DISINFECTION BYPRODUCTS in DRINKING WATER

Formation, Analysis, and Control

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Dedication

This work is dedicated to my parents; my wife, Janet; and my son, Zhen

Preface

Since chloroform was detected as a disinfection byproduct (DBP) in chlorinated waters in the 1970s, many studies have been conducted in the area of DBP analysis, formation, and control. Because of potential health risks of DBPs the United States Environmental Protection Agency promulgated the Stage 1 Disinfectants and Disinfection Byproducts Rule in December 1998. To help water systems better control the formation of DBPs in their finished water, several books have been published, including those on water chlorination, the American Chemical Society symposium series books, and American Water Works Association's *Formation and Control of Disinfection By-Products in Drinking Water*. These books are compiled with hundreds of chapters written by well known professors, scientists, and engineers and are great technical resources for many water professionals in the DBP field. However, all these books are products of a conference or symposium and there are very few interactions among various chapters. For many entry-level scientists, engineers, students, and even professors, an introductory book in the area of DBPs is needed.

For the past 15 years, the author has been intimately involved in various aspects of DBP studies. As a graduate student, a postdoctoral researcher, an engineer, a college professor, and a trainer, the author has gained first-hand experiences in DBP analysis, DBP formation and stability studies, operator training, undergraduate and graduate teaching, and bench scale, pilot scale, and full-scale testing. Between 1994 and 1995, the author conducted a series of training workshops for water quality chemists and engineers. Seminars for engineers covered basic DBP chemistry, DBP formation and control, and DBP data evaluation. Seminars for chemists and analysts covered DBP chemistry, DBP analytical methods, and data evaluation. Many attendees suggested that a book, which covers the workshop content, would be a great technical resource for people who could not attend the workshops. In 1997, the author and his graduate student, Marcus Horne, put together a web site "Disinfection Byproducts: Chemical Information and Molecular Modeling," which provides introductory information on DBPs. The feedback from the web site suggests that this type of introductory information could benefit many people in the field. The encouragement from many colleagues, friends, and graduate students finally inspired the author to write this book, which officially started in January 2000. As expected, the process of writing this book was interrupted many times, especially in the year before the author received his promotion and tenure at Penn State Harrisburg. The generous words and encouragement from colleagues, friends, and family members stayed with the author throughout the arduous process.

This book has 10 chapters. Chapter 1 gives a brief introduction to all DBPs, including their nomenclature, molecular structures, and formation. Chapter 2 discusses the formation of DBPs, including the effects of various water quality parameters. Chapter 3 gives a discussion on the stability of DBPs in drinking water. The

chapter focuses on four typical DBP degradation reactions, including hydrolysis, oxidation, dehalogenation, and biodegradation. Chapter 4 discusses the effects of various water treatment processes on the formation and removal of DBPs. Chapter 5 discusses various DBP removal and control technologies, including enhanced coagulation, carbon adsorption, alternative disinfectants, preoxidation, biologically active carbon, and membrane technology. Chapter 6 gives a discussion on the formation and control of inorganic DBPs, including bromate, chlorite, and chlorate. Chapter 7 provides a review over several past, current, and future regulations on DBPs, including the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules. Chapter 8 summarizes analytical methods and explores data evaluation for DBPs. Chapter 9 provides various informational resources for DBPs, including books, web pages, video tapes, journals and conferences. Chapter 10 summarizes conventional water treatment processes. This chapter could be valuable for analytical chemists and professionals who have limited background in drinking water treatment.

This book could be a valuable reference for entry-level scientists and engineers in the water industry and could also serve as a reference book for graduate and undergraduate students in environmental engineering. In addition, the information in this book could benefit regulators, health professionals, and chemists, as well as water operators.

The author would like to thank his M.S. advisor, Professor Zhu Qingshi, and Ph.D. advisor, Professor Wang Zhansheng, for their early introduction to the water and wastewater treatment field; Dr. David Reckhow for his many years of mentoring on DBP studies; and Dr. Charles Cole for his mentoring and friendship. The author thanks Drs. Philip Singer, James Symons, and Erwin (Mel) Suffet, who conducted many earlier studies in DBPs, for their many years' guidance and encouragement. The author also thanks many of his colleagues and those who attended his DBP workshops for their encouragement and his students for their inspirations and hard work.

As an introductory book, this book compiles the findings of many great researchers in the field of DBPs. Many findings have been well recognized and citations are indeed unnecessary. In addition, too many references could also reduce the readability of this book. The author incorporated major references into Chapter 9 that provide the readers with comprehensive information sources in the area of DBPs. Finally, the author would like to take this opportunity to thank all the people who have contributed to this book directly or indirectly, especially researchers in the field of DBPs.

The Author

Yuefeng F. Xie, **Ph.D., P.E., DEE,** is Associate Professor of Environmental Engineering, Co-Director of Small Public Water Systems Technology Assistance Center, and Co-Director of the Environmental Training Center at Penn State Harrisburg.

Dr. Xie received his B.S. degree in Chemical Engineering in 1984, M.S. degree in Environmental Engineering in 1986, and Ph.D. degree in Environmental Engineering in 1989 from Tsinghua University, Beijing, China. He held a postdoctoral position in the Department of Civil Engineering at the University of Massachusetts at Amherst from 1989 to 1994. As a trainer, Dr. Xie organized and taught more than 10 workshops in the area of disinfection byproducts across the country between 1994 and 1995. In 1995 he joined the Environmental Programs at Penn State Harrisburg as Assistant Professor of Environmental Engineering.

A registered environmental engineer and certified water operator in Pennsylvania, Dr. Xie is a Diplomate of the American Academy of Environmental Engineering. He was a member of the United State Environmental Protection Agency Information Collection Rule Chemical Analysis Joint Task Work Group. He is currently a committee member of Standard Methods for the Examination of Water and Wastewater and was a Joint Task Group member for Standard Method 4410, Inorganic Anions by Capillary Ion Electrophoresis, and Method 6251, Disinfection By-Products: Haloacetic Acid and Trichlorophenol.

Dr. Xie was the Chair of the American Chemical Society, Southeastern Pennsylvania Section in 1999. He is currently a member of the Organic Contaminant Control Committee and Water Quality Laboratory Committee of American Water Works Association. He is also a member of the Research Committee of the American Water Works Association, Pennsylvania Section. Currently, he serves as Chair of Strategic Planning and Budget Advisory Committee at Penn State Harrisburg.

Dr. Xie received the Penn State Harrisburg Excellence in Research Award in 2001. He also received the American Water Works Association, Pennsylvania Section Victor A. Appleyard Award in 1999 and in 2000. His bar theories, Xie's Bar Theory for Water Coagulation and Bar Theory II Chemical Dosage Calculation, won first place "Gidgets and Gadgets Contest Award" at the Water Works Operators' Association of Pennsylvania annual meetings in 2000 and in 2001.

Dr. Xie has 20 years research, teaching, and training experiences in disinfection byproduct analysis and control. His work has been published in the *Journal of the American Water Works Association*, *Water Research*, *Environmental Science and Technology*, and *Ozone Science and Engineering*, *Journal of Mass Spectrometry*, and *Water Environment Research*. He has been the recipient of research and training grants from the United States Environmental Protection Agency, American Water Works Association Research Foundation, and Pennsylvania Department of Environmental Protection. His research and training interests include disinfection byproduct analysis and control, water reuse, and water operator training.

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Prelude

WHAT ARE DBPs?

The purpose of drinking water treatment is to remove pathogens, toxic chemicals, and aesthetic contaminants from raw water. For surface water sources, including rivers, lakes, and reservoirs, a conventional water treatment process is commonly used. The process includes coagulation, flocculation, sedimentation, filtration, and disinfection. Coagulation neutralizes the charge on the surface of particles and flocculation combines small particles into large settleable or filterable flocs. Sedimentation and filtration removes these flocs and other neutralized particles, including pathogens.

The final process is disinfection and it serves two main purposes. The primary purpose of disinfection is to kill or inactivate pathogens. The secondary purpose is to provide a disinfectant residual in finished water and prevent microbial regrowth in water distribution systems. Although the majority of pathogens (99 to 99.9%) are removed by coagulation, flocculation, sedimentation, and filtration, disinfection is a critical process to protect the public from contracting waterborne diseases. Common disinfectants are chlorine, chloramines, ozone, chlorine dioxide, and ultraviolet radiation.

In addition to pathogen kill or inactivation, disinfectants also react with natural organic matter (e.g., humic and fulvic substances) or bromide in water to produce various organic and inorganic byproducts. These byproducts are commonly referred to as disinfection byproducts, or DBPs. Many disinfectants are also commonly used as oxidants to control color, taste, and odor compounds, biological growth inside various treatment units, iron and manganese, and other organic and inorganic compounds. The process is commonly referred to as preoxidation or prechlorination when chlorine is used. The byproducts of various oxidation processes are also commonly referred to as DBPs.

Trihalomethanes (THMs) and haloacetic acids (HAAs) are common DBPs in chlorinated and chloraminated waters. Bromate is an ozonation byproduct in water high in bromide. Chlorite is a degradation product of chlorine dioxide. Other chlorination DBPs include chloral hydrate, haloacetonitriles, halopropanones, and chloropicrin. Cyanogen chloride is a unique DBP in chloraminated waters. Aldehydes, ketoacids, and carboxylic acids are organic byproducts commonly detected in ozonated waters. Chlorate could be formed in chlorine stock (hypochlorite) solution, and in water treated with ozone and chlorine dioxide. Many of these DBPs occur in finished drinking water at μg/L levels.

WHY SHOULD DBPS BE CONTROLLED?

Since the detection of chloroform in chlorinated drinking water, numerous epidemiological studies have been conducted to investigate the potential health risks of chlorinated or chloraminated waters. Many epidemiological studies indicated an association between water chlorination and bladder cancer and rectal cancer. By evaluating 12 epidemiological studies, a 1992 report[1] indicated that 9% of bladder cancer cases and 15% of the rectal cancer cases, that is 10,000 additional cancer cases per year, could be attributed to chlorinated water and its byproducts. The correlation between trihalomethanes in drinking water and spontaneous abortion was also reported.[2] The United State Environmental Protection Agency (U.S. EPA) concluded that the usual exposure to DBPs in drinking water could result in an increased cancer risk at levels encountered in some public water supplies.[3]

Many toxicological studies have been conducted to investigate the mutagenic and carcinogenic properties of various DBPs. Under the classification of the 1986 U.S. EPA Weight-of-the-Evidence Categories, chloroform, chlorodibromomethane, bromoform, dichloroacetic acid, and bromate are placed in group B2, probable human carcinogens.[3] This is based on sufficient evidence in animals and inadequate evidence in humans. Chlorodibromomethane, trichloroacetic acid, and chloral hydrate are placed in group C, possible human carcinogens. This is based on limited evidence in animals in the absence of human data. Chlorite is placed in group D, not classifiable as to human carcinogenicity. This is based on inadequate evidence or no data concerning carcinogenicity in animals in absence of human data. However, chlorite, chlorate, and chlorine dioxide have shown adverse hematological effects in animal studies. The potential health risks of various DBPs are also shown in Table 1.[4]

Because of their high occurrences in drinking water and potential health risks, DBPs are regulated in drinking water by the U.S. EPA. The Total Trihalomethane Rule established a maximum contaminant level (MCL) of 100 μg/L for four THMs in finished water.[5] The Stage 1 Disinfectants and Disinfection Byproducts Rule established MCLs at 80 μg/L for four THMs, 60 μg/L for five HAAs, 10 μg/L for bromate, and 1 mg/L for chlorite,[6] as shown in Table 1. The upcoming Stage 2 Disinfectants and Disinfection Byproducts Rule may not change the MCLs for these DBPs. However, Stage 2 rule may change the method for computing DBP levels and use locational running annual averages (verse running annual average) for total THMs and five HAAs compliance. This will make the DBP requirements much stricter than that under the Stage 1 rule.

WHEN: THE DISINFECTION BYPRODUCT CHRONICLE

Dr. J.M. Symons gave two excellent reviews over the early DBP history.[7–9] His earlier career with the U.S. EPA gave him first hand experiences on DBP detection, regulation, and many of the early studies and surveys. The following DBP chronicle gives readers a quick review of the DBP history.

TABLE 1
National Primary Drinking Water Regulations on DBPs

Disinfection Byproducts	MCLG (mg/L)	MCL (mg/L)	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Bromate	zero	0.010	Increased risk of cancer	Byproduct of drinking water disinfection
Chlorite	0.8	1.0	Anemia: infants and young children: nervous system effects	Byproduct of drinking water disinfection
Haloacetic acids (HAA5)	n/a	0.060	Increased risk of cancer	Byproduct of drinking water disinfection
Total Trihalomethanes (TTHMs)	None[a] …….. n/a[a]	0.10[a] …….. 0.080[b]	Liver, kidney or central nervous system problems; increased risk of cancer	Byproduct of drinking water disinfection

[a]Total Trihalomethane Rule.

[b]Stage 1 Disinfectants and Disinfection Byproducts Rule.

Notes: MCLG = Maximum Contaminant Level Goal; MCL = Maximum Contaminant Level; HAA5 = five haloacetic acids; n/a = not applicable; TTHMs = total trihalomethanes.

Source: From United States Environmental Protection Agency, National Primary Drinking Water Regulations, http://www.epa.gov/safewater/mcl.html, 2003.

1972 Rook reported the detection of chloroform in chlorinated drinking water.[10] This was also reported by the same author in a non-English paper in 1971.[9]
1974 Rook reported the relationship between natural organic matter and formation of chloroform.[11]
1975 The National Organics Reconnaissance Survey was conducted by the U.S. EPA.[12]
1975 First Chlorination Conference was organized by Jolly et al. and held in October.[13]
1979 Total Trihalomethane Rule was promulgated by the U.S. EPA.[4]
1983 U.S. EPA published a list of best-available technologies for THM control.[14]
1983 Formation of haloacetic acids and chloral hydrate in chlorinated drinking water was reported by Uden and Miller.[15]
1983 The formation of bromate in ozonated water containing bromide was reported by Haag and Hoigne.[16]

1986 Formation of a strong mutagen, MX, in chlorinated water was reported by Hemming, Holmbom, Reunanen, and Kronberg.[17]
1989 Formation of aldehydes in ozonated water was reported by Yamada and Somiya,[18] and Glaze, Koga and Cancilla.[19]
1992 A group of new ozonation byproducts, ketoacids including glyoxylic acid, pyruvic acid, ketomalonic acid, were reported by Xie and Reckhow.[20,21]
1992 Chloral hydrate and its three brominated analogues were reported in chlorinated water by Xie and Reckhow.[22]
1993 First American Chemical Society (ACS) Disinfection Byproducts Symposium was organized by Minear and Amy and held in August.[23]
1994 Information Collection Rule was proposed by the U.S. EPA.[24]
1994 Stage 1 Disinfectants and Disinfection Byproducts Rule was proposed by the U.S. EPA.[3]
1996 Information Collection Rule was promulgated by the U.S. EPA.[25]
1998 Stage 1 Disinfectants and Disinfection Byproducts Rule was promulgated by the U.S. EPA.[6]
1999 *Formation and Control of Disinfection By-Products in Drinking Water*, edited by Singer, was published by the American Water Works Association.[26]

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1 Disinfection Byproducts

OBJECTIVES

This chapter gives a brief overview of various disinfection byproducts (DBPs), including their formation and occurrence in drinking water. The chapter also provides an extensive discussion on the nomenclature and molecular structures for various groups of DBPs. With these molecular structures, this chapter will help water professionals to better understand the behavior of DBPs during their analyses and control.

This chapter is written for people who are new in the DBP field. It clearly identifies the basic chemical formula of all major DBPs. In comparison to other chapters, especially Xie's Bar Theory for Water Coagulation in Chapter 10, this chapter is theoretical but essential. A good understanding of the nomenclature and molecular structures for various groups of DBPs lays a solid foundation for proficient DBP analysis and control.

NOMENCLATURE

DBP disinfection byproduct
D-DBP disinfectants and disinfection byproducts
E-MX (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid
HAA haloacetic acid
ICR Information Collection Rule
MX 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
NDMA *N*-Nitrosodimethylamine
NOM natural organic matter
THM trihalomethanes
TOX total organic halide
U.S. EPA United States Environmental Protection Agency

Disinfection byproduct (DBP) is a term used to describe a group of organic and inorganic compounds formed during water disinfection. These byproducts are formed by the reactions between disinfectants and natural organic matter (NOM) or inorganic substances in water. For oxidation processes such as ozonation, their byproducts are also referred to as DBPs even though the main purpose of the processes is oxidation. Because of their potential health risks, currently, four groups of DBPs are regulated under the United States Environmental Protection Agency (U.S. EPA) Stage 1 Disinfectants and Disinfection Byproducts (D-DBP) Rule. These four groups are trihalomethanes (THMs), haloacetic acids (HAAs), chlorite, and bromate. Additional DBPs were also monitored under the U.S. EPA Information

Collection Rule (ICR). They are halopropanones, haloacetonitriles, trichloroacetaldehyde hydrate, trichloronitromethane, and cyanogen chloride. Ozone, a powerful disinfectant and oxidant, has been increasingly used in drinking water treatment. In addition to bromate, three types of organic DBPs, including aldehydes, ketoacids, and carboxylic acids are commonly detected in ozonated drinking water.

Although there are many DBPs detected in drinking water, based on their molecular structures, formation, and chemical properties, these DBPs are often categorized into the following groups.

1.1 TRIHALOMETHANES

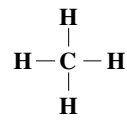
Trichloromethane, or chloroform, was the first DBP identified in chlorinated water. Trihalomethanes are commonly abbreviated as THMs. There are four common THMs. Their names, chemical formula, and common acronyms are listed in Table 1.1.

As illustrated in Figure 1.1, a methane molecule contains four hydrogen atoms. By replacing three hydrogen atoms with halogen atoms, including chlorine and bromine, a total of four THMs are obtained, as shown in Figure 1.2.

With three chlorine atoms, the THM is trichloromethane ($CHCl_3$). Trichloromethane is also commonly called chloroform. Bromodichloromethane ($CHBrCl_2$) contains one bromine atom and two chlorine atoms and chlorodibromomethane ($CHBr_2Cl$) contains one chlorine atom and two bromine atoms. Tribromomethane ($CHBr_3$) contains three bromine atoms and is also commonly called bromoform.

TABLE 1.1
Names and Acronyms for THMs

Names	Common Names	Formula	Acronyms
Trichloromethane	Chloroform	$CHCl_3$	TCM, CF
Bromodichloromethane	—	$CHBrCl_2$	BDCM
Chlorodibromomethane	—	$CHBr_2Cl$	CDBM
Tribromomethane	Bromoform	$CHBr_3$	TBM, BF
Trihalomethane	—	CHX_3	THM



methane

FIGURE 1.1 Molecular structure of methane.

trichloromethane bromodichloromethane chlorodibromomethane tribromomethane

FIGURE 1.2 Molecular structures of four THMs.

Although chloroform and other THMs are illustrated as chlorinated or brominated methanes, the formation of THMs in chlorinated water is not due to reactions between chlorine and methane or chlorinated methanes. Instead, it is due to a complex reaction between chlorine and NOM, including humic or fulvic substances, as shown in Equation 1.1. The formation of brominated THMs is due to the bromide ion in chlorinated water.

$$\text{NOM} + \text{chlorine} + \text{bromide} \rightarrow \text{THMs} \tag{1.1}$$

In addition to four bromo- and chloro-THMs, iodo-THMs have also been identified in chlorinated water containing iodide, especially in sea water. The introduction of iodine significantly increases the number of THMs. Considering the different combinations of chlorine, bromine, and iodine, theoretically there could be a total of 27 THMs.

1.2 HALOACETIC ACIDS

Haloacetic acids are another major group of DBPs, following THMs, in chlorinated drinking water. Haloacetic acids are commonly abbreviated as HAAs. There are nine common HAAs. Their names, chemical formula, and common acronyms are listed in Table 1.2.

As shown in Figure 1.3, an acetic acid molecule contains three hydrogen atoms at the alpha position, or the position next to the COOH group.

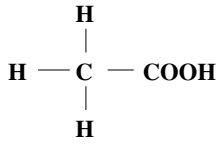
By replacing the hydrogen atoms with halogen atoms, partially or completely, a total of nine HAAs are obtained. Historically, haloacetic acids have been categorized as one single group. However, there are actually three groups of haloacetic acids. With one halogen the HAAs are called monohaloacetic acids (CH_2XCOOH). With two halogens the HAAs are called dihaloacetic acids (CHX_2COOH). With three halogens the HAAs are called trihaloacetic acids (CX_3COOH). It is important to remember that there are three different types of HAAs because their formation and chemical and biological properties are significantly different.

1.2.1 Monohaloacetic Acids

With one chlorine or bromine, there are two monohaloacetic acids. They are monochloroacetic acid ($CH_2ClCOOH$) and monobromoacetic acid ($CH_2BrCOOH$), as shown in Figure 1.4.

TABLE 1.2
Names and Acronyms for HAAs

Names	Formula	Acronyms
Monochloroacetic acid	$CH_2ClCOOH$	ClAA, MCAA
Monobromoacetic acid	$CH_2BrCOOH$	BrAA, MBAA
Dichloroacetic acid	$CHCl_2COOH$	ClAA, MCAA
Bromochloroacetic acid	CHBrClCOOH	BrClAA, BCAA
Dibromoacetic acid	$CHBr_2COOH$	Br_2AA, DBAA
Trichloroacetic acid	CCl_3COOH	Cl_3AA, TCAA
Bromodichloroacetic acid	$CBrCl_2COOH$	$BrCl_2$AA, BDCAA
Chlorodibromoacetic acid	$CBr_2ClCOOH$	$ClBr_2$AA, CDBAA
Tribromoacetic acid	CBr_3COOH	Br_3AA, TBAA
Monohaloacetic acid	CH_2XCOOH	XAA, MHAA
Dihaloacetic acid	CHX_2COOH	X_2AA, DHAA
Trihaloacetic acid	CX_3COOH	X_3AA, THAA
Haloacetic acid	—	HAA



acetic acid

FIGURE 1.3 Molecular structure of acetic acid.

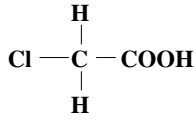
1.2.2. Dihaloacetic Acids

Dihaloacetic acids contain two halogens, chlorine and/or bromine, and there are three possible combinations. They are dichloroacetic acid ($CHCl_2COOH$), bromochloroacetic acid (CHBrClCOOH), and dibromoacetic acid ($CHBr_2COOH$), as shown in Figure 1.5.

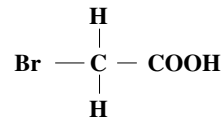
1.2.3 Trihaloacetic Acids

Trihaloacetic acids contain three halogens of either chlorine, bromine, or a combination of the two and being similar to THMs, there are four possible combinations. They are trichloroacetic acid ($CHCl_3COOH$), bromodichloroacetic acid ($CHBrCl_2COOH$), chlorodibromoacetic acid ($CHBr_2ClCOOH$), and tribromoacetic acid ($CHBr_3COOH$), as shown in Figure 1.6.

Again, the formation of haloacetic acids in chlorinated water is not due to the reaction between acetic acid and chlorine. HAAs are formed by the reaction between natural organic matter and chlorine, as shown in Equation 1.2.

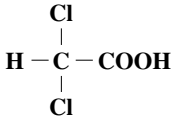


monochloroacetic acid

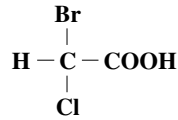


monobromoacetic acid

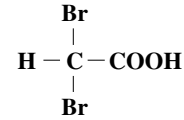
FIGURE 1.4 Molecular structures of two monohaloacetic acids.



dichloroacetic acid

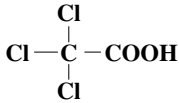


bromochloroacetic acid

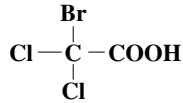


dibromoacetic acid

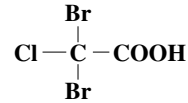
FIGURE 1.5 Molecular structures of three dihaloacetic acids.



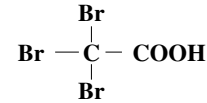
trichloroacetic acid



bromochloroacetic acid



chlorodibromoacetic acid



tribromoacetic acid

FIGURE 1.6 Molecular structures of four trihaloacetic acids.

$$\text{NOM} + \text{chlorine} + \text{bromide} \rightarrow \text{HAAs} \tag{1.2}$$

Further chlorination of monohaloacetic acids and dihaloacetic acids is not the formation mechanism for dihaloacetic acids and trihaloacetic acids in chlorinated water. They are formed through different precursors, as discussed in Chapter 2.

1.3 INORGANIC DISINFECTION BYPRODUCTS

Two inorganic disinfection byproducts are currently regulated under the Stage 1 D-DBP Rule. They are chlorite (ClO_2^-) and bromate (BrO_3^-).

Chlorite is a common DBP found in water treated with chlorine dioxide. The formation of chlorite is due to the degradation of chlorine dioxide, which is an alternative oxidant and disinfectant for drinking water treatment. In the presence of natural organic matter or other reducing agents, chlorine dioxide is reduced to chlorite as shown in Equation 1.3.

$$ClO_2 \rightarrow ClO_2^- \tag{1.3}$$

Bromate is a common DBP found in ozonated water containing inorganic bromide. The formation of bromate is due to the ozonation of the bromide ion in water, as shown in Equation 1.4.

$$Br^- + O_3 \rightarrow BrO_3^- \quad (1.4)$$

In actuality, the formation of chlorite and bromate in water involves many complex reactions. Further discussion of this topic/subject is provided in Chapter 6.

1.4 OTHER HALOGENATED DISINFECTION BYPRODUCTS

In addition to THMs, HAAs, chlorite and bromate, and many organic DBPs have been detected in chlorinated, chloraminated, or ozonated waters. These DBPs include trihaloacetaldehydes, haloacetonitriles, haloacetones, trihalonitromethane, and cyanogen halides. Their names, chemical formula, and common acronyms are listed in Table 1.3.

These DBPs are not regulated in the Stage 1 D-DBP Rule. Some of them were included under the ICR monitoring. Because many of these DBPs could lead to the formation of THMs and HAAs through various reactions, a good understanding of these DBPs will help us better understand the formation, analysis and control of trihalomethanes and haloacetic acids. Many of these DBPs could be regulated in future regulations.

1.4.1 Trichloroacetaldehyde and Its Brominated Analogues

Trichloroacetaldehyde is commonly detected in chlorinated water. Even though its concentration is significantly lower than that for THMs and HAAs, trichloroacetaldehyde and its brominated analogues are the third largest group of organic DBPs found in chlorinated water. Since trichloroacetaldehyde is also called chloral and readily forms trichloroacetaldehyde hydrate in water, the name chloral hydrate is commonly used. As shown in Figure 1.7, acetaldehyde contains three hydrogen atoms at the alpha position, the position next to the CHO group.

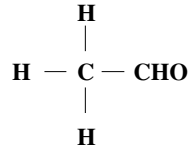
When all three hydrogen atoms are replaced with chlorine, trichloroacetaldehyde (Cl_3Ald) is obtained, as shown in Figure 1.8. Similar to THMs, brominated analogues of trichloroacetaldehyde, or brominated trihaloacetaldehydes (X_3Ald), are also formed in water containing bromide. Three brominated trihaloacetaldehydes are bromodichloroacetaldehyde ($BrCl_2Ald$), chlorodibromoacetaldehyde ($ClBr_2Ald$), and tribromoacetaldehyde (Br_3Ald). Tribromoacetaldehyde is commonly called bromal. Due to a lack of commercial standards and their stability, these brominated trihaloacetaldehydes are not commonly reported in drinking water.

Monohaloacetaldehydes and dihaloacetaldehydes can also be formed in chlorinated drinking water, but since they can be subsequently oxidized into trihaloacetaldehydes, their occurrence and dominance in chlorinated water are relatively limited.

In contrast to THMs and HAAs, trihaloacetaldehydes can be formed by the reaction between acetaldehyde and chlorine, as shown in Equation 1.5. The reaction between acetaldehyde, an ozonation DBP, and chlorine is one of the main mechanisms for the formation of high levels of trichloroacetaldehyde in ozonated water.

TABLE 1.3
Ozonation Disinfection Byproducts

Names	Common Names	Formula	Acronyms
Trichloroacetaldehyde	Chloral	CCl_3CHO	Cl_3Ald,CH
Bromodichloro-acetaldehyde	—	$CBrCl_2CHO$	$BrCl_2$Ald
Chlorodibromo-acetaldehyde	—	CBr_2ClCHO	Br_2ClAld
Tribromoacetaldehyde	Bromal	CBr_3CHO	Br_3ClAld
Trihaloacetaldehyde	—	CX_3CHO	X_3Ald
Dichloroacetonitrile	—	$CHCl_2CN$	Cl_2AN, DCAN
Bromochloro-acetonitrile	—	$CHBrClCN$	BrClAN, BCAN
Dibromoacetonitrile	—	$CHBr_2CN$	Br_2AN, DBAN
Trichloroacetonitrile	—	CCl_3CN	Cl_3AN, TCAN
Bromodichloro-acetonitrile	—	$CBrCl_2CN$	$BrCl_2$AN, BDCAN
Chlorodibromo-acetonitrile	—	CBr_2ClCN	Br_2ClAN, CDBAN
Tribromoacetonitrile	—	CBr_3CN	Br_3AN, TBAN
Dihaloacetonitrile	—	CHX_2CN	X_2AN, DHAN
Trihaloacetonitrile	—	CX_3CN	X_3AN, THAN
Haloacetonitrile	—	—	HAN
Dichloropropanone	Dichloroacetone	$CHCl_2COCH_3$	Cl_2PN
Bromochloropropanone	Bromochloroacetone	$CHBrClCOCH_3$	BrClPN
Dibromopropanone	Dibromoacetone	$CHBr_2COCH_3$	Br_2PN
Trichloropropanone	Trichloroacetone	CCl_3COCH_3	Cl_3PN
Bromodichloro-propanone	Bromodichloro-acetone	$CBrCl_2COCH_3$	$BrCl_2$PN
Chlorodibromo-propanone	Chlorodibromo-acetone	$CBr_2ClCOCH_3$	Br_2ClPN
Tribromopropanone	Tribromoacetone	CBr_3COCH_3	Br_3PN
Dihalopropanone	Dihaloacetone	CHX_2COCH_3	X_2PN
Trihalopropanone	Trihaloacetone	CX_3COCH_3	X_3PN
Halopropanone	Haloacetone	—	HPN, HKs
Trichloronitromethane	Chloropicrin	CCl_3NO_2	Cl_3NM, CP
Bromodichloronitro-methane	—	$CBrCl_2NO_2$	$BrCl_2$NM
Chlorodibromonitro-methane	—	CBr_2ClNO_2	Br_2ClNM
Tribromonitromethane	—	$CBrCl_2NO_2$	Br_3NM
Trihalonitromethane	—	CBr_3NO_2	X_3NM
Cyanogen chloride		ClCN	—
Cyanogen bromide	—	BrCN	—
Cyanogen halide	—	XCN	—



acetaldehyde

FIGURE 1.7 Molecular structure of acetaldehyde.

trichloroacetaldehyde bromodichloroacetaldehyde chlorodibromoacetaldehyde tribromoacetaldehyde

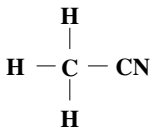
FIGURE 1.8 Molecular structures of trihaloacetaldehydes.

$$\text{aldehyde} + \text{chlorine} + \text{bromide} \rightarrow \text{trihaloacetaldehydes} \tag{1.5}$$

1.4.2 Haloacetonitriles

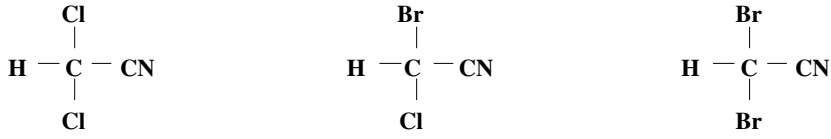
Haloacetonitriles are commonly detected in chlorinated and chloraminated waters at much lower levels than THMs or HAAs. Common haloacetonitriles include dihaloacetonitrile (CHX_2CN) and trihaloacetonitrile (CX_3CN). As shown in Figure 1.9, acetonitrile contains three hydrogen atoms at the alpha position, the position next to the CN group.

When two or three hydrogen atoms are replaced with halogen atoms, dihaloacetonitriles or trihaloacetonitriles are obtained. Similar to dihaloacetic acids, there are three dihaloacetonitriles, including dichloroacetonitrile ($CHCl_2CN$), bromochloroacetonitrile (CHBrClCN), and dibromoacetonitrile ($CHBr_2CN$), as shown in Figure 1.10.



acetonitrile

FIGURE 1.9 Molecular structure of acetonitrile.



dichloroacetonitrile bromochloroacetonitrile dibromoacetonitrile

FIGURE 1.10 Molecular structures of three dihaloacetonitriles.

trichloroacetonitrile bromodichloroacetonitrile chlorodibromoacetonitrile tribromoacetontrile

FIGURE 1.11 Molecular structures of four trihaloacetonitriles.

Similar to THMs, there are four trihaloacetonitriles, including trichloroacetonitrile (CCl_3CN), bromodichloroacetonitrile ($CBrCl_2CN$), chlorodibromoacetonitrile ($CClBr_2CN$), and tribromoacetonitrile (CBr_3CN), as shown in Figure 1.11. Due to a lack of commercial standards, these brominated trihaloacetonitriles are not commonly reported in drinking water.

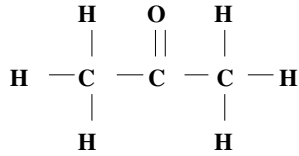
Again, in contrast to THMs and HAAs, haloacetonitriles can be formed by the reaction between acetonitrile and chlorine. Monohaloacetonitriles and dihaloacetonitriles can be further chlorinated into dihaloacetonitriles and trihaloacetonitriles.

1.4.3 Halopropanones

Halopropanones are commonly detected in chlorinated drinking water at very low levels. Since propanone is commonly called acetone, halopropanones are also called haloacetones or haloketones. As shown in Figure 1.12, propanone contains three hydrogen atoms at the alpha position, the position next to the CO group.

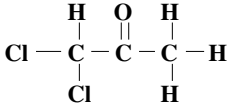
When two or three hydrogen atoms are replaced with halogen atoms, dihalopropanones (CHX_2COCH_3) or trihalopropanones (CX_3COCH_3) are obtained. Similar to dihaloacetic acids, there are three dihalopropanones, including dichloropropanone ($CHCl_2COCH_3$), bromochloropropanone ($CHBrClCOCH_3$), and dibromopropanone ($CHBr_2COCH_3$), as shown in Figure 1.13.

Similar to THMs, there are four trihalopropanones, including trichloropropanone (CCl_3COCH_3), bromodichloropropanone ($CBrCl_2COCH_3$), chlorodibromopropanone ($CBr_2ClCOCH_3$), and tribromopropanone (CBr_3COCH_3), as shown in Figure 1.14. Due to a lack of commercial standards, two brominated dihalopropanones and three brominated trihalopropanones are not commonly reported in chlorinated drinking water.

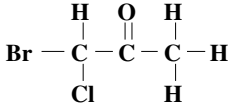


propanone (or acetone)

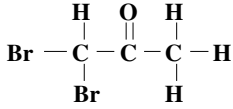
FIGURE 1.12 Molecular structure of propanone.



dichloropropanone

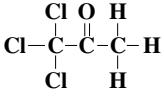


bromochloropropanone

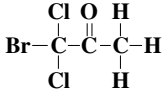


dibromopropanone

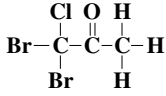
FIGURE 1.13 Molecular structures of three dihalopropanones.



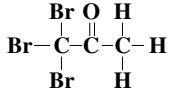
trichloropropanone



bromodichloropropanone



chlorodibromopropanone



tribromopropanone

FIGURE 1.14 Molecular structures of four trihalopropanones.

In addition to dihalopropanones and trihalopropanones, monohalopropanones (CH_2XCOCH_3), tetrahalopropanones (CHX_2COCHX_2 or CX_3COCH_2X), pentahalopropanones (CX_3COCHX_2), and hexhalopropanones (CX_3COCX_3) can also be formed in chlorinated water. Monohalopropanones could be further oxidized into dihalopropanones and trihalopropanones. Tetrahalopropanones, pentahalopropanones, and hexhalopropanones are not stable at natural for high pH conditions and undergo degradation. Again, due to a lack of commercial standards, they are not commonly reported in chlorinated drinking water.

In contrast to THMs and HAAs, halopropanones can be formed by the reaction between propanone and chlorine, as shown in Equation 1.6.

$$\text{propanone} + \text{chlorine} + \text{bromide} \rightarrow \text{halopropanones} \tag{1.6}$$

The reaction between propanone, an ozonation DBP, and chlorine is one of the main mechanisms for the formation of high levels of dichloropropanone and trichloropropanone in ozonated water.

1.4.4 Trichloronitromethane and Its Brominated Analogues

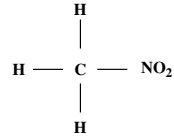
Trichloronitromethane (CCl_3NO_2) is another DBP commonly detected at low levels in chlorinated drinking water. A commonly used name for trichloronitromethane is chloropicrin. As shown in Figure 1.15, nitromethane contains three hydrogen atoms. When all three hydrogen atoms are replaced with halogen, trihalonitromethanes (CX_3NO_2) are obtained.

Similar to THMs, in addition to trichloronitromethane, there are three brominated trihalonitromethanes, including bromodichloronitromethane ($CBrCl_2NO_2$), chlorodibromonitromethane (CBr_2ClNO_2), and tribromonitromethane (CBr_3NO_2) or bromopicrin, as shown in Figure 1.16. Due to a lack of commercial standards, these brominated trihalonitromethanes are not commonly reported in chlorinated drinking water.

1.4.5 Cyanogen Chloride and Its Brominated Analogue

Cyanogen chloride is commonly detected in chloraminated drinking waters. The molecule of hydrocyanic acid contains one hydrogen atom, as shown in Figure 1.17. When the hydrogen is replaced with a halogen atom, cyanogen halides are obtained, as shown in Figure 1.17. When the substituent is chlorine or bromine, the product is called cyanogen chloride or cyanogen bromide, respectively, as shown in Figure 1.17. Cyanogen bromide is commonly detected in chloraminated water containing bromide.

Since hydrocyanic acid, or hydrogen cyanide, is an inorganic compound (highly toxic), some people consider cyanogen chloride and cyanogen bromide inorganic compounds. Both cyanogen chloride and cyanogen bromide are organic compounds.



mononitromethane

FIGURE 1.15 Molecular structure of nitromethane.

trichloronitromethane bromodichloronitromethane chlorodibromonitromethane tribromonitromethane

FIGURE 1.16 Molecular structures of trihalonitromethanes.

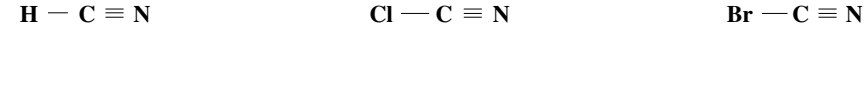


FIGURE 1.17 Molecular structures of hydrocyanic acid and two cyanogen halides.

1.4.6 MX

The full name of MX is 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone. E-MX, (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid, is a geometric isomer of MX. The molecular structures of MX and E-MX are shown in Figure 1.18.

Both MX and E-MX have been identified in chlorinated waters. Like THMs and HAAs, they are formed by the reaction between natural organic matter and chlorine. Their brominated analogues are also formed in water high in bromide. However, due to the complexity of the analytical method, very limited information is available on the occurrence and dominance of MX in chlorinated drinking water in the United States. The cancer potency of MX is much higher than that of THMs and HAAs. MX, E-MX, and their brominated analogues are the major contributing DBPs to the mutagenicity of chlorinated waters.

1.4.7 Total Organic Halide

Due to the limitation of current analytical technologies, many halogenated DBPs are not yet identified in chlorinated waters. The halogenated DBPs discussed above account for only a fraction of the total disinfection byproducts formed in water. Total organic halide (TOX) is a measurement for the total halogens, including chlorine, bromine and iodine but not fluorine, which are contained in all halogenated organic compounds. Similar to total organic carbon (TOC) and chemical oxygen demand (COD), TOX does not yield information on the chemical structures of the organic compounds. In comparison to detection methods for individual DBPs, TOX is an inexpensive measurement to screen a large number of samples for halogenated organic components. This measurement is important especially when the sample contains a large quantity of unidentified halogenated organic compounds.

MX **E-MX**

FIGURE 1.18 Molecular structures of MX and E-MX.

Due to the analytical procedure design, TOX analysis only measures the halogenated organic compounds that can be retained on the activated carbon adsorbent. This measurement is commonly called absorbable organic halogen (AOX). When water samples are filtered before carbon adsorption, this measurement is called dissolved organic halogen (DOX).

1.5 OZONATION DBPs

In addition to bromate and other bromated DBPs, ozone also reacts with NOM to form additional organic DBPs. Three common types of these organic DBPs are aldehydes, ketoacids, and carboxylic acids, as shown in Table 1.4. These organic DBPs are also referred to as oxidation products since in many applications ozone is not used as a disinfectant but rather as an oxidant.

1.5.1 Aldehydes

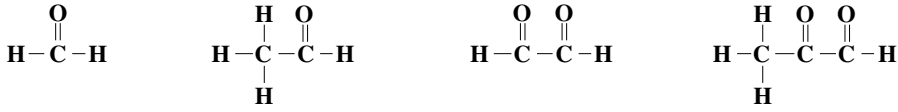
Aldehydes are commonly detected in ozonated drinking water. Formaldehyde and acetaldehyde are two common simple aldehydes detected in ozonated water. Glyoxal and methyl glyoxal are two common dialdehydes detected in ozonated water. Their molecular structures are shown in Figure 1.19. Other less common aldehydes include propanal, butanal, and pentanal.

1.5.2 Ketoacids

Ketoacids are another group of DBPs commonly detected in ozonated water. In general, the concentration of total ketoacids is five or ten times higher than that for total aldehydes. Ketoacids are also referred to as aldoacids or oxoacids. The author suggests that the name, ketoacid, be used since ketoacid is more accurate than aldoacid and more common than oxoacid to name these compounds. Three

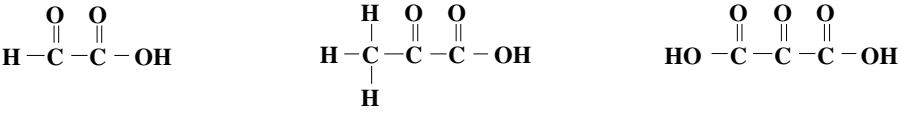
TABLE 1.4
Other Halogenated Disinfection Byproducts

Common names	Molecular formula	Systematic names
Formaldehyde	HCHO	Methanal
Acetaldehyde	CH_3CHO	Ethanal
Glyoxal	OHCCHO	Ethanedial
Methyl glyoxal	CH_3COCHO	2-oxo-Propionaldehyde
Glyoxylic acid	HCOCOOH	Oxoacetic acid
Pyruvic acid	$CH_3COCOOH$	2-oxo-Propionic acid
Ketomalonic acid	HOOCCOCOOH	Oxopropanedioic acid
Formic acid	HCOOH	Methanoic acid
Acetic acid	CH_3COOH	Ethanoic acid
Oxalic acid	HOOCCOOH	Ethanedioic acid



formaldehyde acetaldehyde glyoxal methylglyoxal

FIGURE 1.19 Molecular structures of common aldehydes.



glyoxylic acid pyruvic acid ketomalonic acid

FIGURE 1.20 Molecular structures of common ketoacids.

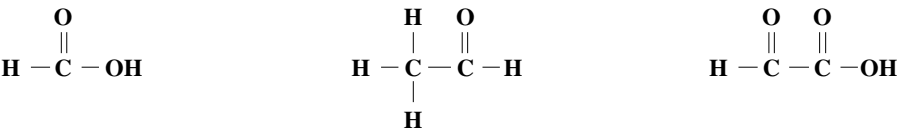
ketoacids that are commonly detected in ozonated water are glyoxylic acid, pyruvic acid, and ketomalonic acid. Their molecular structures are shown in Figure 1.20.

1.5.3 Carboxylic Acids

Carboxylic acids are another group of DBPs commonly detected in ozonated water. There is very little information available on their levels in ozonated drinking water. However, oxalic acid, a common diacid detected in ozonated water, has been reported at levels of hundreds μg/L. Formic acid and acetic acid are two common simple acids detected in ozonated drinking water. Their molecular structures are shown in Figure 1.21.

