration in Utah Water Treatment Plants Using Surface Water (June 1990)

System Size	Number of Samples	TTHM (µg/L)		
		Range	Mean	Median
Plant Effluent				
All Systems	35	1.4 – 97.2	31.3	22.4
>10,000	14	16.2 – 59.1	28.8	21.6
<10,000	21	1.4 – 97.2	33.0	25.4
Distribution System				
All Systems	35	2.3 – 215.4	60.0	82.1
>10,000*	14	28.8 – 81.5	50.7	51.8
<10,000	21	2.3 – 215.4	66.2	62.9

Source: Nieminski et al., 1993

* SDS samples

TTHMs accounted for 64 percent by weight of all Utah's identified DBPs. In June 1990, the average TTHM concentration in the 35 plant effluents was 31.3 µg/L, while the average TTHM concentration in the distribution system was 60.0 µg/L. Seasonal variations at many of the plants were also summarized. Mean and median values were calculated from data provided for 14 plants. Exhibit 4-12 provides seasonal ranges.

Exhibit 4-12. Seasonal Total Trihalomethane Variation in Utah Plant Effluents

Date	Number of Samples	TTHM (µg/L)		
		Range	Mean	Median
June 1990	14	16.2 – 59.1	28.8	21.6
September 1990	14	11.0 – 55.1	30.9	32.4
November 1990	11	7.0 – 37.5	20.9	15.9
March 1991	8	7.7 – 33.4	16.6	15.9

Source: Nieminski et al., 1993

Utah Pre-ICR Data. Data provided from a pre-ICR survey from the State of Utah were aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. Samples were taken from seven large surface water systems serving more than 100,000 persons. Each treatment plant was sampled at several locations in the treatment process and distribution system four to six times between October 1994 and September 1996.

The individual and total THM results from two average distribution system samples were analyzed. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median TTHM concentrations in the distribution systems were 31.3 and 32.1 µg/L respectively. The range was 5.20 to 87.4 µg/L TTHM, and the 90th percentile concentration was 46.8 µg/L. Exhibit 4-1, presented previously, summarizes these statistics.

4.3.6 Monochloroacetic Acid

Monochloroacetic acid occurs in drinking water as a byproduct of disinfection. Monochloroacetic acid has been found to occur as a disinfection byproduct in public water systems that chlorinate water containing natural organic material. Similar to other chlorination byproducts, such as THMs, monochloroacetic acid levels can be lessened, although not eliminated, when chloramines are used to disinfect. The reduction is less, however, when chloramination involves a pre-chlorination step in which a free chlorine residual is maintained through a portion of the water treatment process prior to the addition of ammonia. In industry, monochloroacetic acid is used as a herbicide, in the synthesis of synthetic caffeine and as a preservative.

National Surveys

The AWWSCo study included monochloroacetic acid analysis. Monitoring data from winter and summer 1991 were used to make statistical estimates. The mean and median monochloroacetic acid concentrations in the distribution systems were 1.38 and 1.19 µg/L, respectively (Arora et al., 1994, 1997). The data ranged from BDL to 3.98 µg/L and the 90th percentile concentration was reported as 2.65 µg/L. Exhibit 4-1, presented previously, summarizes these statistics.

State Studies

Utah Pre-ICR Data. Data provided from a pre-ICR survey from the state of Utah were aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. The individual

and total HAA results came from two average distribution system samples. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median monochloroacetic acid concentrations in the distribution systems were 0.08 µg/L and BDL, respectively. The data ranged from BDL to 3.80 µg/L monochloroacetic acid, and the 90th percentile concentration was BDL.

4.3.7 Dichloroacetic Acid

Dichloroacetic acid occurs in drinking water as a byproduct of disinfection. In industry, dichloroacetic acid is used as a chemical intermediate and in the manufacture of pharmaceuticals and has been used as an agricultural fungicide, and as a topical astringent. The medical uses of dichloroacetic acid include experimental treatment of diabetes and hypercholesterolemia and it is being investigated for possible use as a hypoglycemic, hypolactemic, and hypolipidemic agent (Merck Index, 1989).

Dichloroacetic acid occurs as a disinfection byproduct in public water systems that chlorinate water containing humic and fulvic acids. Although dichloroacetic acid levels can be lessened, when chloramines are used to disinfect byproduct formation is not controlled. The reduction is less, however, when chloramination involves a pre-chlorination step in which a free chlorine residual is maintained through a portion of the water treatment process prior to the addition of ammonia.

National Surveys

In the nationwide 35 Utility Study, clearwell effluent samples were analyzed for dichloroacetic acid. The overall median for the quarterly sampling was 6.4 µg/L, with the medians of the individual quarters ranging from 5.0 to 7.3 µg/L. The maximum detected value was 46 µg/L. The detection limit for the survey was 0.6 µg/L. Overall, 75 percent of the data was detected below 12 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

Dichloroacetic acid was sampled in finished water at the treatment plant and in the distribution system for the TSD survey. For surface water systems, the mean concentration in finished water for systems serving more than and less than 10,000 people was 20.7 and 21.8 µg/L, respectively, with the 90th percentile of 33.4 and 50.0 µg/L for 42 samples and 20 samples, respectively. In the distribution system, the mean was 22.1 and 27.7 µg/L for plants serving more than and less than 10,000, respectively, with a 90th percentile concentration of 48.0 and 41.0 µg/L for 39 samples and 11 samples, respectively. The groundwater systems serving less than 10,000 had a mean dichloroacetic acid concentration in finished water samples and

distribution system samples of 2.7 and 1.9 µg/L, respectively, for seven and five observations, with a 90th percentile of 12.5 and 4.7 µg/L, respectively. For systems serving more than 10,000, dichloroacetic acid was not detected in single samples taken at the plant and from the distribution system based on a detection limit of 0.4 µg/L (EPA, 1992b).

HAA analyses were conducted with EPA Method 552 for the AWWSCo study. Monitoring data from winter and summer 1991 were used to make statistical estimates. The mean and median dichloroacetic acid concentrations in the distribution systems were 17.3 and 17.0 µg/L, respectively (Arora et al., 1994, 1997). The date ranged was from BDL to 45.2 µg/L for monochloroacetic acid, and the 90th percentile concentration was 35.6 µg/L (Arora et al., 1994, 1997).

State Studies

North Carolina. Drinking water from six North Carolina utilities was evaluated to assess the occurrence of DBPs in the state (Singer et al., 1995). Dichloroacetic acid was measured in 24 plant effluent samples and 42 distribution system samples in the six utilities. Exhibit 4-13 presents the means, medians, and ranges for the study.

Exhibit 4-13. Dichloroacetic Acid Concentrations from Six North Carolina Surface Water Systems

Sampling Location	Number of Samples	Dichloroacetic Acid (µg/L)		
		Range	Mean	Median
Plant Effluent	24	6 – 44	25	24
Distribution System	42	9 – 60	30	28

Source: Singer et al., 1995

Utah Pre-ICR Data. The mean and median concentrations for dichloroacetic acid were reported as 17.28 and 17.00 µg/L, respectively. The 75th percentile concentration was reported at 24.24 µg/L, while the 90th percentile concentration was 35.59 µg/L. The data ranged from BDL to 45.23 µg/L.

4.3.8 Trichloroacetic Acid

Trichloroacetic acid, a major byproduct of chlorinated drinking water, is used as a pre-emergence herbicide and a reagent for synthetic medicinal products. In the laboratory, it has been used to precipitate

proteins. Trichloroacetic acid is also used in the medical field as a peeling agent for damaged skin, cervical dysplasia, and tattoo removal (Pringle et al., 1975; Merck Index, 1990).

Trichloroacetic acid occurs in public water systems that chlorinate water containing humic and fulvic acids. Similar to other chlorination byproducts, such as the THMs, trichloroacetic acid levels can be lessened, although not eliminated, when chloramines are used to disinfect. The reduction is less, however, when chloramination involves a pre-chlorination step in which a free chlorine residual is maintained through a portion of the water treatment process prior to the addition of ammonia. In addition, the formation of trichloroacetic acid is lessened substantially at high pH levels (i.e., approximately pH 9) (Stevens et al., 1989).

National Surveys

In the nationwide 35 Utility Study, clearwell effluent samples were analyzed for trichloroacetic acid. The overall median for the four quarters was 5.5 µg/L, with the medians of the individual quarters ranging from 4.1 to 5.8 µg/L. The detection limit for the survey was 0.6 µg/L. Seventy-five percent of the data was reported below 15.3 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

The TSD survey sampled for trichloroacetic acid in finished water at the treatment plant and in the distribution system. For surface water systems, the mean concentration in finished water for systems serving more than and less than 10,000 people was 14.4 and 14.8 µg/L, respectively, with the 90th percentile of 28.7 and 30.4 µg/L for 42 samples and 20 samples, respectively. In the distribution system, the mean was 17.0 and 16.6 µg/L for plants serving more than and less than 10,000 people, respectively, with the 90th percentile concentration of 30.6 and 28.9 µg/L for 39 samples and 11 samples, respectively. The groundwater systems serving less than 10,000 people had a mean trichloroacetic acid concentration in finished water samples and distribution system samples of 1.9 and 1.1 µg/L, respectively, for seven observations and five observations, with the 90th percentile of 10.7 and 4.2 µg/L. For systems serving more than 10,000 people, trichloroacetic acid was not detected in single samples taken at the plant and from the distribution system based on a detection limit of 0.4 µg/L (EPA, 1992b).

- The AWWSCo study reported mean and median trichloroacetic acid concentrations in the distribution systems of 19.79 and 16.74 µg/L, respectively (Arora et al., 1994, 1997). The data ranged was from BDL to 83.07 µg/L of trichloroacetic acid with a 90th percentile concentration of 37.93 µg/L (Arora et al., 1994, 1997). Exhibit 4-1, presented previously, summarizes these statistics.

State Studies

North Carolina. Drinking water from six North Carolina utilities was evaluated to assess the occurrence of DBPs in the state (Singer et al., 1995). Samples were collected and analyzed as described in Section 4.3.7. In the distribution system, the mean and median trichloroacetic acid concentrations were 36 and 37 µg/L, respectively. The 42 distribution system samples ranged from 12 to 79 µg/L of trichloroacetic acid. Exhibit 4-14 presents the means, medians, and ranges for the plant effluents and distribution systems.

Exhibit 4-14. Trichloroacetic Acid Concentrations from Six North Carolina Surface Water Systems

Sampling Location	Number of Samples	Trichloroacetic Acid (µg/L)		
		Range	Mean	Median
Plant Effluent	24	8 – 58	28	28
Distribution System	42	12 – 79	36	37

Source: Singer et al., 1995

Utah Pre-ICR Data. The mean and median trichloroacetic acid concentrations in the distribution systems were 14.2 and 14.5 µg/L, respectively. The data ranged from BDL to 32.2 µg/L of trichloroacetic acid, and the 90th percentile concentration was 25.3 µg/L.

4.3.9 Monobromoacetic Acid

National Surveys

The AWWSCo study reported mean and median monobromoacetic acid concentrations in the distribution systems of 0.77 and 0.40 µg/L, respectively (Arora et al., 1994, 1997). The data ranged from BDL to 4.55 µg/L of monobromoacetic acid, and the 90th percentile concentration was 2.48 µg/L (Arora et al., 1994, 1997). Exhibit 4-1, presented previously, summarizes these statistics.

State Studies

Utah Pre-ICR Data. The mean and median monobromoacetic acid concentrations in the distribution systems were 0.10 µg/L and BDL, respectively. The data ranged from BDL to 2.40 µg/L of monobromoacetic acid, and the 90th percentile concentration was reported as BDL. Exhibit 4-1, presented previously, summarizes these statistics.

4.3.10 Dibromoacetic Acid

National Surveys

The AWWSCo study reported mean and median dibromoacetic acid (DBAA) concentrations in the distribution systems of 1.41 and 0.58 µg/L, respectively. The data ranged from BDL to 20.0 µg/L of DBAA, and the 90th percentile concentration was 2.16 µg/L (Arora et al., 1994, 1997).

State Studies

Utah Pre-ICR Data. The individual and total HAA results came from two average distribution system samples. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median dibromoacetic acid concentrations in the distribution systems were 0.71 µg/L and BDL, respectively. The data ranged from BDL to 4.70 µg/L of DBAA, and the 90th percentile concentration was 2.55 µg/L. Exhibit 4-1, presented previously, summarizes these statistics.

4.3.11 Haloacetic Acids 5

HAAs occur in drinking water as byproducts of disinfection along with the presence of chlorine or bromide ions in the system. HAA formation tends to decrease with increasing pH, the opposite formation from THMs (Singer, et al., 1996). There are nine chloride and bromide containing HAAs: however, occurrence data are only provided for five of these compounds, including monochloroacetic acid, dichloroacetic acid, trichloracetic acid, monobromoacetic acid, and dibromoacetic acid. HAA5 refer to the sum of the concentrations of these five compounds.

Summers et al. (1997) reported that HAA5 formation decreased when chlorination was moved further downstream in the coagulation, flocculation, and sedimentation process. This allowed for additional natural organic matter removal before chlorine could react to form DBPs. Similar to other chlorinated byproducts, such as THMs, HAA5 can be lessened when chloramines are used to disinfect. Known effects of HAA5 on humans include reduced blood glucose, reduced plasma levels, reduced plasma cholesterol levels, and reduced triglyceride levels (EPA, 1994b).

National Surveys

In the nationwide 35 Utility Study, clearwell effluent samples were analyzed for HAAs. The overall median for all four quarters was 5.5 µg/L, with the medians of the individual quarters ranging from 4.1 to

5.5 µg/L. The detection limit for the survey was 0.6 µg/L. The study reported that 75 percent of the data was below 15.3 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

The AWWSCo study reported that the mean and median HAA5 concentrations in the distribution systems were 41.3 and 37.0 µg/L, respectively. The data ranged was from 4.7 to 134.3 µg/L for HAA5 and the 90th percentile concentration was 72.3 µg/L (Arora et al., 1994, 1997). Exhibit 4-1 summarizes these statistics.

The most recent version of Water Stats (AWAA, 1997) provide HAA5 data for 146 systems. The mean value was 28.1 µg/L. The median value was 25 µg/L. The values ranged from BDL to 91 µg/L.

State Studies

Missouri. The only state to provide HAA5 data was Missouri. Exhibit 4-15 presents HAA5 data by source water for systems serving greater than 10,000 and fewer than 10,000 people, respectively. In January 1997, the State of Missouri Department of Natural Resources initiated quarterly monitoring of HAA5 at all surface water systems and groundwater systems serving 10,000 or more people. Results from the first two quarters of data are presented in Exhibit 4-15. The means and medians ranged from 32 to 46 µg/L and 29 to 42 µg/L, respectively. As expected, the concentrations of HAA5 in groundwater systems serving greater than 10,000 people were substantially lower. Limited data was available for HAA5 in small systems. In surface water systems serving over 10,000 people, the state of Missouri had mean and median levels of HAA5 of 28 and 24 µg/L, respectively. The state of Missouri also reported HAA5 data from surface water systems serving fewer than 10,000 people. For 81 public water systems, the mean and median HAA5 concentrations were 88 and 80 µg/L HAA5 respectively. The range of HAA5 values for these 81 systems was 0.1 to 284 µg/L. The high levels are attributed to high source water TOC levels and the fact that these small systems are not required to comply with the TTHM MCL.

Exhibit 4-15. Haloacetic Acids 5 Concentrations in Missouri Water Treatment Plants (1/97–6/97)

System Type and Size	Number of Systems	HAA5 (µg/L)			
		Range	Mean	Median	90th Percentile
Surface Water Systems >10,000	11	0.1 – 95.8	28	24	63
Surface Water Systems <10,000	81	0.1 – 284	88	80	165
Groundwater Systems >10,000	14	0.1 – 43.2	7	3	17
All Systems	106	0.1 – 284	69	56	150

Source: Missouri compliance data

North Carolina. Samples were collected and analyzed as described in Section 4.3.7 (Singer et al., 1995). A total of 93 samples were analyzed for four HAAs: chloroacetic acid, dichloroacetic acid, trichloroacetic acid and bromoacetic acid. Dibromoacetic acid was not analyzed because it was assumed that it would not be formed to any significant degree with the low-bromide ion source waters. This was indeed the case with bromoacetic acid, whose concentrations were barely above the detection limits in all samples analyzed.

Exhibit 4-16 presents results from the HAA analyses. The authors noted that the mean and median dichloroacetic acid and trichloroacetic acid concentrations were almost as high as the corresponding chloroform concentrations, unlike other studies in other regions where HAAs were approximately half of the TTHM concentrations. The HAAs, consisting mostly of dichloroacetic acid and trichloroacetic acid, comprised an average of 15 percent of the TOX on a chlorine equivalent basis, the same percentage as TTHMs.

Exhibit 4-16. Haloacetic Acids Concentrations from Eight North Carolina Surface Water Plants

Sampling Location	Number of Samples	HAA4 (µg/L)		
		Range	Mean	Median
Plant Effluent	24	39 – 80	63	64
Distribution System	42	36 – 106	77	81

Source: Singer et al., 1995

Utah. Nieminski et al. (1993) studied DBPs, including HAAs, in water treatment facilities in Utah. Samples were collected from 35 water utilities, 14 of which serve at least 10,000 people and 21 that serve less than 10,000 people. About 30 percent of all DBPs detected in Utah waters were HAAs. The HAAs were analyzed using a micro extraction method similar to that developed by Metropolitan Water District (now Standard Methods) and EPA Method 552.

HAA5 concentrations were reported for the mean, median, and 25th and 75th percentiles. The mean plant concentration for the 35 utilities was 17.3 µg/L, with a median concentration of 13.2 µg/L of HAA5. The 25th and 75th percentiles were 7.13 and 22.60 µg/L HAA5, respectively. The authors noted that monochloroacetic acid and trichloroacetic acid were the major HAAs detected in the distribution systems. HAA concentrations reported were somewhat lower than nationwide medians, and the authors attributed reduced medians to the lower TOC in Utah waters. The statistics were calculated from data provided by the authors for plant effluent and distribution systems and are presented in Exhibit 4-17.

The authors also noted that although seasonal variation was seen in the results from the 14 large plants, no season was significantly lower or higher than the other seasons. Exhibit 4-18 presents data from the seasonal analysis.

Exhibit 4-17. Haloacetic Acids 5 Concentrations from Thirty-Five Utah Surface Water Systems

System Size	Number of Systems	HAA5 (µg/L)		
		Range	Mean	Median
Plant Effluent				
All Systems	35	0.3 – 60.6	17.3	13.2
Medium and Large Systems	14	5.0 – 24.3	12.6	11.3
Small Systems	21	0.3 – 60.6	20.5	14.6
Distribution System				
All Systems	35	1.0 – 89.8	29.8	20.8
Medium and Large Systems	14	8.1 – 51.5	18.6	17.7
Small Systems	21	1.0 – 89.8	37.3	42.2

Source: Nieminski et al., 1993

Exhibit 4-18. Seasonal Analysis of Haloacetic Acids 5 Concentrations from Thirty-Five Utah Surface Water Systems' Plant Effluents

Date	HAA5 (µg/L)		
	Range	Mean	Median
June 1990	6.9 – 24.3	12.6	11.3
September 1990	6.9 – 42.1	21.1	15.5
November 1990	2.1 – 22.0	11.9	14.3
March 1991	4.0 – 18.8	11.9	12.9

Source: Nieminski et al., 1993

The mean and median values were calculated from the data presented in the report.

Utah Pre-ICR Data. Data provided from a pre-ICR survey from the state of Utah were aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. Samples were taken from seven large surface water systems serving more than 100,000 persons. Each treatment plant was sampled at several locations in the treatment process and distribution system four to six times between October 1994 and September 1996.

The individual and HAA5 results came from two average distribution system samples. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median HAA5 concentrations in the distribution systems were 25.87 and 47.1 µg/L, respectively. The range was from 1.5 to 57.4 µg/L of HAA5, and the 90th percentile concentration was 47.2 µg/L.

4.3.12 Chloral Hydrate

Chloral hydrate, also known as trichloroacetaldehyde monohydrate, is used as a hypnotic or sedative drug in humans and in the manufacture of DDT. Chloral hydrate occurs as a disinfection byproduct in public water systems that chlorinate water containing humic and fulvic acids. Ozonation prior to chlorination increases the levels of chloral hydrate compared to chlorine disinfection alone. In addition, pre-ozonation followed by chloramines produces levels of chloral hydrate below that of chlorine disinfection (Jacangelo et al., 1989; Merck Index, 1989).

National Surveys

In the 1992 occurrence document, two studies described the occurrence of chloral hydrate in the nation's drinking water. In the 35 Utility Study, clearwell effluent samples were analyzed for chloral hydrate for 4 quarters (spring, summer, and fall 1988 and winter 1989). The overall median for the quarterly samples was 2.1 µg/L, with the medians of the individual quarters ranging from 1.7 to 3.0 µg/L. The maximum detected value was 22 µg/L. For all four quarters, 75 percent of the chloral hydrate levels were below 4.1 µg/L. The detection limits for the survey were 0.02 µg/L in the first quarter and 0.1 µg/L thereafter (Krasner et al., 1989; EPA and AMWA, 1989).

In the TSD survey, finished waters at the treatment plant and distribution system waters were sampled and tested for chloral hydrate. Concentrations ranged from less than 0.2 to 25 µg/L, with a mean of 5.0 µg/L and a median of 2.5 µg/L for the 67 finished water samples. For the 53 distribution system samples, concentrations ranged from less than 0.2 to 30 µg/L; with a mean and median of 7.8 and 4.4 µg/L, respectively (EPA, 1992b).

Chloral hydrate analyses were conducted with EPA Method 551 for the AWWSCo study. The mean and median chloral hydrate concentrations in the distribution systems were 6.3 and 4.4 µg/L, respectively (Arora et al., 1994, 1997). The data ranged was from BDL to 27.3 µg/L of chloral hydrate, and the 90th percentile concentration was 14.1 µg/L. Exhibit 4-1, presented previously, summarizes these statistics.

State Studies

Utah. Nieminski et al. (1993) studied DBPs in water treatment facilities in Utah. Samples were collected from six large water utilities in Utah (serving more than 10,000 people). The first set of samples from each facility was preserved using 4.6 mg ammonium chloride to 40 mL water to quench the free chlorine. The second set of samples from all facilities was stored at a temperature and time simulating distribution system conditions to allow free chlorine to react with the precursors. At the end of this period, the chlorine residual was measured. The third set was held for seven days before quenching and then was analyzed. Chloral hydrate concentrations between 0.7 and 3.8 µg/L were reported from the four samples collected in June 1990.

Utah Pre-ICR Data. The chloral hydrate results came from two average distribution system samples. Monitoring results from all sampling events were used. Data points reporting below the detection limit were converted to zeros and included in the analyses. The mean and median chloral hydrate

concentrations in the distribution systems were 3.4 and 3.4 µg/L, respectively. The data ranged from BDL to 8.6 µg/L of chloral hydrate, and the 90th percentile concentration was 6.3 µg/L. Exhibit 4-1, presented previously, summarizes these statistics.

4.3.13 Bromate Ion

Bromate ion and organobromine compounds occur in public water systems that treat raw water containing bromide ion and ozone. Bromide ion occurs in raw waters due to both natural and anthropogenic sources. Bromide ion can be oxidized to bromate ion or hypobromous acid; however, in the presence of excess ozone, bromate ion is the principal product (von Gunten and Hoigne, 1994). In laboratory studies, the rate and extent of bromate ion formation depend on the ozone concentration used in disinfection, pH, and contact time. Bromate ion can also be produced during chlorination reactions. However, its formation is expected to be limited under conditions normally found in drinking water (Glaze, 1988; Singer, 1988; Cooper et al., 1985). Bromate has been found as a contaminant in sodium hypochlorite and can therefore also be found in low bromide waters treated with sodium hypochlorite.

