

Precursor Compounds and the Haloform Reaction

Since 1975, many investigators have assumed that the ubiquitous appearance of chloroform (CHCl_3) and other THM's (trihalomethanes, or haloforms) in chlorinated water can be explained by the mechanisms involved in the "haloform reaction" and that the principal precursors of THM's that are found in natural waters are humic substances. As discussed subsequently in the section pertaining to chlorine chemistry, the haloform reaction will proceed only if specific functional groups are present in the available pool of organic compounds. It is likely that the haloform reaction does occur when natural waters are chlorinated and that humic substances provide the necessary functional groups, but it is not certain that either of these postulates is true. For that reason, both topics—the haloform reaction and humic substances—merit further discussion.

The Haloform Reaction

The terms "trihalomethanes" and "haloforms" are synonymous, but the term "haloform reaction" is often misused in discussions of THM formation in natural waters. In recent literature, it has been used to mean any reaction between aqueous solutions of organic compounds and hypohalous acids that results in THM formation, but it actually has a classic chemical definition that is more restrictive. In the future, the expanded meaning may be preferred, but at present the term "haloform reaction" is inappropriate from a strict chemical interpretation, unless one is sure that the THM's are formed by reactions between hypohalous acids and compounds containing acetyl groups or substituents that can be converted to acetyl groups.

The classic haloform reaction, which is actually a series of well-defined reactions, has been known since the 1800's (Fuson and Bull, 1934). The earliest studies were conducted with nonaqueous solvents, high

concentrations of organic compounds, and chlorine gas, but research since 1974 has focused more on defining the reactions that yield THM's under conditions that are closer to those more commonly encountered during the treatment of drinking water supplies.

Compounds, or classes of compounds, with the general formula CH_3CHOHR or CH_3COR , which includes ethanol, acetaldehyde, methyl ketones, and secondary alcohols, can participate in the haloform reaction. So may olefinic substances with the general structure $\text{CH}_3\text{CH} = \text{CR}_1\text{R}_2$, which will be oxidized by hypochlorous acid (HOCl) first to secondary alcohols and then to methyl ketones. The site of attack by chlorine is the carbon adjacent to the one bearing oxygen, and this attack, wherein the hydrogen atoms are successively replaced by chlorine, is preceded by a dissociation of one hydrogen (as H^+) to produce a carbanion ($-\text{CH}_2^-$) that can react with Cl(I) , from hypochlorous acid. Chlorine substitution continues until all hydrogen atoms on the same carbon have been replaced. The final step involves a hydrolytic cleavage of the trihalogenated carbon (the trichlorinated carbon, in this example) to form the THM, which in this example would be chloroform (Morris, 1975).

While it is well known that compounds containing acetyl groups are reactants in the haloform reaction, methyl ketone (acetone, CH_3COCH_3) itself is not a likely precursor during water treatment. According to Morris and Baum (1978), who cited a study by Bell and Lidwell (1940), the half-life for chloroform formation from acetone at pH 7 and room temperature is nearly a year. Stevens *et al.* (1978) also discounted acetone as a precursor of THM because of the slow reaction rate. The rate-limiting step in the haloform reaction is the ionization that produces carbanions, and, apparently, simple ketones are not representative of those which react quickly to produce chloroform under conditions in water treatment plants. Studies with model compounds, which are discussed in the section pertaining to chlorine chemistry, have shown that other types of compounds, including other ketones, may react more rapidly than the simple ketones.

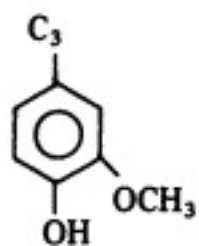
Humic Substances

As was mentioned previously, it is an attractive assumption that naturally occurring humic substances, which are derived from the structural components of living and decaying plants and/or soil dissolution and runoff, provide the most ubiquitous source of haloform precursors in natural water systems. Only limited information is available concerning the structure of these complex natural products, and it is not yet known whether all the *major* structural features have been identified, if any structural differences exist among the humic substances in waters from different geographic areas, and if these substances are closely or distantly related to soil humic and marine humic materials.

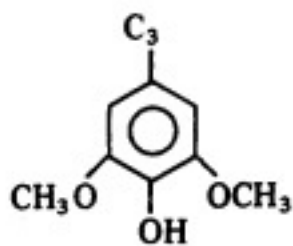
The term "humic acid" is generic and refers to that fraction of soil organic material that is soluble in alkaline solutions but insoluble in acid and ethyl alcohol (Christman and Oglesby, 1971). The fraction that is soluble in acid is commonly labelled "fulvic acid," and that material precipitated by acid but soluble in ethyl alcohol is "hymatomelanic acid." Soils vary widely in their relative compositions of these acids, but aquatic organic material behaves operationally as fulvic acid (Black and Christman, 1963), which typically contains more oxygen and less nitrogen than the humic acid fraction in both soil and aquatic organic matter. Marine organic matter (including sedimentary material) is derived largely from marine organisms and contains more sulfur than its fresh water equivalent (Nissenbaum and Kaplan, 1972; Stuermer and Harvey, 1978). Christman and Oglesby (1971), Steelink (1977), Schnitzer and Kahn (1972), and Dubach *et al.* (1964) have reported the presence of carboxyl, phenolic and alcoholic hydroxyl, carboxyl, and methoxyl functional groups in humic material. It would appear that the more oxygenated fulvic acid fraction has a greater carboxyl acidity than the humic acid fraction.

