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GEOCHEMICAL DISPERSION
OF
ELEMENTS VIA ORGANIC COMPLEXING

by

KEITH SIDNEY JACKSON, B.Sc. (HON), M.Sc.

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

June, 1975.

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LONG LAKE

LEGEND

PALAEOZOIC

ORDOVICIAN

TRENTON and BLACK RIVER

TIAWA FORMATION: limestone with some shale;
dolomite; some sandstone in basal part

TRENTON

COBOURG, SHERMAN, FAIRFAX, KIRKFIELD FORMATIONS

limestone gray and grey, massive

COBOURG, DENMARK, SHERMAN, KIRKFIELD AND
BIRCHLAND FORMATIONS IN NEW YORK STATE

BLACK RIVER

COBOURG, MOORE HILL, GULF RIVER, SHADOW
LAKE FORMATIONS: light to dark gray to brown to grey
limestone, basal formation massive and light grey
shale, some conglomerate

CHAUMONT, LOWVILLE AND PAMELIA IN NEW
YORK STATE

BECKMANTOWN

DEFOY FORMATION: dolomite and limestone
OGDENBURG DOLOMITE IN NEW YORK STATE

MARCH FORMATION: interbedded
sandstone and sandy dolomite

UPPER THERESA FORMATION IN NEW YORK
STATE

Mafic dykes

Nepheline gneiss, pegmatite, nepheline syenite

Granite, granodiorite, tonalite, massive and foliated,
associated migmatite

Leucocratic granite, massive and foliated

Quartz monzonite

Granodiorite, tonalite, massive and foliated

Hornblende, biotite and pyroxene syenites, corundum
syenite, pegmatitic syenite, hornblende quartz syenite,
pyroxene quartz syenite, monzonite (foliated varieties
common)

Pegmatite, white pegmatite associated with marble

Diorite, gabbro, anorthosite, melagabbro, massive and
foliated

Marble, lime silicate rocks, interbedded amphibolite

ORDOVICIAN AND CAMBRIAN

LOWER THERESA FORMATION: sandstone and dolomite
(Cambrian)

NEPEAN FORMATION: sandstone
(Ordovician)

MOIRA RIVER

CALUMET ISL.

MAP 1: FIELD

(Mc D

R

LAVANT-CLYDE

SULPHIDE CK.

SL.

MAP 1: FIELD AREA GEOLOGY

[REDACTED]

POTSDAM FORMATION conditions
(Continued)

Areas of heavy overgrazing

* Includes younger dykes one of which at Verry Lake
(76°49' 44" N) is FRIASSIC

Monite de fer et pyroxène spinels corundum
spinel pyroxène spinel hornblende quartz spinel
pyroxène quartz spinel monite (isolated varieties
common)

Pyramite white pyramite encrusted with marble

Direct public authorities responsible measure and
related

Mylonite line separates rocks interbedded amphibolite
where appears granulite minor quartzite

Amphibolite, biotite hornblende schist and gneiss
pyroxene gneiss associated in gneiss in places
Garnet for ore

Saline water volcanism and hydroclastic rocks

Major and intermediate volcanic rocks.

Paragneiss pelitic and plomine - pelitic
whists and gneisses (includes some layered
amphibolite of uncertain origin)

Compliments

Plumbeous metasediments of probable volcanic origin

Quartzite quartzose schist and paragneiss, quartzite
interlayered with paragneiss, quartzite interlayered with
mudstone

Position of rock unit in the column does not imply the relative age of the unit

CALUMET ISL.

MAP 1: FIEL

(Mc

Miles

Kilometres

SULPHIDE C.K.

P 1: FIELD AREA GEOLOGY

(Mc Donald, 1967 & 1970)

SCALE

(1:250,000)

Areas of heavy iron boulders

Mafic and intermediate volcanic rocks

Paragneiss: pelitic and psammitic, pelitic
schists and gneisses (includes some layered
amphibolite of uncertain origin)

Conglomerate

Psammitic metasediments of probable volcanic
origin

Quartzite, quartzose schist and paragneiss, quartzite
interbedded with paragneiss, quartzite interbedded with
marble

*2

Includes younger dykes, one of which at Valley Lake
(76°49' 30"25" N, 78°15' 10"25" W)

*1

Position of rock units in the column does not imply the relative age
of the unit

1 of 1

MAP 3 SAMPLE LOCALITIES
LONG LAKE

MAP 5 SAMPLE
SULPHIDE

MAP 5 SAMPLE LOCALITIES
SULPHIDE CK.

MAP 3 SAMPLE LOCALITIES
LONG LAKE

MAP 5 SAMPLE
SULPHID

MAP 6 SAMPLE
CALUM

MAP 5 SAMPLE LOCALITIES
SULPHIDE CK.

MAP 6 SAMPLE LOCALITIES
CALUMET ISL.

1 OF 1

2

3 of

MAP 2

SAMPLE LOCALITIES

MOIRA RIVER

Allan

MOIRA RIVER

III

II

1 of 1

MAP 4
SAMPLE LOCALITIES
LAVANT-CLYDE

3 of

The undersigned hereby recommend to the
Faculty of Graduate Studies acceptance of this thesis,
submitted by Keith S. Jackson, B.Sc., M. Sc., in
partial fulfilment of the requirements for the degree
of Doctor of Philosophy.

.....
Supervisor

.....
Chairman of Department

.....

.....

Carleton University,
Ottawa, Ontario
June 27, 1975.

ABSTRACT.

A knowledge of an element's behaviour at a sediment-water boundary is a prime concern in the development of an understanding of what may be the significant chemical controls on an element's dispersion. Previous studies have indicated that the ubiquitous, naturally occurring, soluble humic and fulvic acids have the ability to stabilize metallic cations in solution in competition with hydrolysis, carbonate and sulphide precipitation.

Laboratory model experiments were conducted which extended the range of these experiments to include possible sorption on a clay surface over a pH range of 4 to 9 with the interference due to carbonate being introduced within a set of experiments. The metal to organic acid sites milliequivalence was another variable studied. The ability of humic and fulvic acids to desorb metal previously adsorbed onto clay and metal from metal hydroxide precipitates were also investigated. Cu, Pb, Zn and Ni were the metallic cations studied. Under the experimental conditions, Cu is strongly stabilized in solution but is the most kinetically hindered in desorption reactions. Pb is the least retained in solution by organic complexing but is apparently susceptible to colloidal coagulation phenomena. The solubilities of Zn and Ni are enhanced by organic complexing but are pH dependent with hydrolysis leading to decreased solubilities. Ni solubility is also decreased by carbonate precipitation. The kinetic barriers to desorption of Ni, Pb, and Zn were almost equivalent.

A field study of the dependence of the stream sediment to stream water distribution ratios for 10 elements (Na, K, Mg, Ca, Fe, Mn, Cu, Pb, Zn and Ni) on sediment cation exchange capacity and total dissolved organic carbon was also conducted. Predicted behaviour, based on a reaction scheme involving sorption and organic complexing only, was compared with observed behaviour. It is concluded that this reaction scheme is not adequate for Na, K, Mg, Ca and Mn. The dispersion of Pb and Fe in natural waters is favoured by organic complexing. Cu is strongly governed by sorption to organic-rich stream sediments. The behaviour of Ni is strongly influenced by interfering reactions, particularly with the inorganic ligands carbonate and hydroxide. The proposed reaction scheme may not be adequate for Zn, but, it is suggested that Zn exhibits almost equal reactivity in sorption and organic complexing.

A comparison of the laboratory model with the field results indicates that two significant modifications would be the use of an organic-bearing adsorbent phase and of soluble organics extracted from natural waters.

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INTRODUCTION.

The transport of elements in solution as complexed species has received wide acceptance in the geologic literature. However, there is no unanimous agreement on the nature of the complexed species. For example, Barnes (1962), in looking at sulphide mineralization, supported the proposal that metals are transported as sulphide complexes whereas Helgeson (1969), in a consideration of hydrothermal solutions, proposed chloride species as the most significant species involved. Pittwell (1973) has concluded that the most common coordinating ligands present in groundwaters are water itself, carbonate, chloride, fluoride and some organic acids. He also shows that it is possible to account for the formation of many ores using only these complexes as starting materials and active compounds. Saxby (1973) suggests that, on diagenesis, metal-organic complexes may form concentrations of metallic sulphides.

This thesis is concerned with the chemical processes of trace element dispersion within surficial waters where much significance has been attributed to metal-organic matter interactions in the transport and concentration of trace elements (for example, Szalay, 1964; Manakaya and Drozdova, 1968; and Saxby, 1969).

- Organic compounds constitute only 2 to 3% of sediments and their concentration in natural waters rarely exceeds a maximum of 20mg./l. (Rashid and Leonard, 1973). Nevertheless, there is a considerable literature documenting organic participation in various geochemical processes such as solubility, mobility, concentration and accumulation of metals.

Within surficial waters, the most significant form of inorganic-organic interaction is generally accepted to involve chelation of trace elements with the complex, polymeric organic compounds called humic matter. (Saxby, 1969; and Bowen, 1966). The literature supports the proposition that, in rivers, swamps and soils, much of the organic carbon is present as humic matter. Humic matter (humic and fulvic acids) in the environment has been reviewed by Swain (1963), Schnitzer and Khan (1972) and Jackson (1975).

Experimental studies have shown that, in comparison with model organic compounds likely to find their way into natural waters, soluble humic matter has the highest potential to form soluble, stable metal complexes in competition with hydrolysis reactions. Humic matter in a sedimentary or particulate phase exhibits exceptionally strong cation exchange properties thus concentrating trace elements from solution onto the solid phase. As a further experimental note, humic matter is capable of dissolving many metallic mineral phases.

To a geochemist, the trace element distribution between sediment and natural water and the chemical factors influencing this are of a prime concern. The dominant interactions here are suggested to be cation hydrolysis, cation exchange reactions and cation complex formation (inorganic and organic). To study this, laboratory model experiments will be described in which metallic cations, humic and fulvic acids and clays in suspension were allowed to equilibrate. By doing this, it was hoped that data

would be obtained indicating whether or not metallic cations can be maintained in solution as organic complexes in competition with hydrolysis and exchange reactions with clay. The four metals investigated were Cu, Pb, Zn and Ni. By varying conditions (pH, metal to organic acid ratio and the introduction of soluble carbonate), it was hoped that some differentiation in the reactivities of the four metals might become apparent.

The above experiments were designed to model the reactions of the four metals in a stream water. An equally important geochemical process is the liberation of sediment bound metal into a stream. Experiments, with bulk chemistry analogous to the above, were set up to study the ability of humic and fulvic acids to remobilize Cu, Pb, Zn and Ni from their hydroxide precipitates and from a clay adsorbed phase.

Literature data relating to the behaviour of metals in the presence of soluble organics and a solid adsorbent phase at pH values pertinent to natural waters are not available. From the data obtained in the model experiments, an insight into what are the chemical controls on the behaviour of Cu, Pb, Zn and Ni, at a sediment-water boundary, was being sought.

To assess the validity of conclusions made from the laboratory data and determine the deficiencies of the model, a field programme was undertaken. There is good literature evidence indirectly implying that metal-organic complexing does occur within natural waters. The characterisation of metal and metal-organic species in natural waters is, however, rarely reported in the

literature due to the lack of precise analytical techniques. Nevertheless, it is concluded, on the basis of available information, that metal-organic complexing in natural waters does occur.

The effect of organic complexing on an element's sediment-water distribution ratio was the object of the field study. Stream waters and sediments were sampled from five drainage systems, and the sediment-water distribution ratio for Cu, Pb, Zn, Ni, Fe, Mn, Mg, Ca, Na and K studied as a function of total dissolved organic carbon (TOC), sediment organic content (OC) and sediment cation exchange capacity (CEC). From the field data obtained, the behaviour of the elements in natural waters will be discussed. A comparison will be made between the behaviours of Cu, Pb, Zn and Ni in the laboratory and in the field. From this comparison, an assessment of the model used in the laboratory experiments is possible.

Chapter 1 - Literature Review.

1.1 Definitions of humic and fulvic acid.

Humic substances are defined by Stevenson and Butler (1969) as "a series of acidic, yellow to black coloured, moderately high molecular weight polymers which have characteristics dissimilar to any of the organic compounds occurring in living organisms." Division of these materials into three categories has been generally accepted in the literature. The three divisions are (a) fulvic acids; substances soluble in both acid and alkali, (b) humic acids; substances soluble in alkali but insoluble in acid, and (c) humins; insoluble in acid and alkali.

A further subdivision of humic acids has been noted by Stevenson and Butler (1969). Brown humic acids are not coagulated by an alkaline, electrolytic solution and are characteristic of humic acids in brown coals, peats and podzolic soils. Grey humic acids are precipitated in this electrolytic solution; this humic acid is characteristic of chernozems and rendzinas.

However, such divisions - useful in practice - are quite arbitrary. No sharp division exists between humic acid, fulvic acid and humins. They are part of an extremely heterogeneous polymer system and the differences between the subdivisions are due to variations in elemental composition, acidity, degree of polymerization and molecular weight. That fulvic and humic acids are indeed mixed polymeric systems is further evidenced by their subdivision into fractions by techniques such as

continuous electrophoresis (Manskaya and Drosdova, 1968).

1.2 Humification process.

Humic substances are formed in the natural environment during the degradation of dead organisms and plants. The overall process is referred to as humification. The actual chemical processes involved here are complex and imperfectly understood. The degradation products are thought to be simpler organic compounds such as carbohydrates, proteins and phenolic compounds such as lignin. From the synthesis and condensation reactions involving these simpler compounds, the high molecular weight humic substances can be formed. Many authors have speculated on the various synthetic pathways involved (Ishiwatari, 1966; Jackson, 1975; Manskaya and Drosdova, 1968; Swain, 1963; Kononova, 1966; and Flaig, 1971). Perhaps the most accepted theory (for example, Ogner, 1973) is that the humic substances represent modified lignin. However, Jackson (1975) points out that, based on a study of sedimentary humic matter, lignin is not an essential starting material for the formation of humic compounds. Kononova and Alexandrova (1973) have suggested a possible chemical method for assessing the degree of humification of soil organic matter.

Stevenson and Butler (1969) consider that humic acids can degrade directly to fulvic acids or else may degrade to the structural units which can polymerize to the simpler fulvic acids. Further condensation of fulvic acids could in turn be responsible for the formation of humic acids. The formation of fulvic acids from humic acids via an increase

in oxygen - containing functional groups at the expense of aliphatic and/or acyclic material is not favoured but still cannot be excluded. Stevenson and Butler (1969) also suggest that fulvic acids and possible humic acids can be formed by microorganism activity.

It is of interest to note that humic acids may be precursors to the formation of coal in natural environments (Chakrabartty et al. 1974). The conversion of humic acids to coal during diagenesis might be accomplished by the progressive loss of COOH , OCH_3 , and OH groups.

A detailed account of the complex processes that lead to the formation of humic and fulvic acids in nature is beyond the scope of this thesis. It is clear, however, that there will be a substantial variation in the chemical nature of humic substances depending on the source materials as well as biological, chemical and physical factors that have acted during the transformation of decaying organic matter into humic and fulvic acids.

1.3 Chemical and physical properties of humic and fulvic acids.

(a) Molecular weight.

Molecular weight determinations for fulvic and humic acids range in value from less than 1,000 to greater than 300,000. This is to be expected considering the proposed complex polymeric structures of humic and fulvic acids and the influence of source material on this result. Ishiwatari (1966, 1971), Tan and Giddens (1972), and Kemp and Wong (1974) have calculated molecular weight distributions of humic substances from lake and marine sediments

and soils. For both humic and fulvic acids, wide molecular weight distributions were obtained. The fulvic acids had consistently lower molecular weights. A commonly cited term is the number average molecular weight which is usually in the range 900 to 1,000 for both humic and fulvic acid.

(b) Elemental analyses.

Elemental analyses of humic and fulvic acids have been quoted by many authors. In Manakaya and Drosdova (1968), the analytical compilation, shown below, has been established on the basis of numerous sample analyses.

<u>Acid</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%O</u>
humic acids	52-62	3.0-4.5	3.5-4.5	32-39
fulvic acids	44-48	4.0-5.5	1.5-2.5	44-48

The authors also quote data which indicate that elemental analyses not only vary with sample location but also vary with depth in a peat bog. Schnitzer and Desjardins (1965), in an analysis of seventeen organic soil samples, found variation in the N content with sample type. However, some distinction between humic and fulvic acids is possible from elemental analyses. From any location, fulvic acids consistently show decreased C contents and increased O contents compared with humic acids.

(c) Molecular structure.

The molecular structure of humic and fulvic acids has been the subject of much investigation. Shurygina et al. (1971), in an investigation of humic and fulvic acids from chernozem and podsollic soil, concluded that both aromatic and aliphatic

structures exist in these molecules. Humic acids had a predominance of aromatic units whereas fulvic acids had aliphatic structures in predominance. Jackson et al. (1972), used a phenolic degradation technique to identify linkage units. They concluded that the most probable linkage units between aromatic moieties would be:

Specific chemical attack of humic and fulvic acids has proved useful in identifying basic skeletal units (for example, Khan and Schnitzer, 1972; Schnitzer and Skinner, 1974; Ogner, 1973; Chakrabartty et al. 1974; and Gamble and Schnitzer, 1973). Manskaya and Drozdova (1968) have collated much of the earlier work. The major oxidation products, benzenecarboxylic acids and phenolic acids, would appear to be important skeletal units.

As summarized by Manskaya and Drozdova (1968), X-Ray data have shown that humic acids have variable structures, but, basically, all have aromatic nuclei in the form of flat lattices of cyclic polymerized C connected to which are side chains that carry various functional groups. Humic acids differ in the quantitative relationships between the chains and the aromatic nuclei in the C skeleton. The elucidation of functional groups within the humic acid molecule has been attained by instrumental analyses (e.g. infra-red and UV-visible spectroscopy) and chemical methods. Molecules of humic acid are now known to contain carboxyl, phenolic and alcoholic hydroxyl, methoxyl, carbonyl and quinone groups.

Figure 1.1 (a) Structure of humic acid according to Fuchs (see Swain, 1963).

(b) Structure of humic acid according to Dragunov (see Manskaya and Drozdova, 1968).

Figure 1.2 Possible fulvic acid structure (Gamble and Schnitzer, 1973).

The humic acid structure is likely to be based primarily on six membered aromatic and heterocyclic rings. Certainly no single structural formula, such as that of Fuchs (figure 1.1) appears acceptable. The literature would favour a "type" molecule consisting of micelles of polymeric nature, the basic structure of which is an aromatic ring of the di- or trihydroxyl phenol type bridged by $-O-$, $-CH_2-$, $-NH-$, $-N-$, $-S-$, and other groups, and containing both free $-OH$ groups and the double linkages of quinones (Manskaya and Drozdova, 1968). Dragunov's formula (figure 1.1), as presented in Manskaya and Drozdova, meets many of these requirements but still seems to lack significant amounts of aromatic $COOH$ groups. Humic acids from lignite will differ from humic acids from soil and peat in that they are more highly condensed and have fewer side chains and functional groups.

Fulvic acids have been subjected to similar structural analyses. The functional groups identified in humic acids are also identified in fulvic acids but fulvic acids contain considerably more groups of an acidic nature, particularly $COOH$ (Stevenson and Butler, 1969). Gamble and Schnitzer (1973) concluded from X-Ray and chemical evidence that fulvic acids contain aromatic rings which form an open structure in a 2 or 3 dimensional array. The open structure is held together at least partly by hydrogen bonds among the functional groups. They have proposed a potential structure as shown in figure 1.2.

(d) Functional groups.

More important than the structural networks of humic and

fulvic acids are their functional group content. It is the functional groups of these molecules which determine their reactivity. The important determinations are of total acidity, carboxyl groups, hydroxyl groups and carbonyl groups. Both carboxyl and phenolic hydroxyl groups will contribute to total acidity. As previously stated, it has been concluded that fulvic acids contain more functional groups, particularly carboxyl, per molecule than do humic acids. Manskaya and Drozdova (1968) report the numbers of functional groups per molecule of soil humic acid to be:

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

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

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

This is a significant result as the carboxyl and hydroxyl groups of humic substances are the most likely to react with cations. Fulvic acid should then have a higher capacity for interactions with metals.

(e) Colloidal and polyelectrolyte properties.

Two further important aspects of humic substances are their polyelectrolyte character and their colloidal properties.

It is not surprising, considering the molecular weight of humic substances, that humic and fulvic acids display colloidal chemical properties. These are discussed in detail by van Dijk (1971a).

Humic and fulvic acids behave as negatively charged species due to the ionization of their acidic carboxyl and hydroxyl groups. Neutralization of this charge or repression of the ionization can lead to their flocculation. Gamble (1970) and Gamble and Schnitzer (1973) point out that humic and fulvic acids found in soils have molecular weight ranges and chemical properties quite comparable to those of synthetic polyelectrolyte systems (for example, polyacrylic and polymethacrylic acids). One, however, cannot assume, for humic and fulvic acids, that any two of the ionisable functional groups are chemically identical. This can be significant when attempting to calculate an ionisation constant or "complexation" constant for a humic or fulvic acid. (Gamble and Schnitzer, 1973).

1.4 Interaction mechanisms.

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

A general reaction scheme to describe the interaction of metal ions (M^{X+}) with dissolved organic matter (ORG) and particulate matter (CP) has been proposed by Curtis (1966) and outlined in figure 1.3. According to the Curtis scheme, metal ions can show a positive, zero or negative correlation with carbon from particulate or sedimentary material. A positive correlation arises when metal ions interact in solution with dissolved organic matter forming complexes that in turn are concentrated by adsorption onto particulate matter such as clay particles. Zero and negative correlations result from no interaction between metal ions and organic in solution. The dissolved organic matter alone may then be adsorbed onto particulate matter to produce zero correlation or the metal ions and dissolved organic matter may compete for adsorption onto the particulate matter hence producing a negative correlation.

Another reaction scheme proposed by Ong and Bisque (1968) and Ong et al. (1970) is perhaps best regarded as a refinement of the Curtis scheme. Ong et al. (1970) consider colloids formed from organic acids as possible transporting agents of metal ions although they do concede that the literature favours soluble complex formation rather than colloidal phenomena as the principle means of metal transport. The reaction scheme is presented in figure 1.4. The Fuoss effect refers to a change in shape of the humus or organic acid macromolecule upon the addition of salts. The change in shape causes the expulsion of part of the water of hydration and thus the humus macromolecule changes to a hydrophobic type of colloid. In effect, the addition of cations

Figure 1.3 Generalized metal-organic-solid reaction scheme
as proposed by Curtis (1966).

Figure 1.4 Metal-organic interaction scheme as proposed
by Ong et al. (1970).

has reduced the charge of the polyelectrolyte and thus reduced the water of hydration held by the colloids. In aqueous solution, this leads to the precipitation of metal humates as neutral colloids.

The terms, metal-organic complex and metal-organic chelate, are often treated as synonymous in the literature. The term complex applies to a compound formed when a metal ion combines with an electron donor. If the ligand contains two or more donor groups, then one or more rings may be formed with the resulting structure being termed a chelate compound. Within the structures of humic and fulvic acids, salicylic acid and/or phthalic acid type sites are generally thought to be the most significant centres for metal reaction. These are bidentate sites and hence chelate would be the more accurate description of the resulting compound. However, there is considerable evidence suggesting that minor but not insignificant reaction is feasible via quinone sites which are electron donors but not polydentate. For this, the term complex is correct.

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

the reaction.

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

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

van Dijk (1971b) concluded that metal humates belong to the polynuclear chelates with cations binding predominantly to the negatively charged ligand groupings of the humic acids. He also discusses a dependence on pH. At low pH, acidic and weakly acidic groups are thought to bind metals directly. At high pH, transition metals may form hydroxo-complexes with humic acids.

The acid ionization equilibria of humic and fulvic acids

are pertinent to the present discussion. Gamble (1970) observed two general types of carboxyl groups in a fulvic acid sample. One of these is ortho to the phenolic hydroxyl while the other can be meta or para to the phenolic hydroxyl. For both types, whether in aqueous solution or 0.1M KCl, ionization is almost total by pH⁴. In both cases, an increasing degree of ionization resulted in a decreased acid strength. Theng *et al.* (1967) report the presence of carboxyl groups ionizing above pH7 and extending to as high as pH11. However, it has also been reported that humic acid contains two types of weakly acid groups. Firstly, there are carboxyl groups dissociating up to pH5-6 and, secondly, phenolic OH groups dissociating beyond pH7 (Chuvelava *et al.* 1962).

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

Electrovalent bonds from carboxyl groups to metals and coordinate covalent bonds from phenolic oxygen atoms to metals will be involved. Under natural conditions where trace metal concentrations exist, reaction (a) via the salicylate linkage, is considered to be more feasible (Gamble and Schnitzer, 1973). Potentiometric titrations of fulvic acids complexed by metallic cations indicated that cations released an otherwise untitratable proton (Khanna and Stevenson, 1962; and Schnitzer and Skinner, 1963). From this, reaction (a) is considered to be the correct description of cation - fulvic acid chelation. However, Manning and Ramamoorthy (1973), on the basis of their experimental data, suggest that bonding via phthalate type group (b) is more likely for the Cu^{2+} - fulvic acid reaction. The concentration of the salicylic acid type, bidentate sites can be calculated according to the data of Gamble (1972) to give an average of about 3 sites per molecular weight.

1.5 Laboratory experimental studies of metal-organic interactions.

(a) Element concentration by organics via sorption processes.

The geochemistry of trace elements in soils and in stream sediments is of great significance in geochemical prospecting. The formation of a geochemical anomaly within soils and sediments is dependent upon the retention of heavy metals by inorganic and/or organic components. Several factors, including pH, redox potential, inorganic mineralogy and humus content, will

affect this retention mechanism.

It has also been observed that a number of base metal sulphide deposits have organic carbon contents considerably above the average for shales and this has prompted several authors to propose "organic" processes as playing a significant, possibly critical role, in the concentration and transport of the ore metals (Krauskopf, 1955; Brongersma-Saunders, 1965; and Roberts, 1973). The primary source of organic carbon, although uncertain, may well be algae (Brongersma-Saunders, 1965; and Roberts, 1973). Ferguson and Bubela (1974) conducted laboratory experiments designed to test this hypothesis. Using aqueous solutions of Cu(II), Pb(II) and Zn(II) interacting with organic matter derived from fresh algae specimens, they were able to show that, under suitable conditions, a significant proportion of the metals is removed from solution by sorption onto the particulate organic matter of the algal suspension. The chemical characteristics of the metal sorption are considered similar in some respects to those of the metal-humic matter reactions. It was concluded that such an organic process could form a sedimentary ore deposit if the metal "saturation" values of the algal materials were reached, but this could only be approached in solutions already enriched in metals.

However, the role of the solid adsorbent phase in forming geochemical anomalies within sedimentary materials is of more relevance to this thesis. More specifically, the influence of sedimentary organic material will be reviewed. This is not directly related to the experiments conducted by the author

where clay minerals are used as the solid ion exchange media. However, it is a valuable exercise in giving the reader an overall insight into the geochemical role of metal - humic matter reactions.

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

Chowdhury and Bose (1970) investigated the reactions and equilibria of suspended soil humic matter with dilute solutions of the heavy metals, Cu, Pb, Zn, Ni and Co, at pH values up to 5. The stability of the metal - particulate organic

species formed increased in the order $\text{Co} < \text{Ni} < \text{Zn} < \text{Cu} < \text{Pb}$ which is consistent with the data of Rashid (1974). At pH less than one, there was an almost complete release of all metals. However, at pH values pertinent to natural conditions, Pb and Cu proved most resistant to leaching from the soil humus. This organic retention mechanism would then favour the formation of geochemical anomalies due to enrichment in Cu and Pb.

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

The kinetics of the ion exchange phenomena involving solid humic matter and metallic cations is poorly understood. Bunzl (1974) studied the ion exchange between solid humic substances and Pb(II) . The uptake of Pb by both humic substances and an ion exchange resin proceeded, as a function of time, according to a characteristic sigmoidal curve. The ion exchange characteristics were found to be consistent with theoretical consideration based on a film diffusion process as the rate determining step.

Another aspect of humic acid sorption phenomena is their capacity to absorb hydrophobic organic compounds. Khan and

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

(b) Mineral dissolution and element solubility as affected by organic acids.

The ability of organic acids to leach and dissolve minerals has been studied by many authors including the very early work of Harrar (1929) and Fetzer (1946). The dispersion of elements as affected by this mechanism has considerable geochemical significance.

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

Soluble humic matter reactions with sulphide minerals are

most relevant to a study of gossan formation and to the dispersion of base metals produced from organic attacks of sulphide ores. Bondarenko (1968) studied the reaction of fulvic acid with galena. Fulvic acid was found to dissolve galena 10 to 60 times more rapidly than water containing no organic matter at the same pH. Baker (1973) found that the humic acid attack on sulphide minerals was quite variable with, for example, chalcopyrite yielding $140 \mu\text{g}$ Cu per day whereas chalcocite released $15,000 \mu\text{g}$ Cu per day. A tentative correlation with bond strength has been suggested from the data as evidenced by the increased reactivity of galena compared with sphalerite. Baker also found that humic acid readily attacked hematite and pyrolusite. This might inhibit gossan formation under appropriate conditions. Base metals were strongly attacked by humic acid solutions; a far weaker but still significant release of Ag and Au was also observed.

The ability of humic compounds to weather silicate minerals is uncertain (Krauskopf, 1967; and Loughnan, 1969). The data of Schalscha et al. (1967), Baker (1973), Kodama and Schnitzer (1973), and Boyle et al. (1974) provide some evidence for increased silicate weathering in the presence of humic compounds. Their effect on silicate minerals, while not as pronounced as the effect on sulphide minerals, is still significant when compared with non-organic, aqueous solutions.

The reactions of soluble organic compounds on carbonate solids have been investigated by Rashid (1972) and Rashid and

Leonard (1973). Quinone groups have been found to be one of the major oxygen - containing functional groups present in humic and fulvic acids. In the metal - organic interaction mechanism, quinone groups may take part in secondary, metal complexing reactions. Rashid (1972) found that several quinone compounds had a dissolution effect on the solid carbonates of Cu, Co, Zn, Ni and Mn. The dissolution order for benzoquinone was $\text{Cu} < \text{Zn} < \text{Mn} < \text{Co} < \text{Ni}$ whereas, for humic acid, Rashid observed that the order was $\text{Mn} < \text{Cu} < \text{Zn} < \text{Ni} < \text{Co}$. Rashid suggests that from 1.5 to 8.5% of the total metal solubilizing capacity of humic acid can be attributed to the quinone type reaction. Rashid and Leonard (1973) again demonstrated that the ability of humic acid in the dissolution of carbonates increases in the order $\text{Mn} < \text{Cu} < \text{Zn} < \text{Ni} < \text{Co}$.

Rashid and Leonard (1973) also studied the dissolution of metallic sulphides by humic acid. The order of metal solubility was found to increase in the order $\text{Ni} < \text{Zn} < \text{Cu} < \text{Co} < \text{Mn}$.

Banat et al. (1974) investigated the effect of organic complexing agents in re-mobilizing pollutant metals sorbed to river sediments. They used nitrilotriacetic acid (NTA), a synthetic complexing agent used in detergents which may find its way into a drainage system. Using polluted river sediments, Cu, Cd, and to a lesser extent Ni exhibited a high percentage mobilization. Pb and Zn were also mobilized by NTA solutions. Cr showed no reaction with NTA.

It can be concluded that soluble humic matter has the potential to act as a strong weathering agent on many mineral

species including sulphides, silicates and carbonates with mineral stability and metal - organic affinity the probable controlling factors. The effect of organic acids on sediment adsorbed metals is of considerable interest to this thesis. Banat et al. (1974) have investigated the interaction model with regard to the ability of soluble organic acid (NTA) to desorb sediment adsorbed metal. It is assumed that, in their system, the metals are adsorbed by both inorganic (clay) and organic mechanisms. They do not have any data on the interaction involving initially dissolved metallic cations, dissolved organic acid and a sediment phase. As a further point, they have not considered in their study the more ubiquitous humic compounds.

The fate of trace elements, once liberated from weathering mineral phases, is further influenced by soluble organic compounds. Baker (1973) observed that many heavy metal humates, formed by the organic weathering processes, displayed low solubility in water with a resultant lowering of the metal mobility. In the presence of a humic acid solution, the metal humates were readily mobilized. The presence of inorganic salts in an aqueous, non-organic solution favoured the precipitation of the humates, probably through colloidal coagulation.

The stabilization of various metallic ions in solution by organic acids has been experimentally investigated by several authors (for example, Ong et al. 1970; Bondarenko, 1972; and Theis and Singer, 1973). In no case was the stability of a soluble metal humate or fulvate in competition with sorption

reactions studied. The influence of carbonate, sulphide and hydroxide ions on the metal - organic stability has been investigated.

Duursma (1970) has studied the effect of soluble amino acids on the sorption of metals by marine and river sediments at pH8. The data showed that the sorption of Co and Zn is reduced by the addition of 10^{-2} to 10^{-3} M leucine with the reduction almost equalling that calculated from known stability constants for metal - leucine complexes. Duursma, in extrapolating to the lower concentrations of a natural system, concluded that such an organic influence on the metal distribution between sediment and water could only be a result of humic matter interactions. This is based on the higher natural concentrations of humic compounds and their greater chelating capacity.

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

Bondarenko (1972) found that Cu fulvates and humates are stable up to 240 days in a freshwater system. Fulvates were found to be more stable at weakly acid pH while the humates were more stable at neutral and weakly alkaline pH. In an

artificial seawater, the presence of divalent cations caused the precipitation of the Cu fulvates and humates. The presence of H_2S in seawater produced a marked decrease in the stability of the Cu complexes.

Rashid and Leonard (1973) studied the precipitation behaviour of various metals by gradually adding Cu, Ni, Mn or Fe divalent cation solution to an inorganic ligand (carbonate, sulphide or hydroxide) both in the presence of humic acid and in its absence. At the point of metal precipitation as the inorganic salt, the metal content was noted. The presence of humic acid strongly inhibited the metal precipitation. In the carbonate and sulphide systems studied at pH 8.5, the effect was particularly pronounced increasing in the order of $Ni < Cu < Mn < Fe$. For hydroxide, a significant but not as pronounced effect was observed with the order now $Cu < Fe < Mn < Ni$. The pH of the hydroxide system was not adjusted with each metal addition and varied from 10.7 to a final value of 3.0. Hydroxide would certainly appear the most effective in causing metal precipitation, in competition with soluble metal humate formation, followed by sulphide and then carbonate. However, at the lower final pH of the hydroxide reactions, H^+ ions can interfere in the precipitation reactions.

The data of Rashid and Leonard (1973) are relevant to the solution phase experiments conducted by the author. The influence of hydroxide and bicarbonate/carbonate anions on the stability of metal fulvates and humates, as observed by the author, will be compared where possible to the data of Rashid and Leonard.

Ong et al. (1970) reported evidence that demonstrates the ability of organic acids (an alkali-soluble fraction of peat) to stabilize in solution Cu(II), Zn(II), Pb(II), Al(III), and Fe(III). Experiments were conducted over the pH range 5 to 9 using solid Na_2CO_3 to adjust pH. For Cu, stability in solution was a function of pH and organic carbon concentration. For 8 ppm organic carbon and initial Cu content 20 ppm, a distinct minimum in stability occurs around pH6. For 40 ppm organic C and the same initial Cu, Cu is strongly retained in solution throughout the pH range. The authors relate the observed minimum to stabilities of the insoluble Cu hydroxide and carbonate. The increase in Cu solubility at pH greater than 6 is not clarified. The other metals were studied by the precipitation method (i.e. addition of metallic cation to the solution until precipitation is observed); the Cu results cannot be related to these metals. The amount of metal needed to produce precipitation was again a function of pH and organic acid content. Zn was the most stable but its stability decreased sharply at alkaline pH. Pb stability increased to pH8 and then decreased slightly. Fe and Al stabilities increased steadily from pH5 to 9. The dependence of metal solubility on pH and organic content is further emphasized in the experimental studies conducted by the author. The correlation with the Cu data presented by Ong et al. is most pronounced.

Organic acids appear to play an important role in stabilizing Fe in solution. The data presented by Rashid and Leonard (1973) imply that the precipitation of Fe inorganically is strongly

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inhibited by humic compounds. However, the possible coprecipitation by Fe(II) and Fe(III) hydroxides of organic matter under reduced conditions will not favour the organic stabilization of Fe in solution (Akiyama, 1973). The complex organic matter obtained by bacterial degradation of green algae was coprecipitated whereas, with simpler pigment and lipid materials, coprecipitation was rarely observed with Fe(III) now being held in solution. It is interesting to speculate on possible humic matter involvement in such a coprecipitation reaction. Of the two organic fractions studied by Akiyama, humic matter is likely to relate more closely with the bacterial degradation products which are indeed prone to coprecipitation.

Theis and Singer (1973) found that the oxidation of Fe(II) is completely inhibited in the presence of tannic acid, gallic acid and pyrogallol. The results are indicative of the formation of thermodynamically stable Fe(II) - organic complex. Conversely, the presence of these compounds in aqueous solution with Fe(III) produced an almost instantaneous reduction to Fe(II) which was subsequently stabilized in solution by the organic complexing agent. Under conditions where ferric hydroxide was forming, the tannic acid had a very much diminished reduction effect. Similar results were observed using natural humic acids. Consequently, organic matter appears capable of stabilizing Fe(II) in well oxygenated environments.

Much interest is presently centred on the mobility and fixation of U. The mobilization of U, along with Mo and V, is most commonly considered inorganically with anionic species being the mobile forms of the three elements (Bloomfield and

Kelso, 1973). U could also be mobile as the uranyl cation, UO_2^{++} . The enrichment of these three elements in organic sediments is quite common with the enrichment being considered due to the organic matter (for example, Brookins and Lee, 1974; Williams and Brown 1971; and Szilagyi, 1971a). The enrichment has been considered to involve reduction by the organic matter of the mobile anionic species to exchangeable cationic forms which can then be retained by the organic matter (Szalay, 1964; and Szalay and Szilagyi, 1967). The ability of humic matter to reduce complex anions and some cations has been experimentally demonstrated (Alberts et al., 1974; Szilagyi, 1971b; Szalay and Szilagyi, 1967; and Szilagyi, 1973). However, Bloomfield and Kelso (1973) conducted experiments which showed that U, Mo and V can be transported and fixed by organic matter as anions; thus a reduction step is not essential to the enrichment. Bloomfield and Kelso do, however, propose that, under the conditions in which Mo enriched sediments are formed, H_2S reduction followed by precipitation/coprecipitation of the sulphides is probably the dominant mechanism.

The evidence would suggest then a mechanism of U and Mo transport as anionic species possibly protected by a humic colloid. Coagulation of the humic colloid or adsorption onto pre-existing organic matter could then take place. Concurrently, reduction of the mobile species by the organic matter would aid the U and Mo immobilization with the produced sulphide strongly fixing the elements to the sedimentary phase.

(c) Stability constants.

Quantitative estimates of the stability and formation constants of several metal fulvates and humates have been frequently reported in the literature. Stability constants are thermodynamic quantities based on activities of the reacting species. In the case of humic and fulvic acid complexation reactions, activities are difficult to estimate. As a consequence, the stability constants reported are, in general, concentration stability constants. As a further point, the reactants are prone to several competing side reactions, such as hydrolysis, which are rarely accounted for in the determination. Hence, the great bulk of the data presented are more correctly termed conditional (i.e. dependent on the experimental conditions) stability constants. Gamble and Schnitzer (1973) provide a working example of thermodynamically derived stability constants which will have the advantage of being applicable under any set of experimental conditions. The order of stability for various metals is the same for thermodynamic and conditional stability constants. Within the natural environment, conditional stability constants are more likely indicative of the humic matter - cation interactions (Cheam and Gamble, 1974; and Malcolm et al., 1970).

A further complication exists when comparing literature stability constants. The calculations of humic and fulvic acid concentrations have been based on either the number average molecular weight (for example, Schnitzer and Hansen, 1970) or on the total complexing sites (for example, Gamble et al., 1970; and

Cheam, 1973). Cheam and Gamble (1974) report an increase in $\log K$ from 3.2 for the complexing sites method to 3.7 for the molecular weight method based on the Cu - fulvic acid reactions.

The experimental procedures employed are varied and include ion exchange (Schnitzer and Hansen, 1970; Malcolm et al., 1970; Schnitzer and Skinner, 1966 and 1967; and Ardakani and Stevenson, 1972), continuous variations (Gamble et al., 1970; and Schnitzer and Hansen, 1970), specific ion electrodes (Cheam and Gamble, 1974; Cheam, 1973; and Manning and Ramamoorthy, 1973), potentiometric titrations and atomic absorption (Khanna and Stevenson, 1962; Khan, 1969; Coleman et al., 1956; van Dijk, 1971b; Rashid, 1971; and Stevenson et al., 1973). The chelates formed in these determinations are generally accepted to be 1:1 type complexes involving the bidentate salicylic acid type site. The calculations for the ion exchange equilibrium technique are dependent on the formation of mononuclear complexes (Clark and Turner, 1969; and Schnitzer and Hansen, 1970).

pH is an important parameter due to its influence on the acid ionization and, at alkaline pH, the possible formation of metal-hydroxy organic complexes (van Dijk, 1971b). Ionic strength is also most significant with $\log K$ generally decreasing linearly with increasing ionic strength (Schnitzer and Hansen, 1970; and figure 1.5). Decreasing ionic strength causes the fulvic acid to cation ratio to fall below 1 and hence mixed or polynuclear (with respect to cation) complexes may form.

Figure 1.5 Effect of ionic strength on log K values of metal-fulvic acid complexes at pH3 (Schnitzer and Khan, 1972).

Irving and Williams (1948) published a stability order for complexes of bivalent metal ions which applied regardless of the complexing agent involved. The order of stability would be $\text{Pd} > \text{Cu} > \text{Ni} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}$. Some of the reported data does follow this predicted stability order (Beckwith, 1959; Khanna and Stevenson, 1962; and Khan, 1969). However the bulk of the data would suggest that this stability order is not generally applicable to the humic and fulvic acid - metallic cation reactions.

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

Table 1.1 reports some of the available stability constant data for metallic cation - humic acid complexing.

Table 1.1: Stability constant data for humic acid - metallic cation complexing.

<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 (1965b)
5.6	Zn(II)	6.18	" " "
7.0	Zn(II)	6.80	" " "

The reported data shows reasonable agreement, with the data of Bandhawa and Broadbent (1965b) being somewhat higher. van Dijk (1971b) concluded, on the basis of his experiments, that variation between stability constants using humic acids from different sources is slight.

Schnitzer and Hansen (1970) reported stability constant data for fulvic acid - metallic cations experimentally determined by both an ion exchange and a continuous variation method. The determinations were carried out at an ionic strength of 0.1; hence all the organo-metallic species will be mononuclear with respect to the metal. Their data are in good agreement with the literature. Although little variation was seen for the two methods (table 1.2), the authors favoured continuous variation procedures because of the lower susceptibility to analytical errors.

Table 1.2: Stability constant data for metallic cation - fulvic acid complexes from Schnitzer and Hansen (1970).

