Earth-Science Reviews, 14 (1978) 97—146

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The Nature of Metals–Sediment–Water Interactions in Freshwater Bodies, with Emphasis on the Role of Organic Matter

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ABSTRACT

Jackson, K.S., Jonasson, I.R. and Skippen, G.B., 1978. The nature of metals—sediment—water interactions in freshwater bodies, with emphasis on the role of organic matter. Earth-Sci. Rev., 14: 97—146.

A review with 227 references of the title subject is presented. It is divided into two main sections, viz., nature and properties of humic matter, and water—metal—sediment interactions.

The first section deals with the essential properties of organic matter which occurs naturally in drainage sediments and waters. Discussion of the basic molecular structure of humic and fulvic acids is followed by some details of the chemical nature of functional groups within these structures which are important in metal-ion adsorption and complexing reactions which these materials can undergo. Information is also presented for colloidal and polyelectrolyte properties, complexation properties, and finally a summary discussion of metal-ion—humic-acid, metal-ion—fulvic-acid stability constants for both single ligand and mixed ligand systems completes the section.

The second section comprises discussions of some specific aspects of interactions between metals, sediments and waters, including metal and organic speciation studies; sorption interactions between organic matter, clays and humic acids; chemical reaction between humic acids, heavy-metal minerals, clays and other silicate minerals; metal-ion adsorption—desorption studies, oxidation—reduction reactions between metal ions and humic acids; effects of sulphide ion on some of the above interactions and finally a summary of some relevant field geochemical dispersion studies.

This second section describes both laboratory and field studies for each aspect.

INTRODUCTION

This review attempts to cover a number of aspects of the hydrogeochemistry of naturally occurring organic acids as they relate to metal—sediment—water interactions. It is generally restricted to freshwater systems; the influences of seawater are noted only when they bear directly on some aspect of metal mobilization from sediments derived from freshwater systems.

It is apparent from the information contained in this review that much basic chemical information relevant to the nature of interactions between natural organic acids and metals is not yet available in the literature. There-

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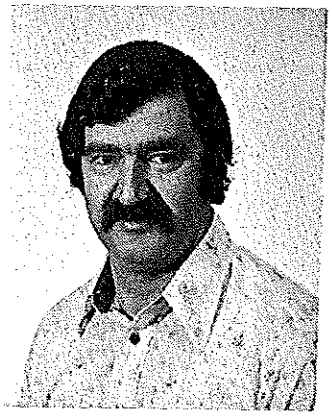

Ian R. Jonasson is a graduate of the University of Melbourne from the Department of Chemistry. He moved to the University of Adelaide where he completed his Ph.D. degree in 1967. Following a period of Post-Doctoral fellowships in Adelaide and in Ottawa he joined the Geological Survey of Canada in 1971. His research interests lie in a number of fields including geochemistry of sulphide ore deposits, studies of geochemical mechanisms of element dispersion in surficial environments and the development of methods for use in geochemical exploration.

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fore, it has proved to be a difficult task to provide a proper assessment of the quality of the information summarized here, given the diversity of data sources and the complexity of the natural systems described therein.

Firstly, the essential nature and structure of humic and fulvic acids, here considered to be the most important organic chemical entities in freshwaters, are summarized. Information pertinent to metal-organic complex formation, including some stability constants, is presented to provide a background for subsequent discussion of some organic chemical processes involved in metal mobilization and dispersion under field conditions.

Secondly and principally, the review is concerned with interaction processes and mechanisms where known. Some selected relevant literature has been gathered to embrace as wide a range of laboratory and field observations as possible. However, it is not practicable to include reference to *all* available information in the earth science literature, especially that which is essentially descriptive in character.

The great complexity of these interactions effectively precludes systematic categorization of different processes. However, the various sections which comprise this work are laid out in an order designed to illustrate different aspects of interaction mechanisms and the increasing complexities of the various natural systems which have been studied.

Within surficial waters, one significant process involves the interaction of trace elements with the complex, polymeric organic compounds which comprise humic matter (Bowen, 1966; Saxby, 1969). In rivers, swamps and soils, much of the organic carbon is present as humic matter. Humic matter in the environment has been reviewed by Swain (1963), Schnitzer and Khan (1972). Jackson, T.A. (1975) has also reviewed the literature on the nature and physicochemical properties of aquatic humic matter as well as its interactions with metals, metal oxides, clay particles and non-humic organic compounds.

The trace-element distribution between sediment and natural water and the chemical factors influencing this are of prime concern here. The dominant interactions involved are suggested to be cation hydrolysis, cation-exchange reactions, related absorption—desorption processes, and complex species formation with both organic and inorganic moieties. Effects of bacterial interactions on metals in sediments seem to be limited but nevertheless remain of prime importance for certain heavy metals (e.g., Wong et al., 1975: Pb; Chau et al., 1976: Se; Wood, 1974, 1975: Sn, Hg, As, Se). These last interactions, which deal with the production of alkyl-metals will not be discussed at length here.

NATURE AND PROPERTIES OF HUMIC AND FULVIC ACIDS

Introductory remarks

Humic matter is divided into three components: humic acid which is soluble in basic solutions, fulvic acid which is soluble in acidic and basic solu-

tions, and insoluble humins. It is important to note that no sharp divisions exist between humic acid, fulvic acid and humins. They are all part of an extremely heterogeneous polymer system and the differences between the subdivisions are due to variations in elemental composition, acidity, degree of polymerization and molecular weight. That fulvic and humic acids are indeed mixed polymer systems is further evidenced by their susceptibility to fractionation by techniques such as continuous electrophoresis (Manskaya and Drozdova, 1968).

Kemp and Wong (1974) determined the molecular-weight distribution of humic matter in some sediments from the Great Lakes region. Whilst humic acids are most prevalent in the high molecular-weight (M.W. >5000) range, fulvic acids are apparently evenly distributed over the entire M.W. range, 300—200,000. The organics in swampwaters and sediment interstitial waters are largely confined to the lowest M.W.'s i.e., >300.

Micro-organisms are, in part, responsible for the decomposition of organic materials in bottom sediments (Kuznetsov, 1975). In this way, interactions within bottom sediments are dynamic and continuous, low molecular-weight material is produced by the breakdown of higher polymeric forms which in turn may be formed by condensation of smaller molecules. Kuznetsov (1975) has observed that the products of such microbial activity depend largely on the amount and nature of the organic substances present. The importance of these reactions as controls on metal binding in sediments and metal release from sediment should not be overlooked.

Basic structure of humic and fulvic acids

A detailed discussion of the structural nature of humic and fulvic acids is not possible here. Reference should be made to the works of Khan and Schnitzer (1972), Ogner (1973), Gamble and Schnitzer (1973), Chakrabarty et al. (1974), Schnitzer and Skinner (1974), Kemp and Wong (1974) and also Manskaya and Drozdova (1968).

As summarized by Manskaya and Drozdova, X-ray data have shown that humic acids have variable structures, but basically, all have aromatic nuclei in the form of flat lattices of cyclic polymerized C connected to which are side chains which carry various functional groups. Humic acids differ in the quantitative relationships between the chains and the aromatic nuclei in the C skeleton. The elucidation of functional groups within the humic-acid molecule has been attained by instrumental analysis, e.g., infra-red and UV-visible spectroscopy, and chemical methods. Molecules of humic acid are now known to contain carboxyl, phenolic and alcoholic hydroxyl, methoxyl, carbonyl and quinone groups.

The humic-acid structure is likely based primarily on six-membered aromatic and heterocyclic rings. Certainly no single structural formula, such as that of Fuchs (Fig. 1) appears acceptable. Literature evidence favours a 'type' molecule consisting of micelles of polymeric nature, the basic structure of which is an aromatic ring of the di- or trihydroxyl phenol type

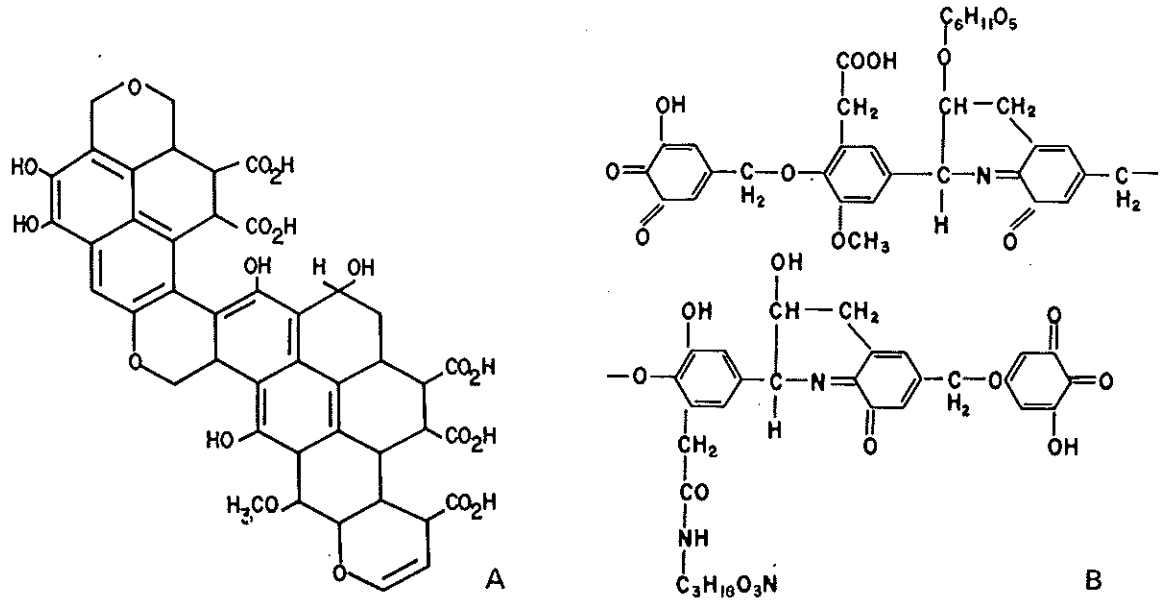


Fig. 1. A. Structure of humic acids according to Fuchs (see Swain, 1963). B. Structure of humic acid according to Dragunov (see Manskaya and Drozdova, 1968).

bridged by —O, —CH_2—, —NH—, —N=, —S—, and certain other groups, and containing both free —OH groups and the double linkages of quinones (Manskaya and Drozdova, 1968). Dragunov's formula (Fig. 1), as presented in Manskaya and Drozdova, meets many of these requirements but still seems to lack significant amounts of aromatic —COOH groups. Humic acids from lignite will differ from humic acids from soil and peat in that they are more highly condensed and have fewer side chains and functional groups.

Fulvic acids have been subjected to similar structural analyses. The functional groups identified in humic acids are also identified in fulvic acids but fulvic acids contain considerably more groups of an acidic nature, particularly — COOH (Stevenson and Butler, 1969). Gamble and Schnitzer (1973) concluded from X-ray and chemical evidence that fulvic acids contain aromatic rings which form an open structure in a two- or three-dimensional array. The open structure is held together at least partly by hydrogen bonds among the functional groups. They have proposed a potential structure as shown in Fig. 2.

Functional groups

More important than the structural networks of humic and fulvic acids are their functional group content. It are the functional groups of these molecules which determine their reactivity towards metals, other organic compounds and solid sediments. The important determinations are of total acidity, carboxyl groups, hydroxyl groups and carbonyl groups. Both carboxyl and phenolic hydroxyl groups will contribute to total acidity. As previously

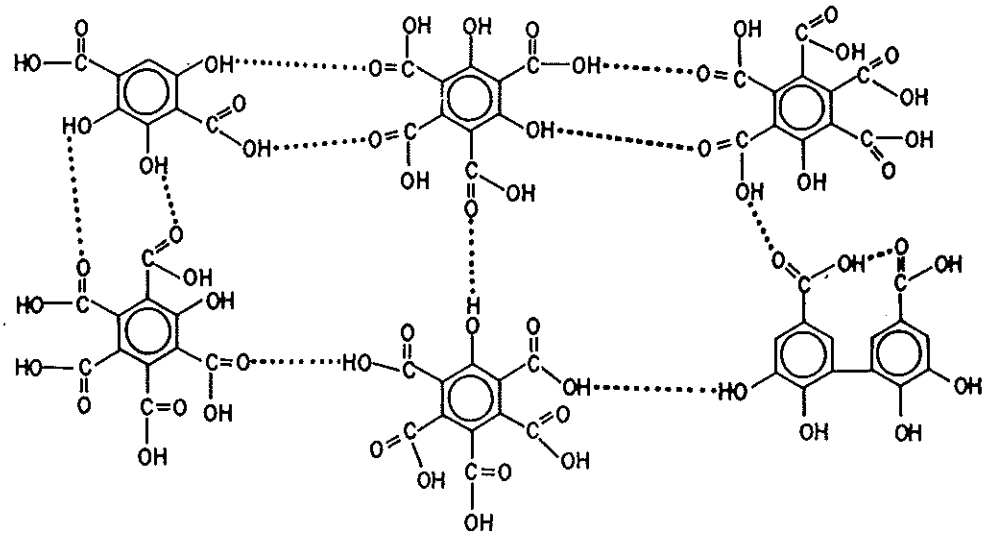


Fig. 2. Possible fulvic acid structure (Gamble and Schnitzer, 1973).

stated, it has been concluded that fulvic acids contain more functional groups, particularly carboxyl, per molecule than do humic acids. Manskaya and Drozdova report the numbers of functional groups per molecule of soil humic acid to be:

carboxyl	3—4
phenolic hydroxyl	3—4
methoxyl	up to 1—2% by weight
quinones	3—4

From the work of Schnitzer and Skinner (1965) and Gamble and Schnitzer (1973), the result for soil fulvic acid is:

carboxyl	6—8
phenolic hydroxyl	2—4
alcoholic hydroxyl	3—4
carbonyl	2—3

The absence of readily oxidizable quinone and amine groups in fulvic acids is compatible with a chemical degradation model for the formation of fulvic acid from humic materials. Bacterial degradation could achieve the same result. This is a significant result as the carboxyl and hydroxyl groups of humic substances are the most likely to react with cations. Fulvic acid should then have a higher capacity for interactions with metals.

