



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

This chapter provides theoretical background and literature review on dissolved organic carbon, disinfection by-products and their precursors, the formation of haloacetic acids, and the predictive model for the formation of HAAs.

2.1 Dissolved organic carbon

Natural organic matter (NOM) is a complex mixture of organic compounds presented in all potable water sources. NOM is typically dominated by humic substances generated by biological activities both in watershed surrounding a water source (allochthonous NOM) and within the water source itself (autochthonous NOM) (Croue *et al.*, 2000). In addition to humic substances, protein, polysaccharides, and other classes of biopolymers also contribute to NOM. Although the name implies that NOM is of natural origin, as a practical matter, NOM includes many organic compounds contributed by human activities. NOM is often expressed in terms of total organic carbon (TOC) and one of the well-known subdivisions of TOC is dissolved organic carbon (DOC) which excludes organic particles with diameter greater than 0.45 μm .

DOC in natural water can be derived from various different sources; for instance, agricultural drainage, surface runoff (including urban storm water runoff), wastewater treatment discharge, etc. DOC can undergo several reactions during the water treatment as the by-products can significantly affected the welfare of human being and environment. To understand these processes better and to control their effects on drinking water quality, it is necessary to understand the chemistry of DOC. However, due to the diversity of chemical compounds in DOC and its reactivities, several approaches are needed to characterize DOC. Conventionally, DOC characterization can be achieved through the isolation technique based on the polarity of the substances, where the resulting organic fractions are: (i) humic

(hydrophobic), and (ii) non-humic (hydrophilic). These two fractions are described in detail as follow.

Humic substance (Hydrophobic constituents)

Humic substances are the organic portion of soil that remains after prolonged microbial decomposition, and that is formed by the decay of animal, leaves, wood, and other vegetative matters. They can impart a yellowish-brown to brownish-black color to water. Most dissolved humic substances have molecular weight of a few hundred to thousand atomic mass units (McIntyre *et al.*, 1997). Humic molecules mostly exhibit hydrophobic property and they are comprised of several components such as aromatic, carbonyl, carboxyl, methoxyl, and aliphatic units (Stevenson, 1982, Perdue, 1985, and Christman *et al.*, 1989). Common functional groups for this organic category are phenolic and carboxylic which provide most of the protonation and metal complexation sites. In addition, the terms hydrophobic (humic) substances are frequently used in reference to an aggregate of humic and fulvic acids, where humic acid is soluble in dilute alkaline media but is precipitated upon acidification whilst fulvic acid remains in solution at pH < 1-2 (Steelink, 1977). In general, fulvic acid is less hydrophilic and contains lower molecular weight compounds than humic acid (Rebhun *et al.*, 1996). Fulvic acids have molecular weights in the range of 200 – 1000 g/mol and therefore exhibit a much higher charge density than their humic acids which have molecular weights in the 200,000 g/mol range (Kavanaugh, 1978). Thurman and Malcolm (1981) stated that hydrophobic species are polar, straw-colored, organic acids that are derived from soil humus, and terrestrial aquatic plants, which typically dominate the DOC on a mass basis, contributing from approx. 50 % to more than 90% of natural water. A more elaborate fractionation of hydrophobic organic results in three organic fractions, i.e. hydrophobic acid, hydrophobic base, and hydrophobic neutral, as described in this work.

Non-humic substance (Hydrophilic constituents)

Hydrophilic fractions mainly contain carboxylic acids, carbohydrates, amino acids, amino sugars, proteins, and nutrients (Marhaba and Van, 1999). Moreover, hydrophilic fractions were also discovered to have higher COOH, phenolic-OH, and organic -N content compared to the hydrophobic fractions. The presence of phenolic-OH could lead to trihalomethanes (THMs), the most well-known disinfection by-products (DBPs), due in part to the existence of an electron-donating substitute, i.e. -OH group. The -OH activates the ring that favors reaction with chlorine resulting in the formation of THMs and other chlorinated by-products (Rockwell and Larson, 1978). Also, hydrophilic organics can be separated into three fractions, hydrophilic acid, -base, and -neutral.

