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CORRELATION OF GEOCHEMICAL DATA ON ORGANIC MATTER AND
METAL IONS IN THE INDIAN RIVER

by

Tahir R. Khan

A thesis submitted to the Faculty of Graduate
Studies in partial fulfilment of the
requirements for the degree of
Doctor of Philosophy

Carleton University

Ottawa, Ontario

July 1979

The undersigned hereby recommends to the Faculty of Graduate Studies the acceptance of this thesis submitted by Tahir R. Khan, M.Sc., in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Geochemical studies of Indian river, a stream of relatively high organic content, flowing over Precambrian marble in the Lanark county (Ontario) area of the Granville Province are described in this thesis. Samples from 31 stations over a distance of about 15 km were analyzed for Cu, Ni, Mn and Fe, and organic solutes. The material passed through 0.45 μ m membrane filter is defined as dissolved, and that retained is called particulate. The average C content of dissolved organic matter (DOM) is estimated 20 ppm, and the average concentrations of Cu, Ni, Mn and Fe are 7.1, 20.0, 19.5 and 68.3 ppm respectively.

Stratified chromatographic columns composed of macroreticular resin XAD-8 and XAD-2 fractionated quantitatively (within 10%) DOM into hydrophobic acids and bases and hydrophillics. The hydrophobic acid fraction comprising about 20% of DOM resembles soil extract fulvic acid. It is the prime fraction that binds metal ions in Indian river water and has a binding capacity 0.01 meq/L at pH 5 estimated by Cu(II) potentiometric titration.

Dissolved Fe shows a statistically significant correlation 0.7, to DOM; a relatively insignificant correlation 0.3 is observed between dissolved Mn or dissolved Ni and DOM, whereas Cu shows a negative correlation, if significant, to DOM. The influence of hydrophobic acids in mobilizing these metal ions in the river water appears to follow the order $Fe > Ni \sim Mn > Cu$ on the basis of correlations stronger than those in the total DOM.

Complexation of metal ions by dissolved organics has been suggested to be responsible for the observed mobilizing trend.

However, an evaluation of theoretical complexation order emphasizes a complementary role for reduction. Both reduction and complexation probably affect the transfer of Fe into solution, while reduction is the principal mechanism for the solubilization of the weakly complexing ion of Mn. Complexation is the only mechanism available for Ni interaction with organics in the river water.

As regards to the particulate phase a significant correlation is not observed between the particulate metal and the particulate organics. No attempt is made at detailed evaluation of the interactions in particulates in the samples.

CHAPTER 1

HUMIC SUBSTANCES IN AQUATIC ENVIRONMENT; THEIR ORIGIN AND INTERACTION WITH INORGANIC SOLUTES

a) Introduction

Although the origin and the nature of terrestrial organics and their interaction with metals has been a subject of interest to geochemists for several decades, our understanding of the problem is still superficial. The lack of coordination between the two principal disciplines, chemistry and geology, and the poor articulation of laboratory scale observations of the former with field observations of geological processes have retarded growth of our knowledge.

The magnitude, scale, and complexity of problem can be put into perspective by considering together the simplified geochemical cycle (Saxby 1969) and biogenic cycle (Jansson 1972) in the manner suggested in Fig. 1. The original block in Saxby's cycle representing "organic matter from biosphere" is replaced by the biogenic cycle, shown by dashed lines in the composite diagram Figure 1. The important feature of the biogenic cycle is that non-living material may accumulate off the main pathway of the cycle. The accumulates are organic as well as inorganic.

The dark-colored organic material which makes up the major part of soil organic matter is called humus. The transformation of humus accompanies processes such as oxidative degradation, polymerization, condensation, and

Adapted from Saxby

Adapted from Jansson

Figure 1. Association of organic matter with the earth's crust.

metabolic activity of soil organisms. Soluble humic material is subdivided into two general classes: humic acids (HA) and fulvic acids (FA). The humic acid fraction is defined as that part of soil organic matter which is soluble in dilute base and insoluble in acid. Fulvic acid is the water-soluble portion which remains in solution at low pH, and after all the humic acid has precipitated out.

The humus, which constitutes an important part of organics, becomes a component of the geochemical cycle by incorporation with igneous rocks. In the geochemical cycle, it is subjected to weathering, undergoes diagenesis and may ultimately end up as graphite by metamorphic events. Humus, as shown in Figure 1, enters the geochemical cycle where it is subject to weathering and transportation, diagenesis and may ultimately be converted to graphite as a result of metamorphism. The fate of humus after its initial formation thus depends upon the environment in which it forms, the distance it is transported, the rapidity with which it is buried below microbial activity levels as well as processes affecting sedimentary and metamorphic rocks. Aquatic humus is one stage of this transformation. The part of humus associated with aquatic sediments is called kerogen.

Humus and kerogen-bearing sedimentary rocks are known in the geological column from about 3.3 billion years ago to the present. The large accumulations of petroleum in Ordovician and Silurian rocks give evidence for increased organic productivity in the seas of those periods as

compared with the Cambrian and Precambrian.

Although records of Pre-Devonian terrestrial fauna are mainly limited to megaspores, the bio-geochemical data suggest that small but significant numbers of lower plants occurred on the land surface in Ordovician time and probably earlier times (Swain 1970, Chap. 11). Fungi, bacteria and algae are known to have been present then. Humus is therefore a product of biogeochemical agents which have been acting upon plant materials for as much as 3.5 billion years.

b) Dynamics of Humic Substances

Organic evolution has been intimately connected to aqueous systems. The aquatic system is a highly dynamic one. It is reasonable to expect a rapid turnover of simple organic structures and to anticipate that the build-up of appreciable quantities of dissolved organic material is the result of long term processes leading to the formation of complex, chemically and biologically stable compounds. Labile organic matter including carbohydrates, proteins, hydrocarbons and to a certain extent, tannins and lignins are slowly mineralized, and the residual refractory materials constitute the organic component of the aquatic system. From the ecological standpoint, this means that the heterotrophic phase (especially mineralization) of nutrients cycle is not able to keep pace with the autotrophic phase (immobilization; especially, assimilation). Dead organic residues and their nutrient elements, primarily

nitrogen, phosphorus, and sulfur, accumulate in the environment. These residues constitute humus. A further complicating feature of the humus reservoir is that it is intimately intermixed with the living heterotrophic biomass of the soil.

It does not come as a surprise that different ecosystems create different types of organic residues or wastes, and therefore different types of humus (Jansson 1972). Thus, the different soil groups (podzols, chernozems, etc.), cultivated soils, bogs, marine and non-marine sediments are characterized by special types of humus. For example, the work on the characterization of total humus components of soil, particularly humic and fulvic acid fractions, reviewed by Kónonova (1966), show that some of the properties investigated (humus reserves, reserves of nitrogen, humic acid content, ratio of humic to fulvic acid, the C:H ratio, exchange capacity, etc.) are most strongly developed in deep chernozem.

On the other hand, metal porphyrin appear to be dominant in sediments. Saxby (1969) reviewing metal-organic chemistry of the geochemical cycle, lists a number of sediment types from which metal-porphyrin complexes have been isolated. These include oil shale, bituminous sediment, petroleum, shale, etc., and the metal is found coordinated to a derivative of porphyrin (Hodgson et al. 1967).

c) Organic Compounds in Aquatic Environment

The characteristics of humus vary greatly, depending on the plant cover, the source organisms and the mode of decomposition the humus has undergone. Microbiological processes are responsible for most humus formation. Plant carbohydrates supply the source of energy for the micro-organisms and the latter themselves are thought to contribute considerable amounts of humic residue (Flaig 1966). Fungi are thought to be important humus producers in lakes and rivers, whereas bacilli are important in bogs. On the other hand, wholly chemical humus formation may take place by: reaction of mineral acids with carbohydrates to form furfurals, condensation of amino acid and peptides with carbohydrates to form melanoids, aldol condensation of amino acids with methyl glyoxal, oxidation of phenols, quinones and other aromatic compounds, and opening of lignin rings.

The bulk of organic matter in surface waters is derived from natural leaching of soil and leaf litter in the drainage basin. The total input of allochthonous organic matter (Wetzel 1975) includes biopolymers derived from the decay of plant matter and geopolymer (humic substances) generated by the random polymerization of biomonomers. The biopolymers are predominantly polypeptides and polysaccharides and since both these classes of compounds are degraded easily by hydrolytic enzyme systems, their concentrations remain low approximately to 10% (Semenov et al. 1967). Their breakdown

products, free amino acids, are always found in extremely low concentrations, since they are rapidly assimilated. Dissolved polysaccharides often occur in close association with dissolved colored geopolymers (humic substances) and can make up to 10% of dissolved organic matter (Leenheer et al. 1973, Semenov 1967). Individual carbohydrate monomers, resulting from hydrolysis of polysaccharides, are almost immediately metabolized. Simple organic acids are subject to the same fate as carbohydrates, and their abundance is therefore very low. Thus, on the average, about 60-80% of organic matter consists of humic substances (Reuter et al. 1977). Most common organic acids in rivers and lakes are butyric, valeric, pyruvic, lactic, succinic, adipic, oxalic, malonic, citric, tartaric, and malic acids. These appear to constitute less than 2 ppm in lakes (Khomenko et al. 1971) and 0.5 ppm in rivers (Lamar et al. 1964) out of a normal 20-30 ppm range of total organic carbon in surface waters. Most of them are good chelators of transition metal ions.

Tannins are found in lakes and rivers as a result of leaching of bark and leaf litter. They add color to water and possess adsorption properties. Their concentration can reach to high levels, 3.4 ppm in a Florida lake (Martin et al. 1976). An important property of tannic acid is that it reduces Fe^{3+} at pH below 3 and forms a stable complex with Fe^{2+} (Theis et al. 1973). At pHs higher than 3, tannic

acid must compete with $-OH$ for Fe^{2+} ; thus both Fe^{2+} -tannin complexes and hydrous iron oxide are expected to be found in fresh water systems.

Tannins are normally resistant to microbial attack because of their ability to inactivate enzymes.

d) Chemistry of Humus

Preliminary Considerations.

The humic substances impart a dark brown to yellow color to water. Comparison of structural interpretations for the soil humic substances and the colored aquatic matter show that both are chemically and genetically closely related (Christman et al. 1971, Stevenson et al. 1971, Bordovskiy 1965). Beck et al. (1974) found that amino acids released by acid hydrolysis from river water humic substances constitute 4.4% of organic matter, whereas those released from soil can constitute up to 10% (Felbeck 1971). The relative molar distribution of amino acids in the acid hydrolyzates of river water humic matter closely resembles that found for soil fulvic acids (Khan et al. 1971, 1972), in that glycine is the most abundant amino acid followed by aspartic acid and alanine.

A meaningful relationship between fulvic acid from the two sources can be ascertained by comparing oxygen containing functional groups, which largely determine properties of one of these molecules, including complexing capacity, redox

properties, hydrophilicity, or hydrophobicity. Reuter et al. (1977) have very elegantly made such a comparison Figure 2. The figure shows that the values for unfractionated river water organic matter fall well within the range reported for soil fulvic acids. An even more important revelation is that the high molecular weight fraction (obtained by gel chromatography) closely resembles soil humic acid.

The striking similarity between aquatic humic and soil humic substances suggests a soil origin for at least part of the aquatic humic matter. Reuter (1977) presents strong evidence in support of this. Shallow ground waters generally exhibit very low organic carbon concentrations 0.1 to 1.3 mg/L, which are an order of magnitude lower than those found in rivers. Vertical transport of dissolved humic matter in soils is generally restricted downward to the B horizon. Observations on some southern U.S. coastal plain streams show that during prolonged periods of low discharge, the organic carbon concentrations decrease. On the other hand, sharp increases in discharge are usually correlated with increases in organic carbon concentrations. This suggests that the bulk of the organic carbon, and specifically of humic substances, is derived from the soil after the water levels have risen upward through the profile during rain storm and overland flow has become a significant fraction of the total run off.

Figure 2. Distribution of acidic functional groups in soil fulvic acids (S-FA), soil humic acids (S-HA), unfractionated organic matter from river water (DOC-UF), and the high molecular weight fraction of organic matter from river water (DOC-HF).

Structural Considerations.

The conventional type of humus fractionation is illustrated in Figure 3. By the use of alkali and ethanol as extracting agents and precipitation with acid, soil organic matter is fractionated into humatomelanic acid, fulvic acids, humic acids, and humin. Total soil organic matter is separated into these four fractions.

Schnitzer and co-workers (1972) carried out extensive investigations of Humus fractions using mainly two methods: 1) "non-degradative" fractionation of humic and fulvic acids, followed by GLC-Mass Spec. analysis, and 2) permanganate oxidation followed by GLC-Mass Spec.

Christman (1967) isolated the colored material from aquatic sources and subjected it to oxidative degradation. The chemical nature of sedimentary humic material has been studied by many workers (Degens et al., 1964; Ishiwatari 1967, 1969, 1970, 1971) (see Ishiwatari 1972). Knowledge of sedimentary humic substances, however, is relatively fragmentary. Structural parameters of humic fractions from different origins, soil, sediment, and water obtained by workers mentioned above are presented in Tables 1 and 2.

Elemental analysis shows that, in general, soil humic fractions have a slightly higher C content than marine fractions, and that stream water fulvic acid approximates more closely to soil fulvic acid than that originating from a marine source. On the contrary the H/C ratio of

Figure 3. Scheme of traditional humus analysis.

TABLE 1. Ultimate analysis and atomic ratios of humus fractions.
Adapted from Ishiwatari 1972.

	Soil F.A.	Soil H.A.	Sed F.A.	Sed H.A.	Water F.A.	Peat H.A.
C	45.6- 51.0	52.3- 58.1	41.3- 48.7	50.2- 63.6	46.2	57.1- 62.7
H	3.2- 5.3	4.9- 5.6	6.0- 6.6	5.6- 7.3	5.9	5.2- 6.6
O	44- 47.3	34.6- 38.4	41.8- 48.3	24.1- 40.6	45.3	30.7- 37.7
N	.8- 2.3	1.6- 5.6	2.8- 6.8	3.6- 6.3	2.6	1.04- 2.86
H/C	.8- 1.4	1.0- 1.3	1.3- 1.7	1.1- 1.5	--	1.1- 1.2
O/C	.65- .77	.5- .6	.6- 1.0	.3- .6		.4- .5

TABLE 2. Functional groups and some important components of humus substances. All values in m equiv/g except as noted.

	Marine ^b	Soil HA ^a	Soil FA ^a	Remarks
>C=O	3-6	3-5	1-3	Marine slightly higher than soil.
Quinone Content	1.8-4.7	-	Nil	Marine higher than peat HA (0.6-0.8).
Phenolic OH	0.5-2.5	2.1-5.5	2.7-5.7	Marine lower than soil.
Alcoholic OH		2.8-3.5	3.4-4.9	
-COOH		1.5-4.7	8.5-9.1	
Carbon Aromaticity %	36	48-49		Marine lower than soil.
Protein Content %	28			
Carbohydrates %	2-6			
Fatty Acid Distribution	C ₁₆ predominating	Range from C ₁₆ -C ₃₆ with C ₂₄ predominating.		

^a Schnitzer and Khan 1972

^b Ishiwatari 1972

soil-derived material is lower than that of marine fractions. It is also noted that the N content of soil F.A. is lower than soil H.A. and marine fractions and is comparable to water fulvic acid.

One of the most significant characteristic apparent from Table 2 is that F.A. extracted from soil has a distinctly higher carboxyl content and slightly higher phenolic OH. This characteristic is important in producing negative charges on the fulvic acid molecule in alkaline solutions, in favouring interaction with metal ions, having dispersive properties, and probably changing redox properties. Magnetic spectroscopy shows that humic substances are stable organic free radicals as evidenced by unpaired electrons whose spin content increases with pH. This paramagnetism as measured by ESR Spectrometry has been ascribed to quinhydrone structures (Steelink et al. 1967). These are normally extremely reactive. Riffaldi et al. (1972) examined the concentrations of free radicals, their g values, and ESR line widths for HA, FA and humin originating from soils of widely different geographical origins and pedological histories. Their results show free radical content decreased in the order humins > HA's > FA's. Plots of spin concentrations vs %H and of spin concentrations vs %O showed inverse and direct statistically significant correlations between the parameters respectively. This was interpreted as that free radicals were formed via the oxidative removal of H from -OH groups.

X-ray diffraction methods have been evaluated for elucidating the structure of soil humic substances. Although humic substances are amorphous, X-ray diffraction patterns do provide limited information regarding nature of packing, ordering of condensed layers, interplanar distances, type of condensation, etc. Kasatochkin et al. (1964) concluded from X-ray studies that humic substances contain flat condensed aromatic networks to which side chains and functional groups are attached. Diffraction patterns of HA's extracted from chernozem soils exhibit distinct 002 reflections, suggesting that most of their carbon is in the condensed "nucleus" and little in the side chains. By contrast, the patterns of FA's extracted from turfy-podzolic soils show little 002 reflection but distinct γ -bands, which is interpreted to mean that most of their carbon is inside chains and little in condensed "nuclei". It may be noted here that elemental analyses also show (Tables 1 and 2) that fulvic acid has more aliphatic carbon than humic acid and less aromatic carbon than humic acid.

Molecular weight measurements are not precise and vary widely among sources, investigators, and methods. In general, molecular weights of humic substances measured by number-average methods (osmotic pressure, cryoscopy) and weight-average methods (viscosity, gel-filtration) are lower than those determined by Z-average (sedimentation) methods, but there are also wide discrepancies among values obtained

within each method. This is not surprising when differences in origin, extractants, degree of purification, etc., are taken into account. For homogeneous systems $\bar{M}_n = \bar{M}_w = \bar{M}_z$, while for heterogeneous systems such as humic materials $\bar{M}_n < \bar{M}_w < \bar{M}_z$ (Schnitzer et al. 1972). By gel filtration, the most common method, humic acids range from 5 000 - 100 000; fulvic acids range from 300 - 2 000.

Schnitzer (1976) carried out extensive degradative studies (oxidative, reductive, thermal and biological) on humic substances from widely differing environments expecting to produce simpler compounds that could be related to those of the starting materials.

The most abundant aliphatic degradation products consist of n-fatty acids, especially the n-C₁₆ and n-C₁₈ acids, di- and tri-carboxylic acids; the prominent benzene polycarboxylic acids are tri-, tetra-, penta- and hexa-forms; and major phenolic acids isolated include those with between 1 and 3 OH groups and between 1 and 5 COOH groups on the aromatic ring.

The main chemical structures identified in a number of humic substances from different sources by KMnO₄ oxidation of unmethylated as well as methylated materials were all aromatic rings substituted at C. The aromaticity of those substances averages 70%.

The important result of this study is that these "building blocks" are similar in HA's, FA's, and humins,

regardless of the origin and climatic conditions under which humic substances are formed. The major difference between the two humic materials is that F.A. is richer in phenolic structures than is the H.A.

Christman et al. (1966) reported similar oxidative degradation products viz., o-, m-dihydroxy benzenes, 3-4 dihydroxy benzoic acids etc. Weber and Wilson (1975) also reported analogous properties of humic substances from the two environments, soil and aquatic.

It was stated earlier that in addition to chemical means, soil microbes may contribute significantly to the formation of humic compounds. Two processes are involved: one is the extracellular transformation of plant and animal constituents into humic compounds, which primarily involve lignin humification; the other is the synthesis of humic precursors within the cells starting with simple aliphatic compounds.

Many fungi, actinomycetes, and bacteria synthesize by secondary metabolic processes either simple or more condensed structures. A great number of fungi belonging to the Imperfecti group synthesize phenols from non-aromatic precursors and transform them into dark colored polymers inside and outside the cells. Orsellinic acid and 6-methyl salicylic acid are two important phenols, the former is formed by *Epicoccum nigrum* (Haider et al. 1967), *Stachybotrys chartarum* (Martin et al. 1969), *Aspargillus sydowi* (Haider and Martin 1970), and by *Hendersonula toruloidea* (Martin et

al. 1972). Orsellinic acid can be converted to a number of phenols, by chemical as well as biosynthesis, which are similar to the compounds considered by Schnitzer (1976) as building blocks of humic substances (Figure 4). These fungal phenols are oxidized to quinones or reactive radicals and react with other phenols, with amino acids or peptides, and with amino sugars or other compounds with amino groups. Bu'lock et al. (1961, 1962) isolated from the young fruiting bodies of *Polyporus hispidus*, which grows on trees, a phenolic material which they named "hispidin". The authors showed that hispidin was oxidized to a lignin-like polymer by a phenol oxidase which develops in the ripening fruits as shown in Figure 5.

Soil particles, especially the clays, exert a marked effect on the activities of soil microbes. Adsorption of nutrients or enzymes by clays are often reported (Skujens 1967). Clays exert, furthermore, a more direct effect on the activity of micro-organisms: these minerals have been reported to enhance respiration and conversion of glucose to CO_2 (Lahar et al. 1962, Stotzky et al. 1966). Furthermore growth stimulation of bacteria in soil or in liquid cultures was observed (McCalla 1940, Conn et al. 1940, Filip 1968), and growth of fungi was reported to be stimulated by the addition of clays to liquid cultures (Haider et al. 1970).

Figure 4. Transformation of Orsellinic acid. Adapted from Haider et.al. 1975.

Figure 5. Formation and polymerisation of hispidin by polyporus hispidus.
Adapted from Bu'Lock 1967.

e) Structure of H.A. and F.A.

On the basis of phenolic and benzene carboxylic acids building blocks; X-ray findings that F.A. consists of a broken network of poorly condensed aromatic rings with appreciable numbers of disordered aliphatic chains around the edges of the aromatic rings; similar information from electron microscopy, which shows that F.A. has a sponge-like structure of variable thickness ($100-300 \text{ \AA}$), perforated by voids of widely differing sizes ($200-1000 \text{ \AA}$ in diameter), thus suggesting a relatively "open", flexible structure; from variability in molecular weight estimates, it becomes more and more apparent that humic substances are not single molecules but rather associations of molecules held together by weak linkages such as hydrogen-bonding, van der Waal's forces and possibly π -binding. These evidences led Schnitzer (1976) to propose a chemical structure for F.A. given in Figure 6.

In higher-molecular-weight fractions, i.e., H.A. and humin, the building blocks appear to be more complex and more stable (Neyroun et al. 1974). The increased stability of each building block may arise from more energetic linkages of F.A. type and/or from additional chemical bonding via C-O and c-o bonds. The structure for H.A. given by Fuchs (Figure 7) does not account for all of the structural parameters (some of these mentioned above) present in the literature, Dragunov's formula (Figure 7), however, meets

Figure 6. The structure of Fulvic Acid.

Figure 7. a. Structure of Humic Acid according to Fuchs.
 b. Structure of Humic Acid according to Dragunov.

many requirements, and the actual structures may be intermediate between those of the a and b structures. The chemistry of humic substances is thus far from fully understood.

f) Spectral Characteristics

Humic substances, like many relatively high molecular weight materials, yield generally uncharacteristic spectra. Absorption spectra of neutral, alkaline, and acidic aqueous solutions of H.A. and F.A. are featureless (Schnitzer and Khan 1972).

Flaig (1972) performed model experiments to explain the absence of discrete maxima in H.A. absorption curves. The isosbestic property shown by 1,4 diquinonyl-benzene (Figure 8) clearly demonstrates transformation of quinonoid structure. The conversion of quinonoid structure to hydroxy-hydroquinone via quinone radical, accompanied by oxidation, forms a deeply colored intramolecular quinhydrone.

