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Introduction

Our immediate environment – the atmosphere, soils, surface water and groundwater – is host to a vast number of chemical reactions, even leaving aside the biochemical reactions of living organisms. Environmental chemists aim to define and quantify these reactions, make analytical determinations of reactants and products, construct predictive models, and relate their findings to the functioning of ecosystems. A major part of the research effort is to take account of natural organic matter and mineral particulates, because these abundant, poorly defined, components exert a powerful and ubiquitous chemical influence on the environment. This book focuses on the most chemically significant fraction of natural organic matter, humic substances.

Humic substances are complex, acidic organic molecules formed by the decomposition of plant, animal and microbial material. They are abundant and persistent in the biosphere and immediate subsurface, being present in particulate and dissolved forms in soils, waters and sediments. They interact with a variety of solutes, adsorb at surfaces, and are photochemically active. Humic substances first came to prominence in agriculture, because of their positive influence on the structure, water retention properties, and nutrient status of soils. More negatively, they pose problems to the water supply industry, requiring removal to minimise water colour, and giving rise to potentially mutagenic by-products as a result of chlorination. There is interest in using humic substances to recover metals from wastewaters and from seawater. Schnitzer (1991) lists a variety of uses of humic matter, in agriculture, industry, environmental engineering, and medicine. However, over and above these practical and utilitarian matters, the greatest present interest in humic substances concerns their rôles in the natural environment. They are recognised to be important in a

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range of issues (Table 1.1), and consequently there is a considerable worldwide research effort aimed at characterising them and understanding their environmental behaviour.

Pre-eminent among the interactions of humic substances with solutes are those involving cations, i.e. protons (H^+) and metallic cations such as Na^+, Al^{3+}, Ca^{2+}, Cu^{2+}, Pb^{2+} and Am^{3+}. The interactions involve both immobile organic matter, in the solid phases of soils and sediments, and dissolved humic substances, which may be mobile and transport the ions. Cation–humic interactions exert control on the reactivity of the cation, including its bioavailability. But this is a two-way process, since cation binding influences the physico-chemical state of the humic matter, and thereby its interactions with other components of the environmental system. Therefore it is important to describe not only how humic substances influence cations, but also how cations influence humic substances.

Table 1.1. Environmental issues involving humic substances. Those for which cation binding is recognised to be an important factor are marked with an asterisk.

Issue	Role of humic substances
Carbon cycling	Major C pool, transformations, transport and accumulation
Light penetration into waters	Absorption and attenuation of light by humic chromophores
Soil warming	Absorption of solar radiation by soil humic matter
Soil and water acidification*	Binding of protons, aluminium and base cations in soils and waters
Nutrient source	Reservoir of carbon, nitrogen, phosphorus and sulphur
Nutrient control*	Binding of iron and phosphate
Microbial metabolism	Substrate for microbes
Weathering*	Enhancement of mineral dissolution rates
Soil formation (podzolisation)*	Translocation of dissolved humic substances and associated metals (Al, Fe)
Properties of fine sediments*	Adsorption at surfaces and alteration of colloidal properties
Soil structure*	Aggregating effect on soil mineral solids
Photochemistry	Mediation of light-driven reactions
Heavy metals*	Binding, transport, influence on bioavailability, redox reactions
Pesticides, xenobiotics*	Binding, transport, influence on bioavailability
Radioactive waste disposal*	Binding and transport of radionuclide ions in groundwaters
Ecosystem buffering*	Control of proton and metal ion concentrations, persistence

The aim of the present volume is to draw together current knowledge about cation interactions with humic matter, and to show how it can be used to understand and predict the natural environment. The book is structured as follows. Chapter 2 reviews information about humic substances, emphasising those aspects of most relevance to cation–humic interactions. The reviews of environmental and solution chemistry in Chapters 3–5 define the chemical territory within which cation–humic interactions take place. Chapter 6 surveys methods available for determining the extents of interaction of cations with humic substances. Chapter 7 reviews available quantitative information, and Chapter 8 discusses knowledge about the physico-chemical natures of cation–humic complexes. Chapters 9–11 address the mathematical modelling of cation–humic reactions, which is a key requirement if information from laboratory studies is to be applied to the natural environment. Chapter 12 looks at how cation binding influences other environmentally significant physico-chemical interactions. Chapters 13 and 14 examine the implications of cation–humic interactions in natural waters and soils respectively. Finally, Chapter 15 considers research needs and wider applications.

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Humic substances – a brief review

An appreciation of the formation and properties of humic substances is needed to understand their interactions with cations, and the influence of those interactions within the natural environment. This chapter presents a summary of current knowledge, emphasising those aspects of most relevance to cation binding. More detailed, wider-ranging, information can be found in the books of Aiken *et al.* (1985a), Hayes *et al.* (1989), Averett *et al.* (1989), Beck *et al.* (1993), Stevenson (1994), Piccolo (1995) and Gaffney *et al.* (1996). Jones & Bryan (1998) reviewed the colloidal properties of humic substances. Thurman (1985) is an essential text on the organic matter of natural waters, and includes much information on humic substances.