Apart from DOC, other parameters commonly used to characterize the organic carbon are ultraviolet (UV) absorbance and specific ultraviolet absorbance (SUVA). UV is simply obtained from evaluating the light absorbance spectrum of the unaltered sample and therefore requires much less time and effort per analysis than other techniques. SUVA, on the other hand, is the ratio between UV at 254 nm and the organic content of the same organic sample ($SUVA = UV/TOC$, L/mg-m), and therefore requires also the evaluation of TOC. Only carbons in aromatic form have been shown to unambiguously affect the UV absorbance spectrum of DOC. Therefore, SUVA is often employed to provide a relative index of humic content. Higher SUVA values were reported to indicate higher molecular weight, humic, hydrophobic, and aromatic character (Krasner *et al.*, 1996 and Li *et al.*, 2000). Normally, SUVA values of less than 3 L/mg-m are representatives of a large amount of nonhumic substances, whereas SUVA values in the range of 4-5 L/mg-m represent mainly humic substances (Edzward and Van Benschoten, 1990). It is interesting to note that enhanced coagulation was usually reported to be able to remove the humic fraction of the natural organic matter in water and therefore a water sample with high SUVA level indicates a potential of using the enhanced coagulation as the primary treatment technique. This is reflected in the EPA Disinfectant and Disinfection By-

product (D/DBP) Rule which proposes a SUVA of 2 L/mg-m as a criterion that triggers the use of enhanced coagulation (Marhaba and Kochar, 2000).

Recent characterization techniques include the use of chemical properties of the functional groups within the molecular structure of the organic substance which could be identified through the analysis with Fourier Transform InfraRed technique (FTIR). The fundamental rationale of this method was to find the functional groups associated in the structure of organic matters (Galapate *et al.*, 1999, Wu *et al.*, 2000, Croue *et al.*, 2000, and Galapate *et al.*, 2001). This method, however, involves the complicated sample preparation method prior to the test by the FTIR and this area has still been researched actively (Tanaka *et al.*, 2001, Howe *et al.*, 2002, and Wai Ting Tang and Turner, 2003). One of the latest characterization techniques is to keep track of the fluorescence absorption bands which were illustrated to have consistent fingerprints for each organic compound (Orlov *et al.*, 1985, Marhaba *et al.*, 2000, Marhaba, and Kochar, 2000, and Marhaba *et al.*, 2002). However, a complete database of the fluorescent fingerprints was still in the early stage of the research (based at the time this thesis was written) which limited the application of this technique.

2.2 Disinfection by-products

2.2.1 Disinfection processes

The primary goal of the disinfection process in potable water treatment is the inactivation of microbial pathogens. These pathogens comprise a diverse group of organisms which might cause waterborne diseases. Included in this group are bacteria, viral, and protozoan species. Although other unit processes such as coagulation, clarification, and filtration may dramatically reduce the number of microbial pathogens, the efficiency of the disinfection is often regarded as the most crucial one as this is the final step that prevents the escape of potential pathogens with the finished potable water product.

There are numerous disinfection methods formed in water, depending on the type of disinfectant used. Chlorine was introduced in the early 1900s. It quickly becomes the most widely used among the oxidative disinfectants due to its excellent bactericide, viricide, and cysticide capabilities. Chlorine also presents attractive economical solution with adequate disinfection effectiveness. However, there is a drawback in using chlorine as disinfectant because the addition of chlorine to water in the presence of naturally or anthropogenic occurring organic matters can result in the formation of numerous disinfection by-products, which have the potential of causing adverse health effects.

2.2.2 Disinfection by-products: Health issues

Several disinfection by-products (DBPs) were reported to have potential adverse health effects by the U,S, National Academy of Sciences (National Academy of Sciences, 1987). The U,S, Federal-Provincial Subcommittee on Drinking Water established the current guideline for DBPs in 1993. The guideline was based on the risk of cancer reported in animal studies of chloroform where trihalomethanes (THMs) are most often presented in greatest concentration in drinking water whereas haloacetic acids (HAAs) usually the second. Since then, new epidemiological (human) studies had been published which reported associations between DBPs and bladder and colon cancer, and adverse pregnancy outcomes including miscarriage, birth defects and low birth weight. Table 2-1 summarizes MCLs and the health effects of DBPs in accordance with classification scheme.

2.2.3 Formation of disinfection by-products

The formation of disinfection by-products (DBPs) due to reactional oxidants with DOC has been under investigation since the discovery of DBPs in chlorinated drinking water by Rook (1974). Since then, several studies have led to a better understanding of the identity of the by-products, their precursors, the kinetics, and yields of DBP forming reactions (Kavanaugh *et al.*, 1980, Christman *et al.*, 1989, Miller and Uden, 1983, and Steven, 1982). DOC contains precursors for DBP

formation during water treatment disinfection operations (Marhaba and Washington, 1998), such as chlorination or ozonation processes. The amount of chlorine that reacts with various substances or impurities in the water, e.g. organic materials, sulfides, ferrous iron, and nitrites is known as a chlorine demand. In other words, chlorine demand is a measure of the amount of chlorine that will combine with impurities and is therefore available to act as a disinfectant. The chlorination of water containing DOC produces the major disinfection by-products (DBPs), e.g. trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), halo ketones (HKs), chloral hydrate (CH), and chloropicrin (CP). The general reaction of DOC with chlorine is as follows (Marhaba and Washington, 1998):