Colloidal and polyelectrolyte properties

Other important aspects of the chemistry of these substances, as it bears upon water—sediment interactions and metal transfer, include their polyelec-

trolyte character and their colloidal properties (Van Dijk, 1971a).

Humic and fulvic acids behave as negatively charged species due to the ionization of their acidic carboxyl and hydroxyl groups. Neutralization of this charge, perhaps by interacting metal ions, can lead to flocculation of their colloids and further coprecipitation of metals.

Mechanisms by which metallic ions from natural waters are adsorbed or complexed by non-living organic matter have been discussed by many authors (e.g., Krauskopf, 1955; Curtis, 1966; Schnitzer and Khan, 1972). The attractive interaction of ions with soluble, colloidal or particulate organic material may range from weak forces leaving the ion easily replaceable (physical adsorption) to strong forces indistinguishable from chemical bonds (chemisorption or specific adsorption).

A general reaction scheme to describe the interaction of metal ions (M^{X+}) with dissolved organic matter (ORG) and clay particles (CP) has been proposed by Curtis (1966) and outlined in Fig. 3. According to the Curtis scheme, metal ions can show a positive, zero or negative correlation with carbon from particulate or sedimentary material. A positive correlation arises when metal ions interact in solution with dissolved organic matter forming complexes that in turn are concentrated by adsorption onto particulate matter such as clay particles. Zero and negative correlations result from no interaction between metal ions and organics in solution. The dissolved organic matter alone may then be adsorbed onto particulate matter to produce zero correlation, or the metal ions and dissolved organic matter may compete for adsorption onto the particulate matter hence producing a negative correlation.

Another reaction scheme proposed by Ong and Bisque (1968) and Ong et

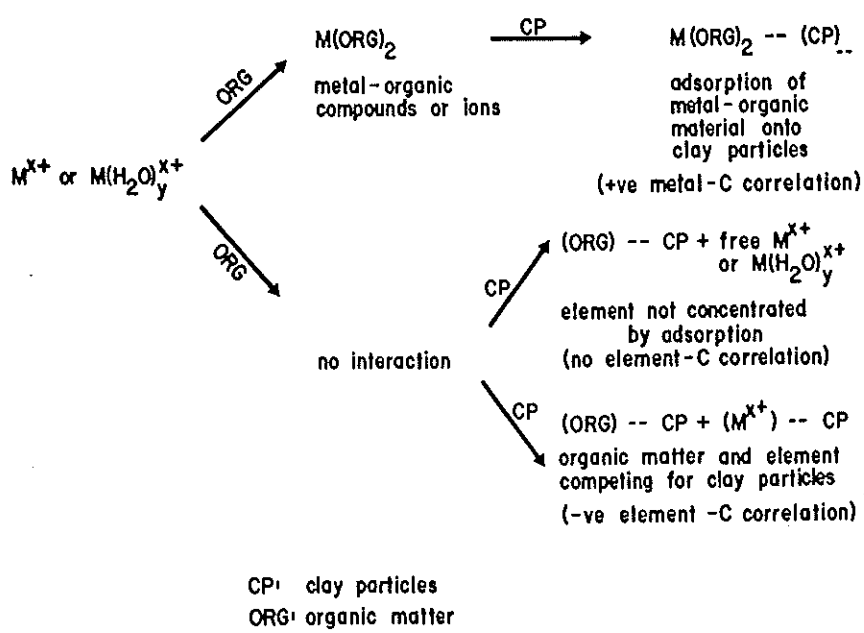


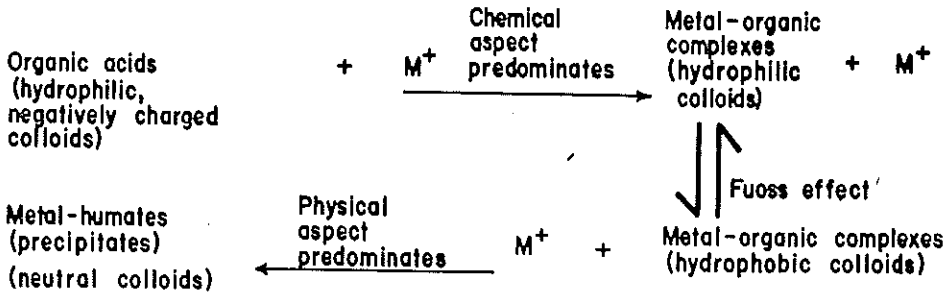
Fig. 3. Generalized metal—organic—solid reaction scheme as proposed by Curtis (1966).

al. (1970) is perhaps best regarded as a refinement of the Curtis scheme. The reaction scheme is presented in Fig. 4. The Fuoss effect refers to a change in shape of the humus or organic acid macromolecule upon the addition of salts. The change in shape causes the expulsion of part of the water of hydration and thus the humus macromolecule changes to a hydrophobic type of colloid. In effect, the addition of cations has reduced the charge of the polyelectrolyte and thus reduced the water of hydration held by the colloids. In aqueous solution, this leads to the precipitation of metal humates as essentially 'neutral' colloids.

Complexing properties

The terms metal—organic complex and metal—organic chelate are often treated as synonymous in the literature. In the strictest sense the term complex applies to a compound formed when a metal ion combines with an electron donor, although it is commonly used to refer to all types of interaction resulting in compound formation. If the ligand contains two or more donor groups, then one or more rings may be formed with the resulting structure being termed a chelate compound. Within the structures of humic and fulvic acids, salicyclic acid and/or phthalic acid type sites may be significant centres for metal reaction. These are bidentate sites and hence chelate would be the more accurate description of the resulting compound. However, minor but not insignificant reaction is feasible via sites which are electron donors but not polydentate. For this, the term complex is correct. However, in this review the term complex will be used in its general sense except where more specific information on the nature of the metal—organic compound is known.

Much evidence is in the literature to support chelation or complex formation as an important means of metal—organic interaction (for example, Mortensen, 1963). This was proposed as early as 1956 when Coleman et al. suggested that the binding of metal ions to acid-washed peat was similar to the retention of metals by polymeric acids, and by Broadbent (1955) who invoked acidic functional groups such as —COOH and coordinating func-



Fi.g 4. Metal—organic interaction scheme as proposed by Ong et al. (1970).

tional groups such as amino, cyclic amino or carbonyl as essential to the reaction.

The chemical blocking of specific functional groups has been reported by several authors in attempts to elucidate the interaction mechanism (Broadbent and Brandford, 1952; Schnitzer and Skinner, 1965; Davies et al., 1969; Gamble and Schnitzer, 1973). Of the functional groups present in humic and fulvic acids, it is generally agreed that three types control the organic complexing (Gamble and Schnitzer, 1973): (a) phenolic hydroxyl groups; (b) carboxyl groups particularly those ortho to the phenolic groups; and (c) all other ionizable functional groups probably including some carboxyl meta to the phenolic hydroxyl groups.

Infra-red spectroscopy has also demonstrated the presence of —COOH groups and carboxylate interaction with metals. The data of Theng et al. (1967) and Thompson and Chesters (1970) represent two examples of such work. The 1,720 cm^{-1} band characteristic of C=O, displays a shift to the 1600—1500 cm^{-1} region indicative of metal-carboxylate formation.

Van Dijk (1971b) concluded that metal humates belong to the polynuclear chelates with cations binding predominantly to the negatively charged ligand groupings of the humic acids. He also discusses a dependence on pH. At low pH, acidic and weakly acidic groups are thought to bind metals directly. At high pH, transition metals may form hydroxo-complexes with humic acids. Thus pH is expected to play a significant part in determining the strength of metal—organic interactions both in solution and at solid surfaces.

However, it should not be overlooked that because of the generally very low concentrations of trace elements in natural-water systems, such complexes may well be largely dissociated in solution with a significant proportion of the metal existing in ionic form (Stumm and Bilinski, 1972; Martell, 1975). On the other hand, influences of hydrolytic reactions on these free metal ions, coupled with natural-water pH near neutral, will ensure that much metal in hydrolysate form will be absorbed or otherwise bound to particulate matter such as metal oxides and clay, and to colloids. Thus studies in the total metal—organic—particulate system become difficult. Conventional chemical approaches to elucidate mechanisms of metal transport, metal fixing to sediments and metal or ligand remobilization are not particularly successful because of the heterogeneous nature of the various phases involved and the fact that such systems can be in a state of disequilibrium over the time of an experiment.

The acid ionization equilibria of humic and fulvic acids are pertinent to the present discussion. Gamble (1970) observed two general types of carboxyl groups in a fulvic acid sample. One of these is ortho to the phenolic hydroxyl while the other can be meta or para to the phenolic hydroxyl. For both types, whether in aqueous solution or 0.1 *M* KCl, ionization is almost total at pH 4. In both cases, an increasing degree of ionization resulted in a decreased acid strength. Theng et al. (1967) report the presence of carboxyl

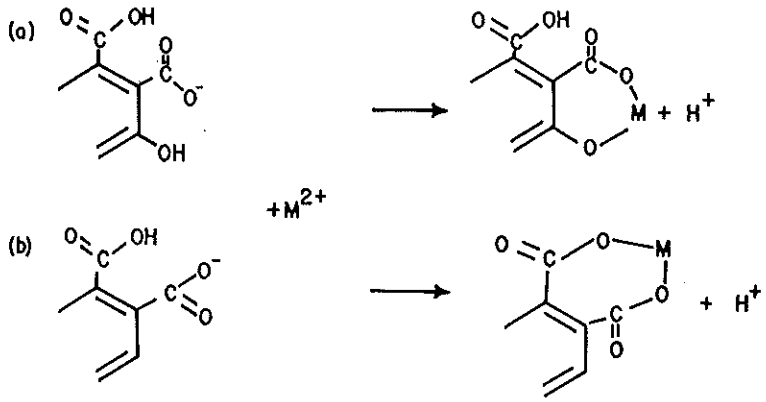


Fig. 5. Model mechanisms for complex formation.

groups ionizing above pH 7 and extending to as high as pH 11. However, it has also been reported that humic acid contains two types of weakly acid groups. Firstly, there are carboxyl groups dissociating up to pH 5—6 and secondly, phenolic OH groups dissociating beyond pH 7 (Chuveleva et al., 1962).

Two possible mechanisms, based on the Cu chelation reactions with salicylic and phthalic acids, have been proposed (Schnitzer and Skinner, 1965; Schnitzer and Hoffman, 1967; Gamble et al., 1970; Gamble and Schnitzer, 1973) and are shown in Fig. 5.

Electrovalent bonds from carboxyl groups to metals and coordinate covalent bonds from phenolic oxygen atoms to metals will be involved. Under natural conditions where trace-metal concentrations exist, reaction (a) via the salicylate linkage, is considered to be more feasible (Gamble and Schnitzer, 1973). Potentiometric titrations of fulvic acids complexed by metallic cations indicated that cations released on otherwise untitratable proton (Khanna and Stevenson, 1962; Schnitzer and Skinner, 1963). From this, reaction (a) is considered to be the correct description of cation—fulvic acid chelation. However, Manning and Ramamoorthy (1973), on the basis of their experimental data, suggest that bonding via phthalate type group (b) is more likely for the Cu^{2+}-fulvic acid reaction. The concentration of the salicylic-acid type, bidentate sites can be calculated according to the data of Gamble (1972) to give an average of about three sites per molecular weight.

Stability constants

Quantitative estimates of the stability and formation constants of several metal fulvates and humates have been reported frequently in the literature. Stability constants are thermodynamic quantities based on activities of the reacting species. In the case of humic and fulvic acid complexation reactions, activities are difficult to estimate. As a consequence, the stability constants reported are, in general, concentration stability constants. As a further point,

the reactants are prone to several competing side reactions, such as hydrolysis, which are rarely accounted for in the determination. Hence, the great bulk of the data presented are more correctly termed conditional stability constants, i.e., dependent on the experimental conditions. Gamble and Schnitzer (1973) provide a working example of thermodynamically derived stability constants which will have the advantage of being applicable under any set of experimental conditions. The order of stability for various metals is the same for thermodynamic and conditional stability constants. Within the natural environment, conditional stability constants are more likely indicative of the humic matter—cation interactions (Malcolm et al., 1970; Cheam and Gamble, 1974).