And since EPR measurements have shown paramagnetism in humic acids, the latter may very well be intramolecular quinhydrone (Flaig 1972).

Figure 8. The transformation of 1,4-diquinonyl benzene: an example of the use of polymeric quinones as models of Humic Acids.

Many spectral properties have been explored in an attempt to quantitatively characterize humic substances. The ratio of optical densities or extinctions at 465 and at 665 nm, generally called E_4/E_6 , has been commonly used, as this parameter is independent of concentration, but depends upon the source type of humic substances. The values for different soil groups vary between 3 and 5.

Absorption spectra in the ordinary u.v. and visible region, which is chiefly caused by electronic transitions of the type $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ (written in increasing order of excitation energies), is featureless due to overlap of absorption bands of a series of substituted but closely related aromatic compounds. Occasionally an indication of maxima (shoulder) can be discerned in the 260-300 nm region (Sato et al. 1967; Schnitzer 1968). It is noteworthy that UV spectra of humic compounds of diverse origins are very similar in spite of differences in elementary composition, and other properties. Due to this property and greater sensitivity of absorbance with wavelength in u.v. region, a suitable wavelength can be chosen to correlate absorbances with analytical concentrations of colored material in fresh waters.

g) Organic-Metal Interactions in Aquatic Environment

Total organic carbon (TOC) values in natural waters vary between 10-40 mg/L (higher limit is fixed from the results of the present study), depending upon the organic activity in the drainage basin. Reuter and Perdue (1977),

according to a survey of organic substances in some river waters in the Soviet Union, report that some 60-80% of TOC consists of humic substances. This figure, of course, can not be assumed for rivers flowing in environments different from that surveyed. The present study, for example, indicates that humic substances in the Indian river, which flows over Precambrian marble, vary between 20-30% of TOC. The remaining portion, which would vary over a wide range, consists of amino acids, residual carbohydrates, simple organic acids, etc. Humic substances, irrespective of their concentration variation, are expected to dominate metal-organic interactions observed in natural waters due to appropriate functionalities (coordination sites) as described earlier.

The metal ions included in the present study belong to first transition series and as expected show strong interaction with humic substances. This aspect is fully developed in Chapter III. The solubility of these metals is a complex function of competing ligands, both inorganic and organic, present in the aquatic environment. The Eh and pH in surface waters are such that divalent metal ions may oxidize to a higher valence state. The concentration levels and state of these metals in solution and in suspension as defined by solubility are determined in turn by physical as well as chemical factors prevailing in the aquatic system. Mn, for example, exists as Mn^{4+} since Mn^{3+} is unstable and disproportionates according to the reaction,

with a log K value of approximately 9 (Stumm et al. 1970). Among the hydrous oxides of Fe the species of importance are Fe_3O_4 (magnetite) and amorphous goethite FeOOH . It is quite possible that freshly precipitated hydroxide is the familiar $\text{Fe}(\text{OH})_3$, which deactivates into a stable micro crystalline structure by exclusion of a water molecule according to the reaction,

Speculation! The process may be fast on the time scale of measurement and escape identification.

Aqueous chemistry of Fe and Mn is quite intriguing. These metals, due to low solubility precipitate almost quantitatively in neutral to alkaline solution (complexation is not considered for the sake of argument) and stay as suspended hydrous oxides. These suspensions have large surface area. The degree of interaction of dissolved species with inorganic and organic molecules suppressed by the phase transformation is partly compensated for by the large surface area in the solid phase.

It has been shown recently, that basic carbonates of Fe^{3+} may be precipitated from carbonate solutions (Bvorak 1969).

Inorganic ligands e.g., OH^- , SO_4^{2-} , CO_3^{2-} , and Cl^- , compete with organic ligands, particularly in waters flowing over sulfide or carbonate bed rock. Manning et al. (1973) speculate, from their model study, that mixed inorganic-organic ligands are more significant than organic ligands.

On the other hand Gardner (1974) showed that humic substances bind Cd(II) to a greater extent than any of the major inorganic ligands (CO_3^{2-} , SO_4^{2-} , Cl^- , OH^-) in natural waters, particularly where humic ligands are predominant. Our knowledge regarding the mixed ligand systems, which undoubtedly are very common in natural waters, is limited, and before any such study is undertaken, simple inorganic ligand-metal complexes at an appropriate pH range and possibly the matrix have to be characterized. The reason is very simple; the major complexes that are formed and their concentrations will be determined by the stability constants of all possible complexes, the pH of the solution, the pKa of complexing ligands and the total concentration of each metal and each complexing agent present.

Pickering (1977) has attempted to show some competing equilibria and interactions schematically, which can be operative in a natural water system (Figure 9). The nature and role of these natural water components will now be examined in some detail.

h) Humic Substances

The gel filtration technique is widely used for fractionation of humic substances, and determination of molecular weights of these fractions. Molecular weights of HA and FA extracts from soil of the order of 300 to >200 000 (Schnitzer and Khan 1972) have been reported. For humic substances in natural waters values varying from 700 to >200 000 have been reported.

Figure 9. Diagram showing some of the competing equilibria and interactions which can be operative in a natural water system.

Gjessing (1965) separated two fractions from humic substances on sephadex column G-100: one with molecular weight $<10\ 000$, and the other $>100\ 000$, and found both fractions containing Fe^{2+} . His further studies indicate that between 20 to 40% humic acids are present in fractions of molecular weight $>200\ 000$ and that $>52\%$ Fe is present in this fraction (Gjessing 1970). Pennanen (1975) carried out similar studies on dissolved humic substances from dystrophic Finnish lakes and quoting his words "Using either Sephadex G-100 or G-150, I have constantly found that one fraction is completely excluded, while the other is retained". The excluded fraction's molecular weight is above $100\ 000$, and can be precipitated with mineral acid, whereas the one retained remains soluble at low pH's. He designated former fractions 'colloidal fraction', and the latter 'electrolyte fraction', and found that the cations studied (Na, K, Ca, Mg, Mn and Fe) were eluted with the electrolyte fraction.

The author of the present thesis believes that electrolyte fraction (low molecular weight) is similar to fulvic acids which show strong affinity towards alkali, alkaline earths, and transition metals of interest in aquatic systems. In a comprehensive study of the distribution of organic and inorganic constituents in natural waters, Beck *et al.* (1974) on the basis of chemical analysis (total acidity, $-\text{COOH}$, amino acid residues, and CHN analysis), and spectroscopic analysis (IR and NMR) concluded that river water organic matter is chemically similar to soil fulvic acid.

It is however important to note that both fractions (F.A. and H.A.) are part of a 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 polymers is further evidenced by their susceptibility to fractionation by techniques such as continuous electrophoresis (Jackson et al. 1978). It is therefore not surprising to observe that both fractions show affinity towards metals varying only in degree and not in type.

Inasmuch as the major fraction of dissolved organic matter in most natural waters closely resembles soil fulvic acids (Reuter 1977), it should be possible to use the extensive information available on metal-fulvic acid interaction to approximately describe those between metals and dissolved humic substances in natural waters.

Relevant to any analysis of metal fulvic acid interactions is a knowledge of the acid base equilibrium and redox properties characteristic of fulvic acid. Gamble (1970, 1972) treats fulvic acid as a polyelectrolyte, and considers it as an irregular polymer of moderately low molecular weight with a number of chemically non-identical acidic functional groups, whose respective dissociation constants are a function of the overall degree of ionization of the fulvic acid polymer. According to this model, the acid dissociation functions for the ionization of individual functional groups can be calculated. He reports two types of acidic groups in

fulvic acid extracted from Prince Edward Island B horizon podzolic soil type I ortho to phenolic -OH, estimated from conductometric titration, corresponds to the first equivalence point value of 3.14 meq/gm F.A. Type II, other than ortho to phenolic-OH, estimated from the total -COOH gps evaluated by potentiometric titrations. With the aid of Gran's equivalence point calculation method for a weak acid having two end points, an equivalence point value of 7.27 meq total -COOH groups per gm of F.A. was computed. Type II acidic gps are then equal to $(7.27 - 3.14)$ 4.13 meq per gm of F.A. Borggaard (1974) in a similar potentiometric study indicated the presence of 1.5-3.0 meq/g of highly acidic ($pK_1 = 2.8 - 3.4$) carboxylic groups, 2.7-4.2 meq/g of moderately acidic ($pK_2 = 4.9 - 5.1$) carboxylic groups, and 1.1-1.7 meq/g of weakly acidic ($pK_3 = 9.4 - 9.7$) phenolic hydroxal groups. The value of latter for P.E.I. fulvic acid is 3 meq/gm. The great amount of information thus obtained suggests that the standard acid base titration may indeed be very useful in characterizing the acidic functional groups of humic substances. These acidic groups are the potential binding sites for metal ions.

i) Type of Interactions

The type of interactions involved in natural waters include the formation of coordination complexes (inner and outer sphere) in the case of transition metals and electrostatic interactions in other cases. The inner-sphere

complexes, generally characterized by large stability constants as a result of crystal field stabilization energies (CFSE), can be considered due to strong interactions. Outer-sphere complexes, on the other hand, involve weak interactions, because ligands do not enter the first coordination shell of the metal; there is no overlapping of metal and ligand orbitals to effect σ or π bonding. In other cases, for example, alkali and alkaline earths, metal ions acquire inert gas structure having no orbitals available to overlap with or occupy the ligand orbitals. The positive charge of these cations interact electrostatically with negatively charged ligands and the resulting compounds are classified as ionic. The interaction in ionic compounds is weak as compared to coordination complexes which gain extra stabilization due to CFSE.

Another type of very weak interaction is due to Van der Waal forces. These account for association between neutral molecules which do not have permanent dipoles. These interactions arise from an imperfect balance of positive and negative charges within the molecule.

Since the present work is limited to the transition metals Fe, Mn, Cu, and Ni, the mechanism describing the formation of coordination complexes is relevant.

Metal F.A. Complexes.

The three functional groups that influence any metal-fulvic acid complexation are: (1) phenolic - OH gp, which

remain un-neutralized except by reaction with concentrated strong base (Schnitzer et al. 24), (2) Type I -COOH, defined as those ortho to the phenolic groups, (3) all other ionizable functional groups, probably including some -COOH groups meta to the phenolic -OH.

Two mechanisms have been postulated for the interaction of metal ion and fulvic acid type ligands, the first strongly favoured is based by selective blocking

functional groups. Schnitzer et al. (1965) blocked functional groups in various combinations, followed by metal retention measurements. Their results show

- (a) The largest reduction in metal ion retention by the fulvic acid occurred when carboxyl groups and phenolic groups were both blocked;

- (b) The second largest effect was obtained when either carboxylic or phenolic groups were blocked;
- (c) No effect resulted from the blocking of alcoholic OH groups.

However, it should not be overlooked that this mechanism is pH dependent, and that at pHs dominant in fresh waters, organic ligands have to compete with -OH groups or form mixed hydroxo-organic-metal complexes. Thus overall stability constant β should increase with pH, which is observed by Schnitzer and Hansen (1970).

A large number of data is available on metal-fulvic and metal-humic acid complexes. The subject is reviewed by Schnitzer and Khan (1972).

Some interesting facts were revealed recently from ion-selective-electrode study of F.A. and Cu(II), Hg(II), Cd(II) ions (Cheam 1973 and Cheam and Gamble 1974). Cheam (1973) reported that the stability constant for Cu(II)-F.A. complex is a function of the mole fraction of Cu(II) (x_{Cu}) particularly if $x_{Cu} < 0.3$. Much of the discrepancy in reported stability constant values for Cu(II)-F.A. system was shown to result from the dependence of the stability constant on x_{Cu} .

Gamble (1973), using an ion-selective electrode, has demonstrated that F.A. binds both Na^+ and K^+ . This raises a very interesting point, that this ability of humic substances must undoubtedly effects the measurement of

binding of other metals (e.g., transition metals), particularly when Na^+ and K^+ salts are used as supporting electrolytes. The importance of metal-fulvic acid complex in natural water has been questioned by Stumm and Morgan (1970) on the grounds of greater abundance of Ca^{2+} and Mg^{2+} (2-3 orders of magnitude) as compared to dissolved organic matter. This question, according to him, is well justified because in natural water systems the stability of a complex is influenced not only by OH^- and H^+ , but also by other metal ions, especially Ca^{2+} and Mg^{2+} . It is instructive here to compare stability constants of Fe^{3+} - EDTA (strongly complexed system) with that of Ca^{2+} - EDTA.

In a mixed system, Fe^{3+} will replace Ca^{2+} according to the equilibria

$$\log K = \frac{K_{\text{FeY}}}{K_{\text{CaY}}} = 14.4$$

This means that FeY^- cannot be formed to any significant extent if the ratio of $[\text{Ca}^{2+}]/[\text{Fe}^{3+}]$ is sufficiently large. This is a simple account, for an exact calculation the hydroxo complexes e.g., FeYOH^{2-} have to be considered in addition to CaY^{2-} and FeY^- . It is apparent, however, that in natural water systems Ca^{2+} and Mg^{2+} would suppress trace metal-organic solute interaction to a limited extent.

Humic acid-metal complexes have also been investigated. Although humic acids form stronger complexes with trace metals than fulvic acid, they may not play a significant role in mobilizing trace metals because of their insoluble (colloidal) character. Tables 3 and 4, taken from Jackson et al. (1978), lists available data on stability constants of humates and fulvates, and show stronger complexing ability of humic acids, the difference between the two sets of data, however, is not too large.

The evidence presented so far suggest that chelation is an important mechanism of interaction between trace metal and organics in natural waters. Other mechanisms, such as chemisorption, have been suggested to explain the coagulative behaviour of dispersed colloids. Multivalent cations are able to form soluble and insoluble complexes with substances containing $-COOH$, $-OH$, $=SO_4$, and $\equiv PO_4$ by the fixation of cation onto the ionized group (possibly bond formation), accompanied by a reduction of the effective charge of the particles and by alteration of their surface solvation and in turn their solubility. The process may be visualized by the following reaction

Further, hydrolytic products of multivalent cations (Fe, Mn) are adsorbed more strongly at particle-water interface than non hydrolyzed metal ion (Stumm and Morgan 1970), due to the following reasons:

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

Table 3. Some Stability constants for Humic acid-metallic cation complexing.

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. Cheem and Gamble, 1974

Table 4. Stability constants for Fulvic acid-metallic cation complexes at 0.1 ionic strength.

1. Hydrolyzed species are larger and less hydrated than non-hydrolyzed species.
2. The enhancement of adsorption is due to the presence of -OH group. Since many solid surfaces are found containing bound -OH groups, hydroxo metal complexes may be favourably adsorbed to the solid surface.
3. Adsorption becomes especially pronounced for poly hydroxo - poly metal species because more than one -OH group per 'molecule' can become attached at the interface.

It is interesting to note that adsorption of poly hydroxo metal complexes can occur against electrostatic repulsion forces, ie. the chemical adsorption energy can outweigh the electrochemical work involved in the adsorption. Stumm and Morgan (1970) conclude that it is more probable that insoluble organic-hydroxy iron species are present in stable colloidal dispersion.

Considerable work has been done on adsorption of metals by humic substances. Rashid (1974) and Guy (1975) have shown that trace metals are readily adsorbed on the surface of particulate humic substances. In the former's experiments, peatmoss (a rich source of humic compounds) and humic acid was allowed to react with Co, Cu, Mn, Ni, and Zn and it was found that Cu was preferentially adsorbed. More important, leaching showed that Cu was far more strongly sorbed than the other metals, implying predominance of chemical adsorption

over physical. Several other workers (Broadbent 1957; Davies et al. 1969, etc.) have shown varying degrees of metal retention on humic matter by leaching experiments. Results similar to Rashid (1974) were obtained by Chowdhury and Bose (1970); they found that the stability of the metal-particulate organic species formed increased in the order $\text{Co} < \text{Ni} < \text{Zn} < \text{Cu} < \text{Pb}$. These metals were almost completely released at pH less than 1, at pH values pertinent to natural conditions, however, Pb and Cu proved most resistant to leaching from soil humus.

Many organic hydrophilic colloids form highly colored complexes with ferric iron. In natural surface waters, high concentrations of organic material are frequently found associated with high concentrations of iron (Shapiro 1957).

The metal hydrous oxides or hydroxides can be compared, at least operationally, with polyelectrolytes (humic, fulvic acids etc.). Because of the pH-dependent charge characteristics, these oxides can exhibit either cation or anion exchange characteristics, depending upon pH. These hydroxides, in addition to their purely electrostatic effects on the ionic solutes, show a strong tendency to interact chemically with anions as well as cations (Stumm and Morgan 1970).

The chemical interactions have been explained in terms of complex formation (Stumm 1970). If a surface group of hydrous metal oxide is represented by $-\text{M}-\text{OH}$, the interactions with anions can be interpreted as ligand exchange

process, for example,

In ligand exchange process, the replacement of metal -OH group by another anion will depend upon the affinity of metal ion for its coordinated hydroxal group and the exchanging anionic ligand. A qualitative evaluation can be made by comparing the formation constants of metal and the ligands in question. For example in the case of hydrous ferric oxide that may interact with phosphates, we may compare the following reactions:

These formation constants show that OH^- has a stronger affinity for Fe^{3+} than does HPO_4^{2-} or PO_4^{3-} . However, the extent of complex formation of Fe^{3+} with HPO_4^{2-} or PO_4^{3-} depends upon the ratio of $[HPO_4^{2-}]/[OH^-]$ or $[PO_4^{3-}]/[OH^-]$ respectively. With decreasing pH phosphate will have an increasing tendency to enter into the coordinate sphere of the surface Fe^{3+} ion. Work done in this laboratory (Kay et al. 1977) indicates that when one equivalent of phosphate is present in the solution of Fe-F.A. (1:1) at pH 4, ferric phosphate precipitated and did not settle in 24 hours. The suspension dissolved completely after 24 hours producing

Fe(III) in solution. The results suggest precipitation of ferric phosphate takes precedence over iron hydrolysis and Fe-F.A. complexation. The results also show that phosphate inhibits reducing properties of F.A. which has been observed in phosphate free solutions.

The interaction with cations can be interpreted as coordination with electron acceptor metal ions. The process in this case involves (a) ionization of the surface group -M-OH according to

and the coordination with solute cation, for example Zn, according to the reaction.

The tendency to complex formation, thus increases with increasing pH.

Kinetics of Fe(II) and Mn(II) redox reactions.

Some useful information regarding the mechanism of Fe^{2+} and Mn^{2+} oxidation has been obtained from kinetic measurements in solutions of concentration less than 5×10^{-4} M (Morgan et al. 1964). The results indicate that the oxidation of both Fe^{2+} and Mn^{2+} ions is strongly pH dependent and that Mn^{2+} oxygenation does not follow the same rate law as Fe^{2+} oxygenation. The auto-catalytic oxidation mechanism in the case of Mn^{2+} has been proposed to follow the following mechanism:

The interpretation of this scheme is that (a) not all Mn^{2+} removed from the solution is oxidized to insoluble MnO_2 and that (b) the products of Mn^{2+} oxygenation are non stoichiometric, showing various degrees of oxidation ranging from $\text{MnO}_{1.3}$ to $\text{MnO}_{1.9}$. The implication of these results is that suspended MnO_2 in oxygenated surface waters carry some adsorbed Mn^{2+} ions.

The case of Fe is slightly different from that of Mn and presents interesting implications with regards to Fe-organic chemistry in natural water systems. It has long been observed that sulfur containing compounds (cysteine etc.) as well as variety of organic substances, especially those that contain hydroxy and/or carboxylic functional groups (e.g., phenols, gallic acid, tannic acid, fulvic acid, and humic acid) can reduce both Fe^{3+} and MnO_2 reasonably fast in synthetic solution (minutes to hours). Such observations are especially interesting in the case of iron, where the same type of substance that reduce ferric iron can also catalyze the oxygenation rate. This apparent contradiction may be explained by the following reaction mechanism:

If conditions of pH and concentration are such that the rate of Fe^{2+} oxygenation is slow in comparison to the Fe^{3+} reduction by the organic material, a relatively high steady-state concentration of Fe^{2+} is built up in the system as long as the organic material is not fully oxidized. Under such circumstances organic material retards the overall oxidation of Fe^{2+} . In natural waters of relatively high organic content and pH, the presence of Fe^{2+} cannot, therefore, be disregarded.

Adsorption and Coprecipitation on Oxide

Kinniburgh et al. (1976) studied adsorption from a mixed solution of light divalent cations (each 0.125×10^{-3} M) in suspensions of freshly precipitated Fe and Al gels (0.093 M with respect to Fe and Al) as a function of pH, and found that gels strongly specifically adsorb divalent cations. The selectivity sequence (lower pH = greater selectivity) for the retention of alkaline earth cations by Fe gel was $\text{Ba} > \text{Ca} > \text{Sr} > \text{Mg}$, but for Al gel was $\text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$. The selectivity sequence for heavy metals adsorbed on Fe gel was $\text{Pb} (3.1) > \text{Cu} (4.4) > \text{Zn} (5.4) > \text{Ni} (5.6) > \text{Cd} (5.8) > \text{Co} (6.0) > \text{Sr} (7.4) > \text{Mg} (7.8)$, whereas the sequence for the Al gel was $\text{Cu} (4.8) > \text{Pb} (5.2) > \text{Zn} (5.6) > \text{Ni} (6.3) > \text{Co} (6.5) > \text{Cd} (6.6) > \text{Mg} (8.1) > \text{Sr} (9.2)$. Figures in parentheses indicate pH for 50% retention. The adsorption-pH sequences are related to cation hydrolyses and hydroxide precipitation pH values.

Murray (1975) measured adsorption of metal ions on synthetic hydrous MnO_2 (which resemble closely naturally occurring manganese minerals), and found that the affinity of the metals for the surface followed the order:

and that the interaction can be characterized by its pH dependence. A comparison of the amount of metal adsorbed with the amount of acid released by the surface was interpreted as complex formation between hydrous MnO_2 and metal ion with subsequent release of proton.

Similar findings have been reported by Taylor et al. (1966) and Taylor (1968), that the concentrations of Co, Zn, and other agriculturally important heavy metals in the soils are quite high in the hydrous manganese oxides. Jenne (1968), in reviewing the available information on the controls of Mn, Fe, Co, Ni, Cu, and Zn in soils, sediments, and fresh water, concluded that the hydrous oxides of Mn and Fe furnish the principal controls on the fixation of these heavy metals. Morgan et al. (1964) explained the high sorption capacities of $\delta\text{-MnO}_2$ for metal ions are due either to surface complex formation or ion exchange. Murray et al. (1968) studied the sorption of metal ions on a $10 \text{ \AA}$ manganite at a pH close to the isoelectric point, and found that Co, Cu, and Ni were sorbed even at pH values lower than the isoelectric point, whereas the alkali metals Na, K, and Li did not sorb under the same conditions. Loganathan et al. (1973), while studying sorption of Co, Zn, Ca, and Na by $\delta\text{-MnO}_2$, computed the

sum of all sites occupied by these metal ions. They observed that during the sorption of Co and Zn, Mn was released to the solution phase, however, Mn release was not detected during the sorption of Ca and Na. It was proposed that there was only one site where Ca interchanged with surface bound H. Zn was postulated to interchange not only with these bound H sites, but also with another site where it interchanged with structural Mn^{2+} . Co was postulated to interchange with both of these sites, and additionally, with a third site where it interchanged with structural Mn^{3+} . It was also determined that approximately 2 moles of H were released per mole of Co or Zn sorbed at bound H sites.

