

CHAPTER 19

FORMATION AND CONTROL OF DISINFECTION BY-PRODUCTS

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INTRODUCTION

Disinfection (and oxidation) by-products (DBPs) are chemical compounds produced as an unintended consequence of disinfection or oxidation processes in drinking water treatment. Most of the compounds of greatest concern contain chlorine and bromine atoms; however, the formation of iodinated compounds also has been noted (Weinberg et al., 2002). Some of these compounds have been found to be carcinogenic or to cause adverse reproductive or developmental effects in animal studies (see Chap. 2). Others have been shown

to be mutagenic and hepatotoxic. As a result, the U.S. Environmental Protection Agency (USEPA) promulgated rules in 1979, 1998, and 2006 regulating DBP concentrations in finished drinking waters (see Chap. 1).

This chapter focuses on a group of chemical contaminants (DBPs in this case), rather than on treatment process technology. As a result, we will refer the reader to specific chapters on treatment processes as they are brought into the discussion of DBPs. In some cases we will provide supplemental information on the performance of treatment processes as they pertain specifically to the control of DBPs. The chapter opens with a summary of the types of by-products formed from each of the commonly used disinfectants, followed by a discussion of factors affecting their formation. Next, the chapter turns to DBP control, including removal of precursors, use of modified disinfection practices, and removal of DBPs after formation. The chapter concludes with a discussion of DBP concentrations and losses in distribution systems.

FORMATION OF DISINFECTION (AND OXIDATION) BY-PRODUCTS

General Considerations

Water treatment oxidants/disinfectants derive their effectiveness from their general chemical reactivity. The same attributes that give disinfectants the ability to react with cell membranes, nuclear materials, and cellular proteins also lead to reactions with abiotic dissolved organic matter and extracellular biomolecules. Except for the occasional source with high ammonia or sulfide concentrations, most of the oxidant/disinfectant demand in raw and treated drinking water can be attributed to reactions with such dissolved organic molecules in water.

Most organic matter in surface and groundwater is of natural origin. Some of this natural organic matter (NOM) is highly reactive with a wide range of oxidants. The reaction products include reduced forms of the oxidants (e.g., chloride, hydroxide, and chlorite when using chlorine, ozone, and chlorine dioxide, respectively) and oxidized forms of the organic or inorganic reactants (e.g., bromate) (Fig. 19-1).

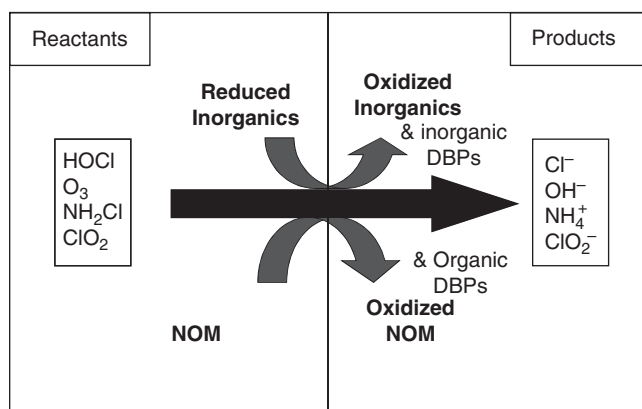


FIGURE 19-1 Schematic illustration of reactions of various oxidants with natural organic material (NOM) and reduced inorganic substances.

The sites of disinfectant (oxidant) attack on NOM are often carbon-carbon double bonds and reduced heteroatoms (e.g., N and S). The organic by-products formed are more highly oxidized, often containing more oxygen atoms. As the extent of the reaction increases, the organic matter becomes more fragmented, and the specific by-products are simpler in structure. General oxidation by-products include the C₁-C₃ acids, diacids, aldehydes, ketones, and ketoacids (e.g., Griffini and Iozzelli, 1996). Specific examples include oxalic acid, pyruvic acid, and formaldehyde.

Several of the disinfectants are capable of producing by-products that have halogen atoms (i.e., chlorine, bromine, and iodine) incorporated into their structure. Aqueous chlorine and bromine do this to the greatest extent, followed by chloramines and ozone. In the case of ozone, high concentrations of bromide are required for substantial bromine incorporation. The organic halide by-products can be measured collectively by the total organic halide analytical method (abbreviated TOX, or more accurately, dissolved organic halide, DOX; for more on this method, see APHA et al., 2005). Because NOM contains very low levels of TOX, this analysis presents an opportunity to easily measure a large and diverse group of compounds that are indisputably DBPs. It also targets a subset of the total DBPs (i.e., just the halogenated ones) that are viewed as the compounds of greatest concern, allowing the calculation of halogen mass balances (e.g., see Singer and Chang, 1989; Shukairy et al., 2002).

Aqueous chlorine, chloramines, and ozone are all capable of oxidizing naturally occurring bromide to form active bromine [i.e., hypobromous acid (HOBr) or bromamines; see Chap. 7]. The latter will react with NOM to form brominated organic compounds (e.g., bromoform and dibromoacetic acid) and, in the presence of free chlorine, mixed bromochloro-organics. The same is true with respect to the formation of iodinated DBPs in the presence of iodide, although iodinated DBPs tend to be found only in chloraminated waters (see section on chloramine by-products). These halogenated by-products all contribute to the TOX concentration of the water. Furthermore, it is possible to measure halogen-specific TOX (e.g., TOCl, TOBr, and TOI) by replacing microcoulometric detection with ion chromatography (e.g., Hua and Reckhow, 2007).

Identity of Disinfection By-Products

Since the discovery of trihalomethanes (THMs) in chlorinated drinking water in the early 1970s (Rook, 1974; Bellar et al., 1974), hundreds of specific compounds have been identified as DBPs. Many of the major groups are summarized in Table 19-1. More detailed listings of individual compounds can be found in the review by Richardson (1998).

Each of the four disinfectants presented in the table has its own unique chemistry. For example, ozone is the only disinfectant that produces measurable quantities of bromate. Nevertheless, many by-product classes and specific compounds are common to two or more of the major disinfectants. This is illustrated by the simple aliphatic carboxylic acids (e.g., acetic acid), which are universal by-products regardless of the disinfectant/oxidant. Itoh and Matsuoka (1996) found that all oxidants produce carbonyls (e.g., formaldehyde), with ozone and chlorine dioxide producing the most and chlorine and inorganic chloramines only slightly behind. Some halogenated compounds, such as dihaloacetic acids, may be produced by all four disinfectants, but the amounts produced range over several orders of magnitude, depending on the disinfectant, the disinfectant dose, and the bromide level. For this reason, an attempt has been made in the table to classify by-product abundance based on an order-of-magnitude scale (very high >100 µg/L; high = 10–100 µg/L; medium = 1–10 µg/L; low = 0.01–1 µg/L; very low < 0.01 µg/L) as assessed for an average drinking water under typical treatment conditions.

TABLE 19-1 Chemical By-Products of the Four Major Disinfectants

By-product class	Examples	Chlorine	Chloramines	Chlorine dioxide	Ozone
<i>Compounds with O-X Bonds</i>					
Oxychlorines	Chlorate, Chlorite			V.High ^{34,35}	
Oxybromines	Bromate, hypobromate				Med ^{51-53,58}
<i>Compounds with C-X Bonds</i>					
	Chloroform, bromodichloromethane, chlorodibromomethane	High	Low		
Trihalomethanes	Bromoform Dichloriodomethane	Med	Low Low		Med ^{49,52}
Other haloalkanes	1,2-Dibromoethane, 1,2-dibromopropane	Low ^{14,15}			
Haloalcohols	3-Bromo-2-methyl-2-butanol, 9-chloro-10-hydroxyl methyl stearate	(NOM ²⁰)	(Models ^{3,23})	(Models ³⁷)	Med ⁶²
Haloacids	Dichloroacetic acid, trichloroacetic acid	High	Med ^{17,18}	(NOM ²⁹)	
	Monochloroacetic acid, bromochloroacetic acid, bromodichloroacetic acid, monobromoacetic acid, dibromoacetic acid, tribromoacetic acid, diiodoacetic acid, 6,6-dichlorohexanoic acid	Med Low	Low		Med ⁵⁰
Haloacids (unsaturated)	3,3-Dichloropropenoic acid	(NOM ¹⁵)	(NOM ^{17,18})		
Halodiacids	2,2-Dichlorobutanedioic acid, 2,3-dichlorobutanedioic acid	(NOM ^{15,16})	(NOM ^{17,18})		
Haloaldehydes	3,3,3-Trichloro-2-hydroxypropanoic acid, 2-chloro-4-hydroxybutanoic acid, 2,3-dichloro-3,3-dihydroxy propanoic acid, 4-chloro-4-hydroxypentenoic acid	(NOM ¹⁵)	(NOM ^{17,18})		
Haloketones	1,1,1-Trichloropropanone	Med ^{1,2,3}			
	Chloropropanone Bromopropanone 1,1,3,3-Tetrachloropropanone		(NOM ^{17,18})		Unkn ⁶⁰
	1,1,1-Trichloro-2-butanone, pentachloro-3-buten-2-one	(NOM ⁴)		Unkn ²⁸	
Haloaldehydes	Chloral	Med			
	Chloroacetaldehyde, dichloroacetaldehyde		(NOM ^{17,18})		
	Dichloropropanal, 3-chlorobutanal, 2,3,3-trichloropropenal	(NOM ⁴)	(NOM ^{17,18})		

(Continued)

TABLE 19-1 Chemical By-Products of the Four Major Disinfectants (*Continued*)

By-product class	Examples	Chlorine	Chloramines	Chlorine dioxide	Ozone
Haloketoacids	2,3-Dichloro-4-oxopentenoic acid, 2,5-dichloro-4-bromo-3-oxopentanoic acid	(NOM ¹⁵)			
Halonitriles	Dichloroacetonitrile, trichloroacetonitrile, dibromoacetonitrile	Med ^{1,2,5}			
Cyanogen aalides	Cyanogen chloride Cyanogen bromide	Low	Med Low (Models ^{3,21})		
C-Chloro amines					
Halophenols		(NOM ^{1,6})			
Chloroaromatic acids	5-Chloro-2-methoxybenzoic acid, dichloromethoxybenzoic acid	(NOM ^{7,8})			
Halothiophenes	Tetrachlorothiophene	(NOM ¹)			
Chlorinated PAHs		Unkn ⁹			
MX and related compounds	MX, EMX, red-MX, ox-EMX 2,2,4-Trichlorocyclopentene-1,3-dione	Low ^{11,12,13} Low ¹⁰	(NOM ^{17,18,27})		
Halo-nitromethanes	Chloropicrin Bromopicrin	Med Low			Med
<i>Compounds with N—X Bonds</i>					
N-Chloro-amino acids	N-Chloroglycine	(Models)			
N-Chloro-amines		(Models ²⁶)	(Models ^{22,24,25})		
<i>Compounds without Halogens</i>					
Aliphatic	Formic acid, acetic acid, butyric acid, pentanoic acid	High		High ^{28,29,38,40}	High ^{43,58}
Monoacids	Hexadecanoic acid				Low ⁶⁰
Aliphatic diacids (saturated)	Oxalic acid Succinic acid, glutaric acid, adipic acid	High		High ^{32,40} (NOM ²⁹)	V.High ⁵⁸ Unkn ⁴⁷
Aliphatic diacids (unsaturated)	Butenedioic acid 2- <i>tert</i> -Butylmaleic acid, 2-ethyl-3-methylmaleic acid	(NOM ^{15,16})		Unkn ^{28,32}	
Aromatic acids	Benzoic acid, 3,5-dimethylbenzoic acid <i>p</i> -Benzoquinone	(NOM ^{15,16})		Unkn ²⁸ (Models ³³)	Unkn ^{44,47}
Other aromatics	Hydroxy-PAHs 3-Ethyl styrene, 4-ethyl styrene Naphthalene, 1-methylnaphthalene			(Models ³⁶) Unkn ²⁸ Unkn ²⁸	
Aldehydes	Formaldehyde, acetaldehyde, propanal Glyoxal, methylglyoxal Benzaldehyde, ethylbenzaldehyde Acetone, propyl ethyl ketone		(Models ¹)	Unkn ³⁰	High Unkn ^{47,57} Med ^{41,54}

(Continued)

TABLE 19-1 Chemical By-Products of the Four Major Disinfectants (*Continued*)

By-product class	Examples	Chlorine	Chloramines	Chlorine dioxide	Ozone
Ketones	Dioxopentane, 1,2-dioxobutane				Unkn ⁴¹
	Acetophenone, 4-phenyl-2-butanone				Unkn ⁴⁷
	2-Hexenal, 6-methyl-5-hepten-2-one				Low ⁶⁰
	2,3,4-Trimethylcyclopent-2-en-1-one, 2,6,6-trimethyl-2-cyclohexene-1,4-dione			Unkn ²⁸	
	Pyruvic acid, glyoxalic acid, ketomalonic acid				High
Ketoacids	Oxobutanoic acid, 4-oxo-2-butenic acid				Unkn ^{41,47}
	Ketosuccinic acid, ketoglutaric acid				Unkn ^{41,61}
	Dioxopropanoic acid, dioxopentanoic acid				Unkn ⁴¹
Hydroxyacids	Hydroxymalonic acid				(NOM ⁴⁴)
Hydroxy-carbonyls	Hydroxyacetaldehyde				(Models ⁵⁹)
Furans	Methylfurancarboxylic acid			(NOM ²⁹)	
Epoxides			(Models ²³)	(Models ^{31,39})	(Models ^{42,55})
Organic Peroxides					(Models)
Nitriles			(Models ^{1,19})		
Nitrosamines	Nitrosodimethylamine	V. low	Low		
Nitramines	Dimethylnitramine	(Models ⁶³)			
Hydrazines	1,1-Dimethylhydrazine		(Models)		
Miscellaneous	5-Methoxy- α -pyrone				(NOM ⁴⁴)

Notes:

1. Data marked "NOM" and "Models" are from studies using solutions of natural organic matter extracts and model compounds, respectively.

2. All other data are from treated drinking waters and unaltered natural waters. Concentrations are classified as follows: V. high (very high): >100 $\mu\text{g/L}$; High: 10–100 $\mu\text{g/L}$; Med (medium): 1–10 $\mu\text{g/L}$; Low: 0.01–1 $\mu\text{g/L}$; V. low (very low): <0.01 $\mu\text{g/L}$; Unkn (not quantified).

Sources:

- | | | |
|--------------------------------|-------------------------------|---------------------------------|
| 1. Le Cloirec & Martin, 1985 | 22. Scully 1986 | 43. Lawrence, 1977 |
| 2. Brass et al., 1977 | 23. Carlson & Caple, 1977 | 44. Benga, 1980 |
| 3. Minisci & Galli, 1965 | 24. Jensen & Johnson, 1989 | 45. Paramisigamani et al., 1983 |
| 4. Smeds et al., 1990 | 25. Crochet & Kovacic, 1973 | 46. Killips et al., 1985 |
| 5. Kanniganti, 1990 | 26. Kringstad et al. 1985 | 47. Glaze, 1986 |
| 6. Shank & Whittaker, 1988 | 27. Backlund et al., 1988 | 48. Edwards, 1990 |
| 7. Backlund et al., 1988 | 28. Richardson et al., 1994 | 49. Cooper et al., 1986 |
| 8. Kronberg & Vartiainen, 1988 | 29. Colclough, 1981 | 50. Daniel et al., 1989] |
| 9. Burttschell et al., 1959 | 30. Stevens et al., 1978 | 51. Haag & Hoigne, 1983 |
| 10. Fielding & Horth, 1986 | 31. Legube et al., 1981 | 52. Glaze et al., 1993 |
| 11. Franzén & Kronberg, 1994 | 32. Masschelein, 1979 | 53. Krasner et al., 1993 |
| 12. Peters et al., 1994 | 33. Wajon et al., 1982 | 54. Fawell et al., 1984 |
| 13. Franzén & Kronberg, 1994 | 34. Steinbertg, 1986 | 55. Chen et al., 1979 |
| 14. de Leer et al., 1985 | 35. Werdehoff & Singer, 1987 | 56. Chappell et al., 1981 |
| 15. Oliver, 1983 | 36. Luikkonen et al., | 57. Lawrence et al., 1980 |
| 16. Kanniganti et al., 1992 | 37. Ghanbari et al., 1983 | 58. Griffini & Iozzelli, 1996 |
| 17. Kanniganti, 1990 | 38. Somsen, 1960 | 59. Le Lacheur & Glaze, 1996 |
| 18. Kanniganti et al., 1992 | 39. Carlson & Caple, 1977 | 60. Richardson et al., 1996 |
| 19. Hausler, | 40. Griffini & Iozzelli, 1996 | 61. Hwang et al., 1996 |
| 20. Havlicek et al. 1979 | 41. Le Lacheur et al., 1993 | 62. Cavanagh et al. 1992 |
| 21. Neale, 1964 | 42. Carlson & Caple, 1977 | 63. Mitch, 2007 |

Many worthwhile studies have been conducted with solutions of isolated NOM (e.g., aquatic fulvic acids). Since these studies are often conducted under extreme conditions (i.e., high TOC, high chlorine dose, and sometimes high or low pH) designed to maximize DBP formation, no attempt has been made to render a judgment on the likely concentration level expected in tap water based on such studies. Also useful, but further removed from practice, are the studies using model compounds (designated "Models" in Table 19-1). Entries that are not labeled with "NOM" or "Model" refer to expected occurrence levels in typical finished drinking water.

Chlorination By-Products. The chlorination by-products include a wide range of halogenated and nonhalogenated organic compounds. Regulatory agencies have focused on the halogenated compounds, especially the THMs and haloacetic acids (HAAs) (see Chap. 1 on regulations). These are small, highly substituted end products of the reaction of chlorine with organic matter. In waters with low bromide levels, the fully chlorine-substituted forms predominate (e.g., chloroform and di- and trichloroacetic acid). Waters with high levels of bromide are likely to contain elevated levels of the bromine-containing analogues (e.g., bromoform and dibromoacetic acid) following chlorination. Waters with moderate levels of bromide will contain the mixed bromo/chloro analogues (e.g., bromodichloromethane and bromodichloroacetic acid).

Nearly all DBP studies in the 1970s focused on the THMs. Given their volatility, chemical stability, and high halogen-carbon ratio, this class of compounds could be easily analyzed with minimal analytical equipment and expertise. Consequently, the THMs were the first by-products to be found in finished drinking waters (Rook, 1974; Bellar et al., 1974), the first to be the subject of an established analytical method, and the first to be included in a large survey of public water supplies (Symons et al., 1975). In a matter of just a few years, it was recognized that the THMs were always present whenever chlorine was used as a disinfectant.

The discovery of HAAs in chlorinated waters (Miller and Uden, 1983; Christman et al., 1983) and subsequent occurrence studies trailed the THMs by several years. One early survey (Krasner et al., 1989) showed the HAAs, like the THMs, to be ubiquitous in chlorinated waters, although present at somewhat lower levels. More recent data have supported this finding. However, the lack of available standards for all the HAAs in these earlier studies may have resulted in underestimation of their concentrations (Cowman and Singer, 1996).

