

## PREFACE

**H**UMIC SUBSTANCES ARE UBIQUITOUS IN NATURE. They represent a unique category of natural products in which the essence of the material appears to be its heterogeneity. Because of their complex, multicomponent nature, humic substances cannot be described in specific molecular terms; rather, they must be treated in a more operational manner. Thus, when dealing with humic substances, researchers are forced by circumstances to express the amount of material in terms of organic matter or as dissolved organic carbon. Despite these difficulties in the study of humic substances, this book presents many compelling, practical reasons for their study. Furthermore, the unique difficulties associated with the study of humic substances make the investigation of these materials a particularly challenging and exciting endeavor.

The influence of aquatic humic substances on the fate and treatment of pollutants has not been explored in a cohesive and comprehensive manner, and we are only beginning to understand the multifarious ways in which humic substances influence the fate of chemicals in the aquatic environment. At present, the literature on the environmental influences of humic substances is scattered. It is frequently hidden as the secondary issue in numerous research publications. Therefore, we saw the need to consolidate the theoretical and experimental approaches to investigation of the environmental impacts of humic substances in order to develop a consistent body of knowledge in this important area. This book serves to partially fulfill that need.

Humic substances directly exert many environmental influences because of their interactions with other species in the environment. Specifically, humic substances can influence the transport of metals and the redox state of metal ions. Humic substances also interact with nonionic compounds and thus immobilize such compounds in sedimentary organic matter; conversely, the association of slightly soluble organic compounds with dissolved or suspended organic matter in the aquatic environment contributes to the mobilization of these compounds. These considerations are certainly relevant to the mobilization of pesticides and other contaminants in the environment. Whereas such association between

contaminant species and humic substances can lead to a greater persistence of contaminants in the environment, the binding may actually cause them to have a decreased availability to organisms and consequently a diminished toxicity.

Understanding the environment is the essence of this discourse. It is a theme open to several frames of reference, running the gamut from understanding the natural environment to environmental protection. The concept of the environmental fate and treatment of pollutants attempts to bridge these various approaches. It illustrates how each thought process evolves and becomes interconnected within the confines of "Planet Earth". In pursuit of the fate of pollutants, we observe how one pollutant's fate can become another pollutant's source and how humic substances affect them. Humic substances are like Joseph's coat of many colors: They are different from place to place and may form and react differently, but nevertheless, they are still part of the same environmental fabric. Finding the common threads and defining and scientifically evaluating the differences are the challenges to the authors of this book.

The welcome interaction of fresh viewpoints continually reshapes the traditional disciplinary approach to science. This is especially true in the environmental area, and for the study of humic substances in particular. This treatise emphasizes the value of fruitful interdisciplinary endeavors in an attempt to break the bonds of tradition by focusing on the need to fulfill the goal of understanding our environment and to ensure environmental protection in a technological society. We took advantage of the desire of workers from different disciplines to focus their message on a common theme: humic substances. The result is the first integrated sourcebook that draws together perspectives that overlap in a synergistic manner and relate to the fate and treatment of hazardous chemicals in the environment.

## Acknowledgments

This book is based on a symposium entitled "The Influences of Aquatic Humic Substances on the Fate and Treatment of Pollutants" that was held in Denver, CO, April 5-10, 1987, at the National Meeting of the American Chemical Society, in the Division of Environmental Chemistry. Individual chapters are based on invited and contributed papers that were presented at that symposium. A few additional chapters were included to give balance to the book. The symposium was sponsored jointly by the International Humic Substances Society (IHSS) and the Division of Environmental Chemistry of the American Chemical Society.

A project such as this one requires the expertise and help of many people. Unfortunately, there is not sufficient space to thank everyone. We

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Many individuals have participated in the preparation of this book. Each chapter has been technically reviewed by at least two outside referees and the editors to ensure that the content meets the scientific rigor of a technical or review journal and that the combination of papers is within the framework of the goal of the book. We commend the reviewers for their candor. We are deeply indebted to the speakers and session chairpersons of the symposium for their contributions and efforts before, during, and after the symposium. The symposium on which this book is based was exceptionally well attended and required double the projected space that was planned to accommodate the overflow. We thank Barbara (Hodsdon) Ulyot of the ACS Meetings and Divisional Activities Department and Bob Jolley of the ACS Division of Environmental Chemistry for helping us accommodate the larger-than-expected audience that was interested in this symposium.

