Impact of Bromide Ion Concentration, Time, Dissolved Organic Carbon and Molecular Weight Cutoff on Haloacetonitrile, Haloketone, Chloropicrin and Trihalomethane Formation Potentials

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IMPACT OF BROMIDE ION CONCENTRATION, TIME, DISSOLVED ORGANIC CARBON AND MOLECULAR WEIGHT CUTOFF ON HALOACETONITRILE, HALOKETONE, CHLOROPICRIN AND TRIHALOMETHANE FORMATION POTENTIALS

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(ABSTRACT)

This research investigated the formation potential (FP) for haloacetonitriles (HANs), haloketones (HKs), chloropicrin (CP) and trihalomethanes (THMs) under conditions of constant DOC, constant Cl:DOC ratio, variable [Br^-] and variable apparent molecular weight (AMW) for coagulated water from a full-scale water treatment plant. Coagulated, high humic water (4.5 mg DOC/L) was fractionated into <1K, <10K, and <30K MWCO fractions. The DOC of the fractions was adjusted to the same value (e.g., ~ 2 mg/L). Fractions were chlorinated at 3:1 Cl_2:TOC ratio under varying [Br^-]. Observed, non-THM species occurred at low concentrations (<0.3-9.0 ug/L). As expected THMFP speciation was strongly affected by Br^-:Cl ratio; this research demonstrated similar effects on specific HANs and HKs. Increasing quantities of brominated HANs and HKs were observed with increasing [Br^-]. DCANFP remained relatively constant while BCANFP and DBANFP increased with increasing [Br^-]. Increases in brominated species resulted in a larger relative change in THANFP than TTHMFP, suggesting that more HAN precursor material reacted when Br^- was present. Elevating Br^-:Cl to 0.03 resulting in HANFPs comparable to $CHBr_3$FP. Change in HAN and HK species with respect to molecular weight cutoff (MWCO) and coagulated-raw water comparisons suggest that HANFP results from reaction with small, reactive, nitrogen containing compounds (<1K AMW) and larger (<30,000 MWCO) proteinaceous matter.

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Chapter 1. Introduction

Throughout the world, the production of drinking water frequently entails the use of chlorination to insure adequate disinfection. Chemical disinfection has been practiced in the U.S. since 1908; installations at Bubbly Creek Filter Plant in Chicago, Il. and Jersey City Water Supply Company, Jersey City, NJ, were some of the first locations to use chlorine. Introducing chlorine into water at levels adequate to insure water quality also results in the formation of chemicals known as disinfection byproducts (DBPs). The group "disinfection byproducts" includes a diversity of organic compounds, many of which have not been adequately described. The common attributes defining DBPs are related to chlorination:

1. Halogenation, the presence of one or more atoms of either chlorine, bromine, iodine, or fluorine.
2. A base structure of organic origin, either cyclical or chain structure.
3. Believed to represent a threat to human health due to toxic or carcinogenic properties.

Several categories of halogenated DBPs have been enumerated including: trihalomethanes (THMs), haloacetic acids (HAAs), haloketones (HKs), and haloacetonitriles (HANs). There are potential health effects associated with ingestion of DBPs, and these risks are believed to be different for different classes of DBPs.

Regulatory History

In 1979, health risks associated with halogenated DBPs resulted in the promulgation of a National Primary Drinking Water Standard for total trihalomethanes, under the Safe Drinking Water Act in 1979 (Means and Krasner, 1993). As a result, THMs have been managed in the United States at a level not to exceed a value of 0.10 mg/L. This is a composite standard which includes four compounds: chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$).

In July 1994, the U.S. Environmental Protection Agency (EPA) proposed revising its regulations expanding the number of DBPs subject to regulation and increased compound specificity within the standard. The Disinfectant/Disinfection Byproduct (D/DBP) Rule, as proposed (59 *Federal Register* 38668), emphasized enhanced coagulation as a DBP formation prevention strategy. Stage I, to be promulgated in December 1996, reduces the existing THM MCL to 0.080 mg/L and establishes an MCL of 0.060 mg/L for the sum of five specified HAAs. With Stage II, to be implemented in the year 2000, these MCLs will decrease to 0.040 and 0.030 mg/L for THMs and HAAs respectively, and HANs, HKs and other DBPs will be considered for regulation.