A 1995 review of the conditions for bromate ion formation was conducted by Siddiqui et al. (1995) to summarize the global occurrence of bromate ion, methods for quantification, chemical formation pathways, and treatment conditions conducive to bromate ion formation. This review also focused on identifying methods of minimizing bromate ion formation in drinking water supplies. Bromate ion forms through reactions with molecular ozone, which contributes 30 to 80 percent of the overall bromate ion formation in waters containing natural organic matter. Siddiqui referenced three articles that reported normal water treatment conditions bromate ion can form in ranges from 1 to 150 µg/L during the ozonation of natural waters containing bromide ion (Krasner et al.; Siddiqui and Amy; and Daniel, et al.). Section 3.1.2 summarizes the occurrence of bromide ion. Although bromate ion occurrence data are limited by analytical detection limits and no comprehensive surveys have been conducted, the data identified are presented below (Singer, 1998).

National Surveys

In 1990, the University of North Carolina conducted AWWARF sponsored pilot-plant and full-scale studies at 10 utilities that treat surface and groundwater with ozone to produce drinking water (Krasner et al., 1989; Glaze, 1993). The purpose was to survey ozonation facilities to determine the occurrence and control of DBPs, including aldehydes, bromate ion, and chlorinated DBPs.

The 10 full-scale utilities surveyed provided a matrix of bromide ion levels, ozone dosages, pH levels, and ammonia concentrations. Bromate ion was analyzed by ion chromatography. Over the course of the study, the minimum reporting level (MRL) was lowered from 10 to 5 µg/L. For four of the six utilities with background levels of bromide ion of at least 0.06 mg/L, bromate ion was not detected above the MRL value at the ozone dosages investigated. For the other two low-bromide ion detection was inconsistent over space and time. Values ranged from 5 to 8 µg/L (Krasner et al., 1989).

Bromate ion concentrations of 5 to 20 µg/L were observed when ozonation (0.94 to 9.3 mg/L) was conducted at ambient pH (5.6 to 9.9), bromide ion (less than 0.01 to 0.33), and TOC (0.9 to 26 mg/L) levels. Ozone dose was determined to be critical in bromate ion formation, although appropriate staging of ozone through two to three contractors can minimize ozone residual and bromate ion formation while still meeting concentration time (CT) criteria. Ozone oxidizes bromide ion to hypobromous acid that dissociates into hypbromite, that, in turn, is oxidized by ozone to bromate ion. Hydrogen peroxide acts as a reducing agent reducing hypobromous acid, thus preventing the formation of hybromate ion and bromate ion (Symons and Zheng, 1997). The highest levels of bromate ion correlated with high bromide ion levels and high ozone doses. As the pH of ozonation was lowered, the required ozone dose dropped, and less bromate ion was produced.

Bromate ion testing was conducted on state project water (SPW) at MWD's 5.5 million gallons per day (MGD) demonstration plant in September and October 1992 and April and May 1993 (Grammith et al., 1993). The formation of bromate ion was evaluated for ambient and spiked bromide ion levels (0.17 to 0.49 mg/L), pH levels of 6 to 8.4 and ozone doses ranging from 0.75 to 2 mg/L. Samples for bromate ion were collected at the contactor effluent. At ambient pH (7.6 to 8.4), ozonation of SPW containing high levels of bromide ion (0.3 to 0.5 mg/L) produced bromate ion concentration greater than 10 µg/L. When bromide ion levels were 0.2 to 0.3 mg/L bromate ion formation ranged from 5 to 10 µg/L. At bromide ion levels below 0.2 mg/L, less than 5 µg/L bromate ion was detected. When the pH of ozonation was lowered to 6.0, bromate ion levels were below 5 µg/L for all bromide ion concentrations. Higher bromate ion occurrence correlated with higher ozone doses.

Sorrell and Hautman (1992) developed a concentration technique for analyzing bromate ion at low levels in drinking water. This procedure used a rotovap to concentrate drinking water samples, followed by ion chromatography. Bromate ion was detected with a combination of suppressed conductivity and ultraviolet absorbance. A minimum detection level of 0.4 µg/L was achieved. This rotary evaporator

concentration technique was applied to several surface drinking water sources before and after ozonation. Bromate ion levels ranged from less than 0.4 to 6.3 µg/L after ozonation. No ozone dosages or bromide ion levels were reported.

State Studies

Nieminski et al. (1993) studied DBPs in water treatment facilities in Utah. Although analyses for bromate ion were conducted, the authors noted that bromate ion was not detected above the detection level of 7 µg/L from any of the 35 water utilities plants that use liquid chlorine (sodium hypochlorite). None of the systems characterized in the study used ozonation, typically a major source of bromate ion.

4.3.14 Chlorite Ion

Chlorine dioxide (ClO_2), commonly used as a disinfectant for drinking water purposes since it does not form THMs, is a good oxidant, and treats taste and odors. However, its use is restricted because of the potential health risks associated with its presence and the presence of its byproducts, chlorite and chlorate ions in finished water. The main health effects associated with ClO_2, and its byproducts include oxidative damage to red blood cells, delayed neurodevelopment and decreased thyroxine hormone levels (EPA, 1994).

Chlorite ion (ClO_2^-) is formed as an end-product of oxidation-reduction reactions when ClO_2 reacts with organic matter and reduced iron and manganese (Gallagher et al., 1994). ClO_2^- concentrations can, however, be potentially controlled through the addition of a ferrous iron or remove it through the use of powdered activated carbon (PAC) or granular activated carbon (GAC). ClO_2^- has the potential to form ClO_2 or chlorate ion (ClO_3^-) when it reacts with free chlorine in the distribution system (Gallagher et al., 1994) Chlorite (as the sodium salt) has been used by industry as a bleaching agent and in the manufacture of shellacs, waxes, and varnishes (EPA, 1994).

National Surveys

Hoehn et al. (1990) conducted a study to determine the role that drinking water disinfected with chlorine dioxide played in contributing to household odors reported at houses located in Lexington, Kentucky, and Charleston, West Virginia. The Lexington plant adds chlorine dioxide to the raw water at doses of approximately 1.0 mg/L. Three customer houses were sampled during the Lexington visit, but, the sampling results were sampled were not discussed. Two customer houses were sampled during the Charleston visit; the results are discussed here. The Charleston plant is divided into two identical treatment trains. Chlorine dioxide can be added to raw water on one side of the treatment plant, typically at 2.0 mg/L.

Chlorine is then added on the other side and, after filtration, the water from each side of the treatment plant is blended in a common clearwell. Exhibit 4-19 provides the chlorite ion results from the two Charleston houses and the distribution system.

Exhibit 4-19. Chlorite Ion Concentrations at Charleston Plant and Customer Houses

Oxidant Species	Below Filter at Plant		Clearwell at Plant	Customer D		Customer E
	November 3	November 4	November 3	November 3	November 4	November 3
Chlorite Ion	1.67	1.04	0.71	0.90	0.31	0.93

Source: Hoehn et al., 1990

Bolyard et al. (1993) reported the occurrence of chlorite ion in source water and finished water from four utilities that use chlorine dioxide. Exhibit 4-20 presents data from systems that use chlorine dioxide. These data show a wide range of concentrations for chlorite ion. The study concluded that chlorine dioxide is the source of inorganic contaminants in these sites since the source water for these systems did not contain measurable concentrations of chlorite and chlorate ions and because gaseous chlorine was used for chlorination. The estimated chlorine dioxide varied from 0.07 to 2.0 mg/L. Additional gaseous chlorine was also added to provide a residual disinfectant level in the distribution system. The concentrations of chlorite ion in the finished water ranged from 0.02 to 0.74 mg/L.

Exhibit 4-20. Occurrence of Chlorite Ion in Utilities Using Chlorine Dioxide

Utility ID Number	Date	Source Water	Chlorine Dioxide Dose (mg/L)[a]	Plant Effluent Chlorite (mg/L)[b]
37	9/90	Stream	2	0.50
37	9/91	Stream[c]	1	0.74
44	8/91	Reservoir[c]	0.1 – 0.2	0.02
62	8/91	Stream[c]	1	0.17
80	9/91	Mixed[c]	0.07	0.05

Source: Bolyard et al., 1993

a. Chlorine dioxide dosage was calculated based on feed rates of raw materials, plant flow on day of sampling, and approximate purity of feed material. Dosage is only an estimate, since these data were obtained from the utilities several months after the samples collection.
b. The samples were assumed to have no detectable chlorine dioxide residual on the basis of information from utility personnel. Therefore, the samples were not purged with an inert gas to remove chlorine dioxide. All samples contained 50 mg EDA/L as a preservative.
c. Source water was analyzed for chlorite ion and chlorate ion, and none was detected above the 10 mg/L reporting limit.

Gallagher et al. (1994) evaluated chlorine dioxide byproduct (chlorite ion and chlorate ion) levels within the water treatment plant and the distribution systems of six utilities in the United States. Only five of the utilities were sampled in the distribution system and that data is presented in Exhibit 4-1. The chemical composition of the chlorine dioxide generator effluents was closely monitored, and the effects of generator optimization on byproduct residuals within the treatment plants and distribution systems were determined. The study also evaluated different analytical methods and sample preservation techniques. The resulting data provide an indication of chlorine dioxide and its byproducts concentrations in water treated with chlorine dioxide.

Most utilities that apply chlorine dioxide at dosages of 1.0 mg/L or slightly greater were able to meet the currently recommended level of 1.0 mg/L for the sum of chlorine dioxide, chlorite ion, and chlorate ion concentrations. The level of chlorite ions that appears following chlorine dioxide treatment can be as much as 70 percent of the applied chorine dioxide dose. During the study, the median concentration of chlorite ion in the distribution system at locations where the dosage of chlorine dioxide to the raw water was 1.0 mg/L or less ranged from 0.03 to 0.78 mg/L. The highest levels were observed at a location where the dosage was 2.0 mg/L but was applied to only one-half of the plant flow. Incomplete mixing between the water treated with chlorine dioxide and the other half of the plant flow was responsible for higher chlorite ion concentrations. Exhibit 4-21 presents the range and mean concentrations of chlorite in distribution systems.

Exhibit 4-21. Chlorite Ion Concentrations in Water Treatment Plant and Generator Effluents

Plant/Date	Range in Plant Effluent (mg/L)	Mean ClO_2^- in Plant Effluent (mg/L)
Skagit, WA 1990	0.35–0.40	0.4
Columbus, GA 1991	0.21–0.40	0.3
New Castle, PA 1990	BDL–0.11	0.04

The Chlorine Dioxide Panel of the Chemical Manufacturer Association (CMA) provided EPA with data for chlorite ion occurrence at 65 water treatment facilities that are serviced by one generation company. CMA estimates that the 65 facilities represent between five to 10 percent of the facilities nationwide that use chlorine dioxide treatment. Greater than 50 percent of the 65 facilities are located in the state of Texas. The rest of the facilities are located in the states of Kentucky, Missouri, Rhode Island, Georgia, South Dakota, Oklahoma, and Kansas.

Most of these facilities provided monthly monitoring results collected between January 1995 and January 1997. The double blinded data set did not indicate exact sample locations, source water characteristics, nor chlorine dioxide dosages or residuals. EPA Method 300.0 was used to determine chlorite ion concentrations. The practical quantitation level is 10 µg/L, and the method detection limit is approximately 1.0 µg/L for chlorite ion. Exhibit 4-22 presents the data.

Exhibit 4-22. Chlorate Ion and Chlorite Ion Concentrations at Sixty-Five Utilities Using Chlorine Dioxide

DBP Contaminant	Concentrations (mg/L)			
	Range	Mean	Median	90th Percentile
Chlorate Ion	0.01 – 4.42	0.40	0.23	1.07
Chlorite Ion	0.01 – 5.36	0.58	0.52	1.02

Source: CMA dataset, 1997

4.3.15 Chlorate Ion

Not only is chlorate ion (ClO_3^-) a byproduct of the inefficient generation of chlorine dioxide and oxidation reactions between ClO_2^- and the free chlorine residual in the distribution system, it may also be present as a contaminant in liquid sodium hypochlorite solutions (Gallagher et al., 1994; Gages, 1997). Chlorate ion can not readily be moved from the water once it is produced. Like the chlorite ion, chlorate (as the sodium salt) has been used by industry as a herbicide, to tan leather, and in the manufacture of dyes, matches, and explosives (EPA, 1994).

National Surveys

As mentioned in Section 4.2.14, Hoehn et al. (1990) evaluated the role that chlorine dioxide played in contributing to household odors reported at houses in Lexington, Kentucky, and Charleston, West Virginia. Exhibit 4-23 presents the chlorate ion results from the two Charleston houses and the distribution system.

Exhibit 4-23. Chlorate Ion Concentrations (mg/L) at Charleston Plant and Customer Houses

Oxidant Species	Below Filter at Plant		Clearwell at Plant	Customer D		Customer E
	November 3	November 4	November 3	November 3	November 4	November 3
Chlorate Ion	0.14	*	*	0.28	0.22	0.28

Source: Hoehn et al., 1990
*Sample interference during analysis – no valid data.

As reported in Section 4.2.14, Bolyard et al. (1993) reported the occurrence of chlorate ion in source water and finished water from four utilities that use chlorine dioxide and 15 sites that use hypochlorination (Cl_2 + HOCl). Analyses for chlorate ions were performed by direct injection into an ion chromatograph with suppressed conductivity detection.

Exhibit 4-24 presents data from systems that use chlorine dioxide. These data show a wide range of concentrations for chlorate ions in these waters. The estimated doses of chlorine dioxide varied from 0.07 to 2.0 mg/L. Additional gaseous chlorine was also added to provide a residual disinfectant level in the distribution system. The concentrations of chlorate ions in the finished water ranged from 0.02 to 0.33 mg/L. The concentration of chlorate ions was much higher than the concentration of chlorite ions in the finished water collected from sites 44 and 62. Both systems use chlorine dioxide as a pre-oxidant. At site 62, the water is chlorinated before the secondary sedimentation basins and passed through granular activated carbon (GAC) filters after sedimentation. Powdered activated carbon (PAC), added to the raw water at site 44, is in contact with the water throughout the sedimentation basins. When PAC acts in a manner similar to GAC, chlorite ions and excess chlorine from the chlorite ion generator or free available carbon, there is the potential to form high concentrations of chlorate ions. This may have attributed to the chlorate ion concentration at site 44. The creation of chlorate ions was higher than would be predicted from the chlorine dioxide dosage for this site, suggesting that the estimated dosage may be low.

Exhibit 4-24. Occurrence of Chlorate Ion in Waters from Utilities Using Chlorine Dioxide

Utility ID Number	Date	Source Water	Chlorine Dioxide Dose (mg/L)[a]	Plant Effluent Chlorite (mg/L)[c]
37	9/90	Stream	2	0.11
37	9/91	Stream[c]	1	0.14
44	8/91	Reservoir[c]	0.1 – 0.2	0.33
62	8/91	Stream[c]	1	0.31
80	9/91	Mixed[c]	0.07	0.02

Source: Bolyard et al., 1993

a. Chlorine dioxide dosage was calculated based on feed rates of raw materials, plant flow on day of sampling, and approximate purity of feed material. Dosage is only an estimate, since these data were obtained from the utilities several months after the samples collection.
b. The samples were assumed to have no detectable chlorine dioxide residual on the basis of information from utility personnel. Therefore, the samples were not purged with an inert gas to remove chlorine dioxide. All samples contained 50 mg EDA/L as a preservative.
c. Source water was analyzed for chlorite ion and chlorate ion and none was detected above the 10 µg/L reporting limit.

Exhibit 4-25 presents occurrence data for 15 utilities for 11 systems that use hypochlorination as a source of chlorine for disinfection. The levels of chlorate ions detected in these finished waters are generally in the same range as those for systems that use chlorine dioxide during treatment. The levels of chlorate ions in the finished water from sites 77 and 87 were much higher than the rest, but the significance of this is not known because of the limited number of samples analyzed. In two sites, 82 and 83, chlorate ions were present in the source water. In both cases, however, higher levels were present in the finished water.

Onsite analysis used amperometric titration from standard methods for analysis of chlorine dioxide and its byproducts concentrations in generator effluent. Ion chromatography (modified EPA Method 300.0b) is recommended for the analysis of chlorate at levels as low as those expected in the distribution system when dosages of chlorine dioxide are in the range of 0.5 to 1.0 mg/L. Preservation with sodium oxalate or ethylene diamide stabilized samples during shipping and storage for one week. Carbonate and borate effluents were used to provide better separation of ion chromatography peaks.

As reported in Section 4.2.14, Gallagher et al. (1994) evaluated chlorine dioxide byproducts (chlorite ion and chlorate ion) levels within the water treatment plant and the distribution systems of five utilities in the United States.

Exhibit 4-25. Occurrence of Chlorate Ion in Fifteen Utilities Using Hypochlorite Solution for Disinfection

Utility ID Number (Date)	Water Source	Chlorate Ion Concentration mg/L	
		Source Water	Plant Effluent
57	Stream	BDL	0.05
72 (7/91)	Stream	NA*	0.06
72 (9/91)	Stream	BDL	0.04
73	Stream	BDL	0.09
74	Ground	BDL	0.05
75	Stream	BDL	0.10
76	Reservoir	BDL	0.13
77	Stream	BDL	0.63
78	Reservoir	BDL	0.32
81	Ground	BDL	0.19
82	Ground	0.019	0.04
83	Ground	0.023	0.08
84	Ground	BDL	0.01
85	Ground	BDL	0.13
86	Ground	BDL	0.01
87	Reservoir	BDL	0.66

Source: Bolyard et al., 1993

* No sample was collected at this sampling point.

The median concentrations for the observed distribution systems ranged from 0.1 to 0.39 mg/L. A substantial source of chlorate ions during this project was the chlorine dioxide generator; reactions between residual chlorite ions and free chlorine most often can be expected to produce the majority of chlorate ions. These reactions can occur rather rapidly after post-chlorination. Concentrations of chlorate ions in the distribution systems monitored during this project were not appreciably greater than those in the clearwells at the treatment plants. Exhibit 4-26 presents the chlorate concentrations collected at three plants.

Exhibit 4-26. Chlorate Concentrations in Water Treatment Plant Effluent

Plant/Date	Range iin Plant Effluent (mg/L)	Mean ClO_2^- in Plant Effluent (mg/L)
Skagit, WA 1990	0.05–0.20	0.09
Columbus, GA 1991	0.06–0.24	0.10
New Castle, PA 1990	0.32–0.58	0.39

The CMA provided data for chlorate ion occurrence at 65 water treatment facilities that are serviced by one generation company. Many facilities provided monthly monitoring results from January 1995 and January 1997. The double blind data set did not indicate exact sample locations, source water characteristics, nor chlorine dioxide dosages or residual levels. EPA Method 300.0 was used to determine concentration. The practical quantitation level is 10 µg/L and the method detection limit is approximately 1.0 µg/L, chlorate. Exhibit 4-22, presented previously, provides the data.

Gordon et al. (1995) developed a survey asking water utilities to describe their treatment systems and to submit finished water samples for chlorate ion analysis. Chlorate ion concentrations was evaluated in raw, feedstock, and finished water submitted to the laboratory from 111 of these water utilities that use hypochlorination. The samples were analyzed using EPA Method 300.0 for ion chromatography. Approximately 78 percent of the raw water samples and five percent of the finished water treated with hypochlorite ion tested BDL for chlorate ion. The study concluded that water treated through hypochlorination exhibits the same or greater levels of chorlate ions than water treated with chlorine dioxide. Exhibit 4-1, presented previously, provides the mean, median, and data range for this study.

5. NATIONAL OCCURRENCE OF DBPs

The purpose of this section is to characterize the national occurrence of the disinfection byproducts (DBPs) for the Stage I Disinfectant/Disinfection Byproduct (D/DBP) rule which will be promulgated by November 1998. Occurrence assessments are required in the regulatory development process for contaminants with proposed Maximum Contaminant Levels (MCLs). In the proposed Stage I D/DBP rule (59 FR 38668), MCLs and Maximum Contaminant Level Goals (MCLGs) were proposed for the following contaminants:

Exhibit 5-1. Stage I D/DBP Rule MCLs

Contaminants	MCL	MCLG
Total trihalomethanes (4)	0.080 mg/L	--
Haloacetic acids (5)	0.060 mg/L	--
Bromate ion	0.010 mg/L	0.0 mg/L
Chlorite ion	1.0 mg/L	0.8 mg/L

For the most recent national occurrence data on total trihalomethanes (TTHMs) and haloacetic acids 5 (HAA5), a number of sources were available. Of these sources, which are summarized in Section 4 of this document, the American Waterworks Association (AWWA) WaterStats and the American Water Works Service Company (AWWSCo) datasets were selected for the *Regulatory Impact Analysis for the Stage I Disinfectants/Disinfection Byproduct Rule* because they are national in scope, contain recent data, and have a large sample size with sufficient accuracy. These datasets are used in Chapter 4 of the *Regulatory Impact Analysis for the Stage I Disinfectant/Disinfection Byproducts Rule* document to estimate pre-regulatory baseline concentrations, which factor into the national costs of complying with the new MCLs and treatments are calculated.

State compliance monitoring data are included here to provide a sense of regional variability throughout the nation for TTHMs and HAA5 and to provide supplementary occurrence data since no true comprehensive DBP survey has been done. The state datasets contain information of excellent quality. They are not, however, national in scope. Sufficient data were not available to characterize the national occurrence of chlorite ion or bromate ion. The available data are presented in this section for comparison.

5.1 DATA SOURCES

Summary information and summary statistics were generated for the AWWA WaterStats, AWWSCo compliance data, and state compliance monitoring data for TTHM and HAA5. Information regarding the data sources, including purpose, objective, and scope, are summarized below. Information for chlorate ion and bromate ion, although not national in scope, are also summarized. Sections 4.2.13 and 4.2.14 also discuss the bromate ion and chlorate ion data, respectively.

5.1.1 AWWA WaterStats

WaterStats was initiated through a joint effort by the AWWA and the AWWA Research Foundation (AWWARF). The purpose of this database is to support the regulatory and legislative efforts of AWWA, assist AWWA in focusing research activities, and support the educational endeavors of AWWA and interested parties. In 1996, AWWA surveyed approximately 3,162 drinking water systems serving populations exceeding 10,000 in the United States. The response rate was better than 30 percent, resulting in TTHM, HAA5, and population-served information for approximately 300 systems in the United States. The survey covered a wide spectrum of information, including utility characteristics and finances, surface and groundwater treatments, water quality monitoring, and water distribution characteristics. The data gathered in this survey comprise WaterStats.

The data in WaterStats characterize distribution system concentrations for TTHM and HAA5. These distribution system data were also characterized by source water and the population served. The data represented annual averages based on quarterly sampling for TTHMs and HAA5 in systems that chlorinate. WaterStats was examined for data consistency and outliers, assumptions associated with the data, and possible analysis methods. The WaterStats data base was assumed to be a representative sample of the water systems in the United States serving greater than 10,000 people.

Many systems in WaterStats had multiple records for an individual plant. The data were presented as plant concentration values. The samples, however, were taken from the distribution systems. The values for shared distribution systems were presented for each plant contributing to the finished water. TTHM data for all plants within a single distribution system were compared. This comparison showed that TTHM and HAA5 data were the same among all plants within a single distribution system. Therefore, system data were extracted from the database and the analyses were conducted on a system, not a plant, level.

Further examination of the data showed that several TTHM and HAA5 values were reported as zero. These values were excluded from the analysis because they were believed to represent data entry error and not to be reflective of detection limits. In addition, obviously incorrect data points, systems outside the United States, and systems with incomplete data were excluded from the analysis. After applying these restrictions to the data, 460 systems with valid TTHM data and 146 systems with valid HAA5 data were available for analysis.