1.6 *N*-Nitrosodimethylamine (NDMA)

N-Nitrosodimethylamine (NDMA) is a semi-volatile organic compound that has been detected in both water and wastewater. The source of NDMA in water varies. NDMA was used as a commercial chemical for decades in the United States. More



formic acid acetic acid oxalic acid

FIGURE 1.21 Molecular structures of common carboxylic acids.

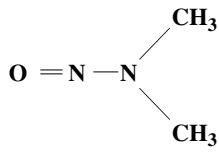


FIGURE 1.22 Molecular structure of NDMA.

recent studies also indicated that NDMA might be a disinfection by-product, especially in chloraminated water. However, there is little information available on the formation mechanism of NDMA in drinking water. The molecular structure of NDMA is shown in Figure 1.22.

1.7 NOMENCLATURE

Many organic DBPs have a systematic name devised by the International Union of Pure and Applied Chemistry (IUPAC) and one or two common names. The systematic name provides information on the carbon number of the main part of the molecule, the functional group that the molecule belongs to, and the locations of various substituents. The common name, in many cases, was given by the discoverer and does not provide much information on the molecule itself. Since many DBPs are referred to by their common names, it is important to know their correlating systematic names. For example, in comparison to chloroform, the name trichloromethane indicates that it belongs to the trihalomethane family, and bromodichloromethane, chlorodibromomethane, and tribromomethane are its brominated analogues. However, for many ozonation byproducts, their common names are accepted by the International Union of Pure and Applied Chemistry and/or are commonly used. Since these common names are so well known it makes little sense to use their systematic names. The systematic names and common names of the DBPs discussed in this book are listed in Tables 1.1 to 1.4.

Acronyms are commonly used in many environmental publications and regulations. In many cases, the authors are trying to use acronyms to increase their oral or written communication efficiencies. However, arbitrarily using acronyms has caused more confusion among readers, especially for those new in the field or from another discipline. Even many professors or experienced researchers cannot finish reading some of the publications or regulations without flipping the page back and forth. The use of acronyms is also subject to potential confusions and inaccuracies. Nevertheless, many publications, including some written by the author, are embedded with acronyms. Common acronyms for DBPs are also listed in Tables 1.1 to 1.4. The author of this book strongly discourages the arbitrary use of acronyms in publications except for tables and figures. Symbols, such as A, B, C, are commonly used for various chemicals in figures due to the limited space. In this case, the author suggests that acronyms, such as Cl_3AA, be used.

This book is written with a minimum use of acronyms. For common acronyms, they are defined in each chapter and listed right after the objective of each chapter.

This repeat listing of acronyms enables reader to read selected chapters without flipping the page back and forth. Acronyms commonly used in the field but not used by the author in this book are defined in each chapter for a reference purpose.

SELECTED SUPPLEMENTARY READINGS

Cowman, G.A. and Singer, P.C., Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances, *Environ. Sci. Technol.*, 30, 16, 1996.

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Xie, Y.F. and Reckhow, D.A., Formation and control of trihaloacetaldehydes in drinking water, in *Proceeding of American Water Works Association Water Quality Technology Conference*, Toronto, 1992.

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2 Formation of Disinfection Byproducts

OBJECTIVES

The focus of this chapter is on the formation of disinfection byproducts in drinking water. The formation mechanisms of trihalomethanes, haloacetic acids, and other DBPs will be first discussed to be followed by the effects of water quality conditions on the formation of DBPs. This chapter will also discuss three tests that are commonly used to evaluate the formation of DBPs in treated water. This chapter will help water professionals to demystify the formation of DBPs in drinking water.

NOMENCLATURE

DBP disinfection byproduct
D-DBP disinfectants and disinfection byproduct
DOC dissolved organic carbon
FP formation potential
HAA haloacetic acid
NOM natural organic matter
SDS simulated distribution system
THM trihalomethane
TOC total organic carbon
TOX total organic halide
UFC uniform formation conditions

The formation of disinfection byproducts (DBPs) in drinking water is caused by the reaction between natural organic matter (NOM) and chlorine or other disinfectants. The speciation and concentration of DBPs in water are affected by many water quality parameters and operating conditions, including natural organic matter, chlorine residual, reaction time, inorganic bromide, and pH. To better control DBPs in finished water, it is important to understand the DBP formation and speciation. This chapter will review the DBP formation mechanisms and the effects of water quality parameters on DBP formation.

Several laboratory test procedures were developed to simulate the formation of DBPs in drinking water. By controlling chlorination conditions, these procedures are designed to measure the DBP precursors and estimate DBP formation and speciation in finished waters and distribution systems.

2.1 FORMATION MECHANISMS

The formation of DBPs are caused by the reaction between natural organic matter, including humic and fulvic substances and disinfectants. Because of very limited information on the chemical structures of humic and fulvic substances, the mechanisms of DBP formation in chlorinated water are not well understood. Organic compounds with a simple molecule, including propanone (or acetone), benzene, and resorcinol, are generally used to illustrate the mechanisms of DBP formation in drinking water.

2.1.1 Trihalomethanes

The formation of THMs can be illustrated by the reaction between propanone and chlorine. In chlorinated water, propanone can be readily oxidized into trichloropropanone, as shown in Equation 2.1. Trichloropropanone undergoes a hydrolysis reaction to form chloroform, especially at high pH, as shown in Equation 2.2.

$$CH_3COCH_3 + HOCl \rightarrow CH_3COCCl_3 \quad (2.1)$$

$$CH_3COCCl_3 + H_2O \rightarrow CH_3COOH + CHCl_3 \quad (2.2)$$

If bromide is present, brominated propanones can be formed. The brominated propanones then result in the formation of brominated THMs. THMs can be formed by the hydrolysis of many other trihalogenated DBPs or intermediate products, which will be discussed further in Chapter 3. These trihalogenated DBPs include trihaloacetonitriles, trihaloacetaldehydes, and brominated trihaloacetic acids. For example, tribromoacetic acid undergoes a hydrolysis reaction to form bromoform at high pH.

2.1.2 Haloacetic Acids

The formation of haloacetic acids (HAAs) can also be demonstrated with the reaction between propanone and chlorine. In addition, trichloropropanone can be further oxidized into tetra-, penta-, and hexchloropropanones, especially at low pH. These chloropropanones undergo hydrolysis reactions to form mono-, di-, and trichloroacetic acids. Equations 2.3 and 2.4 illustrate the formation of pentachloropropanone and dichloroacetic acid.

$$CH_3COCCl_3 + HOCl \rightarrow CHCl_2COCCl_3 \quad (2.3)$$

$$CHCl_2COCHCl_3 + H_2O \rightarrow CHCl_2COOH + CHCl_3 \quad (2.4)$$

Trichloroacetic acid can also be formed by the reaction between a generalized organic matter, CH_3-CO-R, and chlorine, as shown in Equations 2.5 and 2.6, where R is an oxidizable group.[1]

$$CH_3COR + HOCl \rightarrow CCl_3COR \quad (2.5)$$

$$CCl_3COR \rightarrow CCl_3COOH \quad (2.6)$$

If bromide is present, brominated propanones or intermediate byproducts can be formed. These brominated intermediate products then result in the formation of brominated HAAs.

2.1.3 Other Halogenated DBPs

The formation of halopropanones can be illustrated by the reaction between propanone and chlorine, as shown in Equations 2.7 to 2.9. Propanone is a common ozonation byproduct.

$$CH_3COCH_3 + HOCl \rightarrow CH_2ClCOCH_3 \quad (2.7)$$

$$CH_2ClCOCH_3 + HOCl \rightarrow CHCl_2COCH_3 \quad (2.8)$$

$$CHCl_2COCH_3 + HOCl \rightarrow CCl_3COCH_3 \quad (2.9)$$

The formation of trihaloacetaldehydes can be illustrated by the reaction between acetaldehyde and chlorine, as shown in Equation 2.10. Acetaldehyde is a common ozonation byproduct.

$$CH_3CHO + HOCl \rightarrow CCl_3CHO \quad (2.10)$$

The formation of cyanogen chloride can be illustrated by the reaction between hydrogen cyanide and monochloramine, as shown in Equation 2.11. Hydrogen cyanide is a product of the reaction between formaldehyde and monochloramine.

$$HCN + NH_2Cl \rightarrow CNCl \quad (2.11)$$

2.1.4 Ozonation Byproducts

The formation of aldehydes is due to the reaction between ozone and natural organic matter. Aldehydes can be formed via the additional reaction on unsaturated bonds of organics, as shown in Equation 2.12.

$$R_1R_2C{=}CR_3R_4 + O_3 \rightarrow R_1COOH + R_1COR_2 + R_3COR_4 \quad (2.12)$$

The formation of ketoacids and carboxylic acids could be due to further oxidation of dialdehydes and ketoacids, respectively. As shown in Equation 2.13, further oxidation of methyl glyoxal can result in the formation of pyruvic acid.

$$CH_3COCHO + O_3 \rightarrow CH_3COCOOH \quad (2.13)$$

Further oxidation of glyoxylic acid results in the formation of oxalic acid, as shown in Equation 2.14.

$$OHCCOOH + O_3 \rightarrow HOOCCOOH \quad (2.14)$$

2.2 FACTORS AFFECTING DBP FORMATION

The DBP concentration and speciation can be affected by many water quality parameters and operating conditions, including NOM concentration, chlorine residual, reaction time, pH, and bromide concentration.

2.2.1 Effects of NOM

NOM is the precursor for DBPs in treated drinking water. The NOM concentration and characteristics significantly affect the formation of DBPs. NOM levels generally are measured as total organic carbon (TOC) or dissolved organic carbon (DOC). In general, increasing NOM levels in chlorinated water increases the formation of DBPs,[2] as shown in Figure 2.1.

Increasing the NOM level affects DBP formation in two ways. First, increasing the NOM level will increase the level of DBP precursors, which increases DBP formation. Second, increasing the NOM level will increase the chlorine demand of the water. A high chlorine demand in turn requires a high chlorine dosage to maintain a proper chlorine residual in distribution systems. This high chlorine dosage leads to a further increase in the formation of DBPs.

NOM can be separated into several fractions, including humic acids, fulvic acids, hydrophobic acids, hydrophobic neutrals, transphilic acids, transphilic neutrals,

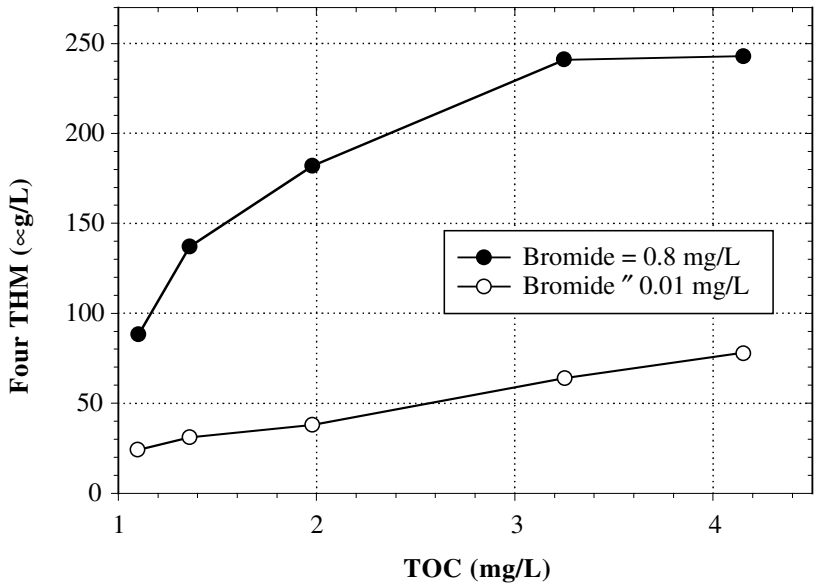

FIGURE 1.1 Effect of TOC on the formation of four THMs. (From Krasner, S.W., Sclimenti, M.J., and Means, E.G., Quality degradation: implication for DBP formation, *J. Am. Water Works Assoc.*, 86(4), 34, 1994.)

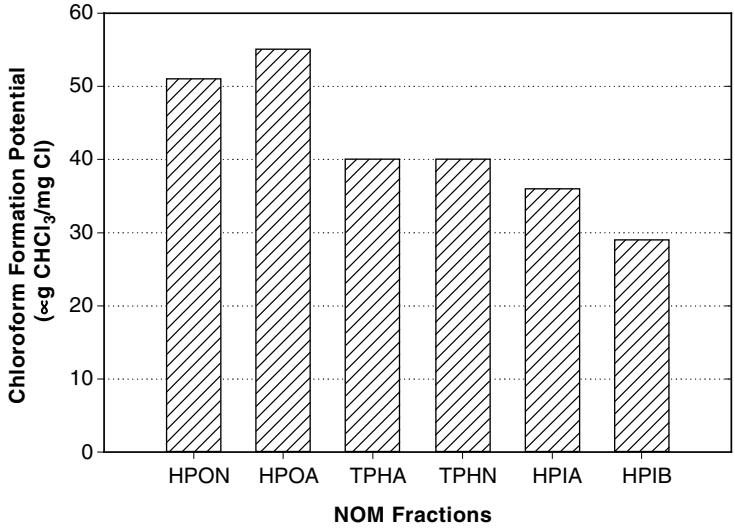

FIGURE 1.2 Chloroform formation potential of Suwannee River NOM fractions. HPON = hydrophobic neutrals; HPOA = hydrophobic acids; TPHA = transphilic acids; TPHN = transphilic neutrals; HPIA = hydrophilic acids; HPIB = hydrophilic bases. (From Croue, J.-P., Debroux, J.-F., Amy, G.L., Aiken, G.R., and Leenheer, J.A., Natural organic matter: structural characteristics and reactive properties, in *Formation and Control of Disinfection By-Products in Drinking Water*, Singer, P.C., Ed., American Water Works Association, Denver, 1999.)

hydrophilic acids, and hydrophilic neutrals. Under the same chlorination conditions, each fraction results in a different DBP yield,[3] as shown in Figure 2.2.

The sources of NOM also significantly affect the DBP formation,[4] as shown in Figure 2.3.

There is limited information on the effects of NOM on DBP speciation. In water containing bromide, in general, a low level of NOM results in a higher percentage of the brominated DBPs than that for a high level of NOM. This is due to the fact that a higher NOM level requires a higher chlorine dosage, which results in a lower ratio between bromide and chlorine.

In typical drinking water, a high level of NOM results in a high level of DBPs, including THMs, HAAs, and ozonation byproducts. Therefore, removing NOM from water before chlorination is an effective way to control DBP formation in chlorinated waters.

2.2.2 Effects of Chlorine Dose

Chlorine is one of two major reactants for the formation of chlorinated DBPs. Chlorine dosage is the key factor for DBP formation. Some DBPs are intermediate products of chlorination reaction and others are end products. These intermediate

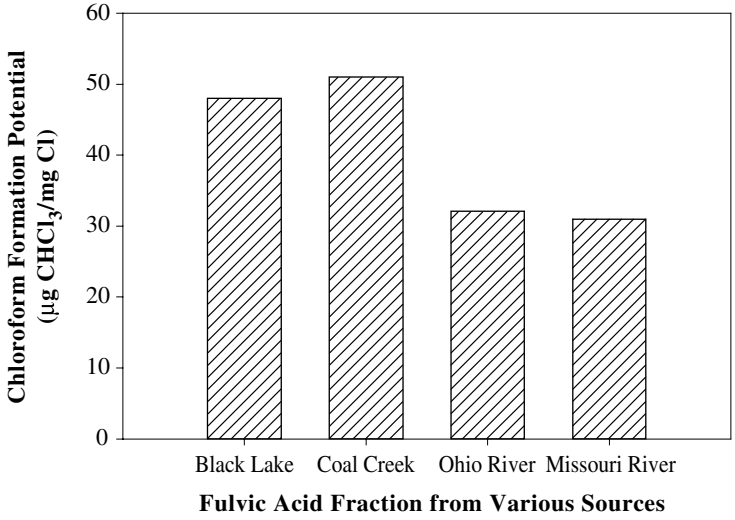

FIGURE 1.3 Chloroform formation potential of the fulvic acid fraction from various sources. (From Reckhow, D.A., Singer, P.C., and Malcolm, R.L., Chlorination of humic materials: byproduct formation and chemical interpretations, *Environ. Sci. Technol.*, 24, 1655, 1990.)

products can be further oxidized by chlorine into end products, as shown in Equations 2.15 and 2.16.

$$\text{NOM} + \text{HOCl} \rightarrow \text{Intermediate products} \tag{2.15}$$

$$\text{Intermediate products} + \text{HOCl} \rightarrow \text{End products} \tag{2.16}$$

In general, increasing chlorine dose increases the formation of end products of chlorination in treated water. THMs are typical end products of chlorination reaction. Increasing chlorine dose increases the formation of chloroform,[5] as shown in Figure 2.4.

Except for monohaloacetic acids and dihaloacetic acids, many monohalogenated and dihalogenated DBPs are intermediate products. Further chlorination of these intermediate byproducts can result in the formation of dihalogenated, trihalogenated, and other DBPs, as shown in Figures 2.5 and 2.6. At a moderate level of chlorine residual, dihalogenated DBPs are formed. Further increasing the chlorine dosage will result in a reduction of dihalogenated DBPs and an increase of trihalogenated DBPs. The effect of chlorination on the concentration of dichloropropanone, a typical intermediate product,[5] is shown in Figure 2.6.

For HAAs, both monohaloacetic acids and dihaloacetic acids are end products. As discussed in Chapter 1, dichloroacetic acid is not an intermediate product for trichloroacetic acid. The reaction between dichloroacetic acid and chlorine is not the mechanism for the formation of trichloroacetic acid. For dichloroacetonitrile, an

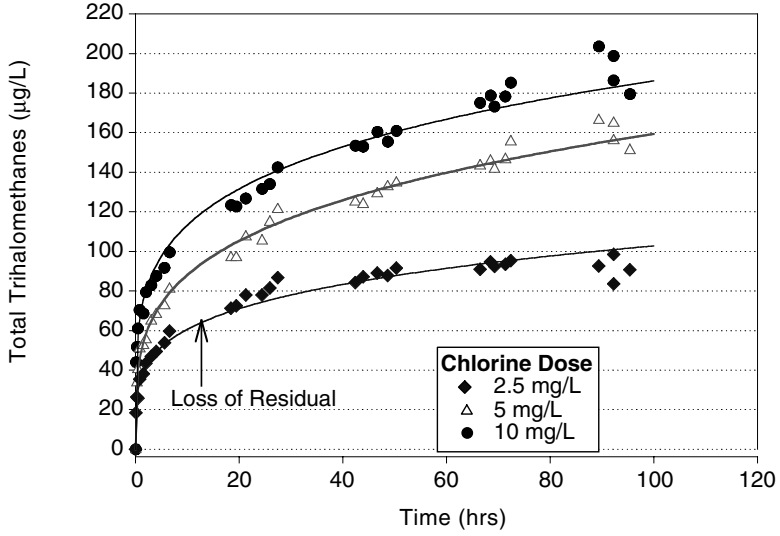

FIGURE 1.4 Effects of chlorine dose and chlorination time on chloroform formation. (From MacNeil, A. and Reckhow, D.A., personal communication, 1996. With permission.)

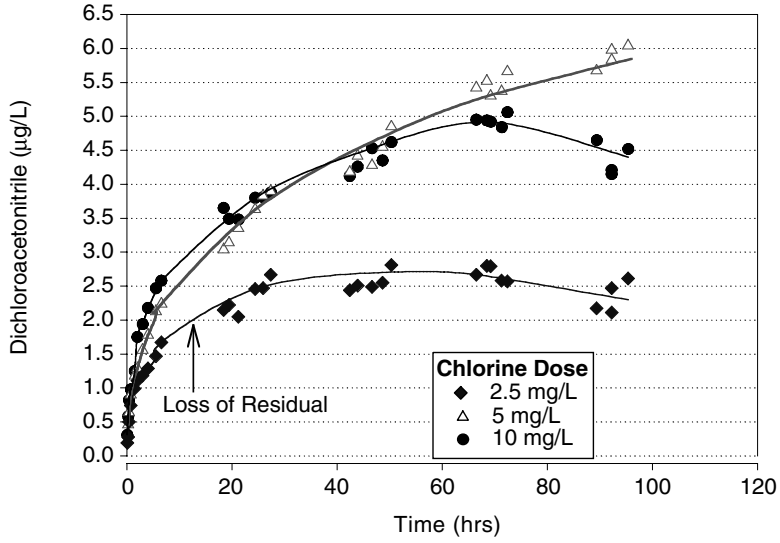

FIGURE 1.5 Effects of chlorine dose and chlorination time on dichloroacetonitrile formation. (From MacNeil, A. and Reckhow, D.A., personal communication, 1996. With permission.)

increase in free chlorine residual may result in formation of chloroacetic acid, as shown in Figure 2.5.

Cyanogen chloride, a DBP of chloramination, can react with chlorine to form cyanate. Therefore, an increase in free chlorine residual will result in a reduction of the cyanogen chloride concentration. Further discussions on the chlorination of cyanogen chloride will be provided in Chapter 3.

In summary, in typical drinking water, increasing the chlorine dose increases the formation of THMs, HAAs, and many other chlorinated disinfection byproducts. One effective way to control DBPs formation is to lower the chlorine dosage.

2.2.3 Effect of Chlorination Time

As shown in Equations 2.15 and 2.16, many DBPs are formed by a series of reactions. If the DBP is an end product, increasing the reaction time will increase the formation of the DBP, as shown in Figures 2.4. This is true for both THMs and HAAs. However, if the DBP is an intermediate product, increasing the reaction time may decrease the formation of the DBP, especially at high chlorination dosages. The effect of chlorination time on two typical intermediate products, dichloroacetonitrile and dichloropropanone, is shown in Figures 2.5 and 2.6

Some DBPs, including trihalopropanones, trihaloacetaldehydes, and trihalonitromethanes, undergo hydrolysis reactions. Increasing the reaction time, especially after chlorine and/or DBP precursors are exhausted, will benefit the hydrolysis reaction and reduce the concentration for these DBPs, as shown in Figure 2.7. Since THMs are typical hydrolysis products and chlorination end products, the formation of THMs are generally increased by increasing the reaction time.

2.2.4 Effects of pH

pH affects the formation of DBPs in many ways. In general, a high pH results in a higher level of THMs but a lower level of HAAs and other halogenated DBPs including total organic halide (TOX),[6] as shown in Figure 2.8.

Many DBPs undergo hydrolysis reactions to form THMs. These DBPs include trihalopropanones, trihaloacetonitriles, trihaloacetaldehydes, trihalonitromethanes, and trihaloacetic acids. Cyanogen halides also undergo hydrolysis reactions to form cyanate. In general, increasing pH increases these hydrolysis reactions. Therefore, for many DBPs that undergo hydrolysis reactions, increasing pH reduces their formation. Since THMs are common hydrolysis products, increasing pH increases their formation.

The effects of pH on THM and HAA formation can be illustrated with one of their precursors, propanone. As discussed earlier, the hydrolysis of pentachloropropanone results in the formation of dichloroacetic acid. At a high pH, the hydrolysis of trichloropropanone significantly reduces the formation of pentachloropropanone and dichloroacetic acid. At a low pH, due to its slow hydrolysis reaction, trichloropropanone can be further oxidized into pentachloropropanone, which results in the formation of dichloroacetic acid.

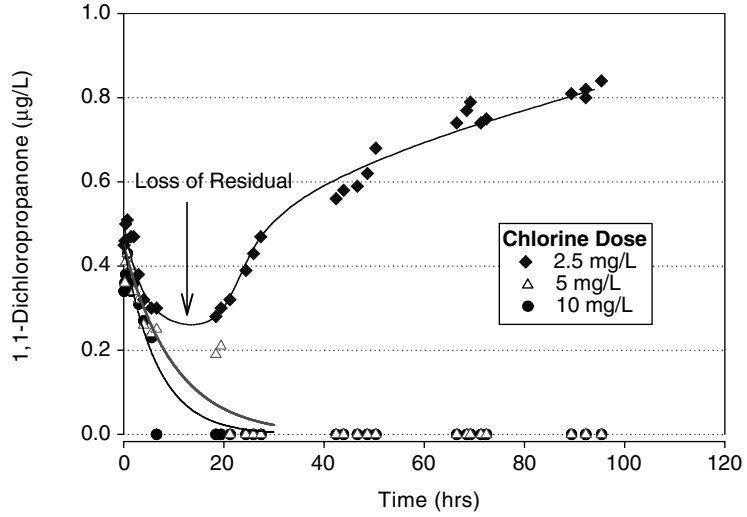

FIGURE 1.6 Effects of chlorination time on the formation of dichloropropanone. (From MacNeil, A. and Reckhow, D.A., personal communication, 1996. With permission.)

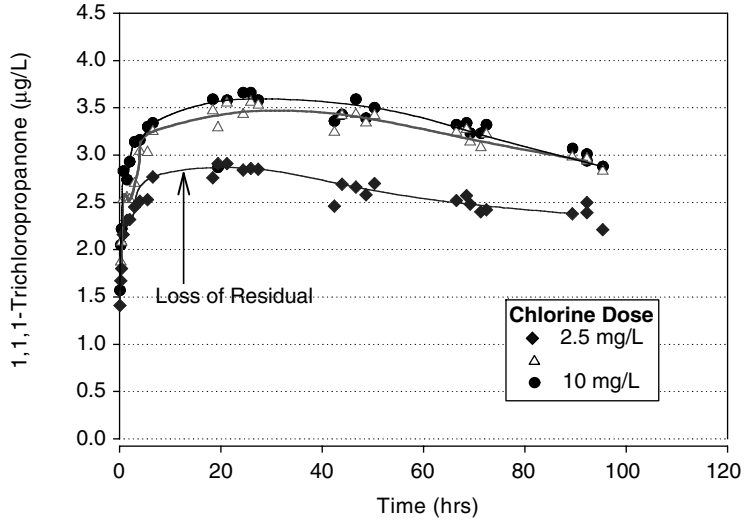

FIGURE 1.7 Effects of reaction time on the formation of trichloropropanone. (From MacNeil, A. and Reckhow, D.A., personal communication, 1996. With permission.)

The speciation of chlorine can also be affected by pH. At low pH, the dominant chlorine species is HClO. At high pH, the dominant chlorine specie is ClO^-. Due to the reaction between hypochlorite (ClO^-) and cyanogen halides, chlorine significantly reduces the concentration of CNCl and CNBr at high pH.

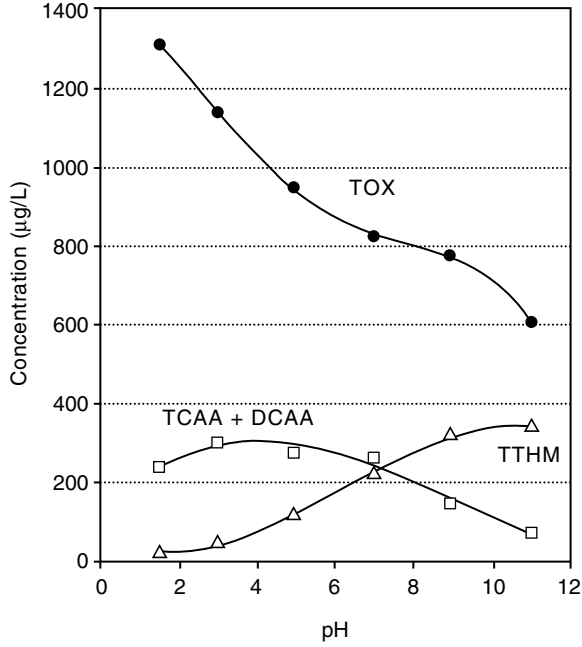

FIGURE 1.8 Formation of chlorination byproducts as a function of pH. (From Reckhow, D.A., and Singer, P.C., Mechanisms of organic halide formation during fulvic acid chlorination and implications with respect to preozonation, in *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Jolly, R.L., Bull, R.J., Davis, W.P., Katz, S. Roberts, M.H., and Jacobs, V.A., Eds., Lewis Publishers, Chelsea, MI, 1985. With permission.)

In general, a low pH water favors the formation of HAAs, trihaloacetaldehydes, trihalopropanones, and cyanogen halides and a high pH water favors the formation of trihaloamethanes.

2.2.5 Effects of Bromide

Bromide, an inorganic ion, does not react with NOM directly. However, inorganic bromide can be oxidized by chlorine or ozone to hypobromous acid or hypochlorite depending on the pH. Like hypochlorous acid and hypochlorite, both hypobromous acid and hypobromite react with NOM to form brominated DBPs. In general, bromine is much more reactive to NOM than chlorine. In water containing bromide, upon chlorination and ozonation, brominated DBPs will be formed. Since bromine will occupy the site for chlorine substitution, the formation of chlorinated species will be reduced. The effects of bromide on the formation of many DBPs were well studied. The effects of bromide on THMs, HAAs, and cyanogen halides are shown in Figures 2.9, 2.10, and 2.11, respectively.[7]

As shown in Figure 2.11, the increase of inorganic bromide in water has little effect on the total molar concentration of cyanogen chloride and cyanogen bromide.[8] It is also expected that the total molar concentration of trihaloacetic acids are lower

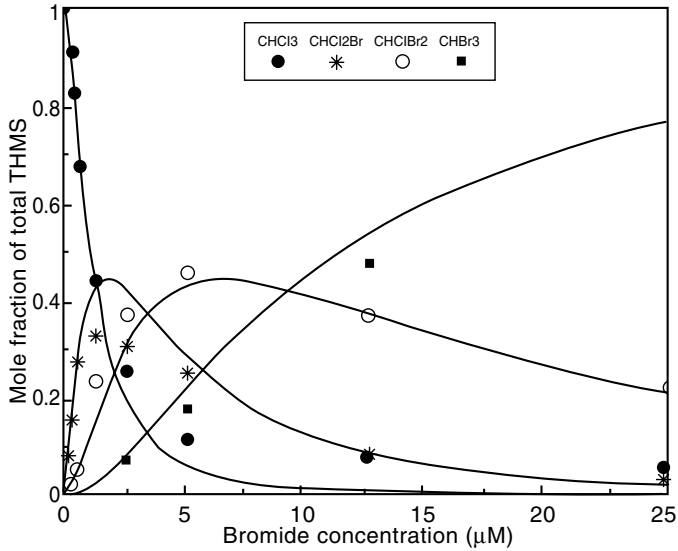

FIGURE 1.9 Effects of bromide on the formation of trihalomethanes. (Reprinted with permission from Cowman, G.A. and Singer, P.C., Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances, *Environ. Sci. Technol.*, 30, 16, 1996. Copyright ©1996, American Chemical Society.)

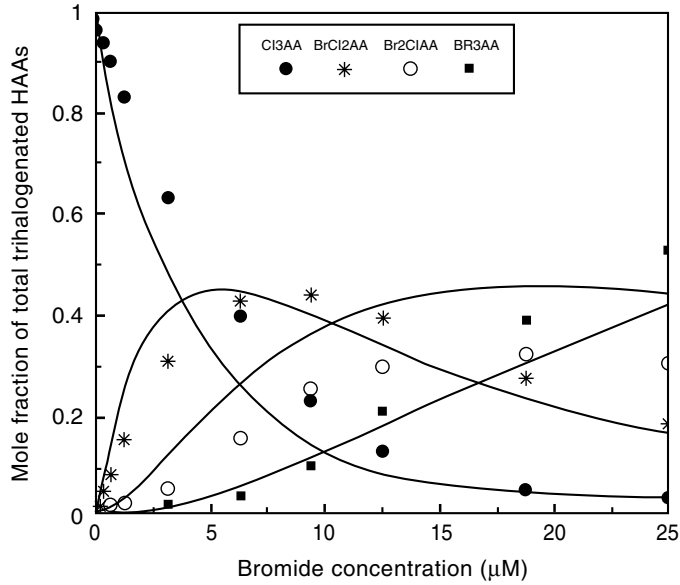

FIGURE 1.10 Effects of bromide on the formation of trihaloacetic acids. (Rerprinted with permission from Cowman, G.A. and Singer, P.C., Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances, *Environ. Sci. Technol.*, 30, 16, 1996. Copyright ©1996, American Chemical Society.)

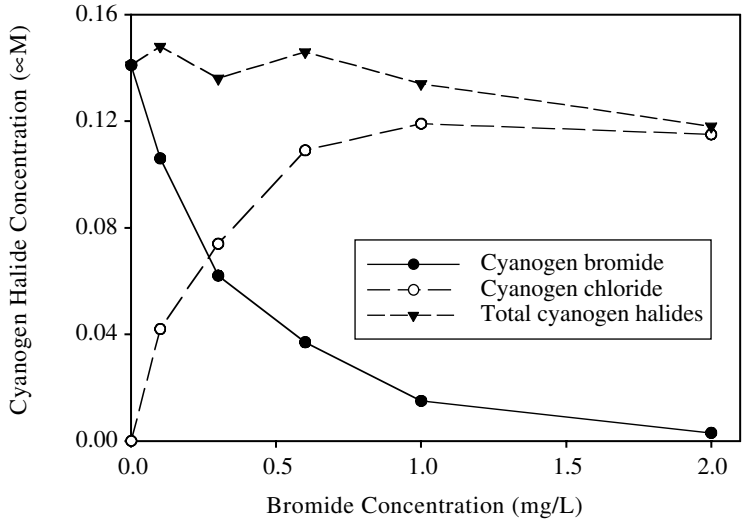

FIGURE 1.11 Effects of bromide on the formation of cyanogen halides. (Reprinted from *Water Research*, Vol. 27, Xie, Y., and Reckhow, D.A., A rapid and simple analytical method for cyanogen chloride and cyanogen bromide in drinking water, 507, Copyright ©1993, with permission from Elsevier.)

at a high bromide level than that at a low bromide level, especially at a high pH. This is due to the instability of brominated trihaloacetic acids, especially tribromoacetic acid, which undergoes hydrolysis reactions to form brominated THMs. It is also expected that the molar concentration of THMs, common hydrolysis byproducts of many brominated DBPs, is higher at a high bromide level. Chapter 3 will provide further discussion on the hydrolysis degradation of DBPs.

Nevertheless, since the mass of bromine (with an atomic weight of 80) is much heavier than chlorine (with an atomic weight of 35.5), the μg/L concentration of the correlated bromoform will be twice that for chloroform. Therefore, at similar chlorination conditions, increasing bromide could significantly increase the concentration of the four THMs regulated by the United State Environmental Protection Agency under the Stage 1 Disinfectants and Disinfection Byproducts (D-DBP) Rule. An increase in bromide levels also reduces the formation of chlorinated HAAs and increases the formation of brominated HAAs. The three brominated trihaloacetic acids and bromochloroacetic acid currently are not regulated in the D-DBP regulation. An increase in bromide levels generally reduces the level of the five HAAs, which are regulated under the Stage 1 D-DBP Rule.

2.3 EVALUATION OF DBP FORMATION IN TREATED WATER

To better control the formation of DBPs in finished water and distribution systems, there is a need to evaluate the DBP precursors, or NOM. TOC, or DOC, which measures the organic carbon content, does not provide information on DBP yield of the NOM. As discussed earlier, the fraction and origin of the NOM also significantly affect DBP

formation. Because the main purpose of NOM control is to control DBP formation it is important to measure NOM based on their DBP yield. Three standardized tests are commonly used for this purpose. They are the formation potential (FP) test, simulated distribution system (SDS) test, and uniform formation conditions (UFC) test.

2.3.1 Formation Potential Test

Formation potential test is a procedure to evaluate the DBP precursors rather than the formation of DBPs in finished water. In this test, excess chlorine is added to assure the maximum formation of DBPs. The test conditions are generally standardized. For THM formation potential, the standard reaction conditions in Standard Method 5710B[9] are listed in Table 2.1. The total THMs formed during the test, or the difference between the final concentration and the initial concentration, is the THM formation potential. The samples can also be used for determining the HAA formation potential and other DBP formation potentials.

For DBP formation potential test, other reaction conditions have been used. These conditions include a chlorine dose of 20 mg/L, an incubation time of 3 days, and/or a temperature of 20°C. As discussed earlier, a higher incubation temperature results in a higher THM formation or THM formation potential and a shorter incubation time results in a lower THM formation potential. Since excess chlorine is added (>3 mg/L), the variation of chlorine residuals does not significantly affect the THM formation potential. For the incubation pH, a higher pH results in a higher THM formation potential and a lower HAA formation potential.

However, the level of DBPs formed during the formation potential test could be significantly different than in finished water or distribution systems. Due to the excess chlorine and long incubation time, the level of DBPs, especially for THMs and HAAs are much higher than that in finished water or distribution systems. Because of the high chlorine dose used in the test, in general, the levels of chlorinated DBPs are much higher than that in finished water. The relative brominated DBP levels could be much lower than that in finished waters due to the much lower bromide to chlorine ratio. The level of intermediate DBPs, including mono- or dichloro-propanone and mono- or dichloro-acetonitrile, could be much lower than that in finished waters due to the high chlorine dose.

In summary, the DBP formation potential test is a good test for evaluating the DBP precursors. It is an excellent tool to evaluate the effects of water treatment processes on DBP precursor removal. Since all reaction conditions generally are standardized, the formation potential test also allows comparison of results from system to system or laboratory to laboratory. However, the DBP formation potential results cannot be used to estimate the DBP formation under actual chlorination conditions. In addition, the formation potential cannot be used to evaluate how a treatment process change affects the DBP formation under actual conditions.

2.3.2 Simulated Distribution System Test

The simulated distribution system test was developed to simulate the DBP formation in actual distribution systems.[10] The test uses the water quality conditions, including

TABLE 1.1
Standard Reaction Conditions for THM Formation Potential

Incubation time	7 days
Incubation temperature	25 ± 2°C
Chlorine residual$_{7\ day}$	3–5 mg/L
pH	7.0 ± 0.2
pH buffer	Phosphate

Source: *Standard Methods for the Examination of Water and Wastewater*, 20th ed., APHA, AWWA, and WEF, Washington, DC, 1998.

pH, temperature, and time, in an actual distribution system. The test can be done in two ways. In a full-scale or pilot treatment plant, the samples can be taken after chlorination, incubated in the laboratory, and analyzed for DBPs. For bench top treatment studies, the reaction conditions need to be adjusted to simulate the actual distribution system. A pH buffer may be needed for pH control. After incubation, the samples are analyzed for DBPs. The final DBP concentrations, including initial DBPs before the incubation and DBPs formed during the incubation, are the simulated distribution system DBPs.

The simulated distribution system DBPs compare well with DBPs in an actual distribution system. The comparison includes both DBP concentration and speciation. The water utility can use results to evaluate the regulation compliance of the finished water. The results can also be used to evaluate how a treatment process addition, removal, or modification affects the DBP regulation compliance. Since the simulated distribution system test generally uses a lower chlorine dose or residual, the simulated distribution system DBPs are much lower than the DBP formation potentials. Because disinfection conditions vary from system to system, it is impossible to compare simulated distribution system DBPs in various systems or laboratories. Even in the same system, the variation of the water temperature from season to season could significantly limit the utility's ability to evaluate the DBP precursor removal efficiency. Due to the biological degradation of some DBPs in distribution systems, which will be discussed in Chapter 3, the simulated distribution system HAAs and other biodegradable DBPs could be much higher than that in the actual distribution systems.

2.3.3 Uniform Formation Conditions Test

In comparison to the DBP formation potential test, the uniform formation conditions test was developed to better simulate the DBP formation in finished waters. In contrast to the DBP simulated distribution system test, the uniform formation conditions test uses standardized conditions that allow comparisons between various systems, laboratories and seasons.[11] The standardized conditions for the uniform formation conditions are listed in Table 2.2.

TABLE 1.2
Conditions for the Uniform Formation Conditions Test

Incubation time	24 ± 1 hour
Incubation temperature	20 ± 1°C
Chlorine residual$_{24\ hours}$	1.0 ± 0.4 mg/L
pH	8.0 ± 0.2
pH buffer	Borate

Source: Summers, R.S., Hooper, S.M., Shukairy H.M., Solarik, G., and Owen D., Assessing DBP yield: uniform formation conditions, *J. Am. Water Works Assoc.*, 88(6), 80, 1996.

Under the uniform formation conditions, the DBP speciation and concentration are much closer to actual chlorination conditions. The variation of chlorination conditions under the uniform formation conditions has limited effects on DBP formation.

The uniform formation conditions test can be used to compare the DBP formation in different water under similar conditions. The test could also be used to compare DBP formation after various water treatment processes and assess the seasonal variability of DBP precursors.[11] However, because the uniform formation conditions represent average conditions in U.S. distribution systems, one should be cautious when using the DBP data to evaluate compliance with DBP regulations.

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3 Stability of Disinfection Byproducts

OBJECTIVES

This chapter discusses the stability of disinfection byproducts (DBPs) in drinking water. The typical DBP degradation reactions, including hydrolysis, oxidation, dehalogenation, and biodegradation, are the focus of this chapter. The effects of water quality and DBP speciation on the stability of DBPs are discussed as well.

NOMENCLATURE

AOC assimilable organic carbon
BDOC biodegradable dissolved organic carbon
DBP disinfection byproduct
D-DBP disinfectants and disinfection byproducts
GAC granular activated carbon
HAA haloacetic acid
THM trihalomethane

Finished drinking water generally takes hours or days to reach its customers, especially in large distribution systems. To protect public health, it is important to control DBPs in distribution systems as well as in treatment processes. Under the Stage 1 Disinfectants and Disinfection Byproducts (D-DBP) Rule, water utilities need to monitor the DBP concentration in their distribution systems, as well as in the finished water. To better comply with the D-DBP regulation and protect public health it is necessary to understand the stability of DBPs during water treatment and in distribution systems. The stability of DBPs is also important for DBP sample storage, preservation, and analysis. Many DBPs undergo degradation reactions in distribution systems. Typical reactions are hydrolysis, oxidation, dehalogenation, and biodegradation.

3.1 HYDROLYSIS

Hydrolysis is a common degradation reaction for many DBPs, especially for trihalogenated DBPs. A typical example is the hydrolysis degradation of trichloropropanone, which leads to the formation of chloroform. This reaction, as shown in Equation 3.1, is a critical step of the chloroform formation, as discussed in Chapter 2.

$$CCl_3COCH_3 \rightarrow CHCl_3 \quad (3.1)$$

The hydrolysis degradation of other trihalopropanones has been studied as well. The hydrolysis products of bromodichloropropanone, chlorodibromopropanone, and tribromopropanone are bromodichloromethane, chlorodibromomethane, and tribromomethane (or bromoform), respectively. These hydrolysis reactions can be described as pseudo-first-order reactions and the degradation rates can be described using Equation 3.2.

$$d[CX_3COCH_3]/dt = k\ [CX_3COCH_3] \quad (3.2)$$

The reaction rate constant, k, indicates the rate of the hydrolysis reaction. A higher k value indicates a faster degradation. The hydrolysis rate can also be described using the half-life, $t_{1/2}$. The half-life is the time required for 50% of the compound to be degraded. The reaction rate constant for tribromopropanone, k, is 6.34×10^{-2} min^{-1} and the half-life is 10.9 min at pH 7.[1] This indicates that at pH 7, it takes 10.9 min for tribromopropanone to degrade from 20 µg/L to 10 µg/L, and another 10.9 min to 5 µg/L. The half-life for bromodichloropropanone is 217 min and 69.1 min for chlorodibromopropanone.[1] The degradation of all three brominated trihalopropanones at pH 7 is shown in Figure 3.1. At this pH level, the hydrolysis reaction rate of trichloropropanone was insignificant when compared with that of its brominated analogues.

As shown in Figure 3.1, increasing the bromine substitution significantly increases the trihalopropanones' hydrolysis instability and their hydrolysis reaction rates. Increasing water pH also increases the hydrolysis degradation. The hydrolysis

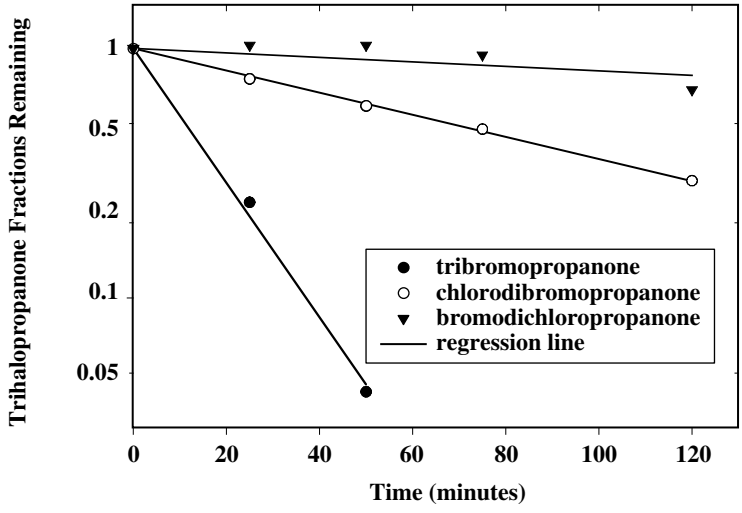

FIGURE 3.1 Hydrolysis degradation of three brominated trihalopropanones. (From Xie, Y.F. and Reckhow, D.A., unpublished report, 1993.)

degradation of trichloropropanone was only observed at high pH. For water high in pH, no trihalopropanone, especially brominated trihalopropanone, should be detected at a significant level. Instead, a higher level of THMs should be expected. For the analysis of trihalopropanones, especially tribromopropanone, the samples should be preserved at low pH.