A parallel regulation, known as the Information Collection Rule (*59 Federal Register 6332*), will establish monitoring requirements for HANs and HKs, for the specific purpose of assessing the extent of their formation in U.S. drinking water treatment systems. The absence of such information was one of the factors which shaped the current D/DBP proposal.

Since the mid-20th century, conventional water treatment plant design has consisted of coagulation-flocculation-filtration and disinfection. After raw water is screened and in some instances a treated with a preoxidant (e.g., chlorine, potassium permanganate), then alum, iron salts, and/or organic polymers are added as coagulants in a rapid mix, which is followed by gentle mixing in a flocculator. Lime or sodium hydroxide addition may take place during rapid mix to optimize pH. Floc, consisting partially of DBP precursor material is allowed to settle in sedimentation basins where removal of contaminants occurs as a result of particle surface chemistry and sweep floc formation. Clarified water is filtered through rapid sand filters and chlorine added for disinfection prior to treated water entering the distribution system. Final disinfection is typically accomplished with chlorine but other oxidants are also used.

The draft D/DBP Rule establishes "enhanced coagulation" as best available technology (BAT) for water treatment plants that: (1) are of conventional design with sedimentation basins, (2) utilize a water source that is influenced by surface water, and (3) experience

total organic carbon (TOC) greater than 2 mg/L prior to disinfection. Enhanced coagulation is defined as addition of a coagulant at a dose beyond which addition of 10 mg/L more will remove less than 0.3 mg TOC/L. While pursued as an economical DBP precursor removal method, implementation of enhanced coagulation will increase operational costs due to increased coagulant demand and sludge management costs.

Randtke *et al.* (1994) surveyed 350 drinking water utilities and found that 75 percent of the coagulation facilities employed chlorine for residual disinfection. Table 1.1 summarizes selected DBP management parameters characterized by the study.

Table 1.1. Summary of Water Quality Parameters and Treatment Conditions at 350 Drinking Water Utilities

Parameter	Sample Size	Quartile 0	25	50	75	100
Raw water TOC, mg/L	95	1.0	2.6	4.0	6.0	25.0
Percent Removed TOC, %	85	0	28	41	58	94
Coagulation pH	225	4.8	6.6	7.2	8.0	9.1
Finished pH	243	6.3	7.3	7.6	8.0	9.1
Bromide, mg/L	43	0.00	0.04	0.05	0.10	0.75
Free Cl_2 Residual, mg/L	175	0.2	1.0	1.3	1.7	4.0

Source: Randtke *et al.*, 1994.

The ability of coagulation to remove DBP precursors depends primarily upon the characteristics of the natural organic matter (NOM). NOM with larger apparent molecular weight (AMW) (>30,000 AMW) and a hydrophobic nature is more readily removed compared to small molecular weight (<1,000 AMW), hydrophilic NOM.

Because THMs were recognized as a public health risk in the early 1970s, there is substantially more research in the literature for this category of DBPs. Expansion of the regulations to more organic contaminants has created a need for additional research into the formation potential of DBPs, particularly those DBPs that are proposed to be regulated. Three such classes of DBPs are the HANs, HKs and chloropicrin. HANs include trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), dibromochloroaceto-

nitrile (BCAN), and dibromoacetonitrile (DBAN); two haloketones of interest are dichloropropanone (DCP) and 1,1,1-trichloro-2-propanone (TCP).

Research Objectives

Flocculation-coagulation-filtration is the dominant treatment method in the water treatment industry for suspended solid, colloidal particle, and DBP precursor removal. Therefore, the research undertaken here investigated the DBP formation potential associated with chlorination of coagulated waters.