Many other halogenated by-products have been widely reported in chlorinated drinking waters. The most intensively studied of these nonregulated compounds are the halopropanones, the haloacetonitriles, chloropicrin, and chloral hydrate. This group owes its large industry-wide database to the analytical method that it shares with the THMs (i.e., like the THMs, they are all volatile neutral compounds that respond well to analysis by gas chromatography with electron-capture detection). The haloacetonitriles are thought to be largely derived from the chlorination of amino acids and proteinaceous material (Bieber and Trehy, 1983). Nitrogenous structures in humic substances also will form haloacetonitriles via cyano acid intermediates (Backlund et al., 1988). The halopropanones (e.g., 1,1,1-trichloropropanone) and chloral hydrate (a haloaldehyde) are halogenated analogues of some common ozonation by-products. They are commonly found at elevated concentrations in waters that had been previously ozonated (Reckhow et al., 1986; McKnight and Reckhow, 1992).

From July 1997 to December 1998, a comprehensive set of data on DBP occurrence in U.S. drinking waters was collected as part of the Information Collection Rule (ICR). All large drinking water utilities (defined as those serving populations > 100,000) provided DBP occurrence information and corresponding water quality characteristics and treatment conditions for six quarters. A total of 299 utilities participated, encompassing 500 water treatment plants. The following DBPs were measured: THMs, HAAs, haloacetonitriles (HANs), haloketones such as the chloropropanones (CPs), chloral hydrate (CH), chloropicrin

(CP), cyanogen chloride (CNCl), and TOX. Bromate, chlorite, chlorate, and aldehydes, which are oxidation by-products of ozone and chlorine dioxide (see Chap. 7 and below), also were measured in the utilities employing these oxidants. The ICR data set was generated with a high degree of quality assurance and was used to finalize the stage 1 and stage 2 DBP rules (see Chap. 1). A description of the ICR activity and its results is provided in an ICR data analysis report (McGuire et al., 2002). Figures 19-2 to 19-4 illustrate the occurrence findings from the ICR database. It should be noted that the majority of the ICR utilities had raw water sources with relatively low bromide concentrations, a characteristic shared by many high-quality surface waters, so the distribution of DBPs was skewed toward the chlorine-containing species.

About 50 percent of the TOX produced on chlorination can be attributed to the major by-products discussed earlier (Singer and Chang, 1989). The remainder is largely unknown and has been the subject of research for the past 20 years. A similar balance on mutagenic activity (Ames test) reveals that more than 50 percent of the activity can be accounted for among the known by-products. Much of the identified mutagenicity is found in a single compound given the abbreviated name MX (Backlund et al., 1988; Meier et al., 1988), a chlorinated furanone that readily undergoes ring opening. It is produced in small quantities along with several related compounds by free chlorine and chloramines. Relatively little is known about its occurrence because it is difficult to measure. Early studies showed finished water concentrations as high as 60 ng/L (Kronberg and Vartiainen, 1988). Wright and colleagues (2002) conducted a focused study of MX in U.S. finished waters and found concentrations up to 80 ng/L. Weinberg et al (2002) documented a median value of 20 ng/L and a maximum of 310 ng/L.

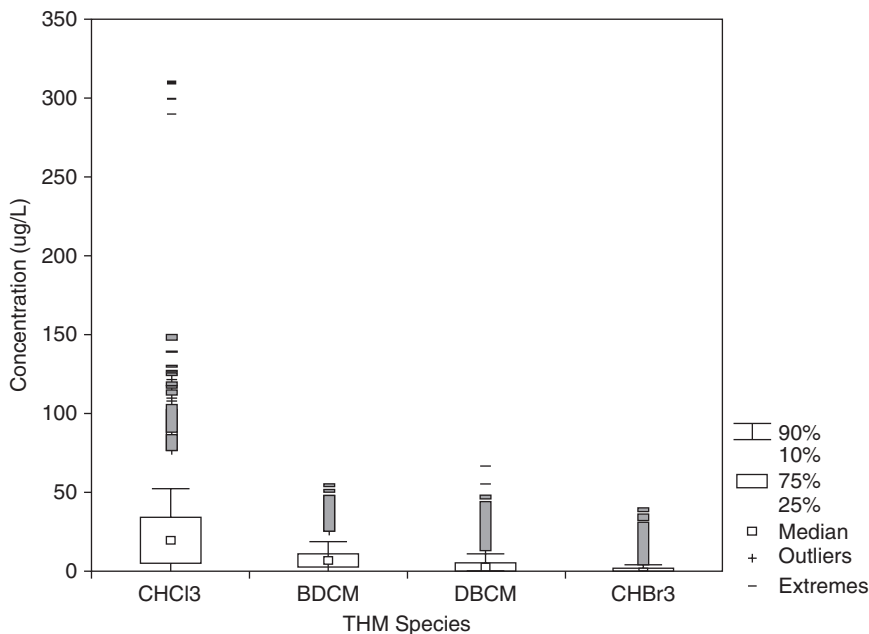


FIGURE 19-2 Distribution of ICR results for individual trihalomethane species. (Source: McGuire et al., 2002, AWWA Research Foundation.)

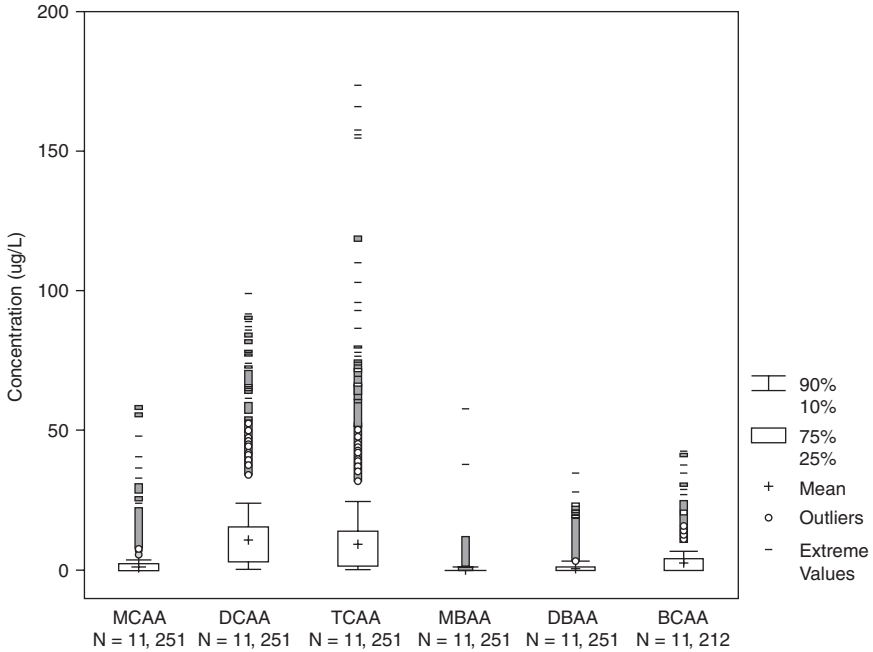


FIGURE 19-3 Distribution of ICR results for individual haloacetic acid species. Note that only six of the nine bromine- and chlorine-containing HAAs were measured by all the participating utilities. (Source: McGuire et al., 2002, AWWA Research Foundation.)

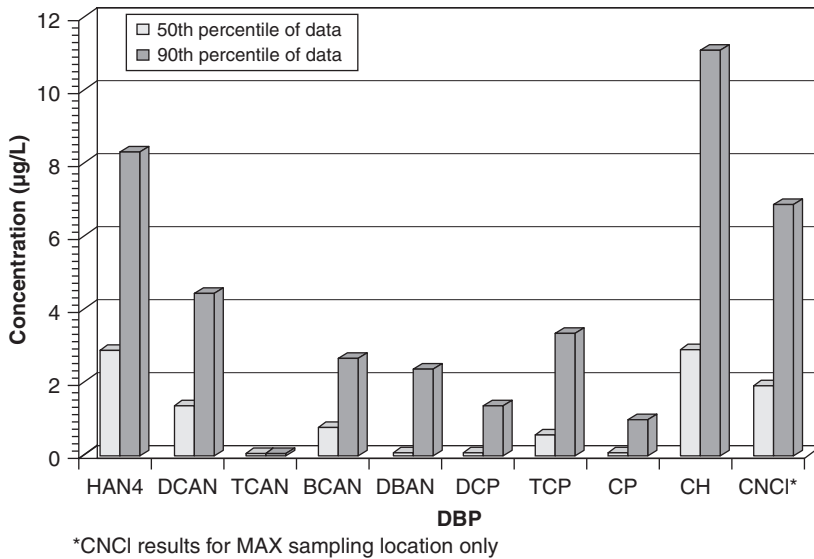


FIGURE 19-4 DBP concentrations in ICR distribution systems. (Source: McGuire et al., 2002, AWWA Research Foundation.)

Because TOX formation represents only a small fraction of the total chlorine consumed (typically < 10 percent), it can be concluded that most of the organic chlorination by-products do not contain chlorine and that most of the chlorine consumed leads to the formation of chloride. A number of these nonhalogenated by-products have been identified (Table 19-1). Most are aliphatic mono- and diacids and benzenepolycarboxylic acids. Because these compounds probably are not of health concern, they have not been studied extensively. It should be noted, however, that many of these compounds are readily biodegradable and therefore contribute to the biodegradable dissolved organic carbon (BDOC) content, sometimes measured as assimilable organic carbon (AOC). Hence, in the absence of a disinfectant residual in the distribution system, the presence of these compounds can encourage the growth of biofilms.

Chloramine By-Products. Although monochloramine and dichloramine are less reactive than free chlorine with NOM and most model compounds, inorganic chloramines can form some of the DBPs commonly associated with free chlorine. Identifiable by-products include dichloroacetic acid (DCAA), cyanogen chloride, and small amounts of chloroform and trichloroacetic acid (TCAA; see Table 19-1). While it's not clear that TCAA and the THMs are true by-products of chloramines (i.e., they may be formed owing to the presence of a small free chlorine residual), it does seem that DCAA and cyanogen chloride are true by-products (Singer et al., 1999). Cyanogen chloride concentrations generally are higher in systems using chloramines, and this is due, at least in part, to the greater stability of this compound in the presence of chloramines compared with free chlorine. Both mechanistic and occurrence studies have shown that haloacetonitriles also can be formed as true by-products of inorganic chloramines (e.g., Young et al., 1995; Weinberg et al., 2002). Backlund and colleagues (1988) found that monochloramine forms MX from humic materials, although the amount measured was less than 25 percent of that formed during chlorination.

Weinberg and colleagues (2002) found iodoacetic acid, bromoiodoacetic acid, (*E*)-3,3-bromoiodopropenoic acid, (*Z*)-3,3-bromoiodopropenoic acid, and (*E*)-2-iodo-3-methylbutenedioic acid in a drinking water system using chloramines with no free chlorine contact time. When there is a substantial free chlorine contact time preceding ammonia addition, lower levels of iodinated organics are produced (e.g., von Gunten et al., 2006; Hua et al., 2007). This is attributed to the rapid oxidation of reactive iodine to the nonreactive iodate anion by pretreatment with free chlorine (see Chap. 7). Inorganic chloramines are not capable of this rapid oxidation, so precursor organics have a greater exposure to reactive iodine and thereby produce more iodinated organic by-products (Fig. 19-5).

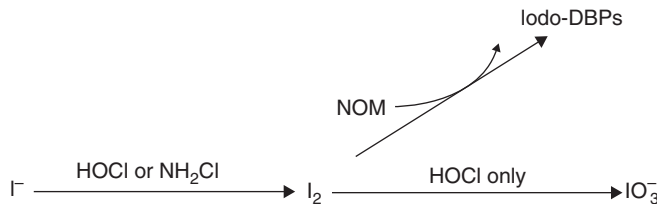


FIGURE 19-5 Pathway for elevated levels of iodinated DBPs from chloramines.

Jensen and colleagues (1985) found that at high monochloramine-carbon ratios (~10 mg Cl₂/mg C), about 5 percent of the oxidant demand goes toward TOX formation. This is identical to the results for chlorine at an equally high chlorine-carbon ratio. Most of the chlorinated organic by-products remained tied up in high-molecular-weight

compounds. This contrasts with free chlorine because monochloramine is a much weaker oxidant than free chlorine and is much less likely to create the smaller fragments that can be analyzed by gas chromatography.

Monochloramine is known to transfer active chlorine to the nitrogen of amines and amino acids, forming organic chloramines (Scully, 1986). This reaction also occurs with free chlorine. Model compound studies have shown that monochloramine also can add chlorine to activated aliphatic carbon-carbon double bonds (Johnson and Jensen, 1986). The adjacent carbon may become substituted with an amine group or with oxygen. Other types of reactions involve the simple addition of amine or chloramine to unsaturated organic molecules. Under certain conditions, chlorine substitution onto activated aromatic rings has been observed. For example, monochloramine will slowly form chlorophenols from phenol (Burttschell et al., 1959). Inorganic chloramines also will add chlorine to phloroacetophenone, a highly activated aromatic compound, to produce chloroform (Topudurti and Haas, 1991). However, the rate of reaction for this compound is low, and the molar yield (i.e., moles DBP formed per mole precursor) is only 3 percent compared with 400 percent for free chlorine.

In addition to chlorine transfer, inorganic chloramines also undergo addition reactions with many types of organic molecules. This results in the formation of new organic amines and organic chloramines where the nitrogen atom originates from the inorganic disinfectant. Studies designed to determine if this is a major pathway for DBP formation in drinking water have produced mixed results. Hirose and colleagues (1988) found that this was not the case when looking at cyanogen chloride (CNCl) formation from the chloramination of the amino acid leucine. Their findings are supported by Krasner and colleagues (1989). On the other hand, chloramination of formaldehyde does produce CNCl, a clear indication of the ammoniation reaction (Pedersen et al., 1999). Using ^{15}N -labeled monochloramine, Young and colleagues (1995) studied this question with natural waters and dichloroacetoneitrile (DCAN) formation. They concluded that most of the nitrogen in DCAN came from the inorganic chloramines and not from naturally occurring nitrogen in the NOM.

One possible result of ammoniation reactions is the formation of carcinogenic nitrosamines from organic amines. Among this group, it is nitrosodimethylamine (NDMA) that has been observed most commonly and studied most widely. NDMA levels in finished drinking water are rarely above the low nanogram per liter level, and it is observed more often in systems using chloramines, especially those affected by wastewater. Although cationic polymers and anion exchange resins used in water treatment can harbor NDMA precursors (e.g., Najm and Trussell, 2001), it now seems clear that a significant amount of organic precursors to NDMA formation originate from municipal and domestic wastewater. Schreiber and Mitch (2006) have formulated a mechanism for NDMA formation from dimethylamine precursors (Fig. 19-6). This explains many of the observations surrounding NDMA formation in drinking water, including the elevated concentrations under conditions that favor dichloramine formation (e.g., high $\text{Cl}_2:\text{N}$ ratios). Since some NDMA formation has been observed at plants using free chlorine, there may be other important mechanisms not involving inorganic chloramines.

When used in water treatment, chloramines are formed in situ, that is, within the plant. This usually involves addition of ammonia after or at the location of addition of chlorine. While the reaction between chlorine and ammonia is rapid at near-neutral pH (Weil and Morris, 1949), yields of the intended product (i.e., monochloramine and dichloramine) typically are less than 100 percent, especially at high $\text{Cl}_2:\text{N}$ ratios. Nitrogen species of elevated oxidation state have long been postulated as necessary intermediates in the formation of the final breakpoint products (i.e., nitrogen gas and nitrate). These include $\text{N}(-\text{I})$ species (e.g., hydroxylamine, NH_2OH) and $\text{N}(+\text{I})$ species (e.g., nitroxyl, HNO , and hyponitrous acid, $\text{H}_2\text{N}_2\text{O}_2$) (Chapin, 1931; Wei and Morris, 1974; Saunier and Selleck, 1979). There is also strong evidence for at least one related $\text{N}-\text{Cl}$ species (Leung and Valentine 1994a, 1994b).

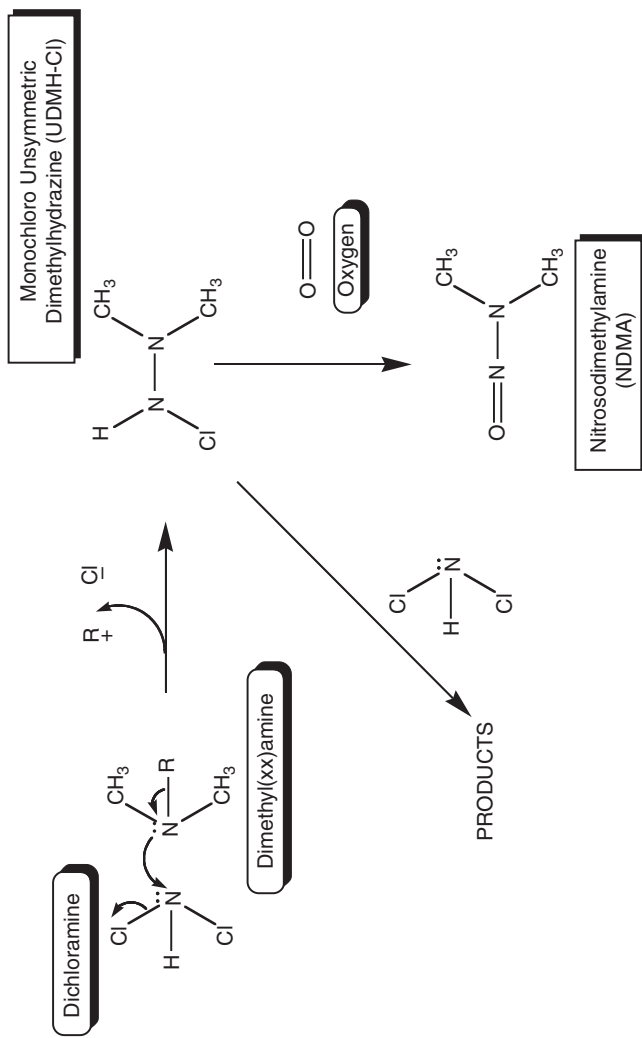


FIGURE 19-6 Proposed pathway for NDMA formation during chloramination. (Based on work by Schreiber and Mitch, 2006.)

Little is known about the reactivity of these compounds or their occurrence in drinking water systems.

Although dismissed by Saunier and Selleck (1979), Shank and Whittaker (1988) asserted that small amounts of the known carcinogen hydrazine ($\text{H}_2\text{N}-\text{NH}_2$) could be formed by reaction of ammonia with monochloramine when drinking waters are chloraminated. Models based on known hydrazine formation rates predict that 10 ng/L concentrations could form in chloraminated waters at pH above 9 (Najm et al., 2006). However, little data exist on actual hydrazine concentrations in drinking water distribution systems.