A further complication exists when comparing literature stability constants. The calculations of humic and fulvic acid concentrations have been based on either the number average molecular weight (for example, Schnitzer and Hansen, 1970) or on the total complexing sites (for example, Gamble et al., 1970; Cheam, 1973). Cheam and Gamble (1974) report an increase in log K from 3.2 for the complexing-sites method to 3.7 for the molecular weight method based on the Cu—fulvic-acid reactions.

The experimental procedures employed are varied and include ion exchange (Schnitzer and Skinner, 1966, 1967; Schnitzer and Hansen, 1970; Malcolm et al., 1970; Ardakani and Stevenson, 1972), continuous variations (Gamble et al., 1970; Schnitzer and Hansen, 1970), specific ion electrodes (Cheam, 1973; Manning and Ramamoorthy, 1973; Cheam and Gamble, 1974), potentiometric titrations, spectrophotometry (Andreyeva and Rybakova, 1974) and atomic absorption (Coleman et al., 1956; Khanna and Stevenson, 1962; Khan, 1969; Van Dijk, 1971b; Rashid, 1971; Stevenson et al., 1973). The chelates formed in these determinations are generally assumed to be 1 : 1-type complexes involving the bidentate salicylic-acid-type site. The calculations for the ion-exchange equilibrium technique are dependent on the formation of mononuclear complexes (Clark and Turner, 1969; Schnitzer and Hansen, 1970). A critical discussion of the measurement of metal complexing ability of polyfunctional macromolecules and of the experimental validity of reported stability constant data is available in Zunino et al. (1975).

pH is an important parameter due to its influence on the acid ionization and, at alkaline pH, the possible formation of metal-hydroxy organic complexes (Van Dijk, 1971b). Ionic strength is also most significant with log K generally decreasing with increasing ionic strength (Schnitzer and Hansen, 1970, and Fig. 6). Decreasing ionic strength causes the fulvic acid/cation ratio to fall below 1 and hence mixed or polynuclear (with respect to cation) complexes may form.

Irving and Williams (1948) published a stability order for complexes of bivalent metal ions which applied regardless of the complexing agent involved. The predicted order of stability would be Pd > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg. The Irving-Williams sequence cannot be expected

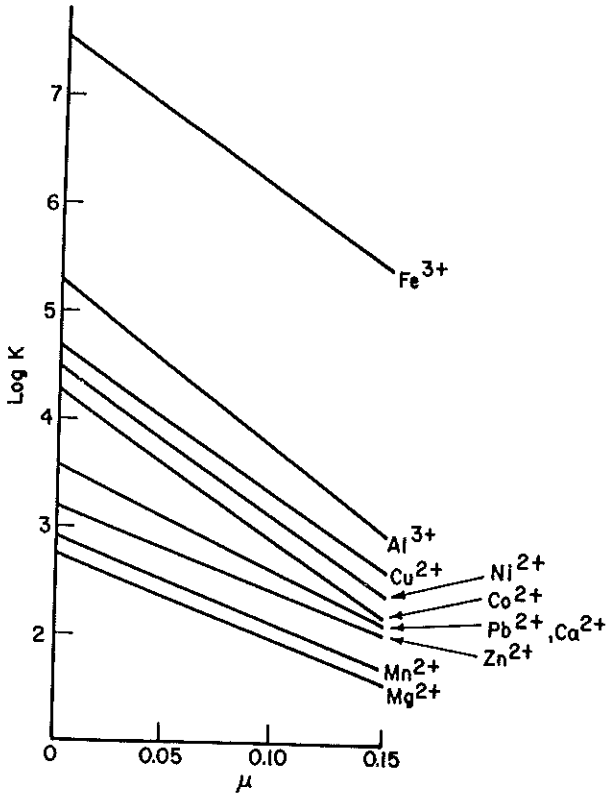


Fig. 6. Effect of ionic strength on log-K values of metal—fulvic acid complexes at pH 3 (Schnitzer and Khan, 1972).

to hold in general as stabilities change with temperature (e.g., Helgeson, 1969) and the order of conditional stability constants can change with ionic strength. Some of the reported data do follow this predicted stability order (Beckwith, 1959; Khanna and Stevenson, 1962; Khan, 1969); however, the bulk of the data would suggest that this stability order is not generally applicable to the humic- and fulvic-acid—metallic-cation reactions. It would be of interest to separate these metal complexes into those which form true inner-sphere chelates, e.g., Fe(II) with fulvic acid and those which form weaker outer-sphere complexes, e.g., Mn(II).

From the literature data, it is concluded that humic acid will form stronger complexes with cations than will fulvic acid, (see Tables I and II). Van Dijk (1971b) observed at pH 5 that humic-acid—divalent-ion binding strengths increased slightly in the order Ba, Ca, Mg, Mn, Co, Ni, Fe, and Zn. Pb(II), Cu(II), and Fe(III) were more firmly bound with stability increasing in the order, Pb, Cu, Fe.

Table I reports some of the available stability constant data for metallic cation-humic acid complexing. The reported data show reasonable agreement, with the data of Randhawa and Broadbent (1965b) being somewhat higher. Van Dijk (1971b) concluded, on the basis of his experiments, that variation between stability constants using humic acids from different sources is slight.

TABLE I

Some stability-constant data for humic acid-metallic cation complexing

pH	Cation	Log K	Reference
4.7	Cu(II)	6.05	Chmielewska (1969)
5.8	Cu(II)	8.08	Chmielewska (1969)
4.7	Co(II)	4.65	Chmielewska (1969)
5.8	Co(II)	6.90	Chmielewska (1969)
4.7	Zn(II)	4.18	Chmielewska (1969)
5.8	Zn(II)	5.82	Chmielewska (1969)
5.0	Cu(II)	7.00	Coupron (1967)
3.6	Zn(II)	4.42	Randhawa and Broadbent (1956b)
5.6	Zn(II)	6.18	Randhawa and Broadbent (1956b)
7.0	Zn(II)	6.80	Randhawa and Broadbent (1956b)
—	Hg(II)	5.23	Strohal and Huljev (1970)

Schnitzer and Hansen (1970) reported stability constant data for fulvic-acid—metallic-cations experimentally determined by both an ion exchange (I.E.) and a continuous variation (C.V.) method. The determinations were carried out at an ionic strength of 0.1; hence all the organo—metallic species will be mononuclear with respect to the metal. Their data are in good agreement with the literature. Although little variation was seen for the two methods (Table II), the authors favoured continuous variation procedures because of the lower susceptibility to analytical errors.

Cheam and Gamble (1974) have reported conditional stability constants for Hg(II), Cd(II) and Cu(II) fulvic acid complexes in 0.1 *M* $NaNO_3$ solutions. Their results are also included in Table 2.

At low pH, the stability order then is Fe(III) > Hg(II) > Al(III) > Cu(II) > Ni(II) > Co(II) > Pb(II) = Ca(II) > Zn(II) > Mn(II) > Mg(II). At pH 5, the order is Ni(II) = Co(II) > Pb(II) > Cu(II) > Zn(II) = Mn > Ca(II) > Cd(II) > Mg(II). It is interesting to note the promotion of Ni(II) and Pb(II) in the stability order with increasing pH although pH values of 5 are still outside the range of most natural surface waters.

Mixed ligand systems

Manning and Ramamoorthy (1973) studied the formation and stabilities of mixed ligand complexes of the type Cu(II)—fulvate—secondary ligand. The secondary ligands investigated were citrate, meso-tartrate, dl-tartrate, salicylate, phosphate, nitrilotriacetate (NTA), aspartate and glycine. For the Cu^{2+} system, the stability constants obtained were in good agreement with the data of Schnitzer and Hansen (1970). It was found that in neutral and weakly acidic solutions, mixed complexes predominate. The citrate, phosphate and NTA mixed complexes were particularly stable in comparison with the simple complex. The authors speculate on the possible significance

TABLE II

Stability constant data for metallic-cation—fulvic-acid complexes at 0.1 ionic strength

Metal	pH	Log K			Reference
		C.V.	I.E.	S.I.E.	
Cu(II)	3.0	3.3	3.3	—	1
	3.0	—	—	3.22	2
	4.0	—	—	3.72	2
	5.0	4.0	4.0	—	1
	5.0	—	—	4.35	2
Ni(II)	3.0	3.1	3.2	—	1
	5.0	4.2	4.2	—	1
Co(II)	3.0	2.9	2.8	—	1
	5.0	4.2	4.1	—	1
Pb(II)	3.0	2.6	2.7	—	1
	5.0	4.1	4.0	—	1
Ca(II)	3.0	2.6	2.7	—	1
	5.0	3.4	3.3	—	1
Zn(II)	3.0	2.4	2.2	—	1
	5.0	3.7	3.6	—	1
Mn(II)	3.0	2.1	2.2	—	1
	5.0	3.7	3.7	—	1
Mg(II)	3.0	1.9	1.9	—	1
	5.0	2.2	2.1	—	1
Hg(II)	3.0	—	—	4.86	2
	4.0	—	—	5.08	2
Cd(II)	4.9	—	—	3.04	2
	5.95	—	—	3.64	2
Fe(III)	1.70	6.10	—	—	1
Al(III)	1.70	—	3.7	—	1
	2.35	3.7	—	—	1

Notes: C.V. = continuous variation; I.E. = ion exchange; S.I.E. = specific ion electrode.
References: 1 = Schnitzer and Hansen (1970); 2 = Cheam and Gamble (1974).

of other oxyanions, SO_4^{2-} and HCO_3^- in similar mixed ligand complex systems. The formation of mixed complexes can apparently inhibit precipitation of metallic cations as phosphates, possible sulphates and carbonates, and as hydrolysed species.

Only recently has any real attempt been made to characterize metal—bicarbonate complexes which are clearly important participants in metal ion transport in fluvial systems. Before a meaningful study of mixed ligand systems, which are likely very common in natural waters, can be undertaken, further data to elucidate the nature of simple interactions such as the forma-

tion of metal—HCO_3^- complexes at appropriate pH ranges must become available. Bilinski et al. (1976) have published some stability constant data on CO_3^{2-} and OH^- complexes of Pb(II), Cu(II), Cd(II) and Zn(II) ions using anodic stripping voltammetry and differential pulse polarography.

They found an order of complex stability of MCO_3^0, viz., Pb > Cu > Zn > Cd and that only Pb(II) and Cu(II) formed $M(CO_3)_2^{2-}$ complexes. They concluded that relative to hydroxocomplexes, the carbonate complexes of Zn and Cd can have no significance in natural waters. These metals probably are present in natural waters mainly as hydroxo- or aquo-ions. Bicarbonate complexes likely do not exist for Pb(II), Cu(II), Zn(II), and Cd(II). Thus, in natural waters, especially springwaters, which contain considerable dissolved CO_3^{2-}, Pb and Cu could become more solubilized and rendered more mobile. However, Stumm and Bilinski (1972) found out that $PbCO_3^0$ adsorbs more strongly to silica surfaces than aquo-Pb ion. It is also likely that $PbOH^+$ adsorbs more strongly than aquo-Pb ion. These processes would effectively restrict Pb mobility and tend to counteract complexation effects.

The complexities of natural systems, such as a stream drainage system or a soil, cause one to view with caution the stability constants quoted in the literature. Perrin (1965) points out that in any system, the major complexes that are formed, and their concentration, will be determined by the stability constants of all possible complexes, the pH of the solution, the pK_a value of the complexing species and the total concentrations of each metal and each complexing species present. The mixed ligand systems studied by Manning and Ramamoorthy (1973) represent a simple example of this effect with a predominance of mixed ligand systems predicted. To handle complex systems, Perrin (1965) describes a computer programme which will calculate equilibrium concentrations of both free and complexed metals and ligands. The application of such a programme to a geochemical field problem suffers from a lack of many of the required parameters such as a knowledge of organic ligand speciation. Stumm and Bilinski (1972) set up such a programme for mixed metal-mixed ligand systems (9 × 9) at pH 8. It was designed to simulate a natural water where ligands are usually in concentrations $<10^{-6}$ M. Their calculations suggested that aquo, hydroxo- and carbonato-complexes would predominate. However, simulated models as described by Stumm and Bilinski (1972) may be inadequate because stability constants for natural organic ligand-metal complexes have not been satisfactorily measured at alkaline pH (7—9); this is especially true for humic and fulvic acid complexes. Therefore their role as complexers in natural waters should not yet be disregarded.

Nevertheless, such models should be tested for natural waters more enriched in soluble organic matter, e.g., simulated marsh and swampwaters, where ligand concentrations may be one or two orders of magnitude greater than 10^{-6} M. Under these conditions organic chelates might be expected to become more significant in metal binding and dispersion processes.