Separation with or without competition by simple ligand is frequently accompanied by coprecipitation. Separation of M^{3+} hydroxides (Fe^{3+} , Al^{3+} , La^{3+} etc.) from solutions containing M^{2+} ions (Cu^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} and Ni^{2+}) at pH = 8 co-precipitate M^{2+} with $M(OH)_3$. Addition of a ligand, for example aminoacetic acid (AAA) and ethylene diamine (EDA) leads to considerable drop in the co-precipitation of M^{2+} . Teodorovich (1975) explained this effect in the first instance by the capacity of AAA and EDA to form stable soluble complexes with M^{2+} ; in the process precipitation of M^{3+} as $M(OH)_3$ is still complete. He further examined sorptive affinity and sorptive capacity parameters for M^{3+} sorbent - M^{2+} sorbate systems and concluded that M^{2+} - $Fe(OH)_3$ have greater stability than M^{2+} - $Al(OH)_3$ systems. The information obtained on these systems also confirm that co-precipitation of M^{2+} in the volume of the precipitate is greater for systems involving

Zn^{2+} , Cd^{2+} , Co^{2+} and smaller for systems involving Cu^{2+} and Ni^{2+} ; this is in agreement with the stabilities of the respective $\text{M}^{2+}-\text{M}(\text{OH})_3$ bonds.

Metal Organic Colloids

There are other forces between atoms and molecules which are always attractive. These are known as London-van der Waals forces. The energy of interaction resulting from these forces (2-10 K cal/mole) is small compared to that of covalent bond or electrostatic (ion pair) bond ($>> 10$ K cal/mole). The van der Waals attraction energy between two atoms is inversely proportional to the sixth power of distance over small distance, and hence dissipate rapidly with distance.

Weak interactions are commonly encountered in processes of co-precipitation. Separation of M^{3+} hydroxides (Fe^{3+} , Al^{3+} , La^{3+} etc.) from solutions containing M^{2+} ions (Cu^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} and Ni^{2+}) at $\text{pH} \approx 8$ co-precipitate M^{2+} with $\text{M}(\text{OH})_3$. Addition of a ligand, for example aminoacetic acid (AAA) and ethylene diamine (EDA) leads to considerable drop in the co-precipitation of M^{2+} . Teodorovich (1975) explained this effect in the first instance by the capacity of AAA and EDA to form stable soluble complexes with M^{2+} ; in the process precipitation of M^{3+} as $\text{M}(\text{OH})_3$ is still complete. He further examined sorptive affinity and sorptive capacity parameters for M^{3+} sorbent - M^{2+} sorbate systems and concluded that $\text{M}^{2+}-\text{Fe}(\text{OH})_3$ have greater stability than $\text{M}^{2+}-\text{Al}(\text{OH})_3$ systems. The information obtained on these systems also confirm that co-precipitation of M^{2+} in the volume of the precipitate is greater for systems involving Zn^{2+} , Cd^{2+} , Co^{2+} and smaller

for systems involving Cu^{2+} and Ni^{2+} ; this is in agreement with the stabilities of the respective $\text{M}^{2+}-\text{M}(\text{OH})_3$ bonds.

As regards to the dissolved organic matter in natural waters, these type of interactions have been proposed to control the particle size. Humic substances in solution considered negatively charged macro-ions or negatively charged hydrophilic colloids, exhibiting properties characteristic to colloids; coagulation and peptization. Ong and Bisque (1968) report that at pH 7 trivalent ions are more effective in coagulating humus than are divalent, and that divalent are more effective than monovalent ions. Further, among cations of the same valence, those with the largest ionic radius are the most effective coagulants. This observation is in accordance with the Schulze-Hardy rule and can be explained in terms of reduction or screening of the charge on the polyelectrolyte that keeps the molecule from collapsing into a coagulated mass.

More convincing evidence of metal-organic interactions, called in this presentation 'weak interaction' is derived from natural systems consisting of mixed iron oxide-organic matter colloids. Stumm and Morgan (1970) strongly favour the thesis that high concentrations of Fe attainable in solution in natural waters are due to colloidal dispersion of hydroxy iron stabilized by anionic organic molecules. Following this model and bearing in mind that the colloid is held dispersed by weak interactions, coagulation of the dispersed phase by the introduction of an electrolyte can

be readily explained.

In a recent study Boyle et al. (1977) surveyed U.S. east coast estuaries and confirmed that large scale rapid removal of iron from river water is a general phenomenon during estuarine mixing. The river-borne iron consists almost entirely of mixed iron oxide-organic matter colloids of diameter less than $0.45\ \mu\text{m}$ stabilized by the dissolved organic matter (Boyle et al. 1977). Precipitation occurs on mixing because the sea water cations neutralize the negatively charged iron-bearing colloids allowing flocculation.

Another study on naturally occurring organic material from a lake in the southeastern U.S. shows weak interactions between organic matter and hydrated Mn^{2+} ion (Albert et al. 1976). The organic material was isolated by ultrafiltration and analyzed by IR and ESR spectrometry and for its elemental composition without chemical pre-treatment. The results indicate that the isolate is an apparent high molecular weight fulvic acid (10 000-300 000) with associated hydrated Mn^{2+} ion which does not appear strongly bound to the organic moiety.

It must be stated before leaving this section, that the material presented above is an attempt to show that there are organic (humic substances) and inorganic (hydrated manganese and iron oxides) moieties in natural waters constituting dispersed phase of size varying over a wide range and that these interact with metal ions by forming strong coordination complexes, by ion-exchange, and by weak

electrostatic attraction depending upon both physical and chemical factors. Resultant force acting in such a complex mixture of solutes as natural waters indeed result from strong interactions (coordinated bonds) to weak interactions of van der Waal type depending upon the complexity of the solute present. A realistic evaluation of the degree and nature of binding between organic and inorganic species would have to wait until our knowledge of natural speciation in aquatic environment is developed. This would require a concerted interdisciplinary effort, which should help to clarify the role of metal-organic compounds in the geochemical cycle. For the chemist, greater knowledge of the actual reactants present in a specific naturally-occurring system is needed, together with an understanding of the atomic, molecular, and ligand-field parameters which decide the course of geochemical and biogeochemical reactions (Saxby 1969).

j) Measurement of Complexing Capacity of Natural Waters

The titration of natural water samples with metal ions to measure the "chelating capacity" (or complexing capacity) follows from work by Chau et al. (1974) as a first response to their important observation that total toxic metal ion concentrations were relatively poor measure of biological effects. Earlier, metal ion titration of sewage effluents was introduced by Bender et al., (1970). In the sewage

effluent study, organic ligands were fractionated prior to the titration in order that complexing capacity could be linked to specific types of constituents. This has not always been done for natural water samples because of the very low level of complexing capacity. Nevertheless, the idea of chelating capacity or complexing capacity of natural waters has attracted a good deal of attention and appears to be becoming an important concept.

Ramanmoorthy (1975) measured complexing capacity of Ottawa river water for heavy metals (Cu, Pb, etc.) by adding a known quantity of metal ion in question, and determining concentration of free metal with ion-selective electrode. For Hg^{2+} , the ion was strongly bound until 15 p.p.m. had been added, after which the bound fraction decreased rapidly. They interpreted this as the saturation of binding capacity at 15 p.p.m. Other metal ions showed different behaviour, e.g., Pb^{2+} saturation of binding capacity spread over a much wider range.

They also calculated equilibrium binding constants and compared these with those obtained for fulvic acid isolated from soil. Both these steps are open to question on fundamental grounds. If the ligands which are the source of complexing capacity are of the fulvic acid type, they are polyelectrolytes. As Gamble and Schnitzer (1973) remark, "no two carboxyl groups are inherently chemically identical". Calculations of binding constants have assumed a homogeneous sample of a chemically uniform ligand. This is not appro-

priate for fulvic acids as the theory of polyelectrolyte titrations given by Gamble and Schnitzer shows. An especially important point is that conditional binding constants calculated for natural water have been compared to those determined for model compounds at larger and more convenient concentration of the model compound (fulvic acid). Burch, Langford, and Gamble (1978) have recently shown that one surprising consequence of the polyelectrolyte situation is that conditional constants calculated are a function of the fulvic acid concentration and that this is an important factor in the comparison of materials from differing soil origins. The concepts applicable to simple electrolytes therefore, may not be valid for polyelectrolytes.

Chau's (1973) work on the subject is classical, and the technique he employed, D.P. ASV*, is more sensitive (to a fraction of ppb concentration levels) and may be claimed precise, but the results are based on an assumption that is critical to the validity of the technique in that the polarized electrode distinguishes between the labile and non-labile metal ions. The matter is discussed in detail in Chapter 2. His results do show the expected result that labile metal component was very significant in lakes of relatively low pH and that Cu and Pb are more strongly bound in lake waters than Zn in compliance with Irving-William series, provided the bound metal is in the form of metal-organic complex.

* Differential Pulse Anode Stripping Voltammetry

In a similar study and employing the same technique Smith (1976) recently measured complexing capacities of estuarine water components obtained by ultra-filtration fractionation. The complexing capacity of each molecular weight fraction was determined after the fraction was diluted to its in situ concentration. The results indicate that the molecular weight range designated $< 1\ 000$ has an increasing ability to complex copper.

Yet in another study Shuman et al. (1977) reported conditional formation constant for Cu-organic chelates in fresh water samples at controlled pH. Titration curves were constructed using ASV to detect unreacted copper. The ligand in the water samples responsible for Cu binding according to the report was characteristic of a conjugate base of a weak acid, the acid being almost entirely ionized at neutral pH. Estimates of the conditional formation constants for these complexes ranged in value from $.32 \times 10^5$ to 5.2×10^5 at pH 6.3. It is interesting to compare this result (which corresponds to pond water, near Chapel Hill, N.C.) with that obtained by Ramanonthy for Ottawa river, $K_{Cu} = 5.01 \pm 1.58 \times 10^3$. The difference in the two constants by two orders of magnitude may indicate the weakness of the method of data reduction.

Hanck et al. (1977) applied three voltametric methods, anode stripping voltametry (ASV), differential pulse polarography (D.P.P.), and low temperature dual-cell ASV (LT ASV)

to determine free metal concentration in Cu^{2+} , Cd^{2+} , Pb^{2+} , In^{3+} and EDTA model. They found that room temperature ASV yields results that were consistently low with a relative error ranging from -14% to -34% depending upon which ion was used as titrant. Low temperature ASV did not improve the results, not to say the added procedural complexities. Results from D.P.P. were also low and subject to kinetic effects. Low results were no surprise, as noted by Hanck, due to depletion of metal ion at the electrode surface, a concentration gradient develops between the electrode and the bulk driving the equilibrium

to the left. This perturbation of equilibrium is true in all cases where voltametric methods of analysis have been employed. In a later communication Hanck (1977) claims to have eliminated the problem complex lability by choosing to complex organic ligands with Co(II) followed by oxidation to inert Co(III)-complex. The method failed to detect concentration levels of amino acids, however, an improvement in the results was claimed in cases where the method was applicable.

CHAPTER 2

A PROBLEM AND A RESEARCH PLANa) Identification of the Problem and the Research Plan

The last Chapter has described the significant source and the nature of organic matter which enters stream waters and has catalogued the complexities of the relation between dissolved organic matter and metal ions. To illuminate the relationship between dissolved metal ions and organic matter more fully is the aim of this thesis. In approaching the question at the start of this work, the most significant gap in the literature appeared to be an attempt to correlate dissolved metals with specific fractions of organic matter in the water. This is because fractionation and quantitative recovery of the low concentration of dissolved organic matter is a delicate task. But it is an important one. Subsequent to fractionation and quantitative recovery is the identification of significant fraction(s), and investigation of their properties, particularly complexation with trace metals. It is also the object of this work to separate the particulate matter from the dissolved, estimate the organic and inorganic content and make an attempt to correlate the two parameters. A field site was sought which would have relatively high dissolved organic matter, geologically interesting metal sources, and minimal contamination from human activity.

Indian river stream chosen for the study meets the above requirements and is conveniently located for sampling. The

geology and the soil characteristics of the field area are described in the next two sections of this Chapter.

The trace metals chosen for study were Cu, Fe, Mn and Ni. The chemical as well as the physical form of these metals and their concentration levels are a complex function of a number of variables characteristic of the water stream. Important among these are the organic substances and the inorganic counter ions prevalent under the existing Eh, pH conditions. These substances determine the speciation and fix the concentration levels of metal ions in the stream.

The problem therefore involves

- (a) Characterization of organic solutes in the stream, and an estimate of their concentrations.
- (b) Determination of concentration levels of metal ions chosen for the study.
- (c) Determination of parameters specific to metal ion-organic phase interactions.

The last two aspects of the research involve an analytical approach, and have been described in Chapter 3. The first part, however, requires an evaluation of methods available for the fractionation of organic material present in stream water.

Many schemes have been devised, advocated and tested, but no perfect system has been devised. Most analytical schemes are based on methodology which incorporates liquid-liquid extraction or carbon adsorption to extract and concentrate organic solutes prior to analysis. These

techniques have their limitations and drawbacks.

For example, liquid-liquid extraction is an efficient method of extracting certain classes of compounds from water, particularly those non polar solutes which have low water solubility, but high solubility, in organic solvents. A basic assumption of the extracting technique is that the distribution coefficient of an organic solute between two immiscible liquids is constant. This does not always follow, and generally the distribution coefficient varies with the concentration of the solute. Liquid-liquid extraction is difficult for highly polar organic solutes, which is the case with organic solutes found in natural waters.

Activated carbon is an efficient agent for removing organic solutes from water by adsorption; however, its use in quantitative analytical schemes is limited by the fact that many organic solutes are not desorbed from the activated carbon (Baker and Malo 1967, Burnham et al. 1973). Another consideration is that once all available sorption sites are filled, selective organic sorption occurs and previously sorbed solutes are desorbed. The recovered organic fraction then, may not represent the original sample composition. Also, certain organic solutes, such as polysaccharides, and amino acids are not adsorbed on activated carbon. Because neither adsorption nor desorption are quantitative, activated carbon cannot be used to measure total organic solute concentrations and to achieve mass balance of separated fractions in aqueous systems. Another characteristic of a

strong adsorber like activated carbon that is not desirable for the purpose of fractionation is that elution of the material adsorbed on the column is not efficient. The elution peaks are generally very wide and excessively large eluent volume is required for a satisfactory elution.

Synthetic resin are free from these limitations and generally display reversible, low energy processes and are capable of selective adsorption. In addition to these advantages, the favourable physical properties, e.g., large surface area, structural stability, and good hydraulic flow led Leenheer and Huffman (1976) to the selection of macroreticular styrene-divinylbenzene copolymers for the fractionation of aquatic organic solutes. These resins are available with non polar surfaces (Amberlite XAD-2 and XAD-4), intermediate polarity surfaces (Amberlite XAD-7 and XAD-8), and highly polar surfaces (XAD-12).

Using XAD-2 and XAD-8 resins, the fractionation scheme divides aquatic organic solutes into hydrophobic and hydrophilic classes. The hydrophobic solutes are defined in this classification procedure as those organic solutes which are adsorbed on the resin surfaces of low and intermediate polarity. The hydrophilic solutes are those which are not adsorbed on these resins, i.e. those which are not retained by XAD-2 and XAD-8 stratified columns. The hydrophobic fraction, which is the major component of organic solutes and is of interest to the present study is thus isolated from the

original water sample. The hydrophobic fraction can then be further divided into hydrophobic acids and hydrophobic bases components by the elution process.

Leenheer and Huffman (1976) describe the analytical procedure of fractionation after testing it on a model solution. The compounds used for test standards were: benzoic acid, fulvic acid, p-methyl benzyl alcohol, aniline, representing a range from hydrophobic acids through to hydrophobic bases. Acetic acid, sucrose, and ethylenediamine represented hydrophilic acids through to hydrophilic bases. The carbon analyses of the components provided evidence for the quantitative nature of the scheme. This scheme was employed in the present study. A complete description of the scheme together with the results of Indian river sample analyses are given in Chapter 3.

b) Description of the Field Area

The Indian river system was chosen for this study on the basis of accessibility and the recent publication (Liberty and Reinhardt 1974) of an accurate geological map of the bedrock. The Indian river drains an area underlain by Precambrian rocks of the Grenville Series (Logan 1863; Moore and Thomson 1974): the river flows eastwards into Clayton Lake near the village of Clayton and then continues eastwards to join the Mississippi river approximately five kilometers north of the village of Almonte, Ontario. The location of

the Indian river and its relationship to bedrock geology are shown on the map.

The vegetation of the area sampled is described by Hoffman et al. (1967). It is well forested and is composed of mixed deciduous trees and conifers. Silver birch, sugar maple, white cedar, white and red pines, white spruce, aspen poplar, red oak and bur oak are common. The surface water, which was sampled for the study, was often turbid and filled with aquatic vegetation, except at a few locations where the flow was moderate. The swamps are usually cedar, bulrush and reed filled. The rich forestation of the region is conducive to a significant organic input into the stream. The light brown coloration observed in the majority of the collected water samples is indicative of this organic input. The relief of the area is generally low.

Sampling of stream water was carried out during July of 1977 with 19 samples collected along the 25 kilometer length of the main stream and a further 12 samples collected from a tributary draining northwards from the Wolf Grove area into the Indian river. Sample locations are shown on the map. Bedrock geology is dominated by tremolite-dolomite marble along the Indian river and in the vicinity of Clayton Lake. The tributary draining from Wolf Grove flows through garnet amphibolite intercalated with granitic rocks; Runhardt (1974) states that the amphibolites are of mainly sedimentary origin.

c) Soil Description

The soil of Lanark county has been described by Hoffman et al. (1967). The surface geological deposits are the parent materials from which the soils of the county have developed. The unconsolidated surface deposits in Lanark county are of glacial origin, and are commonly referred to as till, kame, etc., which denote the mode of deposition, (to some extent, the textural composition of the deposit) and the land form. Glacial till, which covers a large part of the county, is non-sorted material, a mixture of broken rock fragments and soil particles that range in size from sand to clay. The till cover is thin over most of the county and in many places the bedrock is exposed. Areas of deeper unconsolidated material do exist, however; sandy kames are scattered throughout the area west of Mississippi lake and river.

A vertical cut through the soil exposes a characteristic sequence of layers (soil profile), which are called in pedological terms - A horizon, B horizon, and C horizon. These horizons can be further subdivided into Ah, Ae, etc. Soils are principally classified by the kind, number and arrangement of horizons in the soil profile.

Thirty-three soil series differing from one another in one or more of the soil profile features were mapped in the county (Hoffman 1967). The Tweed Series occurs in close association with Precambrian marble (the principal rock type of the sandy area) and therefore there are large amounts of

calcite in their C horizons. The C horizons also contain quantities of material from adjacent granitic and gneissic rocks. The bedrock is never far away from the surface. Areas of Tweed sandy loam usually have three feet or more of unconsolidated materials over the bedrock.

Tweed soils are well drained. Moisture percolates readily through the sandy, stony materials or run rapidly off the slopes. Erosion is not severe. The steeper slopes are usually kept under a permanent cover of grass or trees and soil loss is kept to a minimum. Tweed soils have the typical brown column which becomes somewhat lighter in color with depth.

The largest portion of the county in which Tweed soils occur consists of thin soils with numerous rock exposures. The complex contains about 50 percent bare rock and rock with a thin covering of organic materials, 20 percent of shallow Tweed sandy loam, and 20 percent of deep Tweed sandy loam. The remaining 10 percent consists of Muck, Monteagle sandy loam, and Christy sandy loam.

CHAPTER 3

EXPERIMENTAL

A. Apparatus

1. Treatment of Glass Ware

Two litre nitric acid winchesters were used as sample bottles for field collection. The winchesters were washed thoroughly by forcing tap water through them in inverted position for 10-15 minutes, followed by tap distilled water rinse for about 2 minutes. Finally these were rinsed six times with organic-free doubly distilled water (DDW), and were stored bottom up on the bench for drying. All other glass ware was soaked overnight in concentrated nitric acid before it was washed according to the above procedure.

2. Collection Procedure and Storage

Samples were collected from the stream by slow displacement of air until the bottle was flooded and the lid was screwed tight immediately, while the bottle was still in the stream. Normally 10 samples were collected in a day's field trip. At the end of the collection, samples were brought to the laboratory and were filtered immediately. Samples were first passed through acid-treated and thoroughly washed glass wool, and then filtered through 0.45 μ membrane filter. A portion (10-15 ml) of the filtrate was collected in acid-treated vials, acidified to pH of about 2 with Ultrex quality hydrochloric acid, and stored in a refrigerator (5°C) overnight for metal analysis. All metal

analysis was done within 60-70 hours of sample collection. Only five samples at a time were taken out of the refrigerator for analysis. After metal analysis these vials were replaced in the refrigerator until dissolved organic carbon (DOC) analysis was done. Preliminary experiments (described below) established that dissolved organics remain stable over a period of months.

3. Filtration

Filtration of about a litre of water through 0.45 μ membrane filter using millipore filtering equipment was inconvenient. A number of modifications for the filter-bed were explored to improve flow rate, placing membrane filter between Whatman filters, varying pore size, varying negative pressure inside the filter flask, and increasing positive pressure. None of these modifications worked to our satisfaction. A filter-press was then designed, which worked ~~very~~ well for filtering one to two litres of water sample.

The filter-press, shown in the photograph, consists of three parts: the filter-press A, the 200 ml plexiglass syringe B, and millipore filter unit C. The filter unit C unscrews into two parts; the lower one carries a perforated disc to support the membrane filter. The syringe, filled with water and with the filter unit screwed on, is placed in the press, and the lever is worked manually to achieve a satisfactory filtration rate.

Filter Press

4. Fractionating Columns

Both resins, XAD-2 and XAD-8 were purified by extracting organic contaminants with spectrograde ether, acetonitrile, and methanol in a soxlet apparatus. The resin was slurried in methanol, the supernatant decanted, and the procedure repeated three times. Wet resin was then placed in a thimble, which was previously treated with methanol in the soxlet apparatus for about three hours, and soxlet was run with each solvent, viz., ether, acetonitrile, methanol (in that order) separately over a total period of twelve hours. The resin was then removed from the thimble and dried under vacuum. The glass columns equipped with a backflushing device were fabricated in the glassblowing workshop in the Department of Chemistry. 2.5 gms of XAD-8 were placed in the column, followed by 2.5 gms of XAD-2, with a glass-wool plug between the two strata. The stratified column was flushed with doubly distilled water until zero absorbance was recorded at 240 nm. The column was then considered ready for fractionation.

5. Flameless Atomic Absorption Spectrophotometer

A Perkin-Elmer flameless atomic absorption spectrophotometer, model 603, was employed for metal ion determinations. Pyrocoated graphite tubes were used and were discarded either after 200-250 firings or earlier if high (> 10 absorbance units) background readings on a three digit scale were observed. The sensitivities of metal ions defined by the

manufacturer as weight of metal in pico-grams that gives an absorbance of 0.004 are given below:

<u>Metal</u>	<u>Sensitivity</u>
Fe	30
Mn	8
Ni	140
Cu	50

The instrument is therefore quite sensitive to the concentrations in 10 μ L injected into the graphite furnace.

6. Carbon Analyser

A Beckman model 915A Total Organic Carbon Analyser was used for DOC determinations. The instrument was calibrated against standard 50 ppm potassium hydrogen phthalate full deflection (one absorbance unit) and was checked every 15-20 injections. The acidified water samples were bubbled with nitrogen for 10 minutes immediately before analysis.