5.1.2 AWWSCo Monitoring Data

AWWSCo, the largest investor-owned water utility in the United States, owns and operates more than 100 water systems in 21 states. The utility generated a system-wide summary of DBPs in the distribution systems of their water treatment plants. Upon request, AWWSCo provided a summary to EPA of TTHM and HAA5 data for approximately 92 systems 1991 and 1992. For many of these systems, AWWSCo also provided source water and population information. The data for TTHM and HAA5 were reviewed for source water and population information. In the complete data set, 92 systems had TTHM data and 85 systems had HAA5 data. Only 52 surface water systems, however, provided both TTHM and HAA5 data and the corresponding population and source water data. The data from these systems are used to characterize TTHM and HAA5 occurrence. These data were summarized by Arora et al. (1994 and 1997).

5.1.3 State Compliance Monitoring Data

EPA requested TTHM compliance monitoring data and HAA5 data, if available, from nine states. These states were selected to provide regional, demographic, and source type diversity. THM monitoring is required in all surface water plants serving 10,000 or more people. The same is true for groundwater systems that add a disinfectant in the treatment process. Section 4 includes summary reviews of the state data.

The states of Massachusetts, Missouri, New Jersey, Oregon, Pennsylvania, and Texas submitted quarterly or annual TTHM sample results, Public Water Supply Identification Numbers, populations served, source water types and sample collection dates for the 3-year period between January 1994 and December 1996. The state of Missouri provided the same information for January 1996 through June 1997. Although TTHM monitoring at systems serving fewer than 10,000 people is discretionary, the states of Massachusetts, Missouri, New Jersey, Pennsylvania, and Texas submitted TTHM results from smaller systems that disinfect. Compliance with the TTHM MCL may or may not be required in these states for systems serving fewer than 10,000 people. Missouri is the only state that has provided HAA5 data.

5.2 TTHM DATA

TTHM data were available from several sources representing various cross sections of the nation. WaterStats, a national survey of public and private water systems, represents data from across the county. The AWWSCo data, representing the largest private water utility in the nation, were compiled from water systems from approximately 18 states. Exhibit 5-2 presents the mean, median, and 90th percentile of the occurrence data. A discussion and comparison of the TTHM results from these two datasets appears in Chapter 4 of the *Stage 1 Regulatory Impact Analysis for the Stage 1 Disinfectant/Disinfection Byproducts Rule*.

Exhibit 5-2. Summary Statistics on TTHM Based on WaterStats and AWWSCo

Data Source	Number of Systems	TTHM (µg/L)		
		Mean	Median	90th Percentile
WaterStats 1996	308	44	45	72
AWWSCo 1991	52	54	59	83
AWWSCo 1992	52	64	65	87

In addition to the data in WaterStats and AWWSCo, state monitoring data, including information from many small systems, were collected from six states. For comparison purposes, Exhibits 5-3 and 5-4 present the assembled TTHM data by source water and population served. In Exhibit 5-3, which focuses on surface water and groundwater systems serving more than 10,000 people, the TTHM means and medians ranged from 29 to 64 µg/L and 26 to 65 µg/L, respectively for surface waters. The 10th percentiles from all of the different data sets ranged from 13 to 35 µg/L, and the 90th percentiles ranged from 42 to 89µg/L. As expected, the TTHM concentrations for groundwater systems serving more than 10,000 people were substantially lower. The ranges of means and medians were 8 to 44µg/L and 3 to 15 µg/L, respectively. The 10th percentiles dropped to a range of 0 to 2 µg/L, and the range of 90th percentiles fell to 17 to 60 µg/L.

For systems serving fewer 10,000 people (Exhibit 5-4), large sample sets of TTHM data were available only from state monitoring data. For surface water systems, the states of Missouri and North Carolina had means of 118 and 64 µg/L, respectively. Missouri exhibited high TTHM values for small systems with a median of 102 µg/L and a 90th percentile of 206 µg/L. Because these systems are not required to comply with the TTHM MCL, the concentrations are much higher than in large surface water systems. The small systems in North Carolina, however, had TTHM levels similar to the large systems with a 10th percentile of 18.3 µg/L, a median of 43.8 µg/L, and a 90th percentile of 89.6 µg/L.

Exhibit 5-3. TTHM Compliance Monitoring Data (1994–1996): Surface and Groundwater Systems Serving Greater Than 10,000 People

Source	Number of Systems	Mean (µg/L)	Percentile (µg/L)*				
			10	20	50	80	90
Surface Water							
Massachusetts	21	54	18	27	50	75	89
Missouri	11	45	13	21	37	68	83
New Jersey	23	42	15	21	39	61	71
Oregon	27	29	17	19	26	40	42
Pennsylvania	119	40	15	20	42	58	64
Texas	114	41	15	22	37	56	70
Waterstats, 1996	308	44	17	24	45	64	72
AWWSCo, 1991	52	57	28	39	59	74	83
AWWSCo, 1992	52	64	35	47	65	83	87
Groundwater							
Massachusetts	8	44	–	–	–	–	–
Missouri	14	14	1	2	3	27	46
New Jersey	86	9	0	1	3	11	31
Oregon	7	16	–	–	–	–	–
Pennsylvania	25	8	1	2	6	9	17
Texas	102	24	2	5	15	39	60

*Percentiles were not calculated for sources reporting less than 10 systems for a category.

Exhibit 5-4. Comparison of State TTHM Data for Systems Servings Fewer Than 10,000 People

Source	Number of Systems	Mean (µg/L)	Percentile (µg/L)*	
			50	90
Surface Water				
Massachusetts	3	42	–	–
Missouri	81	118	102	206
North Carolina	66	64	44	90
New Jersey	5	48	–	–
Pennsylvania	54	46	45	84
Groundwater				
Missouri	1	49	–	–
North Carolina	1,217	8	2	18
New Jersey	37	7	3	16
Pennsylvania	25	14	2	36
Texas	11	26	19	52

*Percentiles were not calculated for sources reporting fewer than 10 systems for a category.

The groundwater TTHM levels for small systems in New Jersey and North Carolina exhibited TTHM levels lower than those for medium and large groundwater systems. The mean and median TTHM values for New Jersey were 6.8 and 2.6 µg/L, respectively. The mean and median TTHM values for North Carolina were 7.8 and 2.0 µg/L, respectively.

5.3 HAA5 DATA

HAA5 data were also available in the WaterStats and the AWWSCo data. The only state to provide HAA5 data was Missouri. Exhibit 5-5 presents HAA5 data by source water for systems serving greater than 10,000 people. In January 1997, the state of Missouri Department of Natural Resources initiated quarterly monitoring of HAA5 at all surface water systems and groundwater systems serving 10,000 or more people. Exhibit 5-6 presents results from the first 2 quarters of data. The means and medians ranged from 32 to 46 µg/L and 29 to 42 µg/L, respectively. As expected, the concentrations of HAA5 in groundwater systems serving greater than 10,000 people were substantially lower than the concentrations in surface water systems.

Exhibit 5-5. Comparison of HAA5 Data for Systems Serving Greater Than 10,000 People

Source	Number of Systems	Mean (µg/L)	Percentile (µg/L)*				
			10	20	50	80	90
Surface Water							
Missouri, 1997	11	28	9	11	24	45	63
WaterStats, 1996	78	32	11	18	29	50	60
AWWSCo, 1991	52	46	19	24	42	56	88
AWWSCo, 1992	52	41	18	21	34	56	79
Groundwater							
Missouri	14	7	1	2	3	11	17

*Percentiles were not calculated for Sources reporting less than 10 systems for a category.

Exhibit 5-6. Available Data on Bromate Ion Occurrence in Drinking Water Supplies

Study	Range (µg/L)	Mean (µg/L)	Comments
Sorrell, Hautman, 1992	< 0.4 – 6.3	2.5	Median = 0.75 µg/L
Krasner et al.,1992	< 5 – 20	--	Pilot-plant and full-scale studies of six utilities
Grammith, 1993	< 5 – > 10	--	*

* No information.

Limited data were available for HAA5 in small systems. Only the state of Missouri has collected HAA5 data from systems serving fewer than 10,000 people. For 81 public water systems (<10,000) that use surface water, the mean and median HAA5 concentrations were 88 and 80 µg/L HAA5, respectively. The range of HAA5 values for these 81 systems was 0.1 to 284 µg/L. The high levels are attributed to high source water total organic carbon levels and because these small systems are not required to comply with the TTHM MCL.

5.4 CHLORITE AND BROMATE IONS

Characterizations of national occurrence were not generated for the chlorite ion and bromate ion because of the lack of nationally representative data sets. For these DBPs, a discussion of their occurrence in various studies and surveys is provided. This discussion summarizes the available anecdotal occurrence data for chlorite ion and bromate ion. Additionally, the commentary identifies typical concentrations of these DBPs in public water supplies based on the available studies, where possible.

5.4.1 Bromate Ion

Several studies were summarized in Section 4 of this document and in the 1992 Occurrence document addressing the occurrence of bromate ion in public drinking water supplies. Exhibit 5-6 identifies the ranges of bromate ion concentrations found in these studies.

Bromide ion levels in the range of 50 to 180 µg/L may yield measurable levels of bromate ion (Krasner et al., 1993c). Low levels of bromide ion concentrations may yield bromate ion concentrations of less than 5 µg/L. A lowering of pH levels to 6 has lessened bromate ion formation fourfold in pilot studies. Staging of ozone addition through the use of multiple ozone contractors may also reduce bromate ion formation.

5.4.2 Chlorite Ion

Section 4 of this document and the 1992 occurrence document summarized several studies addressing the occurrence of chlorite ion in public drinking water supplies. Exhibit 5-7 identifies the ranges of chlorite ion concentrations found in these.

Exhibit 5-7. Available Chlorite Ion Occurrence in Drinking Water Supplies

Study	Range (mg/L)	Comments
Gallagher et al., 1994	0 – 2.41	Five water treatment plants using ClO_2
Bolyard et al., 1993	0.052 – 0.74	Four sites using ClO_2
Hoehn et al., 1990	0.31 – 0.93	Two houses, same surface water treatment plant
CMA Dataset, 1997	0.01 – 2.60	Mean = 0.58 mg/L; n = 855, 65 utilities

6. SUMMARY OF EXPOSURE DATA FROM SOURCES OTHER THAN DRINKING WATER

This section provides information gathered from published articles about potential exposure to D/DBPs from routes other than drinking water through food and air via processes such as showering, bathing, cooking, washing dishes, eating, washing clothes, or swimming. The majority of the reviewed articles did not provide exposure data that directly indicates the concentration of disinfectants or DBPs with which an individual could come in contact. The articles typically provided data on the occurrence of disinfectants and DBPs in ambient air and food. Any relevant occurrence and/or exposure information for these non-drinking water sources can be used to establish the relative source contribution (RSC) for drinking water. The RSC can then be used in setting the maximum contaminant level goal (MCLG) or maximum residual disinfection level goal (MRDLG), as described in Section 7. Any adequate occurrence data for individual chemicals can be used, with standard assumptions about the amount of food and air an individual would ingest or inhale, to estimate exposure to disinfectants and DBPs from these non-drinking water sources. THMs are the only volatile DBP compounds, therefore they are the only DBPs expected to be found in any significant concentrations in air.

6.1 DISINFECTANTS

Of the four disinfectants considered for this report, chlorine, chloramines, and chlorine dioxide can remain in process water, food, and air after disinfection. Ozone residuals do not remain in the water after disinfection due to their short half-lives.

6.1.1 Chlorine, Hypochlorite Ion, and Hypochlorous Acid

Dietary Intake

Based on the literature reviewed, little information is available concerning the occurrence of chlorine, hypochlorite ion, and hypochlorous acid in food in the United States. The U.S. Food and Drug Administration (FDA) does not analyze for these chemicals in foods. Chlorine is used extensively in the food production industry to: sanitize food processing equipment and food containers that convey raw and uncooked vegetables, cool heat-sterilized canned foods, wash meats and nuts, and process seafoods, poultry, and red meats. According to the FDA, chlorine is widely used in the poultry industry (DiNovi, 1997). Whole birds are placed in "chiller" tanks, where they soak in water containing 50 to 100 ppm of chlorine. This chlorine soak can add an additional 12 percent to the bird's body weight while in the tank, however, neither the FDA nor the U.S. Department of Agriculture has analyzed chlorine concentrations in poultry

products (DiNovi, 1997). In addition, chlorine is used in chlorinating water at soda and beer bottling plants and for oxidizing and bleaching flour (Wei et al., 1985; Borum, 1991). Therefore, the dietary exposure to chlorine and its hydrolysis products is possible due to its use in food production.

Air Intake

Based on the literature reviewed, no information has been found concerning the occurrence of chlorine in ambient or indoor air or at swimming pools in the United States. The Air Division of the U.S. Environmental Protection Agency's (EPA's) Office of Air and Radiation is not actively studying the ambient effects of chlorine. However, chlorine volatilization from tap water can contribute to exposure in air. Volatile chlorine gas exists in water, but only at pH values well below those found in finished drinking water. It is likely that other chlorinated organics (e.g., chlorine monoxide) volatilize and become potential airborne exposure compounds. Furthermore, Shaw et al. (1982) indicates that road salting with sodium chloride can also lead to volatilization of reduced chlorine (i.e., chloride - I oxidation state) in air.

6.1.2 Chloramines

Dietary Intake

Based on a review of the published literature, no information is currently available on chloramine occurrence in food in the United States. Currently, the FDA does not analyze for chloramine concentrations in foods and is not aware of any specific uses in foods, either direct or indirect. Therefore, it is assumed that exposure to chloramines through food consumption is negligent.

Air Intake

Only one of the reviewed studies discussed chloramine concentrations with regards to air intake. The study measured chloramine concentrations in the atmosphere surrounding 13 swimming pools (Hery et al., 1995). A two-day pollution measurement campaign was carried out at all of the pools, with three exceptions: one pool where the assessment was restricted to one day, and two other pools where spring and autumn campaigns were carried out instead. A total of 309 samples were taken from the pools on the first day. The mean concentration of chloramines was 0.43 mg/m^3. The second day, a total of 317 samples were collected from the swimming pools and the mean chloramine concentration was 0.40 mg/m^3. Chloramine concentration from both days ranged from below the detection limit (BDL) to 1.49 mg/m^3.

6.1.3 Chlorine Dioxide

Dietary Intake

Based on a review of the published literature, no information is currently available on the occurrence of chlorine dioxide, chlorate, and chlorite in food products in the United States. Currently, the FDA does not analyze for chlorine dioxide, chlorate, or chlorite in foods. However, the FDA is aware of uses of chlorine dioxide in food processing (DiNovi, 1997). Various vegetables including sugar beets, lima beans, corn, carrots, peas, potatoes, and tomatoes, are disinfected with chlorine dioxide, followed by a potable water rinse. In addition, the use of chlorine dioxide is approved for flour bleaching. A current proposal would replace the poultry industry's use of chlorine with chlorine dioxide. Sodium chlorite has generally been considered safe for use in bleaching cherries.

Chlorine dioxide is a highly reactive chemical and is likely to transform readily to chlorite and chlorate during contact with food (DiNovi, 1997). The FDA requires that fruits and vegetables that come into contact with chlorite and chlorate must undergo further processing. The FDA acknowledged that some raw vegetables can be exposed to chlorite and chlorate and is currently conducting an analysis on residual amounts in these vegetables (DiNovi, 1997).

Air Intake

Based on a review of the published literature, no information is currently available on the occurrence of chlorine dioxide in air in the United States. However, chlorine dioxide is used as a sanitizer in air ducts, thus ambient air concentrations are possible where this sanitation method is practiced (Borum, 1991).

6.2 DISINFECTION BYPRODUCTS

This section discusses thirteen disinfection byproducts and their potential occurrence in food and/or air. These byproducts may remain in process water, food, and air after disinfection.

6.2.1 Chloroform

Dietary Intake

No exposure estimates were found for chloroform in food; however, seven studies analyzed foods for chloroform content. This section summarizes these seven studies, data collected for six studies reported in a 1993 Department of Health and Human Services (DOHHS) toxicology profile document, and data collected for four studies reported in an EPA drinking water criteria document (EPA, 1994d). Given the use

of chlorine in processes such as the one previously described by the poultry industry, chloroform formation and the formation of other halogenated DBPs is possible and, therefore, so is exposure to this compound. The possibility of exposure remains unquantified, however, due to the lack of analysis.

In accordance with the FDA's Total Diet Study program, Entz et al. (1982) purchased 39 different food items at retail markets in three geographical areas (i.e., Elizabeth, New Jersey; Chapel Hill, North Carolina; and Washington, D.C.). Twenty food composites representing four different food groups (i.e., dairy, meats, oils and fats, and beverages) were analyzed. Chloroform was detected in one dairy composite at 17 ppb, one oils and fats composite at trace levels (less than 12 ppb), and four beverage composites at concentrations of 6, 12, 12, and 32 ppb. Subsequent analysis of individual food items detected chloroform in four cola soft drink samples (178, 22, 9, and 36 ppb), two non-cola soft drink samples (32 and 14.5 ppb), milk (17 ppb), ice cream (23 ppb), processed American cheese (17 ppb), natural cheese (15 ppb), butter (56 ppb), and mayonnaise (34 ppb).

Wallace et al. (1984) analyzed chloroform levels of the air, water, and food for nine volunteers from New Jersey and three volunteers from North Carolina over a six-month period between June and December, 1980. This study was conducted to study seasonal variations. Volunteers were visited three different times during the monitoring period for three days at a time. Food samples from community grocery stores were analyzed to determine if exposure through food was sufficiently important to collect individual food samples. About 40 food items were collected from stores in New Jersey and North Carolina on four occasions. Composites of dairy, meats, fatty foods, and beverages were taken and analyzed for THMs. Chloroform was detected in all beverage composites at concentrations of 32 and 12 ppb in the North Carolina samples and at 10 and 6 ppb in the New Jersey samples.

Heikes (1987) analyzed 19 table-ready food items (including drinking water), which were representative of the 234 items in the FDA Total Diet Study. Fifty-three percent of the sampled foods tested positive for chloroform. The results of this analysis are presented in Exhibit 6-1.

Those items shown to be high in volatile halocarbons (i.e., butter and margarine, cheese, ready-to-eat cereal, peanut butter, and highly processed foods) were designated for further analysis. Samples of individual food items, which were representative of two or three regions of the country, were analyzed. These results are presented in Exhibit 6-2.

Exhibit 6-1. Chloroform Levels in Foods

Food Product	Chloroform Level (ppb)
Chocolate chip cookies	22
Plain granola	57
Cheddar cheese	80
Butter	670
Peanut butter	29
Fried breaded shrimp	24
Scalloped potatoes	7.1
Cream style corn	6.1
Frozen fried chicken dinner	29
High meat baby food dinner	17

Source: Heikes, 1987

Exhibit 6-2. Mean Chloroform Concentrations in Samples Designated for Further Analysis

Food Product	Mean Chloroform Concentration (ppb)
14 butter and margarine samples	364
8 samples of four types of cheeses	182
11 samples of ready-to-eat cereal products	60
7 samples of peanut butter	51.3
12 samples of highly processed foods	122

Source: Heikes, 1987

Uhler and Daichenko (1987) sampled food products from 15 food processing plants located in nine different states as part of a FDA study. Plants were chosen from areas where the presence of chloroform in the process water would be most probable. Results of analysis indicated that out of 39 food items tested, chloroform was present in 13 samples ranging from 2.3 to 31.2 ng/g: two samples of clear sodas, 2.3 and 15.6 ng/g; one sample of dark cola, 12.3 ng/g; four samples of cheese, ranging from 2.4 to 10.9 ng/g; and six samples of ice cream, ranging from 4.6 to 31.2 ng/g.

Daft (1987-89) analyzed foods in three different studies, the most recent and comprehensive of which analyzed 549 food items. Foods were chosen from the FDA's Total Diet Study program list and were made table-ready (e.g., cooking, peeling) prior to analysis. Chloroform was detected in 302 of the food items (about 55 percent), with concentrations ranging from 2 to 830 ng/g with a mean of 71 ng/g (Daft, 1989). The 1988 study analyzed 231 food items obtained from the FDA's Total Diet Study collection. Chloroform was detected in 94 food items (about 17 percent) with a mean concentration of 52 ng/g and a range of 4 to 312 ng/g. In the 1987 study, chloroform was detected in five samples collected as part of a 100-sample grain survey. Chloroform was also detected in seven samples of a combined study that included fortified split peas, seasoned salt, sugar, grapefruit, lime, coffee grounds, coffee beans, spaghetti, flour, bread, two cereals, and crackers.

The Total Exposure Assessment Methodology (TEAM) study measured chloroform in five composite food sample collections from New Jersey, North Carolina, and Washington, D.C. (Wallace, 1988). Four of the composite samples showed measurable levels of chloroform in soft drinks, tea, and coffee. One of the composite samples contained chloroform in dairy products. Cola soft drinks had an average concentration of 50 µg/L, non-cola soft drinks had an average concentration of 10 µg/L, and milk had an average concentration of 4 µg/L.

The DOHHS document, entitled, A *Toxicological Profile for Chloroform*, summarizes the results of six studies involving chloroform concentrations in food (DOHHS, 1993). The results of these studies are presented in Exhibit 6-3. The Heikes (1987) includes results from further analysis conducted on foods containing high levels of volatile hydrocarbons.

EPA's Office of Science and Technology prepared a document entitled, *Drinking Water Criteria Document on Trihalomethanes*, that summarizes the results of a study exploring the occurrence of disinfection byproducts in air and food (EPA, 1994d). This document presents study results discussed previously in this document. The studies were conducted by Daft (1987-89), Entz et al. (1982), Heikes (1987), and Uhler and Daichenko (1987). Exhibit 6-4 summarizes the chloroform levels detected in food by four other studies also discussed in this document.

Exhibit 6-3. Chloroform Levels in Food

Reference	Food	Chloroform Level
Abdel-Ranman, 1982; Heikes, 1987; Entz et al., 1982; Graham and Robertson, 1988; Heikes and Hopper, 1986; Lovegren et al., 1979	Soft drinks/beverages Dairy products Oils and fats Dried legumes Grains/milled grain products	2.7 – 178 µg/L 3 – 1,110 ppb < 12 ppb 6.1 – 57.2 µg/kg 1.4 – 3,000 µg/kg
Heikes, 1987	Butter Mixed cereal Infant/junior food Cheddar cheese	1,100 ppb 220 ppb 230 ppb 80 ppb

Source: DOHHS, 1993

Exhibit 6-4. Chloroform Levels in Food

Reference	Food	Chloroform Level
Abdel-Rahman, 1982	Colas Clear soft drinks	9 – 6.1 µg/L 2.7 – 10.9 µg/L
Entz and Daichenko, 1988 (cited in Wallace, 1992)	37 samples	15 – 150 ng/g
Kroneld and Reunanen, 1990	Pasteurized milk	BDL – 3.1 µg/L
Toyoda et al., 1990	90 samples - summer 90 samples - winter	3.6 – 106.8 ng/g 2.6 - 80.9 ng/g

Sources: Listed in exhibit

McNeal et al. (1995) purchased foods from local markets in the Washington, D.C., area and analyzed the products for total trihalomethanes (TTHMs) with EPA Method 524.2 using gas chromatography and electron capture detection. The researchers observed that the same products from different lots (i.e., produced on different dates) had significantly different contaminant concentrations. Of the individual THMs, chloroform was detected most often in these samples. Exhibit 6-5 summarizes the results for chloroform. The detection limit for chloroform was 0.02 ng/g.

