Mineral weathering by dissolved organic carbon in subarctic fens

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Abstract

The contribution of dissolved organic carbon (DOC) to mineral weathering was investigated under the changing Eh and pH conditions in three subarctic fens, near Schefferville, Quebec. No evidence of increased weathering rates nor different weathering patterns were found in the fen basal sediment despite DOC-rich and low Eh (0 to +200 mV) conditions.

Solutions containing 50 mg DOC/L derived from subarctic fen peat, and of 50 and 300 mg DOC/L, derived from deciduous leaf litter were used as weathering agents. Clinochlore, microcline and the Fe-rich basal till from the Schefferville fens were used as weatherable mediums. The DOC rich solutions and controls (made of distilled water buffered to the same initial pH) were used to invetigate the relative weathering ability of DOC-rich waters under aerobic and anaerobic conditions. The relative ability was determind by comparing the changing cation concentrations in the solutions.

The DOC-rich solutions were 1.5 to 3 times more effective at weathering than the control solutions under aerobic (+600 mV) conditions, but equal under anaerobic conditions (+200 mV). This inability of DOC to increase the weathering rate could only be attributed to a decrease in the number of

complexing functional groups of the DOC molecules (organic acids), brought on by the anaerobic condition.

The Fe rich sediment was the most easily weathered of the mediums, releasing large amounts of Fe into "solution". Fe and other metals were retained in "solution" (filtered through a 0.1 μm cellulose membrane filter) beyond mineral stoichiometric levels in the aerobic DOC-rich solutions, suggesting that DOC preferentially removes these cations and retains them in solution thereby increasing their mobility. Studies using o-pnenanthroline and the thermodynamically-based program SOILCHEM, indicated the metals are complexed by DOC, are involved in exchange reactions with DOC, and are adsorbed as inorganic complexes onto the surfaces of DOC molecules.

Résumé

Le rôle du carbone organique dissous (COD) dans le processus de météorisation des minéraux a été étudié en rapport avec les variations de pH et de Eh dans trois tourbières en milieu subarctique près de Schefferville (Québec). En dépit des faibles valeurs de Eh (0 à +200 mV) et de l'importante quantité de COD dans les horizons minéraux à la base de la tourbe, on a décelé ni augmentation du taux de météorisation ni différence de processus par rapport à la forêt environnante.

Des solutions riches en COD dérivées de tourbe de fen subarctique (50 mg COD/L) et de litière de forêt décidue (50 et 300 mg/L) ont été utilisées comme agents de météorisation afin de déterminer l'effet de l'eau riche en COD dans des conditions d'aérobie et d'anaérobie. Ces solutions ont été comparées à des solutions de référence de même pH initial (5 à 7). Les minéraux clinochlore et microcline et un till de base riche en Fe ont été utilisés comme matériaux altérables. En aérobie (+600 mV), les solutions riches en COD ont été de 1,5 à 3 fois plus efficaces que les solutions de référence. Aucune différence n'a toutefois été observée en anaérobie (+200 mV). Cette inefficacité du COD à accroître le taux de météorisation peut être attribuée à une diminution du nombre des groupes séquestrants fonctionnels des molécules de COD (les acides organiques) en milieu d'anaérobie.

Les sediments riches en Fe ont été plus sensibles à la météorisation, comme en font foi les grandes quantités de Fe mises en solution. En conditions d'aérobie, les concentrations de Fe et d'autres métaux dans les solutions riches en COD (filtrées dans une membrane de cellulose de 0,1 μm) dépassaient les niveaux stochiométriques dans les minéraux. Cela tend à démontrer que le COD détache préférentiellement ces cations et qu'il en augmente la mobilité en les gardant en solution. La méthode o-phenanthroline et le logiciel SOILCHEM (fondé sur des principes de thermodynamique) ont servi de base à des études qui indiquent que les métaux sont complexés par le COD, qu'ils réagissent avec ce dernier et qu'ils sont adsorbés sous forme de complexes inorganiques par les surfaces réactives des molécules de COD.

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Chapter 1

Dissolved Organic Carbon (DOC) and Mineral Weathering Research: a literature review and scope of research

1.1 Introduction

The weathering environment within and beneath wetlands possesses two important characteristics which separate it from weathering in well-drained soils. These characteristics are the continuously high concentrations of dissolved organic carbon (DOC) in peatland water and the often anaerobic (low redox potential) nature. Although considerable research has been done in field and laboratory studies of mineral weathering in well drained environments, little work has been done on weathering under peatland conditions. This is despite the fact that wetlands cover 1.27×10^{6} Km^{2} or 14% of the land surface of Canada (National Wetlands Working Group, 1988).

A field study and a series of laboratory experiments were conducted to investigate the effectiveness of DOC as a weathering agent under aerobic and anaerobic conditions. The field studies were conducted on fens in the Schefferville region of Quebec. Emphasis was placed on solution chemistry (ie. Eh, pH, conductivity, and DOC and cation concentrations), stratigraphy and surface morphology. The spatial relationships between DOC solution chemistry and the influence of other fen characteristics (ie. hydrology) was established.

To limit the number of factors influencing weathering under peatland conditions, pure minerals (clinochlore and microcline) and basal till from beneath a subarctic fen were weathered, under laboratory conditions using DOC-rich water. Overall weathering rates, specific element release rates and DOC adsorption were determined under different DOC concentrations and, Eh and pH regimes. The computer program SOILCHEM (Sposito, 1988), which employs thermodynamic stability constants and mole balance equations, was used to investigate the effect of DOC on element speciation. A comparison of the DOC fractions enriched in Fe from the till and microcline samples was performed using a cascade membrane filtration technique.

1.2 Weathering of Minerals with Inorganic Acid

An understanding of mineral surface processes is paramount in mineral dissolution studies. This has been achieved mainly through the addition of highly concentrated inorganic acids to pure ground minerals. Such studies of mineral dissolution now follow the general formula of a bulk chemical analysis of the weathering solution, followed by petrographic or SEM observations of minerals which are combined to produce theoretical models. Together these studies have produced a basic understanding of mineral alteration and rate limiting steps.

For example, Busenberg and Clemency (1976) based their conclusion of a weathered layer developing on the surface of feldspar grains solely on incongruent changes in the bulk chemistry of the weathering solution and the changing nature of the dissolution rate curve. However, later petrographic observations, using a scanning electron microprobe, revealed only a thin layer of hydrogen feldspar about two unit cells thick coating the majority of the mineral surface (Berner and Holdren, 1979; Drever, 1982; Gardner, 1983). Much of the parabolic effect, suggesting a surface weathered horizon, has been attributed to laboratory procedures, specifically those related to the grinding process (Holdren and Berner, 1979). The general weathering model was further developed when pH changes were observed to effect the release rates of cations. For example, Holdren and Speyer (1985) determined that in alkali feldspar, lowering the solution pH increased the rate of Al release, and further lowering increased the rate of Si release, by hydrolysis reactions. These reactions were most intensive along planes of weakness, forming a weathered layer at these locations. Since the overall dissolution rate increased with decreasing pH; pH was determined to be the rate limiting step in dissolution of alkali feldspars.

In studies of other minerals, mica was observed by Lin and Clemency (1981) to weather in a step-wise manner and pyroxene and amphiboles display etch pits indicating dissolution is controlled by a surface reaction phenomenon (Schott and Berner, 1983). These larger holes in the surfaces of the minerals fill with clays or oxyhydroxides whose genesis, as in the case of feldspar, are not necessarily but more likely related the hole they occupy (e.g. Nahon and Colin, 1982; Velbel, 1984). Surface oxidation layers do build up on iron-rich pyroxene, amphibole and olivine, resulting in diffusion becoming a rate-limiting step (Schott and Berner, 1983). However, these rates are far from consistent and are greatly influenced by small changes in mineralogy which can result in major differences in mineral kinetics (Holdren and Speyer, 1985).

1.3 Weathering of Minerals with Organic Acids

Keller (1957) recognized that mineral stability depends not only on the thermodynamic stability of a mineral but also on the chemistry of the reactant solution. In many natural waters, the dominant acids are organic (Thurman, 1985). Organic acids have been identified as enriching waters in Fe well above the thermodynamically predicted levels for natural waters (Mill, 1980). This Fe and other cation enrichment is the result of organic acids contributing H^+ ions to solution promoting hydrolysis reactions, and providing sites for element complexation, exchange, and adsorption (Huang and Keller, 1970; Rashid, 1985). In response to potential pH increases, water acidity is maintained by the further release of H^+ ions upon metal complexation, the organic acids behaving like weak inorganic acids (Broadbent and Bradford, 1952). Oliver et al. (1983) estimate a contribution of 10 ueq of acidity per mg of fulvic and hydrophillic acids which make up 90% of organic acids in solution. Organic acids also buffer the effect of inorganic acids (McColl and Pohlman, 1976).

Boyle et al. (1974) and Manley and Evans (1986) used a variety of organic acids to weather biotite and feldspars, respectively. Boyle et al. (1974) used organic acids in concentrations that created extremely low pH (<2) conditions, under which, small changes of pH were not correlated with the amount of cations released into solution. Under a northern boreal forest temperature regime (13°C) and using organic acids with concentrations that yielded a pH of approximately 4, Manley and Evans (1986) determined that pH was highly correlated with the ability of the acids to release cations. Holdren and Speyer (1985) noted feldspars were dissolved non-stoichiometerically by organic acids when the pH was decreased. In all cases an affinity for divalent and trivalent cations, by organic acids with high complexing abilities was observed in acidic solutions. However, since the complexing ability of organic acids is tied to pH it becomes difficult to separate the effects.

The carboxylic and phenolic functional groups of organic acids are the main sites of metal complexation. The ability of an organic acid to complex a metal depends on the strength of the bond between the metal and the functional group. To examine the complexing ability of organic acids, a means of comparing such metal-organic interactions is required. Since, in a thermodynamic sense, the interaction between an organic acid and a metal is not any different from the interaction between an inorganic acid and a metal, the stability constant of formation (K) for a metal and organic acid provides a measure of their affinity. Therefore, the greater the stability constant, the greater the complexing ability or power of an acid with respect to a particular metal.

Schalscha et al. (1967) determined that ethylenediamine tetraacetic acid (EDTA), an identified complexing acid, was more effective than HCl in pulling Fe from magnetite, haematite and granodiorite; the reverse was true, however, for goethite, augite, epidote and biotite. The chelating ability of organic acids has been known for sometime. A chelate is a form of complexation that specifically refers to an organo-metal complex with a ring structure that forms more than one bond, an ionic and covalent bond or an ionic and coordinate bond, between the metal and the ligand (Lehman, 1963). Hydrogen ion is released from the chelate upon metal complexation therefore contributing to hydrolysis reactions (Birkeland, 1984; Schalscha et al., 1967). Chelates are just one group of many possible metal-organic complexes that can form in soils but their significance derives from their high stability constants (K).

Huang and Keller (1970) determined that low molecular weight organic acids increased the solubility of Si, Al, Fe, Mg and Ca compared to distilled water and CO_2-rich water. Baker (1973) determined that humic acid, as a whole, was comparable to low molecular weight organic acids in weathering silicate and metallic minerals. Cascade ultrafiltration, sephadex chromatography and small angle x-ray scattering have been used to fractionate organic acids. Fractionation of organic acids based on size can be related to molecular weight (Thurman et al., 1982). Rashid (1971) determined that the greatest amount of complexation occurs in the low molecular weight size fraction (<1,000) where the greatest number of OH^- and $COOH^-$ groups occur. However, significant amounts of cations were found to accumulate in other size fractions and the order of concentration did not necessarily decrease with increasing size. Therefore it appears that a molecular size fraction of organic acids maybe more effective in complexing a particular cation.

The sorption of humic and fulvic acid onto mineral surfaces may restrict weathering (Greenland, 1971). Zutic and Stumm (1984) determined that the presence of organic acids in solution inhibited the weathering of Al-oxide through the formation of Al-organic surface complexes. Significant adsorption appears restricted to specific clay minerals, such as kaolinite, and Fe and Al hydroxides. However, if these secondary minerals coat the surface of a parent mineral the weathering of the parent mineral would be curtailed.

If organic acids can adsorb onto the surfaces of minerals perhaps the converse is true. With the aid of electron micrographs, Buffle (1988) describes the surfaces of organic acids as being sieves which according to Rashid (1985) are capable of adsorbing cations and inorganic complexes.

Violante and Violante (1980) showed that organic acids influenced the precipitated form of $Al(OH)_3$ by slowing down the speed of crystallization. In fast reactions, bayerite precipitates, intermediate reactions favour nordstrandite and slow reactions produce gibbsite. The strongest influence was exerted by organic acids with the greatest complexing power.

Kodama and Schnitzer (1977, 1980) found similar results for Al and Fe oxides. Since ions apparently go into solution before precipitating to form clay minerals or oxides, the complexing power of organic acids may have a profound effect on what minerals precipitate and therefore mineral speciation.

Organic acids can either adsorb, bind or complex metal cations in order to increase the amount in solution (Buffle, 1988). Inorganic colloids that adsorb on to the surfaces of higher molecular weight organic acids (Rashid, 1985), notably Al and Fe oxides, are labelled inert as opposed to labile which implies being complexed (Buffle, 1988). These two terms are not as easily separable as one first imagines. Mixed complexes may develop intramolecular bonds, were bonds occur between the metal of the adsorbing molecule and ligand, and/or intermolecular bonds were only supporting bonds develop. These and other uncertainties, such as the strength of these bonds, make experimental determination of complexing power (K) difficult and the separation of complexing capacity (C) into complexation, exchange and adsorption nearly impossible (e.g. Buffle, 1988; Weber, 1988)

1.4 Weathering Studies of Natural Systems

Graustein (1976) showed that organic anions can attain high concentrations in soil water and the breakdown of primary minerals is strongly influenced by their presence. He proposed that oxalate ion was responsible for the congruent dissolution of plagioclase feldspar by complexation of Al, an ability that was later confirmed by Manley and Evans (1986). However, such low molecular weight organic acids account for only a very small portion of the total amount of DOC in soil and natural waters.

DOC is defined as that organic carbon that pass through a filter of less than 0.45 μm pore size. The 0.45 μm pore size is an arbitrary one and does not separate groups defined by any other meaning. Both the method and conditions of separation can result in differences in experimental results.

Within this broadly based definition lie an almost inexhaustible list of organic acids. Thurman (1985) cites numerous studies, mainly of natural water systems, where the composition and concentration of DOC is analyzed. The major components of DOC in these water systems were classified as humic substances (humic and fulvic acid), hydrophilic acids (simple and complex organic acids) and simple compounds (carbohydrates, carboxylic acid, amino acids and hydrocarbons). The percentages of each component varied but approximately 50% were humic and fulvic acids, 30% hydrophilic acids and 20% simple acids. Of this breakdown, only about 25% of DOC could be further identified, 1-6% being proteins, and 6-24% polysaccharides (Buffle, 1988).

Two major components of DOC that are often used as "natural weathering solutions" are humic and fulvic acids. Humic acids are defined as organic acids that precipitate when the solution is acidified to a pH of 1 or 2 (commonly using H_2SO_4) with fulvic acids remaining in solution. Other differences that have been cited include the average fulvic acid having more carboxylic and hydroxyl functional groups and a lower average molecular weight (generally 800 to 2000 mw for fulvic, > 2000 for humic). If separated by size, the terms fulvic and humic fractions should be used. Although these fractions fall well within the 0.45 μm limit, the operational definitions of these two classifications of DOC, however, are of little value when applied to mineral weathering. The complexing ability (power and capacity), molecular weight, surface area, and source or availability are not fully addressed in this definition, only implied after the fact. Therefore, measurable divisions based on useful definitions are required. Unfortunately, the complex nature of DOC has delayed such developments.

The difference between DOC in soil interstitial water and precipitated, inactive DOC is not often made. In downward percolating water, humic and fulvic acids become insoluble and precipitate onto clay surfaces and with oxides. The result is a decrease of soil solution DOC concentrations from 20 - 30 mg/L in the A horizon to 0 - 2 mg/L in the C horizon (Thurman, 1985). Baker (1973) emphasized the relative importance of humic acids in mineral weathering, as humic acid were the major component of organic acids in the Tasmanian soils he studied. Age fractionation of DOC in soils places fulvic acid at an average of 450 years, humic acid 750-1230 years and humins 1100-2400 years, whereas the age of DOC in natural waters is less than 30 years (Buffle, 1988, after Cheshire et al., 1967; Campbell et al., 1967; Thurman, 1985). The increasing average age of the fractions indicate a metamorphism from fulvic acid to humins. This evidence provokes the question: what is the active role of these organic acids? Once precipitated, the soil humic and fulvic acids appear to evolve into less soluble substances, limiting any further contribution to mineral weathering. Carbon is potentially lost as CO_2, which is a product of microbial activity.

The DOC concentration in soil interstitial water is seasonal, peaking during the spring run off (Thurman, 1985). The source of DOC found in the soil interstitial water was the overlying litter layer (Antweiler and Drever, 1983; Tate and Meyer, 1983). The bulk of DOC that aids in mineral weathering and transports cations from the soil probably originates from decomposing organic matter in the overlying litter layer and not, as Baker (1973) implies, the soil humic and fulvic acids.

Antweiler and Drever (1983) determined that soluble organics derived from the decomposing vegetation controlled the release and transport of Fe and Al cations by lowering the solution pH and through complexation reactions. Fe, Al, Mg, Ca, Na and K concentrations in solution were all correlated with DOC concentrations that averaged 50 mg/L and peaked at 260 mg/L. Weathering of the same volcanic ash with water in a laboratory study, Antweiler and Drever (1983) discovered Fe and Al concentrations were below detectable limits but no experiments were mentioned that involved DOC rich water.

In studies of different types of forest litter leachates, Pohlman and McColl (1988) observed a strong correlation between DOC leachate and the release of Fe and Al from soils. A subdivision of the acids revealed hydrophobic and hydrophilic acids, which are the strongest complexers, were most strongly correlated with the amount of Fe and Al cations in solution.

1.5. Wetlands: A unique reducing DOC-rich environment

DOC concentrations, although variable, are generally higher in wetlands than DOC concentrations in other natural surface waters (e.g. Moore, 1987a; Thurman, 1985; Wheeler, 1976). However, the prolonged saturation and the fewer adsorption sites compared to mineral soils allows DOC from decomposing plant matter to accumulate in solution. Climate, vegetation and hydrology appear to have a significant impact on individual wetland DOC concentrations (Thurman, 1985). In bogs, organic acids are the dominant ligand, outnumbering the inorganic ligands by approximately 3:1 (Thurman, 1985). If fulvic acid is the dominant organic acid in the system, as Thurman (1985) suggests, the average pK_a value of approximately 4.2 maybe used as the lowest achievable acidity for an organic acid-dominated wetland. However, this will vary with type of DOC (ie. dominated by humic or fulvic acids) and may change with inorganic acid inputs such as those of acid rain.

In wetlands, redox potentials (measured as Eh) generally decrease with depth. Postma (1983) reported near surface Eh measurements of +600 mV (pO_2 10^{-35}) while those made at depth were +200 mV (pO_2 10^{-55}) at a pH of 3. In comparison, Garrels and Christ (1965) indicate the Eh in saturated soil zones is between +300 and -300 mV. After oxygen becomes undetectable at about +330 mV, specific zones of reduction can be identified by further decreases in Eh. For example, although pH-dependent, most N is reduced at +220 mV, Mn at +200 mV, Fe at +120 mV, and S at -150 mV (e.g. Connel and Patrick, 1968; Gotoh and Patrick, 1974; Turner and Patrick, 1968). Such reduction leads to the formation of different inorganic complexes and precipitates (e.g. Garrels and Christ, 1965; Gotoh and Patrick, 1974; Ponnamperuma, 1972). But, more importantly, the reduction of Fe^{3+} to Fe^{2+} causes instability in mineral lattice making the whole mineral susceptible to weathering (Zutic and Stumm, 1984). Bloomfield (1953) suggested that organic acids reduced large quantities of Fe and Al upon complexation and, as suggested by Zinder et al. (1989), is a potential mechanism by which organic acids weather minerals more effectively than inorganic acids. Such evidence invites the question how is mineral weathering influenced under the combination of low Eh and high DOC concentration conditions?

Staub and Cohen (1978) determined that a strong relationship existed between peat thickness and the alteration of montmorillonite to kaolinite in sediment beneath Snuggedy Swamp, South Carolina. They believe the alteration was associated with DOC-rich water leaching the substrate. This, although an isolated example, suggests that conditions in overlying peatlands can significantly influence weathering reactions in the basal sediment.

Laboratory studies have been the focus of mineral weathering investigations. The lack of field based studies stems mainly from the general inability of such studies to identify mechanisms for observed phenomena. Laboratory studies involving specific inorganic acids interacting with pure minerals have successfully led to the development of weathering models (e.g. Holdren and Speyer, 1985; Lin and Clemency, 1981; and Schott and Berner, 1983). However, organic acid mineral interactions under the variability of natural conditions are still at more of a pioneering stage because of the complicated nature of organic acids (e.g. Zinder et al., 1986; Zutic and Stumm, 1984).

1.6 Research Aims and General Hypothesis

1.6.1 Research Aims

Other than Staub and Cohen (1978), little work on the effects of DOC on wetland basal sediments has been performed. The aim of this thesis is to investigate DOC-related weathering, particularly under peatland conditions, through field, experimental and theoretical approaches.

Initially, visual evidence of mineral alteration at the base of wetlands was sought. However, as clear evidence of mineral alteration in the young Schefferville fens seemed unlikely, measurements were made to establish the existing relationship between DOC and element concentrations in solution within the peat and substrate profiles. Profiles of three subarctic fens to characterise the Eh, pH, water conductivity, DOC concentrations, hydrochemistry and sediment morphology were constructed to empirically evaluate the effectiveness of DOC as a weathering agent in light of the other fen characteristics, such as hydrology (Chapter 2).

The interaction between two pure minerals with different chemical compositions and structures (clinochlore and microcline) and Fe-rich basal sediment from a fen, and DOC rich waters formed the experimental component of the study. Two different solutions of DOC-rich water: one of 50 mg/L DOC, pH 6.7, derived from fen peat and a second of the same concentration but pH 5.1 and derived from leaf litter were used. A more concentrated leaf litter solution of 300 mg/L and pH 5.1 was also used. Distilled water buffered to the same pH values as the DOC-rich solutions were used as controls. Mineral dissolution and DOC adsorption rates were examined under aerobic (+600 mV) conditions for all the solutions, and in addition, an anaerobic (+200 mV) environment was created with the peat-DOC solution. The aim of the experiment was to empirically examine mineral weathering by DOC-rich solutions and the effect of the DOC type, concentration and the variable Eh conditions found in fens (Chapter 3).

An investigation of the element speciation using the thermodynamic model SOILCHEM and Fe speciation was experimentally determined using o-phenanthroline (O'Connor et al., 1965) (Chapter 4). SOILCHEM incorporates measured stability constants for organic acids as well as inorganic complexes and modelled stability constants for fulvic acid derived from sewage sludge (Sposito et al., 1981; Sposito et al., 1982; Sposito and Coves, 1988). As up to 90% of wetland DOC is characterized as fulvic acid (Thurman, 1985), an attempt was made to use these stability constants to assess mineral speciation under the influence of DOC derived from peat and leaf litter. In an attempt to reconcile differences between results obtained from SOILCHEM and the empirical data from experiments, a determination of the particle size distribution of Fe and DOC in the microcline and Fe sediment 300 mg/L leaf-DOC solutions was made (Chapter 5).

1.6.2 Hypothesis

Does the presence of naturally occuring quantities of DOC (ie. that present in fens and being produced by leaf litter) increase the ability of water to weather minerals under both the aerobic and anaerobic conditions such as those found in wetlands? If so, how is the solution enriched in metals and what mechanisms are involved?