<u>Metal</u>	<u>pH 3.0</u>		<u>log K</u>	<u>pH 5.0</u>	
	CV	IE		CV	IE
Cu(II)	3.3	3.3		4.0	4.0
Ni(II)	3.1	3.2		4.2	4.2
Co(II)	2.9	2.8		4.2	4.1
Pb(II)	2.6	2.7		4.1	4.0
Ca(II)	2.6	2.7		3.4	3.3
Zn(II)	2.4	2.2		3.7	3.6
Mn(II)	2.1	2.2		3.7	3.7
Mg(II)	1.9	1.9		2.2	2.1
Fe(III)	6.1*				
Al(III)	3.7**	3.7*			

notes: CV continuous variation, IE ion exchange,

* determined at pH 1.70, ** determined at pH 2.35)

Cheam and Gamble (1974) have reported conditional stability constants for Hg(II) , Cd(II) and Cu(II) fulvic acid complexes in 0.1M NaNO_3 solutions. The log K values reported are 4.86 and 5.08 at pH 3 and 4 for Hg; 3.04 and 3.64 at pH 4.9 and 5.95 for Cd; and 3.22, 3.72 and 4.35 at pH 3, 4 and 5 for Cu.

At low pH, the stability order then is $\text{Fe(III)} > \text{Hg(II)} > \text{Al(III)} > \text{Cu(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Pb(II)} = \text{Ca(II)} > \text{Zn(II)} > \text{Mn(II)} > \text{Mg(II)}$. At pH 5, the order is $\text{Ni(II)} = \text{Co(II)} > \text{Pb(II)} > \text{Cu(II)} > \text{Zn(II)} = \text{Mn(II)} > \text{Ca(II)} > \text{Cd(II)} > \text{Mg(II)}$.

Manning and Ramamoorthy (1973) studied the formation and stabilities of mixed ligand complexes of the type Cu(II) - fulvate - secondary ligand. The secondary ligands investigated were citrate, meso-tartrate, dl - tartrate, salicylate, phosphate, NTA, aspartate and glycine. For the Cu^{++} - fulvate system, the stability constants obtained were in good agreement with the data of Schnitzer and Hansen (1970). It was found that in neutral and weakly acidic solutions, mixed complexes predominate. The citrate, phosphate and NTA mixed complexes were particularly stable in comparison with the simple complex. The authors speculate on the possible significance of other oxyanions, SO_4^{--} and HCO_3^- , in similar mixed ligand complex systems. The formation of mixed complexes can apparently inhibit precipitation of metallic cations as phosphates, possibly sulphates and carbonates, and as hydrolysed species.

The complexity of natural systems, such as a drainage system or a soil, causes one to view the stability constants quoted in the literature carefully. Perrin (1965)

points out that⁶ in any system, the major complexes that are formed, and their concentration, will be determined by the stability constants of all possible complexes, the pH of the solution, the pK_a value of the complexing species and the total concentrations of each metal and each complexing species. The mixed ligand systems studied by Manning and Ramamoorthy (1973) represent a simple example of this effect with a predominance of mixed ligand systems predicted. To handle complex systems, Perrin (1965) describes a computer programme which will calculate equilibrium concentrations of both free and complexed metals and ligands. The application of such a programme to a geochemical field problem suffers due to a lack of many of the required parameters.

Data presented by Gardner (1974) emphasize the effects of sulphur species on the metal complexing in natural waters. The author developed a model to deal with trace metal solubility in H_2S - rich marine waters involving many inorganic and organic ligands (amino acids and hydrocarboxylic acids). The results indicated that bisulphide and polysulphide complexes, and not the organics, are the important ligands for trace metal solubility under these conditions. The author suggested that the effect, if any, of dissolved organic matter in trace metal solubility under these conditions would be due to humic and fulvic acids. The influence of metal sulphide and organic complex formation on Cu and Zn accumulation in organic lake sediments is discussed by Timperley and Allan (1974).

1.6 Field Observations.

(a) Metal and organic speciation.

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

The vast majority of reported humic and fulvic acid chemical characterizations have been for soil extracted material. Christman (1970; Beck et al., (1974); and Shapiro (1964) have spectroscopically characterized the organic matter observed in some natural waters as being fulvic acid type compounds due to their complex, polymeric nature and an abundance of phenolic and benzenecarboxylic groups. Nissenbaum et al., (1971) observed that polymerized organic matter (possibly humic substances) accounted for about half of the total dissolved organic matter in interstitial waters of the reducing Saanich Inlet (British Columbia) sediments. The main constituents of river water organic matter are generally considered to be humic substances

(Lamar, 1968). Simpler organic compounds, for example amino acids, carbohydrates and sterols (Prashnowsky et al., 1971), are commonly detected within natural waters but their potential metal chelation capacity is well below that of the humic substances. The available evidence indicates that aquatic humic substances are essentially identical to the humic substances of soils, particularly podzols (Christman, 1970; Stevenson and Goh, 1971; and Bordovskiy, 1965). Sedimentary humic matter tends to be more highly aliphatic, less condensed, poorer in phenolic groups but richer in carbonyl and carboxyl groups than soil humic matter (Nissenbaum and Kaplan, 1972; Otsuki and Hanya, 1967; Ishiwatari, 1966; Bordovskiy, 1965; Rashid and King, 1970).

As pointed out by Stumm and Morgan (1970), the formation of metal-organic complexes within natural waters is frequently postulated to account for the occurrence of trace metals at concentrations higher than those expected from known solubility products. On a molar basis, the concentration of potential organic metal complexing agents is significantly higher than the concentrations of such metals as Cu, Zn, Pb, Ni, Cd and Co. However, the effect of the usually more abundant inorganic ligands such as SO_4^{--} , Cl^- , OH^- , CO_3^{--} must also be taken into account when discussing metal speciation within natural waters. Morel et al., (1973) have developed computer programmes aimed at speciation of metal ions and ligands, inorganic and organic, in natural waters. In inorganic systems, the general pattern found was free metal

ions at low pH with carbonates, oxides, hydroxides and silicate becoming predominant in this order with increasing pH. For a reducing environment, insoluble sulphides dominate. Computation of the inorganic system in the presence of citrate, nitrilotriacetate, cysteine and glycine led to the conclusion that organic ligands can play a major role in natural waters by forming soluble metal complexes but, due to the numerous uncertainties involved, little else could be said.

Lerman and Childs (1973) considered the effects of nitrilotriacetate (NTA) and citrate on the distribution of ionic species in a model fresh water. These two organic ligands are considered significant as they are feasible substitutes for phosphates in detergents. Chloride ion and potassium do not form strong complexes with other anions and cations in natural waters and were left out in the computations. The computations, based on thermodynamic equilibria, showed that NTA and citrate complex virtually all available Cu, Fe, Pb, Ni, Co and Zn. Once these elements are complexed, excess NTA and citrate may then complex Ca and, to a lesser extent, Mg. The authors concluded that any complexing agent, including humic and fulvic acids, with strong affinities for metal ions will have a similar effect. The presence of solid mineral phases was also considered. Provided the conditions of elemental input to, and removal from the water system are such that a steady - state can exist, it was concluded that chemical exchange between a solution and a solid sediment phase will slow down the rate of approach to a steady-state without affecting the steady-state concentration.

From the theoretical consideration outlined in the preceding two paragraphs it is possible to conclude that organic complexing in natural waters is feasible. Literature evidence for the direct identification of such complexes is, however, unavailable due to the lack of precise analytical and spectroscopic procedures. Nissenbaum et al. (1971) have suggested the occurrence of metal-organic complexes in interstitial waters based on the observation of large concentrations of Fe, Zn, Co, Ni, Pb and Ag associated with the soluble organic matter. Barsdate (1970) and Shapiro (1964) also reported evidence which, indirectly, suggests that various metals in lake water are to a large extent bound to humic substances. The association between Fe and humic matter in natural waters has been discussed by several authors (Shapiro, 1964; Akiyama, 1971; Christman and Minear, 1971; Plumb and Lee, 1973; and Lamar, 1968). The iron may be in the form of peptized ferric hydroxide sols as well as organically chelated ions. Curtin et al. (1970) have tentatively suggested the presence of gold as soluble organic complexes within a forest humus layer. Stiff (1971), in analyses of polluted surface freshwaters including river water concluded that soluble Cu would consist almost entirely of complexed species. Humic matter complex species were identified as hexanol extractable Cu; chromatographic procedures separated amino acid and polypeptide Cu complexes. Carbonate and cyanide complexes were also indicated. Carbonate and amino acid-polypeptide complexes were most abundant.

Many cases have been reported in the literature of

metal enrichment within sedimentary materials directly related to organic complexation. Fraser (1961a) described a syngenetic copper deposit at Sackville, New Brunswick, located in a swampy terrain. In a later paper, Fraser (1961b) suggested that a Cu-organic sequestering mechanism produced the observed Cu enrichment of the swamp. Szilagyi (1971a) analysed for Mo, Cr and V in many Hungarian coals and showed that the enrichment of these elements was related to the organic carbon. Szalay and Szilagyi (1968) discuss the accumulation of several elements, particularly U, in peats and have concluded that the peat humic matter is directly involved.

(b) Geochemical dispersion studies:

Field studies on the effect of dissolved organic matter in trace element dispersion processes are not commonly encountered. de Groot (1971) and de Groot et al. (1971) have published the most pertinent data. A study was undertaken on the behaviour of various elements in the Rhine River and Ems River (Western Europe), particularly in the deltas prior to their entrance into the Wadden Sea. The Rhine River has been subject to industrial pollution and, as a consequence, the reported Hg, Zn, Cr, Pb, Cu and As levels of the sediments were high. But, in both rivers, starting at the freshwater tidal area and downstream from there, a mobilization of these elements from the sediments was observed. This was apparent when compared with sediment metal contents upstream from this tidal area. The change in chemical conditions at this point produced intensive decomposition of the organic material related to the

sediments. From this, deGroot strongly suggests that the formation of soluble metal-organic complexes is mobilizing the pollutant metals from the sediments. For the Rhine River, it produced the striking result that the highly polluted sediments from the upper reaches of the estuary were reduced to normal levels in the lower courses. A definite order in the degree of mobilization was observed. Hg was the highest with a maximum of 90% mobilization from the sediment being attained. There was then a moderate decrease in the order $\text{Cu} > \text{Zn} > \text{Pb} > \text{Cr} > \text{As}$ which reached a maximum of 75% mobilization. Co came next with 60% maximum mobilization followed by Fe with 45%. Sm, Sc, La and Mn showed no mobilization. The authors considered that this order should reflect the stability constants of the metal-organic complexes formed. Comparison with the data of Schnitzer and Hansen (1970), as presented in table 1.2 for metal fulvate stabilities shows that such a relationship is not apparent. Considering the complexity of the natural system in relation to the conditions employed for the stability constant determinations, this is not surprising. As the authors point out, certainly the mobilization of Hg is likely to be affected by the formation of soluble chloride as well as organic complexes.

Bugelskii (1965) and Bugelskii and Tsimlyanskaya (1966) present data on the behaviour of Ni during the weathering of a serpentinite massif in the Central Urals. The presence of humic substances in the natural surface waters greatly facilitated the dissolution of Ni and its subsequent migration as an assumed Ni-organic complex. In response to hydrogeological, physico-

chemical and biochemical conditions, the organic matter may be altered and coprecipitated from aqueous solution with Ni. Depending on the nature of the organic matter to which Ni is bound, the authors concluded that the Ni-organic compounds, during migration, can be either further dispersed or accumulated.

Beck et al., (1974) produced a wealth of data on organic and inorganic geochemistry of some coastal plain rivers of the southeastern United States. A predominance of acidic organic matter over inorganic constituents, including anionic species, was observed; this is certainly not the normal situation. Fe, Al and pH were directly related to the total dissolved organic matter; Na, K, Mg, Ca and Mn were not obviously complexed by the organic matter. Unfortunately, base metal analyses were not reported.

The hydrogeochemistry of any drainage basin is subject to several interacting parameters. The roles of dissolved and sediment organic carbon are two such parameters. Other at least equally important parameters include bedrock geology (Reeder et al., 1972; and Schwartz, 1974), hydrodynamic and biological factors (Andelman, 1973), inorganic sorption processes (Jenne, 1968; Loganathan and Burau, 1973; and Chao and Anderson, 1974), and mechanisms of trace metal transport in river including transport via suspended particulate matter (Gibbs, 1973; Perhac, 1972; Perhac and Whelan, 1972; and German and Knight, 1973). In the light of such complexity, it is not surprising that attempts to explain the field relationships between trace metals and organic carbon are usually tentative.

1.7 Summary.

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

From laboratory evidence, metal-humic matter interactions are potentially important in the following geochemical processes: (a) leaching of metals from solid mineral phases and soil horizons, (b) dispersion along drainage systems as soluble metal-organic species, and (c) concentration and fixation of many elements within organic rich sediments.

The existence of metal-organic complexes within natural waters and sediments is very strongly implied from field observations. However, the interfering effects of various inorganic and hydrodynamic processes will seriously mask the metal-organic matter system in a field study.

The data reviewed and its potential significance do justify continued research into the metal-organic-sediment interactions. However, the author obviously considers that the direction of this research should move towards more direct consideration of the influence of dissolved organic matter on the metal sediment-water distribution by investigating heterogeneous systems involving soluble organic acids and metallic cations in reaction with a solid adsorbent phase.

Chapter 2 - Experimental Procedures.

Part A - Laboratory Model Experiments.

2.1 Introduction.

In designing experiments which hope to model a natural process, in this case, the effect of organic acids on the geochemical dispersion of trace elements, a detailed insight into the natural system and its interacting components is an invaluable asset. Geological processes rarely offer such insight. From the literature review, it is apparent that humic and fulvic acid complexing will be the dominant organic mechanism affecting trace element dispersion. Hence, humic and fulvic acids were used in these experiments.

Ion exchange reactions or sorption, along with hydrolysis, are the most obvious inorganic reactions to consider. But the choice of an adsorbent solid phase is not easy. Sediment organic content and clay mineralogy will be actively involved in sorption reactions. Local occurrences of Fe and Mn oxides and hydroxides will strongly influence the ion exchange capacity of a sediment. Two clay minerals, kaolinite and montmorillonite, were chosen although it is accepted that the ion exchange capacity of a sediment is dependent upon many factors. Kaolinite was selected because of its wide distribution as evidenced by the clay mineralogy of the sediments collected as part of this thesis. Montmorillonite was selected because of its greater cation exchange capacity.

In many field situations, streams drain through large

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areas of carbonate rocks thus increasing the carbonate content of the waters. This was encountered in the field programme presented in this thesis. The influence of carbonate and bicarbonate ions in solution on the metal-organic-clay reactions has not been studied previously. Experiments were designed to investigate this problem.

The effect of organic acids on leaching clay bound metals and metal hydroxide precipitates must also be considered in an overall view of this geochemical process. Desorption experiments were set up to consider this.

2.2. Isolation and characterization of humic and fulvic acids.

In order to conduct laboratory model experiments, it was necessary to extract and characterize humic (H) and fulvic acid (F) fractions from natural materials. Shoreline humic sediments were collected from Lake Fortune in the Gatineau Hills area, Quebec, a few miles north of Ottawa. It was thought that these humic substances might better represent stream water humic matters than a soil extract. The mud samples were collected in polyethylene bags and refrigerated immediately on return to the laboratory. The mud was then air dried in a fume hood and crushed lightly by mortar and pestle to greater than 100 mesh. Obvious vegetation contained in the samples was removed in the sieving procedure. The crushed and dried mud was stored in plastic vials prior to extraction.

Various procedures for extraction and isolation of humic and fulvic acid fractions from humic materials have been proposed in the literature. In choosing a procedure, three main

points were considered, (i) isolation of unaltered material, (ii) completeness to ensure representation of fractions of the whole molecular weight range and (iii) extraction of humic substances free from contaminants. The most commonly used extraction reagents include NaOH, $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$. The merits of the various methods are reviewed by Smith and Lorimer (1964), Posner (1966), Theng et al. (1967), Schnitzer and Skinner (1968) and Yefimov and Vasil'kova (1970). The humic and fulvic acid fractions obtained by these various procedures show little variation in the characteristic humic properties. However, a procedure employing sodium pyrophosphate was decided upon as the more alkaline reagents result in a high yield of fulvic acids and a subsequent decrease of the humic: fulvic acid ratio (Yefimov and Vasil'kova, 1970).

10 gms. of the crushed and dried mud were placed in a screw cap glass jar. 500 mls. of 0.1M $\text{Na}_4\text{P}_2\text{O}_7$ were added, the jar sealed and the mixture was manually shaken at intervals over a 12 hour period. The supernatant extract was separated by centrifuge. A fresh 500 mls. of 0.1M $\text{Na}_4\text{P}_2\text{O}_7$ were added to the solid residue and the process repeated. A third extraction was then carried out. The 1500 mls. of total extract were acidified to pH2 with concentrated HCl thus separating the acid insoluble humic acid fraction from the soluble fulvic acid fraction. The acidified extract was allowed to sit overnight under refrigeration. The humic acid fraction was separated by centrifuge. The fulvic acid extract was allowed to air dry in the fume hood. The humic and fulvic fractions were washed with distilled water

twice, taken into solution and passed through cation exchange resin, Rexyn 101H, supplied by Fisher Scientific Company. The humic and fulvic acid eluates were allowed to air dry in a fume hood and then stored as a dried, crushed solid in screw capped, glass vials.

The isolated solids were subjected to a C analysis, acid-base titrations and an infra-red analysis. The C content was determined by the combustion-gravimetric procedure described in section 2.6. The black humic acid contained 49.5%C whereas the light yellow fulvic acid contained 40.5%C.

Infra-red spectra were recorded on a Beckman IR 33 Spectrophotometer. The organic acid was first crushed to a fine power; 1 to 2 mgs. were mixed with 200 mgs. of KBr and pressed into a disc. The IR spectra obtained are reported in figure 2.1. Comparison with IR spectra reported in the literature (Theng et al., 1967; Ishiwatari, 1973; Stevenson and Goh, 1971; Wagner and Stevenson, 1965; and Schnitzer, 1965) showed no significant differences to the spectra obtained. Assignments of the main absorption bands are based on these references.

<u>Absorption band (cm^{-1})</u>	<u>Interpretation.</u>
3400	Hydrogen-bonded OH groups
2900	aliphatic C-H stretch
1720	C=O of COOH and ketonic carbonyl
1630	aromatic C=C, hydrogen-bonded C=O of carbonyl, double bond conjugated with carbonyl.
1400 (diffuse)	probably OH deformation and C-O stretching of phenolic OH or C-H

Figure 2.1 Infrared spectra of humic and fulvic acids
isolated from Lake Forture (Quebec) shoreline mud.

	deformation of CH_2 and CH_3 groups.
1700 (diffuse)	C-O stretching and OH deformation of COOH groups.

The majority of fulvic acid IR spectra reported have a more intense band at 1720 cm^{-1} than does humic acid with this being directly related to the higher number of COOH groups in fulvic acid. This is not the case for the Lake Fortune organic acids. The aliphatic C-H stretching absorption at 2900 cm^{-1} is more pronounced for the Lake Fortune fulvic acid than for the majority of spectra from the literature. It is concluded that the fulvic acid isolated from Lake Fortune humic mud contains more aliphatic groups but less carboxyl groups than the "average" fulvic acid described in the literature.

The potentiometric (pH) titrations are shown in figure 2.2. They were carried out with 100 ml. aliquots of 0.1% (by weight) humic and fulvic acid solutions being titrated with 0.1M KOH. The pH was measured by a Beckman Zeromatic pH meter equipped with a combination glass electrode.

The titration curves for both acids indicate the probable existence of 2 equivalence points related to the presence of two general types of carboxyl groups within the humic and fulvic acid molecules (Schnitzer and Khan, 1972). However, experimental error does cast doubt on the validity of the proposed first equivalence point. pH measurement is only accurate to ± 0.1 units. The second equivalence point, representing total COOH groups present, is more reliable. From the observed second equivalence points, calculations would indicate approximately 6.7

Figure 2.2 pH titrations for humic and fulvic acids
isolated from Lake Fortune (Quebec) shoreline mud.

milliequivalents of COOH per g. of fulvic acid and 3.4 milliequivalents of COOH per g. of humic acid.

2.3 Preparation of reagents.

(a) Organic acid solutions.

The organic acid solutions were prepared on the basis of the percentage weight of solid acid to volume of solvent. Fulvic acid, being soluble at both acidic and alkaline pH, was dissolved in distilled, deionized water. Humic acid was dissolved in distilled, deionized water which had been made mildly alkaline, pH 8 to 9, with the addition of several drops of 0.1M NaOH. Salicylic acid solutions were prepared by dissolution in warm, distilled, deionized water. The salicylic acid used was a "Baker Analyzed" reagent supplied by the J.T. Baker Chemical Company. Solutions contained no detectable metal

(b) Metal solutions.

All metal solutions were prepared by the dilution of atomic absorption standard reference solutions supplied by Fisher Scientific Company. The reference solutions used were all initially 1,000 ppm divalent element prepared as nitrate solutions. Cu, Pb, Zn and Ni solutions were employed.

(c) Carbonate/bicarbonate solutions.

A carbonate/bicarbonate solution of pH9 was obtained by preparing a solution of 0.30M NaHCO_3 (25.200g/litre) and 0.014 M Na_2CO_3 (1.484 g/litre). Another solution was prepared by a 1:10 dilution of the above.

(d) Solid adsorbent.

For a sedimentary or solid adsorbent phase in the experiments, two materials, Flint clay and bentonite, were used. The bentonite was supplied by Fisher Scientific Company. X-Ray diffraction showed it to be a montmorillonite clay. The Flint clay was supplied by the National Bureau of Standards, Washington. It was identified by X-Ray diffraction as kaolinite, both ordered and disordered. Prior to use, the Flint clay was crushed lightly by mortar and pestle in order to obtain a homogeneous mixture. The cation exchange capacities, determined according to the procedure described in section 2.6, of the bentonite and Flint clay were found to be 78.20 ± 1.60 and 7.84 ± 0.24 m.e./100g. respectively.

2.4 Design of experiments.

The basic requirement of the experimental system was to enable cation solutions, in the presence and absence of organic acids, to interact effectively with a solid phase. To achieve this, both time and a form of mechanical shaking were considered important. The procedures adopted are described below according to the system being investigated.

(a) Unbuffered, low ionic strength systems.

The systems referred to as unbuffered imply that no pH buffering reagent has been added. Each individual system of cation (s), organic acid and sediment was investigated in four reaction sequences:

- (i) cation solution alone - hydrolysis,
- (ii) reaction of cation (s) and organic acid - hydrolysis and organic complexing,

- (iii) reaction of cation (s), organic acid and sediment - hydrolysis, organic complexing and sorption, and
- (iv) reaction of cation (s) and sediment - hydrolysis and sorption.

For all four reactions, five pH values were initially set between 4 and 9. All reactions were carried out in 4 dram plastic vials with snap caps.

For each system, stock solutions of the cation mixture and of the organic acid involved were prepared. The four reactions were then set up as follows:

- (i) by pipette, 5 ml. of cation stock solution were mixed with 5 ml. of distilled, deionized water. The pH was adjusted by dropwise addition of 0.1M and/or 0.01M NaOH or HCl solutions.
- (ii) As above, except that the 5 ml. of cation stock solution were mixed with 5 ml. of the organic acid solution.
- (iii) the cation and organic acid solutions were mixed as in (ii) followed by the addition of a known weight of sediment material. pH was adjusted as before.
- (iv) The cation mixture was prepared as in (i) followed by addition of a known weight of sediment phase. pH was then adjusted.

The four reactions as outlined may be abbreviated in future discussion. The following example will indicate the terminology used for the reactions (i) to (iv):

- (i) M (M-metal)
- (ii) M + F (F = fulvic acid)

(iii) M + H + K (K = Flint clay, H = humic acid)

(iv) M + B (B = bentonite).

All symbols employed will be further defined in chapter 3.

The mixtures were then allowed to equilibrate with gentle shaking over a period of thirty days. The data shown in Appendix 1, using initially 25 ppm each of Cu, Pb, Zn and Ni, imply equilibration well within the 30 day time limit. At the end of this time, and after final pH had been measured, the reaction vials were allowed to stand until the supernatant solution was visibly clear. Occasionally, centrifuging at 200 r.p.m. was necessary to achieve this. The total metal content of the supernatant solution was then determined by atomic absorption using a Jarrell-Ash atomic absorption unit.

The precision of the AA analysis suffered most at low ppm values. An error of ± 1 ppm for the Cu, Pb, Zn and Ni analyses was estimated from numerous duplicate analyses.

The ionic strength of these solutions was always low and is determined partly by the sodium and chloride ions added during the pH adjustment step. The cation solution, 25 ppm M, will have no measurable effect as, under the experimental conditions, little free metallic cations will exist. The ionic strength attributed to the sodium and chloride ions is 0.002 ± 0.001 , based on the observed volumes of acid and base necessary in adjusting pH. A calculation is required for the humic and fulvic acids. Assuming an average molecular weight of 1,000 for these acids, then a 0.5% (w/v) solution is $5 \times 10^{-3} M$. If it is assumed that the ionized and complexed

organic acids contain a single negative charge, then the ionic strength of the solution, 0.5% organic acid plus the cation solution, is 0.0045 ± 0.001 . For a 0.2% organic acid solution, the overall ionic strength would be 0.003 ± 0.001 . These calculations will be further complicated by the metal-organic chelation reaction and sorption of organic species onto clay surfaces. Nevertheless, a good estimate of the ionic strength of the solutions involved here would be 0.002 to 0.005. Low ionic strength solutions were desired because of the correlation with the low ionic strengths encountered in natural waters.

(b) Carbonate systems:

The effect of bicarbonate/carbonate anions on the metal-organic acid - clay system was investigated by setting up reactions analogous to the four discussed above but now including the bicarbonate/carbonate solutions. To do this, it was necessary to first adjust the pH of the cation alone (M) and cation plus organic (M+Org) reaction aliquots to about 9 prior to addition of the carbonate/bicarbonate solution. To achieve this, three equal volumes of cation stock solution, organic acid stock solution (or distilled water) and carbonate stock solution were mixed. The initial pHs of the reactions were set at about 7.60, 8.10 and 8.50 by dropwise addition of HCl or NaOH. This will alter the initial carbonate/bicarbonate ratios of the two stock solutions by the loss of carbonate anion due to its reaction with acid. After the setting up of these

reactions, the procedures regarding time of interaction and subsequent analyses are identical with those described for unbuffered systems.

The ionic strength of these reaction solutions will be determined by the bicarbonate/carbonate system and, in particular, the bicarbonate anion. For the system containing a large excess of bicarbonate anions (i.e. the carbonate/bicarbonate solution initially 0.30M in NaHCO_3 and 0.014M in Na_2CO_3) the ionic strength for the reaction solutions is approximately 0.1, bearing in mind that the carbonate ion will be considerably less than 0.014M under conditions now established. For the reaction system employing the ten fold diluted carbonate/bicarbonate solution, the ionic strength is estimated to be 0.01

(c) Desorption systems.

The ability of humic and fulvic acids to desorb both adsorbed metals and hydroxide precipitates was studied in the laboratory. This study was carried out using the following procedure:

- (i) Set up cation and clay suspension at $\text{pH}_1 5.5$ and $\text{pH}_1 8.5$.
Allow these suspensions to equilibrate over a period of 14 days which, as indicated in Appendix 1, is more than adequate.
- (ii) To evaluate the effect of pH on desorption, take 5 cation-clay suspensions of each pH_1 and adjust pH (using the NaOH and HCl solutions) to five values over the pH 4 to 9 range.
- (iii) To evaluate the effect of humic and fulvic acids on the

desorption, take 5 cation-clay suspensions of each pH₁, add appropriate aliquots of the organic acid and adjust pH to 5 values over pH₄ to 9 range.

At the end of a 30 day equilibration period, analyses of the supernatant solution were carried out as previously described. Analyses were carried out at longer time intervals to test that desorption process was indeed in an equilibrated state.

Desorption studies on the carbonate/bicarbonate systems were also conducted. A similar procedure was followed. However, it was now necessary to add the organic acid to the equilibrated cation-clay suspensions and adjust pH to about 8.5 to 9. The appropriate carbonate/bicarbonate solution aliquot was then added to three reaction suspensions and the pH adjusted to three values in the 7.5 to 8.5 range.

The ionic strength calculations for these desorption study solutions will be identical to their analogues in the previously discussed unbuffered and carbonate/bicarbonate "adsorption" study solutions.

Part B - Field Procedures.

2.5 Sampling techniques.

It was hoped that the materials collected in the field would truly reflect an equilibrated water-sediment system thus facilitating the investigation of an element's distribution ratio (sediment to water) and the dependence of this on dissolved organic carbon and sorption capacity of a sediment. In an attempt to attain this, stream flow and type of sediment were considered the important criteria to establish. Firstly, sampling stations were selected only where stream flow, as

judged by visual observation, was apparently negligible. Secondly, the sediment phase was defined to be only the fine surficial material down to a depth of approximately one inch.

It should be noted that, for a stream environment, the equilibration between water and suspended load would appear the most desirable one to investigate. 0.45 μ Millipore filters were used in an attempt to filter out the suspended load. However, it was quickly realized that the streams in question had a very low suspended load content. As a consequence, several hours were required to collect the minimal requirement of 100 mg. suspended load. Two possible solutions to this problem - the use of a portable pump for filtration or the collection of 30-40 litres of water plus suspended load for filtration in the laboratory - were considered. The first possibility was ruled out due to the unavailability of a suitable pump. Several problems, both chemical and practical in nature, arise with large volume collection. The most severe problem is the possible change in the water - suspended particle equilibration during storage of this large volume. For these reasons, a suspended load was not collected.

The following procedure was then adopted at each sampling station: (i) Measure water pH using a Corning Model 610A portable pH meter equipped with a Corning combination glass electrode, (ii) collect 1 litre of water with 10 ml. of concentrated Baker Analysed HNO_3 added, (nitric acid addition can add up to a maximum of 0.5 ppb heavy metal) in a

brown plastic bottle, and (iii) fill one 15 in. x 6 in. polyethylene bag with surficial sediment, seal this as air tight as possible and then seal the sample in a second polyethylene bag. Factors such as stream width and depth, vegetation, water colour and temperature were recorded as a matter of routine.

2.6 Stream sediment.

(a) Preparation.

The stream sediments were air dried in the laboratory. This was followed by light crushing with a mortar and pestle thus breaking up any lumps developed during the initial drying. Air drying was then completed. If necessary, light crushing was again employed. Cloth sieves were used to size the sediment to 100 mesh. The dry, 100 mesh fraction was stored for analysis.

(b) Element analyses.

All element analyses reported, with the exception of C, were carried out by Barringer Research Limited, Toronto. Contents of both total and adsorbed element were considered essential. Hence analyses for Cu, Pb, Zn, Ni, Fe, Mn, Mg, Ca, Na and K were conducted via two extraction procedures. The total element was determined by HF/HClO₄ treatment whereas the adsorbed element was given by warm IN HCl leaching.

(c) Organic C analysis.

The combustion-gravimetric procedure described below was adapted from Maxwell (1968, p.230). A Lindberg Hevi-duty

combustion furnace with a porcelain combustion tube was used. The volatile gases emitted from the combustion were led into a Burrell Carbotrane fitted with a CO_2 absorption vessel and vessels for the removal of sulphur oxides and water vapour. Pumice, saturated with CuSO_4 , was inserted to remove any acidic gases emitted during combustion. Suction from a water pump was used to draw air, purified via a lime tower, through the system.

Procedure:

- (i) Weigh a sample of suitable size such that not less than 10mg. of CO_2 will be produced during the combustion (0.10g. for humic sediments, 0.60g. for sandy sediments).
- (ii) Place sample on a watch glass and mix with 2 to 3 mls. of 10% HCl thus destroying carbonate. Once reaction has ceased, allow to air dry in a fume hood.
- (iii) Add 0.5g. of reagent grade V_2O_5 and mix well.
- (iv) Spread the mixture on the bottom of a clean ceramic combustion boat (boats are ignited in a furnace at 800°C for several hours and then stored in a sealed glass jar).
- (v) Insert the weighed CO_2 absorption vessel into the carbotrane.
- (vi) Insert the boat into the central portion of the combustion tube and open the system to suction at a rate of about 2 bubbles per second as measured by a bubble trap.
- (vii) Continue the heating at $1,000^\circ\text{C}$ for 30 minutes.
- (viii) Close off the suction, disconnect the absorption vessel and allow it to equilibrate in the balance room for 10 minutes before weighing.

- (ix) Insert glass connector in place of absorption vessel and flush for 10 minutes before making another determination.

From the weighed uptake of CO_2 , it is now possible to determine percentage, by weight, of C in the sample. Background levels were determined by one blank run performed daily. Uptake of CO_2 in blank determinations never exceeded 2 mg. The accuracy and precision of the determination were checked by frequently analysing salicylic acid for organic C according to the procedure. The precision was estimated to be 5% with an accuracy of better than 8%.

(d) X-Ray diffraction.

The determination of detrital mineral phases present in the stream sediments was adapted from the experimental procedures of Carrol (1970). Carrol's work was designed specifically for clay mineral identification and thus involved a preliminary clay particle concentration step. This would lead to a reduction in and possible loss of other residual minerals in the sediment. The preliminary concentration step was therefore omitted. This worked to the detriment of clay mineral identification but an overall view of the residual minerals present was obtained. Even if no clay minerals are reported for a sediment, it is still possible that a preliminary concentration step might reveal the presence of clay mineral (s), but evidently in low concentration.

The dried and sieved stream sediment required further crushing with an agate mortar and pestle.. A small amount of

the powder obtained was placed on a glass slide and slurried in water. The solid was allowed to settle out and the suspension air dried. The powder X-Ray pattern was run from 10° to 60° . The pattern between 3° and 10° was recorded with the inclusion of a monochromator. The sample slide was then placed in a dessicator with sufficient ethylene glycol in its base so that heating in an oven at $70-80^{\circ}\text{C}$ for 5 or more hours lead to glycolation of any expanding clays, in particular, montmorillonite. The X-ray pattern was run again from 3° to 10° for the glycolated sample. All X-ray patterns were recorded on a Siemens diffractometer using Cu K_{α} radiation.

The identification of the detrital minerals was facilitated by reference to the compilation of Chao (1969). The identification of kaolinite and chlorite proved difficult. Kaolinite has its basal d spacing at $7.15\text{\AA}$ whereas, for chlorite, it will be $14\text{\AA}$. In the integral series of basal spacings for chlorite, chlorite will often display a peak corresponding to $7\text{\AA}$. This peak is easily confused with the kaolinite basal spacing peak. Carroll (1970) indicates that heating at $550-560^{\circ}\text{C}$ for one hour destroys the crystal structure of kaolinite and hence the $7.15\text{\AA}$ peak. However, as shown by Ross and Kodama (1974) and confirmed in this laboratory, the $7\text{\AA}$ chlorite peak is also destroyed by heating. Apart from the peaks discussed, and the occasional identification of a chlorite peak at 2θ of around 35.5° , no other kaolinite and chlorite peaks were identified. The identifications were assigned, therefore, with some ambiguity. The identification of the $14\text{\AA}$ and $7\text{\AA}$ peak was attributed to

kaolinite and/or chlorite. The identification of a peak in the $14\text{\AA}$ region only, which showed no shift on glycolation, was attributed to chlorite. The presence of mixed layer clays, while remaining a likely prospect, could not be experimentally determined.

(c) Cation exchange capacities.

The experimental determination of a cation exchange capacity for any solid material involves several factors which must be given consideration. Ion exchange may, in fact, involve three distinct processes - physical adsorption, chemical adsorption and, for organic rich materials, a "chelation type" adsorption which may be particularly significant for the transition metals. The term sorption is often used to embrace all three processes. The possible selective adsorption of a cation must also be considered; for example, the possible selective adsorption of potassium ions by micaceous minerals. For organic rich sediments, the dissolution of organic matter during the determination must be kept to a minimum as the organic matter content is recognized as a major influence on the total cation exchange capacity of a sediment.

The two most significant variables in the determination of a cation exchange capacity then are pH at which the determination is carried out and the index cation employed. The absolute value obtained will be dependent upon the method applied. The sediments involved in this study were extremely variable in nature ranging from sands to silts to humic muds.

The method decided upon was taken from Hesse (1971, p. 102) who considered it applicable to a wide range of materials including calcareous or organic samples. Ba^{++} is used as the index cation.

Reagents:

- (i) triethanolamine solution: dilute 90 mls. of triethanolamine to 1l. and adjust to pH8.1 with 2M HCl (requires about 150 mls. of acid). Dilute to 2l. and stopper well.
- (ii) Barium chloride solution: 244g./l. of $BaCl_2 \cdot 2H_2O$.
- (iii) Buffered barium chloride solution: mix equal volumes of the above two solutions.
- (iv) Magnesium sulphate solution: 6.2g./l. of $MgSO_4 \cdot 7H_2O$.
- (v) EDTA solution: 3.723g./l. of the disodium salt of EDTA.
- (vi) Eriochrome Black T indicator solution: made up as 0.4% (w/v) Eriochrome Black T and 4% hydroxylamine hydrochloride in methanol. Solution made fresh each week.

Procedure:

- (i) Weigh 1g. of dry, crushed and sized sediment into a 50 ml. centrifuge tube; stopper the tube and record the weight (w_1).
- (ii) Treat the sediment sample in the tube with 40mls. of buffered barium chloride solution overnight; centrifuge and discard the liquid. For a calcareous sediment, treat the sediment initially with 20mls. of buffered barium chloride with gentle shaking for 1 hour; centrifuge and discard the liquid.
- (iii) Add approximately 40mls. of distilled water, thoroughly shake the tube, centrifuge and discard the washings.

Reweigh the stoppered tube (w_2).

(iv) Pipette 20mls. of the magnesium sulphate solution into the tube, shake the mixture for 2 hours, centrifuge and transfer the supernatant liquid into a snap cap vial prior to titration.

(v) Take 5 mls. of the final extract; add 5mls. of 2M triethanolamine to raise the pH and 2 - 3 drops of indicator solution. Titrate with the standard EDTA solution. Let the titre obtained be A_1 mls.; this is corrected (A_2) for the effect of volume of liquid retained by the centrifuged soil. 5 ml. aliquots of the starting magnesium sulphate solution were titrated under the same conditions giving a titre, B mls., Calculations were then made as follows:

$$\text{corrected titre, } A_2 = A_1 (100 + w_2 - w_1) / 100 \text{ mls.}$$

$$\text{cation exchange capacity (CEC)} = 8(B - A_2) \text{ m.e./100g. sediment.}$$

(Note: if the CEC exceeded 50 m.e./100g. calculated on the basis of lg., then it is necessary to repeat the determination using less weight of sediment and modifying the calculation accordingly.)

The precision of the CEC measurements was determined on the basis of 5 separate CEC calculations for both the Flint clay and bentonite samples used in the laboratory model experiments. On this basis, a precision of 3% was observed. Hesse gives an accuracy of 5% for this method.

2.7 Stream water.

Element analyses for Cu, Pb, Zn, Ni, Fe, Mn, Mg, Ca, Na and K were carried out on the water samples by Barringer Research Limited, Toronto. Total organic carbon (TOC) analyses were also conducted by Barringer Research on the water samples.

Chapter 3 Experimental Study of the Metallic Cation-
Organic Acid - Clay Interaction: Unbuffered,
Low Ionic Strength Solutions.

3.1 Introduction.

The importance of metal-organic interaction to the geochemical dispersion of elements has already been emphasized in chapter 1.5. Previous studies of this interaction in the laboratory have been primarily concerned with the dissolution of mineral phases by humic substances and the stability of metal-organic complexes in solution. In order to evaluate the role of organic complexing in geochemical transport, it has been necessary to design experiments that model natural geological systems more closely than previous experimental studies. In particular, the present study has introduced an inorganic adsorber to determine what effect this might have on the ability of humic and fulvic acids to hold metals in solution. Clay minerals were chosen as they represent a particularly common inorganic adsorber in the surficial environment. Flint clay (US Bureau of Standards number 97) consists essentially of kaolin, which along with chlorite was the most common clay mineral in stream sediments from the field areas studied in this work. Bentonite has also been used because of its substantially greater cation exchange capacity when compared to kaolin.

The metal ions chosen for the study were Cu, Pb, Zn and Ni. These elements were known from previous studies to show an affinity for humic and fulvic acids. In selecting metal

and organic acid concentrations, field analytical data for Cu, Pb, Zn, Ni and C were taken into consideration. A reasonable estimate for an average trace metal content in stream waters was taken as 10 parts per billion (ppb). This estimate is probably somewhat low for Zn and high for Pb, Cu and Ni. A similar estimate for total organic carbon was taken as 10 parts per million (ppm). A problem with relating field organic carbon analyses to an experimental system arises from an unknown relationship between total organic carbon measurements and the actual number of functional groups or active organic acid sites that are present in the organic carbon. In the absence of such information, it has been assumed that humic and fulvic acids isolated from Lake Fortune provide a representative number of active sites for organic carbon from streams.

A series of experiments was also conducted using salicylic acid as the soluble organic. The rationale for this is the general acceptance in the literature of the dominant role played by salicylic acid type sites, within the humic and fulvic acid molecules, in metal chelation reactions. These experiments would hopefully give some information on the usefulness of salicylic acid, as a model organic compound, in continued studies of geochemical processes.

A lack of analytical facilities for ppb levels of metal detection in the laboratory study required metal concentration to be raised to the ppm range. Metal levels were therefore set at either 25 or 50 ppm in the experiments and organic acid concentrations were set in the range 100 to 5,000 ppm. As

described in the previous chapter, these levels of concentration correspond to experimental solutions with ionic strength in the range, 0.002 to 0.005. The ionic strength in the experimental solutions correlate reasonably with natural stream waters which typically have ionic strengths of approximately 0.01 (Carrels and Christ, 1965, p. 57). A further advantage to the choice of ionic strength made for the experimental solutions arises from the insensitivity of organic complex stability constants to variations of ionic strength within the quoted range. Consideration of figure 1.5 demonstrates this point clearly.

An additional factor that was taken into account in the experimental studies was the milliequivalence of metallic cation and organic acid. Within lakes and streams, the milliequivalence of active sites in dissolved organic carbon should greatly exceed the milliequivalence of Zn, Cu, Pb or Ni. However, the milliequivalence of total dissolved metals, including for example, Na, K, Mg, Ca is in excess of the active sites for dissolved carbon. In order to test the effect of different relative milliequivalences, two experimental "systems" were considered. The first, referred to below as mix A, was established such that a milliequivalence calculation indicates a slight excess of metallic cation over the organic acid active sites. A second set of experiments, referred to as mix B, involved organic acid potential binding sites well in excess of metallic cation.

For the estimation of the organic acid bidentate active site milliequivalence, two assumptions were necessary. Based

on the humic matter characterisations reported by Schnitzer and Khan (1972) and Gamble and Schnitzer (1973), a number average molecular weight of 950 was assumed for the Lake Fortune humic and fulvic acids with each acid containing 3 bidentate active sites.

A third type of experimental system, to be referred to as mix C, involved solutions containing all four metals (Cu, Pb, Zn and Ni). The direct competition of the four cations for fulvic and humic acid chelating sites, along with the inorganic reactions, was designed to emphasize the distinctions among the reactivities of the cations.

In order to investigate the effect of pH variation on each of the systems described above, it was necessary to add either HCl or NaOH to adjust the initial pH in each experiment. The possibility of chloride complexes as well as organic and hydroxy complexes therefore exists. Chloride ion content was, however, reasonably constant for reactions conducted at a particular pH and should not therefore affect the arguments in favour of organic reaction. The solution of clay minerals was also tested and found to contribute no detectable Cu, Zn, Pb and Ni to the solutions.

The three experimental systems outlined above were designed to test the ability of organic acids to hold trace metals in solution in a simplified geochemical environment. Thus, for those experiments involving both organic acid plus clay, the organic acid was present at the beginning of each experiment.