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The lilting Irish brogue of the Galway native and the nasal New York accent of the Brooklyn native did harmonize, joining forces many times to accomplish a common goal and, surprisingly, without any squabbles. In fact, the biggest problem we faced, considering the equal effort that had been put forth by both editors, was the choice of whose name would appear first on the cover. In our typical approach to scientific problem solving based on undisputable statistical logic, we agreed to flip a coin

transcontinentally between Golden and Philadelphia with the help of the Denver Nuggets basketball team. A game was chosen; the first author would be Suffet if Denver scored an odd number of points, MacCarthy if Denver scored an even number of points. In this prodigious battle, Denver tied the score at the buzzer of regulation time (even point score), but won in overtime by an odd point score, and the rest is folklore. Unfortunately, disputes about the nature of humic substances and their environmental influences are not so readily resolved.

We both gratefully acknowledge, with deepest affection and appreciation, the understanding, support, and encouragement of our wives, Eileen Suffet and Helen MacCarthy. They remain our sources of perspective, understanding, and patience. Without their concern and help, this book would not have been possible.

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To Our Wives and Families  
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# Introduction

## Aquatic Humic Substances and Their Influence on the Fate and Treatment of Pollutants

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**T**HE TERM *HUMIC SUBSTANCES* refers to organic material in the environment that results from the decomposition of plant and animal residues, but that does not fall into any of the discrete classes of compounds such as proteins, polysaccharides, and polynucleotides. Humic substances are ubiquitous, being found in all soils, sediments, and waters. Although these materials are known to result from the decomposition of biological tissue, the precise biochemical and chemical pathways by which they are formed have not been elucidated.

An endeavor to establish such pathways is a formidable task because humic substances consist of an extraordinarily complex mixture of compounds. As an indication of the molecular heterogeneity and complexity of humic substances, these materials have defied all attempts at separation into discrete components. Virtually every separation technique that has been developed by chemists and biochemists has been applied to humic substances. Many of these attempts at fractionation have succeeded in diminishing the degree of heterogeneity of the samples, but none of them comes close to isolating a material that could be referred to as a *pure* humic substance in the classical meaning of the term *pure* chemical or even a *pure* group of chemicals. In this regard, humic substances represent a unique category of natural products in which the essence of the material appears to be heterogeneity *per se*.

This inability to define humic substances in specific chemical terms forces us to use a more vague operational-type definition, such as that given in the opening sentence of this chapter. A more detailed discussion of the heterogeneous nature of humic substances and of the concomitant difficulties in their study is given in ref. 1.

Because of the poorly defined nature of humic substances, compared to the more discrete types of materials that most chemists and biochemists are familiar with handling, it might appear that any fundamental study of humic substances would be a rather futile endeavor. Adoption of such a viewpoint might be further provoked by the realization that there is, in fact, no analytical method for uniquely assaying humic substances. How could one develop a quantitative chemical analysis for a material that is so complex and ill-defined that researchers must be satisfied with a rather vague operational definition? Thus, when dealing with humic substances, researchers must resort to such crude measures as expressing the amount of material in terms of organic matter (e.g., as determined by loss on ignition), or expressing the concentration of humic substances as dissolved organic carbon (DOC).

Even the term *dissolved* in this context lacks the precise meaning that it usually has in chemistry. In this environmental context, *dissolved* generally refers to materials in an aqueous system that pass through a 0.45- $\mu\text{m}$  (or other arbitrarily chosen pore size) filter. In reality, some of these materials may be in colloidal suspension rather than in solution.

Constraints in dealing with humic substances are evident throughout the chapters of this book. However, despite these difficulties in the study of humic substances, this book presents many compelling, practical reasons for studying humic substances. Furthermore, the unique difficulties associated with the study of humic substances make the investigation of these materials a particularly challenging and exciting endeavor.

It should not be surprising that a material that occurs in all soils, sediments, and waters exerts significant influences on many agricultural, geochemical, environmental, and pollutant-treatment processes. The agronomic importance of humus was recognized long before the chemistry of humic substances was ever addressed. Humic substances are vital for maintaining the agriculturally important crumb structure of soils, for sustaining the water regime of soils, for holding micronutrients for plant growth in the soil, and for acting as an acid-base buffer in the soil.

In geochemical and environmental contexts, humic substances can influence the transport of metals and the redox state of metal ions and other species. Humic substances interact with metal ions by complexation and ion-exchange mechanisms. Depending upon the circumstances, this interaction may lead to solubilization or immobilization of the metal.