Chapter 2

Field Study

2.1 Regional Setting

Folding and faulting of the sedimentary units of the Labrador Trough during the Hudsonian Orogeny created a series of narrow, steeply dipping beds. Subsequent erosion of the softer units, usually shale or dolomite, has resulted in a series of parallel northwest southeast trending ridges and valleys (Dimroth, 1978). Wetlands occupy local depressions in valley bottoms where impedance of the natural drainage network and/or ground water upwelling create the saturated conditions for their development. Fens are the dominant wetland type in the Schefferville region of the Labrador Trough. These fens are numerous, easily accessible, and vary in character. Till forms the basal sediment of the wetlands and provides an easily-weatherable medium, rich in Fe. Fe has the properties of being easily complexed by organic acids and reduced at commonly observed redox potentials.

A short active period in the upper portion of the wetland profile, the majority being unfrozen for only 4 to 5 months, limits the production of DOC. Deeper in the fen, low water temperature, between 2 and 5°C at the wetland sediment interface recorded by Moore (1987b), will decrease microbial activity, which in turn restricts DOC production, as well as the overall solubility of elements. Until the frozen surface layer is thawed, DOC produced in the warmer surface horizons cannot migrate toward the basal sediment. The cool temperatures would also restrict chemical weathering through kinetic inhibition. Therefore, cooler water temperatures experienced in the subarctic fens may reduce the overall effectiveness of fen water in mineral dissolution compared to their southern counterparts restricting the applicability of the study to subarctic regions.

2.2 Location and Description of the Three Fens Studied

2.2.1 Location

Three sites were chosen based on logistics, the presence of on going hydrological studies and achieving site diversity but remaining within the fen classification (Figure 2.1). The sites were designated "String Fen" (also known as the Pelletier Fen), "Rich Fen" (also known as the north arm of Astray Fen), and "Poor Fen" (also known as the southern arm of Astray Fen) based on the single most distinguishing characteristic of the sites.

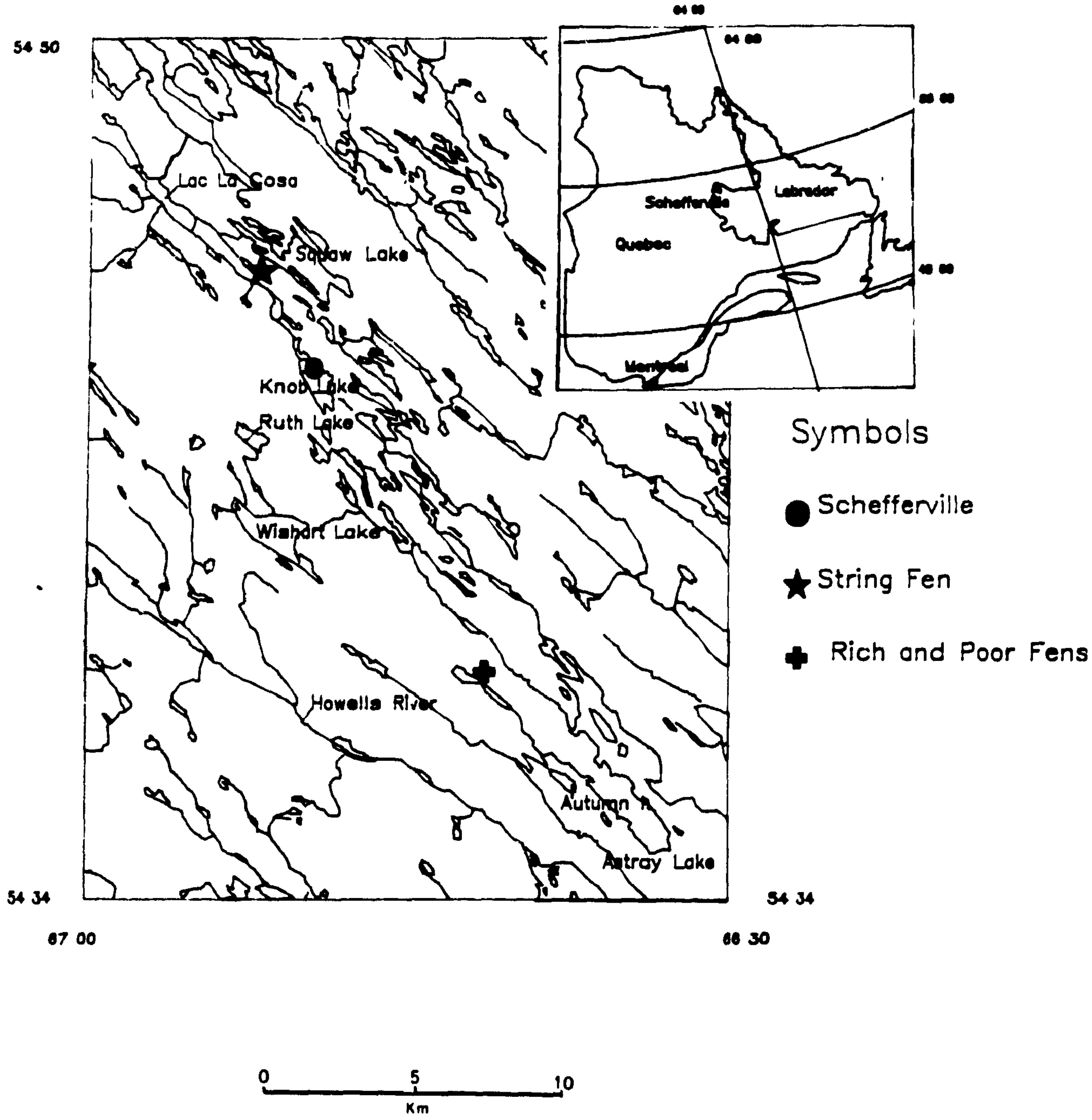


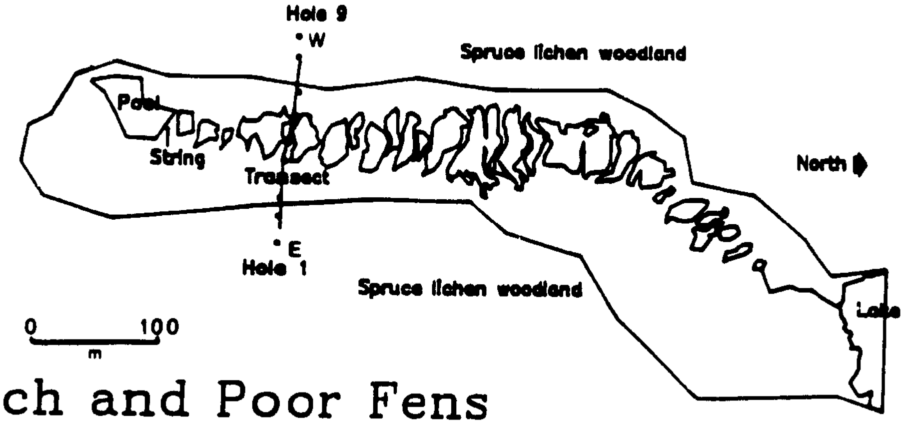
Figure 2.1. Schefferville study area.

2.2.2 The String Fen

The String Fen is located approximately 5 km north of Schefferville and lies within a small shallow drainage basin of less than 0.2 km^2, underlain by slate of the Le Fer Formation (Dimroth, 1978). The fen's dimensions are approximately 0.5 km by 0.1 km with the surface plain tilting slightly northward (surface grade <0.4%) into a small lake (Figure 2.2a). The fen's surface morphology consists of alternating strings and pools creating a unique hydrological setting. No source of recharge other than atmospheric and catchment runoff were observed. Little hydrologic interaction between the pools is likely, except during spring melt, therefore the source of outflow water is probably restricted to the northern portion of the fen (Roulet, pers. comm. 1988). Vertical piezometric gradients of 3mm/day over the length of the fen were recorded by Roulet from snow melt to freeze up (Roulet, pers. comm. 1988). Therefore the inputs of water into the fen after the spring melt must be dominated by local ground water with the pools being surface reflections of ground water seepage points.

The vegetation within the drainage basin is composed of spruce lichen woodland (*Picea mariana, Picea glauca* and occasional *Larix larcina*) with small areas of spruce feather-moss forest.

a) String Fen



b) Rich and Poor Fens

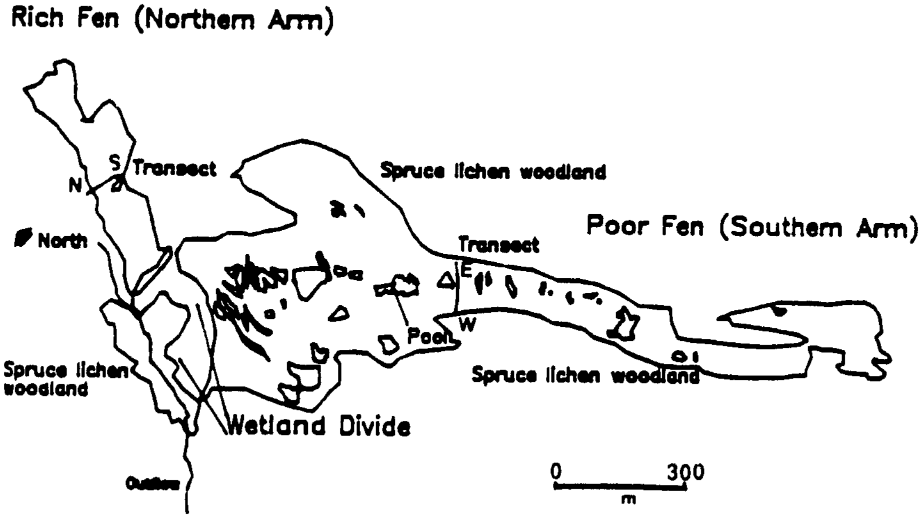


Figure 2.2. Transect locations.

The fen is covered by _Carex spp._ and _Sphagnum spp._ with sporadic _Picea_ and _Betula glandulosa_ on the strings and fen periphery.

2.2.3 The Rich Fen

The Astray Fen lies approximately 12 km south southeast of Schefferville, north of Astray Lake. The fen drains a catchment of approximately 1.0 km^2 and is composed of two arms spanning from a central divide (Figure 2.2b). The Rich Fen occupies the northern arm and the Poor Fen occupies the southern arm.

The Rich Fen lies in a small basin confined to the west and north by a small fault scarp that rises 2 m above the fen surface, and to the east by a gradual slope. A few small pools interrupt a lush vegetation mat that dominates the vast majority of the fen. Spring melt water drains from the wetland southwestward through poorly developed drainage channels. However, during the remainder of the thawed season a large portion of the water in the outflow channel discharges from a spring in the fault scarp.

As in the String Fen, no obvious supply of water recharge other than atmospheric inputs and related runoff were observed. It was felt the fens geological setting, at the junction of a cross-cutting fault and a sedimentary conformity, that large volumes of ground water were entering the fen (from sources who's proximity were only generally known) and being the dominant hydrological factor after spring melt subsided. This was later confirmed in the hydrological studies by Roulet (pers. comm. 1988).

The vegetation of the Rich Fen is lush, with a few lines of spruce trees spanning its width. Carex spp., Sphagnum spp., Picea spp., Betula spp. and Salix spp. dominate the fen surface. An open spruce lichen woodland with patches of feather-moss surround the fen.

2.2.4 The Poor Fen

The "Poor Fen" appears as a long finger running parallel to the tilted sedimentary beds and is exemplary of how the region's surface landforms reflect the underlying geology. All the fen boundaries are marked by distinct changes in vegetation regardless of morphology. However a significant scarp of approximately 2 m defines most of the eastern side of the fen and a northeast facing slope helps define the western side of the fen. The angle of this slope decreases steadily southward until nearly becoming extinct by fens end. Fen water drains slowly northward along the arm and out through the drainage network near the wetland divide (Figure 2.2b). A large number of pools are present that increase in size as the fen widens northward. As in the case of the String Fen, there is evidence to suggest the pools to the NW of the transect, in the central portion of the fen, are related to ground water seepage (Roulet, pers. comm. 1988).

The surrounding vegetation is the same as in the northern arm, but tree density decreases southward. The fen vegetation is less prolific than in the northern arm, with the dominant species being Betula spp., Carex spp., and Sphagnum spp. with some Scirpus cespitosus, Picea spp., and Larix larcina. in the wider central fen section.

2.3 Methods of Sampling and Analysis

Peat and sediment cores were taken across the width of each fen (Figure 2.2). A peat auger was used to remove the upper layer of poorly decomposed peat to a depth of approximately 1 m and the remaining peat and sediment was extracted using a cobra drill with a flow through sampler. Additional cores, 3 on the east side and 2 on the west side, extended the transect line of the String Fen to 25 m beyond each side of the wetland boundary. Soil profiles (<0.7 m deep) were taken at each end of all the transects.

To extract water samples, piezometers of different lengths made from ABS piping were installed at the bore hole sites. Additional water samples were gathered from around the bore hole to a maximum depth of 2.0 m using a perforated metal rod. A high pressure pump was used to withdraw the water samples through tygon tubing into rigid polythene sampling bottles. Insufficient water for analysis was extracted from many peripheral and surface areas of the peat. This was probably a result of the record low precipitation received that summer and prevented a more rigorous sampling scheme. Samples of outflow and surface pool water were also taken.

Redox potentials (Eh) were recorded using electrodes of up to 1.2 m in length with platinum coated wire tips and a calomel half cell coupled to a portable Orion 407A specific ion meter. The electrodes were cleaned, replatinized using platinum chloride and calibrated daily as electrode failure was common after the tips were damaged during insertion. The calibration standard used was a 300/N potassium ferrocyanide, 300/N potassium ferriccyanide and 10/N potassium chloride solution (ZoBell, 1946). Any significant departure ±20 mV from the original correction factor resulted in that data being discarded. Undamaged electrodes generally registered well within this range where-as damaged electrodes often varied by more than +100 mV to +200 mV. The ±20 mV threshold was chosen because it was generally smaller than the variability recorded at any point within the peat and seemed to be the upper bracket of what could be attributed to normal wear.

Organic carbon content and pH of peat, soil and sediment subsamples were determined at regular intervals (approximately every 20 cm) along the length of the core, with additional measurements in areas of boundaries and visible change. Organic carbon was determined by ignition at 850°C for 30 minutes after oven drying at 105°C for 24 hours. pH of air dried samples in both water and 0.01 M $CaCl_2$ was measured using a Fisher Accumet model 210 pH meter. pH of water samples was measured using the same pH meter as above and water conductivity was measured with a YSI Model 32 Conductance meter. A modified Walkley Black method was used to determine the DOC concentrations of the water samples (Appendix I) and major cation analysis was carried out using flame atomic absorption spectrometry (AA).

2.4 Fen Characteristics

2.4.1 Morphology

The maximum depth of peat in the String Fen was approximately 2.3 m, roughly at the transect centre. From this point the peat thins steadily toward the periphery (Figure 2.3a). The Rich Fen is the deepest of the three wetlands, the bottom being beyond the reach of the sampling equipment (>3.75 m) at the three central holes (Figure 2.3b). The Poor Fen is shallow with a maximum depth of 1.2 m recorded along the transect (Figure 2.3c). In general the peat was poorly decomposed, the peat of the Poor Fen appearing slightly more decomposed than that of the other two fens. Most plant matter, although becoming less entwined and finer with depth, remained easily identifiable and even tree trunks were encountered at levels below 1.0 m in the Rich Fen.

The till underlying the String Fen and adjacent forest soil and moss mat was remarkably uniform varying between 1.0 m and 1.5 m in thickness. The same type of sediment was present around the Rich and Poor fens, although it was considerably shallower averaging 40 cm in thickness, and the uniformity of cover was often broken especially beneath the fens.

The till or what will be referred to as sediment or Fe sediment, was generally a compact and saturated red (ie. 2.5YR 3/6 - 2.5YR 4/2) silt loam to silty clay loam. When dried, the samples became very hard and the colour became lighter increasing in both value and chroma (ie. 2.5YR 4/2 - 2.5YR 5/6) in forest till and in hue value and chroma (ie. 5YR 4/8 - 5YR 5/6) in String Fen basal till. The colour of the sediment beneath the Rich and Poor Fens was slightly browner (ie. 5YR

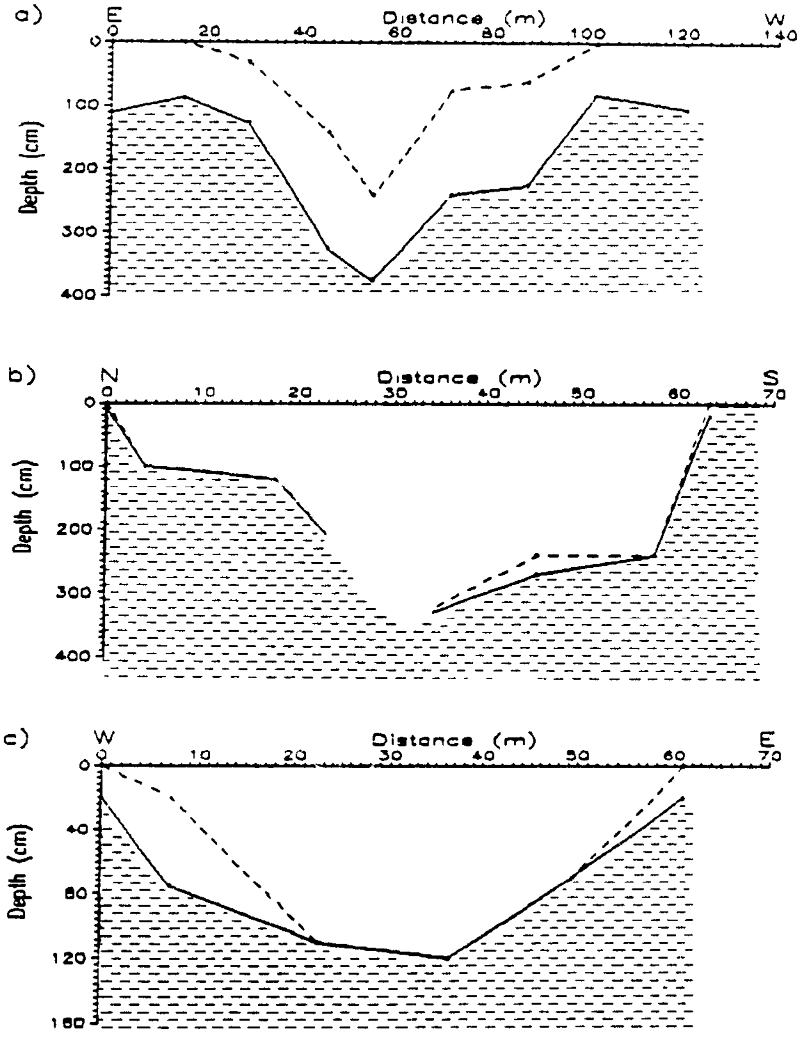


Figure 2.3. Morphological cross sections of the : a) String Fen; b) Rich Fen; and c) Poor Fen; showing the sediment boundary (dashed line) and the bedrock boundary (solid line).

4/4). The sediment becomes slightly coarser with increasing depth, mainly as a result of an increase in the > 2 mm fraction (pebbles). At the sediment bedrock interface up to 50% of the till by volume were pebbles. One anomaly in the uniform till was found at the base of holes 6 and 7 where a sand and fine gravel horizon of less than 20 cm was encountered immediately above the bedrock. The origin of this horizon is unclear, but its unconsolidated nature and fining upward tendency gives the appearance of a lakeshore deposit.

Bedrock samples were obtained from a number of holes in the String and Poor Fens. The samples were a grey green laminated slate consistent with that exposed outside the fen border. This verifies the underlying bedrock of the String Fen is the Le Fer Formation. The formation lying beneath the Poor Fen could not be identified from existing maps but the samples suggest it is the same formation.

No evidence of gleying or unconformity in the sediment was observed with one exception. Just within the eastern border of the String fen, a thin discontinuous gleyed horizon (0 - 5.0 cm thick) existed at a depth of 35 cm beneath the surface. The gleyed horizon separated a more decomposed almost muddy peat from saturated conditions that existed in the till below. It appears where water table fluctuations cross the peat-sediment interface, such as at the fen periphery, gleying can occur.

The organic carbon content of the String Fen peat averaged 42% varying a couple of percentage points over the profile. The organic carbon contents of the Rich and Poor Fens were comparable averaging 38% and 41% respectively. The organic carbon content of the sediment was dramatically lower. A gradient of approximately 7.0% to 0.0% was observed from just beneath the peat-sediment interface to > 1.0 m below the boundary in holes 3 and 4 of the String Fen; and a gradient from 0.2% to 0.0% in the other three holes of the String Fen. In the Rich and Poor fens a similar gradient to holes 3 and 4 of the String fen was observed. Organic carbon content of the forested sediment was 0.0% in all but the upper 5 cm were it varied from 0.0% to 2.0% except where the spruce moss or lichen composed a significant portion of the fraction.

2.4.2 Patterns of Redox Potential (Eh)

Redox potentials, recorded across the transect to a maximum depth of 1.2 m, were plotted as contoured Eh profiles to display general trends in the fens (Figure 2.4). A substantial variation in measurements, up to +100 mV within 1 m^2, at any one depth was recorded and attributed to the natural inherent variability of peat. The Eh of the String Fen decreases from +400 mV to 0 mV both laterally and vertically

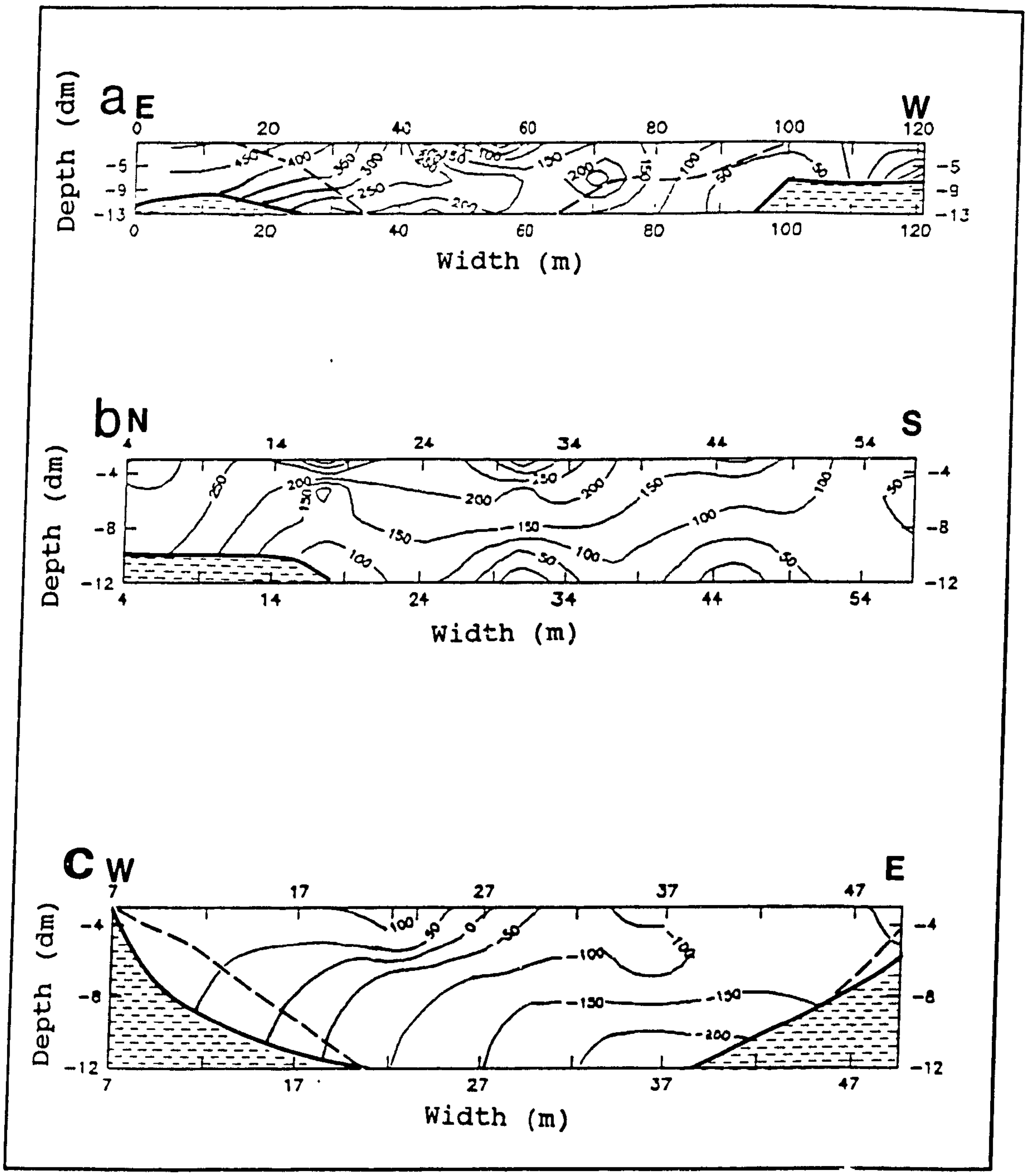


Figure 2.4. Eh profiles of the: a) String Fen; b) Rich Fen; and c) Poor Fen(mV).