The hydrolysis of trihaloacetaldehydes was also well studied. The hydrolysis byproducts for trichloroacetaldehyde, bromodichloroacetaldehyde, chlorodibromoacetaldehyde, and tribromoacetaldehyde are trichloromethane (or chloroform), bromodichloromethane, chlorodibromomethane, and tribromomethane (bromoform). At pH 9.0, the half-life of bromodichloroacetaldehyde is 11 h, 2.5 h for chlorodibromoacetaldehyde, and 0.5 h for tribromoacetaldehyde.[2]

The hydrolysis degradations of three brominated trihaloacetaldehydes at other pH levels are shown in Figure 3.2. The hydrolysis degradation of trichloroacetaldehyde was insignificant at these pH. Increasing bromine substitution increases the hydrolysis degradation of trihaloacetaldehydes. Increasing water pH also increases the hydrolysis degradation. In comparison to trihalopropanones, the hydrolysis degradation of trihaloacetaldehydes is slower. No brominated trihaloacetaldehyde,

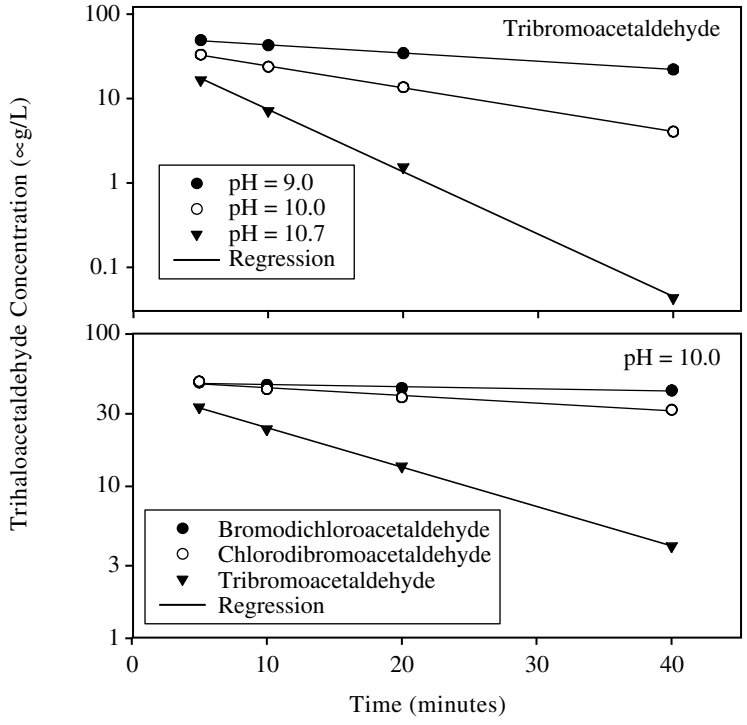

FIGURE 3.2 Hydrolysis degradation of three brominated trihaloacetaldehydes. (From Xie, Y.F. and Reckhow, D.A., Hydrolysis and dehalogenation of trihaloacetaldehydes, in *Disinfection By-Products in Water Treatment,* Minear, R.A. and Amy, G.L., Eds., Lewis Publishers, Boca Raton, FL, 1995. With permission.)

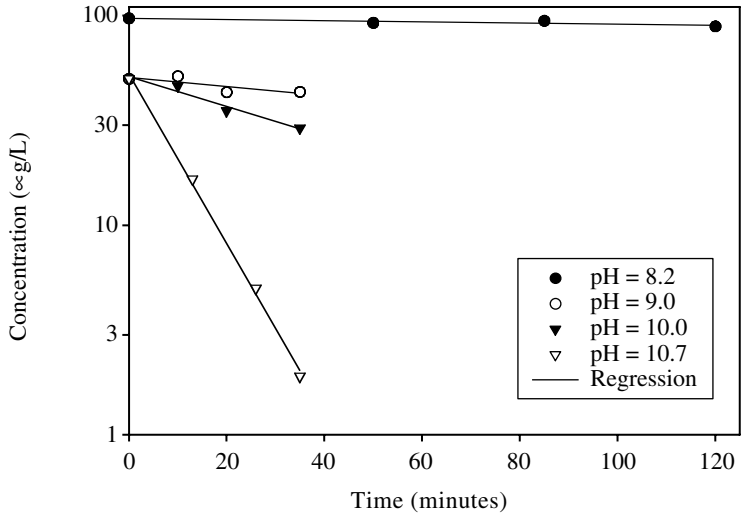

FIGURE 3.3 Hydrolysis degradation of cyanogen chloride. (Reprinted from *Proceedings of 1992 AWWA Water Quality Technology Conference*, by permission. Copyright ©1992, American Water Works Association.)

especially tribromoacetaldehyde, should be detected at a significant level in water high in pH. For brominated trihaloacetaldehydes, especially tribromoacetaldehyde, their water samples should be preserved at low pH before analysis.

The hydrolysis of cyanogen halides, including cyanogen chloride and cyanogen bromide, was also studied. Unlike other trihalogenated DBPs, the hydrolysis product of cyanogen halides is cyanate. As shown in Figure 3.3, increasing pH increases the hydrolysis degradation of cyanogen chloride. At pH 10, the half-life of cyanogen chloride is 42.8 min.[3] For cyanogen bromide, the hydrolysis degradation rates are similar to those of cyanogen chloride.

The hydrolysis of trihaloacetic acid has also been observed. Tribromoacetic acid is unstable in high pH water. Bromoform is the degradation product. Other HAAs are relatively stable under drinking water conditions at room temperature. However, at an elevated temperature (e.g., 70°C) all brominated trihaloacetic acids undergo degradation reactions.[4] Trihalomethanes (THMs) are their degradation byproducts.

In summary, many trihalogenated DBPs undergo rapid hydrolysis reactions in drinking water. THMs are their common products. Increasing water pH increases these hydrolysis reactions. Increasing bromine substitution also increases the hydrolysis reactions. Cyanogen halides undergo hydrolysis degradation to form cyanate. The hydrolysis behaviors of these trihalogenated DBPs significantly affect their occurrence and dominance in finished water, especially in distribution systems. These hydrolysis reactions could well explain why higher THMs levels are detected in distribution systems than in the plant finished water. These hydrolysis reactions also explain why increasing pH levels increases the levels of THMs.

The hydrolysis of DBPs significantly affects their analysis including sample preservation and storage. For trihalogenated DBP analysis, samples should be

processed and analyzed as soon as practical, especially for brominated DBPs. If samples need to be stored, a low pH condition is generally recommended, especially for tribrominated DBPs.

3.2 OXIDATION

Many DBPs undergo further oxidation or chlorination reactions. These reactions will reduce the concentration of these DBPs and result in the formation of new DBPs. These oxidation reactions commonly occur in both chlorinated and ozonated waters.

Many DBPs are subject to further oxidation or chlorination. For example, halopropanones, especially monochloropropanone and dichloropropanone, can be further chlorinated, as shown in Equations 3.3 and 3.4. Haloacetaldehydes are also subject to further chlorination.

$$ClH_2COCH_3 + HOCl \rightarrow Cl_2HCOCH_3 \quad (3.3)$$

$$Cl_2HCOCH_3 + HOCl \rightarrow Cl_3COCH_3 \quad (3.4)$$

Cyanogen halides, including cyanogen chloride and cyanogen bromide, undergo degradation reactions to form cyanate in the presence of free chlorine. This chlorination degradation rate is much greater than that of the hydrolysis degradation. Increasing pH generally increases the degradation since hypochlorite is the active chlorine speciation for the chlorination reaction,[3] as shown in Figure 3.4. At a

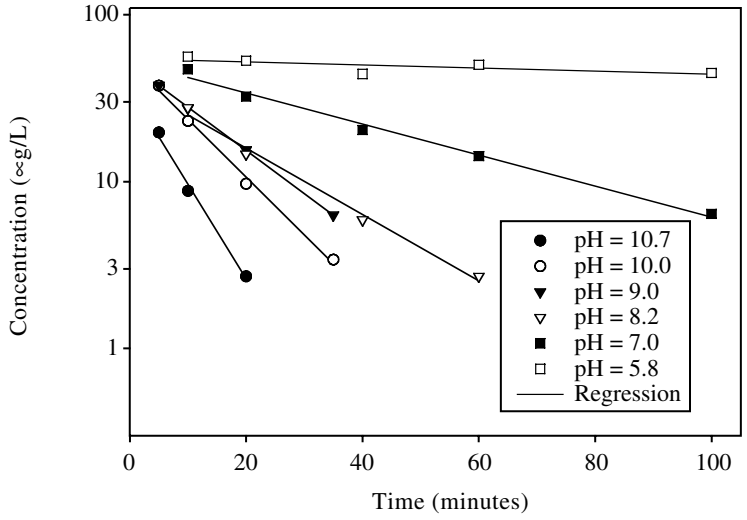

FIGURE 3.4 Degradation of cyanogen chloride in the presence of chlorine. (Reprinted from *Proceedings of 1992 AWWA Water Quality Technology Conference*, by permission. Copyright ©1992, American Water Works Association.)

residual free chlorine concentration of 0.5 mg/L and pH 7, the reported cyanogen chloride chlorination reaction rate constant is 1.08×10^{-2} min^{-1} and the half-life is approximately 60 min. For a sample containing 20 μg/L of cyanogen chloride, the final concentration will be less than 1 μg/L after 5 h, or five half-lives. This could well explain why cyanogen chloride and cyanogen bromide are rarely detected in water containing free chlorine.

Many ozonation byproducts, including aldehydes and ketoacids, can be further oxidized or chlorinated. As shown in Equation 3.5, glyoxal can be further oxidized into a ketoacid, glyoxylic acid.

$$\text{OHC-CHO} \rightarrow \text{OHC-COOH} \tag{3.5}$$

Glyoxylic acid, a ketoacid, is also subject to further oxidation and therefore can form oxalic acid, a carboxylic acid, as shown in Equation 3.6.

$$\text{OHC-COOH} \rightarrow \text{HOOC-COOH} \tag{3.6}$$

Carboxylic acids resist further oxidation and are the common final products of ozonation. In general, carboxylic acids are dominant byproducts in ozonated water, followed by ketoacids and aldehydes. The carboxylic acid domination can be more significant at a high ozone dosage.

Some aldehydes, ketoacids, and carboxylic acids can be further chlorinated in the presence of chlorine residual. Acetaldehyde is a precursor of trihaloacetaldehydes. In general, ozonation results in the formation of acetaldehyde, which leads to a higher chloral hydrate (trichloroacetaldehyde hydrate) formation.[5] Upon chlorination, pyruvic acid can be chlorinated and lead to the formation of chloroform. Malonic acid, a carboxylic acid, can be chlorinated into dichloromalonic acid, which leads to the formation of dichloroacetic acids and trichloroacetic acid.[6]

In general, a disinfectant residual is required in distribution systems. Multiple oxidation and/or disinfection processes are also common in water treatment. Further chlorination or oxidation will affect the level and speciation of existing DBPs and results in the formation of new DBPs. To accurately analyze DBPs in water samples, chlorine, ozone, or other oxidant/disinfectant residuals should be properly quenched to minimize the continuing formation or reduction of DBPs.

3.3 DEHALOGENATION

Many halogenated DBPs undergo dehalogenation degradations in water to form less halogenated DBPs. These degradations include chemical dehalogenation and biological dehalogenation. Biological dehalogenation will be discussed in the following section.

In the presence of sulfite, many DBPs, especially brominated DBPs, undergo chemical dehalogenation degradation. These DBPs include halopropanones, trihaloacetaldehydes, trihalonitromethanes, and cyanogen halides.

In the presence of sulfite, trihalopropanones undergo dehalogenation degradation to form dihalopropanones,[1] as shown in Equation 3.7 and Figure 3.5.

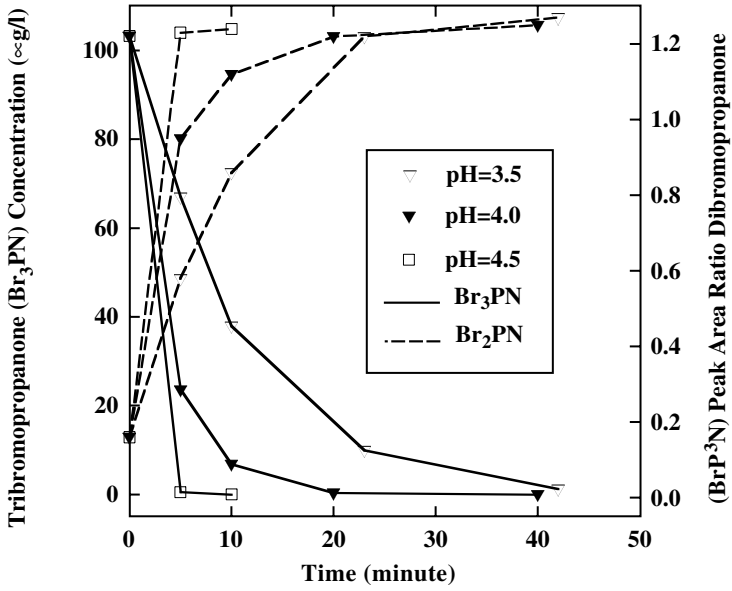

FIGURE 3.5 Dehalogenation degradation of tribromopropanone. (From Xie, Y.F. and Rechhow, D.A., unpublished report, 1993.)

$$CX_3COCH_3 \rightarrow CHX_2COCH_3 \tag{3.7}$$

Dihalopropanones can undergo further dehalogenation degradation to form monohalopropanones or propanone.[1] As shown in Figure 3.6, pH also affects the dehalogenation degradation since it affects the speciation of sulfite (e.g., SO_3^{2-}, HSO_3^-, and H_2SO_3). In general, increasing pH increases the rate of dehalogenation degradation. Because bromine atoms are more subject to dehalogenation reaction than chlorine atoms, bromine atoms will be eliminated first for those DBPs containing both chlorine and bromine atoms. Increasing bromine substitution increases the rate of dehalogenation degradation. Increasing the concentration of sulfite also increases the rate of dehalogenation degradation.

Compared to hydrolysis degradation, sulfite dehalogenation is a much faster reaction. At pH 7, tribromopropanone undergoes an instantaneous sulfite dehalogenation degradation. Even at lower pH, its sulfite dehalogenation degradation is much faster than hydrolysis degradation, as shown in Figure 3.6. At pH 4.0, the half-life of tribromopropanone dehalogenation is approximately 40 seconds, as compared to its half-life, 10.9 min, for hydrolysis at pH 7.[1]

Cyanogen halides also undergo a degradation reaction in the presence of sulfite. Both pH and bromine substitution affect the degradation reaction of cyanogen halides. Increasing pH increases the sulfite degradation of cyanogen chloride,[3] as shown in Figure 3.7. In the presence of sulfite, cyanogen bromide undergoes an instantaneous degradation at pH 7 and pH 4.[7] The concentration of sulfite also affects the degradation rate of cyanogen halides. The degradation rates of cyanogen chloride

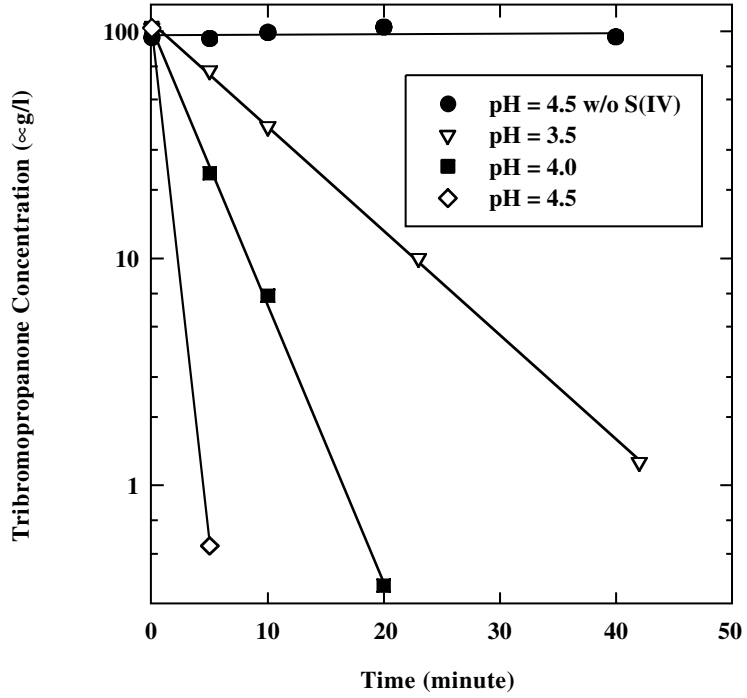

FIGURE 3.6 Dehalogenation degradation of tribromopropanone at various pH levels. (From Xie, Y.F. and Reckhow, D.A., unpublished report, 1993.)

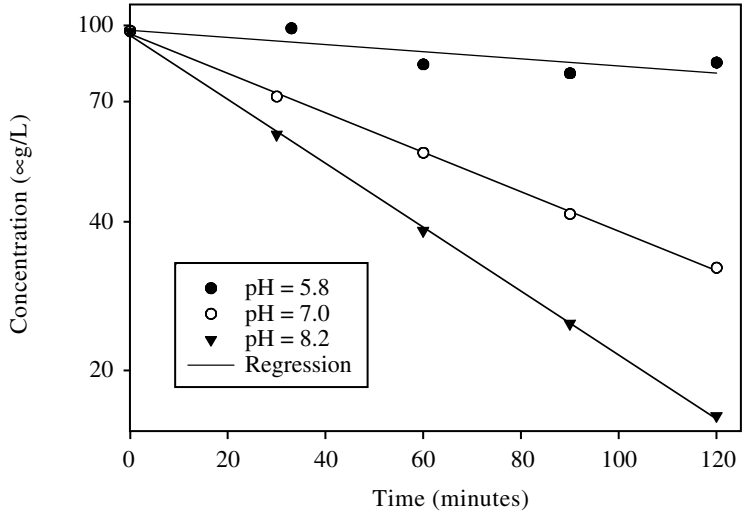

FIGURE 3.7 Degradation of cyanogen chloride in the presence of sulfite. (Reprinted from *Proceedings of 1992 AWWA Water Quality Technology Conference*, by permission. Copyright ©1992, American Water Works Association.)

in the presence of sulfite are similar to its chlorination degradation rates at the sulfite and chlorine levels tested.[3]

Dehalogenation of DBPs has little impact on the DBP levels in drinking water. However, DBP dehalogenation is important for wastewater treatment since dechlorination with sulfite, thiosulfate, or sulfur dioxide is commonly practiced for chlorinated wastewater. Dehalogenation is critical for DBP analysis. For many years, sulfite was used to quench residual chlorine for sample preservation or before DBP analysis. Many DBPs, especially brominated DBPs, were not accurately analyzed due to their rapid dehalogenation reactions. For example, sulfite addition will result in an instantaneous decomposition of tribromopropanone and cyanogen bromide. This also explains why many brominated DBPs were not detected in early studies.

Haloacetic acids (HAAs) also undergo dehalogenation degradation in the presence of elemental iron or zero-valent iron.[8] For example, tribromoacetic acid undergoes a series of dehalogenartion reactions to form acetic acid via intermediate products, dibromoacetic acid and monobromoacetic acid, as shown in Equations 3.8, 3.9, and 3.10.

$$CBr_3COOH \rightarrow CHBr_2COOH \tag{3.8}$$

$$CHBr_2COOH \rightarrow CH_2BrCOOH \tag{3.9}$$

$$CH_2BrCOOH \rightarrow CH_3COOH \tag{3.10}$$

The pseudo-first-order reaction rate constant is 1.41 h^{-1} or a half-life of 0.5 h for the disappearance of tribromoacetic acid.[8] The reported final product is monochloroacetic acid for other chlorinated HAAs. The dehalogenation degradation of trichloroacetic acid is shown in Equations 3.11 and 3.12.

$$CCl_3COOH \rightarrow CHCl_2COOH \tag{3.11}$$

$$CHCl_2COOH \rightarrow CH_2ClCOOH \tag{3.12}$$

The dehalogenation reduction of HAAs in the presence of elemental iron could lead to the development of a new treatment technology for HAA control. This reduction may also contribute to the HAA loss in distribution systems since unlined cast iron pipes are commonly used in many systems.[8]

3.4 BIOLOGICAL DEGRADATION AND DEHALOGENATION

Biodegradation has been investigated for controlling total organic carbon, biodegradation organic carbon (BDOC), assimilable organic carbon (AOC), and ozonation byproducts including aldehydes, ketoacids, and carboxylic acids. These ozonation DBPs are the major contributors to BDOC and AOC. Aldehydes, ketoacids, and carboxylic acids, undergo biological degradation in drinking water, especially in

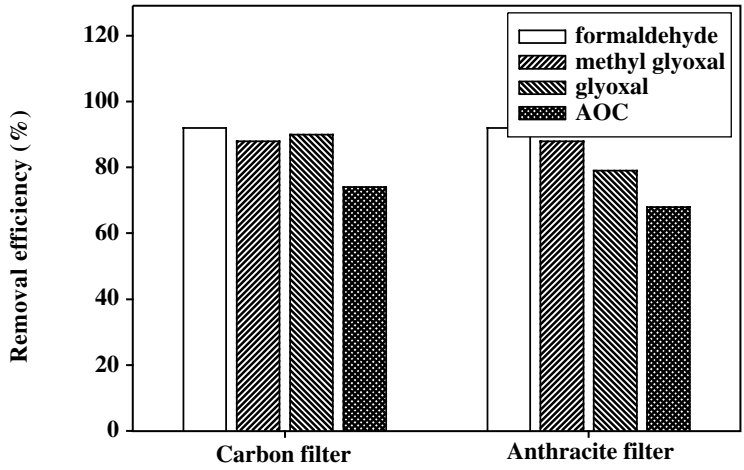

FIGURE 3.8 Removal of aldehydes in biologically active filters. (From Krasner, S.W., Sclimenti, M.J., and Coffey, B.M., Biologically active filters for the removal of aldehydes: an ozone pilot-plant study, in *Proceedings of 1992 American Water Works Association Water Quality Technology Conference*, Toronto, 1992.)

biologically active filters. The filter media can be sand, anthracite, or granular activated carbon (GAC).

The biodegradation of aldehydes was reported in many studies. Aldehydes undergo biological degradation in biologically active filters, including sand, anthracite, or carbon filters. As shown in Figure 3.8, after 56 days of operation, all three aldehydes, including formaldehyde, glyoxal, and methyl glyoxal, were effectively removed by both the carbon filter and the anthracite filter.[9] The biologically active filters are also effective in removing AOC,[9] as shown in Figure 3.8.

Ketoacids undergo biological degradation in biologically active filters with a filtration rate of 1.5 gpm/ft^2 (3.8 m/h),[10] as shown in Figure 3.9. The type of filter medium significantly affects the removal efficiency. Granular activated carbon greatly outperformed anthracite. Reducing the filtration rate also improves the removal efficiency.

HAAs also undergo biological degradation. The rapid elimination of HAAs in treated water during aquifer storage and in distribution systems suggests that HAAs are not stable in the presence of bioactivity. The bacteria that are responsible for HAA biodegradation commonly exist in treated drinking water. In water containing no disinfectant residual, HAAs undergo biological degradation reactions,[11] as shown in Figure 3.10. A complete reduction of dichchloroacetic acid with an original concentration 88 μg/L was observed in 256 h. Meanwhile the heterotrophic bacteria count increased 6000 times (from 1.9×10^3 to 1.14×10^7). The heterotrophic bacteria count increased to 1.12×10^7 for trichloroacetic acid. However, only 30% reduction of trichloroacetic acid concentration was observed. This indicates that heterotrophic bacteria count may not be the proper indicator for biological activity for HAA degradation. The biological degradation for monochloroacetic acid is faster than that for dichloroacetic acid.

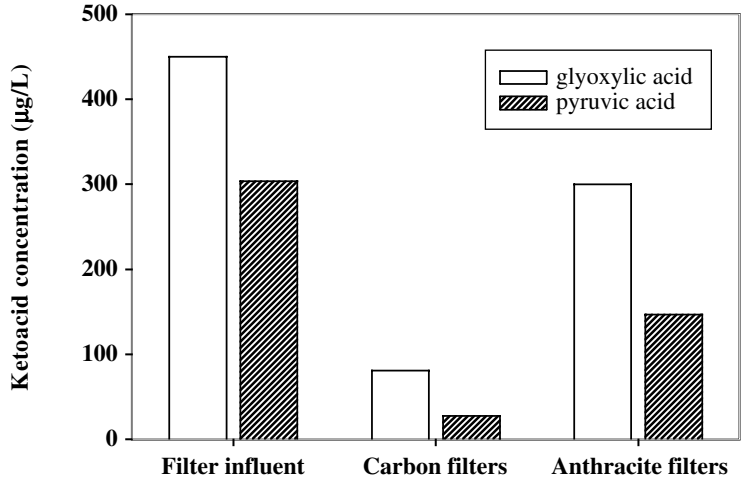

FIGURE 3.9 Removal of ketoacids in biologically active filters. (From Xie, Y.F. and Reckhow, D.A., A new class of ozonation by-products: the ketoacids, in *Proceedings of 1992 American Water Works Association Annual Conference: Water Quality,* Vancouver, 1992.)

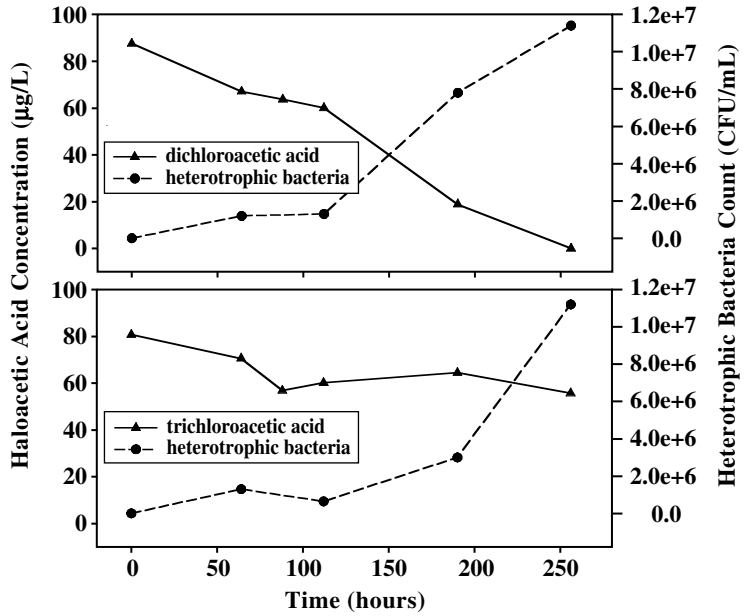

FIGURE 3.10 Biological degradation of haloacetic acids. (Reprinted from *J. Am. Water Works Assoc.*, 94(4), (April 2002), by permission. Copyright ©2002, American Water Works Association.)

In general, increasing the halogen atom number increases the biological stability of HAAs.[11] Bromine substitution also increases their biological stability. Biological degradation of HAAs in the absence of a disinfectant residual can significantly affect the HAA concentration and speciation in distribution systems. The biological degradation also affects HAA analysis since chlorine residual is commonly removed during sample storage. A new technology for HAA removal could be developed based on the current information concerning the biological instability of HAAs.[12] Currently, the author's group is investigating the removal of HAAs using biologically active carbon filters. The preliminary results indicate that biological degradation is a cost-effective technology for HAA control in drinking water.

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4 Effects of Treatment Process on Disinfection Byproducts

OBJECTIVES

The focus of this chapter is on the effects of common water treatment processes on the formation and removal of DBPs. These treatment processes include preoxidation, coagulation, carbon adsorption, biofiltration, and membrane filtration. Information presented in this chapter will help readers to better understand the formation, removal and speciation of disinfection byproducts during water treatment processes.

NOMENCLATURE

AOC assimilable organic carbon
BAC biologically active carbon
BDOC biodegradable dissolved organic carbon
DBP disinfection byproduct
DOC dissolved organic carbon
EBCT empty bed contact time
GAC granular activated carbon
HAA haloacetic acid
NOM natural organic matter
PAC powdered activated carbon
THM trihalomethane
TOC total organic carbon
TOX total organic halide

In addition to water quality parameters, as discussed in Chapter 2, treatment processes also significantly affect the formation, removal, and speciation of DBPs in drinking water. These treatment processes could affect disinfection byproducts directly or indirectly by affecting first water quality and then impacting disinfection byproducts. These treatment processes include preoxidation, coagulation, carbon adsorption, biofiltration, and membrane filtration.

4.1 PREOXIDATION

Preoxidation is a critical treatment process which greatly affects the formation of disinfection byproducts. In the past, prechlorination was commonly used to control taste, odor, color, iron and manganese in water, and algae growth inside treatment units. Due to the high natural organic matter (NOM) concentration and the high chlorine demand in raw water, prechlorination significantly increases the concentration of disinfection byproducts (DBPs) in finished water.

As shown in Figure 4.1, two treatment trains were used in the same treatment plant in Pennsylvania. One treatment train uses prechlorination because of disinfection requirement. Another train uses intermediate chlorination and chlorine is added to the settled water. With prechlorination the concentration of four trihalomethanes (THMs) in the finished water was 106.4 μg/L and without the prechlorination the concentration was 22.5 μg/L.[1]

To control the formation of DBPs, many water utilities have stopped the prechlorination practices and moved the chlorine addition points further down along their treatment processes. Intermediate chlorination or postchlorination are commonly used to replace prechlorination.

For many water treatment plants, prechlorination or preoxidation is necessary for iron and manganese or taste and odor control. Preoxidation with alternative oxidants, including ozone, potassium permanganate, or chlorine dioxide, is commonly used to replace prechlorination. At the dosage commonly used in water treatment, preoxidation has little impact on the concentration of natural organic matter (NOM). However, these oxidants could significantly change or modify the reactivity of NOM toward chlorine and affect subsequent chlorination and DBP formation.

Preoxidation could affect DBP formation in several ways. First, preoxidation reduces chlorine demand. After treatment with alternative oxidants, many NOM reaction sites can become inactive to further chlorination. This will significantly reduce the chlorine demand and lower the chlorine dosage. This will reduce DBP formation potentials and reduce the formation of DBPs after intermediate or postchlorination.

In addition, preoxidation also affects the formation of disinfection byproducts through its effects on NOM. The effects of preoxidation on DBP formation depend on many factors, including type and dose of the oxidant, characteristics of the NOM, and water quality parameters. The effects of preoxidation on various DBP species are also different. Effects of preozonation on DBP formation potential have been widely studied. Typical effects of preozonation on various DBP formation potentials are illustrated in Figure 4.2.

As shown in Figure 4.2, preozonation at a dose of 0.5 mg/L or above significantly reduced the formation potential for THMs, trichloroacetic acids, dichloroacetonitrile, and total organic halides (TOX).[2] However, preozonation had little impact on the formation potential of dichloroacetic acid and significantly increased the formation potential for trichloroacetone. The increase of trichloroacetone formation potential is due to the formation of acetone in ozonated water, as shown in Equations 4.1 and 4.2.

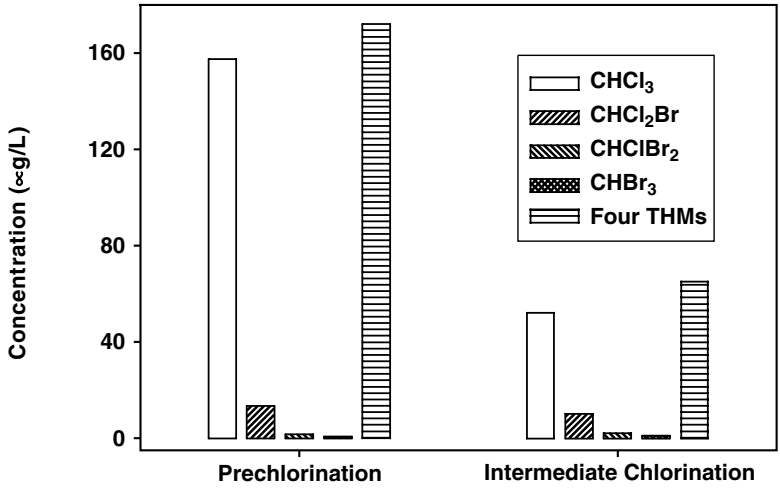

FIGURE 4.1 Effects of prechlorination on the formation of THMs in finished water. (From Xie, Y.F., unpublished data, 2002.)

$$\text{Ozone + NOM} \rightarrow \text{CH}_3\text{COCH}_3 \text{ (actone)} \tag{4.1}$$

$$\text{CH}_3\text{COCH}_3 + \text{Chlorine} \rightarrow \text{CCl}_3\text{COCH}_3 \text{ (trichloroacetone)} \tag{4.2}$$

Preozonation also increases the formation of chloral hydrate (or trichloroacetaldehyde hydrate) in chlorinated water. In water with 4 mg/L dissolved organic carbon (DOC), preozonation at a dose of 4 mg/L doubled the formation potential of chloral hydrate,[3] as shown in Figure 4.3. The increase of chloral hydrate formation potential is due to the formation of acetaldehyde in ozonation water, as shown in Equations 4.3 and 4.4.

$$\text{Ozone + NOM} \rightarrow \text{CH}_3\text{CHO (acetaldehyde)} \tag{4.3}$$

$$\text{CH}_3\text{CHO} + \text{Chlorine} \rightarrow \text{CCl}_3\text{CHO (trichloacetaldehyde or chloral)} \tag{4.4}$$

Preoxidation also improves the treatment efficiency of subsequent treatment processes, including coagulation, sedimentation, and filtration. Preoxidation could improve the particle removal and result in a higher removal efficiency for pathogens. This could reduce the chemical disinfection requirement and lower the chlorine residual or dose, then result in a lower DBP formation in the finished water.

Preoxidation also improves the treatment efficiency for NOM in subsequent treatment processes, including coagulation and biofiltration. For example, preozonation can convert nonbiodegradable NOM fractions to biodegradable fractions. This could enhance NOM removal through biological filtration and result in a reduction of DBP formation. The removal of NOM also reduces the chlorine demand in distribution systems. In Lake Austin water, ozonation alone at 3 mg O_3/mg TOC

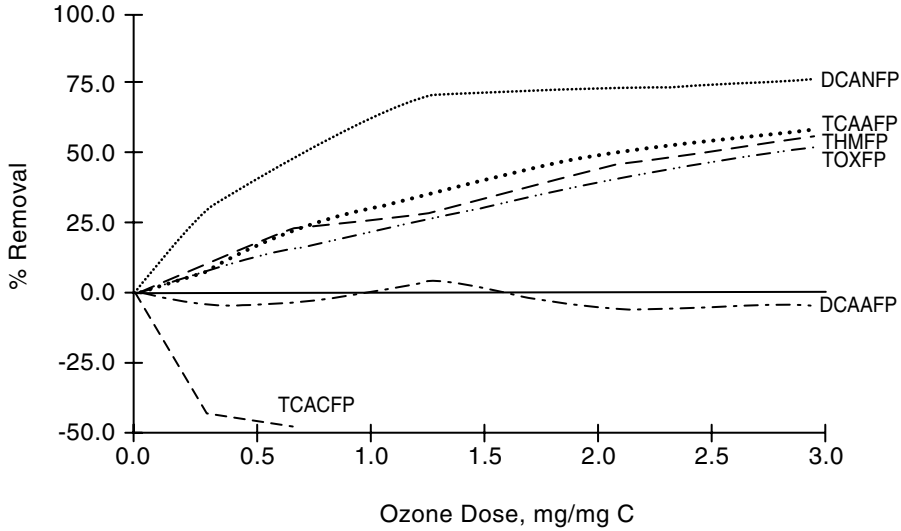

FIGURE 4.2 The effect of ozone dose on various chlorination byproduct precursors. (DCANFP = dichloroacetonitrile formation potential; TCAAFP = trichloroacetic acid formation potential; THMFP = trihalomethane formation potential; TOXFP = total organic halide formation potential; DCAAFP = dichloroacetic acid formation potential; TCACFP = trichloroacetone formation potential.) (From *Ozone in Water Treatment: Application and Engineering*, Langlais, B., Reckhow, D.A., and Brink, D.R., Eds., Lewis Publishers, Chelsea, MI, 1991. With permission.)

resulted in a 25% reduction of the formation potential of trihalomethanes.[4] The combination of ozonation and biodegradation resulted in over 50% reduction of the formation potential of THMs, as shown in Figure 4.4.

4.2 COAGULATION

The main function of coagulation is to destabilize suspended particles by neutralizing the negative charge and aggregate destabilized particles into flocs, which could be removed by subsequent sedimentation and/or filtration. Coagulation affects the NOM levels in two ways. First, NOM can combine with coagulants, the aluminum or ferric ions, to form a complex and precipitate out from water, especially at low pH. Second, at high coagulant doses, the metal hydroxyl precipitate can trap or adsorb NOM. Therefore, a substantial level of NOM could be removed by coagulation, sedimentation, and filtration, especially at a lower pH and/or a higher coagulant dose. A coagulation process optimized for a specified NOM removal has been defined as enhanced coagulation under the U.S. EPA Disinfectants and Disinfection Byproducts (D-DBP) Rule. More details on enhanced coagulation will be given in Chapter 5.

By removing NOM, coagulation significantly reduces the chlorine demand and DBP formation potential. Therefore, moving the chlorine addition points from before coagulation (e.g., prechlorination) to after coagulation (e.g., intermediate or postchlorination) could significantly reduce the formation of DBPs in finished water.

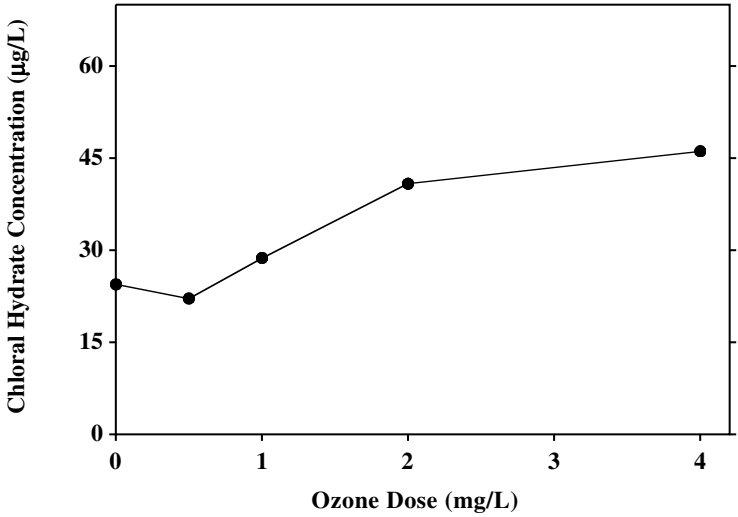

FIGURE 4.3 Effect of preozonation on chloral hydrate formation potential. (Reprinted from *Proceedings of 1992 AWWA Water Quality Technology Conference*, by permission. Copyright ©1992, American Water Works Association.)

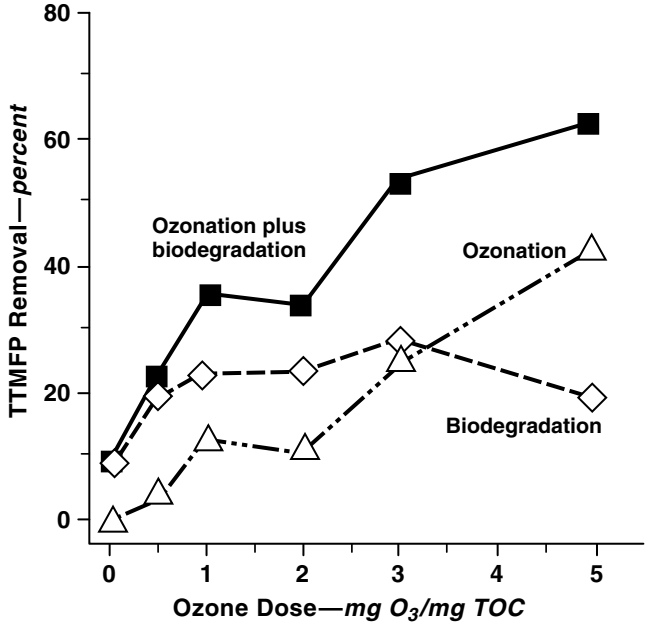

FIGURE 4.4 Trihalomethane formation potential removal from Lake Austin water. (TTHMFP = total trihalomethane formation potential.) (Reprinted from *J. Am. Water Works Assoc.*, 85(5), (May 1993), by permission. Copyright ©1993, American Water Works Association.)

Many studies have been conducted on enhanced coagulation and its effects on DBP formation and speciation.

Coagulation also affects the speciation of DBPs, especially in water containing a low or medium level of bromide. Upon chlorination, bromide will be oxidized into highly reactive hypobromous acid and hypobromite. Prior to coagulation, a large quantity of NOM is available to react with both free chlorine and reactive hypobromous acid and hypobromite. At a low bromide level, a large quantity of chloroform and some brominated THMs will be formed upon chlorination. Coagulation selectively removes NOM but not bromide in water. Because of the reduced level of NOM and a relatively higher level of bromide after coagulation, more brominated THMs will be formed while the total THMs levels, especially chloroform, are reduced. This is well illustrated in Figure 4.5.

As shown in Figures 4.5, coagulation can significantly reduce THM formation potential in water.[5] The concentration of four THM formation potentials was 120 μg/L in raw water and 67 μg/L after coagulation. Before coagulation, trichloromethane accounted for 55% (by weight) of the four THM. After coagulation, trichloromethane accounted for 37% (by weight) of the four THM. After coagulation, both bromodichloromethane and tribromomethane were increased from 14 μg/L and 0.7 μg/L to 16 μg/L and 1.6 μg/L, respectively.

This effect of coagulation on DBP formation and speciation could be more dramatic when the simulated distribution systems and uniform formation condition test protocols (see Chapter 2) are used. Reduction of NOM after coagulation will lower the chlorine demand and chlorine dose. This could result in a significant reduction of chlorinated DBPs and potentially a dramatic increase of brominated DBPs.

4.3 CARBON ADSORPTION

Granular activated carbon (GAC) and powdered activated carbon (PAC) are commonly used for removing taste, odor, pesticides, herbicides, and other natural and synthetic organic compounds. Most existing carbon adsorption studies have been focused on the removal of DBP precursors. A few studies were done on the GAC adsorption for THM removal. However, information on carbon adsorption for the removal of other DBPs, especially haloacetic acids (HAAs), is very limited.