Humic substances can also interact with nonionic compounds and thus cause the immobilization of such compounds in sedimentary organic matter;

conversely, the association of slightly soluble compounds with dissolved or suspended organic matter in the aquatic environment imbues an enhanced solubility on these compounds. Such enhanced solubility can result in an increased mobility of these compounds in rivers and other aquatic environments. These considerations clearly are relevant to the mobilization of pesticides and other contaminants in the environment.

The potential impact of a contaminant in the environment depends not only on the concentration and mobility of the species, but also on its bio-availability. The association of inorganic and organic species with humic substances can lead to a masking of these species by the organic matter, with a concomitant decrease in the toxicity of the contaminants to organisms in the environment. This association may contribute to a greater persistence of the contaminants, but to a diminished toxicity. The multifarious roles of humic substances in influencing the fate of chemicals in the aquatic environment are only beginning to be understood, and much further research remains to be done in this area.

In addition to the more direct environmental effects of humic substances resulting from their interaction with potential pollutants, these materials also have an environmental impact on water- and waste-treatment processes. For example, chlorination of indigenous humic substances during municipal water disinfection can produce carcinogenic compounds; ozonation of the biologically refractory humic substances can produce biodegradable byproducts and thereby promote microbial growth; and humic substances can compete with hazardous chemicals during the adsorption process in activated-carbon treatment, as well as cause fouling of ion-exchange resins and reverse-osmosis membranes. An understanding of the mechanisms by which humic substances interfere with treatment processes, and the development of protocols to eliminate these problems, has considerable economic advantage.

This book is directed to studies of the environmental influences of humic substances in aquatic environments, with an emphasis on how these materials affect the fate of organic and inorganic pollutants and how their presence in natural waters impacts on treatment processes.

### *Historical Perspective*

Humic substances have been studied for more than 200 years (2). Most of these studies have dealt with humic substances isolated from soils, although Berzelius in the early 1800s did investigate humic substances isolated from water (3). Since the early 1970s, there has been a major upsurge in the number of studies dealing with humic substances isolated from water. A significant factor leading to this increased focus on aquatic humic substances was the report by Rook in 1974 (4) that chlorination of natural waters leads to the formation of chloroform and other potentially hazardous chlorinated hydrocarbons. Chlorination is one of the most universal disinfection proc-

esses in water and waste treatment, and many chlorinated chemicals are suspected carcinogens.

Development of new technologies for the isolation of reasonable quantities of humic substances from natural waters (5) has helped to promote research on these aquatic materials. However, many workers like to study the interaction of humic substances with pollutants without concentrating the samples, to observe their effect in a more natural state. This approach has become possible because of the ability to analyze nanogram-per-liter to microgram-per-liter concentrations of pollutants routinely by modern analytical chemical techniques. The obvious difference in the approaches is determined by the end objectives of the particular study.

### *Isolation of Humic Substances*

Humic substances do not occur alone in the environment. Rather, they are mixed with, or chemically or physically associated with, other classes of materials. For example, in the dissolved state in natural waters, humic substances are mixed with amino acids, sugars, various aliphatic and aromatic acids, and a host of other organic compounds. In soils and sediments, and in suspension in aquatic systems, humic substances are frequently bound to the mineral components. Of course, the ultimate objective in the present context is to understand the role of humic substances in the real environment, where all of these other substances and interactions occur. Consequently, some researchers choose to work with whole water or with unextracted soil and sediment samples when evaluating the environmental impact or treatment of humic substances. Other investigators believe that all studies should actually be conducted *in situ* without removing the substrate from its natural location.

Most researchers isolate the humic substances from the nonhumic materials and independently evaluate the characteristics and behavior of the isolated materials. These researchers believe that a part is simpler than the whole, and that the chemistry of these materials can be evaluated more rigorously in the controlled conditions of a laboratory. In this regard, humic-substance researchers generally devote considerable effort to obtaining low-ash samples. These efforts can be contrasted with those of researchers whose primary focus is on the mineral constituents of soils and sediments and who make correspondingly intense efforts to isolate the mineral constituents with as little organic "contamination" as possible. These approaches focus upon two extremes of the true situation, and are largely a manifestation of the research interests of the individual investigators. Ideally, in the long run the data from both approaches can be merged to provide a more meaningful picture of the true environmental situation.