(Figure 2.4a). Similar Eh patterns were observed in the Rich and Poor Fens, the Eh dropping from +300 mV and +100 mV just below the surface to +100 mV and -200 mV at a depth of 1.2 m respectively (Figures 2.4b, 2.4c). Therefore the Poor Fen appears to be completely anaerobic given the Eh measurements and the presence of a sulphide odour emanating from the water and peat samples.

2.4.3 pH Profiles

In both calcium chloride and water based pH measurements the same trends were evident; however, the calcium chloride based measurements averaged 0.6 pH units less than the water based. Therefore only the data from the distilled water pH measurements will be discussed here. The pH of the String Fen peat increased steadily with depth from 3.6 through the peat-sediment interface to 4.4 just above bedrock (Figure 2.5a). The pH of the forest sediment is variable, the western side of the fen being less acidic than the eastern side. The pH of the Rich Fen peat remained fairly consistent decreasing slightly with depth (Figure 2.5b). The underlying sediment pH values followed the same pattern as in the peat, however, the soil adjacent the fen was more alkaline. The pH gradient in the Poor Fen is horizontal as opposed to vertical ranging from 4.4 to 6.0, with sediment pH blending with the peat-pH gradient (Figure 2.5c). A small region of more acidic peat (pH

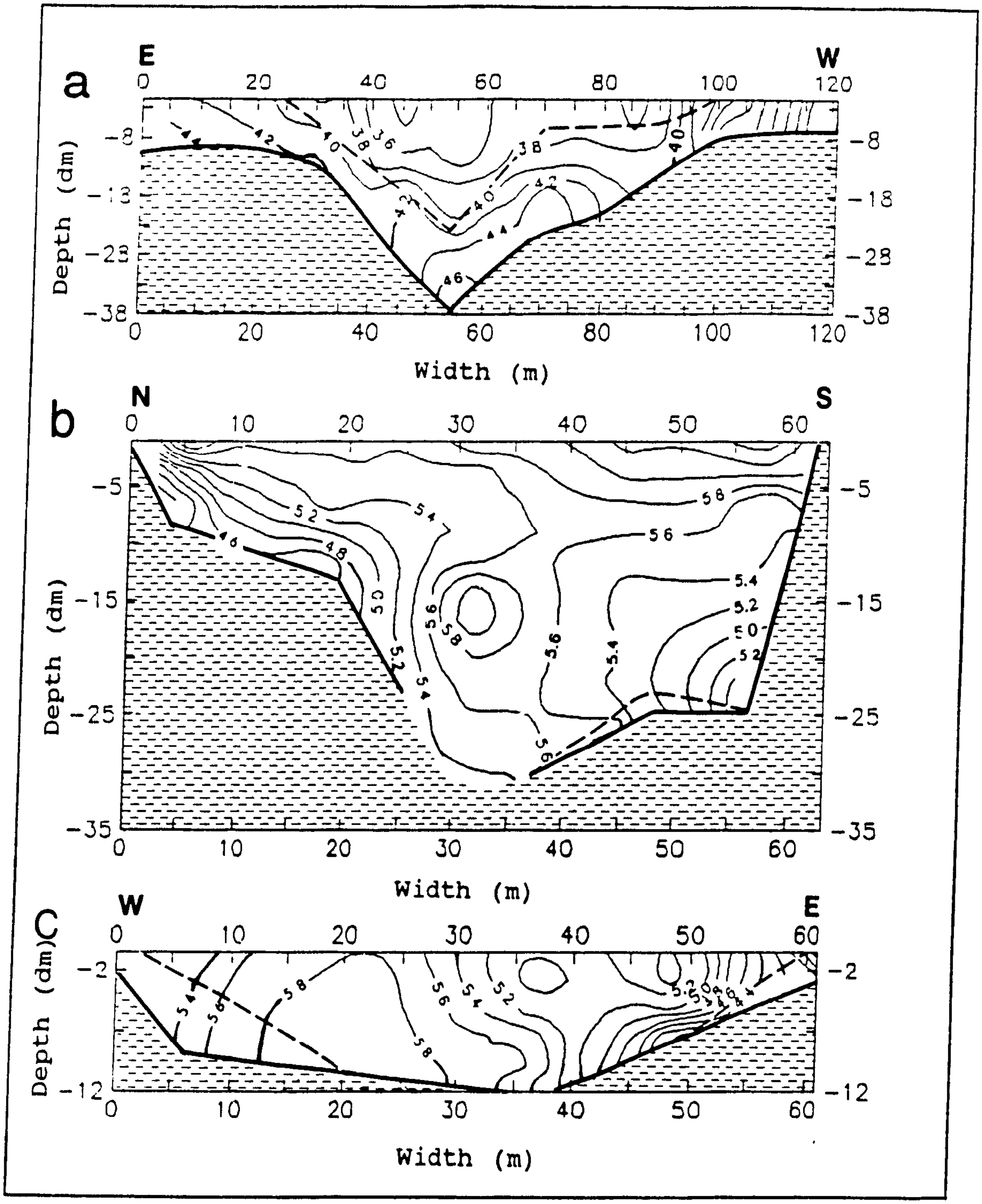


Figure 2.5. Peat and sediment pH profiles of the: a) String Fen; b) Rich Fen; and c) Poor Fen.

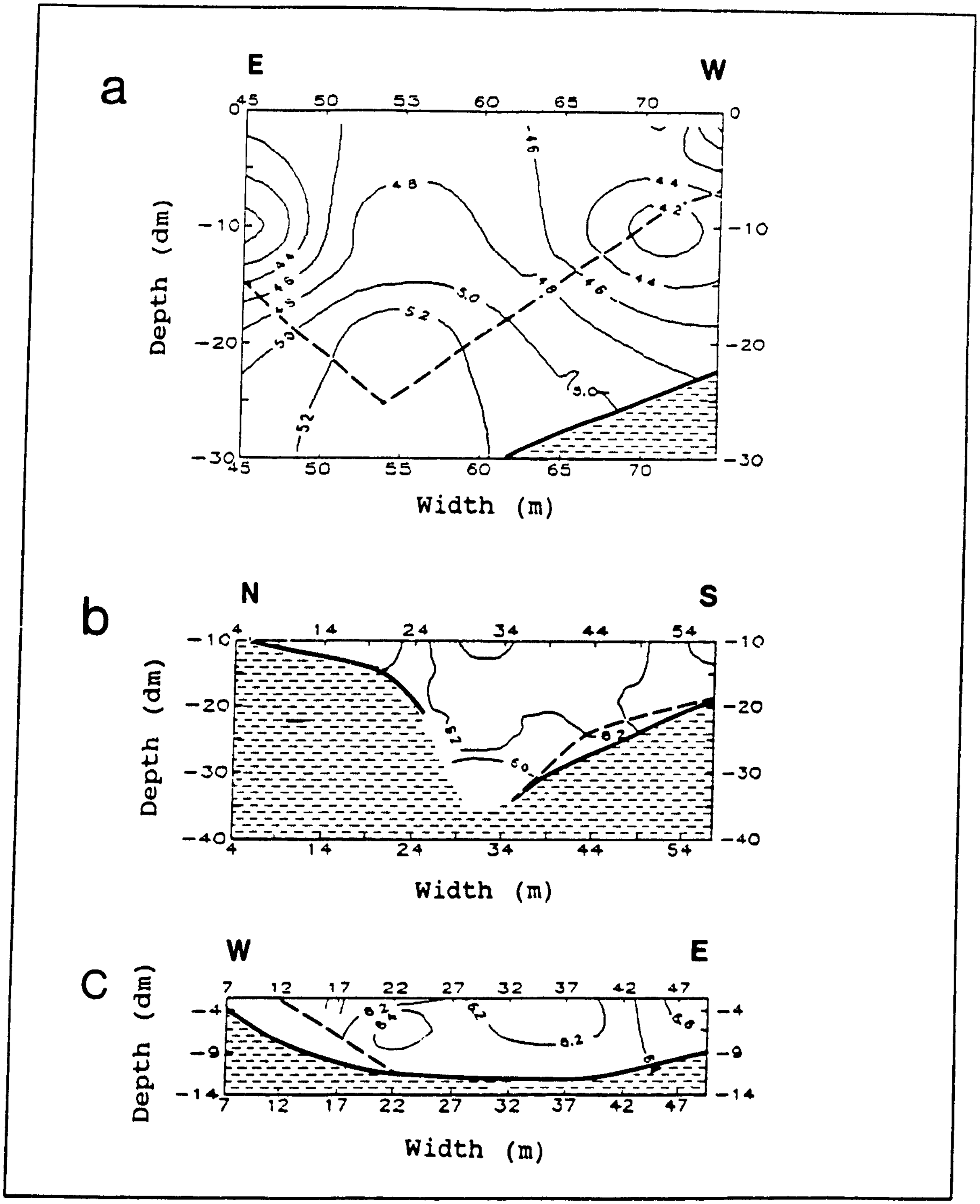


Figure 2.6. pH profiles of the peat water from the: a) String Fen; b) Rich Fen; and c) Poor Fen.

5.0) at the 40 m mark is associated with surface water pools.

The pH of the String Fen interstitial water increases from 4.2 to 5.2 toward the basal centre of the profile (Figure 2.6a). The pH of the Rich Fen water is fairly constant, at 6.2, for the vast majority of the profile varying by only 0.4 pH units (Figure 2.6b). The Poor Fen water has a similar pH to the water of the Rich Fen with the exception of the western edge (Figure 2.6c), where the pH of the Poor Fen water decreases rapidly from 6.0 to 5.0 toward the fen boundary.

2.4.4 Water Conductivity Measurements and Element Analysis

The water conductivity of the String Fen was low, averaging 30 μmhos cm^{-1} and no discernible or significant pattern was evident in the data (Figure 2.7a). The Rich and Poor Fen water had a much higher conductivity, averaging 200 μmhos cm^{-1} (Figure 2.7a and b). The Poor fen conductivity values increase from the west side of the transect to the east side displaying a complex pattern that is uninterpretable from one profile. This trend is unfortunately common of much of the data regarding this transect.

The highest total element concentrations occurred in the Rich Fen with Mg and Ca ions accounting for up to 80% of the

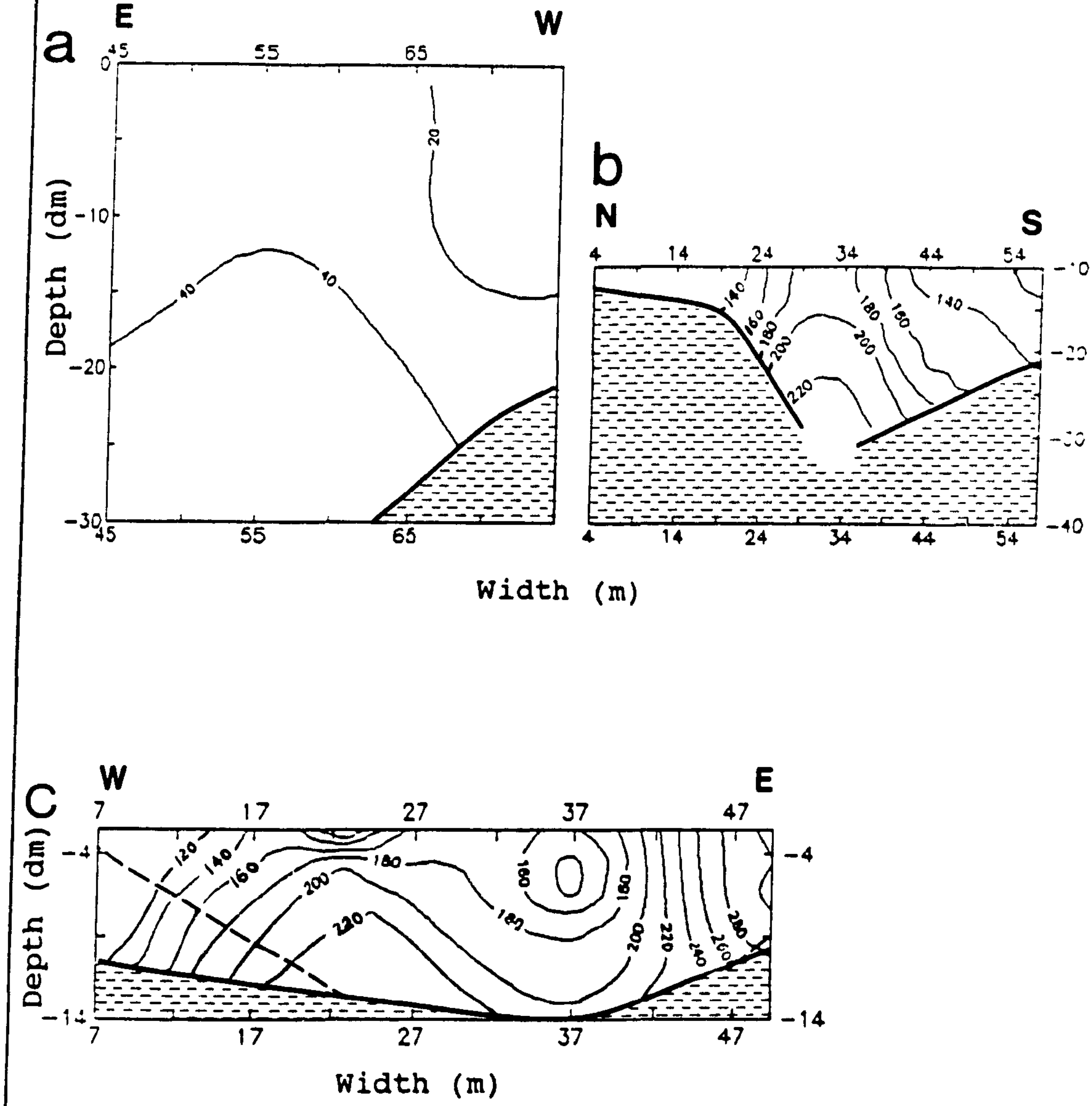


Figure 2.7. Water conductivity profiles of the: a) String Fen; b) Rich Fen; and c) Poor Fen.

total (Table 2.1, Figure 2.8a). In the Poor Fen Mg values were lower and the Ca concentrations considerably lower than in the Rich Fen which may partially explain the differences in the "lushness" of vegetation. K, Na and Si values were approximately the same in the Rich and Poor Fens and Fe was not present in measurable quantities (>0.1 ppm to register, >0.2 ppm to be accurate), which was surprising given its prominence in the surrounding till.

The total element concentration in the String Fen is lower than both the Rich Fen and the Poor Fen and the relative concentrations of individual elements is very different (Figure 2.8b). Lower concentrations of Mg and Ca are offset by increases in Fe, Al and Na. The concentrations of elements in the String Fen outflow are considerably lower than the concentrations water in the southern portion of the fen. This difference is probably a result of a limited horizontal flow in the summer (the time of sampling), making the outflow in this season representative of only the northern portion of the wetland. The drainage channel allows dissolved species to be lost unlike in the southern portion of the fen were evaporation is the primary source of water removal, which allows elements to accumulate. The high Mg and Ca values in Pelletier Lake water, the sink of the wetland outflow, suggest sources other than the fen dominate the lake water supply.

Poor Fen

Hole Pos(m)	Depth (m)	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	DOC
						ppm					mg/L
1 (7)	0.2	Tr*	1.4	2.1	1.8	0.1*	0.6*	4.1	10.1	4.7	8[a]
1 (7)	0.4	0.1*	0.4	3.2	1.0	0.1*	0.2*	5.2	10.2	4.4	10[a]
3 (36)	0.5	Tr*	10.3	2.6	1.1	0.2*	4.2	5.4	23.8	6.0	9[a]
3 (36)	1.4	0.0*	20.8	3.1	1.4	0.1*	12.8	6.4	44.5	6.3	8[a]

Rich Fen

Hole Pos(m)	Depth (m)	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	DOC
						ppm					mg/L
1 (4)	1.0	0.0	8.4	3.5	1.3	0.1	6.5	3.1	22.7	5.3	10
2 (18)	1.0	0.0	9.1	3.2	1.0	0.1	7.2	3.6	24.0	5.8	15
2 (18)	2.0	0.0	12.2	2.1	0.8	0.1	11.0	4.3	30.4	6.1	5
3 (31)	1.0	0.0	16.0	2.7	1.3	0.1	17.1	4.7	41.8	6.5	9
3 (31)	2.0	0.0	18.8	3.7	2.7	0.0	17.4	4.7	47.3	6.2	11
3 (31)	2.5	0.0	17.4	3.2	1.2	0.0	15.1	5.8	42.7	6.4	9
3 (31)	3.0	0.0	19.0	3.2	1.2	0.0	19.1	6.4	51.2	5.8	8
3 (31)	4.0	0.0	23.8	3.1	2.4	0.1	21.1	5.1	55.6	5.8	11
4 (45)	2.0	0.0	13.2	2.7	0.8	0.0	12.2	4.2	33.0	6.2	-
5 (57)	1.0	0.0	7.5	2.5	1.0	0.1	7.4	2.1	20.6	6.0	-

String Fen

Hole Pos(m)	Depth (m)	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	DOC
						ppm					mg/L
4 (45)	1.0	1.2	0.1	4.6	1.2	0.6	0.4	3.7	11.9	4.0	50
5 (45)	1.0	1.8	0.3	7.5	1.9	0.2	3.0	1.6	16.2	4.9	74
5 (55)	2.0	0.0	0.7	4.0	1.1	0.0	1.2	4.4	11.3	5.4	9
5 (55)	2.5	1.4	1.0	3.3	1.3	0.8	0.8	8.4	16.9	5.3	5
5 (55)	3.0	0.0	0.6	3.4	0.9	0.1	1.0	3.9	9.9	5.3	4
6 (72)	0.1	5.8	0.1	3.6	1.0	0.2	0.9	1.6	13.2	4.3	27
6 (72)	1.0	3.8	0.1	3.0	1.6	2.2	0.1	5.5	16.2	4.1	24
Outflow		0.7	0.8	1.7	0.3	0.0	1.5	3.2	8.2	5.8	11
Pelletier Lake		0.0	1.8	3.7	0.8	0.1	2.5	2.0	10.9	6.4	6

* Concentrations are below accurate detection levels but the numbers represent good approximations.

[a] These DOC concentrations were determind by absorbance at 330 nm and correlated using a calibration curve.

Pos(m) = width grid reference.

Table 2.1 Major element analysis of the Fen water samples and the associated DOC concentrations.

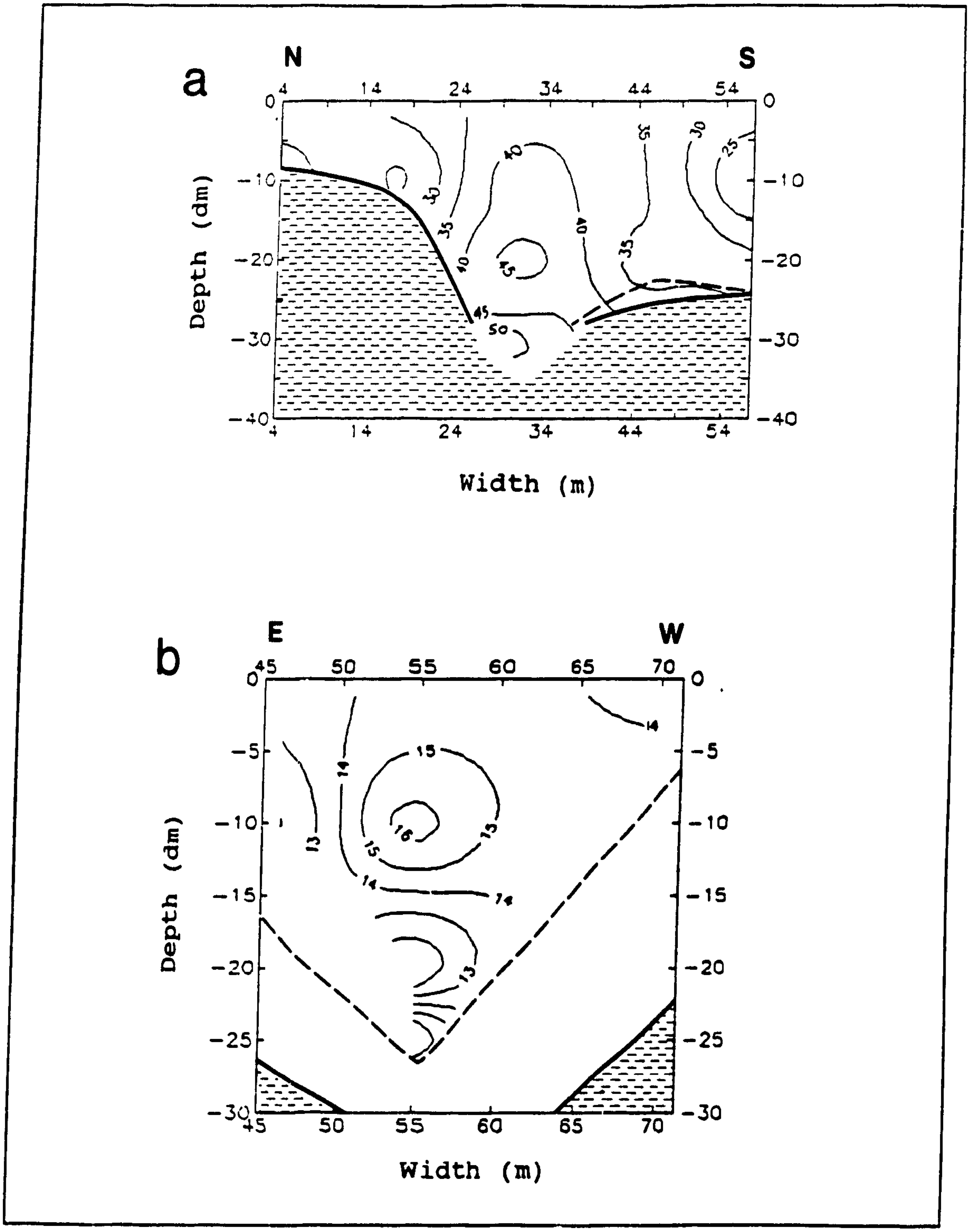


Figure 2.8. Total element concentration (Na, K, Mg, Ca Fe, Al, Si) profiles of the: a) Rich Fen; and b) String Fen(ppm).

2.4.5 DOC concentrations

DOC concentrations of the String Fen peat-water increase toward a focus of approximately 70 mg/L, at a depth of 1 m, forming a bulls eye pattern (Figure 2.9a). The pattern is somewhat exaggerated as a result of the less than desired sampling intensity. Concentrations in the water extracted from the basal sediment were much lower, ranging from 8 to 10 mg/L.

The DOC values recorded in the Rich Fen were between 8 - 14 mg/L (Figure 2.9b) and the two DOC concentrations determind by the Walkley Black Method for the Poor Fen (only two because of insufficient sample volume) were 6 mg/L and 9 mg/L. It is felt these two values are representative of the Poor Fen as preliminary measurements using absorbance gave the indication that any variance from these values would be small. However, taking into account analytical errors in determining DOC concentration and the small variability described above, little can be said about the patterns of DOC concentration in either of these two fens.