2.1 Natural organic matter and humic substances

Most (99.95%) of the Earth's carbon is held in sedimentary rocks, to and from which it cycles on geological time scales. The remaining carbon (about 4×10^{19} g) is in the biosphere or shallow subsurface, 90% of it in the form of carbonate dissolved in seawater, and about 9% in organic forms (Table 2.1). In soils, natural waters and their sediments, the majority of the organic carbon is present in humic matter.

Stevenson (1994) considers natural organic matter in soils to consist principally of litter (macroorganic material lying on the soil surface), the light fraction (plant residues within the soil proper), soil biomass (predominantly microorganisms living in the soil), and stable humus. Of these pools, the last predominates in most agricultural, forest and moorland soils. In peatlands, plant residues may constitute most of the organic matter, but there are nonetheless large amounts of humic substances. Humus consists of humic substances and non-humic substances. The latter comprise identifiable classes of biochemicals (amino acids, carbohydrates, fats, waxes, resins, low molecular weight organic acids etc.). Stevenson defines humic substances as: ‘a series of relatively high-molecular-weight, yellow to black colored substances formed by secondary synthesis reactions’.

Natural waters contain a range of identifiable solutes, together with humic substances. Thurman (1985) lists the main classes of identifiable compounds as carboxylic acids, phenols, amino acids, carbohydrates and hydrocarbons. There are also many trace compounds, of both natural and anthropogenic origin. A similar range of compounds is found in soil waters (Qualls & Haines, 1991). Thurman (1985) points out the difficulty of defining ‘in some limited yet useful way’ what aquatic humic substances are, and he offers:

> (Aquatic humic substances) are colored, polyelectrolytic, organic acids isolated from water on XAD resins, weak base ion-exchange resins, or a comparable procedure. They are nonvolatile and range in molecular weight from 500 to 5000; their elemental composition is approximately 50 percent carbon, 4 to 5 percent hydrogen, 35 to 40 percent oxygen, 1 to 2 percent nitrogen, and less than 1 percent for sulfur plus phosphorus. The major functional groups include: carboxylic acids, phenolic hydroxyl, carbonyl, and hydroxyl groups. Within aquatic humic substances there are two fractions, which are humic and fulvic acid. Humic acid is that fraction that precipitates at pH 2.0 or less, and fulvic acid is that fraction that remains in solution at pH 2.0 or less.

The suspended and bed sediments of rivers consist chiefly of material

Table 2.1. Pools of organic carbon in the Earth’s surface and subsurface.

Pool	$g \times 10^{-15}$
Seawater	1700
Soils	1500
Terrestrial plants	560
Groundwater	15
Surface freshwater	0.5

The data are mainly taken from the compilation by Schlesinger (1997), also from Aiken *et al.* (1985b).
The approximate value for groundwater is based on an assumed average concentration of 1 mgC dm^{-3} and a total groundwater volume of 1.5×10^{16} m^3 (Schlesinger, 1997). The value for freshwater assumes an average concentration of 5 mg dm^{-3} and a total volume of 10^{14} m^3 (Smith, 1981; Schlesinger, 1997).

derived from the land, and the organic matter is therefore related to soil material. Humic substances are the principal forms of organic carbon in marine and lake sediments. In both cases they can be derived from both terrestrial and aquatic sources (Vandenbroucke *et al.*, 1985; Ishiwatari, 1985).

Two definitions of humic substances for soils and waters have already been given. To emphasise that definition is difficult, a third attempt, that of Aiken *et al.* (1985b), can be mentioned: '(Humic substances are) naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight and refractory'. For the most part, the three definitions are summaries of the properties of compounds obtained when natural samples (waters, soils, sediments) are subjected to defined extraction procedures, the principal ones being (a) solubilisation with base and (b) adsorption or precipitation from acid solution (see Section 2.2). The definitions do not include any recognition of function, i.e. they do not say what the rôle(s) of humic substances might be. A contrast can be drawn with biochemical definitions of enzymes, which are primarily defined in terms of the reaction that they catalyse. Much of the research on humic substances aims to determine their functions under different environmental circumstances, and the study of cation binding is an important part of that research effort.

2.2 Isolation and classification of humic substances

Traditionally, humic substances have been considered to comprise three main fractions, distinguished by their solubility and adsorption properties. Humic acids are soluble in base but insoluble in acid, while fulvic acids are soluble in both base and acid. A third fraction, humin, is readily soluble in neither acid nor base. Humin may consist of humic acid in strong association with mineral matter, highly condensed insoluble humic matter, fungal melanins, and paraffinic substances (Stevenson, 1994). Broadly speaking, humic acids and humin occur mostly in soils and sediments as part of the solid phase, while fulvic acids are more mobile and account for a major part of the dissolved organic matter in natural waters. The word 'humic', used generically, encompasses all humic substances.