Over the years, many subfractions of humic substances have been isolated and given special names. Of these, only three fractions have stood the



test of time as being generally useful, namely, humic acid, fulvic acid, and humin. Because of the difficulty in establishing a uniform set of definitions that is applicable to a complicated mixture that can be isolated from a solid substrate (e.g., soil) and a nominally dissolved substrate (natural waters), these three fractions are operationally defined as follows (6):

- **Humic acid:** the fraction of humic substances that is not soluble in water under acidic conditions (pH <2.0) but is soluble at higher pH values
- **Fulvic acid:** the fraction of humic substances that is soluble in water under all pH conditions
- **Humin:** the fraction of humic substances that is not soluble in water at any pH value

These definitions reflect the methods of isolating the various fractions from the original substrate. Although there are literally hundreds of variations of the extraction techniques for humic substances, the essential features embodied in all of these techniques are as follows.

**Isolation from Solid Substrates.** When dealing with a solid substrate (e.g., soil or sediment), the sample is mixed with a sodium hydroxide solution; after centrifugation, the alkaline supernate contains humic and fulvic acids in the salt form. This solution is decanted and acidified to pH 2.0 with HCl. The humic acid precipitates, and the fulvic acid, which remains in solution, is decanted after centrifugation. The humic acid and fulvic acid are then desalted by any of various techniques. The insoluble residue remaining after the alkaline extraction of the organic substrate contains the humin, generally mixed with insoluble mineral matter or undecomposed fibrous plant material. Any soluble nonhumic material that is mixed with the humic acid is removed during the subsequent washing with water during desalting of the humic acid.

The supernate that remains following acidification of the alkaline extract is more correctly referred to as the fulvic acid fraction, rather than as fulvic acid. The fulvic acid fraction contains discrete compounds such as amino acids and simple sugars, in addition to the humified material (fulvic acid). These discrete compounds can be separated from the fulvic acid by passing the fulvic acid fraction through a hydrophobic resin. The more hydrophilic compounds (e.g., amino acids, sugars) pass through the column, and the less hydrophilic constituents (fulvic acid) sorb to the resin. The fulvic acid can subsequently be eluted from the resin with dilute base. The distinction between fulvic acid and fulvic acid fraction is not always made, even within chapters of this book, but such a distinction needs to be recognized if data are to be properly interpreted and compared. Methods for extracting and

fractionating humic substances from soils are discussed in refs. 7 and 8, respectively. These techniques are also applicable to sediment samples.

**Isolation from Aqueous Substrates.** Isolation of humic substances from natural waters is a much more formidable task, even for those waters that have a relatively high concentration of humic substances. Generally, the water is acidified to approximately pH 2.0 with HCl and is passed through a column containing an essentially hydrophobic resin, such as the methyl methacrylate cross-linked polymer, XAD-8. The humic substances sorb to the column while the more hydrophilic, nonhumic materials pass through the column. The column is then eluted at pH 7.0 to remove the fulvic acid. Subsequent elution with 0.1 M NaOH desorbs the humic acid. The humic and fulvic acids are then converted to the hydrogen form by passage through a strong cation exchanger in the hydrogen form. Any humin in the water is removed by a prior filtration. Methods for the isolation and fractionation of humic substances from waters are reviewed in refs. 5 and 9, respectively.

Because of the low concentration of humic substances in natural waters, the isolation of reasonable quantities of humic and fulvic acids can be a very time-consuming and tedious task. Nevertheless, it is a necessary and critical step in the investigation of aquatic humic substances.

Some workers have chosen to avoid the difficulty of isolating real aquatic humic substances. Instead, they have used surrogate humic acids as substitutes for aquatic humic and fulvic acids in an attempt to assess the environmental influences of humic substances in natural water. For example, commercial humic acids have been used by many researchers as analogues of true water and soil humic substances, as is evident from reading some of the chapters in this book. It has been shown (10) that the commercial humic acids are not representative of water or soil humic and fulvic acids; this subject is discussed further in Chapter 4 of this book.

## ***Composition of Humic Substances***

Despite the limitations in our knowledge of the chemical nature of humic substances, a great deal is known about the occurrence and composition of these materials. This compositional information affords a basis for understanding many of the environmental and geochemical effects of humic substances. Humic substances vary in composition, depending on their source, method of extraction, and other parameters. Overall, however, the similarities between different humic substances are more pronounced than their differences.