Five related objectives investigating DBP formation potential were formulated, specifically exploring:

1. Species specific haloacetonitrile, haloketone, trihalomethane and chloropicrin formation potential for a representative water as a function of time.

2. The effect of organic substrate:bromide ion ratio on haloacetonitrile, haloketone, trihalomethane and chloropicrin formation potential.

3. The relationship between NOM nominal size fraction, and haloacetonitrile, haloketone, trihalomethane, and chloropicrin formation potential for raw and coagulated waters under conditions of variable NOM AMW distribution and constant bromide concentration, dissolved organic carbon (DOC) concentration, and chlorine dose.

4. The impact of bromide ion (Br^-) concentration:chlorine dose ratio on haloacetonitrile, haloketone, trihalomethane and chloropicrin formation potentials.

5. The likelihood that DCAN is an intermediate product in the formation potential of other DBPs.

Experimental design focused on ultrafiltration partitioned natural and coagulated waters (<1,000, <10,000, <30,000, and <4,500,000 AMW) obtained at Harwood's Mill Reservoir, where TOC values of 4.9 mg/L are typical. Coagulated water used in the study was subject to the water treatment plant's full scale treatment scheme, prior to pre-

filtration chlorination. DOC and bromide ion concentrations were controlled in the laboratory through fortification, concentration, and dilution. Unless chlorine concentration was varied purposefully in an experimental matrix, an initial ratio of free available chlorine (measured as Cl_2/L) to DOC of 3:1 was maintained.

Chapter 2. Literature Review

Chlorination is the predominant disinfection method used in the drinking water supply industry. Over 64 percent of current water works, which serve more than 46 percent of the drinking water customers in the United States, rely on chlorine as the primary disinfectant in the water treatment process (59 *Federal Register* 145). Chlorine is readily available, inexpensive, effective at low concentrations, and forms a disinfectant residual (Reynolds, 1982.).

An AWWA survey conducted in 1989-1990 to determine the distribution of disinfectants in use, found that chlorination was the dominant disinfectant practice in the U.S.. The survey reflects data from 280 water utilities in the U.S. Figure 2.1 summarizes this survey, while Figure 2.2 compares the practices observed in the 1989-1990 survey to the results of a similar effort made in 1978 by Hoehn.

Background

Within the pH range present in typical, coagulation-flocculation water treatment plant, chlorine reacts with water to form hypochlorous acid (HOCl).

$$Cl_2 + H_2O \Leftrightarrow HOCl + HCl \qquad \text{(Eq. 2.1)}$$

Dissociation of HOCl yields hypochlorite ion (OCl^-).

$$HOCl \Leftrightarrow H^+ + OCl^- \qquad \text{(Eq.2.2)}$$

The relative abundance of these two aqueous forms is pH and temperature dependent; HOCl and OCl^- being equally abundant at pH 7.58 at 20°C (Fair *et al.*, 1948; Johnson and Jensen, 1986). Both HOCl and OCl^- are reactive with organic matter and reduced substances, including Fe^{2+}, Mn^{2+}, and NO_2 (Reynolds, 1982). The reaction of chlorine species with organic matter during the disinfection process results in the formation of disinfection byproducts, some of which are believed to adversely affect human health.