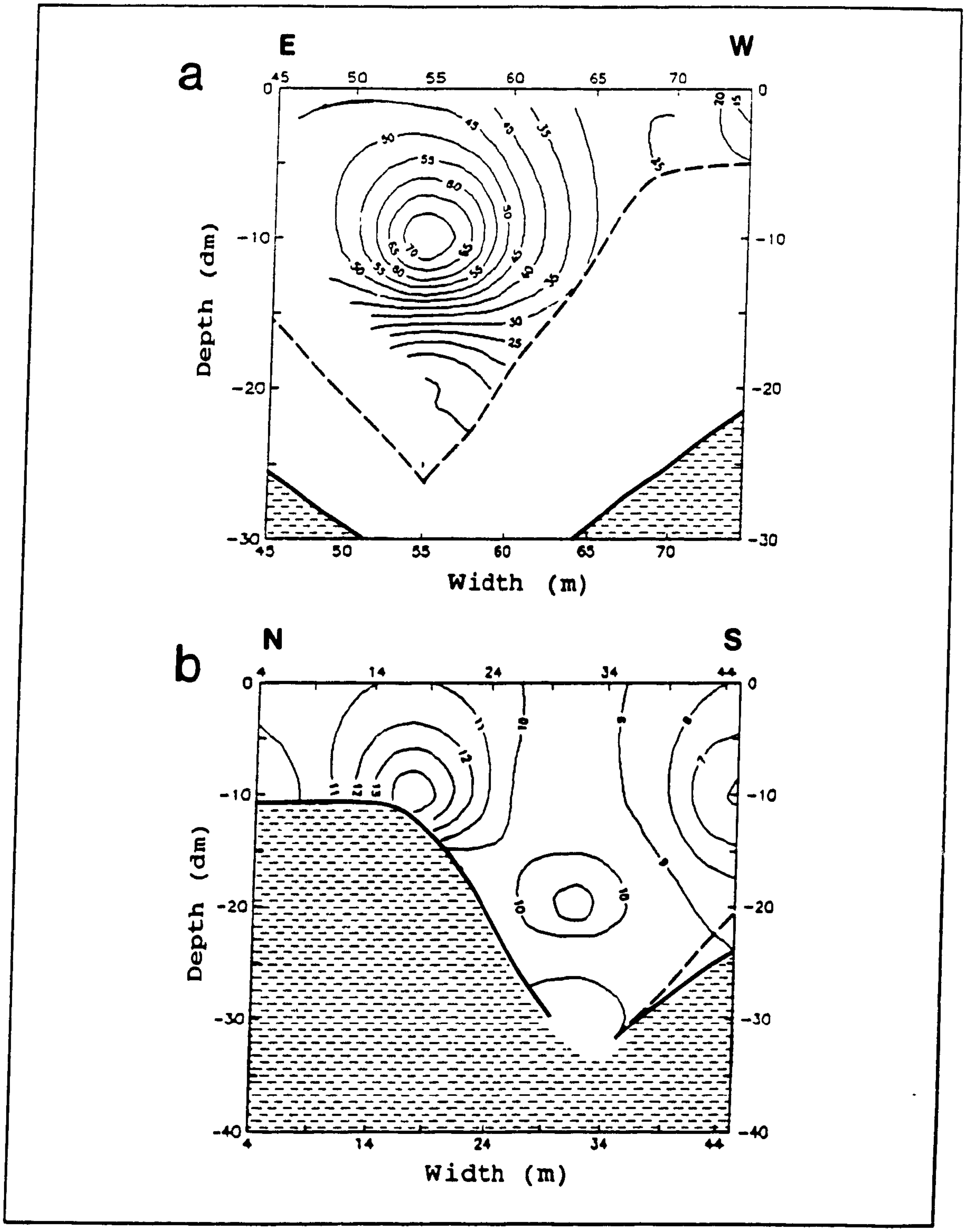


Figure 2.9. DOC concentrations in the a) String Fen; and b) the Rich Fen.

2.5 Discussion

All three fens studied are influenced by ground water in some way. In the String Fen, the impression of an upwelling plume of less acidic water is created by the interpolated isolines (Figure 2.6a). The sparse data set maybe partly responsible for the image as a great deal of emphasis is placed on a few, although precise, points. A significant difference exists between peat-pH or potential acidity, and that of the fen water indicating the acidity of the peat is offset by a base rich inorganic solution. Red, water rich in iron particulates filled the fen bore holes when the sediment was perforated by the drill bit. All these factors combine to support Roulet's (pers. comm., 1989) hypothesis of the existence of a plume of more alkaline water intruding through the bottom of the deepest portion of the String Fen.

The pH of the peat in the Rich and Poor Fens was considerably higher than that of the String Fen. Differential adsorption of cations onto the surface of organic matter from ground water and the release of cations from decomposing vegetation once richer in cations (from the same ground water source) could readily explain the between fen and within fen differences in peat-pH. An enrichment of cations in the Rich Fen (Figure 2.8a) corresponds to the maximum peat-pH values (Figure 2.5b) and a high, although more expansive due to a lack of sensitivity, in the conductivity profile (Figure 2.7b). The largest concentration of cations is near the base of the fen and corresponds to a high, although not the highest, pH value. This suggests ground water, rich in cations probably having past through dolomitic rock, is entering the base of the fen at some point north of the transect and moving laterally through the fen at the transect line. A greater amount of cation accumulation in the peat is probably related to slower moving water in the mid central portion of the fen transect compared to basal flow. At the periphery of the fens the pH values are lower, probably as a result of acidic surficial runoff waters entering the peat from the surrounding woodland.

The Eh measurements obtained for half of the String Fen and all of the Rich Fen are not really basal; but since ground water dominates the system, the effects of which easily reach the depth measured, this is probably of little consequence. The rate of fen water movement allows the fens to develop a slight anaerobisim, but is sufficient to prevent further reduction of these systems. In the case of the Poor Fen, the sulphide odour was prominent in all regions regardless of depth. The longer water residence time, given the fetch of the fen and slow percolation rates, allows the water to become anoxic. The transect selected is either some distance from a ground water seepage zone or "up stream" of the main source of fen water flow. The relatively high cation concentrations measured suggest that the area is influenced to some degree by ground water but this influence may be seasonal. The low oxygen content of the water in this region is probably a major contributor to the poor state of the vegetation.

The highest DOC values in the field, 74 mg/L, were recorded in the String Fen but concentrations over 150 mg/L were obtained from the peat of the Rich Fen in laboratory studies (3.1). Although the peat of the other two fens was not tested, it appears potential DOC levels are not being achieved in the environment. Low redox potentials, in the case of the Poor Fen, colder water temperatures, ground water dilution and high number of dissolved cations in solution, particularly Ca and Mg causing coprecipitation, may be responsible for the lower concentrations.

In the summer, evaporation is the main mechanism for water removal from the portion of the String Fen in which the transect lies. This, in conjunction with a vertical flow regime, may allow DOC to concentrate in the near surface layers of the fen instead of flowing out through a drainage network as in the case of the Rich Fen. An investigation of the DOC and cation concentrations in solution cross sections of the String Fen water (Figures 2.9a and 2.8b) shows the peak DOC concentration matches remarkably well with peak cation concentration. This sparse evidence, unfortunately, does not suggest anything about the relationship between DOC and the cations in solution particularly regarding binding and transport. Not unexpectedly, the cation composition of the fen water does not resemble the composition of the sediment (Chapter 3.1.2) given the dominance of ground water from some other source. The focal point of cation concentrations also corresponds remarkably well with the position of the frost table, which persisted for the entire summer in parts of the fen. It may have served as a barrier for downward migrating DOC or upward migrating cation rich water, as below this level an upward gradient in element concentrations is observed, with Mg offering a slight inverse relationship. The DOC and cation peaks, therefore, are probably coincidental. The upward moving water may render all but the DOC produced at depth ineffective as a weathering agent. A reduction in DOC concentration of between 50% and 75% occurs shortly below the peat-sediment interface suggesting any DOC entering the sediment is quickly adsorbed. Sediment organic carbon contents suggest this amount is small, restricted to near the interface, and are not any greater than in the forest sediment.

2.6 Conclusions

In the fen basal till there were no visible signs of a weathering profile that was different than that which exists in the same till of the surrounding woodland. No correlation was found between DOC and dissolved cation concentrations, as hydrological complexities made the interpretation of DOC:sediment interactions most difficult. Therefore, there is no evidence to suggest the consistant presence of DOC-rich water is accelerating the weathering of the fen basal till nor creating a different weathering profile. It is felt a long term study of the fen hydrology, and DOC and cation migration may improve the current understanding of the influence of DOC on the fen substratum, but it is unlikely to be able to separate the effects of single factors. This is best handled in a laboratory investigations were these factors maybe controlled individually.

CHAPTER 3

Mineral Weathering by DOC-Rich Water: a laboratory study

3.1 Introduction

Laboratory grade minerals and an Fe-rich sediment, collected from the Schefferville area, were subjected to DOC solutions of different concentration, origins, and redox potentials (Eh). The DOC solutions were compared with control solutions of distilled water and a weak solution of HCl, the latter being an inorganic weathering agent. Weathering was assessed through the determination of changes in element concentrations in the weathering solution.

3.2 Materials and Methods

3.2.1 The Solutions

Two DOC-rich solutions of 50 and 300 mg/L DOC were derived from leaf litter to represent average and high DOC concentrations, respectively, that enter the soil from decomposing leaf matter (Antweiler and Drever, 1982). Maple (Acer saccharum) and Beech (Fagus americana) leaves were placed in pails with distilled water at a 1:4 ratio and after two weeks the DOC concentration of the leachate produced was 500 mg/L. It was noted that with approximately a 1:1 leaf-water ratio, a concentration of over 1000 mg/L DOC was possible after 1 month. The 500 mg/L was passed through a 1.4 μm GFC filter and diluted to DOC concentrations of 50 and 300 mg/L with respective pH values of 5.3 and 5.1.

DOC concentrations observed in the Schefferville peatlands approached but did not often exceed 50 mg/L (Moore, 1989; Koprivnjak, 1990). Immersions of sections of peat, representative of the upper 50 cm of the Rich Fen, in distilled water resulted in DOC concentrations of 90 mg/L after 10 days. The solution was decanted, filtered (1.4 μm) and diluted to 50 mg/L with a pH of 6.7. Greater concentrations of DOC could be achieved after prolonged immersion, for example 170 mg/L after 30 days. The pH of 6.7, although within the range expected for fens of the Schefferville region, 4.8 to 6.9, is higher than the pH of 6.0 measured for both pore water and peat of the Rich Fen. The explanation for the disparity lies in the complicated origin of the Rich Fen peat water and the short immersion times used to determine peat pH (1 hr) did not allow for the modification of pH by the addition of DOC and cations to solution by peat degradation. Both leaf and peat DOC solutions were analyzed by AA for the initial concentrations of elements to be studied and the data is presented in Table 3.1.

	Fe	Mg	Na	K ppm	Al	Ca	Si
50 mg/L Peat-DOC	1.24	3.81	0.97	2.06	0.23	1.13	3.01
50 mg/L Leaf-DOC	0.00	0.16	0.64	3.07	0.18	1.53	0.00
300 mg/L Leaf-DOC	0.00	0.96	3.84	18.40	1.08	9.18	0.00

Table 3.1. Initial concentrations of weatherable elements in the DOC-rich solutions.

To reflect the aerobic environment, solutions were equilibrated with the atmosphere, at a Eh of approximately +600 mV. To represent anaerobic weathering, a complementary set of peat-DOC solutions were reduced to an Eh of approximately +200 mV by adding 250 mg/L of dextrose, therefore adding an additional 125 mg/l of DOC. After approximately 4 days, the redox potential dropped to between 0 and +200 mv at pH 5.1 and DOC concentrations of samples taken just prior to mineral addition were 71 mg/L. It is likely CO_2 gas was the major byproduct of the reactions resulting in the loss of organic carbon. The solution will continue to be referred to as having 50 mg/L peat-DOC, ignoring the presence of the DOC produced by the dextrose. The +600 mV and +200 mV Eh's are characteristic of the aerobic and anaerobic zones of the Schefferville fens respectively (Figure 2.7). The +200 mV Eh falls within the zone of potential iron reduction, observed to be between +300 mV and

+100 mV at pH 5 to 7 respectively (Gotoh and Patrick, 1974). Two control solutions, one of distilled water, with pH 6.9 approximately equal to the pH of the aerobic peat-DOC, and a second buffered with $5x10^{-5}$ M HCl to a pH of 5.1, approximately equal to the pH of the leaf and anaerobic peat-DOC, were also used.

3.2.2 The Minerals

Three weathering mediums, microcline, clinochlore, and an Fe-rich sediment were selected and their molar concentration of elements is listed in Table 3.2. Microcline and clinochlore, although structurally very different, were observed to be comparable in resisting weathering under low temperature and pressure regimes depending on the solution (Goldrich, 1938). Microcline is the common feldspar that is most resistant to weathering and has a structure of $(Si,Al)O_4$ tetrahedra linked by shared oxygens, forming two linked parallel chains with Na and K occupying the interstices. Impurities such as Ca, Fe and Mg also occupy some of these interstitial sites and provide the opportunity to investigate the selectivity of the DOC in mineral dissolution.

Clinochlore, a chlorite, is a sheet silicate with two sheets, a "brucite" sheet $Mg_6(OH)_{12}$ and a "talc" sheet $Mg_6Si_8O_{20}(OH)_{12}$. In clinochlore, the substitution of Al for Si,

Minerals	Fe^{2+}	Fe^{3+}	Mg	Na	K	Al	Ca	Si
				%				
Fe Sediment	0.9	24.8	1.1	0.6	4.0	10.6	0.4	57.8
Clinochlore	7.9	3.0	30.6	<0.1	0.8	27.9	0.3	29.7
Microcline	<0.1	<0.1	<0.1	3.4	19.0	18.8	<0.1	58.6

Table 3.2. Mineral composition shown as percent molar concentration of elements. Composition was determined using X-Ray fluorescence. The actual analytical data is listed in Appendix I.

and Fe for Mg and Al, provides a means of investigating the selective nature of DOC weathering. The third material chosen was a sample of the extremely Fe-rich sediment collected from beneath the Schefferville fens. The mineralogy was described by Nicholson and Moore (1977) as being quartz, mica, chlorite and kaolinite with low concentrations of magnetite. Fe-oxalate concentrations were recorded as being 1% and Fe-dithionite concentrations 5%.

There is no consistency regarding the particle size of minerals used in weathering experiments, though Schalsha et al. (1967) indicated the importance of particle size in absolute dissolution rates. Particle sizes have ranged from 90 - 110 μm (Holdren and Berner, 1979), 106 to 500 μm (Manley and Evans, 1986), 149 to 297 μm (Huang and Keller, 1970) and 37 to 53 μm (Boyle et al., 1974). The bulk of the Fe rich Schefferville sediment is naturally in the silt clay loam to silt loam fraction (USDA), which corresponds to 84% <57 um.

Since most of the sediment is silt and coarse clay, the whole sediment fraction <200 um was used. In an effort to create particle size uniformity, the clinochlore and microcline were ground to between 57 and 200 um. Comparisons of cation release rates between the two pure minerals and the Fe sediment should take into consideration differences in particle size.

Mineral-solution ratios vary in the literature from 0.7 g/L (Kodama et al., 1983) to 20g/L (Huang and Keller, 1970) and 50 g/L (Busenberg and Clemency, 1976). In this experiment a concentration of 20 g/L of sediment or mineral was selected ensuring a reasonable sediment reservoir for which the DOC could interact as in natural environment. The minerals were untreated after grinding although an extensive mineral preparation is suggested by Manley and Evans (1986) to remove carbonates sulfides and soluble salts.

3.2.3 Experimental Conditions, Sampling and Element Analysis

Aerobic chambers consisted of 1 L polyethylene bottles at maintained at approximately 25°C and 1 Atm. To increase the interaction between the minerals and DOC, the solutions were stirred gently for alternate 12 hr periods. 150 ml samples were pipetted from approximately 10 cm above mineral mass, after 10, 20, 50, 100 and 400 hr. Eh, pH and conductivity were measured at the same point after every 12 hr for approximately the first 100 hr, every 24 hr for the next 200 hr, and finally every 48 hr for the last 100 hr. The pipetted samples were then centrifuged at 4500 rpm in an International Clinical table top centrifuge for 1 hr to remove suspended matter and the pH measured again. Absorbance was measured using an LKB BIOCHROM ultraspec 4050 spectrophotometer in 1 cm cells at 330 and 510 nm. The cations Fe, Mg, Na, K, Al, Ca, and Si were determined by flame AA analysis without modifying the solution. Prior to analysis, samples were stored in polyethylene bottles at 4°C.

A slightly different method was employed for the anaerobic peat-DOC solution. To minimize the effect of the air space left vacant in the chamber after sample extraction, three 500 ml polyethylene bottles were used as reaction chambers for each mineral solution combination. The first bottle was sampled after 10 and 20 hr, the second after 50 and 100 hr and the third after 400 hr. The samples were stored in Vacutainers after centrifuging, to minimize further oxidation.

The DOC concentrations of all the samples was determined using a method modified from Stainton (1973). 10 ml of sample, 0.1 g $K_2S_2O_8$ and 1 drop of H_3PO_4 were placed in a glass ampule. Nitrogen was bubbled through the solution removing excess CO_2, after which the ampule was sealed and autoclaved at 121°C for 30 minutes to combust organic matter. The ampules were opened in a sealed rubber tube, the gas and fluid extracted into a 60 ml syringe, shaken and the liberated CO_2 measured using a Perkin Elmer 3920 gas chromatograph. Two injections were required from each sample as only 50% of the CO_2 was liberated from solution in the syringe from one shaking. The total amount of CO_2 was calculated by multiplying the counts from the first injection by the distribution coefficient of the two measurements, then converted to CO_2 using a calibration curve prepared from standards.

3.3 Results

3.3.1 Colour Changes in the Weathering Solutions

Colour changes of the centrifuged supernate provide the first evidence of mineral solution reactions (Figure 3.1.) A lightening of the solution colour with time is observed in the 50 mg/L aerobic peat and leaf-DOC solutions in the presence of clinochlore (Figure 3.1a and c) and to a lesser degree microcline but not in the case of the anaerobic solutions (Figure 3.1b). Little change is visible in the 300 mg/L leaf-DOC solutions, perhaps because being so dark, changes are not visible to the eye. Absorbance measurements, taken at 510 nm in a 1cm cell for the 300 mg/L leaf-DOC solutions, indicate a marginal increase in absorbance for the microcline and clinochlore solutions of 10 to 20% on average

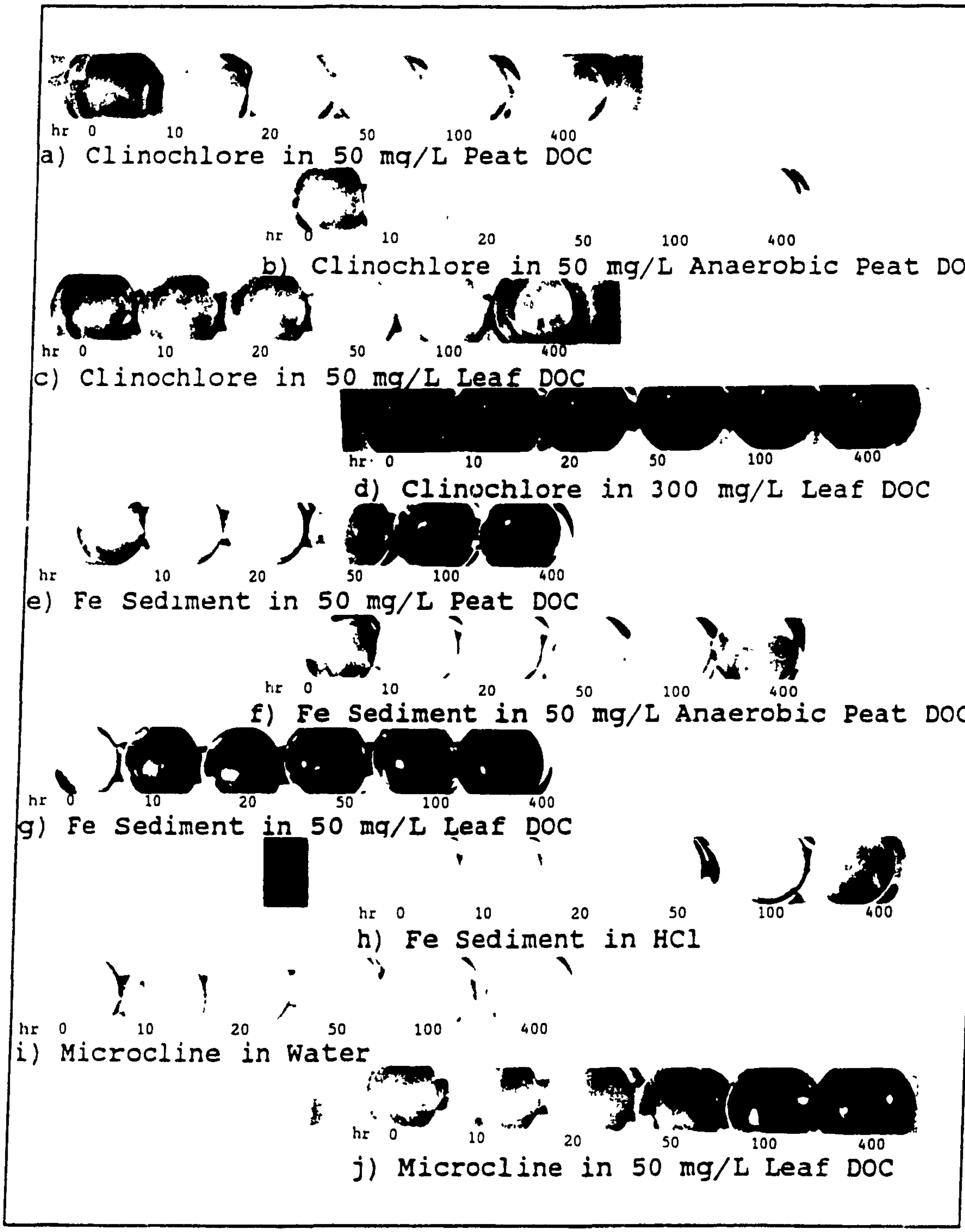


Figure 3.1. Examples of colour changes in the weathering solutions over the course of the experiment.

(ie. 0.44 to 0.63 for microcline) but substantial increases from 0.36 to 1.16 were recorded for the Fe sediment solutions after 400 hr. Any lightening of the Fe sediment solution by DOC adsorption, Figure 3.1 e-g, is obscured by the reddening of the solution from the release of Fe complexes. A slight orange tinge is present in the Fe sediment control solutions, here represented by the HCl solution (Figure 3.1h) but microcline and clinochlore have no visible effect on changing the colour of the control solutions and only a small change of 0.008 in absorbance was recorded (Figure 3.1i).

3.3.2 Eh and pH of Weathering Solutions (Supernates)

After a small initial peak, the Eh of the aerobic weathering solutions stabilize and the five Eh-time curves produced for each of clinochlore, microcline and the Fe sediment appear to converge at +505 mV, +535 mV, and +570 mV, respectively (Figure 3.2). The Eh of the anaerobic solutions or leachates increase from an initial value of +200 mV to +485 mV, +505 mV, and +505 mV after 400 hr in the clinochlore, microcline and Fe sediment cases, respectively.