Carbon adsorption can be used for DBP control in several ways. First, carbon adsorption is an effective process for NOM, or DBP precursor removal. For a GAC adsorption process, the removal of DBP precursors is very effective at the beginning of a carbon adsorption operation. However, the effectiveness will begin to diminish when the GAC is exhausted. The removal of THM precursors was studied using simulated distribution systems, as shown in Figure 4.6. Without GAC adsorption the THM formation potential was 151 μg/L.[6] At the beginning of the carbon adsorption a complete removal of THM precursors was achieved. After 50 days operation, the reduction for THM precursors was only 15%. GAC adsorption also affected the speciation of THMs, favoring the formation of brominated species.[6]

Under the D-DBP rule, GAC adsorption (with an empty bed contact time of 10 min and reactivation frequency of no more than 6 months) is one of the best available

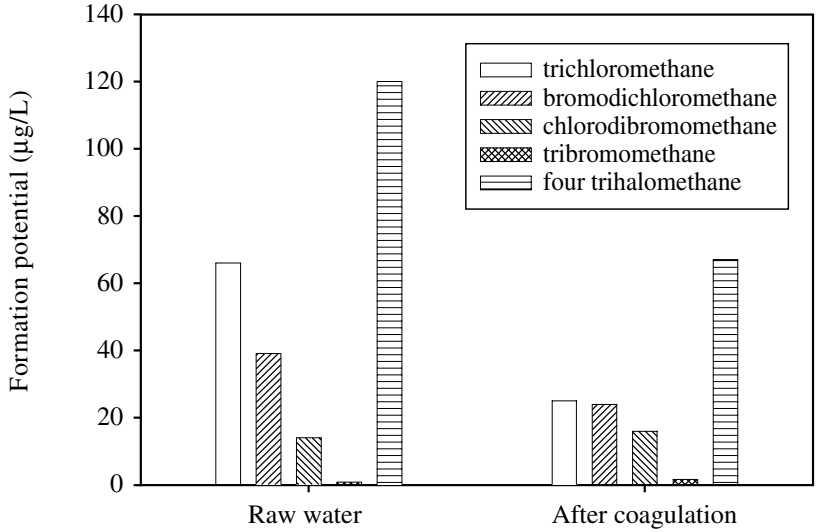

FIGURE 4.5 Impact of coagulation on THM precursors and speciation. (From Krasner, S.W., Sclimenti, M.J., Means, E.G., Symons, J.M., and Simms, L., The impact of chlorine dose, residual, chlorine, bromide, and organic carbon on trihalomethane speciation, in *Proceedings of AWWA Water Quality Technology Conference*, 1992.)

technologies for DBP control. The effectiveness of using GAC for NOM removal is dependent on empty bed contact time (EBCT), physical and chemical properties of the carbon, type of the NOM, and water metrics. The carbon adsorption process could be illustrated using a DOC breakthrough curve, as shown in Figure 4.7. At the beginning of the GAC operation, the best removal efficiency generally is not 100% because some NOM fractions are nonadsorbable.[7] The TOC removal efficiency gradually decreases during the GAC contactor operation. A significant TOC removal may still be observed after the GAC adsorption capacity is exhausted. This removal generally is due to the biodegradation of biodegradable NOM fractions. A reactivation of GAC is required after the GAC is exhausted.

PAC generally is used in water treatment plants for taste, odor, and color, and herbicide and pesticide control. PAC is also effective in the removal of DBP precursors, especially at a high dosage and a longer contact time. A PAC study was conducted with Ohio River water, as shown in Figure 4.8. With a PAC dosage of 50 mg/L, a 50% reduction in THM formation potential was achieved.[8]

Carbon adsorption can also be used directly for DBP removal. However, because THMs are poorly adsorbed, a frequent reactivation of GAC is required when GAC is used for THM removal. For two common THMs, chloroform and bromodichloromethane, their reported Freundlich K values are 93 and 241 $(\mu g/g)(L/\mu g)^n$, respectively.[9] These low values indicate that they are poorly adsorbed onto GAC. A set of typical breakthrough curves for THMs are shown in Figure 4.9. In this study, both GAC column 1 and GAC column 2 had an EBCT of 7.5 min.[10] Both GAC columns were completely exhausted after in operation for approximately 2 months when the

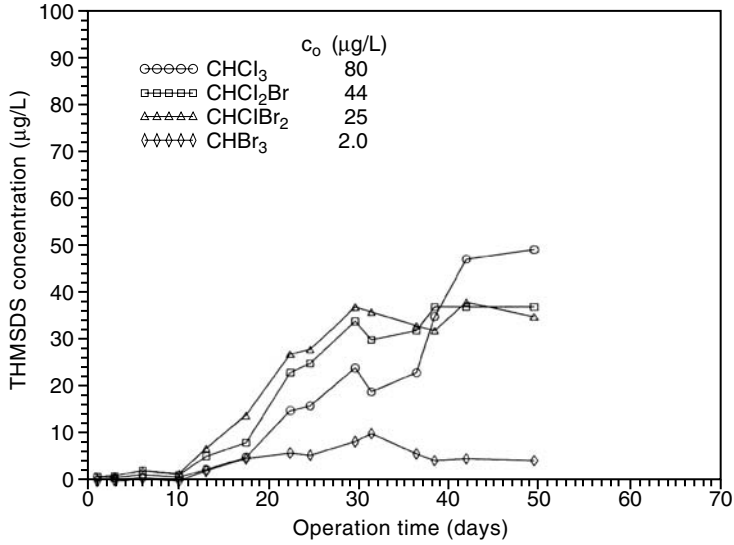

FIGURE 4.6 Removal of THM precursors in a field scale GAC column. (THMSDS = trihalomethane simulated distribution system.) (Reprinted from *Proceedings of 1992 AWWA Water Quality Technology Conference*, by permission. Copyright ©1992, American Water Works Association.)

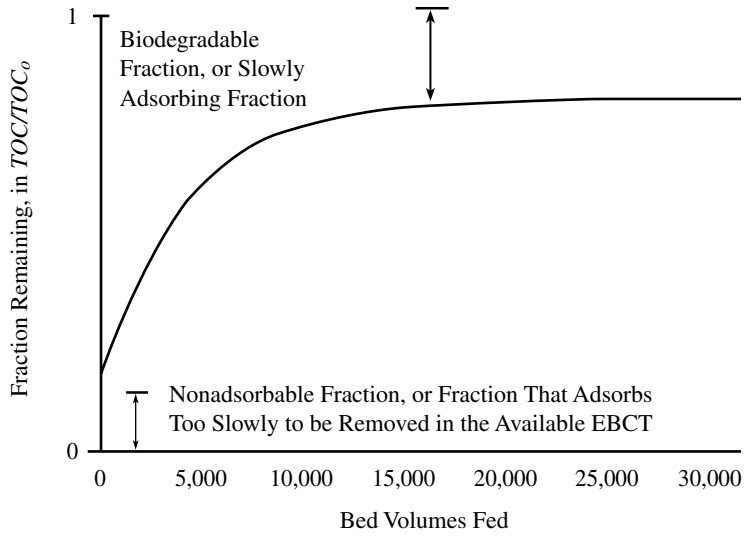

FIGURE 4.7 Typical breakthrough curve for total organic carbon removal by GAC (TOC=total organic carbon). (Reprinted from *Formation and Control of Disinfection By-Products in Drinking Water*, by permission. Copyright ©1999, American Water Works Association.)

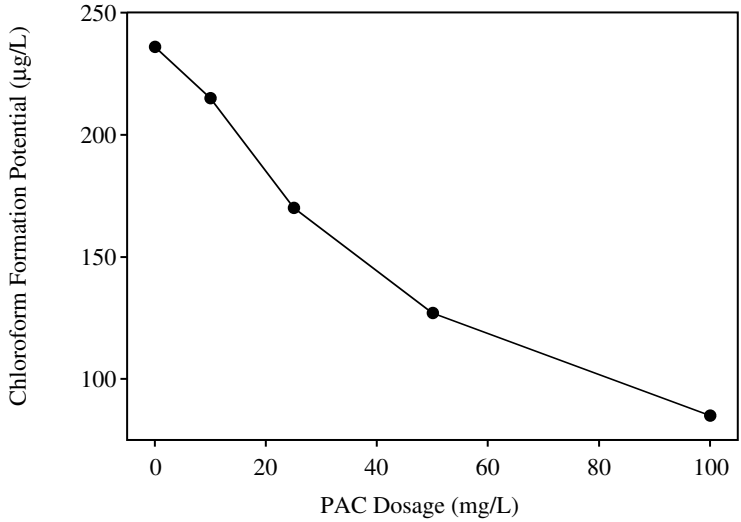

FIGURE 4.8 Effects of PAC on chloroform formation potential. (From Najm, I.N., Snoeyink, V.L., Lykins, B.W., and Adams, J.Q., Using powdered activated carbon: a critical review, *J. Am. Water Works Assoc.*, 83(1), 65, 1991.)

effluent total THM concentration exceeded the influent THM concentration, as shown in Figure 4.9.

The information on GAC adsorption for HAA removal is very limited. HAAs are ionized at pH often found in drinking water. Because of this hydrophilic characteristic, it is commonly assumed that HAAs are poorly adsorbed on GAC. However, Freundlich K values, 1630 and 11,700 $(\mu g/g)(L/\mu g)^{-}$, have been reported for dichloroacetic acid and trichloroacetic acid, respectively.[11] These relatively higher Freundlich K values indicates that HAAs are much better adsorbed than THMs on GAC and could be effectively removed by GAC adsorption.

However, a GAC column study indicated that a much shorter exhaustion time for dichloroacetic acid.[12] The column influent was prepared with finished water obtained at a treatment plant in Pennsylvania and spiked with approximately 50 µg/L of dichloroacetic acid. The column was operated with an EBCT of 20 min. The GAC column was completely exhausted in less than 30 days, as shown in Figure 4.10. This is approximately 50 times shorter than that estimated by the published Freundlich K value for dichloroacetic acid. The removal after 40 days was due to biodegradation of dichloroacetic acid. Currently, the author's research group is conducting a study to determine the Freundlich K values for HAAs at various conditions.

4.4 BIOFILTRATION

Biofiltration is an effective process for removing biodegradable organic matter and biodegradable DBPs. GAC, anthracite, sand, and garnet are common media for

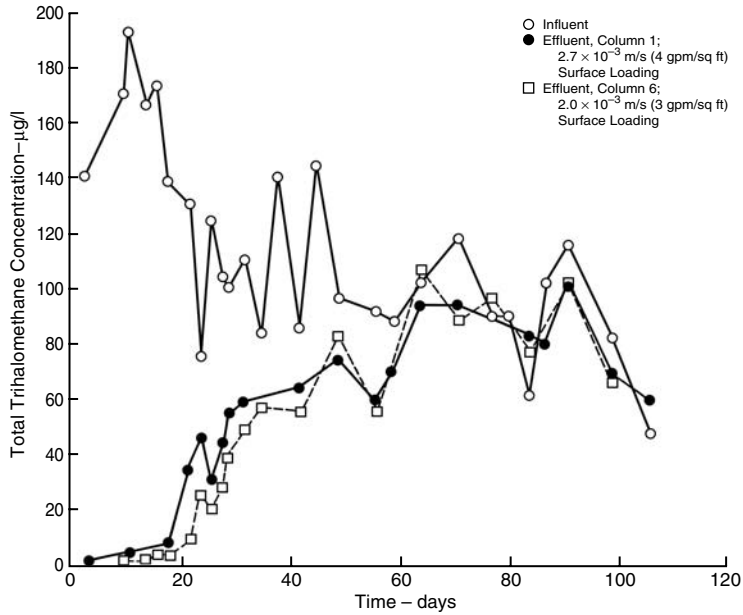

FIGURE 4.9 Breakthrough curves for total THMs in GAC columns. (Reprinted from *J. Am. Water Works Assoc.*, 70(11), (November 1978), by permission. Copyright ©1978, American Water Works Association.)

biological filters. Biologically active carbon (BAC) is a common term for acclimated GAC process.

Biofiltration could be used for NOM removal, especially with preozonation. The removal of NOM in biofilters is affected by many factors, including NOM sources and characteristics, ozone dose, EBCT, backwashing, filter media, and temperature. Most biofilters could be operated using the filtration rates (2 to 6 gpm/ft^2) for typical rapid granular media filters.[13] The removal of NOM at three different filtration rates (4, 10, and 20 gpm/ft^2) is shown in Figure 4.11. Preozonation (2.2 mg O_3/mg total organic carbon [TOC]) was used in this study.

Many ozonation byproducts, including aldehydes, ketoacids, and carboxylic acids, are readily biodegradable organics. Biofiltration is effective in removing these ozonation byproducts. As shown in Figure 4.12, two ketoacids, glyoxylic acid and pyruvic acid, spiked in the influent at 500 µg/L each, were significantly reduced after the GAC biological filters.[14] The removal in the anthracite filter was significant but much less than that in four GAC filters. A better removal was achieved with a lower hydraulic loading.

Biodegradable dissolved organic carbon (BDOC) or assimilable organic carbon (AOC) are commonly used to evaluate the biological stability or treatability of drinking water. Aldehydes, ketoacids, and carboxylic acids are the major identified components of AOC and BDOC. Therefore, biological filtration is also effective in the removal of BDOC and AOC, as shown in Figure 4.13. In this pilot study, both biological filters, GAC/sand filters, were effective in removing AOC.[15]

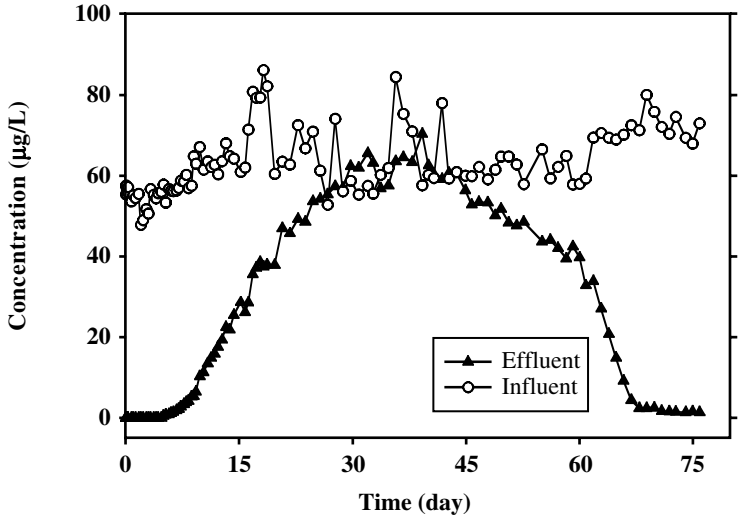

FIGURE 4.10 Removal of dichloroacetic acid in a GAC column. (Reprinted from *J. Am. Water Works Assoc.*, 94(5), (May 2002), by permission. Copyright ©2002, American Water Works Association.)

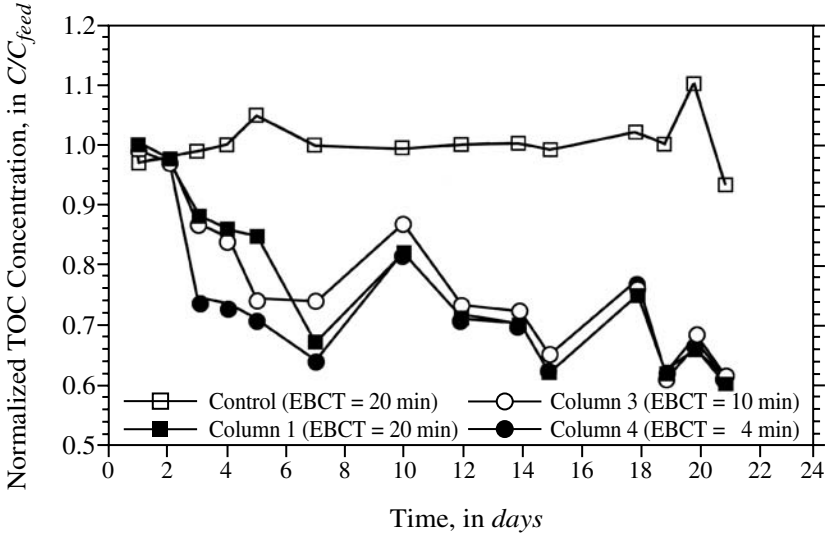

FIGURE 4.11 Removal of natural organic removal in biofilters (TOC = total organic carbon; EBCT = empty bed contact time). (Reprinted from *Formation and Control of Disinfection By-Products in Drinking Water,* by permission. Copyright ©1999, American Water Works Association.)

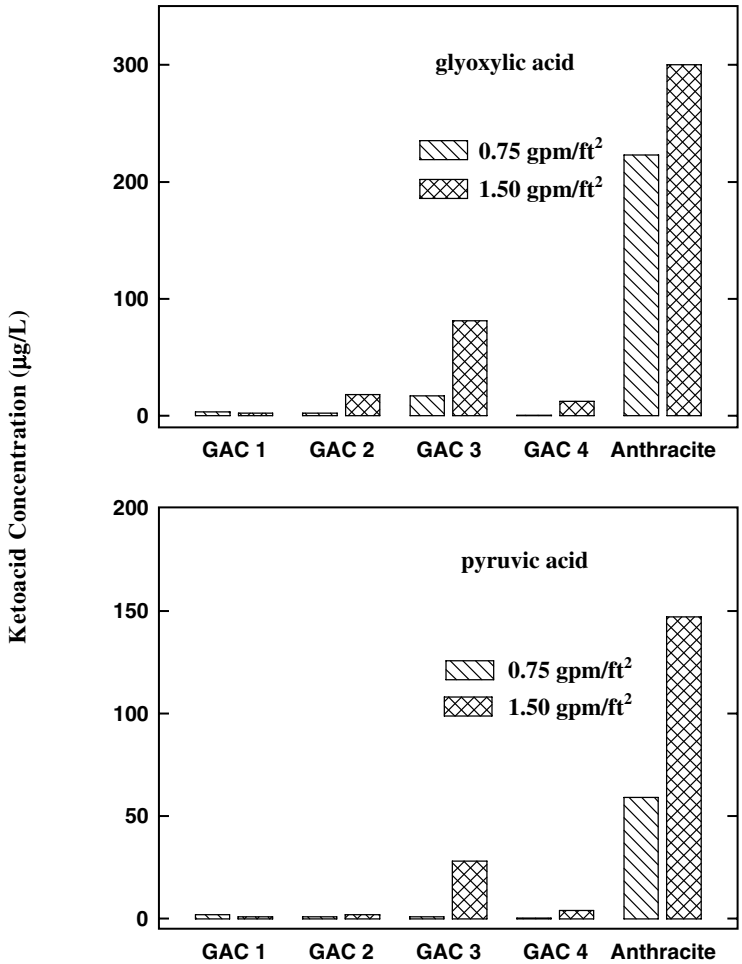

FIGURE 4.12 The removal of glyoxylic acid and pyruvic acid in biofilters. (GAC = granular activated carbon columns). (Reprinted from *Proceedings of 1992 AWWA Annual Conference*, by permission. Copyright ©1992, American Water Works Association.)

There is limited information available on the removal of HAAs using biofiltration. Preliminary studies conducted by the author's research group indicated that biologically active carbon (BAC) is an effective process for HAA removal, as shown in Figures 4.10 and 4.14. In Figure 4.14, the BAC was collected at a local water treatment plant and the carbon had been online for 26 months.[16] Influent was spiked with five HAAs at 50 µg/L each. For monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, and dibromoacetic acid, the effluent concentrations were less than 1 µg/L. For trichloroacetic acid, the effluent concentration was 7.5 µg/L but its removal efficiency was still higher than 80%. Further studies are under way at the author's laboratory.

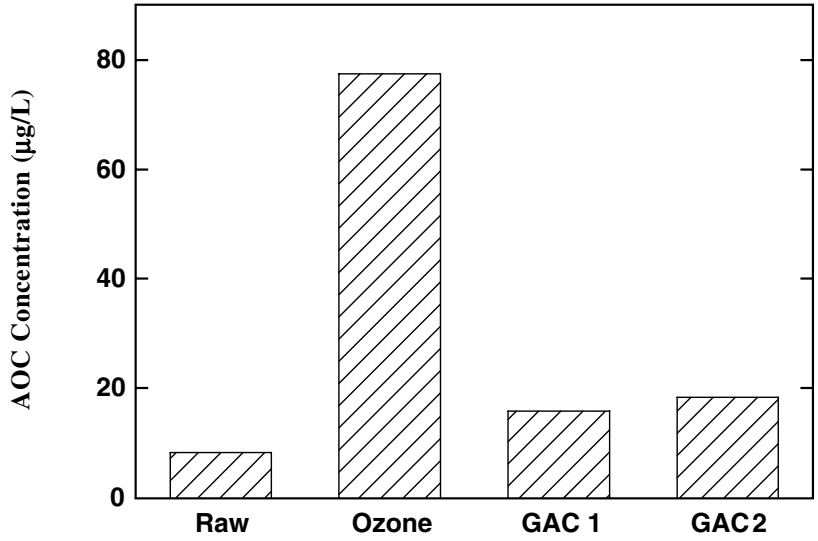

FIGURE 4.13 Assimilable organic carbon removal in biological filters (GAC = granular activated carbon columns; AOC = assimilable organic carbon). (From McEnroe, R.L., Pre-ozonation and in-line direct filtration: impact on the bacterial regrowth potential, M.S. thesis, University of Massachusetts, Amherst, 1993.)

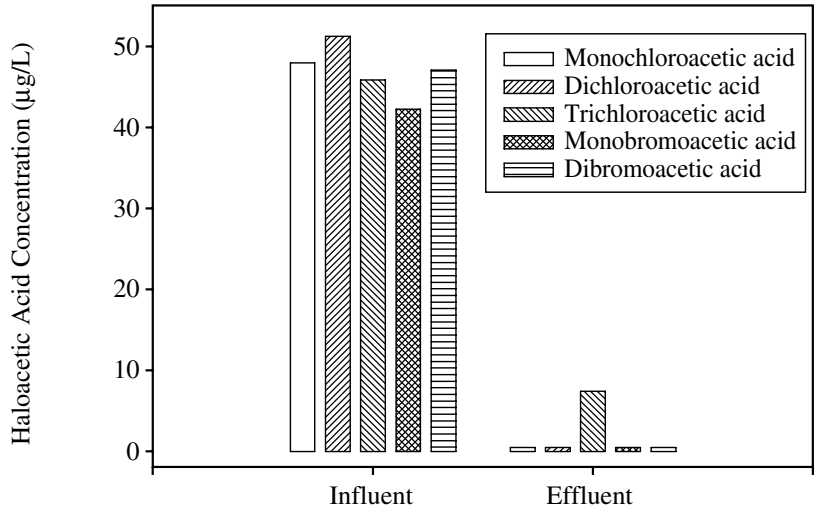

FIGURE 4.14 Haloacetic acid removal in BAC filters. (From Zhou, H.J. and Xie, Y.F., Biologically active carbon for HAA removal: part I, Batch study, *J. Am. Water Works Assoc.*, 94(4), 194, 2002.)

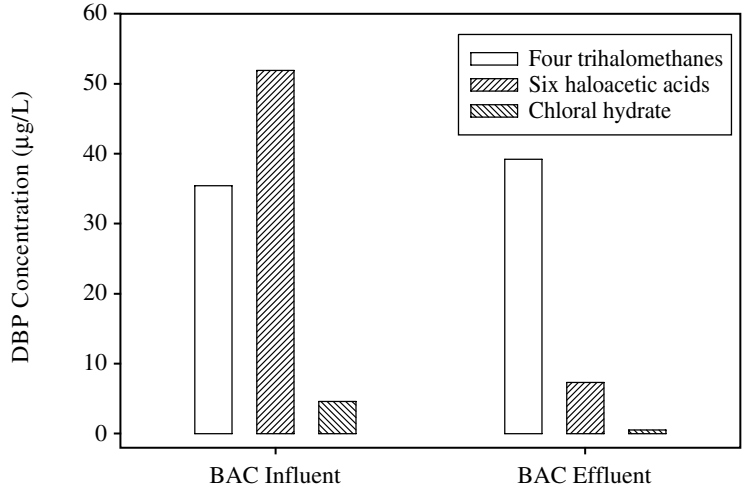

FIGURE 4.15 Effect of biofiltration on DBP speciation (BAC, biologically active carbon). (From Xie, Y.F., unpublished data, 2002.)

Biofiltration, in general, is not an effective treatment process for THMs. Because biofiltration only removes selective DBPs, it could also affect the speciation of DBPs. Because of its selective removal of HAAs and chloral hydrate, as shown in Figure 4.15, biofiltration generally increases the ratio between THMs and HAAs or chloral hydrate.[17] For HAAs, biofiltration could increase the ratio between trihaloacetic acids and dihaloacetic acids or monohaloacetic acids because of a less effective removal of trihaloacetic acids.[16]

4.5 MEMBRANE FILTRATION

In recent years, the application of membrane technologies in water treatment has been significantly increased. Common membrane filtration technologies include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis.

Microfiltration is a common membrane filtration technology used in drinking water treatment. In general, microfiltration is effective in the removal of pathogens and particular NOM. Due to its large pore size, however, microfiltration is not effective in removing dissolved NOM and other small organic and inorganic compounds. Nanofiltration, with much smaller pore sizes, is effective in both hardness and NOM removal. Ultrafiltration has a membrane pore size between microfilter and nanofilter. Depending on its pore size, ultrafiltration can remove a substantial amount of NOM. Reverse osmosis is an effective process in the removal of NOM. However, due to its high capital and operating costs, reverse osmosis is primarily used in seawater desalinization. Table 4.1 summarizes results from several studies conducted on the removal of NOM and DBP precursors using membrane filtration.[17]

As shown in Table 4.1, nanofiltration is an excellent process for DBP precursor removal. The removal efficiency of NOM by microfiltration and ultrafiltration is low. However, it could be significantly improved by the pretreatment of influent with a coagulant or PAC. With a proper pretreatment, the removal of NOM or DBP precursors by microfiltration and ultrafiltration could be increased from 10 to 20% to as high as 60 to 80%.[18]

Membrane filtration, especially nanofiltration, effectively removes NOM from water. This could significantly reduce the DBP formation in treated water when chlorine is applied. By contrast, the removal efficiency for inorganic bromide is significantly lower than that for NOM. This could significantly increase the ratio between inorganic bromide and NOM and result in a relatively higher level of brominated DBPs.

As shown in Figure 4.16, THMs speciation in the feed water is in the order: chloroform > bromodichloromethane > chlorodibromomethane > bromoform. After a nanofiltration (membrane III), THMs speciation was shifted in the order: chlorodibromomethane > bromoform > bromodichloromethane > chloroform.[19] Nanofiltration also caused a similar shift in monohaloacetic acid, dihaloacetic acid, and trihaloacetic acid species.

TABLE 4.1
Summary of DBP Precursor Studies with Membrane Processes

Water Source	Pretreatment	Membrane technology	Feed water THMFP (μg/L)	Treated THMFP (μg/L)	Percent THMFP removal
Ground	Antiscalant,	NF	961	28–32	97
	Prefiltration	NF	961	31–39	96–97
		UF	961	326–947	2–66
Surface	Prefiltration	NF	157–182	55–84	49–70
Ground	Prefiltration	NF	176–472	6–95	78–98
Surface	None	MF	60–630	40–420	20
	Coagulation	MF	70–80	30–40	40–60
Ground	Prefiltration	NF	259	39	85
Ground	pH adjustment Prefiltration	NF	120	6	95
Surface	Prefiltration	UF	40–460	NA	<10
	Prefiltration	NF	40–460	NA	30–90
	UF	NF	40–460	NA	90

Source: From Taylor, J.S., and Wiesner, M., Membranes, in *Water Quality and Treatment 5th ed.*, Letterman, R.D., Ed., Copyright ©1999 by The McGraw-Hill Companies, Inc. Reprinted by permission of the publisher.

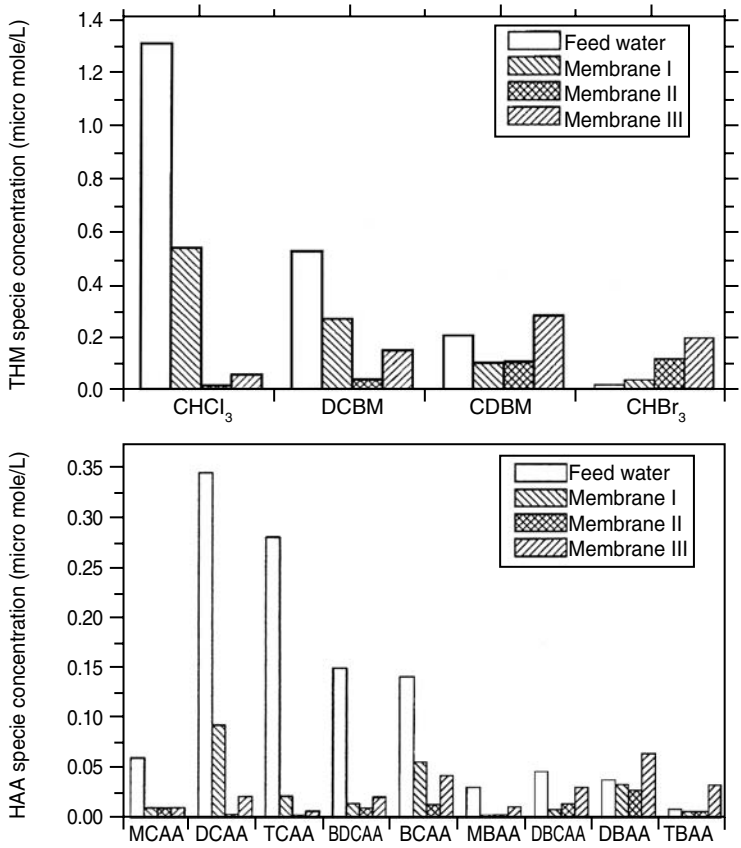

FIGURE 4.16 Effect of nanofiltration on THM and HAA speciation. (DCBM = bromodichloromethane; CDBM = chlorodibromomethane; MCAA = monochloroacetic acid; DCAA = dichlororoacetic acid; TCAA = trichloroacetic acid; BDCAA = bromodichloroacetic acid; BCAA = bromochloroacetic acid; MBAA = monobromoacetic acid; DBCAA = dibromoacetic acid; DBAA = dibromoacetic acid; TBAA = tribromoacetic acid.) (Reprinted with permission from Chellam, S., *Environ. Sci. Technol.*, 34, 1813, 2000. Copyright ©2000, American Chemical Society.)

4.6 SUMMARY

Preoxidation, coagulation, carbon adsorption, biofiltration, and membrane processes are effective processes for removing DBP precursors and/or DBPs. When optimized, these processes are excellent for DBP control. In addition to DBP reduction in finished water, these processes also affect the speciation of DBPs in finished water. Many of the processes will increase relative levels of brominated DBPs and some of the treatment processes will alter the ratio between THMs and HAAs or other DBPs.

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5 Disinfection Byproduct Control

OBJECTIVES

This chapter discusses two best-available technologies, enhanced coagulation and granulated activated charcoal (GAC) adsorption, for disinfection byproduct (DBP) control. Other technologies, including alternative disinfectants, preoxidation, biologically active carbon, and membrane, are discussed as well. Information presented in this chapter provides the reader of this book with an array of choices for DBP control.

NOMENCLATURE

AOC assimilable organic carbon
BAC biologically active carbon
BAT best-available technology
DBP disinfection byproduct
D-DBP disinfectants and disinfection byproducts
DOC dissolved organic carbon
EBCT empty bed contact time
GAC granular activated carbon
GAC10 granular activated carbon with an empty bed contact time of 10 minutes
HAA haloacetic acid
NOM natural organic matter
PAC powdered activated carbon
PODR point of diminishing returns
POU point-of-use
SUVA specific ultraviolet adsorption
THM trihalomethane
TOC total organic carbon
U.S. EPA United States Environmental Protection Agency
UV ultraviolet

Because of the widespread occurrence of disinfection byproducts (DBPs) in chlorinated drinking water and their potential health risks, the United States Environmental Protection Agency (U.S. EPA) promulgated Stage 1 Disinfectants and Disinfection Byproducts (D-DBP) Rule in 1998. The maximum contamination level is 80 μg/L for total four trihalomethanes (THMs), 60 μg/L for five haloacetic acids (HAAs), 1 mg/L for chlorite, and 10 μg/L for bromate.[1] U.S. EPA also identified two best

available technologies (BATs) for DBP control. The discussion in this chapter will help water professionals to better understand these best-available technologies and other potential technologies for DBP control and removal.

5.1 ENHANCED COAGULATION

Enhanced coagulation is one of two BATs for DBP control under the Stage 1 D-DBP Rule.[1] The enhanced coagulation process is defined as an optimized coagulation process for removing DBP precursors, or natural organic matter (NOM). NOM is measured as total organic carbon (TOC) or dissolved organic carbon (DOC). In general, enhanced coagulation is practiced at a higher coagulant dose and a lower pH.

5.1.1 Enhanced Coagulation Requirements

Specific UV adsorption (SUVA) is an important water quality criterion for enhanced coagulation. SUVA is defined as UV adsorption (per m or m^{-}) at 254 nm per mg/L of DOC, as expressed in Equation 5.1. Because most of UV measurement is done with 1-cm UV cells (per cm or cm^{-}), the SUVA is often multiplied by 100 to be expressed as L/mg-m.

$$SUVA = \frac{UV}{DOC} \tag{5.1}$$

SUVA could be used to evaluate the treatability of water. In general, water with a SUVA of 2 L/mg-m or less is considered difficult-to-treat water. By contrast, water with a higher SUVA is considered easy-to-treat water. Because TOC can be easily measured and monitored, TOC removal is used to evaluate enhanced coagulation.

For enhanced coagulation, there is a two-step standard specified in the Stage 1 D-DBP Rule.[1] Under the step 1 requirement, a treatment system that meets the TOC removal criteria listed under Table 5.1 complies with the enhanced coagulation requirements. The TOC removal criteria listed consider the effects of alkalinity in source waters. For a higher alkalinity source water, in general, it is more difficult to lower the pH and achieve a better TOC removal. Therefore, a lower TOC removal is required for high alkalinity waters. TOC removal requirements are also affected by the source water TOC.

The step 2 requirement provides alternative percent removal of raw water TOC for water systems that may not be able to meet the TOC removal criteria listed in Table 5.1. The alternative TOC removal percentage is determined by conducting jar tests on at least quarterly basis for 1 year. The jar tests should be conducted by adding alum ($Al_2(SO_4)_3 \cdot 14.3\ H_2O$) or an equivalent dose of ferric salts, as shown in Table 5.2, in a 10 mg/L interval until the pH is lowered to the target pH value.[2] The target pH values for waters with various alkalinity ranges are listed in Table 5.3.

The alternative TOC removal percentage is set at the point of diminishing returns (PODR). The regulation defines the PODR as the point where the removal of TOC for every 10 mg/L alum added changes from greater than 0.3 mg/L to less than 0.3 mg/L and remains less than 0.3 mg/L.

TABLE 5.1
Required Removal of Total Organic Carbon by Enhanced Coagulation

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	0 to 60	>60 to 120	>120
>2.0–4.0	35.0%	25.0%	15.0%
>4.0–8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

Source: From United States Environmental Protection Agency, National Primary Drinking Water Regulations; Disinfectants and Disinfection Byproducts; Final Rule, *Federal Register,* 63, 69392, 1998.

TABLE 5.2
Equivalent Dose of Coagulants under the Step 2 Requirement (mg/L)

Regular grade alum, $Al_2(SO_4)_3{\cdot}14\ H_2O$	10	20	30	40	50	60
Reagent grade alum, $Al_2(SO_4)_3{\cdot}18\ H_2O$	11.2	22	34	45	56	67
Ferric chloride, $FeCl_3{\cdot}6\ H_2O$	9.1	18	27	36	46	55
Ferric chloride, $FeCl_3$	5.5	11	16	22	33	38
Ferric sulfate, $Fe_2(SO_4)_3{\cdot}9\ H_2O$	9.5	19	28	38	47	57
Ferrous sulfate, $FeSO_4{\cdot}7\ H_2O$	9.4	19	28	37	47	56

Source: Modified from United States Environmental Protection Agency, Enhanced Coagulation and Enhanced Precipitate Softening Guidance Manual, EPA 815-R-99–012, U.S. EPA Office of Water, 1999.

The PODR generally is determined graphically.[2] First, plot the TOC removal (mg/L) vs. regular grade alum dose (10, 20, 30… mg/L). For other coagulants, plot the TOC removal vs. equivalent regular grade alum dose (10, 20, 30… mg/L) instead of their actual dose. Second, determine the PODR as the point where the slope changes from >0.3/10 to <0.3/10 and remains <0.3/10. Alternatively, plot the TOC removal vs. the actual dosage of other coagulants. The slope criteria will not be 0.3/10 but 0.3/11.2, 0.3/9.1, 0.3/5.5, 0.3/9.5, and 0.3/9.4 for reagent grade alum ($Al_2(SO_4)_3{\cdot}18\ H_2O$), ferric chloride ($FeCl_3{\cdot}6\ H_2O$), ferric chloride ($FeCl_3$), ferric sulfate ($Fe_2(SO_4)_3{\cdot}9\ H_2O$), and ferrous sulfate ($FeSO_4{\cdot}7\ H_2O$), respectively.

Actually, the slope criterion is –0.3 mg/L TOC/10 mg/L alum, not 0.3/10. However, the removal of TOC, not TOC concentration, is the goal of this determination. Therefore, the slope is commonly referred to in EPA documents and publications as 0.3/10 even though it is not mathematically correct, especially in the graphical format.

TABLE 5.3
Target pH Values under the Step 2 Requirement

Alkalinity (mg/L)	0–60	>60 to 120	>120–240	>240
Target pH	5.5	6.3	7.0	7.5

Source: Modified from United States Environmental Protection Agency, Enhanced Coagulation and Enhanced Precipitate Softening Guidance Manual, EPA 815-R-99–012, Office of Water, 1999.

A typical jar test result is shown in Figure 5.1.[2] The dashed line with a slope of 0.3/10 is added to aid the visual identification of the PODR. As shown in Figure 5.1, the section of the plot for doses of 20 and 30 mg/L has a slope higher than 0.3/10. The section for the plot for doses of 30 and 40 mg/L has a slope lower than 0.3/10. Therefore, the PODR is determined at 2.8 mg/L TOC or 33% removal.

The sections of the plot for some water may fall below 0.3/10 slope criteria twice,[2] as shown in Figure 5.2. Both sections, for doses of 20 to 30 and 50 to 60 mg/L, have a slope higher than 0.3/10. Both sections, for doses of 30 to 40 and 60 to 70 mg/L, have a slope lower than 0.3/10. The regulation states the PODR as the point where the removal of TOC for every 10 mg/L alum changes from >0.3 mg/L to <0.3 mg/L and remains <0.3 mg/L. Therefore the PODR for this water is determined at 3.05 mg/L TOC (or 27% removal), not 3.55 mg/L TOC (or 15%).

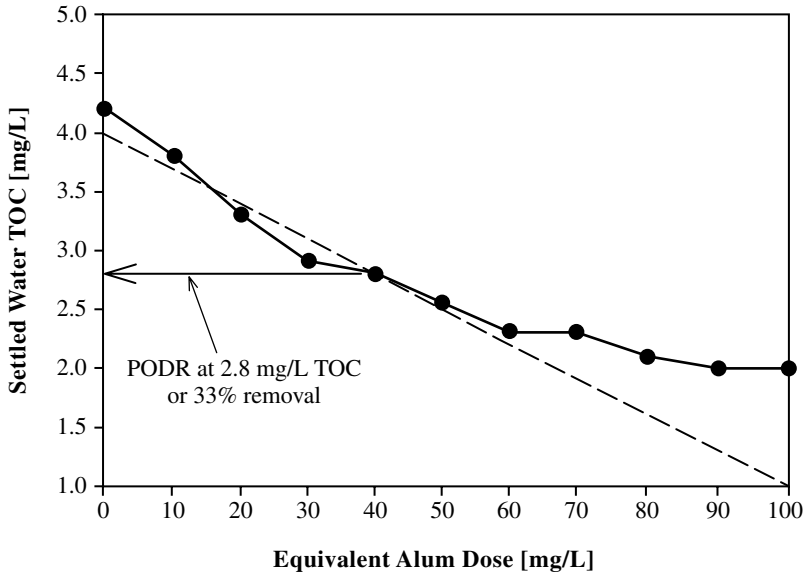

FIGURE 5.1 Determining the step 2 removal requirement. (From United States Environmental Protection Agency, Enhanced Coagulation and Enhanced Precipitate Softening Guidance Manual, EPA 815-R-99–012, Office of Water, 1999.)

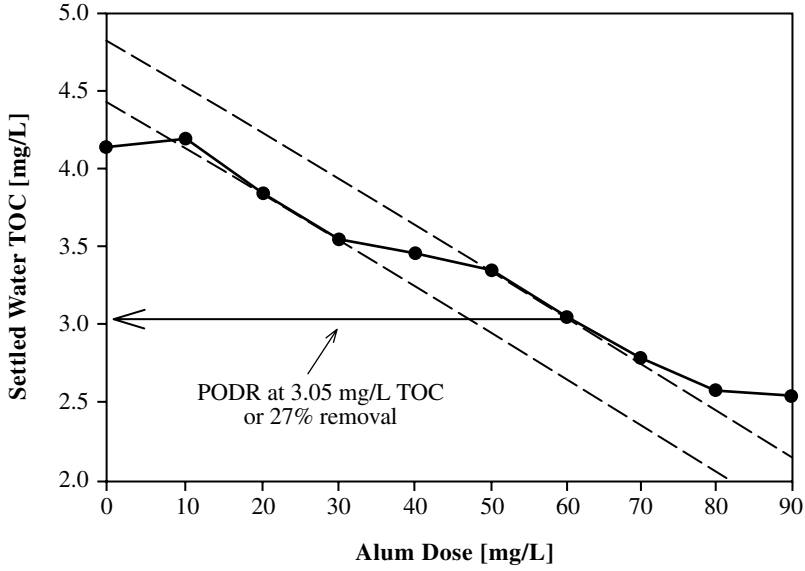

FIGURE 5.2 Determining the step 2 removal requirement. (From United States Environmental Protection Agency, Enhanced Coagulation and Enhanced Precipitate Softening Guidance Manual, EPA 815-R-99–012, Office of Water, 1999.)

Some utilities may have water that is not amenable to enhanced coagulation,[2] as shown in Figure 5.3. No section of the plot has a slope higher than 0.3/10. Therefore the PODR for this water is never met. This indicates that this water is indeed not amenable to enhanced coagulation. The water utility could apply for a waiver from enhanced coagulation.

5.1.2 Practices of Enhanced Coagulation

Many water quality conditions and operating conditions affect TOC removal. The water quality conditions include alkalinity, pH, turbidity, TOC concentration, origin of NOM, and temperature. The design and operating conditions include coagulant dosage and type, pH, preoxidation, coagulation aids, mixing and mixing time, sedimentation process, and sludge handling. Two operation conditions greatly affect TOC removal. They are coagulant type and pH preadjustment.

5.1.2.1 Coagulants

Most enhanced coagulation studies were conducted using alum or ferric salts (e.g., ferric chloride or ferric sulfate). In general, both coagulants are commonly used in the water industry and perform well for TOC removal. For some water, ferric salts perform better than alum. Figure 5.4 shows a jar test result obtained in the author's laboratory.[3] Based on the TOC and alkalinity of the raw sample, a 25% TOC removal is required under the step 1 requirements. A 50 mg/L alum addition meets this removal requirement. To meet the same removal requirement, only 30 mg/L (equiv-

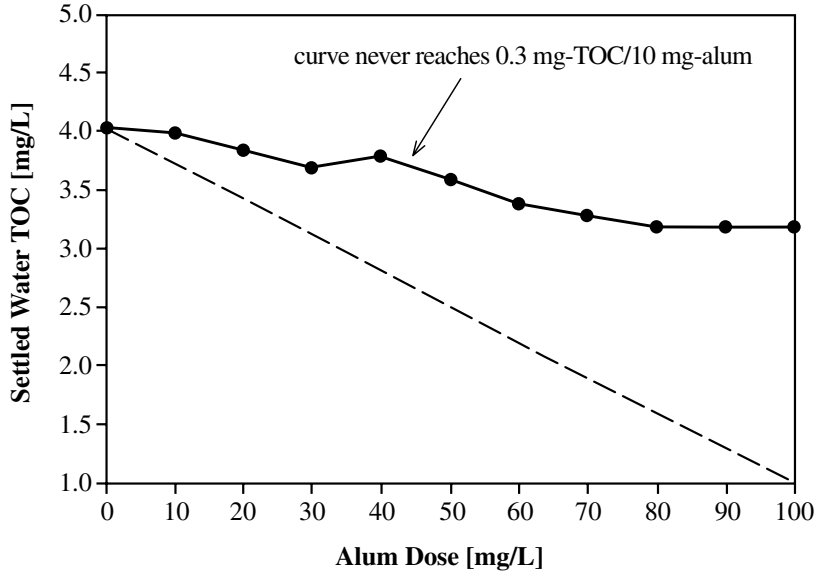

FIGURE 5.3 Determining the step 2 removal requirement. (From United States Environmental Protection Agency, Enhanced Coagulation and Enhanced Precipitate Softening Guidance Manual, EPA 815-R-99–012, Office of Water, 1999.)