The experiment was continued until the concentration of metal in solution reached a constant value indicating that equilibrium had been reached with regard to adsorption of metal onto the clay. Alternatively, the equilibrium position can be approached by first allowing metal ion to be adsorbed onto the clay in the absence of an organic acid and then subsequently introducing the organic reagent to determine the amount of metal that can be desorbed from the clay and back into solution. Such experiments were carried out on solutions containing all four metals, as described above for mix C, and will be referred to below as mix C*.

3.2 pH.

The analytical data for the reactions described above are presented in appendices 11 a, b, c, d and e. Before considering the metal solubility data for each reaction system, the pH data presented in the appendices will be discussed. The pH data have been presented as pH_I and pH_F . pH_I is the pH of the reaction solution initially set by addition of HCl or NaOH. pH_F is the final pH of the solution measured after the 30 day equilibration period.

The pH variations (i.e. the differences between pH_I and pH_F) over the course of the reactions proves to correspond well for a particular reaction irrespective of the reaction mix. For the metal hydrolysis reactions (M), the initially acidic solutions tend to increase slightly in pH although this increase is usually within experimental error (± 0.1 pH). The initially

alkaline solutions exhibit a marked decrease in pH towards neutrality. For the metal plus organic acid reactions, the pH increase for the initially acidic solutions is generally more evident than was observed for the metal hydrolysis reactions but is only considerably larger than experimental error for humic acid. However, the initially alkaline solutions of the organic reaction exhibit a smaller decrease in pH than was observed for the metal hydrolysis.

For the metal plus clay reactions, the initially alkaline solutions exhibit a decreased pH, similar in value to the metal hydrolysis. The initially acidic solutions show a considerable increase in pH with the increase generally greater for pH_I around 4. The only variation from the metal plus clay trends exhibited by the metal plus organic plus clay reactions is a lesser decrease in pH for the initially alkaline solutions.

To explain the observed pH variations on a mechanistic basis is a difficult task. One can only speculate on the effects of the various competing reactions on the pH of the solutions. The reactions involved will include metal hydrolysis, ion exchange at the clay surface, metal-organic complexing and possibly further interactions between the organic species.

3.3. Salicylic acid reactions.

The components of the salicylic acid reactions were;

M: 50 ppm divalent cation

K: 120mg. Flint clay. (kaolin)

O: 0.1% salicylic acid. (w/v)

Milliequivalence calculations indicate that the salicylic acid

was in excess by a factor of about 8 for Cu, Ni and Zn, and about 26 for Pb. The analytical data for these reactions are given in appendix 11A and presented in figures 3.1, 3.2, 3.3 and 3.4.

The Cu reaction curves (figure 3.1) strongly imply the occurrence of a Cu-salicylic acid reaction. The metal hydrolysis curve (M) shows a rapid decrease in soluble Cu content with increasing pH; this is accompanied by the appearance of a blue precipitate assumed to be cupric hydroxide. However, the metal plus organic curve (M+O) indicates that the salicylic acid reaction is capable of strongly retaining Cu in solution over the hydrolysis reaction. In the presence of kaolin, but in the absence of salicylic acid, the M+K curve shows a further decrease in soluble Cu content compared with the hydrolysis curve. This is due to the sorption of Cu by the clay which will occur concurrently with hydrolysis. In the presence of salicylic acid and kaolin (M+O+K), the salicylic acid has the effect of retaining Cu in solution compared with M+K. However, when compared to M+O, the ion exchange reactions at the clay surface have decreased the soluble Cu content of the M+O+K reaction. Whether the Cu salicylate is involved in the ion exchange reactions is uncertain. The kaolin surface is negatively charged (Wayman, 1967) and, for significant Cu salicylate sorption onto the clay, the complex needs to be positively charged. The solubility decrease between M+O and M+O+K is suggestive of Cu salicylate sorption which would imply that the complex is positively charged.

Figure 3.1 Cu reaction curves for salicylic acid mix
(data points subject to an error of ± 1 ppm)

○ M, ● M+K, □ M+O, ■ M+O+K

Figure 3.2 Ni reaction curves for salicylic acid mix
(data points subject to an error of ± 1 ppm)

○ M, ● M+K, □ M+O, ■ M+O+K

Figure 3.3. Pb reaction curves for salicylic acid mix
(data points subject to an error of ± 1 ppm)

○ M, ● M+K, □ M+O, ■ M+O+K

Figure 3.4 Zn reaction curves for salicylic acid mix
(data points subject to an error of ± 1 ppm)

○ M, ● M+K, □ M+O, ■ M+O+K

Ni behaves differently to Cu (see figure 3.2). The metal hydrolysis curve (M) and metal plus clay curve (M+K) show the rapid decrease of soluble Ni content with increasing pH. The metal plus salicylic acid curve (M+O), when compared to the M curve, shows a decrease in Ni solubility at pH greater than 6.2. For Ni then, salicylic acid reaction has apparently decreased the Ni solubility. For the clay reactions, the presence of salicylic acid in the M+O+K reaction, when compared to M+K, produces an increase in Ni solubility up to pH 6.6. At pH greater than this, the salicylic acid reaction again shows the effect of a decrease in Ni solubility. Before attempting to interpret this result, the discussion will continue with the Pb and Zn data.

For Pb (figure 3.3), comparison of metal hydrolysis (M) with metal plus salicylic acid (M+O) would indicate no effect on Pb solubility due to the organic reaction. However, the data point at pH 8.15 for the M+O reaction records 9.5 ppm soluble Pb. A comparison of the clay reaction curves, M+K and M+O+K, would indicate that the presence of salicylic acid diminishes the Pb solubility. For both reactions at pH greater than 6, soluble Pb is not detected.

The Zn reaction curves (figure 3.4) reflect some aspects of the Ni reactions. Comparison of the hydrolysis curve (M) with the metal plus salicylic acid (M+O) implies a very considerable decrease in Zn solubility. For example, at pH 6, 10 ppm soluble Zn is recorded for the M+O reaction with 43 ppm being recorded for the hydrolysis (M) reaction. This trend is repeated in the clay reactions. Comparison of the M+K

reaction with $M+O+K$ shows a decreased Zn solubility for the organic reaction.

Before considering the organic reactions, the metal hydrolysis reactions will be considered. The order of metal hydroxide precipitation observed in these reactions with increasing pH is Cu and Pb occurring at almost identical pH followed by Zn and then Ni. Solubility products for the hydroxides of Cu, Pb Zn and Ni are recorded in Sillen and Martell (1964 and 1971). However, the values of the solubility products presented vary considerably with the technique and conditions of the determination. This is prohibitive to a theoretical calculation of the pH for which the metal hydroxides will precipitate under the experimental conditions used here. It is observed that the solubility products given for a particular set of conditions increase in the order Cu, Zn and Ni. The position of Pb in this order is variable again depending on the conditions and technique but it usually corresponds fairly well with Cu. The metal hydrolysis curves obtained are consistent then, with the solubility product data for at least the order of hydrolysis. It is to be noted that the hydrolysis order obtained for all reaction mixes is consistent with these data.

Of more importance is the interpretation of the salicylic acid effects on the metal solubilities. To summarize, Cu has an increased solubility for the reactions carried out in the presence of salicylic and for Ni, reactions carried out in the presence of salicylic acid at pH around 6.5 and greater, a decreased solubility is observed. Zn too shows a decreased

solubility in the presence of salicylic acid. Over all, salicylic acid does not have a pronounced effect on the Pb reactions. In attempting to understand these data, two factors are considered significant. Firstly, there is the stability constant of the metal salicylate and, secondly, the solubility in aqueous solution.

Salicylic acid is a ligand of the type H_2L with phenolic and carboxylic protons ionizable. From the acid dissociation constants for salicylic acid (Sillen and Martell, 1964 and 1971), in the pH range of the reaction solutions, the predominant salicylic acid species available for complexing will be HL^- with the carboxyl proton ionized. The metal - salicylic acid complexing reactions are $M^{2+} + HL^- = M(HL)^+$ (a)

$$M(HL)^+ + HL^- = M(HL)_2 \quad (b)$$

and $M^{2+} + HL^- = ML + H^+$ (c)

The third reaction involves the bidentate salicylic acid site and the release of the phenolic proton. ML and $M(HL)_2$ have zero charge and hence will be insoluble in aqueous solution. Sillen and Martell (1964 and 1971) report Cu, Zn and Ni stability constants for reactions (a) and (b), termed K_1 and K_2 respectively. Pb data are not available. The values reported, for the same method of determination, are

	$\log K_1$	$\log K_2$
Cu	12.03	8.67
Ni	8.41	7.04
Zn	9.2	not determined

Data applicable to reaction (c) were not available.

The increase in Cu solubility is explicable perhaps on the basis of its K_1 value. This predicts that substantially more Cu is complexed in solution. The relatively higher concentrations of free Ni and Zn contribute to their precipitation by hydrolysis. The higher stability constant (K_1) for Cu salicylate cannot, however, be the only factor that sets Cu apart from the behaviour of Ni and Zn. If this were so, the presence of salicylic acid would not decrease the solubility of Zn and Ni when compared with the inorganic reactions.

The solubility of metal salicylates now seems to play a role. The evidence suggests that Zn and Ni form insoluble salicylates whereas Cu salicylates are soluble. The K_1 and K_2 data for Cu are at a significant variance indicating that Cu is likely involved predominantly in reaction (a) forming a positively charged, soluble complex. This is consistent with the discussion pertinent to Cu salicylate sorption by kaolin. K_1 and K_2 correspond more closely for Ni perhaps indicating that Ni is involved to a considerable extent in reaction (b) forming an insoluble complex. The K_2 value for Zn is not determined. Reaction (c), involving chelation at a bidentate site, cannot be evaluated due to the lack of data. However, at higher pH, reactions involving the ionisation of the phenolic proton such as (c), become more probable. This also forms a zero charged, aqueous insoluble complex. Pb would appear to show the least reaction with salicylic acid of the four elements but a lack of literature data prevents a similar discussion of the Pb result.

Nevertheless, on the basis of the evidence and its discussion, Ni and Zn are apparently preferentially involved in reactions (b) and (c) compared with Cu. Reaction (c), via the salicylic acid bidentate site, is commonly cited as the reaction characteristic of the humic and fulvic acid active sites (see chapter 1.4). From the literature quoted in chapter 1.4, Cu is at least equally reactive with the humic and fulvic acid sites as are Ni and Zn. The difference may then depend more importantly on the different reactivities of the metals in reactions (a) and (b).

The use of salicylic acid in this type of model experiment proved interesting. However, due to the uncertainty of the aqueous solubility of metal salicylates, metal-organic reactions can lead to a decreased metal solubility. Since it was hoped to study the ability of soluble organics to retain metal in solution, the experimental emphasis was placed on the reactions involving humic and fulvic acids.

3.4 Mix A - metal in excess of organic acid.

The metal and organic concentrations were established such that a milliequivalence calculation, based on the assumptions outlined in the introduction to this chapter, indicates a slight excess of metallic cation over the organic acid sites for Cu, Zn and Ni and an almost 1:1 ratio for Pb. The milliequivalence ratios (metal to organic active sites) are estimated to be about 2.5, to 1 for Cu, Ni and Zn, and 0.75 to 1 for Pb. The mix A components are:

M: 50 ppm divalent cation

K: 120mg. Flint clay (kaolin)

F: 0.01% fulvic acid (w/v)

H: 0.01% humic acid. (w/v)

The analytical data are presented, in tabular form, in Appendix 11b and presented in figures 3.5, 3.6, 3.7 and 3.8.

The reaction curves for Cu (figure 3.5) include the metal hydrolysis (M) and the metal plus organic acid (M+F, M+H). The production of cupric hydroxide accounts for the slope of the M reaction curve. This is verified by the observation of a blue precipitate in the solutions at pH greater than 6.1. However, each of the metal plus organic reaction curves exhibits a distinct minimum. The minimum occurs around pH 5.85 for M+F and around 6.3 for M+H. For the reaction solutions at pH values close to the minima, light to dark brown flocculate precipitates are observed. Up to pH 6, the presence of organic acid in the M+F and M+H reactions produces a decrease in Cu solubility compared with the hydrolysis reaction (M). However, at higher pH values, the organic acids lead to a substantial increase in Cu solubility.

As discussed in the literature review, Ong et al. (1970) observed a minimum around pH 6 in the reaction curve for Cu (11) with an alkali soluble fraction of peat. Their organic fraction then will represent both fulvic and humic acids. The concentrations were such that Cu (20ppm) will be in excess of organic carbon (8ppm). The Cu solubility increases rapidly at pH greater than 6. The authors speculate that this behaviour is

Figure 3.5 Cu reaction curves for mix A (metal in excess of organic sites). Data points subject to an error of ± 1 ppm.

Δ M, $\triangle$ M+K, $\circ$ M+F, $\square$ M+H, $\bullet$ M+F+K, $\blacksquare$ M+H+K

observed in response to hydroxide and carbonate precipitation at lower pH and the increased stability of the metal-organic colloid at higher pH. However, a different explanation will be offered for the very similar Cu behaviour obtained in the results described as part of this thesis.

The explanation that is offered for this behaviour is related to the polyelectrolytic, colloidal properties of humic and fulvic acids in conjunction with the excess of metal ion in the reaction solutions. If the ionizable functional groups of the organic acids are effectively complexed by metal cations, then the precipitation of uncharged, polynuclear (with respect to metal) humates and fulvates is the probable result. The observed development of light to dark brown flocculate precipitates in reaction solutions around the minima supports this explanation. The reaction curves in figure 3.5 do indicate a strong pH effect on the humate and fulvate precipitation. At lower pH, all functional groups may not be ionized. At higher pH, the possibility of soluble metal hydroxy organic complexing exists to account for the rapid increase in metal solubility. To invoke increasing stability for the metal-organic complex with increasing pH is reasonable over the pH range 3 to 5 (for example, Schnitzer and Hansen, 1970). At pH values above 5 , this information is lacking. Nevertheless, a pH effect on stability constants may well be of significance.

The Flint clay (kaolin) reaction curves for Cu (figure 3.5) indicate that fulvic acid in the M+F+K reaction leads to a

decrease in Cu solubility compared with the M+K reaction up to pH 6.2. At higher pH, Cu is insoluble in both reactions. However, humic acid in the M+H+K reaction leads to a slightly increased Cu solubility (3 to 6 ppm) at pH greater than 6 compared to M+K but to a decreased solubility at lower pH. The explanation of this behaviour will involve the formation of uncharged complexes but, superimposed on this, are the sorption or ion exchange reactions with kaolin. Due to the presence of clay, the light to dark brown Cu humate and fulvate precipitates were not able to be observed. The humic acid stock solution was dark brown in colour; the fulvic acid was a light yellow solution. For the M+H+K reaction, an indication of metal-organic precipitation or sorption is found in the loss of the reaction solution organic colour. This too is observed in the M+H reaction along with the brown precipitate. For M+F+K, the original organic solution colour is such a light yellow that it is not possible to detect a clear colour change over the course of the reaction. The cations in solution will be involved in sorption reactions with the negatively charged clay surface (Wayman, 1967). However, what involvement the organic acids and the metal-organic complexes have in ion exchange is speculative.

No attempt was made to experimentally evaluate the sorption of organic acid and metal-organic onto clay. However, interlamellar adsorption of humic and fulvic acids by clays was found to be possible only at acidic pH values

(pH less than 4) where the organic acids were almost totally unionized and hence behave like an uncharged molecule (Kodama and Schnitzer, 1968; and Schnitzer and Kodama, 1966). For the reactions considered in this study, pH is always greater than 4; hence the fulvic and humic acid functional groups will be strongly ionized. Rashid et al. (1972) concluded that adsorption of humic acids on clay minerals in weak ionic solution, such as fresh water, would be minimal. They found the percentage by weight adsorption of humic acid to be 0.04, 0.2 and 0.33 for chlorite, illite and kaolinite respectively. As the surface of clay minerals is negatively charged, the forces between the clay surface and the ionized humic and fulvic acids will be repulsive. In strong electrolyte solutions (3.5% NaCl), the adsorption was enhanced due to the compression of the double layer and subsequent increased significance of the attractive Van der Waals' forces (Rashid et al., 1972). Rashid and his co-workers further noted, on the basis of desorption experiments, that most of the adsorption is indeed of a physical nature through Van der Waals' attraction. Some chemical adsorption is possible through the carboxyl groups of the organic acid and positive sites on the clay mineral. Edge effects of the clay minerals are likely to be important in this adsorption process due to the generation of positive sites by broken bond formation at edges. This latter mechanism may be of some limited significance for the kaolin sorption.

The adsorption of metal-organic complexes is more difficult

to evaluate. Under the conditions of slight metal excess over organic acid active sites, the author has suggested that uncharged polynuclear colloids may form. However, if metal is in large enough excess, then the complexation of metal via void filling and secondary groups may occur. Such a complex could have an overall positive charge and be susceptible to adsorption onto the negatively charged clay surface. As suggested by Greenland (1971), humic and fulvic acid adsorption by clay minerals may take place through association with polyvalent metals at the clay surface. However, considering the low cation contents and ionic strength of the solutions in this present study, a mechanism involving possible metal-organic reaction at a clay surface is likely to be minimal. This system is quite analogous to the low ionic strength system of Bashid et al. (1972).

The above discussion of sorption effects will be pertinent to the two systems (mix B and mix C) presented later in this chapter. The critical factors of cation content and ionic strength are quite analogous. However, mixes B and C have organic in excess with the result that metal-organic complexes formed will likely be negatively charged due to incomplete reaction of the organic active sites, which themselves are negatively charged. Hence, sorption of metal-organic complexes in mixes B and C is considered to be negligible. For mix A, the possibility of the formation of a positively charged complex does exist and this would then be susceptible to sorption.

Comparison of the hydrolysis curve (M) with the metal plus

Figure 3.6 Ni reaction curves for mix A (metal in excess of organic sites). Data points subject to an error of ± 1 ppm

ΔM , $\triangle M+K$, $\circ M+F$, $\square M+H$, $\bullet M+F+K$, $\blacksquare M+H+K$

Figure 3.7 Zn reactions curves for mix A (metal in excess of organic sites). Data points subject to an error of ± 1 ppm

Δ M; $\blacktriangle$ M+K, $\circ$ M+F, $\square$ M+H, $\bullet$ M+F+K, $\blacksquare$ M+H+K

Figure 3.8 Pb reaction curves for mix A (metal in excess of organic sites). Data points subject to an error of ± 1 ppm.

Δ M, $\triangle$ M+K, $\circ$ M+F, $\square$ M+H, $\bullet$ M+F+K, $\blacksquare$ M+H+K

organic curves (M+F and M+H) for Ni (figure 3.6) shows a different result than was observed for Cu. In the presence of humic acid, the Ni solubility is increased between pH7 and 8 but, at higher pH, it drops off rapidly with a brown precipitate being observed at the last data point (pH8.25). However, the fulvic acid produces a decreased Ni solubility up to pH7.7 and then a slight increase is observed. A light green precipitate is observed for M+F at pH6.7 and greater. The observation of a precipitate is again taken as evidence for the formation of insoluble humates and fulvates of zero charge. The precipitation of Ni hydroxide may also be involved but this precipitate, as observed in the M reaction, is quite distinct from the precipitates observed in the M+F and M+H reactions.

Comparison of the clay reaction, M+K with M+F+K and M+H+K indicates that the organic acids have quite small effects on the Ni solubility. An average decrease of about 5ppm is observed for the humic acid curve (M+H+K) compared to M+K. Fulvic acid gives an increase in Ni solubility up to pH6.3; the maximum increase is 6ppm at pH5. At pH greater than 6.3, the Ni solubility is not enhanced and may even be decreased by the presence of fulvic acid. At pH greater than 7, Ni has a zero solubility for all three clay reactions. The loss of organic colour for the M+H+K solutions is observed at pH greater than 6; again, this is interpreted as evidence for Ni humate precipitation or sorption.

Some correlation between the Ni reaction curves and the Zn reaction curves (figure 3.7) is observed. Comparison of the

metal hydrolysis curve (M) with the metal plus organic (M+F and M+H) leads to conclusions similar to the Ni reactions. The humic acid increases the Zn solubility at pH greater than 6.2; the effect of Zn humate precipitation is not observed for Zn but it must be noted that the most alkaline data point for Zn is pH 7.95. For Ni plus humic acid, the effect of humate precipitation is observed at pH greater than 8. The fulvic acid leads to a decreased Zn solubility up to pH 7.4; at higher pH, Zn solubility increases up to a few ppm. A light green precipitate is observed in reaction solutions at pH greater than 6.4. The effect of zero charged colloid formation for Zn fulvates, as for Ni fulvates, is a plausible explanation for the observed Zn solubility in M+F. Zn and Ni humates exhibit considerable aqueous solubility up to pH 8.

In the presence of fulvic acid and clay (M+F+K), Zn solubility is decreased compared to M+K. Humic acid (M+H+K) slightly increases the Zn solubility compared to M+K; for example, at pH 6.5, M+K records 0 ppm soluble Zn whereas M+H+K records 13 ppm soluble Zn. This represents the maximum discrepancy between the two curves. The organic colour of the M+H+K reaction solutions is diminished considerably.

Comparison of the Pb reactions, M, M+F and M+H (figure 3.8) implies a strong retention in solution for the fulvic acid reaction over the full pH range. It is concluded that soluble Pb fulvate formation occurs. In the presence of humic acid, the Pb solubility curve exhibits a possible minimum value although this is far less distinct than for the Cu results.

At pH greater than 5.4, the humic acid retains Pb in solution. Pb is the largest of the four divalent cations, Cu, Pb, Zn and Ni, and would be expected to be the most efficient in coagulation of a humic or fulvic colloid. No precipitate is detected, however, in both M+F and M+H. Nevertheless, the formation and coagulation of zero charged complexes would appear to have some effect on the M+H reaction for Pb but not for M+F reaction. The Pb fulvates formed are particularly soluble and are concluded to be charged species. The charge is unlikely to be due to unreacted, ionized sites within the fulvic acid molecule; this is based on the almost equal metal to organic milliequivalences. The possible reaction of Pb with secondary sites of the fulvic acid molecule (such as quinone groups) now is invoked with the formation of a positively charged complex. However, the possibility of this should be equal for all four cations. As a further point, the formation of charged Pb hydroxy fulvates may also be involved.

For the clay reactions, it is humic acid (M+H+K) which retains Pb in solution compared to M+K; precipitation of Pb humate is indicated by the loss of organic colour. For fulvic acid (M+F+K), except for one data point at pH 8.15 (3.5ppm), Pb is insoluble. If a positively charged Pb fulvate is being formed, then it will be sorbed onto the negatively charged kaolin surface.

Pb is not unique in the fact that it exhibits a high metal solubility for M+F but a dramatic decrease in solubility

is seen upon the introduction of clay. A similar result is observed for Zn plus humic acid, Cu plus humic and fulvic acids at pH greater than 7, and Ni plus humic acid. In each of these cases, in the M plus organic reaction, an increase is observed in the metal solubility compared with hydrolysis (M). It has been concluded that soluble metal-organic complexes are formed. On the introduction of a clay, the metal solubility decreases. In each case, the interpretation proposed involves the formation of positively charged metal-organic complexes which, in the presence of clay, will be involved in sorption phenomena. Due to the ion exchange reactions with kaolin, the metal-organic acid milliequivalence ratio is possibly altered, by a drop in free metal cation activity, such that conditions now favour the precipitation of zero charged metal-organic complexes. This too can account for the observed result. This argument, however, does imply an initial metal excess which, if in reaction with an organic acid, a soluble charged complex forms, then it should be positively charged.

The most significant conclusion to be drawn from the above data is that, under conditions of slight metal excess over organic acid sites, metal organic complexes of zero charge may form. This, in effect, leads to the precipitation, in aqueous solution, of metal humates and fulvates. From the data presented, the effect is variable for the metals and for the organic acid used. However, in the presence of clay, the organic acids show low to no ability to hold metal in solution. In accord with complex precipitation, the presence of organic acid in the clay reactions

conducted at acidic pH values generally leads to a decreased metal solubility. The geochemical significance of this is likely to be observed in streams high in soluble base metals but dilute in soluble organics. One might then expect a slight excess of the base metals over the organic active sites. Metal-organic reaction in this situation, based on the laboratory data, would lead to metal-organic complex precipitation. It has generally been considered that metal-organic reaction in natural waters enhances the metal solubility.

3.5 Mix B - organic acid in excess.

The components of the reaction system termed mix B are:

M: 25 ppm divalent cation.

F: 0.5% fulvic acid. (w/v)

H: 0.2% humic acid (w/v)

K: 100mg. Flint clay. (kaolin)

For fulvic acid, the organic active sites are in excess of Cu, Ni and Zn by a factor of approximately 40; the factor for Pb is increased to about 130. With humic acid, the active sites are in excess of Cu, Ni and Zn by a factor of approximately 16; the factor for Pb increases to about 50. Based on these data, precipitation of zero charged complexes, as seen in mix A, is considered unlikely to occur for mix B. Analytical data are given in Appendix 11 B and presented in figures 3.9, 3.10, 3.11 and 3.12.

The Cu reaction curves (figure 3.9) show clear evidence of the formation of soluble Cu fulvate and soluble Cu humate

in competition with hydrolysis and sorption. Comparison of the hydrolysis curve (M) with the metal plus organic curves (M+F and M+H) indicates that the organic acids have the effect of a total retention of Cu in solution over the entire pH range studied. In the presence of clay, fulvic acid almost totally retains Cu in solution; this is evident from a comparison of the M+K and M+F+K curves. The M+H+K reaction exhibits a pH dependence with Cu solubility increasing from pH5 to pH6. Humic acid, in comparison to M+K, strongly retains Cu in solution. The pH dependence may be attributable to an increase in the humate stability constant with pH (Schnitzer and Hansen, 1970).

It is possible that a decrease in metal solubility for a metal-organic acid - clay reaction will result from sorption reactions. It has been concluded previously that direct involvement of metal-organic complexes and the organic acids in sorption is most unlikely. However, the free metal cations in solution will be involved in sorption. The metal-organic chelation reaction can be simply represented by

where M is the free metal cation,

L is the organic ligand (humic or fulvic acid)

and ML is the metal organic complex.

Sorption of free metal cation by the clay will decrease the activity of M thus displacing this reaction to the left with a resultant decrease in ML activity and hence metal solubility. The magnitude of this effect will be dependent on the equilibrium

Figure 3.9 Cu reaction curves for mix B (organic sites in excess of metal). Data points subject to an error of ± 1 ppm

○ M, ● M+K, △ M+F, □ K+H, ▲ M+F+K, ■ H+H+K

Figure 3.10 Ni reaction curves for mix B (organic sites in excess of metal). Data points subject to an error of ± 1 ppm

○ M, ● M+K, △ M+F, □ M+H, ▲ M+F+K, ■ M+H+K

Figure 3.11 Zn reaction curves for mix B (organic sites in excess of metal). Data points subject to an error of ± 1 ppm

$\circ$ M, $\bullet$ M+K, $\triangle$ M+F, $\square$ M+H, $\blacktriangle$ M+F+K, $\blacksquare$ M+H+K

Figure 3.12 Pb reaction curves for mix B (organic sites in excess of metal). Data points subject to an error of ± 1 ppm

○ M, ● M+K, △ M+F, □ M+H, ▲ M+F+K, ■ M+H+K

constant of the above reaction (i.e. the stability constant for ML) with the effect being minimized for more stable complexes. A lack of stability constant data applicable to the experimental conditions prohibits a further evaluation of this effect.

It should also be noted that the effect of increasing metal hydrolysis with increasing pH, in competition with metal chelation, will also push the above reaction to the left. This effect is again dependent on the stability of the metal-organic complex.

The Cu data show no effects due to hydrolysis. Sorption does have a moderate effect on the M+H+K reaction as evidenced by its comparison with M+H. This suggests that, under these experimental conditions, the Cu fulvate has a higher stability.

The Ni reaction curves (figure 3.10) indicate that the organic acids increase the Ni solubility. In competition with hydrolysis (M), fulvic acid (M+F) totally retains Ni in solution up to pH 8.4; humic acid (M+H) has the same effect with the only deviation being the decreased solubility at pH 8.7. The fulvic acid curve does not go beyond pH 8.4. No precipitate is observed for the M+H reaction solution, pH 8.7. This moderate decrease is interpreted as being a result of the Ni hydrolysis on the humate stability.

The fulvic acid (M+F+K) and humic acid (M+H+K) retain Ni in solution in competition with hydrolysis and sorption. However, both organic curves show a decrease in solubility compared with the organic reactions in the absence of clay (M+F and M+H).

The solubility decrease is pH dependent, increasing with pH. This suggests that the stabilities of Ni humate and fulvate are low enough for the competing reactions of hydrolysis and sorption to produce this measurable drop in Ni solubility. The data indicate that the Ni humate is more stable than the Ni fulvate (the solubility decrease is less for M+H+K compared to M+F+K).

Fulvic³ and humic acid totally retain the Zn in solution in competition with hydrolysis (compare the M, M+F and M+H curves in figure 3.11). In the presence of clay, fulvic acid (M+F+K) almost totally retains Zn in solution compared with M+K. This suggests that Zn fulvate has considerable stability. A comparison of the humic acid reaction, M+H+K, with M+K indicates a significant increase in Zn solubility in the presence of humic acid. However the Zn solubility in M+H+K is significantly influenced by pH. The nature of the curve is indicative of a hydrolysis effect on the Zn humate formation. Certainly, Zn humate appears to be less stable than Zn fulvate.

The Pb reaction curves are given in figure 3.12. Humic acid and fulvic acid retain Pb in solution in competition with hydrolysis (compare M with M+F and M+H). The presence of clay in the organic reactions decreases the Pb solubility compared to M+F and M+H. However, a comparison of M+F+K and M+H+K with M+K, indicates that the behaviour is different for each organic acid. The Pb solubility increases with pH in M+F+K but decreases with pH for M+H+K. The humate would appear more stable at lower pH with the fulvate and humate stabilities approaching a

similar value at higher pH. The large ionic size of Pb(II) also opens up the possibility of humic and fulvic acid coagulation by the Pb. There is no observed change in solution organic colour to suggest this takes place.

For the fulvic acid-metal-clay reactions, the increasing order of metal solubility is Pb, Ni, Zn and Cu. Zn and Cu have almost equal solubilities. The positions of Pb and Ni reverse at pH 8.5. For humic acid, at pH greater than 6, the increasing solubility order is Cu, Ni, Zn and Pb. The pH effects on the solubility order are quite variable but, as a summary, Pb and Cu solubilities increase with pH, Zn and Ni solubilities decrease with pH.

The above data imply that, under the conditions of considerable organic excess, metal-organic reaction will retain Cu, Pb, Zn and Ni in solution in competition with hydrolysis and sorption. The solubilities are pH dependent with sorption and hydrolysis being apparently effective in decreasing Ni and Zn solubilities; Pb and Cu solubilities are affected predominantly by sorption. The organic excesses used in mix B are probably too great to represent most natural waters; the humic acid reactions with Cu, Ni and Zn are more realistic. Mix C was then designed to have an organic excess but, hopefully, a metal to organic ratio now more relevant to natural systems.

3.6. Mix C - mixed cations, organic acid in excess.

In this system, the stock cation solution contained all four divalent cations (Cu, Pb, Zn and Ni). It was hoped that the

direct competition of the four cations for the fulvic and humic acid chelating sites, along with the inorganic reactions, would emphasize distinctions among the reactivities of the cations. The effects of two solid phases, Flint clay and bentonite, added in weights of both 100 mg. and 250 mg. were also investigated. By using bentonite with its higher cation exchange capacity, a broader application to natural systems was being sought. The use of an increased weight of adsorbent solid was also designed to test the effect of increased sorption on the overall reactions.

The components of mix C are:

M: 25 ppm each of Cu(II), Pb(II), Zn(II) and Ni(II).

F: 0.5% fulvic acid (w/v)

H: 0.2% humic acid (w/v)

K: 100mg. Flint clay; K^I: 250mg. Flint clay (kaolin)

B: 100mg. bentonite ; B^I: 250mg. bentonite

The data are presented in Appendix IId and figures 3.13, 3.14, 3.15, 3.16, 3.17, 3.18, 3.19, 3.20 and 3.21.

Milliequivalence ratios for the four metals and fulvic acid (using the previously discussed assumptions for the organic acid) are approximately 3 : 3 : 3 : 1 : 130 for Cu: Ni: Zn: Pb: fulvic acid active sites. For the humic acid, the ratios are about 3 : 3 : 3 : 1 : 50 for Cu: Ni: Zn: Pb: humic acid active sites. In both cases, the organic acid is in excess of each cation and the total cation content. On the basis of total cation content, the organic excess is less than that of mix B.

The pH variations during the course of the reactions are as previously discussed. The metal hydrolysis curves (figure 3.13) for mix C are similar to mix B; the Cu hydroxide precipitation occurs at a slightly higher pH for mix C.

The M+K reaction curves (figure 3.14) prove interesting. The effect of hydrolysis on these curves is evident with increasing pH. Increasing the solid weight of kaolin to 250mg. leads to increased sorption of all four elements, as reflected by the decrease in soluble metal content, but this decrease is most pronounced for Pb and Zn. This indicates an increased reactivity in sorption phenomena for these two elements compared with Cu and Ni.

The metal plus bentonite (M+B) reaction curves (figure 3.15), in comparison with the M+K reaction, clearly reflect the increased cation exchange capacity of bentonite. With increased weight of bentonite, the metal sorption is increased but it is difficult to discern preferential ion exchange for the elements involved.

Compared with mix B, the organic acid reactions with and without clay, for mix C are more revealing. For the M+F and M+H reactions of mix B, all four metals were almost totally retained in solution; Ni showed a drop in solubility at pH around 8.5. The metal plus humic acid reaction for mix C (figure 3.16) shows that, with the four metals in competition for the humic acid, only Cu is strongly retained in solution. Ni and Zn solubilities exhibit a dependence on hydrolysis. The Pb solubility at acidic pH falls below the Pb hydrolysis curve. Such a solubility

Figure 3.13 Metal hydrolysis curves for mix C (data points subject to an error of ± 1 ppm)

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.14 Metal-kaolin sorption reaction curves for mix C (data points subject to an error of ± 1 ppm)

(a) 100mg kaolin (b) 250 mg. kaolin

○ Cu, ■ Ni, □ Pb ● Zn

Figure 3.15 Metal-bentonite sorption reaction curves for
 mix C (data points subject to an error of
 ± 1 ppm)
 (a) 100 mg. bentonite (b) 250 mg. bentonite
 $\circ$ Cu, $\blacksquare$ Ni, $\square$ Pb, $\bullet$ Zn

Figure 3.16 Metal-humic acid reaction curves for mix C

(organic sites in excess of metal). Data points
subject to an error of ± 1 ppm

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.17 Metal-fulvic acid reaction curves for mix C
(organic sites in excess of metal). Data
points subject to an error of ± 1 ppm
○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.18 Metal-humic acid-kaolin reaction curves for mix C (organic sites in excess). Data points subject to an error of ± 1 ppm

(a) 100mg. kaolin, (b) 250mg. kaolin

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.19 Metal-humic acid-bentonite reaction curves for mix C (organic sites in excess). Data points subject to an error of ± 1 ppm

(a) 100mg. bentonite, (b) 250mg. bentonite

○ Cu, ■ Ni, □ Pb, ● Zn

figure 3.20 Metal-fulvic acid-kaolin reaction curves for
mix C(organic sites in excess). Data points
subject to an error of ± 1 ppm

(a) 100mg. kaolin, (b) 250mg. kaolin

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.21 Metal-fulvic acid-bentonite reaction curves
for mix C(organic sites in excess). Data points
subject to an error of $\pm$ ppm
(a) 100mg. bentonite, (b) 250mg. bentonite
 $\circ$ Cu, $\blacksquare$ Ni, $\square$ Pb, $\bullet$ Zn

decrease has been, for mix A, attributed to metal-organic complex precipitation. The ionic size of Pb does imply that Pb is likely to cause colloid coagulation in preference to Cu, Zn or Ni. It is concluded that Pb humate precipitation is occurring in this reaction. However, in competition with hydrolysis at alkaline pH, the humic acid reaction holds Pb in solution. In the presence of fulvic acid (figure 3.17), Zn and Cu are almost totally retained in solution. The increased milliequivalence of organic active sites for the M+F reaction compared with M+H may explain the increased Zn solubility for fulvic acid. However, Ni and Pb behave in a similar manner for both humic and fulvic acids.

In the presence of kaolin, humic acid retains all four metals in solution (figure 3.18). Cu is strongly retained in solution. It is apparent that sorption processes with kaolin have little effect on the Cu humate stability. Cu humate sorption by kaolin must also be negligible as the weight of kaolin used has little effect on Cu solubility. The decreased Cu solubility around pH5, in the presence of 250mg. kaolin, is interpreted to be a result of a decreased Cu humate stability at this pH combined with an increased sorption. The Ni solubility is influenced by hydrolysis and also by sorption. The latter point is demonstrated by the decreased Ni solubility with the increased kaolin weight. Zn, however, is more strongly affected by sorption. The decrease in solubility with increased kaolin weight is most pronounced for Zn. Pb is also affected by the increased kaolin weight. Pb humate is apparently influenced by colloid coagula-

tion and sorption; hydrolysis does not have a pronounced effect on the Pb solubility. Although the distinction among the elements for mix C is more evident than for mix B, the order of metal retention in solution ($\text{Cu} > \text{Ni} > \text{Zn} > \text{Pb}$) is the same for both mixes.

The M+H+B reaction curves (figure 3.19) show metal behaviour similar to the above discussed M+H+K reaction curves. In the presence of bentonite, all four metals show decreased solubilities in accord with the increased bentonite sorption capacity. Considering that the data points are subject to an error of $\pm 1 \text{ ppm}$, the increased weight of bentonite has little apparent effect on the metal solubilities; of the four elements, Zn is most effected by the increased clay weight but this is only apparent at pH less than 6. The Cu solubility more clearly shows a pH dependence (being lower around pH 5) but, as for M+H+K, it demonstrates the highest solubility. The solubility of the other three metals decreases in the order Ni, Zn and Pb with Pb and Zn having almost equal solubilities at higher pH. This is the same order as for M+H+K.

The behaviour of the metals in the fulvic acid, M+F+K, reactions (figure 3.20) differs in some ways from the humic acid-kaolin reactions. Cu and Ni show similar behaviour for both acids. Cu is strongly retained in solution whereas the Ni solubility is affected by increasing hydrolysis. However, Zn and Pb, in the fulvic acid reaction, show a marked increase in solubility at pH greater than 6. With 100mg. of kaolin minima are evident

in the Pb and Zn curves; this behaviour was not encountered in mix B. As a further point, the Pb and Zn curves show decreased solubility, at low pH, when compared to the M+K reaction curves (see figure 3.14). The Pb result is similar to the M+F curve for Pb (see figure 3.16). The precipitation of Pb and possibly Zn fulvates is offered as the explanation of this behaviour. No detectable colour change was noted as was the case for mix A but this is not surprising considering the metal fulvate solubility attributed to Ni and Cu which will retain the organic colour. The fact that the Zn curve in M+F+K does not follow the M+F result indicates that sorption reactions will also play a dominant role in determining Zn solubility. Of the four elements, Zn is most strongly affected by the increase in kaolin weight further emphasizing the significance of sorption reactions in determining Zn solubility.

Cu, Pb, Zn and Ni are retained in solution for the M+F+B reactions (figure 3.21). Compared to M+F+K, metal solubility is reduced for the four metals in the bentonite reactions. The increased weight of bentonite causes a pronounced drop in Cu solubility implying that sorption processes with bentonite do cause a destabilization of Cu fulvate. The Ni behaviour is again characterized by decreased solubility with increasing pH for 100mg. bentonite. This is not so for 250mg. bentonite suggesting that sorption is now the predominant inorganic factor. The increased weight of bentonite has most influence on the Cu and Ni solubilities. The Zn solubility for the M+F+B

reaction does not increase with pH as observed for M+F+K. At pH greater than 6, the decrease in metal solubilities observed when comparing M+F+K and M+F+B is most pronounced for Zn. This is further evidence of the dependence the Zn solubility has on sorption reactions. The Pb solubility for the bentonite reaction is low and is attributed to the combination of sorption processes and fulvate coagulation.

For bentonite and kaolinite, the fulvic acid reactions show a similar order of soluble metal retention, $Cu > Zn - Ni > Pb$; Zn and Ni exhibit crossover points in both reactions.

As for mix B, these results further imply the potential ability of humic and fulvic acids to maintain Cu, Pb, Zn and Ni in solution in competition with hydrolysis and clay sorption. In comparison to mix B, the metals did show more differentiation in their behaviour. The bentonite experiments and the use of increased weights of solid did imply that clay sorption reactions do decrease the solubilities of Cu, Pb, Zn and Ni in the presence of organic acid. However, the effect is most pronounced for Zn with possibly Ni being the next most affected.

By combining the data of mixes A, B and C, conclusions pertinent to the geochemical behaviour of Cu, Pb, Zn and Ni have been made:

- (1) Organic acids have the potential to retain Cu, Pb, Zn and Ni in solution; an excess of organic acid active sites is an important consideration here.
- (11) In a situation of metal excess, soluble metal may be reduced by metal-organic precipitation.

- (iii) Cu shows the highest affinity of the four elements for organic reaction in solution in competition with clay sorption and hydrolysis.
- (iv) In the presence of organic acids, clay sorption processes may decrease the Cu, Pb, Zn and Ni solubility but this effect is most pronounced for Zn.
- (v) Increasing pH (hydrolysis) is the more significant competing inorganic parameter affecting Ni solubility.
- (vi) Of the four elements, Pb is most prone to colloidal coagulation phenomena.

3.7 Desorption study.

Desorption experiments have been carried out using the same bulk chemistry as in mix C. The effect of an increased solid weight (250mg.) was excluded from the desorption study. In reference to the desorption experiments, these components will be referred to as mix C*. The objective of the desorption study was to study the reversibility of the following reaction:

where M represents metallic cation,

MO represents metal-organic complex,

C represents inorganic absorber including clay and hydroxide precipitate

(M--C) represents clay-bound metal species,

and (MO--C) represents clay-bound metal-organic species.

Such a study tests the extent to which equilibrium has been approached in the experiments and also presents an alternative

model for geochemical processes. For the adsorption study of mix C, the starting point was M + MO in solution over a range of pH values with subsequent addition of clay to determine how much metal was taken out of solution by adsorption onto the clay. At alkaline pH, the extra influence of hydroxide precipitation on metal solubility was also determined. The adsorption experiments therefore model the ability of an inorganic phase to inhibit the dispersion of metal in organic-rich waters.

For the desorption study, the reaction is set up, in one case ($\text{pH}_1 5.5$), with (M--C) initially present by adding clay to dissolved metal ion in the absence of organic reagent at $\text{pH} 5.5$. After the adsorption of metal onto the clay is completed, the organic acid and pH adjustment are introduced. In the second case ($\text{pH}_1 8.5$), the reaction is set with predominantly metal hydroxide and also possibly (M--C) initially present by adding clay to dissolved metal ion in the absence of organic acid but with pH set at 8.5. After the suspension has equilibrated, the addition of organic acid and pH adjustment steps are again carried out. The desorption experiments then model the ability of an organic acid to remobilize metals that have been previously taken out of solution by clay sorption and hydroxide precipitation. Given sufficient time to reach equilibrium, the adsorption and desorption experiments should reach the same point of equilibrium. However, kinetic factors can prevent the achievement of equilibrium for either adsorption or desorption in geochemical processes. The comparison of adsorption and desorption reactions

that is presented in this section is intended to identify metals that might be susceptible to this problem.