A rise of 2 pH units in the clinochlore based uncentrifuged solutions (Figure 3.3a) is followed by recession and stabilization at a pH between 6.8 and 8. The fluctuations in these curves are the result of mixing, measurement error

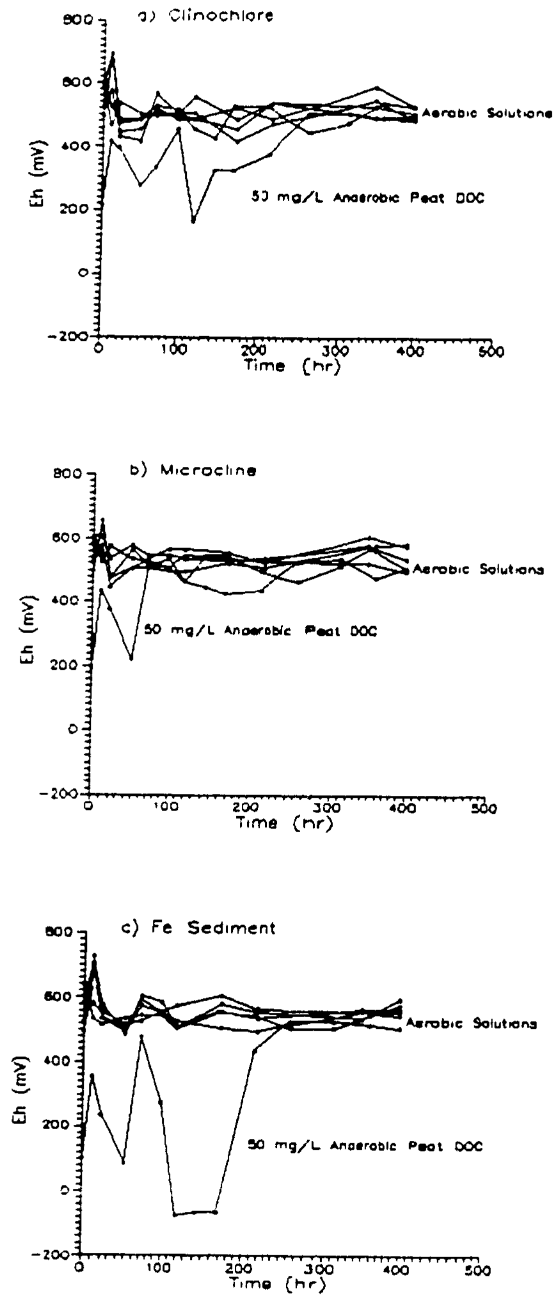


Figure 3.2. Changes of Eh in the: a) clinochlore; b) microcline; and c) Fe sediment based reaction chambers over the duration of the experiment.

and on going solution mineral reactions. A similar pattern exists in the pH of the microcline based matrices (Figure 3.3b) but the initial pulse is only 1 pH unit and stabilization occurs between a pH of 6 and 7. In the case of the Fe sediment based solutions, solutions with pre-sediment addition pH values of approximately 7 decrease upon sediment addition, yet those with an original pH 5 increase. The mean pH appears to be 6 with the Fe sediment matrix solutions appearing the most stable after 400 hr. No ordering of solutions based on pH transgressing mineral type is apparent, except that the anaerobic solutions always have the lowest pH.

3.3.3 The pH of the Supernate after Centrifugation

A rapid increase in pH over the first 50 hr is observed in the centrifuged clinochlore samples (Figure 3.3d) and a similar but smaller scale increase is observed in the microcline extracts (Figure 3.3e) with a broader spectrum of final pH values (2 pH units). After 50 hr, the pH stabilizes in most solutions, the small fluctuations attributed to solution equilibria adjustments and/or measurement error. The pH of the aerobic clinochlore based samples appear to converge toward a pH of 7.2, compared to a pH of 6.4 for the microcline based samples, suggesting clinochlore has a greater effect on solution pH. Small increases in pH are observed in the aerobic Fe sediment solutions of initial pH 5 but decreases are

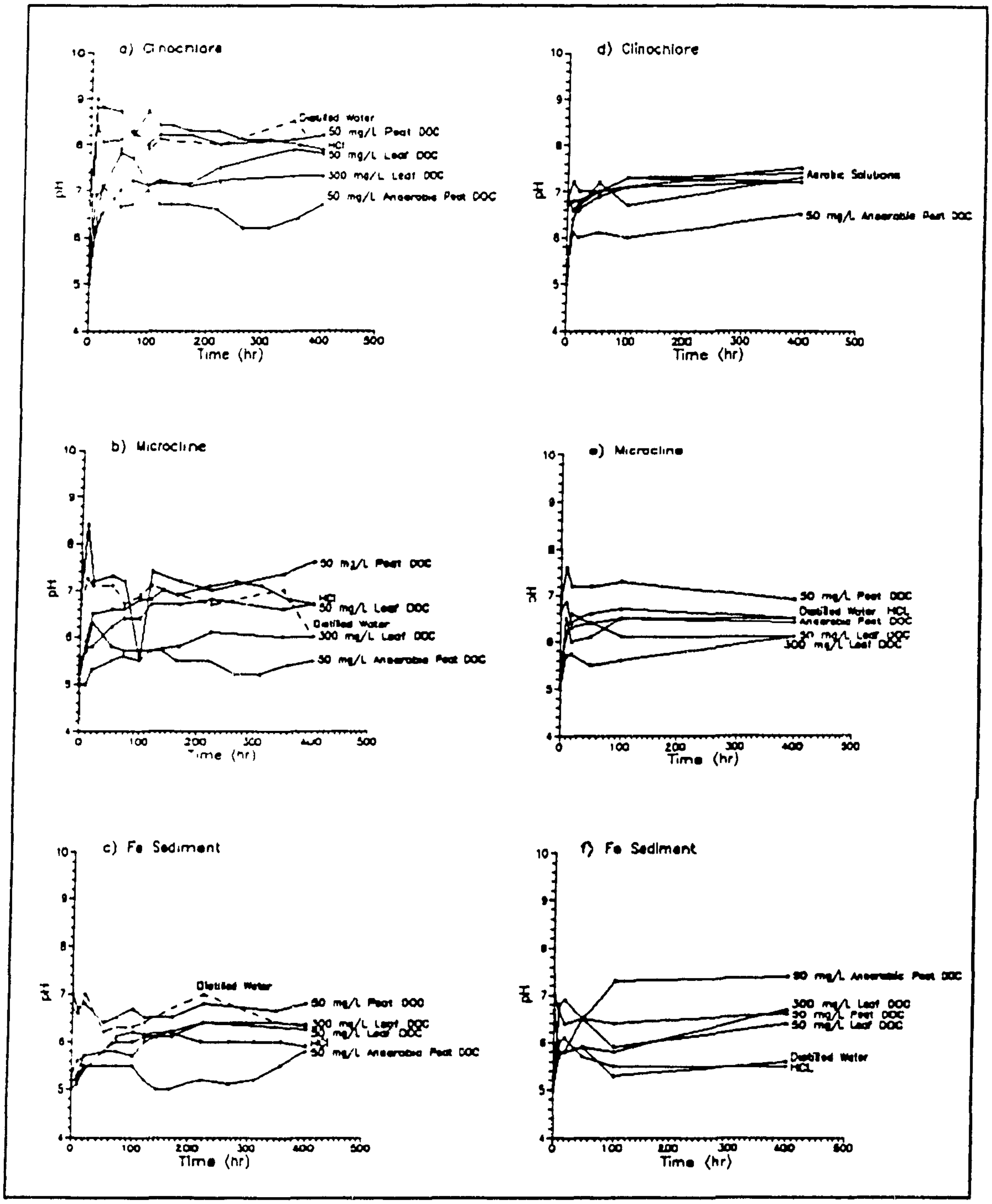


Figure 3.3. Change of pH in: a) clinochlore; b) microcline; and c) Fe sediment; based reaction chambers, and d) clinochlore; e) microcline; and f) Fe sediment; solutions after centrifugation, over the duration of the experiment.

observed in those of initial pH 7 (Figure 3.3f). The pH of DOC-rich solutions tend to pH 6.4 and the distilled water and HCl solutions tend toward a pH of 5.4, the latter pH being close to the sediment pH values recorded in Chapter 2.

The pH of the centrifuged anaerobic peat-DOC samples increases rapidly from 5.1 early in the experiment to approximately 6.4 in the clinochlore and microcline based solutions but >7.0 in the Fe sediment based. In comparing both types of pH data, centrifuged and uncentrifuged, it is apparent that anaerobic solutions behave very differently than the aerobic solutions.

3.3.4 Mineral Dissolution Rates

The total number of elements measured in solution, taken at the five sampling intervals, were used to plot total mineral dissolution rate curves (Figure 3.4). In clinochlore and microcline two periods of weathering took place. In the first stage of 10 to 20 hr, as much as 50% and 65% of the elements respectively were released into solution. This was followed by a second stage of slower but steady cation release (Figure 3.4). The first phase is described as the nonparabolic kinetics phase by Busenberg and Clemency (1976) and can be seen even more clearly as a horizontal line displacement in Figure 3.4 d-f.

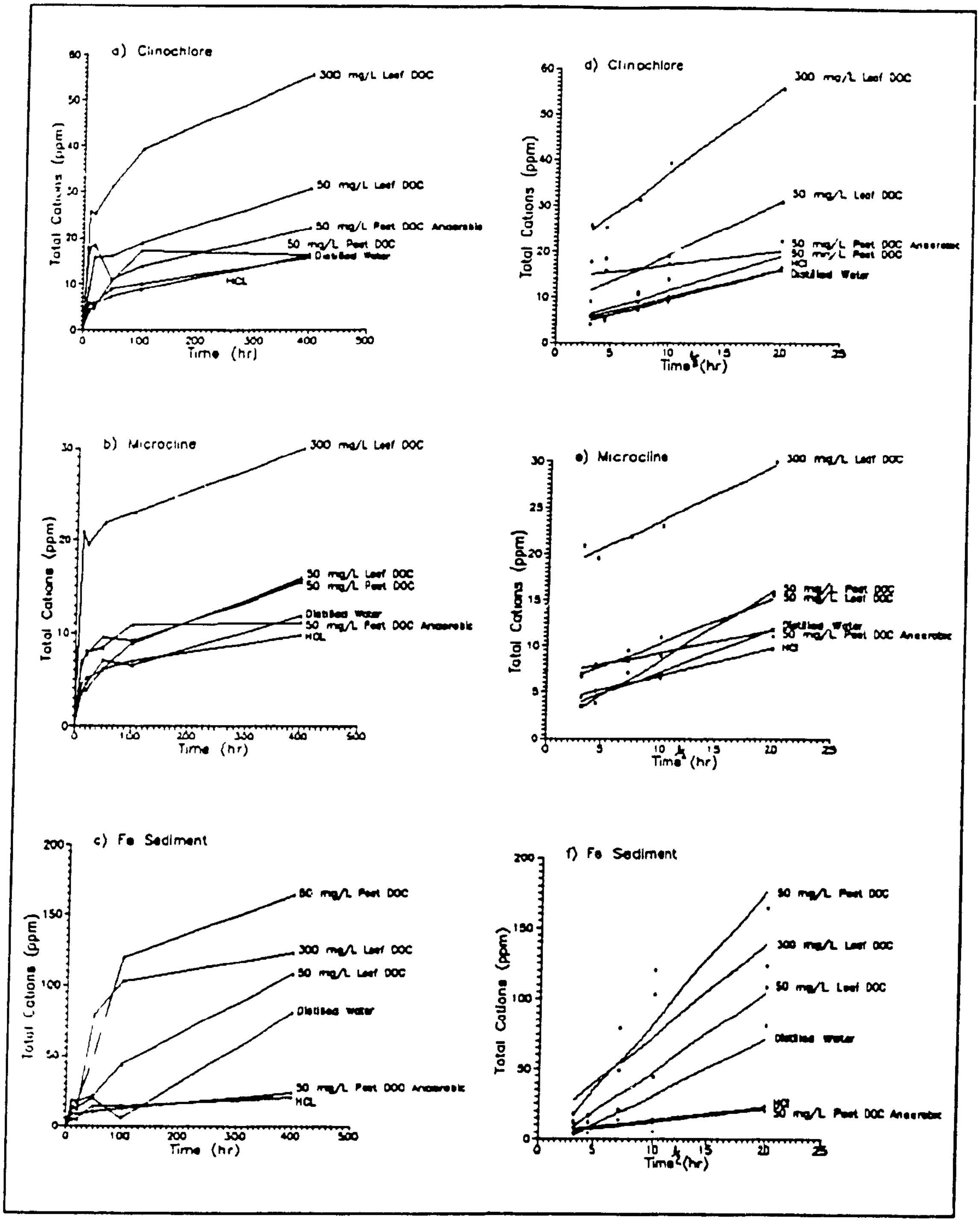


Figure 3.4. The relative effectivness of the 6 weathering solutions with clinochlore, microcline and Fe sediment, portrayed as mineral dissolution curves. Total cations are plotted against time a-c and $t^{\frac{1}{2}}$d-f.

Types of solutions	Clinochlore	r
50 mg/L Peat-DOC	$TC = 0.76t^{1/2} + -12.31$	0.66
Anaerobic Peat-DOC	$TC = 0.31t^{1/2} + 13.90$	0.23
50 mg/L Leaf-DOC	$TC = 1.16t^{1/2} + 7.72$	0.94
300 mg/L Leaf-DOC	$TC = 1.87t^{1/2} + 18.67$	0.99
Water	$TC = 0.62t^{1/2} + 3.66$	0.98
HCl	$TC = 0.65t^{1/2} + 2.90$	0.99
	Microcline	**r**
50 mg/L Peat-DOC	$TC = 0.75t^{1/2} + 0.86$	1.00
Anaerobic Peat-DOC	$TC = 0.25t^{1/2} + 6.78$	0.73
50 mg/L Leaf-DOC	$TC = 0.49t^{1/2} + 5.34$	0.96
300 mg/L Leaf-DOC	$TC = 0.59t^{1/2} + 17.70$	0.96
Water	$TC = 0.47t^{1/2} + 2.48$	0.94
HCl	$TC = 0.31t^{1/2} + 3.70$	0.99
	Fe Sediment	r
50 mg/L Peat-DOC	$TC = 9.46t^{1/2} + -12.30$	0.90
Anaerobic Peat-DOC	$TC = 0.93t^{1/2} + 4.22$	0.98
50 mg/L Leaf-DOC	$TC = 5.67t^{1/2} + -9.08$	0.97
300 mg/L Leaf-DOC	$TC = 6.63t^{1/2} + 6.59$	0.75
Water	$TC = 4.08t^{1/2} + -10.27$	0.78
HCl	$TC = 0.93t^{1/2} + 2.87$	0.83

Table 3.3. Equations of the Root Time ($t^{1/2}$) vs Total Cations (ppm) (TC) lines of best fit of Figure 3.5 and the associated r values.

In the case of Fe sediment, a parabolic weathering rate was initiated from onset in all but that of the aerobic peat-DOC and 300 mg/L leaf-DOC solutions, where the two phase cation release pattern is evident. The slopes of the total cations in solution curves of these two solutions change after 100 hr, perhaps signifying a change in release kinetics. This relationship is very evident in Table 3.3 were the r value of the $T^{1/2}$ vs concentration for aerobic solutions is generally 0.95 for all but these two of the mineral solution combinations.

The rapid release of Na, K and Ca cations in the first 10 to 20 hr or stage 1 is a result of the rapid weathering of jagged and damaged mineral surfaces created by the grinding process (Holdren and Berner, 1979). Although overshadowed by the Na, K and Ca; Fe, Al, Si and Mg solution concentrations in the first 100 hr are also attributed by Holdren and Berner (1979) to this process described as the pseudo-parabolic effect. Linear dissolution rates do not appear to develop as described by Busenberg and Clemency (1976), perhaps with the exception of the Fe sediment control solutions, because the duration of the experiment was not long enough.

In the Fe sediment samples, the pseudo-parabolic effect is not as apparent. Consider the intercept of the best fit lines of the HCl, anaerobic peat-DOC and 300 mg/L leaf-DOC cross the axis near the x,y intercept indicating immediate parabolic dissolution. The lack of a weathering pulse is most likely the result of the natural size characteristics of the Fe sediment and its previous exposure to weathering. Being silt sized already, minimal damaged to the grain surfaces could be inflicted by grinding and sieving the sediment. The aerobic peat-DOC, 50 mg/L leaf-DOC and distilled water seem almost "inhibited" early in the weathering process as indicated by their negative y intercepts in Figure 3.4f. There appears to be a relationship between the pH of the solutions and the early dissolution rates. The initial pH of the three "inhibited" solutions being higher than the "uninhibited" solutions, however, this pattern is lost over the duration of the experiment.

3.3.5 The Relative Effectiveness of DOC Solutions

In general, the least effective weathering agent was 10^{-5} M HCl (Figure 3.4). The aim of using such a dilute acid was to have an uncomplicated inorganic weathering solution with a pH similar to that of the DOC solutions. Essentially no difference was found in the ability of distilled water of pH 7 and that acidified with HCl to pH 5 to weather clinochlore or microcline. However, in the case of Fe sediment, the acidified water proved to be the least effective of all solutions, being substantially less effective than its distilled water counterpart after 400 hr. This suggests the Fe sediment dissolution rates are sensitive to pH changes, in this pH range, barring a measurement error of this final point. Both control inorganic solutions tend toward the same pH suggesting the solution pH is controlled by the sediment within 400 hr. The DOC-rich solutions however, offer some resistance, the solution pH not being dominated by the presence of the sediment, at least within the duration of the experiment.

The anaerobic peat-DOC was generally less effective than its aerobic counterpart as a weathering agent, being 7 times less effective in the case of the Fe sediment (Figure 3.4c). Leaf-DOC was the most effective of the weathering agents used on microcline and clinochlore. However, the 300 mg/L leaf-DOC concentration was only 1.9 times as effective on microcline and 1.8 times as effective on clinochlore, after 400 hr, than 50 mg/L leaf-DOC and not 6 times as effective suggesting a nonlinear effect of concentration with probably a threshold level. In contrast, the aerobic peat-DOC was the most effective weathering agent of the Fe sediment.

3.4 The Stoichiometry of Mineral Dissolution

3.4.1 Clinochlore

Mg is the dominant cation released from clinochlore in all but the aerobic peat-DOC solution where it is surpassed by K on a mass but not molar basis (Table 3.4, Figure 3.5).

	Mg :	Fe :	Al :	Si :	K
50 mg/L Leaf-DOC	6.1	0.3	1.0	1.7	1.3
300 mg/L Leaf-DOC	5.0	0.4	1.0	0.6	2.4
50 mg/L Peat-DOC	6.1	0.0	1.0	1.7	0.3
50 mg/L Anaerobic Peat-DOC	3.4	0.0	0.1	1.9	1.7
Distilled Water	8.6	0.0	0.1	1.3	4.3
HCl	3.4	0.0	0.0	0.4	1.3
Clinochlore	1.3	0.2	1.0	1.1	0.2

Table 3.4. The stoichiometric ratios of the elements measured in the clinochlore solutions after 400 hr and the original mineral clinochlore, with Al being the reference.

The molar ratios in table 3.4 were calculated by dividing the cation concentrations (Appendix III) by the respective molar masses and reduced to ratios based on Al. The data of the individual elements can not be compared directly (column wise), but relative deviations from the whole rock composition with respect to Al concentrations, can be used to examine the stoichiometry of dissolution. It should be emphasized that Al is still a variable although used as a reference. It is clear dissolution of clinochlore is incongruent and considering the absolute data (Figure 3.5), it is mainly the result of low Al

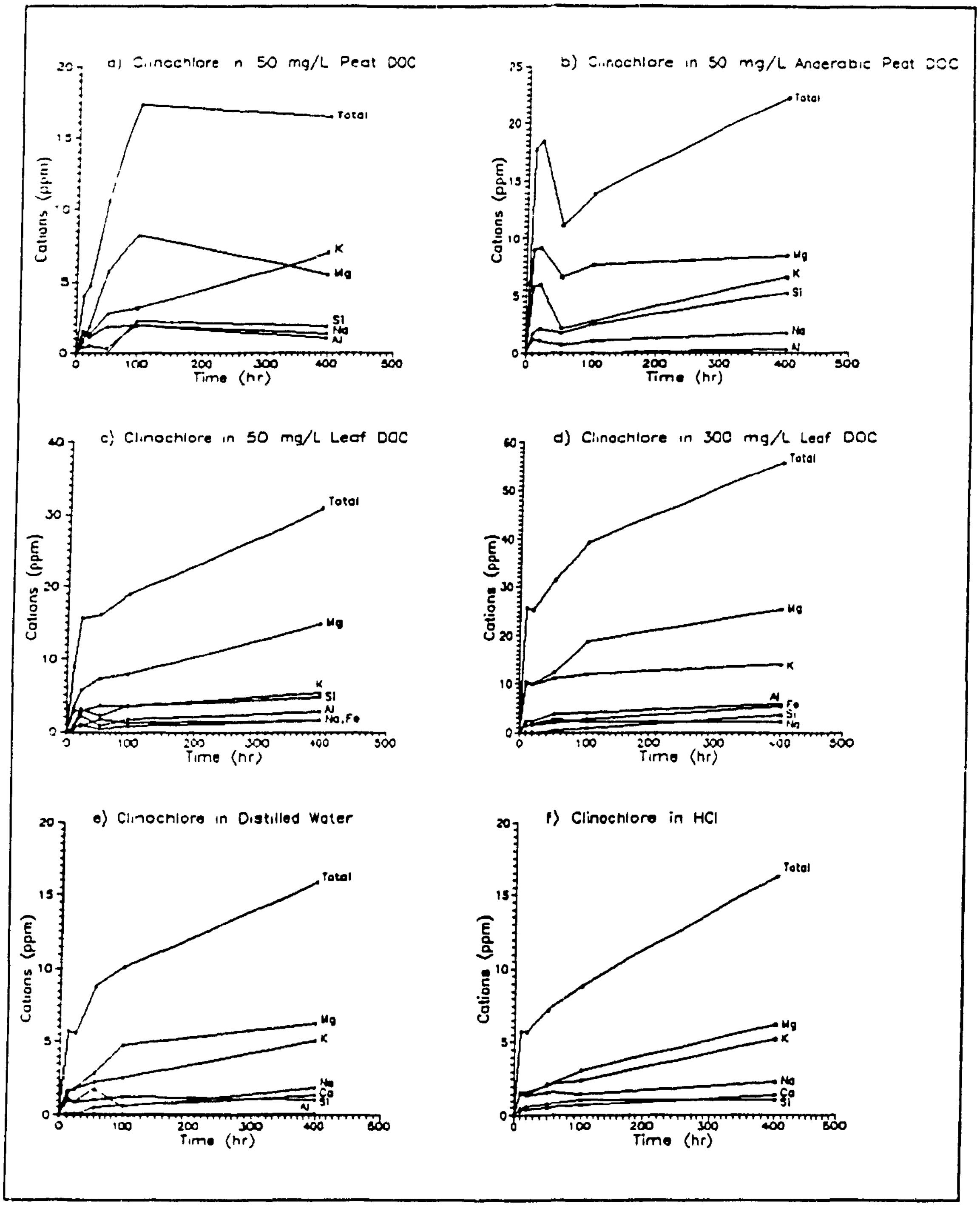


Figure 3.5. Changes in concentration of K, Na, Mg, Ca, Fe, Al, and Si in the 6 weathering solutions exposed to clinochlore.

and Si concentrations in solution.

3.4.2 Microcline

K is the most dominant cation released both in mass and molar mass terms, except in the case of the peat-DOC, where it is replaced by Fe (Table 3.5, Figure 3.6). K and Na remain in the centrifuged solution at levels more than twice that of the microcline composition even after the pseudo-parabolic stage. The concentration of Fe in solution is remarkably high, being 200 times the original mineral concentration (Appendix II; Table 3.5) but in the control solutions only traces of Fe were found. The weathering of microcline, as in the case of clinochlore, is incongruent in all cases (Table 3.5). Al and Si appear in levels below accurate detection by the AA method used and although they

	Fe :	Na :	K :	Al :	Ca :	Si
50 mg/L Leaf-DOC	1.0	2.3	4.0	1.0	0.3	2.5
300 mg/L Leaf-DOC	1.4	2.6	8.0	1.0	1.6	0.0
50 mg/L Peat-DOC	2.8	2.5	2.3	1.0	0.0	2.6
50 mg/L Anaerobic Peat-DOC	2.8	4.2	24.0	1.0	0.0	9.2
Distilled Water	0.1	2.2	3.2	1.0	0.2	1.6
HCl	0.0	11.0	6.0	1.0	0.8	10.0
Microcline	Tr	0.2	0.7	1.0	Tr	3.0

Table 3.5. The Stoichiometric ratios of the elements measured in the microcline solution after 400 hr and the original mineral microcline with Al as a reference (Tr=trace).