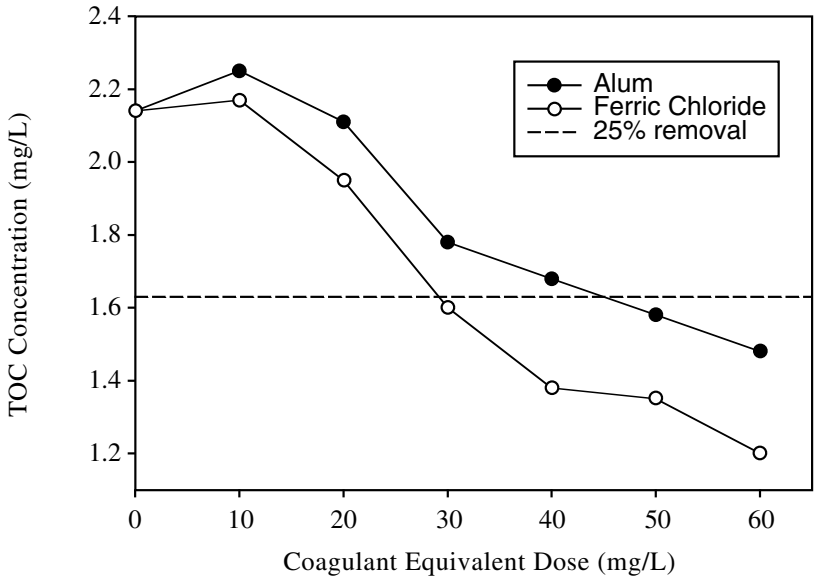

FIGURE 5.4 Enhanced coagulation with alum and ferric chloride. (From Xie, Y.F. and Fillmann, S.L., unpublished data, 1997.)

alent dose) ferric chloride is needed. The actual dose is 27.3 mg/L of ferric chloride ($FeCl_3 \cdot 6\ H_2O$). However, the use of ferric salts could cause more serious corrosion problems to the treatment facilities. The potential introduction of heavy metals, which are often impurities in ferric salts, could be a concern for finished water quality and sludge disposal.

Organic or inorganic polymers are commonly used for water coagulation. Very few studies were reported on the use of organic polymers for enhanced coagulation. The use of inorganic polymers for enhanced coagulation was not recommended by the U.S. EPA. The guidance manual did not provide information on the equivalent doses for these chemicals. However, studies have demonstrated that polymerized aluminum chloride or sulfate could be more effective in enhanced coagulation for some water. Figure 5.5 shows a jar test result obtained in the author's laboratory.[3] Based on the TOC and alkalinity of the raw sample, a 35% TOC removal is required under the step 1 requirements. A 60 mg/L alum addition meets this removal requirement. For polymerized aluminum chloride, however, only 40 mg/L (equivalent dose) is needed. The actual dose is 29.2 mg/L determined using the aluminum content. Unlike alum and ferric salt, polymerized aluminum chloride does not significantly affect the pH of the process water. In some cases an acid addition may be required to achieve a better TOC removal. The cost of polymerized aluminum chloride or sulfate is significantly higher than that of alum or ferric salts. A lower polymerized aluminum chloride or sulfate dosage will reduce the sludge production. This can significantly reduce the cost for sludge handling and disposal.

5.1.2.2 pH Preadjustment

Recognizing the importance of water pH in enhanced coagulation, U.S. EPA set target pH values under the step 2 requirements. Sufficient amount of alum or ferric salts are needed to reach these pH values. Acid addition is an alternative way of lowering the pH and achieves a better TOC removal. Sulfuric acid is commonly used for this purpose. Figure 5.6 shows a jar test result obtained in the author's laboratory.[3] Based on the TOC and alkalinity of the raw water sample, a 45% TOC removal is required under the step 1 requirements. A 60 mg/L alum addition meets this removal requirement. When the water pH was preadjusted to 6.2, a much better TOC removal was achieved. With pH preadjustment, only 40 mg/L of alum is needed to meet the 45% TOC removal requirement. For some high alkalinity water, the acid addition will achieve a better TOC removal. For low alkalinity water, however, a base addition may be needed to maintain the minimum pH and achieve a better TOC removal.

5.1.3 Impacts of Enhanced Coagulation

Enhanced coagulation reduces NOM and DBP precursors. Practicing enhanced coagulation will reduce the formation of DBPs in finished water. However, it can also significantly impact other water treatment processes. Enhanced coagulation generally enhances water disinfection. At a lower pH value, hypochlorous acid, a stronger chlorine species, will become the predominant species. This could lower

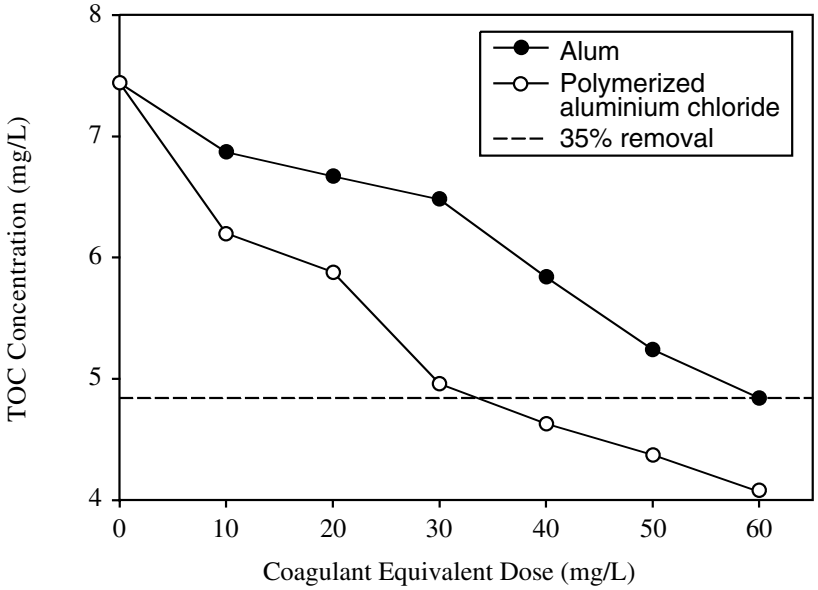

FIGURE 5.5 Enhanced coagulation with alum and polymerized aluminum chloride. (From Xie, Y.F. and Fillmann, S.L., unpublished data, 1997.)

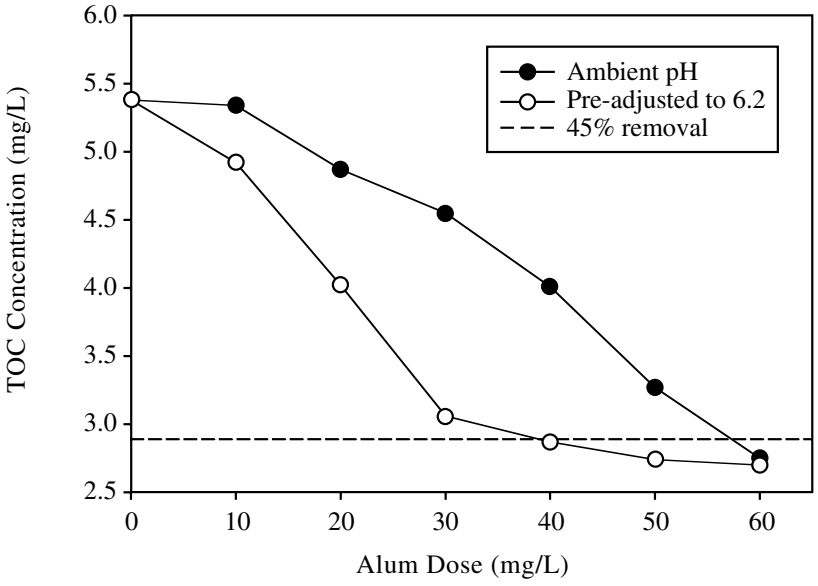

FIGURE 5.6 Enhanced coagulation with pH preadjustment. (From Xie, Y.F. and Fillmann, S.L., unpublished data, 1997.)

the CT requirement (see Chapter 10) and enhance water disinfection. Because of the better TOC removal, the chlorine demand by NOM will be reduced. This could significantly improve the stability of chlorine residual in the distribution systems.

Enhanced coagulation will significantly compromise the removal of manganese as a result of the lower pH conditions. The typical manganese removal process includes preoxidation, sedimentation, and filtration. Therefore, the degree of impact depends on the type and dose of the preoxidant, oxidation time before coagulation, and pH of coagulated water. The main reason for incomplete manganese removal was incomplete oxidation of the soluble manganese (Mn^{2+}) at the low pH conditions. The oxidation could be improved by using a fast oxidant (e.g., ozone and chlorine dioxide), a higher oxidant dosage, and a longer contact time before coagulation. For enhanced coagulation with pH preadjustment, acid should be added after the complete oxidation of manganese. Trace amounts of manganese in ferric salts is another concern when a ferric salt is used at a high dosage.

Enhanced coagulation also increases sludge production and may alter the sludge characteristics. This could significantly increase the cost and difficulty of the sludge handling and disposal. By lowering the pH, enhanced coagulation could potentially result in more corrosion problems in the distribution systems and compromise the compliance of the Lead and Copper Rule. A final pH adjustment with soda ash (Na_2CO_3) or caustic soda (NaOH) generally is needed to raise the plant effluent pH to proper levels. Without enhanced coagulation many utilities raise pH during the coagulation process. This could be done with a cheaper alkaline chemical, lime ($Ca(OH)_2$). Therefore, enhanced coagulation will increase the cost of the pH adjustment of finished water. Enhanced coagulation may also cause higher levels of aluminum in finished water. Raising pH before filtration may be needed to mitigate the problem.

In summary, enhanced coagulation is a coagulation process optimized for TOC removal. Practicing enhanced coagulation could compromise particle (or turbidity) and pathogen removal in subsequent sedimentation and filtration. Coagulation aid or filter aid should be investigated to minimize the particle removal problem resulting, from enhanced coagulation. Using plate settlers or tube settlers may enhance performance of a sedimentation tank. Replacing old filter media or changing monomedia to dual-media may also enhance filtration efficiency.

5.2 CARBON ADSORPTION

Carbon adsorption is a process that can remove both DBPs and DBP precursors. Both granular activated carbon (GAC) and powdered activated carbon (PAC) are commonly used in the water industry.

5.2.1 DBP Precursor Removal

Under the Stage 1 D-DBP Rule, GAC with an empty bed contact time (EBCT) of 10 min (GAC10) was chosen as one of the two BATs for DBP control. GAC10 is defined as GAC adsorption with an EBCT of 10 min and GAC reactivation frequency of no more than 6 months.[1] The EBCT is the water detention time in the empty

GAC contactor. It is calculated by dividing the GAC volume by water flow rate, as shown in Equation 5.2. Because of a much smaller void space inside the GAC contactor, the actual contact time between GAC and water is much shorter.

$$EBCT = \frac{V_{GAC}}{Q_{water}} \tag{5.2}$$

In general, GAC10 is effective in removing natural organic matter (NOM). However, DBP precursors, low-molecular-weight fractions of NOM, are poorly absorbable. This results in a nonproportionally poor removal of DBP precursors. Many studies have demonstrated that the ratios between DBP precursors and TOC were significantly increased after GAC adsorption. Figure 5.7 shows that a 70% removal of TOC is required to achieve a 20% reduction of THM formation potential.[4]

GAC could be used as the top media in dual or tri-media filters. This process is commonly referred to as filter adsorbers or GAC filters. Typical EBCTs are between 5 to 15 min. Many GAC filters will not meet the 10 min requirement. A GAC contactor could be used for carbon adsorption. When it is used after filter, it is referred to as postfilter adsorbers. Typical EBCTs are between 10 to 30 min. Both filter adsorbers and postfilter adsorbers with a minimum EBCT of 10 min can be used for DBP precursor removal.

For GAC adsorption design and operation, bench scale and/or pilot scale studies should be conducted. A bench scale test, rapid small-scale column test (RSSCT),[5] is a cost-effective technology for predicting carbon adsorption performance and carbon usage rate. A pilot study is another way, though more expensive, to evaluate the carbon adsorption performance and carbon usage rate.

GAC could also be used as biologically active carbon (BAC). As discussed in Chapter 4, BAC could reduce biodegradable DBP precursors by biodegradation. Biologically active carbon could be promoted using nonchlorinated influent and nonchlorinated backwash water. Preozonation could convert nonbiodegradable NOM into biodegradable organics and improve the effectiveness of BAC for DBP precursor removal.

5.2.2 DBP Removal

GAC could be used for DBP removal, as well. Under the Total THM Rule, GAC adsorption was one of the BATs for THM removal.[6] A frequent GAC regeneration is required for most GAC contactors. Shorter EBCTs (e.g., filter adsorbers) require much more frequent GAC regenerations.

Several studies have been conducted and have reported a higher GAC adsorption capacity for HAAs than that for THMs. However, a much lower adsorption capacity was observed for HAAs than THMs in the author's laboratory.[7] For monochloroacetic acid, GAC generally reached saturation in a few days, as shown in Figure 5.8.

Because HAAs are readily biodegradable, BAC, or acclimated GAC, can be used for an effective removal of HAAs.[8] A rapid development of bioactivities on GAC could lead to an effective HAA removal through biological degradation and compensate for the rapid breakthrough of HAAs. In a laboratory column study,[7]

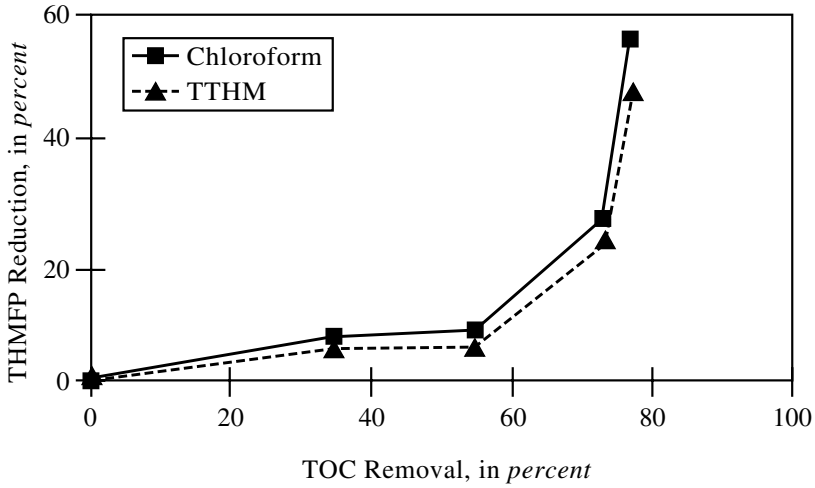

FIGURE 5.7 GAC Adsorption for trihalomethane precursor removal. (Reprinted from *Water Research,* vol. 21, El-Rehaili, A.M. and Weber, W.J., Control of humic substance trihalomethane formation potential and adsorption behavior to molecular weight distribution in raw and chemically treated waters, 573, Copyright ©1987, with permission from Elsevier.)

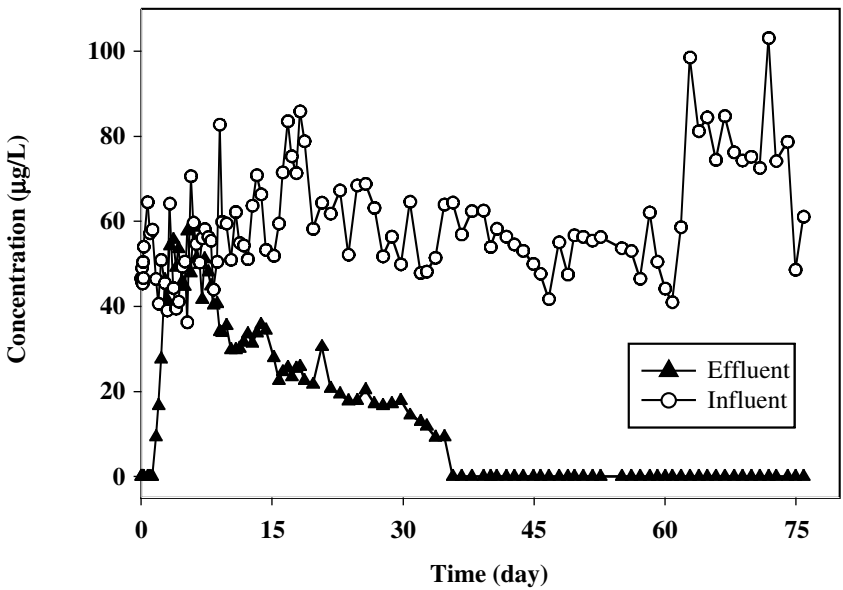

FIGURE 5.8 Monochloroacetic acid removal in a GAC column. (Reprinted from *J. Am. Water Works Assoc.,* 94(5) (May 2002), by permission. Copyright ©2002, American Water Works Association.)

a minimum 40% removal of five HAAs was observed in the first 2 months, as shown in Figure 5.9. After 2 months, a near complete removal of five HAAs was observed.

The combination of GAC adsorption and biological degradation of DBPs could be used to effectively control DBPs in finished water. For a GAC treatment plant with a 3-year regeneration cycle, GAC replacement could be staggered over 3 years. One-third new GAC each year could reduce THM concentration by a third for 2 to 3 months. Two-thirds older GAC (biologically active carbon) could be used for HAAs removal. Based on the study in the author's laboratory, early summer is the best time for GAC replacement. This provides for the best THM control in summer months. The warmer water temperature in summer months also promotes a rapid biological activity development on GAC. Various research activities are carried out in the author's laboratory to explore the use of GAC for DBP control.

5.2.3 Point-of-Use Carbon Devices

The application of point-of-use (POU) devices in residential houses has grown substantially in the recent years. Carbon devices are commonly used for taste and odor control and chlorine removal. A recent study[9] conducted in the author's laboratory shows that POU carbon devices are effective in reducing DBP levels in tap water, as shown in Figure 5.10. The filter was run for 66 days, about 120% of the filter usage (based on water filtered) suggested by the manufacturer. Throughout the operation period, the POU carbon devices are effective in removing THMs. For HAAs, an early breakthrough was observed. However, a substantial reduction of

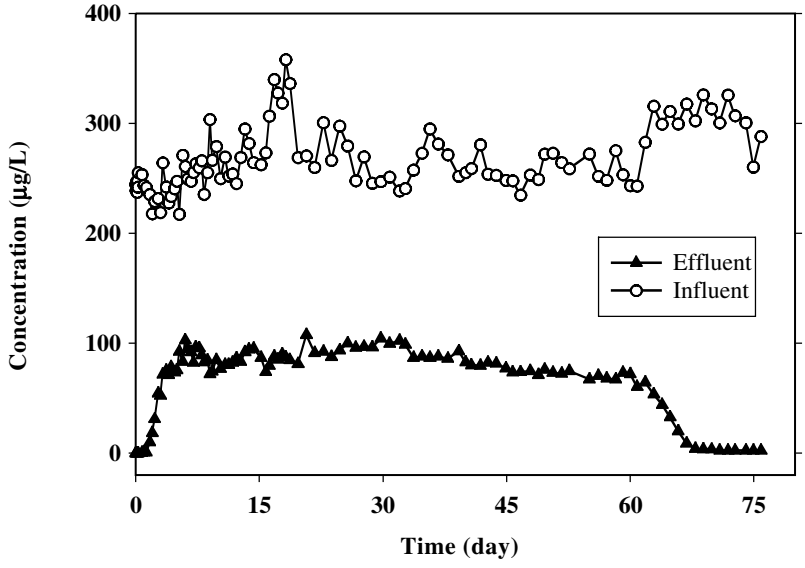

FIGURE 5.9 Haloacetic acid removal in a GAC column. (Reprinted from *J. Am. Water Works Assoc.,* 94(5) (May 2002), by permission. Copyright ©2002, American Water Works Association.)

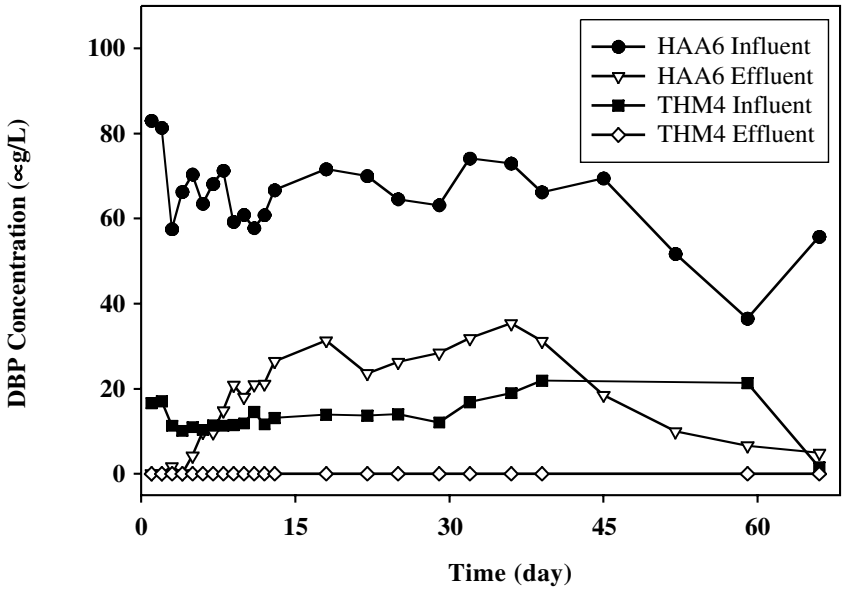

FIGURE 5.10 DBP removal in a POU carbon filter. (From Xie, Y.F., Tung, H.-H., and Yeung, M.Y., unpublished data, 2002.)

HAAs was seen in the later stage. This removal is due to the biological degradation of HAAs. This also indicated the development of biological activity inside these devices in the later stage.

Under the Drinking Water Act Amendments 1996, centrally managed POU devices are allowed for regulation compliance. Currently, U.S. EPA allows the use of point-of-use devices for Arsenic Rule compliance.[10] The use of POU devices for DBP regulation compliance could be a cost-effective technology for small water systems.

5.3 CHANGING THE CHLORINATION POINT

Since the publication of Total THM Rule, many water systems, especially large water systems, have eliminated prechlorination and moved back the chlorination point to intermediate or postchlorination. For many medium and small water systems, prechlorination is still commonly used. As discussed in Chapter 4, changing the chlorination point, or eliminating prechlorination, is one of the most effective ways to control DBP levels in finished water.

Moving back chlorination point could significantly impact the subsequent water treatment processes. First, it will reduce the CT values (see Chapter 10) and affect water disinfection. Many water systems use prechlorination to achieve additional credits for disinfection. Eliminating prechlorination may compromise the CT requirement. Second, eliminating prechlorination could affect iron and manganese removal. Third, eliminating prechlorination may cause algae and biofilm growth inside the treatment units.

To minimize the potential impact of prechlorination elimination on the subsequent treatment processes, preoxidation with alternative oxidants or disinfectants could be used to replace prechlorination. Preoxidation with potassium permanganate or chlorine dioxide is commonly used in treatment plants for iron and manganese removal. Chlorine dioxide is also an effective disinfectant and may provide additional disinfection. Preozonation is used in some treatment plants. Although an expensive technology, ozone is effective in iron and manganese removal, as well as taste, odor, and color control. Preozonation also contributes to CT credit and is effective in *Giardia* and *Cryptosporidium* inactivation. Preozonation also reduces DBP precursors and promotes biological active degradation in the late stage. Preozonation may benefit coagulation and enhance NOM removal.

5.4 ALTERNATIVE DISINFECTANTS

Using alternative disinfectants is another effective way to control DBPs in finished water. These alternative disinfectants include chloramines, ozone, chlorine dioxide, and UV. Switching to alternative disinfectants affects water disinfection, the DBP formation and speciation, and other treatment processes.

5.4.1 Chloramines

Chloramine is a much weaker disinfectant than free chlorine. Free chlorine can be converted into chloramine by adding ammonia in water. As a primary disinfectant, as discussed in the Prelude, chloramine requires a much longer contact time for adequate disinfection. Because of its low reactivity, chloramine can last longer, especially in large distribution systems. This makes chloramine an ideal choice as a secondary disinfectant. Water chloramination also produces DBP. A unique chloramination byproduct is cyanogen chloride. In water high in bromide, cyanogen bromide will be produced. Cyanogen chloride is not included in the current Stage 1 and proposed Stage 2 D-DBP Rules. However, cyanogen chloride was monitored in chloraminated water under the Information Collection Rule. Chloramination also produces low levels of THMs and HAAs, especially dihaloacetic acids (e.g., dichloroacetic acid).[11] The formation of these DBPs largely depends on the ratio of chlorine to ammonia.

Nitrification is a big concern for chloramination systems. Nitrification of ammonia depletes chloramine residual and cause Total Coliform Rule violations. High water temperatures and low chlorine to ammonia ratios favor nitrification. Nitrification could be controlled by increasing the ratio of chlorine to ammonia. Switching back to free chlorine for a few days could also be used to combat nitrification. Taste and odor problem is another big concern for chloraminated systems. Dichloramine and trichloramine are two major taste and odor contributors and can be minimized by adjusting the ratio of chlorine to ammonia.

5.4.2 Ozone

Ozone is a stronger disinfectant than free chlorine. Ozonation is especially effective in inactivating *Giardia* and *Cryptosporidium*. Because of its high reactivity, ozone

does not provide a long lasting ozone residual in distribution systems. In general, ozone is commonly used as a primary disinfectant, not a secondary disinfectant. Like chloramines, ozone also produces byproducts. Ozone reacts with inorganic bromide to produce bromate and hypobromous acid. Hypobromous acid reacts with NOMs to produce bromoform, monobromoacetic acid, dibromoacetic acid, tribromoacetic acid, cyanogen bromide, and other brominated DBPs. Bromate, bromoform, monobromoacetic acid and dibromoacetic acid are regulated under the Stage I D-DBP Rule.[1] Ozone also reacts with NOM to form aldehydes, ketoacids, carboxylic acids and other biologically degradable organics. Except for aldehydes, which were monitored under the Information Collection Rule, there is little health risk information for these organics. However, these biologically degradable organics could significantly increase the level of assimilable organic carbon (AOC) and result in bacteria regrowth in distribution systems.

5.4.3 Chlorine Dioxide

Chlorine dioxide is a stronger bactericide and viricide than chlorine over a wide pH range. Chlorine dioxide also produces long lasting residual in distribution systems. Therefore, chlorine dioxide could be used as a primary disinfectant as well as a secondary disinfectant. Chlorine dioxide is also effective in controlling taste and odor compounds, iron and manganese, and DBPs. The degradation of chlorine dioxide results in the formation of chlorite. Under the Stage I D-DBP Rule, chlorite is regulated at a maximum contaminant level of 1.0 mg/L. Residual chlorine dioxide also reacts with ozone or chlorine to produce another inorganic byproduct, chlorate. Impurities in chlorine dioxide also affect chlorite and chlorate levels in finished water.

Due to its high cost, application of chlorine dioxide in large water systems is limited to preoxidation in the United States. The use of chlorine dioxide for primary and/or secondary disinfection is limited to small water systems. The use of chlorine dioxide in large water systems for disinfection, however, is common in many European countries.

5.4.4 Ultraviolet

Ultraviolet (UV) radiation is a physical process for water disinfection and is an effective technology for inactivating bacteria and viruses. Many earlier studies indicated that UV radiation may not be a viable choice for *Giardia* and *Cryptosporidium* inactivation. However, recent studies indicated that UV radiation could achieve 3-log (99.9%) inactivation of *Giardia* and *Cryptosporidium* at a UV dose of 40 mJ/cm^2.[12] Many early studies used an unreliable *in vitro* excystation procedure to pretreat *Giardia* and *Cryptosporidium* and might provide misleading results on UV disinfection. Methods using infectivity in susceptible animals should be used for *Giardia* and *Cryptosporidium* inactivation using UV radiation.

The effectiveness of UV disinfection, especially on *Cryptosporidium*, has brought more attention to the technology. As a physical process, UV radiation does not provide a disinfectant residual. Therefore, UV radiationcan only be used as a

primary disinfectant. A secondary disinfectant, including chlorine, chloramines or chlorine dioxide, must be used in conjunction with UV disinfection to provide a disinfection residual in distribution systems.

5.4.5 Combinations of Disinfectants

To better balance DBP control and water disinfection, it is common to use a combination of two or three alternative disinfectants. Common combinations are chlorine/chloramines and ozone/chloramines. In comparison to traditional chlorine/chlorine treatment processes, these combinations could assure microbial disinfection and reduce DBPs in finished water. As shown in Table 5.4, changing chlorine/chlorine to chloramines/chloramines and ozone/chloramines reduced total THMs from 225 μg/L to 9.4 μg/L and 3.2 μg/L, respectively.[13] In another study, as shown in Table 5.5, switching chlorine/chlorine to ozone/chloramines resulted in a 96% reduction in total THMs and 89% in HAAs in 2 waters.[13] Switching chloramines/chloramines to ozone/chloramines also reduced THMs by 23 to 95% and HAAs by 8 to 59% in three waters.

TABLE 5.4
Effects of Ozone and Chloramines on DBP Formation

Combined disinfectants	TOC (mg/L)	THM (μg/L)	HAA6 (μg/L)
Prechlorine and postchlorine	3.2	225	146
Prechloramines and postchloramines	3.2	9.4	14
Preozone and postchloramines	2.9	3.2	8.7

Source: From Lykins, B.W., Koffsey, W.E., and Patterson, K.S., 1994, Alternative disinfectants for drinking water treatment, *Journal of Environmental Engineering*. Copyright ©1994, ASCE, with permission.

TABLE 5.5
Effects of Chloramination on DBP Reduction

Combined disinfectants	TOC (mg/L)	THM (%)	HAA (%)
Chlorine to ozone and chloramines	2.46	96	89
Chlorine to chloramines and chloramines	3.91	95	89
Chloramines to ozone and chloramines	2.46	95	80
Chloramines to ozone and chloramines	5.51	84	64
Chloramines to ozone and chloramines	3.91	23	8

Source: Reprinted from *Formation and Control of Disinfection By-Products in Drinking Water,* by permission. Copyright ©1999, American Water Works Association.

There are many other combinations of alternative disinfectants for DBP control. They are ozone/chlorine dioxide, UV/chloramines, and UV/chlorine dioxide. As an effective disinfection process for *Giardia* and *Cryptosporidium* inactivation, UV has attracted more attention in the water industry.

5.5 MEMBRANE TECHNOLOGIES

Many studies have been conducted on the use of membranes for DBP control in recent years. Nanofiltration is extremely effective in DBP precursor removal. With proper pretreatment, ultrafiltration and microfiltration are also effective in DBP precursor removal. Traditionally, membrane technology is used for groundwater treatment. The application of membrane filtration for surface water treatment has been increased since the 1990s. For surface water treatment, most membrane filtration systems require special pretreatment and post-treatment of water. The generation of membrane wastewater, or concentrate, also presents a new challenge for plant residual management and disposal. Due to their high capital and operation costs, membrane technologies are not identified as the best-available technologies for DBP control under the D-DBP regulation.

5.5.1 Pretreatment

Membrane fouling is a major operational problem for membrane filtration. Membrane fouling reduces water production and requires frequent membrane cleaning. Improving influent water quality is an effective way to control membrane fouling. Typical pretreatment processes for controlling membrane fouling include pH adjustment, acid or antiscalant addition, coagulant or polymer addition, turbidity or particulate reduction, NOM reduction, and disinfection. Nanofiltration commonly requires pretreatment with microfiltration and/or conventional water treatment processes, including coagulation, sedimentation, and filtration. It is important to point out that many of these pretreatment processes provide a good removal of DBP precursors. As shown in Figure 5.11, the overall removal of THM precursors for membrane A and membrane B processes were 99 and 95%, respectively.[14] However, 73% of THM precursors were removed during the pretreatment processes (microfiltration and dual media filtration).

For ultrafiltration and microfiltration, a proper pretreatment is essential for an effective removal of DBP precursors. Coagulation using alum and ferric salts is a common pretreatment process to enhance DBP precursor removal. Powdered activated carbon (PAC) adsorption is another common pretreatment process for ultrafiltration and microfiltration. Both coagulation and carbon adsorption could also improve membrane water production and minimize membrane fouling.

5.5.2 Post-Treatment

Low pH, low alkalinity, and high carbon dioxide content are typical characteristics for membrane treated water or filtrate. Because of it high corrosivity, membrane filtrates need to be stabilized before being delivered into distribution systems. Adding

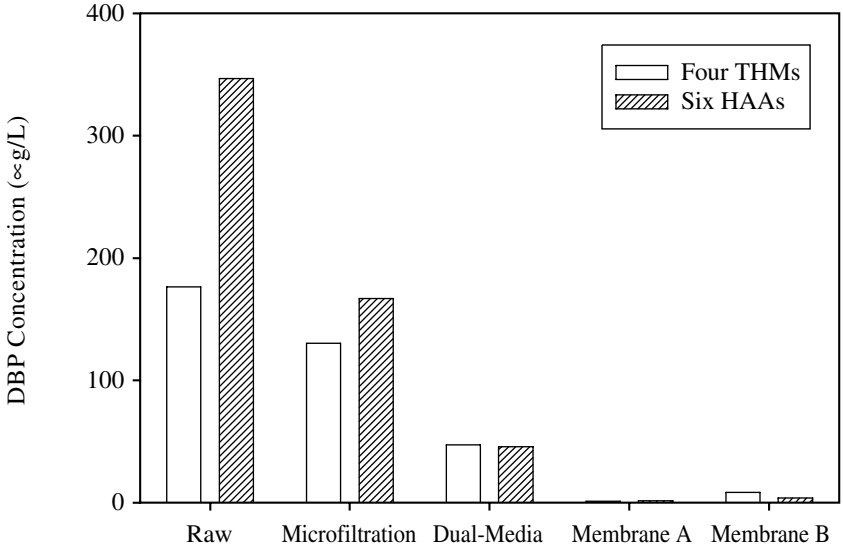

FIGURE 5.11 Removal of DBP precursors by microfiltration, conventional treatment, and nanofiltration. (From Chellam, S., Jacangelo, J.G., Bonacquisti, T.P., and Schauer, B.A., *J. Am. Water Works Assoc.*, 89(10), 77, 1997.)

alkali chemicals to raise water pH and convert carbon dioxide into bicarbonate alkalinity is a common post-treatment process. Disinfection with chlorine or other alternative disinfectants is another essential post-treatment process.

Mixing or blending membrane filtrate with nonmembrane treated water is a common post-treatment practice for many systems. Because of extreme high quality of the membrane filtrate, treating a portion of water and blending it with untreated water is an effective way to reduce the overall cost of membrane filtration. In addition, blending could provide an effluent with a proper alkalinity and pH and avoid post-treatment of membrane filtrate.

5.5.3 Waste Disposal

Waste disposal is a big concern for many membrane filtration facilities. Because of its quantity and waste strength, membrane wastewater, or reject, may have a big impact on ecological systems in the receiving stream. For a 10 mgd (million gallon per day) membrane facility with a 90% recovery and a 80% rejection of 100 mg/L chloride in feed water, it will produce a 1.11 mgd waste concentrate stream with a chloride level at 820 mg/L.[15] Disposal of this concentrate stream in sewer could easily upset the wastewater treatment processes. Stream discharge could have a significant impact on the ecological systems in the receiving stream. A National Pollution Discharge Elimination System (NPDES) permit is required for discharging membrane wastewater into surface waters.

5.6 COSTS OF DBP CONTROL TECHNOLOGIES

As discussed above, many technologies could be used for DBP control in finished water. Of all technologies, using chlorine as the primary disinfectant and chloramines as the secondary disinfectant generally has the lowest cost for both small and large water systems. One of the best available technologies, enhanced coagulation, is also very cost effective. GAC10, another best available technology (BAT), has a lower cost than membrane technologies, especially for medium and large systems, but a higher cost than chloramination and enhanced coagulation.

Table 5.6 presents the unit cost estimates in dollars (in 1998) for various DBP control technologies in various system size categories.[1] The unit costs are presented in dollar ($) per 1000 gallons produced, including operation, maintenance, and amortized capital costs. Four typical population size categories were presented. The unit costs for other categories can be found in the D-DBP Rule. Increasing the population size reduces the unit cost of all DBP control technologies. Chlorine/chloramines and enhanced coagulation have a low cost for various population sizes. Membrane technology could be a very cost-effective technology for very small water systems (population size, 25 to 100). However, it has the highest cost for large water systems (population size, >1 million). For ground water systems, the combination of chlorine/chloramines also has the lowest cost for various population sizes.

TABLE 5.6
Surface Water Systems Costs for DBP Control Technologies

DBP Control Technologies	Population Size Category			
	25–100	1K–3.3K	75K–100K	>1M
Chlorine/Chloramine	0.71	0.03	0.01	0.01
Enhanced coagulation (EC)	0.15	0.11	0.07	0.06
EC/Chloramine	0.87	0.14	0.08	0.07
Ozone/Chloramine	12.67	0.52	0.08	0.04
EC + ozone, chloramine	12.82	0.63	0.15	0.10
EC + GAC 10	6.24	0.81	0.29	0.16
EC + GAC 20	14.11	2.45	0.90	0.41
Chlorine dioxide	24.33	0.64	0.06	0.04
Membranes	3.40	2.65	0.87	0.87

Source: Data from United States Environmental Protection Agency, National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts; Final Rule, Federal Register, 63:69390, 2001.

Note: $ per thousand gallons produced (K = thousand, M = million).

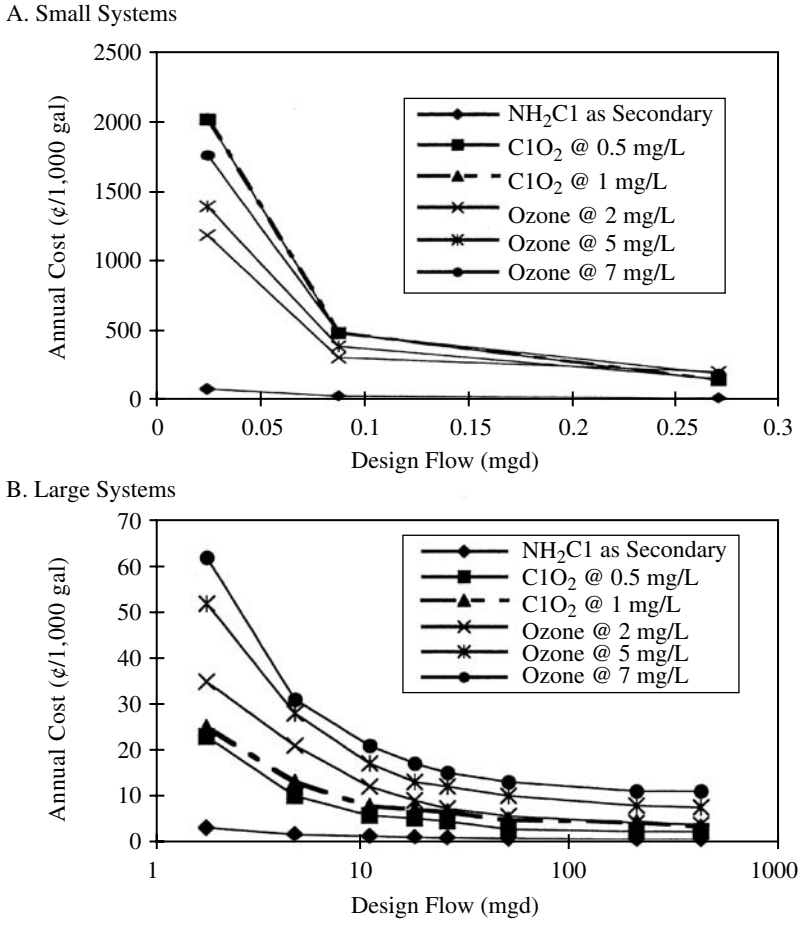

FIGURE 5.12 Upgrade cost of using alternative disinfectants. (Reprinted from *Formation and Control of Disinfection By-Products in Drinking Water*, by permission. Copyright ©1999, American Water Works Association.)

Figure 5.12 illustrates the upgrade cost of using alternative disinfectants for DBP control.[16] The unit cost includes amortized capital cost, operation, and maintenance cost. Chloramines as the secondary disinfectant has the lowest cost for both small and large systems. Chlorine dioxide has the highest cost for small systems and ozone has the highest cost for large systems. For DBP precursor or NOM removal, the unit costs of various technologies are shown in Figure 5.13.[16] Increasing coagulant dosage, or enhanced coagulation, has the lowest cost for both small and large water systems. GAC adsorption has the highest cost for small water systems and nanofiltration has the highest cost for very large water systems (20 mgd).

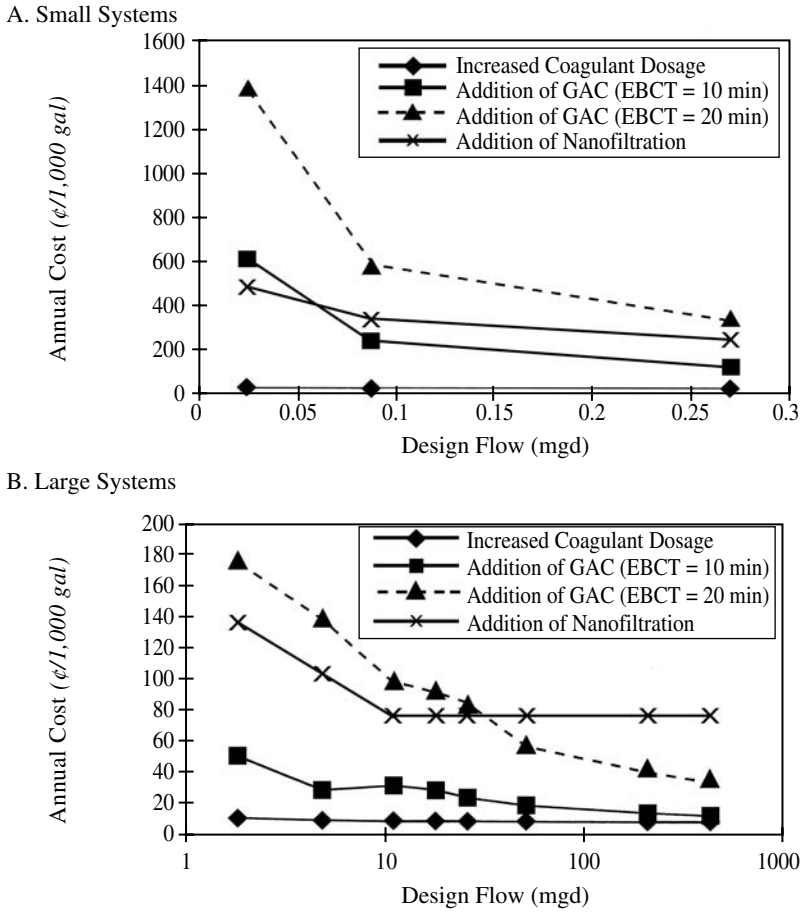

FIGURE 5.13 Upgrade cost of improved NOM removal. (Reprinted from *Formation and Control of Disinfection By-Products in Drinking Water*, by permission. Copyright ©1999, American Water Works Association.)

The application of membrane in drinking water treatment has been significantly increased in recent years. Both capital cost and maintenance and operation cost have been reduced. Nevertheless, membrane is an expensive technology for DBP control, especially for large water systems.

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6 Inorganic Disinfection Byproducts

OBJECTIVES

The objective of this chapter is to provide an overview of inorganic disinfection byproducts (DBPs), including bromate, chlorite, and chlorate. The formation mechanisms and control strategies for these inorganic DBPs are discussed. As a group of inorganic compounds, their formation and control are significantly different from organic DBPs.

NOMENCLATURE

DBP disinfection byproduct
D-DBP disinfectants and disinfection byproducts
DOC dissolved organic carbon
NOM natural organic matter
U.S. EPA United States Environmental Protection Agency

In addition to trihalomethanes and haloacetic acids, two inorganic DBPs, bromate and chlorite, are regulated under the Stage 1 Disinfectants and Disinfection Byproducts (D-DBP) Rule. Bromate is a common DBP in ozonated water high in bromide. Chlorite is a degradation byproduct of chlorine dioxide.

6.1 BROMATE

Under the Stage 1 D-DBP Rule, bromate is regulated at a maximum contaminant level of 10 μg/L.[1] Due to the occurrence of bromide in many surface and ground water sources, the formation of bromate causes significant concern when ozonation is considered for water disinfection.

6.1.1 Formation of Bromate

6.1.1.1 Formation Mechanisms

Inorganic bromide reacts with ozone to form hypobromite and other bromite-containing intermediate products. Further reactions between ozone and hypobromite or other intermediate products result in the formation of bromate. Many models have been developed to illustrate the bromate formation pathways or mechanisms.