Chlorine Dioxide By-Products. Chlorine dioxide undergoes a wide variety of oxidation reactions with organic matter to form oxidized organics such as aldehydes, ketones, and acids, as well as inorganic chlorite, ClO_2^- (see Table 19-1 and Chap. 7). The concentration of the resulting chlorite accounts for 50 to 70 percent of the chlorine dioxide consumed (Rav Acha et al., 1984; Werdehoff and Singer, 1987). Chlorite also may be formed, along with chlorate (ClO_3^-), by the disproportionation of chlorine dioxide (see Chap. 7). All three of the oxidized chlorine species (chlorine dioxide, chlorite, and chlorate) are considered to have adverse health effects, and their presence in finished water above regulated levels is a source of concern; see Chaps. 1 and 2 for coverage of regulations and health effects.

Chlorine dioxide also can undergo a limited number of chlorine substitution reactions. For example, reaction with dimethoxyphenylethanol, a lignin model compound, produces many initial products, including a ring-chlorinated derivative (Svenson et al., 2002). Trihalomethanes, however, have not been detected as reaction products when water containing NOM is treated with chlorine dioxide. As with the other chlorine-containing oxidants, chlorine addition/substitution products are favored at low oxidant-carbon ratios, and oxidation reactions are favored at high ratios. Studies using drinking waters and NOM have shown that small amounts of TOX form on treatment with typical levels of chlorine dioxide (e.g., Hua and Reckhow, 2007). Aside from direct reactions between NOM and molecular ClO_2 , as noted earlier, this also may be due to the formation of HOCl when chlorine dioxide reacts with NOM and subsequent reaction with other NOM compounds (Werdehoff and Singer, 1987). The relatively small amount of HOCl formed in this manner probably leads to sparsely halogenated macromolecular TOX, which would account for the lack of identifiable organohalide by-products.

Ozonation By-Products. Ozonation can lead to the formation of brominated by-products when applied to waters with moderate to high bromide levels. This is a direct result of ozone's ability to oxidize bromide to hypobromous acid and related species (see Chap. 7). Some of this oxidized bromine continues to react to form bromate ion. Much of the remaining hypobromous acid reacts with NOM to form brominated organic compounds. These by-products encompass the same general classes reported for the halogenated by-products of chlorine [i.e., THMs (bromoform), HAAs (dibromoacetic acid), HANs (dibromoacetonitrile), and halonitromethanes (bromopicrin)]. It has been estimated that 7 percent of the raw water bromide becomes incorporated as TOX (or total organic bromide, TOBr) following ozonation under conditions typical of drinking water treatment (Song et al., 1997). The extent of TOBr formation from HOBr versus further oxidation of HOBr to form bromate depends markedly on pH, with elevated pH values (above 6.5–7) favoring bromate formation.

In contrast to the situation with bromide, ozonation will not lead to the formation of iodinated DBPs when water containing iodide is ozonated. This is so because ozonation rapidly oxidizes the hypoiodous acid formed to iodate (see Chap. 7).

Most ozonation by-products are not halogenated, and the majority of these are similar to the general oxidation products reported for other disinfectants. For example, field studies with ozone and chlorine dioxide showed that both produced about the same level of low-molecular-weight carboxylic acids (Griffini and Iozzelli, 1996). Nevertheless, there

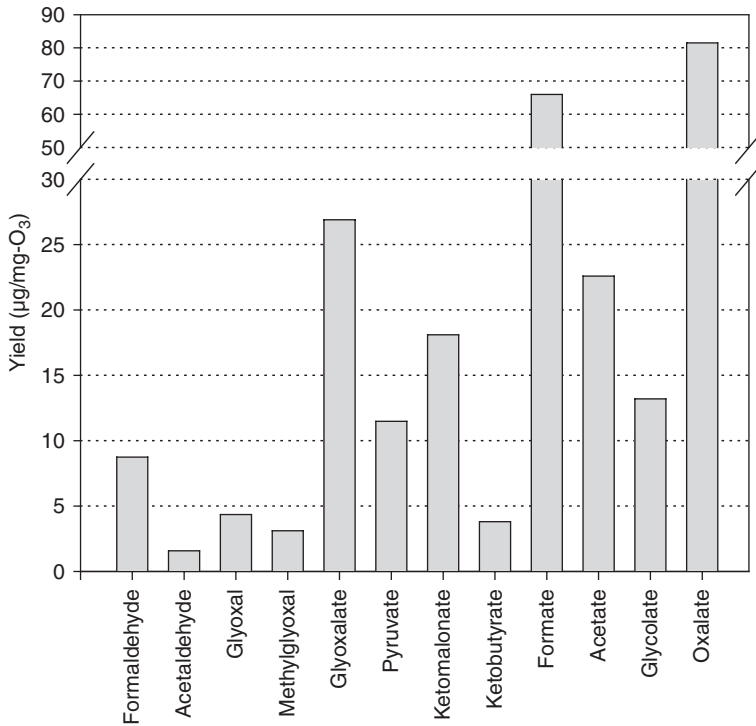


FIGURE 19-7 Yields of major ozonation by-products normalized per milligram of ozone applied, as reported in the literature. (Source: Reckhow, 1999, AWWA Research Foundation.)

are a number of studies that suggest ozone produces higher levels of simple aldehydes and ketoacids (or aldoacids) than the other major disinfectants. Figure 19-7 presents some dose-specific yield data for these major by-products. High levels of aldehyde and ketone by-products are characteristic of ozonation and generally are attributed to the Creigee ozonolysis mechanism (Fig. 19-8).

Other oxidation by-products attributed to ozone include hydroxyacids (e.g., pyruvic acid), aromatic acids (e.g., benzoic acid), and hydroxyaromatics (e.g., catechol) (see Table 19-1). Organic peroxides and epoxides are also expected ozonation by-products, although their detection in treated drinking waters has proved to be a challenge.

Because of the strong correlation between ozonation by-product formation and biodegradable organic matter (BOM) concentrations, attempts have been made to attribute this BOM to specific compounds. Krasner and colleagues (1996) have shown that as much as 40 percent of the assimilable organic carbon (AOC) and 20 percent of the BDOC can be assigned to known major ozonation by-products. However, these known by-products still represent less than 5 percent of the overall DOC concentration.

UV By-Products. Given the recent growth of ultraviolet (UV) disinfection technology in drinking water treatment (see Chaps. 17 and 18), questions have arisen as to how UV treatment might affect finished water DBP levels. Many also have asked whether UV irradiation produces unique DBPs. While it is widely acknowledged that THMs and HAAs do not

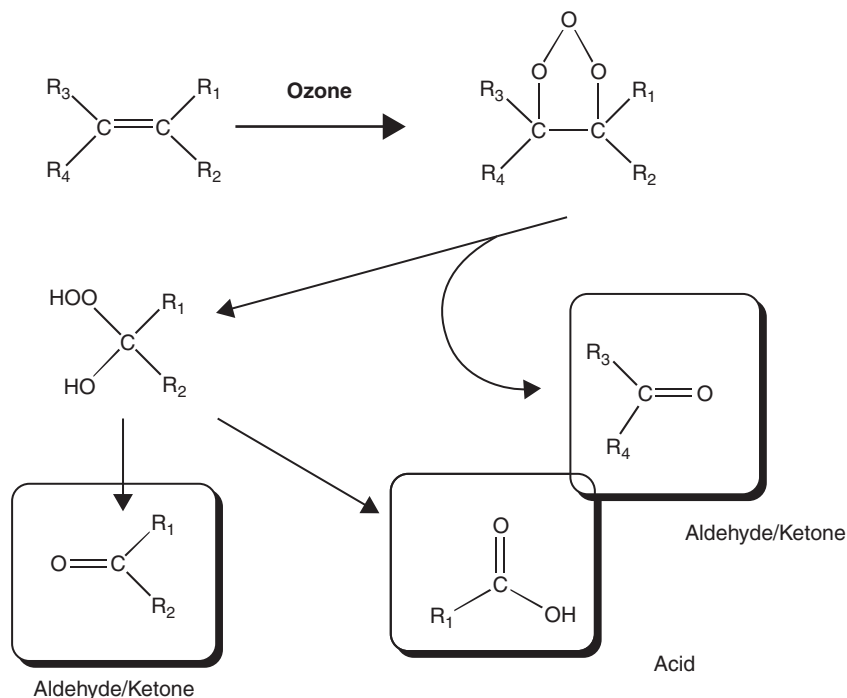


FIGURE 19-8 Creigee ozonolysis mechanism, which results in the formation of acids, aldehydes, and ketones. (Source: Reckhow, 1999, AWWA Research Foundation.)

form from UV irradiation, several researchers have shown that low levels of aldehydes and carboxylic acids can form from UV irradiation (Malley et al., 1995; Peldszus et al., 2000; Thomson et al., 2002; Liu et al., 2002).

Most studies also have shown that UV irradiation at doses typical of drinking water disinfection (i.e., ≤ 40 mJ/cm²) does not significantly affect THM and HAA formation from subsequent chlorination and chloramination (Malley et al., 1995; Liu et al., 2002; Reckhow et al., 2010). Nevertheless, there are indications that UV treatment can alter the structure and reactivity of NOM in measurable ways (e.g., the formation of aldehydes and acids, as mentioned previously). Others have studied the overall effect of UV irradiation on organic matter from treated surface waters using high-performance size-exclusion chromatography (Frimmel, 1998; Frimmel et al., 2005) and electrospray mass spectrometry (Magnuson et al., 2002). The results suggested that the molecular size distribution of NOM shifts toward smaller molecules after UV irradiation at levels typical of drinking water disinfection. Changes in NOM size and functional group content would be expected to have an impact on its reactivity with chlorine. Most studies to date on UV/Cl₂ have focused on the two major regulated groups, the THMs and the HAAs. Far less has been done with other known DBPs. However, Reckhow and colleagues (2010) have shown recently that medium-pressure UV can cause elevated chloropicrin concentrations during subsequent chlorination. These authors have attributed this effect to formation of nitroorganic precursors by photolysis reactions.

Factors Influencing By-Product Formation

Time. Reaction time is among the most important factors determining DBP concentrations under conditions where a disinfectant residual persists. Because the major halogenated DBPs (e.g., THMs and HAAs) are chemically stable, their concentrations typically increase with reaction time for as long as a disinfectant residual exists (Fig. 19-9). However, there are cases where HAA concentrations drop to near zero after long residence times in drinking water distribution systems. This phenomenon is generally attributed to biodegradation, which does not appear to occur with the THMs (the latter appear to be biodegradable only under anoxic conditions).

Laboratory tests have shown that HAAs form somewhat more rapidly than THMs. Studies also have shown the brominated analogues to form more rapidly than the purely chlorinated compounds. This causes the HAA-THM or the THM-chloroform ratio to be high in the early stages of the reaction and drop slowly with reaction time. These observations are supported by data collected from full-scale treatment plants and distribution systems.

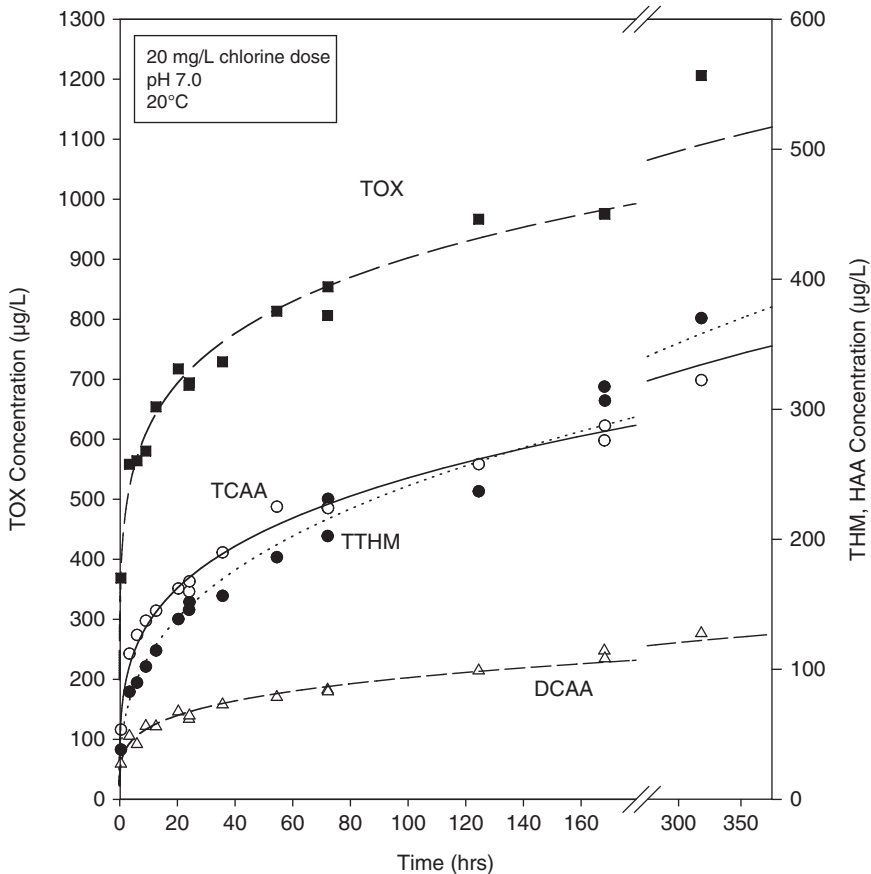


FIGURE 19-9 Effect of reaction time on the major chlorination by-products. (Data from Reckhow and Singer, 1984.)

In contrast to the case for chlorine, ozonation by-products form quickly and show little increase with time. This is due to the rapid dissipation of ozone residuals. Once dissolved ozone is depleted, by-product formation can continue only by means of hydrolysis reactions, which represent a relatively minor contribution to the total formation of these by-products.

In contrast to the THMs and HAAs, many other halogenated DBPs are chemically unstable and are subject to hydrolysis or further oxidation. For these compounds, the concentration reaches a maximum value, after which the concentration declines with time (see discussion on pH effects below). Some DBPs, such as dichloroacetonitrile, decompose slowly and reach a maximum concentration after reaction times on the order of days. Others (e.g., 1,1-dichloropropanone) are more reactive and decrease to undetectable levels within minutes to hours through hydrolysis or halogenation pathways.

Disinfectant Dose and Residual. Disinfectant dose has a variable impact on DBP formation. Small changes in the dose used for residual disinfection often have minor effects on DBP formation. This is so because these systems have an excess of disinfectant, and therefore, the DBP formation reaction is precursor limited.

When the disinfectant residual drops below about 0.3 mg/L, DBP formation becomes disinfectant limited. Under these circumstances, changes in disinfectant dose have a large effect. Figure 19-10 shows that when 3 and 5 mg/L of chlorine is added to Connecticut River water, THMs are produced in direct proportion to that dose. However, when an excess is added (>5 mg/L), a residual persists, and the extent of THM formation with increasing dose levels off. The other two waters in this figure show only the latter behavior because they had lower TOC values and their chlorine demand was less than the minimum dose tested (3 mg/L).

As a general rule, disinfectant dose plays a greater role in DBP formation during primary disinfection than during secondary disinfection. This is so because primary disinfectants usually are added in amounts well below the long-term demand. Therefore, the disinfectant is the limiting reactant, not the organic precursors. Figure 19-10 shows a near-linear

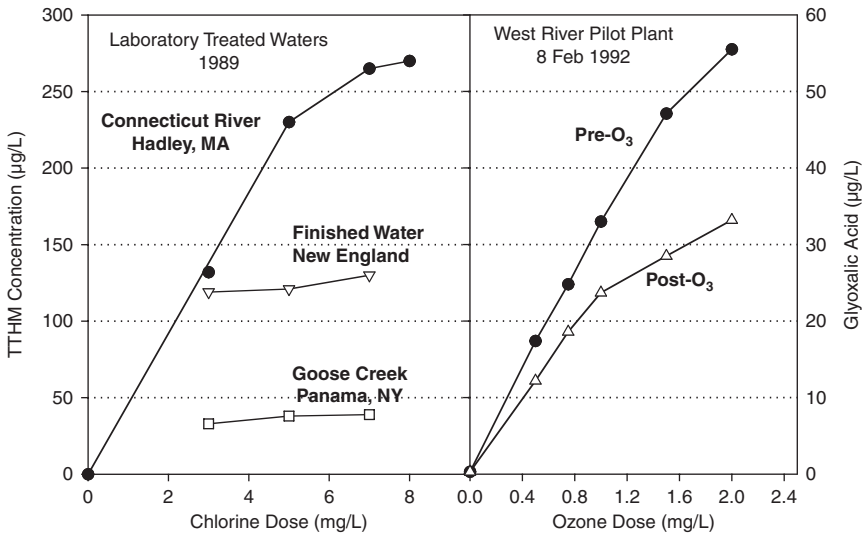


FIGURE 19-10 Observations on effect of disinfectant dose on DBP formation (chlorination conditions: pH 7, 20°C, 3-day reaction time). (Figures redrawn from Coombs, 1990, and Reckhow et al., 1993.)

relationship between ozone dose and glyoxalic acid formation. When the ozone is applied after coagulation and filtration (postozone in the figure), glyoxalic acid formation starts to plateau. This is a reflection of the removal of ozone-demanding organics and the approach to precursor-limiting conditions.

The relationship between disinfectant dose and DBP formation can be illustrated with a simple kinetic model. Figure 19-11 shows the results of a kinetic simulation for the simple second-order reaction (Eq. 19-1):



where A represents the NOM precursor material, B is the disinfectant, C is the particular DBP, and k is the second-order rate constant. If the initial precursor level (A_0) is held constant, and a rate constant and reaction time t is arbitrarily chosen, the extent of DBP formation can be calculated as a function of the disinfectant dose (B_0). The three curves in Fig. 19-11 are the result of this calculation for three different combinations of k and t .

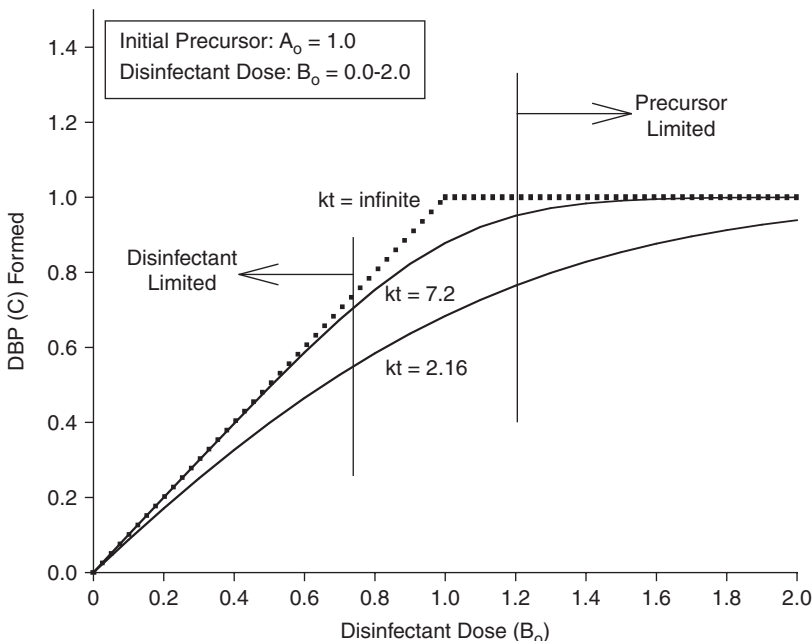


FIGURE 19-11 Theoretical second-order kinetic plot showing effect of reactant dose on product formation.

the product of k and t gets large, the DBP formation curve approaches two straight lines (one where DBP formation increases linearly with dose and one where DBP formation is independent of dose). The upward-sloping line corresponds to the disinfectant-limiting case. The horizontal line corresponds to the precursor-limiting case. This model is consistent with the experimental observations in Fig. 19-10.