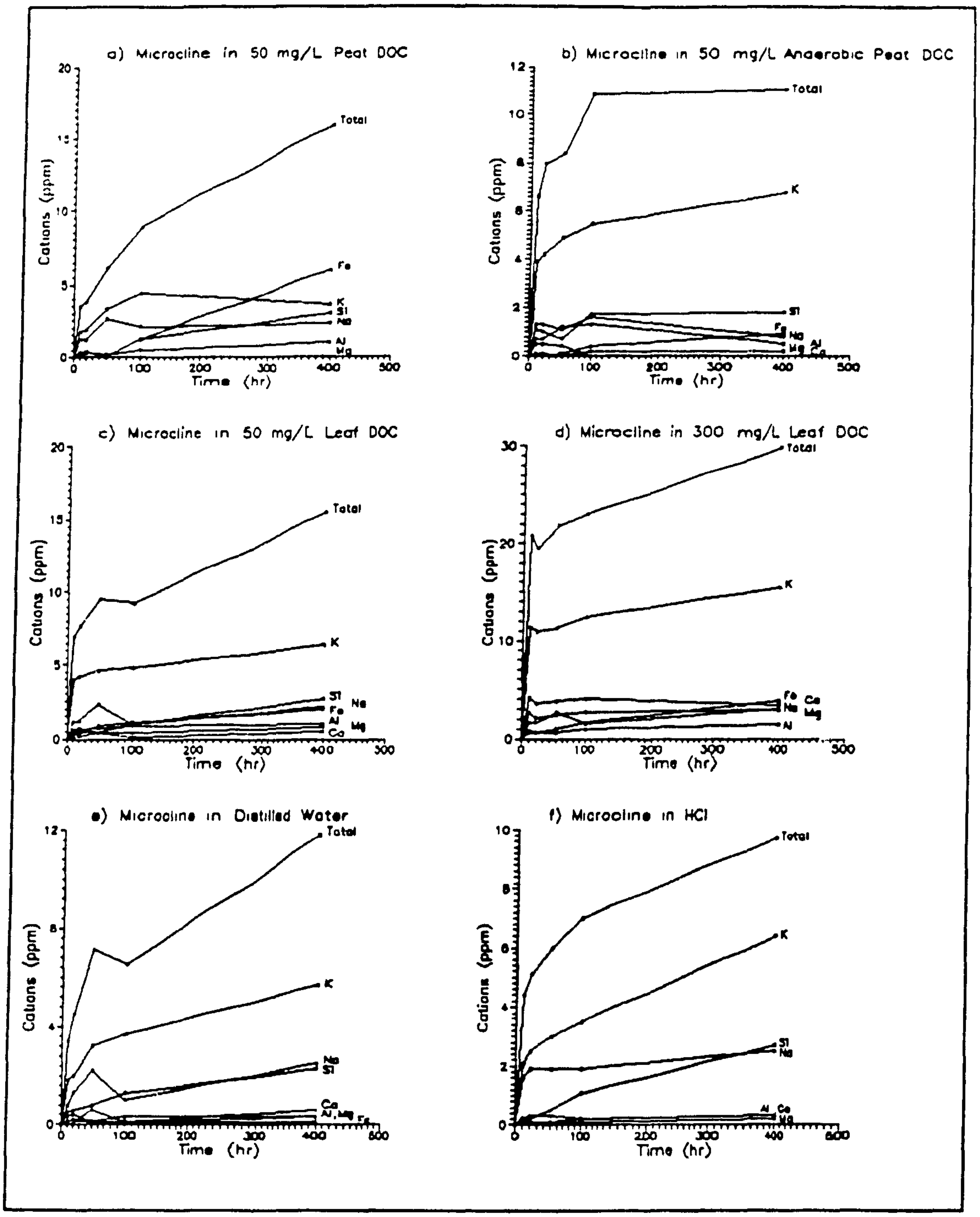


Figure 3.6. Changes in the concentrations of K, Na, Nq, Ca, Fe, Al and Si in the 6 weathering solutions exposed to microcline.

provide a qualitative means of comparison being precise results should be treated with caution.

3.4.3 Fe Sediment

Fe and Si are the dominant cations released from the Fe sediment. Concentrations of Fe are highest in the DOC solutions and Si in the inorganic controls and the anaerobic DOC solution (Figure 3.7). The element concentrations in solutions released from the Fe sediment, although incongruent, were much closer to the mineral ratios than the microcline or clinochlore. The Fe sediment incongruence appeared to be mainly due to low Si concentrations in solution. Much of the Si in the Fe sediment is in the form of quartz which is almost inert to chemical weathering at low temperature and pressure (Nicholson and Moore, 1977). The large volumes of Si released

	Fe :	Mg :	Na :	K :	Al :	Ca :	Si
50 mg/L Leaf-DOC	1.2	0.1	0.1	0.2	1.0	0.0	1.7
300 mg/L Leaf-DOC	0.8	0.2	0.1	0.3	1.0	0.0	4.7
50 mg/L Peat-DOC	1.0	0.0	0.04	0.2	1.0	0.0	1.7
50 mg/L Anaerobic peat-DOC	1.0	0.6	0.7	1.1	1.0	0.0	2.9
Distilled Water	0.6	1.7	0.2	0.3	1.0	0.0	2.2
HCl	0.6	0.3	1.0	0.8	1.0	0.06	4.6
Fe Sediment	1.3	0.1	0.05	0.3	1.0	0.03	5.3

Table 3.6. The stoichiometric ratios of the elements measured in the Fe sediment solution after 400 hr and original Fe Sediment, with Al as the reference.

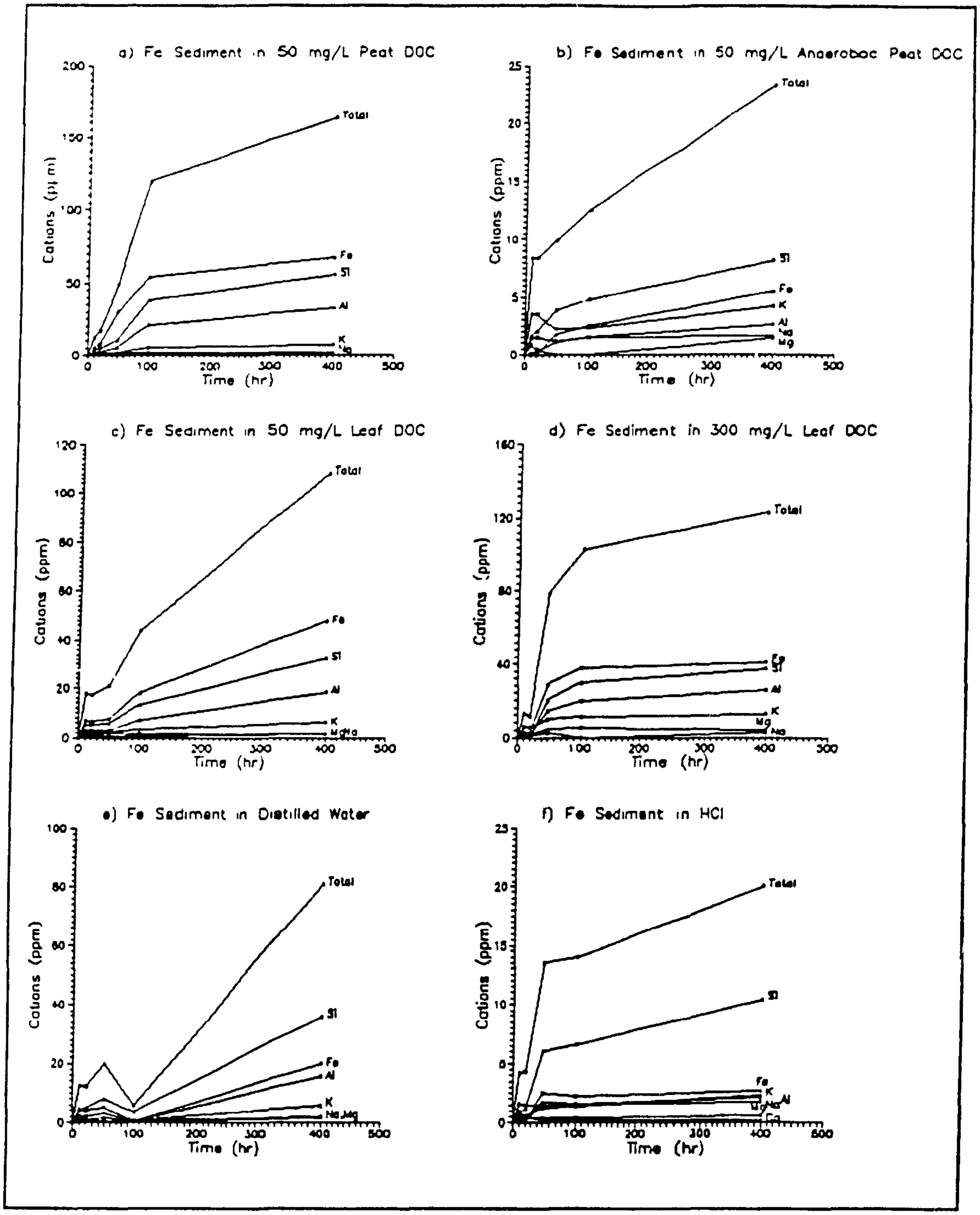


Figure 3.7. Changes in concentrations of K, Na, Mg, Ca, Fe, Al, and Si in the 6 weathering solutions exposed to the Fe sediment.

probably came from mica or chlorite, with lower relative Si concentrations, therefore biasing the solution stoichiometry. A significant difference between control solutions in total cations released occurs only in the 400 hr extract, and may well be the result of incomplete centrifugation, as the distilled water solution was much redder than the HCl solution. Therefore this point being anomalous should be treated with care in interpreting results.

3.5 Discussion

3.5.1 Noise in Eh and pH Measurements Created by the Methodology

Small scale fluctuations in measured pH and Eh (section 3.2.2) can be explained by variations in suspended sediment concentrations at the time of measurement. Centrifugation lessened the influence of the sediment resulting in more stable measurements, however, its effect on pH varied between solutions and mineral types. For example, the pH was lowered by centrifugation in the clinochlore solutions, but increased in the case of Fe sediment solutions. Such discrepancies created by the treatment, in this case centrifugation, emphasize the importance of recording the conditions under which measurements are made to prevent incorrect assumptions on the part of the reader.

The erratic Eh curve of the anaerobic peat-DOC may be related to the use of multiple containers and the presence of an air space above the DOC solutions created by sample extraction (Figure 3.2). In preliminary studies without minerals, it was noted that DOC solutions could be maintained at Eh levels of between 0 and +200 mV for approximately 600 hr, before air entering the container during Eh and pH measurement or through container leakage, was enough to oxidize the environment. However, Eh of the final chambers, sealed for the first 100 hr, became elevated to atmospheric levels (+600 mV) after 200 hr without sample extraction, the dissolution of the minerals contributing to the oxidation of the weathering solution.

3.5.2 Weathering Models of the Minerals

A mineral to mineral comparison revealed the Fe sediment was more soluble than the clinochlore in every solution but the anaerobic peat-DOC, and the clinochlore was more soluble than the microcline in every case (Figure 3.4). The ease by which the Fe sediment dissolves is probably a result of easily soluble oxides and Fe oxides in particular. A small fraction of the difference in the DOC solution between clinochlore and microcline maybe a result of the increased presence of K. K decreases the ability of DOC to complex cations when the K concentration greatly exceeds the amount of divalent cations

(Rashid, 1985 after Bolter and Butz, 1977). For the most part however, the greater solubility of clinochlore compared to microcline is attributed to differences in mineral structure and composition. Unfortunately, the differences may, in part, reflect how the mineral resisted grinding, the average particle of clinochlore appearing smaller (within the defined particle range) and edges more readily damaged than microcline. Comparisons to other studies are hindered by different methods of accelerating dissolution, the variable definition of "in solution", and the structural differences within mineral families and continuums effecting the dissolution kinetics (e.g. Holdren and Speyer, 1985; Kittrick, 1982).

Holdren and Berner (1979), prescribed the incongruent weathering of feldspars to the dissolution of small <1.0 μm particles affixed to the mineral grains whose presence was promoted by grinding. Once the mineral preparation caused phenomena were filtered through the use of pretreatments, the incongruence was reduced to levels that could be explained by surface controlled-reaction phenomena and element precipitation. The dissolution curves (Figure 3.6e) appear to support this hypothesis, after the first 10 to 20 hr, the linear dissolution patterns indicate the dominance of surface-controlled reactions. Increasing the concentration of DOC 6 times catalyzed dissolution but only doubled the rate, suggesting a threshold rate ultimately determined by surface controlled reactions, regardless of DOC concentrations.

The presence of gibbsite or pseudomorph such as norstrandite (Violante and Violante, 1980), at concentrations of 0.11 ppm at pH 8, appear as "mud cracks" (Velbel, 1984) on mineral surfaces and in fractures of both weatherable and inert minerals suggest dissolved Al can precipitate rapidly from solution. The precipitation of Al could explain a great deal of the observed incongruencies in both DOC and control solutions. Even so, the Al concentrations in the DOC solutions are elevated above thermodynamically calculated solubility levels, suggesting complexation or chelation (McColl and Pohlman, 1986) and adsorption by DOC, increasing the "total solubility" of Al, and/or the presence of uncentrifuged colloids.

Kodama et al. (1983) discovered incongruent reactions in weathering chlorites Mn-Mg chamosite and Fe clinochlore in open and closed systems. The incongruence in the Fe clinochlore open system was the result of greater metal enrichment, including Al, compared to Si. The incongruence in the Mn-Mg chamosite closed system was mainly the result of an enrichment in Mg compared to Si, Al and Fe. The data obtained in this experiment for clinochlore reveal 2:1 and 1:1 Si:Al ratios depending on the solution, but the main incongruence is caused by Mg enrichment as in Kodama et al. (1983), therefore the DOC solutions behave like Kodama's fulvic acid derivatives. Overall, the linear dissolution patterns of Figure 3.6d, indicate surface controlled reactions.

Clinochlore is composed of an outer Brucite layer $(Mg,Al,Fe)_6OH_6$ and an inner Talc (octahedral) layer $(Mg,Fe)_6(Si,Al)_8O_{20}(OH)_4$. Kodama et al. (1983) suggests Mg and Fe are easily removed from octahedral sites of the chlorites. Mg^{2+} is replaced by Fe^{2+} in the mineral lattice as 73% of Fe is in the ferrous state; however, this replacement is probably not uniform, as Mg and Fe do not dissolve congruently. Therefore, it appears the sheet without Fe is being preferentially weathered. The release of hydroxyls and Mg from either layer could easily account for the observed solution pH increase. The low rates of Al and Fe (27% of Fe can substitute for Al) release compared to Mg and K from this experiment suggests extraction of octahedral cations before breakdown of the sheet itself. Norrish (1973) has suggested the removal of K^+ and Mg^{2+} ions would result in the reorientation of hydroxyls resulting in the stabilization of cations in the adjacent layer inhibiting further weathering. It is possible excess Al precipitated from solution to form large aluminum hydroxide colloids that were centrifugeable and the higher Mg values are the result of pseudo-parabolic effects. However, the latter is unlikely given the steady increase in Mg concentrations in the latter portion of the experiment. Kittrick (1982) determined through mineral solubility experiments that neither brucite nor talc individually controlled the dissolution of chlorite, but rather it was chlorite as a whole. The apparently selective weathering capability of a DOC enriched solution may disrupt the uniform chlorite dissolution preferring to dissolve one layer, perhaps the talc layer, given the 2:1 Si:Al ratio. Kittrick (1982) also pointed out that individual smectites vary in layer completeness, therefore weathering of any particular layer maybe pronounced on an individual basis. Since a structural analysis of the mineral particles is lacking, this theory can not be tested.

A traditional weathering model can not be developed from the Fe sediment data because of the diverse mineralogy. However, the linearity of the root time vs concentration of elements plot (Figure 3.6) suggests surface controlled dissolution rates as in the case of microcline and clinochlore. Perhaps more importantly the net result of prolonged leaching of the Fe sediment suggested by the dissolution curves is an Al and Si enriched sediment with the Al being in the form of gibbsite or perhaps kaolinite and the silica as quartz.

Microcline as a framework silicate has K^+, Na^+ and Ca^{2+} ions occupying the interstices of the aluminosilicate frame where they are potentially more easily leached. The trace Fe found in microcline is nearly equally distributed between the ferric and ferrous forms (Table 3.2), the ferric form replacing Al^{3+} cations in the aluminosilicate frame and ferrous form the interstitial Ca^{2+}. These isomorphous substitutions create an imbalance of charge in the mineral structure weakening the lattice and allowing cations to be easily leached. Therefore, the structure of microcline aids the organic acids in creating a incongruence between mineral and solution by conveniently placing the Fe cations at its most vulnerable sites. Since the total Fe released, by mass, is greater than Al, and more than 100 times the original mineral stoichiometry, it is presumed the Fe released was mainly ferrous, and according to Bloomfield (1953) more easily organically complexed.

A major weakness in interpreting dissolution experiments is assuming that what is in solution is what has been weathered which as indicated by Velbel (1984) is clearly not the case. Calculating the precipitation rates of cations would be extremely important in determining absolute dissolution rates of minerals, but it is that which remains in solution in one form or another that is transportable and probably of greatest significance in natural systems.

3.5.3 The Potential Effect of pH in Inorganic and Organic Weathering Solutions

The majority of the DOC-rich solutions showed an increase in pH during the experiment, which allows more phenolic groups of the DOC molecules to dissociate and allows OH^- ligands to become active thereby increasing the number of sites for complexation and cation exchange (Rashid, 1985). The organic acids behave more like weak than strong inorganic acids, suggesting measuring acidity using the hydrogen electrode may not be a good means of selecting a control solution or measuring the potential acidity of organic rich natural waters. Therefore, HCl may not be the best inorganic acid to use for comparison with organic acids in weathering experiments not having the same number of available H^+ ions but its use does limit potentially undesirable reactions. What is required is an acid that releases H^+ ions at a rate similar to that of the organic acids with the same total acidity.

3.5.4 The Effect of Redox Potential

The anaerobic (Eh +200 mV) conditions of the peat-DOC rich solutions inhibited the weathering of minerals, decreasing the rate of dissolution to that of water of the same pH (the control HCl solution). It is not clear from this experiment whether the low Eh is stabilizing mineral surfaces in the presence of DOC, which is unlikely given that cations become more mobile after reduction (Zutic and Stumm, 1984) or the complexing capabilities and/or acid exchange abilities of the peat-DOC are being altered. Even when the Eh rose to levels of the aerobic peat-DOC, weathering did not accelerate, suggesting the effect was irreversible or long lived. The solution appearance does not provide a visual indication of any change in form, the brown colour of the water diagnostic of complex organic acids prevailing.

It is assumed that mineral-solution interactions in natural environments such as soils, and perhaps those of the Fe sediment, are dominated by Fe and Al oxides. Zinder et al. (1986) found ferrihydrite, goethite and hematite to have a higher dissolution rate in the presence of oxalate, a strong complexing acid, under reducing (<+420 mV at pH 4-5, achieved using ascorbic acid) rather than under oxidizing conditions. The results of Zinder et al. (1986) seemingly conflict directly with the results of this study, however the conflict stems from methodological differences starting with the organic acid used.

Oxalic acid is a simple organic acid not nearly as large or as complex as DOC type molecules. Under anaerobic conditions, humic compounds tend to be poorly developed with fewer, approximately 1/3, carboxylic and phenolic groups and more carbynol groups. Upon oxidation the pattern is reversed, the carboxyl and phenolic groups become dominant and suggest a major change in the complexing ability of the humic acid (Rashid, 1985). Further complications in comparing this study with that of Zinder et al. (1986) stem from: the complexity of the DOC molecules; the variability of the Fe sediment mineralogy; array of other cations in solution; and differences in the way reduction was achieved, particularly the unknown role of ascorbic acid. Since reduction in most near surface environments, both terrestrial and aquatic, is microbially induced it is felt the dextrose invoked microbial reduction best mimics the natural setting. Furthermore, specific oxide studies have suggested retardation of dissolution may be explained by: the DOC forming multinuclear surface complexes (e.g. Matijevic' and Kallay, 1983; Rubio and Matijevic', 1979); or through the creation of new surface phases on the mineral, in the presence of phosphate or Si at near neutral pH, which protect the original phase (Zinder et al., 1986). Si is found in lower concentrations in anaerobic solutions than in the control solutions suggesting that Si precipitation may have occurred. However, Mg appears in greater quantities in the anaerobic than the aerobic peat-DOC solutions suggesting not all cations are inhibited. Therefore, it is likely an alteration in the structure of peat-DOC molecules is responsible for the decreased weathering of all three materials tested, although ascorbic acid invoked reduction had the opposite effect on the ability of a single organic acid (oxalate) to bring Fe into "solution" from a single cation mineral.

3.5.5 DOC Adsorption, Co-adsorption, and Co-precipitation

The observed change in colour of the weathering solutions was not only the result of an increase in the number of ions in solution but the result of a loss of DOC. The possible effects of DOC co-precipitation with Ca became very obvious when preparing standards for atomic absorption. When Ca standard (calcium carbonate in nitic acid) was added to DOC, especially peat-DOC, within 24 hr an organic precipitate was found at the base of the test tube and supernate was nearly clear, probably devoid of DOC. After a considerably longer period, small amounts of precipitate occurred in the Mg, Fe, and Al DOC standards. A similar effect was evident in the clinochlore weathering experiment where Ca was present in the centrifuged distilled water and HCl solutions but absent in the DOC solutions. In the o-phenanthroline study of Chapter 4, Fe concentrations decreased below levels inherent in the peat-DOC. In both cases it is likely the cations were adsorbed onto clinochlore particles. Tipping (1981) determined that Mg and Ca are susceptible to co-adsorption with organic acids onto mineral surfaces. Although other cations did not show any effects of co-adsorption or co-precipitation with DOC, based on comparisons to the control solutions, this is not conclusive evidence for saying they were unaffected.

Clinochlore	Time (hr) 10	20	50	100	400
50 mg/L Peat-DOC	26	22	26	29	28
50 mg/L Anaerobic Peat-DOC	53	48	64	50	31
50 mg/L Leaf-DOC	23	17	15	X	X
300 mg/L Leaf-DOC	135	116	109	137	101
Microcline					
50 mg/L Peat-DOC	29	26	27	28	25
50 mg/L Anaerobic Peat-DOC	78	75	65	59	67
50 mg/L Leaf-DOC	37	35	29	29	26
300 mg/L Leaf-DOC	160	155	175	159	X
Fe Sediment					
50 mg/L Peat-DOC	26	20	21	20	21
50 mg/L Anaerobic Peat-DOC	77	75	65	59	67
50 mg/L Leaf-DOC	22	26	24	18	14
300 mg/L Leaf-DOC	108	118	100	152	106

X = no measurement

Table 3.7. DOC concentrations (mg/L) taken over the course of the experiment. After the initial drop, a small decrease in DOC concentration in solution is noted but any conclusive evidence is obscured by fluctuations in the data probably caused by the stirring and standing cycles and, in the case of the anaerobic solutions, the changing of reaction chambers.

The least amount of DOC adsorption occurred in the microcline samples probably because its larger average grain size and, if any, Fe or Al oxides present (ie, Davis, 1980; Tipping, 1981). The DOC concentration in the +600 mV solutions halved within the first 20 hr of the experiment but in the +200 mV solutions, the DOC adsorption was restricted until the Eh of the solution began to rise (Table 3.7).

The anaerobic Fe sediment solution maintained the <+200 mV Eh levels the longest which resulted in the DOC concentration decreasing by only 20% regardless of the presence of Fe and Al oxides. It is not clear if the Eh is affecting the ability of DOC to adsorb or the surface characteristics of the minerals.