The concentrations of DBPs in the finished water are correlated to the DOC concentrations in the raw water as DOC is often a major component that reacts with chlorine to form DBPs. The DBPs precursors are generated via several sources. For instance, water treatment chemicals were shown to be a source of organic matter that led to the formation of DBPs (Feige *et al.*, 1980). The release of industrial chemicals and minerals is also largely an unknown contributor to DBP formation. In this case, the type of DBPs is highly site-specific. Furthermore, foodstuffs, occasionally, can also potentially be DBP precursors (Raymer *et al.*, 1999).

The formation of DBPs depends on several environmental factors. In particular, the presence of other ions such as bromide can have a profound impact on the nature and distribution of the DBPs formed during water treatment. Temperature, pH, and oxidant dosing rates can also affect DBP formation. Literature regarding the effects of environmental factors on the formation of DBPs, especially HAAs, will be provided later in this chapter.

DBPs control can commonly be achieved using three strategies: (i) DBP precursor removal accomplished by precipitation, adsorption, and membrane processes, (ii) disinfectant modification, e.g. replacing free chlorine with other

alternative disinfectants such as ozone, chlorine dioxide, chloramines, or potassium permanganate (Marhaba and Washington, 1998), and (iii) DBP removal which is not really a control technique but an abatement technique rather, which can generally be accomplished by either GAC adsorption or by air stripping (Stanley *et al.*, 2000). The detail on control strategies, although is important for the actual treatment facilities, is omitted here for brevity purposes as they are not the main purpose of the work.

2.3 Haloacetic acids

THMs and HAAs were found to be the most common DBPs in finished chlorinated drinking water (Krasner *et al.*, 1983). Early studies have mainly focused on formation of THMs. Although HAAs are also listed as other main potentially hazardous substances DBPs, very little work has been done on them. This is perhaps due to the complicated methods of estimation of HAAs which requires a long and tedious experimental procedure.

HAAs are acetic acids that include one, two or three atoms of fluorine, chlorine or bromine. HAAs are capable of dissociating in water. They are more than 99% ionized (de-protonated) to the haloacetic anions under drinking water conditions. However, they are regulated and usually reported in terms of the parent acids rather than the carboxylate anions. HAAs have long been known as pesticides with varying degrees of persistence. They also exhibit herbicidal properties and even one of the early herbicides, trichloroacetic acid, is a haloacetic acid. Possible sources of HAAs in the environment include municipal water and industrial effluents. Some of these acids are believed to be breakdown products of hydrochlorofluorocarbon compounds (HCFCs), promoted as a replacement for ozone-depleting CFCs.

HAAs are toxic species of increasing environmental interest due to their formation during drinking water chlorination, as well as through microbial processes. HAAs are naturally detected in atmospheric depositions throughout the world but at a concentration range that is unlikely to present a problem to aquatic organisms and terrestrial plants. However, at high concentration, HAAs are

considered potentially harmful to human health and have diverse toxicological effects in laboratory animals, including carcinogenic, reproductive and developmental effects. Concerns regarding the carcinogenic effects of HAAs led the US Environmental Protection Agency (USEPA, 1994) to promulgate the state II DBP rule that limits the release of five HAAs species at a maximum contaminant level of 60 µg/L in finished drinking water. Various types of HAAs are listed in Table 2-2. The five regulated HAA species in the United States are monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acids (TCAA) (see Figure 2-1). In Thailand and in the European community, HAAs are currently not regulated.

Statistically, HAAs accounted for about 13% of the halogenated organic matter after disinfection (Weinberg, 1999). However, levels of HAAs were found to vary and were generally highest in treated water from sources with high organic matter content, such as rivers and lakes. Lower levels of HAAs were usually found when the source water is groundwater (Dalvi *et al.*, 2000). HAAs levels can vary within a single water supply depending on the season, water temperatures, amount of natural organic matter in water, pH, amount of chlorine added, point of chlorination, time in distribution system, and other factors such as treatment processes. Clark and Boutin (2001) summarized some of the factors that influenced both the formation of HAAs and the demand for chlorine as follows:

- (i) disinfectant dose: the formation of HAAs increased with chlorine concentration,
- (ii) reaction time: a longer reaction time generally led to greater HAAs formation,
- (iii) pH: HAAs were found to decrease when pH increased, and
- (iv) temperature: an increase in temperature increased the rate of HAAs formation.