Air Intake

This section summarizes twelve studies that reported chloroform levels in air. Some of these studies measured chloroform concentrations in the breath of individuals. In addition, this section summarizes data from five studies reported in the DOHHS toxicology profile document (DOHHS, 1993), data from six studies reported in an EPA drinking water criteria document (EPA, 1994d), and data from a 1997 literature review document on human exposure to chloroform and other THMs, compiled by Wallace. Singh et al. (1981)

Exhibit 6-5. Chloroform Concentrations in Food and Beverages

Food Analyzed[a]	$CHCl_3$ (ng/g)
Spring water	1
Mineral water	1
Flavored sparkling water	38
Dry beer A	1
Dry beer B	1
Apple juice A	1
Fruit drink A	21
Fruit drink B	1
Sport drink	12
Cola A (3 samples)	36 – 94
Diet orange soda (4 samples)	10 – 65
Diet white grape soda	50
Diet lemon lime soda	38
Diet raspberry soda	57
Diet cherry berry soda	23
Diet grapefruit soda	56
Diet tangerine soda	49
Pizza sauce (canned)	50
Green beans (vegetable water)	1
Sweet corn (vegetable water)	1
Duck sauce	3
Beef extract	3
Lite syrup product	2

Source: McNeal et al. (1995)

[a] Letters for food products designate different brands

reported results from field studies conducted in three cities: Los Angeles, California; Oakland, California; and Phoenix, Arizona. Ambient air samples were collected at each site over a two-week period in 1979 and analyzed for chloroform. Results of the analysis indicated that for the Los Angeles area, the mean concentration was 88.2 ppb and the range was 24.3 to 223.5 ppb. In Phoenix, a mean of 111.4 ppb and range of 27.1 to 514.0 ppb were reported, while Oakland had a mean of 32.1 ppb and a range of 13.1 to 60.1 ppb.

From November 1982 to December 1983, ambient air samples at four urban/industrial sites in the California South Coast air basin were surveyed for the presence of halogenated hydrocarbons (Shikiya et al., 1984). Chloroform was detected above the quantitation limit of 0.02 ppb in 96 percent of the samples. Concentrations generally increased in the summer months equally throughout the sites, but the highest value of 3.0 ppb was recorded for downtown Los Angeles. Los Angeles also reported the highest monthly mean of 0.78 ppb and the highest composite mean of 0.13 ppb.

Wallace et al. (1984) analyzed the air, water, and food of nine volunteers from New Jersey and three volunteers from North Carolina over a six month period between June and December 1980 to study seasonal variations in chloroform exposure. The New Jersey subjects were expected to have occupational exposure to volatile organic compounds; the North Carolina subjects were not. Subjects were monitored during different times of the day, during six weekdays and three weekend days. Air samples were analyzed using a purge and trap method, followed by gas chromatography/mass spectrometry (GC/MS) techniques. The detection limit was 0.01 $\mu g/m^3$. Exhibit 6-6 summarizes the monitoring results.

Exhibit 6-6. Summary Statistics of Chloroform in Ambient Air of New Jersey and North Carolina Subjects ($\mu g/m^3$)

Location	Number of Samples	Number of Samples Below Detection Limit	Number of Samples at Trace Levels	Median	Range
New Jersey	165	31	2	2.1	0.03 – 129.00
North Carolina	59	9	0	3.4	0.09 – 17.60

Source: Wallace et al., 1984

Wallace et al. (1984) also analyzed breath samples of these same individuals. Samples were collected using a specially designed spirometer. Samples were analyzed using a purge and trap method, followed by GC/MS techniques. The detection limit was 0.01 $\mu g/m^3$. Exhibit 6-7 summarizes the monitoring results.

Exhibit 6-7. Summary Statistics of Chloroform in Breath of New Jersey and North Carolina Subjects ($\mu g/m^3$)

Location	Number of Samples	Number of Samples Below Detection Limit	Number of Samples at Trace	Median	Range
New Jersey	49	7	2	3.5	0.09 – 53.00
North Carolina	17	1	0	50	0.11 – 685.00

Source: Wallace et al., 1984

Several studies surveyed inhalation exposure to chloroform from indoor and outdoor air. The major source of data is EPA's five-year TEAM study. This study measured the personal exposures of urban populations to a number of organic chemicals in air and drinking water of several U.S. cities (Wallace, 1992). As part of the study, personal air samples and outdoor air samples were analyzed for chloroform. Personal air samples were collected for each individual for two 12-hour periods, excluding showers, and outdoor samples were collected from the residences of study participants, also during two 12-hour periods. Exhibits 6-8 and 6-9 present chloroform concentrations in personal air samples and in outdoor air samples, respectively.

Exhibit 6-8. Chloroform in Personal Air Samples from the EPA TEAM Study (μg/m³)

Location	Date Sampled	Number of Samples	Mean	Median	Range
Elizabeth/Bayonne, New Jersey	Fall 1981	345	8.0	3.20	0.06 – 215
	Summer 1982	145	4.3	0.8	0.05 – 140
	Winter 1983	48	4.0	2.2	0.23 – 40
Los Angeles, California	Winter 1984	112	1.9	1.25	0.02 – 9.7
	Spring 1984	50	1.2	0.48	0.02 – 20
Antioch/Pittsburgh, California	Spring 1984	68	0.6	0.03	0.02 – 6.3
Devils Lake, North Dakota	Fall 1982	23	2.0	0.38	0.11 – 50
Greensboro, North Carolina	Fall 1982	24	2.2	1.7	0.13 – 7.5

Source: Wallace, 1992

Exhibit 6-9. Chloroform in Outdoor Air Samples from the EPA TEAM Study (μg/m³)

Location	Date Sampled	Number of Samples	Mean	Median	Range
Elizabeth/Bayonne, New Jersey	Fall 1981	85	0.28	3.2	0.04 – 21.5
	Summer 1982	55	4.4	52	–
	Winter 1983	9	0.17	–	–
Los Angeles, California	Winter 1984	24	0.72	0.45	–
	Spring 1984	23	0.34	0.03	–
Antioch/Pittsburgh, California	Spring 1984	10	0.33	0.42	–
Devils Lake, North Dakota	Fall 1982	5	–	0.05	Max 0.78
Greensboro, North Carolina	Fall 1982	5	–	0.14	Max 11.0

Source: Wallace, 1992

McKone (1987) quantified inhalation exposure to chloroform and six other VOCs resulting from the transfer of these VOCs from tap water to indoor air. The author developed a time dependent, three-compartment model that simulated the 24-hour VOCs concentrations within the shower, bathroom, and remaining household volumes of a dwelling. Average and maximum concentrations of the VOCs in the air

of three household compartments were calculated by using a 1 mg/L of tap water concentration. Chloroform concentrations in the shower air averaged 2.0×10^{-2} mg/L. Average concentrations in the bathroom air and household air were 5.8×10^{-3} mg/L and 1.2×10^{-4} mg/L, respectively. This model, along with data on water use in the U.S. homes, and a range of exposure parameters, were used to estimate reference and upper-bound lifetime daily equivalent human dose. The calculated doses for all the VOCs, except for DBCP were 0.04 and 0.2 (mg/kg.d)/(mg/L). Based on these dose factors, the author suggested that, for a 70 kg adult, indoor inhalation exposures to contaminated tap water can be between 1.5 and 6.0 times the exposure from ingesting 2 liters of tap water a day. Calculated doses for chloroform were comparable to the measured values obtained by Wallace et al. for the non-bathroom pathway in studies published in 1984 and 1986.

Jo et al. (1990a) conducted a study to determine the chloroform dose to an individual based on exhaled breath analysis. This study team also demonstrated that chloroform is absorbed by the body as a result of dermal exposure during showering (Jo et al, 1990b). The researchers quantified a person's mean absorbed chloroform dose for a 10-minute shower as being 0.47 µg/kg/day. A chloroform absorption efficiency rate of 0.77 was used for inhalation to conduct the analysis.

McKone (1993) developed a model to estimate chloroform concentrations in breath samples from individuals exposed to this chemical during showering through both inhalation and dermal routes and inhalation only. This model combined two dermal uptake models, the McKone-Howd model and the EPA model (1992); and a revised PBPK model. Model predictions were evaluated against previously reported ratios of air and breath concentrations to tap water concentrations. The resulting ratio ranged from 0.25 to 0.66 mg per mg/L. Effective permeability of the skin during a ten-minute shower was between 0.16 and 0.42 cm/hr. The model also allowed for the calculation of the ratio between dermal and inhalation exposure to the metabolized dose in the liver. This ratio of metabolized dose to water concentration was 0.41 mg/mg/L, at conditions of linear metabolism.

Wallace (1992) reported the results of a 1983 study conducted by Singh et al. in which 2,577 short-term measurements of ambient air in 10 cities were collected between 1979 and 1981. The 25th percentile, median, and 75th percentile values were 0.14, 0.20, and 0.78 µg/m^3, corresponding to exposures of 2.8, 4.0, and 16 mg/day, respectively, for these measurements.

Although TEAM studies do not collect breath samples during showers, attempts have been made to measure the contribution of shower water to airborne chloroform levels. Wallace (1992) reported results from a 1987 EPA study that indicated that chloroform levels increased from 2 to 100 ppb (about 10 to

500 µg/m³ during a 10-minute shower with chlorinated water. Furthermore, these studies have shown that 50 percent of the chloroform present in water is expected to volatilize from water during showers.

Exhibit 6-10 presents the results of five studies of exposure to chloroform monitored in air summarized in a *Toxicological Profile for Chloroform* (DOHHS, 1993).

Exhibit 6-10. Exposure Levels of Chloroform Monitored in Air

Study	Sampling Location	Exposure Level
Class and Ballschmidter, 1986	Northern Atlantic ocean ranges	25 – 50 ppt
Singh et al., 1982	Seven U.S. cities between 1980 and 1981	Maximum: 5.1×10^{-3} ppm Background: 2.0×10^{-5} ppm
Brodzinsky and Singh, 1982	U.S. cities between 1980 and 1981	Mean: $2 \times 10^{-5} - 2 \times 10^{-3}$ ppm
	Source dominated areas in U.S. between 1977 and 1980	Median: 8.2×10^{-4} ppm
Barkley et al.,1980	Outside houses in Love Canal, New York in 1978*	1,000 – 110,000 ng/m³
Wood and Porter, 1987	20 California Class II nontoxic municipal landfills	Maximum: 0.61 ppm

Sources: Listed in exhibit

* It should be noted that these samples were collected in an area underlain by a previous toxic chemical dump.

The *Drinking Water Criteria Document on Trihalomethanes* summarizes study results for occurrence and exposure of disinfection byproducts in air and food (EPA, 1994d). This document presents previously discussed study results, conducted by Shikiya et al. (1984) and Singh et al. (1981). Exhibit 6-11 presents the results of chloroform exposure from outdoor air for four studies, and Exhibit 6-12 summarizes the results of chloroform occurrence in indoor air reported by three studies.

Exhibit 6-11. Chloroform Exposure from Outdoor Air

Study	Sampling Location	Chloroform Exposure
Singh et al., 1983 (cited in Wallace, 1992)	10 cities	Median: 4.0 µg/m³
Shikiya et al., 1994	California South	Maximum: 14.0 µg/day
Singh et al. 1986	Los Angeles and Oakland, California, Phoenix, Arizona	3.7 – 10.5 µg/day
Armstrong and Golden, 1986	Outdoor pools	Maximum: 1 µg/m³

Sources: Listed in exhibit

Exhibit 6-12. Chloroform Concentration in Indoor Air

Study	Sampling Location	Chloroform Concentration ($\mu g/m^3$)
Jo et al., 1990	Shower – with individual	119 – 313.4
Wallace, 1992	House after washing clothes and dishes	BDL – 44
Armstrong and Golden, 1986	Indoor pools	Mean: 90
	Hot tubs	Mean: 12

Sources: Listed in exhibit

Andelman (1985a) compared chloroform concentrations in outdoor and indoor air, previously reported in field studies. The range of means for outdoor air was 81-900 ppt, and the range for indoor air was 14-730 ppt. Background chloroform concentration was 20 ppt at remote sites. These values showed that indoor concentrations are considerably higher than background concentrations, but are similar to outdoor measurements. The author concluded that indoor volatilization of chloroform and other chemicals, and inhalation exposure, especially during bathing and showering, should be of concern as water supplies become increasingly contaminated.

In another study, Andelman et al (1986) studied the extent to which chloroform is volatilized in a laboratory bath-shower system, and the factors affecting the volatilization process. The authors continuously injected known concentrations of chloroform into this system for a period of one hour, while effluent air and water samples were monitored. Results demonstrated that an increase in the water temperature, the chloroform concentration in the water, and the diameter of the shower head hole are all factors that increased the rate of chloroform volatilization. During the injection period, chloroform air concentrations were much lower in the bath than in the shower, due to the larger surface area of the shower droplets resulting in a larger rate of volatilization. However, after injection stopped, the rate of decay of air concentration was much greater in the shower mode. While only residual chloroform was present in the water from the shower, the bath water volume contained chloroform concentrations that could volatilize. The authors concluded that, in this study, chloroform volatilization was approximately 50 percent, and suggested that inhalation exposure could be potentially greater than that from ingestion.

Andelman (1985b) used the single compartment air model to analyze maximum indoor air chemical concentrations resulting from the volatilization of the chemicals from tap water brought to a home. Taking an adult man with a daily respiratory volume of 20 m^3 and a daily water intake of 2 liters, the author concluded that the air exposure to chloroform is higher than that from water by a factor of 6. This calculation indicates that inhalation exposure is substantial if compared to exposure attributed to the ingestion route.

Researchers in Canada (Lévesque et al., 1994) studied 11 male swimmers to quantify their exposure to chloroform from the indoor air of a swimming pool. Water from the indoor ambient air at the pool and exhaled breath (alveolar air) were sampled. Data were collected over seven days in the pool area. Exhaled breath data were collected over five days from the subjects, ages 19 to 38 years (median age = 23 years) during and after 55-minute swimming workouts. The detection limit was 10 ppb. The mean alveolar air concentration was 52.6 ppb (0 to 200 ppb, standard deviation 50.8 ppb) because of air contamination in the locker room. Mean chloroform body burden (concentration of chloroform in the air of the lungs) after 35 minutes of exercise ranged from 100 to 950 ppb. Mean chloroform body burden after 55 minutes of exercise ranged from 103.9 to 1093.6 ppb.

Weisel and Shepard (1994) studied chloroform occurrence and exposure in swimming pools disinfected with sodium hypochlorite. Breath samples were taken from one individual following 30 minutes of exposure during five separate visits to an indoor pool in New Brunswick, New Jersey. During three of the visits, the individual swam for the 30-minute period and remained at rest in the water. During the other two visits, the individual remained three meters from the pool edge but out of the water. Breath samples were taken within five minutes after leaving the pool area and compared to a pre-exposure breath sample prior to entry in the pool. Water samples were analyzed by purge and trap coupled with GC/MS. Air samples were collected on an adsorbent trap filled with 0.5 g Tenax GC.

Chloroform concentrations in the swimming pool water ranged between 32 and 150 μg/L, with a mean of 85 μg/L. Air samples revealed chloroform concentrations ranging from 23 to 120 $\mu g/m^3$, with a mean of 87 $\mu g/m^3$. The pre-exposure breath concentrations were less than 0.5 $\mu g/m^3$ on all but one day, when a value of 1.6 $\mu g/m^3$ was measured. Initial concentrations of chloroform in breath increased immediately after the 30 minute swimming and resting period and generally declined as more time passed. Chloroform concentrations in breath were higher after swimming than after resting. Chloroform concentrations in breath ranged from 0.76 to 26.5 $\mu g/m^3$.

Using these concentrations, the authors made a conservative estimate of chloroform exposure due to swimming and from ingesting chlorinated drinking water. The inhalation exposure to an adult who swims one hour/day, three days/week, in a pool with a chloroform air concentration of 100 $\mu g/m^3$ and assuming a respiration rate of one m^3/h would be 300 μg. The respiration rate used in this study is higher than the EPA standard of 20 m^3/day (0.833 m^3/h) and results in a more conservative internal dose than if the EPA standard was used. These assumptions would result in an internal chloroform dose of 210 μg. The same person who

daily ingests two liters of water with a chloroform concentration of 25 µg/L would have a weekly exposure from ingestion of 350 µg, assuming 100-percent absorption.

Lindstrom et al. (1997) assessed the exposure of collegiate swimmers to chloroform during a two-hour training session in an indoor natatorium at the University of Montana. Alveolar breath samples from one female and one male were collected before, during, and three hours after the swimming session. A total of fifty samples were obtained by using the single breath canister technique. Six whole-air grab samples and two pool water samples were collected to obtain background concentration data. Pool water chloroform concentrations were 68 and 73 µg/L. Chloroform concentration in the air was 145 µg/m^3 during the exposure period.

Chloroform concentrations in pre-exposure breath samples ranged from 3.07 to 3.46 µg/m^3. At two and at eight minutes of exposure, breath concentrations rapidly increased to 71.2 and 160 µg/m^3, respectively, peaking 371 µg/m^3 at ninety minutes. This peak concentration was more than two times the maximum concentration possible (i.e., 145 µg/m^3) considering an inhalation route only, suggested the importance of the dermal exposure route. Body burden of chloroform during the three hours following the exposure period showed breath levels more than five times higher than pre-exposure levels.

Based on the post-exposure results, the authors used a three-compartment model, which allowed estimation of compartmental half-lives, resulting minimum bloodborne dose, and an approximation of the duration of elevated body burden. The authors concluded that at an air chloroform concentration of 145 µg/m^3 and a 0.33 steady state breath/environmental equilibrium ratio, the inhalation exposure route alone should contribute about 48 µg/m^3 to the final breath concentration at the end of the exposure period. The dermal exposure route was considered to be the dominant estimated to account for 80 percent of the blood chloroform concentration.

Weisel and Jo (1996) collected and analyzed time series samples of expired alveolar breath to evaluate changes in concentrations of chloroform being expired after showering. Analyses of chloroform in expired breath were used to determine uptake from tap water by inhalation and dermal exposure. Each route of exposure contributed to the total exposure of these compounds from daily water use. The chloroform concentrations in the exhaled breath were elevated in each subject after both inhalation and dermal exposures during showering and bathing. Chloroform concentrations in the water ranged from 10 to 50 µg/L for the inhalation exposure experiments and from BDL to 41 µg/L for the dermal exposure experiments. The bath water ranged from 11 to 15 µg/L for the dermal exposure experiments. Expired

breath concentrations ranged from 0.02 to 0.05 µg for the inhalation-only exposure, 0.02 to 0.13 µg for the dermal-only shower exposure, and from 0.33 to 0.56 µg after the dermal bathing study. The larger amount expired after bathing is due to the longer exposure time (60 minutes for a bath versus 10 minutes for a shower).

Wallace (1997) summarized existing information on human integrated exposure to chloroform (i.e., exposure through drinking water, diet, indoor air, inhalation from shower, and dermal absorption from shower). The author found that each of these exposures provides chloroform amounts ranging from 10 to 40 µg/d to an individual whose water supply is chlorinated, for a total chloroform intake of 100 to 150 µg/d for an adult.

Another exposure route is dermal absorption from swimming in indoor pools. According to studies reviewed by Wallace (1997) and carried out by Weisel and Shepard (1994), Levesque et al. (1994), and Lindstrom et al. (1995), 25 percent to 50 percent of the total chloroform exposure in swimming pools comes from the dermal exposure route. Additionally, Weisel and Shepard calculated that for an adult swimming for a period of one hour a day, three days a week, in a pool water with chloroform air concentration of 100 µg/m^3, the weekly dose from inhalation would be 210 µg. They also estimated a similar inhalation and dermal dose from showering and a similar ingestion dose per week for the same individual.

Wallace (1997) reported the results of a 1979 study conducted by Krotoszynski et al. (1977, 1979) in which measurements of the pulmonary elimination of chloroform through the exhaled breath in 54 individuals revealed a geometric mean of 23.3 µg/m^3, and a range of 7.4 to 73.7 µg/m^3.

6.2.2 Bromodichloromethane

Dietary Intake

No exposure estimates were found for bromodichloromethane in food; however, five studies analyzed foods for bromodichloromethane content. This section summarizes these studies, as well as data collected for an EPA drinking water criteria document. Given the use of chlorine in processes such as the ones used by the poultry industry, bromodichloromethane formation is possible and, therefore, exposure from such sources is also possible. However, exposure remains unquantified due to the lack of analysis.

Entz et al. (1982) analyzed food samples from Elizabeth, New Jersey; Chapel Hill, North Carolina; and Washington, D.C., for bromodichloromethane. A total of 39 different food items from each city were

collected according to standards set for the FDA Total Diet Study program. From 20 food composites representing four food groups, bromodichloromethane was detected in one dairy composite at 1.2 ppb and two beverage composites at 0.3 and 0.6 ppb. Individual food analysis detected bromodichloromethane in three samples of cola soft drinks at concentrations of 2.3, 3.4, and 3.8 ppb and one butter sample at 7 ppb.

Uhler and Daichenko (1987) sampled food products from 15 food processing plants located in nine states. Plants were chosen from areas in which the presence of chloroform in the process water would be most probable. Results of analysis showed that out of 39 food items tested, bromodichloromethane was detected in six samples ranging from BDL to 2.3 ng/g: two samples of clear sodas, 1.2 and 2.3 ng/g; one sample of dark cola, 1.2 ng/g; and three samples of ice cream, 0.6 to 2.3 ng/g.

Howard (1990) reported the results of a 1982 study conducted by Brodzinsky and Singh that analyzed various soft drinks for bromodichloromethane concentrations. The researchers found that average levels ranged from 0.9 to 5.9 ppb for colas and 0.1 to 0.2 ppb for clear soft drinks.

Graham and Robertson (1988) reported the results of a study that analyzed THM concentrations in soft drinks. These researchers found bromodichloromethane concentrations ranging from 1.20 to 4.00 µg/L in the cola drinks that they sampled.

The EPA Office of Science and Technology's *Drinking Water Criteria Document on Trihalomethanes* (EPA, 1994d) summarized study results for the occurrence of disinfection byproducts in air and food. This document presents study results discussed previously in this document. The studies were conducted by Entz et al. (1982), Abdel-Rahman (1982), Uhler and Daichenko (1987), Toyoda et al. (1990), and Kroneld and Reunanen (1990). Exhibit 6-13 summarizes the bromodichloromethane levels detected in food reported by the latter two studies.

Exhibit 6-13. Bromodichloromethane Levels in Food

Study	Food Item	Bromodichloromethane Concentration
Toyoda et al., 1990	90 samples – summer 90 samples – winter	BDL – 1.7ng/g BDL – 1.2 ng/g
Kroneld and Reunanen, 1990	Pasteurized milk	BDL – 0.07 µg/L

Sources: Listed in exhibit

McNeal et al. (1995) purchased foods from local markets in the Washington, D.C., area and analyzed the products for THMs using EPA Method 524.2. The detection limit for bromodichloromethane was 0.05 ng/g. The researchers observed that the same products from different lots (i.e., produced on different dates) had significantly different contaminant concentrations. Exhibit 6-14 summarizes the bromodichloromethane concentrations detected in the food and beverages. Bromodichloromethane was not detected in six types of noncarbonated bottled waters, two types of beer, two types of apple juice, one sport drink sample, three different canned tomato and pizza sauces, one vegetable juice, three different vegetable waters, and three other foods.

Exhibit 6-14. Bromodichloromethane Concentrations in Food and Beverages

Food Analyzed*	$CHBrCl_2$ (ng/g)
Flavored sparkling water	38
Fruit drink A	5
Cola A (3 samples)	2 - 4
Diet orange A soda (4 samples)	2 - 12
Diet white grape soda	2
Diet lemon lime soda	1
Diet raspberry soda	3
Diet cherry berry soda	2
Diet grapefruit soda	3
Diet tangerine soda	2

Source: McNeal et al., 1995

*Different letters for the same food indicate different brands

Air Intake

This section summarizes four studies that reported bromodichloromethane levels in air. Some of these studies measured bromodichloromethane concentrations in the breath of individuals. In addition, this section presents data from one study reported in an EPA drinking water criteria document (EPA, 1994d).