When using chloramines, the chlorine-nitrogen ratio is also an important consideration. As the $Cl_2:N$ ratio increases from 2 to 5 (on a weight basis), the presence of transient free chlorine residuals increases substantially. For example, at a $Cl_2:N$ ratio of 2 mg/mg and a chlorine dose of 2 mg/L (pH 7, 10°C), the measurable free chlorine residual should

disappear (i.e., drop below 10 $\mu\text{g/L}$) at about 8 seconds after initial mixing, whereas it takes about 4 minutes at a $\text{Cl}_2\text{:N}$ ratio of 5 mg/mg (calculation based on data from Morris and Isaac, 1983). This results in a shift in the DBP character (yields and types) from that typical of pure chloramines to that of free chlorine. Model compound studies (Merlet, 1986) have shown that highly reactive precursors (e.g., resorcinol) will experience this shift at lower $\text{Cl}_2\text{:N}$ ratios than the slower-reacting compounds (e.g., acetone). It is likely that the same could be said for waters with highly reactive NOM versus less reactive waters. This observation regarding transient free chlorine residuals attests to the importance of mixing when ammonia is added to convert a free chlorine residual to a combined residual.

pH. The overall reaction between chlorine and NOM is relatively insensitive to pH over the range of typical water treatment practice. However, the formation of TOX and specific halogenated by-products is strongly influenced by pH (e.g., Fleischacker and Randtke, 1983; Reckhow and Singer, 1984). Nearly all the by-products (e.g., trihaloacetic acids, halo-propanones, haloacetonitriles, etc.) decrease in concentration with increasing pH, but one important exception is the THMs. Although pH can influence chlorination reactions in many ways, it is probably base-catalyzed hydrolysis mechanisms that have the greatest overall effect. Many DBPs (e.g., 1,1,1-trichloropropanone) are decomposed by base-catalyzed hydrolysis. These compounds are less prevalent in waters with high pH, and they tend to decrease in concentration at long residence times. The THMs increase at high pH because many hydrolysis reactions actually lead to THM formation. Other by-products are themselves unaffected by base hydrolysis (e.g., the HAAs), but their formation pathways may be altered at high pH, resulting in lesser formation. It is important to note that the dihaloacetic acids have a different pH dependency than the trihaloacetic acids. Their pathway of formation is different, and dihaloacetic acid formation tends to be relatively independent of pH, whereas trihaloacetic acid formation, as indicated earlier, decreases with increasing pH.

Chloramines exhibit some unique pH behavior that ultimately affects DBP formation from these disinfectants. pH values below 7 tend to favor the formation of dichloramine over monochloramine, especially at chlorine-nitrogen values near the breakpoint (Palin, 1975). This may affect DBP formation because monochloramine and dichloramine react differently with precursor materials. For example, the NDMA formation pathway in Fig. 19-6 suggests that conversion of monochloramine to dichloramine should increase the formation of this DBP. Also, chloramine decay is acid catalyzed, so the total residual drops rapidly at pH values of 6 and below. If not compensated with higher doses, the resulting loss of residual could lead to suspension of DBP-forming reactions and growth of DBP-degrading organisms.

None of the major ozonation by-products are subject to alkaline hydrolysis. Instead, pH plays a role by altering the rate of decomposition of ozone to hydroxyl radicals (see Chap. 7). As pH increases, ozone decomposition accelerates, and this is thought to be responsible for a decrease in the classical by-products of ozonation (e.g., aldehydes) (Schechter and Singer, 1995). However, the chemistry of ozone and hydroxyl radical reactions with NOM is not well understood, and there may be cases where some carbonyl by-products increase with pH (e.g., Itoh and Matsuoka, 1996).

Bromate is formed in ozonated waters from a series of reactions between ozone and/or hydroxyl radicals and naturally occurring bromide (see Chap. 7). A key intermediate in the formation of bromate is hypobromite ion (OBr^-). At lower pH, more of the hypobromite becomes protonated, forming hypobromous acid (HOBr), which is less reactive with respect to bromate formation. This causes the overall concentration of bromate to decrease as pH is decreased. On the other hand, lower pH favors the formation of TOBr during ozonation (Song, 1997). This is probably due to suppressed decomposition of ozone, changes in the speciation of the oxidized bromine favoring HOBr , and less base-catalyzed hydrolysis of brominated by-products.

Temperature. The rate of formation of DBPs generally increases with increasing temperature. Laboratory and full-scale plant data suggest that chloroform formation is more sensitive to temperature than DCAA formation. The relationship is not as clear for TCAA formation. At high temperatures, accelerated depletion of residual chlorine slows DBP formation even though the rate constants for DBP-producing reactions might increase. This may be especially true for TCAA because its formation is more sensitive to chlorine residual than is chloroform or DCAA formation. This is another example that suggests that dihaloacetic acid chemistry is quite different from trihaloacetic acid chemistry. Nevertheless, because more chlorine typically is added to compensate for the more rapid depletion of residual chlorine at high temperatures, overall DBP formation increases with increasing temperature.

High temperatures also may accelerate DBP degradation processes. Biodegradation of HAAs (see below) would be expected to proceed more quickly at high temperature. Reactive DBPs, such as the haloacetonitriles and halopropanones, would undergo abiotic reactions with bases or active chlorine at a faster rate as temperature increases. For this reason, increases in temperature actually may cause a decrease in the concentration of certain DBPs.

Bromide and Iodide. Bromide is readily oxidized by aqueous chlorine and ozone to form hypobromous acid (see Chap. 7). The hypobromous acid reacts with NOM to form brominated DBPs. In the presence of residual free chlorine, mixed chloro-bromo DBPs are formed. As bromide levels increase, formation of the more heavily brominated DBPs increases. Figure 19-12 shows how increasing bromide concentration causes shifts in the THM speciation from chloroform to progressively more brominated members of the group.

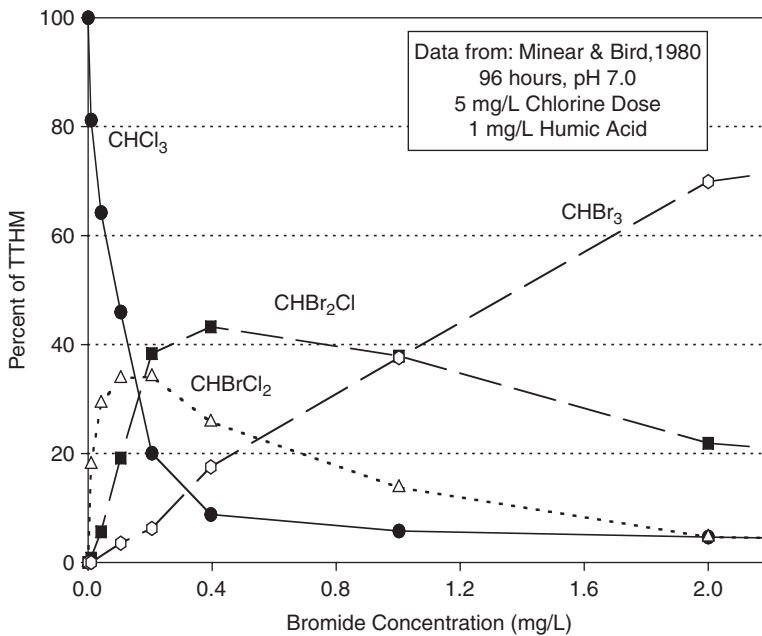


FIGURE 19-12 The effect of bromide concentration on THM speciation. (Redrawn from Minear and Bird, 1980.)

A similar effect has been observed for the HAAs, halopicrins, halopropanones, haloacetaldehydes, and haloacetonitriles (e.g., Trehy and Bieber, 1981; Pourmoghaddas and Dressman, 1993; Xie and Reckhow, 1993; Cowman and Singer, 1996). Although Fig. 19-12 extends to high bromide levels rarely seen in practice, Fig. 19-13 presents some actual occurrence data on bromine content of THMs. Note that both indicate a bromide concentration of just over 100 $\mu\text{g/L}$ as the point where the THMs become more heavily populated with bromine atoms. Figure 19-13 also suggests that this characteristic bromide level drops

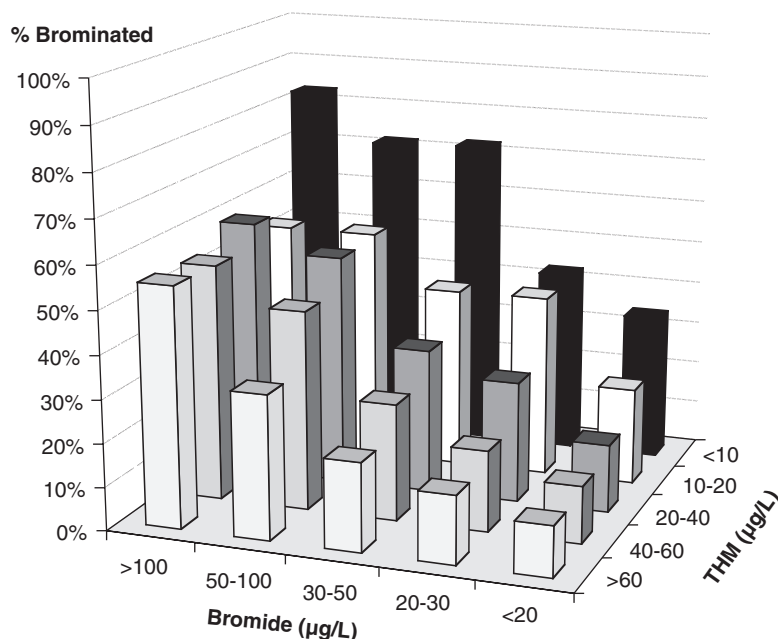


FIGURE 19-13 Dependence of bromine incorporation among trihalomethane species on bromide concentration in ICR waters. (Source: McGuire et al., 2002, AWWA Research Foundation.)

considerably as the THM level, and therefore the precursor level, drops. Most laboratory studies also have shown that the molar formation of THMs increases slightly with bromide concentration. Since the brominated forms are heavier than their chlorinated analogues, the mass-based THM level (e.g., micrograms per liter) increases even more sharply with increasing bromide level. The formation of nonhalogenated DBPs is probably insensitive to varying bromide levels. One study of ozonation by-products showed only minor effects of bromide on aldehyde concentrations (Schechter and Singer, 1995).

Bromine (and iodine) incorporation among species in different DBP classes occurs in a predictable fashion. Cowman and Singer (1996) presented a simple competitive model that results in a binomial distribution function describing the relative concentrations of the different bromine-containing species. This model has been shown to accurately reflect actual full-scale THM concentrations (Fig. 9-14). The x axis in this figure represents the mole ratio of bromine to total halogen averaged over all THM molecules in any particular sample [sometimes called the *bromine substitution factor* (BSF)]. This is related to the *bromine incorporation factor* (BIF), which is the average number of bromine atoms per molecule. Plant-scale data from the ICR database show that the extent of bromine

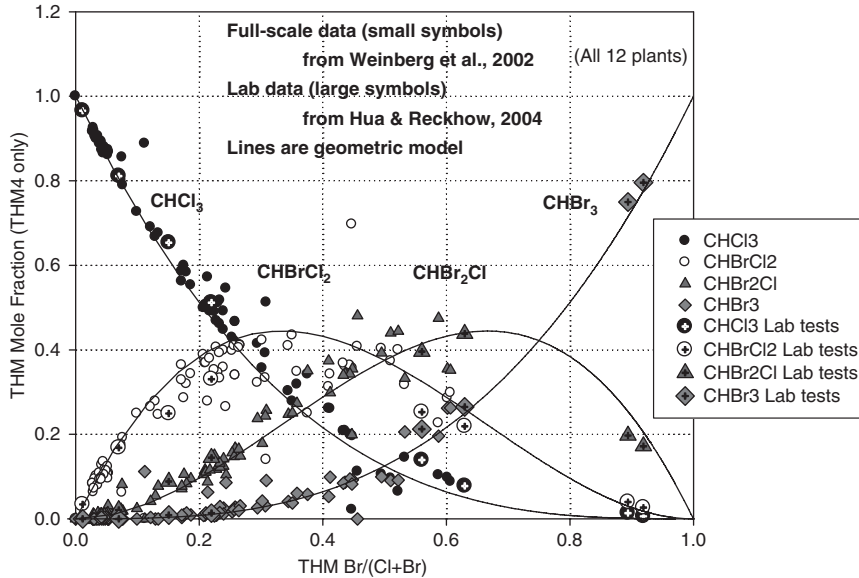


FIGURE 19-14 Relationship between THM species and degree of bromine incorporation. (The x axis is the molar ratio of bromine incorporated in the THM species to the total THM concentration.) (The geometric model is after Cowman and Singer, 1996.)

incorporation among the dihaloacetic and trihaloacetic acid species closely matches bromine incorporation among the THM species (Obolensky and Singer, 2005). In fact, this parallelism has allowed researchers to predict overall HAA formation (all nine bromine- and chlorine-containing HAAs) from measured values of the four THMs and the five regulated HAAs (Roberts et al., 2002).

The impact of iodide on DBP speciation is qualitatively similar to that of bromide. As inorganic iodide levels increase, the formation of iodinated DBPs is greater, as is the incorporation of iodide into the THMs. Because iodine is more volatile than chlorine or bromine, continental waters (i.e., surface waters and groundwaters that have not been affected by salt water) tend to be enriched in iodide compared with seawater. Nevertheless, iodide levels are thought to be roughly correlated with bromide levels. As a result, Weinberg and colleagues (2002) showed about 10 percent molar ratio of I:Br in THM species.

Organic Precursor Material. It is well established that halogenated DBP formation is strongly correlated with the DOC concentration of the water being chlorinated. For this reason, many calculations regarding DBP formation are based on specific yields normalized to a fixed organic carbon level (e.g., micrograms of chloroform per milligram of DOC). While the relationship between TOC or DOC and DBP formation may be quite strong for selected waters, the correlation becomes much weaker when considering waters of different character, originating from different ecoregions (i.e., geographic areas differing in hydrology, landforms, soil types, and vegetation), different climatic conditions, and different times of the year. The reasons for this can be seen in model compound studies. Common biological molecules such as carbohydrates and sugars are relatively poor DBP precursors, whereas tannins and lignins produce large amounts of measurable by-products on a per-carbon basis. Waters collected from different locations and at different times of the year will have distinctly different mixtures of these biomolecules. As a result, the specific DBP yields can vary substantially between natural waters.

Chlorination studies with NOM extracts and whole waters have suggested that the activated aromatic content of the organic material is an important determinant in its tendency to form major chlorination by-products (Reckhow et al., 1990). This probably explains why UV absorbance is such a good predictor of a water's tendency to form THMs and HAAs because UV absorbance by NOM generally is attributed to activated aromatic chromophores. Accordingly, UV absorbance is a better predictor of chlorine reactivity and halogenated DBP formation potential than overall DOC. See Chap. 3 for coverage of UV absorbance as a surrogate parameter for TOC/DOC and DBP precursors.

Lignin is a major constituent in terrestrial vascular plants. It is quite resistant to biodegradation yet reactive with oxidants owing to a high density of activated aromatic rings. This combination of high terrestrial production, persistence, and high level of reactivity makes lignin an extremely important source of aquatic NOM and DBP precursors.

Perdue and Ritchie (2004) have summarized five literature sources and found a mean of 1 percent of total DOC attributable to phenolic lignin monomers. This is probably an underestimate because direct analysis of commercially derived lignin results in low recoveries of the monomeric compounds (Kim and Reckhow, 2009). If recoveries with commercial lignin and aquatic NOM are assumed to be comparable, aquatic fulvic acid could be in the range of 15 to 50 percent lignin derived.

Terpenoids are hydrocarbons produced in large quantities by a wide range of plants, both terrestrial and aquatic. There are indications that these compounds, which exist in various linear, branched, and cyclic forms, may account for a major fraction of the NOM in fresh waters (Leenheer et al., 2003; Lam et al., 2007). In particular, they may be dominant in waters of low aromaticity. These compounds are not likely to be as reactive as the activated aromatic structures in lignin. However, they certainly will react with oxidants by virtue of their abundant olefinic bonds. Given their presumed abundance and likely reactivity, it seems that the terpenoids could play a major role in oxidant demand and by-product formation in many types of waters.

General NOM reactivity often is expressed as some measure of the tendency to form major organic by-products. For chlorination, this means formation of THMs and HAAs, among others, and it is commonly done by means of an empirical laboratory chlorination test. To assess DBP formation in a valid reproducible fashion requires the use of a standard set of chlorination conditions. Standardized conditions facilitate the comparison of data from different investigators and allow the evaluation of precursor characteristics of different types of raw water sources at different times of the year. Since the 1970s, researchers have used a wide range of chlorination protocols, some calling for fixed chlorine doses and high residuals, some using fixed chlorine dose–TOC ratios, and some aiming for fixed chlorine residuals that are more representative of real systems. The former frequently has been called a *formation potential (FP) test*, and it is intended to maintain a relatively constant Ct (concentration times time) product in the face of changing chlorine demands. While each has its own advantages, the lack of standardization has hindered direct comparisons.

In an effort to solve this problem, many researchers are now using a single low-dose precursor test protocol called the *uniform formation conditions (UFC) test*. Summers and colleagues (1996), based on a meeting with several DBP researchers, developed this test, in which a sufficient amount of chlorine is applied to the water to produce a 1 mg/L free chlorine residual after 24 hours of contact at pH 8.0 and 20°C. This protocol is especially useful for assessing the effectiveness of various types of treatments on DBP precursor removal while using conditions that are typical of many systems. Because the chlorine doses are typical of those used in practice (on the order of 1.5–2 mg Cl₂ per milligram of C) (Obolensky et al., 2007), the distribution among bromine- and chlorine-containing DBP species is not distorted by use of an excessive chlorine dose. A related protocol using a 7-day reaction time at 25°C, pH 7.0, and a target chlorine residual of 4 mg/L also has been widely endorsed (APHA et al., 2005).