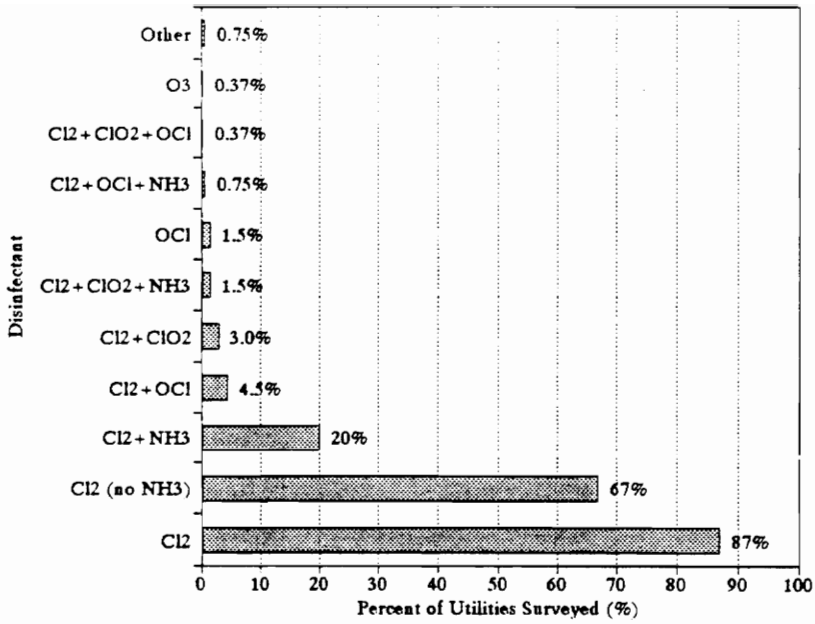

Figure 2.1. Drinking Water Disinfection Practices Observed in Survey of 280 Water Utilities in United States, 1990 (AWWA, 1990)

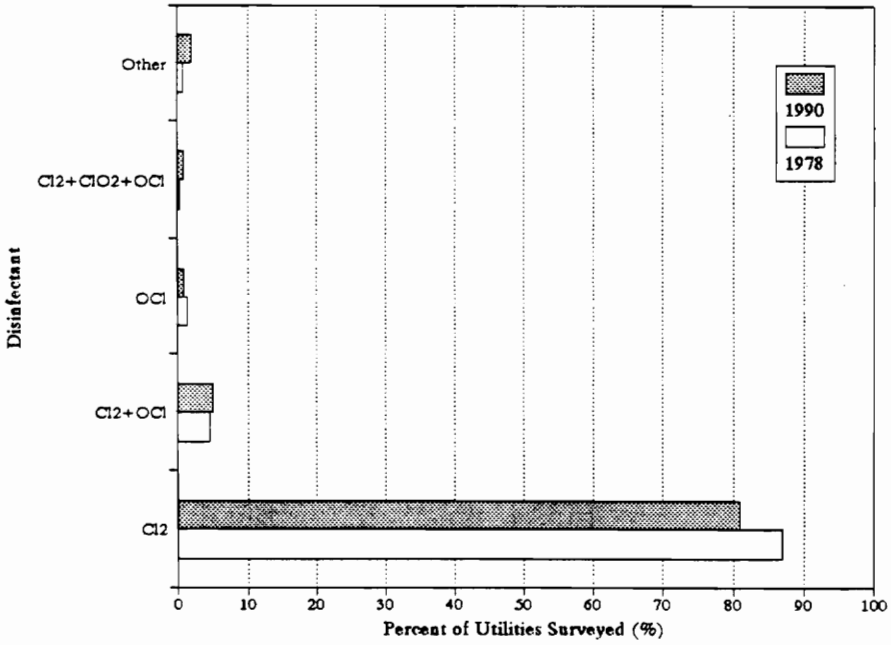

Figure 2.2. Comparison of Drinking Water Disinfection Practices Observed in Industry Surveys, 1978 and 1990 (Hoehn, 1978; AWWA, 1990)

The formation of halogenated disinfection byproducts (DBPs) was reported by Rook in 1974 with the identification of chloroform and other trihalomethanes (THMs) due to chlorination of natural waters. Subsequent research (Rook, 1980; Christman, 1983; Singer and Reckhow, 1990) indicated that THMs represent a small fraction of the halogenated organics created by chlorination. Stevens *et al.* (1989) conducted a survey of 10 water works and identified 196 compounds attributable to chlorination in finished water. Another more comprehensive study of 35 utilities provided a broad based assessment of DBP formation and is summarized in Table 2.1 (Metropolitan Water District of Southern California *et al.*, 1989) .