After the initial adsorption step conducted at the two pH values (pH₁ 5.5 and 8.5) and prior to the addition of the organic acid, the initial soluble metal contents of the desorption solutions used in the kaolin and bentonite reactions were obtained from the metal plus kaolin and metal plus bentonite reaction curves for mix C (see figures 3.14a and 3.15a, respectively). The initial metal concentrations for the desorption stock solutions are given in table 3.1

Continuation of the experiments for mix C* involved the addition of organic acid to the stock solution and adjustment of the pH by the addition of HCl or NaOH. The results obtained, after allowing 30 days for reaction, are shown in figures 3.22, 3.23, 3.24, 3.25, 3.26 and 3.27 with the analytical data presented in tabular form in Appendix IIe. To facilitate comparison of the adsorption and desorption reactions, the comparable adsorption curve obtained for mix C is presented along with data points and desorption curves obtained for mix C*.

The effect of pH variation alone in the absence of organic reagent has been tested on the desorption studies with the results shown in figures 3.22 and 3.23. Figures 3.22a and 3.23a show the results for metal adsorbed onto clay in the absence of hydroxide precipitate (pH₁ 5.5). The absence of metal hydroxides is predicted by the hydrolysis curves for mix C (see figure 3.13). For both the M+K and M+B reactions, the

Table 3.1 Initial metal concentrations (in ppm) for
reaction solutions used in desorption studies.

		<u>Cu</u>	<u>Ni</u>	<u>Pb</u>	<u>Zn</u>
M+K	pH ₁ 5.5*	3.0	20.0	3.0	20.0
	pH ₁ 8.5*	0	0	0	0
M+B	pH ₁ 5.5*	1.5	4.5	1.5	4.0
	pH ₁ 8.5*	0	0	0	0

*Note: An allowance was made for the change in pH during the adsorption step when obtaining the metal concentrations from the reaction curves. pH5.9 was used for the acidic adsorption (pH₁5.5) and pH7.8 for the alkaline adsorption (pH₁8.5).

Figure 3.22 Metal-kaolin reaction curves for desorption

mix c*. Data points subject to an error of ± 1 ppm

(a) pH₁ 5.5, (b) pH₁ 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.23 Metal-bentonite reaction curves for desorption mix C*. Data points subject to an error of ± 1 ppm

(a) $pH_1 5.5$, (b) $pH_1 8.5$

$\circ$ Cu, $\blacksquare$ Ni, $\square$ Pb, $\bullet$ Zn

Figure 3.24 Metal-fulvic acid-kaolin reaction curves for desorption mix C*. Data points subject to an error of ± 1 ppm.

(a) pH_i 5.5, (b) pH_i 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.25 Metal-fulvic acid-bentonite reaction curves for desorption mix C*. Data points subject to an error of ± 1 ppm

(a) $pH_1 5.5$, (b) $pH_1 8.5$

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.26 Metal-humic acid-kaolin reaction curves for desorption mix C*. Data points subject to an error of ± 1 ppm

(a) pH_i 5.5, (b) pH_i 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 3.27 Metal-munic acid-bentonite reaction curves

for desorption mix C*. Data points subject
to an error of ± 1 ppm

(a) pH_i 5.5, (b) pH_i 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

adsorption and desorption data agree within experimental errors indicating that no kinetic barrier exists in achieving equilibrium with respect to adsorption and desorption of metal from clay. Figures 3.22b and 3.23b show that in the presence of a hydroxide precipitate ($\text{pH}_1 8.5$), equilibrium is not achieved. For M+K and M+B, Cu and Pb show zero desorption; Ni and Zn are desorbed to 50% or less of the values obtained for adsorption experiments. The failure to attain equilibrium for initially alkaline pH values is attributed to unfavourable kinetics for the dissolution of the hydroxide precipitates.

Humic and fulvic acids prove capable of desorbing metal from both a clay and metal hydroxide precipitates. When compared to the adsorption reactions, kinetics effects are evident becoming more pronounced with increasing pH.

For the M+F+K reactions (figure 3.24)', the order of metal solubility is quite similar for adsorption and desorption. The shape of the reaction curves is also similar with the slight drop in Cu solubility at alkaline pH in the desorption being the only significant difference. The desorption of adsorbed metal ($\text{pH}_1 5.5$) does suffer from unfavourable kinetics at pH greater than 6. The discrepancies between the adsorption and desorption curves are greatest for Cu and Zn suggesting that these elements are most susceptible to kinetic effects. Fulvic acid does dissolve the metal hydroxides ($\text{pH}_1 8.5$) to a significant extent. Unfavourable kinetics strongly affect the solubilities of all four metals, particularly at pH greater than 6.

For the M+F+B reactions, desorption of both clay adsorbed metal ($\text{pH}_1 5.5$) and metal hydroxides ($\text{pH}_1 8.5$) leads to a similar metal solubility. Comparison with the adsorption reactions for the four metals indicates that agreement is within experimental limits up to pH about 8 and greater; at the higher pH, the metal solubility is less for the desorption reactions. Kinetic effects seem important only at higher pH for the bentonite desorption reactions.

In the presence of kaolin, kinetic effects are also apparent for the M+H+K reactions (figure 3.26). For the desorption of clay adsorbed metal ($\text{pH}_1 5.5$), all four metals show significant solubility with kinetic effects becoming apparent at pH 6 and greater. There is no evidence of a differential kinetic effect for the four metals; the decrease in solubility for desorption, compared with adsorption, is similar for the four metals. Humic acid has a considerable dissolution effect on the metal hydroxides (figure 3.26b). In comparison, with adsorption, the metal solubilities are decreased implying a kinetic barrier to the hydroxide desorption. Cu appears the most affected by the kinetic effect.

As observed for M+F+B, desorption at $\text{pH}_1 5.5$ and $\text{pH}_1 8.5$ leads to a similar result in the M+H+B reaction (figure 3.27). Comparison of the adsorption and desorption curves shows agreement within experimental limits for Pb, Zn and Ni. The decreased Cu solubility observed in the desorption experiments at pH greater than 6 implies that Cu desorption from both a clay adsorbed

phase and Cu hydroxide is kinetically unfavoured.

In summary, the experimental evidence indicates the following:

- (i) Humic and fulvic acids are capable of remobilizing Cu, Pb, Zn and Ni from a clay adsorbed phase and their metal hydroxide precipitates.
- (ii) The metal desorption is generally kinetically unfavoured, particularly at alkaline pH; desorption from a metal hydroxide phase is the more unfavourable process.
- (iii) Of the four metals, Cu desorption appears to be the most kinetically unfavoured.
- (iv) The order of metal solubility for adsorption and desorption for each reaction is essentially the same.

It is interesting to speculate on the closer correlation observed between the adsorption and desorption for the bentonite reactions than is observed for the kaolin reactions. Bentonite has a ten times greater ion exchange capacity than kaolin hence it may be postulated that sorption of metals by bentonite, even at alkaline pH in competition with hydrolysis, is far more effective than the equivalent kaolin reactions. Hence, desorption would be from a predominantly clay bound phase. The closer correlation observed then may be interpreted as evidence in favour of the above conclusion that desorption from a metal hydroxide phase is the more kinetically unfavoured process.

The geochemical significance of the desorption study is clear. Fulvic and humic acids prove capable of not only stabilizing Cu, Pb, Zn and Ni in solution (as seen in mix C), but also of

remobilizing Cu, Pb, Zn and Ni from a sediment phase including both metal hydroxides and metal adsorbed to clay. The geochemical dispersion of an element within a natural water is vitally dependent upon its aqueous solubility. However, it is first necessary for an element to be taken up into solution from a solid phase before organic complexing can influence its dispersion. Humic and fulvic acids also prove effective in this geochemical process. Compared with the adsorption experiments, kinetic factors affecting the level of metal solubility reached are less favourable for the desorption experiments with Cu being the most affected. This might lead to the situation where Cu, in comparison to Ni, Zn, and Pb, is released from a sediment phase at a considerably lower rate and is hence less available for organic complexing in solution. ➤

Chapter 4 Experimental Study of the Metallic Cation
-Organic Acid-Clay Interaction: Bicarbonate/
Carbonate Solutions of Varied Ionic Strength.

4.1 Introduction.

Stream waters from the field areas investigated in this study frequently cross bedrock that contains a high proportion of marble. As a result, the stream waters are often alkaline with a significant amount of dissolved carbonate. Because of this characteristic of the geology of eastern Ontario, it was decided to extend the experimental investigations reported in the previous chapter to investigate the effect of possible metal-bicarbonate and carbonate precipitation on the ability of humic and fulvic acids to hold Cu, Ni, Zn and Pb in solution. Two types of reaction solutions were involved in this study. Mix D was designed to have an approximately equivalent ratio of organic acid active sites and bicarbonate anion, both of which are in excess compared with metallic cations. In mix E, the bicarbonate anion is in about a ten fold excess of the organic acid sites which are in turn in excess over the metallic cations. Of the low ionic strength solutions described in the previous chapter, mix C is the most similar to the carbonate-bearing systems reported in the present chapter; mixes C, D and E have identical metal to organic acid active site milliequivalences.

Livingstone (1963) reports analytical data for several streams in Ontario and Quebec. None of the analyses reported were for streams sampled as part of this thesis. However for the

streams in eastern Ontario reported by Livingstone, HCO_3^- contents were in the range 100 to 230 ppm. Streams from Quebec contained 6 to 30 ppm HCO_3^- . For a stream with 10ppm total dissolved organic carbon (which is an approximation to the average for stream waters collected as part of this thesis) and assuming a molecular weight of 300 per organic active site, then, for 6ppm HCO_3^- , a milliequivalence ratio calculation indicates an approximate three fold excess of bicarbonate over the organic sites. Mix D is the better model for this situation. However, for 200ppm HCO_3^- , bicarbonate is in excess by a factor of about 90. Mix E, although not an accurate model of this situation, is a better approximation than mix-D, and is considered a better model for the eastern Ontario streams sampled in the field study to be reported. The ionic strength effect on humate and fulvate stabilities would become a considerable problem if bicarbonate concentration was raised to 1M in order to simulate the large excess calculated above.

4.2. Equal excess of bicarbonate and organic acid (mix D).

The mix D components are:

M: 25ppm each of Cu(II) , Pb(II) , Zn(II) and Ni(II)

F: 0.5% fulvic acid (w/v)

H: 0.2% humic acid (w/v)

K: 100mg. Flint clay (kaolin)

B: 100mg. bentonite.

All reactions are 0.01M in HCO_3^- and 5×10^{-4} M in CO_3^{--} . Ionic strength is estimated to be 0.01. The analytical data are

presented in Appendix IIIa and in figures 4.1, 4.2 and 4.3.

pH changes during the course of the reactions were minor and in the range 0.2 to 0.4.

Direct comparison to mix C is further justified when figure 1.5 is consulted. It can be seen from this that the variations in $\log K$ stab for Cu(II), Ni(II), Pb(II) and Zn(II) fulvates for an ionic strength change from 0.005 (mix C) to 0.01 are not significant. It is assumed that similar trends will be observed by both humate and fulvate complexes at alkaline pH. Obviously, the comparison between mixes C and D is only possible over the pH range common to both.

For the metal hydrolysis (M) and metal sorption reactions (M+K, M+B), no metal is retained in solution at the alkaline pH values involved here. The same result is found for mix C. This can be attributed to all three inorganic reactions of hydrolysis, sorption and bicarbonate-carbonate precipitation.

The M+F and M+H reaction curves are shown in figure 4.1. For the fulvic acid reaction, a comparison with mix C (figure 3.17) reveals no significant changes in the Cu, Zn and Ni solubilities; Pb does show a marked decrease in solubility for mix D. For the humic acid reaction, a comparison with mix C (figure 3.16) now indicates no significant change for Cu, Ni and Pb but Zn shows an increased solubility in the carbonate solution (mix D).

The metal-fulvic acid-clay reaction curves for mix D (figure 4.2) bear a marked similarity to the analogous reactions for mix C (figures 3.20 and 3.21). For the kaolin reaction

Figure 4.1 Metal-organic acid reaction curves for mix D
(bicarbonate and organic sites in excess). Data
points subject to an error of ± 1 ppm
(a) fulvic acid, (b) humic acid

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.2 Metal-fulvic acid-clay reaction curves for mix D (bicarbonate and organic sites in excess). Data points subject to an error of ± 1 ppm

(a) kaolin, (b) bentonite

○ Cu, ■ Ni, □ Pb, ○ Zn

Figure 4.3 Metal-humic acid-clay reaction curves for mix D
(bicarbonate and organic sites in excess). Data
points subject to an error of ± 1 ppm
(a) kaolin, (b) bentonite

$\circ$ Cu, $\blacksquare$ Ni, $\square$ Pb, $\bullet$ Zn

(M+F+K), Ni and Pb are slightly less soluble (a decrease of 2 to 3ppm) in the carbonate solutions. The Pb decrease is consistent with the M+F reaction. The trend is continued in the bentonite reactions (M+F+B) with no significant variation being observed between mixes C and D. The solubility order for M+F+K and M+F+B is $Cu > Zn > Ni > Pb$. For M+F+K, Pb becomes more soluble than Ni at pH greater than 8.5 in the carbonate solutions.

The metal-humic acid-clay reactions for the carbonate system (figure 4.3) and for the low ionic strength mix C (figures 3.18 and 3.19) are again similar. For the M+H+K reactions, Zn (in accord with the M+H reaction) has a slightly increased 1 to 2ppm solubility in the carbonate system whereas Ni has a decreased solubility (2 to 5ppm). The bentonite reactions (M+H+B) follow a similar pattern with Ni now showing no variation between mixes C and D. This leads to an order of solubility $Cu > Ni > Zn >$

Pb for the carbonate system which is the reverse of the order for Pb and Zn observed in mix C.

The data indicate that carbonate complexing has no effect on the metal solubility under these experimental conditions. This is consistent with the conclusion that hydroxide will precipitate metals more effectively in competition with organic complexing than will carbonate (Rashid and Leonard, 1973). Carbonate and bicarbonate are weak ligands but their involvement in mixed ligand complex formation is possible (Manning and Ramamoorthy, 1973). The data presented do not permit an assessment of possible mixed ligand complex formation. Variations observed between the

carbonate system, mix D, and the carbonate-free system, mix C, can probably be accounted for by the ionic strength effect on the humate and fulvate stabilities and experimental errors.

4.3 Bicarbonate in excess of organic acid and metallic cation (Mix E).

The mix E components are:

M: 25ppm each of Cu(II), Ni(II), Pb(II) and Zn(II)

F: 0.5% fulvic acid (w/v)

H: 0.2% humic acid (w/v)

K: 100mg Flint clay

B: 100mg. bentonite.

In this system, all reactions are carried out in 0.1M NaCO_3 and 0.005M Na_2CO_3 . Ionic strength is 0.1. Hence, the bicarbonate anion is approximately six times in excess of the fulvic acid sites and 15 times in excess of humic acid sites. The data for this mix are presented in Appendix IIIb and figures 4.4, 4.5 and 4.6. The pH variation is similar to that observed for mix D with pH increasing slightly during the reactions.

When comparing this carbonate system with the carbonate-free system, mix C, ionic strength considerations are important. The change in ionic strength here is significant varying from 0.005 for mix C to 0.1 for mix E. From the data of Schnitzer and Khan (1972) presented in figure 1.5, it can be seen that this ionic strength increase produces an almost ten fold decrease in the stability constants for Cu, Pb, Zn and Ni fulvates at pH3. Under the experimental conditions used, a similar reduction in

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fulvate and humate stabilities in the carbonate system may be anticipated.

The metal hydrolysis (M) and metal-sorption (M+K, M+B) reactions for mix E show an insignificant solubility for the four metals. For the M and M+K reactions, 1 to 2ppm of Cu and Pb are detected in solution. Ni and Zn are not detected in solution for any of these reactions.

The data for the metal-organic acid reaction curves (figure 4.4) indicate a decreased metal solubility in the presence of excess carbonate for mix E when compared to the data for mix D (figure 4.1). For the fulvic acid reactions, Pb solubilities are almost identical. Ni shows the greatest decrease (6 to 10ppm) with Cu and Zn being affected to a lesser extent (3 to 5ppm). For the humic acid reactions, all four metals exhibit a significant decrease (4 to 8ppm) in solubility with Zn being the most strongly affected. The solubility order for M+F is $Cu > Zn > Ni > Pb$ for mix E but $Cu > Zn > Ni > Pb$ for mix D. For M+H, the order $Cu > Ni > Zn > Pb$ is the same for both mixes.

The preferential destabilization of Ni in the fulvic acid reactions can be related to the data of Rashid and Leonard (1973). As discussed in the literature review (chapter 1.5), these workers found that, at pH8.5, the order of carbonate precipitation in the presence of humic acid was Ni followed by Cu, Mn and Fe. The humic acid reactions, however, more clearly reflect the decreased humate stability, due to ionic strength considerations, leading to almost equal decreases in solubility for all four metals.

Figure 4.4 Metal-organic acid reaction curves for mix E
(excess bicarbonate). Data points subject to
an error of ± 1 ppm

(a) fulvic acid, (b) humic acid

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.5 Metal-fulvic acid-clay reaction curves for mix E (excess bicarbonate). Data points subject to an error of ± 1 ppm

(a) Kaolin, (b) bentonite

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.6 Metal-humic acid-clay reaction curves for mix E
(excess bicarbonate). Data points subject to an
error of ± 1 ppm

(a) kaolin, (b) bentonite

○ Cu, ■ Ni, ▲ Pb, ◆ Zn

Increased carbonate excess may also be a factor in the general decrease. The fulvic acid reactions are influenced by the decreased fulvate stabilities but for Ni, at least, preferential carbonate precipitation is superimposed on this.

Consideration of the data for the metal-fulvic acid-clay reactions (figure 4.5) leads to the same conclusion. All four metals show a decreased solubility for mix E but the effect is most pronounced for Ni. In the bentonite reaction, Ni shows a zero solubility for mix E. The data suggests then Zn, in comparison to Cu and Pb, is also affected by the presence of carbonate. Cu and Pb solubilities decrease for mix E, compared to mix D (see figure 4.2), but the decreases are within experimental limits (± 1 ppm). The Zn solubility, in M+F+K and M+F+B, shows a uniform decrease of about 5 ppm.

For the metal-humic acid-clay reactions (figure 4.6), the decreased solubility of all four metals in mix E compared with mix D (see figure 4.3) is evident. The variations in Pb solubility are within experimental limits. Cu solubility decreases by 2 to 3 ppm for both bentonite and kaolin. Zn solubility decreases by about 2 ppm for the kaolin reaction but by 6 to 7 ppm in the bentonite reaction. Ni solubility decreases by about 3 ppm in the kaolin reaction and by about 5 to 6 in the bentonite reaction. This represents further evidence of the preferential destabilization of Ni and possibly Zn in the presence of bicarbonate.

It was concluded for mix D that, with equal milliequivalences of bicarbonate and organic acid, no decrease in metal solubility

due to bicarbonate/carbonate complexing is observed. With an average ten fold excess of bicarbonate, decreased solubility of all four metals is observed. The decrease is minimal and often within experimental limits for Cu and Pb. Ni appears the most affected by the presence of bicarbonate/carbonate but Zn is also strongly affected. It is difficult to assess to what extent the preferential decrease in solubility for Zn and Ni can be attributed to the change in humate and fulvate stabilities with ionic strength. Data on humate and fulvate stabilities in the pH range of this study are not available. The data of Schnitzer and Khan (1972, see figure 1.5) predicts an almost equivalent decrease in fulvate stabilities for Cu, Pb, Zn and Ni; however, these data were obtained at pH3.

Ionic strength effects are perhaps greatest for Zn considering that Zn exhibits the lowest affinity for organic complexing of the four elements. It is concluded that bicarbonate/carbonate has a very significant effect on Ni solubility, and possibly on Zn solubility, in the presence of soluble organic acids and solid clay. Pb and Cu solubilities are concluded to decrease slightly in response to decreased humate and fulvate stabilities.

Streams draining through carbonate terrains are likely to be low in soluble Ni content, according to the experimental results, irrespective of soluble organic carbon content. Zn dispersion in natural waters might also respond to carbonate units in the bedrock geology. Cu and Pb should not be influenced by carbonate. This is a significant consideration when studying

the geochemistry of natural waters draining through varied bedrock geology featuring carbonate units.

4.4. Desorption studies.

Desorption studies were carried out on systems analogous to mixes D and E. When referring to the appropriate desorption mix, the nomenclature D* and E* will be used. Considering the alkaline pH values of the solutions, the effect of pH variation alone on desorption was not studied as undoubtedly no metal would be released. The results of this study are given in Appendices 111c and 111d, and in figures 4.7, 4.8, 4.9, 4.10, 4.11, 4.12, 4.13 and 4.14.

It has already been observed that for the low ionic strength carbonate-free system (mix C), a comparison of adsorption and desorption reaction curves suffers from a kinetic effect, being particularly evident at alkaline pH. With bentonite, a closer comparison for adsorption and desorption resulted. For the carbonate systems, a comparison of the data for the adsorption and desorption reactions leads to similar conclusions. The results will be briefly summarized for this comparison:

1. Decreased solubilities for the desorption of clay adsorbed bed metal, pH₁ 5.5, are less than those observed for the desorption from metal hydroxides, pH₁ 8.5.
2. Decreased metal solubilities for the various reactions are consistently greatest for Cu.

It is concluded that desorption for the carbonate systems

Figure 4.7 Metal-fulvic acid-kaolin reaction curves for desorption mix D*. Data points subject to an error of ± 1 ppm

(a) $pH_1 5.5$, (b) $pH_1 8.5$

Figure 4.8 Metal-fulvic acid-bentonite reaction curves for desorption mix D*. Data points subject to an error of ± 1 ppm

(a) $pH_1 5.5$, (b) $pH_1 8.5$

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.9 Metal-humic acid-kaolin reaction curves for desorption mix D*. Data points subject to an error of ± 1 ppm

(a) pH₁ 5.5, (b) pH₁ 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.10 Metal-humic acid-bentonite reaction curves for desorption mix D*. Data points subject to an error of ± 1 ppm

(a) pH_i 5.5, (b) pH_i 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.11 Metal-fulvic acid-Raolin reaction curves for desorption mix E*. Data points subject to an error of ± 1 ppm

(a) pH₁ 5.5, (b) pH₁ 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.12 Metal-fulvic acid-bentonite reaction curves for desorption mix E*. Data points subject to an error of ± 1 ppm

(a) pH_i 5.5, (b) pH_i 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.13 Metal-humic acid-kaolin reaction curves for desorption mix E*. Data points subject to an error of ± 1 ppm

(a) $pH_i 5.5$, (b) $pH_i 8.5$

○ Cu, ■ Ni, □ Pb, ● Zn

Figure 4.14 Metal-humic acid-bentonite reaction curves for desorption mix E*. Data points subject to an error of ± 1 ppm

(a) pH_i 5.5, (b) pH_i 8.5

○ Cu, ■ Ni, □ Pb, ● Zn

or Zn, was any carbonate complexing effect noticeable for the desorption reactions.

In a natural system, soluble carbonate is unlikely to suppress the ability of soluble organic matter to leach metals from sedimentary materials. However, soluble carbonate is predicted to suppress the effects of organic complexing of Ni, and possibly Zn, once in the stream water, by carbonate precipitation.

Chapter 5 - Field Study of Element Distribution
between Stream Water and Stream
Sediment.

5.1 Introduction.

In any study of element dispersion within a drainage system and the distribution of these elements between the sediment and water, many parameters are involved. These will include both inorganic and organic chemical controls and physical factors. The studies conducted in the laboratory have been based on the effects of organic complexing on the metal (Cu, Pb, Zn and Ni) solubility in competition with the inorganic reactions of metal hydrolysis, carbonate precipitation and ion exchange with clay. The results indicated that organic complexing in solution can retain these metals in solution in competition with these inorganic reactions.

How applicable the interaction model involving solution phase organic complexing is to a field situation is uncertain. In an attempt to investigate this, stream water and sediment sampling were undertaken. 149 stations were sampled from 5 drainage systems. The sediment-water distribution ratios for the elements were of prime concern as it was hoped that the field data would relate to the laboratory experiments. Water and sediment analyses were translated into distribution ratios and their relationship to total dissolved organic carbon (TOC) and sediment cation exchange capacity (CEC) investigated.

5.2 Field areas.

The field areas were chosen on the basis of their accessibility and the extent of geological understanding of the areas. It was considered most desirable that the geological, here considered distinct from geochemical, influences on the trace element dispersion were well documented before attempting to discuss any chemical effects. Four areas in south-east Ontario and one in Quebec were chosen for study and sampled between June and August, 1974. Stream discharge was moderate to low. Figure 5.1 shows the area locations.

The most extensive area involved part of the Moira River drainage system, Hastings County. 62 stream water samples and 61 stream sediment samples were collected; in the treatment of the analytical data, this area is referred to as area E. The sample stations (see map 2) cover the river's drainage from Wolf Lake in the north to 2 or 3 miles west of its drainage from Moira Lake. The major communities in the area are Bannockburn, Keller Bridge, Eldorado, Malone, Deloro, Marmora and Madoc. The area is covered by the Tweed, Campbellford and Bannockburn National Topographic sheets.

37 stream water samples and 35 stream sediment samples were collected from the drainage system to the west and north west of Long Lake, Frontenac County. Sampling locations are shown on map 3; the area may be referred to as area I. The presence of the now inoperative Lynx mine is of most interest. At the time of sampling, the mine was operative; water samples 35 and 36 were collected from the outflows of the pumps draining the under-

Figure 5.1 Location map for field areas

E: Moira River, Z: Long Lake,

L: Lavant Creek-Clyde River, S: Sulphide Creek

CI: Calumet Island

ground workings and the mill respectively. The Tichborne National Topographic sheet covers the area. There are no major rural communities in the sampling area.

30 stream water samples and 29 stream sediment samples were collected along the Lavant Creek - Clyde River system, Lanark County. Lavant Creek was sampled from Robertson Lake to its junction with the Clyde River (see map 4). The Clyde River has been sampled from east of Clyde Forks to its intersection of highway 511. This area may be referred to as L and is covered by the Clyde National Topographic Sheet. There are no major rural developments in close proximity to the drainage.

13 stream water and stream sediment samples were collected along the course of Sulphide Creek, Hastings County, from 1 mile east of the community of Sulphide to its drainage into Stoco Lake (see map 5). The area is covered by the Kaladar and Tweed National Topographic sheets.

9 stream water and stream sediment samples were collected from the stream draining past Larawla and the abandoned New Capumet mine site, Pontiac County, Quebec (see map 6). The stream finally enters the Ottawa River. The contamination from the abandoned mine site was obvious. The area is covered by the Cobden National Topographic sheet.

The areas sampled are well forested with varying degrees of agricultural development. The climate is best described as temperate. The forests of the area are composed of mixed deciduous trees and conifers. White birch, white cedar, white

pinus, poplar, white spruce and maples are predominant. The stream channels are often bullrush filled with water lilies also common. The swamps are usually cedar, bullrush and reed filled. The rich forestation of the region is conducive to a significant organic input into the drainage systems. The light yellow to light brown colouration observed in the majority of the collected water samples is indicative of this organic input. The relief in all five areas is generally low.

5.3 Geology.

Geological aspects of each area will be considered in some detail particularly with regard to economic geology. The geology of the region embracing all five areas has been reviewed in the geologic compilation maps of the Ottawa-Kingston area produced by McDonald (1967 and 1970). The geology of each field area, shown in map 1, has been directly transcribed from McDonald's maps. All five areas are within the Grenville geological province. A table of formations generalizing the regional geology is presented in table 5.1. Carbonate rocks commonly outcrop in all areas. This has geochemical significance as the waters are likely carbonate enriched.

(a) Moirs River (area E).

The geology pertinent to the Moirs River drainage area has been reported by Hewitt (1964 and 1968). A Precambrian-Paleozoic contact passes along the south side of Moirs Lake with Paleozoic sediments outcropping south of the lake. To the north near Wolf Lake, Precambrian metasediments consisting of marble and

Table 5.1 Table of formations from Hewitt (1968)

Cenozoic

Pleistocene till, sand, gravel, clay, marl

-----Unconformity-----

Paleozoic

Trenton and Black River limestone

----- Unconformity-----

Precambrian

Plutonic rocks:

granite, syenite, diorite, gabbro

Intrusive contact

Metasedimentary and volcanic rocks:

Marble

Conglomerate, pelitic and psammo-

pelitic rocks quartzite.

Acid and basic volcanic rocks.

lime-silicate rocks outcrop. These overlie the pelitic and psammo-pelitic schists and gneisses. The oldest rocks are the Precambrian mafic metavolcanics which outcrop to the north east and north west of Madoc. Rhyolitic and felsic metavolcanic rocks overlie the mafic metavolcanics locally. In the Deloro area, the Deloro pluton of Precambrian age intrudes the metamorphosed basement rocks with the plutonic rocks being described as leucocratic granites. The Moira granite extends over the north eastern end of Moira Lake. Paleozoic sediments (limestone) overlie the Deloro granite to the east. In the Marmora area and extending south of Moira Lake, the youngest rocks of the Black River sedimentary group (Ordovician) outcrop. The Black River group consists predominantly of limestone and argillaceous limestone. Within the area, there are numerous mineral showings of economic interest. An example of these are the numerous fluorite veins in the Madoc area which have been previously studied (in this department) by Lalonde (1973).

Eldorado has a history of mining activity related to gold, copper and iron. In 1866, the first discovery of gold in Ontario was made in Eldorado at what was to be called the Richardson mine. Hematite, chalcopryite and chalcocite have been mined from vein occurrences between 1902 to about 1907.

The Hollandia lead mine, about 2 miles north of Bannockburn, operated at the turn of the century. Drilling was carried out on the property as recently as 1956. The ore is galena with minor sphalerite and pyrite occurring within calcite veins.

Many small arsenical gold deposits are clustered along the west contact of the Deloro granite near the village of Deloro. Some of these deposits were worked in the early 1900's. However, the ore processing plant in Deloro continues to be a source of possible pollution of the Moira River which drains through the site. Ore brought in from Cobalt, Ontario, was processed on this site until more recent times. The extensive waste dumps in the area are being actively weathered.

Numerous iron showings are reported for the area. The only one of significance is the contact metamorphic magnetite deposit located 3 miles east of Marmora. This is presently being mined by Bethlehem Mines.

The numerous fluorite veins in the Madoc area are a potential source of base metals for the drainage. The vein material consists of fluorite, calcite and barite with minor celestite, quartz, marcasite, pyrite, sphalerite and bituminous material (Lalonde, 1973).

(b) Long Lake (area 2)

The geology of the Long Lake area is reviewed by Harding (1951) and Hewitt (1964). The rocks in this area are predominantly the Precambrian mafic plutonic rocks (diorite and gabbro) along with granite and granite-gneiss. The carbonate metasediments locally outcropping in the area are of most economic significance. The Lynx Canada Zn deposit, located to the north of Long Lake, is hosted in a carbonate lens. Other carbonate lenses within the intrusive rocks have also proved

Zn rich.

Zn production from the Long Lake site has been intermittent over the past 75 years. The major sulphide minerals are sphalerite, galena, pyrite with minor pyrrhotite and chalcopyrite. High Ag values have been occasionally reported for the galena.

(c) Lavant Creek - Clyde River (area L).

The geology of the Lavant Creek-Clyde River area has been described by Peach (1956). Lavant Creek drains along the Robertson Lake shear zone. The granitic intrusive rocks outcrop predominantly along the creek along with metasedimentary rocks (marble). Along the course of the Clyde River, the predominant rock types are diorites, quartz diorites and gabbros. Metasedimentary carbonates outcrop locally.

The economic geology is restricted to several Cu showings along the Robertson Lake shear zone in close proximity to Lavant Creek. The showings have never proved economic for mining and, apart from their presence, little else has been reported.

(d) Sulphide Creek (area S).

The geology of the Sulphide area has been reported by Hewitt (1964). The course of Sulphide Creek in question runs almost parallel to the Clare River syncline axis. The outcropping rocks are predominantly metavolcanics and metasediments including carbonates, schists and amphibolites.

Of economic interest are the three pyrite deposits in proximity to the village of Sulphide. Pyrite was mined from these deposits in the early 1900's.

(c) Calumet Island (area CI).

The geology of the Calumet Island area has been reported by Osborne (1944) and Sangster (1967). The most significant geological influence here is the massive sulphide deposit hosted by marble and lime-silicate rocks. Sangster (1967) described the sulphide deposit as massive pods and disseminations of sphalerite, pyrrhotite and galena confined to a thin, discontinuous marble horizon within highly deformed Grenville paragneiss and amphibolites. The ore mineralogy is sphalerite, pyrrhotite, galena, pyrite, marcasite, chalcopyrite, tetrahedrite and arsenopyrite.

5.4 Treatment of data.

Analytical data have been tabulated for each area in Appendix IV. The data included here are:

- (a) sediment analyses for Cu, Pb, Zn, Ni, Fe, Mn, Mg, Ca, Na and K by HF/HClO₄ attack (total element),
- (b) sediment analyses for the same ten elements by HCl leaching (adsorbed element),
- (c) water analyses for the same ten elements,
- (d) water pH readings measured in the field,
- (e) total dissolved organic content of water (TOC),
- (f) sediment organic carbon content (OC),
- (g) sediment cation exchange capacity (CEC),
- and
- (h) sediment mineralogy.

Before considering the data, some further explanation of the meaning of the analyses will be given. This applies to the water element analyses and the meaning of TOC.

The water samples were analysed without filtration. Livingstone (1963) discusses the possible error involved in water analyses without prior filtration to remove suspended solids and colloidal particulates. Analyses of unfiltered water will always produce higher values but the magnitude of this increase is dependent upon the sorption capacity of the suspended load and on how much of this suspended load is incorporated into the analysis. Perhac (1972) and Perhac and Whelan (1972) studied the distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn in dissolved and particulate (colloidal and coarser) solids from two streams draining an area of exposed minor Zn mineralization. They observed that the colloidal particulates exhibit greatly increased metal concentrations compared with the dissolved state and coarse particulates. Yet, generally, over 90% of each metal occurs in the dissolved state; less than 10% occurs with the coarse particulates and less than 1% as colloids. The streams of interest to this thesis have particularly low suspended loads; this was observed when filtration through Millipore 0.45 μ filters was attempted. It is concluded that the increase due to incorporation of the element content of a suspended load will be insignificant in the data presented.

However, at times of high flow with increased suspended load, it would be interesting to study the partition of elements between a dissolved state and a suspended particulate state.

The more intimate contact between the particulate phases and the aqueous medium might lead to a better equilibrated system than the solution-fine sediment phase system studied in this work.

The analyses carried out on the field samples have been discussed in chapter 2. No duplicate samples were sent for analysis and hence precision cannot be estimated. However, a precision of 1% has been stated by Barringer Research Ltd.. The TOC value is worthy of comment. The accuracy of this figure, according to Barringer Research Ltd., is $\pm 10\%$. However, it is the meaning of the analysis which is important. What is most desirable is a measure of the total organic chelating capacity of a natural water. Some attempts at measuring metal-organic chelation capacities for natural waters are now being made (for example, Chau et al. 1974). However, this persists as a basic analytical problem. The assumption will be made in this work that TOC is directly related to the organic chelating capacity. This is justified on the grounds that fulvic acid type compounds represent the predominant organic chelators in natural waters and the variance in chelation capacities of these compounds, derived from different sources, will not be large (see literature review).

It is assumed that warm HCl leaching of the sediments will release adsorbed elements whereas the HF/HClO₄ attack will release the total metal content of the sediment including mineral bound elements. Chemically, this assumption is reasonable and one would expect the total element contents to exceed the HCl

-adsorbed element contents. However, there are instances where adsorbed element content is greater. This is particularly evident for Mn and somewhat less recurring for Mg and Ca. This may be a result of experimental error but the Mn trend is quite perplexing and may be inherent in the analytical procedure. The element distributions between the sediment and water were processed by means of a Fortran IV computer programme. The first programme (statements listed in Appendix Va) was designed to perform the following tasks:

- (a) convert the sediment and water analyses into two ratios, for each element, defined as:

$$R = \frac{\text{sediment adsorbed element content}}{\text{water element content}}$$

$$\text{and } R^I = \frac{\text{sediment total element content}}{\text{water element content}}$$

- (b) print out R and R^I values in tabular form,
- (c) plot R and R^I against TOC, OC and CEC with sample stations identified on the plot;
- (d) plot R and R^I against TOC, OC and CEC with frequency reported (i.e. if two stations plot at one point then this is recorded as 2 on the computer print out), and
- (e) a sub-routine was included which, if necessary would omit any anomalous ratios (defined as greater than 2.5 times the average) from the plot with this station now being recorded at the top line of the plot. This achieved a more desirable spread of the vertical axis.

It became evident that, if any relationship between the element distribution ratios and the three parameters was to be proposed without a strong personal bias affecting the outcome, the plots needed to be handled statistically via a regression analysis programme (see Appendix Vb). The regression analysis produces a polynomial equation of best fit to the data under consideration. Equations of degree 1 and 2 were selected as the most reasonable to apply to the data. Anything beyond degree 2 is likely to produce a regression function which has no obvious application to a natural system.

The available data, then, included plots of R and R^I against TOC, OC and CEC and regression analyses for these plots. Variation between the R and R^I was most evident for Na, K, Mg and Ca. This is obviously related to their role as essential elements in the silicate minerals making up the bulk of the sediment samples. The distribution ratio, R , involving loosely bound (adsorbed) element is the one of interest to this study. The laboratory experiments, in effect, studied the influence of soluble organic acids on an element's distribution between a solution phase and a sediment (clay) adsorbed phase. Hydroxide and carbonate precipitates were also involved in the laboratory model. However, the effect of organic acids on mineral bound element was not considered as part of this model. For this reason, the ratio R does relate to the laboratory model whereas R^I does not. Only the data pertinent to R will be reported and discussed.

5.5. Metal dispersion patterns.

The dispersion patterns observed for the alkali and alkaline earth elements within a drainage system are not of primary interest to this study. It is expected their sediment and water contents will bear a strong relationship to sediment detrital mineral content and lithology of the surrounding rocks. It is not a prime concern of this thesis to study in detail the dispersion of the elements but rather, as already pointed out, the factors influencing the sediment - water distribution. Nevertheless, some attention will be given to the dispersion patterns of the base metals Cu, Pb, Zn and Ni.

(a) Calumet Island (area CI).

As to be expected, sediment Pb and Zn values are anomalous in all stations with the exception of station 9, upstream from the abandoned mine workings. The adsorbed Cu and Ni sediment contents show little variation throughout with the exception of anomalous Cu at station 1. In fact station 1, on the Ottawa River, is the most anomalous for Cu, Pb and Zn. There are signs of what was probably an ore loading dock in the vicinity of station 1 and contamination from ore material is quite likely. The water analyses show high Zn (200ppb) and Pb (12ppb) at station 6. This is an interesting result as the sediment here had a fine, easily suspended film of red Fe oxides. It would appear from the high water Fe content (6,600ppb) and the visible suspended load that suspended Fe oxide is having a marked effect on these water analyses. Station 9 is apparently anomalous

in Cu 60ppb , Pb 32ppb with 110ppb Zn. This is upstream from the mine and from a drainage culvert. The high Cu and Pb create suspicions of a contamination source, such as a rotting pipe, in close proximity to the station.

(b) Moirra River (area E).

From HCl sediment analyses, Cu-Ni mineralisation in the Deloro area is indicated. Stations 31, 32 and 33 show high Cu (5,100, 690 and 540 ppm respectively) and high Ni (1,100, 560 and 920ppm respectively). High Ni in the sediments along the Moirra River continues in stations 36, 34, 38, 39 and even to Moirra Lake at stations 46 and 40. However, stations 25 and 26 from the Moirra River within the Deloro site record background Ni values. Stations 23 and 24, further downstream, are anomalous for Ni (510 and 1,100ppm respectively). The source of the Ni and Cu is almost certainly from the Ni arsenides and Cu sulphides within the tailings material near the swampy beginning of the creek containing stations 31 and 32 which enters the Moirra River just upstream from station 33.

No evidence of Cu mineralisation in the Eldorado area is revealed by the analyses. The fluorite veins in the Madoc area do not have a detectable effect on the base metal contents of the sediment. The Marmora iron mine has little effect on sediment iron content at station 27; its total Fe content of 7.2% is the highest of all the sample stations but this does not represent an anomalously high value.

The water analyses show little variation for Zn (10-30ppb)

throughout the area. Cu and Ni are rarely above the detection limits (2ppb). For the stations with anomalous Ni sediment contents, Ni is not detectable in the water; pH of these waters is around 7. Yet, at station 3, water pH 6.80, a very organic locality near Eldorado, 38ppb Ni is recorded. Pb rarely exceeds 2-4ppb but of interest is the increased soluble Pb content in stations 53 to 62, all of which were collected after several days of heavy rain.

(c) Lavant Creek-Clyde River (area L).

Cu, Pb, Zn and Ni sediment contents show little variation within the area. The Cu showings along Lavant Creek have no detectable effect on the Cu dispersion. Station 22, on the Clyde River in close proximity to cottages, has an anomalous adsorbed Zn content (530ppm). This one spurious result is most likely related to the cottage development.

The Cu, Pb, Zn and Ni water analyses are also quite uniform throughout. Cu is equal to or less than the detection limit of 2ppb for all stations except number 4 which records 6ppb. This may be related to the Cu mineralization or to the culvert about 400 yards upstream. The Pb values at stations along the Clyde River are consistently higher than the Lavant Creek stations. The proximity of county roads and cottages along the Clyde offer sources of increased Pb. The sediment Pb contents do not show this variation.

(d) Long Lake (area Z).

Cu and Ni are not anomalous in the sediments of this area.

Zn is strongly dispersed from the Lynx mine site. Station 19 has 5,600ppm adsorbed Zn and 44,000ppm total. Zn persists up to 2 miles downstream in stations 20,24,25,26,27,28 and 29 until it is dispersed in the swamps around station 30. The Zn showing near station 10 is not evident in the Zn analyses. The Pb dispersion from the Lynx mine site as detected in the stream sediments is similar to Zn but is less persistent. Stations 19, 20 and 24 are anomalous for Pb with station 25 high (97ppm adsorbed, 115ppm total).

Cu and Ni water analyses are also low. Station 34, at the east end of Long Lake near a public beach, has spurious values of 28ppb Cu and 14ppb Ni, both well above the background. The station location is indicative of a contaminant source for the Cu and Ni. The Zn dispersion from the Lynx mine in stream waters is not as pronounced as for the sediment data. Even at station 20, Zn is barely anomalous (69ppb). Pb is not above detection limits at stations 19 and 20. High Pb values are spread over the area - station 1, 24ppb; station 15, 38ppb and station 23, 28ppb. Stations 1 and 15 are near roads; station 23 may be affected by a culvert upstream.

(c) Sulphide Creek (area 8).

A correlation is observed between the Cu, Pb, Zn and Ni contents and the pyrite deposit at the village of Sulphide. The sediment analyses, both total and adsorbed, show considerably higher Cu, Pb, Zn and Ni values for stations 1 to 5 compared with stations 6 to 13. Station 6 was not collected in Sulphide Creek but from a small creek draining into Sulphide Creek. These data

are suggestive of metal dispersion from the plainly visible pyrite rich basic metavolcanics. Station 11, collected in a swamp floodplain, also shows increased base metal contents now probably related to enrichment via organic sorption.

The water analyses for Pb and Zn are subject to this variation going downstream. The Zn analyses for stations 1 and 3 are considerably higher than all other stations. However, Ni water analyses show a most pronounced drop from stations 6 to 13 compared with stations 1 to 5.