The preceding tests are distinguishable from the *simulated distribution system (SDS) test*, in which treated water is held under the specific conditions (pH, temperature, and chlorine residual) of distribution (e.g., APHA et al., 2005). The SDS test is useful to predict the extent of THM and HAA formation in a given water at various distribution system water ages. Comparisons between SDS tests and actual distribution system measurements made as part of the ICR effort were found to be good (McGuire et al., 2002). Although useful for predictive purposes in a specific system, the SDS test cannot be used in a more generic sense to predict DBP formation at conditions other than those used in the actual test.

Several researchers have examined THM precursor levels across a broad geographic distribution of sites. One of the largest of these studies encompassed 133 data points from five literature sources (Chapra et al., 1997). They concluded that the THM formation potential (THMFP) of this broad spectrum of natural waters increases with TOC in a nearly linear fashion. Reckhow and colleagues (2007) have reanalyzed these data, correcting for differences in chlorination conditions, and they found almost no relationship between THMFP and TOC. Not surprisingly, laboratory tests have shown that THM formation from dilutions of a single sample of NOM is constant when expressed on a per milligram of carbon basis. This is only true when the conditions are held reasonably constant, including the profile of chlorine residual versus time. For this reason, a normalized THM yield, defined as the specific THM formation under a UFC protocol (specific THM-UFC), has been used by Reckhow and colleagues (2007) as the characteristic measure of THM yield. This value is the concentration of THMs formed from reaction under the uniform formation conditions divided by the initial TOC of the water. Analysis of the preceding data by Chapra and colleagues (1997) show a regressed value of 21.5 $\mu\text{g}/\text{mg}$ of C at 1 mg/L TOC, which increases only slightly with TOC (Eq. 19-2). The yield is expected to change for different conditions of temperature, pH, and contact time, as discussed below.

$$\text{Specific THM-UFC} \equiv \frac{\text{THM-UFC}}{\text{TOC}} = 21.5(\text{TOC})^{0.095} \quad (19-2)$$

There are many other good databases that can be incorporated into a statistical analysis of THM formation. Reckhow and colleagues (2007) have compiled 27 data sets from the open literature and critically assessed the THM formation potential under the standardized specific conditions cited earlier in connection with Eq. 19-2. Within these 27 papers and reports were hundreds of single water assessments. A visually direct way of presenting the data is through a cumulative frequency plot, as found in Fig. 19-15. This reinforces the belief that groundwaters generally have lower specific formation potentials than surface waters, albeit not that much lower. In addition, one can extract median values and population percentiles from these data. Note that the median THM yield for surface waters is about 24 $\mu\text{g}/\text{mg}$ of C under the standardized conditions.

Figure 19-15 illustrates clearly that even when normalized to the organic carbon level and subject to the same set of reaction conditions, there still remains a substantial range in THM formation from one NOM sample to the next. The same has been observed for dihaloacetic acid and trihaloacetic acid formation (Reckhow et al., 2007). Some of this variability can be captured with the specific UV absorbance, as will be shown below.

In an effort to better understand the extent of DBP formation from NOM (DOC) in different types of waters and at different times of the year, many investigators have resorted to methods of fractionating the DOC into different subgroups. The most common and one of the simplest of these fractionation methods uses a series of macroreticular resins with different degrees of hydrophobicity and is based on an extraction procedure by Thurman and Malcolm (1981). Most often the organic material is fractionated into hydrophobic acids, transphilic acids, and hydrophilic constituents. Chlorination of the different fractions tends to show that, in most waters, the THM and HAA yield on a per milligram

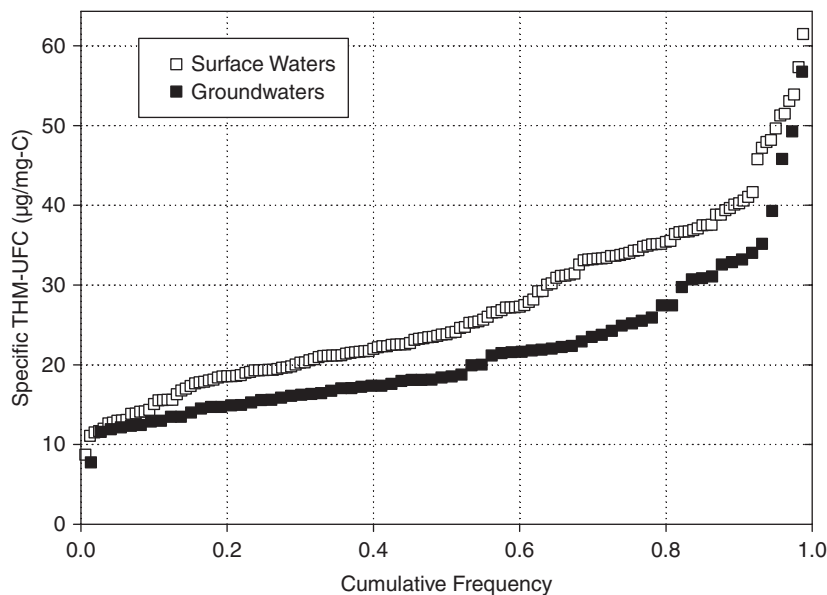


FIGURE 19-15 Specific precursor content in North American waters. (Source: Reckhow et al., 2007, AWWA Research Foundation.)

of C basis is greatest for the hydrophobic acid fraction (e.g., Liang and Singer, 2003). More recent studies have focused on fractionating dissolved organic nitrogen (DON) and assessing the formation of nitrogenous DBPs from these fractions (Leenheer et al., 2007; Dotson et al., 2009).

Another common, simple metric for characterizing DOC in waters with respect to its DBP formation potential is UV absorbance, with units of cm^{-1} . As indicated earlier, UV absorbance measurements reflect the activated aromatic content of organic carbon, and it is these activated aromatic structures that are dominant contributors to THM and HAA formation. While UV absorbance reflects the bulk concentration of precursors in a water (Fig. 19-16), the nature and reactivity of the precursors can be assessed by normalizing the UV absorbance, dividing it by the DOC concentration, and multiplying that number by 100 cm/m . The resulting specific UV absorbance (SUVA, in units of $\text{L}/\text{mg} \cdot \text{m}$) is a good indicator of the specific DBP formation potential of a water, as shown in Fig. 19-17 for three independent data sets. See Chap. 3 for additional coverage of the use of UV absorbance as a surrogate parameter for DOC and DBP precursors and coverage of SUVA.

Seasonal Effects. DBP concentrations are strongly influenced by season. The underlying factors are temperature and seasonally induced changes in water quality (NOM concentrations and characteristics, bromide, pH). In general, DBP concentrations are highest in summer. This is at least partly attributed to high temperatures, which accelerate DBP-forming reactions. Furthermore, disinfectant demand reactions are faster, requiring higher disinfectant doses to maintain target residuals. Competing with this are the facts that chemical degradation of selected DBPs (see below) is faster at high temperatures, and biodegradation may play a larger role in warmer waters.

With some sources, water quality changes also may be important. For example, in many watersheds, heavy spring rains cause allochthonous (terrestrial-derived) NOM, which has

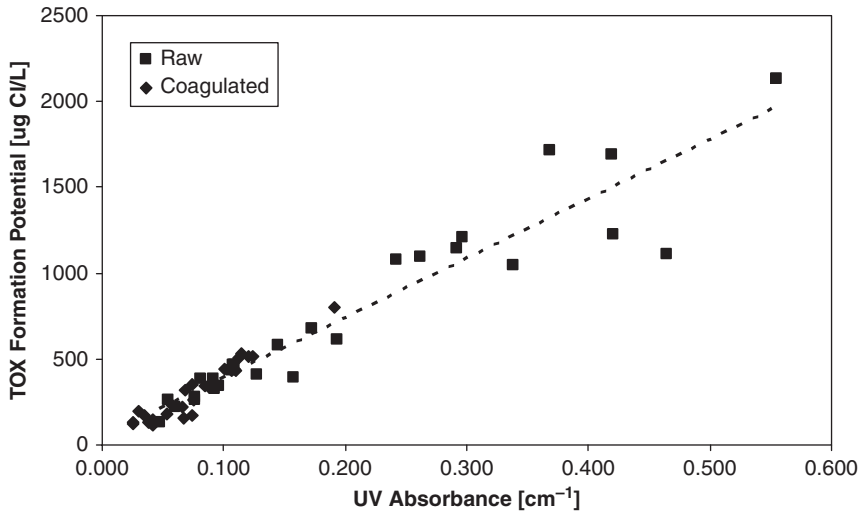


FIGURE 19-16 Relationship between total organic halide formation potential and UV absorbance for 27 different raw and coagulated waters from across the United States. (Source: Archer and Singer, 2006.)

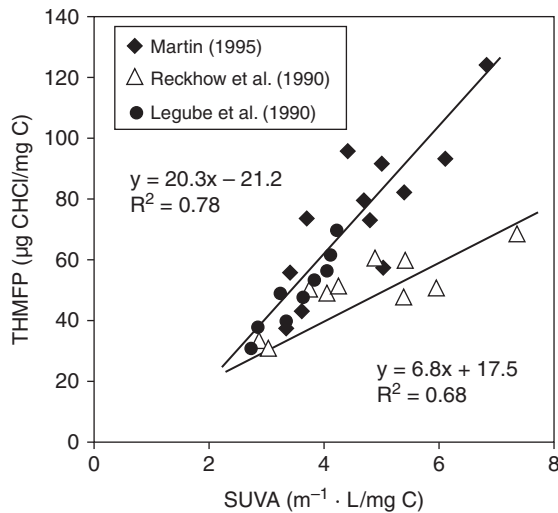


FIGURE 19-17 Correlations for normalized THM formation potential versus SUVA. (Source: Croué et al., 1999.)

a high lignin content and is rich in hydrophobic organic acids, to run off into the water source. In the summer, a larger portion of the NOM is autochthonous and hydrophilic in nature, arising from algal activity. In the fall, decomposed leaf litter washes into source waters. Hence the seasonal DBP signatures resulting from the application of disinfectants are expected to be different.

Likewise, the San Francisco Bay Delta, which provides raw drinking water for a large portion of the population in central and southern California, experiences significant seasonal variations in bromide concentration. During the spring season, high freshwater flows from the Sierra Nevada Mountains keep salt water, with its concomitant high bromide content, out of the delta so that chlorinated DBPs comprise most of the DBP content of the treated drinking water. In contrast, during the summer and early fall when fresh water flows are low, more salt water intrusion into the delta occurs, and bromine-containing species are the dominant DBPs formed.

Disinfection By-Product Formation Models

Since the very earliest work on DBPs, researchers and practitioners have proposed mathematical models to describe the formation of these compounds at different contact times and as a function of treatment conditions (e.g., disinfectant dose, pH, temperature) and treated water quality (e.g., DOC, UV absorbance, bromide). Fully empirical models composed of multiplicative power terms have proven to be useful and robust tools (e.g., Amy et al., 1987). This approach has been used in formulating a more general water treatment model that has been valuable in assessing central tendencies on a regional and national basis (Harrington et al., 1992; Solarik et al., 2000; Swanson et al., 2002). Unfortunately, the complex and diverse nature of naturally occurring DBP precursors requires that these DBP models be partially recalibrated before they can be used on specific systems. Models based on simplified chemical rate laws have been proposed in an effort to improve model performance (e.g., McClellan et al., 2000). These are more computationally intensive, and their development is an ongoing area of research.

CONTROL OF OXIDATION/DISINFECTION BY-PRODUCTS

There are three general approaches to controlling DBP concentrations: (1) minimize DBP formation by reducing the concentration of organic precursor material at the point of disinfection, (2) minimize DBP formation by reducing the disinfectant dose or contact time, changing the nature of the disinfectant or optimizing the conditions of disinfection, and (3) remove DBPs after their formation. Most efforts have focused on approach 1, as represented by optimizing the coagulation process (see Chap. 8) for removal of both TOC and particles (turbidity), and approach 2, reflected by changing from free chlorine to ozone or UV for primary disinfection and from free chlorine to chloramination for secondary disinfection. The third approach (DBP removal) is most appropriate for control of biodegradable by-products, especially those produced by ozonation, and possibly for removal of highly volatile DBPs such as chloroform.

Removing Organic Precursors

The objective of this particular strategy is to minimize the amount of organic precursors at the point of disinfection. This can be done by either reducing the precursor content of the raw water, improving precursor removal through the plant, shifting the point of disinfection to a later stage of treatment after precursors have been removed, or some combination of the three. It has been suggested that watershed management practices that help to reduce primary productivity in impoundments also will result in reduced THM precursor

levels (Karimi and Singer, 1991; Chapra et al., 1997). Reductions in organic precursor and bromide levels also may be achieved through careful source water selection, blending, or storage. Once they have entered the plant, DBP precursors may be removed or rendered less active by coagulation, adsorption, anion exchange, oxidation, biodegradation, or membrane separation. Each of these is discussed in the text that follows, with special focus on DBP control. For a broader and more comprehensive discussion of each process, the reader should consult the appropriate chapters earlier in this book.

Source Control. Control of DBP precursors at the source is an option that has received some attention, but with little practical experience to date. Cooke and Carlson (1989) prepared an early summary of established methods for reservoir and watershed management, including the likely impacts on DOC levels. Their ideas were based on a general understanding of allochthonous and autochthonous sources of NOM. Techniques intended to minimize terrestrial inputs (e.g., buffer strips) would control the former, and techniques intended to reduce algal and macrophyte contributions (e.g., application of copper sulfate) would control the latter. If DOC could be reduced, so would the levels of DBP precursors.

Twenty years later, we still know very little about the long-term impacts of watershed management practices on DBP precursor levels. However, we have made progress on one of the most fundamental questions—the relative importance of terrestrial versus aquatic sources of precursors. Water quality investigations and watershed modeling studies across the United States have revealed that some supplies are dominated by terrestrial or allochthonous sources, whereas others are largely algal or autochthonous in nature (e.g., Palmstrom et al., 1988; Canale et al., 1997; Stepczuk et al., 1998; Fuji et al., 1998; Speiran, 2000; Waldron and Bent, 2001; Nguyen et al., 2002; Garvey and Tobiasson, 2003; Reckhow et al., 2007).

Aquifer storage and recovery (ASR) has been used as a method of source water control (see Chap. 15). By storing high-quality treated water in the subsurface when raw water quality is good, this stored water later can be withdrawn when the raw water quality is poor, with only a minor degree of additional treatment. Similar raw water storage concepts can be considered in cases where the raw water is affected by high bromide concentrations. Storage of raw (or treated) water during times of the year when bromide levels are low allows utilities to use the stored water when bromide levels are elevated. ASR also may result in lower DOC and reduced DBP precursor levels as a result of long storage times in contact with aquifer minerals and microorganisms.

Oxidation. Pretreatment with a nonhalogenating oxidant can result in a net destruction of precursor sites and thereby reduce the subsequent formation of chlorinated DBPs after final disinfection with chlorine or chloramines. This phenomenon has been most widely studied with ozone, although the effect also has been demonstrated with chlorine dioxide, permanganate, and several advanced oxidation processes. From model compound studies, it has been shown that preozonation most often results in intermediates with lower DBP formation potential, although the reverse does sometimes occur. Since NOM is a broad mix of molecules with different structures and reactivities, it is not surprising that most types of NOM seem to show a downward trend in DBP formation with oxidation, much like the majority of model compound studies. Because of its selectivity for olefinic bonds, molecular ozone appears to be more effective than the less selective hydroxyl radicals. Oxidative precursor destruction is minor for most waters at typical oxidant doses used in water treatment. For example, Reckhow and colleagues (1986) showed that ozone doses of 0.25 to 0.5 mg of O₃ per milligram of C can result in THM precursor destruction of about 5 to 25 percent depending on the concentration of bicarbonate. The role of bicarbonate is to suppress ozone decomposition (by serving as a hydroxyl radical scavenger), thereby

enhancing the persistence of molecular ozone and possibly encouraging the formation of bicarbonate radicals.

The tendency of ozone to destroy DBP precursors is greater for systems where chlorine is added at acidic pH. The effect of ozone may disappear entirely or even reverse for systems that chlorinate at pH above 8 (Reckhow et al., 1986). Impacts of ozonation on subsequent trihaloacetic acid formation (e.g., TCAA) generally follow its impact on THMs. In contrast, precursors of dihaloacetic acids (e.g., DCAA) are far less affected by preoxidation.

Chlorine dioxide has been shown to produce similar removals of THM precursors as ozone at the same dose levels (Fig. 19-18).

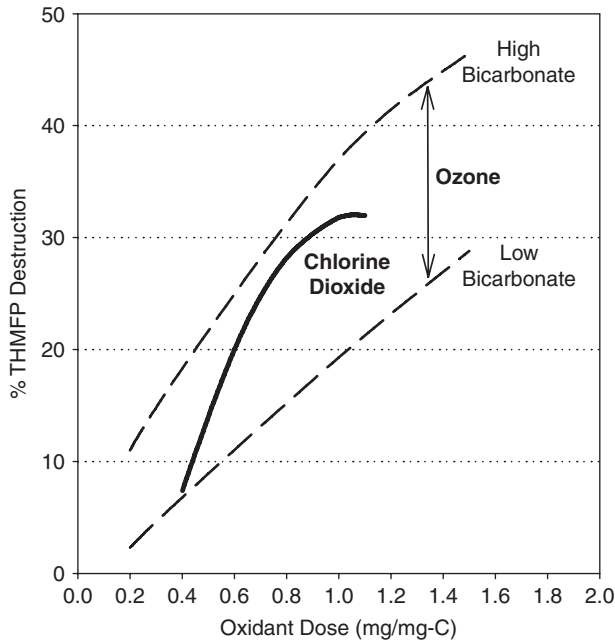


FIGURE 19-18 Comparison between ozone and chlorine dioxide in the destruction of THM precursors. (Data from: Reckhow, 1984; Werdehoff and Singer, 1987.)

Permanganate also appears to be capable of oxidizing THM precursors to a limited degree, although effective removal has been observed in hard waters owing to calcium-assisted adsorption of NOM on the manganese oxides produced (Colthurst and Singer, 1982).

Ozonation also has been shown to most effectively destroy the fastest-reacting DBP precursors. This has the effect of making ozonation appear more effective in systems where the chlorine contact time is short. Figure 19-19 shows the relative destruction of TCAA precursors by ozonation when the results are evaluated at different chlorine contact times. Precursor destruction in this case is as high as 75 percent when the chlorine is allowed to react for only 30 minutes. Precursor destruction was only 35 percent when the chlorine contact time was 1 week.