Table 2.1. Finished Water DBP Type and Concentration Determined from a Seasonal Survey of 35 U.S. Water Utilities

Disinfection Byproduct	Median Concentration (ug/L)
Trihalomethanes	36.50
Haloacetic Acids	17.00
Aldehydes	5.77
Haloacetonitriles	3.28
Chloral Hydrate	2.07
Haloketones	1.18
Cyanogen chloride	0.60
Trichlorophenol	0.40
Chloropicrin	0.12

Source: 59 *Federal Register* 38732
Metropolitan Water District of Southern California *et al.*, 1989

Observed values in Table 2.1 reflect finished water concentrations from four seasonal sampling quarters. Facilities with treatment trains involving ozonation were included in the study; higher levels of some species, like aldehydes, were observed at those facilities. Current regulatory emphasis by the U.S. Environmental Protection Agency (EPA) reflects an increased awareness of DBPs other than THMs.

DBP formation is dependant on a number of parameters including available precursor material, oxidant type, oxidant dose, contact time, pH, and temperature. The following sections summarize previous research particularly relevant to this study and the research objectives outlined in Chapter 1. The last section in Chapter 2 describes the source water utilized in this investigation.

Impact of Organic Carbon Concentration

The abundance of NOM in water subjected to treatment is an important parameter in determining the extent of DBP formation (Singer *et al.*, 1989). Kavanaugh *et al.* (1980, p. 578) noted that a wide variety of reactions occur between chlorine and organic matter including: "double bonds, ionic substitutions, {and} partial oxidation." A review of the American Water Works Association's water industry database indicated that surface water total organic carbon (TOC) levels range from non-detectable to 30 mg/L for surface waters in the continental United States (59 *Federal Register* 38714). This same review found that TOC levels at the 25th, 50th and 75th percentiles were 2.6, 4.0 and 6.0 mg/L respectively. TOC concentrations in natural waters vary with geography; higher TOC values tend to occur in the southeastern United States (Table 2.2).

In a simulated distribution system study Meyer *et al.* (1993) found that a one milligram per liter increase in TOC concentration resulted in a 8.5 ug/L increase in total THM formation potential (TTHMFP) (initial TOC, 6.1 mg/L; initial Cl_2 residual, 1.6 mg/L; 4 day formation potential). Reckhow and Singer (1990) reported a TOC normalized TTHMFP (72 hour, pH 7, 20°, 20 mg Cl_2/L) of 52 ug TTHM/mg carbon. Peterson *et al.* (1993) found average THM yields of 11 ug/mg TOC (168 hour, pH 7, 5 mg Cl_2/L residual) in a survey of water treatment systems in Alberta employing

Table 2.2. Total Organic Carbon Concentration Distribution in Raw Waters

EPA Region		n	Minimum Value (mg/L)	Maximum Value (mg/L)
1.	New England	6	3.00	9.00
2.	Northeast	10	2.10	20.00
3.	Mid-Atlantic	20	nd	25.00
4.	Southeast	11	1.60	30.00
5.	Midwest	14	nd	9.17
6.	Central	10	2.00	10.00
7.	South Central	2	7.00	10.00
8.	West	7	1.00	14.00
9.	Southwest	16	nd	5.90
10.	Northwest	4	1.25	3.30

Source: 59 *Federal Register* 38716, 1994.

conventional treatment (sedimentation-coagulation-filtration and chlorination). Reckhow and Singer (1990) found normalized THM, trichloroacetic acid (TCAA), TCP, and total organic halide (TOX) formation to vary less than 23 percent among eight colored, raw waters. HAN and dichloroacetic acid (DCAA) formation were more variable, particularly DCANFP which had a coefficient of variance of 40 percent. Peters *et al.* (1991) found a positive correlation between available organic carbon and total HAA concentration in finished Dutch waters. While a positive correlation between DBPFP and TOC has been established, only 10-20 percent of dissolved organic matter (DOM) in natural waters has been described with respect to chemical character (Servais *et al.*, 1987) providing limited insight into the precursor material to DBPs.