Contradictory result was reported by Chen and Weisel (1998) who observed a decrease in HAAs with an increase in chlorine contact time. In addition, algae in the source water, especially under bloom conditions, also contributed

significantly to the formation of HAAs (Hanson and Solomon, 2004). Literature reviews of HAAs formation and its precursors in various sources are briefly summarized in Table 2-3.

2.4 Mathematical model for the estimation of disinfection by-products

A number of past reports have been done on the evaluation of the nature of DBPs and the conditions that governed their formation in source water. Often, an empirical mathematical model was proposed as a tool to the estimation of the amount of disinfection by-products under various environmental conditions. Although the application of the model is only limited to specific water sources, it helps greatly in reducing the time required for the time-consuming fractionation and formation potential tests which needs a minimum of two weeks.

In the earliest scenario, a number of investigators focused on the models for chlorine decay in drinking water. For instance, Hao *et al.* (1991) demonstrated the kinetic reaction of chlorine with organic and inorganic matters, Zhang *et al.* (1992) the chlorine modeling in sand-filtered water, and Lyn and Taylor (1993) the description of the entire disinfectant reaction for one groundwater treated in a particular plant. The summary of literature regarding this type of model is given in Table 2-4. Despite the availability of a great number of works, the identification of the reactive sites on organic molecules, the reaction pathways, and a number of the end products were still only poorly understood.

More recent works focused on the formation of disinfection by-products, mostly THMs and THM formation potential (or THMFP). Several forms of empirical mathematical models were proposed for the estimation of such quantities and these are briefly summarized in Table 2.5. In most cases, the macroscopic parameters such as DOC, UV-254, SUVA, pH, chlorine demand, etc. were employed as surrogates for the calculation of the quantity of by-products formed during the disinfection processes. The effect of each surrogate on the formation of disinfection by-products depended notably on several environmental conditions and even the same

surrogate could lead to a very different result when presented in different water sources. DOC or TOC were among the most common surrogates as they represented the quantity of the main reactants (organic compounds) that underwent the disinfection reaction. However, some researchers claimed that UV was a better surrogate than DOC as it specifically referred to the quantity of aromatic organic species which were believed to be the major contributor for disinfection by-products (Krasner and Amy, 1995).

From the result obtained by Marhaba and Kochar (2000), it was observed that TOC and UV-254 showed strong and similar correlations to the total trihalomethane formation potential (TTHMFP) and total haloacetonitrile formation potential (TTHNFP) of water sources. Moreover, researchers have shown good correlations between the HAAFP and TOC of natural drinking water (Singer, 1981, and Edzwald *et al.*, 1985). Others have also shown UV-254 absorbance to be a better surrogate than TOC for DBPs formation potential in chlorinated drinking water (Najm *et al.*, 1994). Other wavelengths of UV absorbance were also reported to the correlation with DBPs. However, some prior publication (Harrington *et al.*, 1992, Rathbun 1996, and Gracia Villanova *et al.*, 1997) reported that the relationships between the formation of DBPs and chlorine dose, DOC concentration, hydrophobicity were non-linear.

The formation potential (FP) test is an evaluation of the maximum quantity of DBPs that could possibly be formed during the disinfection processes. This is achieved by using a relatively large dose of chlorine (in the chlorination, or other disinfectants for other disinfection processes) and providing an extremely long reaction time (one week). The test also requires that the final chlorine concentration in the sample must be within the range found in potable water to simulate the actual system that might take place if the water remains in the distribution system for a long time period.

In terms of the model development, a much less number of works have been done on the HAA formation. In all cases, UV and SUVA were employed as

surrogate of the HAAFP. Interestingly, the relationships between UV or SUVA and HAAs and HAAFP were found to be well represented by a straight line. For instance, Li *et al.* (1998) and Korshin *et al.* (2002) reported that the relationship between UV_{272} and three species of HAAs (MCAA, DCAA, and TCAA) concentrations was reasonable fit by a straight line. Croue *et al.* (2000) presented data indicating a reasonable linear correlation between SUVA for both HAAFP and THMFP. Similar trend was reported by Kitis *et al.* (2002) who stated that strong trend ($R^2 = 0.92$) were observed between SUVA and HAAs. However, there was also some contradictory result for which a non-linear was found to be a better correlation between HAA and SUVA (Weisheer *et al.*, 2003).