Advanced oxidation processes (AOPs) may be less effective for precursor destruction than simple ozonation. Frimmel and colleagues (2000) examined the use of moderate ozone doses (~1 mg/mg C) with waters of low TOC (1.2–2.3 mg/L) and found that increasing

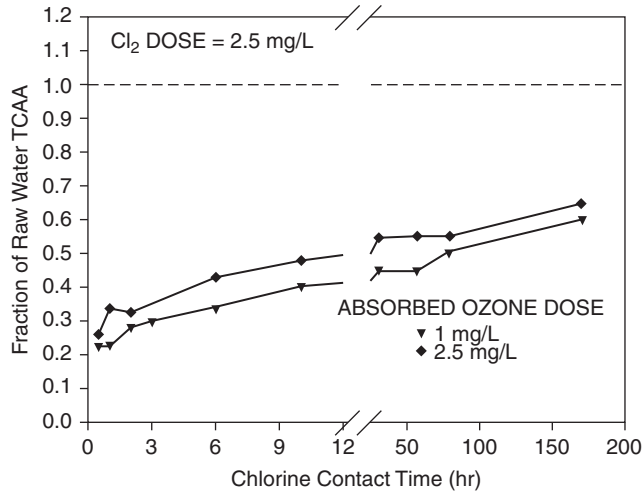


FIGURE 19-19 Destruction of TCAA precursor by ozone, as determined at various chlorine contact times. (Data from Reckhow et al., 1993.)

levels of peroxide caused a decrease in the destruction of THM precursors (Fig. 19-20). In related work, Kleiser and Frimmel (2000) explored the impacts of peroxide and UV irradiation on Ruhr River water (2.3 mg/L DOC). They found that UV treatment caused a small increase in THM precursor content even though the UV absorbance was partly destroyed (Fig. 19-21). Parallel experiments with ozone alone showed a monotonic decrease in THM precursor with increasing ozone dose.

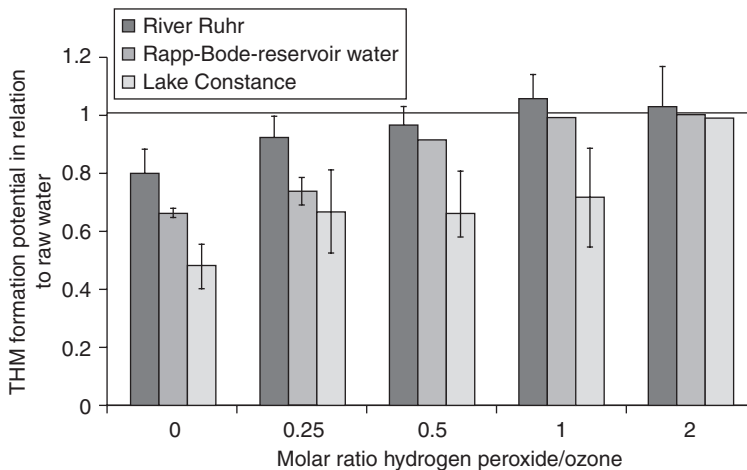


FIGURE 19-20 Impact of peroxide on destruction of THM precursors by moderate doses of ozone. (Reprinted with permission from Frimmel et al., 2000. Copyright © 2000 American Chemical Society.)

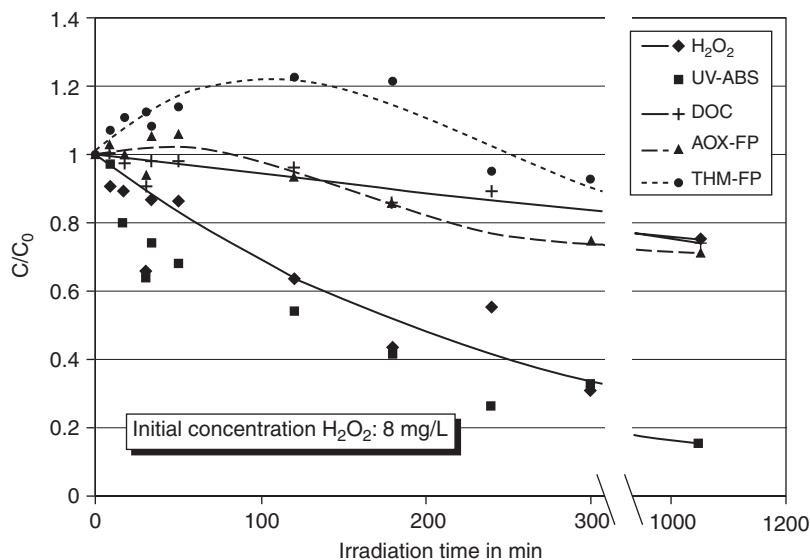


FIGURE 19-21 Impact of UV dose on THM precursor control from combined UV-peroxide treatment. (Source: Kleiser and Frimmel, 2000.)

Use of ozone and UV light may present some unique disadvantages, especially with respect to halonitromethane formation. The highest levels of halonitromethanes (e.g., chloropicrin) have been reported for plants with preozonation followed by chlorine/chloramines. It has been proposed that nitration reactions may be partly responsible (e.g., Choi and Richardson, 2004), although there also may be some activation of preexisting N organics. Thibaud and colleagues (1986) have shown that *m*-nitrophenol can produce halonitromethanes at 5 to 50 percent yield depending on pH. UV light from medium-pressure lamps has been shown to enhance halonitromethane formation substantially, probably due to photonitration reactions resulting in the incorporation of ambient nitrate into the NOM (Reckhow et al., 2009).

Coagulation and Clarification. The reader is also referred to Chap. 8 for additional coverage of this subject. Coagulation with alum or ferric salts generally is quite effective for removal of NOM (e.g., as measured by DOC) and its constituent DBP precursors (Kavanaugh, 1978; Young and Singer, 1979; Babcock and Singer, 1979; Edzwald et al., 1985). In fact, there is a tendency for the humic and fulvic fractions of NOM to be removed more completely during coagulation and subsequent settling or filtration than the more hydrophilic NOM (Liang and Singer, 2003; Archer and Singer, 2006). Since these humic materials bear a higher density of THM, trihaloacetic acid, and TOX precursor sites, this leads to slightly higher removals of THM, trihaloacetic acid, and TOX precursors on a percentage basis than bulk DOC (e.g., see Reckhow et al., 2005; Archer and Singer, 2006) (Fig. 19-22).

There are indications that some DBP precursors are more closely aligned with the hydrophilic fraction of organic carbon. One example is the 1,1,1-trichloropropanone precursors, which are probably associated with aliphatic ketones and related compounds. Figure 19-23 shows that these precursors are less amenable to removal by alum coagulation than the bulk organic carbon.

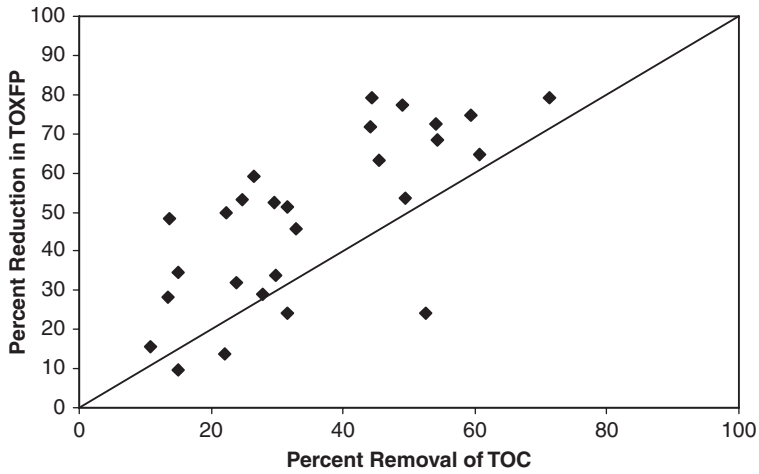


FIGURE 19-22 Comparison of the reduction in total organic halide formation potential and removal of TOC by coagulation for 27 raw waters across the United States. (Source: Archer and Singer, 2006.)

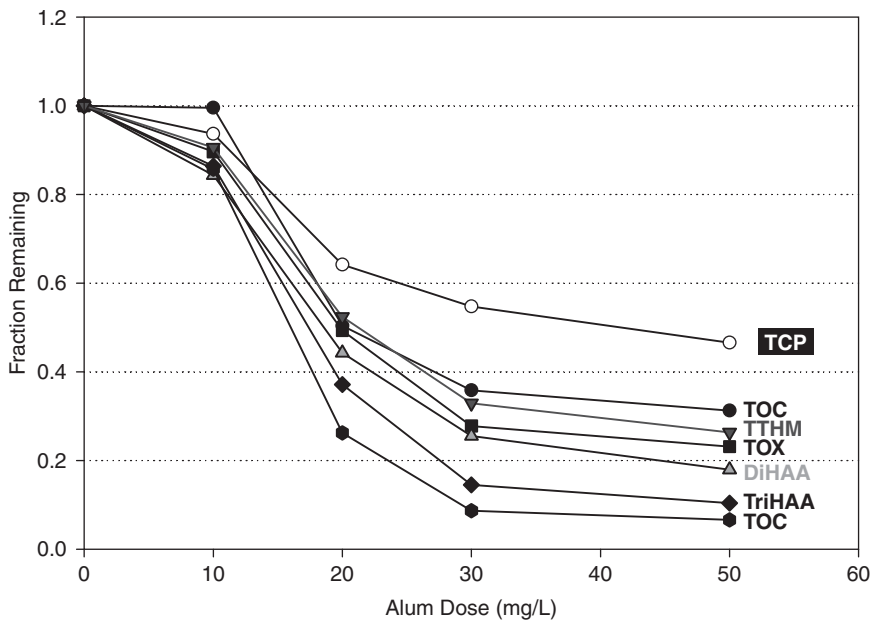


FIGURE 19-23 Removal of NOM and DBP precursors by alum coagulation, settling, and filtration. (Source: Reckhow and Singer, 1990.)

The effectiveness of coagulation for the removal of NOM and DBP precursors is the basis for including “enhanced” coagulation as a requirement of the Stage 1 Disinfectants/Disinfection By-Products Rule (see Chaps. 1 and 8). In addition to promulgating specific maximum contaminant levels for THMs and HAAs, the Stage 1 Rule requires a specified degree of TOC removal prior to disinfection. The objective of this requirement is to limit the formation of unidentified DBPs that may have an adverse public health effect. The TOC removals specified depend on the TOC concentration and alkalinity of the raw water (see Chap. 8). In general, raw waters with high SUVA values (and high DBP formation potentials) are more amenable to TOC removal by coagulation than waters with low SUVA values. This is in recognition of the general consensus that raw waters with higher TOC concentrations tend to contain higher concentrations of hydrophobic organic carbon that is more amenable to TOC removal by coagulation than waters with low TOC concentrations.

Ion Exchange. Because much of the NOM that harbors DBP precursor structures contains carboxylic acid functional groups and therefore is anionic in nature, anion exchange has been proposed as a promising technology for precursor control. Most recently, this interest has been directed toward the use of magnetic ion exchange resins (MIEX) of low particle size. Early batch tests suggested that MIEX could remove both hydrophilic and hydrophobic organic acids from water (Boyer and Singer, 2005) and thereby offer some advantages over coagulation, which removes primarily the hydrophobic fractions. Additional studies (Johnson and Singer, 2004; Boyer and Singer, 2006) also showed that MIEX could remove bromide in waters with low levels of competing anions (e.g., bicarbonate and sulfate). These studies also demonstrated THMF, HAAFP, and DOC removals of 70 percent or more (Fig. 19-24). There are concerns, however, that iron and hydrophobic

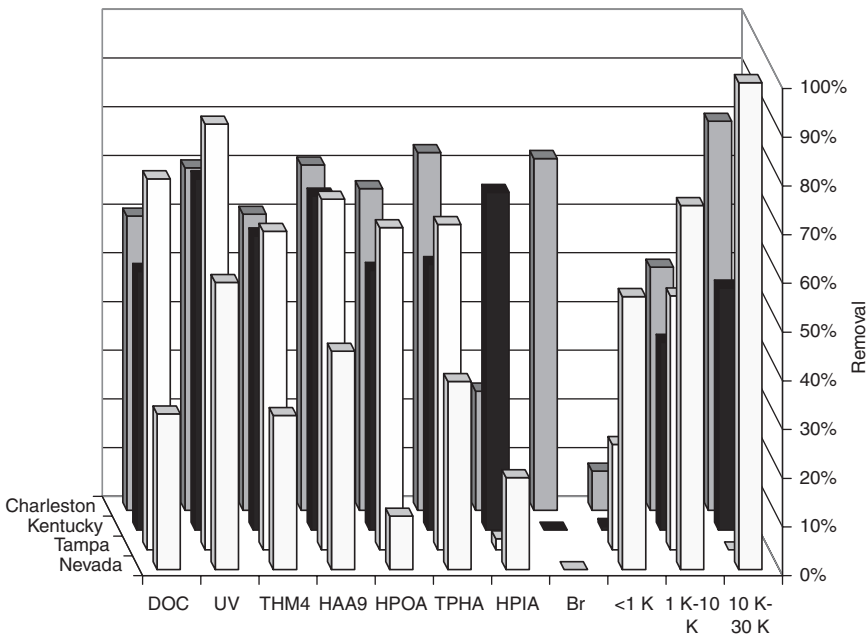


FIGURE 19-24 Summary of optimal MIEX treatment from four pilot-plant studies. (Source: Singer et al. 2007.)

organic matter in some waters may foul the MIEX resin and limit its reuse (Mergen et al., 2008). Ion exchange processes are discussed more extensively in Chap. 12.

Adsorption. Use of granular activated carbon (GAC) for adsorption of NOM has been studied widely, including its impacts on the removal of constituent DBP precursors. Because biological activity occurs so readily in GAC beds, it is sometimes difficult to separate removal owing to adsorption from loss to microbial degradation. Nevertheless, fresh GAC medium is effective at removing DBP precursors through abiotic adsorption. Important variables are the empty-bed contact time, GAC surface area, pore size distribution of the GAC, and temperature. In general, THMFP breakthrough parallels DOC breakthrough. Sometimes it lags the DOC breakthrough, making DOC a good conservative surrogate (e.g., Summers et al., 1995). Nevertheless, it should be recognized that use of GAC in a strictly adsorptive mode to control DBP precursors is relatively expensive for most systems, although it has been shown that biodegradation of DBP precursors in biologically active GAC beds can remove on the order of 20 percent of these precursors.

Powdered activated carbon (PAC) also can be used for the removal of DBP precursors. However, at typical water treatment doses and contact times, a limited degree of precursor removal can be expected. Processes that increase the standing concentration of PAC in the contactor or its residence time, such as contact clarifiers containing suspended PAC, are expected to be more effective. For greater coverage of adsorption, the reader should consult Chap. 14.

Biological Filtration. Biological filtration generally refers to the use of granular media filters in a way that encourages growth of attached biomass and results in high levels of biodegradation in the filter bed. Biological filtration has been practiced for more than a century in the form of slow sand filtration. More recently, rapid media filters have been operated for biological activity, especially when following ozonation. Important parameters that affect the performance of biological filters include pretreatment, contact time in the filter bed, oxidant/disinfectant residuals, media surface properties, and temperature.

There are numerous reports in the literature documenting the effectiveness of biological filtration for removing DOC and DBP precursors (e.g., Wang et al., 1995; Urfer et al., 1997; Niquette et al., 1999). These types of studies usually are designed to isolate the impacts of biological activity, separating biological effects from physicochemical adsorption. For GAC processes, this is sometimes done by assuming that long-term (postbreakthrough) removal of DOC represents the steady state biological removal. The extent of this steady state removal will depend on the fraction of biodegradable organics in the influent water, as determined by raw water quality and impacts of upstream treatment (e.g., ozonation). As an example, Snoeyink and Knappe (1994) found that 30 percent of the THM precursors were removed on GAC columns through long-term biodegradation.

In general, removal of THM precursors by biologically active GAC parallels the removal of DOC. While studied less commonly, the removal of precursors to other DBPs appears to reflect the gross removal of DOC, with some notable differences. These are illustrated here using pilot-plant studies conducted for the Massachusetts Water Resources Authority (MWRA). The raw water is a low-DOC, low-alkalinity surface water. Three trains were examined, all including preozonation, with one going directly to filtration, one with dissolved air flotation (DAF) and granular media filtration, and one with an upflow roughing filter (contact adsorption clarifier) with GAC media. Three types of filters were studied: an anthracite single-medium filter operated intermittently and two GAC/sand filters, one operated intermittently and one operated continuously. The intention was to limit biological activity in some of the filters by “starving” them via intermittent operation. The acclimated dual-media filters resulted in substantially lower precursor levels than the nonacclimated single-medium filter in the direct filtration train. Table 19-2 shows average precursor

TABLE 19-2 Average Precursor Removal from Wachusett Pilot-Plant Studies

Treatment process or change in process	TTHM	DCAA	TCAA	Choral hydrate
<i>Percent removal across process</i>				
DAF alone	13	27	38	20
DAF + anthracite bed filtration	37	40	65	27
Anthracite bed filtration	37	40	58	30
Acclimated anthracite bed filtration	49	54	70	67
Acclimated GAC bed filtration	62	65	76	78
<i>Additional percent removal across process</i>				
Acclimated anthracite bed filtration	12	14	9	38
Anthracite → GAC	13	9	6	11

Source: From Reckhow et al. (1992).

removal at various stages of the different process trains. Removals shown are calculated as the difference between the concentration in the ozone contactor effluent and the indicated process effluent divided by the concentration in the ozone contactor effluent.

Table 19-2 shows that removals by DAF always were less than removals by treatment trains that included some form of filtration. Some of this difference was due to removal of particulate organic carbon that escaped DAF, and some was due to biodegradation in the filters. As expected, pretreatment with DAF did not ultimately result in better filtered water quality (compare “DAF + Anthracite Bed Filtration” with “Anthracite Bed Filtration”), although it certainly would reduce head-loss buildup in the filters. The acclimated anthracite filters showed better removal of all four classes of precursors than the intermittently operated (i.e., nonacclimated) filters. This difference is shown in the second to last row in Table 19-2. Note that the difference is greatest for the chloral hydrate precursors, a group that is expected to be dominated by aliphatic aldehydes, which are readily biodegradable. The acclimated GAC media seems to have supported a higher level of removal for all the precursors compared with the acclimated anthracite filters. This difference is shown in the bottom row of Table 19-2. Elevated biological activity with GAC media relative to sand or anthracite has long been noted (e.g., Wang et al., 1995) and has been attributed to differences in the pore size distribution or surface chemistry of the GAC.

While ozonation and biofiltration ultimately will result in lower overall DBP levels in the finished water, they also will result in a shift toward a higher fraction of brominated species. This is especially noticeable in waters that contain high levels of bromide because ozone will oxidize some of the bromide to hypobromous acid and bromate. The hypobromous acid will react with NOM in the water to form low levels of brominated DBPs, even before the addition of any halogen-containing disinfectants. Second, improved removal of DOC by the GAC will result in higher ratios of bromide to DOC in the finished water. This has the unintended consequence of more heavily populating precursor carbon with bromine atoms rather than chlorine atoms. The end result is a higher level of bromine incorporation (e.g., Shukairy and Summers, 1996). This same phenomenon exists for most processes that target DOC removal, for example, coagulation, GAC adsorption, anion exchange, nanofiltration (see below).