In a pilot study designed to field test personal air quality monitoring methods, Wallace et al. (1982) collected personal air samples from students at two universities: Lamar University, Texas, which is located near petroleum refineries, and the University of North Carolina (UNC), which is located in a nonindustrialized area in Chapel Hill, North Carolina. In personal air samples collected from 11 Lamar students, bromodichloromethane was detected in 64 percent of the samples, with a mean of 1.23 $\mu g/m^3$, a

median of 1 μg/m³, and a range of 0.12 to 3.72 μg/m³. At UNC, 17 percent of the samples from six students had detectable levels of bromodichloromethane. Concentrations ranged from 0.12 to 4.36 μg/m³, with a mean of 0.83 μg/m³ and a median of 0.12 μg/m³.

Another study conducted by Wallace et al. (1984) analyzed the air, water, and food of nine individuals from New Jersey and three individuals from North Carolina over three seasons. The New Jersey subjects were expected to have occupational exposure to volatile organic compounds; the North Carolina subjects were not. Subjects were monitored during different times of the day, over a period of six weekdays and three weekend days. Air samples were analyzed using a purge and trap method, followed by GC/MS techniques. The detection limit was 10 μg/m³. Exhibit 6-15 summarizes the monitoring results.

Exhibit 6-15. Summary Statistics of Bromodichloromethane in Ambient Air of New Jersey and North Carolina Subjects (μg/m³)

Location	Number of Samples	Number Below Detection Limit	Number of Samples at Trace Levels	Median	Range
New Jersey	164	136	16	0.44	0.10 – 13.40
North Carolina	60	48	7	–	0.10 – 3.66

Source: Wallace et al., 1984

Wallace et al. (1984) also analyzed breath samples of the same individuals. Breath samples were collected using a specially designed spirometer. Samples were analyzed using a purge and trap method, followed by GC/MS techniques. The detection limit was 10 μg/m³. Exhibit 6-16 presents the monitoring results.

Exhibit 6-16. Summary Statistics of Bromodichloromethane in Breath of New Jersey and North Carolina Subjects (mg/m³)

Location	Number of Samples	Number Below Detection Limit	Number of Samples at Trace Levels	Median	Range
New Jersey	49	49	0	0.17	0.17 – 2.20
North Carolina	17	17	0		0.14 – 2.20

Source: Wallace et al., 1984

From November 1982 to December 1983, ambient air samples at four urban/industrial sites in the California South Coast air basin were surveyed for the presence of halogenated hydrocarbons (Shikiya et al., 1984). Thirty-five percent of the samples detected bromodichloromethane above the quantitation limit of

0.01 ppb. Peaks in the concentration of bromodichloromethane were observed at the various sites in June and July, with downtown Los Angeles and Dominguez registering the highest monthly means of 0.03 ppb. The maximum reported value was 0.04 ppb, while the composite means ranged from 0.02 to 0.1.

Howard (1990) reported the results of a 1982 study conducted by Brodzinsky and Singh. Ambient air samples from Magnolia, Arizona; El Dorado, Arkansas; Chapel Hill, North Carolina; and Beaumont, Texas, were measured. Bromodichloromethane was detected at mean concentrations of 0.76, 1.4, 120, and 180 ppt, respectively.

In *Drinking Water Criteria Document on Trihalomethanes*, EPA summarized study results for the occurrence of disinfection byproducts in air and food (EPA, 1994d). The criteria document presents results of outdoor air studies already discussed in this document. The studies were conducted by Brodinsky and Singh (1983) and Shikiya et al. (1984). In addition, the document summarizes a study by Armstrong and Golden (1986), which presents both occurrence and exposure data. Exhibits 6-17 and 6-18 present the bromodichloromethane concentrations and exposure from outdoor air and indoor air, respectively, reported by Armstrong and Golden.

Exhibit 6-17. Bromodichloromethane Occurrence and Exposure from Outdoor Air

Study	Location	Bromodichloromethane Concentration (mg/m^3)	Bromodichloromethane Exposure (µg/day)
Armstrong and Golden, 1986	Outdoor swimming pool	1 – 72	0.12 – 26

Source: Armstrong and Golden, 1986

Exhibit 6-18. Bromodichloromethane Occurrence and Exposure from Indoor Air

Study	Location	Bromodichloromethane Concentration (µg/L)	Bromodichloromethane Exposure (µg/day)
Armstrong and Golden, 1986	Indoor swimming pool	1 – 90	0.12 – 26
	Hot tubs	BDL – 105	0.12 – 26

Source: Armstrong and Golden, 1986

6.2.3 Dibromochloromethane

Dietary Intake

No exposure estimates were found for dibromochloromethane in food. The FDA does not analyze for dibromochloromethane in foods, however, chlorine is used for several purposes (e.g., disinfection of chicken in poultry plants, as described previously) and for the chlorination of water at soda and beer bottling

plants (Borum, 1991). Therefore, dietary exposure is possible from the byproducts of chlorination in food production. This section summarizes data from two studies reported in an EPA drinking water criteria document (EPA, 1994d) and two other studies that reported dibromochloromethane in food products.

EPA's *Drinking Water Criteria Document on Trihalomethanes* summarizes study results for occurrence and exposure of disinfection byproducts in air and food (EPA, 1994d). Exhibit 6-19 presents the results of two studies analyzing dibromochloromethane occurrence in food.

Exhibit 6-19. Dibromochloromethane Levels Found in Food

Study	Food Item	Dibromochloromomethane Concentration
Toyoda et al., 1990	90 food samples – summer 90 food samples – winter	BDL – 0.5 ng/g BDL – 0.7 ng/g
Kroneld and Reunanen, 1990	Pasteurized milk	BDL – 0.3 µg/L

Sources: Listed in exhibit

Graham and Robertson (1988) reported the results of THM analysis on soft drinks. Dibromochloromethane concentrations ranged from BDL to 5 µg/L in the sampled soft drinks.

McNeal et al. (1995) purchased foods from local markets in the Washington, D.C., area and analyzed the products for TTHMs using EPA Method 524.2. The detection limit for dibromochloromethane was 0.05 ng/g. The researchers observed that the same products from different lots (i.e., produced on different dates) had significantly different contaminant concentrations. Dibromochloromethane was detected in five of the 37 food samples analyzed. Exhibit 6-20 presents these results. Dibromochloromethane was not detected in six types of noncarbonated bottled waters, two types of beer, five different flavored noncarbonated beverages, nine of the 13 types of soft drinks, three different canned sauces, seven types of canned vegetables and vegetable juices, and three other foods.

Exhibit 6-20. Dibromochloromethane Concentrations in Food and Beverages

Food Analyzed	$CHBr_2Cl$ (ng/g)
Flavored sparkling water	1
Diet orange soda (3 samples)	1 – 2
Diet white grape soda	0.5

Source: McNeal et al., 1995

Air Intake

Limited information is available concerning dibromochloromethane levels in air. This section summarizes four studies that reported dibromochloromethane levels in air. Some of these studies measured dibromochloromethane concentrations in the breath of individuals. In addition, this section summarizes data from a study reported in an EPA drinking water criteria document (EPA, 1994d).

Wallace et al. (1982) conducted a pilot study designed to field test personal air quality monitoring methods. Personal air samples were collected from students of two universities: Lamar University, which is located near petroleum refineries, and UNC, which is located in a non-industrialized area. Dibromochloromethane was not detected above 0.12 $\mu g/m^3$.

In a another study (Shikiya et al., 1984), ambient air samples were collected from November 1982 to December 1983 at four urban/industrial sites in the California South Coast air basin and analyzed for halogenated hydrocarbons. Dibromochloromethane was detected above the quantitation limit of 0.01 ppb in 17 percent of the samples. The maximum reported value, highest monthly mean, and highest mean composite were 0.29, 0.28, and 0.05 ppb, respectively, all of which were recorded in downtown Los Angeles in July. Mean concentrations ranged from BDL to 0.05 ppb.

Howard (1990) reported the results of a 1982 study conducted by Brodzinsky and Singh. Dibromochloromethane levels were reported in ambient air samples from Magnolia and El Dorado, Arizona; Chapel Hill, North Carolina, Beaumont, Texas; and Lake Charles, Louisiana, at concentrations of 0, 0.48, 14, 14, and 19 ppt, respectively.

In another study (Atlas and Schauffler, 1991), replicate air samples were collected at various locations on the island of Hawaii during a month-long field experiment to test an analytical method for determining halocarbons in ambient air. Dibromochloromethane was detected at a mean of 0.27 ppt on the island.

The EPA Office of Science and Technology's *Drinking Water Criteria Document on Trihalomethanes* summarizes study occurrence results for disinfection byproducts in air and food (EPA, 1994d). This document presents the results of outdoor air studies discussed previously in this document. The studies were conducted by Brodzinsky and Singh (1983), Shikiya et al. (1984), and Atlas and Schauffler (1991). In addition, the document summarizes a study by Armstrong and Golden (1986) which presents both occurrence

and exposure results. Exhibits 6-21 and 6-22 present the results of dibromochloromethane occurrence from outdoor air and occurrence and exposure from indoor air, respectively, from the Armstrong and Golden study.

Exhibit 6-21. Dibromochloromethane Occurrence from Outdoor Air

Study	Location	Dibromochloromethane Occurrence (µg/m3)
Armstrong and Golden, 1986	Outdoor swimming pool	BDL – 8

Source: Armstrong and Golden, 1986

Exhibit 6-22. Dibromochloromethane Occurrence and Exposure from Indoor Air

Study	Location	Dibromochloromethane Occurrence (µg/L)	Dibromochloromethane Exposure (µg/day)
Armstrong and Golden, 1986	Indoor swimming pools	0.3 – 30	0.18 – 94
	Hot tubs	BDL – 48	0.18 – 94

Source: Armstrong and Golden, 1986

6.2.4 Bromoform

Dietary Intake

Based on a review of the literature reviewed, one study concerning the occurrence of bromoform in food was available. This section includes the results of this study which is summarized in an EPA drinking water criteria document (EPA, 1994d). The FDA does not analyze for bromoform in foods, however, chlorine is used for several purposes in food production (e.g., disinfection of chicken in poultry plants, as described previously) and for the chlorination of water at soda and beer bottling plants (Borum, 1991). Therefore, dietary exposure is possible from the byproducts of chlorination in food processing. However, exposure from foods has not been extensively quantified.

EPA's *Drinking Water Criteria Document on Trihalomethanes* summarizes the results of one study of bromoform levels found in food (EPA, 1994d). Exhibit 6-23 summarizes the results of this study.

Exhibit 6-23. Bromoform Levels Found in Food

Study	Food Item	Bromoform Concentration(ng/g)
Toyoda et al., 1990	90 food samples – summer 90 food sample – winter	BDL – 3.1 BDL – 8.1

Source: Toyoda et al., 1990

Air Intake

Brominated THMs are usually found in air at low concentrations. This section summarizes three studies that reported bromoform levels in air, as well as data from one study reported in an EPA drinking water criteria document (EPA, 1994d).

From November 1982 to December 1983, ambient air samples at four urban/industrial sites in the California South Coast air basin were surveyed for the presence of halogenated hydrocarbons (Shikiya et al., 1984). Thirty-one percent of the samples detected bromoform above the quantitation limit of 0.01 ppb. Peaks in the concentration of bromoform were observed at the various sites in May and June, with the downtown Los Angeles site registering the highest composite mean of 0.04 ppb and the highest monthly mean of 0.31 ppb in June 1983.

EPA (1989, 1991) reported the results of a 1983 Brodzinsky and Singh study of ambient air concentrations for several urban locations across the United States. From 1976 to 1977 in El Dorado, Arizona, bromoform was detected in 76 percent of 46 samples at a mean of 0.81 ng/m^3, with a range from BDL to 2.7 ng/m^3. In samples from Lake Charles, Louisiana, bromoform was detected in all four samples, with a mean of 50 ng/m^3 and a range from 6.6 to 71 ng/m^3 in 1978. In 1977, bromoform was detected in 89.3 percent of 28 ambient air samples collected from Magnolia, Arizona. Concentrations ranged from BDL to 8.3 ng/m^3, and the mean was 1.5 ng/m^3. Overall, the average bromoform concentration was 37 ng/m^3.

In a third study, replicate air samples were collected at various locations on the island of Hawaii during a month-long field experiment to test an analytical method for determining halocarbons in ambient air. Bromoform was detected at a mean concentration of 1.9 ppt (Atlas and Schauffler, 1991).

EPA's *Drinking Water Criteria Document on Trihalomethanes* summarizes study results for the occurrence of disinfection byproducts in air and food (EPA, 1994d). This document presents the results of outdoor air studies, discussed previously. The studies were conducted by Brodzinsky and Singh (1983), Shikiya et al. (1984), and Atlas and Schauffler (1991). In addition, the EPA document discusses a study presenting both occurrence and exposure results. Exhibits 6-24 and 6-25 summarize the bromoform concentrations and exposure from outdoor and indoor air reported by Armstrong and Golden (1986).

Exhibit 6-24. Bromoform Occurrence and Exposure in Outdoor Air

Study	Location	Bromoform Occurrence (µg/L)	Bromoform Exposure (µg/day)
Armstrong and Golden, 1986	Outdoor swimming pools	BDL	0.42 - 70

Source: Armstrong and Golden, 1986

Exhibit 6-25. Bromoform Occurrence and Exposure in Indoor Air

Study	Location	Bromoform Occurrence (µg/L)	Bromoform Exposure (µg/day)
Armstrong and Golden, 1986	Indoor swimming pools	BDL - 20	0.42 - 70
	Hot tubs	BDL - 62	0.42 - 70

Source: Armstrong and Golden, 1986

6.2.5 Total Trihalomethanes

Dietary Intake

Based on a review of the published literature, one study concerning the occurrence of total trihalomethanes in food in the United States was available. Currently, the FDA does not analyze for total trihalomethanes in foods. Studies with information on these individual THMs were discussed previously, but only one reference was found that contained information about the total group of THMs. As previously stated, given the use of chlorine in such processes as those used by the poultry industry, the formation of trihalomethanes is possible and, therefore, so is exposure from these sources. However, these possibilities remain unquantified.

Toyoda et al (1990) analyzed the daily intakes of TTHMs in Japanese housewives. Exhibit 6-26 presents these results.

Exhibit 6-26. Total Trihalomethanes Levels in Food

Food Item	Total Trihalomethanes Concentration (ng/g)
90 food samples - summer	3.8 - 108.2
90 food samples - winter	1.6 - 81.0

Source: Toyoda et al., 1990

Air Intake

No information is available concerning the occurrence of total trihalomethanes in air; however, individual compounds have been discussed in previous sections.

6.2.6 Monochloroacetic Acid

Dietary Intake

Based on a review of the published literature, no information is available on the occurrence of monochloroacetic acid in food in the United States. Currently, the FDA does not analyze for monochloroacetic acid in foods. However, chlorine is used for several purposes in food production (e.g., disinfection of chicken in poultry plants) and the chlorination of water at soda and beer bottling plants. Therefore, dietary exposure is possible from the byproducts of chlorination in food products. Also, monochloroacetic acid has a limited use as a herbicide (Borum, 1991).

Air Intake

Based on a review of the published literature, no information is available concerning the occurrence of monochloroacetic acid in air.

6.2.7 Dichloroacetic Acid

Dietary Intake

Based on a review of the published literature, no information is available on the occurrence of dichloroacetic acid in food in the United States. Currently, the FDA does not analyze for dichloroacetic acid in foods. However, chlorine is used for several purposes in food production (e.g., disinfection of chicken in poultry plants) and for the chlorination of water at soda and beer bottling plants. Therefore, dietary exposure is possible from the byproducts of chlorination in food products. In addition, dichloroacetic acid has a limited use as a herbicide (Borum, 1991).

Air Intake

Based on a review of the published literature, no information is available concerning the occurrence of dichloroacetic acid in air.

6.2.8 Trichloroacetic Acid

Dietary Intake

Based on a review of the published literature, no information is available concerning the occurrence of trichloroacetic acid in food in the United States. The FDA does not analyze for trichloroacetic acid in foods. However, chlorine is used for several purposes in food production (e.g., disinfection of chicken in

poultry plants) and for the chlorination of water at soda and beer bottling plants. Therefore, dietary exposure is possible from the byproducts of chlorination in food products. In addition, trichloroacetic acid has a limited use as a herbicide (Borum, 1991).

Air Intake

No information is identified in the review of published literature concerning the occurrence of trichloroacetic acid in ambient or indoor air in the United States (Borum, 1991).

6.2.9 Monobromoacetic Acid

Dietary Intake

Based on a review of the published literature, no information is available on the occurrence of monobromoacetic acid in food in the United States. Currently, the FDA does not analyze for monobromoacetic acid in foods. However, chlorine is used for several purposes in food production (e.g., disinfection of chicken in poultry plants) and for the chlorination of water at soda and beer bottling plants. Therefore, dietary exposure is possible from the byproducts of chlorination in food products. In addition, monobromoacetic acid has a limited use as a herbicide (Borum, 1991).

Air Intake

Based on a review of the published literature, no information is available concerning the occurrence of monobromoacetic acid in air.

6.2.10 Dibromoacetic Acid

Dietary Intake

No information in the published literature is available on the occurrence of dibromoacetic acid in food in the United States. Currently, the FDA does not analyze for dibromoacetic acid in foods. However, chlorine is used for several purposes in food production (e.g., disinfection of chicken in poultry plants) and for the chlorination of water at soda and beer bottling plants. Therefore, dietary exposure is possible from the byproducts of chlorination in food products. In addition, dibromoacetic acid has a limited use as a herbicide (Borum, 1991).

Air Intake

Based on a review of the published literature, no information is available concerning the occurrence of dibromoacetic acid in air.

6.2.11 Haloacetic Acids 5

Dietary Intake

Based on a review of the published literature, no information is available on the occurrence of total haloacetic acids in food in the United States. Currently, the FDA does not analyze for dibromoacetic acid in foods; however, chlorine in food production (e.g., disinfection of chicken in poultry plants) and for the chlorination of water at soda and beer bottling plants. Therefore, dietary exposure is possible from the byproducts of chlorination in food products. In addition, each of the haloacetic acids has a limited use as a herbicide (Borum, 1991)

Air Intake

Based on a review of the published literature, no information is available concerning the occurrence of haloacetic acids in air.

6.2.12 Chloral Hydrate

Dietary Intake

Based a review of the published literature, no information is available on the occurrence of chloral hydrate in food in the United States. The FDA does not analyze for chloral hydrate in foods. However, chlorine is used for several purposes in food production, including sanitizing equipment and containers, conveying vegetables, cooling heat-sterilized foods, washing meats and nuts, processing seafoods and poultry and red meats, oxidizing and bleaching flour and for the chlorination of water at soda and beer bottling plants (Wei et al., 1985; Borum, 1991). Therefore, dietary exposure to chloral hydrate is possible as a result of its formation as a result of chlorination in food products.

Air Intake

No information in the published literature is available concerning the occurrence of chloral hydrate in ambient or indoor air in the United States. However, chlorine volatilization from tap water may contribute to chloral hydrate exposure in air (Borum, 1991).

6.2.13 Bromate

Dietary Intake

Based on a review of the published literature, no information is available concerning the occurrence of bromate levels in food in the United States. Currently, the FDA does not analyze for bromate in foods. However, bromate has been used as a maturing agent in malted beverages, as a dough conditioner, and in confectionery products. Therefore, exposure to bromate is possible through ingestion of foods processed using bromate (Borum, 1991). According to the FDA, American beer producers have stopped using bromates in the manufacturing process (DiNovi, 1977). However, bromate can still be used for malting barley in imported beers and is used as a preservative by the bakery industry.

Air Intake

Based on the studies reviewed, no information is available concerning the occurrence of bromate in air in the United States. Bromate is not a volatile compound and therefore is not expected to be found in high concentrations in air.

6.2.14 Chlorate and Chlorite

Based on a review of the published literature, no information is available on the occurrence of chlorate or chlorite in food in the United States. Currently, the FDA does not analyze for chlorine dioxide in foods. However, the FDA is aware of uses of chlorine dioxide in food processing (DiNovi, 1997). Various vegetables including sugar beets, lima beans, corn, carrots, peas, potatoes, and tomatoes, are disinfected with chlorine dioxide, followed by a potable water rinse. In addition, the use of chlorine dioxide is approved for flour bleaching. A current proposal would replace the poultry industry's use of chlorine with chlorine dioxide. Sodium chlorite has generally been considered safe for use in bleaching cherries.

Chlorine dioxide is a highly reactive chemical and is likely to transform readily to chlorite and chlorate during contact with food (DiNovi, 1997). FDA regulations are written such that fruits and vegetables in contact with chlorite and chlorate are required to undergo further processing. The FDA acknowledged that some raw vegetables could be exposed to chlorite and chlorate and is currently conducting an analysis on residual amounts in these vegetables (DiNovi, 1997). Cooking processes convert chlorite and chlorate to chloride; therefore, exposure to these chemicals is not anticipated after cooking.

Air Intake

Based on a review of the published literature, no information is available on the occurrence of chlorate or chlorite in air in the United States. However, chlorine dioxide is used as a sanitizer in air ducts, thus ambient air concentrations are possible where this sanitation method is practiced (Borum, 1991). Due to the chemical and physical properties of chlorite and chlorate, it is not anticipated that these two compounds will occur in a gaseous form and, therefore, air intake of these two compounds should be nonexistent.

7. RELATIVE SOURCE CONTRIBUTION EVALUATION

The occurrence and exposure data for drinking water and other sources presented in Sections 3 through 6 can be used to develop maximum residual disinfectant level goals (MRDLGs) and maximum contaminant level goals (MCLGs) using a relative source contribution (RSC) approach. This section describes the RSC approach and the types of exposure assumptions that would be used with occurrence data (when adequate occurrence data are available) to estimate exposure. In addition, this section presents the RSCs chosen for each disinfectant and disinfection byproduct for which the RSC approach is applicable.

7.1 OVERVIEW OF THE RELATIVE SOURCE CONTRIBUTION APPROACH

The RSC is the fraction of total exposure attributable to a given environmental source. The portion of total exposure attributable to drinking water (the RSC for drinking water) is multiplied by the reference dose for noncarcinogens to set the MCLG or MRDLG. The rationale for using the RSC approach to set the MRDLG or MCLG is based on the idea that an individual's total exposure to a chemical should not exceed the reference dose (RfD) established for noncarcinogens (or, more recently, the dose reflecting the chosen margin of exposure for nonlinear carcinogens). The reference dose for noncarcinogens is formally defined as "an estimate (with uncertainty spanning approximately an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects over a lifetime" (EPA, 1988). The RfD is estimated by dividing the experimental no observed adverse effect level (NOAEL) or the lowest observed adverse effect level (LOAEL) by an appropriate uncertainty factor. The NOAEL is the highest experimental dose at which there is no biologically or statistically significant increase in the frequency or severity of a critical effect in an exposed group occurred when compared with an appropriate control group. If all doses in the available data resulted in adverse effect, thereby precluding the determination of a NOAEL, the RfD may be determined from the LOAEL. The NOAEL or the LOAEL is then divided by an uncertainty factor (UF). The UF is based on the data set and variability in sensitivity among humans, uncertainty in extrapolating effects data collected on animals to effects in humans, uncertainty associated with extrapolating chronic levels from exposure levels from studies using less than chronic exposure, uncertainty in extrapolating from LOAELs, and uncertainty in the toxicological data. The resulting value (NOAEL or LOAEL / UF) is the RfD.