Table 2-1 United State primary drinking water regulations with maximum contaminant levels (MCLs) and maximum contaminant level goals (MCLGs) for DBPs

Compound	MCL (mg/L)	Cancer classification	Potential health Effects	Sources of water contamination
Bromodichloromethane	See TTHMs	B*	Cancer, liver, kidney, Reproductive effects	Drinking water chlorination and chloramination by-product
Bromoform	See TTHMs	B*	Cancer, nervous system, liver, kidney effects	Drinking water ozonation, chloramination, and chlorination by-product
Chloroform	See TTHMs	B*	Cancer, liver, kidney, reproductive effects	Drinking water chlorination and chloramination by-product
Dibromochloromethane	See TTHMs	C*	Nervous system, liver, kidney, reproductive effects	Drinking water chlorination and chloramination by-product
Dichloroacetic acid	See HAA ₅	B*	Cancer and other effects	Drinking water chlorination and chloramination by-product
Haloacetic acids ^b (HAA ₅)	0.060 ^a	-	Cancer and other effects	Drinking water chlorination and chloramination by-product
Trichloroacetic acid	See HAA ₅	C*	Possibility cancer and reproductive effects	Drinking water chlorination and chloramination by-product
Total trihalomethanes ^c	0.08 ^a	-	Cancer and other effects	Drinking water chlorination and chloramination by-product

Source: 63 Federal Register 69390

^a Finalized on December 16, 1998 (63 *federal Register* 69390) as established in 40 CFR 141.64.

^b HAA₅ is the sum of the concentrations of mono-, di-, and trichloroacetic acids and mono-, dibromoacetic acids expressed in mg/L.

^c Total trihalomethanes are the sum of the concentrations of bromodichloromethane, dibromochloromethane, bromoform, and chloroform expressed in mg/L.

* B = Probable humic carcinogen (Sufficient evidence from animal studies)

C = Possible humic carcinogen (Limited evidence from animal studies and inadequate or no data in humans)

Table 2-2 Haloacetic acids found in potable water

HAA	Formula
Monochloroacetic acid	ClCH ₂ CO ₂ H
Dichloroacetic acid	Cl ₂ CHCO ₂ H
Trichloroacetic acids	Cl ₃ CCO ₂ H
Monobromoacetic acid	BrCH ₂ CO ₂ H
Dibromoacetic acid	Br ₂ CHCO ₂ H
Tribromoacetic acid	Br ₃ CCO ₂ H
Monobromochloroacetic acid	BrClCHCO ₂ H
Dibromochloroacetic acid	BrCl ₂ CCO ₂ H
Tribromochloroacetic acid	Br ₂ ClCCO ₂ H

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
Hill Creek, Utah	7.4	Hydrophobic Neutral = 18 Hydrophobic Base = 1 Hydrophobic Acid = 30 Hydrophilic Base = 5 Hydrophilic Acid = 22 Hydrophilic Neutral = 24		Leenheer, 1979
Lake Bret, France	2.81	Humic = 46 (fulvic:humic = 43:3) Other Hydrophobic = 5 Hydrophilic = 49		Krasner <i>et al.</i> , 1996
WTP in Canada	1.1		Approx. 23 µg/mg	William <i>et al.</i> , 1997
The canal road WTP		Hydrophobic Acid = 0.42 Hydrophobic Base = 0.21 Hydrophobic Neutral = 0.63 Hydrophobic Acid = 1.67 Hydrophilic Base = 0.13 Hydrophilic Neutral = 0.72	22 µg/mg 22.5 µg/mg 21.5 µg/mg 8 µg/mg 11 µg/mg 5 µg/mg	Marhaba and Van, 1999

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
Zegrzynskie lake	7-17		Approx. 0.6-7.5 µg/mg	Dojlido <i>et al.</i> , 1999
South Platte River, Colorado	7.5	Hydrophobic Neutral = 31.6 Hydrophobic Base = 1.2 Hydrophobic Acid = 18.0 Hydrophilic Base = 25.4 Hydrophilic Acid = 18.1 Hydrophilic Neutral = 5.6		Marhaba <i>et al.</i> , 2000
Water source, NJ	4.0	Hydrophobic Neutral = 18 Hydrophobic Base = 6 Hydrophobic Acid = 12 Hydrophilic Base = 4 Hydrophilic Acid = 48 Hydrophilic Neutral = 21		Marhaba <i>et al.</i> , 2000
Passaic Valley WTP, NJ	4.6	Hydrophobic Neutral = 10 Hydrophobic Base = 7 Hydrophobic Acid = 12	Hydrophobic Neutral = 56 Hydrophobic Base = 5 Hydrophobic Acid = 26	Marhaba and Van, 2000