Characterizing Dissolved Organic Matter

DBP formation is believed to result from the halogenation of NOM particularly "humic substances." Humic substances are precursors of sixty percent of TTHMFP in colored waters (Reckhow, 1994). Both autochthonous sources of organic matter, principally extracellular products released by algae (Davis and Gloor, 1981; Hoehn *et al.*, 1984) and allochtanous humic substances contribute DOC in most natural waters.

Numerous authors (Uden and Miller, 1983, Thurman, 1985; Peterson *et al.*, 1993) identified allochtanous sources of aquatic DOC. Randtke *et al.* (1987) identified impoundments where aquatic weeds were a primary source of THM precursors. Hoehn (1980, *et. al*; 1984) identified specific THM precursor production by algal biomass. There has been significant and unresolved debate as to which component of "humic substances" contribute most to the formation of DBPs.

Humic Substances

Humic substances are a group of physical and biodegradation products within the DOC fraction of natural waters (Thurman, 1985). Humic substances are present at different concentrations as a function of conditions in each individual watershed, but in general humic substances can be anticipated at concentrations of 0.5 - 4 mg C/L in larger rivers (Thurman, 1985). Because humic substances are the product of organic decomposition, they include the major functional groups found in organic structures. carboxyl, hydroxyl, carbonyl, and phenolic hydroxyl (Thurman, 1985; Peshel and Wildt, 1988). Carbohydrates and amino acids are present at trace levels, one to three percent of the humic fraction reflecting humic source material: carbohydrates (50-60 percent), protein (1-3 percent), and lignins/phenolics (10-30 percent) (Choudhry, 1984; Thurman, 1985).

This diverse chemical character is reflected in efforts either to fractionate DOC into its individual components or coagulate natural waters to remove DBP precursors. To facilitate discussion of humic substances, this broad category is typically divided into two components; fulvics and humics. Humic and fulvic substances are functional definitions derived from soil science, and based on acid solubility (Choudhry, 1984). In typical riverine, raw waters the fulvic and humic fractions are 82 and 15 percent of the dissolved NOM present (Thurman, 1985). Fulvic substances tend to be smaller than humic substances and are acid soluble; the fulvic fraction is generally viewed as more reactive than the humic fraction. The fulvic fraction is typically composed of substances less than

2,000 AMW, while humic materials are typically greater than 2,000 AMW (Thurman, 1985; Amy *et al.*, 1992). Others suggest a larger AMW distribution for fulvics and hydrophilic neutral fraction, 1,000-5,000 AMW. There is general consensus that the 1,000-10,000 AMW fraction is a major source of TTHMFP (Reckhow, 1992).

There are differences in the abundance of functional groups between the humic and fulvic substances (Table 2.3).

Table 2.3. Characteristics of Fulvic and Humic Substances

Characteristic	Fulvic	Humic
Acidic Functional Groups	More	Less
Carboxyl Functional Groups	More	Less
Aromatic Structures	More	Less
Polysacchridelike Structures	More	Less

Source: after Blondeau, 1986.

J de Laat (1982) found that aliphatic, acid, aldehyde, and alcohol structures are relatively inert to chlorination. Thurman (1985) estimated the aromatic:aliphatic ratio in the fulvic fraction to be 1:2. He also noted that while total nitrogen content was only one percent by weight, amino acids were the source of 15 to 20 percent of the nitrogen present. Nitrogen and amino acid content in the humic fraction was typically twice that observed in the fulvic fraction (Thurman, 1985).

Color and UV absorption are attributable to the structural composition of the DOC present in the water. Oliver and Thurman (1983) found strong correlations between THMFP and water color. UV absorbance is particularly attributable to the aromatic structures, which are active as precursors for THM formation (J de Laat, 1982; Reckhow *et al.*, 1990; Amy *et al.*, 1992). Observing coagulation effects, Najm *et al.* (1994) noted a stronger correlation between UV absorbance reduction and DBP formation than DOC removal, suggesting a larger role for UV absorbing precursors in DBPFP. Analyzing trends in bench scale and field data tests, Harrington *et al.* (1992) found that an increase in UV 254 nm absorbance was correlated with decreasing THM precursor apparent

molecular weight. A 15 hour reaction study by J de Laat (1982) indicated that the presence of activating groups, -OH and $-NR_2$, enhanced chlorine reactivity with aromatic precursor molecules.