WATER—METAL—SEDIMENT INTERACTIONS

Metal and organic speciation in surface waters

The ubiquity of organic carbon within stream and lake sediments and waters is well known. Bordovskiy (1965) considers that, as has been observed in soils, the great bulk of organic matter within sediments and natural waters comprises complex, polymeric humic matter. Within natural waters, the organic carbon content is commonly in the range 0.1—10 mg carbon/l (Stumm and Morgan, 1970) and is negatively charged (Black and Christman, 1963). This is consistent with a humic, polyelectrolytic character. The humic matter of natural waters and sediments is derived, in part, by leaching or eroding of soil (allochthonous origin) and, in part, from the cellular constituents and exudates of indigenous aquatic organisms (autochthonous origin) (Bordovskiy, 1965; Nissenbaum and Kaplan, 1972).

The vast majority of reported humic and fulvic acid chemical characterizations have been for soil extracted material.

However, a number of attempts have been made to characterize the dissolved yellow organic matter commonly observed in natural waters of streams, lakes and marshes. The methods for extraction of these materials have often been described (e.g., Milanovich et al., 1975). Humic materials from marsh waters were studied by Fotiyev (1971) who found that they comprise mainly fulvic acids in which silica was a common constituent. He concluded that silica was solubilized and stabilized as some adduct with fulvic acid. Maier et al. (1975) discussed the occurrence, nature and reactivity of yellow organic matter in some surface waters of the U.S.A. Their summary of the relevant literature suggests that fluvial organics are a mixture of aliphatic polyhydroxy carboxylic acids, fulvic acids and other aromatic polyhydroxy carboxylic acids, various phenols and some amines. The reactivity of these yellow organics towards metal ions is apparent with such complexing ligands present.

Shapiro (1964), Christman (1970) and Beck et al. (1974), have characterized spectroscopically the organic matter observed in some natural waters as being fulvic-acid-type compounds due to their complex, polymeric nature and an abundance of phenolic and benzenecarboxylic groups. Nissenbaum et al. (1971) observed that polymerized organic matter (possibly humic substances) accounted for about half of the total dissolved organic matter in interstitial waters of the reducing Saanich Inlet (British Columbia) sediment. The main constituents of river-water organic matter are generally considered to be humic substances (Lamar, 1968). Simpler organic compounds, for example amino acids, carbohydrates and sterols (Prashnowsky et al., 1971), are commonly detected within natural waters but their potential metal chelation capacity is well below that of the humic substances. The available evidence indicates that aquatic humic substances are essentially identical to the humic substances of soils, particularly podzols (Bordovskiy, 1965; Christ-

man, 1970; Stevenson and Goh, 1971). Aqueous humic matter tends to be more highly aliphatic, less condensed, poorer in phenolic groups but richer in carbonyl and carboxyl groups than soil humic matter (Bordovskiy, 1965; Ishiwatari, 1966; Otsuki and Hanya, 1967; Rashid and King, 1970; Nissenbaum and Kaplan, 1972).

As pointed out by Stumm and Morgan (1970), the formation of metal—organic complexes within natural waters is frequently postulated to account for the occurrence of trace metals at concentrations higher than those expected from known solubility products. On a molar basis, the concentration of potential organic—metal complexing agents is significantly higher than the concentrations of such metals as Cu, Zn, Pb, Ni, Cd, and Co. However, the effect of the usually more abundant inorganic ligands such as SO_4^{2-}, Cl^-, OH^-, CO_3^{2-} must also be taken into account when discussing metal speciation within natural waters (Bilinski et al., 1976). Morel et al. (1973) have developed computer programmes aimed at speciation of metal ions and ligands, inorganic and organic, in *natural* waters. In inorganic systems, the general pattern found was free metal ions at low pH with carbonates, oxides, hydroxides and silicates becoming predominant in this order with increasing pH. For a reducing environment, insoluble sulphides dominate. Computation of the inorganic system in the presence of citrate, nitrilotriacetate (NTA), cysteine and glycine led to the conclusion that organic ligands *can* play a major role in natural waters by forming soluble metal complexes but, due to the numerous uncertainties involved, little else could be said.

On the other hand, Stumm and Bilinski (1972) have published an eloquent discussion of the problems involved in the elucidation of the nature of metal speciation in natural waters. The authors consider that most trace-metal ions are present as aquo-, hydroxo- or carbonato-complexes, sols and colloids, rather than as truly soluble metal—organic chelates. They consider it doubtful whether individual ligands are present in high enough concentrations, typically less than 10^{-6} *M*, to influence the speciation of trace metals at similar concentrations. Moreover, the presence of relatively overwhelming quantities of say, Ca^{2+} and Mg^{2+}, themselves prone to strong complexing, would likely account for the consumption of all available ligand. Stumm and Bilinski (1972) consider that the significant role of dissolved organic matter may well be confined to the generation of humic protected colloids of very finely dispersed particles of oxides and simple inorganic complexes. But whatever the true mechanism of metal binding and transport, it is clear that dissolved organic matter is a key participant. Solutions to the problems of metal ion speciation in very dilute solution will have to await more detailed research.

More recently, some very powerful analytical tools have come into use whereby metal ion speciation in natural waters can now be studied directly. Anodic stripping voltammetry (e.g., Zirino and Healy, 1972; Nürnberg and Valenta, 1975) can be used to demonstrate the importance of complexation reactions and to measure apparent stability constants for the complexes

formed between metal ions and dissolved organics in lake (Chau et al., 1974) and river waters (Ramamoorthy and Kushner, 1975). But as Langford and Gamble (1974) have pointed out, this application is limited to relatively 'non-labile' metal complexes with large organic ligands. Langford and Gamble suggest that a study of the kinetics of formation of such metal—organic complexes would be informative in speciation studies in that mechanisms of reaction can help to predict natural solution equilibria. Faster reactions involving the formation of kinetically more labile complexes could be studied by fast reaction techniques such as stopped flow spectroscopy.

Other methods which permit the study of rapidly established equilibria include anodic stripping at a ring disc electrode and technique called 'medium exchange' (for details see Shuman and Michael, 1975). Raspov et al. (1975) studied the formation of a Cd(II)—NTA complex in seawater using differential pulsed polarography. Experiments were carried out where the stability of the complex was determined in the presence of Cl^- which competes for Ca^{2+}, and Ca^{2+} and Mg^{2+} which compete for the NTA ligand. Bilinski et al. (1976) used similar techniques to measure stability constants for some hydroxo- and carbonato-complexes of Pb(II), Cu(II), Cd(II) and Zn(II), important species in most surficial waters.

Benes and Steinnes (1974) have described in situ dialysis experiments which permit characterization of truly dissolved and colloidal forms of trace elements in natural waters without influence from adsorption processes. Analyses of trace elements in equilibrated dialysis cells were by neutron activation. A river-water specimen was analyzed in situ for a number of elements including Mn, Zn, Sb, V, Cr, Fe, and Co, and except for Mn which became subject to oxidation during the experiment, losses due to adsorption onto cell walls were not significant. Surface adsorption of Mn is promoted by oxidation of the Mn(II) state. Sb and Co were found to be present in dissolved form at 80%; Mn, Zn, V, Cr were present as 50% dissolved. Fe was present mainly in colloidal form and only 20% dissolved.

Chau et al. (1974) devised a method for measuring 'apparent complexing capacity' of lake waters utilizing Cu^{2+} ion. Free of 'labile' Cu^{2+}, present in the system under study, was measured by anodic stripping voltammetry after a water spiked with Cu was allowed to come to solution equilibrium. The masking of aquo-Cu^{2+} ion was attributable to the presence of complexing ligands in the lake water at pH ~8. Metal ions such as Fe^{3+} and Pb^{2+} which form complexes at least as strong as Cu^{2+}, interfered with the measurement. Apparently Cu^{2+} could not displace them from the complexing ligands in the time of the experiment, or perhaps not at all. Experiments such as these have limited application; however, they do indicate that small quantities of organic matter do interact with metal ions in natural waters.

Similar work by Ramamoorthy and Kushner (1975) yielded similar results for river water. In this case, specific ion electrodes were used to determine 'free' or 'labile' metal ion when spikes of Hg^{2+}, Pb^{2+}, Cu^{2+}, or Cd^{2+} were added. They found that 'apparent complexing capacity' measured depends

on the strength of binding of a given metal ion. In this case, binding strength decreases in the order Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}. Complexing capacity was attributed to soluble organic matter, perhaps fulvic acids. It follows that the use of Hg^{2+} ion would be a good choice for ion competition or ion displacement experiments since its very strong binding character, or rather the inability of many other cations to displace it, (e.g., Strohal and Huljev, 1970) will likely yield maximal 'apparent complexing capacity'. The principal objection to these types of experiments lies in the highly variable nature of dissolved organic matter in natural waters; it is difficult to apply conclusions drawn from one particular environment, e.g., marsh or swamp, to another, e.g., lake or river water.

Pauli (1975) conducted experiments with 'aqua humus' to determine some other important parameters, viz., those which relate to the kinetics of metal sorption into the humus. Pauli compared the extent of complex formation after 20 days for a number of metals and found an order of increasing quantity of complexed metal ions, $UO_2^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Pb^{2+} > Cd^{2+}$. UO_2^{2+} formed complexes very much faster than any of the others, an observation indicative of the relatively greater strength of binding of UO_2^{2+} to humic acids. The ability of dissolved humic matter to mobilize and disperse UO_2^{2+} in natural systems is well known. In view of these results it can be suggested that UO_2^{2+} would also be an ideal ion on which to base comparative studies of metal ion binding, especially over a wide pH range, in view of its strength of adherence and the fact that it is relatively unaffected by competing hydrolytic reactions up to about pH 7.0.

Cline et al. (1973) concluded that Hg can be mobilized in fluvial systems as soluble species, viz., metal—organic complexes or as organic colloids and suspensions. Distribution studies between waters and sediments of the St. Clair River system suggested that particulates were likely more important. Pore waters were thought to contain Hg as organic complexes in a colloidal state.

Matson et al. (1969) have shown that Cd, Pb, Cu does not exist in free ionic form in waters of the Great Lakes, but rather as organic complexes. Relative strengths of complexes of Fe^{3+}, Co^{2+}, Pb^{2+}, and Cu^{2+} were measured. Dissociation rates of such complexes and exchange rates with H^+ and other metal ions ranged from minutes to hours.

Nissenbaum et al. (1971) have suggested the occurrence of metal—organic complexes in interstitial waters based on the observation of large concentrations of Fe, Zn, Co, Ni, Pb and Ag associated with the soluble organic matter. Barsdate (1970) and Shapiro (1964) also reported evidence which, indirectly, suggests that various metals in lake water are to a large extent bound to humic substances. The association between Fe and humic matter in natural waters has been discussed by several authors (Shapiro, 1964; Lamar, 1968; Akiyama, 1971; Christman and Minear, 1971; Plumb and Lee, 1973). The iron may be in the form of peptized ferric hydroxide sols as well as organically chelated ions. Curtin et al. (1970) have tentatively suggested the

presence of gold as soluble organic complexes within a forest humus layer. The work of Boyle et al. (1975) confirms this proposal. Experimental work showed that Au forms soluble humic compounds. Stiff (1971), in analyses of polluted surface freshwaters including river water, concluded that soluble Cu would consist almost entirely of complexed species. Humic-matter complex species were identified as hexanol-extractable Cu; chromatographic procedures separated amino acid and polypeptide Cu complexes. Carbonate and cyanide complexes were also indicated. Carbonate and amino acid-polypeptide complexes were most abundant.

It is apparent from the above summaries that little progress has been made in identifying specific organic and metal—organic species in natural waters. Weight of evidence seems to indicate that metal—organic 'complexes' do exist in interstitial waters and that some strong associations are detectable in surface waters. However, it is unclear whether true co-ordination complexes, ion-pairs or loose ion-colloid assemblages are the dominant species. In view of the work of Benes and Steinnes (1974), it would seem likely that organic-colloid—metal-hydrolysate-colloid interactions could be more important for metals such as Fe^{3+} in natural waters. However, experiments to test this model have yet to be devised.

Element concentration by organics via sorption processes

The formation of a geochemical anomaly within soils and sediments is dependent upon the retention of heavy metals by inorganic or organic components or both. Several factors, including pH, redox potential, inorganic mineralogy and humus content, will affect this retention mechanism. It has also been observed that a number of base-metal sulphide deposits have organic-carbon contents considerably above the average for shales and this has prompted several authors to propose 'organic' processes as playing a significant, possibly critical role, in the concentration and transport of the ore metals (Krauskopf, 1955; Brongersma-Sanders, 1965; Roberts, 1973, Pauli, 1975). The primary source of organic carbon, although uncertain, may well be algae (Brongersma-Sanders, 1965; 1966; and Roberts, 1973). Ferguson and Bubela (1974) conducted laboratory experiments designed to test this hypothesis. Using aqueous solutions of Cu(II), Pb(II), and Zn(II) interacting with organic matter derived from fresh algae specimens, they were able to show that, under suitable conditions, a significant proportion of the metals is removed from solution by sorption onto the particulate organic matter of the algal suspension. The chemical characteristics of the metal sorption are considered similar in some respects to those of the metal-humic matter reactions. It was concluded that such an organic process could form a sedimentary ore deposit if the metal 'saturation' values of the algal materials were reached, but this could only be approached in solutions already enriched in metals. Such conditions might be approached in some geothermal and fumarolic fluids. However, the role of the solid adsorbent phase in forming

geochemical anomalies within sedimentary materials is of more relevance to this review. More specifically, the influence of sedimentary organic detrital material will be discussed.