About 50% of the dissolved organic carbon in uncolored surface waters of the United States consists of humic substances. The average concentration of the humic substances in these surface waters is 2.2 mg of C/L or 4.4 mg of humic substances/L. (The humic substances are approximately 50% car-

**Table I. Elemental Compositions of Representative River and Soil Humic Substances**

Sample	C	H	O	N	S	P	Total	Ash (%)
Ohio River, dissolved fulvic acid	55.03	5.24	36.08	1.42	2.00	0.34	100.35	0.38
Ohio River, dissolved humic acid	54.99	4.84	33.64	2.24	1.51	0.06	98.76	1.49
Sanhedron Al, soil fulvic acid	48.71	4.36	43.35	2.77	0.81	0.59	100.59	2.25
Sanhedron Al, soil humic acid	58.03	3.64	33.59	3.26	0.47	0.10	99.09	1.19

NOTE: Elemental compositions are expressed on a percent-by-weight, ash-free, and moisture-free basis; adapted from ref. 10.

bon by weight.) Although the DOC of colored surface waters is extremely variable, it typically ranges from about 5 to more than 50 mg of C/L. Also, in these colored waters, the fraction of the total DOC in the form of humic substances varies considerably and can be as large as 80%. Typically 90% of the dissolved humic substances in natural waters consists of fulvic acid, and the remaining 10% consists of humic acid. This composition is in contrast to humic substances from soils, where the humic acid is in very large excess over the fulvic acid. These data are taken from Malcolm (11), who presents a detailed discussion of the occurrence and distribution of humic substances in streams.

Many workers use the terms DOC and humic substances interchangeably. Such usage is not correct and fails to make the appropriate distinction between humic substances and a mixture of humic substances plus nonhumic substances. With the growing awareness of the subtleties involved in humic substances research and terminology, important distinctions between terms such as *humic substances* and *DOC* should be more adequately accommodated in the future.

Aquatic humic acids differ from aquatic fulvic acids in elemental and functional group compositions, average molecular weights, and other characteristics. Aquatic humic and fulvic acids also differ from their corresponding soil counterparts. Elemental compositions of representative water and soil humic substances are given in Table I. The major functional groups in humic substances are carboxyl, phenolic hydroxyl, and alcoholic hydroxyl. Typical number average molecular weights of aquatic fulvic acids are 800–1000 daltons, and those of aquatic humic acids are 2000–3000 daltons. In contrast, the molecular weights of soil humic acids are reported to be as large as several hundred thousand daltons (8, 12).

It is not possible to integrate all of the compositional data into neat structural models for humic substances. These data are, nevertheless, very useful in accounting for many of the environmental influences of these materials. For example, materials with a greater oxygen content will have a greater concentration of functional groups. This composition will be likely to cause the material to be more hydrophilic, and consequently less effective in the uptake of nonionic organic compounds. However, the higher concentration of oxygen-containing functional groups will likely render this ma-

terial more acidic and more effective in complexing metal ions. Refs. 13–15 contain more detailed discussions of the chemistry of humic substances.

### ***Standard Humic Substances***

A major problem that has confronted researchers in the area of humic substances has been the lack of standard material through which they could objectively compare their results (16–18). This lack of standard material is apparently why commercial humic materials are used in research, but it has now been remedied by the International Humic Substances Society, which has established standard humic substances from water, soil, peat, and leonardite. Information relating to the nature and availability of these standard humic substances is available from the society.

### ***Environmental Effects of Aquatic Humic Substances***

Evaluation of the fate of potentially hazardous pollutants in the environment or during water treatment is concerned with how, where, in what form, and in what concentration pollutants are distributed (19). This concern for an understanding of pollutant impact or removal generally involves dealing with a trace concentration of a pollutant in solution (microgram-per-liter concentrations or less) within the background matrix of milligram-per-liter concentrations of other natural organic materials. The influence of the background organic matter on the fate and treatment of pollutants is potentially great and is only beginning to be understood.

Influences of aquatic humic substances on the fate and treatment of pollutants have been investigated only recently. The remainder of this introduction will indicate how humic substances behave in the aquatic environment and during treatment processes, and how they affect the fate and treatment of hazardous chemical pollutants.