The RSC is employed to establish a MCLG or MRDLG for Category II and III compounds using EPA's three-category approach. As described in the 1994 proposed rule, the three-category approach classifies compounds as carcinogens (Category I) or noncarcinogenic compounds (Category III) based on evidence of carcinogenicity, pharmacokinetics, potency, and exposure. Compounds that exhibit carcinogenic

endpoints, but have limited evidence, and exhibit noncarcinogenic endpoints are classified as Category II compounds. The assessment of carcinogenic health effects is based on EPA's five-tiered general carcinogenic classification scheme (EPA, 1986). The MCLG or MRDLG for Category I compounds is set at zero because it is assumed, in the absence of other data, that there is no threshold dose for carcinogenicity. For Category II compounds, the MCLG or MRDLG is established using one of two options. The first option uses the RfD and then applies an additional safety factor of 1 to 10 to establish the MCLG or MRDLG. This accounts for the possible carcinogenicity of the compound. The second option sets the MCLG or MRDLG using a theoretical lifetime excess cancer risk of 10^{-5} to 10^{-6} using a conservative mathematical extrapolation model. EPA generally uses the first option to establish MCLG or MRDLG values. However, EPA uses the second option when valid noncarcinogenic data are not available to calculate the RfD and adequate experimental data are not available to quantify the cancer risk.

The RSC approach used in setting drinking water standards involves several general steps. First, the population of concern to be protected by the MCLG or MRDLG is chosen. Next, data on the occurrence of the pollutant in each medium are used (if available) with assumptions about the intake of water, food, and air for the chosen population to estimate exposure levels from these environmental sources. These estimated exposure levels are then used to estimate total exposure to a given disinfectant or disinfection byproduct. As noted above, the fraction of total exposure attributable to drinking water (the RSC) is then multiplied by the reference dose for the chemical and is used in the following equation to set the MCLG or MRDLG for noncarcinogenic chemicals:

$$MCLG \text{ or } MRDLG = \frac{RfD \times BW \times RSC}{WC}$$

where:

RfD	=	Reference dose for noncarcinogens (mg/kg per day),
BW	=	Body weight of the individual to be protected (kg), and
WC	=	Water consumption (L/d).
RSC	=	Fraction attributed to drinking water.

When adequate exposure data from drinking water and other sources are available and the data indicate that drinking water exposure contributes between 20 and 80 percent of the total exposure, EPA uses the actual percentage contributed by drinking water exposure to determine the RSC for drinking water (59 FR, 38668). When data indicate that the exposure from drinking water is between zero and 20 percent

or 80 and 100 percent. EPA uses a floor and ceiling value of 20 percent or 80 percent, respectively. When adequate exposure data for the chemical are not available, EPA typically uses a 20 percent default as the RSC for drinking water exposure (59 FR, 38668). However, the 1994 proposed rule used the 80 percent default value to set the RSC for all relevant disinfectants and disinfection byproducts (DBPs) because, based on available information, the drinking water source was anticipated to contribute the vast majority of overall exposure.

7.2 CHOICE OF THE POPULATION OF CONCERN

Exposure to disinfectants and DBPs possibly may have different effects on the subpopulations being served by the water treatment system. Thus, assessments of the exposure to disinfectants and DBPs should consider sensitive subpopulations. Some common sensitive subpopulations include infants, the elderly, pregnant women, people with cardiovascular disease, malnourished individuals, enzyme deficient individuals, and immuno-compromised individuals. The health effects from disinfectants and DBPs have been generally characterized as long-term exposure illnesses and are assumed to pose limited additional risk to most subpopulations. Based on these considerations, the population of concern for exposure from disinfectants and DBPs was characterized as adults with long-term exposure.

7.3 ESTIMATION OF EXPOSURE FROM DRINKING WATER

The RSC approach uses central tendency estimates of occurrence and exposure when estimating the contribution of exposure from drinking water for an average adult. However, it is also important to note that exposure to disinfectants and DBPs in drinking water may vary according to regional water quality and disinfection practices and also with residual disinfection concentrations is also important . Residual disinfectant concentrations decrease from the point of entry to the terminal portions of the distribution system (Haas, 1990). The formation of most DBPs increases with time in the distribution system (Stevens and Symons, 1977). The inverse relationship of residual disinfectant and most halogen-substituted DBP concentrations creates a range of exposures within a distribution system. Consumers closer to the treatment plant may have higher exposures to disinfectants and lower exposure to DBPs, while populations at the terminal sections of the distribution system may be exposed to higher concentrations of DBPs and lower concentrations of disinfectants.

EPA believes that the 2 L/d assumption is representative of a majority of the population over the course of a lifetime. This assumption has been used in numerous drinking water regulations and also with the human health methodology for setting ambient water quality criteria. Although a policy decision, 2 L/d

is a reasonable and protective determination that represents the intake of most water consumers in the general population according to available drinking water studies, as discussed below.

The National Academy of Sciences (NAS) specifically undertook a study to meet the needs expressed in the 1974 Safe Drinking Water Act (SDWA). Under the SDWA, EPA was required to establish federal standards for protection from harmful contaminants in the drinking water supplies of the nation. Congress directed EPA to arrange with NAS to study the adverse effects on health attributable to contaminants in drinking water. In 1977, NAS produced a multivolume study entitled, *Drinking Water and Health*. In this study, 2 L were taken as the average amount of water consumed per day. While the average per capita water consumption, as calculated from a survey of nine different literature sources, was 1.63 L/d NAS adopted 2 L/d as better representation of the intake of the majority of water consumers. EPA adopted 2 L/d as the drinking water exposure for its human health criteria methodology, understanding that it included a margin of safety that would ensure that most water consumers would be protected.

Another significant and more recent study by the National Cancer Institute (NCI) estimated intake from tapwater using data from the USDA's National Food Consumption Survey (Ershow and Canter, 1989). For 11,700 adults aged 20 to 64 years, this study reports the 50th, 75th, and 90th percentile tapwater intakes to be 1.3, 1.7, and 2.3 L/d, respectively. This study indicates that 2 L/d is the 84th percentile value.

Because EPA's purpose in selecting a higher than statistical average value is to provide a margin of safety sufficient to protect most people, a finding that 2 L is representative of 84 percent of the population is consistent with EPA's approach in setting human health criteria. EPA is also aware that certain individuals who work or exercise in hot climates may consume water at rates significantly higher than 2 L/d. EPA still believes that the 2 L/d assumption continues to represent an appropriate risk management decision. If occurrence data are adequate, the estimate of 2 L can be combined with occurrence data to estimate the daily amount of a chemical from drinking water to which an adult is exposed.

7.4 ESTIMATION OF EXPOSURE FROM SOURCES OTHER THAN DRINKING WATER

As noted previously, occurrence data for sources other than drinking water can be used to develop exposure levels that are then used in the development of MRDLGs and MCLGs. Only limited data on occurrence in sources other than drinking water were available for the disinfectants and disinfection byproducts considered in this document. When adequate data are available to estimate exposure, however,

the amount of food an adult eats per day and the amount of air an individual breathes are used with occurrence data from nondrinking water sources to estimate intake from these sources.

7.5 RELATIVE SOURCE CONTRIBUTION VALUES CHOSEN FOR INDIVIDUAL DISINFECTANTS AND DBPS

The RSC approach is used only for those disinfectants and disinfection byproducts that are not evaluated as carcinogens and that have sufficient toxicity data to establish an MCLG or MRDLG. The following sections describe whether the RSC approach is applicable to the chemical described, based on whether the chemical is a carcinogen and whether adequate toxicity data were available at the time of the 1994 proposed rule to set an MCLG or MRDLG for the chemical.

Of the chemicals that are not carcinogens and that have sufficient toxicity data to establish an MCLG or MRDLG, the available data on occurrence and exposure were reviewed for the chemical for potential use in estimating the RSC for the chemical. Data were available for only two noncarcinogenic chemicals, chloramines and chlorodibromomethane, regarding concentrations in sources other than drinking water. The data for these two chemicals were determined to be too limited to use in estimating the RSC. Therefore, for all disinfectants and disinfection byproducts for which the MRDLG and the MCLG were based on noncarcinogenic endpoints, the RSC was set at 80 percent (see Section 7.1).

7.5.1 Disinfectants

Chlorine

The U.S. Food and Drug Administration (FDA) does not currently analyze for this compound in food. Although chlorine is used extensively in food preparation, no monitoring data are available to adequately characterize exposure. Limited additional data were identified for chlorine since the 1994 proposed rule. Exposure to chlorine from the inhalation of ambient or indoor air is also insufficient to develop an RSC based on available data. Although EPA requested additional data on nondrinking water exposure in the 1994 proposed rule, no comments were received. Because no additional information are available to estimate exposure, the RSC will remain at 80 percent.

Chloramines

The 1994 proposed rule set the RSC for chloramine at 80 percent exposure from drinking water. Little information on dietary or ambient air intake exposures was published since the proposed rule. Although EPA requested additional data on nondrinking water exposure in the 1994 proposed rule, no

additional data were received in response to the request. Data characterizing exposure to chloramine from dietary intake and inhalation of ambient or indoor air are insufficient to develop an RSC. Therefore, the RSC will remain at 80 percent.

Chlorine Dioxide

Little information is available on the occurrence of chlorine dioxide in food in the United States. However, the FDA, anticipates that no typical exposure to chlorine dioxide in foods will occur because of its reactive nature. Although chlorine dioxide is approved for use as a sanitizer in air ducts (Borum, 1991), insufficient information exists to develop an RSC based on the data. The RSC was set at 80 percent in the proposed rule, and no comments were received from the proposed rule request for additional data on nondrinking water exposure. Therefore, the RSC will remain at 80 percent for chlorine dioxide.

7.5.2 Disinfection Byproducts

Total Trihalomethanes

The toxicological data for bromodichloromethane, bromoform, and chloroform supported a Category I classification for these compounds as carcinogens. Therefore, EPA proposed MCLGs of zero for these compounds. RSCs are not necessary for these carcinogenic compounds.

In the 1994 proposal, the RSC for chlorodibromomethane was set at 80 percent because there were no significant levels detected in ambient air. Although, the EPA requested additional information in the 1994 proposed rule, no additional information was received. Limited additional data on nondrinking water exposure have been identified for chlorodibromomethane since the 1994 proposed rule. Therefore, the RSC will remain at 80 percent for chlorodibromomethane.

Haloacetic Acids 5

The five haloacetic acids include mono-, di-, and trichloroacetic acid and mono- and dibromoacetic acids. EPA proposed MCLGs for two of these compounds, dichloroacetic acid and trichloroacetic acid. EPA proposed zero for dichloroacetic acid and 0.3 mg/L for trichloroacetic acid. Dichloroacetic acid was classified as a Category I carcinogenic compound, and no RSC was necessary.

The MCLG for trichloroacetic acid was based on an RSC of 80 percent. Little additional information has been identified for trichloroacetic acid since the 1994 proposed rule. Although the proposed rule

requested additional data on the concentration of trichloroacetic acid in food, water, and air, no additional studies or data were received. Therefore, the RSC will remain at 80 percent for trichloroacetic acid.

Chloral Hydrate

The proposed MCLG of 0.04 mg/l for chloral hydrate was based on an RSC of 80 percent. Although the proposed rule requested additional data on the concentration of chloral hydrate in water, food, and air, no additional studies or data were received. Only limited information on the exposure to chloral hydrate has been identified since the 1994 proposed rule. Therefore, the RSC will remain at 80 percent for chloral hydrate.

Chlorite

The 1994 proposed MCLG for chlorite was 0.08 mg/L. EPA based this MCLG on an RSC of 80 percent. Although EPA requested additional information in the proposed rule and NODA, no additional data on non-drinking water exposure were submitted and no additional information was identified in the literature searches. Therefore, the RSC will remain at 80 percent for chlorite.

Bromate

EPA proposed an MCLG of zero for bromate based on a Category I classification as a carcinogen. Therefore, an RSC is not necessary.

Exhibit 7-1 summarizes the RSCs for disinfectants and DBPs. Note that RSCs are not developed for class I carcinogens and are not provided in the exhibit.

Exhibit 7-1. Relative Source Contribution for Disinfectants and Disinfection Byproducts

Compound	RSC
Disinfectants	
Chlorine	80
Chloramines	80
Chlorine Dioxide	80
Disinfect Byproducts	
Bromodichloromethane	*
Bromform	*
Chloroform	80
Chlorodibromoform	80
Monochloroacetic acid	*
Dichloroacetic acid	80
Chlorite	80
Bromate	80
Chloral hydrate	80

* Compound is classified as a class I carcinogen

APPENDIX A

Summary of Surveys and Studies

SUMMARY OF SURVEYS AND STUDIES

This appendix provides summaries of the major surveys and studies cited in Sections 3 and 4 of this occurrence assessment document. The summaries extract details from the published literature on sampling, analytical methods, and the evaluations of the data. It should be noted that these data may have a wide degree of validity. For example data from some of the surveys were provided by public water systems (PWSs) in response to requests for data from the Agency or associations funding the survey. Data from the monitoring compliance reports and local studies may have received a more thorough degree of quality assurance. The summaries are organized in alphabetical order by author for studies and by title for surveys.

American Water Works Association Disinfection Survey, 1991: The Disinfection Committee of AWWA's Water Quality Division conducted the AWWA's 1991 Disinfection Survey and collected data from 283 utilities. Each facility was asked to respond to questions involving disinfection and quality control, including: control methodology, chlorine demand, filtration, chlorine dose, contact times, and TTHM levels. The survey results indicated that mean free chlorine residuals in drinking water entering distribution systems ranged from 0.07 to 5.00 mg/L, with a median of 1.10 mg/L.

American Water Works Association, 1997: This survey for the American Water Works Association (AWWA) Survey was conducted in January 1997 by McGuire Environmental Consultants. The survey includes data from 298 Information Collection Rule (ICR) utilities. One of the objectives was to gather TOC data for use in the Microbial Disinfection Byproducts (M-DBP) stakeholder process to develop the final Stage 1 DBP rule. For this study, data were requested from surface water systems serving more than 100,000 people and groundwater systems serving more than 50,000 people in 50 states. Two hundred seventy-five utilities provided 3 months of TOC data from September, October, and November 1996.

American Water Works Association Research Foundation, 1987; McGuire and Meadow, 1988: In 1987, the American Water Works Association Research Foundation (AWWARF) sponsored a national survey of trihalomethanes (THMs) conducted by the Metropolitan Water District of Southern California. As part of this survey, alternate treatment technologies were investigated that would lower THM levels.

According to survey results, typical chlorine dosage in drinking water was 2.2, 2.3, 1.2, and 1.0 mg/L for systems using lakes, flowing streams, groundwater, and mixed-supplies, respectively, as their raw water sources. Overall, doses ranged from 0.1 to more than 20 mg/L. Typical chloramine concentrations in drinking water were 1.5 mg/L for systems using lakes and 2.7 mg/L for systems using flowing streams as

their raw water sources. Typical chlorine dioxide dosage used in drinking water was 0.6 mg/L for systems using lakes and 1.0 mg/L for systems using flowing streams as their raw water sources (McGuire and Meadow, 1988).

American Water Works Service Companies, 1991. The American Water Works System Company (AWWSCo) is the largest investor-owned water utility in the United States. It owns and operates more than 100 water systems in 21 states. In 1989, AWWSCo initiated a project to evaluate the occurrence and formation of DBPs at approximately 20 of their 100 water systems (the majority of which have surface water treatment plants) and to observe seasonal differences in these occurrences. Investigators collected samples in three phases: phase I in the fall of 1989 for 16 systems; phase II in the winter of 1991 for 16 systems; and phase three summer 1991 for 21 systems. Overall, sampling represented systems in 10 states, 9 of which are located east of the Mississippi River. In this study, AWWSCo characterizes TOC and bromide ion occurrence in raw water. For dibromochloromethane and cloral hydrate sampling, water was collected from source waters (mostly surface waters) throughout the treatment train and in the distribution system; chloral hydrate analyses were conducted with EPA Method 551.

AWWSCo provided EPA with a summary of TTHM and haloacetic acid 5 (HAA5) data for approximately 52 systems for 1991 and 1992. For many of these systems, information on source water and population was also provided. For the purpose of this occurrence assessment, precursor and disinfection by product data were aggregated by sample location to obtain a range of statistics.

Amy et al., 1994; Westerhoff et al., 1994: This is a study from the University of Colorado on bromide ion occurrence. Source water samples from 101 drinking water utilities across the United States were collected from October 1991 to April 1993 and analyzed for bromide ion. Except for 10 utilities known to have bromide ion-related problems, the utilities were randomly selected from the Water Industry Database to obtain geographical and source type diversity.

The population-weighted averages for bromide ion for the randomly chosen large utilities and randomly chosen small utilities were 0.078 and 0.006 mg/L, respectively. Lake and reservoir sources were generally lower in concentration than rivers and groundwater. The 10th and 90th percentile distribution values were 0.0055 and 0.102 mg/L, respectively, for bromide ion. The authors of the University of Colorado Study suggested that connate seawater may occur ubiquitously and affect the distribution of bromide ion in drinking water sources.

Seasonal variations in bromide concentrations were minimal. The concentration range across the groundwater samples was higher, however, than across the samples from lakes and rivers. When the data included the targeted samples (average of 0.210 mg/L), the overall average increased to about 0.100 mg/L. The authors suggested that the values excluding the targeted facilities were probably more representative of random sampling.

Arora et al., 1994: This survey analyzed water samples from 20 utilities (mostly surface waters) in the fall of 1989, winter of 1991, and the summer of 1991 to observe seasonal differences in TOC and THM. THM analyses were conducted by EPA Method 501.1. Monitoring data from winter and summer 1991 were used to make statistical estimates.

Bolyard et al., 1993: Bolyard et al. (1993) reported the occurrence of chlorite ion in source water and finished water from four utilities that use chlorine dioxide and 15 sites that use hypochlorination. Analyses for chlorate ions were performed by direct injection into an ion chromatograph with suppressed conductivity detection. Because the source water for these systems did not contain measurable concentrations of chlorite ion and chlorate ion and because gaseous chlorine was used for chlorination, chlorine dioxide is the source of DBP contaminants in these sites. The estimated dose of chlorine dioxide doses varied from 0.07 to 2.0 mg/L. Additional gaseous chlorine was also added to provide a residual disinfectant level in the distribution system. The concentrations of chlorite ion in the finished water ranged from 0.015 to 0.740 mg/L.

Results for chlorate ions in these waters show a wide range of concentrations. The estimated doses of chlorine dioxide varied from 0.07 to 2.0 mg/L. Additional gaseous chlorine was also added to provide a residual disinfectant level in the distribution system. The concentrations of chlorate ions in the finished water ranged from 0.021 to 0.330 mg/L. The concentration of chlorate ions was much higher than the concentration of chlorite ions in the finished water from two specific sites (sites 44 and 62). Both systems use chlorine dioxide as a pre-oxidant. At site 62, the water is chlorinated before the secondary sedimentation basins and passes through granular activated carbon (GAC) filters after sedimentation. Powdered activated carbon (PAC), added to the raw water at site 44, is in contact with the water through the sedimentation basins. If PAC acts in a manner similar to GAC, chlorite ions and excess chlorine from the chlorite ion generator or free available chlorine as the residual disinfectant probably react to form the high concentration of chlorate ions detected in the finished water at site 44. The creation of chlorate ions was higher than would be predicted from the chlorine dioxide dosage for this site, suggesting that the estimated dosage may be low.

Data for 11 systems (15 sites) that use hypochlorination as a source of chlorine for disinfection demonstrates that the levels of chlorate ions detected in these finished waters are generally in the same range as those for systems that use chlorine dioxide during treatment. The levels of chlorate ions in the finished water from sites 77 and 87 were much higher than the rest, but the significance of this is not known because of the limited number of samples analyzed. In two sites, 82 and 83, chlorate ions were present in the source water. In both cases, however, higher levels were present in the finished water.

Chemical Manufacturers Association Dataset, 1997: The Chlorine Dioxide Panel of the Chemical Manufacturer Association (CMA) provided EPA with data for chlorite ion occurrence at 65 water treatment facilities that are serviced by one generation company. CMA estimates that the 65 facilities represent between 5 to 10 percent of the facilities nationwide that use chlorine dioxide treatment. More than 50 percent of the 65 facilities are located in the states of Texas, Kentucky, Missouri, and Rhode Island; with a few in Georgia, South Dakota, Oklahoma, and Kansas.

Many facilities provided monthly monitoring results between January 1995 and January 1997. The double blinded data set did not indicate exact sample locations, source water characteristics, nor chlorine dioxide dosages or residuals. EPA Method 300.0 was used to determine chlorite ion concentrations. The practical quantitation level is 10 µg/L, and the method detection limit is approximately 1 µg/L for chlorite ion. Data showed a range for chlorate ion concentration from 0.01 to 4.42 mg/L and a range for chlorite ion that varies from 0.01 to 5.36 mg/L. Mean values for chlorate and chlorite ions were of 0.40 and 0.58 mg/L, respectively.

Community Water System Survey, 1978 (Brass et al., 1981): The U.S. EPA conducted the Community Water Supply Survey (CWSS) in 1978. Drinking water samples provided by 452 systems, including 388 utilities serving populations of less than 10,000, were taken at the treatment plants and in the distribution systems. The survey included analyses for chloroform, bromoform, bromodichloromethane, and dibromochloromethane. It should be noted the samples were 1 to 2 years old prior to analysis.

The CWSS results show that 97 percent of the surface water supplies and 34 percent of the groundwater supplies were positive for chloroform. For the surface water supplies, the mean of the positives and the overall median were 90 and 60 µg/L, respectively. For the groundwater supplies, the mean of the positives was 8.9 µg/L, and the overall median was below the minimum reporting limit of 0.5 µg/L. The CWSS was conducted before the enactment of the total trihalomethane regulation; therefore, these results

may be higher than current levels in systems that disinfect and serve more than 10,000 people (Brass et al., 1981).

EPA/AMWA/CDHS (35 utility study), 1988-1989; (Krasner et al., 1989): In 1987, EPA funded a cooperative agreement with the Association of Metropolitan Water Agencies (AMWA) to study the formation and control of disinfection byproducts (DBPs) in drinking water systems. Twenty-five utilities nationwide participated in the study performed by the Metropolitan Water District of Southern California and James M. Montgomery Consulting Engineers, Inc. The California Department of Health Services also contracted with Metropolitan Water District of Southern California to include 10 California utilities in the baseline phase of the study. Samples of plant influent and clearwell effluent were collected from each utility on a quarterly basis during 1988-89. The clearwell effluent samples were analyzed for chlorine residuals; surrogate parameters; and several chlorination DBPs, including THMs, chloral hydrate, dichloroacetic acid, and trichloroacetic acid. Appropriate dechlorinating agents were added to all samples at the time of collection.

Krasner et al. (1989) reported bromide ion levels in the 35 utility nationwide DBP study. Bromide ion concentrations in groundwater and surface water samples ranged from less than 0.1 to 3.0 mg/L, with a median of 0.1 mg/L. High levels may have been due to saltwater intrusion or connate waters. In addition, clearwell effluent samples were analyzed for chloroform. Samples were taken for 4 quarters (spring, summer, and fall 1988 and winter 1989). The median for all 4 quarters was 14 µg/L, with the medians of the individual quarters ranging from 9.6 to 15 µg/L. The maximum value detected was 130 µg/L. For all 4 quarters, 75 percent of the data was below 33 µg/L (Krasner et al., 1989; EPA and AMWA, 1989).