The work of Förstner and his colleagues (Förstner and Müller, 1973; Förstner and Patchineelam, 1976; Förstner, 1977) in their studies of metal remobilization in the waters and sediments of some German river systems illustrates the great complexity of the problem. They suggested that metal transport is via solid or particulate dispersion of detritus, calcareous and hydrolysate precipitates of Fe and Mn oxides, and ionic or complex adsorbed phases on clays and humic matter. Remobilization into true solution is promoted by decrease in pH, decrease in dissolved oxygen and increase in salinity.

The ability of solid humic matter to adsorb metals physically and chemically from aqueous solution has been well documented. Rashid (1974) investigated metal absorption onto sedimentary and peat humic acids. A solution adjusted to pH 7.0 and containing equal concentrations of Co, Cu, Mn, Ni, and Zn was brought into contact with humic acid and also peatmoss, a rich source of humic compounds. Cu was preferentially adsorbed. Leaching, by various reagents, of the metal—solid organic matter phase implied that the Cu was far more strongly sorbed than the other metals. Little variation in the strengths of Co, Mn, Ni and Zn sorption was observed. It is apparent that the chemical aspect of sorption is predominant over the weaker physical sorption in the case of Cu. An experiment to absorb base metals from seawater by peatmoss failed, probably due to the low content of these metals and the supersaturation with respect to the alkali and alkaline earth elements. This is an important consideration when interpreting field data because, as for seawater, natural surface waters are loaded with Na, K, Ca, and Mg compared with the base metals Cu, Pb, Zn, and Ni.

Chowdhury and Bose (1970) investigated the reactions and equilibria of suspended soil humic matter with dilute solutions of the heavy metals, Cu, Pb, Zn, Ni, and Co, at pH values up to 5. The stability of the metal—particulate organic species formed increased in the order, Co < Ni < Zn < Cu < Pb, which is consistent with the data of Rashid (1974). At pH < 1, there was an almost complete release of all metals. However, at pH values pertinent to natural conditions, Pb and Cu proved most resistent to leaching from the soil humus. This organic retention mechanism would then favour the formation of geochemical anomalies due to enrichment in Cu and Pb.

Several other workers have investigated the variability of metal—humic matter binding strengths by leaching experiments (Broadbent, 1957; Lewis and Broadbent, 1961; Randhawa and Broadbent, 1965a, b; Davies et al., 1969). The differences in stabilities of the various metal—humic matter complexes were indicated by varying degrees of metal retention against the acids and buffers used.

The kinetics of the ion-exchange phenomena involving solid humic matter and metallic cations is poorly understood. Bunzl (1974) studied the ion

exchange between solid humic substances and Pb(II). The uptake of Pb by both humic substances and an ion-exchange resin proceeded, as a function of time, according to a characteristic sigmoidal curve. The ion-exchange characteristics were found to be consistent with theoretical consideration based on a film diffusion process as the rate-determining step.

Garkusha et al. (1974) investigated the nature of binding of Fe(III), Ni(II), Co(II) and Cu(II) ions by lignin. They consider that uptake is likely as an ion-exchange process with complexation taking place via phenolic hydroxyl and carboxyl groups. Kishk and Hassan (1973) prepared adsorption isotherms for Cu^{2+} ions on humic acids at pH 2—6. Data could be fitted readily to Freundlich curves, again suggesting that ion exchange mechanisms may be involved.

Reimers et al. (1973) and Reimers and Krenkel (1974) observed the adsorption—desorption kinetics of Hg ions onto organic sediments at different pH. The adsorption of mercuric ions is diminished by high chloride concentration indicating that chloro-complexes are less strongly adsorbed by organic substrates. The organic sediments used in these experiments were synthetic, consisting of sand surfaces doped with stearic acid, octadecylamine or dodecanethiol. Sorption of mercuric ions and methylmercury ions was very rapid, but desorption was not observed in the time of the experiments. The degree and strength of metal ion adsorption onto organic-covered sands was much greater than for metals interacting only with sand, kaolinite or montmorillonite. These experiments support the thesis that specific adsorption of Hg ions takes place on organic matter; perhaps complex formation also occurs.

Uptake of organic matter by humic acids

Another aspect of humic acid sorption phenomena is the capacity to absorb hydrophobic organic compounds. Khan and Schnitzer (1972) concluded that 100 g of humic acid can firmly retain up to 2 g, and possibly more, or hydrophobic organic compounds. Adsorption on external surfaces and in internal voids of a molecular-sieve type structure is thought to be involved. Other authors have published data which confirm the ability of particulate humic matter in absorbing organic compounds, some of which may be toxic pollutants (Ogner and Schnitzer, 1970; Hsu and Bartha, 1973; Khan, 1973a, b; Pierce et al., 1974; Khan and Mazurkewich, 1974). This mechanism could be particularly significant in controlling the mobility of persistent organic pollutants and their subsequent concentration upon sedimentation.

Reactions of humic matter with mineral surfaces

Organic matter also interacts strongly with clay (Greenland, 1971) and other mineral surfaces forming very stable entities upon which further metal

or organic sorption reactions may take place (e.g., Gucket et al., 1975).

Theng (1976) studied interactions in the system metal ion—montmorillonite—fulvic acid at pH 7. Metal-saturated fulvic acid is postulated to absorb to the clay surface by hydrogen bonding via the acid anion and the hydration shell of the metal ion, e.g., for Ba^{2+}, Cu^{2+}, Ca^{2+}, Zn^{2+}, and La^{3+}. Evidence for loose binding is indicated by the fact that most of the metal ion can be desorbed from the clay by washing with water. For Al^{3+}, Cu^{2+}, and Fe^{3+}, surface interaction is strong and suggests further specific binding of the metal—fulvic-acid chelate to the clay surface involving complexation between clay and metal. Similar results are described by Schnitzer and Kodama (1972) who observed the system fulvic acid—Cu(II) ion—montmorillonite. Fulvic acid interacts strongly with Cu^{2+} adsorbed on montmorillonite but the effects decreased with increasing pH perhaps indicating the increasing importance of competitive hydrolytic influences. Apparently montmorillonite imposes unusual strained molecular configurations upon the adsorbed fulvic acid which in turn induces strong chelation with Cu^{2+} ions.

These effects of clays upon metal-ion binding, in which the clay behaves as a template for selected adsorption and chemical interactions, may well be very important in a number of respects. A clay template may promote specific metal-ion complexation interactions as noted above or alternatively they may promote cleavage of the fulvic acids in certain well-defined ways. Such processes have been proposed from time to time as models for specific decomposition behaviour of organic substances adsorbed on clays in processes which eventually may lead to the formation of petroleum during sediment diagenesis. However, the situation is further complicated by the fact that humic and fulvic acids also are instrumental in decomposing the clay on which they are sorbed (Tan, 1975).

Another important aspect of organic matter reactions with mineral surfaces deals with the use of calcium carbonate (or limestone particles) as a scavenger of dissolved yellow organic acids in natural waters. Otsuki and Wetzel (1973), who sought such methods of cleaning natural waters, found that the organic acids adsorbed very strongly to crystallizing calcium carbonate particles and were thus effectively co-precipitated from solution. Moreover, the similar behaviour observed for both the natural organic acids and added lipid materials towards calcium carbonate particles lends support to their idea that these compounds are chemically similar. Work by Suess (1973) along similar lines supports the observation that strong adsorption of dissolved organic acid takes place on calcite surfaces. Inspection of the data of Cheam and Gamble (1974) reveals that Ca^{2+} forms strong associations with fulvic acid. It seems likely that Ca^{2+} may exhibit similar affinities towards these yellow organic acids during the co-precipitation process.

The effects of natural heterogeneous interactions such as these on the mobility of heavy-metal ions and their complexes with organic matter, are apparent.

Mineral dissolution by organic acids

The ability of organic acids to leach, reduce and dissolve minerals has been studied by many authors including the very early work of Harrar (1929) and Fetzer (1946). The dispersion of elements as effected by this mechanism, which probably involves oxidation—reduction reactions as well as complexation phenomena, has considerable geochemical significance. Some examples of typical experimental studies follow.

Evans (1964) used sodium adenosine triphosphate (ATP) to dissolve calcite, apatite, augite, rhodonite, malachite, rhodochrosite, galena, siderite, dolomite, kaolinite and gypsum. Alumina, gelatinous silica and hydrated ferric oxides were not soluble. Similar results were obtained with other biochemical compounds which may find their way into natural waters.

Soluble humic matter reactions with sulphidic minerals are most relevant to a study of gossan formation and to the dispersion of trace metals produced from organic acid attacks of sulphide ores. Bondarenko (1968) studied the reaction of fulvic acid with galena. Fulvic acid was found to dissolve galena 10—60 times more rapidly than water containing no organic matter at the same pH. Baker (1973) found that the humic acid attack on sulphide minerals was quite variable with, for example, chalcopyrite yielding 140 μg Cu per day, whereas chalcocite released 15,000 μg Cu per day. A tentative correlation with bond strength has been suggested from the data as evidenced by the increased reactivity of galena compared with sphalerite. Baker also found that humic acid readily attacked hematite and pyrolusite. This process might inhibit gossan formation under appropriate conditions or alternatively, promote their disintegration once formed. Base-metal sulphides were strongly attacked by humic acid solutions and a far weaker but still significant release of Ag and Au was also observed. Humic acids are clearly very powerful agents in leaching solutions.

Evidence such as this from the literature suggests Ni, Cu and Pb are rendered the most mobile, i.e., they probably form the most stable, soluble complexes with humic acid. Fisher et al. (1974) noted that natural organic acids react with Au to form very stable fulvate complexes. They consider that the anion complex $AuCl_4^-$ is involved in the reaction.

Humic acids also appear to have the ability to mobilize a wide variety of metal ions in rock weathering processes. Mitskevich et al. (1975) have reported on the influences of humic and fulvic acids on Be migration, whilst Kovalev and Generalova (1968) discussed the interactions between hydrolysate ions of Fe, Th, Ti, and Zr and natural organic acids. In all cases, soluble complex humates and fulvates are the result of weathering by organic matter.

The ability of humic compounds to weather silicate minerals is considered uncertain by some (Krauskopf, 1967; Loughnan, 1969). However, the data of Schalscha et al. (1967), Baker (1973), Kodama and Schnitzer (1973), Boyle et al. (1974), and Singer and Navrot (1976) provide strong evidence

for increased silicate weathering in the presence of humic compounds. Their effect on silicate minerals, while not as pronounced as the effect on sulphide minerals, is still significant when compared with non-organic, aqueous solutions.

Huang and Keller (1972) conducted over 2000 analyses of solutions resulting from interaction of augite, muscovite, labradorite, microcline, kaolinite, illite, flintclays and montmorillonite with organic acids. It was shown that the acids were quite efficient at removing framework cations such as Si, Al, Fe and Mg. Weak complexing acids like acetic acid exert an efficiency up to 10 times greater than water; stronger complexing acids like citric acid are up to 90 times more effective than water. It was observed that mineral stabilities with respect to organic acid attack were quite different from those operative for water attack. Perhaps this can be taken to indicate that different reaction mechanisms are involved.

By taking the discussion of their results a step further, Huang and Keller (1972) suggested that the complexing properties of fulvic acids on Al^{3+} (a hexacoordinate chelate) are such that it may be possible to form kaolinite if there is an interaction between soluble (or colloidal) organic complexes of both Al and Si, or between soluble Al complexes and dissolved silica. Fotiyev (1971) has demonstrated that aqueous humus from marsh waters contains considerable dissolved silica perhaps forming some kind of addition complex with fulvic acid mixtures in the ratio 1 part silica to 2 parts fulvic acid. Huang and Keller (1972) also considered that bauxite could form from accumulation and breakdown of Al-fulvate complexes.

It would seem to be reasonable to conclude, in the light of the above studies, that soluble organic acids are not only capable of decomposing sulphide minerals or promoting the dissolution of silicate minerals, but can also yield precursor species which may eventually lead to the formation of new minerals. Such processes are clearly important in soil formation as well as in lateritization and related deep leaching phenomena.

The leaching effects of organic matter which occurs in lake or streambed sediments are likely similar processes to those described above. Reaction is probably slow and prolonged and of importance to mechanisms by which metals might be released from sediments. Coey et al. (1974) used Mössbauer spectra in an attempt to characterize iron compounds found in some dried surface lake sediments of Canada. Results indicate that cryptocrystalline ferric hydroxide accounts for much of the iron present. The main source of ferrous iron which would produce this material upon air-drying the sediment would seem to be chlorite particles. Prolonged leaching of Fe from chlorite and other clay minerals is one of the major reactions which takes place in sediments under reducing conditions. Other workers have also noted the ability of organic matter to leach clay minerals. For example, Tan (1975) has studied the decomposition of clay minerals by humic and fulvic acids. It might be expected that this attack would also take place in bed sediments.