Membrane Separation. Although low-pressure membranes (microfiltration and ultrafiltration) generally are not effective at removing dissolved organic substances, high-pressure processes can be quite effective. Nanofiltration (NF) membranes typically reject 50 to 95 percent of the THM precursors depending on the molecular weight cutoff of the membrane (Chellam, 2003). Since NF is capable of removing a large fraction of the organic

DBP precursors, but not bromide, NF-treated water can be expected to have high Br:DOC ratios. This leads to higher levels of bromine incorporation during subsequent chlorination (e.g., Chellam, 2003; Ates et al., 2009), similar to that observed for biofiltration. Reverse-osmosis (RO) processes are capable of removing essentially all the THM and HAA precursors, as well as rejecting some of the bromide. The performance, design, and operational considerations for NF and RO are covered in detail in Chap. 11.

Modifying Disinfection

Various elements of the disinfection step sometimes can be changed to help control DBP formation. One obvious approach is to reduce the disinfectant dose or contact time to the extent possible within the constraints of good disinfection practice. For example, primary and secondary disinfectant doses may be reduced in some plants while relying on booster disinfection out in the distribution system to take care of areas susceptible to low residuals (see Carrico and Singer, 2009). Additionally, disinfectant addition may be delayed until after a substantial portion of the DBP precursors have been removed, for example, by coagulation, anion exchange, adsorption, or membrane filtration. pH adjustment also can be used to favorably affect DBP formation. Base addition for corrosion control might be delayed until after disinfection with chlorine to help depress formation of THMs (see earlier section on the effects of pH). A widely used approach to control the formation of currently regulated DBPs is to substitute an alternative disinfectant for chlorine. Common examples include the use of chloramines as a secondary disinfectant in place of free chlorine or the use of ozonation, UV irradiation, or chlorine dioxide as a primary disinfectant in place of chlorination. Implementation of any of these options must be done in such a manner that disinfection is not compromised.

Moving the Point of Chlorination. It is well established that halogenated DBP formation is, by a first approximation, proportional to the TOC concentration at the point of chlorination. This is why, in waters with high DBP precursor concentrations, shifting the point of chlorination from before coagulation to after clarification yields substantial reductions in DBP formation. This was first demonstrated in full scale by Young and Singer (1979). These authors monitored the Durham, NC, water treatment plant over the time period when they switched from addition of chlorine prior to rapid mix to addition at a point between sedimentation and dual-media filtration. The drop in THMs after the switch (early January 1977) was quite clear and was based on a series of bench-scale chlorination tests using raw and coagulated water (Fig. 19-25). The Stage 1 Disinfectants/Disinfection By-products Rule requirement that certain levels of TOC removal be achieved prior to final disinfection is based on recognition that chlorinating after effective coagulation and clarification substantially reduces the formation of THMs and HAAs and most (if not all) other halogenated DBPs.

Furthermore, a 40 percent reduction in TOC across conventional treatment often translates to a 50 percent or more reduction in some DBPs when this switch is made. This is partly attributed to preferential removal of precursor organics by coagulation and the accompanying shift in the nature of the NOM at the point of chlorination to less reactive compounds (see Fig. 19-23).

Delaying the addition of chlorine until after filtration may serve to further reduce finished-water DBP concentrations. Organic precursors deposited on filter media are subject to reaction with chlorine in the water applied to the filters. The end result is that these retained organic precursors are converted to DBPs at a high yield (Corbin et al., 2003). However, the need to control manganese by means of catalytic removal on filter media may preclude this option in some plants (see Chap. 7).

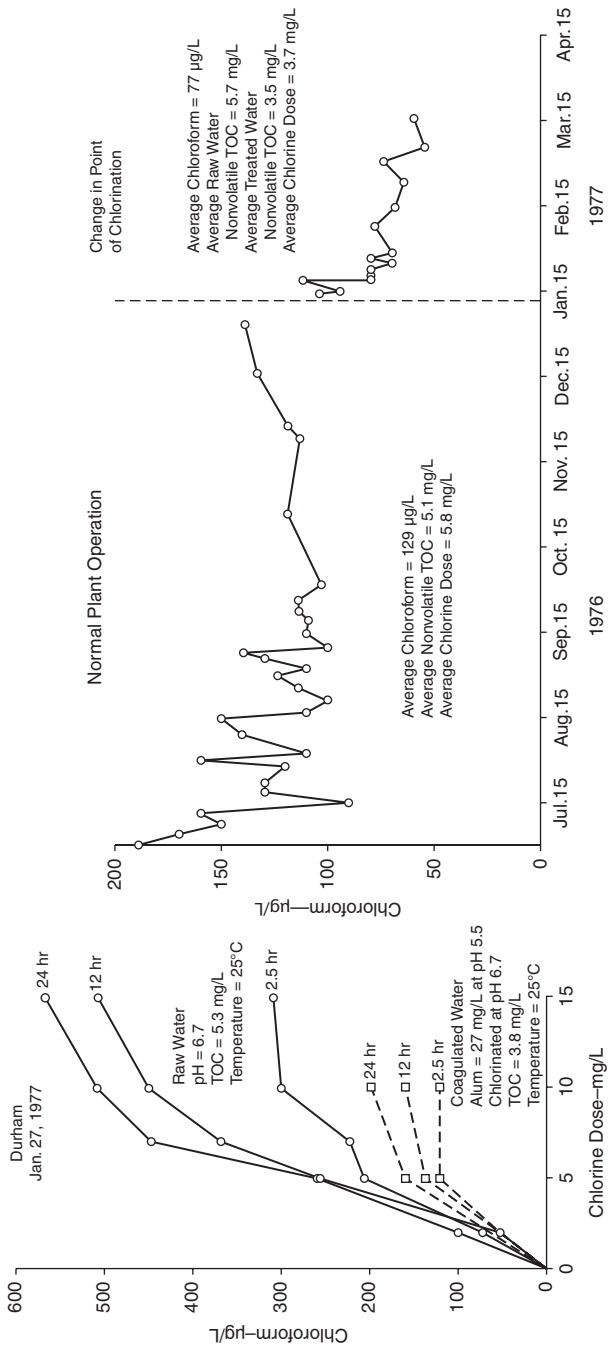


FIGURE 19-25 Impact of moving the point of chlorination from before to after coagulation and sedimentation. (Source: Young and Singer, 1979.)

Alternative Primary Disinfectants. A number of utilities have adopted the use of ozone, UV irradiation, or chlorine dioxide as alternative primary disinfectants in place of free chlorine. These agents, although more expensive, generally are better disinfectants than free chlorine (see Chap. 17). As noted earlier and in Chap. 7, however, while these alternative disinfectants do not form THMs and HAAs to any appreciable degree, ozone is associated with the formation of bromate in bromide-containing waters, and chlorine dioxide produces chlorite as a by-product. Both bromate and chlorite are public health concerns and are regulated in finished drinking water.

Alternative Secondary Disinfectants: Chloramines. Research has shown that inorganic chloramines result in little or no formation of trihalogenated species, that is, THMs and the trihaloacetic acids (Cowman and Singer, 1996, Zhang et al., 2000). In contrast, monochloramine produces dichloroacetic acid, but at much lower concentrations than free chlorine. The addition of preformed monochloramine, however, is not commonly practiced. Still, because chloramines are almost always applied after a period of free chlorine contact (or use of an alternative primary disinfectant), they have the effect of greatly reducing the formation of THMs and HAAs (e.g., Speitel, 1999). Figures 19-26 and 19-27 demonstrate the impact of ammonia addition to chlorinated finished water from three water treatment plants in North Carolina (Singer et al., 1998). Ammonia was added at a 1:4 weight ratio relative to chlorine, and waters were held at pH 8.0 and 20°C for the times indicated. As shown, little additional THM or HAA6 formation is apparent.

As a result of the Stage 2 Disinfectants/Disinfection By-products Rule and the shift to a locational running annual average instead of the historical system-wide running annual average as a basis for regulation and the fact that chloramines essentially stop the continuing formation of THMs and HAAs, many utilities have switched or are planning to switch to the use of chloramines as a secondary disinfectant to comply with the Stage 2 Rule.

Changing the Chemistry of Disinfection. A good example of how knowledge of the chemistry of DBP formation can be used to effect DBP control is the case of bromate. This

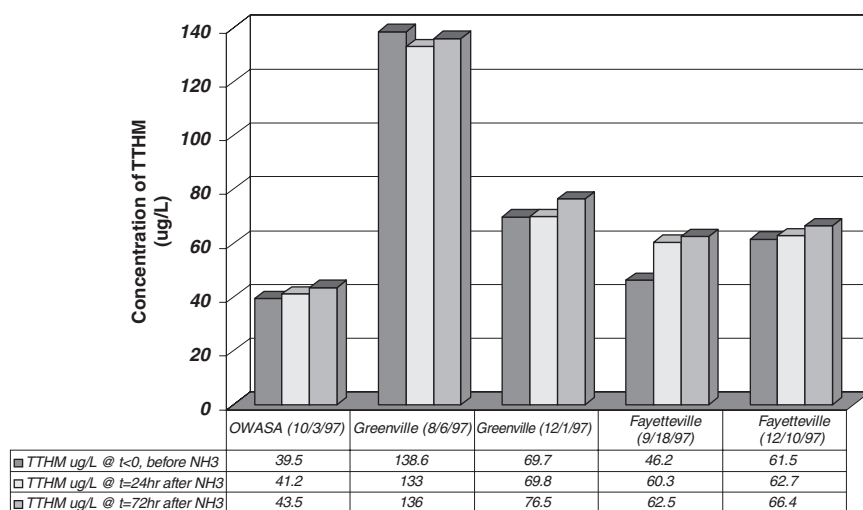


FIGURE 19-26 Impact on THM formation from ammonia addition to chlorinated finished water from three water treatment plants in North Carolina. (Source: Singer et al., 1998.)

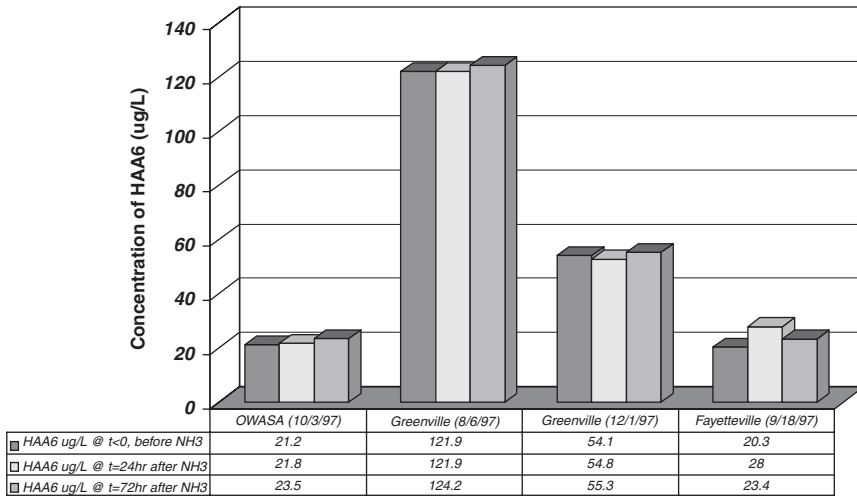


FIGURE 19-27 Impact on HAA formation from ammonia addition to chlorinated finished water from three water treatment plants in North Carolina. (Source: Singer *et al.*, 1998.)

inorganic DBP is produced almost exclusively from the ozonation of inorganic bromide ion. Von Gunten and Hoigne (1994) have shown that multiple pathways are important in bromate formation in drinking water, involving some combination of molecular ozone and the hydroxyl radical (see discussion in Chap. 7 and Fig. 19-28).

With this knowledge, it is easy to see that there are at least three feasible strategies for interrupting the formation of bromate: (1) prechloramination: depress bromide (Br^-) concentrations by adding chlorine to produce HOBr/OBr^- and ammonia to convert the HOBr/OBr^- formed to bromamines prior to ozonation; (2) acidification: depress hypobromite (OBr^-) concentration by lowering the pH and forming HOBr , which is less reactive than OBr^- with respect to bromate formation; and (3) preammoniation: add ammonia to convert hypobromous acid and hypobromite formed from the oxidation of bromide by ozone to bromamines. All three of these have been tested and found to be effective to varying degrees, with prechloramination attracting the most attention (e.g., Buffle *et al.*, 2004; Wert *et al.*, 2007).

Removing Disinfection By-Products after Formation

In general, DBPs are hydrophilic and have low molecular weights, characteristics that make them difficult to remove by most physicochemical processes. For example, the removal of THMs in chlorinated water requires either air stripping or GAC adsorption with frequent regeneration. On the other hand, some DBPs are biodegradable and therefore may be removed by biologically active filtration. The most common example of this is the removal of aldehydes, acids, and ketoacids produced by ozonation. There is also evidence that HAAs produced from chlorination can be removed in this way. These postdisinfection options are discussed below.

Adsorption. Granular active carbon (GAC) is the adsorbent of choice for removing trace levels of organic compounds, especially synthetic organic contaminants, from drinking

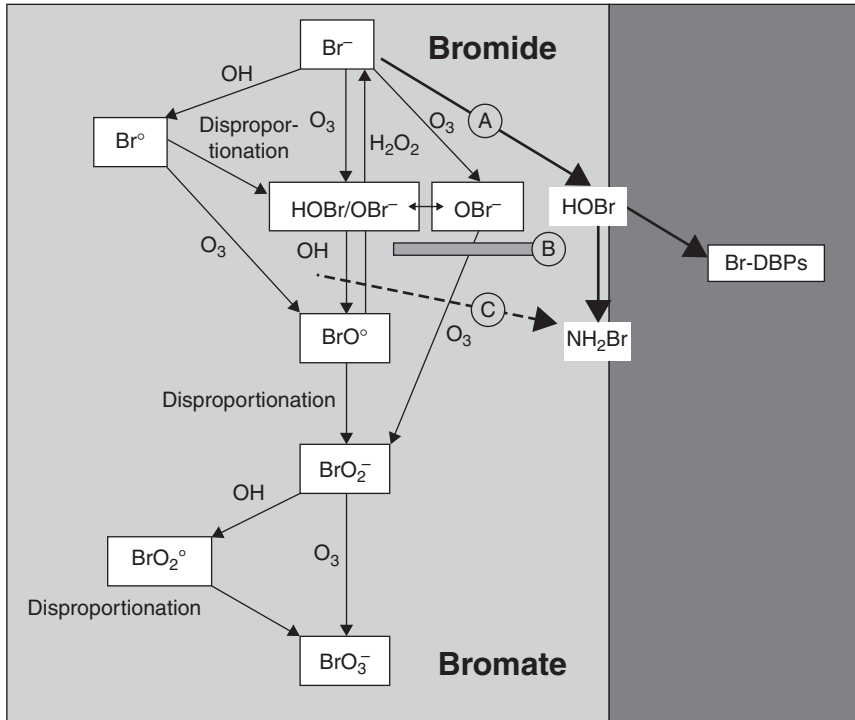


FIGURE 19-28 Bromate formation pathways and strategies for bromate control.

water. Batch isotherm tests show that the capacity and affinity of GAC for low-molecular-weight polar organic compounds is limited, rendering GAC adsorption an expensive solution for removal of many DBPs. While chloropicrin and 1,1,1-trichloropropanone are strongly adsorbed, chloroform and the other THM species are not. The HAAs are also poorly removed largely because they are almost completely ionized at pH conditions typical of drinking water treatment.

Pilot- and full-scale adsorber studies support the conclusions from bench-scale testing. Graese and colleagues (1987) showed that only 5000 to 6000 bed volumes (BV) of water could be processed before reaching 20 percent breakthrough (80 percent chloroform removal), corresponding to 50 to 100 days of service (Fig. 19-29). Throughput and bed life diminish as the empty-bed contact time (EBCT) drops below 8 to 10 minutes owing to changes in the length of the mass transfer zone. Nevertheless, Savitz and colleagues (2005) have shown that several point-of-use devices containing GAC have the ability to remove substantial amounts of THMs and HAAs for extended periods of time.

It has been suggested that bromate can be removed by GAC (Kirisits et al., 2000). Such removal probably occurs through reaction of bromate with reduced sites on the carbon, and as a result, competition exists with NOM and some inorganics for those sites. There are indications that preozonation may help to improve bromate removal via this mechanism because ozone can render NOM more hydrophilic and less readily adsorbable.

Biological Filtration. While biodegradation has been used for enhancing removal of NOM and DBP precursors in filters, it also may be used to remove preformed DBPs. The

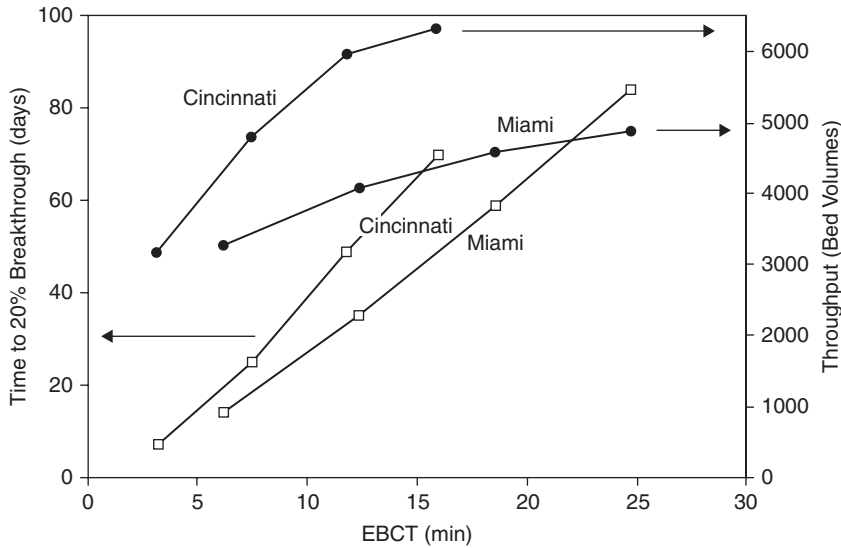


FIGURE 19-29 Field data on chloroform removal by GAC. (Source: Adapted from Graese et al., 1987.)

most widely studied cases involve ozonation by-products such as the low-molecular-weight aldehydes and ketones. Reckhow and colleagues (1992) conducted biofiltration pilot studies in a Connecticut utility where they challenged the filters with high levels of ozonation by-products. They found that common by-products such as glyoxalic acid are removed almost completely at conventional filtration rates (Fig. 19-30). They also found that backwashing the filters with water containing a chlorine residual could be detrimental to the activity of the attached growth; thus filters 2 and 3 were less effective than filters 1 and 4. Similar findings have been reported by DiGiano and colleagues (2001) for removal of formaldehyde, glyoxal, and methyl glyoxal at EBCTs of 10 minutes.