Gallagher et al., 1994: In an AWWARF report Gallagher et al. (1994) evaluated chlorine dioxide byproduct (chlorite ion and chlorate ion) levels within the waste water treatment plant and the distribution systems of five utilities in the United States. These included Charleston, WV; New Castle, PA; Gulf Coast Water Authority; Skagit, WA; and Columbus, GA. At each utility, the chemical composition of the chlorine dioxide generator effluents was closely monitored, and the effects of generator optimization on byproduct residuals within the treatment plants and distribution systems were determined. The study also evaluated different analytical methods and sample preservation techniques. The resulting data provide an indication of chlorine dioxide and its byproducts concentrations in water treated with chlorine dioxide.

Onsite analysis used amperometric titration from standard methods for analysis of chlorine dioxide and its byproducts concentrations in generator effluent. Ion chromatography (modified EPA Method 300.0b)

is recommended for the analysis of chlorite and chlorate ions at levels as low as those expected in the distribution system when dosages of chlorine dioxide are in the range of 0.5 to 1.0 mg/L. Preservation with sodium oxalate or ethylene diamine stabilized samples during shipping and storage for 1 week. Carbonate and borate eluants were used to provide better separation of ion chromatography peaks. Reductive flow injection analysis with colorometric detection is useful in determining levels of chlorine dioxide and chlorite ion. was accomplished using a Tecator 5020 analyzer with a Tecator Chemifold II manifold.

Most utilities that apply chlorine dioxide at dosages of 1 mg/L or slightly greater were able to meet the currently recommended level of 1 mg/L for the sum of chlorine dioxide, chlorite ion, and chlorate concentrations. Furthermore, most utilities were able to meet the maximum disinfectant residual level (MRDL) of 0.8 mg/L, which is the level EPA proposed in 1994 for chlorine dioxide. Concentrations of ClO_2 in the range of 0.1 to 0.3 mg/L were not uncommon in systems where chlorine dioxide had been added to raw water and the finished water was dosed with free chlorine. During the study, concentrations approaching 0.6 mg/L were observed in some clearwells after free chlorine had been added. Exhibit 3-10 identifies the concentrations of ClO_2 at three utilities.

During the study, the median concentration of chlorite ion in the distribution system at locations where the dosage of chlorine dioxide to the raw water was 1.0 mg/L or less ranged from 0.03 to 0.78 mg/L. The highest levels were observed at a location where the dosage was 2.0 mg/L but was applied to only one-half of the plant flow. Incomplete mixing between the water treated with chlorine dioxide and the other half of the plant flow was responsible for higher chlorite ion concentrations. Exhibit 4-1 presented previously, gives study results.

The median concentrations for the observed distribution systems ranged from 0.1 to 0.39 mg/L. A substantial source of chlorate ions during this project was the chlorine dioxide generator; reactions between residual chlorite ions and free chlorine most often can be expected to produce the majority of chlorate ions. These reactions can occur rather rapidly after post-chlorination. Concentrations of chlorate ions in the distribution systems monitored during this project were not appreciably greater than those in the clearwells at the treatment plants. Exhibit 4-20, presented previously, gives study results.

Glaze et al., 1993: Glaze et al. (1993) reported sample results for seven full-scale water systems across the country in an AWWA report that discusses drinking water ozonation treatment plants. A total of nine samples were taken from two plants sampled on two separate occasions. Samples of raw water were

collected and analyzed for bromide ion. The analytical method used was ion chromatography, which had a detection level of 0.01 mg/L bromide ion.

Gordon et al., 1993 This 1991 study evaluated the concentration chlorate ion as a disinfection byproduct for in 16 systems using hypochlorination. Twenty-five samples showed a residual chlorate ion concentration ranging from 0.08 to 0.30 mg/L and a median of 0.12 mg/L. The 25 and 75 percentiles were 0.08 and 0.18 mg/L, respectively.

Gordon et al., 1995a: From 1993 to 1995, Gordon et al. collected and analyzed water samples from 111 systems using hypochlorination. The objective was to evaluate disinfection byproduct concentrations, specifically of chlorate ion, in the drinking water samples. Results demonstrated a residual chlorate ion concentration in the distribution system varying from <0.01 mg/L to 9.18 mg/L and mean and median concentrations of 0.49 and 0.16 mg/L, respectively.

Grammith, 1993: In this study, Grammith evaluated bromate concentrations in water samples from a MWD demonstration plant of 5.5 MGD. Ozonation water sampling was performed at contactor effluent. Results showed a residual bromate concentration range in the distribution system varying from <5 to >10 µg/L.

Groundwater Supply Survey 1980-1981: The Groundwater Supply Survey (GWSS) is an EPA national study on groundwater TOC occurrence. It reports data by EPA Region for 945 utilities. GWSS is not applicable to the occurrence of chloroform in distribution systems...

GWSS data presented in this ocurrence assessment indicates that sixty-nine percent of these utilities or 654 chlorinated their water, while 31 percent or 291 utilities did not. When the TOC data were combined to present values for all groundwater systems, the 25th, 50th, and 75th percentiles were 0.3, 0.6, and 1.4 mg/L TOC, respectively. These results were presented in Tables VI-3 A, B, and C from the 1994 D/DBP proposed rule.

Hoehn, 1990: Hoehn et al. (1990) conducted a study to determine the contribution of drinking water disinfected with chlorine dioxide to household odors reported at houses, in Lexington, Kentucky (three houses, samples not specified), and in Charleston, West Virginia. Source waters at both plants were rivers, and samples were collected from the plants and from houses. The Lexington treatment adds chlorine dioxide

to raw water at doses of 1.0 mg/L; the treatment process in Charleston adds 2.0 mg/L of chlorine dioxide. Samples were analyzed using the amperometric method of Aieta et al. and the flow injection analysis of Gordon et al. Chlorine dioxide concentrations in the Charleston treatment plant and distribution system, and chlorite and chlorate ion results from two houses and the distribution system were examined. Results from sampling at Lexington were not specified.

Massachusetts Compliance Monitoring Data: During the period from 1994 to 1996, the State of Massachusetts collected data on total trihalomethanes (TTHMs) from statewide drinking water systems that used groundwater, surface water, and mixed water as the source. A total of 53 samples were analyzed for TTHM. Results indicate that the highest TTHM concentrations were for the 21 samples from those systems using surface water as the source and serving more than 10,000 people, with values ranging from 2 to 502 µg/L and mean and median values of 54 and 50 µg/L, respectively. These TTHM concentrations were followed by those from 19 samples in systems using mixed water as a source and serving more than 10,000 people, which showed values varying from 0 to 524 µg/L and mean and median values of 50 and 45 µg/L, respectively. The lowest TTHM concentrations were found in systems serving less than 10,000 people in systems using surface water and mixed water as the source. Two samples from the smaller systems (serving less than 10,000 people), that use mixed water as the source, showed the lowest TTHM mean value, 28 µg/L, and median value, 12 µg/L.

Missouri Compliance Monitoring Data: The State of Missouri evaluated the concentrations of total trihalomethanes (TTHM) reported for 107 groundwater and surface water systems statewide during 1996 and 1997. Surface water samples comprised 86 percent of the 107 samples, and groundwater samples the other 14 percent. Results indicate the highest average TTHM concentrations for those systems serving less than 10,000 people, regardless of their source. Eighty-one samples from surface water systems serving less than 10,000 people showed the highest average and mean TTHM concentrations, 118 and 102 µg/L, respectively. Fourteen groundwater systems (>10,000 people) demonstrated an average TTHM concentration of 15 µg/L and a median TTHM concentration of 3 µg/L. These were the lowest values reported.

New Jersey Compliance Monitoring Data: The New Jersey Department of Environmental Protection provided compliance monitoring data for average TTHM concentrations at 151 public water systems from 1994 through 1996, the majority (123 systems) of these being groundwater systems. Data reported from surface water systems, regardless of population served, showed the highest average and mean TTHM concentrations, varying from 42 to 48 µg/L and from 27 to 39 µg/L, respectively. Groundwater

average TTHM concentrations were lower than those form surface water, 9 µg/L for small (<10,000 people served), and 7 µg/L for large systems (>10,000 people served).

Nieminski et al., (1993): The Utah Department of Environmental Quality and the Utah Department of Health studied DBPs in surface water treatment facilities in Utah. All plants used chlorine for primary and secondary disinfection. The study analyzed treated water for individual THMs, HAAs, and other halogenated DBPs. Samples were collected from 35 water utilities, including 14 serving more than 10,000 people and 21 serving fewer than 10,000 people.

At the 14 larger systems, testing for DBPs was conducted quarterly to observe seasonal variations. These samples were collected at locations just prior to distribution and held for various periods to simulate conditions in the distribution system samples (SDSs). At the small plants, samples were collected annually from the plant effluents and at the end of the distribution system. All samples were collected in triplicate.

Three sets of samples were collected: plant effluent, distribution system or SDS samples and 7-day formation potential. The first set of samples from each facility was preserved using 4.6 mg ammonium chloride to 40 mL water to quench the free chlorine. The second set of samples from 14 facilities was stored at a temperature and time simulating distribution system conditions to allow free chlorine to react with the precursors. At the end of this period, the chlorine residual was measured. The third set was held for 7 days before quenching and then was analyzed. EPA Method 551 with a methyl-tert-butyl ether (MTBE) extraction rather than the pentane was used to analyze individual THMs.

The HAAs were analyzed using a micro extraction method similar to that developed by Metropolitan Water District (now Standard Methods) and EPA Method 552. To prevent MTBE from boiling over, the method was modified. The water was shaken for 20 seconds after the addition of the acid, and then the MTBE was added after another 5 to 10 seconds. Copper sulfate was not added, because it contained impurities that interfered with chromatography of monochloroacetic acid. Only 6 grams of sodium sulfate was added (not 12 as per the method) to avoid caking.

Results showed no significant differences in DBP occurrence in large versus small utilities. The authors also noted that although seasonal variation was seen in the results from the 14 large plants, no season was significantly lower or higher than the other seasons. In a representative large plant, chloroform was the major THM compound detected, representing 77 percent THMs by weight. The authors provided EPA with analytical results of individual THM species from the plant effluents not published in the article. It should

be noted that concentrations in the distribution system were up to 40 percent greater than concentrations in the plant effluents.

Total HAA concentrations were reported for the mean, median, and 25th and 75th percentiles. The mean plant concentration for the 35 plants was 17.3 µg/L, with a median concentration of 12.8 µg/L of HAA5. The 25th and 75th percentiles were 7.13 and 22.60 µg/L HAA5, respectively. The authors noted that monochloroacetic acid and trichloroacetic acid were the major HAAs detected in the distribution systems. HAA concentrations reported were somewhat lower than nationwide medians, and the authors attributed reduced medians to the lower TOC in Utah waters. The statistics were calculated from data provided by the authors for plant effluent and distribution systems.

Chloral hydrate concentrations between 0.7 and 3.76 µg/L were reported from the four samples collected in June 1990. Although analyses for bromate ion were conducted, the authors noted that bromate ion was not detected above the detection level of 7 µg/L from any of the 35 water utilities plants that use liquid chlorine. However, none of the systems characterized in the study used ozonation, the major source of bromate ion.

National Organics Monitoring Survey, 1976-1977 (Bull and Kopfler, 1990): The National Organics Monitoring Survey (NOMS) is one of two surveys performed by EPA to obtain information on the occurrence of trihalomethanes (THMs) and other organic compounds in the United States prior to the promulgation of the maximum contaminant level (MCL) of 0.10 mg/L for total trihalomethanes (TTHMs) in 1979.

EPA conducted the National Organics Monitoring Survey from March 1976 to January 1977 to identify sources and frequency of occurrence of organics and inorganics in drinking water supplies. NOMS was conducted in three phases: Phase I – March to April 1976, Phase II – May to July 1976, and Phase III – November 1976 to January 1977. NOMS involved sampling and analyzing finished water from 113 public water supplies across the United States.

Results show that surface water was the major source for 92 of the systems, and groundwater was the major source for the remaining 21 systems. Two analytical methods were used to measure chloroform concentrations at the time of sampling and to measure the maximum chloroform concentrations due to the reaction of all the chlorine residual. During the three phases, chloroform was detected in 92 to 100 percent of the systems sampled. The median concentrations of the maximum chloroform in the three phases ranged

from 22 to 54.5 µg/L. The maximum value detected was 540 µg/L. NOMS was conducted before the enactment of the total trihalomethane regulation; therefore, these results may be higher than current levels in systems that disinfect and serve populations of more than 10,000 people (Bull and Kopfler, 1990).

National Organics Reconnaissance Survey, 1975; (Symons et al., 1975): The National Organics Reconnaissance Survey is one of two surveys performed by EPA to obtain information on the occurrence of trihalomethanes (THMs) and other organic compounds in the United States prior to the promulgation of the maximum contaminant level (MCL) of 0.10 mg/L for total trihalomethanes (TTHMs) in 1979. The NORS primary objective was to characterize the extent and presence of TTHMs in the United States.

The NORS collected drinking water samples from 80 cities nationwide, geographically distributed and representing a wide variety of raw water sources and treatment technologies. This survey sampled for several organics, including THMs, at the water treatment facilities. Results indicated chlorine residuals ranging from 0 to 2.8 mg/L, with an approximate median concentration of 0.6 mg/L (Symons et al., 1975). In addition, it was found that eighty percent of the systems had surface water sources, and the remaining 20 percent had groundwater sources. The median concentration for chloroform was 23 µg/L, and the maximum level detected was 311 µg/L.

The NORS no longer represents occurrence of THMs in water systems serving more than 10,000 people, because of changes in disinfection practices required in the Surface Water Treatment Rule, which became effective in 1993. However, data could be indicative of THM occurrence in small systems. NORS was performed prior to the 1979 total trihalomethane regulation; therefore, these results may be higher than current levels for systems that disinfect and serve more than 10,000 (Symons et al., 1975).

Oregon Compliance Monitoring Data: Information reported by the State of Oregon from 1994 to 1996 included TTHM data for 34 Oregon's public water systems serving more than 10,000 people. Of these systems, 27 are surface water and 7 are groundwater. Results indicate that the mean TTHM concentration in surface water systems is 29 µg/L, approximately twice of that found in groundwater systems, 16 µg/L. Ranges for surface water and groundwater systems are 7-76 µg/L and 5-31 µg/L, respectively.

Pennsylvania Compliance Monitoring Data: The State of Pennsylvania provided compliance monitoring results, including TTHM concentration data for 223 systems statewide for the years 1994 through 1996. Surface water systems, a total of 173, comprised the majority of the systems studied. Of these, 63

systems purchase surface water. A total of 10,312 samples were collected from the distribution system only on a quarterly basis and analyzed using EPA Methods 551, 502.2, and 524.2. The results showed higher TTHM concentrations in samples collected from surface water systems than those in groundwater systems. TTHM concentrations from surface water systems serving more than 10,000 people ranged from 1 to 113 µg/L, with a 90th percentile of 64 µg/L. Surface water systems showed a TTHM concentration range of 0-162 µg/L, and a 90th percentile of 84 µg/L. In groundwater systems, TTHM concentrations ranged from 0-41 µg/L in systems serving more than 10,000 people, and 0-158 µg/L in those serving less than 10,000. Their 90th percentiles were 17 and 36 µg/L, respectively.

Rural Water Survey, 1978-1980: The Rural Water Survey (RWS), conducted by EPA between 1978 and 1980, assessed the occurrence of organic compounds in public water supplies from rural areas serving less than 10,000 people. The samples were collected from more than 2,000 households, representing more than 600 rural water supply systems. Data collected showed that most of the systems (i.e., 494) sampling for TTHMs used groundwater as their source water, and 154 used surface water. Of the 2,655 samples obtained, 800 were analyzed for purgeable halocarbons, including the four THMs. It should be noted that some samples were up to 27 months old prior to analysis.

The RWS sample analyses demonstrated that 82 percent of the surface water supplies and 17 percent of the groundwater supplies were positive for chloroform. For the surface water supplies, the mean of the positives and the overall median concentrations were 84 and 57 µg/L, respectively. For the groundwater supplies, the mean of the positives was 8.9 µg/L, and the overall median was below the minimum reporting limit of 0.5 µg/L (Brass, 1981).

Singer et al., 1995: This study evaluates the occurrence of DBPs in drinking water from six North Carolina utilities. Eight water treatment plants provide water for the six utilities. Because North Carolina has a relatively high TOC concentration in surface water sources of drinking water (average of 5 mg/L TOC in systems serving populations greater than 50,000), DBP levels were expected to be higher than levels reported in other studies. Source waters were characterized as relatively low in bromide ion levels. All plants used chlorine for disinfection; most plants applied chlorine to the settled water prior to filtration. Sample sets were collected three times from each utility between June 1991 and February 1992 to encompass high- and low-temperature periods. A total of 93 samples were collected from representative locations in the distribution systems and analyzed for four THMs, four HAAs, and other DBPs. The sampling locations were those used for THM compliance monitoring. DBP analysis was performed by liquid-liquid extraction and capillary column gas chromatography with electron capture detection.

The average chloroform concentrations in the plant effluents and the distribution systems were 32 and 41 µg/L, respectively. The 42 distribution system samples had a median of 38 µg/L chloroform, with a range of 8 to 91 µg/L of chloroform. The average chloroform/TTHM ratio was 0.79, indicating that chloroform represented 79 percent of the TTHMs measured.

Sorrell and Hautman, 1992: In their 1992 study, Sorrell and Hautman report on the development of a concentration technique for analyzing bromate ion at low levels in drinking water. This procedure used a rotovap to concentrate drinking water samples, followed by ion chromatography. Bromate ion was detected with a combination of suppressed conductivity and ultraviolet. A minimum detection level of 0.4 µg/L was achieved. This rotary evaporator concentration technique was applied to several drinking water surface water sources before and after ozonation. Bromate ion levels ranged from less than 0.4 to 6.3 µg/L in samples from nine surface water plants using ozone. No ozone dosages or bromide ion levels were reported.

Technical Support Division, 1992: The Technical Support Division (TSD) of the U.S. EPA Office of Groundwater and Drinking Water conducted a water chlorination byproduct field study from October 1987 to March 1989 and compiled a database with the information collected. Twenty-one community water supplies provided samples of source water, plant effluent, and water from a far point in the distribution system. Disinfection processes and concentrations of the four individual THMs (i.e., chloral hydrate, dichloroacetic acid, and trichloroacetic acid) were characterized.

In the distribution system, the mean chloroform concentration was 58.7 and 77.2 µg/L for plants serving above and below 10,000, respectively, with the 90th percentile concentration of 141.0 and 110.0 µg/L for 39 samples and 11 samples, respectively (EPA, 1992b). The groundwater systems serving less than 10,000 had a mean chloroform concentration of 3.6 µg/L for five observations, with the 90th percentile of 9.4 µg/L (EPA, 1992b).

Texas Compliance Monitoring Data: Between the years 1994 and 1996, the State of Texas provided compliance monitoring data characterizing TTHM concentrations in 227 water treatment systems, 114 surface water and 113 groundwater systems. In this analysis, 47 systems using purchased water were considered surface water systems. Fifty-three groundwater systems or roughly half of the groundwater systems reported their TTHM results as formation potentials. Samples were collected quarterly and analyzed using EPA Methods 551, 502.2, and 524.2. Data were aggregated by source and the population being served by the public water supply. Actual TTHM results and TTHM results reported as formation potentials were

combined for the purposes of this analysis. The analysis results showed that surface water systems have a slightly higher range, mean, median and 90th percentile than those from groundwater systems. A range of 8-135 µg/L and a 90th percentile of 70 µg/L were obtained for 2,521 surface water system samples. Results from the groundwater system samples indicate that 113 systems serving more than or less than 10,000 people have similar means, medians, and ranges for TTHM concentrations. Large systems showed mean, median and range values of 24, 15 and 0-121 µg/L, while small systems reported 26, 19 and 0-120 µg/L for the same statistics. The 90th percentile in for those serving more than 10,000 people is 60 µg/L and 52 µg/L for smaller systems.

Utah Pre-ICR data, 1996: The state of Utah conducted a survey between October 1994 and September 1996 on seven large surface water treatment plants serving more than 100,000 persons. This survey provides data for disinfection precursors (TOC and bromide ion), and byproducts (individual and total THMs and HAAs). Samples for this study were taken at several locations in the treatment process and distribution system four to six times between October 1994 and September 1996. EPA Method 551 with a methyl-tert-butyl ether (MTBE) extraction rather than the pentane was used to analyze individual THMs. The HAAs were analyzed using a micro extraction method similar to that developed by Metropolitan Water District (now Standard Methods) and EPA Method 552.

For the occurrence assessment, Utah Pre-ICR survey data were aggregated by sample location to provide a range of statistics for precursors and disinfection byproducts. Disinfection precursor and by product data points reporting less than the detection limit were converted to zeros and included in the analyses. The TOC and bromide ion results from the raw water samples were analyzed using all data points reported. Individual and total HAA results came from two average distribution system samples. Chloral hydrate results came from two average distribution system samples. Monitoring results from all total HAA and chloral hydrate samples were used.

WaterStats 1996: WaterStats was initiated through a joint effort by the AWWA and the AWWA Research Foundation (AWWARF). The purpose of this database is to support the regulatory and legislative efforts of AWWA, assist AWWA in focusing research activities, and support the educational endeavors of AWWA and interested parties. In 1996, AWWA surveyed approximately 3,162 drinking water systems serving populations exceeding 10,000 in the United States. The response rate was better than 30 percent, resulting in TTHM, HAA5, and population-served information for approximately 300 systems in the United States. The survey covered a wide spectrum of information, including utility characteristics and finances,

surface and groundwater treatments, water quality monitoring, and water distribution characteristics. The data gathered in this survey comprise WaterStats.

The data in WaterStats characterize distribution system concentrations for TTHM and HAA5. These distribution system data were also characterized by source water and the population served. The data represented annual averages based on quarterly sampling for TTHMs and HAA5 in systems that chlorinate. WaterStats was examined for data consistency and outliers, assumptions associated with the data, and possible analysis methods. The WaterStats data base was assumed to be a representative sample of the universe of systems serving greater than 10,000 people.

Water Industry Database 1989-1990: The Water Industry Data Base (WIDB) is a joint effort by the American Water Works Association (AWWA) and the American Water Works Association Research Foundation (AWWARF). The study, conducted between 1989 and 1990, surveyed approximately 1,300 drinking water systems serving more than 10,000 people in the United States. Sampling was conducted at different times over several years and other water system data were collected based on the professional judgement of utility personnel. The WIDB includes information on utility characteristics and finances, surface and groundwater treatments and disinfection methods, water quality monitoring, and water distribution characteristics. In addition, it provides a large data set of annual average TTHM data, free chlorine, and combined chlorine residuals. Because of the comprehensive nature of the WIDB, the Regulatory Negotiating Committee used this data set in their regulatory impact analysis.

For the occurrence assessment, data on TOC levels from 157 utilities was extracted from the WIDB to analyze TOC occurrence data in groundwater (57 systems) and surface water (100) systems. The ocurrence study used the WIDB to identify the number of utilities that did not provide TOC data; 854 groundwater utilities and 897 surface water utilities did not provide TOC data. Also, it studied the residual chlorine at average consumer from 228 surface water plants and 215 groundwater plants and distribution system average chloramine from 140 utilities nationwide. Other estimates based on WIBD data included the usage of chlorine dioxide for disinfection, chlorine residual in drinking water and population exposed to chlorine residual in drinking water.

APPENDIX B

ANALYTICAL METHODS

ANALYTICAL METHODS

Analytical methods are an important factor in water quality monitoring. When interpreting and comparing data on the occurrence of contaminants, knowing that different studies have used similar methods with comparable precision, accuracy, and sensitivity is useful. Many of the analytical methods used for disinfection byproducts (DBPs) have been improved significantly during the 1990s; hence, the quality of occurrence data has improved as well.

For the disinfectant/disinfection byproduct (D/DBP) rule, the levels of precursors in the source water will determine the extent of treatment required. The quantities of DBPs must remain below the maximum levels specified in the regulation. All of the measurements must be accurate to ensure a safe water supply while avoiding unnecessary treatment.