On the other hand, it can be argued that the interactions between organic

acids and minerals can promote the breakdown of organic materials or impose greater solubility upon humic acids. For example, Sequi et al. (1976) observed that the alkali solubility of soil organic matter is greatly dependent on the nature of metal ions present in the system. These interactions may have the effect of restricting coagulation of colloids or inhibit rates of polymerization of dissolved humic matter which would lead eventually to their precipitation.

The reactions of soluble organic compounds on carbonate solids have been investigated by Rashid (1972) and Rashid and Leonard (1973). Quinone groups have been found to be one of the major oxygen-containing functional groups present in humic and fulvic acids. In the metal—organic interaction mechanism, quinone groups may take part in secondary, metal complexing reactions. Rashid (1972) found that several quinone compounds had a dissolution effect on the solid carbonates of Cu, Co, Zn, Ni, and Mn. The dissolution order for benzoquinone was Cu < Zn < Mn < Co < Ni whereas, for humic acid, Rashid observed that the order was Mn < Cu < Zn < Ni < Co. Rashid suggests that from 1.5 to 8.5% of the total metal solubilizing capacity of humic acid can be attributed to the quinone type reaction. Rashid and Leonard (1973) again demonstrated that the ability of humic acid in the dissolution of carbonates increases in the order Mn < Cu < Zn < Ni < Co. Rashid and Leonard also studied the dissolution of metallic sulphides by humic acid. The order of metal solubility was found to increase in the order Ni < Zn < Cu < Co < Mn. Baker (1973) studied the solubilization rates of the carbonates, calcite (Ca), smithsonite (Zn), malachite (Cu) and cerussite (Pb) by soluble humic acids. The order of reactivity was found to be Zn < Ca < Cu < Pb, although attack was brisk on each metal carbonate.

It can be concluded that soluble humic matter has the potential to act as a strong weathering agent on many mineral species including sulphides, silicates and carbonates with mineral stability and metal-organic affinity the probable controlling factors. In some instances redox reactions would also be important.

Desorption induced by organic acids

The effect of organic acids on sediment and soil-adsorbed metals is of considerable interest to this review. Unfortunately there are few studies described in the literature which use humic and fulvic acids as desorbents for metals in sediments.

Lerman and Childs (1973) considered the effects of nitrilotriacetate (NTA) and citrate on the distribution of ionic species in a model freshwater. These two organic ligands are considered significant as they are feasible substitutes for phosphates in detergents. Chloride ion and potassium ion do not form strong complexes with other anions and cations in natural waters and were left out in the computations. The computations, based on thermodynamic equilibria, showed that NTA and citrate complex virtually all avail-

able Cu, Fe, Pb, Ni, Co, and Zn. Once these elements are complexed, excess NTA and citrate may then complex Ca and, to a lesser extent, Mg. The authors concluded that any complexing agent, including humic and fulvic acids, with strong affinities for metal ions will have a similar effect. The presence of solid mineral phases was also considered. Provided the conditions of elemental input to, and removal from the water system are such that a steady state can exist, it was concluded that chemical exchange between a solution and a solid sediment phase will slow down the rate of approach to a steady state without affecting the steady-state concentration. Banat et al. (1974) have investigated the interaction model with regard to the ability of a soluble synthetic organic acid (NTA) to desorb sediment-adsorbed metal. It is assumed that, in their system, the metals were adsorbed on both inorganic (clay) and organic substrates. Cu, Cd, and Ni were readily desorbed, Pb and Zn to a lesser extent and Cr not at all. They do not have any data on the interaction involving initially dissolved metallic cations, dissolved organic acid and a sediment phase. Furthermore, they have not considered in their study the more ubiquitous humic compounds which may not be comparable with NTA. However, Butz (1976) has made an evaluation of the effects of naturally occurring organic acids (humic) on the mobilization of heavy metals from soils, in this case near Pb ore smelters. Water-soluble organic acids were found to form strong complexes with Cu, Zn, Pb, and Cd, promote their solubilization and desorption from the soils and effectively change the sorption and precipitation characteristics of the metals. Butz observed that at pH 4 the order of complex stability was Cu < Zn < Cd < Pb but at pH 4—8, Pb was demoted and the order became Cu < Pb < Zn < Cd. Similar experiments conducted on stream and lake sediments would be most informative.

Solution interactions between metal ions and dissolved organic matter

The fate of trace elements, once liberated from leached sediment, soil and mineral phases, is further influenced by continual interaction with soluble compounds. The nature of these interactions has been discussed in previous sections of this review. Baker (1973) observed that many heavy-metal humates, formed by the organic weathering processes, displayed low solubility in water with a resultant lowering of the metal mobility. In the presence of a humic acid solution, the metal (Cu, Ni, Mg, Ca) humates were readily mobilized perhaps indicating the formation of higher humate complexes. The presence of inorganic salts in an aqueous, non-organic solution favoured the precipitation of the humates, probably through induced coagulation of humic complexes or protected colloids.

The stabilization of various metallic ions in solution by organic acids has been experimentally investigated by several authors, for example, Ong et al. (1970), Bondarenko (1972), and Theis and Singer (1973). Some examples of

such studies follow. These effectively illustrate the diversity of information available.

Duursma (1970) has studied the effect of soluble amino-acids on the sorption of metals by marine and river sediments at pH 8. The data showed that the sorption of Co and Zn is reduced by the addition of 10^{-2}—10^{-3} M leucine with the reduction almost equalling that calculated from known stability constants for metal—leucine complexes. Duursma, in extrapolating to the lower concentrations of a natural system, concluded that such an organic influence on the metal distribution between sediment and water could only be a result of humic matter interactions. This is based on the higher natural concentrations of humic compounds and their greater chelating capacity. However, Duursma's extrapolation to ligand concentrations more typical of natural waters (i.e., 10^{-6} M) may not be valid.

Rashid (1971) studied the effect of humic acid molecular weight on the chelation of both di- and trivalent metallic cations. It was observed that the lowest molecular-weight fraction (less than 700) was the most efficient, by a factor of 2—6, in complexing the metals. This result is significant as it is the lower molecular-weight humic and fulvic fractions which are likely to be predominant in natural waters due to their greater solubility.

Bondarenko (1972) found that Cu fulvates and humates are stable up to 240 days in a freshwater system. Fulvates were found to be more stable at weakly acid pH while the humates were more stable at neutral and weakly alkaline pH. In an artificial seawater, the presence of divalent cations (cf., Baker, 1973) caused the precipitation of the Cu fulvates and humates. The presence of H_2S in seawater produced a marked decrease in the stability of the Cu complexes probably because of direct competition for Cu ions by sulphide ion.

Some very useful competition studies between cations for complexation sites have been made by Strohal and Huljev (1970) who used radiotracers to study the interaction between Hg^{2+} and humic acids. They found that Hg^{2+} was very strongly bonded to humic acid ($K_{stab} = 1.7 \cdot 10^5$) but that the process was reversible. Competition experiments with ions such as Li^+, Na^+, Rb^+, Co^{2+}, Mn^{2+}, Ba^{2+}, Zn^{2+}, Mg^{2+}, La^{3+}, Fe^{3+}, Al^{3+}, Ce^{3+}, and Th^{4+} showed that none of these could displace it. However, it does exchange fully with radio-Hg^{2+}. Further studies of this kind, but with more competitive ions such as Pb^{2+} and Cu^{2+}, should be made.

Ong et al. (1970) reported evidence that demonstrates the ability of organic acids (an alkali-soluble fraction of peat) to stabilize in solution Cu(II), Zn(II), Pb(II), Al(III), and Fe(III). Experiments were conducted over the pH range 5—9 using solid Na_2CO_3 to adjust pH. For Cu, stability in solution was a function of pH and organic carbon concentration. For 8 ppm organic carbon and initial Cu content 20 ppm, a distinct minimum in stability occurs around pH 6. For 40 ppm organic C and the same initial Cu, Cu is strongly retained in solution throughout the pH range. The authors relate the observed minimum to stabilities of the insoluble Cu hydroxide and carbon-

ate. The reasons for the increase in Cu solubility at pH greater than 6 are not clarified. The other metals were studied by the precipitation method (i.e., addition of metallic cation to the solution until precipitation is observed); however, the Cu results cannot be related to these metals. The amount of metal needed to produce precipitation was again a function of pH and organic acid content. Zn was the most stable but its stability decreased sharply at alkaline pH. Pb stability increased up to pH 8 and then decreased slightly. Fe and Al stabilities increased steadily from pH 5—9.

However, only rarely have attempts been made to investigate the stability of soluble metal humates or fulvates in competition with other complexing ions such as carbonate, sulphide and hydroxide. The adsorption influences induced by the presence of solid substrates are also little known. Some examples of such studies illustrate the complexities involved in interpreting reaction mechanisms.

Rashid and Leonard (1973) studied the precipitation behaviour of various metals by gradually adding Cu, Ni, Mn, or Fe divalent cation solution to an inorganic ligand (carbonate, sulphide or hydroxide) both in the presence of humic acid and in its absence. At the point of metal precipitation as the inorganic salt, the metal content was noted. The presence of humic acid strongly inhibited the metal precipitation. In the carbonate and sulphide systems studied at pH 8.5, the effect was particularly pronounced, increasing in the order of Ni > Cu > Mn > Fe. For hydroxide, a significant but not as pronounced effect was observed with the order now Cu > Fe > Mn > Ni. The pH of the hydroxide system was not adjusted with each metal addition and varied from 10.7 to a final value of 3.0. Hydroxide would certainly appear the most effective in causing metal precipitation, in competition with soluble metal humate formation, followed by sulphide and then carbonate. However, at the lower final pH of the hydroxide reactions, H^+ ions can interfere in the precipitation reactions. Guy et al. (1975) have proposed a model for Cu(II), Cd(II) and Zn(II) ion and complex ion adsorption onto particulates such as clays, manganese oxide and solid humic acid. They studied the absorption characteristics of metals bound by soluble humic acid, tannic acid and bicarbonate, and in particular the effects of pH on metal speciation and related adsorption behaviour. The most interesting result from a practical viewpoint was that at pH 6.0, Cu is distributed equally as adsorbed species and dissolved organic complexes, but below pH 6.0—3.8, the solution species were primarily in an uncomplexed or 'free' form. Similar studies at pH > 6.0 could prove to be very informative in view of the fact that natural waters are frequently neutral or slightly alkaline.

There is little doubt that, at the metal and organic acid concentrations employed in the works summarized above, metal ions and organic acids impose a mutual stabilization upon each other in the same solution. It is not at all clear whether metal ions at levels more typical of natural waters behave in the same ways. It is likely that competition from hydroxide and carbonate ions will be more vigorous and perhaps even dominant especially in solutions

with pH greater than 7. Experiments along the lines described by Ong et al. (1970) should be attempted under these conditions.

There seems to be no evidence in the literature of studies involving heterogeneous interactions between metal ions, natural organic acid clays and solid humic matter. These and related colloidal interactions may well be dominant in very dilute solutions typical of natural freshwaters.

Stabilization of iron and other reduced species

Organic acids appear to play an important role in stabilizing reduced species of some metals in solution to oxidation. The data presented by Rashid and Leonard (1973) imply that the precipitation of Fe as inorganic compounds is strongly inhibited by humic compounds. However, the possible co-precipitation by Fe(II) and Fe(III) hydroxides of organic matter under reduced conditions will not favour the organic stabilization of Fe in solution (Akiyama, 1973). The complex organic matter obtained by bacterial degradation of green algae was co-precipitated whereas, with simpler pigment and lipid materials, as might be found in swamp waters, co-precipitation was rarely observed, with Fe(III) now being retained in solution. It is interesting to speculate on possible studies by Akiyama, humic matter is likely to relate more closely to the bacterial degradation products which are indeed prone to co-precipitation.

Theis and Singer (1973) found that the oxidation of Fe(II) is completely inhibited in the presence of tannic acid, gallic acid and pyrogallol which can act as reductants as well as complexing ligands.

Three possible mechanisms for the stabilization of ferrous ions by dissolved organic acids in natural waters were offered for consideration. The first is that hydroxoferric complexes can induce peptization of the organic molecules, the second concerns chelation of Fe ions by humic ligands followed by polymerization, and the third depends on the reduction of ferric ion to ferrous ion by humic acid followed by chelation. The results were considered indicative of the formation of a thermodynamically stable Fe(II)-organic complex. Conversely, the presence of these compounds in aqueous solution with Fe(III) ions produced an almost instantaneous reduction to Fe(II) which was subsequently stabilized in solution by the organic complexing agent. However, under conditions where ferric hydroxide was forming, the tannic acid had a very much diminished reduction effect. Similar results were observed in experiments using natural humic acids, which therefore appear capable of stabilizing Fe(II) in well-oxygenated environments.