Both situations are important because humic substances themselves are precursors of hazardous chemicals (e.g., chlorination of humic substances is known to produce haloforms in drinking-water treatment; humic substances also contribute undesirable color to drinking water). Humic substances can neutralize hazardous chemicals by complexation with toxic metals or by association with toxic organic chemicals. The presence of humic substances in the environment may have beneficial or deleterious consequences, and therefore an evaluation of the impacts of humic substances in each situation must be carefully conducted. Humic substances, and indeed DOC as a whole, comprise a complex mixture of chemicals that are constantly subject to change by chemical and biological forces. Therefore, only gross primary effects may remain the same from time to time. The chemistry of complex mixtures usually cannot be described as the sum of the properties of the individual constituents because intermolecular interactions can modify component characteristics (Leenheer et al., Chapter 2 in this book).

The concentration of a pollutant as it changes with time is a function of mixing and transport (i.e., turbulent diffusion and advection), emission rate, sinks, and reactivity (e.g., biological and chemical). The continuity of mass and heat must also be satisfied. The fate of hazardous trace organic chemicals in the environment, as well as during treatment processes, is becoming the main criterion for assessing pollution impact. Elucidation of the chemical, physical, and biological influences acting upon compounds in the environment is of primary and immediate concern. Therefore, the impacts of humic substances in the environment and during treatment processes must be described to gain an understanding of hazardous chemical effects. Chemical influences include physicochemical reactions of the compounds (such as sorption, coagulation, acid–base interactions, and complexation reactions) and chemical changes (oxidation, reduction, hydrolysis, and photochemical reactions). Physical influences include processes that transport or disperse chemicals. Biological influences include uptake and depuration by organisms and metabolic changes associated with receptor organisms and food chains.

Models are used to depict simplified segments of the environment or treatment processes on a scale that can be conceptualized and understood. The primary types of models that have been used to describe the behavior of chemicals in the environment are equilibrium, steady-state, and homeostatic models. Equilibrium models involve closed thermodynamic systems (time-invariant), whereas steady-state models involve open thermodynamic systems with equal input and output changes. Homeostatic models include the concept of feedback and feedforward kinetic control. The importance of humic substances in sediments and aquatic environments has only recently been recognized as a factor in the environmental reactivity and treatment of chemicals. As a result, the effects of humic substances are only now beginning to be incorporated into models of environmental fate (e.g., Caron and Suffet, Chapter 9 in this book) and treatment processes (e.g., Weber and Smith, Chapter 30 in this book).

### ***Influences of Aquatic Humic Substances on Fate of Pollutants***

The association or binding of nonpolar highly hydrophobic compounds to DOC has been observed to increase the solubility (20) and thus the mobility of chemical pollutants. However, it was only in the 1980s that Carter and Suffet (21), Landrum et al. (22), and others started to quantify the phenomena. The binding of nonpolar highly hydrophobic compounds to DOC was also observed to decrease sorption of these compounds to sediments and suspended sediments (23–25), to decrease their bioavailability to aquatic organisms (26–30), to decrease the volatility rate of PCBs (31, 32), to decrease the rate of alkaline hydrolysis of certain pesticides (33), and to influence the photochemistry of hazardous chemicals in natural waters (Cooper et al.; Hoigné et al., Chapters 22 and 23 in this book).

Energy from sunlight can cause photochemical changes in certain pollutants. Sunlight can also interact with constituents of natural waters to produce changes in the DOC. The DOC acts as a sensitizer or precursor for the production of reactive intermediates (photoreactants) by producing singlet oxygen, peroxy radicals, hydrogen peroxide, etc., when photooxidized. Thus, sunlight can react with hazardous organic chemicals directly by photochemical pathways or indirectly via photoreactants produced from DOC (Cooper et al.; Hoigné et al., Chapters 22 and 23 in this book).

Carter and Suffet (34), Kile and Chiou (Chapter 10 in this book), and others have concluded that the variability in solubility of hazardous organic chemicals in natural waters is probably caused by the inconsistent structural configuration of aquatic organic matter in the natural environment. Kile and Chiou (Chapter 10 in this book) observed that polarity, size, configuration of the DOC, and hydrophobicity of the solute were controlling factors in solubility enhancement of trace organic substances in aquatic environments.

In aquatic systems, binding of organic or inorganic contaminants to humic substances can alter the bioavailability of the contaminants (28). Organic contaminants associated with humic substances appear to be essentially unavailable for uptake by the biota. This decrease in bioavailable contaminant concentration decreases the toxicity of the hazardous organic chemicals in the environment. The association of nonionic organic solutes to humic substances is more pronounced for the most hydrophobic compounds (i.e., those compounds with octanol-water partition coefficients  $>10^4$ ). In most cases, toxic metals associated with humic substances have reduced uptake and less toxic effects. However, interactions among complexing metal ions, major cations in solution, and the carrier proteins on biological membranes make it difficult to generalize and predict any reduction in accumulation and toxicity of metals.