5.6 Element distribution between sediment and water.

(a) Introduction.

The focal point of the field study will now be discussed. This involves the interpretation of the field data in order to determine the significance that dissolved organic matter (TOC) and cation exchange capacity of a sediment (CEC) have on the behaviour of an element at a sediment-water boundary. To do this, the reader could view the numerous computer plots for R against CEC and TOC for the five areas but it was felt that study of tabulated regression data would achieve the same end result without introducing a personal bias, and with far more convenience.

Plots of R against the organic content (OC) of the sediment were available. However, as shown in figure 5.2, CEC and OC show a strong linear relationship. The regression data for R against CEC and R against OC led to the same conclusion. It is apparent that, for the areas sampled, the sediment organic content

Figure 5.2 Relationship between sediment organic C content (%OC) and cation exchange capacity (CEC, me/100g).
 (a) Moira River, (b) Lavant-Clyde, c) Sulphide, (d) Long Lake and (e) Calumet Island

Figure 5.2 cont'd

Figure 5.2 cont'd

has a strong influence on the total exchange capacity of the sediment. For this reason, the R against OC data will not be reported.

The terms involved in the regression are defined as follows:

N : number of observations or pairs of variables,

D : the degree of the fitted polynomial(1 and 2 in this study),

Y_i : the i^{th} observed value of the dependent variable (R),

y_i : the i^{th} calculated value of the dependent variable,

and

r : the correlation coefficient defined as

$$r = 1 - \frac{\sum_{i=1}^{1-N} (Y_i - y_i)^2}{\sum_{i=1}^{1-N} (Y_i)^2 - \frac{1}{N} \left[\sum_{i=1}^{1-N} Y_i \right]^2}$$

The closer the correlation coefficient, r, is to unity, the better is the fit of the observed data points to the calculated function. Alternatively, as the difference between observed and calculated values for the dependent variable increases, the value of r tends towards zero. The limiting values of r are, therefore, 1 and 0.

(b) Predicted element behaviour.

In predicting the behaviour of an element at a sediment-water boundary where the competing processes of sorption and organic complexing in solution are considered as the only reactions taking place, then an idealized set of reactions can

be envisaged. In doing this, the assumption that free metal ion in solution is the only metal species directly reacting in sorption will be made. This is reasonable in consideration of the laboratory data reported and the probability that metal-organic species in solution will be negatively charged with the sorption sites also negatively charged. The activity of the metal-organic species will, however, change in response to the free metal ion sorption. The proposed reactions are:

and

where M_F is a particular metal cation, uncomplexed in solution,

M_S is a particular metal sorbed onto sediment,

O is soluble organic complexing reagents,

MO is the soluble organic complex of a particular metal cation,

R_a is the adsorption distribution coefficient at the

R sediment-water boundary for a particular cation,

and

K_{Stab} is the metal-organic species stability constant for a particular metal cation.

The distribution ratio, R , measured in the field is defined

as:

$$R = \frac{M_S}{\text{total metal in solution}}$$

From (i) and (ii), total metal in solution is comprised of M_F plus MO . Therefore, R can be expressed as:

$$R = \frac{M_S}{M_F + MO}$$

This can then be expressed as:

$$(iii) \quad R = \frac{R_a}{1 + MO/M_F}$$

A major advantage of plotting the variable R, rather than M_S or total dissolved metal ($M_F + MO$) arises from the fact that R expresses the distribution of metal between water and sediment independently of the total metal supply to a particular station. If, for example, M_S were plotted against CEC, no relationship would be anticipated because M_S depends on the vagaries of metal supply as well as CEC. Similarly, total metal in solution plotted against TOC will not produce an obvious relationship because of varying concentrations of metal supplied to the various stations.

According to equation (iii), R will vary with changing R_a and MO/M_F (ratio of complexed to free metal). R_a will be dependent on CEC and TOC will be taken as a measure of MO/M_F . The magnitude of R_a variation for a given CEC change will be dependent upon the reactivity of an element in sorption processes. If the relationship between R_a and CEC is linear over the range of concentrations encountered in a field study, then, for constant MO/M_F (i.e. constant TOC), equation (iii) predicts a linear relationship between R and CEC, i.e.

$$(iv) \quad R = k (CEC)$$

The constant, k, will be positive as increasing cation exchange capacity leads to increased metal content in the sediment and,

hence, an increase in R . Equation (iv) also predicts that at zero CEC, there will be no adsorbed metal and so R is zero. In practice, however, it is possible that any observed linear relationship will not pass through the origin. The determination of the amount of sorbed metal in the sediment involved an HCl digestion and, therefore, includes not only sorbed metal, but also metal in phases such as carbonates and sulphides that are soluble in HCl but that do not contribute to the CEC of the sediment. The intercept of any observed linear relationship is therefore assumed to result from the analytical procedure.

An additional factor that may mask a linear relationship between R and CEC is varying TOC from station to station. It is readily seen from equation (iii) that a simple linear relationship between R and CEC does not arise except for a specific value for the ratio MO/M_F . The extent to which varying TOC will affect the relationship between R and CEC will be dependent on the magnitude of R_a and the relationship between TOC and MO/M_F for a particular element. For elements with a strong affinity for sorption (i.e. large R_a) and low organic reactivity, MO/M_F will show little variation with TOC. Conversely, elements that have a low affinity for sorption and a strong tendency to form organic complexes may be expected to show more scattering of points on a plot of R versus CEC.

Further complications are likely to arise from factors that have not been explicitly considered in deriving equation

(iv). These additional factors will include:

- (i) pH,
- (ii) variation in the nature of sediment adsorption sites (inorganic versus organic),
- (iii) variation in the nature of soluble organic chelating sites,
- (iv) reaction with inorganic ligands (for example, carbonate and sulphide),
- (v) temporal effects such as rainfall,
- and (vi) analytical errors.

To take account of the possibility that such additional chemical factors might introduce systematic deviations from a linear relationship, a function of degree 2 has been fitted to the field data. The degree 2 function is of the following type:

$$y = ax^2 + bx + C$$

The geochemical significance, if any, of the additional coefficients in the degree 2 equation has not been investigated. Those elements that approach a linear relationship between R and CEC will have low values for the coefficient, a, in the degree 2 equation.

A relationship between R and TOC can also be predicted from equation (iii). Since R varies inversely with TOC, a hyperbolic relationship is predicted. Thus, a second degree function would be expected to produce a better fit than a first degree function to the field data. Equation (iii) indicates that variations in CEC will produce scatter in the R versus TOC

plots and the relationship between R_a and CEC will determine the extent of this deviation. It is predicted that for an element with high reactivity in organic complexing but little dependence on cation exchange, the effect of CEC variation will be minimal. Additional chemical factors such as those listed in a preceding paragraph will also complicate the observed relationship between R and TOC.

It is expected that, for elements exhibiting considerable reactivity in sorption and in organic complexing and for elements with a low reactivity in sorption and organic complexing, a random scatter of points for both R versus CEC and R versus TOC will result.

The preceding discussion indicates that, even for elements exhibiting considerable reactivity in sorption or organic complexing, a close fit of the data points to the regression function is not likely. This was considered when interpreting the r values obtained. Conclusions as to whether the behaviour of an element at the sediment-water boundary is influenced by CEC or TOC were based on the degree 1 and degree 2 functions obtained and the r value. Correlation coefficients, r, were assessed by consideration of the maximum and minimum r values reported among the 10 elements for one area in the TOC or CEC plot. N was also considered, because of geological variation, r values will tend to increase with a decreasing N. The regression data are tabulated in tables 5.2 and 5.3 for CEC functions, and tables 5.4 and 5.5 for the TOC functions.

Included in these tables are N , r , the coefficients a , b and c , and a yes or no conclusion as to an element's dependence on CEC or TOC. The shape of the degree 2 function is also indicated in the inset figures.

(c) Observed element behaviour with CEC and TOC.

Na, K, Mg and Ca can be treated as a group. For their degree 1 functions, the values of the coefficient b are consistently the lowest of the ten elements. In fact, in certain instances (for example, Ca from Moira River), the degree 1 function is virtually a constant. The correlation coefficient, r , is also consistently low implying large deviations from the degree 1 functions. There are certain instances where reasonable r values are obtained. In these cases, b values are low (for examples, Ca and Na for Long Lake, and Ca, Na and K from Sulphide Creek). The degree 2 functions do not fit the accepted behaviour. A factor influencing the values reported for b is the considerably lower R values obtained for these elements in response to their inorganic solubility. This implies that a significant change in R will still be a relatively low absolute value. Taking this into account, the data are suggestive of a weak Na and K dependence on sorption. This is likely in response to sorption on clay minerals and not organic matter, the predominant sorbing material.

Fe and Mn show no relationship with CEC. Explanation of the Mn random plots is not possible on the basis of the available analytical data. The Fe data do tend to respond to high

Table 5.2 Regression data for R vs. CEC, degree 1

Area	Cu	Pb	Zn	Ni	Fe
Long Lake	N14 b0.016 c2.94 r0.07 No	N8 b0.066 c0.76 r0.16 Yes(r?)	N35 b0.03 c9.74 r0.0069 No	N8 b0.050 c1.64 r0.32 Yes(b?)	N35 b-0.065 c43.24 r0.0095 No
Lavant Clyde	N6 b0.11 c2.38 r0.40 Yes	N15 b0.049 c0.30 r0.066 No	N29 b-0.26 c25.65 r0.042 No	N2 Insuff. data	N29 b0.82 c104.25 r0.027 No
Sulphide Creek	N6 b0.28 c1.49 r0.61 Yes	N13 b0.12 c2.44 r0.13 Yes(r?)	N13 b0.043 c0.84 r0.23 Yes(b?)	N8 b0.35 c0.28 r0.43 Yes	N13 b0.10 c28.16 r0.014 No
Moirs River	N5 b69.89 c-2440.64 r0.48 No(C?)	N21 b-0.014 c12.65 r0.0018 No	N61 b0.038 c5.91 r0.043 No	N8 b-0.12 c18.63 r0.042 No	N61 b0.35 c72.60 r0.020 No
Calumet Island	N9 b-0.74 c38.28 r0.14 No	N4 b-6.98 c211.06 r0.21 No	N9 b-0.26 c16.52 r0.17 No	N3 b-0.65 c17.70 r0.89 No	N9 b-0.55 c46.82 r0.10 No

Table 5.2 cont'd

Area	Mn	Mg	Ca	Na	K
Long Lake	N35 b-0.018 c4.82 r0.018 No	N35 b-0.0059 c1.51 r0.058 No	N35 b0.0082 c0.13 r0.27 No	N35 b0.0092 c0.21 r0.20 No	N35 b0.0019 c0.45 r0.039 No
Lavant-Clyde	N29 b0.0006 c14.25 r9.07x10 ⁻⁷ No	N29 b0.00005 c1.01 r3.30x10 ⁻⁶ No	N 29 b0.0021 c0.39 r0.0057 No	N29 b0.018 c0.19 r0.27 Yes	N29 b-0.0004 c0.35 r0.0023 No
Sulphide Creek	N13 b0.0031 c1.45 r0.0006 No	N13 b0.013 c0.25 r0.23 Yes	N13 b0.0004 c0.17 r0.0033 No	N13 b0.0072 c0.046 r0.52 No	N13 b0.049 c-0.097 r0.37 Yes(c?)
Moir River	N61 b0.10 c7.84 r0.068 No	N61 b-0.021 c2.49 r0.068 No	N61 b-0.0008 c0.65 r0.0009 No	N61 b0.0013 c0.16 r0.019 No	N61 b0.0041 c0.31 r0.13 No
Calumet Island	N9 b-0.25 c13.69 r0.15 No	N9 b-0.023 c1.19 r0.88 No	N9 b-0.035 c1.46 r0.17 No	N9 b-0.0005 c0.087 r0.053 No	N9 b-0.0045 c0.39 r0.081 No

Table 5.3 Regression data for R vs. CEC, degree 2

Area	Cu	Pb	Zn	Ni	Fe
Long Lake	N14	N8	N35	N8	N35
	a-0.0006	a0.0088	a-0.0041	a-0.0013	a0.00016
	b0.12	b-0.38	b0.70	b0.18	b-0.091
	c0.12	c0.49	c-6.40	c-0.44	c43.89
	r0.33	r0.47	r0.25	r0.50	r0.0096
	Yes	No	No	Yes(c?)	No
Lavant Clyde	N6	N15	N29	N2	N29
	a0.0027	a-0.0007	a0.010		a0.018
	b-0.086	b0.13	b-0.015	Insuff.	b-1.35
	c5.55	c1.38	c57.17	Data	c158.43
	r0.44	r0.072	r0.092		r0.036
	Yes	No	No		No
Sulphide Creek	N6	N13	N13	N8	N13
	a-0.021	a-0.013	a-0.0013	a-0.009	a-0.015
	b1.28	b0.71	b0.10	b0.77	b0.77
	c-5.88	c-2.23	c0.39	c-0.66	c22.92
	r0.96	r0.31	r0.25	r0.46	r0.045
	Yes(c?)	Yes	Yes	Yes(c?)	No
Moirs River	N5	N21	N61	N8	N61
	a11.52	a0.0044	a-0.0023	a-0.0068	a-0.0016
	b-904.4	b-0.58	b0.33	b0.75	b0.55
	c17016.5	c24.64	c-0.14	c-1.81	c68.40
	r0.98	r0.077	r0.26	r0.14	r0.021
	No	No	Yes(c?)	Yes(c?)	No
Calumet Island	N9	N4	N9	N3	N9
	a0.061	a-2.34	a0.032		a0.058
	b-4.31	b64.93	b-2.13	Insuff.	b-3.93
	c64.17	c-260.09	c30.10	Data	c71.37
	r0.31	r0.81	r0.60		r0.29
	No	No	No		No

Table 5.3 cont'd

Area	Mn	Mg	Ca	Na	K
Long Lake	N35 a- 9.62×10^{-6} b-0.016 c4.79 r0.018 No	N35 a- 3.15×10^{-5} b- 8.52×10^{-4} c1.38 r0.061 No	N35 a0.00023 b-0.029 c1.02 r0.66 No	N35 a 4.5×10^{-6} b0.0085 c0.22 r0.20 No	N35 a- 7.0×10^{-5} b0.013 c0.18 r0.14 No
Lavant-Clyde	N29 a-0.0019 b0.23 c8.40 r0.0065 No	N29 a-0.00005 b0.0061 c0.86 r0.0027 No	N29 a0.00005 b-0.0044 c0.55 r0.0085 No	N29 a0.00008 b0.0074 c0.45 r.028 No	N29 a0.00001 b-0.0021 c0.39 r0.0038 No
Sulphide Creek	N13 a-0.004 b0.19 c0.0090 r0.12 No	N13 a-0.0011 b0.065 c-0.15 r0.42 No	N13 a-0.00044 b0.020 c0.017 r0.39 No	N13 a0.00005 b0.0046 c0.066 r.053 Yes(b?)	N13 a-0.0004 b0.068 c-0.24 r0.37 Yes(c?)
Moir River	N61 a-0.0014 b0.27 c4.16 r0.087 No	N61 a0.00049 b-0.084 c3.81 r0.12 No	N61 a0.00012 b-0.016 c0.94 r0.026 No	N61 a-0.00003 b0.0052 c0.077 r0.037 No	N61 a-0.00006 b0.012 c0.15 r0.17 Yes
Calumet Island	N9 a0.019 b-1.37 c21.83 r0.31 No	N9 a0.0017 b-0.12 c1.92 r0.17 No	N9 a0.0028 b-0.20 c2.65 r0.36 No	N9 a0.00005 b-0.0032 c0.11 r0.12 No	N9 a0.0002 b-0.017 c0.48 r0.11 No

Table 5.4 Regression data for R vs. TOC, degree 1

Area	Cu	Pb	Zn	N1	Fe
Long Lake	N14 b-0.019 c4.21 r0.0016 No	N8 b-0.064 c3.54 r0.023 No	N35 b-0.15 c13.30 r0.0035 No	N8 b-0.02 c3.88 r0.0018 No	N35 b-2.20 c70.03 r0.21 Yes
Lavant-Clyde	N6 b0.33 c3.36 r0.32 No	N15 b-0.40 c0.91 r0.14 Yes(r?)	N29 b0.29 c9.19 r0.0011 No	N2 Insuff. Data	N29 b-7.65 c220.34 r.047 Yes
Sulphide Creek	N6 b0.67 c-0.69 r0.37 No	N13 b-0.31 c8.14 r0.12 Yes(r?)	N13 b-0.05 c2.16 r0.043 No	N8 b-0.54 c15.99 r0.13 Yes(r?)	N13 b-0.52 c36.09 r0.047 No
Moirs River	N5 b-54.12 c1266.11 r0.12 No	N21 b0.29 c7.97 r0.033 No	N61 b-0.13 c9.28 r0.015 No	N8 b-0.53 c20.30 r0.029 No	N61 b-5.46 c166.17 r0.17 Yes(r?)
Calumet Island	N9 b1.31 c12.48 r0.016 No	N4 b-21.06 c316.82 r0.53 Yes(N?)	N9 b0.86 c2.98 r0.063 No	N3 b-1.89 c31.61 r0.95 Yes(N?)	N9 b-0.14 c40.11 r0.00022 No

Table 5.4 cont'd

Area	Mn	Mg	Ca	Na	K
Long	N35	N35	N35	N35	N35
Lake	b-0.15	b-0.04	b0.044	b0.018	b0.00018
	c5.99	cl.77	c-0.076	c0.41	c0.54
	r0.025	r0.053	r0.15	r0.015	r7.2x10 ⁻⁶
	No	No	No	No	No
Lavant-	N29	N29	N29	N29	N29
Clyde	b-1.47	b-0.05	b-0.025	b0.0088	b-0.022
	c28.16	cl.48	c0.74	cl.05	c0.54
	r0.10	r0.073	r0.017	r0.0013	r0.11
	Yes(r?)	No	No	No	No
Sulphide	N13	N13	N13	N13	N13
Creek	b0.22	b0.05	b0.0099	b-0.0073	b-0.0016
	c-1.10	c-0.11	c0.063	c0.26	c0.77
	r0.44	r0.45	r0.25	r0.074	r5.7x10 ⁻⁵
	No	No	No	No	No
Moirs	N61	N61	N61	N61	N61
River	b0.17	b0.023	b-0.019	b0.015	b0.0044
	c9.31	cl.32	c0.87	c-0.0085	c0.41
	r0.0066	r0.0027	r0.015	r0.091	r0.0048
	No	No	No	No	No
Calumet	N9	N9	N9	N9	N9
Island	b0.72	b0.15	b0.14	b-0.0028	b0.041
	cl.87	c-0.82	c-0.61	c0.11	c-0.14
	r0.045	r0.12	r0.091	r0.052	r0.23
	No	No	No	No	No

Table 5.5 Regression data for R vs. TOC, degree 2

Area	Cu	Pb	Zn	Ni	Fe
Long Lake	N14 a-0.0084 b0.30 c1.4 r0.011 No	N8 a0.062 b-2.26 c1.20 r0.97 Yes	N35 a-0.0078 b0.098 c1.57 r0.0040 No	N8 a0.0077 b-0.31 c6.28 r0.0096 No	N35 a0.16 b-7.50 c106.83 r0.28 Yes
Lavant -Clyde	N6 a0.32 b-0.22 c5.09 r0.37 No	N15 a-0.016 b-0.14 c8.33 r0.15 Yes(r?)	N29 a-0.24 b4.42 c5.57 r0.017 No	N2 Insuff. Data	N29 a-0.29 b2.68 c202.60 r0.048 No
Sulphide Creek	N6 a0.13 b-2.85 c20.03 r0.55 No	N13 a0.12 b-3.24 c24.20 r0.38 Yes	N13 a0.04 b-1.04 c7.58 r0.43 No	N8 a0.17 b-5.02 c40.11 r0.34 Yes	N13 a0.38 b-10.00 c87.99 r0.42 Yes
Moirs River	N5 a1.81 b-113.93 c1,666.71 r0.12 No(N?)	N21 a-0.10 b3.26 c-9.58 r0.14 No	N61 a-0.035 b0.91 c2.52 r0.052 No	N8 a-0.18 b4.78 c-13.83 r0.15 No	N61 a0.13 b-9.36 c191.66 r0.17 Yes
Calumet Island	N9 a-0.60 b15.04 c-61.23 r0.027 No	N4 Notdet'd. Have 3 stations equal TOC value.	N9 a-1.31 b30.80 c-157.80 r0.58 No	N3 Insuff. data	N9 a-2.99 b68.14 c-326.54 r0.37 No

Table 5.5. cont'd

Area	Mn	Mg	Ca	Na	K
Long Lake	N35 a0.067 b-2.31 c21.00 r0.31 Yes	N35 a-0.0099 b-0.0083 c1.55 r0.055 No	N35 a0.0085 b-0.23 c1.82 r0.48 No	N35 a0.0023 b-0.058 c0.93 r0.029 No	N35 a-0.0016 b0.051 c0.18 r0.032 No
Lavant-Clyde	N29 a-0.034 b-0.89 c26.08 r0.10 Yes(?)	N29 a0.016 b-0.33 c2.50 r0.25 No	N29 a0.000075 b-0.027 c0.75 r0.017 No	N29 a0.018 b-0.30 c2.16 r0.12 No	N29 a0.000022 b-0.022 c0.54 r0.11 No
Sulphide Creek	N13 a0.0013 b0.19 c-0.92 r0.44 No	N13 a0.0083 b-0.16 c1.01 r0.63 No	N13 a0.0029 b-0.062 c0.46 r0.54 No	N13 a0.0016 b-0.046 c0.47 r0.12 No	N13 a0.0051 b-0.13 c1.46 r0.0078 No
Moir River	N61 a0.066 b-1.80 c22.24 r0.037 No	N61 a-0.016 b0.50 c-1.78 r0.043 No	N61 a-0.0036 b0.088 c0.17 r0.032 No	N61 a0.00039 b0.0035 c0.066 r0.093 No	N61 a0.0011 b-0.03 c0.63 r0.015 No
Calumet Island	N9 a-0.69 b16.54 c-83.06 r0.19 No	N9 a-0.033 b0.91 c-4.90 r0.14 No	N9 a-0.087 b2.13 c-11.30 r0.22 No	N9 a-0.0014 b0.028 c-0.058 r0.094 No	N9 a-0.021 b0.53 c-2.77 r0.45 No

TOC values. As predicted by equation (iii), deviations will result in a CEC plot if the element has a strong affinity for organic reaction. This can be interpreted as evidence for a TOC influence on the Fe ratios; however, there are exceptions to this observation.

The data for Ni suggest sorption reactions to be of significance for at least Long Lake and Sulphide Creek. The Moira River data exhibit a low r . This is in response to pH and possibly carbonate and sulphide precipitation at 2 stations and to high TOC values recorded at 2 other stations. This is reflected in the TOC plot shown in figure 5.3. The carbonate and sulphide interference occurs for two stations (61 and 43) on Moira Lake where pH has increased to about 7.9 compared with 7 in the river. As it is a lake sediment with probably a more reduced environment, sulphide precipitation may also interfere. The result of this is a far larger R value than would be expected based on CEC values.

The Cu data for the Moira River are strongly influenced by an anomalous Cu source producing Cu precipitation. This occurs at station 31 downstream for the tailings at the Deloro site. Analytical error is probably a factor for the Cu data as water contents are often around the detection limit of 2 ppb. The data do, however, imply a Cu dependence on sorption. Degree 1 functions for Sulphide Creek and Lavant-Clyde suggest this. The degree 2 function for Long Lake is also acceptable as the curvature occurs in response to 3 stations plotting

anomalously low at high CEC. The explanation for this is not obvious from the available data.

Pb and Zn are not strongly influenced by CEC. The exceptions are Sulphide Creek for Pb, and Sulphide Creek and Molra River for Zn. TOC appears a major interference on the CEC plots as several stations with high TOC and high CEC plot with lower R values than would be expected based on CEC alone. The degree 2 function for Zn from Molra River proved acceptable with high TOC proving an important variable.

The data for Calumet Island are worth consideration. The stream drains through the tailings pond of the abandoned New Calumet mine site. The carbonate host rock for this ore is being weathered with an expected high influx of carbonate to the stream. This is evidenced by the detectable carbonate at the seven stations below the pond (stations 1 to 7). In conjunction with this, anomalously high metal is being supplied to the system. The regression data consequently show negative slopes and high intercepts. A high intercept is consistent with the anticipated high rate of metal precipitation in the stream. The negative slopes are interpreted as being a result of decreased metal precipitate content and increased organic and clay content away from the mine site.

As for the CEC plots, Na, K, Mg and Ca exhibit generally low b and r values. The available data do not lead to any conclusions regarding the nature of the interfering reactions. It is concluded that these elements are not controlled by

Figure 5.3 Plot of R versus TOC for Ni (Moira River).

Figure 5.4 Plot of R versus TOC for Pb (Long Lake).

Figure 5.5 Plot of R versus TOC for Pb (Moira River).

sorption reactions. The data for Mn suggest that it is subject to several reactions in addition to sorption and organic complexing.

Of all the 10 elements studied, Fe shows the most pronounced dependence on TOC. The degree 2 function for Sulphide Creek is acceptable but one anomalous station with a higher than expected R, is observed. This may be a spatial problem as a railroad runs within thirty feet of this station possibly increasing the precipitated Fe in the sediment. The Fe result is in accord with known metal-humate and fulvate stability constants; of the 10 elements, Fe has the highest stability. This result also supports the reviewed field evidence in favour of Fe-organic complexing in natural waters.

The organic complexing reaction has little effect on the Cu. High CEC values are the most obvious cause for deviations from a predicted TOC plot. This is in accord with the conclusions based on the CEC data.

The Pb data suggest that its behaviour is strongly influenced by the organic complexing. Leland et al. (1973) also propose organic complexing as an important mechanism in Pb dispersion. The degree 2 function for Long Lake is acceptable but one anomalous station is observed (number 27). Figure 5.4 illustrates this; the curve shown is fitted by observation only. The interfering reaction may involve Mn precipitation and coprecipitation as the sediment content of station 27 is highly anomalous in Mn. The Pb data from the Moira River illustrate

the possible interfering reactions brought out by temporal factors, in this case, rainfall (see figure 5.5). Stations 53, 54, 55, 56, 57, 58, 61 and 62 are anomalous with low R values and low TOC. This sampling took place after several days of heavy rainfall. The effect of this has been to increase the soluble Pb content but not via organic reaction. Station 59 is also anomalous with a large R. It is suggested that contamination is likely, considering its location within the village of Madoc, thus giving high precipitated Pb content in the sediment.

The degree 1 and 2 functions for Zn are characterized by low r values. However, from the available data, it is not possible to suggest what the interfering reactions are. The degree 2 functions appear meaningless.

The Ni data for Long Lake are apparently influenced by the competing reaction involving the high Mn content for station 27 as previously discussed for Pb. However, the influence of low CEC is also reflected in the data leading to lower R than predicted. Ni is apparently influenced by both sorption and organic complexing. The Moira River data (see figure 5.3), as observed for CEC, are influenced by competing reaction due to presence of hydroxide, carbonate and possibly sulphide at stations 61 and 43.

(d) Conclusions.

From the above discussion the behaviour of the elements as observed in the field can be summarized as follows;

1. Na, K, Mg, Ca and Mn are not dominantly influenced by CEC or TOC. Failure to identify any consistent influences due to CEC or TOC indicates that, for these elements, the scheme involving reactions (i) and (ii) is inadequate. This is to be expected for Na, K, Mg and Ca considering their inorganic solubilities and low affinity for organic complexing.
2. The proposed reaction scheme does give an insight into the behaviour of Fe. Of the two reactions, organic complexing is the more dominant with sorption having little apparent effect on the distribution ratio, R. This implies that, with increased soluble organic matter, the dispersion of Fe in natural waters will be enhanced considerably.
3. The behaviour of Pb is similar to that of Fe with organic complexing being the more dominant reaction. However, the influence of sorption is more evident for Pb compared with Fe. While an increase in soluble organic matter will favour the dispersion of Pb in natural waters, an accompanying increase in the exchange capacity of a sediment would tend to suppress somewhat the Pb dispersion.
4. Cu shows the opposite behaviour to Pb. Its dispersion in natural waters is decreased as the sediment exchange capacities increase leading to Cu partitioning to the sediment phase. However, for an accompanying increase in soluble organic matter, the Cu partitioning to the sediment is suppressed implying that Cu is involved in organic complexing.

5. The behaviour of Ni is under some influence due to sorption, reaction (1). However, its behaviour is characterized by the effect of interfering reactions which have no measurable effect on the other 9 elements. Of particular importance are the reactions with competing ligands, hydroxide, carbonate and possibly sulphide.

The data for Sulphide Creek are worthy of further consideration (see table 5.6). The pH for stations 1 to 5 is in the 6.30 to 6.40 range; the pH changes to 6.75 up to 7.60 for stations 6 to 13. The change from metavolcanics to leucocratic granites represents the only geological boundary crossed by the creek. However, it might be possible that carbonate rocks outcropping in the area have an increased influence on the creek's elemental composition in the lower reaches of its drainage; the geology does not help here. Consideration of the Ni content of the waters shows a decrease with increasing pH (table 5.6). Except for stations 1 and 3, the Zn content of the waters shows little variation. If hydrolysis was the important consideration leading to decreased metal solubility with increased pH, then, based on the laboratory model, Ni and Zn should both be affected. However, carbonate reactions preferentially affect Ni solubility.

It has been previously suggested that stations 1 to 5 are influenced by a source enriched in Cu, Pb, Zn and Ni. However, if it was source alone that leads to an increased soluble Ni content, then the effect should be stronger for water samples 31, 32 and 33 collected from the Moira River at

Table 5.6 Selected analytical data from Sulphide Creek.

Sample Station	pH	<u>Water</u>			<u>Sediment</u>	
		TOC (ppm)	Ni (ppb)	Zn (ppb)	Ni (HCl, ppm)	CEC (me/100g).
1	6.30	16	2	368	22	34.3
2	6.35	7	12	35	46	14.0
3	6.35	6	8	144	180	26.2
4	6.30	8	16	90	280	43.6
5	6.40	7	4	50	55	12.9
6	6.75	16	<2	36	5	18.3
7	7.00	12	<2	35	18	9.6
8	6.90	15	<2	40	17	8.2
9	6.90	16	<2	37	20	11.2
10	7.00	9	<2	83	6	6.6
11	7.00	20	3	35	22	26.3
12	7.25	12	2	36	7	8.1
13	7.60	10	2	60	5	4.6

locations downstream from Deloro as source here is more enriched in Ni than the Sulphide Creek localities. The sediments from these sample locations record up to 1100ppm adsorbed Ni whereas the waters do not have detectable Ni contents ($< 2\text{ppb}$). The pH of these waters is in the range 6.70 to 7.10. For the Moira River samples, increased sulphide levels, being introduced with the Ni, may also be a factor in the low Ni solubility. However, effects of pH and carbonate precipitation on Ni solubility are well evidenced in the Sulphide Creek data.

6. The behavioural controls for Zn are difficult to determine on the basis of the data. The reaction scheme proposed does appear to have some application to Zn with sorption (CEC) and organic complexing (TOC) having an influence on the distribution ratio, R, for Zn. Similar reactivities in sorption and organic complexing could explain the scattering of points observed for the Zn plots. However, unknown interfering reactions might also produce the same result.

SUMMARY AND CONCLUSIONS.

In summary, a comparison of the laboratory predictions with the behaviour observed in the field will be made. However, a point which must be taken into account is the abundance of dissolved organic carbon compared with water trace element content. The TOC values for the streams sampled, fall within a range of 1 to 30ppm which is consistent with the literature values. This will be an excess compared with the ppb levels of Cu, Pb, Zn, Ni, Mn and Fe. However, Mg, Ca, Na and K are in the ppm range. Complexing of the dissolved organic matter by these elements, particularly Ca and Mg (Duursma, 1970), will reduce the number of organic active sites available for further reaction. Beck et al. (1974) have, however, concluded that, for coastal plain rivers rich in soluble organics, Mg, Ca, Na and K undergo little, if any, reaction with soluble organic matter. Hence, the extent of the organic complexing by these elements in natural waters is uncertain. The laboratory experiments have emphasized the significance of the metal-organic acid site milliequivalences. In the field systems studied, where the soluble organics are considerably more difficult to characterize, the metal-organic acid active site ratio is not known. The possibility of a metal excess and, hence the formation of insoluble metal-organic species, cannot be ruled out.

From the laboratory model experiments, the following predictions were made with regard to the behaviour of Cu, Pb, Zn and Ni at a sediment-water boundary with hydroxide (pH) and

carbonate present as competing ligands:

- (i) All four elements are stabilized in solution by organic complexing; the magnitude of this effect generally decreases in the order Cu, Ni, Zn and Pb.
- (ii) The solubility of Zn and Ni via organic complexing is pH-dependent decreasing with increasing pH. Hydrolysis and clay sorption processes affect their solubilities with hydrolysis having a more significant effect for Ni.
- (iii) Ni solubility, and possibly Zn solubility, are decreased even further in the presence of soluble carbonate.
- (iv) The solubility of Pb-organic complexes appears susceptible to colloidal coagulation phenomena.
- (v) Organic acids are capable of remobilizing Cu, Pb, Zn and Ni from a sediment phase. Of the four elements, Cu desorption is the most kinetically hindered process.

A comparison of the laboratory predictions and field observations proves useful. Soluble organics in the field lead to Pb partitioning to a solution phase. While this is not inconsistent with the laboratory data, it does suggest a modification in the laboratory model. Pb-organic solubility in the laboratory is affected by the molecular size of the humic and fulvic acids used (colloidal coagulation). A comparison of the Pb field data with those of Cu, Zn and Ni (which do not show a strong correlation with TOC) indicates that the solubility of Pb-organic complexes, in stream waters, is enhanced over the laboratory model. This implies that stream water organic

chelating compounds will have lower molecular weights than the humic mud extracts used and will approach true solution as distinct from colloidal dispersion. It is consistent with solubility considerations that the lower end of the molecular weight spectrum for humic and fulvic acids will be predominant in stream waters. The introduction of stream water organics into the model experiments, in place of mud or soil extracts, is the logical modification. However, the techniques involved in isolating such material, in useable quantities, are poorly understood.

The field observation that the Cu distribution ratio is not positively correlated with TOC and, in fact, for Sulphide Creek and Lavant-Clyde, is adversely affected by TOC (i.e. higher TOC values produce a Cu partitioning to the sediment) but is related to sorption (CEC), is compatible with aspects of the laboratory model although a further modification in the model is indicated by the field data. Of the four metals, Cu showed the strongest retention in solution for the laboratory model; however, the adsorbent phase used was clay. The field sorption processes are very dependent on sediment organic content. The literature reviewed (chapter 1.5) indicated that the sorption of Cu by solid and particulate organic matter was a particularly efficient process. Highly organic sediments, collected from swampy terrains, will also often have high TOC values in the associated waters (due to leaching of sediment organic content). This leads to the observation that TOC may have an

adverse effect on Cu partitioning to solution as it is the more efficient solid organic sorption which controls the Cu behaviour. As a further point, highly organic sediments are likely to be enriched in sulphide due to organic degradation. Timperley and Allan(1974) have shown that Cu is strongly fixed by sulphide in organic lake sediments. This mechanism further works in favour of Cu partitioning to the sediment. The modification suggested from this is the use of a solid, organic-bearing adsorbent phase. This was considered during the course of the experimental work. A problem is anticipated with leaching of the solid organic material during the course of the reactions which would require continual monitoring of the soluble organic content and solid phase organic content available for reaction. The introduction of sulphide into the model would help clarify whether organic sorption or Cu sulphide formation is the more important process partitioning Cu to the sediment.

The fact that Cu humate and fulvate formation in solution are not affected by clay sorption processes in the laboratory does imply that the sorption mechanism in the field is indeed related to the sediment organic and/or sulphide content. A further point is the kinetics operative within the field. The desorption studies in the laboratory indicated that Cu release from a sediment phase is the most kinetically hindered. The sediment-water equilibration in the field may be such that little Cu is being released from the sediment for reaction with

the soluble organic matter. If this is so, then it implies that it is not the stability of Cu-organic complexes in solution which is the important consideration but it is the rate of Cu release from a sediment or solid phase which is the more significant factor. This kinetic consideration is possibly amplified in the field areas where Cu is more strongly sediment bound compared with the Cu-clay sorption of the laboratory experiments.

The field observation that the distribution ratio of Zn is not strongly related to TOC does suggest that, in this case, the laboratory model is a reasonable one. The Zn ratios in fact plot quite randomly (low r values) with TOC. This can be related to pH of the waters in the field areas. The laboratory model predicted that the solubility of Zn will decrease with increasing pH. The pH values for the water samples collected are predominantly around 7 and fall in the range 6.6 to 7.6. It is around this pH range in the laboratory experiments that the solubility of Zn is susceptible to hydrolysis and sorption. This effect is more pronounced for the humic acid reactions which perhaps indicates that, whatever characterizes the humic acid reaction with Zn compared to reaction with fulvic acid, it is a better representation of the organic reactions in natural waters. One possible factor here is the lower functional group content of humic acids compared with fulvic acids. Hence, while (for solubility reasons) the organic content of natural waters is better represented by the fulvic

acid molecule, it may not have the characteristic fulvic acid functional group content. This leads to the same modification suggested on the basis of the Pb data, i.e. the use of stream water organic material in place of soil and mud extracts.

The laboratory model suggested that Zn solubility is more influenced by sorption processes with clay than hydrolysis. The field observation that the Zn distribution ratio for the Moira River and Sulphide Creek are influenced by CEC is consistent with the laboratory model only if clay sorption processes are involved. The plots of OC against CEC (figure 5.2) indicate an exchange capacity of about 5 me/100g. can be attributed to the clay content. This is perhaps too low to be of significance. Timperley and Allan (1974) have shown that organic sorption and possibly sulphide precipitation are the significant mechanisms involved in fixing Zn to organic lake sediments. The modification, suggested on the basis of the Cu data, of using an organic-bearing solid phase would also prove useful in the interpretation of the Zn data.

The regression analysis of the field data for Ni suffers from a paucity of observations. Yet, this is compatible with the predictions based on the laboratory model. Except for Sulphide Creek, Ni is rarely detected in the waters collected. The pH of the waters and the ubiquity of carbonate rocks in the field areas are important considerations. The laboratory

model predicted that Ni solubility is decreased more significantly by hydrolysis with sorption also having an effect; the introduction of soluble carbonate further decreases Ni solubility. For the natural waters sampled, pH and probably the carbonate content (although this has not been analysed) are such that Ni solubility is likely to be low, irrespective of the total dissolved organic carbon content (TOC).

The reaction scheme proposed in the interpretation of the field data proved useful in gaining an understanding of the behaviour of the ten elements studied. Continued use of this approach to the problems of geochemical dispersion would benefit greatly from laboratory model experiments designed to delineate the relationship between Ra and CEC for a particular element at constant TOC, and ~~the~~ relationship between MO/M_F and TOC at constant CEC for a particular element. The effects of varying TOC and CEC respectively could then be studied. With this type of information, a more accurate prediction of expected field relationships would be feasible. It may also prove possible to include a more definite estimate of how additional competing reactions will influence the predictions. Laboratory model experiments could allow such refinements.

Appendix 1: Time study for experimental reaction systems.

(Note: mix C components used

M: 25 ppm of each divalent cation

F: 0.5% fulvic acid,

H: 0.02% humic acid

K: 100mg Flint clay (kaolin)

B: 100mg. bentonite.)

REACTION	INITIAL pH	TOTAL METAL IN SOLUTION (ppm)					
		TIME (days)					
		2.0	4.0	5.5	15	30	60
<u>M</u> metal	4.00	Cu	24.5	25.0	24.0	23.5	24.0
		Ni	25.0	24.0	24.5	23.0	23.0
		Pb	23.0	22.0	22.0	22.5	22.0
		Zn	25.0	25.0	24.5	24.0	24.0
	6.00	Cu	18.5	17.5	17.5	18.0	18.0
		Ni	24.0	23.5	23.5	24.0	22.5
		Pb	14.0	13.0	13.0	14.0	13.5
		Zn	23.0	22.5	22.5	21.5	22.0
	8.00	Cu	0	0	0	0	0
		Ni	11.0	10.5	11.0	9.0	10.0
		Pb	0	0	0	0	0
		Zn	6.5	5.5	5.0	4.5	7.0
<u>M+F</u> metal fulvic	4.10	Cu	24.0	24.5	24.5	23.0	24.0
		Ni	25.0	24.5	24.0	23.5	24.0
		Pb	6.0	5.0	5.5	6.0	5.0
		Zn	25.0	24.0	25.0	23.5	24.0
	6.00	Cu	24.5	24.0	24.0	24.0	24.5
		Ni	24.0	24.0	24.5	24.0	22.0
		Pb	6.0	6.5	7.0	6.5	6.0
		Zn	24.5	25.0	24.0	24.0	23.5
	8.00	Cu	24.0	23.5	24.0	25.0	23.5
		Ni	23.5	22.5	22.0	22.5	22.5
		Pb	17.0	16.0	15.5	14.0	16.5
		Zn	24.0	24.0	22.5	24.0	24.5

<u>M+H</u> metal humic	4.00	Cu	24.5	24.0	24.0	23.5	24.0	24.0
		Ni	24.0	25.0	24.0	24.5	24.0	24.0
		Pb	16.0	14.0	15.5	14.0	15.0	15.0
		Zn	25.0	24.5	24.0	24.5	25.0	25.0
	6.10	Cu	23.5	24.0	24.0	21.0	23.5	24.0
		Ni	24.0	24.0	23.0	22.5	23.5	23.0
		Pb	14.0	11.0	12.0	12.0	13.0	12.0
		Zn	24.0	22.0	22.5	23.0	22.0	23.0
	8.00	Cu	25.0	24.0	24.0	22.0	23.0	23.5
		Ni	22.0	19.0	20.0	20.5	20.0	19.5
		Pb	14.0	16.0	13.0	13.0	14.0	13.0
		Zn	16.0	14.0	14.5	15.0	14.5	15.0
<u>M+K</u> metal kaolin	4.00	Cu	16.0	15.5	16.0	16.5	16.0	16.0
		Ni	23.0	22.5	23.0	22.5	20.5	23.0
		Pb	10.0	9.5	9.0	8.0	7.0	9.5
		Zn	24.0	23.5	23.0	23.0	20.5	23.5
	6.10	Cu	0	0	0	0	0	0
		Ni	18.0	17.0	17.5	17.0	14.5	17.0
		Pb	0	0	0	0	0	0
		Zn	16.0	16.0	15.0	16.5	14.0	15.5
	8.00	Cu	0	0	0	0	0	0
		Ni	0	0	0	0	0	0
		Pb	0	0	0	0	0	0
		Zn	0	0	0	0	0	0

<u>M+B</u> metal bent.	4.00	Cu	6.0	7.0	6.5	7.0	6.0	6.5
		Ni	9.0	8.0	8.5	8.5	6.0	8.0
		Pb	4.0	3.0	3.5	3.0	2.5	3.0
		Zn	8.0	8.0	7.0	7.5	6.0	7.5
	6.00	Cu	0	0	0	0	0	0
		Ni	3.0	3.5	3.0	2.5	3.0	3.0
		Pb	0	0	0	0	0	0
		Zn	3.5	3.5	3.0	3.0	5.0	3.0
	8.00	Cu	0	0	0	0	0	0
		Ni	0	0	0	0	0	0
		Pb	0	0	0	0	0	0
		Zn	0	0	0	0	0	0
<u>M+F+K</u> metal fulvic kaolin	4.00	Cu	20.5	18.5	17.0	17.0	14.0	16.0
		Ni	18.0	19.0	18.0	15.0	18.5	18.0
		Pb	4.0	4.0	3.0	2.5	3.0	3.0
		Zn	16.0	14.0	15.0	14.5	12.0	14.5
	6.00	Cu	20.5	20.0	19.5	15.0	18.0	19.0
		Ni	19.5	19.0	17.0	18.0	17.5	17.0
		Pb	7.0	5.0	5.5	4.5	5.0	5.0
		Zn	15.0	13.0	11.0	10.5	12.5	12.0
	8.00	Cu	21.0	21.0	20.0	18.0	19.5	20.0
		Ni	18.5	18.0	17.0	17.0	16.0	17.0
		Pb	15.5	14.0	13.0	10.5	13.0	12.0
		Zn	20.5	18.5	19.0	17.5	19.0	19.5

metal fulvic bent.	<u>M+F+B</u>		Cu	18.5	16.0	15.0	14.0	16.0	14.5
	4.10		Ni	17.0	16.0	15.0	15.5	13.5	15.0
			Pb	5.0	4.0	4.0	3.5	3.0	3.5
			Zn	17.0	16.5	16.0	16.0	14.0	16.0
			Cu	18.5	16.5	13.5	14.0	10.5	14.0
	6.00		Ni	17.0	15.0	12.5	16.0	13.5	14.0
			Pb	4.0	2.0	2.0	2.0	1.0	2.0
			Zn	10.5	11.0	8.5	7.0	9.0	8.5
			Cu	18.5	17.0	13.5	14.0	14.0	13.0
	8.10		Ni	16.0	14.0	13.0	14.0	12.5	13.0
			Pb	4.0	5.5	4.0	3.5	3.0	4.0
			Zn	11.0	9.5	8.0	9.0	10.0	9.0
Cu			20.0	18.0	17.5	16.0	19.0	18.5	
metal humic kaolin	<u>M+H+K</u>		Ni	22.0	24.0	21.0	22.0	20.5	22.0
	4.00		Pb	12.0	12.0	10.5	12.0	10.0	9.5
			Zn	22.0	21.5	20.0	22.0	20.5	20.0
			Cu	20.5	20.5	21.0	23.5	21.0	21.5
			Ni	22.0	20.0	20.5	20.0	22.0	20.0
	6.00		Pb	10.0	8.0	8.5	10.0	9.0	8.5
			Zn	18.0	17.5	15.0	14.0	14.0	14.5
			Cu	20.0	21.0	21.0	23.5	20.0	21.0
			Ni	16.0	15.0	14.0	10.5	13.5	13.0
	8.10		Pb	10.0	9.0	5.0	8.0	7.5	7.5
			Zn	8.5	8.0	6.5	7.0	7.5	7.0

metal humic bent.	<u>M+H+B</u> 4.00	Cu	17.0	12.0	12.0	13.0	10.0	12.5
		Ni	18.0	17.0	16.0	17.5	15.0	17.0
		Pb	9.0	8.5	8.0	9.0	7.5	7.5
		Zn	19.0	18.0	14.0	17.5	17.0	17.0
	6.10	Cu	20.5	16.0	15.0	16.5	16.0	16.0
		Ni	16.0	13.0	14.0	12.5	15.0	14.0
		Pb	7.0	6.0	5.0	8.0	4.5	5.0
		Zn	10.0	7.0	8.0	7.5	7.0	7.5
	7.90	Cu	20.5	16.5	15.5	14.0	16.0	16.5
		Ni	8.0	7.5	6.0	9.5	7.0	7.0
		Pb	8.0	6.0	5.0	7.0	5.0	5.0
		Zn	4.0	3.0	1.5	1.0	1.0	1.0

Appendix 11 - Analytical data for the low ionic
strength, unbuffered reactions discussed
in Chapter 3.