It is likely that the reducing and complexing properties of humic acids will confer similar stabilization on other reduced metal species. Zajicek and Pojasek (1976) found that the Mn oxides, pyrolusite and hausmannite, are readily solubilized by fulvic acids extracted from pond water and forest debris. The amount of Mn in solution was found to be directly related to the organic colouration of the water. The process of solubilization is considered

by the authors to be one of reduction by the organic matter to Mn(II) followed by complexation with fulvic acids. Similar observations have been made on the stabilization of Mn(II) solutions to hydrolysis upon complexation by dissolved organic matter (Koshy et al., 1967).

Ingols and Enginum (1968) have studied the remobilization of MnO_2 in lake sediments. They concluded that bacterial action was not involved and that reduction of Mn(IV) to Mn(II) by a wholly chemical reaction with organic-rich mud, was the true mechanism.

Some structural work by Gamble et al. (1976) on the Mn^{2+}-fulvic-acid complex sheds some light on the reasons for different reactivities of Fe and Mn fulvates. Their ion exchange and n.m.r. studies have shown that the Mn^{2+}-fulvic-acid structure is an outersphere electrostatic complex, i.e., loose bonding. On the other hand the Fe^{3+}-fulvic-acid structure is definitely an inner-sphere type, i.e., strongly bound as a chelate (Langford and Gamble, 1974). To complete the picture, similar studies on the nature of a Fe^{2+}-fulvic-acid complex would be very informative indeed.

The importance of these studies should not be overlooked because of their relevance to the mechanisms by which lake and stream sediment-hosted Fe—Mn nodules and precipitates are formed and re-dissolved. The fate of metal ions whose dispersion is controlled by adsorption and desorption and dissolution from hydrous Fe and Mn oxides is therefore dependent on this type of process.

Humic acid is also capable of reducing Hg^{2+} (mercuric) ion to elemental mercury (Alberts et al., 1974), a reaction of some significance of the widespread problem of Hg migration and contamination in river and lake sediments. By this means, Hg^{2+} which is usually considered to be strongly complexed by organic matter (e.g., Strohal and Huljev, 1970) and thereby largely immobilized, can be rendered free from its ligand and pass back into solution again as dissolved metal. Chemical and biochemical transformations which likely take place via organic complexes would therefore be moderated.

Much interest is presently centred on the mobility and fixation of U. The mobilization of U, along with Mo, V, and P is most commonly considered to be by inorganic processes with oxyanionic species being the mobile forms of these three elements (Bloomfield and Kelso, 1973). U can also become mobile as the free uranyl cation, UO_2^{2+} and as complex bis- or tris-carbonato anions. The enrichment of these three elements in organic sediments, and for that matter in ancient sediments now present as carbonaceous shales, is quite common with the enrichment being considered due to the organic matter (for example, Williams and Brown, 1971; Szilagyi, 1971a; Brookins and Lee, 1974). The enrichment has been considered to involve reduction by the organic matter of the mobile anionic species to exchangeable cationic forms which can then be retained by the organic matter (Szalay, 1964; Szalay and Szilagyi, 1967). The ability of humic matter to reduce complex anions and some cations has been experimentally demonstrated (Szalay and Szilagyi, 1967; Szilagyi, 1971b; Alberts et al., 1974). However, Bloomfield and Kelso

(1973) conducted experiments which showed that U, Mo, and V can be transported and fixed by organic matter as anions; thus a reduction step may not be essential to the enrichment. Nonetheless, Bloomfield and Kelso do propose that, under the conditions in which Mo-enriched sediments are formed, H_2S-induced reduction followed by precipitation—coprecipitation of the sulphides is probably the dominant mechanism.

The evidence available suggests a mechanism of U and Mo transport as very stable anionic species, possibly protected by a humic colloid. Coagulation of the humic colloid by aging or by an increase in, say, Ca^{2+} concentration, could lead to precipitation or adsorption onto pre-existing organic matter. Subsequent reduction of the mobile species by the organic matter would ensure U and Mo immobilization with sulphide strongly fixing the elements to the sedimentary phase. The work of Kovalev and Generalova (1968) who have studied other metals which commonly take a hydrolyzate form, viz., Th, Ti, and Zr, confirms the possibility that U may yield soluble complexes while in the form of UO_2^{2+} and U^{4+} (c.f., Th^{4+}) as well, perhaps an important process in remobilization of U during diagenesis of organic-rich sediments.

The presence of radioactive hydrocarbon relicts in certain sedimentary U occurrences may well be a consequence of humic acid transport of UO_2^{2+}, U^{4+} or both into cracks and fractures during or following solution controlled mineralization processes. These hydrocarbons, commonly and perhaps erroneously referred to as 'thucolites' since they are not always enriched in U or Th, have been described recently by Jonasson et al. (1977).

Influence of sulphide

The interactions between sulphide species and organic matter are complex. Boulegue and Michard (1974) noted that polysulphide ions serve as good acidity and redox buffers in reduced organic sediments. Reactions between humic materials and polysulphides serve to stabilize the organics by incorporation of polysulphides chains into their structures. Polysulphides are strong complexing ions in their own right, thus their enhancing effects on complexation properties of humic materials are likely to be significant. Interactions with metals would be expected to be strong and retentive against metal remobilization. Subsequent aeration of such sediments would lead to the release of heavy metals as the polysulphides are oxidized and solubilized, perhaps in the form of thiosulphate and sulphate. Humic materials may also become more soluble and mobile as linking chains are destroyed.

Of some interest in this regard is the work of Listova (1966) who conducted some experiments on the solubility of lead sulphide under slightly oxidizing conditions. Pb forms thiosulphate complexes under conditions of restricted acidity (pH ~ 5). Resultant species are quite soluble and may well become important entities in Pb migration. Exposed sulphidic muds containing heavy metals, including Pb, could follow a similar reaction pathway upon aeration and washing with rainwater.

Such effects were observed by Jonasson and Timperley (1973) who made some preliminary studies of the remobilization of metals in lake sediments which had undergone sudden exposure to atmospheric oxygen from previously strongly reduced conditions. In this instance a small lake was drained of water following the collapse of a retaining beaver dam. It was apparent that samples collected from the same location a few weeks apart had lost more than half of their original trace contents of Zn, Cu, Pb, Ni, and As from sulphidic (2%) organic muds and more than 80% of their original S and Hg contents. C content remained roughly constant. It is considered that such processes may be operative in lake or marsh sediments which undergo similar seasonal exposure to oxygenated waters or atmosphere. Water—sediment interactions under these circumstances are rapid and vigorous and result in the release of metals previously bound as sulphide or a sulphidic organic complex, to the water. Jonasson and Timperley (1973) further suggested that similar remobilization of metals may occur in dredged muds from, for example, the Rhine estuary when these are dumped on shore (De Groot and Allersman, 1973).

Data presented by Gardner (1974) emphasize the effects of sulphur species on metal complexing in natural waters. He developed a model to deal with trace-metal solubility in H_2S-rich marine waters, which involves many inorganic and organic ligands such as amino acids and hydrocarboxylic acids. The results indicated that bisulphide and polysulphide complexes, and not the organics, are the important ligands for trace-metal solubility under these conditions. The author suggested that the effect, if any, of dissolved organic matter in trace-metal solubility under these conditions would be due mainly to humic and fulvic acids.

The influence of metal sulphide and organic complex formation on Cu and Zn accumulation in organic lake sediments is discussed by Timperley and Allan (1974). This work represents an attempt to determine the forms of binding of metals such as Cu, Fe and Zn in reducing, organic-rich (~50%) muds and gels. They concluded that the accumulation of Cu was mainly by sulphide precipitation whereas organic complexing was more important to the binding of Zn and Fe. Their preliminary work suggests that the controlling factor may be direct competition between sulphide ion or perhaps its adducts with organic matter (Jonasson and Timperley, 1973) and organic ligands for the metal, so that some predictive value on the behaviour of other metal ions may be possible on the basis of simple metal sulphide solubilities. For example, Cd may behave like Zn, but As and Hg are likely bound largely as sulphide species. The accumulation of Fe in anoxic lake sediments and its interactions with sulphide ion have also been discussed by Emerson (1976).

Geochemical dispersion studies

The hydrogeochemistry of any drainage basin is subject to several interacting parameters. The roles of dissolved and sediment organic carbon are

two such parameters. Other at least equally important parameters include bedrock geology (Reeder et al., 1972; Schwartz, 1974), hydrodynamic and biological factors (Andelman, 1973), inorganic sorption processes (Jenne, 1968; Loganathan and Burau, 1973; Chao and Anderson, 1974), and mechanism of trace-metal transport in river including transport via suspended particulate matter (Perhac, 1972; Perhac and Whelan, 1972; Gibbs, 1973; German and Knight, 1973; Förstner, 1977). In the light of such complexity, it is not surprising that attempts to explain the field relationships between trace metals and organic carbon are usually tentative. Field studies on the effect of dissolved organic matter on trace element dispersion processes are not commonly encountered. De Groot (1971) and De Groot et al. (1971) have published the most pertinent data. A study was undertaken on the behaviour of various elements in the Rhine River and Ems River (Western Europe), particularly in the deltas prior to their entrance into the Wadden Sea. The Rhine River has been subject to industrial pollution and, as a consequence, the reported Hg, Zn, Cr, Pb, Cu, and As levels of the sediments were high. But, in both rivers, starting at the freshwater tidal area and downstream from there, a remobilization of these elements into solution from the sediments was observed. This was apparent when compared with sediment metal contents upstream from this tidal area. The change in chemical conditions (i.e., oxygenation, increased salinity) at this point promoted intensive decomposition of the organic material related to the sediments. From this, De Groot concluded that the formation of soluble metal-organic complexes was mobilizing the pollutant metals from the sediments. For the Rhine River, it produced the striking result that the highly polluted sediments from the upper reaches of the estuary were reduced to normal levels in the lower courses. A definite order in the degree of mobilization was observed. Hg was the highest with a maximum of 90% mobilization from the sediment being attained. There was then a moderate decrease in the order Cu > Zn > Pb > Cr followed by Fe with 45%, whereas Sn, Sc, La and Mn showed no mobilization. The authors reasoned that this order should reflect the stability constants of the metal-organic complexes formed. Comparison with the data of Schnitzer and Hansen (1970), as presented in Table II for metal fulvate stabilities shows that such a relationship is not apparent. Considering the complexity of the natural system in relation to the conditions employed for the stability constant determinations, this is not surprising. As the authors point out, certainly the mobilization of Hg is likely to be affected by the formation of soluble chloride as well as organic complexes.

However, the differences between field observation and laboratory experiment possibly may be explained otherwise. The apparent immobility of Mn compared with Hg as measured by De Groot provides a clue. It is likely that this element is present in some hydrous oxide-phase complexes with fulvic acid (Gamble et al., 1976) which might be expected to dissociate readily and undergo oxidation to MnO_2, perhaps reprecipitating in situ in the sediments. By comparison Fe, initially present as Fe(II)-organic complexes, is more

stable to oxidation and may remain temporarily intact as a solubilized species before undergoing similar dissociation and oxidation.

It has been noted elsewhere in this review that Hg(II) forms very strong and stable complexes with macromolecular organic acids, so too does Cu(II). Thus it may be that simple solubility of these organic complexes is a key to the order of mobilization reported. In his original work, De Groot made no allowance for dilution of river sediments by materials brought into the estuary from the open sea. While this process would result in a general reduction in metal levels giving the appearance of remobilization, in no way can it satisfactorily explain the order of remobilization observed. Thus his conclusions although less clear-cut seem to remain valid (see also Jonasson and Timperley, 1973). On the other hand, what is virtually the reverse order of mobilization was observed by Engler and Patrick (1975) who found that the stabilities of heavy-metal sulphides (MnS, FeS, ZnS, CuS, HgS) in aerobic and anaerobic flooded soils were directly related to their respective solubilities. The order of reactivity, i.e., release of S-35 used to label the sulphides, was MnS > FeS > ZnS > CuS > HgS.

Thus for lake and stream muds, the order of mobilization is roughly the reverse of that which would be predicted from a consideration of the solubilities of simple sulphides. It does seem likely that the greater complexing powers of, e.g., Hg(II) and Cu(II), towards organic ligands are more important to the kinetics of remobilization than the solubilities of their simple sulphides, in seeking an explanation for field observations.

Quite a number of papers have been written giving qualitative descriptions of heavy-metal associations with organic matter in natural waters. For example, Cooper and Harris (1974) reported high levels of heavy metals associated with organic phases of a river sediment. By comparison, metal levels in mineral phases were low. Metals bound in this way include Zn, Ni, Cu, Cd, Pb. Changes in acidity of river waters had a marked effect on the actual levels of metals observed, especially Zn.