### ***Influences of Aquatic Humic Substances on Treatment Processes***

The presence of humic substances in a water supply is undesirable for a number of reasons (Vik and Eikebrokk, and Baker et al., Chapters 24 and 31 in this book). Major problems result from the fact that humic substances:

1. produce esthetically undesirable problems such as color in the water;
2. serve as precursors of potentially hazardous trihalomethanes during chlorination processes;
3. act as precursors of other low- and high-molecular-weight chlorine-containing organic compounds that are produced during chlorination;

4. serve as precursors of low- and high-molecular-weight organic compounds that are formed by oxidation during ozonation processes;
5. stabilize dispersed and colloidal particles during coagulation processes;
6. lead to the formation of biodegradable organic compounds during ozonation and thereby enhance regrowth of microorganisms within the water-distribution systems;
7. can compete with pollutant compounds for adsorption sites in GAC adsorption; and
8. can precipitate in the distribution system; this precipitation can lead to deterioration of tap water quality and increase the need for interior cleaning of pipes.

The health effects of high concentrations of humic substances per se (mixtures containing high-molecular-weight materials) are unknown.

Water-treatment processes have been designed primarily to remove pathogens and turbidity through the use of coagulation–floculation–sedimentation–filtration and disinfection with ozone and chlorine processes. As is true in any serial set of processes, the efficiency of the first (coagulation) process will affect subsequent processes. Because humic substances stabilize dispersed and colloidal particles, the removal of humic substances has been a focus of the coagulation process.

During coagulation, stabilization of dispersed and colloidal particles can occur through the adsorption of the higher-molecular-weight humic substances on the surface of the mineral particles. A strong interaction has often been observed between the dissolved humic substances and the flocculants. In most cases, higher humic-substance concentrations mean larger flocculant dosages and therefore higher treatment costs.

An alternative to coagulation for particle removal during water treatment is membrane filtration. The main problem with membrane filtration is irreversible fouling of the membrane by complex mixtures of inorganic materials and humic substances. The characterization and control of membrane fouling is currently under investigation (Mallevalle et al., Chapter 41 in this book).

Chlorine can combine with aquatic humic substances to form chlorinated organic compounds, such as chloroform (3, 35), other low-molecular-weight disinfection byproducts (e.g., haloacetonitriles, haloacids, haloaldehydes, haloketones, chlorophenols, chloropicrin, and cyanogen chloride) (Stevens et al., Chapter 38 in this book), and complex high-molecular-weight chlorinated compounds (36). All of these compounds may have adverse effects on human health.

Oxidation processes also can change the chemical structure of humic substances and alter the biodegradability of these compounds. In German waterworks, ozonation is very often used to render humic substances from surface water more biodegradable. However, the biodegradable compounds need to be removed before entering the water-distribution system, where they can enhance regrowth of microorganisms (Kruithof et al., Chapter 37 in this book).

Background DOC can also influence the treatment of pollutants by reducing the capacities and rates of the carbon adsorption unit process for the removal of smaller molecules that present a known health hazard (Weber and Smith, Baker et al., Chapters 30 and 31 in this book). Thus, the lower the concentration of humic substances present in the influent water to a GAC contactor, the more efficient the process will be for pollutant removal.

## Conclusions

Although humic substances have been studied for many years, it has only been since the early 1970s that a major research effort has been devoted to the investigation of aquatic humic substances and their environmental influences. As in the case of humic substances from other environments, one cannot assign unique compositions or formulas to aquatic humic substances. However, the compositional and other data that are available allow us to understand many of the environmental effects of these materials.

If evaluation of the fate of potential hazardous pollutants in the environment and during treatment is concerned with how, where, in what form, and in what concentration pollutants are distributed (19), then an understanding of the background DOC matrix as it directly influences the fate of pollutants must be carefully developed. At present, the understanding of the influences of humic materials is only sufficient to define site-specific effects on the pollutants. Thus, site-specific investigations must be completed to define the fate of hazardous chemicals. In the future, as information is accumulated, it is hoped that a more general understanding of the effects of humic substances on hazardous chemicals will be developed to help predict effects in unknown situations.

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