7. Potentiometric Titrations

Potentiometric titrations were performed on the filtered whole samples and on the samples obtained after successive removal of individual fractions by setting up a manual version of a potentiostat. Cu^{2+} activity was monitored to ± 0.1 mV using an Orion Research Cu-ion selective electrode and a Metrohm digital meter. Micro-combination electrodes (glass and calomel) and a Beckman pH meter were used to measure the pH of the titrant solution. The pH was maintained at 5.00 by making small additions of strong acid or base as required after each addition of Cu-solution. The titration

cell was thermostated at 25°C and an atmosphere of nitrogen was maintained over the solution.

B. Establishment of Experimental Conditions

Fresh water samples from the Rideau river, which flows along the University campus, were chosen for preliminary studies in order to establish the conditions for fractionation of organic solutes and for the measurement of metal ions and DOC.

The spectrum of Rideau water is given in Figure 1. It shows a rising band in the u.v. region and an absorbance of about 0.366 at 240 nm. Since aromatic conjugated systems give absorption peaks in the u.v. region, a wavelength of 240 nm was considered appropriate to monitor concentrations of organic solutes. Water and inorganic species of interest are transparent in this region.

1. Fractionation of Dissolved Organics

The scheme for the fractionation of dissolved organics into hydrophobic acid, hydrophobic bases, and hydrophillics discussed in Chapter 1 is given in Figure 2.

The procedure adopted was as follows: one litre, 0.45 μ filtered Rideau river sample was passed through a clean column at a flow rate of 4 ml/minute. The sample reservoir and the column were rinsed twice with 10 ml alkaline permanganate double distilled water (DDW), collecting the sample and the washings together in a beaker. The column

Figure 1. Spectrum of the Rideau river sample I and its fractions.
 1. Rideau Water 2. Hydrophobic acid fraction
 3. Hydrophilic fraction

Figure 2. Fractionation scheme of organics in Indian river water due to Leenheer and Huffman (1976).

was then back-flushed with 50 ml of 0.1 M HCl followed by 50 ml DDW. The hydrophobic bases thus eluted were collected in a 100 ml flask. The sample and washings were acidified to pH 2 with HCl and passed again through the column. Adsorbed hydrophobic acids were back-flushed with 50 ml 0.1 M NaOH and 50 ml DDW, collecting the eluate in a 100 ml flask. It is interesting to note that the acid fraction was dark brown in color. The sample after second pass contains hydrophilic solutes. About 10 ml of each fraction was stored as such at 5°C in 20 ml vials for DOC analysis, except hydrophobic bases which were acidified to pH 2 before storage, as these fractions were basic. The conditions of fractionation are summarized in Table 1.

The elution peaks of hydrophobic acids and bases generated are shown in Figure 3. As can be seen from the figure, complete elution of bases and 99% of acids were achieved with a 100 ml elution volume.

2. Analysis of Metal Ions

The optimum conditions for each metal ion analyzed were determined by observing peak absorbances under varying drying time and temperature, charring time and temperature, and atomization time and temperature. The effect of deuterium background corrector for the light scattering and molecular absorption were also investigated, and were found to have no significant effect on peak absorbance. All measurements were

Table 1. The Characteristics of the Stratified Column and
the Conditions of Fractionation

<u>Parameter</u>	<u>Column</u>
Dimensions	30" X 0.9"
XAD - 8	2.5 gm (Lower Strata)
XAD - 2	2.5 gm (Upper Strata)
Dead Volume	~ 5 ml
Downward Flow Rate	4 ml/Minute
Upward Flow Rate	2 ml/Minute
Sample Volume	1 L
Volume of 0.1 M HCl to Desorb Hydrophobic Acids	50 ml
Volume of 0.1 M NaOH to Desorb Hydrophobic Bases	50 ml
Washings After Passage of the Solution	2, 10 ml Each
Absorbance at 240 of Clean Column	.003 or Less

Figure 3. Elution profile of hydrophobic acids (peaks on the left) and hydrophobic bases (peaks on the right) fractions of the Rideau sample 2.
 Solid curves -- Column 1
 Dotted curves -- Column 2

therefore done without corrector. The matrix of the standard and the samples is the only variable that is unmatched, and on account of the complex nature and low (20-30 p.p.m. C) concentration levels of solutes, it is beyond the scope of this project to examine the matrix effect on the atomization of the analyte. It is presumed that the matrix effects are negligible in the present analysis. However, these effects may be significant in solutions where background concentrations and its nature cannot be ignored. For example, a recent study (ref.99) indicates that the time characteristics of carbon furnace atomic absorption signals of Cu and Mn in the presence of $Mg(NO_3)_2$, $MgSO_4$, $MgCl_2$, $Ca(NO_3)_2$, $CaCl_2$, and NaCl are not comparable, suggesting that it is probable that different atomizing mechanisms are operating in the presence of different salts. Standard solutions in DDW were considered the safest way to by-pass the problem, and were adopted in all measurements. The instrument settings are given in Table 2.

Rideau river water was analyzed for Fe, Cu, Mn and Ni and the sample was stored at 5°C in the refrigerator immediately after the analysis was completed. The analyses were repeated every day in order to observe changes in concentrations with time. It was found that the absorbance signal for these metals remains steady over a period of 60-70 hours and starts decreasing after this period.

Samples from the Indian river were collected in such a way that all metal analyses were done within 72 hours of

Table 2. Instrument Settings for ~~6~~ White Furnace A.A.Spectrophotometry

<u>Element</u>	<u>Drying</u>	<u>Ashing</u>	<u>Atomising</u>	<u>Volume Injected</u>
Fe	110°C, 30 Sec.	600°C, 20 Sec.	2700°C, 7 Sec.	10 µ L
Cu	110°C, 20 Sec.	500°C, 20 Sec.	2500°C, 7 Sec.	10 µ L
Ni	110°C, 30 Sec.	400°C, 30 Sec.	2700°C, 7 Sec.	10 µ L
Mn	110°C, 30 Sec.	600°C, 20 Sec.	2700°C, 7 Sec.	10 µ L

collection and every precaution was taken to avoid unnecessary exposure to the room temperature.

3. Analysis of Dissolved Organic Carbon (DOC)

Samples for DOC had to be stored in a refrigerator (5°C) for a period of about 4-8 weeks before analysis due to limited access to the Beckman Carbon Analyzer, and it was therefore necessary to investigate the stability of these samples with time. A shoulder at 265 nm in the u.v. spectrum of Rideau water was identified as due to fulvic acid by Schnitzer and Khan (1972). This wavelength was chosen to monitor the variation of DOC concentration with time. In the latter section more experimental evidence is presented to correlate A_{265} with DOC. The results are presented in Table 3, and show that DOC is not lost over a period of at least 1½ to 2 months.

4. Measurement of Complexing Capacity of Water by Ion-Selective Electrode Potentiometry

The measurement of complexing capacity of these water samples by Cu Ion-Selective Electrode potentiometry was chosen mainly for two reasons: one, Cu shows the strongest tendency of complexation with organic ligands (Leads Irving William Series) among M^{2+} ions, and two, Cu Ion-Selective Electrode is commercially available and its performance in respect of probing free Cu ion in aqueous solutions has been reported as satisfactory.

Table 3. Stability of Organic Solutes in Rideau River
with Time

<u>Time (Days)</u>	<u>Abs. (265 nm)</u>
0	.185
1	.190
2	.187
3	.188
9	.191
15	.191
23	.188
30	.190
45	.197
60	.191

The author of this thesis favours this technique over others e.g., anodic stripping voltametry, or even more sensitive technique, differential pulse anode stripping voltametry, ESR, and Ion-exchange techniques that have been employed to measure trace metal concentrations for the following reasons:

- 1) Electrode measurements are rapid and virtually instantaneous in favourable cases. Time responses are frequently as fast as ten milliseconds, and even under unfavourable conditions, a reading can be obtained within two minutes.
- 2) An electrode measurement is non-destructive. The number of ions transported across the membrane in order to establish the equilibrium potential is infinitesimal relative to the number present even in the most dilute solutions. With appropriate electrode geometry, therefore, very small samples can be handled.
- 3) In most cases, no sample pre-treatment is necessary. Opaque solutions and even the viscous slurries can be measured directly.
- 4) The equipment required is simple, and can be assembled within a price range of a thousand dollars.
- 5) Although an electrode senses ionic activity, it can usually be used to determine free ion and total concentrations.

The copper-selective electrode is a mixed Cu S-Ag₂ S membrane electrode, whose Nernstian response is given by the equation

$$E = \text{constant} + \frac{.05916}{2} \log [a_{\text{Cu}^{2+}}] \quad (1)$$

where a represents the activity of Cu^{2+} . It predicts a slope of 29.58 millivolts at 25°C, and a constant intercept for a curve constructed by plotting electrode potential versus Cu-ion concentrations. This curve is of analytical importance, as unknown concentrations can be estimated by referring measured voltages to this curve. This curve can also be used to estimate the uncertainty in the measurements. Ross* translates the uncertainty in the potential into the corresponding percent uncertainty in the ion activity as follows:

Precision in E	% Uncertainty Monovalent Ion	% Uncertainty Divalent Ion
0.1 mV	0.4	0.8
2.0 mV	7.5	15

Conditions of measurements of the present work insure a precision of 0.1 mV, indicating an uncertainty of approximately 1%. In theory two factors contribute to the uncertainty of the measurement of analytical concentrations. One is the temperature dependent Nernst factor $\frac{RT}{F}$, and the other arises from the Nernst constant (equation 1). Even

* Ross, J.W., Jr., Solid-state and liquid membrane ion-selective electrodes, special communication of Orion Research Incorporated, Cambridge, Mass. 02139.

with temperature controlled to within ± 0.2 degrees, measurements of Cu-electrode potentials showed a variation of about 1% in the Nernstian factor (slope) in preliminary as well as subsequent experiments. The uncertainties in the Nernst constant (intercept) arise from a number of sources since the constant is a complex term, as seen from the following considerations. The Cu^{2+} -selective electrode potential E is given by

$$E = E^0 + \frac{RT}{F} \ln a_{\text{Ag}^+} \quad (2)$$

since $\text{Ag}/\text{Ag}_2\text{S}$ is the sensor electrode in the Cu^{2+} -selective electrode assembly. The electrode responds to the Ag^+ activity, as the silver ion is the conducting ion in the membrane and is sensed by a Ag/AgCl sensor electrode mounted inside the Cu^{2+} -selective electrode. Because the electrode is a mixed $\text{CuS}/\text{Ag}_2\text{S}$ electrode, the Ag^+ activity level at the sample/membrane interface, assuming that the sample contains no silver ion initially, is determined by the following two equilibria:

$$K_{\text{sp}}(\text{Ag}_2\text{S}) = a_{\text{Ag}}^2 \cdot a_{\text{S}}$$

$$K_{\text{sp}}(\text{CuS}) = a_{\text{Cu}} \cdot a_{\text{S}}$$

Eliminating a_{S} and solving for a_{Ag} gives:

$$a_{\text{Ag}^+} = \left[\frac{K_{\text{sp}}(\text{Ag}_2\text{S})}{K_{\text{sp}}(\text{CuS})} \times a_{\text{Cu}} \right]^{1/2}$$

Substituting in (2), we get

$$E = E^0 + \frac{RT}{2F} \ln \left[\frac{K_{sp}(Ag_2S)}{K_{sp}(CuS)} \right] + \frac{RT}{2F} \ln [a_{Cu}]$$

or

$$E = E^0 + \frac{RT}{2F} \ln \left[\frac{K_{sp}(Ag_2S)}{K_{sp}(CuS)} \right] + \frac{RT}{2F} \ln [\gamma_{Cu^{2+}}] + \frac{RT}{2F} \ln [Cu^{2+}]$$

The Nernstian constant is then given by the combination of the following terms:

$$E^0 + \frac{RT}{2F} \ln \left[\frac{K_{sp}(Ag_2S)}{K_{sp}(CuS)} \right] + \frac{RT}{2F} \ln [\gamma_{Cu^{2+}}]$$

The solubility constant term $K_{sp}(CuS)$ corresponds to the equilibrium

that exists at the sample/membrane interface. In acid solutions, however, this equilibrium may not represent adequately the reaction taking place at the interface due to the formation of HS^- and H_2S ,

This would result in an increased solubility of CuS and the solubility constant would show pH dependence. The last term in the constant, the activity coefficient is also a variable and depends largely upon the total ionic strength. The Nernstian constant is thus subject to a variation, unless

Cu-concentrations are determined under carefully controlled conditions of temperature, ionic strength, and pH.

The present study departs significantly from conventional practices in that the complexing capacity was measured without fixing the ionic strength of the sample solution to an arbitrary value. This is done to match the natural conditions. The intercept of the standard curve was found to vary up to 6% of the total voltage change of the electrode potential.

Measurements of the complexing capacity involve two titrations, one with the DDW and the other with the river sample. A standard curve was constructed by titrating 100 ml DDW against the standard Cu-solution at 25°C under the nitrogen atmosphere. 100 ml Bideau sample was then titrated under similar conditions. The pHs of the DDW and the sample were 6.00 and 8.85 respectively and the titration was performed in ion buffered solutions.

The titration curves shown in Figure 4 show two distinct features; one, the distilled water titration curve (standard curve for Cu^{2+} ion) shows a slope close to the theoretical value of 30, and secondly, the sample shows a curvature similar to conventional titration curves for the case in which the titre (Cu^{2+} soln) reacts with the titrant (water sample). The curves do not yield the required information, since the reaction and the products in both titrations are different due to different pHs of the two solutions. It

Figure 4. Titration of distilled water (curve 1) and Rideau water, against Cu(II) solution (curve 2) at pH 8.85.

was also noted at the end of the sample titration that copper precipitated in the titration cell. Although it was desired to carry on titrations at the natural pH, this was not possible due to the precipitation of Cu-hydroxide. A pH of 5.00 was chosen to avoid possible Cu precipitation.

Method of Measurement

A titration cell was set up on a magnetic stirrer immersed in a water bath operating at 25°C, in which two sets of electrodes were plunged. One set consisting of a glass and a calomel was connected to a Beckman pH-meter and the other, consisting of a Cu-selective electrode and a calomel, was connected to an Orion Research pH-meter employed as a voltage measuring device. 100 ml DDW were introduced into the cell, the magnetic stirrer was activated along with the nitrogen flow, and pH was fixed at 5.00 by adding required amounts of hydrochloric acid or base. An aliquot of the standard copper solution was added from a semi-micro buret, pH was adjusted to 5.00, and the steady value of the electrode potential was noted. The criterion for a steady value was no change over a one-minute period. These steps were repeated after the addition of each aliquot.

It was observed that the titration employing the copper solution of one concentration would not resolve the details of the titration curve. Three solutions of different concentrations, namely 0.1 M, 0.01 M, and 0.001 M were

prepared from the stock, and these solutions were employed in a wide range titration, starting from the most dilute one, depending upon the uptake by the river sample titrated.

C. Experiments and Results (Indian River)

Water samples were collected from the Indian river at 30 stations, shown in the map. Samples were filtered and analyzed at the end of each day of collecting as described in Section B2. Table 4 presents field data relevant to the samples.

1. Determination of Cu, Fe, Mn, and Ni Concentrations in Indian River Samples

Preparation of Standards

Standard solutions for these metals were prepared by dissolving accurately weighed amounts of pure metal in 35% v/v water solution of Baker ultrax grade HNO_3 and making up the solution in a 250 ml volumetric flask. Analar grade Fe and Mn metals, 5-N quality electrolytic Cu and Ni metals were used. The stock standards were acidic (approximately 1 N in HNO_3), and were stored in a refrigerator. Each flask was wrapped in aluminum foil to avoid any possible photolysis.

The analysis was performed in three sets corresponding to three sample collection trips. The standard curves of Cu, Fe, Mn, and Ni for these sets are given in Figures 5, 6, and 7. The results of the unfiltered (total metal ion)

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Table 4. Physical Parameters of the Sampling Stations.

Trip 1, June 15, 1977

Station No.	Temp. °C.	pH	Color ^a Index	Total ^b Phosphate	Stream
IR1(1)*	23	8.2	--	--	Slow moving over vegetation, turbid.
IR2(2)	22	8.24	--	--	As above
IR3(3)	20	7.87	--	--	Tributary, slow moving, dirty
IR4(4)	20	8.28	--	--	Very slow moving, clear
IR4(5)	20	8.20	--	--	As above
IR6(6)	20	8.40	--	--	Fast flow over rocks, clear
IR7(7)	20	8.30	--	--	Fast flow, clear
IR8(8)	23	8.56	--	--	Moderate flow over vegetation, turbid
IR9(9)	22.5	8.26	--	--	Slow moving, swampy
IR10(10)	21.5	8.64	--	--	Fast flow over rocks, clear

Trip 2, July 19, 1977

IR3(11)	27	8.02	--	1.9ppm	Very slow moving, dirty brown
IR11(12)	31	8.32	--	2.85ppm	Flowing over vegetation, clear
IR12(13)	31	8.42	--	--	As above
IR13(14)	28	7.90	95	2.85ppm	Fast moving, clear, yellow colored
IR14(15)	28	8.17	--	--	Slow moving

Station No.	Temp. °C.	pH	Color ^a Index	Total ^b Phosphase	Stream
IR15(16)	29.5	7.81	45	--	Moderate flow
IR16(17)	31.5	8.13	60	--	Moderate flow, fallen trees in the stream
IR17(18)	30.5	8.14	72	--	Moderate flow, little veg- itation in the bed
IR18(19)	31 ⁶	7.97	11	2.75ppm	Moderate flow, muddy, veg- itation and log in the stream

Trip 3, August 22, 1977

IR19(20)	32	8.16	--	--	Fast flow, clear
IR20(21)	--	7.50	--	3.05ppm	Lake water vegetation under- neath
IR21(22)	--	6.42	--	--	Dirty
IR22(23)	--	7.65	--	--	Very slow moving (Beaver Dam)
IR23(24)	16	7.65	--	4.05ppm	Moderate flow over rocks, clear
IR24(25)	17	7.6	--	--	Slow moving, clear
IR25(26)	18	7.3	--	--	Slow moving, marshy brown
IR26(27)	22	7.3	--	--	--
IR27(28)	23	8.4	--	--	--
IR28(29)	23	8.35	--	--	--
IR29(30)	19	7.7	--	--	--
IR30(31)	17	7.4	--	--	--

* - Number in paranthesis refer to sample number

a - Color was measured by Heath Kit at the sampling station

b - Total phosphate was estimated by Hach Kit at the sampling station

Figure 5. Standard curves for Ni, Cu, Fe, and Mn.

Figure 7. Standard curves for Ni, Cu, Fe, and Mn.

and the 0.45 μ filtered (dissolved metal ion) sample analyses are given in Table 5. The standard deviation S of the individual determination was estimated by the formula

$$S = \frac{w^*}{d}$$

where w is the spread and d is a constant proportional to the number of analyses N performed on the sample. The values of d listed below are taken from Skoog and West (1976).

N	d
3	1.693
4	2.059
5	2.326
6	2.534

The standard deviations were then averaged over 31 analyses (31 being the number of total samples analyzed) and the average figure thus obtained represents an estimate of the precision of the method employed. These figures are listed below.

Metal	Metal Average Value ppb	S Average Value	% Average S
Cu	7.7	0.3	3.7
Mn	31.5	0.5	1.7
Fe	144.0	3.5	2.4
Ni	30.8	1.2	4.0

* The equation
$$S = \frac{\sqrt{\sum_{i=1}^N (x_i - \bar{x})^2}}{N - 1}$$
 which yields a somewhat

more reliable estimate of S , was not considered necessary, since the number of accepted results of an individual analysis was small (usually 3). Absorbance values not agreeing within 3-4% were rejected.

Table 5. Analysis of Indian River Water Samples for Fe, Mn, Cu, and Ni. The Numbers are in ppb. T = Total Metal Concentration, D = Dissolved Metal Concentration

Sample No.	TFe	DFe	TMn	DMn	TCu	DCu	TNi	DNi
1	137.00	2.00	34.20	24.20	8.50	7.10	39.00	7.00
2	139.00	3.00	32.90	20.20	6.60	7.10	8.00	0.00
3	244.00	110.00	80.00	75.00	4.10	4.20	12.00	0.00
4	85.00	0.00	30.60	24.90	11.00	6.20	0.00	0.00
5	120.00	8.00	40.80	32.00	5.20	5.10	16.00	0.00
6	18.00	0.00	18.90	8.60	14.10	9.60	0.00	0.00
7	9.00	0.00	20.00	6.60	6.20	4.70	0.00	0.00
8	21.00	0.00	8.50	0.00	8.70	5.10	0.00	0.00
9	64.00	6.00	23.90	0.00	6.80	5.10	0.00	0.00
10	87.00	34.00	17.90	9.90	5.50	3.80	0.00	0.00
11	313.00	52.00	54.40	49.80	3.00	3.00	27.00	27.00
12	53.00	31.00	34.40	4.90	1.50	1.40	16.00	10.00
13	46.00	25.00	36.60	4.80	0.00	0.00	15.00	13.00
14	178.00	120.00	34.10	5.00	0.00	0.00	18.00	18.00

Sample No.	TFe	DFe	TMn	DMn	TCu	DCu	TNi	DNi
15	203.00	167.00	45.30	3.20	3.90	4.00	25.00	21.00
16	316.00	210.00	58.60	32.70	0.00	0.00	26.00	25.00
17	258.00	163.00	28.40	5.00	5.00	5.00	25.00	22.00
18	205.00	132.00	16.20	2.60	3.40	3.40	17.00	17.00
19	178.00	78.00	25.50	2.80	5.40	5.00	28.00	27.00
20	94.00	63.00	16.90	2.00	4.70	4.30	24.00	24.00
21	57.00	42.00	28.90	0.00	13.60	13.60	70.00	66.00
22	273.00	263.00	120.00	100.00	6.50	6.50	3.00	3.0000
23	160.00	137.00	15.30	8.10	3.30	3.30	3.00	3.00
24	206.00	185.00	23.80	12.50	3.20	3.20	5.00	5.00
25	186.00	27.00	57.80	52.40	15.50	15.50	65.00	66.00
26	87.00	31.00	9.50	9.50	25.90	18.50	74.00	75.00
27	120.00	45.00	68.10	68.10	14.80	14.80	57.00	56.00
28	172.00	35.00	21.20	16.40	12.60	12.60	47.00	47.00
29	185.00	5.00	28.20	23.80	14.50	13.50	47.00	47.00
30	55.00	32.00	27.30	26.40	19.30	12.70	40.00	40.00
31	198.00	111.00	55.80	50.00	13.10	10.40	25.00	25.00

2. Fractionation of Dissolved Organic Solutes in Indian River Samples and Determination of DOC

The fractionation of organic solutes in the 0.45 μ filtered samples was done as described in Section B.1. The fractionation control and the fractions data are given in Table 6. Each fraction was acidified to pH 2 or less before storing the analysis for dissolved organic carbon, as described in Section B.3. The carbon concentration in each fraction was corrected to the initial volume of the sample, which was 1 L. The carbon analysis results are given in Table 7.