- (a) data for salicylic acid reactions
- (b) data for mix A reactions
- (c) data for mix B reactions
- (d) data for mix C reactions
- (e) data for mix C^{*} (desorption) reactions.

Note: pH_I : initially set pH of solution
 pH_F : final measured pH of solution
TM : total metal in solution.

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App. 11a	Cu					
REACTION	pH and total metal in solution (ppm)					
<u>M</u>	pH _I	4.10	5.30	6.20	7.20	8.50
metal	pH _F	4.15	5.30	6.20	7.00	7.40
	TM	50.0	41.0	1.0	0	0
<u>M+K</u>	pH _I	4.25	5.60	6.75	7.75	8.75
metal	pH _F	5.00	5.60	6.60	7.00	7.20
kaolin	TM	36.5	21.0	0	0	0
<u>M+O</u>	pH _I	4.00	5.10	6.40	7.80	9.15
metal	pH _F	4.10	5.20	6.45	7.60	8.10
sal. acid	TM	48.0	47.0	39.0	37.0	36.0
<u>M+O+K</u>	pH _I	4.00	5.30	6.65	7.70	9.10
metal	pH _F	5.00	5.70	6.95	7.45	8.00
sal. acid	TM	38.0	30.0	21.0	16.0	14.0
kaolin						

App 11a

N1

REACTION		pH and Total Metal in Solution (ppm)				
<u>M</u> metal	pH _I	4.00	5.60	6.90	7.50	9.00
	pH _F	4.25	5.90	6.75	6.90	7.55
	TM	50.0	47.0	45.5	47.5	21.0
<u>M+K</u> metal kaolin	pH _I	4.20	5.60	6.80	8.00	9.05
	pH _F	5.05	6.10	6.65	7.20	7.90
	TM	37.5	30.0	21.5	0	0
<u>M+O</u> metal sal. acid	pH _I	4.25	5.40	6.65	7.85	9.00
	pH _F	4.90	6.00	7.30	7.65	8.25
	TM	50.00	49.0	7.5	2.0	1.5
<u>M+O+K</u> metal sal. acid kaolin	pH _I	4.10	5.30	6.40	7.70	8.80
	pH _F	5.20	5.95	6.80	7.80	8.25
	TM	45.0	41.0	1.0	0	0

App. 11 a Pb

REACTION		pH and Total Metal in Solution (ppm)				
<u>M</u> metal	pH _I	4.30	5.45	6.80	8.20	9.05
	pH _F	4.50	5.85	6.95	7.30	7.45
	TM	50.0	12.5	0	0	0
<u>M+K</u> metal kaolin	pH _I	4.20	5.50	6.60	7.95	9.00
	pH _F	5.20	6.15	7.00	7.45	7.75
	TM	12.5	0	0	0	0
<u>M+O</u> metal sal. acid	pH _I	4.25	5.50	6.55	7.60	8.85
	pH _F	4.70	6.10	7.15	7.55	8.15
	TM	49.5	0	0	0	0
<u>M+O+K</u> metal sal. acid kaolin	pH _I	4.25	5.45	6.65	7.85	8.85
	pH _F	5.20	6.05	7.10	7.75	8.25
	TM	5.5	0	0	0	0

App. 11a

Zn

REACTION

pH and TOTAL METAL IN SOLUTION.

<u>M</u> metal	pH _I	3.80	5.65	6.80	7.70	8.70
	pH _F	4.55	5.70	6.85	7.10	7.20
	TM	45.0	46.0	22.0	3.0	2.0
<u>M+K</u> metal kaolin	pH _I	3.90	4.95	6.10	7.40	8.75
	pH _F	4.90	5.70	6.25	6.90	7.20
	TM	38.5	30.0	14.5	0	0
<u>M+O</u> metal sal. acid	pH _I	4.20	5.65	6.70	7.80	9.10
	pH _F	4.90	6.15	6.90	7.60	8.20
	TM	50.0	2.5	0	0	0
<u>M+O+K</u> metal sal. acid kaolin	pH _I	4.20	5.45	6.50	7.65	8.85
	pH _F	5.10	5.50	6.55	7.70	8.20
	TM	38.5	19.0	0.0	0	0

App. 11b Mix A, Cu

Metal (M) and metal + kaolinite (M+K) reactions
for mix A are as recorded in appendix 11 a for all
four metals.

REACTION		pH and TOTAL METAL IN SOLUTION (ppm)				
<u>M+F</u>						
metal fulvic	pH _I	3.90	5.40	6.55	7.55	8.65
	pH _F	3.95	5.30	6.40	7.45	7.95
	TM	49.0	8.0	8.0	48.0	49.0
<u>M+H</u>						
metal humic	pH _I	4.25	5.45	6.45	7.75	8.55
	pH _F	4.30	5.50	6.50	7.00	7.90
	TM	40.0	22.0	7.0	23.0	44.0
<u>M+F+K</u>						
metal fulvic kaolin	pH _I	3.95	5.20	6.40	7.60	9.00
	pH _F	5.00	6.10	6.80	7.40	8.00
	TM	17.5	0	0	0	0
<u>M+H+K</u>						
metal humic kaolin	pH _I	4.05	5.40	6.60	7.75	8.95
	pH _F	5.00	5.60	7.00	7.70	8.40
	TM	22.5	7.5	5.0	4.0	3.0

App. 11b

Mix A, Ni

REACTION

pH and TOTAL METAL IN SOLUTION (ppm)

<u>M+F</u>	pH _I	4.05	5.50	6.70	7.60	8.80
metal	pH _F	4.45	5.70	7.00	7.50	8.20
fulvic	TM	50.0	49.0	14.5	6.0	3.0
<u>M+H</u>	pH _I	3.95	5.50	6.70	7.80	8.85
metal	pH _F	4.25	6.10	7.00	7.90	8.25
humic	TM	48.0	49.0	48.5	47.0	17.0
<u>M+F+K</u>	pH _I	4.10	5.40	6.50	7.60	8.90
metal	pH _F	5.00	6.00	6.90	7.50	8.10
fulvic	TM	42.5	31.5	4.0	0	0
kaolin						
<u>M+H+K</u>	pH _I	4.20	5.40	6.60	7.90	8.85
metal	pH _F	5.20	6.10	6.70	7.50	8.00
humic	TM	34.0	26.0	12.5	0	0
kaolin						

App. 11b MixA, Pb

REACTION pH and TOTAL METAL IN SOLUTION (ppm)

<u>M+F</u>						
metal	pH _I	4.30	5.35	6.50	7.75	8.95
fulvic	pH _F	4.80	5.65	6.85	7.60	8.45
	TM	48.0	49.0	49.5	49.5	48.5
<u>M+H</u>						
metal	pH _I	4.15	5.60	6.55	7.65	8.80
humic	pH _F	5.40	7.00	7.50	8.00	8.30
	TM	29.5	22.5	33.5	30.0	39.5
<u>M+F+K</u>						
metal	pH _I	3.95	5.15	6.30	7.50	9.00
fulvic	pH _F	5.20	6.00	6.95	7.60	8.15
kaolin	TM	0	0	0	0	
<u>M+H+K</u>						
metal	pH _I	3.90	5.30	6.50	7.80	8.50
humic	pH _F	5.80	6.90	7.40	7.80	8.20
kaolin	TM	14.0	7.0	5.5	2.0	1.5

App. 11b Mix A, Zn

REACTION		pH and TOTAL METAL IN SOLUTION (ppm)				
M+F	pH _I	4.25	5.70	6.90	7.75	8.90
	pH _F	4.50	6.40	7.00	7.60	8.05
	TM	46.5	1.5	1.0	4.0	6.5
<u>M+H</u>						
metal	pH _I	4.10	5.10	6.70	7.45	8.90
	pH _F	5.10	6.35	6.80	7.20	7.90
	TM	42.0	41.0	40.5	40.0	38.0
<u>M+F+K</u>						
metal	pH _I	4.00	5.35	6.40	7.65	8.70
	pH _F	5.10	5.70	6.70	7.45	7.95
	TM	26.5	12.5	0	0	0
<u>M+H+K</u>						
metal	pH _I	4.25	5.40	6.60	7.80	8.80
	pH _F	5.50	6.10	6.80	7.80	8.20
	TM	34.5	24.5	8.0	1.0	0.5

App. 11c Mix B, Cu

REACTION		pH and TOTAL METAL IN SOLUTION (ppm)				
<u>M</u> metal	pH _I	4.30	5.20	6.10	6.50	7.95
	pH _F	4.15	5.20	5.70	6.20	6.50
	TM	24.5	24.0	15.5	1.0	0
<u>M+K</u>						
metal kaolin	pH _I	4.00	4.80	5.50	6.40	7.20
	pH _F	4.70	5.15	5.65	6.20	7.00
	TM	16.0	12.0	5.5	0	0
<u>M+F</u>						
metal fulvic	pH _I	4.00	5.35	6.60	7.80	9.00
	pH _F	4.10	5.30	6.50	7.50	8.20
	TM	25.0	25.0	24.5	24.7	24.5
<u>M+H</u>						
metal humic	pH _I	4.10	5.30	6.50	7.90	9.10
	pH _F	4.15	6.00	7.00	8.00	8.35
	TM	24.0	24.5	24.2	25.0	24.2
<u>M+F+K</u>						
metal humic kaolin	pH _I	4.10	5.80	6.55	7.70	9.00
	pH _F	4.70	5.90	6.60	7.60	8.30
	TM	23.8	23.5	22.5	23.5	24.0
<u>M+H+K</u>						
metal humic kaolin	pH _I	4.15	5.60	6.65	7.75	8.90
	pH _F	4.80	6.10	7.20	7.85	8.50
	TM	16.0	20.0	20.2	20.5	21.0

App. 11c MixB, N1

REACTION pH and TOTAL METAL IN SOLUTION (ppm)

<u>M</u> metal	pH _I	4.00	5.10	6.10	7.50	8.80
	pH _F	4.10	5.25	6.40	7.30	7.60
	TM	25.0	25.0	25.0	22.5	13.0
<u>M+K</u> metal kaolin	pH _I	4.10	5.70	6.50	7.75	8.90
	pH _F	5.00	6.20	6.40	7.10	7.70
	TM	16.5	10.5	7.5	0	0
<u>M+F</u> metal fulvic	pH _I	4.15	5.50	6.80	7.90	9.00
	pH _F	4.60	5.70	7.10	8.00	8.40
	TM	25.0	25.0	25.0	25.0	25.0
<u>M+H</u> metal humic	pH _I	4.20	5.30	6.50	7.70	9.00
	pH _F	4.60	6.20	7.50	8.20	8.70
	TM	25.0	25.0	25.0	25.0	19.5
<u>M+F+K</u> metal fulvic kaolin	pH _I	4.10	5.60	6.70	7.80	9.10
	pH _F	5.10	6.10	6.90	7.90	8.50
	TM	21.0	20.0	20.0	20.0	11.5
<u>M+H+K</u> metal humic kaolin	pH _I	4.10	5.20	6.50	7.70	9.00
	pH _F	5.00	6.20	7.50	8.10	8.70
	TM	23.0	20.0	22.0	20.7	17.0

App. 11c

Mix B, Pb

REACTION

pH and TOTAL METAL IN SOLUTION (ppm)

<u>M</u> metal	pH _I	4.10	5.40	6.70	7.80	8.90
	pH _F	4.20	5.50	6.80	7.10	7.40
	TM	22.0	19.0	1.0	0	0
<u>M+K</u> metal kaolin	pH _I	4.15	5.25	6.45	7.80	8.90
	pH _F	4.80	5.55	6.50	7.10	7.50
	TM	6.0	2.0	0	0	0
<u>M+F</u> metal fulvic	pH _I	4.00	5.25	6.50	7.70	8.90
	pH _F	4.10	5.30	6.60	7.40	8.30
	TM	23.0	19.0	19.0	22.0	22.5
<u>M+H</u> metal humic	pH _I	4.05	5.30	6.60	7.80	9.00
	pH _F	4.90	6.10	7.20	7.95	8.25
	TM	20.0	22.0	23.0	23.0	23.0
<u>M+F+K</u> metal fulvic kaolin	pH _I	4.00	5.20	6.35	7.60	8.90
	pH _F	5.00	5.70	6.50	7.60	8.40
	TM	10.0	12.0	16.0	15.0	16.0
<u>M+H+K</u> metal humic kaolin	pH _I	4.00	5.30	6.65	7.80	8.80
	pH _F	5.30	6.35	7.50	8.10	8.40
	TM	18.5	17.5	14.5	15.0	14.5

App. 11c Mix B, Zn

REACTION pH and TOTAL METAL IN SOLUTION (ppm)

<u>M</u> metal	pH _I	4.10	5.40	6.70	7.80	8.90
	pH _F	4.20	5.60	6.80	7.10	7.40
	TM	25.0	24.5	17.0	8.0	0
<u>M+K</u> metal kaolin	pH _I	3.95	5.20	6.20	7.40	8.80
	pH _F	4.80	6.10	6.40	7.40	8.00
	TM	21.5	12.5	6.5	0	0
<u>M+F</u> metal fulvic	pH _I	4.20	5.50	6.70	7.70	8.85
	pH _F	4.20	5.50	6.60	7.45	8.10
	TM	24.0	24.5	24.0	24.0	24.5
<u>M+H</u> metal humic	pH _I	4.10	5.50	6.55	7.60	8.80
	pH _F	4.40	6.20	7.30	7.00	8.40
	TM	24.5	24.0	24.5	24.0	24.0
<u>M+F+K</u> metal fulvic kaolin	pH _I	4.20	5.45	6.60	7.80	8.90
	pH _F	5.10	5.80	6.70	7.70	8.20
	TM	22.5	23.0	21.5	24.0	23.0
<u>M+H+K</u> metal humic kaolin	pH _I	4.10	5.60	6.70	8.00	9.00
	pH _F	4.90	6.50	7.60	8.30	8.60
	TM	22.5	21.0	17.5	16.5	11.0

App. 11d Mix C

REACTION pH and TOTAL METAL IN SOLUTION (ppm)

<u>M</u> metal	pH _I	4.20	5.40	6.75	7.85	8.90
	pH _F	4.30	5.60	6.80	7.10	7.40
	TM: Cu	25.0	23.0	1.0	0	0
	Ni	25.0	24.5	21.0	14.0	4.5
	Pb	21.5	21.5	1.0	0	0
	Zn	25.0	25.0	18.5	9.5	0

<u>M+K</u> metal kaolin (100mg.)	pH _I	4.00	5.15	6.45	7.80	9.05
	pH _F	5.00	5.45	6.40	7.00	7.80
	TM: Cu	15.5	10.0	0	0	0
	Ni	23.0	22.0	14.0	2.0	0
	Pb	11.5	9.0	0	0	0
	Zn	23.0	22.5	10.0	0	0

<u>M+B</u> metal bent. (100mg.)	pH _I	4.15	5.45	6.80	7.80	9.05
	pH _F	4.70	6.00	7.10	7.50	8.10
	TM: Cu	6.5	1.0	0	0	0
	Ni	8.5	4.5	0	0	0
	Pb	3.0	1.5	0	0	0
	Zn	7.0	4.0	1.0	0	0

<u>M+F</u> metal fulvic	pH _I	4.10	5.40	6.60	7.80	9.05
	pH _F	4.20	5.60	6.70	7.80	8.20
	TM: Cu	25.0	25.0	23.5	24.0	24.0
	Ni	24.0	24.5	22.0	23.0	18.0
	Pb	5.5	1.0	15.5	16.0	16.0
	Zn	25.0	23.5	24.0	25.0	23.5

<u>M+F+K</u> metal fulvic kaolin 100mg.)	pH _I	4.10	5.45	6.60	7.80	9.10
	pH _F	4.90	5.70	6.70	7.80	8.30
	TM: Cu	18.0	18.5	20.5	21.0	20.0
	Ni	18.5	18.0	18.0	18.5	13.5
	Pb	4.0	1.0	12.0	12.0	11.5

<u>M+F+B</u>						
metal	pH _I	4.20	5.30	6.55	7.80	8.90
fulvic	pH _F	4.90	5.60	6.60	7.80	8.20
bent.	TM: Cu	14.5	13.0	13.0	13.0	13.0
(100mg.)	Ni	15.5	13.5	14.0	14.0	9.0
	Pb	4.0	1.0	1.5	5.0	5.0
	Zn	16.0	9.0	9.0	9.5	8.5

<u>M+H</u>						
metal	pH _I	4.10	5.30	6.60	7.80	9.10
humic	pH _F	4.50	6.20	7.60	8.40	9.00
	TM: Cu	24.0	24.0	25.0	24.0	23.0
	Ni	25.0	25.0	24.5	20.5	19.0
	Pb	14.5	13.0	13.0	10.5	16.0
	Zn	24.0	25.0	21.0	16.5	8.5

<u>M+H+K</u>						
metal	pH _I	4.10	5.40	6.55	7.65	8.90
humic	pH _F	4.80	6.40	7.60	8.40	8.90
kaolin	TM: Cu	18.0	22.5	22.0	21.5	20.5
(100mg.)	Ni	22.0	21.0	17.5	14.5	11.5
	Pb	9.0	8.0	6.5	6.0	6.0
	Zn	20.0	17.5	7.0	5.5	4.5

<u>M+H+B</u>						
metal	pH _I	4.00	5.25	6.50	7.80	8.85
humic	pH _F	4.40	5.90	7.60	8.50	8.80
bent.	TM: Cu	11.5	16.0	16.5	16.5	16.5
(100mg.)	Ni	17.5	16.0	9.0	7.5	6.5
	Pb	6.5	4.0	3.0	4.0	3.0
	Zn	17.0	13.0	2.0	0.5	0

App. IId continued

REACTION pH and TOTAL METAL IN SOLUTION (ppm)

<u>M+K₁</u>						
metal	pH _I	4.15	5.30	6.60	7.70	9.00
kaolin	pH _F	5.00	5.50	6.70	7.00	7.75
(250mg.)	TM: Cu	14.0	4.0	0	0	0
	Ni	21.0	20.0	0	0	0
	Pb	6.0	1.0	0	0	0
	Zn	16.5	13.5	0.5	0	0

<u>M+B₁</u>						
metal	pH _I	4.20	5.50	6.60	7.75	9.00
bent.	pH _F	4.80	5.80	6.80	7.20	7.90
(250mg.)	TM: Cu	4.0	0	0	0	0
	Ni	5.0	4.0	0	0	0
	Pb	2.0	0	0	0	0
	Zn	5.0	2.5	0	0	0

<u>M+F+K₁</u>						
metal	pH _I	4.20	5.50	6.50	7.75	9.00
fulvic	pH _F	5.10	5.90	6.70	7.70	8.30
kaolin	TM: Cu	12.5	14.0	16.5	18.5	18.5
(250mg.)	Ni	18.5	16.5	17.0	17.0	13.0
	Pb	1.0	1.0	4.5	8.0	7.0
	Zn	6.5	6.5	10.0	15.0	16.0

<u>M+F+B₁</u>						
metal	pH _I	4.20	5.50	6.60	7.80	9.00
fulvic	pH _F	5.10	5.75	6.70	7.70	8.40
bent.	TM: Cu	6.0	6.5	7.0	9.5	11.5
(250mg.)	Ni	9.0	9.0	9.5	9.5	9.0
	Pb	3.5	2.5	4.0	4.0	2.0
	Zn	7.5	8.0	9.0	8.5	9.0

<u>M+H+K₁</u>							
metal	pH _I		4.20	5.40	6.70	7.80	9.00
humic	pH _F		5.00	6.00	7.20	7.90	8.90
kaolin (250mg.)	TM:	Cu	20.00	20.5	21.0	20.0	19.5
		Ni	20.0	21.5	20.0	18.0	12.5
		Pb	8.0	8.0	7.0	6.0	5.0
		Zn	16.0	15.0	9.0	6.0	5.0

<u>M+H+B₁</u>							
metal	pH _I		4.20	5.40	6.60	7.80	9.00
humic	pH _F		4.60	5.90	7.20	8.15	8.90
bent. (250mg.)	TM:	Cu	11.5	13.5	14.0	15.0	14.0
		Ni	10.5	12.0	9.0	5.5	5.0
		Pb	5.0	3.5	3.0	3.0	2.0
		Zn	9.0	9.0	3.0	1.0	1.5

App. 11e Mix C*, desorption pH_i 5.5

REACTION pH and TOTAL METAL IN SOLUTION (ppm)

M+K

metal	pH _I	4.05	5.50	6.50	7.65	9.00
kaolin	pH _F	5.10	5.95	6.60	6.90	7.50
	TM: Cu	14.5	0	0	0	0
	Ni	20.0	16.0	12.0	3.0	0
	Pb	9.0	0	0	0	0
	Zn	18.5	14.0	6.0	1.0	0

M+F+K

metal	pH _I	4.10	5.40	6.60	7.70	9.00
fulvic	pH _F	4.95	5.65	6.70	7.55	8.35
kaolin	TM: Cu	16.0	16.0	16.0	14.0	14.0
	Ni	18.0	17.5	15.0	15.5	12.5
	Pb	2.5	1.0	5.5	10.5	10.5
	Zn	13.0	9.0	9.0	12.0	14.0

M+H+K

metal	pH _I	4.20	5.40	6.70	7.90	9.00
humic	pH _F	4.75	5.90	7.25	8.05	8.80
kaolin	TM: Cu	17.5	18.5	17.0	17.0	12.5
	Ni	19.0	17.0	11.5	9.5	7.5
	Pb	7.0	5.5	3.5	3.5	2.5
	Zn	18.5	16.0	5.0	1.5	1.0

M+B

metal	pH _I	3.90	5.25	6.55	7.70	8.80
bent.	pH _F	4.50	5.60	6.85	7.20	7.90
	TM: Cu	6.0	3.5	0	0	0
	Ni	10.5	7.0	0	0	0
	Pb	4.0	2.5	0	0	0
	Zn	8.0	5.0	0.5	0	0

<u>M+P+H</u>						
metal	pH _I	4.10	5.40	6.70	7.90	9.10
fulvic	pH _F	4.85	5.60	6.70	7.55	8.20
bent.	TM: Cu	13.0	10.5	10.5	11.0	6.5
	Ni	15.5	14.0	13.5	13.0	6.5
	Pb	5.5	4.0	4.0	3.5	0
	Zn	12.0	10.0	9.5	8.5	4.5

<u>M+H+B</u>						
metal	pH _I	4.10	5.40	6.80	8.00	9.05
humic	pH _F	4.55	6.10	7.25	7.85	8.75
bent.	TM: Cu	14.5	15.0	13.0	11.0	7.5
	Ni	17.0	16.5	11.5	10.0	4.0
	Pb	6.5	4.0	3.5	3.5	2.0
	Zn	15.0	14.5	3.0	1.0	1.0

App. 11e (continued) desorption pH_i 8.5

REACTION pH and TOTAL METAL IN SOLUTION (ppm)

<u>M+K</u>						
metal	pH _I	4.25	5.25	6.40	7.80	9.05
kaolin	pH _F	5.20	5.80	6.60	7.00	7.60
	TM: Cu	0	0	0	0	0
	Ni	9.0	8.0	0.5	0	0
	Pb	0	0	0	0	0
	Zn	9.5	7.0	0.5	0	0
<u>M+F+K</u>						
metal	pH _I	4.20	5.55	6.60	7.90	9.00
fulvic	pH _F	5.10	5.85	6.75	7.85	8.35
kaolin	TM: Cu	11.5	12.0	14.0	12.0	10.5
	Ni	17.5	15.5	14.0	8.5	4.5
	Pb	1.0	1.0	4.5	6.5	4.5
	Zn	10.0	8.0	8.5	10.0	9.0
<u>M+H+K</u>						
metal	pH _I	4.20	5.40	6.60	7.75	9.00
humic	pH _F	5.00	6.50	7.30	8.05	8.75
kaolin	TM: Cu	13.0	14.5	10.0	9.0	7.5
	Ni	14.5	10.0	6.5	4.5	3.5
	Pb	5.5	5.5	3.5	3.5	2.5
	Zn	18.5	8.5	6.5	5.5	3.0
<u>M+B</u>						
metal	pH _I	4.30	5.30	6.75	7.80	8.85
bent.	pH _F	5.00	5.50	6.80	7.10	7.55
	TM: Cu	0	0	0	0	0
	Ni	5.0	3.0	0	0	0
	Pb	0	0	0	0	0
	Zn	3.0	2.5	0	0	0

4

OF/DE

5

M+P+B

metal	pH_I	4.15	5.50	6.70	7.80	8.80
fulvic	pH_F	4.95	5.85	6.70	7.60	8.00
bent.	TM: Cu	12.0	10.0	9.5	9.5	7.5
	Ni	14.5	14.0	12.0	12.0	9.0
	Pb	6.5	3.5	4.0	3.5	1.5
	Zn	11.5	10.0	9.0	8.0	6.0

M+H+B

metal	pH_I	4.15	5.30	6.60	7.90	9.10
humic	pH_F	5.00	5.95	7.00	7.90	8.85
bent.	TM: Cu	11.0	14.5	12.5	11.0	6.5
	Ni	17.0	18.0	12.0	8.5	4.0
	Pb	4.5	3.0	2.0	2.0	1.0
	Zn	12.0	10.5	1.5	1.0	0

Appendix III - Analytical data for the carbonate
reactions discussed in chapter 4.

- (a) data for mix D reactions
- (b) data for mix E reactions
- (c) data for mix D^{*} (desorption) reactions
- (d) data for mix E^{*} (desorption) reactions

Note: pH_I : initially set pH of solution
 pH_F : final measured pH of solution.
 TM_I : total metal in solution.

App. 111a

Mix D

REACTION

pH and TOTAL METAL IN SOLUTION (ppm)

<u>M</u> metal	pH _I	7.55	8.10	8.60
	pH _F	7.85	8.30	8.80
	TM: Cu	0	0	0
	Ni	0	0	0
	Pb	0	0	0
	Zn	0	0	0
<u>M+K</u> metal kaolin	pH _I	7.50	8.05	8.60
	pH _F	8.00	8.35	8.90
	TM: Cu	0	0	0
	Ni	0	0	0
	Pb	0	0	0
	Zn	0	0	0
<u>M+B</u> metal bent.	pH _I	7.60	8.20	8.60
	pH _F	7.90	8.45	8.85
	TM: Cu	0	0	0
	Ni	0	0	0
	Pb	0	0	0
	Zn	0	0	0
<u>M+F</u> metal fulvic	pH _I	7.55	8.10	8.60
	pH _F	7.90	8.40	8.80
	TM: Cu	22.5	22.0	21.0
	Ni	20.5	19.5	19.5
	Pb	10.0	6.5	6.5
	Zn	21.5	23.5	20.5
<u>M+F+K</u> metal fulvic kaolin	pH _I	7.50	8.10	8.60
	pH _F	8.00	8.40	8.75
	TM: Cu	20.5	21.5	20.5
	Ni	14.0	11.0	6.0
	Pb	10.0	7.5	6.5
	Zn	18.5	19.5	19.5

M+F+B

metal	PH _I	7.55	8.10	8.65
fulvic	PH _F	7.95	8.40	8.70
bent.	TM; Cu	14.0	13.0	14.0
	N1	9.5	7.0	6.0
	Pb	3.0	3.0	3.0
	Zn	10.0	10.0	9.5

M+H

metal	PH _I	7.55	8.10	8.60
humic	PH _F	8.00	8.45	8.80
	TM; Cu	25.0	25.0	24.5
	N1	24.0	22.0	22.0
	Pb	15.0	12.5	13.5
	Zn	21.0	22.5	22.0

M+H+K

metal	PH _I	7.55	8.00	8.60
humic	PH _F	7.90	8.30	8.80
kaolin	TM; Cu	22.0	22.0	22.0
	N1	11.5	9.5	10.0
	Pb	5.5	5.5	4.5
	Zn	8.0	7.0	6.5

M+H+B

metal	PH _I	7.65	8.15	8.65
humic	PH _F	8.00	8.40	8.80
bent.	TM; Cu	17.0	17.5	17.0
	N1	8.5	8.0	8.0
	Pb	3.0	3.0	3.0
	Zn	8.5	7.5	7.0

App. 111b Mix E

REACTION		pH and TOTAL METAL IN SOLUTION (ppm)		
<u>M</u> metal	pH _I	7.60	8.10	8.65
	pH _F	8.15	8.50	8.95
	TM: Cu	1.5	2.0	2.0
	Ni	0	0	0
	Pb	1.0	2.0	2.0
	Zn	0	0	0
<u>M+K</u> metal kaolin	pH _I	7.60	8.10	8.65
	pH _F	8.20	8.50	9.00
	TM: Cu	1.0	1.0	1.0
	Ni	0	0	0
	Pb	1.0	1.0	1.5
	Zn	0	0	0
<u>M+F</u> metal fulvic	pH _I	7.55	8.10	8.55
	pH _F	8.00	8.40	8.85
	TM: Cu	19.0	20.0	19.0
	Ni	14.5	11.0	10.0
	Pb	10.0	8.0	8.0
	Zn	16.5	14.0	15.5
<u>M+B</u> metal bent.	pH _I	7.60	8.10	8.65
	pH _F	8.25	8.50	8.90
	TM: Cu	0.0	0	0
	Ni	0	0	0
	Pb	0	0	0
	Zn	0	0	0
<u>M+F+K</u> metal fulvic kaolin	pH _I	7.65	8.10	8.60
	pH _F	8.10	8.45	8.80
	TM: Cu	19.0	19.0	18.5
	Ni	1.5	1.5	1.5
	Pb	8.5	6.5	7.5
	Zn	13.0	14.0	14.0

M+P+B

metal fulvic bent.	pH _I	7.60	8.10	8.55
	pH _F	8.10	8.45	8.80
	TM: Cu	14.5	14.5	15.0
	Ni	0	0	0
	Pb	2.0	2.0	2.0
	Zn	4.0	5.5	5.0

M+H

metal humic	pH _I	7.60	8.10	8.60
	pH _F	8.10	8.45	8.85
	TM: Cu	20.5	20.5	19.5
	Ni	17.5	15.5	16.0
	Pb	10.0	9.5	10.5
	Zn	16.0	12.0	13.0

M+H+K

metal humic kaolin	pH _I	7.60	8.10	8.65
	pH _F	8.15	8.40	8.75
	TM: Cu	19.0	19.0	17.5
	Ni	7.5	7.5	5.5
	Pb	4.5	4.5	5.5
	Zn	5.0	5.5	4.0

M+H+B

metal humic bent.	pH _I	7.60	8.10	8.60
	pH _F	8.10	8.45	8.65
	TM: Cu	14.5	14.0	14.5
	Ni	3.0	2.5	3.0
	Pb	2.0	2.0	2.0
	Zn	1.0	1.0	1.0

App. 111c Mix D*

REACTION

pH and TOTAL METAL IN SOLUTION

<u>M+P+K</u>	pH _I	7.60	8.00	8.60
(pH ₁ 8.5)	pH _P	7.90	8.25	8.75
metal	TM: Cu	8.5	8.0	9.0
fulvic	Ni	1.5	2.5	1.5
kaolin	Pb	7.0	7.0	5.0
	Zn	7.5	8.0	8.0

<u>M+P+K</u>	pH _I	7.60	8.10	8.60
(pH ₁ 5.5)	pH _P	8.10	8.25	8.80
	TM: Cu	16.0	17.5	18.0
	Ni	8.0	9.0	4.0
	Pb	6.5	7.0	5.5
	Zn	18.0	18.0	17.5

<u>M+H+K</u>	pH _I	7.60	8.10	8.60
(pH ₁ 8.5)	pH _P	7.90	8.30	8.90
metal	TM: Cu	8.0	8.0	7.5
humic	Ni	3.0	2.5	2.0
kaolin	Pb	2.0	2.0	2.0
	Zn	2.5	2.0	2.0

<u>M+H+K</u>	pH _I	7.50	8.00	8.50
(pH ₁ 5.5)	pH _P	7.90	8.20	8.75
	TM: Cu	20.5	19.0	18.0
	Ni	10.5	10.0	11.5
	Pb	3.5	4.0	4.0
	Zn	8.0	6.5	6.0

<u>M+F+B</u>				
(pH_1 8.5)	pH_I	7.60	8.00	8.60
metal	pH_P	7.90	8.25	8.80
fulvic	TM: Cu	8.0	7.5	7.5
bent.	Ni	3.5	2.0	2.0
	Pb	2.0	1.0	1.0
	Zn	9.0	8.5	8.5

<u>M+F+B</u>				
(pH_1 5.5)	pH_I	7.60	8.10	8.60
	pH_P	8.00	8.25	8.80
	TM: Cu	11.0	11.5	10.0
	Ni	7.5	6.5	5.0
	Pb	1.0	0	1.0
	Zn	9.0	8.5	7.5

<u>M+H+B</u>				
(pH_1 8.5)	pH_I	7.50	8.10	8.60
metal	pH_P	8.10	8.40	8.85
humic	TM: Cu	8.0	8.0	7.5
bent.	Ni	3.5	3.0	3.0
	Pb	0	0	0
	Zn	1.5	2.0	1.0

<u>M+H+B</u>				
(pH_1 5.5)	pH_I	7.50	8.00	8.60
	pH_P	8.00	8.30	8.85
	TM: Cu	16.5	16.0	16.5
	Ni	9.0	9.0	7.0
	Pb	2.0	2.5	2.0
	Zn	7.0	7.0	6.5

App. 111d Mix E*

REACTION	pH and TOTAL METAL IN SOLUTION (ppm)			
M+F+K (pH ₁ 8.5) metal fulvic kaolin	pH _I	7.60	8.00	8.45
	pH _F	8.00	8.25	8.75
	TM: Cu	10.0	9.0	8.5
	Ni	0	0	0
	Pb	4.5	4.0	4.5
	Zn	7.0	6.5	5.0
<u>M+F+K</u> pH ₁ 5.5)	pH _I	7.50	8.10	8.60
	pH _F	8.00	8.30	8.85
	TM: Cu	15.5	16.0	15.0
	Ni	2.5	2.0	1.0
	Pb	5.5	5.5	6.5
	Zn	11.5	12.5	12.5
<u>M+H+K</u> (pH ₁ 8.5) metal humic kaolin	pH _I	7.50	8.00	8.50
	pH _F	8.10	8.30	8.85
	TM: Cu	8.5	9.0	8.5
	Ni	2.0	1.5	1.5
	Pb	2.0	2.0	2.0
	Zn	1.5	1.5	1.0
<u>M+H+K</u> pH ₁ 5.5)	pH _I	7.50	8.10	8.60
	pH _F	8.20	8.40	8.80
	TM: Cu	15.0	15.5	14.5
	Ni	7.0	7.0	5.5
	Pb	4.0	4.5	3.5
	Zn	4.5	4.5	3.0

<u>M+F+B</u>				
(pH ₁ 8.5)	pH _I	7.60	8.00	8.50
metal	pH _F	8.10	8.30	8.70
fulvic	TM: Cu	9.5	8.5	8.5
bent.	Ni	0	0	0
	Pb	1.0	1.0	1.5
	Zn	4.0	5.0	5.5

<u>M+F+B</u>				
(pH ₁ 5.5)	pH _I	7.50	8.05	8.60
	pH _F	8.00	8.25	8.80
	TM: Cu	10.5	12.0	10.5
	Ni	1.0	0	0
	Pb	1.0	1.5	1.0
	Zn	4.5	4.0	5.0

<u>M+H+B</u>				
(pH ₁ 8.5)	pH _I	7.60	8.10	8.60
metal	pH _F	8.10	8.30	8.85
humic	TM: Cu	7.00	8.0	7.0
bent.	Ni	1.0	1.0	1.0
	Pb	0	0	0
	Zn	1.0	1.0	1.0

<u>M+H+B</u>				
(pH ₁ 5.5)	pH _I	7.60	8.00	8.50
	pH _F	8.15	8.30	8.80
	TM: Cu	9.5	11.0	10.0
	Ni	4.0	3.0	3.5
	Pb	1.0	1.0	1.0
	Zn	1.0	1.0	1.0

Appendix IV Field analytical data

- (a) Moira River
- (b) Long Lake
- (c) Lavant Creek - Clyde River
- (d) Sulphide Creek
- (e) Calumet Island.