There are three major pathways for bromate formation in ozonated water, including molecular ozone, hydroxyl radical, and direct/indirect mechanisms.[2] A clear understanding of all three pathways is important to the formation and control of bromate in ozonated water. The molecular ozone pathway involves the reactions between ozone and bromide or bromine-containing intermediate products, as shown in Equations 6.1 to 6.3.

$$Br^- + O_3 \rightarrow BrO^- \quad (6.1)$$

$$BrO^- + O_3 \rightarrow BrO_2^- \quad (6.2)$$

$$BrO_2^- + O_3 \rightarrow BrO_3^- \quad (6.3)$$

The hydroxyl radical pathway involves the reactions between hydroxyl radical, an ozone decomposition product, and bromide or bromine-containing intermediate products, as shown in Equations 6.4 to 6.8.

$$Br^- + OH\cdot \rightarrow Br\cdot \quad (6.4)$$

$$Br\cdot + O_3 \rightarrow BrO\cdot \quad (6.5)$$

$$BrO\cdot + OH\cdot \rightarrow BrO_2^- \quad (6.6)$$

$$BrO_2^- + OH\cdot \rightarrow BrO_2\cdot \quad (6.7)$$

$$BrO_2\cdot + OH\cdot + O_3 \rightarrow BrO_3^- \quad (6.8)$$

The third pathway, direct/indirect pathway, involves the following reactions,[3] as shown in Equations 6.9 to 6.11.

$$Br^- + O_3 \rightarrow BrO^- \quad (6.9)$$

$$BrO^- + OH\cdot \rightarrow BrO\cdot \quad (6.10)$$

$$BrO\cdot + OH\cdot \rightarrow BrO_2^- \quad (6.11)$$

$$BrO_2^- + OH\cdot \rightarrow BrO_2\cdot \quad (6.7)$$

$$BrO_2\cdot + OH\cdot + O_3 \rightarrow BrO_3^- \quad (6.8)$$

These multiple pathways to the formation of bromate are summarized in Figure 6.1.[4]

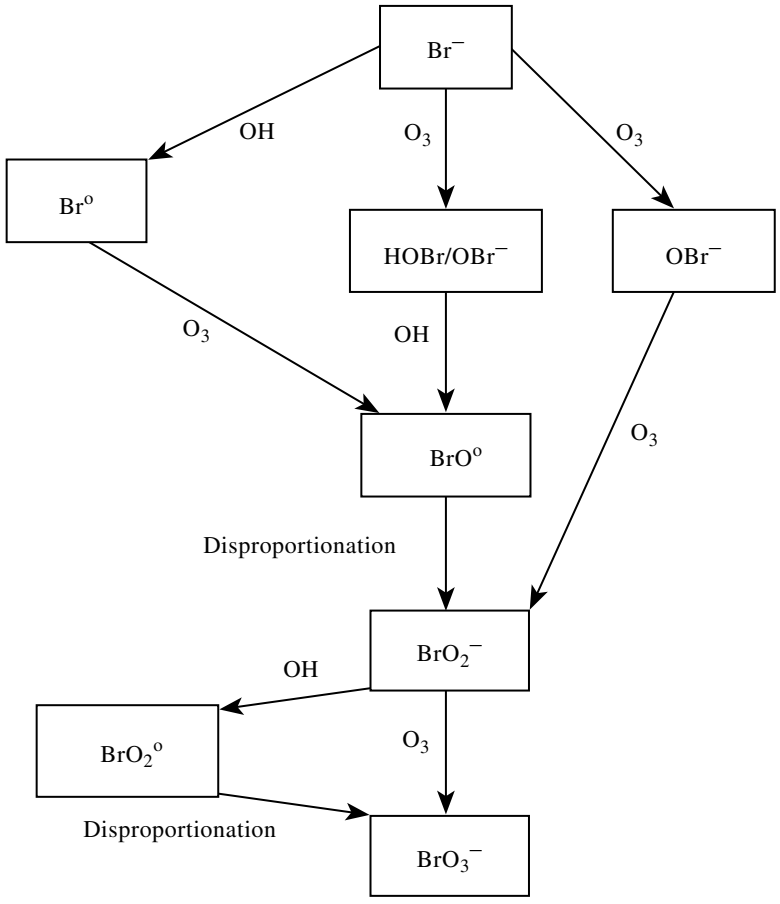

FIGURE 6.1 Multiple pathways to the formation of bromate. (Reprinted from *Formation and Control of Disinfection By-Products in Drinking Water,* by permission. Copyright ©1999, American Water Works Association.)

6.1.1.2 Effect of Bromide Concentration

As illustrated by the bromate formation mechanisms, the formation of bromate is greatly affected by the bromide concentration. In general, increasing bromide level increases the formation of bromate and decreasing bromide level decreases the formation of bromate. The effect of bromide on the formation of bromate is illustrated in Figure 6.2.

In this study, the formation of bromate was investigated in three synthetic water samples prepared with natural organic matter (NOM) isolates at three bromide levels, 0.1, 0.4, and 1.0 mg/L.[5] As one can see in Figure 6.2, increasing bromide levels increases the concentrations of bromate proportionally. There is a threshold level of bromide concentration for bromate formation. Below this threshold no bromate formation is detected. This threshold concentration depends on ozone dosage, NOM,

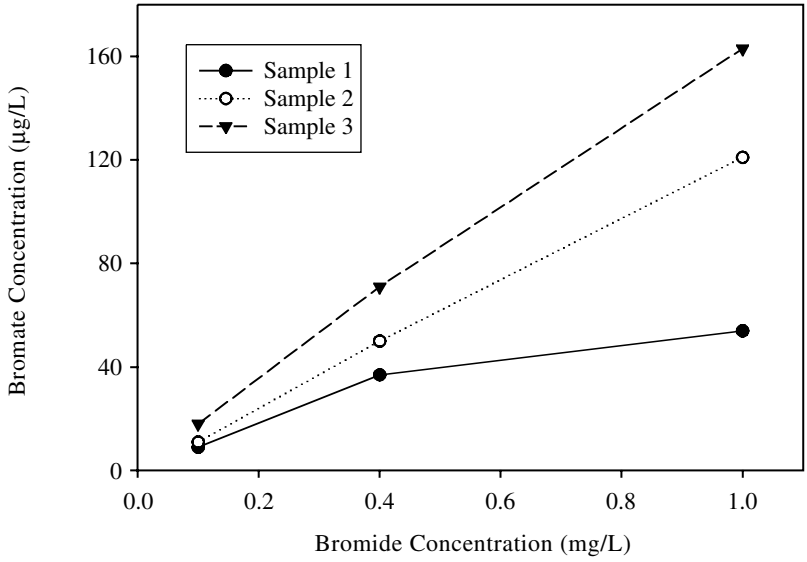

FIGURE 6.2 Effects of bromide concentration on the formation of bromate. (From Song, R., Minear, R., Westerhoff, P., and Amy, G., Ozone-bromide interactions with NOM separated by XAD-8 resin and UF/RO membrane methods, in *Disinfection By-Products in Water Treatment*, Minear, R.A. and Amy, G.L., Eds., Lewis Publishers, Boca Raton, FL, 1996.)

pH, and alkalinity of the water.[6] Typical threshold concentrations vary between 0.1 mg/L and 0.3 mg/L.

6.1.1.3 Ozone Dosage

As illustrated by the bromate formation pathways, bromate formation in ozonated water is also greatly affected by ozone dosage. Increasing ozone dosage increases the formation of bromate if bromide is not fully consumed, as shown in Figure 6.3. At both pH conditions, increasing ozone dosage increased the formation of bromate. An ozone threshold concentration was also reported.[6] Below the threshold concentration, no bromate formation occurs. In the pretreated surface water, ozone threshold was reported at 1 mg/L.[6]

6.1.1.4 Effect of pH

In general, a higher pH leads to a higher bromate formation. As shown in Figure 6.4, increasing ozonation pH significantly increases the formation of bromate. Four different NOM isolates were used in the study.[7] For sample 1, the bromate level was increased from 22 µg/L at pH 6.5 to 62 µg/L at pH 8.5. For sample 4, the bromate level was increased from 43 µg/L at pH 6.5 to 89 µg/L at pH 8.5.

As shown in Equation 6.12, the equilibrium between hypobromite ion and hybromous acid is regulated by pH. At pH < 8.7, hypobromous acid is the predominant species. At pH > 8.7, OBr^- is the predominant species. Because the reaction

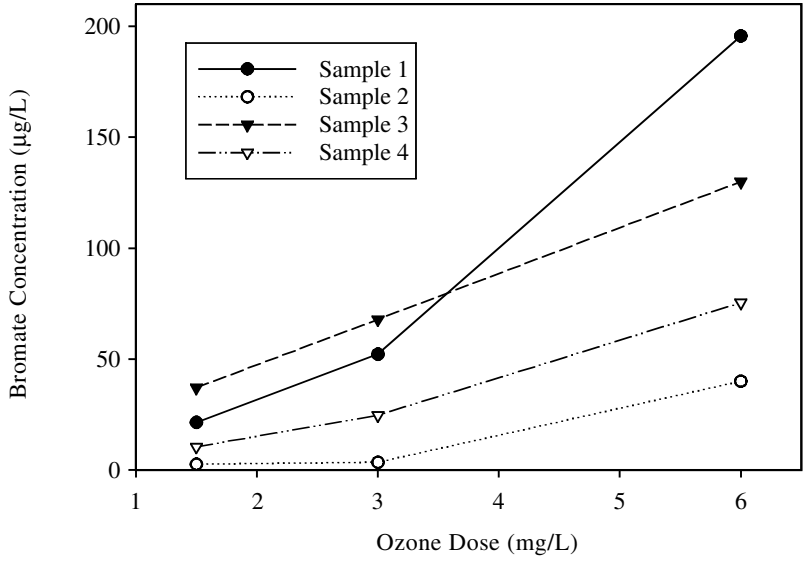

FIGURE 6.3 Effects of ozone dosage on bromate formation. (From Song, R., Westerhoff, P., Minear, R., and Amy, G., Bromate minimization during ozonation, *J. Am. Water Works Assoc.*, 89(6), 69, 1997.)

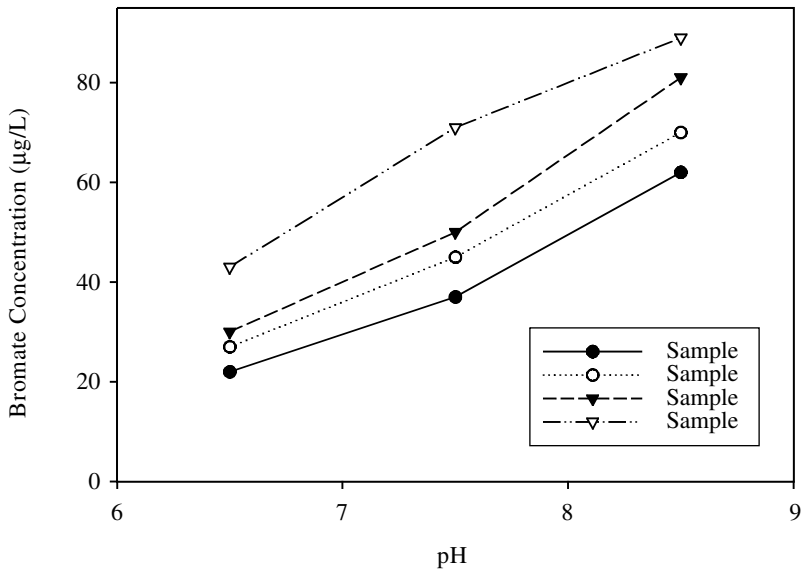

FIGURE 6.4 Effects of pH on bromate formation. (From Song, R., Minear, R., Westerhoff, P., and Amy, G., Ozone-bromide interactions with NOM separated by XAD-8 resin and UF/RO membrane methods, in *Disinfection By-Products in Water Treatment*, Minear, R.A. and Amy, G.L., Eds., Lewis Publishers, Boca Raton, FL, 1996.)

between O_3 and OBr^-, as shown in Equation 6.3, is much faster than that between O_3 and HOBr,[8] a higher pH will result in a higher level of bromate formation.

$$H^+ + OBr^- = HOBr \qquad pK_a = 8.7 \tag{6.12}$$

$$3O_3 + H_2O = 2OH\cdot + 4O_2 \tag{6.13}$$

In addition, a higher pH also results in a higher level of HO radical formation, as shown in Equation 6.13. Increasing the level of hydroxyl radical, OH·, increases the degradation of ozone and the formation of bromate, as shown in Equations 6.4 to 6.8. In natural waters, a higher pH indicates a higher alkalinity. A high level of bicarbonate ions stabilizes the degradation of ozone and favors a high level of bromate formation through the molecular ozone pathway.

6.1.1.5 Effect of Natural Organic Matter

NOM affects the formation of bromate in a number of ways. First, increasing the level of NOM increases the ozone dosage required, thus the formation of bromate. Ozone dose is commonly determined by the ratio of ozone dosage to dissolved organic carbon (DOC). Due to the reaction between NOM and ozone, a proper ozone dosage to DOC ratio is required to achieve the desired ozone residual or CT value (see Chapter 10). Second, the source of NOM affects the formation of bromate. As shown in Figure 6.3, at pH 8.5 the level of bromate was 40 μg/L in sample 2 and 196 μg/L in sample 1. These samples were prepared with 3 mg/L of NOM from various sources. Third, NOM affects the mechanism of bromate formation. Hydroxyl radical pathway is the predominant pathway for bromate formation in NOM containing natural waters. Fourth, the reaction between ozone and NOM may produce a high level of ozonation byproducts, including formate, acetate, and oxalate, as discussed in Chapter 1. These ozonation byproducts are radical scavengers and can react with hydroxyl radicals to inhibit the formation of bromate. In summary, because of the predominance of hydroxyl radical pathway in NOM water, a higher level of NOM may reduce the formation of bromate formation.[6]

6.1.1.6 Effect of Ammonia

Ammonia reacts with BrO^- and HBrO to form the combined bromine, bromamines, as shown in Equations 6.14 and 6.15.

$$NH_3 + HBrO = NH_2Br + H_2O \tag{6.14}$$

$$NH_2Br + HBrO = NHBr_2 + H_2O \tag{6.15}$$

By consuming BrO^- and HBrO, addition of ammonia in ozonated water could inhibit the formation of bromate. As shown in Figure 6.5, the addition of 85 μg/L of ammonia reduced bromate formation from 37, 45, and 71 μg/L to 32, 36, and 48 μg/L in three NOM isolate solutions, respectively.[5] In natural water, however,

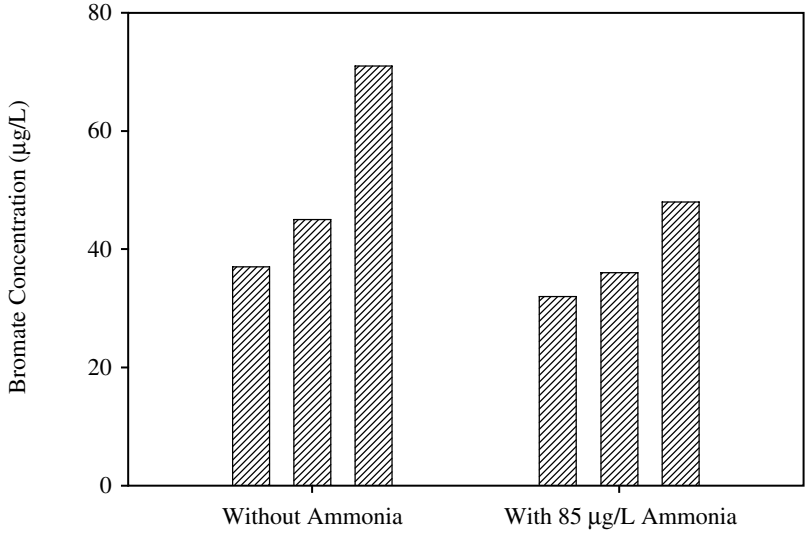

FIGURE 6.5 Effects of ammonia on bromate formation. (From Song, R., Minear, R., Westerhoff, P., and Amy, G., Ozone-bromide interactions with NOM separated by XAD-8 resin and UF/RO membrane methods, in *Disinfection By-Products in Water Treatment*, Minear, R.A. and Amy, G.L., Eds., Lewis Publishers, Boca Raton, FL, 1996.)

ammonia addition for bromate formation control is not as obvious as shown in Figure 6.5. This indicates that hypobromite and hypobromous acid may play very limited roles in bromate formation. The effect of ammonia on bromate formation also depends on NOM concentrations and pH levels.

6.1.1.7 Effect of H_2O_2 Addition

Hydrogen peroxide (H_2O_2) is commonly used with ozonation to enhance the removal of taste and odor compounds, pesticides, herbicides, and other synthetic organics. Hydroperoxide ion (HO_2^-), dissociated from hydrogen peroxide, can react with molecular ozone to produce the superoxide ion (O_2^-) and the hydroxyl radical (OH·), as shown in Equations 6.16 and 6.17.

$$H_2O_2 = HO_2^- + H^+ \tag{6.16}$$

$$HO_2^- + O_3 = OH\cdot + O_2^- + O_2 \tag{6.17}$$

The hydroxyl radical and superoxide ion can participate in the ozone decomposition cycle and result in an accelerated hydroxyl radical production and ozone decomposition.[6] This leads to a lower dissolved ozone concentration and a lower bromate formation. By lowering the ozone concentration, hydrogen peroxide could significantly affect the ozonation disinfection efficiency. Hydrogen peroxide could also react with hypobromite (OBr^-) and produce Br^- and O_2, as shown in Equation 6.18. This will lead to a reduction of the bromate formation.[9]

$$OBr^- + H_2O_2 = Br^- + O_2 + H_2O \quad (6.18)$$

6.1.2 Bromate Removal and Control

Controlling ozone treatment process to reduce production of bromate is identified as the best available technology for bromate compliance under the Stage 1 D-DBP Rule.[1] Bromate formation could be minimized by pH depression, reducing ozone residual, ammonia addition, and H_2O_2 addition. Bromate can also be removed after its formation using various technologies, including granular activated carbon, biologically active carbon, and ferrous iron reduction.[6]

Reducing ozone residual is an effective way to minimize the formation of bromate in ozonated water. However, reducing ozone residual may affect ozonation disinfection efficiency and compromise the specific objectives of the ozonation treatment. Proper dosing and staging the ozonation processes may be used to balance the ozone treatment efficiency and bromate formation. For a two-stage ozonation process, the overall ozone residual can be reduced by adding more ozone in the first stage and less in the second stage.[4] A 40% reduction of bromate was obtained using this approach, as compared to splitting the overall dose evenly between the two stages.

Bromate formation can also be reduced by pH depression. For pre- or intermediate ozonation, pH depression could benefit both bromate control and enhanced coagulation. For postozonation, however, pH depression could compromise corrosion control in the distribution systems. For highly alkaline water, pH depression may require a high dose of acid. This could significantly increase the cost of ozonation treatment.

Bromate can be removed after its formation using various technologies. These technologies include biodegradation using biologically active carbon or chemical reduction using granular activated carbon, ferrous, or sulfite. Biologically active carbon is commonly used after ozonation for biodegradable organic removal. Biological degradation of bromate on the surface of biologically active carbon could provide a solution for bromate removal in finished water.[10] Ferrous reduction can be used to remove bromate produced by preozonation.[11] Ferrous reduction produces ferric precipitates and should be used before sedimentation.

6.2 CHLORITE

Chlorite is a degradation byproduct of chlorine dioxide in drinking water. Because of its developmental neurotoxicity and other adverse health effects, chlorite has been regulated at a maximum contamination level of 1 mg/L under the Stage 1 D-DBP Rule.[1]

6.2.1 Formation of Chlorite

Chlorine dioxide can be reduced to chlorite by reacting with many organic and inorganic reducing compounds in water, as shown in Equation 6.19.

$$ClO_2 + e = ClO_2^- \quad (6.19)$$

In water treated with chlorine dioxide, the formation of chlorite is directly proportional to the degradation of chlorine dioxide, as shown in Figure 6.6. Regardless of the total organic carbon (TOC) concentrations, pH values, and reaction times, the chlorite concentration is approximately 70% of chlorine dioxide added,[12] as shown in Figure 6.7.

The chlorite water treated with chlorine dioxide could also come from the chlorine dioxide stock solution, especially in those generated with chlorite, as shown in Equations 6.20 to 6.22.[13] Incomplete reactions could lead to an elevated level of

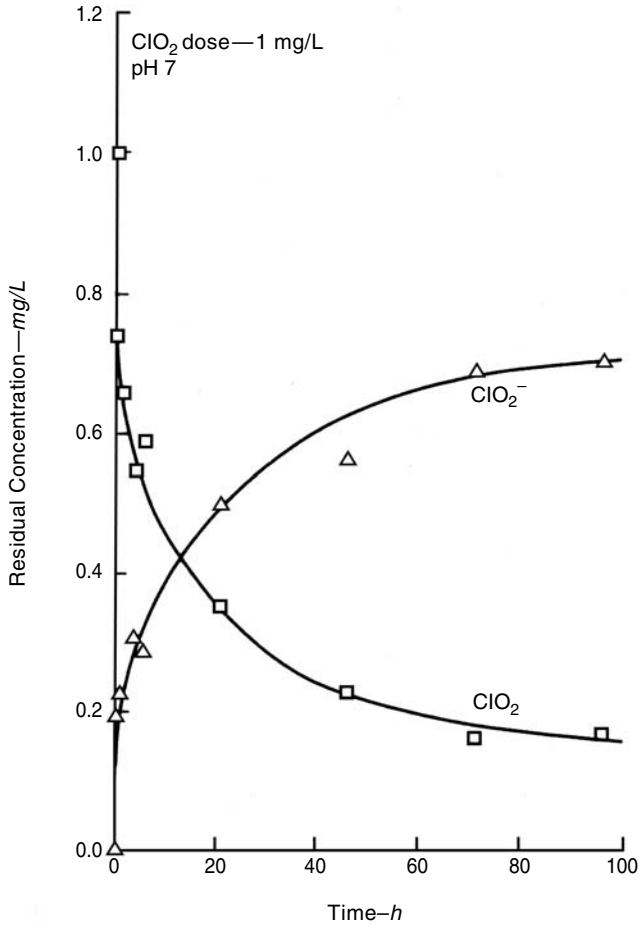

FIGURE 6.6 Chlorine dioxide consumption and chlorite formation in diluted finished water (TOC = 1 mg/L, ClO_2 dose = 1 mg/L, and pH = 7). (Reprinted from *J. Am. Water Works Assoc.,* 79(9) (September 1987), by permission. Copyright ©1987, American Water Works Association.)

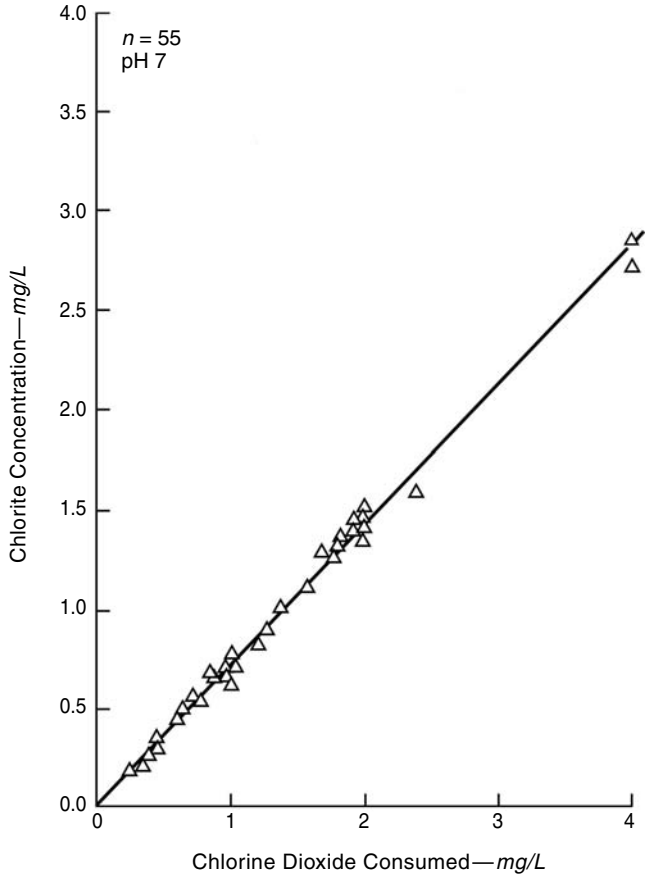

FIGURE 6.7 Chlorite residual resulting from various chlorine dioxide treatment. (Reprinted from *Journal AWWA,* 79(9) (September 1987), by permission. Copyright ©1987, American Water Works Association.)

chlorite in chlorine dioxide solution and result in a high level of chlorite in chlorine dioxide treated water.

$$2NaClO_2 + Cl_{2(g)} = 2ClO_{2(g)} + 2NaCl \tag{6.20}$$

$$2NaClO_2 + HOCl = 2ClO_{2(g)} + NaCl + NaOH \tag{6.21}$$

$$5NaClO_2 + 4HCl = 2ClO_{2(g)} + 2H_2O + 5NaCl \tag{6.22}$$

6.2.2 Chlorite Removal and Control

Because of the direct relationship between chlorite levels in water and chlorine dioxide doses, controlling chlorine dioxide dosage has been identified as the best available

technology for chlorite control under the Stage 1 D-DBP Rule.[1] Because 50 to 70% of chlorine dioxide ends as chlorite, many water utilities use a chlorine dioxide dose below 1.5 mg/L to comply with the 1 mg/L maximum contaminant level for chlorite. Another way for chlorite control is to control the chlorite level in chlorine dioxide solution by optimizing chlorine dioxide generation. This could be done by properly operating chlorine dioxide generators. Like bromate, biodegradation using biologically active carbon and chemical reduction using granular activated carbon, ferrous or sulfite could be used to remove chlorite in chlorine dioxide treated water.

6.3 CHLORATE

Chlorate is another inorganic DBP commonly detected in finished water. It is a degradation byproduct of the hypochlorite (ClO^-) solution and may be produced by the reaction between chlorine dioxide and ozone or chlorine. Chlorate (ClO_3^-) is not regulated under the Stage 1 D-DBP Rule. Because of its potential health risks, however, chlorate was monitored under the Information Collection Rule.[14] A 200 μg/L for chlorate has been proposed in Switzerland as a tolerance limit and by the World Health Organization as a guideline value.[15]

6.3.1 Formation of Chlorate

Hypochlorite stock solution is the main source of chlorate in finished waters. The formation of chlorate involves the degradation of hypochlorite, as shown in Equations 6.23 and 6.24. The formation of chlorate depends on the concentration, pH, and temperature of the hypochlorite solution. The concentration of transition metal ions and sunlight exposure also affect the decomposition of hypochlorite.[16]

$$2ClO^- = ClO_2^- + Cl^- \tag{6.23}$$

$$ClO^- + ClO_2^- = ClO_3^- + Cl^- \tag{6.24}$$

In general, a higher hypochlorite concentration leads to a higher formation of chlorate. For hypochlorite stock solution used for water chlorination, typical hypochlorite concentration could be as high as 150,000 mg/L (as chlorine). The high level of hypochlorite concentration could lead to a high level of chlorate formation during the manufacture and storage of the hypochlorite solution. A survey of 14 water utilities found that chlorate concentrations in hypochlorite solutions ranged between 200 mg/L and 50,000 mg/L. The chlorate levels in finished waters ranged between 10 and 660 μg/L.[17]

Lowering the pH of hypochlorite solution also enhances the degradation of hypochlorite and the formation of chlorate. This is due to the higher degradation rate of hypochlorous acid. Increasing the temperature of the hypochlorite solution also increases the degradation of hypochlorite and results in a high level of chlorate. Shortening the storage time could significantly reduce the formation of chlorate in the hypochlorite solutions.

Chlorate is also commonly detected in chlorine dioxide solutions, especially in those generated with chlorate, as shown in Equation 6.25. Chlorite, a degradation product of chlorine dioxide, also reacts with chlorine or ozone to form chlorate.

$$2NaClO_3 + H_2O_2 + H_2SO_4 = 2ClO_2 + O_2 + Na_2SO_4 + 2H_2O \qquad (6.25)$$

6.3.2 Chlorate Removal and Control

Chlorate is stable in finished water and not readily removed by common treatment processes. For water utilities using hypochlorite solution instead of gaseous chlorine for chlorination, the key is to control the chlorate formation in the hypochlorite stock solution.[16] Because hypochlorite solution addition is based on its chlorine content or concentration, the ratio between chlorate concentration and chlorine concentration should be used to assess the quality of the hypochlorite stocks. One of the quick assessment methods is to measure the chlorine concentration in the solution. If the actual chlorine concentration is significantly lower than that specified, a high level of chlorate in the solution is expected.

Because of the hypochlorite degradation and chlorate formation during storage, water utilities should avoid storing the hypochlorite for prolonged periods and have more frequent chemical delivery, especially during summer months. Lowering the temperature in the hypochlorite storage area is another way to limit the formation of chlorate.

Because of the relative stability of chlorate in drinking water, chlorate cannot be effectively removed by existing water treatment processes. Preventing chlorate formation is the best approach to control chlorate in finished water.

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7 Disinfection Byproduct Regulations

OBJECTIVES

The focus of this chapter is to outline the major disinfection byproduct regulations, including Total Trihalomethane Rule, Information Collection Rule, Stage 1 Disinfectant and Disinfection Byproducts Rule, and the upcoming Stage 2 Disinfectant and Disinfection Byproducts Rule. In addition, other disinfection byproduct related regulations are discussed as well. They are Surface Water Treatment Rule, Interim Enhanced Surface Water Treatment Rule, Filter Backwash Recycling Rule, Long Term 1 Enhanced Surface Water Treatment Rule, Long Term 2 Enhanced Surface Water Treatment Rule, and Ground Water Rule. To precisely describe these regulations, many sentences are the exact sentences from the United States Environmental Protection Agency regulation documents.

NOMENCLATURE

DBP disinfection byproduct
DBPR Disinfectants and Disinfection Byproducts Rule
FBRR Filter Backwash Recycling Rule
GAC granular activated carbon
GWR Ground Water Rule
ICR Information Collection Rule
IDSE initial distribution system evaluation
IESWTR Interim Enhanced Surface Water Treatment Rule
LRAA locational running annual averages
LT1SWTR Long Term 1 Enhanced Surface Water Treatment Rule
LT2SWTR Long Term 2 Enhanced Surface Water Treatment Rule
MCL maximum contaminant level
MCLG maximum contaminant level goal
MRDL maximum residual disinfectant level
MRDLG maximum residual disinfectant level goal
RAA running annual average
SWTR Surface Water Treatment Rule
THM trihalomethane
TOC total organic carbon
U.S. EPA United States Environmental Protection Agency

Since the discovery of trihalomethanes (THMs) in chlorinated drinking water in the 1970s, the United States Environmental Protection Agency (U.S. EPA) has promulgated several regulations to monitor and control disinfection byproducts. Major regulations are Total Trihalomethane (TTHM) Rule, Information Collection Rule, and Stage 1 Disinfectants and Disinfection Byproducts Rule. The Stage 2 Disinfectants and Disinfection Byproducts Rule is currently under development. In conjunction with disinfection byproduct (DBP) regulations, especially Disinfectants and Disinfection Byproducts Rule, other regulations were also promulgated or proposed to balance the chemical and microbial risks in drinking water.

7.1 TOTAL TRIHALOMETHANE RULE

The TTHM Rule[1] was promulgated in November 1979 by the U.S. EPA. Under this rule, an interim maximum contaminant level (MCL) of 100 μg/L was established for TTHMs, including chloroform, bromodichloromethane, chlorodibromomethane, and bromoform in finished drinking water. A running annual average of the quarterly averages of all samples, collected at various locations in the distribution systems, was used for compliance. The TTHM Rule applied to any community water system using surface or groundwater, serving at least 10,000 people, and adding a disinfectant to the drinking water during any part of the treatment process. The final regulation did not specify any technology for THM removal and control.

In 1983, U.S. EPA promulgated regulations specifying best technologies generally available for obtaining variances, or permissions not to meet a certain drinking water standard.[2] For the TTHM Rule, the best technologies include chloramination, using chlorine dioxide, THM precursor reduction by improving existing clarification, eliminating prechlorination, and using powdered activated carbon. Other best technologies, which were not "generally available" at that time, were also specified. They were off-line water storage for THM precursor reduction, THM reduction by aeration, clarification, alternative raw water sources, and ozonation.

7.2 INFORMATION COLLECTION RULE

The Information Collection Rule (ICR)[3] was promulgated in May 1996. The purpose of this rule was to collect information on the occurrence and control of microbial pathogens and DBPs in drinking water. The ICR applied to three types of public water systems, including surface water systems serving more than 100,000 people, groundwater serving more than 100,000 people, and groundwater serving 50,000 to 100,000 people. The duration of the rule was 18 months. There were three ICR requirements. They were monitoring for DBP and related parameters, monitoring for disease-causing microorganisms and microbial indicators, and treatment studies.

The DBP monitoring required water systems serving more than 100,000 people to monitor four THMs, six haloacetic acids (HAAs), and six other halogenated DBPs within the treatment plants and distribution systems, as shown in Table 7.1. The rule also required monitoring for bromate and aldehydes by water systems using ozone, cyanogen chloride by chloramines systems, and chlorite by chlorine dioxide systems.

TABLE 7.1
Information Collection Rule Monitoring Summary

Monitoring Type	Contaminants or water quality parameters
DBPs	THMs, haloacetic acids, chloral hydrate, haloacetonitriles, haloacetones, chloropicrin, bromate (ozone), aldehydes (ozone), cyanogen chloride (chloramines), and chlorite (chlorine dioxide)
Microbial	*Cryptosporidium*, *Giardia*, total culturable viruses, total coliforms, and fecal coliforms or *Escherichia coli* (*E. coli*)
Others	Total organic carbon (TOC), ultraviolet absorbance (UV), specific ultraviolet absorbance (SUVA), assimilable organic carbon (AOC), and biodegradable organic carbon (BDOC)

Source: Data from United States Environmental Protection Agency, *Federal Register,* 61, 24354, 1996.

The microbial monitoring required surface water systems serving more than 100,000 people to monitor their source water at the intake for *Cryptosporidium*, *Giardia*, total culturable viruses, total coliforms, and fecal coliforms or *Escherichia coli* (*E. coli*), as shown in Table 7.1. ICR also required these systems to monitor their finished water for these microorganisms when *Cryptosporidium* and *Giardia* exceed 10 per liter or total culturable virus exceed one per liter in the source water.

The treatment studies required all three types of water systems to monitor total organic carbon (TOC) and determine their treatment study applicability. It also required water systems to conduct bench- and/or pilot-scale treatment studies to determine the effectiveness of granular activated carbon or membranes for DBP precursor and TOC removal. U.S. EPA also published its treatment study protocol *Manual for Bench- and Pilot-Scale Treatment Studies* to aid water systems to select appropriate protocols for their studies.

A total of 296 water systems were involved in the ICR monitoring. The information on the occurrence of DBPs and microbial pathogens was compiled into an ICR database. The database is available on line at the U.S. EPA web site at: http://www.epa.gov/enviro/html/icr/index.html

One can retrieve DBP and microbial pathogens occurrence information for each participating water system and plant. The national levels for these DBPs and microbial pathogens are also available in the database.

7.3 DISINFECTANTS AND DISINFECTION BYPRODUCTS RULE

The Stage 1 Disinfectants and Disinfection Byproducts Rule (Stage 1 DBPR)[4] was promulgated by the U.S. EPA on December 18, 1999. This rule applies to all sizes of community water systems and nontransient noncommunity water systems that add a disinfectant to their drinking water, and transient noncommunity water systems that use chlorine dioxide. The Stage 1 DBPR covers many areas including DBP

monitoring and reporting, best-available technologies for DBP control, and enhanced coagulation provisions, as described in the following list.

1. Maximum residual disinfectant level goals (MRDLGs) and maximum residual disinfectant levels (MRDLs). The U.S. EPA sets MRDLGs and MRDLs for three common disinfectants, including chlorine, chloramines, and chlorine dioxide, as shown in Table 7.2.
2. Maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs). The U.S. EPA sets MCLGs and MCLs for four groups of DBPs, including four THMs, five HAAs, chlorite, and bromate, as shown in Table 7.3. As discussed in previous chapters, THMs and HAAs are chlorination and chloramination DBPs. Bromate is an ozonation DBP, and chlorite is a chlorine dioxide degradation byproduct. The compliance is based on the running annual average levels. Subsequently, the zero MCLG for chloroform was removed from its National Primary Drinking Water

TABLE 7.2
Maximum Residual Disinfectant Level Goals (MRDLGs) and Maximum Residual Disinfectant Levels (MRDLs) for Various Disinfectants

Disinfectant Residual	MRDLG (as Cl_2) (mg/L)	MRDL (as Cl_2) (mg/L)
Chlorine	4	4.0
Chloramine	4	4.0
Chlorine dioxide	0.8	0.8

Source: Data from United States Environmental Protection Agency, *Federal Register*, 63, 69392, 1998.

TABLE 7.3
Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs) for DBPs

DBPs	MCLG (μg/L)	MCL (mg/L)
Total trihalomethanes	N/A	0.080
Chloroform	0	
Bromodichloromethane	0	
Dibromochloromethane	60	
Bromoform	0	
Haloacetic acids (HAA5)	NA	0.060
Dichloroacetic acid	0	
Trichloroacetic acid	300	
Chlorite	800	1.0
Bromate	0	0.010

Source: Data from United States Environmental Protection Agency, *Federal Register*, 63, 69392, 1998.

Regulations by U.S. EPA, effective May 30, 2000, in accordance with an order of the U.S. Court of Appeals for the District of Columbia Circuit.[5] A MCLG of 0.070 mg/L is likely proposed in the Stage 2 Disinfectants and Disinfection Byproducts Rule.

3. Treatment techniques for DBP precursor removal. To better control DBP formation, the rule specifies the removal requirements for DBP precursors (natural organic matter) measured as TOC. A treatment technique using enhanced coagulation or enhanced softening is specified. Because enhanced coagulation is generally performed at low pH conditions, as discussed in Chapter 5, the natural alkalinity in water significantly affects the TOC removal and coagulant dosage requirement. The TOC removal requirements are based on source water alkalinity, as shown in Table 7.4. Another best available technology is GAC 10. The rule specifies the granular activated charcoal (GAC) empty bed contact time of 10 min and GAC reactivation frequency of no more than 6 months.
4. Best available technologies (BATs) for disinfectants and DBPs. To better control chlorite and disinfectants residuals of chlorine, chloramines, and chlorine dioxide, the rule specifies the BATs as control of treatment processes to reduce disinfectant demand and control of disinfection processes to reduce disinfectant dosage. The best available technologies for THM and HAA control are enhanced coagulation, enhanced softening, or GAC 10. For bromate control, the BAT is to control ozonation process.
5. Analytical methods and laboratory certification criteria. The rule lists the approved analytical methods for DBPs and other related water quality parameters. For DBP monitoring there are three methods each for THMs, HAAs, and chlorite, and one method for bromate. The rule also lists laboratory certification criteria for monitoring disinfectants and DBPs. More information on DBP analytical methods will be discussed in Chapter 8.

TABLE 7.4
Required Total Organic Carbon (TOC) Removal (%) by Enhanced Coagulation and Enhanced Softening

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	0–60	>60–120	>120
> 2.0–4.0	35.0	25.0	15.0
> 4.0–8.0	45.0	35.0	25.0
> 8.0	50.0	40.0	30.0

Source: Data from United States Environmental Protection Agency, *Federal Register*, 63, 69392, 1998.

7.4 STAGE 2 DISINFECTANTS AND DISINFECTION BYPRODUCTS RULE

The final Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR) was scheduled to be published in May 2002. This promulgation date has been delayed. At the present time, U.S. EPA has published several documents to unveil the major components of the Stage 2 Disinfectants and Disinfection Byproducts Rule. One of these documents is the Stage 2 Microbial and Disinfection Byproducts Federal Advisory Committee Agreement in Principle.[6] This rule will reduce exposure to peak DBP levels in the distribution systems. It will apply to all community water systems and nontransient noncommunity water systems that add a chemical disinfectant other than ultraviolet or deliver water that has been chemically disinfected.

MCLs will be established for total THMs and five HAAs. There is a major difference for the MCL compliance between the Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules. For the Stage 1 Rule, the compliance is based on the running annual average (RAA) levels for all monitoring locations in the water system. A high DBP level at one location in the system could be offset by lower DBP levels at other monitoring locations and the average DBP level could be significantly lower than the highest DBP level. The Stage 2 Rule will use locational running annual averages (LRAA) for total THMs and five HAAs compliance. Under the Stage 2 Rule, a locational running annual average must be calculated at each monitoring site. For a water system with four monitoring sites, four locational running annual averages will be calculated and each of them must comply with the specified MCL.

This MCL compliance calculation could significantly impact many water systems. Due to hydrolysis reactions in distribution systems, as discussed in Chapter 3, many water systems may have a significantly higher level of total THMs at the maximum residence time site (mostly the end of water distribution systems). For HAAs that undergo biodegradation, a higher level may occur at the entrance of the distribution systems.

The Stage 2 Rule will apply to water systems in two phases. In phase 1, 3 years after rule promulgation, all water systems must comply with a 120/100 (120 μg/L for THMs and 100 μg/L for HAAs) locational running annual average (LRAA) based on Stage 1 monitoring sites and also continue to comply with the Stage 1 80/60 (80 μg/L for THMs and 60 μg/L for HAAs) running annual average. In phase 2, 6 years after rule promulgation, large and medium systems must comply with an 80/60 LRAA based on new sampling sites identified. Small water systems will be given more time to comply with the regulation.

The Stage 2 Rule will also require water systems to conduct an initial distribution system evaluation (IDSE) study. The main goal of this study is to identify new compliance monitoring sites that more accurately reflect sites representing high TTHM or HAA5 levels. For the phase 2 compliance, water systems must use the new compliance monitoring sites identified under the study. For bromate, the MCL remains at 10 μg/L.

7.5 OTHER DBP RELATED REGULATIONS

In addition to Total Trihalomethanes Rule, Information Collection Rule, Stage 1 Disinfectants and Disinfection Byproducts Rule, and the upcoming Stage 2 Disinfectants and Disinfection Byproducts Rule, the U.S. EPA has promulgated or proposed several regulations to balance the chemical and microbial risks in disinfected drinking water. They are Total Coliform Rule, Surface Water Treatment Rule, Interim Enhanced Surface Water Treatment Rule, Filter Backwash Recycling Rule, Long Term 1 Enhanced Surface Water Treatment Rule, upcoming Long Term 2 Enhanced Surface Water Treatment Rule, and proposed Ground Water Rule.

7.5.1 Total Coliform Rule

The Total Coliform Rule (TCR)[7] was promulgated in June 1989. It applies to all public water systems. This rule sets both MCLGs and MCLs for total coliform levels in drinking water. For systems that collect 40 or more samples per month, no more than 5.0% of the samples may be total coliform positive. For those systems that collect fewer than 40 samples, no more than one sample may be total coliform positive. If a system exceeds the MCL, it must notify the state and the public. The rule also suggests actions been taken by water systems to avoid or eliminate microbial contamination. In addition, the rule details the type and frequency of testing that water systems must carry out. For systems that collect fewer than five samples per month, an on-site inspection and a sanitary survey must be performed by the state or by an agent approved by the state.

7.5.2 Surface Water Treatment Rule

The Surface Water Treatment Rule (SWTR)[7] was promulgated in June 1989. This rule applies to all public water systems using surface water sources or groundwater sources under the direct influence of surface water. It has established MCLGs for *Legionella*, *Giardia*, and viruses at zero. The rule requires all systems to filter and disinfect their water to provide a minimum of 99.9% (3 log) combined removal and inactivation of *Giardia,* and 99.99% (4 log) of viruses. This rule also sets turbidity requirements for the combined filtered water. Under the rule, the turbidity must be less than or equal to 0.5 nephelometric turbidity unit (NTU) in at least 95% of the measurements and at no time may turbidity exceed 5 NTU.

7.5.3 Interim Enhanced Surface Water Treatment Rule

The Interim Enhanced Surface Water Treatment Rule (IESWTR)[8] was promulgated in December 1996. This rule applies to water systems using surface water, or groundwater under the direct influence of surface water and serving 10,000 or more people. It sets an MCLG of zero for *Cryptosporidium* and requires water systems with filtration to provide a minimum of 99% (2 log) removal of *Cryptosporidium.* The rule also strengthens the turbidity requirements. Under the rule, the turbidity level of a system's combined filtered water at each plant must be less than or equal to 0.3 NTU in at least 95% of the measurements and at no time may the turbidity

exceed 1 NTU. The rule also includes continuous turbidity monitoring requirements for individual filters. In addition, the rule includes microbial benchmarking/profiling and sanitary survey requirements.