2.2.1 Isolation and fractionation procedures

Isolation procedures have been discussed fully by Hayes (1985), Aiken (1985) and Stevenson (1994). Figures 2.1 and 2.2 show outline schemes of

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the most commonly used methods for the isolation of humic and fulvic acids from soils and waters. To a large extent, the procedures depend upon controlling the electrical charge of the humic matter. When the molecules are highly charged (high pH), they are more soluble. When the charge is decreased (low pH), precipitation and adsorption to hydrophobic surfaces are promoted.

Hatcher *et al.* (1985) considered humin to be the organic residue after successive extraction of sediments by benzene + methanol (to remove lipids), 1 mol dm^{-3} HCl, and 0.5 mol dm^{-3} NaOH. In marine sediments, further treatment with HF + HCl was needed to remove mineral matter.

Within the humic substances research community, there is some unease about how representative isolated humic substances are of the materials in their natural states. The unease arises mainly because the extraction conditions are rather extreme, involving high concentrations of acid and base; if such conditions were used in the isolation of enzymes, for example, most or all of their biological activity would be lost. A number of authors

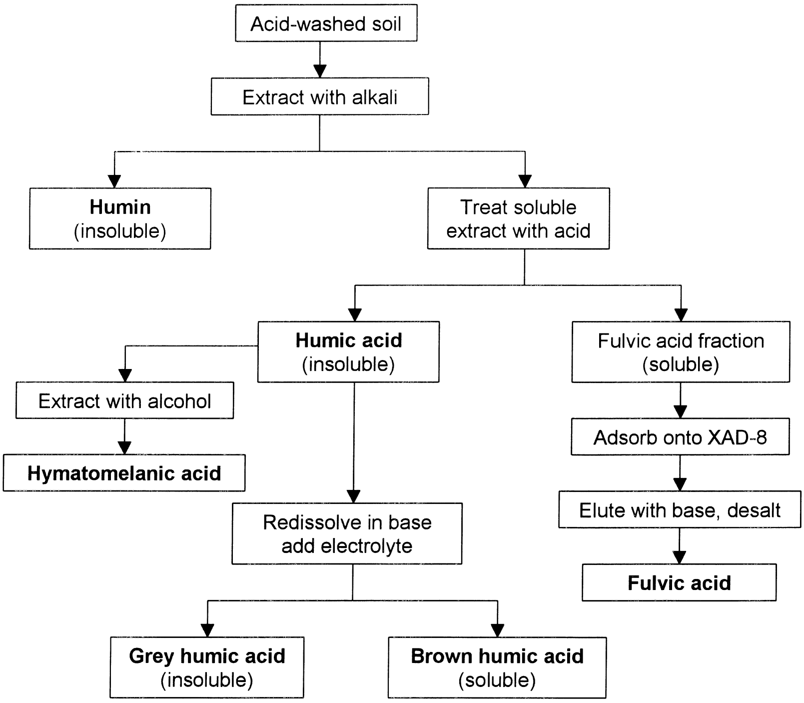

Figure 2.1. Scheme for the isolation of humic substances from soils. [Adapted from Stevenson, F.J. (1994), *Humus Chemistry: Genesis, Composition, Reactions,* 2nd edn., by permission of John Wiley & Sons, Inc.]

have argued that the standard methods of isolation introduce artefacts. According to Hayes (1985), ‘the classical extraction procedures use aqueous alkaline solvents and these give rise to partially oxidised and slightly degraded humic artefacts’. He argued that milder, but still efficient, methods should be sought. Shuman (1990) speculated that the isolation procedure for aquatic humic substances tends to select molecules with certain properties, leading to an unrepresentative, but relatively