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
Canal Road WTP, NJ	4.0	Hydrophilic Base = 5	Hydrophilic Base = 6	Marhaba and Pipada, 2000
		Hydrophilic Acid = 53	Hydrophilic Acid = 4	
		Hydrophilic Neutral = 13	Hydrophilic Neutral = 3	
		Hydrophobic Neutral = 17		
		Hydrophobic Base = 6		
		Hydrophobic Acid = 11		
		Hydrophilic Base = 4		
Raritan-Millstone WTP, NJ	4.0	Hydrophilic Acid = 46		Marhaba <i>et al.</i> , 2000
		Hydrophilic Neutral = 20		
		Hydrophobic Neutral = 16		
		Hydrophobic Base = 4		
		Hydrophobic Acid = 9		
		Hydrophilic Base = 5		
		Hydrophilic Acid = 42		
		Hydrophilic Neutral = 7		

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
Wakarusa river	5.4		Approx. 2.8 µg/mg	Pomes <i>et al.</i> , 2000
Clinton lake	4.1		Approx. 2.4 µg/mg	
Al-Jubail Plant	3.2		Approx. 30 µg/mg	Dalvi <i>et al.</i> , 2000
Suwannee River, Georgia	4.6	Hydrophobic acid = 58.79 Hydrophobic neutral = 0.94 Hydrophobic base = - Hydrophilic acid = 5.04 Hydrophilic neutral = 0.17 Hydrophilic base = 0.04 Transphilic = 12.20 Ultra-hydrophilic = 2.46 Loss = 20.17	Hydrophobic acid = 84 µg/mg Hydrophobic neutral = 75 µg/mg Hydrophobic base = - Hydrophilic acid = 109 µg/mg Hydrophilic neutral = - Hydrophilic base = 70 µg/mg Transphilic = 146 µg/mg Ultra-hydrophilic = 159 µg/mg	Croue <i>et al.</i> , 2000
South Platte River, Colorado	2.6	Hydrophobic acid = 31.08 Hydrophobic neutral = 2.93 Hydrophobic base = - Hydrophilic acid = 5.10	Hydrophobic acid = 42 µg/mg Hydrophobic neutral = 28 µg/mg Hydrophobic base = -	Croue <i>et al.</i> , 2000

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
		Hydrophilic neutral = 0.93 Hydrophilic base = 0.25 Transphilic = 26.02 Ultra-hydrophilic = 1.11 Loss = 32.58	Hydrophilic acid = 40 µg/mg Hydrophilic neutral = 34 µg/mg Hydrophilic base = - Transphilic = 67 µg/mg Ultra-hydrophilic = - Raw water = 44 µg/mg	
Colorado River, Colorado	2.55	Hydrophobic = 41.7 Transphilic = 15.3 Hydrophilic Base = 1 Hydrophilic Acid + Neutral = 13.2 Colloid = 1.8 Loss = 28		Leenheer <i>et al.</i> , 2001
Seine River, France	4.69	Hydrophobic = 22.6 Hydrophilic Base = 1.7 Hydrophilic Acid + Neutral =		Leenheer <i>et al.</i> , 2001

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
		12.6		
		Colloid = 17.1		
		Loss = 45		
Sacramento Delta, California	2.52	Hydrophobic = 48.4		Leenheer <i>et al.</i> , 2001
		Transphilic = 7.5		
		Hydrophilic Base = 1		
		Hydrophilic Acid + Neutral = 6.4		
		Colloid = 24		
		Loss = 12.7		
Pan-Hsin water, Taiwan	Approx. 2.00	Hydrophobic = 43	Hydrophobic = approx. 233	Chang <i>et al.</i> , 2001
		Hydrophilic acid = 41	μg/mg	
		Non-acid hydrophilics = 16	Hydrophilic acid = approx. 79	
			μg/mg	
			Non-acid hydrophilics =	
			approx. 375 μg/mg	
Pan-Hsin river		HPOA = 0.2	HPOA = 150	Chang <i>et al.</i> , 2001

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
Myrtle Beach, US	20.2	HPOB = 0.07	HPOB = 20	Kitis <i>et al.</i> , 2002
		HPON = 0.18	HPON = 40	
		Hydrophilic = 0.02	Hydrophilic = 120	
		Hydrophobic = 66	Hydrophobic = approx. 95	
		Hydrophilic = 34	$\mu\text{g}/\text{mg}$	
Tomhannock WTP, US	3.3	Hydrophobic = 36	Hydrophobic = approx. 62	Kitis <i>et al.</i> , 2002
		Hydrophilic = 64	$\mu\text{g}/\text{mg}$	
			Hydrophilic = approx. 55	
Han river			6.5 $\mu\text{g}/\text{mg}$	} Kim <i>et al.</i> , 2002
Daechung lake			7.7 $\mu\text{g}/\text{mg}$	
Youngsan river			16.3 $\mu\text{g}/\text{mg}$	
Nackdong river			4.7 $\mu\text{g}/\text{mg}$	
South Fork Tolt river, Seattle			0.36 $\mu\text{mol}/\text{mgC}$	