7.5.4 Filter Backwash Recycling Rule

The Filter Backwash Recycling Rule (FBRR)[9] was promulgated on June 8, 2001. This rule applies to all public water systems that use surface water or groundwater under the direct influence of surface water; utilize direct or conventional filtration processes; and recycle spent filter backwash water, sludge thickener supernatant, or liquids from dewatering processes. When the filter backwash water is recycled, it reintroduces contaminants, including pathogens such as *Cryptosporidium*, back into treatment processes. Poor recycle practices could also significantly impair the water system's ability to achieve a 99% removal of *Cryptosporidium.* This rule requires that the recycled filter backwash water, sludge thickener supernatant, and liquids from dewatering processes must be returned to a location such that all processes of a system's conventional or direct filtration are employed. For both conventional and direct filtration, this location is before coagulation process.

7.5.5 Long Term 1 Enhanced Surface Water Treatment Rule

The Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR)[10] was promulgated on January 14, 2002. This rule applies to all small public water systems that serve less than 10,000 people and use surface water or groundwater under the direct influence of surface water. The IESWTR, discussed earlier, only applies to systems serving 10,000 or more people. Under the new rule, many requirements under the IESWTR will also apply to small water systems. These requirements include the 99% removal for *Cryptosporidium*, the turbidity of combined filter effluent less than 0.3 NTU in at least 95% of the measurements and at no time exceed 1 NTU.

7.5.6 Ground Water Rule

The Ground Water Rule (GWR)[11] was proposed on May 10, 2000. The final rule was scheduled to be published in Summer 2002. This promulgation date has been delayed. This rule will apply to all public groundwater systems. This rule will also apply to any system that mixes surface and groundwater if the groundwater is added directly to the distribution system and provided to consumers without treatment. The rule will establish multiple barriers to protect public health against bacteria and viruses in drinking water from groundwater sources and will establish a targeted strategy to identify groundwater systems at high risk for fecal contamination. The rule will require sanitary surveys, hydrogeologic sensitivity assessments, source water microbial monitoring, and/or corrective actions. The rule will also require compliance monitoring for systems that disinfect to ensure that they reliably achieve 4-log (99.99%) inactivation or removal of viruses.

7.5.7 Long Term 2 Enhanced Surface Water Treatment Rule

The Long Term 2 Enhanced Surface Water Treatment Rule (LT2SWTR)[6] will apply to all public water systems that use surface water or groundwater under the direct influence of surface water. This rule was scheduled to be promulgated in May 2002. U.S. EPA has published several documents to unveil the major components of the Long Term 2 Enhanced Surface Water Treatment Rule. One of these documents is the Stage 2 Microbial and Disinfection Byproducts Federal Advisory Committee Agreement in Principle.[6] This document outlines monitoring and treatment requirements for filtered systems. These requirements involve assignment of systems into different categories or bins based on the results of source water *Cryptosporidium* monitoring. Additional treatment will be required depending on the bin to which the system is assigned. These treatment processes, including watershed control, alternative source, pretreatment, improved treatment, and improved disinfection, are listed in the Microbial Toolbox. The rule will also cover unfiltered systems and uncovered finished water reservoirs.

7.6 TECHNICAL GUIDANCE DOCUMENTS

To aid water systems to better comply with the microbial and DBP regulations, a number of technical guidance documents have been published by U.S. EPA. These documents are excellent information resources for readers to better understand various microbial and DBP control technologies.

1. Alternative Disinfectants and Oxidants Guidance Manual, EPA 815-R-99–014/April 1999
2. Disinfection Profiling and Benchmarking Guidance Manual, EPA 815-R-99–013/August 1999
3. Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual, EPA 815-R-99–012/May 1999
4. Guidance Manual for Compliance with the Interim Enhanced Surface Water Treatment Rule: Turbidity Provisions, EPA 815-R-99–010/April 1999
5. Guidance Manual for Conducting Sanitary Surveys of Public Water Systems; Surface Water and Ground Water Under the Direct Influence (GWUDI), EPA 815-R-99–016/April 1999
6. M/DBP Simultaneous Compliance Manual, EPA 815-R-99–015/August 1999
7. Uncovered Finished Water Reservoirs Guidance Manual, EPA 815-R-99–011/April 1999
8. Disinfection profile/CT spreadsheet, April 2001

These technical guidances can be obtained by calling the U.S. EPA Safe Drinking Water Hot Line, (800) 426–4791, or download at the following U.S. EPA Web site: www.epa.gov/safewater/mdbp/implement.html.

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4. United States Environmental Protection Agency, National Primary Drinking Water Regulations; Disinfectants and Disinfection Byproducts; Final Rule, *Federal Register,* 63, 69392, 1998.
5. United States Environmental Protection Agency, Removal of the Maximum Contaminant Level Goal for Chloroform from the National Primary Drinking Water Regulations; Final Rule, *Federal Register,* 65, 34404, 2000.
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9. United States Environmental Protection Agency, National Primary Drinking Water Regulations; Filter Backwash Recycling Rule; Final Rule, *Federal Register,* 66, 31086, 2001.
10. United States Environmental Protection Agency, National Primary Drinking Water Regulations; Long Term 1 Enhanced Surface Water Treatment Rule; Final Rule, *Federal Register,* 67, 1812, 2002.
11. United States Environmental Protection Agency, National Primary Drinking Water Regulations; Ground Water Rule; Proposed Rules, *Federal Register,* 65, 30194, 2000.

8 Disinfection Byproduct Analysis and Data Evaluation

OBJECTIVES

The objective of this chapter is to provide an overview of analytical methods for disinfection byproducts. Typical analytical problems during disinfection byproduct analysis and common approaches for evaluating the integrity of disinfection byproduct data are discussed as well. The information will benefit scientists, engineers, regulators, operators, and laboratory analysts.

NOMENCLATURE

DBP disinfection byproduct
D-DBP disinfectants and disinfection byproducts
GC gas chromatography
HAA haloacetic acid
ICR Information Collection Rule
MTBE methyl tert-butyl ether
MX 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone
NDMA *N*-nitrosodimethylamine
NOM natural organic matter
PFBHA O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine
SPME solid-phase micro-extraction
THM trihalomethanes
TOX total organic halide
U.S. EPA United States Environmental Protection Agency

Since the detection of chloroform in chlorinated drinking water in the 1970s, many methods have been developed for analyzing trihalomethanes (THMs), haloacetic acids (HAAs), and other organic and inorganic disinfection byproducts (DBPs). To assist water utilities to monitor DBPs in their finished water, the United States Environmental Protection Agency (U.S. EPA) published a list of approved methods under the Information Collection Rule (ICR)[1] and Disinfectants and Disinfection Byproducts (D-DBP) Rule.[2]

8.1 APPROVED METHODS FOR DBPS

The approved methods concept was initiated during the development of ICR. Prior to ICR monitoring, there were no certified methods for DBPs except for THMs. In addition, many of the DBP methods at the time were still in the early stage of development. For many states, no laboratories were certified for DBP analyses except for THMs. Because of these limitations, it was unlikely that each individual state could certify methods and laboratories prior to the ICR promulgation. In order to ensure that laboratories be able to conduct DBP analysis according to the ICR monitoring time schedule, approved methods and approved laboratory concepts were proposed. Under this proposal, the approved methods would be issued by the U.S. EPA. Laboratory approval would be conducted by the U.S. EPA under ICR monitoring.

Under the D-DBP regulation, approved methods were used again. Many of the methods under D-DBP Rule are same as those under ICR.[1,2] The approved methods for four groups of DBPs are listed in Table 8.1.

TABLE 8.1
Approved Methods for DBP Analysis

DBPs	Approved Analytical Methods
THMs	EPA Method 502.2,[3] EPA Method 524.2,[3] and EPA Method 551.1[3]
HAAs	EPA Method 552.1,[4] EPA Method 552.2,[3] and Standard Method 6251B[5]
Chlorite	EPA Method 300.0[6] and EPA Method 300.1[7]
Bromate	EPA Method 300.1[7]

8.1.1 Trihalomethanes (THMs)

For chloroform, analytical method played a critical role in its discovery in chlorinated drinking water. Prior to this discovery, two concentration methods, carbon adsorption and liquid-liquid extraction, were commonly used for organic analysis in water.[8] The first method could not detect chloroform because the method involved granular carbon adsorption followed by desorption using chloroform. The second method involved liquid-liquid extraction followed by extract concentration using evaporation. This method could not detect chloroform because chloroform is a volatile organic and was lost during the extract concentration. Using a headspace analytical method that consists of headspace separation and activated silica concentration followed by gas chromatograph (GC) analysis, Rook[9] first observed the chloroform peak as the largest peak in chlorinated water sample. In 1974, the formation of chloroform was reported as the product of the reaction between chlorine and natural organic matter in drinking water.[10]

THMs are one of two major groups of organic DBPs in chlorinated water. As discussed in Chapter 1, there are four common THMs, including trichloromethane (chloroform), bromodichloromethane, chlorodibromomethane, and tribromomethane (bromoform). Other iodinated THMs were also reported in water high in iodide (brackish water and seawater). One of the major concerns was the medicinal

odor caused by iodinated THMs. Because iodinated THMs are not commonly detected in drinking water, the term, THMs, generally refers to the four THMs mentioned above. Under the D-DBP Rule,[2] THMs are regulated at a maximum contaminant level of 80 μg/L.

Currently, there are three approved analytical methods for THMs.[2] They are EPA Methods 502.2, 524.2, and EPA 551.1, as shown in Table 8.1. Both EPA methods 502.2 and 524.2 use purge-and-trap method for sample concentration and GC for sample analysis.[3] For THM detection, EPA Method 502.2 uses photoionization and electrolytic conductivity detectors in series and EPA Method 524.2 uses a mass spectrometer. Both methods can be used for many other regulated and unregulated volatile organic chemicals.

EPA Method 551.1 uses micro liquid-liquid extraction with methyl tert-butyl ether (MTBE), GC separation, and electron capture detection.[3] In addition to THMs, EPA Method 551.1 is also used for monitoring haloacetonitriles, chloral hydrate, chloropicrin, and chloropropanones. EPA Method 551.1 could also be used to analyze 8 chlorinated solvents and 16 halogenated pesticides/herbicides.

In comparison with EPA Method 551,[11] there are several significant modifications in EPA Method 551.1. One of the modifications is the extraction salt. Sodium chloride was used in EPA Method 551. However, because of its high bromide impurity, which reacts with residual chlorine and natural organic matter, sodium chloride causes higher brominated DBP (or artifact) levels and interference for other DBP determination.[12] Sodium sulfate was specified as the extraction salt in EPA Method 551.1. EPA Method 551.1 also allows pentane as a solvent choice if chloral hydrate is not analyzed.

Three analytical methods for THMs are listed in Standard Methods.[5] These are Standard Methods 6232B, 6232C, and 6232D. Standard Method 6232B is a liquid-liquid extraction gas chromatographic method that specifies pentane as the extraction solvent and electron capture detector for detection. This method is similar to EPA Method 551.1. Standard Method 6232C is a purge and trap GC/mass spectrometric method, which is almost identical to EPA Method 524.2. Standard Method 6232D is a purge and trap GC method, which is almost identical to EPA Method 502.2. These three Standard Methods were not listed as approved methods under the D-DBP Rule. Several other analytical methods are under development. These methods employ various sample preparation techniques, including headspace, solid-phase micro-extraction (SPME), and direct aqueous injection. GC/electron capture detection is commonly used for sample analysis.

For THM analysis, the author suggests that EPA Methods 502.2 and 524.2 be used if samples need to be analyzed for other regulated and unregulated volatile organic chemicals. However, if a sample needs to be analyzed for DBP formation and control, EPA 551.1 should be used. In addition to THMs, EPA Method 551.1 provides information on other DBPs.

8.1.2 Haloacetic Acids

HAAs are another major group of organic DBPs in chlorinated water. Like THMs, HAAs are formed by the reactions between chlorine and natural organic matter.

Method development for the detection of HAAs trails behind THMs. HAAs are relatively nonvolatile and hydrophilic organic compounds. These properties make purge trap, headspace, and liquid-liquid extraction less effective for HAA separation, especially at the natural pH. In addition, these acids cannot be easily separated and detected by GC/electron capture detection. For GC/electron capture detection analysis, these acids need to be chemically converted into their methyl esters, or methylated HAAs.

As discussed in Chapter 1, there are 9 common HAAs. They are monochloroacetic acids (ClAA), monobromoacetic acids (BrAA), dichloroacetic acids (Cl_2AA), bromochloroacetic acid (BrClAA), dibromoacetic acid (Br_2AA), trichloroacetic acid (Cl_3AA), bromodichloroacetic acid ($BrCl_2AA$), chlorodibromoacetic acid ($ClBr_2AA$), and tribromoacetic acid (Br_3AA). A maximum contaminant level of five HAAs, including ClAA, BrAA, Cl_2AA, Br_2AA, and Cl_3AA, was set at 60 μg/L under the Stage I D-DBP regulation.[2]

Currently, there are three approved methods for HAA analysis: EPA Methods 552.1, 552.2, and Standard Method 6251B.[2] All three methods include sample extraction, methylation, and GC/electron capture detection. EPA Method 552.2[3] and Standard Method 6251B[5] use micro liquid-liquid extraction with MTBE at acidic conditions. Both sodium sulfate and sulfuric acid are added to samples to increase the extraction efficiency. EPA Method 552.1[4] uses solid phase extraction with ion exchange resins. Standard Method 6251B uses a common methylating reagent, diazomethane, for HAA methylation. Due to its hazardous nature, diazomethane is replaced with acidic methanol in EPA Methods 552.1 and 552.2. A capillary GC/electron capture detection is used in all three methods. The author suggests EPA Method 552.2 or Standard Method 6251B be used due to the poor HAA extraction efficiency using EPA Method 552.1, especially in water containing high levels of sulfate or chloride.

Diazomethane and acidic methanol are two of the chemical choices for HAA methylation. Diazomethane should be freshly prepared. The concentration of the diazomethane could be estimated by checking the color of the solution. For both diazomethane and acidic methanol, incomplete methylation of HAAs, especially traihaloacetic acids, have been reported in several laboratories.[13,14] The author suggests that calibration curves be prepared with each batch of the HAA samples to compensate the effect of the incomplete methylation of HAAs.

A modified EPA Method 552.2, or EPA 552.3, is currently being developed.[15] This method includes two major modifications, increasing acidic methanol volume and increasing methylation temperature, to address the incomplete methylation of trihaloacetic acids. The first modification specifies a higher ratio of the acidic methanol volume to MTBE extract volume. The second modification specifies a higher methylation temperature. Due to the low boiling point of MTBE, another high boiling point extraction solvent, tert-amyl methyl ether (TAME), was specified in the method.

Two methods for direct analysis of HAAs without methylation have been reported. One uses ion chromatography[16] and another uses capillary electrophoresis.[17] Neither sample extraction nor HAA methylation is required under both methods. Both methods can be used for a rapid determination (10 to 20 min) of high

levels of HAAs (mg/L). However, both methods require a time consuming and cumbersome sample concentration process for determination of HAAs at μg/L levels.

8.1.3 Bromate and Chlorite

Bromate is an ozonation byproduct in water high in bromide. Chlorite is a degradation byproduct of chlorine dioxide. The current D-DBP regulation sets a maximum contaminant level of 10 μg/L for bromate and a maximum contaminant level of 1 mg/L for chlorite.[2]

For chlorite analysis, both EPA Method 300.0 and 300.1 are approved methods.[2,6,7] Both methods use ion chromatographic separation, subsequent suppression and conductivity detection. For bromate analysis, only EPA Method 300.1 is approved because EPA Method 300.0 is not sensitive enough to determine μg/L levels of bromate, especially in presence of mg/L levels of chloride. EPA Method 300.1, which specifies a high capacity ion chromatographic column, improves chromatographic resolution and minimizes chromatographic interferences from common anions including chloride. For bromate analysis, aged guard and analytical columns can cause irregular baselines, poor resolution and poor sensitivity.[18] Therefore, the resolution must be closely monitored and the column be replaced immediately when resolution starts to deteriorate. For chlorite analysis, an amperometric titration method, Standard Method 4500-ClO_2 E,[5] could be used for routine daily monitoring in treatment plants. However, chlorite compliance analyses should be conducted using an ion chromatograph.

8.1.4 Haloacetonitriles, Chloral Hydrate, Chloropicrin, and Chloropropanones

Haloacetonitriles, chloral hydrate (or trichloroacetaldehyde hydrate), chloropicrin, and chloropropanones are other major DBPs in chlorinated drinking water. These DBPs were monitored under ICR and could be regulated under future regulations. For ICR monitoring, EPA Method 551.1 was the approved method for these DBPs. For chloral hydrate analysis, due to its poor extraction efficiency with pentane, MTBE should be used as the extraction solvent. Chloramines may cause degradation of chloral hydrate during sample storage. Therefore, ammonium chloride cannot be used for the preservation of chloral hydrate samples.

8.1.5 Cyanogen Chloride

Cyanogen chloride is a DBP commonly detected in chloraminated waters. Cyanogen chloride in chloraminated water was included under the ICR monitoring. However, cyanogen chloride is not included in the D-DBP regulation. There are three methods for analyzing cyanogen chloride in drinking water.[19] They are purge and trap gas chromatography (GC)/mass spectrometry, headspace GC/electron capture detection, and micro liquid-liquid extraction GC/electron capture detection. The purge and trap GC/mass spectrometry method for cyanogen chloride was used under the ICR monitoring. However, this method requires the use of specialized instrument, a purge and trap GC/mass spectrometry system.[20] A heated purge

is also required if the analysis of cyanogen bromide is needed. Developed by Xie and Reckhow,[21] the headspace GC/electron capture detection method is a relatively simple and rapid analytical method. The analysis could be automated using a headspace autosampler. The liquid-liquid extraction GC/electron capture detection method was originally developed for cyanogen bromide analysis. This method was further developed by Sclimenti et al.,[22] for both cyanogen chloride and cyanogen bromide analysis. The sample injection could be easily automated with a common GC autosampler.

8.1.6 Aldehydes

Aldehydes are DBPs formed by the reactions between ozone and natural organic matters in drinking water. The typical levels of aldehydes in ozonated water range from 5 to 20 μg/L. Aldehydes were included under the information collection rule monitoring. Aldehydes, however, are not regulated in drinking water. For aldehyde analysis, two common methods are EPA Method 556 and Standard Method 6252.[5,23] Both methods use O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) to derivatize aldehydes to their pentafluorobenzyl oximes in aqueous phase. Their oxime derivatives are then extracted with hexane and analyzed by GC/ECD (electron capture detector). EPA Method 556.1,[23] a derivative of EPA Method 556, uses fast gas chromatographic technique for oxime detection. For aldehyde analysis, one of the challenges is getting aldehyde-free reagent water to prepare aqueous standards. Formaldehyde and acetaldehyde are commonly present in indoor air or ion exchange resins for generating reagent water. Low background levels of formaldehyde and acetaldehyde in reagent water could be removed by UV radiation or simply boiling the water.

8.1.7 Ketoacids

Ketoacids are another group of ozonation byproducts formed by the reaction between ozone and natural organic matter in drinking water. As discussed in Chapter 1, ketoacids include glyoxylic acid, pyruvic acid, and ketomalonic acid. Although ketoacids are not regulated under the D-DBP regulation, ketoacids could significantly affect the biostability of treated water and bacterial regrowth in distribution systems. There are two established analytical methods that use double derivatization and GC/ECD detection.[24,25] Both methods use PFBHA derivatization to convert ketoacids to their oximes in aqueous phase. Following MTBE extraction, one method uses diazomethane for ketoacid methylation, and another uses acidic methanol. However, acidic methanol is not suitable for ketomalonic acid analysis. Both methods use GC/ECD for separation and detection. Very few laboratories have conducted ketoacid analyses. Both dirty injectors or samples containing PFBHA could cause chromatographic interference and poor sensitivity. A calibration curve should be prepared for each batch of samples. Since ketoacids are easily biodegradable, ketoacid samples should be analyzed within 24 h or properly preserved.

8.1.8 MX

3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) and its analogues are another group of DBPs detected in chlorinated waters at ng/L levels. However, these DBPs may pose great health risks because they can account for 20 to 50%[26,27] of the mutagenicity in drinking water. The original analytical method for MX and its analogues includes resin extraction, acidic methanol methylation, and GC/mass spectrometry detection.[26] This method requires the use of a mass spectrometer and may not be capable of detecting all MX analogues. Recently, a GC/electron capture detection method has been developed. The new method consists of liquid-liquid extraction, boron trifluoride methanol methylation, and GC/electron capture detection.[28] However, this method has higher detection limits (20 to 50 ng/L) and may be subject to matrix interferences.

8.1.9 NDMA

N-nitrosodimethylamine (NDMA) is a potential chloramination DBP, which occurs at ng/L levels, as discussed in Chapter 1. The analysis of NDMA involves sample concentration and GC/mass spectrometer detection. Because of the extremely low level of NDMA in drinking water (ng/L) and metrics effects, mass spectrometry detection in selected ion monitoring mode is required. There are several ways for sample concentration, including resin adsorption, liquid-liquid extraction, continuous liquid-liquid extraction, and solid phase extraction.[29] Due to the great concentration factors, isotope dilution is generally used to quantify NDMA concentration. Currently, there is no EPA approved method for NDMA analysis. Both EPA Methods 625 and 1625 could be used for NDMA determination. For determining NDMA at ng/L levels, however, both methods need to be modified.[29]

8.2 TYPICAL ANALYTICAL PROBLEMS

DBP monitoring in drinking water is critical for health risk assessment and regulation development, as well as water treatment process design and operation. Due to the complexity of DBP analysis, it is also a great challenge for many water quality engineers and chemists to evaluate the integrity of DBP analytical data. Some analytical problems are associated with analytical methods, and some are related to incorrect method modifications done in the analytical laboratories. Because there is very little information on the stability of DBPs, choosing a proper sample preservation method is also a challenging task.

8.2.1 Bromide Contamination

Brominated DBPs are commonly formed in water containing bromide. Increasing bromide level increases the formation of brominated DBPs, as discussed in Chapter 2. In water containing little bromide, the formation of brominated DBPs is insignificant. In drinking water samples, the typical bromide levels range from 0.0 to 0.5 mg/L.

Because sodium chloride can be easily dissolved in water samples, sodium chloride is commonly used as an extraction salt for enhancing the liquid-liquid extraction efficiency. Bromide contamination occurs when sodium chloride (NaCl) is used. Reagent grade sodium chloride contains a high level of inorganic bromide (0.005 to 0.01% by weight). Adding 4 g sodium chloride into 30 mL of water samples can spike in 7 to 13 mg/L of bromide. If the chlorine residual in the sample is properly quenched, in theory, inorganic bromide spiked will not affect the level of brominated DBPs. However, for samples containing residual chlorine, in either free or combined forms, using the sodium chloride could significantly increase the level of brominated DBPs.[12]

Due to the extremely high level of bromide introduced by sodium chloride during the sample extraction, this bromide contamination generally only affects the concentration of brominated species, including tribromomethane, bromoacetic acid, dibromoacetic acid, tribromoacetic acid, dibromoacetonitrile, and cyanogen bromide. This type of data could be easily identified. They exhibit higher levels of chlorinated DBPs and brominated DBPs than mixed bromochloro-DBPs (e.g., bromodichloroethane, chlorodibromomethane, and bromochloroacetic acid). This type of data could also be identified using the V-trap rule discussed later in this chapter.

Sodium chloride was specified as the extraction salt in EPA Method 551.[4] Many DBP data obtained using EPA Method 551, especially those prior to 1995, are subject to potential bromide contamination. Some laboratories also used sodium chloride to replace sodium sulfate in EPA Method 552.2 and other methods. This modification could also result in bromide contamination.[12]

8.2.2 Chloroform Contamination

Chloroform contamination in the extraction solvent, methyl tert-butyl ether (MTBE), is a common problem for THM analysis. This contamination will affect the calibration curve for chloroform and mask chloroform in samples. There are two common ways to further purify the solvent. One is distillation and another granular activated carbon adsorption. Distillation is an effective process for purifying the solvent. However, distillation involves heating the volatile MTBE and needs to be conducted by an experienced chemist. Carbon adsorption could potentially introduce other contaminants and carbon fines into the solvent.

The author suggests two approaches to avoid chloroform contamination. One is choosing residual analysis or pesticide analysis grade MTBE. If no significant amount of chloroform is found in the solvent, place a large quantity of the solvent with the same lot number. Another approach is to use an alternate solvent, pentane, for sample extraction. However, pentane cannot be used for analyzing chloral hydrate and other trihaloacetaldehydes.

8.2.3 Incomplete Methylation

For HAA analysis, a complete conversion of HAAs to their methyl easters is the key to assure the precision and accuracy of the data. Incomplete methylation was

reported in both acidic methanol and diazomethane derivitization procedures.[13,14] For the diazomethane derivitization procedure, excess water in MTBE extracts is the common cause. Drying MTBE extract with magnesium sulfate could significantly increase the methylation efficiency, especially for trihaloacetic acids. For the acidic methanol derivitization procedure, inadequate acidic methanol is the cause of the incomplete methylation. Methylation efficiency of trihaloacetic acids could be improved by increasing the ratio between acidic methanol and MTBE extract. This improvement is likely to be adopted in the upcoming EPA Method 552.3.[15]

8.2.4 Sample Degradation

Sample degradation could be affected by many factors. As discussed in Chapter 3, DBPs undergo many degradation reactions, including hydrolysis, dehalogenation, oxidation, chlorination, and biodegradation. Understanding these degradation reactions is the key for properly preserving DBP samples.

Hydrolysis degradation of many trihalogenated DBPs could result in the formation of THMs. These hydrolysis reactions could affect the quantification of trihaloacetonitriles, trihaloacetones, brominated trihaloacetaldehydes, as well as THMs. A low pH and low temperature condition could prevent or slow down many of these reactions. For trihaloacetic acids, their hydrolysis and dehalogenation reactions are very slow in drinking water samples. However, haloacetic acids may undergo a rapid biological degradation, especially at room temperatures. A chlorine residual or acidic condition may be needed to preserve HAA samples.

The hydrolysis of chloral hydrate, or trichloroacetaldehyde hydrate, is very slow and negligible in drinking water samples. However, chloral hydrate and its brominated analogues undergo a degradation reaction in the presence of chloramines. Therefore, for analyzing chloral hydrate and its brominated analogues, ammonium chloride cannot be used for sample preservation.

8.2.5 Analytical Artifacts

Analytical artifacts are common sources of interferences for DBP determination. Many artifacts are products of impurities in extraction solvents. Unique artifacts can form when residual chlorines or oxidants are allowed to come into contact with these solvents. A number of chlorinated cyclohexene derivatives were reported as reaction products of the cyclohexene preservative in dichloromethane with residual chlorine.[30] Converting free chlorine to combined chlorine by using ammonium chloride cannot prevent the formation of the artifacts. In water high in bromide, brominated artifacts could be formed. By exacting a bromine solution with MTBE, the author detected a number of brominated artifacts in the extract.[31] Three of these artifacts were identified as bromoacetone, 1-bromo-2-methyl-2-propanol, and 3-bromo-2-methyl-2-butanol. Halogenated artifacts were also observed in other chlorinated, chloraminated, and brominated solvents, including MTBE, pentane, and diethyl ether. Many of these artifacts were reported as new DBPs.

Using sodium chloride as the salt to enhance extraction could result in the formation of various brominated and iodinated analytical artifacts. Many of these artifacts have not been identified. The peaks of these artifacts overlap with DBP peaks in gas chromatograms and cause interferences to DBP analysis. At low levels, these artifacts also result in noisy chromatogram baselines.

8.3 EVALUATING THE INTEGRITY OF DBP DATA

Data evaluation is important for analytical chemists, as well as water quality engineers. Understanding the chemistry or typical pattern could help analytical chemists identify problems associated with sample preservation, storage, and analysis.

8.3.1 Typical Data Pattern

Typical data pattern can be very useful to evaluate the integrity of DBP data.[32] DBP data pattern could be affected by many water quality parameters, including total organic carbon, pH, chlorine residual, bromide, and temperature. Bromide concentration has a unique impact on the speciation of DBPs, or distribution of a DBP and its brominated analogues.

In chlorinated water containing no bromide, only chlorinated DBPs are formed. Increasing the bromide level increases the formation of brominated DBPs and reduces the formation of chlorinated DBPs. The relative concentration among a chlorinated DBP and its brominated analogues could be used to estimate the bromide level in water and evaluate the integrity of DBP data. The effects of bromide on DBP speciation were discussed in Chapter 2.

As described in Chapter 1, there are many groups that contain the chlorinated DBPs and their brominated analogues. Many of these DBPs are not analyzed regularly due to the regulation requirements and/or lack of chemical standards. Four groups of DBPs, THMs, dihaloacetic acids, trihaloacetic acids, and dihaloacetonitriles, are commonly analyzed and can be used for DBP data evaluation.

The THM data for four water samples are shown in Table 8.3. For sample one, only the chlorinated THM was detected at 50 μg/L. No brominated THMs were detected. One could conclude that this water does not contain bromide. For sample two, in additon to the chlorinated THM, two brominated THMs were detected at low levels. One could estimate that this water contains very low levels of bromide. For sample three, the THM at the highest level is bromodichloromethane. Trichloromethane, chlorodibromomethane and tribromomethane were detected at lower levels. This indicates that the water contains a moderate level of bromide. For sample four, the tribromomethane is the highest THM. Bromodichloromethane and chlorodibromomethane were detected at lower levels. Trichloromethane was not detected. This indicates that the water contains a high level of bromide. You could use other DBPs (e.g., dihaloacetic acids, trihaloacetic acid, and dihaloacetonitriles) to evaluate the bromide level in water samples. The bromide levels, low, moderate, and high, are arbitrary. As long as you use the same standard for all DBPs, this could be used by you to evaluate the DBP data integrity.

TABLE 8.2
Suggested Analytical Methods for Disinfection Byproducts

DBPs	Analytical Methods
Haloacetonitriles	EPA Method 551.1[3]
Chloral hydrate	EPA Method 551.1[3]
Chloropicrin	EPA Method 551.1[3]
Chloropropanones	EPA Method 551.1[3]
Cyanogen chloride	EPA Method 524.2,[20] Method by Xie and Reckhow[21] and Method by Sclimenti et al.[22]
Aldehydes	EPA Method 556 [23] and Standard Method 6252[5]
Ketoacids	Methods by Xie and Reckhow[24] and Xie et al.[25]
NDMA	Modified EPA Methods 625 and 1625[29]

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TABLE 8.3
Trihalomethane Concentrations and Bromide Levels (μg/L)

Samples	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	Bromide
Sample 1	50	ND	ND	ND	none
Sample 2	45	7	1	ND	low
Sample 3	20	40	20	5	medium
Sample 4	ND	10	20	40	high

Note: ND = not detected.

A set of published DBP data from a membrane-treated water sample is shown in Table 8.4. By evaluating the THM data, one can conclude that the water sample contains moderate levels of bromide. Using the same criteria, however, the dihaloacetonitrile data indicate that the water contains a high level of bromide. Because both THM and dihaloacetonitrile data are from the same water sample, the bromide level should be the same. Therefore, either THM data or dihaloacetonitrile data are questionable. By further investigating the experimental procedure, the dihaloacetonitrile data were questionable. It was due to a bromide contamination resulting from the use of sodium chloride as the extraction salt. THM data were analyzed by a different method and they are indeed reliable.

The second set of DBP data was obtained from an interlaboratory study. The concentrations of trihalomethanes and dihaloacetic acids are shown in Table 8.5. The THMs data indicate that there was little bromide in the water sample. However, the dihaloacetic acid data indicate that the bromide level was between low and moderate levels. Again, these contradictory data indicate that either THMs or dihaloacetic acids were problematic. Further investigation indicated that the THM data were comparable to data from other laboratories. The dihaloacetic acid data were

TABLE 8.4
Problematic Data on Trihalomethanes and Dihaloacetonitriles (μg/L)

Trihalomethanes	**$CHCl_3$**	**$CHBrCl_2$**	**$CHBr_2Cl$**	**$CHBr_3$**
	18	18	17	2.5
Dihaloacetonitriles	**Cl_2AN**	**BrClAN**	**Br_3AN**	
	1.0	2.9	4.4	

TABLE 8.5
Problematic DBP Data on Trihalomethanes and Dihaloacetic Acids (μg/L)

Trihalomethanes	**$CHCl_3$**	**$CHBrCl_2$**	**$CHBr_2Cl$**	**$CHBr_3$**
	31.0	0.8	ND	ND
Dihaloacetic acids	**Cl_2AA**	**BrClAA**	**Br_2AA**	
	22.0	8.3	3.1	

Note: ND = not detected.

indeed questionable since other laboratories reported no detectable level of bromochloroacetic acid and dibromoacetic acid.

When only one analytical method is used, the evaluation procedure above may not be able to identify potential problems with the DBP data. EPA Method 551 could be used for both THMs and dihaloacetonitriles after a single sample extraction and GC run. Bromide contamination from the extraction salt, sodium chloride, could form excess brominated trihalomethanes and brominated dihaloacetonitriles during the sample preparation. Because the same method is used, both data sets will indicate a moderate or high level of bromide, which is different from the bromide level of the water sample. In Table 8.5, dihaloacetic acid data, which are obtained with a different method, could provide a valuable reference for DBP data evaluation. The same limitation may occur when using both dihaloacetic acid data and trihaloacetic acid data. In addition, this evaluation indicates the contradictions among the DBP data. To identify the problematic data, a further examination of the analytical procedure or a repeat analysis is required.

8.3.2 The V-Trap Rule

After studying DBP data evaluation for many years, the author developed a simple rule, the V-trap rule, to identify some problematic DBP data.[32] To use this rule, one must list various groups of DBP data in the following order (from left to right): the chlorinated DBP, the monobrominated analogues, dibrominated analogues, and tribrominated analogues, as shown in Table 8.4. When the pattern of the DBP level from the chlorinated DBP to most brominated analogues resembles a letter V, the DBP data are questionable. For example, the trichloromethane level is 30 μg/L, 5 μg/L for bromodichloromethane, and 20 μg/L for chlorodibromomethane. This set

TABLE 8.6
Problematic DBP Data on Trihalomethanes, Dihaloacetic Acids, Trihaloacetic Acids, and Dihaloacetic Acids

Dihaloacetic acids	**Cl_2AA**	**BrClAA**	**Br_2AA**	
	11.3	ND	6.1	
	21	3.5	8.3	
Dihaloacetonitriles	**Cl_2AN**	**BrClAN**	**Br_2AN**	
	14.0	2.8	5.2	
Trihaloacetic acids	**Cl_3AA**	**$BrCl_2AA$**	**$ClBr_2AA$**	**Br_3AA**
	14	ND	6.1	ND

Note: ND = not detected.

of data resembles the pattern of high, low, and high, or letter V. This set of data is questionable regardless of the level of tribromomethane.

As shown in Table 8.6, four sets of DBP data are summarized from two published papers. The patterns of all four sets of data resemble the letter V and are questionable. Further investigation of the analytical methods indicates that errors were due to bromine contamination in two sets of the data and the use of an unreliable method in others.

The V-trap rule is simple and easy to use. It also shows the importance of properly tabulating DBP data, that is a chlorinated DBP should be grouped with its brominated analogues. There are exceptions for this V-trap rule. First, it cannot be used for spiked DBP samples. Spiking DBPs at various levels could easily change the distribution of a DBP and its brominated analogues. Second, it cannot be used for a mixture of chlorinated high bromide water and chlorinated low bromide water. Third, it cannot be used for a high bromide water that uses preozonation and postchlorination.

There are many other ways for DBP data evaluation. The formation and stability information discussed under Chapters 2 and 3 could be used for this purpose. For example, in water containing a high free chlorine residual, no significant levels of cyanogen chloride should be detected. In presence of biological activities (e.g., biologically active carbon effluent or distribution samples), a lower level of HAAs, especially dichloroacetic acid, is expected. In addition, the above procedure for data evaluation can be used as a simple and quick way to spot potential problems with DBP data. However, the best way to assure the DBP data quality is to have a good understanding of the analytical method and a good quality control and quality assurance program.

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9 Disinfection Byproduct Information Resources

OBJECTIVES

The objective of this chapter is to provide a summary of disinfection byproduct (DBP) information resources in various formats, including books, web pages, video tapes, journals and conference proceedings. These information resources are excellent supplemental reading materials for this book. In addition to traditional reference materials, several DBP web pages were reviewed and sample pages and links were provided. Together, they provide the reader with information on DBP toxicities, regulations, analyses, and control technologies.

NOMENCLATURE

AWWA American Water Works Association
DBP disinfection byproduct
ICR Information Collection Rule
U.S. EPA United States Environmental Protection Agency

The Information Revolution has affected every aspect of our lives. The field of DBPs is no exception. DBP information has been presented in many formats. Books, yes printed books, are still one of the primary information sources for DBPs. Journals, including both printed journals and e-journals, are also common resources for DBPs. Many web sites have been developed in the area of DBPs. Timely maintenance and updating of these web sites is still the biggest challenge. The DBP information resources cannot be complete without listing web pages. However, it is possible that when this book is published some of web pages could be changed and even taken off from their sites. The author has decided to take this risk because of enormous information listed on these web pages

9.1 BOOKS

Formation and Control of Disinfection By-Products in Drinking Water. Edited by an internationally renowned expert in the DBP field, Dr. Philip Singer, this book[1] focuses on the DBP control, and includes several chapters on the chemistry, regulations, and toxicology of DBPs. Most of the authors are nationally well-known researchers in the field. Since its publication, this book has become one of the most important technical guides in the field. Chapter 1, Disinfection Byproducts: a Historical Perspective, authored by Dr. James Symons, provides a historical review of

disinfection byproduct discovery, studies, and regulations. DBP control technologies are discussed in ten chapters of the book. These technologies include the use of chloramines, ozone, chlorine dioxide, ultraviolet light, coagulation and precipitative softening, adsorption, advanced oxidation, membrane processes, biofiltration, and anion exchange. One chapter is focused on the treatment costs for DBPs and another on DBP regulations and treatment in Europe. Other chapters provide discussions on DBP chemistry, DBP formation modeling, natural organic matter, epidemiology and toxicology, and regulatory issues.

Controlling Disinfection By-Products and Microbial Contaminants in Drinking Water. Edited by Robert M. Clark, a nationally known drinking water researcher, and Brenda K. Boutin, this report[2] was produced as part of the U.S. EPA National Risk Management Research Laboratory's strategic long-term research plan. This report includes regulation review, DBP chemistry, alternative disinfectants, biological filtration, activated carbon, membrane, coagulation, modeling, and cost analysis. Each chapter gives an excellent review on the topic. In addition, several chapters provide information on current EPA research projects and future research and policy directions. To order this free report call, 1-800-426-4791, or go to www.epa.gov/ORD?NRMRL/Pubs/600R01110/600r01110.pdf/.

Disinfection By-Products in Drinking Water: Current Issues. Edited by Mike Fielding and Mike Farrimond, this book[3] evolved from the International Conferences, "Disinfection By-Products: The Way Forward," held in Cambridge, UK, in 1998. This book brings together regulators, researchers, and water suppliers from Europe and North America to discuss the current issues associated with DBPs. Five of the sections are: DBP Formation and Occurrence in Treatment and Distribution, Advances in Analysis and Monitoring, Standards and Regulations, Balancing Chemical and Microbiological Risk, and Control of DBPs. Most of the chapters are focused on DBP formation, occurrence, and control. Several chapters discuss chemical analyses, regulations, and risk analysis. This book is a valuable source for DBP occurrence, research, and regulations in Europe.

***Environmental Health Criteria 216: Disinfectants and Disinfectant By-Products*.** This report is one of the Water Health Organization Environmental Health Criteria monographs. Intended to provide critical reviews on the health effects of various chemicals, this report[4] is focused on the toxicology and epidemiology of common disinfectants and DBPs. Chapter 2, Chemistry of Disinfectants and Disinfectant Byproducts, prepared by Drs. Gary Amy and Mohamed Siddiqui, provides an excellent review of the DBP chemistry. This chapter covers DBP formation, analysis, control, and modeling. Both inorganic DBPs and organic DBPs are discussed, as well as nonhalogenated organic DBPs. This chapter gives an excellent discussion on the influence of source water characteristics and water treatment variables on DBP formation.

Disinfection By-Products in Water Treatment: The Chemistry of their Formation and Control. Edited by two internationally well-known experts in the DBP field, Drs. Roger Minear and Gary Amy, this book[5] evolved from an American Chemical Society Environmental Chemistry Division symposium on disinfection byproducts in water treatment, held in Chicago in 1993. The book is focused on the DBP

chemistry, and includes several chapters on the chemistry, regulations, and toxicology of DBPs. Most of the authors are active researchers in the DBP field. Part 1, General Aspects, reviews DBP regulations, removal technologies, and a DBP control study. Part 2, Chlorine By-Products, discusses the effects of bromide on DBP formation and innovative DBP removal technologies. Part 3, Ozone and Brominated Disinfection By-Products, focuses on bromate formation and control and organic DBPs. Part 4, Chloramines and Chlorine Dioxide, focuses on DBP modeling, DBP formation and control using chloramination, and chlorine dioxide. Part 5, Influence of Natural Organic Matter on By-Products, discusses effects of natural organic matter on DBP formation and control.

Water Disinfection and Natural Organic Matter: Characterization and Control. Edited by Drs. Roger Minear and Gary Amy, this book[6] is the continuation of the previous book and evolved from an American Chemical Society Environmental Chemistry Division symposium, "Disinfection Byproducts and NOM Precursors: Chemistry, Characterization, and Control," held in Chicago in 1995. The book focuses on DBP and natural organic matter (NOM) chemistry. Most of the authors are active researchers in the field. Part I, Chlorination-Chloramination Products and Reactions, illustrates disinfectants and DBP modeling. Part II, Natural Organic Matter Relationships and Characterization, focuses on the characterization of NOM and effects of NOM on DBPs. Part III, Ozone and Other Processes, discusses bromate formation and control and another on organic ozonation byproduct analysis.

Natural Organic Matter and Disinfection By-products: Characterization and Control in Drinking Water. Edited by three well-known experts in the DBP field, Sylvia Barrett, Stuart Krasner, and Gary Amy, this book[7] is the continuation of the previous books and evolved from an American Chemical Society Environmental Chemistry Division symposium, "Natural Organic Matter and Disinfection Byproducts: Characterization and Control in Drinking Water," held in Anaheim in 1999. The book focuses on DBP and NOM chemistry and analyses. Most of the authors are active researchers in the field. Part I, Regulatory and Health Effects Background, focuses on DBP toxicity, regulation, and modeling. Part II, Natural Organic Matter Characterization and Reactivity, focuses on the natural organic matter characterization, reactivity, and DBP formation. Part III, Formation of Chlorination Disinfection Byproducts, focuses on chlorination, DBP formation, and modeling. Part IV, Chemistry of Alternative Disinfectants, focuses on ozonation, radiation, other disinfectants, and their effects on DBP formation. Part V, Disinfection Byproduct Method Development, discusses innovative methods for DBP identification and analyses.

Water Chlorination: Chemistry, Environmental Impact and Health Effects. Volumes 1–6. This six-volume Water Chlorination collection,[8–13] edited by Dr. Robert L. Jolly and others, represents the permanent record of the proceedings of six conferences on "Water Chlorination: Chemistry, Environmental Impact and Health Effects." Jolly is a nationally known researcher. Many of the chapters discuss the formation, analysis, and control of disinfection byproducts, and are focused on the toxicology and epidemiology of water chlorination and DBPs. Water disinfection and regulatory issues are discussed as well. Although some of the information is

outdated, these books have been important DBP information resources since the first volume was published.

9.2 WEB SITES

Disinfection Byproducts: Chemical Information and Molecular Modeling. This Web site,[14] shown in Figure 9.1, consists of references on analytical methods and health effects for common DBPs, including aldehydes, cyanogen halides, dihaloacetones, haloacetic acids, ketoacids, trihaloaldehydes, trihaloacetones, trihaloacetonitriles, trihalomethanes, and trihalonitromethanes. One unique feature of the Web site is the two-dimensional and three-dimensional molecular models for these DBPs. The users can change the molecular model display type, display option, and display color. These three-dimensional molecular models can be rotated in any direction automatically, and can be edited and saved. One typical molecular model for dichloroacetic acid is shown in Figure 9.2. This Web page is a great teaching tool for graduate students, entry level engineers, and entry level chemists. The Web page, especially the analytical and health effect references, has been updated regularly and can be accessed at www.hbg.psu.edu/epc/dbp/frames.html

Drinking Water Priority Rulemaking: Microbial and Disinfection Byproduct Rules. This page,[15] shown in Figure 9.3, has been constructed and maintained by the U.S. EPA Office of Ground Water and Drinking Water. It provides information on the Stage 1 Disinfectants and Disinfection Byproducts Rule and other microbial and DBP regulations. These regulations include existing regulations and future microbial and DBP regulations. For each rule, a summary is provided. For many recent regulations, links to the regulations are provided. Links to guidance and implantation documents for these rules are also provided. Many of these rules and documents were presented in Chapter 7, Disinfection Byproduct Regulations. This page is a great information source for existing and future microbial and DBP regulations. The reader can get the regulations and their guidance documents, and even pre-proposal drafts of new regulations. The page also provides links to meeting summaries for DBP regulations and other drinking water regulations. From these summaries, the reader could better understand the rule-making process. The page can be accessed at www.epa.gov/safewater/mdbp/mdbp.html.