Bugelskii (1965) and Bugelskii and Tsimlyanskaya (1966) presented data on the behaviour of Ni during the weathering of a serpentinite massif in the Central Urals. The presence of humic substances in the natural surface waters greatly facilitated the dissolution of Ni and its subsequent migration as an assumed Ni-organic complex. In response to hydrogeological, physicochemical and biochemical conditions, the organic matter may be altered and co-precipitated from aqueous solution with Ni. Depending on the nature of the organic matter to which Ni is bound, the authors concluded that the Ni-organic compounds, during migration, can be either further dispersed or accumulated.

Beck et al. (1974) produced a wealth of data on organic and inorganic geochemistry of some Coastal-Plain rivers of the southeastern United States. A predominance of acidic organic matter over inorganic constituents, including anionic species, was observed; this is certainly not the normal situation. Fe, Al and pH were directly related to the total dissolved organic matter; Na,

K, Mg, Ca, and Mn were not obviously complexed by the organic matter. Unfortunately, base-metal analyses were not reported.

However, the amount of literature published on field measurements of interactions between waters, metals and sediments are fewer, perhaps reflecting a recognition of the difficulties of interpreting the observations made. Martynova (1971) listed three main pathways by which water—sediment interactions occur. These are molecular diffusion, filtration, and the roiling (muddying) of bottom sediments. The principal controls on these processes of mass transport are considered to be adsorption-exchange processes, redox equilibria, biochemical activity of micro-organisms and the hydro-geological condition of the water body. These interactions involving metals can best be studied by radio-tracer techniques, e.g., Zn; isotopic labelling, e.g., P; and by direct chemical measurement using hoods on the floor of the water body, e.g., NH_4^+ and Cl^-, according to Martynova (1971).

Jonasson (1976) has described studies made on the distributions of a number of metals, viz., Zn, Pb, Cu, Fe, Mn, Hg, As, Ni, Mo, and U between organic sediments, silty sediments and waters from two small lakes in an isolated area of eastern Ontario. Data for organic C, S, and carbonate are also given. The distribution patterns observed are discussed qualitatively in terms of interactions between metals in waters and sediments. Of particular interest are the observations that dispersion flows of certain sediment-held metals such as Zn and Pb, and their relationships to organic carbon and sulphur in sediments reflect hydrodynamic processes set up by seasonal variations in water flow. Interaction mechanisms such as the fixing of metal and metal hydrolysate ions by dissolved organic matter, coagulation of organic complexes and subsequent diagenesis to sulphides in bottom muds are also discussed.

The release of heavy metals from bottom sediments has been studied mainly with the use of radioisotopes. Draskovic et al. (1971) have discussed application of these methods to the problem of metal transport in the Danube River. Their colleagues, Radosavljevic et al. (1973) used Co-60 to follow the migration and sorption behaviour of Co in sediments. No mention was made of the nature of Co species thought to be present in the system.

Lenaers (1971) uses U-V irradiation to induce release of Mn-54 held by Columbia River sediment. Organic matter was selectively destroyed with little effect on Zn-65, Sc-46, Co-60 considered to be bound to hydrous Fe and Mn oxides. No effect was noted for Zn-65-labelled montmorillonite. Thus, a useful method for studying trace metal uptake and release by organic matter without disturbing metal loadings on hydrous oxides or clays, becomes available. This could be a particularly useful approach when studying the distribution of a given metal amongst organic and inorganic matter.

Bothner and Carpenter (1973) investigated the influence of the Columbia River suspended matter on the fate of dissolved Hg in the lower river and its estuary. About 50% of the total Hg was found to be transported by the suspended load. Some laboratory experiments were designed, using Hg-203 to

observe adsorption—desorption reactions on some suspended river sediments. These were mainly clays containing about 2% organic-C, perhaps as an adsorbed coating. Half of the radio-Hg was adsorbed in a few hours, indicating rapid surface reactions; the remainder was taken up much more slowly. Desorption experiments, designed to test the strength of metal-substrate binding, showed that roughly 45% of total Hg was easily removed by water washings. Therefore, about half of the adsorbed Hg (rapid uptake) is weakly held, possibly on ion-exchange sites, while the remainder is more strongly bound perhaps at some more specific adsorption or complexation sites. The studies of Strohal and Huljev (1970) who reported that Hg(II) was very tightly bound to fulvic acid bears on these observations. Bothner and Carpenter (1973) also noted that seawater washings (i.e., Cl^- solutions) had little effect on the desorption data. Johnson et al. (1967) reported that Zn-65 was similarly retained by Columbia River bottom sediments in interaction with seawater.

Timofeeva-Resovskay (1963) introduced radioisotopes of Zn, Cd, Hg, Rb, Cs, Co, Y, S, Fe, and Ru into waters of certain freshwater reservoirs and followed their uptake by soils, sand, sediments and suspended particles. Strongest adsorptions and least desorption were shown by Co, Zn, Cd, Y, and Cs. Weakest adsorption and most desorption were shown by S, Fe, Ru, and Ce.

Interesting though these works are, the more immediately useful studies deal with true interactions between known species. Kovalev and Generalova (1974) investigated the effects of humic and fulvic acids on the formation of Fe sulphides. In a series of experiments at different pH, mixtures of ferrous sulphate, sodium carbonate and goethite were saturated with hydrogen sulphide and left to form precipitates of Fe sulphides. The presence of organic acids suppressed the formation of pyrite; FeS formed instead. Fulvic acid, which is a stronger complexer, was found to be more effective than humic acid. Pauli (1975) conducted similar experiments with aqueous humic acids, hydrogen sulphide and Cu, Zn, Ni, Pb, and Cd. In the presence of hydrogen sulphide, more than 60% of all the metal humates, previously prepared, was transformed into metal sulphides, another 30% remained with the acid precipitable humus. These two works are of some relevance to the study of formation of syngenetic sulphide bodies (see also Saxby, 1973), in metal-rich bogs for example (Fraser, 1961a, b).

Jackson, K.S. (1975) designed model laboratory experiments over a pH range 4—9 to simulate interactions in the system dissolved metal ion—clay—dissolved organic acids. The objective was to compare results with data from field studies within carefully selected stream systems. Interferences due to the presence of carbonate were also observed. The ability of soil-derived humic and fulvic acids to desorb metal previously adsorbed onto clay, and also metal from metal hydroxide precipitates was investigated. Cu(II), Pb(II), Zn(II) and Ni(II) were the cations studied.

Results indicated that Cu is strongly stabilized in solution but is the most

kinetically hindered in desorption reactions. Pb is least retained in solution by organic complexing because it is effectively removed by adsorption during colloidal coagulation of organic matter. The solubilities of Zn and Ni are enhanced by organic complexing but are pH-dependent with hydrolysis leading to decreased solubilities. Ni-solubility is also decreased by carbonate precipitation.

Jackson, K.S. (1975) also embarked upon a field study of streams in which similar processes were considered to prevail. Predicted behaviour, based on a reaction scheme involving sorption and organic complexing only, was compared with observed behaviour. The dispersion of Pb and Fe in natural waters seems to be favoured by organic complexing. Cu-dispersion is strongly governed by sorption to organic-rich stream sediments. The behaviour of Ni is strongly controlled by interfering reactions, particularly with carbonate ion and hydroxide at high pH. The reaction scheme derived from the model experiments was found to be inadequate for Zn.

A comparison of the laboratory model with field results indicates that two significant modifications to the laboratory scheme would be the use of an organic-bearing adsorbent phase and of soluble organics extracted directly from natural waters. Competition studies, (c.f., Strohal and Huljev, 1970) using different metal ions for adsorption sites on clays, humic solids, and clay-humates, would also be relevant to a more realistic laboratory study. Cations such as Mg^{2+} and Ca^{2+}, which can be complexed quite efficiently by fulvic acids as evidenced by both complexation and mineral dissolution studies, are among the more important ions to consider. Finally, introduction of sulphide ion into the bed sediments should be considered in order to study the fixing effects it would have with respect to organic acid remobilization of sediment-held metals.

Two articles on the seasonal effects of Fe migration in river systems illustrate the added problems involved in field studies when spread over a full cycle of seasons.

Kovalev et al. (1974) have studied the seasonal variations of Fe content of streams draining from swampy terrain. It was observed that seasonal changes in oxygen content of waters represented one of the causes of Fe variation. When oxygen is depleted in winter, the quantity of Fe carried in streamwaters increases; an observation which suggests that soluble ferrous complexes may be important species of migrations in the winter. In this context, it was also noted that Fe-humus complexes accounted for as high as 90% of all dissolved Fe. Fine suspensions of Fe-humus aggregates accounted for much of the Fe carried in solid phases. Conversely, the data indicated that it are likely ferric species which are dominant in Fe dispersion during summer.

Nikitina (1973) has provided some information on the migration states of Fe, Al, Si, Ca, Mg in 'ultrafresh' (very low total dissolved solids) waters from a permafrosted landscape. Dialysis methods, selective solvent extractions and ion-exchange methods were used to separate colloidal forms from ionic-molecular forms. In highly organic waters and opalescent siliceous water, Fe

was found to migrate predominantly as colloidal forms involving organic matter. Organic matter stabilizes Fe in solution over a wide pH range. Electrophoretic experiments suggested that the Fe forms part of an anionic organomineral.

But in waters of low organic content, Fe migrated entirely in dissolved form. Colloids were not detected. In highly organic waters, the proportion of Fe carried colloidally was lowest in spring (cf., Kovalev et al., 1974) snowmelt waters and highest in late summer when greater quantities of complexing organic ligand are available.

Nikitina (1973) also discussed the migration forms of a number of trace metals including Cr, V, Cu, Ni, Zn. These too were considered to migrate predominantly in organic colloidal form. Fifty percent of all Cu present was extractable with isobutanol, perhaps indicating the presence of zero-charge complexes.

There seem to be very few studies available in the literature which deal with all possible complexities including those outlined by Jackson, K.S. (1975) and those imposed by temporal effects as described above.

One approach to this problem, although it has not yet been used in this way, is the method of Cline and Upchurch (1973) who made an in situ field study of metal—water—sediment interactions. Experiments were devised as test mechanisms by which Cu might migrate through organic lake sediments. It was found that Cu accumulated in the upper strata of the sediment bed. The metal was thought to have been transported upwards on bubble interfaces, by ionic migration and as a result of dewatering of the compacting sediments. Organic-absorption and metal-chelation sites remained active in the upper strata and contributed to the accumulation process.

Beginning with an initially even distribution, Cu(II) spread over a sediment column 60 cm long moved upwards over 3 months. At that time, there was a 30% increase in Cu(II) content in the upper 4.5 cm with a matching decrease over the rest of the column. Sediments at all levels were systematically analyzed for KCl and EDTA-extractable Cu and total Cu. Pore waters were also analyzed. It is interesting to observe that the work of Dunnette et al. (1973), who used S-35 tracer to demonstrate that H_2S production from sulphate and cysteine in anoxic freshwater sediments was confined mainly to the upper 4 cm of sediment, is relevant to the work of Cline and Upchurch (1973). Presumably the Cu(II) in upper sediment strata could also be fixed and accumulated by increased sulphide-ion concentration. Dissolved Cu would be minimal and so a concentration gradient from bottom to top of the column would be established. Moreover bubble movement of H_2S, NH_3, CH_4 and H_2 from deeper levels could promote significant interactions with the soluble Cu(II) species present. Just what these interactions might be and what species are involved are at present speculative but they do seem to have some bearing on the formation of framboidal sulphide ores by humic colloidal growth around structures which have been interpreted as having their origins in bubbles of gas or liquid (Pauli, 1975).

Combining this kind of experiment with in situ measurements of metal-organic species such as those described by Benes and Steinnes (1974) might be worthwhile.

SUMMARY

Humic and fulvic acids are best described as high molecular-weight, weak acid polyelectrolytes. It is not yet possible to assign a molecular structure to these acids; however, benzenecarboxylic acid and phenolic groups are the apparent key structural units. There is much evidence to imply that stable metal humates and fulvates will probably form via a salicylic acid-type bidentate site.

From laboratory evidence, metal—humic-matter interactions are potentially important in the following geochemical processes: (a) leaching of metals from solid mineral phases and soil horizons; (b) dispersion along drainage systems as soluble or colloidal metal—organic species; and (c) concentration and fixation of many elements within organic-rich sediments. But more work needs to be done to establish the nature of organic, inorganic and mixed ligand species involved.

The existence of metal—organic complexes within certain kinds of natural waters and sediments is undoubted from field observations. However, the interfering effects of various inorganic and hydrodynamic processes will seriously mask the metal—organic matter interactions in a field study.

The data reviewed and their potential significance do justify continued research into metal—organic sediment—water interactions. However, it is considered here that the direction of this research should move towards more direct consideration of the influence of dissolved organic matter on the metal—sediment—water distribution by investigating heterogeneous systems involving soluble organic acids and metallic cations in reaction with a solid adsorbent phase. For preference, as many in situ field experiments along these lines as can be devised, should be attempted. Full utilization of the latest analytical chemical instrumentation is mandatory mainly because these experiments should be carried out using metal concentrations more typical of those encountered in natural freshwater systems.

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(Received May 3, 1977; revised version approved May 31, 1978)