Appendix B briefly summarizes the approved analytical methods for the Stage I D/DBP rule and discusses the nationwide capacity of laboratories to perform these analytical methods. This section describes the approved analytical methods for the disinfectants or DBPs. The number of laboratories approved by the U.S. Environmental Protection Agency (EPA) for monitoring under the Information Collection Rule (ICR) are used to estimate the laboratory capacity and availability of analytical services.

Each of the methods described in this section has an associated method detection limit(MDL). By definition, the MDL is specific to the analyte, method, and laboratory. For example, EPA Method 524.2 provides four tables of MDL values. The MDL values are dependent on how the instrument is set up matrix, and analyte. The MDLs provided in this section represent the most sensitive value available for each method from the published methods, not an exhaustive analysis of MDL data that is being collected for the ICR. Under this effort each laboratory approved to work under the ICR ran MDL studies for the analytes and reported all the results. Method detection limits for each of the methods summarized in this section are presented in exhibits following each class of analyte.

DISINFECTANTS

Free and Total Residual Chlorine

Standard Method (SM) 4500-Cl D (APHA, 1996) is an amperometric method for detecting chlorine and chloramines with a detection limit of 2 mg/L. Free residual chlorine is measured by adjusting the pH of the sample to 6.5 to 7.5 and titrating to the endpoint with a phenyl arsine oxide reducing solution. Total

residual chlorine is measured by adding potassium iodide to the sample, adjusting the pH to 3.5 to 4.5, and titrating with phenyl arsine oxide to the endpoint. Microamperometry detects the endpoints in each titration.

SM 4500-Cl E (APHA, 1996) is a low-level amperometric method for detecting chlorine and chloramines measured as total residual chlorine. This method has a detection limit of 10 µg/L and utilizes the same principles as the amperometric titration method (4500-Cl D). This method modifies SM 4500-Cl D by using a more dilute concentration of phenyl arsine oxide titrant and a graphical procedure to determine the endpoint. Use of this method is recommended when the total residual chlorine is less than or equal to 0.5 mg/L as chlorine. A positive bias will be shown if other oxidizing reagents are present in the water sample.

SM 4500-Cl F (APHA, 1996) uses N,N-diethyl-p-phenylenediamine (DPD) as an indicator with ferrous ammonium sulfate titrimetric method for detecting chlorine and chloramines with a detection limit of 18 µg/L Cl as Cl_2. When the proper pH is chosen, this method can differentiate between free chlorine and monochloramine, dichloramine, and total chlorine. The color produced by the reaction of the chlorine species with DPD dye slowly disappears as the sample is titrated with ferrous ammonium sulfate. The amount of titrant corresponds to the concentration of the chlorine species being measured. This method is approved for determinating free, combined, and total residual chlorine.

SM 4500-Cl G (APHA, 1996) is a DPD colorimetric method for detecting chlorine and chloramines. This method has a detection limit of 10 µg/L and utilizes the same principles as the DPD ferrous titrimetric method (SM 4500-Cl F), except that the color produced is read by a colorimeter, and the concentration of free and total chlorine are calculated after standardization. Combined residual chlorine is the sum of the monochloramine and dichloramine measurements. Total residual is the sum of free and combined residual chlorine. This method is used for determining free, combined, and total residual chlorine.

SM 4500-Cl H (APHA, 1996) is a detects free available chlorine test, syringaldazine (FACTS) which is sensitive to free chlorine concentrations of 0.1 mg/L or less. The reagent, syringaldazine, is oxidized by free chlorine on a 1:1 basis to produce a color that is determined colorimetrically. The pH of the sample must be maintained at approximately 6.7 to stabilize the color formed. This method is used for determining free residual chlorine.

SM 4500-Cl I (APHA, 1996) is an iodimetric electrode technique for detecting chlorine and chloramines. This method involves the direct potentiometric measurement of iodine released when

potassium iodide is added to an acidified sample containing chlorine. A platinum-silver, platinum-platinum, or platinum-copper electrode pair is used in combination to measure the liberated iodine. This method is used for determining total residual chlorine.

Chlorine Dioxide Residual

SM 4500-ClO_2 C (APHA, 1996) is an amperometric titration method which is an extension of the amperometric method used for chlorine (SM 4500-Cl D). It consists of four successive titrations using phenylarsine oxide (PAO) in order to determine the concentrations of free chlorine, chloramines, chlorite, and chlorine dioxide. The cell current changes as the titrant reacts with the oxyhalogen as chlorine, or with iodine formed by the addition of iodide to the solution prior to the titration. The four titrations are done using different pretreatment steps, primarily involving pH adjustment and potassium iodide (KI) addition, in order to differentiate between the species. The concentrations of the analytes are calculated through mathematical manipulation of the titration results. Error in one titration step can potentially be propagated to affect multiple analyte determinations. In this method, chlorine dioxide is determined by subtracting the concentration of total available chlorine from the sum of total available chlorine plus one-fifth available chlorine dioxide. Consequently, error in the measurement of chlorine dioxide increases at higher relative concentrations of total available chlorine. This method is also subject to interferences from chloramines, manganese, copper, and nitrite. In addition, loss of chlorine dioxide due to volatilization during sample pretreatment and titrations can be problematic. USEPA removed SM 4500-ClO_2 C from its list of approved methods for monitoring chlorine dioxide to determine compliance with the MRDL.

SM 4500-ClO_2 D (APHA 1996) is a colorimetric titration that involves successive titrations with ferrous ammonium sulfate (FAS) to reduce the color formed upon reaction of oxychlorine species with N,N-diethyl-p-phenylenediamine (DPD). The method is an extension of the standard DPD method used for determination of free chlorine and chloramines in water. Oxychlorine species produce a red color upon reaction with the DPD indicator. As with SM 4500-ClO_2 C, a series of titrations is carried out using different pretreatment steps in order to quantitate free and combined chlorine, chlorine dioxide, and chlorite. Glycine is added to convert free chlorine to nonreactive chloroaminoacetic acid which allows determination of chlorine dioxide at neutral pH. Titration of a separate sample along with successive additions of potassium iodide yields free available chlorine and mono- and dichloramine. Chlorite is determined through acidifying and then neutralizing a sample prior to titration. Oxidized manganese, copper, and chromate are interferences in this method, although these can be suppressed by addition of EDTA or corrected by subtraction of the background color of a reagent blank. Monochloramine reacts with the DPD indicator to

form a colored product and, thereby, interferes with analysis of other oxychlorine species when present in high concentration. EDTA is added to suppress iron activation of chlorite by FAS.

SM 4500-ClO_2 E (APHA 1996) is an amperometric titration much like 4500-ClO_2 C except that the pH is adjusted to 12 and a gaseous purge step to physically remove chlorine dioxide are added. It uses successive titrations of combinations of chlorine species, followed by calculations to determine the concentration of each species. Either phenylarsine oxide (PAO) or sodium thiosulfate can be used as the titrant. Residual chlorine and one-fifth of available ClO_2 are titrated at pH 7. The sample pH is then lowered to 2 and the remaining four-fifths of available ClO_2 plus the chlorite are determined. A separate sample is purged with nitrogen gas to remove ClO_2 and titrated for non-volatilized chlorine after adding KI. The sample is then acidified to pH 2 and titrated to measure chlorite ion. In a final step employing highly acidic conditions, all the oxidized chlorine species, including chlorate ion, are measured.

In this method, the concentration of chlorine dioxide is calculated by subtracting the concentration of chlorite from the sum of chlorite plus four-fifths of available ClO_2. This procedure typically allows quantitation of ClO_2 with far less error than when using 4500-ClO_2 C. Standard Methods (APHA 1996) recommends that the total mass of oxidants should be no greater than 15 mg equivalents of iodine and that all analyses be made in triplicate. The method is also recommend for assessing chlorine dioxide purity as the PQLs are 0.1 mg/L for chlorine dioxide and chlorite and 0.2 mg/L for chlorate.

Exhibit B-1. Method Detection Limits for Disinfectants.

Analyte	Method	MDL
Disinfectants		
Free and Total Residual Chlorine	SM 4500-Cl D	< 0.2 mg/L
	SM 4500-Cl E	< 0.01 mg/L
	SM 4500-Cl F	~ 18 ug Cl as Cl2/L
	SM 4500-Cl G	~ 10 ug Cl as Cl2/L
	SM 4500-Cl H	0.1 mg/L or less
Chlorine Dioxide	SM 4500-ClO2 C	0.1 mg/L
	SM 4500-ClO2 D	> 0.1 mg/L
	SM 4500-ClO2 E	0.1 mg/L

DISINFECTION BYPRODUCTS

Trihalomethanes

EPA Method 502.2 (EPA, 1995) is used for determining the amount of volatile organic compounds (VOCs), including the four trihalomethanes (THMS). EPA Method 502.2 is a purge and trap gas chromatography method utilizing a photoionization detector in series with an electrolytic conductivity detector. The method detection limits range from 0.01 to 3.0 µg/L for concentrations between 0.02 to 200.0 µg/L. Air purged samples are trapped in a tube with sorbent material. The sorbent material in the tube is then heated and backflushed with helium to thermally desorb trapped sample components. Identification of the individual THM species is based on comparison of retention times; concentrations are quantified by standard calibration.

EPA Method 524.2 (EPA, 1995) uses the same purge and trap procedures as EPA Method 502.2; however, this method employs a capillary column gas chromatograph and mass spectrometer quantitate analytes. The method detection limits range from 0.02 to 1.6 µg/L and depend on the sample matrix and analyte. The specific method detection limits are listed in Table 4 of the method.

EPA Method 551.1 (EPA, 1996) is used for determining chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water using liquid-liquid extraction and gas chromatography/electron capture detection (GC/ECD). This method is used to determine 12 commonly observed chlorination DBPs. Method 551.1 offers significant improvements over previous methods for THMs.

In EPA Method 551.1, the ionic strength of a 35- to 50-mL drinking water sample is adjusted using sodium chloride, and the sample is extracted with 2 mL of methyl-tert-butyl ether (MTBE). If only THMs are being measured, pentane can be used as an extraction solvent. Prior to sample analysis, the THM formation reaction must be halted by the addition of a reagent that removes all free chlorine from the sample. Sodium sulfate is used as an extraction salt instead of sodium chloride, which can have trace bromide impurities. Following extraction, 2 µL of the extract is injected into a GC equipped with a fused silica capillary column and linearized electron capture detector for separation and analysis. Gas chromatography/ mass spectrometry (GC/MS) can be used to confirm the presence of the compounds.

Haloacetic Acids

EPA Methods 552.1 and 552.2 (EPA. 1995) and SM 6251B (APHA. 1996) are methods that use gas chromatographic instrumentation to determine the presence of haloacetic acid in drinking water. groundwater. raw water. and water at any intermediate treatment stage. The analytical procedures in these three methods are equivalent and very similar.

EPA Method 552.1 and SM 6251B both use capillary column gas chromatographs with electron capture detectors. The two methods differ in the sample preparation steps. Method 552.1 uses solid phase extraction disks, followed by an acidic methanol derivitization. MDLs, which vary according to analyte, are listed in Table 2 of the method. SM 6251B is a small-volume micro liquid-liquid extraction with MTBE. followed by a diazomethane derivitization. Following the extraction procedures, the concentration extracts are converted to methyl esters, which are partitioned into the MTBE phase. The converted esters are identified, and capillary column gas chromatography is used for quanitification.

EPA Method 552.2 uses capillary column gas chromatography with electron capture detection and combines the micro extraction procedure of SM 6251B with the acidic methanol derivitization procedure of EPA Method 552.1. Following the extraction procedure, this method follows the similar process of converting the concentration extracts to methyl esters for identification and using capillary column gas chromatography for quantification.

Chloral Hydrate

EPA Method 551.1 (EPA, 1996) is used for determining chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water using liquid-liquid extraction and gas chromatography/electron capture detection (GC/ECD). This method is used to determine. 12 commonly observed chlorination DBPs. Method 551.1 offers significant improvements over previous methods for chloral hydrate.

EPA Method 551.1, the ionic strength of a 35- to 50-mL drinking water sample is adjusted using sodium chloride, and the sample is extracted with 2 mL of methyl-tert-butyl ether (MTBE). Prior to sample analysis, the DBP formation reaction must be halted by the addition of a reagent that removes all free chlorine from the sample. Sodium sulfate is used as an extraction salt instead of sodium chloride, which can have trace bromide impurities. Following extraction, 2 µL of the extract is injected into a GC equipped with

Exhibit B-2. Disinfection Byproduct Method Detection Limit

Analyte	Method	MDL
Disinfection Byproducts		
Chloroform	EPA 502.2	0.02 ug/L
	EPA 524.2	0.03 ug/L
	EPA 551	0.002 ug/L
	EPA 551.1	0.075 ug/L
BDCM	EPA 502.2	0.02 ug/L
	EPA 524.2	0.08 ug/L
	EPA 551	0.006 ug/L
	EPA 551.1	0.005 ug/L
DBCM	EPA 502.2	0.3 ug/L
	EPA 524.2	0.05 ug/L
	EPA 551	0.012 ug/L
	EPA 551.1	0.007 ug/L
Bromoform	EPA 502.2	1.6 ug/L
	EPA 524.2	012 ug/L
	EPA 551	0.012 ug/L
	EPA 551.1	0.006 ug/L
Monochloroacetic acid	SM 6233B	0.082 ug/L
	EPA 552.1	0.21 ug/L
	EPA 552.2	0.60 ug/L
Monobromoacetic acid	SM 6233B	0.087 ug/L
	EPA 552.1	0.24 ug/L
	EPA 552.2	0.20 ug/L
Dichloroacetic acid	SM 6233B	0.054 ug/L
	EPA 552.1	0.45 ug/L
	EPA 552.2	0.24 ug/L
Trichloroacetic acid	SM 6233B	0.054 ug/L
	EPA 552.1	0.07 ug/L
	EPA 552.2	0.20 ug/L
Dibromoacetic acid	SM 6233B	0.065 ug/L
	EPA 552.1	0.10 ug/L
	EPA 552.2	0.25 ug/L
Bromide Ion	EPA 300.0	0.1 mg/L
Chlorite Ion	EPA 300.0	0.01 mg/L
Bromate Ion	EPA 300.0	0.02 mg/L

a fused silica capillary column and linearized electron capture detector for separation and analysis. Gas chromatography/mass spectrometry (GC/MS) can be used to confirm the presence of the compounds.

Chlorite Ion, Bromide Ion, and Bromate Ion

EPA Method 300.1 (EPA, 1996) is an improved method used for determining inorganic anions by ion chromatography. This method covers the determination of several inorganic ions in a variety of liquid matrices, including drinking water. The laboratory method detection limit for chlorite and bromide ions is 0.01 mg/L. The MDL for bromate is expected to be 2 µg/L. The MDL for a specific matrix can differ, depending upon the nature of the samples.

Analysis of the sample occurs by introducing approximately 2 to 3 mL of sample into an ion chromatograph. The anions of interest are separated and measured using a system comprising a guard column, analytical column, suppressor device, and conductivity detector. Method 300.1 consists of two parts (i.e., A and B). The part used depends on the anion of concern.

WATER QUALITY PARAMETERS

Total Organic Carbon

EPA has approved three methods for analyzing total organic carbon (TOC). SM 5310B (APHA, 1996) was not originally approved; however, improvements in instrumentation have increased the sensitivity to an acceptable level. SM 5310B, High-Temperature Combustion Method, is suitable for samples with high levels of TOC that would require dilution using the persulfate methods. A sample is injected into a heated reaction chamber packed with an oxidative catalyst. The organic carbon is oxidized to carbon dioxide and is detected with a non-dispersive infrared analyzer. Because both inorganic and organic carbon are detected, the inorganic carbon must be removed prior to detection or measured separately and subtracted from the total carbon measurement.

SM 5310C (APHA, 1996) is a persulfate-ultraviolet oxidation method that measures organic carbon via infrared absorption of the carbon dioxide gas that is produced when the organic carbon in the sample is simultaneously reacted with a persulfate solution and irradiated with ultraviolet light. Inorganic carbon is removed from the sample prior to analysis by acidification using phosphoric or sulfuric acid and purging with nitrogen gas. Chloride and low sample pH can impede the analysis. The MDL is 0.05 mg/L.

SM 5310D (APHA, 1996) is a wet-oxidation method with a detection limit of 0.10 mg/L. This method is subject to the same interferences as the persulfate-ultraviolet method. Inorganic carbon is removed from the sample prior to analysis by acidification using phosphoric acid or sulfuric acid and purging with nitrogen gas. The purged sample is sealed in an ampule and combusted in an oven for 4 hours, causing the persulfate to oxidize organic carbon to carbon dioxide. The ampule is opened inside the TOC analyzer, and carbon dioxide is measured using a non-dispersive infrared analyzer.

UV 254 nm

SM 5910 (APHA, 1996) uses the ultraviolet (UV) light absorbing characteristic of constituents in the water. Data derived using SM 5910 are an aggregate measure of the organic content base where absorbance is proportional to concentration. This method requires filtration to remove particles that create absorbance interference. Results from the spectrophotometric analysis of samples at 254 nm correlate to the concentrations of dissolved organic material in the sample. Note that the correlation between UV absorbance and organic content is site specific and may not be comparable to absorbance values from other sites.

The UV absorbance at 254 nm can be used to further characterize precursors in source water. The specific ultra violet absorbance (SUVA) is a calculated value that is a good indicator of the humic content of water. SUVA is defined as the UV (measured in m^{-1}) divided by the dissolved organic carbon concentration (measured as mg/L). Typically, SUVA values <3L/mg-m are representative of largely nonhumic material, while values in the 4-5L/mg-m represent mainly humic material.

pH

EPA Methods 150.1 and 150.2 are used to determine the hydrogen ion activity with potentiometric measurement using a standard hydrogen electrode and reference electrode. SM 4500-HB and American Society for Testing and Materials (ASTM) D1293-84 are also approved methods for determining pH (ASTM, 1994). All of these methods are relatively free of interference. However, interference may be attributed to sodium interference at pH of more than 10. These methods require two point calibration and standard temperature (e.g., 25°C).

Alkalinity

SM 2320B (APHA, 1996) is the approved method for alkalinity. Total alkalinity is measured by titration of the sample to an electrochemically determined endpoint and reported as milligrams per liter as calcium carbonate. The method ascribes the entire alkalinity concentrations to the equivalent sum of

carbonate, bicarbonate, and hydroxide concentrations and assumes an absence of other alkalinity contributing compounds.

Exhibit B-3. Precursor Method Detection Limits.

Analyte	Method	MDL
Total Organic Carbon	SM 5310B	1 mg carbon/L
	SM 5310C	0.05 mg organic carbon/L
	SM 5310D	0.10 mg organic carbon/L
UV Absorbance at 254 nm	SM 5910	~ 1 mg/L

NATIONAL LABORATORY CAPACITY

This section estimates the number of laboratories that are capable of conducting analyses for the D/DBP rule. It also estimates the number of samples those laboratories can analyze, which is referred to as the laboratory capacity.

Because the ICR requires that DBP testing be conducted by approved laboratories, the number of laboratories approved for ICR analyses may be the best indicator of the national laboratory capacity for DBP monitoring. The ICR laboratory approval process confirms a laboratory's ability to produce data of known accuracy and precision for both DBPs and their precursors. The ICR approval process tracks the number of laboratories that have applied for approval in this program and the number of laboratories that have been approved. Exhibit B-4 lists the number of laboratories that applied and were approved for each analyte. ICR laboratories use the methods summarized previously. Laboratories may have applied for approval of more than one analyte and may be counted in multiple categories. Therefore, Exhibit B-4 should not be used to provide the total number of ICR-approved laboratories.

Each of the 384 ICR laboratory application forms submitted by applying laboratories was examined to determine the laboratory sample capacity for each method. In this approval process, laboratories were required to provide data on their ability to perform each analytical method and estimate the weekly total of analyses performed.

National Capacity for Disinfectant and Precursor Measurements

The Stage 1 D/DBP rule does not require analyses for disinfectants (i.e., chlorine, chloramine, chlorine dioxide) by a certified laboratory. Many of the methods must be performed immediately onsite

Exhibit B-4. Laboratories Applying and Approved for Certification in the ICR Program

Analyte	Laboratories Applied	Laboratories Approved	Percent Approved
Free Chlorine*	328	318	97
Total Chlorine*	324	312	96
Chlorine Dioxide*	36	29	81
Total Trihalomethanes	204	203	99
Haloacetic Acids 5	103	88	85
Chlorite Ion	57	48	84
Bromate Ion	57	48	84
Bromide Ion*	57	48	84
TOC*	181	175	97
UV 254 nm*	163	158	97
Alkalinity*	324	314	99
pH*	359	355	99

*Certification is not federally mandated for these parameters under the Stage I D/DBP rule.

because of the short holding time of the samples. Analyses can be performed by trained operators; therefore, laboratory capacity is not an issue for these parameters.

Similarly, certification is not required for TOC or for specific ultraviolet absorbance (SUVA) – UV absorbance/TOC. A greater degree of skill is necessary to conduct these tests than disinfectant analysis, and state drinking water programs may require certification. Exhibit B-5 provides estimates of the number of samples analyzed per week for TOC and SUVA by method. The overall average was 119 TOC samples per laboratory per week, and the reported average for SUVA was 103 samples per week per laboratory.

National Capacity for Total Trihalomethane Measurements

Since 1979, the Safe Drinking Water Act has required analyses for TTHMs for public water supplies that serve at least 10,000 people and add a disinfectant to their water. Additionally, the methods for VOCs include the four TTHMs. All community and nontransient, noncommunity water supplies are required to analyze for VOCs. Because numerous commercial, state, and municipal laboratories are certified for TTHM and VOC testing, laboratory capacity is considered adequate for the Stage I DBP rule. Laboratories that applied for ICR approval were not asked to provide laboratory capacity for TTHMs.

Exhibit B-5. Laboratory Sample Capacity

Analyte	Method	Lab Approved	Sample Capacity per Week	Average Samples per Lab per Week
Trihalomethanes	EPA 502.2	156	Not Provided	-
	EPA 524.2			
	EPA 551			
	EPA 551.1	47	2,713	-
Haloacetic Acids 5	EPA 552.1	17	940	55
	EPA 552.2	41	1,783	43
	SM 6233B & 6251B	26	1,550	60
Chlorite, Bromide, or Bromate	EPA 300.0	48	7,208	106
Total Organic Carbon	SM 5310B	57	7,373	129
	SM 5310C	94	10,669	114
	SM 5310D	16	1,860	116
UV Absorbance at 254 nm	SM 5910	158	14,250	103

National Capacity for Haloacetic Acids

The ICR was the first EPA regulation requiring analyses for HAAs from about 600 water treatment plants. Prior to the ICR, few laboratories performed HAA analyses. In the ICR laboratory application process, laboratories submitted information on the maximum number of samples that they could analyze per week. Exhibit B-5 lists the number of laboratories approved for HAA analyses under the ICR. The exhibit also shows the number of samples per week for each method employed.

A total of 88 laboratories are approved for analyzing HAAs. These laboratories estimated that they could process a maximum of 4,273 samples per week, or an average of 51 HAA samples per laboratory per week. For the D/DBP Stage I rule, up to 50 percent additional capacity may be expected from State laboratories not involved in ICR testing and from laboratories that applied for ICR approval but failed.

National Capacity for Bromate and Chlorite

EPA approved 57 laboratories for the analyses of bromide, bromate, and chlorite using Method 300.0. These laboratories estimated that they could process a maximum of 7,208 samples per week, or an average of 106 samples per laboratory per week. Not all laboratories will update their instruments as required in the revised method, Method 300.1; however, additional capacity is expected from state laboratories.

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