Information Collection Rule. The Information Collection Rule, promulgated in 1996, was designed to support future regulation of microbial contaminants, disinfectants, and disinfection byproducts. The regulation required large public water systems serving at least 100,000 people to monitor and collect data on microbial contaminants, disinfectants, and disinfection byproducts for 18 months. The information collected for the regulation is available at the U.S. EPA's Envirofacts Warehouse Information Collection Rule Web site,[16] as shown in Figure 9.4. The Web site provides information on four DBPs (trihalomethanes, haloacetic acids, chlorite, and bromate), three disease-causing microbes (*Cryptosporidium*, *Giardia*, and virus), and three indicators of fecal contaminations (total coliform, fecal coliform, and *E. coli*). The occurrence data at both the national and state levels were provided in graphical and tabular formats, as shown in Figure 9.5 and Table 9.1. The reader can

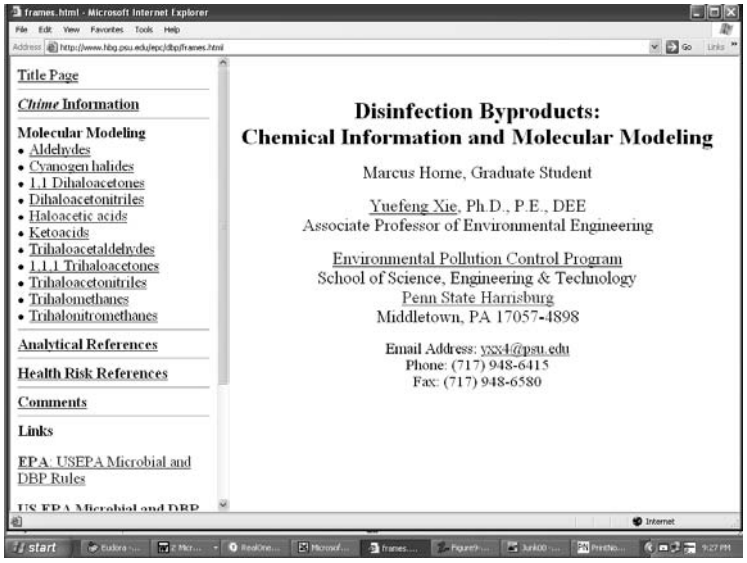

FIGURE 9.1 Disinfection byproducts: chemical information and molecular modeling. (From Horne, M.B. and Xie, Y.F., Disinfection Byproducts: Chemical Information and Molecular Modeling, at www.hbg.psu.edu/epc/dbp/frames.html, 1997.)

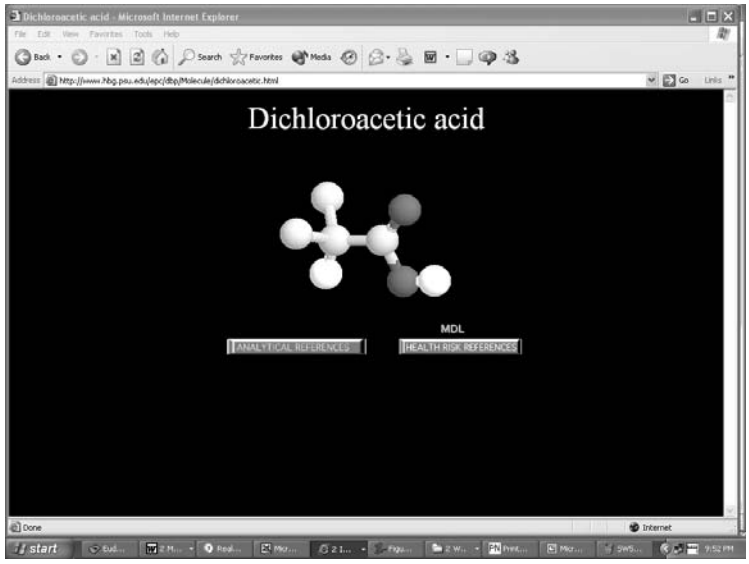

FIGURE 9.2 A typical molecular model for dichloroacetic acid. (From Horne, M.B. and Xie, Y.F., Disinfection Byproducts: Chemical Information and Molecular Modeling, at www.hbg.psu.edu/epc/dbp/Molecule/dichloroacetic.html, 1997.)

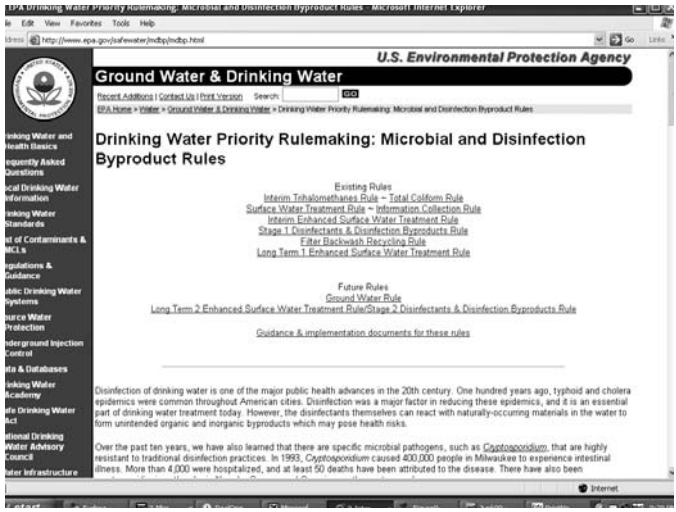

FIGURE 9.3 Drinking water priority rulemaking: microbial and DBP rules. (From United States Environmental Protection Agency, Drinking Water Priority Rulemaking: Microbial and Disinfection Byproduct Rules, at www.epa.gov/safewater/mdbp/mdbp.html, 2003.)

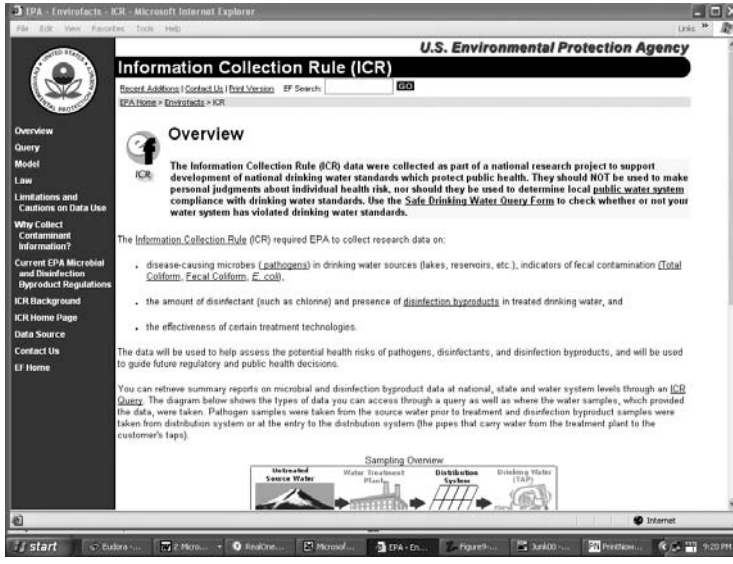

FIGURE 9.4 Information Collection Rule Web site. (From United States Environmental Protection Agency, Information Collection Rule, at www.epa.gov/enviro/html/icr/index.html, 2003.)

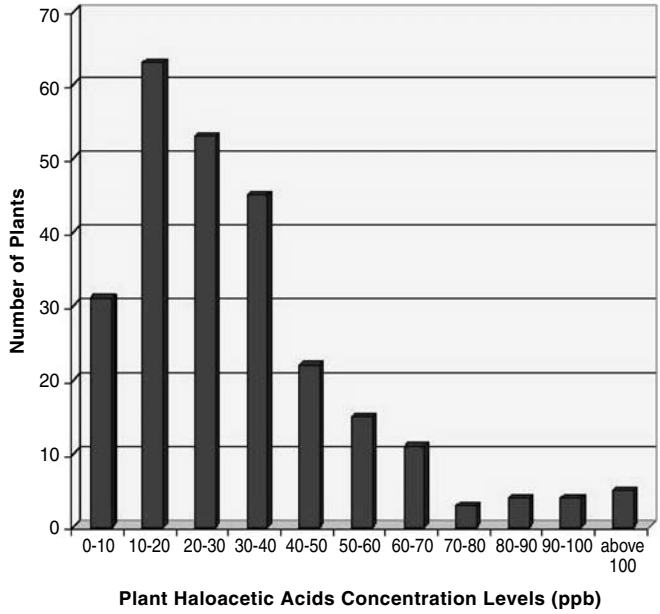

FIGURE 9.5 National haloacetic acid occurrence levels in treated surface water for July 1998 to September 1998. (From United States Environmental Protection Agency, Information Collection Rule, at www.epa.gov/enviro/html/icr/national/report/haa5/5.html, 2003.)

TABLE 9.1
National Haloacetic Acid Occurrence Levels in Tabular Format for July 1998 – September 1998

Levels of Haloacetic Acids 5 (ppb)	Water Type	Number of Plants
0-10	Surface Water	31
10-20	Surface Water	63
20-30	Surface Water	53
30-40	Surface Water	45
40-50	Surface Water	22
50-60	Surface Water	15
60-70	Surface Water	11
70-80	Surface Water	3
80-90	Surface Water	4
90-100	Surface Water	4
above 100	Surface Water	5

Source: From United States Environmental Protection Agency, Information Collection Rule, at www.epa.gov/enviro/html/icr/national/report/haa5/5.html, 2003.

also access the data submitted by each participating water systems. The Web site provides background information on the Information Collection Rule, microbial contaminants, and DBPs. This site is a great information resource to get DBP and microbial occurrences at national and state levels for large water systems. The Web page can be accessed at www.epa.gov/enviro/html/icr/ .

Microbial / Disinfection Byproducts (M/DBP) Center. This Web site,[17] Microbial/Disinfection Byproducts (M/DBP) Center, has been constructed and maintained by the American Water Works Association, as shown in Figure 9.6. The site provides background and regulatory information on the implementation of Interim Enhanced Surface Water Treatment Rule and Disinfectants and Disinfection Byproducts Rule. The site also provides links to various EPA Web sites where the reader could download regulations and guidance documents. The site provides 15 compliance case studies for the regulation compliance. These case studies were presented at the 1999 teleconference. There are six case studies for the DBP regulation compliance. These plants include both groundwater and surfacewater plants, ranging from 2 to 50 million gallon per day. The case studies presented numerous approaches for DBP control, including enhanced coagulation, moving the chlorine addition point, chloramination, ozonation, reducing detention time, and improving sludge handling. The web page can be accessed at www.awwa.org/Science/dbp/.

Projects Related to Special Topics: DBP Projects. This Web site,[18] DBP Projects, is constructed and maintained by the American Water Works Association Research Foundation. Since its establishment, the Research Foundation has funded over 100

FIGURE 9.6 Microbial/Disinfection Byproducts (M/DBP) Center. (Reprinted from AWWA Web site, www.awwa.org/science/dbp, by permission. Copyright © May 13, 2003, American Water Works Association.)

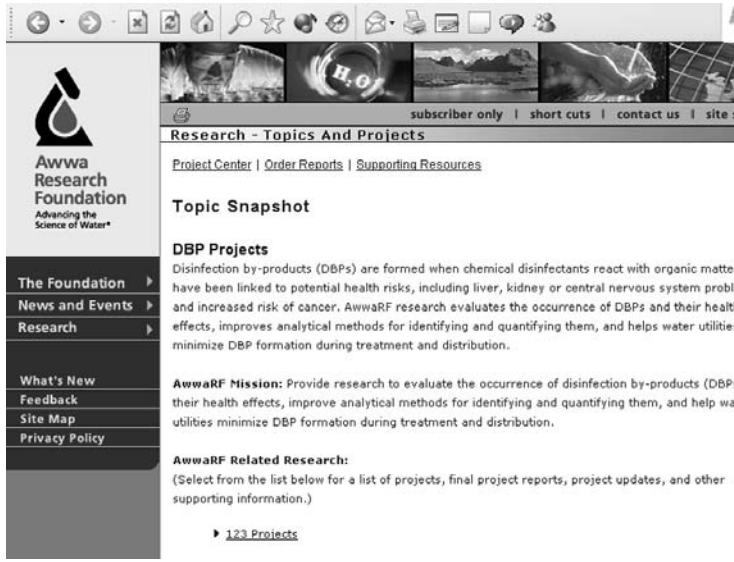

FIGURE 9.7 American Water Works Association Research Foundation DBP projects. (From American Water Works Association Research Foundation, *DBP Projects,* at www.awwarf.org/research/TopicsAndProjects/topicSnapShot.aspx?Topic=DBP, June 24, 2003. With permission.)

projects in the area of DBP analysis and control, as shown in Figure 9.7. For each project, a project summary (1–2 pages) is accessible at the Web site. These summaries provide brief information on the background, methods, results, and conclusion of the project. The Web page can be accessed at www.awwarf.org/research/TopicsAndProjects/topicSnapShot.aspx?Topic=DBP.

A full project report for these DBP projects is also available through the Research Foundation. Research Foundation subscribers may request these reports (indicated by an order number) online or by telephone. Others should order reports by calling 1-888-844-5082 or through the American Water Works Association Bookstore at www.awwa.org/ bookstore or 1-800-926-7337.

9.3 JOURNALS

Journal American Water Works Association (JAWWA). This well-known, monthly journal, published by the American Water Works Association, Denver, is dedicated to safe drinking water and is an internationally recognized authority on drinking water issues. Since the 1970s, the journal has published many articles in DBP formation, analysis and control. In addition to its peer-reviewed articles, it also provides news of federal legislative and regulatory developments.

Environmental Science and Technology. This journal, published biweekly by the American Chemical Society, Washington, DC, publishes peer-reviewed research papers in environmental science and engineering, including air, water, and land. It

includes many papers in the areas of DBP analysis and formation. This journal is a great resource for papers dealing with identification of new DBPs and mechanisms for DBP formation and degradation.

Water Research. The International Water Association publishes this journal in partnership with Elsevier Science. It contains refereed, original research papers on all aspects of the science and technology of water quality and its management worldwide, especially in drinking water and wastewater quality and treatment. Many papers in the areas of DBP analysis, formation, and control have been included. Many of the papers are written by researchers from European and Asian countries. This journal is a great resource for learning the international aspect of DBP research around the world.

Ozone Science and Engineering. Published bimonthly by the International Ozone Association, in partnership with Lewis Publishers, this journal provides peer-reviewed scientific, engineering, or review papers covering various aspects of ozone technology. Many papers include the areas of formation, analysis, and control of ozonation DBPs. The use of ozone for DBP control is also well published in the journal.

Journal of Water Supply: Research and Technology–AQUA. This journal, published by the International Water Association (IWA), contains peer-reviewed papers dealing with research and development in water supply technology and management. It includes many papers in the areas of formation and control of DBPs.

9.4 CONFERENCES

American Water Works Association Water Quality Technology Conference. This conference, organized by the American Water Works Association and held annually in November, is well-attended by chemists, microbiologists, engineers, and professors in the water industry. In recent years, several sessions have been devoted to DBP removal and control technologies, DBP analysis techniques, DBP regulation, and risk assessment. The conference publishes proceedings, however, many papers presented in Sunday seminars and special sessions are not included. This conference is an excellent resource for DBPs and a great place for networking with colleagues in the water industry.

American Water Works Association Annual Conference and Exposition. This conference, organized by the American Water Works Association and held annually in June, is well-attended by engineers, professors, students, managers, operators, regulators, and exhibitors in the water industry. In recent years, several sessions have been devoted to DBP regulations and control technologies. Many graduate student research projects are presented in two special sessions, University Forums, which provides an exclusive opportunity for students to present their research. The conference publishes proceedings, however, many papers presented in Sunday seminars and special sessions are not included. This conference is an excellent resource for

DBP technology and regulations and a great place for networking with colleagues in the water industry.

American Water Works Association Research Foundation Workshops and Technology Transfer Conferences. American Water Works Association Research Foundation is nonprofit and supported by the water industry. In addition to supporting research projects, the foundation also organizes workshops and technology transfer conferences, many focused on DBPs. These programs are great resources for the water utilities, manufacturers, and consultants, especially for foundation subscribers.

International Ozone Association Conferences. The International Ozone Association holds a World Congress every 2 years, which publishes proceedings. In addition, the Association holds other regional or specialty conferences regularly. The formation and control of ozonation byproducts, especially bromate, has been frequently presented at the Congress and other meetings. Many conference sessions address the effects of ozonation on chlorination DBPs, and the use of ozone for chlorination DBP control.

9.5 VIDEO TAPES

1974 Revisited — An Historical Review of the Disinfection By-Product Issue. In this 47-minute video,[19] Dr. James Symons, an internationally well-known DBP expert, gives a first-person account of current research from 1974 to 1995. This makes the material accessible to both novice and expert. With an excellent review of the DBP history, this video tape is a great teaching aid for undergraduate and graduate students, water operators, and analytical chemists.

Water Supply Operations Series: Disinfection Byproducts Control. This 11-minute video[20] gives a brief review of the disinfection byproduct formation and control technologies, including enhanced coagulation, granular activated carbon adsorption, ozonation and biofiltration, and membrane processes for DBP precursor removal. This video is a great teaching aid for undergraduate and graduate students, water operators, and analytical chemists.

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10 Overview of Drinking Water Treatment Processes

OBJECTIVES

The objective of this chapter is to provide an overview of drinking water treatment processes for those with limited experience in this field. For many nonengineers, especially those in analytical and operational fields, this chapter will help them better understand the purpose and fundamentals of common water treatment processes.

NOMENCLATURE

CT mathmatical product of disinfectant residual (C) and contact time (T)
DBP disinfection byproduct
G velocity gradient
GAC granular activated carbon
NOM natural organic matter
PAC powdered activated carbon
U.S. EPA United States Environmental Protection Agency

10.1 INTRODUCTION

The purpose of drinking water treatment is to remove pathogens, toxic chemicals, particles, and aesthetic contaminants from raw water. Typical water sources include ground water and surface water. Generally speaking, ground water is of high quality. Surface water, including water from rivers, lakes, and reservoirs, can contain higher levels of organic chemicals, particles, and pathogens. Because disinfection byproducts (DBPs) are more commonly found in treated surface water than in treated ground waters, this chapter will focus on surface water treatment.

Surface water treatment commonly uses conventional water treatment processes including coagulation, flocculation, sedimentation, filtration, and disinfection, as shown in Figure 10.1. For water low in turbidity, water could be treated without sedimentation and/or flocculation. The terms of direct filtration and direct in-line filtration are commonly used to identify treatment processes without sedimentation, and without flocculation and sedimentation, respectively,[1] as shown in Figure 10.2. Pretreatment including oxidation and carbon adsorption is commonly used prior to coagulation. Intermediate or post-treatment, such as oxidation and carbon adsorption, is also commonly used.

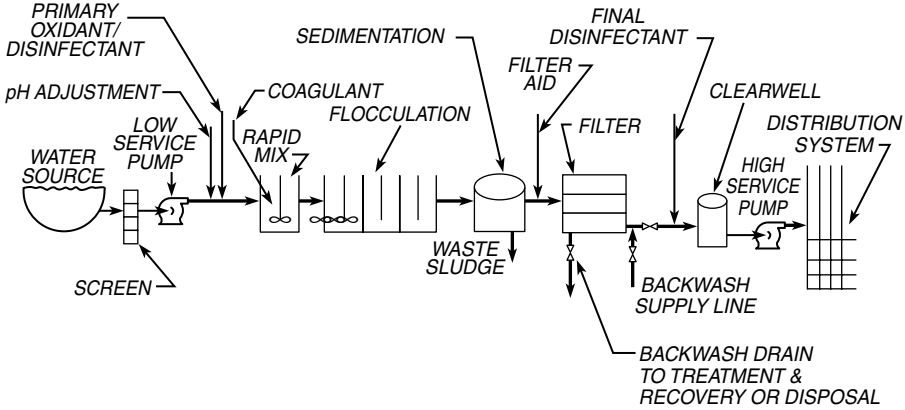

FIGURE 10.1 Conventional water treatment processes. (From Logsdon, G., Hess, A., and Horsley M., Guide to selection of water treatment processes, in *Water Quality and Treatment,* 5th ed., Letterman, R.D., Ed., Copyright ©1999 by The McGraw-Hill Companies, Inc. Reprinted by permission of the publisher.)

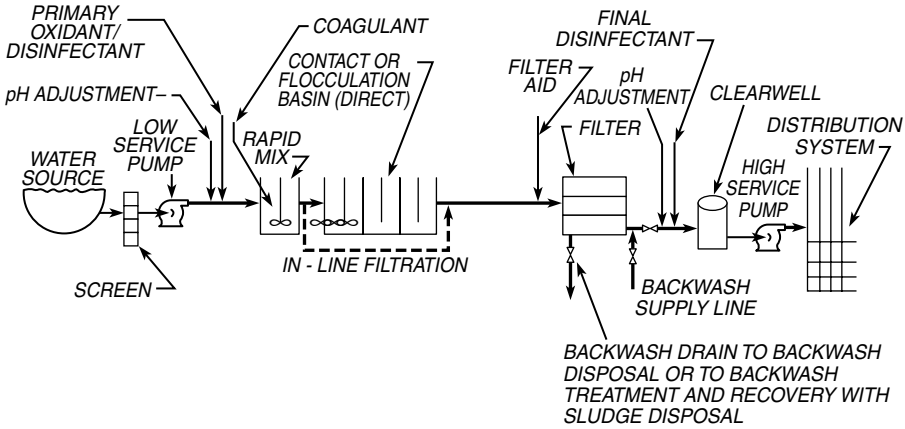

FIGURE 10.2 Direct and direct in-line filtration treatment processes. (From Logsdon, G., Hess, A., and Horsley M., Guide to selection of water treatment processes, in *Water Quality and Treatment,* 5th ed., Letterman, R.D., Ed., Copyright ©1999 by The McGraw-Hill Companies, Inc. Reprinted by permission of the publisher.)

10.2 COAGULATION

In surface water sources, most particles, including silts and pathogens, are very small in size. The reason these tiny particles are suspended in water is that they are negatively charged and repel each other. In order for the subsequent sedimentation and filtration to work, the negative charge on these particles needs to be neutralized first. The objective of a coagulation process is to destabilize colloidal particles.

Coagulants need to be mixed into raw water for effective coagulation. One of the common coagulants is alum or aluminum sulfate with a formula of $Al_2(SO4)_3$•14.3 H_2O. Another common coagulant is ferric chloride, or $FeCl_3$. Both coagulants will consume alkalinity and reduce pH in water, as shown in Equations 10.1 and 10.2. For effective coagulation, in general, the pH range required is approximately 5.5 to 8.0 for alum and 4.0 and 9.0 for $FeCl_3$ and other ferric salts. If natural alkalinity is insufficient in raw water, an alkaline, including lime (CaO), hydrated lime ($Ca(OH)_2$), soda ash (Na_2CO_3), or caustic soda (NaOH), could be added. Other coagulants include cationic polymers, polymerized $AlCl_3$ and $Al_2(SO_4)_3$. These polymers have little impact on water pH.

$$Al_2(SO_4)_3 + Ca(HCO_3)_2 \rightarrow Al(OH)_3\downarrow + CaSO_4 + CO_2 \quad (10.1)$$

$$FeCl_3 + Ca(HCO_3)_2 \rightarrow Fe(OH)_3\downarrow + CaCl_2 + CO_2 \quad (10.2)$$

To neutralize negatively charged particles, Al^{3+}, Fe^{3+}, and other cationic intermediate products should be brought in contact with these particles before they form $Al(OH)_3$ or $Fe(OH)_3$ precipitates. Therefore, an efficient mixing between coagulants and negatively charged particles is essential for an effective coagulation. Either a high speed mechanical mixer or an efficient static mixer can be used for this purpose. Therefore, this coagulation process is also referred to as rapid mixing.

In addition to charge neutralization, the formation of $Al(OH)_3$ or $Fe(OH)_3$ precipitates could also remove particles by enmeshment, especially at high coagulant dosages. This process is usually called sweep flocculation. Another theory for coagulation is double-lay compression, which is commonly described in textbooks. However, this theory is not practical for drinking water treatment.[2]

Natural organic matters (NOM) can also be removed by adsorbing onto the precipitates or settling out as metal-NOM complexes. NOM also has a tendency to stabilize particles or particulates. Therefore, a higher natural organic matter concentration in water requires a higher dosage of coagulant.

For effective coagulation, proper coagulant dosage and efficient mixing are two important operating conditions. The pH of the raw water, type of coagulants, type of contaminant particles, and concentration of NOMs also affect the effectiveness of coagulation. Coagulation conditions, including coagulant type, coagulant dosage, mixing, and pH for an effective coagulation, could be determined in four or six 1- or 2-L square (or round) jars equipped with mixing paddles. This test is commonly referred to as jar test. The charge on the contaminant particles (or zeta potential) could also be determined by measuring the velocity of particles in an electrical field using a zeta meter. A neutral particle will remain still in an electric field. A negatively charged particle will move toward cathode and a positively charged particle will move toward anode. A higher velocity indicates a higher zeta potential or charge. For an effective coagulation, the zeta potential should be reduced to about zero. In water treatment plants, stream current detectors are commonly used to automate the addition of coagulant. The concept of stream current detection is similar to that of zeta potential measurement.

10.3 FLOCCULATION

Flocculation is a process to agglomerate neutralized particles by chemically joining or bridging them together. During this process, a gentle mixing is needed to bring the neutralized particles into contact with each other. Since the electrical repelling force between particles are neutralized, larger particles or flocs will be formed when particles collide. In general, a higher mixing provides more opportunities for particles to collide into each other. However, a very high mixing can also break down large flocs. Therefore, a gentle mixing is used for flocculation.

It is also common to use two or three mixing zones for a more effective flocculation. The process is called two or three-stage flocculation. In the first stage (or zone), since few large flocs are formed, a higher mixing speed is used to increase the rate of particle collision. In a later stage, a slower mixing speed is used to preserve large flocs. Velocity gradient, or G value, is commonly used to describe mixing, or mixing intensity. G value has a unit of fps/ft or s^{-1} and can be calculated from energy dissipated and the volume of flocculation basins,[3] as expressed by Equation 10.3. Typical G values range from 10 to 100 fps/ft or $s.^{-1}$ In comparison, the G values for rapid mixing range from 300 to 1700 fps/f or s^{-1} with a mixing time between 1 and 30 sec.

$$G = [P/(\mu V)]^{1/2} \tag{10.3}$$

P = Power input; μ = absolute viscosity of water; V = volume of flocculation basins

Another important condition for flocculation is the mixing time, or flocculation time. Longer mixing times provide more opportunities for particles to collide. For a given flow, however, a longer mixing time requires a larger flocculation basin. This could result in a higher construction cost, or capital cost. For many water treatment plants, typical flocculation times range from 10 to 30 min.

An effective flocculation also depends on the original particle concentration. Increasing the particle concentration will increase the opportunity for particles to collide, or become larger flocs. When raw water turbidity is extremely low in winter or spring, water generally is hard to treat. It is a common practice to add bentonite, kaolin, and other products to increase raw water turbidity during winter and spring seasons and to improve the particle removal efficiency.

10.4 SEDIMENTATION

Sedimentation, or clarification, is a process to remove flocculated flocs from processed water by gravity. In sedimentation basins, velocity of water flow is reduced to allow flocs to settle. The typical maximum horizontal velocity and detention time of water in sedimentation basins is 0.5 fpm (0.15 m/min), and 2 to 4 h, respectively. The overflow rate is a common design criterion for sedimentation basins. The overflow rate has a unit of gpd/ft^2, which gives the water flow per unit of sedimentation surface area. Mathematically, overflow rate is the settling velocity of flocs in

water. In general, a proper overflow rate and water depth will give a proper horizontal velocity and retention time. Settled flocs, or sludge, need to be removed from the bottom of sedimentation basins for further sludge processing and disposal.

An effective sedimentation depends on many water quality parameters. As shown in Table 10.1, the size of particles or flocs significantly affects sedimentation efficiency. Therefore, the treatment efficiency of coagulation and flocculation will greatly influent the sedimentation efficiency. In many cases, poor sedimentation efficiency, or high settled water turbidity, indicates inadequate coagulation or flocculation.

An effective sedimentation also depends on the hydraulic flow of the processed water in sedimentation basins. A poorly designed basin could cause dead space and short circuiting inside the sedimentation basin and lower the sedimentation efficiency. The dead space and short circuiting could also be a result of a sudden change of water temperature and turbidity. The wind condition could also affect the sedimentation efficiency if sedimentation basins are located in an open field.

Plate or tube settlers are commonly used to enhance the sedimentation efficiency. Plate settlers, or lamella settlers, consist of uniformly spaced panels. The panels are commonly inclined with an angle of 60°. Tube settlers are plastic modules with uniformly spaced, inclined channels. Plate and tube settlers could significantly reduce the size of sedimentation tank and are often referred to as high rate settlers. Figure 10.3 illustrates the installation of plate and tube settlers in rectangular and circular basins.[4]

10.5 FILTRATION

Water filtration is a process to separate non-settable and destabilized particles from process water using a porous medium. Sand and/or anthracite are commonly used as granular media for water filtration. The filtration following coagulation and sedimentation is a physical chemical process. The particle removal mechanism involves physical straining, sedimentation, flocculation, and adsorption. Filtration is also referred to as rapid sand filtration in contrast to slow sand filtration, which is a physical and biological process for water treatment.

The physical straining is not the main mechanism for particle removal in granular media water filtration. The pore size in a layer of typical (1 mm) granular media is approximately 150 μm in size by calculation. However, the filter could effectively remove particles much smaller than 1 μm.[5] Larger particles are removed by physical straining and smaller particles are removed by coagulation and adsorption. To obtain good filtration efficiency, particles in water must be chemically destabilized, or neutralized, prior to filtration. For a proper chemically pretreated water, a 99.7% (2.5 log) removal of *Giardia* can be reliably achieved in filtered water. However, without chemical pretreatment, removal efficiency of *Giardia* by filtration is only 80 to 91%.[3] Therefore, a poor filter effluent generally indicates an improper coagulation.

When two or three types of media are used in a filter, the filter is called dual media, tri-media, or multimedia filter. Generally, dual media consists of sand and anthracite layers with anthracite on top of sand. For tri-media or multimedia filters,

TABLE 10.1
Settling Velocity and Settling Time of Various Particles in 20°C Water

Type of particles	Particle density (kg/m³)	Size in diameter (μm)	Settling velocity	Time to settle for one meter
Bacteria	1010	1	23 μm/h	5 years
Clay	2000	0.1	20 μm/h	6 years
Carbon steel	7860	0.1	134 μm/h	10 months
Alum flocs	1010	50	0.057 m/h	17.3 h
Alum flocs	1010	100	0.23 m/h	4.3 h

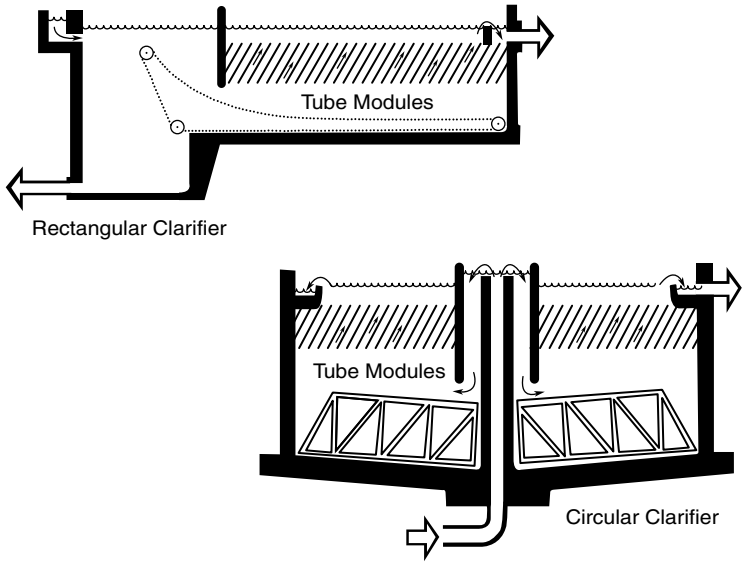

FIGURE 10.3 Tube settlers installed in sedimentation basins. (Courtesy of USFilter Microfloc Products.)

a garnet layer is added beneath the sand. Typically, a filter can be run continuously for 24 to 48 h. Then a back wash is needed to clean the filter media. Backwash water contains pathogens and particles removed by filtration. The recycle of backwash water is regulated under the U.S. EPA Filter Backwash Recycling Rule.[6]

10.6 DISINFECTION

Disinfection is a process to inactivate pathogens in water. Common examples of waterborne diseases are listed in Table 10.2. Waterborne pathogens include bacteria, viruses, protozoans, and helminth eggs. Water disinfection could be achieved through both physical and chemical means. Ultraviolet radiation, a physical disinfection

TABLE 10.2
Common Waterborne Diseases

Waterborne Disease	Causative Organism	Source of Organism in Water	Symptom
Gastroenteritis	*Salmonella (*bacteria)	Animal or human feces	Acute diarrhea and vomiting
Typhoid	*Salmonella typhosa* (bacteria)	Human feces	Inflamed intestine, enlarged spleen, high temperature — fatal
Dysentery	*Shigella* (bacteria)	Human feces	Diarrhea — rarely fatal
Cholera	*Vibrio comma* (bacteria)	Human feces	Vomiting, severe (bacteria) diarrhea, rapid dehydration, mineral loss — high mortality
Infectious hepatitis	Virus	Human feces shellfish grown in polluted water	Yellowed skin, enlarged liver, abdominal pain — low mortality, lasts up to 4 months
Amoebic dysentery	*Entamoeba histolytica* (protozoan)	Human feces	Mild diarrhea, chronic dysentery
Giardiasis	*Giardia lamblia* (protozoan)	Animal or human feces	Diarrhea, cramps, nausea, and general weakness — not fatal, lasts 1 week to 30 weeks
Cryptosproidiosis	*Cryptosporidium* (protozoan)	Human and animal feces	Acute diarrhea, abdominal pain, vomiting, low-grade fever
Legionellosis	*Legionella pneumophila* and related bacteria		Acute respiratory illness

Source: Reprinted from *Principles and Practices of Water Supply Operations — Water Treatment,* by permission. Copyright ©1995, American Water Works Association.

process, has drawn significant attentions because of its effectiveness for *Cryptosporidium* inactivation. For chemical disinfection, chlorination is the most common water disinfection process. Other common chemical disinfectants include chloramines, chlorine dioxide, and ozone.

For chemical disinfection, the two most important design criteria are disinfectant residual concentration (C) and contact time (T). Pathogen kill is proportional to the product of the disinfectant residual (C) and contact time (T), or CT (C times T) value, for a given disinfectant, pathogen, temperature, and pH. To achieve the same disinfection efficiency, water plant operator could use a lower disinfectant residual

TABLE 10.3
CT Values for 99% Inactivation of *Giardia* and Virus by Various Disinfectants

Disinfectants	*Giardia* (mg/L·min)	Virus (mg/L·min)
Chlorine	37	1.0
Chloramines	735	321
Chlorine dioxide	10.0	2.1
Ozone	0.48	0.40

Source: Data from Disinfection Profiling and Benchmarking Guidance Manual, EPA-815-R-99–013, the United States Environmental Protection Agency, August 1999.
Note: 20°C, pH 7, and 1 mg/L disinfectant residual.

and longer contact time, or a higher disinfectant residual and shorter contact time, as long as the product or CT value is maintained. The typical CT values for 99% inactivation of *Giardia* and virus using various disinfectants are listed in Table 10.3.[7]

For *Giardia* inactivation, as shown in Table 10.3, one can see that ozone is the most efficient disinfectants because it requires the lowest CT value, 0.48 mg/L·min, for 99% inactivation. One can also see that *Giardia* is much more resistant to chlorine than virus because *Giardia* inactivation requires a higher CT value, 37 mg/L·min.

Percentage is commonly used to describe disinfection efficiency. In addition to disinfection, sedimentation and filtration are also effective in removing pathogens. Log removal is used as a convenient way to sum the disinfection efficiencies of several consecutive processes. One log removal is equivalent to 90% removal. It is much easier to calculate the overall efficiency for a treatment plant using the log removal. For instance, the removal efficiency for coagulation, sedimentation, and filtration is 99% or 2 logs, and 90% or 1 log for chlorination. The overall removal efficiency is 2 logs plus 1 log, or 3 logs (99.9%). Using percentage the calculation will be slightly more complicated because one cannot add two percentages (99% and 90%) directly. The conversions between log removal (L) and percentage removal (P) are shown in Equations 10.4 and 10.5. Typical log removal values and their corresponding percentage removal values are shown in Table 10.4.

TABLE 10.4
Relationship between Percentage Removal and Log Removal

Log Removal	Percentage Removal
0.5	68.4
1.0	90.0
1.5	96.8
2.0	99.0
2.5	99.7
3.0	99.9

$$L = - \log (1-P) \quad (10.4)$$

$$P = 1–10^{–L} \quad (10.5)$$

L = Log removal value, P = Percentage removal value

A conventional filtration process, including coagulation, sedimentation, and filtration, generally provides 2.5 logs removal for *Giardia*. A direct filtration process, coagulation and filtration, provides 2.0 logs removal. Because of the 3-log *Giardia* removal requirement under the Surface Water Treatment Rule,[8] the disinfection process for conventional filtration must achieve 0.5 log (68%) inactivation, and 1.0 log (90%) inactivation for direct filtration.

Another purpose of disinfection is to provide a disinfectant residual in distribution systems and inhibit bacteria or other pathogen regrowth in distribution systems. The disinfectant used for this purpose is called secondary disinfectant. Chlorine is the most common secondary disinfectant. Due to the concern of DBP formation in distribution systems, more and more water systems are using chloramines as the secondary disinfectant. Some water systems, especially small water systems, use chlorine dioxide as their primary and secondary disinfectant. Ozone and UV radiation do not provide a stable disinfectant residual and are not good choices for secondary disinfectants. More information on the applicability of alternative disinfectant techniques is listed in Table 10.5.[9] Please refer to Chapter 5 for more information on the new development of UV technology in *Giardia* and *Cryptosporidium* inactivation.

10.7 PREOXIDATION

Preoxidation is commonly used to control taste, odor and color, iron and manganese in water and algae growth in various treatment units. Some treatment plants also use preoxidation (prechlorination and preozonation) to achieve required CT, or disinfection requirements. The common preoxidation chemicals are chlorine, potassium permanganate, chlorine dioxide, and ozone. Due to the concerns over DBP formation, many plants have eliminated prechlorination. Ozonation, with an excellent disinfection efficiency, effective iron and manganese oxidation, superior taste and odor control, and little halogenated DBP formation, has been used for preoxidation in many systems. Potassium permanganate and chlorine dioxide are also excellent preoxidation chemicals for taste, odor, color, iron, and manganese control.

Oxidants could also be added after coagulation and before filtration. This is generally referred to as intermediate oxidation. Intermediate ozonation is commonly used to reduce the ozone dosage or promote biological filtration. Intermediate chlorination is commonly used to increase the CT and improve filtration efficiency.

TABLE 10.5
Applicability of Alternative Disinfection Techniques

Consideration	Cl_2	O_3	ClO_2	UV
Equipment reliability	Good	Good	Good	Fair to good
Relative complexity of technology	Simple	Complex	Moderate	Moderate
Safety concerns	Yes	Moderate	Yes	Moderate
Bactericidal	Good	Good	Good	Good
Virucidal	Moderate	Good	Moderate	Good
Efficacy against protozoa	Fair	Moderate	Fair	Fair to moderate
By-products of possible health concern	Yes	Some	Some	None known
Persistent residual	Long	None	Moderate	None
Reacts with ammonia	Yes	No	No	No
pH dependent	Yes	Slight	Slight	No
Process control	Well developed	Developing	Developing	Developing
Intensiveness of operations and maintenance	Low	High	Moderate	High

Source: From Haas, C.N., Disinfection in *Water Quality and Treatment*, 5th ed., Letterman, R.D., Ed., Copyright ©1999 by The McGraw-Hill Companies, Inc. Reprinted by permission of the publisher.

10.8 CARBON ADSORPTION

Carbon adsorption is an effective process to removal taste, odor, and color in drinking water. Carbon adsorption is also effective in removing pesticides, herbicides, humic substances, and other synthetic or natural organic chemicals. Two types of carbon, powdered activated carbon (PAC) and granular activated carbon (GAC), are generally used in drinking treatment. PAC is typically used to combat seasonal taste, odor, color, or organic and inorganic contamination problems. It could be added anywhere before sedimentation. Typically, PAC is added in raw water in order to achieve a longer contact time. Spent carbon is collected in sedimentation basin as sedimentation sludge. GAC is generally used in a separated GAC contactor or as a filtration medium in sand or sand/anthracite filters. GAC is typically used to combat year-around taste, odor, color, or organic and inorganic contamination problems. It is also effective in promoting biological activity on its surface and reducing biologically degradable chemicals. DBP precursors can be removed through carbon adsorption and biological degradation. Adsorption capacity of GAC generally lasts for 2 to 3 years. Upon exhaustion, the GAC needs to be removed from the basins and thermally regenerated on site or off site.

10.9 XIE'S BAR THEORY: WATER COAGULATION

The conventional drinking water treatment process consists of coagulation, sedimentation, filtration, and disinfection. The main objective of these processes is to remove particles including *Giardia*, *Cryptosporidium*, and other pathogens. The coagulation process consists of rapid mixing and flocculation. Rapid mixing introduces chemicals (coagulants) into process water and destabilizes suspended particles. Flocculation combines small particles into large flocs that can be removed by sedimentation.

First, let us picture the water treatment facility as a bar, and men and women as particles. The objective is to pair all men and women. For many men and women, like particles in water, if there are repelling forces between them, nothing will happen between them. To make them attractive to each other we can quickly add a proper dose of alcohol, or chemical. If the dosage is not adequate, the repelling charge is not fully neutralized. If the dosage is too high (or drunk), it will result in a reverse charge that generates a new repelling force.

After a rapid addition of a proper dosage of alcohol, men and women are very much attracted to each other. However, if everyone sits still, nothing will happen. A typical example is a formal restaurant that serves alcohol. A slow mixing between men and women is needed for them to encounter. This is why a bar is designed for people to walk around. Like particles in water, not every encounter will produce a result. The efficiency depends on the attractive force, which in turn depends on the proper alcohol dosage. Regardless of the efficiency, more mixing means more opportunities. However, an extremely high mixing could break up existing pairs. To get better efficiency, two- or three-stage mixing can be used. The first stage should use the fastest mixing and the last one the slowest mixing. A sharp person will walk inside the bar quickly first to identify targets. Then he or she will slow down to focus on a few targets.

Mixing time is also important. If someone stays inside a bar for 5 min, the chance for him or her to pair with someone is very limited. A 30-min stay will provide more opportunities. A 10-h stay may produce the most opportunities, but will cost more money. Therefore, mixing time is governed by economic factors as well as particle encounters.

In winter, raw water generally has a low temperature and low turbidity. Winter is the most difficult time to treat water. Why? A low turbidity means a low particle concentration. Much like the bar scenario where a person will have less chance of meeting others on Monday night than on Friday or Saturday night, because there are fewer people around.

In summary, a successful pairing (floc formation) depends on a rapid addition (rapid mixing) of a proper dosage of alcohol (coagulant), a proper slow mixing (flocculation mixing), adequate mixing time (flocculation time), and a bar full of men and women (a high original particle concentration). The efficiency could be improved by using a two- or three-stage slow mixing (flocculation). Most importantly, an overdose of chemical will result in a reversed charge and a repelling force between you and others, not to mention the economic cost.

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* Page numbers in **bold** refer to molecular structures.

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