(note: minerals identified

Q: quartz, F: feldspar, K: kaolin,

Ch: chlorite

K-Ch or Ch-K: chlorite and/or kaolin,

M: montmorillonite, I: illite or

micaceous mineral, D: dolomite,

C: carbonate detected by HCl treatment)

Sample No.	ppm			ppm			ppm			ppm			ppm			HF/ HClO ₄ K %
	HF/ HClO ₄ Cu	HF/ HClO ₄ Pb	HF/ HClO ₄ Zn	HF/ HClO ₄ Ni	HF/ HClO ₄ Fe %	HF/ HClO ₄ Mn	HF/ HClO ₄ Mg %	HF/ HClO ₄ Ca %	HF/ HClO ₄ Na %	HF/ HClO ₄	HF/ HClO ₄	HF/ HClO ₄				
E 1	24	50	90	32	3.2	230	0.32	1.00	0.42	0.34						
2	22	28	165	36	4.2	590	0.69	0.91	0.42	0.50						
3	38	48	130	26	4.0	245	0.56	1.60	0.86	0.34						
4	22	40	135	18	3.8	760	0.61	1.26	0.40	0.23						
5	26	30	125	20	3.6	330	0.58	0.84	0.34	0.41						
6	20	20	115	26	4.4	540	0.56	0.84	0.69	0.54						
7	22	18	115	32	4.0	330	0.55	0.91	0.77	0.54						
8	30	24	250	54	5.6	1000	0.65	0.68	0.77	0.38						
9	20	26	155	40	4.4	280	0.88	1.26	0.86	0.45						
E10	10	16	94	34	5.2	390	0.69	0.88	1.20	0.45						
11	16	22	115	38	4.6	575	0.78	0.95	0.98	0.45						
12	12	10	86	24	3.8	255	0.58	0.51	0.92	0.60						
13	10	20	100	36	4.0	390	0.65	0.72	0.98	0.50						
14	14	12	96	36	4.8	810	0.85	1.02	1.04	0.60						
15	10	18	110	42	4.2	390	0.71	0.80	1.20	0.66						
16	12	14	88	36	4.0	320	0.63	0.78	1.04	0.66						

17		12	20	94	30	3.8	340	0.69	0.68	1.12	0.66
18		10	16	80	32	5.0	405	0.71	0.95	0.98	0.54
19		46	30	115	66	5.6	1050	1.47	1.58	0.73	0.45
20		26	34	170	26	5.0	820	0.63	0.76	0.92	0.50
21		16	14	105	26	4.0	220	0.67	0.68	1.04	0.60
22		12	14	115	40	4.2	280	0.73	0.74	1.20	0.80
23		110	88	150	640	5.4	820	1.00	1.10	0.98	0.60
24		160	88	175	1250	5.6	450	0.88	0.72	0.98	0.54
25		44	64	130	300	4.4	390	0.85	0.70	1.04	0.54
26		42	42	145	120	4.0	1020	1.02	0.91	1.04	0.66
27		92	58	130	56	7.2	290	0.50	4.50	0.13	0.04
29		74	20	90	34	5.0	390	0.44	6.40	0.14	0.04
30		30	20	110	32	5.0	420	0.63	4.00	0.69	0.45
31		5100	66	175	1050	5.6	180	0.33	0.55	0.48	0.34
32		660	18	170	540	5.2	205	0.29	0.62	0.62	0.23
33		480	46	150	1020	6.6	330	0.56	0.86	0.65	0.41

34		105	44	165	660	5.8	800	0.60	0.84	0.65	0.41
35		34	18	145	110	5.0	355	0.71	0.70	0.69	0.41
36		105	56	190	650	6.4	550	0.63	0.82	0.73	0.45
37		20	22	125	28	4.8	600	0.40	0.84	0.63	0.41
38		130	64	190	750	4.8	490	0.53	0.59	0.62	0.34
39		125	56	185	760	6.8	845	0.50	0.78	0.55	0.34
40		76	76	135	200	5.2	515	0.55	0.89	0.40	0.38
41		16	28	70	52	6.4	450	0.69	1.23	1.00	0.45
42		30	170	110	36	6.4	330	0.61	4.00	0.82	0.45
43		20	18	78	115	3.4	205	0.80	1.50	0.86	0.38
44		34	92	105	125	4.6	255	0.73	4.50	0.77	0.50
45		8	20	66	54	3.0	700	3.05	6.60	0.32	0.18
46		90	56	135	300	2.2	70	0.23	1.26	0.18	0.12
47		24	56	155	26	4.4	750	0.30	0.84	0.58	0.25
48		26	56	240	26	5.0	450	0.32	0.59	0.58	0.23
49		28	76	270	28	4.8	1400	0.40	0.66	0.69	0.23

50		20	28	180	36	6.2	615	0.67	0.72	0.86	0.28
51		28	24	115	38	5.6	400	0.71	0.62	1.15	0.50
51		14	16	90	34	3.8	500	0.44	0.76	0.87	0.60
53		16	16	96	34	5.8	450	0.55	0.91	0.82	0.66
54		14	20	100	30	4.8	525	0.50	1.17	0.77	0.60
55		10	16	74	26	4.6	320	0.47	0.93	0.98	0.54
56		20	24	115	38	5.4	320	0.61	0.84	0.77	0.50
57		14	22	105	28	4.8	600	0.56	1.47	0.65	0.60
58		20	30	130	44	5.8	500	0.65	1.80	0.73	0.54
59		34	92	145	38	4.8	440	0.93	4.30	0.73	0.50
60		20	30	160	28	3.8	145	0.35	1.31	0.49	0.28
61		16	12	110	115	2.4	220	1.21	1.85	0.52	0.80
62		10	12	96	26	4.8	290	0.53	0.68	1.20	0.54

17		7	9	50	8	1.9	400	0.40	0.39	275	200
18		6	9	34	4	1.7	130	0.40	0.64	375	175
19		30	32	83	17	2.9	3200	1.54	6.0	500	600
20		20	32	165	9	3.3	1560	0.66	1.3	600	450
21		9	12	73	9	2.3	200	0.61	0.58	325	325
22		9	12	79	9	2.4	280	0.58	0.58	325	250
23		96	84	125	510	3.4	1360	0.97	0.73	600	375
24		165	91	160	1100	2.3	640	0.50	0.52	225	175
25		38	58	93	265	2.7	560	0.76	0.58	425	450
26		30	42	115	42	2.7	1635	0.87	0.83	425	375
27		37	63	82	11	2.2	100	0.33	7.2	600	200
29		15	28	56	13	1.6	515	0.44	14.4	1500	175
30		14	20	70	9	1.7	480	0.70	5.6	900	300
31		5,100	64	165	1100	2.5	280	0.22	0.79	600	175
32		690	25	175	560	29	280	0.61	0.51	675	325
33		450	50	140	920	29	360	0.48	0.49	375	300

34	89	40	140	530	33	1270	0.46	0.64	675	250
35	22	14	97	75	25	515	0.74	0.67	375	200
36	88	47	165	560	34	835	0.44	0.55	675	175
37	14	18	86	11	27	1140	0.35	0.79	500	200
38	110	54	170	650	30	800	0.56	0.66	1100	375
39	96	48	150	665	32	1420	0.50	0.75	500	325
40	57	77	125	225	29	935	0.65	1.54	425	1350
41	10	8	23	17	17	200	0.64	1.16	225	425
42	9	19	33	58	10	160	1.15	6.7	325	125
43	12	20	42	75	13	200	1.40	3.2	425	175
44	18	80	56	64	14	200	1.24	6.2	675	325
45	2	20	34	24	15	1040	8.25	13.8	150	18
46	55	42	98	235	14	70	0.43	1.8	1500	250
47	15	43	140	8	2.5	1240	0.15	1.02	900	175
48	21	53	230	11	2.9	840	0.50	0.87	1100	800
49	23	71	255	12	3.5	4400	0.07	0.79	675	300
50	14	22	150	13	3.0	660	0.76	0.51	325	175

51	22	19	92	16	3.4	720	1.21	0.70	325	2000
52	9	12	63	9	2.4	760	0.46	1.19	500	425
53	14	15	78	15	2.8	875	0.76	1.85	375	1100
54	10	16	75	11	2.6	875	0.83	1.8	375	700
55	8	10	51	8	1.9	320	0.60	1.19	425	450
56	13	15	78	13	2.6	360	0.78	1.61	600	800
57	8	18	71	8	2.0	915	0.74	3.45	375	375
58	12	22	88	12	2.4	680	0.90	3.85	675	800
59	25	83	115	13	2.2	560	1.67	6.55	375	875
60	17	40	190	12	2.8	280	0.68	5.30	1400	600
61	12	13	90	89	1.8	280	3.0	5.30	500	100
62	6	8	62	7	2.6	280	0.46	0.58	275	250

SAMPLE NUMBER	Cu ppb	Pb ppb	Zn ppb	Ni ppb	Mn ppb	Mg ppm	Fe ppb	Ca ppm	Na ppm	K ppm
E - 1	< 2	4	20	< 2	10	6.5	250	47.5	9.00	0.20
2	< 2	< 2	10	< 2	30	8.5	300	40.0	0.45	0.45
3	< 2	4	30	38	40	8.0	400	47.5	4.00	0.45
4	< 2	2	20	< 2	30	8.5	300	50.5	3.70	0.30
5	< 2	4	20	3	50	9.0	350	50.5	5.40	0.40
6	< 2	2	20	< 2	20	9.0	500	57.2	44.5	0.45
E - 7	< 2	< 2	10	< 2	30	9.5	400	60.0	4.35	0.60
8	< 2	< 2	10	6	150	2.5	500	22.7	1.85	0.65
9	< 2	2	20	< 2	110	1.5	1400	9.7	0.45	0.40
10	< 2	< 2	10	< 2	140	3.0	650	22.0	1.85	0.65
11	< 2	2	20	< 2	110	3.0	600	22.0	2.00	0.70
12	< 2	2	20	< 2	50	9.5	750	63.0	4.55	0.65
13	< 2	< 2	20	< 2	80	4.5	550	26.8	2.30	0.65
14	< 2	< 2	20	< 2	80	4.0	550	25.2	2.30	0.65
15	< 2	< 2	10	< 2	130	4.5	500	29.5	2.25	0.70
16	< 2	< 2	10	< 2	20	6.0	400	30.5	1.28	0.45

17	< 2	< 2	20	< 2	80	4.5	450	28.5	2.10	0.75
18	< 2	< 2	20	< 2	20	5.5	450	27.7	1.20	0.45
19	< 2	< 2	20	< 2	190	2.5	500	18.2	1.42	0.65
20	< 2	< 2	20	< 2	170	2.5	700	23.5	0.60	0.60
21	< 2	< 2	20	2	100	4.5	500	28.7	2.00	0.70
22	< 2	< 2	20	< 2	90	4.5	550	29.5	2.25	0.65
23	< 2	< 2	10	< 2	60	4.5	400	27.7	2.30	0.70
24	< 2	3	20	< 2	100	4.5	500	29.5	2.30	0.85
25	< 2	< 2	20	< 2	90	5.0	500	29.5	2.00	0.75
26	< 2	2	20	< 2	50	5.0	450	28.7	2.10	0.75
27	< 2	< 2	30	2	10	17.3	400	92.0	59.0	2.85
28	< 2	< 2	10	< 2	40	4.0	900	75.0	5.80	0.22
29	< 2	< 2	20	< 2	20	23.9	250	52.0	113	4.20
30	< 2	< 2	20	< 2	50	13.8	300	66.0	56.5	4.15
E - 31	2	< 2	10	< 2	80	2.5	700	23.5	2.45	0.50
32	5	< 2	10	< 2	110	2.5	1200	22.0	5.30	0.65
33	< 2	2	10	< 2	70	5.0	400	31.5	2.25	0.70
34	< 2	2	10	< 2	70	6.5	300	41.2	22.5	0.70

17	< 2	< 2	< 2	20	< 2	80	4.5	450	28.5	2.10	0.75
18	< 2	< 2	< 2	20	< 2	20	5.5	450	27.7	1.20	0.45
19	< 2	< 2	< 2	20	< 2	190	2.5	500	18.2	1.42	0.65
20	< 2	< 2	< 2	20	< 2	170	2.5	700	23.5	0.60	0.60
21	< 2	< 2	< 2	20	2	100	4.5	500	28.7	2.00	0.70
22	< 2	< 2	< 2	20	< 2	90	4.5	550	29.5	2.25	0.65
23	< 2	< 2	< 2	10	< 2	60	4.5	400	27.7	2.30	0.70
24	< 2	3	< 2	20	< 2	100	4.5	500	29.5	2.30	0.85
25	< 2	< 2	< 2	20	< 2	90	5.0	500	29.5	2.00	0.75
26	< 2	2	< 2	20	< 2	50	5.0	450	28.7	2.10	0.75
27	< 2	< 2	< 2	30	2	10	17.3	400	92.0	59.0	2.85
28	< 2	< 2	< 2	10	< 2	40	4.0	900	75.0	5.80	0.22
29	< 2	< 2	< 2	20	< 2	20	23.9	250	52.0	113	4.20
30	< 2	< 2	< 2	20	< 2	50	13.8	300	66.0	56.5	4.15
31	2	< 2	< 2	10	< 2	80	2.5	700	23.5	2.45	0.50
32	5	< 2	< 2	10	< 2	110	2.5	1200	22.0	5.30	0.65
33	< 2	2	< 2	10	< 2	70	5.0	400	31.5	2.25	0.70
34	< 2	2	< 2	10	< 2	70	6.5	300	41.2	22.5	0.70

35	2	< 2	10	< 2	420	9.5	1450	58.0	5.80	0.92
36	< 2	< 2	20	< 2	60	6.5	300	46.2	21.5	1.32
37	< 2	< 2	10	< 2	170	3.0	400	32.5	3.50	0.55
38	2	< 2	20	< 2	90	6.0	350	40.0	8.15	1.20
39	< 2	< 2	10	< 2	70	6.5	200	46.2	7.10	1.10
40	< 2	< 2	20	< 2	80	5.0	150	32.5	3.50	1.20
41	< 2	< 2	10	< 2	60	5.0	80	31.5	3.40	1.02
42	< 2	< 2	20	< 2	60	3.0	350	58.0	30.0	2.40
43	< 2	< 2	10	2	40	5.5	80	21.2	4.45	0.70
44	< 2	< 2	10	< 2	80	5.5	250	34.5	6.05	0.98
45	< 2	< 2	10	< 2	50	5.0	140	31.5	3.60	1.02
46	< 2	< 2	20	< 2	60	6.0	100	43.5	6.65	1.02
47	< 2	< 2	20	< 2	100	2.5	80	18.2	< 0.1	0.20
48	< 2	< 2	10	< 2	450	2.5	900	24.5	0.95	0.50
49	< 2	< 2	10	< 2	130	3.5	250	25.2	2.90	0.70

50	< 2	< 2	20	< 2	410	3.0	450	24.5	2.35	0.98
51	< 2	< 2	20	< 2	160	6.0	300	34.5	2.25	0.92
52	2	< 2	20	< 2	60	6.5	200	62.0	1.90	0.98
53	< 2	7	10	< 2	30	17.2	80	85.0	3.20	1.40
54	< 2	3	10	< 2	70	6.5	350	57.0	2.10	0.98
55	< 2	2	20	< 2	100	7.5	350	64.0	5.15	1.15
56	< 2	2	10	2	80	8.5	350	66.0	4.00	1.15
57	< 2	4	10	< 2	50	19.0	150	64.0	4.20	1.32
58	< 2	4	10	< 2	40	12.0	200	60.0	4.20	1.25
59	< 2	2	20	< 2	40	11.2	200	57.0	4.35	1.25
60	< 2	< 2	10	< 2	60	12.0	650	57.0	5.00	1.45
61	< 2	4	10	2	40	6.5	60	25.2	5.40	0.98
62	< 2	4	10	< 2	70	8.5	200	46.2	3.10	1.10

MOIRA RIVER

Sample No.	pH	TOC (ppm)	% ORG. C	CEC (me/100g.)	MINERALOGY
1	6.90	21	22.07	106.40	Q
2	6.85	20	6.91	41.84	Q, F, K-Ch
3	6.80	24	20.74	109.60	Q, F
4	6.90	24	22.56	113.60	Q, F
5	7.05	17	13.42	67.36	Q, F, Ch
6	6.90	20	7.39	42.72	Q, F, K-Ch
7	7.00	20	7.50	43.52	Q, F, Ch
8	7.10	15	6.99	37.84	Q, F, K-Ch
9	6.90	20	4.39	23.76	Q, F, K-Ch
10	7.00	17	1.47	11.20	Q, F, K
11	6.90	24	2.84	18.24	Q, F, K-Ch
12	7.10	16	3.76	26.64	Q, F, K
13	7.15	20	3.63	23.52	Q, F, K-Ch
14	7.00	19	1.52	12.72	Q, F, K-Ch, C
15	6.95	17	2.64	17.04	Q, F, K-Ch
16	7.00	20	3.97	24.72	Q, F, K-Ch
17	7.10	21	2.59	18.24	Q, F, K-Ch
18	7.00	21	3.42	23.92	Q, F, K-Ch
19	7.25	12	4.91	23.36	Q, F, I, K-Ch
20	7.00	23	6.81	40.24	Q, F, I, K-Ch
21	7.05	14	3.04	20.24	Q, F, K-Ch
22	7.15	15	2.14	17.52	Q, F, K-Ch
23	7.20	12	3.41	21.36	Q, F, K-Ch
24	7.45	16	3.70	26.16	Q, F, K-Ch

MOIRA RIVER cont'd

25	6.95	16	3.36	25.52	Q, F, Ch
26	6.90	15	3.87	24.64	Q, F, K-Ch, M
27	7.40	7	5.27	20.42	Q, F, C
28	7.00	12	-		no sediment
29	7.30	10	18.05	92.00	Q, F, C
30	7.45	10	7.90	36.96	Q, F, C
31	7.00	9	10.07	56.00	Q, F, Ch
32	6.70	11	9.19	46.88	Q, F, Ch
33	7.10	14	3.87	23.52	Q, F, K-Ch, I
34	7.15	14	6.33	35.04	Q, F, K-Ch, I
35	6.60	25	3.54	30.72	Q, F, K-Ch
36	7.20	19	4.61	29.84	Q, F, K-Ch, I
37	6.60	10	9.25	49.20	Q, F, Ch
38	7.00	14	8.80	48.64	Q, F, K
39	7.30	16	10.97	58.72	Q, F, K-Ch, I
40	6.80	10	14.19	61.92	Q, F, K, I
41	7.50	9	0.46	6.48	Q, F, C
42	6.90	17	5.72	25.84	Q, F, C
43	7.90	16	9.98	54.32	Q, F, Ch
44	7.80	14	4.68	18.80	Q, F, C
45	7.90	14	1.72	4.64	Q, D, C
46	7.65	14	27.91	144.64	amorphous
47	7.00	14	18.16	87.84	Q, F
48	7.00	16	16.44	77.28	Q, F, Ch, I
49	7.00	12	12.01	56.64	Q, F, Ch, I
50	6.85	15	4.18	23.92	Q, F, K-Ch, I

MOIRA RIVER cont'd

51	7.20	14	3.53	25.36	Q, F, Ch
52	7.20	7	4.95	31.84	Q, F
53	7.40	5	4.36	29.52	Q, F, C
54	7.25	6	4.56	29.52	Q, F, C
55	7.10	7	3.20	21.12	Q, F, C
56	7.30	7	6.02	37.84	Q, F, Ch
57	7.45	6	4.96	27.84	Q, F, C
58	7.35	8	5.87	35.76	Q, F, C
59	7.40	9	3.43	17.44	Q, F, D, C
60	7.25	12	15.76	75.84	Q, F
61	7.50	11	6.46	31.04	Q, F, I
62	7.25	10	2.24	13.44	Q, F, Ch

Sample No.	ppm			ppm			ppm			HF/ HClO ₄ K %
	HF/ HClO ₄ Cu	HF/ HClO ₄ Pb	HF/ HClO ₄ Zn	HF/ HClO ₄ Ni	HF/ HClO ₄ Fe %	HF/ HClO ₄ Mn	HF/ HClO ₄ Mg %	HF/ HClO ₄ Ca %	HF/ HClO ₄ Na %	
1	22	10	82	48	5.6	465	1.00	1.76	1.12	0.34
2	26	14	110	54	5.6	450	1.06	1.47	0.65	0.45
3	16	12	100	48	5.0	340	0.73	1.22	0.87	0.41
4	14	16	110	44	5.4	365	0.75	1.17	1.04	0.38
5	14	12	105	44	5.8	350	0.73	1.05	0.98	0.38
6	18	26	155	42	6.6	945	0.67	1.02	0.77	0.32
7	22	18	145	56	5.8	690	0.73	1.02	0.82	0.31
8	26	26	120	54	5.2	270	0.53	0.80	0.55	0.32
9	16	24	150	46	5.6	550	0.71	1.37	0.87	0.38
10	24	12	86	44	5.2	280	0.58	1.02	0.73	0.28
11	16	26	115	36	5.4	390	0.69	1.14	0.82	0.35
12	14	32	120	46	6.0	640	0.85	1.14	0.77	0.23
13	20	24	135	36	4.8	450	0.56	0.73	0.77	0.28
14	46	48	125	40	3.6	195	0.28	1.00	0.62	0.10
15	8	18	96	24	5.4	390	0.56	0.91	0.25	0.41
18	16	18	115	22	4.6	270	0.47	1.00	0.98	0.38
19	70	1300	44000	30	6.0	910	1.20	5.90	0.92	0.25

20	34	265	3100	42	6.0	330	0.65	1.14	0.55	0.41
21	14	20	115	28	6.0	330	0.62	0.96	0.69	0.45
22	16	66	180	30	6.6	515	0.48	0.84	1.04	0.31
23	14	40	135	28	6.2	515	0.58	1.14	0.62	0.31
24	26	140	2700	36	6.0	600	0.56	0.96	0.58	0.38
25	34	115	660	26	4.0	230	0.37	1.00	0.52	0.20
26	20	26	310	32	4.8	255	0.54	0.86	0.40	0.38
27	12	30	240	44	8.8	5800	0.67	1.64	0.77	0.20
28	14	32	240	30	6.6	750	0.75	1.22	0.82	0.31
29	24	34	155	36	4.6	305	0.51	0.73	0.92	0.31
30	20	22	115	44	6.4	500	0.80	0.88	0.77	0.41
31	36	50	230	24	4.6	280	0.33	1.22	0.38	0.15
32	130	56	350	36	6.6	450	1.34	0.74	0.62	0.28
33	18	72	155	16	4.0	390	0.44	0.88	0.40	0.19
34	8	14	105	40	6.6	525	1.02	2.20	1.20	0.54
37	8	26	135	32	5.0	450	0.73	1.37	1.12	0.50
38	26	50	96	36	3.4	160	0.14	0.95	0.11	0.06
39	22	20	56	14	2.6	120	0.11	0.97	0.11	0.04

Sample No.	HCl Cu ppm	HCl Pb ppm	HCl Zn ppm	HCl Ni ppm	HCl Fe %	HCl Mn ppm	HCl Mg %	HCl Ca %	HCl Na ppm	HCl K ppm
1	15	7	33	12	2.0	200	0.90	1.54	225	325
2	18	12	66	20	2.8	480	1.62	1.89	325	1600
3	13	9	68	14	2.7	280	0.76	0.65	325	775
4	8	9	70	9	2.1	120	0.48	0.46	325	275
5	10	8	63	10	2.1	160	0.44	0.39	325	275
6	12	24	115	15	3.3	1480	0.50	0.56	600	325
7	13	12	97	15	2.6	680	0.60	0.48	425	275
8	20	24	110	25	3.0	320	0.80	0.54	600	425
9	8	16	125	9	2.9	480	0.64	0.64	325	175
10	15	13	49	12	2.2	70	0.44	0.58	675	100
11	10	24	85	9	1.7	120	0.40	0.56	500	125
12	11	33	91	12	2.8	680	1.0	0.92	775	200
13	14	18	110	11	2.6	560	0.68	0.49	425	200
14	24	37	89	16	2.0	200	0.39	1.14	1275	200
15	5	18	48	6	2.5	280	0.33	0.27	275	200
18	7	35	69	5	1.3	110	0.20	0.29	675	125
19	2	835	5600	10	2.4	800	1.4	9.6	500	325

20	24	260	2650	18	3.3	240	0.85	0.88	775	1100
21	7	10	51	7	1.9	145	0.39	0.26	200	200
22	10	60	155	9	3.6	760	0.54	0.44	775	325
23	9	32	91	9	2.7	440	0.66	0.35	375	375
24	21	160	3300	18	3.8	1100	0.64	0.90	1000	875
25	24	97	660	10	2.1	200	0.52	0.63	1200	450
26	15	28	295	12	2.2	160	0.72	0.53	375	425
27	7	30	190	8	4.5	16100	0.80	0.77	1850	250
28	9	23	175	8	2.6	800	0.56	0.53	375	200
29	16	25	135	16	2.3	360	0.76	0.63	500	600
30	9	10	45	7	3.0	440	1.27	0.65	225	600
31	18	41	110	9	2.0	280	0.18	1.14	1275	200
32	51	38	175	9	3.0	440	1.9	0.56	425	375
33	11	60	135	8	2.2	480	0.60	0.99	775	275
34	4	8	31	4	1.3	110	0.87	1.24	175	275
37	4	16	31	4	0.9	120	0.56	1.14	175	275
38	12	41	82	9	2.1	320	0.21	1.54	1000	200
39	8	17	45	8	1.8	280	0.18	5.4	1850	125

SAMPLE NUMBER	Cu ppb	Pb ppb	Zn ppb	Ni ppb	Mn ppb	Mg ppm	Fe ppb	Ca ppm	Na ppm	K ppm
--- Z - 1	4	24	57	4	70	7.0	1100	19.0	1.85	1.20
2	< 2	12	73	< 2	60	9.0	800	32.5	2.55	1.40
3	< 2	< 2	31	< 2	50	10.0	400	36.5	2.60	1.20
4	< 2	< 2	25	< 2	140	12.0	600	54.7	3.38	1.32
5	< 2	< 2	21	< 2	130	12.5	550	52.2	3.38	1.25
6	< 2	< 2	32	< 2	370	10.0	750	40.0	3.38	1.52
7	< 2	< 2	24	< 2	1050	11.0	900	41.7	4.45	1.60
8	< 2	< 2	26	< 2	460	9.5	750	33.5	3.20	1.45
9	< 2	< 2	23	< 2	320	3.0	1650	9.2	0.80	0.40
10	< 2	2	20	< 2	70	4.5	650	15.5	0.40	0.30
11	< 2	< 2	19	< 2	60	4.5	450	14.2	0.22	0.10
12	< 2	< 2	-19	< 2	50	4.5	450	14.7	0.22	0.20
Z - 13	3	< 2	20	< 2	280	2.5	1600	18.0	0.72	0.35
14	8	< 2	10	< 2	360	4.5	750	18.2	0.72	0.20
15	10	38	19	3	710	3.0	7100	11.5	0.72	1.32
18	2	< 2	15	< 2	50	3.0	750	8.0	0.60	0.35
19	< 2	< 2	280	< 2	30	20.2	300	92.0	33.0	1.20

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20	< 2	< 2	< 2	69	< 2	70	19.8	350	95.0	35.0	1.20
21	< 2	< 2	< 2	50	< 2	40	3.0	550	9.2	0.50	0.60
22	< 2	< 2	< 2	4	< 2	220	4.0	2000	11.5	0.65	1.40
23	6	28		14	4	700	4.5	3750	12.7	0.80	1.40
24	2	< 2		56	2	200	19.8	1050	92.0	33.8	1.40
25	3	< 2		20	< 2	240	17.3	1000	72.0	27.0	0.40
26	< 2	< 2		11	< 2	180	10.0	750	32.5	9.50	0.65
27	4	6		18	2	1100	6.0	2850	17.5	3.20	0.50
28	2	12		4	2	420	5.5	250	17.5	3.10	0.70
29	3	< 2		9	< 2	180	6.5	1550	21.2	1.85	0.50
30	< 2	< 2		14	< 2	200	6.5	900	22.7	1.65	0.55
31	< 2	< 2		13	< 2	100	4.5	450	19.0	0.60	0.15
32	< 2	< 2		12	< 2	40	3.5	300	11.0	0.90	0.88
33	3	< 2		19	2	130	3.5	250	11.5	0.90	1.10
34	28	2		76	14	80	3.5	200	11.5	1.20	1.05
35	10	8		3060	< 2	380	22.8	1900	115.0	32.0	2.50
36	8	10		3336	< 2	540	23.9	3100	125.0	32.0	2.60
37	< 2	< 2		30	< 2	100	3.5	250	11.0	1.20	0.90
38	< 2	< 2		23	< 2	100	4.0	700	14.2	0.98	0.55
39	2	< 2		31	< 2	110	4.0	600	14.7	0.98	0.60

LONG LAKE

Sample No.	pH	TOC (ppm)	% ORG. C	CEC (me/100g.)	MINERALOGY
1	6.55	17	1.07	11.28	Q, F
2	6.80	16	1.37	21.60	Q, F, Ch
3	6.95	10	2.12	21.60	Q, F, Ch
4	7.10	8	2.30	17.44	Q, F,
5	7.30	7	1.59	16.96	Q, F, Ch
6	7.00	16	6.46	37.92	Q, F, Ch
7	6.85	12	2.51	30.64	Q, F, K-Ch
8	6.60	18	7.15	49.20	Q, F, Ch
9	6.20	11	5.49	32.16	Q, F, Ch
10	6.30	9	7.10	42.16	Q, F, Ch
11	6.70	13	6.46	30.16	Q, F, Ch
12	6.60	8	6.40	34.16	Q, F,
13	6.25	12	7.98	51.36	Q, F, Ch
14	6.40	10	23.26	133.12	Q, F
15	6.20	18	3.68	23.04	Q, F, Ch
18	8.30	13	8.14	36.24	Q, F, Ch
19	7.30	4	3.00	21.36	Q, F, Ch, C
20	7.45	7	6.24	43.44	Q, F
21	6.50	14	1.45	14.72	Q, F, Ch
22	6.50	17	8.88	59.12	Q, F, Ch
23	6.30	16	7.50	42.16	Q, F, Ch-K
24	7.40	12	8.22	62.40	Q, F, Ch
25	7.10	22	13.66	81.28	Q, F, Ch
26	6.50	12	5.48	37.44	Q, F, Ch
27	6.50	27	3.68	40.72	Q, F

LONG LAKE cont'd

28	6.50	13	5.68	28.64	Q, F, Ch
29	6.60	14	11.13	58.32	Q, F, Ch
30	6.65	13	2.31	32.72	Q, F, Ch
31	6.60	18	26.84	123.36	Q, F
32	6.75	8	7.38	37.28	Q, F, Ch-K
33	6.70	12	18.28	94.56	Q, F
34	8.10	10	0.75	5.68	Q, F, Ch
35	7.40	2	-	-	Water from pumps draining under ground
36	7.45	7	-	-	Water from pump on mill
37	6.80	8	0.76	6.40	Q, F,
38	6.50	23	28.31	151.52	amorphous
39	6.55	29	33.15	165.44	amorphous

Sample No.	ppm		ppm		ppm		ppm		ppm		ppm		ppm		ppm		ppm	
	HF/ HClO ₄ Cu	HF/ HClO ₄ Pb	HF/ HClO ₄ Zn	HF/ HClO ₄ Ni	HF/ HClO ₄ Fe	HF/ HClO ₄ Mn	HF/ HClO ₄ Mg	HF/ HClO ₄ Ca	HF/ HClO ₄ Na	HF/ HClO ₄ K								
11	32	28	125	44	6.6	760	1.38	0.84	0.69	0.23								
2	20	22	120	32	5.0	490	0.58	0.98	0.86	0.38								
3	14	12	105	34	6.2	760	0.67	0.98	0.98	0.38								
4	22	16	105	46	5.0	895	0.67	0.88	0.77	0.38								
5	24	28	125	28	5.4	1000	0.60	0.95	0.77	0.34								
6	22	34	135	30	4.6	920	0.67	1.00	0.77	0.31								
7	16	24	115	34	4.8	2350	0.58	1.10	0.86	0.41								
8	24	26	130	26	4.6	550	0.56	0.82	0.69	0.28								
9	34	16	135	38	4.8	330	0.51	0.66	0.58	0.28								
10	26	20	190	38	5.4	340	0.71	0.82	0.77	0.20								
11	36	50	125	24	3.4	440	0.36	1.00	0.28	0.19								
12	12	24	120	34	5.2	1000	0.56	1.02	0.98	0.38								
13	110	88	150	36	4.8	340	0.58	0.93	1.00	0.45								
14	18	38	120	16	2.8	465	0.32	0.88	0.32	0.15								
15	24	40	92	28	3.2	205	0.29	0.84	0.43	0.18								

16	28	20	100	36	5.2	580	0.93	1.32	0.73	0.28
17	34	52	125	26	4.2	150	0.48	1.18	0.43	0.16
18	20	18	115	30	6.4	1150	0.63	1.04	0.98	0.34
20	22	32	140	34	6.6	3000	0.48	1.04	0.65	0.25
21	36	40	170	28	4.4	785	0.63	5.50	0.65	0.28
22	46	54	510	40	6.2	440	0.61	1.53	0.86	0.34
23	16	18	94	30	4.4	450	0.53	1.44	0.86	0.31
24	60	14	100	40	5.0	270	0.65	0.97	0.77	0.34
25	16	22	98	38	5.2	420	0.78	1.34	1.04	0.41
26	30	24	110	54	6.2	640	1.10	1.44	0.82	0.38
27	18	18	90	36	6.4	750	0.54	1.80	0.98	0.34
28	28	96	240	44	4.8	1000	0.48	1.07	0.69	0.23
29	20	44	140	30	4.0	400	0.56	1.20	0.52	0.19
30	22	20	120	36	4.8	870	0.61	0.91	0.77	0.34

Sample No.	HCl Cu ppm	HCl Pb ppm	HCl Zn ppm	HCl Ni ppm	HCl Fe %	HCl Mn ppm	HCl Mg %	HCl Ca %	HCl Na ppm	HCl K ppm
L1	23	30	87	17	3.1	1100	1.71	0.32	325	175
2	15	12	80	9	2.8	400	0.50	0.36	500	175
3	9	11	56	7	2.3	920	0.52	0.46	500	150
4	18	7	72	12	2.2	1535	0.62	0.46	425	150
5	16	19	81	10	2.6	2000	0.58	0.56	425	300
6	15	25	92	8	2.5	1360	0.74	0.75	1275	175
7	11	15	78	8	2.5	1610	0.48	0.56	375	1000
8	16	18	85	7	2.1	800	0.50	0.51	775	100
9	23	18	81	9	2.3	320	0.50	0.42	500	75
10	20	16	170	11	2.9	240	0.78	0.54	675	125
11	26	46	98	9	2.3	760	0.56	1.24	1275	100
12	9	15	81	8	2.1	3400	0.50	0.60	675	175
13	96	67	120	8	2.5	160	0.50	0.24	375	250
14	12	34	115	8	2.0	840	0.37	0.86	1400	125
15	18	40	81	8	2.5	320	0.52	1.09	2000	250

16	19	18	55	9	2.9	600	1.33	2.15	425	325
17	22	44	96	9	2.7	1180	0.76	0.96	1700	325
18	13	15	80	9	3.1	3200	0.72	0.66	1000	150
20	13	25	97	9	3.6	7200	0.54	0.60	1225	150
21	23	31	130	9	1.8	1000	0.78	8.6	675	375
22	42	51	530	19	2.9	240	0.83	1.58	775	250
23	9	7	49	6	1.3	240	0.39	0.60	600	100
24	46	13	62	14	2.2	70	0.55	0.75	675	175
25	9	12	52	7	1.8	240	0.46	0.42	375	125
26	20	14	60	16	2.5	720	0.92	0.88	425	275
27	11	11	38	7	1.8	480	1.51	1.72	275	150
28	18	81	195	10	2.6	1920	0.76	1.04	1275	375
29	16	41	125	9	2.2	600	0.88	1.65	775	175
30	18	14	86	10	2.8	1300	0.60	0.58	325	175

SAMPLE NUMBER NATURAL WATER	Cu ppb	Pb ppb	Zn ppb	Ni ppb	Mn ppb	Mg ppm	Fe ppb	Ca ppm	Na ppm	K ppm
L - 1	< 2	2	26	< 2	40	6.0	80	21.2	0.60	0.80
2	< 2	< 2	19	4	50	6.5	120	22.0	0.68	0.70
3	2	4	20	< 2	40	9.0	140	26.0	0.80	0.50
4	6	< 2	25	< 2	70	8.5	200	22.7	0.72	0.45
5	< 2	2	22	< 2	50	8.5	150	22.0	0.50	0.40
6	< 2	< 2	21	< 2	100	8.0	300	20.5	0.80	0.40
7	< 2	< 2	13	< 2	20	16.0	60	114.0	0.42	0.88
8	< 2	< 2	20	< 2	190	7.5	400	19.6	0.67	0.50
9	< 2	< 2	15	< 2	110	8.0	300	19.0	0.60	0.38
10	< 2	< 2	12	< 2	240	8.5	750	27.7	0.50	0.55
11	< 2	< 2	19	< 2	70	7.0	150	16.7	0.80	0.50
12	< 2	< 2	17	< 2	140	15.5	450	37.5	1.85	1.00
13	< 2	< 2	16	< 2	30	5.5	100	20.5	0.80	0.45
14	< 2	< 2	13	< 2	70	4.5	450	12.1	0.68	0.35
15	< 2	< 2	16	< 2	20	6.5	60	14.7	1.17	0.60

16	2	< 2	4	< 2	50	6.5	100	22.0	0.60	0.88
17	< 2	6	14	< 2	50	5.5	80	20.5	0.38	0.88
18	2	< 2	15	< 2	350	5.0	750	19.0	0.52	1.25
19	2	18	14	< 2	10	10.0	40	26.0	0.68	2.32
20	< 2	6	9	< 2	1300	15.5	1900	40.0	1.90	0.92
21	< 2	8	12	< 2	180	11.2	350	22.7	0.72	0.60
22	< 2	6	13	< 2	70	6.5	200	22.0	0.60	0.80
23	< 2	12	10	< 2	60	13.8	200	41.0	0.60	1.32
24	< 2	4	15	< 2	80	8.0	300	24.5	0.80	0.92
25	< 2	8	11	< 2	80	10.0	450	27.7	0.72	0.88
L - 26	2	14	10	2	1950	7.0	3550	33.5	1.10	2.00
27	2	4	20	< 2	60	7.0	200	21.2	0.52	0.88
28	< 2	6	20	< 2	60	3.0	150	11.0	0.45	0.50
29	< 2	6	20	< 2	60	7.0	80	22.0	0.75	0.75
30	< 2	12	40	< 2	360	8.5	900	26.0	0.60	1.25

LAVANT-CLYDE

Sample No.	pH	TOC (ppm)	% ORG. C	CEC (me/100g.)	MINERALOGY
1	7.50	10	5.64	49.12	Q, F, K-Ch
2	7.30	10	7.60	38.88	Q, F, K-Ch
3	7.20	9	3.35	21.12	Q, F
4	7.15	7	4.55	37.12	Q, F, K-Ch
5	7.40	8	5.61	39.20	Q, F
6	7.20	11	9.80	45.84	Q, F, K-Ch
7	6.90	6	6.22	40.00	Q, F, K-Ch
8	7.10	9	8.89	47.84	Q, F, K-Ch
9	7.00	10	7.82	44.88	Q, F, K-Ch
10	6.70	7	9.74	59.20	Q, F, K-Ch, I
11	6.95	10	17.40	94.08	Q, F, I, K-Ch
12	7.05	10	8.50	55.12	Q, F, K-Ch
13	7.20	14	3.98	17.12	Q, F, Ch
14	7.00	12	19.14	110.24	Q, F, K-Ch
15	7.10	6	21.84	101.12	Q, F, Ch
16	7.40	11	10.12	59.20	Q, F, Ch-K
17	6.95	14	15.56	87.52	Q, F
18	7.00	15	5.27	40.72	Q, F, K-Ch
19	7.60	7	-	-	no sediment
20	7.00	10	12.49	84.80	Q, F, Ch-K
21	6.90	10	5.72	39.36	Q, F, Ch-K, C
22	6.80	10	4.40	21.84	Q, F, Ch-K
23	7.20	15	7.38	42.40	Q, F, Ch-K
24	7.00	8	11.24	64.08	Q, F
25	7.25	14	4.67	25.52	Q, F, Ch-K
26	6.50	14	8.47	41.60	Q, F, Ch-K
27	7.05	2	3.10	17.04	Q, F, Ch-K
28	7.10	1	13.86	70.24	Q, F, Ch-K
29	7.20	4	21.01	80.80	Q, F, Ch-K
30	7.30	8	9.41	57.20	Q, F, Ch-K

a

Sample No.	ppm			ppm			ppm			ppm			ppm			HF/ HClO ₄ K %
	HF/ HClO ₄ Cu	HF/ HClO ₄ Pb	HF/ HClO ₄ Zn	HF/ HClO ₄ Ni	HF/ HClO ₄ Fe %	HF/ HClO ₄ Mn	HF/ HClO ₄ Mg %	HF/ HClO ₄ Ca %	HF/ HClO ₄ Na %	HF/ HClO ₄ Mg %	HF/ HClO ₄ Ca %	HF/ HClO ₄ Na %	HF/ HClO ₄ K %			
S 1	34	30	145	54	5.6	330	0.67	0.70	0.86	0.45						
2	46	16	94	66	4.8	390	0.56	1.07	0.98	0.60						
3	16	52	300	200	5.2	800	0.37	0.91	0.77	0.45						
4	60	30	300	250	5.6	650	0.90	0.55	0.58	0.31						
5	24	76	260	110	5.6	380	0.44	0.72	0.92	0.50						
6	6	18	86	36	4.8	600	0.42	0.70	0.86	0.41						
7	6	16	94	38	4.0	380	0.45	0.93	1.20	0.50						
8	6	16	76	44	5.8	640	0.47	1.05	1.20	0.50						
9	18	14	90	50	6.4	1000	0.53	0.91	0.92	0.41						
10	6	10	60	34	4.6	355	0.47	0.68	1.20	0.50						
11	36	30	140	62	5.6	405	0.63	1.00	0.86	0.41						
12	6	14	66	40	4.4	290	0.42	0.91	1.04	0.54						
13	6	12	56	26	3.6	230	0.40	0.84	1.12	0.50						

Sample No.	HCl Cu ppm	HCl Pb ppm	HCl Zn ppm	HCl Ni ppm	HCl Fe %	HCl Mn ppm	HCl Mg %	HCl Ca %	HCl Na ppm	HCl K ppm
1	27	28	120	22	3.0	280	0.52	0.29	375	700
2	17	10	63	46	2.9	440	1.07	1.3	425	1100
3	20	56	285	180	3.3	1390	0.52	0.66	500	200
4	18	28	300	280	4.0	1070	0.62	0.33	775	375
5	13	64	170	55	2.5	360	0.44	0.39	275	275
6	14	9	50	5	2.5	720	0.22	0.33	600	150
7	4	9	52	18	1.7	240	0.22	0.33	325	175
8	3	6	40	17	1.7	720	0.24	0.39	275	150
9	5	7	51	20	2.0	1680	0.35	0.54	325	200
10	3	2	21	6	1.5	120	0.11	0.30	275	200
11	27	28	98	22	2.9	480	0.90	1.32	500	375
12	3	5	34	7	1.7	85	0.22	0.33	225	175
13	2	4	22	5	1.3	85	0.15	0.29	200	125

SAMPLE NUMBER NATURAL WATER	Cu ppb	Pb ppb	Zn ppb	Ni ppb	Mn ppb	Mg ppm	Fe ppb	Ca ppm	Na ppm	K ppm
S - 1	2	4	368	2	130	4.5	1650	18.2	2.45	0.20
2	< 2	4	35	12	2100	18.5	1250	40.0	1.75	0.60
3	< 2	4	144	8	930	18.0	650	41.0	1.90	0.35
4	2	8	90	16	2600	18.5	1350	37.5	1.70	0.28
5	2	6	50	4	1150	18.0	750	40.0	2.10	0.45
6	< 2	6	36	< 2	270	4.0	1050	16.0	1.85	0.45
7	< 2	2	35	< 2	220	6.0	1100*	18.2	2.10	0.60
8	< 2	2	40	< 2	340	7.0	900	20.5	2.55	0.60
9	< 2	4	37	< 2	310	9.0	750	25.2	3.10	0.80
10	< 2	4	83	< 2	230	9.0	500	37.5	4.50	1.40
11	2	6	35	3	220	7.5	650	34.5	4.55	1.10
12	2	2	36	2	300	5.5	450	24.3	3.50	1.05
13	2	2	60	2	130	5.0	350	23.5	3.10	0.88

SULPHIDE CREEK

Sample No.	pH	TOC (ppm)	% ORG. C	CEC (me/100g.)	MINERALOGY
1	6.30	16	5.19	34.32	Q, F, Ch
2	6.35	7	1.50	14.00	Q, F, Ch
3	6.35	6	4.36	26.24	Q, F, Ch
4	6.30	8	7.34	43.60	Q, F
5	6.40	7	2.11	12.88	Q, F, Ch
6	6.75	16	3.36	18.32	Q, F, Ch
7	7.00	12	1.89	9.60	Q, F, Ch
8	6.90	15	1.16	8.16	Q, F, Ch
9	6.90	16	1.37	11.20	Q, F, Ch
10	7.00	9	0.80	6.64	Q, F,
11	7.00	20	5.11	26.32	Q, F, Ch
12	7.25	12	0.99	8.08	Q, F, Ch
13	7.60	10	0.65	4.56	Q, F

SEDIMENTS SAMPLE NUMBER	ppm			ppm			ppm			HF/ HClO ₄ Mg %	HF/ HClO ₄ Ca %	HF/ HClO ₄ Na %	HF/ HClO ₄ K %
	HF/ HClO ₄ Cu	HF/ HClO ₄ Pb	HF/ HClO ₄ Zn	HF/ HClO ₄ Ni	HF/ HClO ₄ Fe %	HF/ HClO ₄ Mn	HF/ HClO ₄ Mg %	HF/ HClO ₄ Ca %	HF/ HClO ₄ Na %	HF/ HClO ₄ K %			
CI1	560	3000	4200	96	7.4	1000	2.15	2.20	0.30	0.28			
2	84	325	1080	64	6.8	820	1.42	1.44	1.16	0.88			
3	130	610	1160	68	6.0	845	1.76	1.90	0.69	0.54			
4	350	1280	2900	145	6.6	1300	1.75	2.80	0.55	0.38			
5	280	1270	1890	105	6.0	1350	1.85	3.40	0.55	0.41			
6	270	1250	1760	130	6.4	1000	1.85	2.70	0.48	0.34			
7	430	1380	1560	135	6.6	1300	1.80	3.00	0.42	0.34			
8	84	225	960	56	6.0	2500	0.48	0.45	0.58	0.34			
9	22	44	140	46	4.8	500	0.78	0.74	1.12	0.60			