Table 2-3 HAAs formation and its precursors in various sources

Water source	DOC of raw water (mg/L)	Fraction (%)	HAAFP	References
Lake Manatee reservoir, Bradenton			0.22 $\mu\text{mol/mgC}$	
Poquonnock reservoir, Groton			0.29 $\mu\text{mol/mgC}$	Liang <i>et al.</i> , 2003
Mississippi, E. St. Louis			0.17 $\mu\text{mol/mgC}$	
White river, Indianapolis			0.21 $\mu\text{mol/mgC}$	
Sainte Foy WTP	2.4		Approx. 4 $\mu\text{g/mg}$	} Serodes <i>et al.</i> , 2003
Charlesbourg WTP	1.6		Approx. 68 $\mu\text{g/mg}$	
Quebec WTP	1.7		Approx. 35 $\mu\text{g/mg}$	
St. Lawrence river			Approx. 20 $\mu\text{g/mg}$	Rodriguez <i>et al.</i> , 2004

Table 2-4 Modeling the decay of chlorine residual

Water source	Equation	Input	Output/ Result	References
Synthesis water	$D_t = D_1 t^n$	$D_1 =$ chlorine consumed after 1 hour $N =$ a constant characteristic of a given water	D_t : chlorine consumed at time t (h)	Feben and Taras, 1951
Synthesis water			First-order decay model yielded the best results.	Haas and Karra, 1984
Synthesis water	$-dCl/dt = k_1[Cl][F_1] + k_2[Cl][F_2]$	$[Cl] =$ free residual chlorine $k_1 =$ rate constant for the fast reaction $k_2 =$ rate constant for the slow reaction $[F_1] =$ concentration of relative sites on the fulvic acids		Qualls and Johnson, 1983
Choisy-le-Roi plant	$-\frac{dx}{dt} = k(a-x)^\alpha (b - \frac{x}{n})^\beta$	$k =$ rate constant $a =$ total residual chlorine at 4 hours $b =$ maximum potential chlorine demand $n =$ stoichiometry $\beta =$ partial orders of reaction	$x =$ chlorine consumption after 4 hours	Jedas-Hecart <i>et al.</i> , 1992

Table 2-5 Models for predicting DBPs in various sources

Source water	DBPs	Equation	Additional data	Reference
	THM	$\frac{dTHM}{dt} = -\frac{dC}{dt} = k_2(Cl_2)(C)m$	C = concentration of organic precursor M = order of reaction with respect to the precursor concentration	Trusell and Umphres, 1978
Seawater distillation process	THM	$\text{Log}(THM) = A*\text{Log}(Cl_2)+B*\text{Log}(TOC)+C$	A, B and C = estimated parameters which depend on seawater chlorine dose.	Tawabini <i>et al.</i> , 1987
Mississippi River	THM	$THM = 14.6(pH-3.8)^{1.01} (Cl)^{0.206}(UV_{254})^{0.849}(t)^{0.306}$		Rathbun, 1996
Finished water	THM	$TTHM = 13.54\ln[chla]-14.47pH+230.25[Br] -139.62[Br]^2-25.28S+110.55Sp - 6.59(T*Sp)+1.48(T*[Cl])$	82 ± 20% of the predicted values	Golfinopoulos <i>et al.</i> , 1998
	THM	$THM = e^{1.49} Cl^{0.48} TOC^{0.18} pH^{0.96} Temp^{0.28}$	R ² = 0.78	Clark and Sivaganesan, 1998
	TTHM	$TTHM = T(C_A - [C_A(1-R) / 1-Re^{-ut}])$	T = dimensionless parameter C _A = initial chlorine residual (mg/L)	Clark, 1998