Removal of chlorination by-products via biofiltration is practiced less commonly. Wu and Xie (2005) demonstrated that all HAAs could be removed effectively by GAC/sand filters at high temperatures. However, at lower temperatures (e.g., $<10^{\circ}\text{C}$), removal of TCAA was poor (<50 percent), except at EBCTs of 10 minutes or more. Kim and Kang (2008) confirmed that TCAA was not as well removed as DCAA by biological filtration. They also confirmed that the THMs are not degraded in biologically active filters.

Based on the limited research on HAA degradation in filters, and by analogy with the larger body of work on ozonation by-products, it seems that the following factors are likely to encourage biodegradation of a broad range of oxidation by-products: (1) absence of a disinfectant residual in the filter bed during normal operation, (2) little or no disinfectant residual in the backwash water, (3) extended EBCTs, that is, 10 minutes or more, (4) warm temperatures, (5) prior acclimation by exposure to the DBPs that are to be removed (this is often accompanied by partial exhaustion of adsorption capacity if GAC is used), and (6) media with high external surface area for good microbial attachment.

Biological filtration also may be effective for control of bromate. Pilot-plant studies have shown removals in the range of 40 to 60 percent (Kirisits and Snoeyink, 1999). Bromate seems to serve as a terminal electron acceptor, and as a result, this process may require that most of the dissolved oxygen be depleted prior to filtration. In like manner, bromate removal has been seen in anoxic groundwaters (Butler et al., 2004).

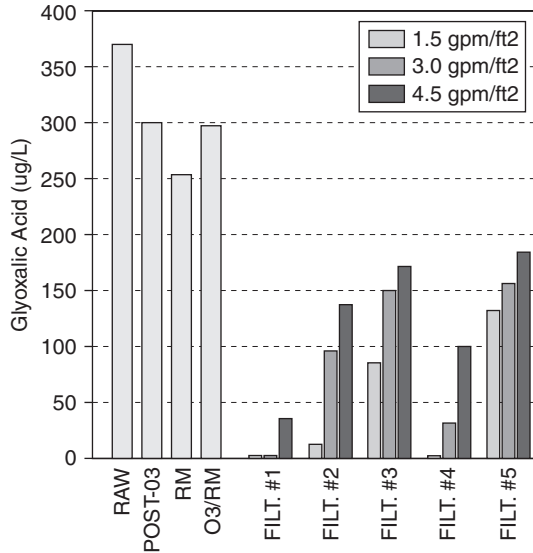


FIGURE 19-30 Impact of filtration rate and backwash on removal of glyoxalic acid by biologically active filters. (Post-O₃, RM and O₃/RM refer to raw water samples treated with ozone, alum, and combined ozone and alum, respectively.) (Source: Reckhow et al., 1992.)

Aeration. THMs are among the most volatile of the chlorination by-products. Accordingly, packed tower aeration has been studied by Umphres and colleagues (1983) for removal of THMs. As the level of bromine incorporation increases, the rate of loss by aeration decreases owing to the lower volatility of the heavier bromine-containing species (Fig. 19-31). Aeration is discussed further in Chap. 6.

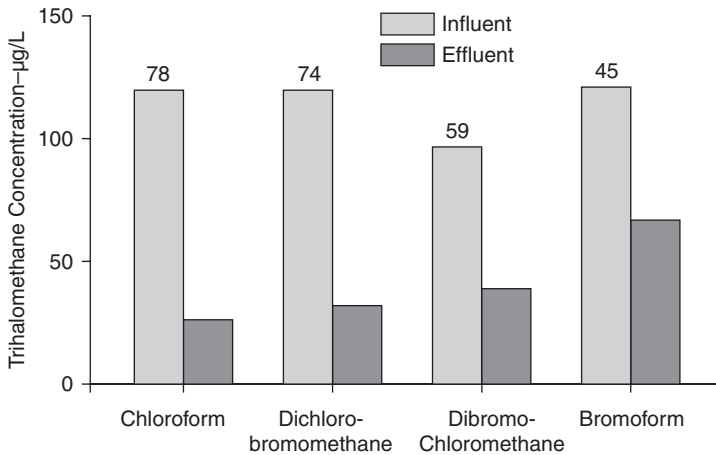


FIGURE 19-31 Comparison of THM removals from pilot-plant studies on packed tower aeration. (Source: Umphres et al., 1983.)

Membrane Separation. While high-pressure membrane processes are quite effective at removing DBP precursors, preformed DBPs usually are much smaller in molecular size and therefore less well removed. Reverse osmosis (RO) has exhibited THM rejections as high as 90 percent (Reinhard et al., 1986). Membrane composition is likely to be more important than molecular weight cutoff ratings. For these small-molecular-weight compounds, rejection depends more on specific chemical properties of both the compound and the membrane and on the affinity between the solute and the membrane. In particular, charge effects may be an important characteristic in determining rejection. For example, Chalati and colleagues (2009) found that high-density negatively charged NF membranes are capable of removing 90 percent or more of the anionic HAAs. On the other hand, uncharged DBPs such as NDMA are poorly removed, even by RO (Steinle-Darling et al., 2007). Partial fouling of membranes may result in improved removal of these difficult solutes. The performance, design, and operational considerations for NF and RO are covered in detail in Chap. 11.

DISINFECTION BY-PRODUCTS IN THE DISTRIBUTION SYSTEM

Stability of Disinfection By-Products

The THMs generally are considered to be stable end products of the reaction between NOM and chlorine. Although the HAAs are also considered to be stable end products of chlorination, they are known to degrade abiotically by decarboxylation or by reductive dechlorination. The rate and extent of their degradation tend to be proportional to their bromine content (Zhang and Minear, 2002), with tribromoacetic acid being the least stable of the bromine- and chlorine-containing trihaloacetic acids. The trihaloacetic acids primarily exchange a bromine atom for a hydrogen atom, forming the corresponding dihaloacetic acids. There also may be some conversion of dibromoacetic acid to bromoacetic acid and bromochloroacetic acid to chloroacetic acid. Loss of bromine atoms is substantially faster than loss of chlorine atoms. Zero-valent iron associated with pipe walls can readily dehalogenate HAAs (Hozalski et al., 2001), with chloroacetic acid being the final product of di- and trichloroacetic acid degradation. Furthermore, linear free-energy calculations by Zhang and Minear (2002) suggest that all iodinated trihaloacetic acids except dichloroiodoacetic acid are also likely to undergo decarboxylation in drinking water distribution systems.

Reports of the biological degradation of HAAs in drinking water distribution systems are well known. Starting with the work of Williams and colleagues (1994), numerous researchers have observed a decrease in HAA concentrations in regions of the distribution system that have no chlorine residual (e.g., Speight and Singer, 2005), especially when the water temperature is high. This loss is particularly noticeable for the dihaloacetic acids. Figure 19-32 illustrates, for a utility in the southeastern United States using combined chlorine as a secondary disinfectant, the loss of HAAs in the system at high residence times when the chlorine residual is depleted. The THM concentration at this same location is essentially unchanged. Nitrification also was observed at this same location, indicating the presence of ammonia-oxidizing bacteria. Figure 19-33 shows a similar situation for a utility in California using combined chlorine. Again, HAA concentrations are decreased at locations where the combined chlorine residual is low. [Note that the water ages (residence times) shown are based on hydraulic modeling, and therefore, the hierarchical order of residence times may not be accurate.] The speciation of the HAAs for this utility is shown in Figure 19-34, which illustrates that the decrease in total HAA concentration is due to loss of the dihaloacetic acid species.

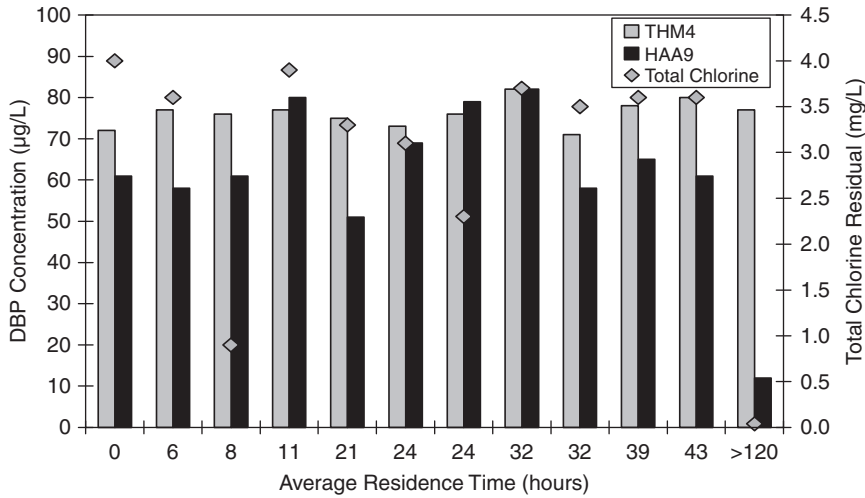


FIGURE 19-32 Trihalomethane and haloacetic acid concentrations and total chlorine residual at various water ages for a utility in the southeastern United States. (Source: Baribeau et al., 2006, AWWA Research Foundation.)

The fact that HAA levels tend to decrease at high water ages in the distribution system means that unlike THM concentrations, which are highest at distribution system locations with the highest residence times, HAA concentrations often tend to peak elsewhere in the system. For many systems, different patterns are observed at different times of the year because biodegradation is limited at colder temperatures, and it is also easier to maintain chlorine residual in remote parts of the system when the temperature is colder. This

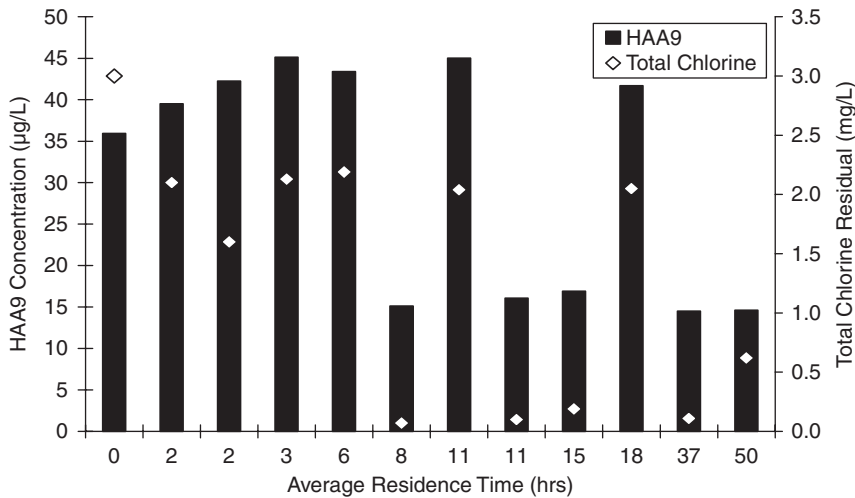


FIGURE 19-33 Haloacetic acid concentrations and total chlorine residual at various water ages for a utility in California. (Source: Baribeau et al., 2006, AWWA Research Foundation.)

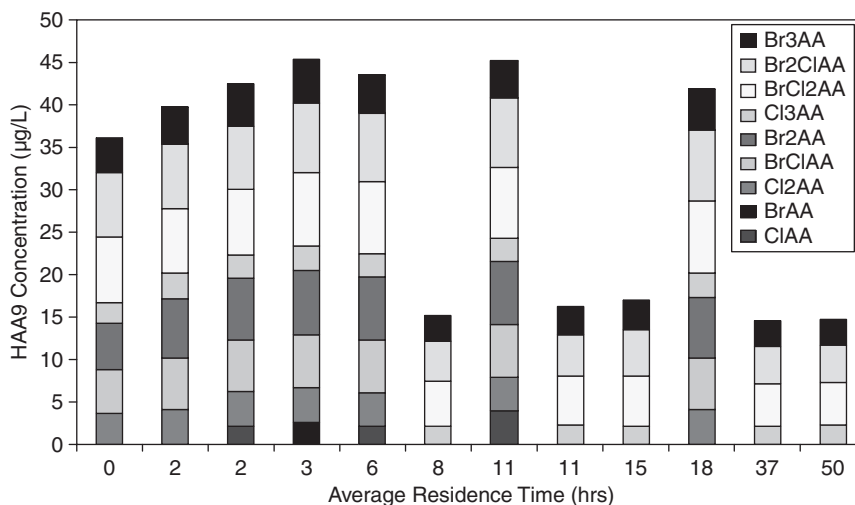


FIGURE 19-34 HAA speciation at various water ages for a utility in California. (Source: Baribeau et al., 2006, AWWA Research Foundation.)

has regulatory implications with respect to choosing locations for compliance monitoring where THM and HAA concentrations are at a maximum.

Many of the other halogenated DBPs normally formed during chlorination are chemically unstable. Once in the distribution system, they will continue to react with constituents of the water or materials attached to pipe walls to form secondary by-products. Examples of reactive DBPs, as noted earlier in this chapter, include the haloacetonitriles, the haloketones, and the cyanogen halides. It is quite likely that many other metastable compounds have eluded detection in finished drinking water because of their innate chemical instability.

Monitoring for Regulatory Compliance

Historically, DBPs have been regulated based on annual average levels in the distribution system. For larger systems, the Stage 1 Disinfectants/Disinfection By-products Rule requires that THMs and HAAs be measured quarterly at four locations in the system for each water treatment plant and that the *system-wide* running annual average (the average of the last four quarters) be below the maximum contaminant levels of 0.08 mg/L for the THMs and below 0.06 mg/L for the HAAs that are regulated—five of the nine bromine and chlorine-containing HAAs. The four locations were designated as three with average distribution system residence times and one remote location. For small systems, compliance is based on monitoring once a year, when the levels are expected to be highest, and at only one location, again where the levels are expected to be highest. The Stage 2 Rule keeps the same maximum contaminant levels but bases compliance on a *locational* running annual average, meaning that compliance must be achieved at all sampling locations. Moreover, the four sampling locations must be at points in the system where THM and HAA levels are expected to be highest.

As noted earlier, because of their stability, THM concentrations in chlorinated systems are expected to be highest where the contact time between free chlorine and the water is greatest, that is, at locations with the highest water age. For HAAs, this is not always the

case, particularly in warmer waters, where biodegradation occurs at high water ages. For chloraminated systems, because monochloramine does not produce THMs and produces only limited amounts of the dihaloacetic acids, THM and HAA levels are expected to be relatively uniform throughout the distribution system, except at high water ages, where biodegradation may affect HAA levels. The fact that THMs and HAAs do not increase appreciably in the system when monochloramine is the residual disinfectant is one of the reasons why many utilities have converted or are planning to convert to a combined chlorine residual for compliance with the Stage 2 Rule.

Spatial Temporal Variability of DBP Levels

Until recently, the temporal and spatial variability in DBP concentrations in distribution systems have not been fully appreciated. While it has always been understood that DBP levels change seasonally because of changes in temperature (kinetics of DBP formation) and the nature and amount of precursors in the raw water and that DBP levels change with increasing residence time in chlorinated systems, short-term (day-to-day and hour-to-hour) variations generally have not been recognized.

Singer (2001) showed that THM concentrations at various locations in chlorinated systems exhibit appreciable diurnal variations that match the diurnal variations in residual chlorine and water age. At times of the day when water demand is low and storage tanks in the system are filling, water age at sampling locations influenced by these tanks is low, and THM concentrations tend to be at a minimum. At other times of the day, when water demand is high and water levels in storage tanks are being drawn down, water age is higher, chlorine residuals are lower, and THM levels are correspondingly higher. Such diurnal variations are not seen in chloraminated systems because DBP levels do not increase appreciably with water age. Of course, as noted earlier, such variations can be seen if biodegradation of HAAs occurs with increased water age.

Short-term variations in DBP levels also have been reported at the point of entry to the distribution system, particularly for THMs (Periera et al., 2004; Obolensky et al., 2008). THM levels were observed to change by a factor of up to 2 over a relatively short period of time. These variations were unexpected and were traced to operational variations in the treatment plants associated with chlorine addition, ammonia addition, and pH adjustment. The findings suggest that water utilities should examine their operations routinely to make sure that their chemical feed systems are designed and operated appropriately.

Accordingly, in view of this short-term variability in DBP levels in the distribution system, regulators and utility personnel may wish to review the current reliance on quarterly averaging to assess DBP exposure and to determine MCL compliance.

ABBREVIATIONS

AOC	assimilable organic carbon
BCAA	bromochloroacetic acid (also BrClAA)
BCAN	bromochloroacetonitrile
BDCM	bromodichloromethane
BDOC	biodegradable dissolved organic carbon
BIF	bromine incorporation factor
BOM	biodegradable organic matter

BSF	bromine substitution factor
CH	chloral hydrate
CP	chloropicrin
DAF	dissolved air flotation
DBAA	dibromoacetic acid (also Br ₂ AA)
DBAN	dibromoacetonitrile
DBCM	dibromochloromethane
DBPs	disinfection by-products
DCAA	dichloroacetic acid (also Cl ₂ AA)
DCAN	dichloroacetonitrile
DCP	dichloropropanone
D/DBP	disinfectants/disinfection by-products
DiHAA	dihaloacetic acids (DCAA + BCAA + DBAA)
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
DOX	dissolved organic halogen
EBCT	empty-bed contact time
FP	formation potential
GAC	granular activated carbon
HAAFP	haloacetic acid formation potential
HAA9	nine haloacetic acids (MCAA + MBAA + DiHAA + TriHAA)
HAAs	haloacetic acids
HAN4	four haloacetonitriles (DCAN + TCAN + BCAN + DBAN)
HANs	haloacetonitriles
HPIA	hydrophilic acids
HPOA	hydrophobic acids
ICR	Information Collection Rule
MBAA	monobromoacetic acid (also BrAA)
MCAA	monochloroacetic acid (also ClAA)
MCL	maximum contaminant level
MIEX	magnetic ion exchange resin
NDMA	nitrosodimethylamine
NF	nanofiltration
NOM	natural organic matter
MW	molecular weight
MWRA	Massachusetts Water Resources Authority
PAC	powdered activated carbon
RM	rapid mix
RO	reverse osmosis
SDS	simulated distribution system

SUVA	specific UV absorbance
TBAA	tribromoacetic acid (also Br ₃ AA)
TCAA	trichloroacetic acid (also Cl ₃ AA)
TCAN	trichloroacetoneitrile
TCP	trichloropropanone
THMFP	trihalomethane formation potential
THM4	four trihalomethanes (chloroform, BDCM, DBCM, and bromoform)
THMs	trihalomethanes
TPHA	transphilic acids
TriHAA	trihaloacetic acids (TCAA + bromodichloroacetic acid + dibromochloroacetic acid + tribromoacetic acid)
TOBr	total organic bromine
TOC	total organic carbon
TOCl	total organic chlorine
TOI	total organic iodine
TOX	total organic halogen
UFC	uniform formation conditions
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
UV ₂₅₄	ultraviolet absorbance at 254 nm

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