3. Spectrum of Indian River Water and its Correlation With DOC

U.V. spectra of a number of water samples from the Indian river and Rideau river were recorded. Representative spectra corresponding to station IR 1 and its hydrophobic acid, hydrophobic base, and hydrophilic fractions are reproduced in Figure 8. The hydrophobic acid (dark brown) and hydrophobic base fractions were collected from the original sample volume of 1 L, and were eluted by 0.1 M NaOH and 0.1 M HCl respectively to a volume of 100 ml; their spectrum were therefore recorded from solutions diluted by ten times. The broad band covering 400 to 200 nm is common to the water investigated in this study. The chemical and genetical similarities between soil humic substances and aquatic colored materials (Christman and Minlar 1971) and the classical structural elucidation of

Table 6. Fractionation Control and Fraction Data

Sample No.	Initial Column A_{240}	Washing After 1st Pass (ml)	P A R A M E T E R				Volume of Base Eluate (ml)
			Volume of Acid Eluate (ml)	A_{240} After Acid Elution	Washing After 2nd Pass (ml)	Volume of Hydrophilics (ml)	
1	.000	20	100	.000	20	970	100
2	.002	20	100	--	--	995	100
3	.001	20	100	.000	20	1073	100
4	.000	20	Lost	.000	20	1016	100
5	.001	0	100	.000	20	997	100
6	.003	0	100	.000	20	1016	100
7	.000	0	100	--	20	1022	100
8	.000	0	100	.000	20	1015	100
9	.001	0	100	.000	20	1023	100
10	.000	0	100	.001	20	1018	100
11	.000	0	100	.000	20	1020	100
12	.000	0	100	.001	20	1020	100
13	.000	0	100	.002	20	1026	100
14	.000	0	100	.002	20	1006	100
15	.000	0	100	.000	20 (incomplete elution)	1019	100
16	.000	0	100	.000	20	1011	100
17	.002	0	100	.000	20	1021	100
18	.002	0	100	.002	20	1010	100
19	.020	0	100	.002	20	1019	100
20	.025	0	100	.005	20	1025	100

PARAMETER

Sample No.	Initial Column A_{240}	Washing After 1st Pass (ml)	Volume of Acid Eluate (ml)	A_{240} After Acid Elution	Washing After 2nd Pass (ml)	Volume of Hydrophilics (ml)	Volume of Base Eluate (ml)
21	.008	0	100	.010	20	1020	100
22	.006	0	100	.005	20	1020	100
23	.010	0	100	--	20	1025	100
24	.000	0	100	.010	20	1013	100
25	.000	0	100	--	20	1015	100
26	.001	0	100	.001	20	1010	100
27	.015	0	100	.005	20	985	100
28	.000	0	100	.000	12	1005	100
29	.010	0	100	.010	20	1020	109
30	.010	0	100	.008	20	1000	100
31	.000	0	100	.005	0	1009	100

Table 7. Analysis of Indian River Samples for Carbon. Numbers in ppm. TOC = Total Organic Carbon, DOC = Dissolved Organic Carbon, HPA = Hydrophobic Acid, HPB = Hydrophobic Base, HPL = Hydrophillics

<u>Sample No.</u>	<u>TOC</u>	<u>DOC</u>	<u>HPA</u>	<u>HPL</u>	<u>HPB</u>
1	17.20	11.90	2.10	9.50	.30
2	15.50	10.70	2.80	9.00	.30
3	13.00	13.00	2.70	10.90	.30
4	12.80	10.40	2.60	9.10	--
5	12.00	10.20	1.80	10.00	.40
6	12.00	11.70	2.50	9.40	.40
7	11.50	11.60	2.60	9.60	.50
8	11.50	11.10	2.30	9.90	.50
9	14.90	13.20	2.90	11.10	.60
10	13.30	13.50	3.80	10.10	.50
11	32.50	30.30	4.50	24.40	.90
12	21.40	21.40	4.60	21.20	.80
13	16.60	16.60	4.40	15.00	.60
14	35.40	33.50	10.30	25.80	1.10
15	32.70	33.00	8.70	19.60	.90
16	23.90	23.90	7.20	16.50	.60
17	81.60	24.60	6.40	16.80	.80
18	26.30	22.90	7.10	20.70	1.10
19	29.00	26.00	5.50	19.20	1.00
20	28.80	27.80	7.60	22.70	1.20
21	29.60	26.20	6.90	20.00	.60
22	29.60	29.60	14.10	18.50	.80

<u>Sample No.</u>	<u>TOC</u>	<u>DOC</u>	<u>HPA</u>	<u>HPL</u>	<u>HPB</u>
23	34.60	33.50	8.60	29.80	.80
24	28.80	27.50	10.40	21.20	.90
25	23.40	23.90	5.70	21.60	.80
26	22.80	21.20	6.20	14.90	.60
27	27.90	26.50	9.70	15.60	.70
28	21.30	21.30	6.40	14.50	.60
29	21.40	20.10	6.50	18.40	.70
30	21.70	21.20	8.60	12.80	.80
31	24.90	22.80	7.20	18.40	.70

Figure 8. Spectrum of the sample I and its fractions.

1. Sample I
2. Hydrophobic acids
3. Hydrophillics
4. Hydrophobic bases (peak around 190).

soil humic substances (Schnitzer 1972) would predict a spectrum for the natural water in which characteristic absorption bands of individual units are masked by the strong interactions among those units, resulting in a broad envelope.

Major oxidative degradation products of humic substances from widely differing environments are aliphatic carboxylic acids, benzenepolycarboxylic acids and polyphenolic acids. In addition, smaller amounts of n-alkanes, substituted furans, fatty acids, and dialkyl phthalates have been identified.

Schnitzer (1976) considers that phenolic and benzene carboxylic structures are the major building blocks of all soil humic materials and proposes a relatively "open", flexible structure for the soluble low-molecular-weight humic fraction (fulvic acid), in which the molecular forces holding the building blocks together are low-energy bonds such as hydrogen bonds and van der Waal's interactions.

Significant concentrations of amino acids in the breakdown products of aquatic humic materials, 4.4% of organic matter (Beck 1974), as compared to 10% of humic material (Felbeck 1971) have been reported. Again, similarity between the two varieties of humic material, soil and aquatic, may be inferred by noting that glycine is the most abundant amino acid, followed by aspartic acid, and alanine (Khan and Sowden 1971, 1972).

The colored soluble organic solutes in the natural water

are thus weakly condensed molecules of character varying widely from simple glycine to poly substituted single or condensed aromatic centres. Although the picture presented above is highly simplistic, it provides some explanation for the "featureless" spectrum. The molecule probably undergoes $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions at various centres in the moderate energy (200-400 nm) region, causing an overlap of the bands with the result that a continuous rising band is observed.

A shoulder around 265 nm appears consistently in most of the samples and the relationship between absorbance and 265 nm (A_{265}) and DOC was investigated. A similar pattern has been reported in other river waters e.g., (Swift et al. 1970) who further observes the resemblance of these spectra to the spectrum of a spruce lignin extract.

It may be noted here, that both hydrophobic acid and hydrophilic fractions retain some degree of similarity to the original water spectrum. Hydrophobic bases however, lose the parent feature, and are transparent up to 210 nm. This transparency may be due to the loss of the aromatic character and hydrophilics are probably aliphatic molecules with functional groups carrying atoms with non-bonding electrons (N, O, etc.). This may account for sharp rise in absorption band around 200 nm.

Attempts have also been made to characterize organic substances in natural water relationships with absorption ratios. The ratio of absorbances at 465 and 665 nm is often used for the characterization of humic substances. The ratio

referred to as A_4/A_6 is independent of the humic concentration and ranges from 6.0 to 8.5 (Kononova 1966) have been quoted. In the present study values range between 11 and 15. It should be noted, however, that the hydrophobic acid fraction (colored), which was investigated in this study, was eluted with 0.1 M NaOH. It is probable that the ionized functional groups of the hydrophobic acid fraction tend to polymerize and account for higher A_4/A_6 ratio. Table 8 lists A_4/A_6 ratios and values of A_{265} . The first four ratios may not be accurate, as the measurement was done after diluting the fraction to 100 ml. Since A_{665} values are low and are inherently uncertain, a small error in measurement would cause significant difference to A_4/A_6 ratio. The rest of the measurements are taken from concentrated fraction and are more reliable.

The relationship between the absorption band at 265 nm and the amount and the nature of organic solutes in these water samples was investigated in an attempt to try to establish some useful criteria by which the amount and the nature of organic solutes in these types of water can be assessed spectroscopically. A linear regression analysis for A_{265} and dissolved organic carbon (DOC) (Table 7) produced a correlation factor of 0.822, indicating a strong correlation between these two variables, with a small intercept of 0.11 on the ordinate range 0 to 1.0. The program source of regression analysis called REGRESS is stored in Carleton University's computer library. An even stronger

Table 8. A_4/A_6 Ratios and A_{265} Values of Indian River Water Samples

HPA1 = Hydrophillic Acid Fraction of Sample No.1

Sample No.	A_{465}	A_{665}	A_4/A_6	A_{265}
1	--	--	--	--
HPA1	.015	.003	5.0	--
3	--	--	--	--
HPA3	.070	.020	3.5	--
5	--	--	--	.170
HPA5	.011	.002	5.5	--
6	--	--	--	.173
HPA6	.013	.004	3.25	--
7	--	--	--	.162
HPA7	.024	.002	12.0	--
8	--	--	--	.164
HPA8	.029	.002	14.5	--
9	--	--	--	.300
HPA9	.790	.065	12.2	--
10	--	--	--	.318
HPA10	1.022	.075	13.6	--
11	--	--	--	.500
HPA11	.433	.032	13.5	--
12	--	--	--	.181
HPA12	.415	.031	13.4	--
13	--	--	--	.194
HPA13	.237	.022	10.8	--
14	--	--	--	.573
HPA14	.547	.047	11.6	--
15	--	--	--	.534
HPA15	.597	.043	13.9	--
16	--	--	--	.415
HPA16	.382	.025	15.3	--
17	--	--	--	.310
HPA17	.273	.021	13.0	--

Sample No.	A_{465}	A_{665}	A_4/A_6	A_{265}
18	--	--	--	.300
HPA18	.348	.029	12.0	--
19	--	--	--	.282
HPA19	.296	.024	12.3	--
20	--	--	--	.420
HPA20	.317	.029	10.9	--
21	--	--	--	.472
HPA21	.265	.025	10.6	--
22	--	--	--	.744
HPA22	.646	.044	14.7	--
23	--	--	--	.571
HPA23	.271	.019	14.3	--
24	--	--	--	.498
HPA24	.330	.023	14.3	--
25	--	--	--	.388
HPA25	.174	.014	12.4	--
26	--	--	--	.412
HPA26	.404	.030	13.5	--
27	--	--	--	.560
HPA27	.563	.037	15.2	--
28	--	--	--	.432
HPA28	.479	.036	13.3	--
29	--	--	--	.380
HPA29	.326	.026	12.5	--
30	--	--	--	.431
HPA30	.509	.033	15.4	--
31	--	--	--	.342
HPA31	.218	.017	12.8	--

correlation was found between A_{265} and the carbon content of the hydrophobic acid fraction, namely 0.880 with a negligible intercept .04 on the ordinate range 0 to 1.0.

The regression lines for both sets of variables are reproduced from computer plots in Figures 9 and 10.

The correlation factor for A_{265} and the carbon content of the hydrophilic fraction, however, weakens significantly to the value 0.587. The regression analysis results are as follows:

	DOC- A_{265}	HPA- A_{265}	HPL- A_{265}
Correlation factor	.822	.880	.587
Regression coefficient	38.33	16.86	20.83
T Statistics for the coefficient	7.21	9.27	3.62
R Square uncorrected	.675	.775	.344
True x-value	$.162 + x(.582)$	$.162 + x(.582)$	--
True y-value	$10.2 + y(23.3)$	$1.80 + y(12.30)$	--

Although these results suggest that A_{265} is a guide to dissolved organics, the correlation is not strong enough for analytical application. Perhaps the most interesting aspect is the indication of non-correlation (perhaps differential origin) between HPA's and hydrophilics. Are the hydrophilics metabolites of aquatic organisms where the HPA's are organic degradation products?

FIGURE 9. The plot of A_{265} vs DOC for the Indian river samples.

FIGURE 10. The plot of A_{265} vs the hydrophobic acid fraction of the Indian river samples.

4. Measurement of Complexing Capacity of Indian River Samples

The standard 0.1 M stock Cu solution was prepared by dissolving an accurately weighed amount of five-9 electrolytic copper metal in 25 ml 20% HNO_3 and diluting the solution to an appropriate volume. 10^{-2} and 10^{-3} M solutions were prepared from the stock solution before titration.

Out of the ten samples collected from the first field trip, the sample from station IR9 was selected for the measurement, as it was the most deeply colored. Titration of the 100 ml 0.45 μm filtered sample was done immediately after the titration of 100 ml DDW at pH 5.01. The results are given in Table 9a and 9b, and the Nernstian plots in Figure 11. The lower part of the curve 1 shows curvature. This deviation from linearity is almost always shown by Cu-electrode at the present stage of development in solutions of concentration 10^{-6} M and lower. As the copper concentration increases progressively, DDW shows the predicted results with a slope of 27.5, whereas Indian river water shows correspondingly lower electrode potentials indicating lower activities of copper. In the later part of the curve, the river water shows potentials similar to the DDW and the two curves merge. This region is comparable to the part of the conventional titration curves past the equivalence point. The potentials are converted to concentrations from the DDW standard curve and these values correspond to free copper. The bound copper is

Table 9a. Titration of DDW at pH 5.09. Initial Volume 100 ml
 a = of Concentration $10^{-3}M$, b = of Concentration $10^{-2}M$
 c = of Concentration $10^{-1}M$

Total mls of Cu-Soln. added	Total Volume ⁴	[Cu] X 10^6	log [Cu]	mV
0 ^a	100.015			128.9
0.1	100.118	0.999	-5.999	133.6
0.2	100.227	1.995	-5.699	136.6
0.3	100.327	2.990	-5.523	139.5
0.4	100.427	3.983	-5.399	141.9
0.5	100.527	4.974	-5.302	144.2
0.6	100.632	5.962	-5.224	145.9
0.7	100.732	6.949	-5.157	147.6
0.8	100.837	7.934	-5.099	148.9
0.9	100.937	8.916	-5.049	150.0
1.0	101.039	9.897	-5.003	151.2
0.1 ^b	101.149	19.77	-4.703	158.0
0.2	101.261	29.63	-4.527	163.5
0.3	101.385	39.45	-4.403	164.4
0.4	101.485	49.27	-4.307	169.5
0.5	101.629	59.04	-4.228	171.2
0.6	101.734	68.81	-4.162	173.4
0.7	101.849	78.55	-4.104	175.1
0.8	101.957	88.27	-4.053	176.4
0.9	102.057	97.98	-4.009	178.0
0.1 ^c	102.224	195.6	-3.708	185.4
0.2	102.394	293.0	-3.533	190.1
0.3	102.559	390.0	-3.409	194.0
0.4	102.731	486.7	-3.313	197.0
0.5	102.859	583.3	-3.234	199.6
0.6	102.990	679.7	-3.168	200.1
0.7	103.133	775.7	-3.110	202.5
0.8	103.260	871.6	-3.060	203.4
0.9	103.385	967.3	-3.014	205.8
1.0	103.512	1063	-2.973	207.0

Table 9b. Titration of Sample No. 9 at pH 5.01. Initial Volume = 100 ml

Initial pH 8.37

Total mls of Cu-Soln. Added	Total Volume	[Cu] X 10 ⁶	log [Cu]	mV
0	100.055	--	--	103.3
0.1 ^a	100.162	0.998	-6.000	118.0
0.2	100.267	1.995	-5.699	121.9
0.3	100.367	2.989	-5.523	125.6
0.4	100.467	3.981	-5.399	129.4
0.5	100.567	4.972	-5.302	131.8
0.6	100.667	5.960	-5.224	133.9
0.7	100.767	6.947	-5.157	136.2
0.8	100.867	7.931	-5.099	137.8
0.9	100.967	8.914	-5.049	139.5
1.0	101.067	9.894	-5.003	140.7
0.1 ^b	101.167	19.77	-4.703	152.5
0.2	101.273	29.62	-4.528	158.0
0.3	101.373	39.46	-4.403	162.6
0.4	101.478	49.27	-4.307	165.6
0.5	101.591	59.06	-4.228	168.3
0.6	101.693	68.83	-4.162	170.8
0.8	101.898	88.32	-4.053	174.2
0.9	102.008	98.03	-4.008	175.6
1.0	102.114	107.7	-3.967	176.6
0.1 ^c	102.234	205.4	-3.687	185.9
0.2	102.361	302.8	-3.518	191.4
0.3	102.487	400.1	-3.397	194.8
0.4	102.619	497.1	-3.303	197.7
0.5	102.750	593.7	-3.226	200.1
0.6	102.872	690.2	-3.160	201.7
0.7	102.999	786.4	-3.104	203.3
0.8	103.124	882.4	-3.054	204.7
0.9	103.258	978.1	-3.009	206.0
1.0	103.380	1074.0	-2.969	207.1

Figure II. Titration of the sample 9 at pH 5.0.
Curve 1. Titration of DDW
Curve 2. Titration of the sample

obtained by difference. The experimental values of free copper can be refined by observing the relationship between free and total copper and can be done by plotting the two sets of values. Table 10 shows results of these calculations. The curvature on the standard curve at the lower concentrations makes the first five river water titration points useless, and introduces some uncertainty into the next four or five points, as concentrations from these points are estimated from the curved portion of the standard curve. These disadvantages are not the source of any error in the estimation of the limiting value of Cu-bound to the organic matter, as these are limited to the initial stages of the binding process.

The limiting value of copper bound to the organic matter in the river water (i.e. the binding capacity) is obtained from the plot of bound Cu against total copper. Bound copper corresponding to the portion of the curve of zero slope gives the binding capacity. The plot is shown in Figure 12, and the value obtained is 1330 milli-equivalents per 100 ml of water sample, or .0133/L.

It should be noted, however, that this result is bound to be erroneous, since the pH of the standard curve differs from that of the sample water. It is included to demonstrate that the simple technique used is workable for the system investigated.

The titration was repeated under carefully controlled conditions at pH 5.00. The results are given in Tables 11a

Table 10. Estimated Free and Bound Cu

[Cu] X 10 ⁶ Total milli- moles	log [Cu] Free	[Cu] X 10 ⁶ Free		[Cu] X 10 ⁶ Bound milli- moles
		molar	milli- moles	
600.0	-6.03	0.93	93.62	506
700.0	-5.74	1.81	182.4	518
800.0	-5.64	2.29	231.0	569
900.0	-5.52	3.01	303.9	596
1000	-5.46	3.46	349.7	650
2000	-4.95	11.20	930.7	1069
3000	-4.70	19.91	2015	985
4000	-4.54	28.78	2920	1080
5000	-4.43	37.09	3765	1235
6000	-4.33	46.69	4744	1256
7000	-4.25	56.14	5705	1295
9000	-4.13	74.00	7540	1460
10000	-4.07	84.97	8670	1330
10998	-4.02	95.34	9732	1266
2999	-3.70	199.22	20365	1992

FIGURE 12. Binding capacity of the sample 9 at pH 5.0.

and 11b and the Nernstian plots in Figure 13. It can be seen that the standard slope (28.7) is closer to theoretical value (29.5), and that better resolution is achieved in the sample curve. The estimated values of free and bound copper are given in Table 12. The plot of total Cu vs bound Cu gives a value for the binding capacity of .0286 milli-equivalents/L as shown in Figure 14.

The binding capacities of the hydrophobic acids and the bases together with the hydrophilic fraction were also estimated. Similar measurements were made on another sample (#5) which was lighter in color than the sample #9. The results for both these sets of experiments showed that total binding capacity of fractions was 25-30% less than that of the whole sample (material imbalance exceeded the uncertainty limits). The effect of sodium hydroxide elution on the hydrophobic acid fraction was investigated, since this fraction carries the major portion of the binding capacity of the whole sample. It was soon discovered that sodium hydroxide is causing structural changes in the hydrophobic acid fraction, and is indicated by higher E_4/E_6 ratios as pointed out in Section C.3.

A different procedure was adopted which is as follows: 200 ml of 0.45 μ m filtered sample was passed through the column. The eluate was divided into two equal portions A and B, 100 ml each. B, which contains total dissolved organics less hydrophobic bases was acidified to pH 2 and passed through the column again. This eluate (C) contains

Table 11a. Titration of 100 ml DDW at pH 5.00

a = mls of 10^{-3} M Soln., b = mls of 10^{-2} M Soln.

<u>Cu-Soln. Added Total, mls.</u>	<u>Total Volume</u>	<u>[Cu] X 10^6</u>	<u>log [Cu]</u>	<u>mV</u>
0 ^a	100.01	--	--	95.4
0.8	100.83	7.93	-5.10	146.6
1.6	101.65	15.74	-4.80	155.4
0.1 ^b	101.80	25.54	-4.59	161.8
0.4	102.16	54.82	-4.26	171.2
0.8	102.62	93.55	-4.03	177.9
1.3	103.20	141.50	-3.85	182.9
2.2	104.23	226.40	-3.64	188.8
3.2	105.37	318.90	-3.50	193.0

Table 11b. Titration of 100 ml, River Sample 9 at pH 5.00

a = mls of 10^{-3} M Cu-Soln., b = mls of 10^{-2} M Cu Soln.

Cu Soln., Added Total mls	Total Volume	Cu Added milli- moles	[Cu] X 10^6	log [Cu]	mV
0	100.26	0	0	0	49.0
0.5 ^a	100.82	.0005	4.95	-5.30	116.0
1.2	101.60	.0012	11.81	-4.93	136.2
2.0	102.55	.0020	19.49	-4.71	146.8
0.15 ^b	102.78	.0035	34.05	-4.47	157.0
0.30	102.97	.0050	48.57	-4.31	163.0
0.50	103.21	.0070	67.82	-4.17	168.2
0.80	103.55	.0100	96.57	-4.01	173.8
1.80	104.65	.0200	191.1	-3.72	184.2
2.50	105.41	.0270	256.1	-3.59	188.7
3.00	106.00	.032	301.88	-3.52	190.5

Figure I3. Titration of the sample 9 at pH 5.0

Table 12. Estimated Free and Bound Cu for Sample 9

Cu X 10 ⁶ Total milli-moles	log [Cu] Free	Cu X 10 ⁶ Free		[Cu] X 10 ⁶ Bound milli-moles
		molar	milli-moles	
500	-6.17	0.67	68	432
1200	-5.47	3.38	343	857
2000	-5.09	8.11	832	1168
3500	-4.73	18.58	1910	1590
5000	-4.53	29.46	3033	1967
7000	-4.35	44.59	4602	2398
10000	-4.15	70.67	7318	2682
20000	-3.79	161.92	16945	3055
27000	-3.64	228.74	24111	2889
32000	-3.56	273.96	29151	2849

Figure 14. Binding capacity of the sample 9 at pH 5.0

hydrophillics as hydrophobic acids were retained on the column. The three portions A, C and the whole sample were then titrated against the standard copper solution as described earlier.

A fresh sample was collected from station IR 34 through ice in early December in two different bottles marked samples 34-1 and 34-2. Those samples were analyzed according to the above procedure. Sample 34-1 was analyzed in duplicate. Data are given in Tables 13 to 28, and the corresponding plots are shown in Figures 15 to 30.

The results are collected in the Table 29. The accuracy of these numbers depends largely upon the slope of standard curve, as discussed in Section B.4, and it is necessary to know the extent of variation of Nerstian slope yielded by the electrode employed in the measurements. At least one standard curve was obtained for each titration; a large number of data is therefore available for an empirical estimate. Two Orion Cu-selective electrodes were used in the study, and the different values given by these electrodes are listed below.