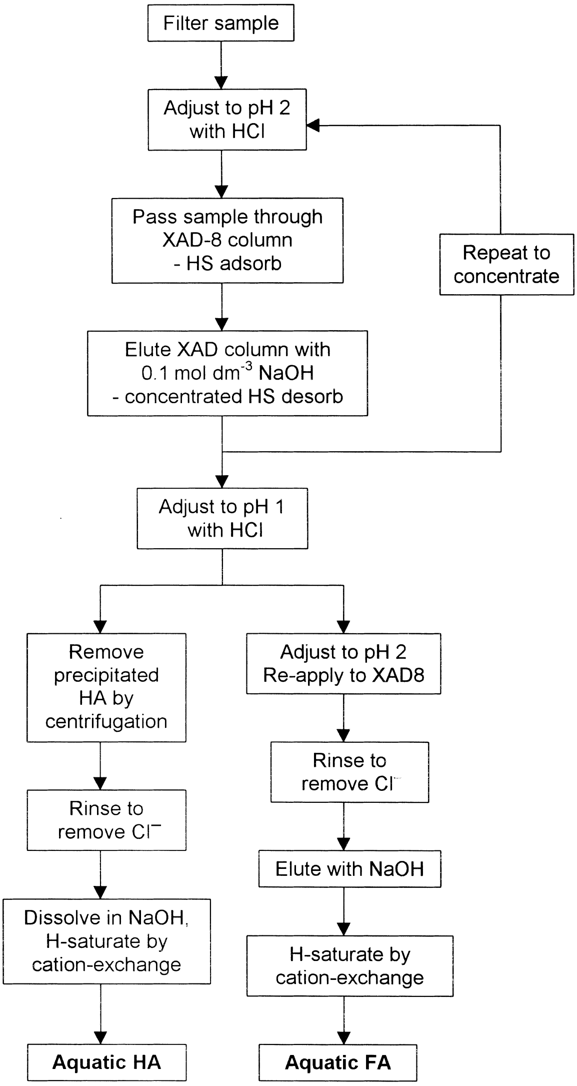

Figure 2.2. Scheme for the isolation of humic substances from waters, based on Aiken (1985).

uniform, isolated material. De Haan (1992) claimed that the extremes of pH to which aquatic humic substances are subjected during isolation (Fig. 2.2) cause artefacts. These concerns have led to alternative isolation methods, including extraction of soil humic matter with acidic dimethylsulphoxide (Hayes, 1985), and acid pyrophosphate (Gregor & Powell, 1987). Reverse osmosis, a purely physical method, has been used to concentrate dissolved organic matter from natural waters (Sun *et al.*, 1995), but other (unwanted) solutes are also concentrated.

Fractionation of humic acid can be achieved by extraction with alcohol, to obtain hymatomelanic acid, and by treatment of its solution in base with electrolyte, to obtain grey humic acid (precipitated) and brown humic acid (not precipitated). Fractionation has also been carried out successfully by gel chromatography, which separates the material by molecular weight (Swift, 1985). More extensive fractionation schemes have been developed for dissolved organic matter, the most well-established being that of Leenheer (1981), in which chromatographic separations are used to divide the sample into hydrophobic and hydrophilic fractions, each sub-divided into acidic, basic and neutral fractions. Table 2.2 shows suggestions for the components of the different fractions.

2.2.2 Buffle's classification scheme for natural organic matter

Buffle (1984, 1988) proposed a classification of natural organic matter that is ecologically orientated, being based on the identification of 'homologous compound groups', which correspond more closely to specific ecosystem functions than do fractions obtained from the analytically based separation schemes described above. Buffle defined natural organic matter as all the organic matter other than living organisms and synthetic compounds. The classification scheme is summarised in Table 2.3. Buffle (1988) explained in detail the natures of the different classes, and showed how they are related to the chemically fractionated humic substances. Buffle's scheme is arguably more logical, less restrictive, and more useful than the classification of humic substances (and non-humic substances) that currently holds sway. As yet there is not much evidence that other workers are adopting it in their research. However, at the very least it serves as a reminder that two samples of humic matter isolated by the same means may not have the same functional properties, and that differences may be related to the origins of the materials.

2.3 Formation and decomposition of humic substances

2.3.1 Formation

In most environments, the majority of dead biomass is converted to carbon dioxide, in the process of mineralisation. However, mineralisation is rarely complete, and therefore organic matter accumulates in the form of humic substances. The extent of accumulation depends upon turnover times, climate, vegetation, parent mineral material, topography and cropping (Stevenson, 1994). Humic substances are especially prevalent in

Table 2.2. Fractions obtained from the Leenheer (1981) fractionation scheme, and some of their likely non-anthropogenic constituents in surface and soil waters, based on Thurman (1985) and Qualls & Haines (1991).

	Hydrophobics	Hydrophilics
Acids	Fulvic acid Humic acid Humic-bound carbohydrates Simple aromatic acids Oxidised polyphenols Long-chain fatty acids Tannins Flavonoids Polyphenols Vanillin Proteins Phospholipids	Hydrophilic acids Simple carboxylic acids Oxidised carbohydrates with COOH groups Proteins Amino acids Adenosine di- and tri-phosphates Inositol and other sugar phosphates
Neutrals	Hydrocarbons Chlorophyll Carotenoids Phospholipids Low-acidity humic compounds Proteins Alcohols Ketones Ethers	Simple neutral sugars Polysaccharides Alcohols Ketones Ethers Proteins Amino acids Urea
Bases	Peptides Proteins	Amino-sugar polymers Pyrimidines Purines Amino acids Peptides Proteins Low molecular weight amines