3.6 Conclusions

Based on concentrations of elements "in solution" after centrifugation, the weathering solutions enriched with leaf and peat-DOC appear to be more effective weathering agents of clinochlore, microcline and Fe sediment at near neutral pH and +600 mV Eh than water adjusted to the same pH with HCl. Solutions containing 50 mg/L DOC were approximately twice as effective as the controls, but increasing DOC concentration to 300 mg/L produced only an increase to 3 times that of the control solutions. Therefore, the degree of dissolution is not directly proportional to the concentration, implying that surface-controlled reactions ultimately control the dissolution rate. Under anaerobic conditions (Eh of +200 mV) the peat-DOC solution was only as effective as the control water solution of the same pH, the complexing capacity of the organic molecules apparently having been lowered at the lower Eh. Approximately half the DOC was adsorbed under aerobic conditions, the greatest adsorption occurring in the Fe sediment where Fe and Al oxides are most plentiful. Under anaerobic conditions, little to no adsorption occurred.

The means by which DOC enriches the solution and the form of the enrichment remains unclear. Some of the increased weathering is probably the result of organic acids having a greater number of available H^+ ions that are undetected by pH measurement. Theoretically, this can not contribute greatly to solution enrichment as the products would simply precipitate when solution saturation is achieved. The DOC preferentially removes di and trivalent cations, however the structure of the mineral inevitably decides which cation is most readily available. The cations have different solubilities therefore early precipitation of cations such as Al result in a stoichiometric imbalance between minerals and solutions naturally. However, many of the cations appear to be in solution in concentrations that are higher than what is thermodynamically possible in both control and DOC enriched solutions. Therefore the cations must form direct organic complexes with DOC or inorganic complexes that may eventually precipitate. This would imply a larger number of complexes in the DOC-rich solutions, which if the precipitated organics are of a very small size being able to avoid centrifugation, perhaps by bonding directly with DOC. Therefore, a theoretical investigation of the solution chemistry based on thermodynamic properties and supported by experimental data is required to determine what the element speciation should be and actually is in both control and DOC-rich solutions, and the role of DOC (Chapters 4 and 5).

Chapter 4

Potential and Measured Element Complexation by DOC

4.1 Introduction

From the results presented in Chapter 3, it is clear that an overall increase in mineral dissolution, with particular emphasis on the release of Fe, Al, and Mg, occurs in waters enriched with DOC under aerobic, near-neutral pH regimes compared to unenriched waters of similar pH. This result evokes the next question; how does the presence of DOC increase the rate of mineral dissolution? It is likely a complex series of processes related to surface interactions are responsible, as examined by Zutic and Stumm (1984) and Zinder et al. (1986); with relative importance varying with DOC composition, solution conditions and mineral types. Research in this field is beyond the scope of a masters thesis and would be best explored by researchers in disciplines other than geography.

However, before being able to begin perusing theories regarding specific mechanisms, it is crucial to know in what form the enrichment takes place, which is the subject of Chapter 4 and 5. The cation enrichment can be grouped into two forms: enrichment caused by ionic dissolution and direct element complexation with DOC (Chapter 4); and enrichment of colloidal and particulate matter (Chapter 5). The enrichment by direct complexation was investigated through an examination of the potential element speciation using the program SOILCHEM (Sposito, 1989) and Fe speciation was experimentally determined using o-phenanthroline (Koenings, 1976; Moore, 1988).

4.2 Methods and Equipment

4.2.1 The o-phenanthroline Method

In an effort to determine the form of iron in solution for the 18 mineral solution combinations of Chapter 3, an o-phenanthroline method was used similar to that outlined by Koenings (1976) and modified by Moore (1988). "Reactive ferrous iron" was determined by measuring the change in absorbency at 510 nm with the LKB BIOCHROM ultraspec in 1 cm cells 24 hr after adding 1% alcoholic o-phenanthroline to the sample solution in a 1:100 ratio by volume. The pH of the solutions was generally between the prescribed 4-6 and therefore was not adjusted using NaOH. "Total reactive ferrous iron" was determined by adding 1 ml of hydroxylamine hydrochloride to the 20 ml of sample in addition to the 0.2 ml of o-phenanthroline. The absorbency was read after 24 hr at 510 nm and the "Total ferrous iron" determined by subtracting the absorbance of the original sample. Total iron had already been determined using AA in Chapter 3.

4.2.2 SOILCHEM: a means of modelling element complexation by DOC

SOILCHEM is an iterative computer program that uses thermodynamic mole-balance equations to asses element speciation in natural solutions (Sposito, 1988). Free ionic concentrations of all metals and ligands and an estimation of solution ionic strength, from solution conductivity, are required as input. Ionic strength and the equilibrium constants for each metal and ligand are concurrently recalculated with each iteration, to account for changes in solution ionic strength, until equilibrium is achieved. The program also has the facility to deal with a range of complexes, mixed solids, redox reactions and, to some extent, surface exchange reactions. However, the use of the additional components requires additional data, such as pE or pO_2, which are easily obtained, or the exchange ability of a surface, which is not so.

The data bank, called GEODATA (Sposito, 1988), contains the required stability constants for most standard experimental applications, although its application to the natural environment is restricted being based on 25°C and 1 atm. However, the program does contain the provision for expansion and updating. GEODATA offers well established stability constants for a wide range of organic acids but the applicability of these acids to natural systems is questionable as they may not be present. To provide more "useful" stability constants for organics, two stability constant categories Ful1 and Ful2, derived through a statistical evaluation of the complexing ability of sewage sludge fulvic acid over a range of cation types and concentrations are provided (Sposito et al., 1981). Both categories have 1:1 metal-complex ratios, but the Ful1 group tends to be composed of the most acidic groups and the Ful2 has three separate categories of functional groups that all behave the same with respect to metals. The respective concentrations, Fu_{Ti}, of Ful1 and Ful2 can be derived using

$$Fu_{Ti} = \frac{DOC}{226} \times n_i \times \frac{2.06\times10^{-3}}{1.21} \quad (i=1,2)$$

(Sposito et al., 1981), where in Ful1 $n_1=0.11$, and Ful2 $n_2=1.1$ per mole of fulvic acid. The stability constants were calculated at a pH of 5.0 and ionic concentration of 0.1 M. The applicability of these stability constants decreases with deviations of pH and ionic concentration and is contingent on the assumption that naturally derived DOC has similar functional groups as the fulvic acid derived from sewage sludge. It should be emphasized that the program assumes concentrations entered are ionic, which is not easy to verify and, at most concentrations, not the case. Therefore any results obtained using SOILCHEM should be interpreted with care, as the actual speciation may be affected by kinetic factors. In this experiment, unreconstituted colloids and particles are likely to exist and classed as ionic in the data entry because of analytical restrictions. Therefore, the absolute concentrations, particularly of precipitated species, derived by the program are most likely high.

The carbonate content of the solutions was required for the SOILCHEM program to determine the involvement of the carbonate ligand. It was determined using the NAQUADAT (No 10110; 1978) total alkalinity method which involves a potentiometric titration using H_2SO_4. No results have been presented as concentrations were extremely low but the activity of the ligand is presented in tables 4.2a and 4.2b.

A cross section of 18 mineral solution combinations were run using different combinations of the program variables. Portraying all the output data would serve little function and require an appendix of extraordinary length. A summary of the results is provided in section 4.4 and Tables 4.2a and 4.2b.

4.3 Results

4.3.1 The Analytically Determined State of Fe in Solution

The "reactive ferrous iron" is ionic Fe^{2+} or Fe^{2+} complexed by organic matter, with stability constants less than those of o-phenanthroline (Koenings, 1976). The "total reactive ferrous iron" includes "reactive ferrous iron", ionic ferric iron and some ferric iron that needs reduction before being released from organic matter complexes. The Fe^{3+} bound to organic matter that avoids reduction will not be available to o-phenanthroline. The complexation of Fe^{2+} creates an equilibrium imbalance in the solution resulting in the reduction of Fe^{3+} and when the ferric:ferrous ratio is high, >10, the dissolution of inorganic Fe particles can occur. Therefore, in solution Fe concentrations determined using o-phenanthroline are usually higher than actual Fe concentrations (O'Connor et al., 1965). These ambiguities have lead to the operational definitions of "total reactive" vs "reactive" ferrous iron. Even operating within the boundaries of these definitions, some relationships between DOC and the state of iron can be seen.

In the microcline experiments the reactive ferrous iron concentration was very low (<1 mg/L) in all solutions, and the total reactive ferrous iron more than double the reactive ferrous iron, suggesting either Fe^{3+} is also bound or present

Clinochlore

	Type of Fe (ppm)		
	Reactive	Total Reactive	Total
Solution			
50 mg/L Peat-DOC	0.1	0.3	0.0
50 mg/L Anaerobic Peat-DOC	Trace	0.1	0.0
50 mg/L Leaf-DOC	0.1	0.2	1.6
300 mg/L Leaf-DOC	0.4	0.8	5.3
Water	0.1	0.1	0.0
HCl	0.1	0.1	0.0

Microcline

	Type of Fe (ppm)		
	Reactive	Total Reactive	Total
Solution			
50 mg/L Peat-DOC	0.9	4.3	5.9
50 mg/L Anaerobic Peat-DOC	1.0	1.5	0.9
50 mg/L Leaf-DOC	0.4	0.8	2.0
300 mg/L Leaf-DOC	0.8	1.0	3.8
Water	0.0	0.0	0.1
HCl	0.0	0.1	0.0

Fe Sediment

	Type of Fe (ppm)		
	Reactive	Total Reactive	Total
Solution			
50 mg/L Peat-DOC	0.5	0.2	67.2
50 mg/L Anaerobic Peat-DOC	0.1	0.3	5.5
50 mg/L Leaf-DOC	0.3	0.5	47.7
300 mg/L Leaf-DOC	1.3	2.5	41.2
Water	0.2	0.9	20.0
HCl	0.1	0.1	2.7

Table 4.1. The relative states of Fe in the experiment solutions after 400 hr. Reactive and total reactive Fe concentrations were determined using o-phenanthroline (3.1.4) and Total Fe concentrations using AA. The o-phenanthroline technique produces ≤0.1 ppm Fe inherently from the chemicals often causing small discrepancies from AA derived totals. Inherent Fe contained in the peat- DOC at experiment onset has not been filtered out of the o-phenanthrolene data, (1.24) as it was for the AA derived totals accounting for the discrepancies in the peat-DOC solutions. Therefore to measure the total reactive iron, 1.24 should b subtracted from the peat-DOC solutions.

in ionic form (Table 4.1). In the peat-DOC microcline solution, Fe originally in the peat-DOC is probably responsible for the higher total ferrous iron concentrations (Table 3.1). The total iron concentration of the peat-DOC clinochlore solution is less than the original concentration of Fe (1.24 ppm) in the peat-DOC, and is probably the result of DOC adsorption.

The total Fe recorded in the leaf-DOC solutions were nearly 10 times the total ferrous iron concentration implying large amounts of Fe is inorganically complexed, perhaps in colloidal or particulate form. This disparity was present in all the Fe sediment DOC solutions where the total iron exceeded the total reactive ferrous iron by factors up to 100, suggesting large amounts of colloids are in solution. This observation is addressed in the filtration experiment of Chapter 5. It seems likely, in the case of microcline and clinochlore, that the colloids or particles were precipitated from solution given the incongruent stoichiometry; but it is also possible, and likely in the case of Fe sediment, that parent particles are also present.

Bloomfield (1953) suggested that Fe^{3+} is reduced upon complexation with organic acids, however, given the total ferrous iron is consistently twice the ferrous iron, this does not always appear to be the case. In fact, a portion of the

Fe^{2+} that enters the solution may be oxidized, given the suggestion that Fe^{2+} is being released from microcline. In anaerobic solutions, reactive iron is approximately equal to total reactive iron but still is far less than total when Fe sediment was weathered, indicating Eh and organic matter had little effect on the "unreactive iron".

4.3.2 Speciation Determined Using SOILCHEM

The general trends of speciation, with the program option of allowing solids to precipitate invoked, is as follows with specific examples in Tables 4.2a and 4.2b. K is ionic except when Mg, Fe, Al, and Si are all present, which results in K being incorporated into illite. Mg is generally ionic except when one of K, Fe, Al, or Si are absent, unless CO_3^{2-} is present. Ca tends to be a free metal or complex with CO_3^{2-}. Fe is found mostly bound with hydroxyls except in the anaerobic chambers, where the ferrous form prefers complexation with $CO_3^{2-}$and or $SiO_2(OH)_2^{2-}$ (listed in the program print out as SiO_3^-). Al is usually complexed with SiO_3^- or is incorporated into mixed solids (clays), but when Si is present in small quantities, Al can complex with hydroxyls. Si is found in clays or simply bound with H^+ in solution or a solid. When mixed solids were ignored the only noticeable change was an expected increase in the percentage of precipitated complexes. Ful1 and Ful2 are not significant agents, generally complexing

Microcline in 300 mg/L Leaf-DOC

	Ca	Mg	K	Na	Fe^{3+}	Fe^{2+}	Al
Free	76.8	82.6	99.8	99.9	0.3	48.6	0.0
CO_3^{2-}	0.7	0.8	0.2	0.1	0.1	0.7	0.0
Solid CO_3^{2-}	0.0	0.0	0.0	0.0	0.0	49.7	0.0
solid OH^-	0.0	0.0	0.0	0.0	99.9	0.0	97.8
Ful1	0.0	0.0	0.0	0.0	0.0	0.3	0.0
Ful2	0.1	0.0	0.0	0.0	0.0	0.7	2.2
Dolomite	22.3	16.5	0.0	0.0	0.0	0.0	0.0

Ful1: as free ligand 0.6%; bound with Ca 46.5%; bound with Mg 21.4%; bound with Fe^{2+} 31.5%.
Ful2: as free ligand 6.7%; bound with Ca 6.6%; bound with Mg 2.4%; bound with Fe^{2+} 7.1%; bound with Al 77.3%.

Fe Sediment in 50 mg/L Leaf-DOC

	K	Na	Fe^{3+}	Fe^{2+}	Al
Free	98.6	98.9	0.0	4.1	0.0
CO_3^{2-}	1.4	1.1	3.0	0.5	0.0
Solid CO_3^{2-}	0.0	0.0	0.0	0.0	95.1
Solid OH^-	0.0	0.0	97.0	0.0	0.0
Solid SiO_3^-	0.0	0.0	0.0	0.0	100.0
Ful1	0.0	0.0	0.0	0.1	0.0
Ful2	0.0	0.0	0.0	0.1	0.0

SiO_3^-: in solid form with Al 53.7%; bound with H 0.5%; in solid form with H 45.8%;
Ful1: as free ligand 24.9%; bound with Fe^{2+} 75.1%.
Ful2: as free ligand 93.5%; bound with Fe^{2+} 5.6%; bound with Al 0.9%.

Clinochlore in HCl

	Ca	Mg	K	Na	Fe^{2+}
Free	64.0	86.5	100.0	100.0	2.7
Solid SiO_3^-	0.0	9.6	0.0	0.0	97.1
Dolomite	36.0	3.9	0.0	0.0	0.0

SiO_3^-: bound with Mg 95.5%; bound with Fe^{2+} 4.4%.
Note: iron was indicated as being Fe^{2+} by o-phenanthroline but may well be Fe^{3+} as it is difficult to differentiate such a small amount.

Table 4.2a. The speciation of the dissolved metals as a percentage of metal cation and the SiO_3, Ful1 and Ful2 ligands as a percentage of ligand as calculated by SOILCHEM. Note, SiO_3^- is the print out for $SiO_2(OH)_2^{2-}$.

Clinochlore in Aerobic 50 mg/L Peat-DOC

	Mg	K	Na	Al
Free	3.2	83.8	91.7	0.0
CO_3^{2-}	2.2	8.5	0.0	0.0
Solid CO_3^{2-}	92.5	0.0	0.0	0.0
OH^-	0.0	0.0	0.0	0.6
Illite	2.1	7.8	0.0	99.3

SiO_3^-: in solid form as illite 100.0%.
Ful1: as free ligand 26.2%; bound with Mg 73.8%.
Ful2: as free ligand 92.5%; bound with Mg 2.6%; bound with Al 4.9%.

Clinochlore in Anaerobic 50 mg/L Peat-DOC

	Mg	K	Na	Fe^{2+}	Al
Free	66.4	96.8	99.6	18.3	0.0
CO_3^{2-}	1.9	0.5	0.4	1.3	0.0
Ful2	0.0	0.0	0.0	0.4	0.0
Solid SiO_3^-	31.2	0.0	0.0	79.9	0.0
Illite	0.4	2.7	0.0	0.0	100.0

SiO_3^-: in solid form with Mg 87.1%; in solid form with Fe^{2+} 0.8%; bound with H 0.6%; in solid form as illite 11.6%.
Ful1: as free ligand 1.1%; bound to Mg 96.2%; bound to Fe^{2+} 2.7%.
Ful2: as free ligand 52.5%; bound to Mg 45.0%; bound to Fe^{2+} 2.5%.

Fe Sediment in Anaerobic 50 mg/L Peat-DOC

	Mg	K	Na	Fe^{3+}	Fe^{2+}	Al
Free	78.2	66.4	99.8	0.0	91.6	0.0
CO_3^{2-}	0.9	0.2	0.2	0.0	1.5	0.0
OH^-	0.0	0.0	0.0	87.7	0.0	0.0
Ful1	0.0	0.0	0.0	0.0	1.3	0.0
Ful2	0.1	0.0	0.0	0.0	5.6	0.0
Illite	20.7	33.4	0.0	12.2	0.0	100.0

SiO_3^-: bound with H 0.7%; in solid form with H 42.7%; in solid form as illite 56.6%.
Ful1: as free ligand 3.1%; bound with Mg 56.3%; bound with Fe^{2+} 40.7%.
Ful2: as free ligand 69.1%; bound with Mg 12.7%; bound with Fe^{2+} 18.3%.

Table 4.2b. The speciation calculated using SOILCHEM of: the dissolved metals as a percentage of metal cation; and the SiO_3^-, Ful1, and Ful2 ligands as a percentage of ligand. Note, SiO_3^- is the printout name for $SiO_2(OH)_2^{2-}$.

less than 1% of the metals available. Ful2, especially in the peat-DOC cases, often existed as a free ligand, therefore a closer examination of the Ful1 and Ful2 data is required.

The complexation data of a ligand maybe misleading. An examination of the reaction intensities (Sposito and Coves, 1988) makes it possible to examine the interdependence of cations and complexes. Reaction intensities are dimensionless quantities defined by

$$x,y = \frac{-\log[\text{free ionic concentration of complex } x]}{-\log[\text{Total concentration of complex } y].}$$

A large absolute value indicates x is sensitive to the presence of y. If the value is >0 and large, the free ionic concentration x increases significantly as y increases. If it is <0 and large, the free ionic concentration x decreases significantly as y increases. The closer the value to 0, the smaller the effect of y on x. A large negative number would therefore signify as y increases, x decreases because it is bound by y.

The values encountered were generally negative. This indicates, as expected, a decrease in ionic ligand concentration with increase in cation concentration. When intensities were compared to the actual outcome, it is apparent that the actual complexation reactions were of a "second choice" nature. The theoretical Ful1 order of preference was to complex Fe^{3+} followed by Al^{3+}, Fe^{2+}, Mg^{2+} and Ca^{2+}. The most common complexation order outlined by SOILCHEM, under the experimental conditions, was Fe^{2+}, Ca^{2+}, and Mg^{2+}, depending on the concentration and availability of the cation. The Ful2 order of preference based on reaction intensities is $Fe^{3+} = Al^{3+}$, Ca^{2+}, Mg^{2+}, and Fe^{2+}. This order changes slightly with variations in pH and ionic concentration of the solution. The actual order of observed complexation was Al^{3+}, Fe^{2+} and Ca^{2+}. Al is complexed by Ful2 only if concentrations are sufficient.

The model DOC prefers to interact with Fe and Al but the SOILCHEM data suggests they are not doing so. An examination of the Fe and Al reaction intensities provides a possible answer. The order of preference for complexation with ligands by Al and Fe place Ful1 and Ful2 behind all the other ligands known to be present in the solution. Therefore, the Fe and Al complex with all other ligands until all sites are occupied, before binding with Ful1 and Ful2. This pattern can also be found by examining the iteration sequence, where it is not until the very end of the run that the organic acids act.

Increasing pH above 5.0 results in an increase in the free ligand concentration of the Ful1 and Ful2. At pH 6.8, 50% of the Ful1 and Ful2 remained as unreactive ligands. This may be the result of greater particle neutrality resulting from lower hydrogen ion activity but is more likely a product of the limitations of the modelled stability constants. It is these stability constants and the way their usage that must next be scrutinized, as presently theoretical and measured data do not correspond.

4.4 Discussion: problems of using a thermodynamic approach

Using the experimental data obtained from the dissolution of microcline in 300 mg/L leaf-DOC as input to SOILCHEM, it was determined that after 400 hr, the DOC concentration was approximately 150 mg/L with a complexing capacity of 1.59×10^{-3} moles, of which 1.5×10^{-3} moles of sites were occupied. The experimental data (Appendix III) indicates an enrichment of 0.47 M of cations in this same solution compared to the HCl control. Fe constituted 6.8×10^{-2} M of this enrichment but was undetectable in the HCl control solution. The difference between theoretically complexed and observed enrichment is even more pronounced in the Fe sediment, where total enrichment, after 400 hr, exceeded the HCl standard by 2.97 M, of which 0.69 M was Fe. The complexing capacity assigned to DOC by substituting Ful1 and Ful2 was of the order of 7×10^{-4} M for Al and Fe, which was 3 orders of magnitude lower than the amount in "solution".

The o-phenanthroline method provides an experimental means of comparing "actual" forms of Fe with the "theoretically" derived species of SOILCHEM. The SOILCHEM program predicts concentrations of Fe^{2+} complexed by Ful1 and Ful2 in the order of $2x10^{-5}$ M and $2x10^{-4}$ M respectively at pH 5. The "reactive ferrous iron", a surrogate for organically complexed Fe^{2+}, ranges from $1.8x10^{-3}$ to $1.6x10^{-2}$ M, which is a significant difference between apparent and theoretically organically complexed Fe^{2+}. More specifically, in the case of Fe sediment in 300 mg/L leaf-DOC after 400 hr, the SOILCHEM predicted organically-bound Fe was in the order of 10^{-5} M compared to the o-phenanthroline measured concentration of $2.3x10^{-2}$ M. A similar pattern existed in the microcline and 50 mg/L peat-DOC solutions, the predicted value being $3x10^{-6}$ M compared to a reactive ferrous iron concentration of $1.4x10^{-2}$ M. SOILCHEM predicts the Fe^{2+} cannot be ionic (accept for trace concentrations) given the Eh of +600 mV, which is consistant with accepted theory (Garrels and Christ, 1965). Yet, Fe^{2+} is available to o-phenanthroline which suggests it is not inorganically bound. The total reactive ferrous iron concentration, however, is generally double that of reactive ferrous iron in most of the solutions studied (Table 4.1), indicating as much Fe^{3+} was either ionic or organically bound. In the Fe sediment 300 mg/L leaf-DOC solution, the total reactive ferrous iron was $4.4x10^{-2}$ M which is three orders of magnitude larger than the SOILCHEM predicted concentrations of $1x10^{-5}$ M. According to SOILCHEM, Fe^{3+} is not likely to be ionic beyond concentrations of $1x10^{-13}$ M, therefore, both ferric and ferrous iron complexed with DOC is underestimated by Ful1 and Ful2.

In the +200 mV peat-DOC solutions the same trends are present. The lower Eh appears to have no effect on the speciation of Fe, mainly because so little of it remains ionic. Since Fe^{3+} can not be ionic, in any quantity, at an Eh of +200 mV, the Fe^{3+} component of the "total reactive ferrous iron" fraction must be organically complexed. Bloomfield's (1953) suggestion that organic acids reduce Fe on binding is not substantiated for DOC as a whole in this experiment, even at this low Eh.