Electrode 1		Electrode 2	
Slope		Slope	
	27.5		28.2
	28.7		28.5
	28.3		28.0
	28.6		28.4
	<u>28.4</u>		<u>28.8</u>
Mean	28.4	Mean	28.4

The maximum deviation from mean for both electrodes is about

Table 13. Titration of 100 ml Sample 34-1 at pH 5.00

$a = 10^{-3}$ M Cu-Soln., $b = 10^{-2}$ M Cu-Soln.

<u>Cu-Soln. Added Total mls.</u>	<u>Total Volume</u>	<u>[Cu] X 10⁶</u>	<u>log [Cu]</u>	<u>mV</u>
0.2 ^a	100.4	1.99	-5.70	95.2
.4	100.6	3.98	-5.40	100.9
.6	100.8	5.95	-5.22	105.0
.8	101.0	7.92	-5.10	108.8
1.0	101.2	9.88	-5.00	111.8
1.3	101.5	12.81	-4.89	115.6
1.6	101.8	15.72	-4.80	118.6
1.9	102.1	18.61	-4.73	121.2
2.5	102.7	24.34	-4.61	125.1
0.1 ^b	102.8	34.05	-4.47	129.9
.2	102.9	43.73	-4.36	134.0
.3	103.0	53.40	-4.27	136.8
.4	103.1	63.05	-4.20	139.0
.6	103.3	82.28	-4.08	142.7
.8	103.5	101.4	-3.99	145.7

Table 14. Estimated Free and Bound Cu Values for Sample 34-1.

Cu X 10 ⁶ Total milli-moles	log [Cu] Free	Cu X 10 ⁶ Free		Cu X 10 ⁶ Bound milli-moles
		molar	milli-moles	
200	-5.9	1.26	127	73
400	-5.68	2.09	210	190
600	-5.54	2.88	290	310
800	-5.39	4.07	411	389
1000	-5.28	5.25	531	469
1300	-5.15	7.08	718	582
1600	-5.02	9.55	972	628
1900	-4.94	11.48	1172	728
2500	-4.80	15.85	1628	872
3500	-4.62	23.99	2466	1034
4500	-4.47	33.88	3486	1014
5500	-4.36	43.65	4496	1004
6500	-4.28	52.48	5411	1089
8500	-4.15	70.79	7313	1187
10500	-4.04	91.20	9439	1061

Table 15. Titration of 105 ml Sample 34-1 Less Hydrophobic Bases

Fraction

a = mls of 10^{-3} M Cu-Soln., b = mls of 10^{-2} Cu-Soln.

<u>Cu-Soln. Added Total mls</u>	<u>Total Volume</u>	<u>[Cu] X 10^6</u>	<u>log [Cu]</u>	<u>mV</u>
0.3 ^a	105.44	2.85	-5.54	94.7
.6	105.72	5.68	-5.24	103.3
.8	105.92	7.55	-5.12	107.0
1.0	106.23	9.41	-5.03	110.7
1.3	106.53	12.20	-4.91	114.5
1.6	106.83	14.98	-4.82	117.8
1.9	107.13	17.74	-4.75	120.4
2.2	107.43	20.48	-4.69	122.6
2.5	107.73	23.21	-4.63	124.5
2.7	107.93	25.02	-4.60	125.6
3.0	108.23	27.72	-4.56	127.3
0.1 ^b	108.35	36.92	-4.43	131.4
0.2	108.47	46.10	-4.34	134.5
0.3	108.57	55.26	-4.26	137.2
0.4	108.69	64.40	-4.19	139.4
0.6	108.91	82.64	-4.08	142.9
0.8	109.23	100.70	-4.00	145.7
1.0	109.46	118.80	-3.92	148.0

Table 16. Estimated Free and Bound Cu Values for Sample 34-1

Less Hydrophobic Base Fraction

Cu X 10 ⁶ Total <u>milli-moles</u>	log [Cu] Free	Cu X 10 ⁶ Free		Cu X 10 ⁶ Bound <u>milli-moles</u>
		<u>molar</u>	<u>milli-moles</u>	
300	-5.85	1.41	149	151
600	-5.55	2.81	297	303
800	-5.42	3.79	401	399
1000	-5.28	5.24	556	444
1300	-5.15	7.06	752	548
1600	-5.03	9.31	995	605
1900	-4.93	11.72	1255	645
2200	-4.86	13.78	1480	720
2500	-4.79	16.19	1744	756
2700	-4.75	17.75	1915	785
3000	-4.69	20.38	2205	795
4000	-4.54	28.79	3119	881
5000	-4.43	37.09	4023	977
6000	-4.34	45.63	4954	1046
7000	-4.26	54.86	5963	1037
9000	-4.13	74.00	8059	941
11000	-4.04	91.05	9945	1055
13000	-3.96	109.16	11946	1054

Table 17. Titration of 100 ml Sample 34-1 at pH 5.00. Duplicate Ru

<u>Cu-Soln. Added Total mls</u>	<u>Total Volume</u>	<u>[Cu] X 10⁶</u>	<u>log [Cu]</u>	<u>mV</u>
1.0	101.50	9.85	-5.01	111.6
1.7	102.20	16.63	-4.78	119.0
2.5	103.00	24.27	-4.61	124.8
3.3	103.80	31.79	-4.50	128.9
4.0	104.50	38.28	-4.42	131.7
5.0	105.50	47.39	-4.32	134.9
0.1	105.62	56.81	-4.25	137.1
.15	105.67	61.51	-4.21	138.6
.20	105.72	66.21	-4.18	139.7
.25	105.78	70.90	-4.15	140.6
.30	105.83	75.59	-4.12	141.6
.35	105.88	80.28	-4.10	142.4
.40	105.94	84.95	-4.07	143.1
.60	106.16	103.60	-3.98	145.8
.80	106.38	122.20	-3.91	148.0
1.3	106.94	168.30	-3.77	152.5

Table 18. Estimated Free and Bound Cu Values for Sample 34-1

Duplicate Run				
Cu X 10 ⁶ Total milli-moles	log [Cu] Free	Cu X 10 ⁶ Free		Cu X 10 ⁶ Bound milli-moles
		molar	milli-moles	
1000	-5.23	5.85	594	406
1700	-4.98	10.57	1080	620
2500	-4.78	16.79	1729	771
3300	-4.63	23.44	2433	867
4000	-4.53	29.51	3084	916
5000	-4.42	38.02	4011	989
6000	-4.34	45.71	4828	1172
6500	-4.29	51.29	5420	1080
7000	-4.25	56.23	5945	1055
7500	-4.22	60.81	6432	1068
8000	-4.18	65.61	6944	1056
8500	-4.16	69.66	7376	1124
9000	-4.13	74.13	7853	1147
11000	-4.04	92.26	9794	1206
13000	-3.96	109.65	11665	1335

Table 19. Titration of 105 ml Sample 34-1 Less Hydrophobic

Base Fraction at pH 5.00. Duplicate Run

a = mls of 10^{-3} M Cu-Soln., b = mls of 10^{-2} M Cu-Soln.

<u>Cu-Soln. Added Total mls</u>	<u>Total Volume</u>	<u>[Cu] X 10^6</u>	<u>log [Cu]</u>	<u>mV</u>
1.0 ^a	106.14	9.42	-5.03	110.2
1.7	106.84	15.91	-4.80	118.6
2.5	107.64	23.23	-4.63	124.5
3.3	108.45	30.43	-4.52	128.5
4.0	109.16	36.64	-4.44	131.3
5.0	110.17	45.38	-4.34	134.3
.05 ^b	110.22	49.90	-4.30	135.3
.10	110.27	54.41	-4.26	136.8
.15	110.33	58.91	-4.23	137.9
.20	110.38	63.42	-4.20	138.9
.25	110.44	67.91	-4.17	140.0
.30	110.49	72.42	-4.14	140.9
.35	110.54	76.90	-4.11	141.9
.40	110.60	81.37	-4.09	142.5
.60	110.82	99.26	-4.00	145.5
.80	110.05	117.06	-3.93	147.8
1.30	111.60	161.29	-3.79	152.1

Table 20. Estimated Free and Bound Cu Values for Sample 34-1

Less Hydrophobic Base Fraction

Cu X 10 ⁶ Total milli-moles	log [Cu] Free	Cu X 10 ⁶ Free		Cu X 10 ⁶ Bound milli-moles
		Molar	milli-moles	
1000	-5.295	5.07	538	462
1700	-5.00	9.93	1060	640
2500	-4.80	16.0	1722	778
3300	-4.66	22.13	2400	900
4000	-4.56	27.86	3041	959
5000	-4.45	35.48	3909	1091
5500	-4.42	38.37	4229	1271
6000	-4.36	43.35	4780	1220
6500	-4.32	47.53	5244	1256
7000	-4.28	52.36	5780	1220
7500	-4.24	56.95	6290	1210
8000	-4.21	61.54	6800	1200
8500	-4.18	65.77	7270	1230
9000	-4.16	68.71	7599	1401
11000	-4.06	87.70	9719	1281
13000	-3.97	106.17	11790	1210
18000	-3.82	150.66	16814	1186

Table 21. Titration of 115 ml Sample 34-1 Hydrophillic Fraction
at pH 5.00

10^{-3} M Cu Soln. Added Total mls	Total Volume	[Cu] X 10^6	log [Cu]	mV
.25	118.56	2.11	-5.67	92.3
.30	118.62	2.53	-5.60	95.1
.35	118.67	2.95	-5.53	96.5
.40	118.72	3.37	-5.47	97.7
.45	118.77	3.79	-5.42	99.0
.50	118.82	4.21	-5.37	100.4
.55	118.87	4.63	-5.33	101.4
.60	118.92	5.05	-5.30	102.5
.65	118.97	5.47	-5.26	103.5
.70	119.02	5.88	-5.23	104.5
.80	119.12	6.72	-5.17	106.0
.90	119.22	7.55	-5.12	107.6
1.00	119.32	8.38	-5.08	109.1
1.20	119.53	10.04	-5.00	111.0
1.40	119.73	11.69	-4.93	113.1
1.60	119.93	13.34	-4.87	115.0
1.80	120.13	14.98	-4.82	116.6
2.00	120.33	16.62	-4.78	118.0

Table 22. Estimated Free and Bound Cu Values for Sample 34-1

Hydrophillic Fraction

$\text{Cu} \times 10^6$ Total milli-moles	$\log [\text{Cu}]$ Free	$\text{Cu} \times 10^6$ Free Molar	milli-moles	$\text{Cu} \times 10^6$ Bound milli-moles
250	-5.72	1.91	226	24
300	-5.62	2.40	285	15
350	-5.58	2.63	312	38
400	-5.53	2.95	350	50
450	-5.48	3.31	393	57
500	-5.44	3.63	431	69
550	-5.40	3.98	473	77
600	-5.36	4.37	519	81
650	-5.32	4.79	569	81
700	-5.29	5.13	610	90
800	-5.23	5.89	701	99
900	-5.18	6.60	788	112
1000	-5.12	7.58	905	95
1200	-5.04	9.12	1090	110
1400	-4.98	10.71	1289	111
1600	-4.905	12.45	1493	107
1800	-4.85	14.13	1697	103
2000	-4.80	15.85	1907	93

Table 23. Titration of 100 ml Sample 34-2 at pH 5.00

$a = \text{mls of } 10^{-3} \text{ M Cu Soln.}, b = 10^{-2} \text{ M Cu Soln.}$

<u>Cu Soln. Added Total mls</u>	<u>Total Volume</u>	<u>[Cu] X 10⁶</u>	<u>log [Cu]</u>	<u>mV</u>
1.0 ^a	101.3	9.87	-5.01	110.0
1.7	102.0	16.67	-4.78	118.3
2.5	102.81	24.32	-4.61	124.4
3.3	103.61	31.85	-4.50	128.4
4.0	104.31	38.35	-4.42	131.3
5.0	105.31	47.48	-4.32	134.4
.05	105.36	52.20	-4.28	135.5
.10	105.41	56.92	-4.24	137.0
.15	105.46	61.63	-4.21	138.2
.20	105.51	66.34	-4.18	139.3
.25	105.56	71.05	-4.15	140.3
.30	105.63	75.74	-4.12	141.1
.35	105.68	80.43	-4.09	142.0
.40	105.73	85.12	-4.07	142.8
.60	105.98	103.81	-3.98	145.5
.80	106.18	122.43	-3.91	148.0
1.30	106.74	168.63	-3.77	152.1

Table 24. Estimated Free and Bound Cu Values for Sample 34.2

$\text{Cu} \times 10^6$ Total milli-moles	$\log [\text{Cu}]$ Free	$\text{Cu} \times 10^6$ Free molar	milli-moles	$\text{Cu} \times 10^6$ Bound milli-moles
1000	-5.27	5.43	550	450
1700	-4.98	10.57	1078	622
2500	-4.77	17.14	1762	738
3300	-4.63	23.61	2446	854
4000	-4.52	29.92	3121	879
5000	-4.42	38.28	4031	969
5500	-4.38	41.69	4392	1108
6000	-4.33	47.10	4965	1035
6500	-4.29	51.64	5446	1054
7000	-4.25	56.62	5974	1026
7500	-4.21	61.24	6464	1036
8000	-4.19	64.86	6851	1149
8500	-4.15	70.15	7413	1087
9000	-4.13	74.82	7911	1089
11000	-4.03	92.47	9798	1202
13000	-3.95	112.07	11900	1100
18000	-3.80	157.86	16850	1150

Table 25. Titration of 105 ml Sample 34-2 Less Hydrophobic Base

Fraction at pH 5.00

a = mls of 10^{-3} M Cu Soln., b = mls of 10^{-2} M Cu Soln.

Cu Soln. Added Total mls	Total Volume	[Cu] X 10^6	log [Cu]	mV
1.0 ^a	106.11	9.42	-5.02	110.1
1.7	106.81	15.92	-4.80	118.5
2.5	107.61	23.23	-4.63	124.4
3.3	108.41	30.44	-4.52	128.5
4.0	109.11	30.66	-4.43	131.3
4.5	109.61	41.05	-4.39	133.1
.05 ^b	109.66	45.60	-4.34	134.4
.10	109.71	50.13	-4.30	135.8
.15	109.76	54.66	-4.26	137.3
.20	109.82	59.19	-4.23	138.3
.25	109.87	63.71	-4.20	139.5
.30	109.93	68.23	-4.17	140.4
.35	109.98	72.74	-4.14	141.3
.40	110.04	77.24	-4.11	142.1
.60	110.25			

Table 26. Estimated Free and Bound Cu Values for Sample 24-2

Less Hydrophobic Base Fraction				
$\text{Cu} \times 10^6$ Total milli-moles	$\log [\text{Cu}]$ Free	$\text{Cu} \times 10^6$ Free molar	milli-moles	$\text{Cu} \times 10^6$ Bound milli-moles
1000	-5.29	5.13	544	456
1700	-5.00	10.0	1068	632
2500	-4.79	16.22	1745	755
3300	-4.65	22.39	2427	873
4000	-4.55	28.18	3075	925
4500	-4.49	32.36	3547	953
5000	-4.44	36.31	3982	1018
5500	-4.39	40.74	4469	1031
6000	-4.34	45.71	5017	983
6500	-4.30	50.12	5504	996
7000	-4.26	54.95	6038	962
7500	-4.23	58.88	6473	1027
8000	-4.20	63.10	6939	1061
8500	-4.17	67.61	7440	1060
10500	-4.07	85.80	9460	1040

Table 27. Titration of 118 ml Sample 34-2 Hydrophillics at
pH 5.00

10^{-3} M Cu Soln. Added Total mls	Total Volume	[Cu] X 10^6	log [Cu]	mV
.25	118.31	2.11	-5.68	93.6
.30	118.37	2.53	-5.60	95.4
.40	118.47	3.38	-5.47	98.6
.50	118.57	4.22	-5.38	101.3
.60	118.67	5.06	-5.30	103.8
.70	118.78	5.89	-5.23	105.9
.80	118.88	6.73	-5.17	107.5
.90	118.98	7.56	-5.12	109.0
1.0	119.08	8.40	-5.08	110.3
1.2	119.29	10.06	-5.00	112.5
1.4	119.49	11.72	-4.93	114.8
1.6	119.69	13.37	-4.87	116.4
1.9	120.00	15.83	-4.80	118.5
2.2	120.30	18.29	-4.74	120.6
2.5	120.61	20.73	-4.68	122.2

Table 28. Estimated Free and Bound Cu Values for
Sample 34-2 Hydrophillics

$\text{Cu} \times 10^6$ milli-moles	$\log [\text{Cu}]$ Free	$\text{Cu} \times 10^6$ Free molar	$\text{Cu} \times 10^6$ Free milli-moles	$\text{Cu} \times 10^6$ Bound milli-moles
250	-4.71	1.95	231	19
300	-5.65	2.24	265	35
400	-5.54	2.88	342	58
500	-5.43	3.72	441	59
600	-5.35	4.47	530	70
700	-5.27	5.37	638	62
800	-5.22	6.03	716	84
900	-5.16	6.92	823	77
1000	-5.12	7.59	903	97
1200	-5.04	9.12	1088	112
1400	-4.965	10.84	1295	105
1600	-4.905	12.45	1490	110
1900	-4.826	14.93	1791	109
2200	-4.75	17.78	2139	61
2500	-4.703	19.82	2390	110

Figure 15. Titration of the sample 34-1 at pH 5.0

Figure 16. Binding capacity of the sample 34-I at pH 5.0

Figure 18. Binding capacity of the sample .34 -1 less hydrophobic bases at pH 5.0

Figure 17. Titration of the sample 34 less hydrophobic bases at pH 5.0

Figure 19. Titration of the sample 34-I at pH 5.0

Figure 20. Binding capacity of the sample 34-I at pH 5.0

Figure 21. Titration of the sample 34-I less hydrophobic bases fraction at pH 5.0

Figure 22. Binding capacity of the sample 34-I less hydrophobic bases at pH 5.0

Figure 23. Titration of the hydrophilic fraction of the sample 34-I at pH 5.0

Figure 24. Binding capacity of the sample 34-I hydrophillics fraction at pH 5.0

Figure 25. Titration of the sample 34-2 at pH 5.0

Figure 26. Binding capacity of the sample 34-2 at pH 5.0

Figure 27. Titration of the sample 34-2 less hydrophobic bases fraction at pH 5.0

Figure 28. Binding capacity of the sample 34-2 less hydrophobic bases fraction at pH 5.0

Figure 29. Titration of the hydrophillic fraction of the sample 34-2 at pH 5.0

Figure 30. Binding capacity of the hydrophilic fraction of the sample 34-2.

Table 29. Complexing Capacities of Fractions in Milli-Equivalent /L.

Sample	Whole Sample	Whole Sample Less Hydrophobic Bases	Hydrophobic Bases By Difference	Hydrophilics	Hydrophobic Acid By Difference
34-1	.0113	.0106	.0007	--	--
Duplicate	.0115	.0121	--	.0011	.0104
34-2	.0115	.0104	.0011	.0011	.0093

1%. The effect of the deviation on the parameter measured by the electrode, the free Cu-concentration, can be estimated by measuring its concentrations from the standard curves of slopes varying by $\pm 1\%$ of the typical value in a titration experiment. A typical titration curve and the standard curve (slope 28.7) are given in Figure 31. Two other standard curves whose slopes, 28.4 and 29.0, show variations of $\pm 1\%$ from the experimental value are also drawn. The free Cu values from each of these curves are given in Table 30 and it is shown that the maximum variation in free Cu concentration associated with 1% deviation in Nernstian slope is about 10%. The complexing capacities of components (Table 29) thus involve an uncertainty of 10%. The agreement between duplicate runs and samples from two bottles is good, except for the hydrophobic base fraction, which is close to the sensitivity of the method.

Figure 3I. A typical titration curve showing the slope of the standard curve varying within $\pm 1\%$. 1. slope=28.4, 2. slope=28.7, 3. slope=29.0

Table 30. Estimated Variation in Free Cu Values with an Uncertainty of $\pm 1\%$ in Standard Curve Slope

Slope=28.4			Slope=28.7			Slope=29.0		
$\log [\text{Cu}]_f$	$[\text{Cu}] \times 10^6$	% Change	$\log [\text{Cu}]_f$	$[\text{Cu}] \times 10^6$		$\log [\text{Cu}]_f$	$[\text{Cu}] \times 10^6$	% Change
-6.84	.145	9	-6.80	.158		-6.72	.1905	18
-6.24	.575	10	-6.20	.631		-6.14	.724	14
-5.52	3.02	7	-5.49	3.24		-5.44	3.63	12
-5.16	6.92	7	-5.13	7.41		-5.09	8.13	10
-4.77	16.98	5	-4.75	17.78		-4.71	19.50	10
-4.56	27.54	0	-4.56	27.54		-4.51	30.90	12
-4.38	41.69	0	-4.38	41.69		-4.35	44.67	7
-4.19	64.57	0	-4.19	64.57		-4.16	69.18	7
Average Change =		5%				Average Change =		11%

CHAPTER 4

RESULTS AND DISCUSSION

a) Stability of Organic and Inorganic Solutes in River Streams

Natural waters acquire their chemical characteristics by chemical reactions with the crust of earth with which they have come into contact during the various parts of hydrological cycle. Weathering reactions, essentially caused by the interaction of water and atmosphere with the rocks in the earth crust, take place because the original constituents of the crust, the igneous rocks, are thermodynamically unstable in the presence of water and the atmosphere. These reactions may be typified by an incongruent dissolution reaction of aluminum silicates, represented by

Most of carbon, that has cycled through organisms and plants and has been incorporated into long-lived biochemical structures is similarly thermodynamically unstable. A familiar example is,

The redox intensity of a system in an aquatic environment is constrained by the redox potential of water in equilibrium at the surface with atmospheric oxygen. The latter quantity is now being expressed (Stuman and Morgan

1970) in terms of the parameter pE , the electron activity, and is defined by the relation

$$pE = \frac{F}{2.3 RT} E_H$$

where E_H is the conventional redox potential of the half cell on the hydrogen scale in accord with the Stockholm convention. Conceptually pE can be regarded just as pH ; large positive values of pE (low electron activity) represent strongly oxidizing conditions while small or negative values (high electron activity) correspond to strongly reducing conditions. Considering the relations

$$\Delta G^0 = -nFE_H^0 \quad \text{and} \quad \Delta G^0 = -2.3 RT \log K$$

where the super script denotes the standard state i.e. the activity of all components is unity, the above equation can be written as

$$pE^0 = - \frac{\Delta G^0}{2.3 nRT}$$

These relations show that pE^0 is directly related to ΔG^0 , and that values for pE^0 can be computed from stability constants (K) for reaction with electrons of the system in question. Stumm and Morgan (1970) have compiled a table of redox processes pertinent in aquatic conditions.

Two constraints can be put on redox systems present in natural waters. Defined as stability limits, one corresponds to complete oxidation and the other to complete reduction of water under varying pH s. These limits can be readily plotted from equations

$$pE = 20.8 - pH + \frac{1}{4} pO_2$$

corresponding to the reaction

$$\text{and } pE = 0 - pH - \frac{1}{2} \log pH_2$$

corresponding to the reaction

The pE^0 value for water at $pH = 0$ and $25^\circ C$ is $+20.8$ (unit less) and those for reactions of organic molecules in water are negative, showing that these organic molecules should exist virtually completely in their highest oxidation state, i.e. CO_2 . Since organic matter is known to persist in waters containing dissolved oxygen, total redox equilibrium is not found in natural water systems. At best these can represent quasi-equilibria. The treatment outlined above can be applied to systems which approximate to equilibrium. In fact, because of the intrinsic instability of organic compounds, organic geochemistry is dominated by non-equilibrium processes. As Blumer (1967) has pointed out, during diagenesis the less stable compounds are eliminated by reactions that tend to scramble the ordered structures created by organisms. Diagenesis thus leads gradually to equilibration of the sedimentary organic matter.