The relative abundance of functional groups, particularly carboxyl groups, and longer fatty-acid chains, results in a tendency for the humic fraction to be hydrophobic (Thurman, 1985). This hydrophobic character contributes to humics associating with iron and aluminum oxides in solution (Thurman, 1985). Reckhow *et al.* (1990) found this hydrophobic fraction to be rich in precursors to TCAA and DCAN and poor in precursors to TCP. Employing 72 hour formation potential tests on ten humic and fulvic acids at high chlorine doses (e.g., 20 mg Cl_2/L), Reckhow (1992) observed that the humic fraction produced more DCAN than the fulvic fraction, while the hydrophilic base fraction produced more DCAN on a weight basis.

Table 2.4 after Reckhow and Singer (1990) compares the chlorination products of humic and fulvic substances. Chlorination produced chlorinated byproduct yields which were very similar to those obtained in similar tests of humic and fulvic substances.

Table 2.4. Relative Chlorination Byproduct Yields for Ten Humic Substances

Fraction	Percent Cl Incorporation	Percent of TOX			
		$CHCl_3$	TCAA	DCAA	DCAN
Fulvic Acid	27.7	19.8	15.3	5.3	0.22
Humic Acid	24.6	19.6	21.0	6.1	0.38
10 City Average	23.0	23.0	22.2	6.8	0.34

After: Reckhow and Singer, 1990.
Notes: Formation potential test conditions were pH 7 and 72 hour.

Characteristics Associated with Apparent Molecular Size

Researchers routinely separate NOM into apparent molecular weight (AMW) size fractions using ultrafiltration. Nominal molecular weight cutoffs (MWCOs) range from 500 to 300,000 AMW. Response to treatment can be segregated into specific AMW bins

(e.g., 1,000-10,000, 10,000-30,000 AMW) using serial filtration or arithmetic manipulation of MWCO fraction responses.

In a summary of research from ultrafiltration and gel separation experiments, Thurman (1985) found little consistency among natural waters in the relative distribution of NOM within the fractions observed. The primary area of agreement in prior research was the appearance of most aquatic NOM in the 10,000 MWCO fraction. Distribution of DBP precursors among AMW fractions is also source water specific. Laine *et al.* (1993) found up to 21 percent variation in TOC removal by nanofiltration membranes (e.g., 200 and 500 MWCO) among three waters; variation in removal of UV absorbing substances was even larger at 39 percent, thus illustrating the source water specificity of NOM AMW distribution and chemical characteristics.

A number of researchers evaluated the linkage between THM formation and AMW. While the structural character of the DOC present is most critical to determining which DBPs will be generated upon chlorination, Table 2.4 illustrates that general trends can be attributable to general characteristics like AMW (Oliver and Thurman, 1983; Veenstra and Schnoor, 1980; El-Rehaili and Weber, 1987; Reckhow *et al.*, 1992). Oliver and Visser (1980) fractionated stream and lake fulvic and humic acids, then they investigated $CHCl_3$ formation as a function of substrate and AMW fraction. This work demonstrated discernable fulvic and humic acid THM formation (72 hours, 15 mg Cl_2/L, 20°C, pH 11, 1 mg DOC/L). $CHCl_3$FP from lake and stream fulvic and humic acids in the 1,000-30,000 AMW fraction was greater than formation potential in larger MWCO fractions. In substrate specific trials of size separated soil, natural water, and yeast culture extracts, $CHCl_3$ formation was only observed in <1,000 AMW fraction, when the substrate was a microbial extract. TOC normalized formation potentials were more evenly distributed across AMW fractions than formation on a per liter of sample basis.

Joyce *et al.* (1984) made more limited but similar findings to Oliver and Visser (1980). Using soil extracted fulvic acid samples and natural waters, a greater $CHCl_3$FP, by weight, was attributed to the greater number of active sites in the <10,000 AMW