Sample No.	HCl Cu ppm	HCl Pb ppm	HCl Zn ppm	HCl Ni ppm	HCl Fe %	HCl Mn ppm	HCl Mg %	HCl Ca %	HCl Na ppm	HCl K ppm
CI 1	210	2800	2000	21	4.0	960	0.83	3.0	150	700
2	38	280	740	23	3.0	1080	1.07	2.45	775	1475
3	43	475	645	24	3.0	1000	0.97	3.30	1100	1350
4	77	855	1400	31	3.1	1840	0.83	3.20	675	1350
5	54	810	745	25	2.5	920	1.13	3.20	600	2700
6	70	810	835	31	4.0	1340	0.78	2.90	600	1750
7	110	910	830	36	3.5	760	0.69	3.40	675	875
8	52	215	775	21	3.9	5600	0.30	0.28	425	500
9	15	29	91	15	2.8	600	0.92	0.42	425	1900

SAMPLE NUMBER NATURAL WATER	Cu ppb	Pb ppb	Zn ppb	Ni ppb	Mn ppb	Mg ppm	Fe ppb	Ca ppm	Na ppm	K ppm
CI - 1	2	< 2	70	< 2	30	2.0	800	7.0	1.20	1.15
2	2	2	90	< 2	90	20.9	600	77.0	7.75	8.70
3	2	2	100	< 2	140	21.5	750	66.0	8.15	9.10
4	6	< 2	130	< 2	400	24.0	1800	66.0	9.70	8.80
5	4	< 2	40	2	100	15.0	400	31.5	7.60	3.40
6	2	12	220	2	1500	48.2	6600	155.0	18.5	28.5
7	4	< 2	30	< 2	40	14.2	400	23.5	7.60	2.60
8	5	< 2	90	< 2	1400	13.8	1350	42.2	6.35	3.20
9	60	32	110	6	620	19.8	5600	51.0	21.8	3.80

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CALUMET ISLAND

Sample No.	pH	TOC (ppm)	% ORG. C	CEC (me/100g.)	MINERALOGY
1	6.90	14	0.43	4.80	Q, F, I, Ch, C
2	7.25	8	0.71	15.04	Q, F, I, Ch, C
3	7.00	8	0.72	11.84	Q, F, I, Ch, C
4	6.90	10	1.61	8.72	Q, F, I, Ch, C
5	6.90	11	1.13	4.80	Q, F, I, Ch, C
6	6.85	8	0.83	7.12	Q, F, I, C
7	7.80	12	0.67	5.12	Q, F, I, C
8	6.80	15	7.19	54.00	Q, F
9	6.75	15	2.73	23.04	Q, F,

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Appendix V - Computer programme statement listings

- (a) calculation and plotting of
element distribution ratios
 - (b) regression analysis.
- 4

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PCL
COPY TEMP TO CP
COPY TEMP TO IP
    DIMENSION ELM(10), IGRAPH(120,4), NOSYMB(20), NOSAMP(62),
    1 RAT(62,10,2), LINE(120), CARBON(62,2), WATHET(62,10), SEDLAT(62,10),
    2 SEDAD8(62,10), HFRAT(62,10), HCLRAT(62,10), PCARB(62), TOC(62),
    3 SCALER(19), FAC(21), TENC(10), VALMAX(10,2), TITLE(8,4), IRAT(7,4),
    4 XFAC(2), IP(3), NPOINT(10,2)
    EQUIVALENCE INFRAT(1,1), RAT(1,1,1,1), HCLRAT(1,1,1), RAT(1,1,2),
    1 (PCARB(1), CARBON(1,1)), (TOC(1), CARBON(1,2))
    COMMON ELM, IGRAPH, NOSYMB, NOSAMP, RAT, LINE, CARBON, WATHET, SEDLAT,
    1 SEDAD8
    COMMON /O/ SCALER, FAC, TENC, VALMAX, TITLE, IRAT, XFAC, IP
    CALL EOFSET(998)
    DATA SCALER/O.1, O.16, O.25, O.4, O.625, 1.0, 1.6, 2.5, 4.0, 6.25, 10.0,
    1 16.0, 25.0, 40.0, 62.5, 100.0, 160.0, 250.0, 400.0/
    DATA FAC/625.0, 400.0, 250.0, 160.0, 100.0, 62.5, 40.0, 25.0, 16.0, 10.0,
    1 6.25, 4.0, 2.5, 1.6, 1.0, 0.625, 0.4, 0.25, 0.16, 0.1, 0.0625/
    DATA TITLE/4H= , 4HDATE, 4H R AN, 4HALYS, 4HES, 4HAS R, 4HEAD,
    1 4HIN , 4H= , 4HMF O, 4HIGES, 4HTION, 4H (TO, 4HTAL, 4HMETA, 4HML) ,
    2 4H= H, 4HCL O, 4HIGES, 4HTION, 4H IAD, 4H SORB, 4HED I, 4HONS),
    3 4HX GR, 4HG C , 4HIN $, 4HEC , 4H , 4H , 4H TOC, 4H PPM/
    DATA IRAT/4H= , 4H RAT(1, 4H O 1 , 4H (TOT, 4HAL M, 4HETAL, 4H) ,
    1 4H= , 4H RAT(1, 4H O 2 , 4H (ADS, 4HORBE, 4H O ME, 4HTAL)/
    READ 60, ELM
    60 FORMAT(10(A2,2X))
    READ 61, NOSYMB
    61 FORMAT(20(A1,1X))
    IPAGE=1
    LINES=50
    NOFILE=0
    NUMBER=0
    C *** PUT AXES IN PLOT
    DO 24 I=1,41
    IGRAPH(I,1)=17
    24 CONTINUE
    DO 25 I=2,110
    IGRAPH(I,41)=16
    25 CONTINUE
    DO 26 I=111,120
    IGRAPH(I,41)=11
    26 CONTINUE

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20 NGE=LE=NOFILE+1
C *** START READING DATA. FIRST CARD TO CONTAIN AREA DESIGNATION IN
C *** COLUMN 1 AND, IF NECESSARY, NEXT THREE COLUMNS. IN SAME CARD,
C *** INDICATE TYPE OF ANALYSIS IN COLUMN 5, 6, 7, OR 8 BY FOLLOWING
C *** NUMBER: 1 FOR WATER ANALYSES
C ***          2 FOR HF DIGESTION (TOTAL METAL)
C ***          3 FOR HCL DIGESTION (ADSORBED METAL)
C *** LEAVE AT LEAST ONE COLUMN BLANK AND STATE NUMBER OF ELEMENTS -
C *** DEFAULT VALUE IS 10, MAXIMUM IS ALSO 10 *****
      READ 3,AREA,ITYPE,NE
      3 FORMAT(A,20.0)
      IF (NE.EQ.0) NE=10
      IF (NE.GT.10) NE=10
      IF (ITYPE.EQ.0) ITYPE=1
      IF (ITYPE.GT.3) ITYPE=3
      IF (LINES.LT.20) GO TO 180
      PRINT 18,AREA,(TITLE(I),ITYPE(I),I=1,8),IPAGE
      18 FORMAT(1H,'AREA ',9A,55X,'PAGE',1A,/)
      IPAGE=IPAGE+1
      LINES=3
      GO TO 182
180 PRINT 18,AREA,(TITLE(I),ITYPE(I),I=1,8)
181 FORMAT(1,/,/, ' AREA ',9A,/)
      LINES=LINES+6
182 DO 11 I=1,12
      READ 9,NOS,(TENOR(J),J=1,NE)
      9 FORMAT(110.0)
      IF (NOS.GT.999) GO TO 12
      IF (LINES.LT.42) GO TO 183
      PRINT 18,AREA,(TITLE(I),ITYPE(I),J=1,8),IPAGE
      IPAGE=IPAGE+1
      LINES=3
183 PRINT 27,NOS,(TENOR(J),J=1,NE)
27 FORMAT(13,418,AFR,2)
      LINES=LINES+1
      GO TO 15,7,9,ITYPE
5 NOSAMP(1)=NOS
      NUMBER=NUMBER+1
      GO 6 J=1,NE
      NATHET(I,J)=TENOR(J)
      6 CONTINUE
      GO TO 11
7 IF (NOS=NOSAMP(1)) GO TO 74,72

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70 PRINT 71, AREA, NOS
71 FORMAT(' SAMPLE MIXUP IN AREA ', A4, ' NEAR NUMBER', I3)
   GO TO 99
72 DO 73 J=1, NE
   SEDLAT(I, J)=0
73 CONTINUE
   I=I+1
   GO TO 7
74 DO 8 J=1, NE
   SEDLAT(I, J)=TENOR(J)
8 CONTINUE
   GO TO 11
9 IF (NOS=NOSAMP(I)) GO TO 94, 92
92 DO 93 J=1, NE
   SEDADS(I, J)=0
93 CONTINUE
   I=I+1
   GO TO 9
94 DO 10 J=1, NE
   SEDADS(I, J)=TENOR(J)
10 CONTINUE
11 CONTINUE
C *** CHECK FOR EXCESS DATA - IF MORE THAN 62 STATIONS IN SAMPLING AREA,
C *** PROGRAM IGNORES THE BALANCE AND PRINTS A WARNING ***
   READ 4, NOS
   IF (NOS.LT.999) CALL EXREAD(AREA)
12 IF (NFILE.LT.3) GO TO 20
C *** PREPARE TO READ PERCENTAGES OF ORGANIC CARBON IN THE SEDIMENTS
C *** AND THE PPM OF TOTAL ORGANIC CARBON IN THE WATER SAMPLES ***
C *** FIRST ACTION IS THE PRINTING OF HEADING FOR CARBON DATA LISTING
   IF (LINES.LT.20) GO TO 120
   PRINT 18, AREA, (TITLE(I, 4), I=1, 8), IPAGE
   IPAGE=IPAGE+1
   LINES=3
   GO TO 121
120 PRINT 18, AREA, (TITLE(I, 4), I=1, 8)
   LINES=LINES+6
121 NCCARD=(NUMBER+9)/10
   IF INISH=0
C *** PERCENTAGE ORGANIC CARBON IS READ IN THE FOLLOWING LOOP. SUPPLY TEN
C *** PERCENTAGES PER CARD - ADDITIONAL ONES WILL NOT BE READ - IN FREE
C *** FORMAT, I.E. REAL OR INTEGER NUMBERS, SEPARATED BY BLANKS ***
   DO 122 J=1, NCCARD

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121 START=IFINISH+1
    IFINISH=IFINISH+10
    IF (IFINISH.GT.NUMBER) IFINISH=NUMBER
    READ A,IPCARB(I),I=1,START,IFINISH)
122 CONTINUE
    IFINISH=0
    C *** TOTAL ORGANIC CARBON IN PPM IN WATER IS READ IN THE NEXT LOOP.
    C *** FORMAT IS SAME AS FOR % ORGANIC C IN SEDIMENT SAMPLES ***
    DO 125 J=1,NOCARD
        125 J=J+1,NOCARD
        121 START=IFINISH+1
        IFINISH=IFINISH+10
        IF (IFINISH.GT.NUMBER) IFINISH=NUMBER
        READ A,ITOC(I),I=1,START,IFINISH)
125 CONTINUE
    CARNAX=0
    ITOCHAX=0
    C *** THE FOLLOWING FOURTEEN STATEMENTS PRINT THE DATA LISTING OF THE
    C *** CARBON CONTENTS AND SIMULTANEOUSLY FIND THE HIGHEST VALUE IN EACH
    C *** OF THE TWO COLUMNS ***
    DO 29 I=1,NUMBER
        PCAR=PCARB(I)
        ITOC(I)
        IF (LINES.LT.42) GO TO 127
        PRINT 18,AREA,TITLE(J,4),J=1,8),IPAGE
        IPAGE=IPAGE+1
        LINES=3
127 PRINT 28,NOSAMP(I),PCAR,TO
        LINES=LINES+1
    28 FORMAT(15,7X,F7.2,15X,I4)
        IF (CARNAX.LT.PCAR) CARNAX=PCAR
        IF (ITOCMAX.LT.ITO) ITOCHAX=ITC
    29 CONTINUE
    C *** METAL RATIOS SEDIMENT/WATER ARE CALCULATED FOR LATTICE=8OUND
    C *** CATIONS (HFRAT) AS WELL AS FOR ADSORBED IONS (HCLRAT) ***
    DO 130 N=1,NUMBER
        DO 13 M=1,4
            HFRATIN,M)=0
            HCLRATIN,M)=0
            IF (WATMETIN,M).LT.2.C) GC TO 13
            WATH=1.0/WATMETIN,M)
            HFRATIN,M)=SEDLAT(N,M)*WATH
            HCLRATIN,M)=SEDAOS(N,M)*WATH
130 CONTINUE
13 CONTINUE

```

*** THE FOLLOWING NINE STATEMENTS SERVE TO STRAIGHTEN OUT A DISCREPANCY

C *** BETWEEN THE SEQUENCE OF ELEMENTS IN THE WATER ANALYSIS REPORTS

C *** AND THAT OF THE ELEMENTS IN THE SEDIMENT ANALYSIS REPORTS

WATH=10000.0/WATMET(N,7)

HFRAT(N,5)=SEDLAT(N,5)*WATH

HCLRAT(N,5)=SEDADS(N,5)*WATH

WATH=1.0/WATMET(N,5)

HFRAT(N,6)=SEDLAT(N,6)*WATH

HCLRAT(N,6)=SEDADS(N,6)*WATH

WATH=10.0/WATMET(N,6)

HFRAT(N,7)=SEDLAT(N,7)*WATH

HCLRAT(N,7)=SEDADS(N,7)*WATH

130 CONTINUE

DO 140 N=1,NUMBER

DO 14 M=8,NE

HFRAT(N,M)=0

HCLRAT(N,M)=0

IF (WATMET(N,M).LT.0.02) GO TO 14

WATH=10.0/WATMET(N,M)

HFRAT(N,M)=SEDLAT(N,M)*WATH

HCLRAT(N,M)=SEDADS(N,M)*WATH

14 CONTINUE

HCLRAT(N,9)=HCLRAT(N,5)*C.0001

HCLRAT(N,10)=HCLRAT(N,10)*C.0001

140 CONTINUE

C *** THE FOLLOWING STATEMENTS PRODUCE THE LISTING OF THE RESULTS

C *** CALCULATED AS RATIO 1. THE FIRST NINE CARDS TAKE CARE OF THE

C *** INITIAL PAGE HEADING - THE NEXT THREE CONTROL THE ACTUAL LISTING *

LINES=50

DO 19 N=1,NUMBER

IF (LINES.LT.42) GO TO 16

PRINT 15,AREA,IRAT(1,1),I=1,7,IPAGE,(ELM(1),I=1,NE)

15 FORMAT(1H,9X,'SAMPLE AREA',8A,'**','PAGE',14,'STATION',5X,

1016X,4A)

PRINT 32

IPAGE=IPAGE+1

LINES=4

16 PRINT,17,NOSAMP(N),(HFRAT(N,M),M=1,NE)

17 FORMAT(13,10F10.2)

LINES=LINES+1

19 CONTINUE

C *** NEXT, RATIO 2 IS LISTED ***

IF (LINES=21,30,33,33

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30 PRINT 31, AREA, (RAT(I,2), I=1,7), (ELM(I), I=1,NE)
31 FORMAT(//10X, 'SAMPLE AREA ', 8A4//5X, 10(6X,A4))
PRINT 32
32 FORMAT(//10X, '
LINES=LINES+6
GO TO 330
33 LINES=50
330 DO 35 N=1,NUMBER
IF (LINES-LT.42) GO TO 34
PRINT 15, AREA, (RAT(I,2), I=1,7), (PAGE, (ELM(I), I=1,NE)
PRINT 32
IPAGE=IPAGE+1
LINES=4
34 PRINT 17, NOSAMP(N), (MCLRAT(N,M), M=1,NE)
LINES=LINES+1
35 CONTINUE
C *** DETERMINE MAXIMA FOR PLOTTING
DO 36 K=1,2
DO 36 I=1,NE
NPINT(I,K)=0
36 CONTINUE
DO 23 K=1,2
DO 23 I=1,NE
RATNUM=0
RAISUM=0
VAL=0
DO 22 J=1,NUMBER
RATJIK=RAT(I,J,K)
IF (RATJIK-LT.0.001) GO TO 22
RATNUM=RATNUM+1.0
RAISUM=RAISUM+RATJIK
IF (RATJIK-VAL)22,22,21
21 VAL=RATJIK
22 CONTINUE
VALMAX(I,K)=VAL
220 IF (RATNUM-LT.1.0) GO TO 23
AVERAG=RAISUM/RAISUM
TOPVAL=2.5*AVERAG
IF (VAL-GT.TOPVAL) GO TO 222
IF (AVERAG-FAC(3))221,221,223
221 VALMAX(I,K)=VAL
GO TO 23
222 RAISUM=RAISUM+VAL

```

	RATNUM=RATNUM-1.0
	AVERAG=RATSUM/RATNUM
	IF(AVERAG.GT.FAC(3)) GO TO 223
	VALMAX(I,K)=2.5*RATSUM/RATNUM
	GO TO 23
	223 CALL REDUCE(I,NUMBER,K)
	M=I+1
	NPOINT(M,K)=3
	23 CONTINUE
	40 DO 42 K=2,19
	IF(CARMAX-SCALER(K))41,41,42
	41 IK=K-1
	XFAC(I)=FAC(IK)
	IP(I)=16-1K
	GO TO 43
	42 CONTINUE
	43 DO 45 K=2,19
	IF(TOCHMAX-SCALER(K))44,44,45
	44 IK=K-1
	XFAC(2)=FAC(IK)
	IP(2)=16-1K
	GO TO 44
	45 CONTINUE
	46 IF(LINES.EQ.42) GO TO 463
	LINES=42-LINES
	DO 462 I=1,LINES
	PRINT 32
	462 CONTINUE
	LINES=42
	463 DO 58 K=1,NE
	DO 58 L=1,2
	VAL=VALMAX(K,L)
	IF(VAL.LT.0.01) GO TO 54
	DO 58 J=1,19
	IF(VAL-SCALER(I))47,47,48
	47 II=I+1
	YFAC=FAC(II)
	IP(3)=I-3
	GO TO 49
	48 CONTINUE
	YFAC=FAC(21)
	IP(3)=17
	49 XF=XFAC(1)

```

MODE=1
JPOINT=POINT(X,L)
CALL PLTROT(XF,YFAC,K,L,MODE,NUMBER,AREA,IPAGE,JPOINT) /
53 YEXEAC(2)

MODE=2
CALL PLTROT(XF,YFAC,K,L,MODE,NUMBER,AREA,IPAGE,JPOINT)
GO TO 58

54 PRINT 55,ELM(K),AREA,L,VAL
55 FORMAT(10H,NO PRINTER PLOT POSSIBLE FOR 'A3',IN AREA 'A4',BECAU
18F ITS HIGHEST TENDR (RATIO(1,12,1)) IS ONLY',F7.5/)

DO 57 M=1,40
PRINT 32
57 CONTINUE
LINES=42
58 CONTINUE
59 NGELLE=0
NUMBER=0
GO TO 20
59 CALL EXIT
END
SUBROUTINE EXREAD(AREA)
PRINT 1,AREA
1 FORMAT('OAREA 'A4,'CONTAINS MORE THAN 62 SAMPLES - EXCESS SAMPLES
1 IGNORED')
2 READ 3,NBS
3 FORMAT(8.0)
IF(NBS.LT.999) GO TO 2
RETURN
END
SUBROUTINE REDUCE(I,N,K)
DIMENSION ELM(10),IGRAPH(120,41),NOSYMB(20),NOSAMP(62),
1 RAT(62,10,2)
COMMON ELM,IGRAPH,NOSYMB,NOSAMP,RAT
DO 1 J=1,N
RAT(J,J,K)=RAT(J,J,K)+C*1
1 CONTINUE
I=I+1
RETURN
END
SUBROUTINE PLTROT(XF,YFAC,NOSYMB,NOSAMP,NOSYMB(20),NOSAMP(62),
1 DIMENSION ELM(10),IGRAPH(120,41),NOSYMB(20),NOSAMP(62),
1 RAT(62,10,2),LINE(120),CARBON(62,2),WATMET(62,10),SEDLAT(62,10),
2 SEDAD(62,10),HERAT(62,10),HCLRAT(62,10),PCARB(62),TQC(62),

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3 SCALER(19),FAC(21),IENER(10),VALMAX(10,2),ITILE(8,4),IRAT(7,4),
* XFAC(2),IP(3)
EQUIVALENCE (HFRAT(1,1),RAT(1,1,1,1)),(MCLRAT(1,1),RAT(1,1,2)),
1 IPCARB(1),CARBON(1,1),ITOC(1),CARBON(1,2))
COMMON ELM,IGRAPH,NGSTPB,NGSAMP,RAT,LINE,CARBON,WATMET,SEOLAT,
1 SEDADS
COMMON/O/SCALER,FAC,IENER,VALMAX,ITILE,IRAT,XFAC,IP
DO 1 I=1,40
DO 1 J=2,120
IGRAPH(I,J)=11
1 CONTINUE
CALL YSCALE(JPOINT)
IGRAPH(115,41)=11
DO 46 N=1,N0
RA=RAT(N,NOFEL,NGRAT)
IF(RA.LT.0.002) GO TO 46
CA=CARBON(N,MODCAR)
IF(CA.LT.0.02) GO TO 46
NUMX=1.5001*XF*CA
NUMY=41.4999*YFAC*RA
KOUNTX=0
KOUNTY=0
IF(NUMY.EQ.41.AND.NUMX.EQ.1) GO TO 45
NGS=NGSAMP(N)
IF(NUMY.GE.1) GO TO 22
NUMY=1
IF(IGRAPH(NUMX,NUMY)=11) 15,16,17
15 IGRAPH(115,41)=20
GO TO 27
16 IGRAPH(NUMX,1)=20
GO TO 5
17 IF(IGRAPH(NUMX,1).LT.18.AND.NUMX.GT.1) GO TO 4
22 IF(NUMY.EQ.41.AND.IGRAPH(NUMX,41).EQ.16) IGRAPH(NUMX,41)=11
IF(NUMX.EQ.1) GO TO 5
3 IGR=IGRAPH(NUMX,NUMY)
IF(IGR.LT.11.OR.IGR.EQ.18) GO TO 14
IF(IGR.EQ.19) GO TO 46
IF(IGR.EQ.20) GO TO 27
IGR=IGR+1
IGRAPH(NUMX,NUMY)=IGR
IF(IGR=12) 46,5,4
* CALL SEARCH(NUMX,NUMY,IPCINT,NGS)
GO TO (27,11),IPCINT

```

```

5 NUMX=NUMX+1
  KOUNTX=KOUNTX+1
  IF (NUMX=110) 6,7,27
6 IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 27
  IF (NOS=10) 8,7,7
7 NUMX=NUMX+1
  KOUNTX=KOUNTX+1
  IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 27
8 IF (NUMX=110) 8,9,27
  NUMX=NUMX+1
  KOUNTX=KOUNTX+1
  IF (IGRAPH(NUMX,NUMY).LT.11) GO TO 27
9 KOUNTX=KOUNTX+2
10 NUMX=NUMX-KOUNTX+1
  NUMY=NUMY-KOUNTY
11 NOS=NOS/10
  IF (NOS) 13,13,12
12 IGRAPH(NUMX,NUMY)=NOS
  NUMX=NUMX+1
13 NOS=NOSAMP(N)-10+NOS
  IF (NOS.EQ.0) NOS=10
  IGRAPH(NUMX,NUMY)=NOS
  GO TO 46
14 NUMY=NUMY-KOUNTY
  KOUNTX=0
  IGRAPH(115,NUMY)=19
27 NUMY=NUMY+1
  KOUNTX=1
  IF (NUMY.GT.40) GO TO 34
  NUMX=NUMX-KOUNTX+1
  KOUNTX=1
  IF (NUMX=1128,29,29)
28 NUMX=NUMX+1
29 IF (IGRAPH(NUMX,NUMY).LT.11) GO TO 34
  IF (NOS.LT.10) GO TO 30
  NUMX=NUMX+1
  KOUNTX=KOUNTX+1
  IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 34
  IF (NUMX=110) 30,34,34
30 NUMX=NUMX+1
  KOUNTX=KOUNTX+1
  IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 34
  IF (NUMX=110) 32,33,34

```


32	NUMX=NUMX+1 KOUNTX=KOUNTX+1 IF (IGRAPH(NUMX,NUMY).LT.11) GO TO 34	
33	KOUNTY=0 KOUNTX=KOUNTX-1 GO TO 10	
34	NUMX=NUMX-KOUNTX-3 KOUNTX=-3 IF (NOS-10) 35,36,36	
35	NUMX=NUMX+1 KOUNTX=KOUNTX+1 GO TO 39	
36	IF (NUMX.LT.1) GO TO 39 NUMY=NUMY-KOUNTY	
	KOUNTY=0 IF (IGRAPH(NUMX,NUMY).LT.11) GO TO 39	
	NUMX=NUMX+1 KOUNTX=KOUNTX+1 IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 39	
	KOUNTS=KOUNTX NUMC=NUMX+1 IF (IGRAPH(NUMC,NUMY).LT.11) GO TO 39	
	IF (NOS-10) 37,37,37	
37	NUMX=NUMX+1 KOUNTX=KOUNTX+1 KOUNTS=0 IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 39	
	NUMC=NUMX+1 IF (IGRAPH(NUMC,NUMY).LT.11) GO TO 39	
	IF (NOS-10) 38,38,38	
38	NUMX=NUMX+1 KOUNTX=KOUNTX+1 KOUNTS=0 IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 39	
	NUMC=NUMX+1 IF (IGRAPH(NUMC,NUMY).LT.11) GO TO 39	
39	KOUNTX=KOUNTS GO TO 10	
	NUMX=NUMX-KOUNTX-1 KOUNTX=-1 NUMY=NUMY-1 KOUNTY=1 IF (NUMY.LT.1) GO TO 45 IF (NUMX-1) 40,41,41	
40	NUMX=NUMX+1 IF (IGRAPH(NUMX,NUMY).LT.11) GO TO 45	
41	IF (NOS.LT.10) GO TO 42 NUMX=NUMX+1 KOUNTX=KOUNTX+1 IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 45	
	IF (NOS-10) 42,42,42	

```

42 NUMX=NUMX+1
   KOUNTX=KOUNTX+1
   IF (IGRAPH(NUMX,NUMY).NE.11) GO TO 45
   IF (NUMX=11013,44,45)
43 NUMX=NUMX+1
   KOUNTX=KOUNTX+1
   IF (IGRAPH(NUMX,NUMY).LT.11) GO TO 45
44 KOUNTY=0
   KOUNTX=KOUNTX-1
   GO TO 10
45 NUMX=NUMX-KOUNTX
   NUMY=NUMY-KOUNTY
   IF (NUMX.LT.2) NUMX=115
   IF (IGRAPH(NUMX,NUMY).NE.11) NUMX=115
   IF (NUMY.GT.40) NUMX=115
   IGRAPH=NUMX,NUMY=19
46 CONTINUE
   IS=4*(MODCAR-1)+1
   IF (IS=3
      DO 47 M=1,120
      L=IGRAPH(M,1)
      LINE(L)=NOSYMB(L)
47 CONTINUE
      PRINT 48,ELM(NOFEL),NCRAT,(TITLE(M,4),M=18,IF),AREA,IPAGE
      48 FORMAT(36X,A32,18A10,12,1 VS, 1A4,1 FOR AREA,1A4,17X,IPAGE,1,1)
      IPAGE=IPAGE+1
      DO 51 M=1,41
      DO 49 M=1,120
      L=IGRAPH(M,N)
      LINE(M)=NOSYMB(L)
49 CONTINUE
      PRINT 50,(LINE(I),I=115,120),(LINE(I),I=1,110)
      50 FORMAT(1X,120A1)
      51 CONTINUE
      LINE(1)=NOSYMB(10)
      18=NOSYMB(11)
      DO 52 I=2,120
      LINE(I)=18
      52 CONTINUE
      IPI=IPIMBDCAR1
      IF (IPI.63,63,53)
      53 IF (IPI-7)54,54,63
      54 NSPOT=1

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ANSPOT=1.5001
NOSYM=0
GO TO (90,55,58,59,60,70,80),IPI
50 INQ=5
INS=5
GO TO 56
55 INQ=5
INS=8
56 NOSYM=NOSYM+INO
NSPOT=NSPOT+INS
NS=NSPOT
NOS=NOSYM/10
IF (NOS.LT.1) GO TO 57
LINE(INS)=NOSYM(NOS)
NS=NS+1
57 NOS=NOSYM-NOS+10
IF (NOS.EQ.0) NOS=10
LINE(INS)=NOSYM(NOS)
IF (NS=110+INR156,56,65
70 INQ=1
INS=10
GO TO 56
80 INQ=1
INS=16
GO TO 56
58 INQ=4
INS=10
GO TO 56
59 INQ=2
INS=8
GO TO 56
60 INQ=2
ANS=12.5
61 INSEANS=0.2922
NOSYM=NOSYM+INO
ANSPOT=ANSPOT+ANS
NSPOT=ANSPOT
NS=NSPOT
NOS=NOSYM/10
IF (NOS.LT.1) GO TO 62
LINE(INS)=NOSYM(NOS)
NS=NS+1
62 NOS=NOSYM-NOS+10

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```

IF (NOS-EG-01, NOS=10)
  LINE(18)=NOSYB(NOS)
  IF (NOS-110, NOS=1, 61, 68)
    DO 44 1=2, 110
    NOS=NOSYB(12)
    LINE(17)=NOSY
  44 CONTINUE
  65 PRINT 66, (LINE(1), I=1, 110)
  66 FORMAT(7X, 110A1)
  DO 2 1=2, 110
    IGRAPH(1, 1)=16
  2 CONTINUE
  21 RETURN
END
SUBROUTINE SEARCH(NUMX, NUMY, IPOINT)
  DIMENSION ELM(10), IGRAPH(120, 41)
  COMMON ELM, IGRAPH
  KOUNT=0
  1 NUMX=NUMX+1
  KOUNT=KOUNT+1
  IF (IGRAPH(NUMX, NUMY)=111, 2, 15)
    15 IF (IGRAPH(NUMX, NUMY)=1818, 1, 8)
    2 IF (NUMX-109) 9, 3, 8
    3 IF (NOS-10) 4, 8, 8
    4 NUMX=NUMX+1
    KOUNT=KOUNT+1
    IF (IGRAPH(NUMX, NUMY)=1118, 5, 8)
    5 NUMX=NUMX+1
    KOUNT=KOUNT+1
    IF (IGRAPH(NUMX, NUMY)=1118, 6, 6)
    6 NUMX=NUMX+2
    7 IGRAPH(NUMX, NUMY)=18
    NUMX=NUMX+1
    IPOINT=2
    GO TO 14
  8 IPOINT=1
  NUMX=NUMX+KOUNT
  GO TO 14
  9 IF (NOS-10) 4, 10, 10
  10 NUMX=NUMX+1
  KOUNT=KOUNT+1
  IF (IGRAPH(NUMX, NUMY)=1118, 11, 8)
  11 NUMX=NUMX+1

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```

KOUNT=KOUNT+1
IF (IGRAPH(NUMX,NUMY)=11) 8,12,8
12 NUMX=NUMX+1
KOUNT=KOUNT+1
IF (IGRAPH(NUMX,NUMY)=11) 8,13,13
13 NUMX=NUMX+3
GO TO 7
14 RETURN
END
SUBROUTINE YSCALE(JPGINT)
DIMENSION ELM(10), IGRAPH(120,4), NOSYMS(20), NOSAMP(62),
1 RAT(62,10,2), LINE(120), CARBON(62,2), WATHET(62,10), SEDLAT(62,10),
2 SEDADS(62,10), HERATI(62,10), HCLRATI(62,10), PCARB(62,10), TDC(62,10),
3 SCALER(19), FAC(21), TENC(10), VALMAX(10,2), TITLE(8,4), IRAT(7,4),
4 XFAC(2), IP(3)
EQUIVALENCE (HERATI(1,1), RAT(1,1,1)), (HCLRATI(1,1), RAT(1,1,2)),
1 PCARB(1,1), CARBON(1,1)), (TDC(1,1), CARBON(1,2))
COMMON ELM, IGRAPH, NOSYMS, NOSAMP, RAT, LINE, CARBON, WATHET, SEDLAT,
1 SEDADS
COMMON /O/ SCALER, FAC, TENC, VALMAX, TITLE, IRAT, XFAC, IP
NP=IP(3)
IF (NP.LT.1) NP=NP+20
NR=2
IF (NP.GT.5) NR=1
IF (NP.GT.17) NR=2
ANPOS=41.001
ANBSYH=0.001
IGRAPH(119,41)=10
GO TO (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,32,33,34,35), NP
33 ANO=0.02
ANS=8
GO TO 24
34 ANO=0.02
ANS=5
GO TO 24
35 ANO=0.05
ANS=8
GO TO 24
1 ANS=0.1
ANS=10
GO TO 24
2 ANO=0.2
ANS=12.5

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3	GO 10-24 ANS=0.25 ANS=10 GO 10-24
4	ANS=0.2 ANS=5 GO 10-24 ANS=8 GO 10-24
5	ANS=12.5 ANS=8 GO 10-24
6	ANS=1 ANS=10 GO 10-17
7	ANS=2 ANS=12.5 GO 10-17
8	ANS=2 ANS=8 GO 10-17
9	ANS=4 ANS=10 GO 10-17
10	ANS=5 ANS=8 GO 10-17
11	ANS=10 ANS=10 GO 10-17
12	ANS=20 ANS=12.5 GO 10-17
13	ANS=25 ANS=10 GO 10-17
14	ANS=40 ANS=10 GO 10-17
15	ANS=50 ANS=8 GO 10-17
16	ANS=50 ANS=5 GO 10-17

22	ANS=100
	ANS=6.25
17	ANOPOS=ANOPOS-ANS
	NOPOS=ANOPOS
18	DO 19 I=1,3
	LINE(I)=11
19	CONTINUE
	ANSYM=ANSYM+ANS
	NOS=ANSYM
	IF(NOS=100)21,20,20
20	ITONOS=NOS
	NOS=NOS/100
	LINE(1)=NOS
	NOS=ITONOS-100*NOS
	ITONOS=NOS
	NOS=NOS/10
	NUS=NOS
	IF(NOS.EQ.0) NUS=10
	LINE(2)=NUS
	NOS=ITONOS-10*NOS
	IF(NOS.EQ.0) NOS=10
	LINE(3)=NOS
	NI=3
	GO TO 23
21	IF(NOS=10)23,22,22
22	STNCS=NOS
	NOS=NOS/10
	LINE(1)=NOS
	NOS=STNCS-10*NOS
	IF(NOS.EQ.0) NOS=10
	LINE(2)=NOS
	NI=2
	GO TO 23
23	LINE(1)=NOS
	NI=1
	GO TO 23
24	ANOPOS=ANOPOS-ANS
	NOPOS=ANOPOS
	IF(ANOPOS)31,31,25
25	DO 26 I=1,4
	LINE(I)=11
26	PANTIME

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ANDSYH=ANDSYH+AND
IF IANDSYH=1.0128,27,27
27 NOS=ANDSYH
LINE(1)=NOS
LINE(2)=12
ANDS=NOS
NOS=10.0+ANDSYH-10.0+ANDS
NUS=NOS
IF (NOS-EG.0) NUS=10
LINE(3)=NUS
BMS=NOS
NOS=100.0+ANDSYH-100.0+ANDS-10.0+8NOS
IF (NOS-EG.0) NOS=10
LINE(4)=NOS
NI=4
GO TO 28
28 LINE(1)=10
LINE(2)=12
NOS=10.0+ANDSYH
NUS=NOS
ANDS=NOS
IF (NOS-EG.0) NUS=10
LINE(3)=NUS
NOS=100.0+ANDSYH-10.0+ANDS
IF (NOS-EG.0) NOS=10
LINE(4)=NOS
NI=4
29 X=130+NI
DO 30 J=1,NI
  IGRAPH(K,NOPGS)=LINE(J)
  K=K+1
30 CONTINUE
  IF (POINT-EG.3) IGRAPH(120,NOPGS)=10
  GO TO 117/231/NR
31 RETURN
  END

```



```

1. IMPLICIT DOUBLE PRECISION (A-H,O-Z)
2. DIMENSION X(485),Y(485),ID(20),PI(485),C(16),ITLE(17),
3. 1 CAR(623),RAT(62,10,2),KHEL(10),ALPHA(16),BETA(16),G(16),S(100)
4. CALL ECFSET(288)
5. KEND=9999999
6. INDEX=0
7. KE=10
8. READ 2,KHEL
9. READ 2,ITLE(3),ITLE(4)
10. 1 READ 2,IC
11. 2 FORMAT(2CA4)
12. 3P(10(4),EG,KEND) GO TO 28
13. DECODE(24,2,10) IP,LP,N,ITLE(5),ITLE(6)
14. 3 FORMAT(3I4,3A4)
15. DO 5 J=1,3
16. READ 4,(CAR(I,J),ICR,N)
17. 4 FORMAT(100.0)
18. 5 CONTINUE
19. DO 6 K=1,2
20. DO 6 J=1,N
21. READ 4,(RAT(I,J,K),I=1,N)
22. 6 CONTINUE
23. DO 23 L=1,3
24. READ 2,ITLE(1),I=7,16)
25. DO 22 K=1,2
26. READ 2,ITLE(1),I=5,6)
27. DO 22 J=1,N
28. DO 3 I=1,N
29. X(I)=CAR(I,L)
30. Y(I)=RAT(I,J,K)
31. 8 CONTINUE
32. M=0
33. DO 9 I=1,N
34. IF(Y(I).EQ.0.0.OR.X(I).EQ.0.0) GO TO 9
35. M=M+1
36. X(M)=X(I)
37. Y(M)=Y(I)
38. 9 CONTINUE
39. DO 21 NN=1P,LP
40. PRINT 10,M,NN
41. 10 FORMAT(1H1,NUMBER OF OBSERVATIONS',I4,', DEGREE',I3/,
42. MIP=NN

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43.      PLP=NN
44.      LIM=MLP+1
45.      KKK=MIP+1
46.      26 IF(KKK,GI,LL) GO TO 57
47.      IF(PLP-MIP)27,28,28
48.      27 PLP=MIP
49.      28 NOP=MLP+1
50.      KKK=MIP+1
51.      IF(15-PLP)29,31,31
52.      29 PRINT 30
53.      30 FORMAT(24X,24HERROR****MAX DEGREE = 15/)
54.      GO TO 22
55.      31 IF(MIP)32,32,34
56.      32 PRINT 33
57.      33 FORMAT(24X,24HERROR****MIN DEGREE = 1/)
58.      GO TO 21
59.      34 IF(485-M)35,35,37
60.      35 PRINT 36
61.      36 FORMAT(24X,27HERROR****NO OF POINTS > 485/)
62.      GO TO 22
63.      37 IF(M-MIP-1)38,38,40
64.      38 PRINT 39
65.      39 FORMAT(24X,26HERROR****INSUFFICIENT DATA/)
66.      GO TO 22
67.      40 SY=SY2=C
68.      GO 41 PI=1,M
69.      PI=1(M)=0
70.      PI(I)=1
71.      YI=Y(I)
72.      SY=SY+YI
73.      SY2=SY2+YI*YI
74.      41 CONTINUE
75.      DO 42 PI=1,16
76.      ALPHA(I)=BETA(MI)-S(MI)=0
77.      42 CONTINUE
78.      A1=0
79.      B1=0
80.      W1=M
81.      M1=1
82.      43 W1=0
83.      DO 44 LL=1,M
84.      W1=W1+Y(LL)*PI(LL)

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```

86. S(MI)=MI/MI
87. IF(PI=NOPI)5,49,49
88. 45 A1=0
89. DO 46 LL=1,M
90. A1=A1+X(LL)*PI(LL)*PI(LL)
91. 46 CONTINUE
92. A1=A1/MI
93. MI=MI+1
94. ALPHA(PI)=A1
95. MI=0
96. DO 47 LL=1,M
97. PIP1=(X(LL)-A1)*PI(LL)-B1*PI(M1(LL))
98. PIM1(LL)=PI(LL)
99. P1(LL)=PIP1
100. MI=MI+PIP1*PIP1
101. 47 CONTINUE
102. B1=MI/MI
103. MIM=MI+1
104. BETA(PIM)=B1
105. MI=MI
106. GO TO 43
107. 48 IF(M=KKK)38,38,49
108. 49 DO 50 LL=3,16
109. G1(LL)=0
110. 50 CONTINUE
111. G11=1
112. G12=-ALPHA12)
113. DO 51 JM=1,KKK
114. S1=0
115. DO 52 LL=1,KKK
116. IF(LL.LI.3) GO TO 51
117. LLJ=LL-1
118. LLJ=LLI-1
119. G1LL=G(LL)-ALPHA(LL)*G(LLI)-BETA(LL)*G(LLJ)
120. S1=S1+G(LL)*G(LL)
121. 52 CONTINUE
122. C(JM)=S1
123. LL=KKK
124. DO 53 I2=2,KKK
125. LLJ=LL-1
126. G1LL=G(LLI)
127. LL=LLI
128. 53 CONTINUE

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```

129.      8(1)=0
130.      54 CONTINUE
131.      ERR2=0
132.      DO 56 LL=1,M
133.          YCALC=0
134.          JM=KKK
135.          DO 55 J2=1,KKK
136.              YCALC=YCALC+X(LL)+C(JM)
137.              JM=JM+1
138.          55 CONTINUE
139.          ERR=Y(LL)-YCALC
140.          ERR2=ERR2+ERR*ERR
141.      56 CONTINUE
142.          ERR=M*KKK
143.          SEE=DSORT(DABS(ERR2/ERR))
144.          ERR=M
145.          R2=1.0-ERR2/(8Y2-SY*SY/ERR)
146.          KKK=KKK+1
147.          IF(KKK-NOP)48,48,26
148.      57 KK=NN+1
149.          PRINT 11,(ITLE(I),I=1,4),KNEL(J),(ITLE(I),I=5,16),(JJ=1,C(JJ),JJ=1
150.              1,KK)
151.          11 FORMAT(1H,17A4//13H COEFFICIENTS/(16X,15,E18.8))
152.          IF(INDEX(14,14,12
153.              12 PUNCH 13,(ITLE(I),I=1,4),KNEL(J),(ITLE(I),I=5,16),(JJ=1,C(JJ),JJ=1
154.              1,KK)
155.          13 FORMAT(1H,17A4//13H COEFFICIENTS/(16X,15,E18.8))
156.          14 PRINT 15,ERR2/R2,SEE
157.          15 FORMAT(16X,8HERR**2 =,E14.7,13X,6HRR**2 =,E14.7,13X,9HSTD=ERR =,
158.              1 F14.7/)
159.          PRINT 11
160.          PRINT 16
161.          16 FORMAT(5X,'ORIGINAL      RECONSTITUTED',/9X,'VARIABLES',/7X,
162.              1 'DEPENDENT',/7X,'IND',/6X,'DEP',/7X,'VARIABLE',/
163.              LINES=14+NN
164.              DO 20 NNN=1,M
165.                  XX=X(NNN)
166.                  SUP=C(1)
167.                  DO 17 JJ=2,KK
168.                      JXP=JJ-1
169.                      SUP=SUP+C(JJ)*XX+IXP
170.              17 CONTINUE
171.              IF(LINES-LI,43) GO TO 18

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172.      PRINT 16
173.      LINES=4
174.      18 PRINT 19,XX,Y(NNN),SUM
175.      19 FORPAT(2F10.2,F12.2)
176.      LINES=LINES+1
177.      20 CONTINUE
178.      21 CONTINUE
179.      22 CONTINUE
180.      23 CONTINUE
181.      GO TO 1
182.      25 CALL EXIT
183.      END
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