Thermally slow reaction and photosynthesis are two causative factors of non-equilibrium. The slow reaction rates of organic solutes interacting with other redox couples

or their isolation from the total environment as a result of slowness of diffusional or mixing processes keep the system from approaching equilibrium. It is important to point out that since both kinetic and hydro-dynamic factors are time dependent, and since the residence time of organic solutes in rivers may be as little as weeks to months, the organics may never have enough time to approach equilibrium. On the contrary, the residence time in lakes may range between tens to hundreds of years and that in the oceans between hundreds to thousands of years. The system may not lack at least the time factor, particularly in the ocean, to approach equilibrium.

Photosynthesis is a major cause of non-equilibrium conditions in natural waters. By trapping light energy and converting it to chemical energy, photosynthesis produces reduced states of higher energy and thus non-equilibrium concentrations of carbon and sulfur compounds (Morris et al. 1967). The conversion of CO_2 to glucose at unit activities

requires $\text{pE}^0 = -0.20$, a very small negative value. Photosynthesis, thus may be conceived as a process producing localized centres of high-electron activity. Two important points emerge from the above discussion: (1) equilibrium considerations provide boundary conditions towards which the system must be proceeding, (2) organic systems generate anaerobic conditions favourable for their preservation as

well as producing reducing environments of high electron activity.

b) Organics in Indian River Water

Samples from Indian river showed the yellow to brown color characteristic of water containing humic material. The "particulate phase" was separated from the dissolved phase by filtering the sample through the conventional 0.45 μ average pore size membrane filter. The dissolved phase, called dissolved organic carbon (DOC) in this presentation, was fractionated on three-dimensional styrene-divinyl benzene copolymer resin into three components: hydrophobic acids, hydrophobic bases, and hydrophillics. It should be noted that DOC is an operational assignment based on the cut-off pore size of the membrane filter and should be understood in this context.

The copolymer Amberlite XAD-2 and XAD-8 provide respectively non-polar and intermediate polarity sites for the absorption of organic molecules of similar character. Since there are no ionized groups involved on the resin surface, hydrophillic organic compounds do not interact and pass through the resin column and collect in the eluate fraction. The non-polar compounds and those of intermediate polarity employed in Leenheer's (1976) test model include benzoic acid, p-methyl benzyl alcohol, aniline, fulvic acid, ethylenediamine, and sucrose describe the type of composition of the hydrophobic faction. This fractionates into hydrophobic

acids and hydrophobic bases upon elution with sodium hydroxide and hydrochloric acid solutions, respectively.

The hydrophobic acid fraction was indeed colored dark brown, very characteristic of dissolved humic material, whose spectral (uv-visible) properties, described in Chapter 3-C.3 support the identification. As evident from Table 7, the hydrophobic acid fraction is the predominant component of DOC, and the major component of total organic material expressed here as total organic carbon (TOC). The range of TOC, 12-35 ppm (excluding the anomalous figure 81.6 for the sample No. 17), is higher as compared to the average value quoted generally, namely 1-10 ppm.

The thought is difficult to avoid that the success achieved in the fractionation and in the mass balance particularly is a new achievement in the study of organic matter of aquatic origin. Further studies on the hydrophobic acid fraction (calling it a fulvic acid fraction may not be too far from reality) would yield information specific to this fraction.

One of the properties of hydrophobic acids that was examined in the present study was the spectral characteristics in the u.v. region, described in Chapter 3-C. As was pointed out there, the correlation between DOC and A_{265} is not strong enough for quantitative analytical applications. It is of interest, however, to calculate molar absorptivity a from the slope of the regression line. This slope can be

expressed by

$$a = \frac{0.628}{9.67 \times 10^{-3}}$$

Assuming C% = 46.2 in aquatic fulvic acid (Steelink 1977), and the molecular weight is approximately 1000, the denominator converts to 4.5×10^{-6} M, giving the slope and hence a value of 1.4×10^5 . This value is of the expected order of magnitude, as polycyclic compounds commonly have a value of the order of 10^5 , e.g., a for pigment trans- β -carotene at 234 nm is 2.80×10^5 .

c) Metal Ions in Indian River Water

The metals investigated in the present study, Fe, Mn, Cu, and Ni are geochemically significant to aquatic systems. Fe and Mn are among the most abundant metals in the crust and the soil of the earth. Their hydrous oxides are ubiquitous and can play a principal role in controlling the fixation of heavy metals, e.g., Mn, Cu, Ni, Co, and Zn in fresh water sediments.

Equilibrium models are helpful in interpreting the stability relations of pertinent redox components in natural water systems. Concentrations of oxidizable and reducible species, however, are found far from the predicted values, because many redox reactions are slow and complicated by the presence of organic and inorganic ligands. Considering Fe as an example, analysis of a large number of river water samples shows that the concentration of Fe is approximately

4×10^{-6} M (Allegre et al. 1974). The simple equilibrium model reactions pertinent to natural water in contact with the atmosphere are:

(2) and (3) yield

(2) and (4) yield

Equations 1, 2, 5 and 6 conveniently give concentrations of species Fe(OH)_4^- , Fe(OH)_2^{3+} , Fe(OH)_2^+ and $\text{Fe(OH)}_5\text{OH}^{2+}$ as a function of pH when set in logarithmic form. For example equation (1) transforms into

$$\log K_{s4} = \log [\text{Fe(OH)}_4^-] + \log [\text{H}^+]$$

$$\text{or } -\log [\text{Fe(OH)}_4^-] = -\log K_{s4} - \text{pH}$$

A plot of $-\log [\text{concentration}]$ vs pH generates a useful diagram depicting the form and concentration of the species as a function of pH. The diagram adapted from Morgan (1970) is shown in Figure 1. It is immediately obvious that the concentrations of Fe^{3+} and Fe(OH)^{2+} are extremely low

Figure 1. The solubility of $\text{Fe}(\text{OH})_3$ as a function of pH.

($<10^{-13}$ M) and do not make any significant contribution to the total Fe concentration at pH 8. This pH has been selected for reference, as it corresponds to median Indian river water. The concentration of the remaining two species Fe(OH)_2^+ and Fe(OH)_4^- roughly adds up to 2×10^{-10} M. This computed total Fe concentration is several orders of magnitude smaller than the average river water figure for Fe quoted above. Equilibrium calculations, as has been stated earlier, can provide boundary conditions towards which the system must be proceeding, however slowly, when the models are sufficiently elaborate. In other words all the species are accounted for in making the calculations. It is therefore important for the present discussion to extend solubility estimations to Mn, Cu and Ni and compare these with experimental results. Before leaving the case of Fe one point should be brought to notice regarding the Fe species, which describe in part the simple equilibrium model used above for solubility calculations. The assignment of the species Fe(OH)_2^+ is not unambiguous. Our kinetic studies on hydrous oxides of Fe at pH 4 (Langford et al. 1977) in comparison to similar studies by Sommer (1973) on acid hydrolysis of the polymeric Fe(OH)_2^+ species indicate that the species is not a monomer.

Since the Indian river flows over carbonate bed rock (precambrian marble) and the observed pHs are neutral to slightly alkaline (recorded pHs of water samples vary

between 7-8), it is reasonable to estimate concentration levels of the carbonate species. The reaction of carbonate rock with dissolved carbon dioxide in equilibrium with the atmospheric carbon dioxide can be written as

and the constant K ,

$$K = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2]} = \frac{K_1 K_s}{K_2} = 4.24 \times 10^{-5},$$

where K_1 , K_2 are the first and second dissociation constants of H_2CO_3 and K_s is the solubility product of calcite.

Substituting the values for K_1 , K_2 , K_s and using the calculated concentration of $[\text{CO}_2]$ ($= 1.028 \times 10^{-5} \text{ M}$), the following concentrations are obtained:

$$[\text{HCO}_3^-] = 9.56 \times 10^{-4}$$

$$\text{pH} = 8.32$$

$$[\text{Ca}^{2+}] = 4.78 \times 10^{-4}$$

$$[\text{CO}_3^{2-}] = 9.35 \times 10^{-6}$$

These values give an upper limit of HCO_3^- and Ca^{2+} concentrations, and suggest that the river represents a diluted version of the equilibrium model, in which fresh water saturated with $[\text{Mg}]\text{CaCO}_3$ is in equilibrium with dissolved carbon dioxide.

The concentrations of Fe(III) bicarbonates are insignificant as compared to hydrous oxides, which predominate in

aqueous solutions. The former can be ignored in solubility estimates. However, in the case of manganese, the situation is different, the MnHCO_3^+ species contribute significantly to the concentration of manganese present in fresh waters.

Figure 2 shows the distribution of various Cu and Mn species in aqueous solutions as a function of pH. The Mn diagram shows that in waters of neutral and slightly alkaline pHs, the predominant species is MnHCO_3^+ , which may be true in the present case as the carbonate bed rock may be contributing to the alkalinity of the river water. Table 1 gives the concentrations of Fe, Mn and Cu at pH 8 estimated from these diagrams and the average values generally accepted for these metals in river waters.

It may be noted that our values are in good agreement with published results. The table shows large differences between the calculated and observed concentrations for Fe and Cu, particularly for Fe, where observed and calculated values differ by several orders of magnitude. These apparent discrepancies are, of course, meaningful only when the equilibrium requirement of the solubility reaction is fulfilled, i.e. the supply of the metal is large enough for the coexistence of the solid and the liquid phase. Analytical results given in Chapter 2 indicate that Ni does not satisfy the requirement. The stoichiometric concentrations are very low; in fact, Ni was not detected at a number of stations. The solubility of Ni is therefore not hydroxide limited.

Table 1. Calculated and Observed Metal Concentrations in River
Streams

Species	Concentration ^a M	Total	Typical Observed ^b	This Work (average)
$\text{Fe}(\text{OH})_4^-$	10^{-10}	2×10^{-10}	4×10^{-6}	1.3×10^{-6}
$\text{Fe}(\text{OH})_2^+$	10^{-10}			
$\text{Fe}(\text{OH})^{2+}$	Negligible			
$\text{Fe}^{3+}_{\text{aq}}$	Negligible			
$\text{Cu}(\text{OH})_4^{2-}$	Negligible	2×10^{-8}	1.1×10^{-7}	1.1×10^{-7}
$\text{Cu}(\text{OH})_3^-$	10^{-12}			
$\text{Cu}(\text{OH})^+$	10^{-8}			
$\text{Cu}^{2+}_{\text{aq}}$	10^{-8}			
MnHCO_3^+	10^{-6}	1×10^{-6}	1.6×10^{-7}	3.2×10^{-7}
MnOH^+	10^{-11}			
$\text{Mn}(\text{OH})_3^-$	10^{-12}			
$\text{Ni}^{2+}_{\text{aq}}$	$10^{-5.2^c}$	--	6.8×10^{-8}	3.4×10^{-7}

^a Figures represent maximum concentration species can have in equilibrium with the solid.

^b Values from Allegre et al. (1974).

^c Calculated from $K_{\text{SO}} = [\text{Ni}^{2+}][\text{OH}^-]^2 = 10^{-17.2}$ (Feitknecht et al. 1963).

Figure 2. Solubility of Mn(II) (calculated for 2×10^{-3} total carbonic species), and amorphous CuO.

This explains the lower observed value 6.8×10^{-8} in comparison with the calculated value $10^{-5.2}$.

The value calculated for total dissolved Mn 1×10^{-6} M shows a similar situation to that described above for nickel although the difference between calculated and observed values is not as large as for Ni. The situation arises from the large solubility of MnHCO_3^+ in acidic and neutral waters. The predominance of MnHCO_3^+ , however, diminishes towards higher pHs as hydroxy species become more important than bicarbonate species in determining the total Mn concentration.

In river waters whose pHs are not controlled by dissolved carbonate, it is noted from Table 1 that the concentration of dissolved Mn is hydroxide limiting and that the observed solubility is several orders of magnitude larger than predicted. In bicarbonate free systems, a situation similar to that observed in the cases of Fe and Cu.

The plausible explanation for these differences has often been thought to be the formation of metal-organic complexes, the evidence for which can be found in the literature discussed in Chapter 1. A positive correlation between dissolved metal and dissolved organics is suggested by the hypothesis of this model. Turning attention to the results of the present work, correlation factors between metal and DOC were evaluated by fitting a set of variables (metal is considered independent variable and DOC dependent variable) to the linear regression program. The results are given in Table 2.

Table 2. Results of Linear Regression Analysis.

D = Dissolved, P = Particulate, HPA = Hydrophillic Acids (fulvic acid), O = Organics

Independent Variable	Dependent Variable	r	z _r	t	p
DFe	DOC	0.7	0.87	4.51	<.001
DMn	DOC	0.1	0.10	0.53	>0.50
DCu	DOC	-0.1	0.10	0.53	>0.50
DNi	DOC	0.2	0.20	1.07	0.20<p<0.4
DFe	HPA	0.7	0.87	4.51	<.001
DMn	HPA	0.3	0.31	1.63	0.10<p<0.20
DCu	HPA	0.1	0.10	0.53	>0.50
DNi	HPA	0.3	0.31	1.63	0.10<p<0.20
PO	PFe	0.1	0.10	0.53	>0.50
PO	PMn	0.1	0.10	0.53	>0.50
PO	PCu	-0.1	0.10	0.53	>0.50
PO	PNi	0.1	0.10	0.53	>0.50

Table 2. Explanation of the Symbols

(Blommers, P. and Lindquist, E. F., Statistical Methods in Psychology and Education, Houghton Mifflin Co., Boston, 1960)

The linear regression analysis (Program REGRESS TSL employed in the present study) generates Pearson's correlation factor r , and is based on the statistical null hypothesis. The hypothesis assumes a normal bivariate model, according to which the mean of the sampling distribution ~~ie~~ the population correlation is in the neighbourhood of zero. However, if the population correlation differs from zero, the sampling distribution departs from normality, unless the sample is extremely large. Fisher's logarithmic transformation of Pearson's r , called z_r , and given by

$$z_r = \frac{1}{2} \ln \left(\frac{1+r}{1-r} \right)$$

is true regardless of the population correlation even for samples that are quite small. Using transformed values of r , t values are calculated from the formula

$$t = \frac{z_r - 0}{1/\sqrt{n-3}}$$

where n = degree of freedom, t -values describe approximately normal sampling distribution curves for the degree of freedom considered. Finally, p is the probability of obtaining a t as large or larger than indicated, given that the population correlation coefficient is zero (i.e. under the statistical null hypothesis). In other words a value of $p < .001$ means that there is one chance in one thousand to obtain population correlation

different from zero, i.e. the correlation factor r is meaningful. A correlation factor, with a p value >0.50 is accordingly statistically insignificant.

There is a moderately strong correlation between DFe and DOC, which remains unchanged for DFe and HPA. The next lower correlation factor in the order was found for Ni. The correlation is weak and shows a slight improvement when DOC is replaced by the specific fraction HPA. The correlation between DMn and DOC is weaker than that for Ni. The factor for the DMn - HPA correlation, however, is slightly larger than DMn - DOC.

Cu presents an interesting anomaly; Cu exhibits a negative correlation between DCu and DOC and a weak, statistically insignificant correlation with HPA.

The correlations between the metal ions and the organic fractions of Indian river water noted above are now explained. This is done by describing the predicted relationship between the metal and the organic fraction and then comparing it with the results of the present work.

The simplest theory that predicts the nature of metal-organic interaction is the ionic theory of complex formation based on the electrostatic model. Since the formation of a complex may be regarded as an interaction between a cation and either an anion or the negative end of a dipole, the magnitudes of the charges are expected to be important as well as the sizes of the metal ions. The smaller the metal ion or the larger the charge on it, the greater the electrostatic attraction and the more stable the resultant complex. It is noted, however, that the theory disregards other types

of interactions. Thus, for cations and hard bases (Basolo and Pearson 1967) the stability constants of complexes of a metal with a base increase as the oxidation state of the metal increases. In a series of ions of approximately the same ionic radius, the stability constants with a given ligand decrease as the charge decreases, for example $\text{Th}^{4+} > \text{Y}^{3+} > \text{Ca}^{2+} > \text{Na}^{+}$. It is customary to express the charge and size as the ratio, instead of just the charge or size. The ratio is then referred to ionic potential of ions. The relationship between stability constants and Z^2/r for some complexes is shown in Figure 3 (Phillip and Williams 1965). The linear relationship shown holds quite well. The elements in the figure are restricted to those of the A sub-group for the simple reason that B sub-group elements and the transition metals deviate from the ionic model. For a given ligand and divalent ions of the first transition series, the stability constants roughly follow an empirically deduced order known as Irving-Williams Order (Nicholls 1974).

Although the order follows the ionic potential of the metal ions, the stability of various complexes is more readily understood with the addition of crystal field theory (C.F.T.) considerations.

Crystal field theory assumes that the bonding in a complex is a result of electrostatic interaction between the positive nucleus of the metal cation and the negative charge

Figure 3. The relationship between stability constants and $Z^2/r_{\text{effective}}$ for some ionic complexes: circles-hydroxides, squares-acetylacetonates.

distribution of the ligands. A perturbation of non-spherically distributed d electrons on the cation is considered. It leads to increase of the energy of electrons directed toward the ligands. Consider, for example, an octahedral complex with the metal at the centre and the ligands along the four-fold axes chosen to be the cartesian axes of the octahedron. The ligands are considered point charges and are assumed to constitute an electrostatic field around the metal ion. In view of the spherical symmetry of s orbitals, the electron in the orbital is affected equally by the electrostatic field in all six directions. The energy of the four s orbitals is merely raised by the presence of the electrostatic field. Similarly the p orbitals of the metal ion, which lie along the cartesian coordinates are equally affected by the field, and their degeneracy is preserved. It is with the d-orbitals, where the e_g symmetry set point directly along the cartesian coordinates and consequently directly at the ligand atoms and the t_{2g} set have their lobes pointing between the axes, that the presence of the crystal field becomes most important. Simple electrostatic forces lift the degeneracy of the d orbitals in a octahedral complex, the e_g set being at higher energy than the t_{2g} set. The consequence of this perturbation is that the octahedral complex may be stabilized when the number of d electrons and energetics of spin pairing allow preferential occupancy of the lower t_{2g} set. The hydration energies shown

in Figure 4 (Basolo and Pearson 1967) provide evidence for this "crystal field stabilization energy" which is confirmed by stability constant trends for divalent metal ions with ethylenediamine type ligands (Basolo and Pearson 1967).

These theoretical considerations predict the stability order for the metal ions investigated in the present work as follows:

Fe^{3+} now form the most stable complex beyond Cu^{2+} in Irving-William Order, since the ionic potential of the former 9/0.61 is much larger than that of the latter 4/0.70. This predicted order then should be the order of correlations observed in the present study, provided complex formation is the mechanism controlling the metal-organic interactions in the river stream. This simply is not the case. The observed order of correlation is

in which it is noted that Cu^{2+} , the leading member in Irving-William order, takes the position of the last member in the observed order and that Mn^{2+} is elevated. This leads to the conclusion that the mechanism involving complex formation cannot fully explain the relationship between the metal ions and the dissolved organics present in the stream and that other factors have to be considered to explain the difference between the observed and the predicted order.

It is noted that the discrepancy between the observed

Figure 4. Uncorrected(dotted line) and crystal field corrected(solid line) hydration energies of divalent(lower) and trivalent (upper) ions of the first transition series.

and predicted trends revealed in the present study is the result of the investigation in which a number of elements of similar properties i.e. transition metals were included. This would not have been possible had fewer elements been investigated or if the number of the elements was large and their chemical properties were widely different e.g., alkali metals and the transition metals.

Very little information is available in the literature on the mechanistic aspect of the metal-organic interactions in natural waters in the solution phase. The literature gives mainly trends for individual metal ions. For example, Beck (1974) reported a moderately good linear correlation for both Fe and Al with dissolved organic matter in Satilla river in south-east Georgia. Tryland and Gjessing (1975) reported a strong association between humus and iron, and Shapiro (1966) concluded that yellow organic matter extracted from natural waters is capable of holding in suspension large quantities of metallic ions which would otherwise settle to the bottom and go out of circulation. He further states that the millipore filtered water contains iron upto 10^8 to 10^9 times the theoretical limit and relates the color of water to the iron concentration. Similarly, Benes (1976) reports a weak association between humus and alkali metals, a relatively high degree of association with alkaline earths and a distinctly high association with transition metals in lake waters.

Fe-fulvic acid systems modeling natural waters have been

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investigated in this laboratory (Langford and Khan 1975). A kinetic method of analysis was employed for the measurement of the binding function of Fe-fulvic acid; the method chosen is unique, since it has the distinct advantage that no treatment of the analyte is required prior to the analysis. Sulfosalicylic acid (SSA) produces a colored product common to all iron species in solution, each characterized by the rate constant at which it forms the SSA complex. The method thus characterizes and estimates concentrations of the species of interest. The conditional formation constants at 25°C and ionic strength 0.1 show a narrow variation $2.8 - 1.5 \times 10^4$ over a pH range 1-2.5. It is important to mention that the observation noted in this work that the rate of formation of the iron-fulvic acid complex is similar to that of SSA and 'normal' (Wilkins 1970) in the sense that it is comparable to rate of complex formation with monodentate ligands. Higher values of the order of 10^6 for the stability constants of Fe^{3+} -soil fulvic acid have been reported in the literature. These results, however, should be taken with caution as noted in Chapter 1.

The work in this laboratory, was also extended to higher pH in order to approach natural water conditions. One of the difficulties encountered in the laboratory study of water chemistry is the preparation of stable iron solutions at higher pHs. However, we succeeded in preparing non-settleable iron colloids at pH 4, and that prompted the extension of

previous work to more realistic conditions (Langford et al. 1977). Two observations are pertinent to the present study.

1. The measurements show two kinetically distinguishable components in solution of FA:Fe = 2:1, the slower reacting one probably represents Fe^{3+} bound strongly to FA at ortho located phenolcarboxylate chelating sites and probably corresponds to the species studied at pH 1-2.5 as described above, the fast component is suggested Fe^{3+} weakly bound to the carboxylate sites of the fulvic acid molecule.
2. Fulvic acid is found to cause substantial reduction of Fe^{3+} to Fe^{2+} , and that it causes complete dissolution and depolymerization of colloidal and particulate iron at 1:1 ratio. The reduction of Fe^{3+} by humic substances has also been reported by other workers as mentioned in Chapter 1.

The observations made in 1 provide sufficient evidence that the ortho situated phenolic and carboxylic functionalities in the fulvic acid molecule are important in providing a suitable site for complexation with the metal ion. The numerical values of conditional constants, reported above, indicate that the complexation is moderate. The observation made in 2 is equally important, because it may explain high concentrations of iron, which otherwise would not be possible at pH values found in natural water, as noted in Table 1. The reduction to Fe^{2+} also provides a mechanism complementary to

complexation for mobilizing the metal ion. Iron and manganese form insoluble hydrous oxides in higher oxidation states (+3 for Fe and +4 for Mn) and soluble species in the reduced states. Fulvic acid causes the reduction and increases the solubility of these oxides. The recognition of the reduction mechanism is important as it provides a new and possibly highly significant perspective on the DFe-DOC correlation of 0.7 observed in the present study.