Whittaker and Likens (1973) estimated that 90% of the terrestrial biospheric carbon (standing biomass) is tied up in woody tissue. Lignin is a dominant

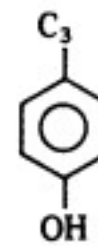
(20%-40%) chemical entity in woody tissue. Because of its refractory nature, it is probably a principal precursor of soil humus, although a myriad of other natural products unquestionably contribute to the complex pool of soil organic matter. Lignin itself is a mixed polymer of guaiacyl (I), syringyl (II), and *p*-hydroxyphenylpropane (III) aromatic moieties:



I



II



III

No other substitution patterns are known in nature and no other length of alkyl side chain has been found in lignin from any source. Oxidative degradation of lignin produces, therefore, only three aromatic substitution patterns (I, II, and III), although the relative amounts of each vary among the gymnosperms, angiosperms, and the grasses. Intermonomeric linkages in the lignin macromolecule are of both carbon-to-carbon and ether linkage types. The largest single contributor is believed to be the *b*-4' ether configuration. Side-chain carbon atoms may be in various states of oxygenation or unsaturation, and may contain methyl ketone, allyl, and secondary alcohol configurations.

Significant changes occur in the humification process as reflected by comparative functional group data for lignin and soil humic acid ([Table III-1](#)).

TABLE III-1 Comparative Functional Group Analysis of Soil Humic Acid and Spruce

Functional Group	Group Content, mMig	
	Lignin	Soil Humic Acid
Methoxyl	5.1	0.2
Total hydroxyl	6.2	5.1
Phenolic hydroxyl	1.6	2.9
Alcoholic hydroxyl	4.6	2.2
Carboxyl	1.0	5.5
Carboxyl	Trace	86.0

^a From Christmas and Ogilby, 1973.
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TABLE III-1

Comparative Functional Group Analysis of Soil Humic Acid and Spruce

Lignin.

This process, which is oxidative in nature, may strongly affect the characteristics of aquatic humic material. Microbial mediation is apparent when there is a marked decrease in methoxyl groups and increases in phenolic hydroxyl and carboxyl acidity.

The contribution of woody tissues to marine humus is not apparent from the results of degradative experiments on marine fulvic acids, which are considered to be autochthonous materials. Degradation of both soil humic acid and aquatic humic material reflects a partial lignitic origin ([Table III-2](#)), although a variety of other aromatic patterns (*m*-dihydroxy) and aliphatic chain lengths (C₂—C₁₇) must result from other natural product sources. The data in [Table III-2](#) indicate key areas of inadequacy in our knowledge of the chemical nature of aquatic humic substances. It is not possible to model natural aquatic humic material with a desirable degree of chemical accuracy, and it certainly is not possible to state that THM's, which appear in chlorinated water containing humic substances, are derived by the classic haloform reaction.

Technique	Marine Humus ¹	Soil Humus ²	
Acid hydrolysis	(FA) 20% amino acids (Gagstein and Steiner, 1977) (FA) 20% organic soluble (not identified)	20 amino acids (Kahn and Sweden, 1972), peptides, sugars, phenolic carboxylic acids (trace) ³	B F
Alkaline hydrolysis	No data	(BA) 11% aliphatic (C ₁₀ -C ₁₂) fatty acids 7% phenolic acids (principally syringic and syringic) 2% polycarboxylic aromatic acids (Keywood and Schlotzer, 1975)	(a a a
Oxidation	Conversion to carbon dioxide and water mixed with strong oxidants.	Alkaline cupric oxide (BA) vanillin, <i>p</i> -hydroxybenzaldehyde, syringaldehyde, <i>p</i> -hydroxybenzoic acid, vanillic acid, 3,5-	A (b

[TABLE III-2](#)

Chemical Degradation Products of Humic Substances.

The ultimate concern for public health protection is, of course, the fact that THM's are formed during the chlorination of drinking water sources.

Consequently, a discussion of chemical mechanisms may appear to be rather academic. However, a precise understanding of the mechanisms by which the

THM's are formed may prove to be truly beneficial by helping water utility personnel avoid the conditions during treatment that promote the appearance of high concentrations of these compounds in finished water. Studies with model compounds under well-defined laboratory conditions have been useful in elucidating these mechanisms and reaction conditions. Examples are given in the section pertaining to chlorine chemistry.