Table 2-5 Models for predicting DBPs in various sources

Source water	DBPs	Equation	Additional data	Reference
			R = dimensionless parameter from chlorine decay u = reaction rate (time ⁻¹)	
Various treated industrial wastewaters	THM	$\text{Log}[\text{THMFP}] = 2.17 + 0.20 \cdot \text{UV}260(\text{nonhumic}) + 0.30 \cdot \text{organic-N}(\text{nonhumic}) + 0.29 \cdot \text{phenolic-OH}(\text{nonhumic}) + 0.59 \cdot \text{log}[\text{UV}260](\text{humic}) + -0.36 \cdot \text{Log}[\text{Org.-N}] (\text{humic})$	UV260 is recommended for specific chemical functional groups COOH and phenolic-OH,	Galapate <i>et al.</i> , 1999
Suwannee River	TTHM	$\text{TTHM} = 135.5 \text{UV}_{\text{humic acid}} + 16.9$ $\text{TTHM} = 3.7 \text{TOC}_{\text{humic acid}} + 18.5$ $\text{TTHM} = 101 \text{UV}_{\text{fulvic acid}} + 19.5$ $\text{TTHM} = 2.5 \text{TOC}_{\text{fulvic acid}} + 19.5$	$R^2_{\text{UV}} = 0.86$ $R^2_{\text{TOC}} = 0.87$ $R^2_{\text{UV}} = 0.88$ $R^2_{\text{TOC}} = 0.87$	Marhaba and Kochar, 2000
	THAN	$\text{THAN} = 15 \text{UV}_{\text{humic acid}} + 3.2$ $\text{THAN} = 0.4 \text{TOC}_{\text{humic acid}} + 3.4$ $\text{C} = 17.6 \text{UV}_{\text{fulvic acid}} + 3$	$R^2_{\text{UV}} = 0.98$ $R^2_{\text{TOC}} = 0.97$ $R^2_{\text{UV}} = 0.82$	

Table 2-5 Models for predicting DBPs in various sources

Source water	DBPs	Equation	Additional data	Reference
		$C = 0.4\text{TOC}_{\text{fulvic acid}} + 3$	$R^2_{\text{TOC}} = 0.78$	
	THM	$[\text{THM}] = k_1(\text{DOC})^a(A_{254})^b(\text{HOCl dose})^c$ $(t)^d(T)^e(\text{pH}-k_2)^f((\text{Br})+k_3)^g$	A_{254} = light absorbance at 253 nm t = time T = temperature	Li <i>et al.</i> , 2000
Water distribution systems	THM	$[\text{TTHM}]_{(t+\Delta t)} = [\text{TTHM}]_t + F*(\text{Cl}_{(t+\Delta t)} - \text{Cl}_t)$	F is a chlorine demand proportionality coefficient	Elshorbagy <i>et al.</i> , 2000
Drinking water	THM	$\text{TTHM} = -0.26[\text{chla}] + 1.57\text{pH} + 28.74[\text{Br}]$ $- 66.72[\text{Br}]^2 - 43.63\text{S} + 1.13\text{Sp}$ $+ 2.62\text{T}*\text{S} - 0.72\text{T}*\text{[Cl]}$		Golfinopoulos <i>et al.</i> , 2002
Water treatment plant	THM	$\text{THM} = a(\text{TOC})^b(\text{pH})^d(\text{D})^e$ $\text{THM} = a + b(\text{TOC}) + c(t) + d(\text{pH}) + e(\text{D})$	t = contact time, D = chlorine dose, a, b, c, d, e = the estimated values of statistical coefficients	Abdullah <i>et al.</i> , 2003
Tsinkias river	THM	$\text{Log THM} = 0.33\text{pH} - 0.02\text{pH}^2 + 0.12t$ $- 0.004t^2$	t = contact time The percentage of observed values within 20% of the values ranged from 84% to 88%	Nikolaou <i>et al.</i> , 2004
Mylopotamos river		$\text{Log THM} = -0.44\text{pH} + 7.53\text{logpH} - 0.01\text{time}$ $\times \text{Cl dose} + 1.59\text{logCl dose}$		

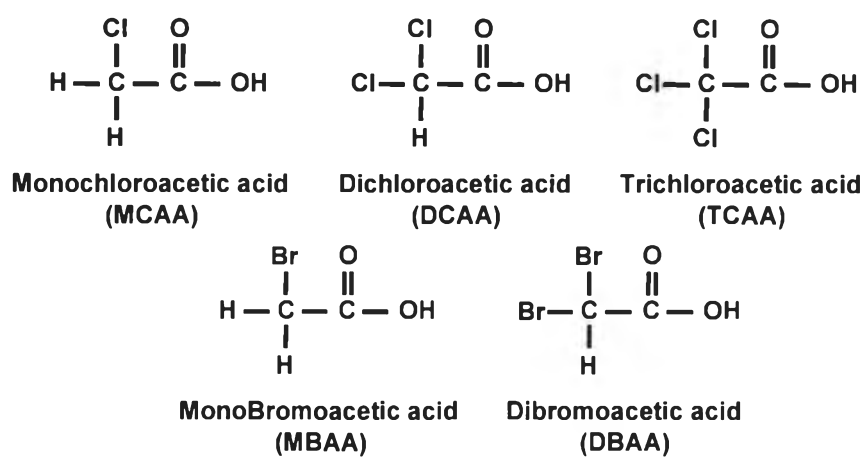


Figure 2-1 Five species of HAAs