The reduction of metal ions in natural waters is consistent with the mechanism that is believed to be operating in several mineral deposits. The sedimentary deposition of iron is believed by many geologists to be the result of mobilization and transportation of large amounts of iron by organic matter present in river waters (Moore et al. 1929). The presence of reduced (Fe^{2+}) is evident from the sedimentary facies like magnetite and siderite forming the deposits. The role of redox processes in uranium transportation and deposition has been recognized by most Colorado Plateau geologists (Park and McDiarmid 1975). Uranium together with vanadium are relatively soluble in the oxidized forms U(VI) and V(IV), as uranyl dicarbonate and tricarbonates complexes and tetravalent vanadium complexes. Geochemical studies indicate that the metals would be most stable in solution within a mildly reducing, and neutral to alkaline environment. Precipitation takes place under more strongly reducing conditions, such as those produced by fluids containing organic material, carbonaceous material, or hydrogen sulfide (Huff and Lesure

1962).

Geochemically Ni is an important element. It is mainly associated with ferro-magnesian minerals, as a result of an ionic potential which is very similar to the most effectively complexing alkaline earth metal, Mg. Its crustal abundance is subordinate to Fe and Mn, but has a small precedence over Cu. In aqueous solutions +2 is the only state of importance and is found in hexaquo-ion $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. The speciation of Ni is limited to complex formation in aqueous solutions. It hydrolyzes at pH 6.5 and above forming $\text{Ni}(\text{OH})_2$ and has highest solubility among the metals included in the present study.

Theoretically Ni^{2+} has complexing properties similar to Cu^{2+} with CFSE substantial for octahedral complexes, which are preferred. Table 2 shows a statistically insignificant correlation of 0.3 between DNi and HPA. Whether or not this is close to expectation depends on comparison to the other metals. The key point is that neither oxidation or reduction is important for Ni(II) so that it represents an almost pure case of the effect of the complexation mechanism.

Manganese is one of the two metals of this study that clearly violated the rules of crystal field theory of transition metals by showing a correlation with DOM better than that of copper. It is the third most abundant transition metal, being widely distributed in the earth's crust and exhibits a large variation of oxidation states, +2 to +7.

The oxidation states higher than +4 are not important to the natural water chemistry as these exist in either strongly acidic or strongly basic conditions. Mn^{3+} is unstable with respect to disproportionation in aqueous solution.

Thus, Mn^{4+} and Mn^{2+} are the only two stable species to be considered in the stream.

The property of manganese important to the observed concentration levels in natural waters (including the present study); and which is similar to the property of iron as noted earlier, is that the higher oxidation state Mn^{4+} is insoluble and the lower one Mn^{2+} is soluble in aqueous solutions. In other words the observed concentrations of manganese exceed the limiting value based on the solubility product model of the hydroxide and do not do so with respect to bicarbonate. Irrespective of the type of the anion associated with Mn^{2+} , the observed concentrations of manganese (of the order of 10^{-7} M) are possible only if one or both of the mechanisms, complexation and reduction, are actively involved. Since crystal-field stabilization energies make no contribution to their overall thermodynamic stability (Mn^{2+} forms mostly high-spin complexes) the complexation mechanism would not be favoured strongly. The NMR study on the interaction of soil fulvic acid with metal ions (Deczky and Langford 1977) shows outer-sphere complex formation in the case of manganese as expected. This suggests that a reduction mechanism may be

the controlling factor in producing relatively large concentrations of manganese (10^{-7} M) in natural waters.

Geochemically, manganese behaves similarly to iron; the two elements accumulate in similar environments and under similar conditions. Chemically both are readily soluble in reduced states, but each favours a very insoluble hydrous oxide. Under oxidizing conditions, pyrolusite or some other form of MnO_2 would be expected to form; at intermediate and low values of Eh and pH, however, divalent manganese is more stable than iron due to the fact that the standard reduction potential of the Mn^{4+}/Mn^{2+} couple (+1.23 v) is much higher than that of Fe^{3+}/Fe^{2+} couple (+0.77). Minerals containing the reduced form of manganese Mn^{2+} e.g., $MnCO_3$, $MnSiO_3$, Mn_2O_3 are common in sedimentary deposits.

A few additional experiments were performed to see the effect of fulvic acid on the solubility of MnO_2 . The experiments and their results are described below.

Manganese dioxide was prepared fresh by reduction of potassium permanganate with ethanol. 30 ml of water were added to 6.7 gms of the permanganate in a beaker, and the contents of the beaker were heated until the salt was dissolved. 33 mls of ethanol were added and the solution was stirred. The reaction initiated vigorously, and continued with the formation of a brown MnO_2 precipitate. The precipitate was filtered and dried at $100^{\circ}C$. It was recrystallized in 1:1 nitric acid, and was dried again.

The fulvic acid sample was supplied by Dr. D. S. Gamble of The Soil Research Institute, Agriculture Canada. It is an unusually well characterized sample of this poorly understood material which is derived from a Bh horizon podzol from Prince Edward Island. For the purpose of this study, its most important characteristics are 3.3 milliequivalents of phenolic functional groups and 7.7 milliequivalents of carboxylate functional groups per gm of FA (Gamble and Schnitzer 1973). This and studies of blocking group inhibitions of the metal complexing functions (Gamble and Schnitzer 1973) imply that strong metal complexes are formed with salicylic acid type functionality.

Small amounts (about 100-200 mgs) of manganese dioxide and varying amounts of fulvic acid solution were added to a series of 50 ml flasks, and the volumes were made to the mark. The contents of the flasks were shaken for three days and were allowed to stand on the bench for a week before the solutions were filtered through 0.45 μ m membrane filter and analyzed for manganese by flame atomic absorption spectrophotometer. The results are tabulated in Table 3 and plotted in Figure 4.

The plot indicates that approximately three moles of the binding sites are involved in dissolving two moles of manganese dioxide. A reaction showing this stoichiometry and involving both redox and complex formation processes can be written as follows:

Table 3: Dissolution of MnO_2 in the Presence of
Varying Concentrations of Fulvic Acid.

Flask No.	F.A. m.moles $\times 10^4$	Dissolved Mn m.moles $\times 10^4$
1	4.65	11.83
2	13.95	35.40
3	25.0	55.06
4	41.84	74.72
5	80.32	223.90
6	160.64	330.90
7	240.90	524.50
8	301.20	558.30

Figure 5. Dissolution of MnO_2 in the presence of F.A.

FA_{ox} represents the oxidized FA molecule.

Turning to the results for copper, it is seen from Table 2 that correlation factors between the metal and DOC and between the metal and HPA are statistically insignificant. Since the insignificant correlation does not suggest an interaction between Cu(II) and dissolved organics, the results apparently contradict the predicted stabilities of Cu²⁺-organic ligand complexes. Ni²⁺, which is next to Cu²⁺ in the descending order of the stability constants among transition metals (Irving-Williams Series), and whose concentration in the stream is limited to the presence of the metal in the bed rock (a number of stations show no detectable concentration of Ni), shows at least a weak correlation with DOC. Copper forms the strongest complexes among divalent transition metals, as discussed earlier, and is next to Fe³⁺ only because a trivalent metal ion is included.

Considering the redox chemistry of copper in aqueous solutions, Cu(H₂O)₆²⁺ is the most stable ion, Cu⁺ is unstable and disproportionates according to the following reaction:

The standard potential indicates that the reduction to Cu²⁺ occurs with one of the products metallic copper.

Following the mechanism that has been developed for other metals, the suggestion that organic matter reduces Cu²⁺ to metallic copper which, being insoluble, separates as a solid phase, is in order. The presence of organic matter would have a negative effect on the solubility of copper,

and would explain the absence of a positive correlation between Cu(II) and DOC as well as the HPA fraction. A parallel between the reduction of Cu^{2+} to metallic copper and the work of Alberts (Alberts et al. 1974), in which elemental mercury was found to be formed in aqueous solutions by the chemical reduction of Hg^{2+} in the presence of humic acid is suggested. According to the authors the reduction mechanism involves the interaction of the ionic metal species with the free radical electrons of the humic acid.

A few experiments were designed to get preliminary information regarding the effects of fulvic acid on the copper solutions in conditions similar to natural water. Same fulvic acid described earlier in the section and standard copper solution described in Chapter 3 were used in these experiments.

A series of eight solutions containing 2.5 ml of 3.012×10^{-3} M copper solution and increasing amounts of 3.012×10^{-2} M F.A. in stoichiometric proportions were prepared in almost neutral conditions and were allowed to age for different periods (see Table 4) at the room temperature. The solutions were filtered through 0.45 μm membrane filter, and both the filtered and unfiltered samples were analyzed for copper by A.A. The results are given in Table 4. A better sensitivity could not be achieved due to non-availability, at the time of experimentation, of flameless A.A.,

Table 4. Effect of Fulvic Acid on the Solubility of Cu
Solutions

Soln. #	Aged for 24 hrs. Cu (ppm)		Aged for 11 days Cu (ppm)	
	Unfiltered	Filtered	Unfiltered	Filtered
1	9.6	9.6	---	9.2
2	9.6	9.6	---	9.2
3	9.6	9.6	9.4	9.2
4	9.6	9.8	9.4	9.2
5	9.6	9.6	9.4	9.0
6	9.6	9.6	9.4	9.2
7	9.6	10.0	9.6	9.2
8	9.6	9.6	---	9.6

which was employed for the main body of work. The loss of copper in the filtered samples after the aging period of eleven days, among other factors, may be in part due to the reduction of Cu(II) to the insoluble metallic phase.

d) Mechanism of Interaction

The necessity of the two mechanisms, complexation and reduction, has been recognized in the above discussion (Section C) to explain the observed correlation between the metal ions and the dissolved organics.

In the case of iron both mechanisms increase the solubility of the metal and favour mobilization. The mobilization of manganese, however, is affected primarily by reduction, and complexation is most likely the mechanism controlling the mobilization of nickel. In the case of copper, complexation favours mobilization whereas reduction favours sedimentation of the metal. Since the observed correlation is insignificant, the two mechanisms appear to counteract each other reducing the overall concentration of the metal in the stream. This is consistent with the low results of the copper analysis. Copper is, therefore, not expected to move long distances from the source. The conclusion is that the contributions of the two mechanisms in fixing the state of the metal vary with the metal and follow the following trend:

Thus in shallow well oxygenated neutral to alkaline streams, as is the case with Indian river stream, inorganic ligands, mainly hydroxide and possibly phosphate, contribute primarily in precipitating the metals. However, in the presence of dissolved organic matter the situation is not simple; the process determining the solubility of metals is modified by organic ligands.

The preceding discussion has outlined some experimental evidence for the possibility that a reduction as well as a complexation mechanism contribute to the correlation between organic substances and metals in stream waters.

The association of manganese with iron in the sedimentary deposits of manganese can be understood readily. The manganeseiferous beds commonly contain oxides concentrated in layers separate from the iron beds, as at Morro do Urueum, Brazil (Park and MacDiarmid 1975). River waters can dissolve and transport enough iron and manganese, since both are readily soluble in reduced states. However, when these loaded waters

enter the oxidizing environment, iron should be precipitated before manganese from the solution, since Fe^{2+} is more easily oxidized than Mn^{2+} under any naturally occurring Eh-pH conditions.

It is very interesting to note that aluminum does not occur in sedimentary deposits because similar argument is not applicable. The diagenetic processes are of no practical importance to the formation of bauxite, since a soluble oxidation state lower than Al^{3+} does not exist; Al^{3+} can only be solubilized as aluminate in strongly alkaline solutions. One explanation of economic bauxite deposits is, therefore, that these are produced by enrichment of aluminum bearing rocks during weathering.

e) Particulate Fe and Mn

It is apparent from the solubility considerations for Fe, Mn, Cu and Ni presented in this Chapter, particularly with reference to Figures 1, 2 and 3, that hydrous oxides of these metals constitute an important phase in the Eh-pH conditions of these natural waters. In the absence of complexing molecules, such as organic ligands, the solubility of these metals would be very low due to the insolubility of metal hydroxides. It has been suggested that the hydroxides of Fe and Mn exert the principal control on the availability of heavy metals (Fe, Mn, Co, Ni, Cu and Zn) in natural waters (Jenne 1968). In other words these hydroxides can act as sinks

for heavy metals.

The stable form of iron hydrous oxide is the micro-crystalline FeOOH (goethite), and can be visualized as the dehydration product of conventional $\text{Fe}(\text{OH})_3$.

The hydrous form of manganese and iron, $\delta\text{-MnO}_2$, and α and $\gamma\text{-FeOOH}$ have high surface areas of up to 300 meter²/gm for $\delta\text{-MnO}_2$ and 230 to 320 meter²/gm for FeOOH.

Cu precipitates as $\text{Cu}(\text{OH})_2$, which reverts to a more stable form, CuO, by dehydration.

It has been suggested that Mn^{4+} can be reduced to Mn^{2+} without the phase change (Feitknecht et al. 1960).

This reaction is suggested to have implications in colored natural waters.

These hydrous oxides specially at pH values higher than pH_{ZPC} (ZPC = zero point charge and is defined by the pH at which surface positive charge equals to surface negative charge) are capable of interacting with cations by two mechanisms:

1. Complex formation
2. Electrostatic interaction.

Physically the electrostatic interaction can be best visualized by Helmholtz electric double layer. The surface of these oxides carries charges that assign a potential to

the surface, which decreases exponentially into the solution. The exposed surface charges orient ligands, metal ions and water dipoles in the layer next to the surface and interact with the solution species. The capacity of this process is pH dependent and decreases rapidly into the bulk solution. The strong interaction, generally shown by trivalent transition metal ions is referred to as specific interaction, whereas weak charge dipole or charge-ion interactions are referred to non-specific interactions. The mechanism of interaction is the same as has been developed in the case of homogeneous solutions, i.e. specific interaction corresponds to complex formation and non-specific to electrostatic interaction. The capacity of complex formation of these oxides in heterogeneous solution does not reach, in principle, to the proportions attained by homogeneous solutions, because of the limitations set by surface potential, and more important the exponential decay of the latter, as mentioned earlier. This factor can be compensated for, in the case of transition metals, by preferential interaction of transition metal ions with the surface. Quoting Morgan (1970): "While adsorption with group I and II elements takes place predominantly in the diffused part of the electric double layer, the transition and heavy metals can become specifically attached to the surface..". A composite diagram depicting the interactions of a metal ion, an organic ligand and water dipole in the double layer has

been outlined and shown p.204. Manganese hydrous oxide is used as an example; the surface of the oxide is shown by the solid boundary. The diffused layer and the bulk, where the process is not well defined is not shown for clarity.

In the present study particulate is operationally defined as the fraction retained on 0.45 μm membrane filter. Linear correlation factors between particulate organic material (PO) and particulate forms of metal ions is given in Table 2. The correlation is very weak among all metals. This excludes the possibility of any detailed evaluation of the interactions in particulates in the samples. We can recognize three mechanisms.

1. Adsorption of particulate metal onto humus. (Humus is defined as that insoluble fraction of organic material present in river water which does not pass through 0.45 μm membrane filter. Most of the fulvic acid and small humic acid particles are therefore excluded from humus.)
2. Adsorption of organic molecules onto particulate metal.
3. Formation of a mixed metal-organic particulate. This, of course, does not mean that organic molecules are forming a protective layer on the suspended metal colloid and inducing coagulation.

Any more detailed description of the nature of interaction in the heterogeneous system is beyond the scope of

the present study, except that the overall mechanism of interaction, i.e. electrostatic complemented by inner sphere complexation.

f) Binding Capacity of Indian River Water

The importance of organic matter which forms soluble complexes with metal ions in the aquatic environment has become a major topic of aquatic studies. Our study has shown that complexation (in addition to redox characteristics) is important in Indian river waters. Consequently it seems important to evaluate the metal ion binding capacity (stoichiometric total) of Indian river waters.

The basic assumption involved in the measurement of the binding capacity of organic material present in Indian river water is that copper would displace all metals already occupying the binding sites, except probably Fe^{3+} . This assumption is theoretically sound (Irving-Williams stability order). The stability rule (Section c) is valid for oxygen containing salicylic acid type ligands shown to be functional in aquatic organic matter. The situation in natural waters, however, is different from the carefully controlled laboratory studies in the sense that the competition between trace metals and the major cations e.g., Ca^{2+} , Mg^{2+} , for the available complexing sites may be significant.

It can be argued that doping the natural water with an excess of Cu ions might not reveal the true complexing

capacity. Very little work has been done on the coordination complexes of metals and the salicylic acid type ligands to prove the validity of the Irving-Williams rule in natural waters. But it can be said that the work done so far does not refute the idea. For example, Gamble (1973) examined the reactions of the most abundant alkali metals, Na and K, with soil extracted fulvic acid and found no evidence of complex formation. The studies indicated that the alkali metals are held by weak electrostatic attraction. The studies at our laboratory referred to earlier show that Mn^{2+} interacts with fulvic acid as outer sphere complex whereas Cu^{2+} and Fe^{3+} form inner sphere complexes.

More pertinent to the present discussion is the work of Gamble and Schnitzer (1973), in which they examined the effect of Ca^{2+} competition on the complexation of Cu^{2+} by fulvic acid. At a fulvic acid concentration of 1 mg/L and at a Ca/Cu ratio of 80, they calculated that the fulvic acid chelating sites would be almost fully evaded with Ca^{2+} , with very little Cu(II) complexation. Reuter et al. (1977) extended the calculations to a range of fulvic acid concentration in order to account for much greater than 1 mg/L fulvic acid concentrations usually found in natural waters. Fulvic acid concentrations ranged from 1 to 100 mg/L (3×10^{-6} - 3×10^{-7} M, assuming 3 m.mole bidentate sites/gm FA) and Cu(II) concentrations ranged from 1×10^{-8} to 1×10^{-5} M. A Ca^{2+} concentration of 4×10^{-4} M and an initial pH of 5 were used in all calculations, along with equilibrium functions for

Figure 6. Degree of complexation of Cu(II) and Ca^{2+} as a function of fulvic acid concentration. Total Cu(II) concentrations 1×10^{-5} (---) and 1×10^{-8} M (—).

Ca^{2+} -FA complex ($\bar{K} = 1.8$) and the Cu(II) -FA complex ($\bar{K} = 23$) which were reported by Gamble and Schnitzer (1974).

The results which are given in Figure 5 predict that the degree of complexation of Cu^{2+} and Ca^{2+} , as well as the fraction of occupied complexing sites in fulvic acid, are essentially independent of the analytical concentrations of Cu(II) . However, these parameters are quite dependent on the concentration of fulvic acid. For example, when 1 mg/L of fulvic acid is present, only about 8% of Cu(II) is complexed; however at a fulvic acid concentration of 10 mg/L, almost half of the Cu(II) will be complexed. Thus the data of Gamble and Schnitzer (1973) predict that substantial quantities of Cu(II) could be complexed by fulvic acid even in the presence of a 40 000 fold excess of Ca^{2+} .

The piece of information presented above affords some support to our basic assumption. It may not be unsafe to conclude then, that most abundant alkali and alkaline earths metal together with most of the divalent transition metals occupying the chelating sites of organic ligands would be displaced by Cu^{2+} when added in excess. Al^{3+} and Fe^{3+} , having a much larger ionic potential as compared to other divalent transition metals, together with other cations carrying higher charges may present tough competition. Since Al and Fe are the only elements abundant in natural waters, the interference due to cations of higher charge may be neglected. Since metals such as Fe and Al bind

strongly to chelating sites, it is possible that measured binding capacity would be different from the true value.

Our measurements (Table 29, Chapter 3) yield values of the order of 11 μ mole/L for Indian river water, and show that this value is almost wholly due to the hydrophobic acid fraction. In other words, the dominant organic fraction responsible for Cu^{2+} binding is clearly the hydrophobic fraction. We can compare the hydrophobic acid fraction more quantitatively to fulvic acid.

A fulvic acid from a Prince Edward Island Podzol has been characterized by Gamble and Schnitzer (1973). The Cu^{2+} binding sites are chelating and appear to involve the 3 meq/gm of phenolic functionality. This fulvic acid analyzes 46% C. According to our DOC measurements, 20% of the carbon is in the hydrophobic acid fraction. Thus our sample contains 2.6 mg/L of hydrophobic acid carbon. If this was composed entirely of the Schnitzer and Gamble fulvic acid it should carry (according to manipulations of the above numbers) 17 μ mole/L of complexation capacity. The degree of agreement is impressive and the difference may correspond to the difference between apparent and real values.

The next aspect pertinent to binding capacity is that of "intensive" parameters. Can a conditional binding constant be calculated for comparison with purified fulvic acid? Despite some earlier efforts, we believe that the answer should be in the negative at present. There are two reasons.

The first is purely technical. We do not believe that data of the resolution (or other similar work at natural water organic concentrations) can support refined analysis. There is too much danger that "best" parameter values will be controlled by error. The second is more fundamental and has been overlooked in earlier work. If the ligands which are the source of complexing capacity are of the fulvic acid type, they are polyelectrolytes. As Gamble and Schnitzer remark (1973): "no two carboxyl groups are inherently chemically identical". Calculations of binding constants have assumed a homogeneous sample of a chemically uniform ligand. This is not appropriate for fulvic acids as the theory of polyelectrolyte titration given by Gamble and Schnitzer shows. An especially important point is that conditional binding constants calculated for natural water have been compared to those determined for model compounds at larger and more convenient concentration of the model compounds (Ramamoorthy et al. 1975). Burch, Langford and Gamble (1978) have recently shown that one surprising consequence of the polyelectrolyte situation is that conditional constants calculated are a function of the fulvic acid concentration and that this is an important factor in the comparison of materials from differing soil origins.

g) Conclusion

Although during the part of the geochemical cycle the

temperature, pressure, and time intervals involved are such as to prevent participation by metal-organic molecules, the evidence presented indicates that during weathering and sedimentation organic matter has a significant role to play in modifying the chemical and physical properties of the metals investigated. Reduction of metal ions by organic matter, in addition to complexation, has been recognized as an important mechanism affecting the mobilization of metal ions. Among metals explored here, Fe is most affected and Cu least in terms of transfer to solution. Extension of the work to other metals with several oxidation states in the same pE range would be very interesting. A notable example is uranium.

The binding capacity of the organic matter 11×10^{-6} mole/L of water has been found largely due to the hydrophobic part of the complex organic matter present in the stream. The properties of this fraction resemble that of the soil fulvic acid.

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MAP 1302A
GEOLOGY
CARLETON PLACE
ONTARIO
Scale 1:50,000

MAP 1362A
GEOLOGY
CARLETON PLACE
ONTARIO
Scale 1:80,000

- LEGEND
- Medium- to coarse-grained, light grey marble; tremolite marble alternating with well-layered, fine-grained, grey marble
 - Garnet amphibolite, garnet gneiss and migmatite
 - Layered, medium-grained amphibolite
 - Metagabbro, dense, massive to schistose, fine-grained, dark amphibolite, possibly equivalent to metagabbro
 - Hornblende migmatite: mainly intercalated amphibolite and granitic rocks
 - Massive, medium- to coarse-grained hornblende metadiorite, which may grade into metagabbro
 - Foliated and massive, pink granodiorite
 - Massive, coarse-grained, pink granite and pink pegmatite

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MAP 1382A
GEOLOGY
CARLETON PLACE
ONTARIO.
Scale 1:84,000

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