When the pH is significantly above (one order of magnitude) and probably below pH 5.0, the majority of the Ful2 ligand is free of metals, restricting the models use to pH values near 5. This is very evident in the case of peat-DOC which achieves pH values of greater than 7.0. At pH values near 5, the Ful ligand complexation sites appear to be 100% occupied, after 10 hr, with Al, Mg, Ca and Fe (as ferrous or ferric depending on Eh) found in ionic forms in almost every scenario provided SOILCHEM. Therefore, the assumption that all species entering the solution were ionic, which was made to use SOILCHEM but suspected of being invalid, is not critical as a dissolution pattern similar to the one observed would be produced regardless. It is felt that changes in speciation resulting from including non-dissolved particles as ionic and not including factors such as their adsorption ability would only be significant if concentrations were much lower than recorded in the experimental solutions. Most importantly, however, since all complexation sites of the modelled DOC, Ful1 and Ful2, are occuppied after 10 hr, further mineral dissolution can not be attributed to metal complexation, according to the SOILCHEM model.

The conditional stability constants and moles of binding sites per mole of Ful1 and Ful2 were calculated by Sposito et al. (1981) using a quasiparticle fulvate model, which employs the use of a mathematical description or hypothetical molecules to mimic the actual organic molecules. The moles of binding sites and conditional stability constants for fulvic acid, derived from sewage sludge, with Cd^{2+}, Pb^{2+}, Ca^{2+} and Cu^{2+} were determined using potentiometric titrations of easily dissociable metal complexes and the Scatchard plot technique. The conditional stability constants for the remaining metals were predicted using linear correlation equations, assuming a linear correlation with the Misono softness parameters. A mixture model, using organic acids whose functional groups were expected to simulate the metal complexing acids of the sewage sludge fulvic acid fraction at a concentration of

2.06×10^{-3} M fulvic acid (equal to 226 g m^{-3} of organic carbon) was compared to the quasiparticle model (Sposito et al., 1982). The mixture model and quasiparticle model did not yield the same predictions for Cu^{2+} and Cd^{2+} complexation because of the mixture model's wide range of stability constants. Therefore the importance of cation concentration in the mixture model is limited, unlike in the fulvate model which it dominates. Since the fulvate model was employed in SOILCHEM, although preferential complexation occurs indicated by the reaction intensities, the actual complexation is generally dominated by the concentration of a particular cation in solution. For example, in the clinochlore solution, Mg is the dominant multivalent cation and also occupies the majority of the Ful sites but is replaced by Ca as the dominant cation in the 300 mg/L Leaf-DOC solutions (Tables 4.2a,b).

An important question is whether the Ful modelled organic acids are indicative of the peat-DOC and leaf-DOC, in both their ability to complex and number of complexation sites. Obvious differences were recorded in the o-phenanthroline study, suggesting at least higher stability constants are required for Fe in the fulvate model. However, changes in the stability constant would only increase the competitiveness of the hypothetical Ful, allowing it to complex cations that are presently modelled to be inorganically complexed. What is also required is an increase in the complexation capacity, because at pH 5.1, all bonding sites were occupied. Complexation capacity, is defined by Buffle (1988) as the number of sites per mole gram of homologous complexant. To increase the concentration of sites in the formula developed by Sposito et al. (1981) would require a lower concentration of carbon per mole of fulvic acid. What this means in terms of the DOC molecules is a lower proportion of carbon atoms in the structure or an overall lower molecular weight. Therefore the complexing power and capacity of the Ful acids molecular weight may not be representative of any other type of DOC other than the sewage sludge from which it was derived.

Rashid (1985) identified the average binding capacity of humic acid from soils to be between 97.5 and 150 mg of metal per gram of organic matter, which translates into about 4.9 to 11.9 mg of metal for 150 mg/L of humic acid. This capacity is much larger than the o-phenanthroline values obtained for Fe bound in microcline and Fe sediment solutions but smaller than the total enrichment of 42.1 mg/L (compared to the total enrichment of the Fe sediment water control; Appendix II).

The stability constants for o-phenanthroline and Fe^{2+}, are $\log k_1$ 5.85, $\log k_2$ 5.25, and $\log k_3$ 10.3, respectively, and Fe3+ are logkl 6.5, $\log k_2$ 11.4, $\log k_3$ 23, respectively (Cheng et al., 1982). Similarly, stability constants (logk) for metals bound with natural organic acids are also tiered for sewage sludge fulvic acid (Sposito et al., 1981). For example, Ful1 and Ful2 were set at 4 and 9 respectively by Sposito et al. (1981), to represent the two types of observed bonding by sewage sludge fulvic acid, but can be as high as 10 according to Rashid (1985). In order to complex one Fe^{2+} molecule from the organic chelates it would appear that in some instances all 3 o-phenanthroline complexation sites would be required achieving a logk of 10.3. Kinetics becomes a major factor when such complicated exchanges are required. The o-phenanthroline molecules may not be able to extract all the organically complexed ferrous iron, particularly that which is strongly chelated, and the hydroxalymine hydrochloride may not be able to reduce a good portion of the iron, therefore underestimating both "ferrous iron" and "total ferrous iron".

The complexation model of Sposito assumes a 1:1 metal ligand ratio, and attempts to ensure complexation is the means of binding were made by using single easily dissociable $metal(NO_3)^2$ titrants. However, complexation models undoubtably include certain aspects of sorption, specifically ligand exchange phenomena where actual ion exchange occurs, and class them as complexation. The SOILCHEM program has a component for cation exchange and adsorption. However, these models require sophisticated analysis of the particles in question and requires a method of investigating the surfaces of DOC molecules. Most adsorption phenomena investigated have focused on adsorption of organics to inorganics, however, adsorption of inorganic colloids onto the surfaces of DOC may increase the concentrations of cations by changing the 1:1 metal ligand ratio.

4.5 Conclusions

The SOILCHEM model and the o-phenanthroline study indicate that at least a portion of the increased cation dissolution was the result of complexation by organic ligands but the exact quantity is unknown. The remainder of the enrichment occurs in the form of inorganic particles and/or colloids. It is the relationship between the DOC and the colloids and particles, which maybe precipitates or small fragments of original mineral, that is not addressed by this thermodynamic approach. This issue will be examined in Chapter 5.

Chapter 5

The Particle Size Distribution of Iron Complexes

5.1 Introduction

In natural waters, the molecular weight (M_w) of aquatic humic substances, which is a major component of DOC, generally ranges from 500 to 10,000 M_w but may be as high as 100,000 M_w and the fulvic fraction ranges from 500 to 2000 M_w (e.g. Buffle et al., 1978; Gjessing, 1965; Thurman et al., 1982). The range of 500 to 10,000 M_w, can be approximated to equal 5 to 33 Å or 4.7×10^{-4} to 3.3×10^{-3} μm respectively, suggesting most of the aquatic humic substance are in the sub-colloidal (<10,000 M_w) fraction (Thurman et al., 1982). Although Buffle et al. (1978) and Thurman et al. (1982) agree on the particle size distribution of organic matter (OM) in most natural fresh waters, Buffles points out that the majority of OM in peat waters and leaf leachates extends from the colloidal fraction, between 10^4 and 10^6 M_w (<0.05 μm) into the particulate fraction (>0.05 μm). In fact, in the case of the leaf extracts, 65% formed "particulate organic matter", being between 0.035 and 0.2 μm.

Koenings (1976) observed the majority of Fe in North Gate Lake, at a pH of 4 to 5, to be in the form of mineral organic "colloids" (0.45 - 4.8×10^{-3}μm). It should be noted Koenings' definition of the colloidal fraction differs from those of Buffles et al. (1978) and Thurman et al. (1982), by defining particles of a larger size. Koenings' findings in North Gate Lake were based on the fact that 90% to 100% of the Fe in the aerobic zone and 99% in the anaerobic zone, was filterable through a 0.45 μm pore size filter but only 8% and 45% to 60%, respectively was filterable through $4.8\text{x}10^{-3}$ μm pore size dialysis tubing. He suggested that in lakes of low pH, colloidal organic matter (COM) is responsible for the "complexation and or sorption" of most Fe, forming clay-organic colloids, given the low concentrations of hydroxyls. This phenomenon is not specific to Fe: Ares and Ziechmann (1988) noted a tendency for Al to "flocculate" in the presence of organic matter at levels beyond the natural decrease in solubility, when the pH was increased from 2 to 5. However, they also noted a decrease in the complexing power of DOC with increasing pH and suggested structural changes in the DOC lead to incorporation of Al into the precipitating organic matter. The structure of the DOC molecule has been observed to be open and flexible, with voids of various sizes which become more ordered and fibrous with increasing pH creating more sites for adsorption (Ares and Ziechman, 1988; Buffle, 1988).

Being derived from poorly decomposed peat and leaf leachates, the DOC used in this study was assumed to be a mixture of humic and fulvic acids of the fractions described by Thurman et al. (1982). Having been filtered through a 1.2 μm GFC filter, it may have a large component of colloidal size fraction described by Buffle et al., (1978). The o-phenanthroline study and SOILCHEM speciation program suggested that the majority of the cation enrichment in the DOC rich solutions of the experiment was similar to that described by Koenings (1976) in North Gate Lake, the DOC interacting with mineral complexes (e.g. Aries and Ziechman, 1988; Buffle, 1988; and Rashid, 1985). To determine the relationship between the particle size fractionation of Fe and DOC, a filtration experiment was conducted on the microcline and Fe sediment solutions.

5.2 Methodology

The boundaries used to group particles based on size tend to be operationally defined and scientifically arbitrary. For example, Buffle et al. (1978), based mainly on apparent groupings established by others and the availability of filters, used both size, 0.2 and 0.035 μm, and molecular weight 10,000 and 210 as divisions. The boundaries employed in this experiment are: 1.2 μm, 0.65 μm, 0.45 μm, 0.22 μm and 0.10 μm; and are likewise somewhat arbitrary being controlled by the availability of the Micron Separations Inc. (MSI) cellulose membrane filters used and the desire to examine the colloidal size fraction. The filters were not pretreated with acid to remove inherent DOC, as is often prescribed, because tests revealed that with the methods employed, any contribution was undetectable. Small samples of the solution being tested were passed through to complex any inherent metal before experimental use, and the filters were changed regularly to prevent pore clogging. Suction of 1.0 atm was applied with a GAST pump to increase the speed of filtration.

Twenty grams of Fe sediment and microcline, of the same composition used in Chapter 3, were each added to the 10^{-5} M HCl in water control solution and the 300 mg/L Leaf-DOC solution used in Chapter 3. The 300 mg/L leaf-DOC was used instead of the 50 mg/L peat-DOC solution because of its lower inherent Fe concentration and it was presumed the higher DOC concentration would make changes induced by filtration easier to observe. The 4 solutions were stirred and left to stand for alternate 12 hr periods (as in 3.2.3) until 200 hr had passed after which a 300 ml aliquot was extracted from the container. To determine the effect of centrifugation, 150 ml of the aliquot was centrifuged for 1 hr at 4500 rpm with an International Clinical Table Top Centrifuge prior to filtering and the remaining 150 ml was filtered directly. A sample of the original 300 mg/L leaf-DOC solution was filtered to determine its initial particle size distribution.

The filtration was carried out by passing each solution through the series of filters from 1.2 μm to 0.1 μm in succession with a 25 ml sub-aliquot being extracted after each filter. The remaining volume was passed through the successive filters with 20 ml sub-aliquots being removed each time, in a form of cascade filtration. The absorbance at 330 and 510 nm was determind using an LKB BIOCHROM ultraspec 4050 spectrophotometer with 1 cm cells, total Fe content using flame AA, and DOC content using both the modified Walkley Black and GC methods of Chapter 3 and 4, respectively, were measured for each sub-aliquot. The used filter papers were oven dried over night at 105°C and the proportional mass of filtered material determined by subtracting an average weight of 4 wetted and oven dried filters.

5.3 Results

Measuring the changes in the filter paper mass was the least effective method in determining changes in concentration of particles and colloids. The variability in weight loss of individual filters, and the ease by which the filters were damaged by oven drying, created unreliable results. Absorbance measurements were effective in displaying changes in Fe and DOC concentrations alone, and given a known concentration for a specific fraction the concentrations of other fractions could be predicted (Figure 5.1a). The correlation coefficient between absorption at 330 nm and the DOC concentration determined by the modified Walkley Black method was 0.80 and GC method was 0.68 (Table 5.1). The correlation coefficient between absorbance at 510 nm and actual Fe concentration determined by AA was 0.97 with the percent change absorbance corresponding very well in both Fe sediment and microcline centrifuged and uncentrifuged control solutions (Table 5.1, 5.2).

In the leaf-DOC a 20% loss of absorbance at 330 nm was observed after filtering but the actual decrease in DOC concentration determined by the Walkley Black method was 16%, and by gas chromatography 6%. The GC method is not accurate at concentrations >100 mg/L because of incomplete recovery of CO_2 gas, but normally has a error of about 2 to 3 mg/L below this concentration. Therefore, the leaf-DOC solutions were diluted 3.5 times lowering the DOC concentration to <100 mg/L which increased the potential error to as large as 10 mg/L or 5% of the original concentration. The modified Walkley Black method yields errors of a similar order, making interpretation regarding individual fractions whose concentration changes by only 1 or 2 percent impossible. On the whole, some portion of DOC was removed, between 6% and 20%, suggesting a small portion of the DOC is likely larger than 0.10 um. It should be pointed out that in higher DOC concentrations, larger

300 mg/L Leaf-DOC

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	288	243	x	0.274	x
<0.65	268	238	x	0.269	x
<0.45	250	228	x	0.260	x
<0.22	246	235	x	0.257	x
<0.10	242	221	x	0.235	x

300 mg/L Leaf-DOC and 20 g/L Fe Sediment

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	216	205	16.70	0.248	0.055
<0.65	186	175	12.87	0.224	0.042
<0.45	216	192	11.74	0.215	0.039
<0.22	247	206	10.76	0.214	0.039
<0.10	239	191	9.09	0.197	0.035

300 mg/L Leaf-DOC and 20 g/L Microcline

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	255	228	1.47	0.248	0.036
<0.65	247	239	1.39	0.246	0.031
<0.45	201	217	1.31	0.237	0.028
<0.22	208	240	1.24	0.227	0.027
<0.10	262	205	1.15	0.214	0.024

10^{-5}M HCl and 20 g/L Fe Sediment

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	x	x	9.72	x	0.312
<0.65	x	x	3.14	x	0.054
<0.45	x	x	2.22	x	0.033
<0.22	x	x	1.30	x	0.018
<0.10	x	x	0.36	x	0.003

10^{-5}M HCl and 20 g/L Microcline

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	x	x	0.00	x	0.023
<0.65	x	x	0.00	x	0.020
<0.45	x	x	0.00	x	0.017
<0.22	x	x	0.00	x	0.016
<0.10	x	x	0.00	x	0.017

*Absorbance measured in a 1 cm cell after diluting 3.5 times. X = no measurement.

Table 5.1. Particle size distribution of Fe-complexes and DOC determined by cascade membrane filtration only.

300 mg/L Leaf-DOC and 20 g/L Fe Sediment

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	170	202	13.13	0.242	0.043
<0.65	208	194	12.54	0.230	0.041
<0.45	201	197	11.92	0.227	0.040
<0.22	262	214	11.18	0.222	0.035
<0.10	239	198	10.33	0.195	0.055

300 mg/L Leaf-DOC and 20 g/L Microcline

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	201	243	1.59	0.284	0.034
<0.65	232	230	1.52	0.251	0.030
<0.45	216	236	1.43	0.247	0.028
<0.22	185	213	1.29	0.221	0.025
<0.10	216	200	1.14	0.205	0.024

10^{-5} M HCl and 20 g/L Fe Sediment

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	x	x	2.05	x	0.016
<0.65	x	x	1.94	x	0.013
<0.45	x	x	1.80	x	0.013
<0.22	x	x	1.56	x	0.014
<0.10	x	x	0.53	x	0.002

10^{-5} M HCl and 20 g/L Microcline

Size Fraction µm	WB. DOC mg/L	GC. DOC mg/L	Fe mg/L	*Abs330 nm	*Abs510 nm
<1.20	x	x	0.00	x	0.017
<0.65	x	x	0.00	x	0.014
<0.45	x	x	0.00	x	0.017
<0.22	x	x	0.00	x	0.016
<0.10	x	x	0.00	x	0.016

*Absorbance was measured in a 1 cm cell after diluting 3.5 times. X = no measurement.

Table 5.2. Particle size distribution of the Fe-complexes and DOC determined by cascade filtration after centrifugation at 4500 rpm for 1 hr. DOC concentrations determined by the modified Walkley Black (WB) and Gas Chromatography (GC) methods, and Fe concentrations by AA.

molecular weight molecules can form that are not normally present in lower concentrations of the same substance (Thurman et al., 1982).

The methods employed for determining DOC concentration lack the sensitivity required for examining the fractionation of DOC and unfortunately this is even more so the case when sediment is present. The overall decrease in DOC observed using absorbance at 330 nm did not always correspond to measured concentrations. The correlation coefficient between changes in DOC and absorbance at 330 nm calculated for the Walkley Black method was 0.06 and the GC method 0.43. The poor correlations are likely the result of the limitations of the methods used to determine DOC concentrations. The correlation coefficient between absorbance at 510 nm and Fe concentration determined by AA is much better, averaging 0.80, with the percent change absorbance corresponding very well in both Fe sediment and microcline centrifuged and uncentrifuged samples (Figure 5.1). But when DOC and Fe are in the same solutions changes in absorption can not be easily assigned to one or another. Wrigley et al. (1988) established the longer wavelengths such as 510 nm are absorbed more by particulate matter than the coloured water of low molecular weight DOC. However, since the DOC lost is of the same size as the Fe, the differences in wavelength do not appear to be useful.

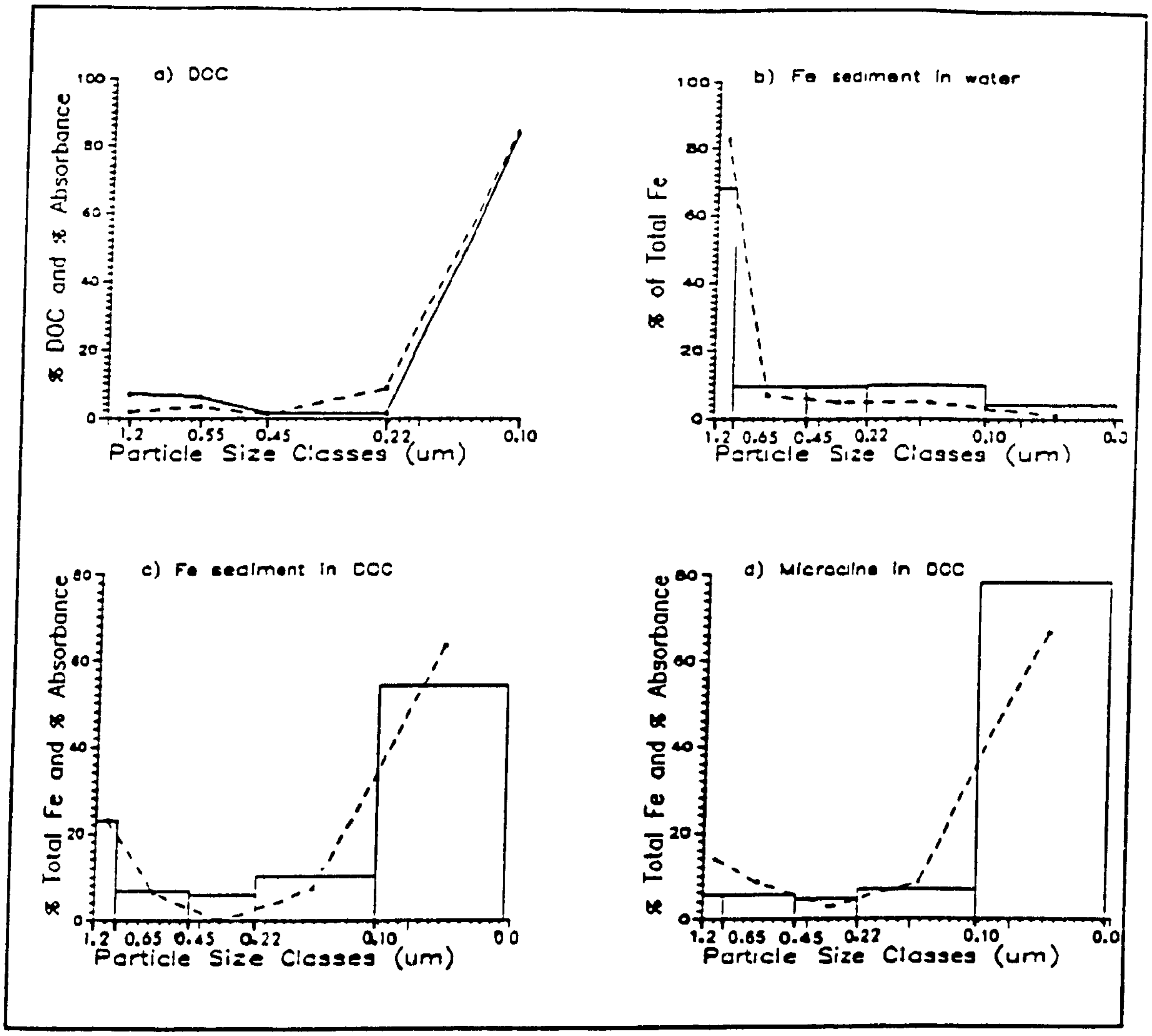


Figure 5.1. The size fraction of: a) 300 mg/L Leaf-DOC determined by filtration followed by the modified Walkley Black (solid line), and absorbance at 330 nm (dashed line); b) Fe complexes from the dissolution of Fe sediment in acidified water determined by filtration followed by AA (bars), and absorbance at 510 nm (dashed line); c) Fe complexes from the dissolution of Fe sediment in 300 mg/L leaf-DOC determined by filtration followed by AA (bars), and absorbance (dashed line) d) Fe complexes from the dissolution of microcline in 300 mg/L leaf-DOC determined by filtration followed by AA (bars), and absorbance at 510 nm (dashed line).

Although filtration had little or no effect on the DOC component of the solutions, it had a strong effect on the Fe complexes. The filters removed Fe complexes steadily and the distribution of the particle sizes are displayed in Figure 5.1b-d. The Fe concentration is small but consistent in the first 4 zones defined by the filters, averaging about 5% but the bulk of the enrichment is in the <0.10 μm fraction. As observed in chapter 3, Fe was not released in a measurable quantity from microcline in water (the control solution) but the leaf-DOC was extremely effective in selectively weathering Fe.

Comparing the centrifuged and uncentrifuged samples, it is obvious that a considerable amount of Fe was lost by centrifugation, mainly in the >0.65 μm fraction. The effect of centrifugation is most obvious in the Fe sediment control solution, Table 5.1 and 5.2, where the <1.2 μm Fe concentration is 20% of its uncentrifuged counterpart. However, in the <1.2 μm fraction of the Fe sediment leaf-DOC solution, the total Fe in the centrifuged solution was 80% of the uncentrifuged. In the microcline 300 mg/L leaf-DOC solution centrifugation increased the concentration of the total Fe by 8% in the 1.2 to 0.65 μm fraction. A slight enrichment of Fe in the finer fractions of all the centrifuged compared to the uncentrifuged samples occurs. This enrichment suggests that the centrifugation process may break up larger particles and also create the slightly higher Fe concentrations in the centrifuged microcline samples.

3.57 mg/L or 21% of Fe from the <1.2 μm fraction of the leaf-DOC Fe Sediment solution was removed by centrifugation. Centrifugation of the control solution resulted in a loss of 7.67 mg/L or 79% in the <1.20 μm fraction. The biased removal of particles from the control solutions by centrifugation may make the DOC-rich solution seem 37% (4.10 mg/L), in this case, more effective at weathering Fe sediment than it actually was. It appears the leaf-DOC reduced the amount of colloidal and particulate Fe being removed by centrifugation. In chapter 3, this form of centrifugation was used to remove suspended particulate matter prior to comparing the element concentration data of the DOC-rich and control solutions. Although not entirely equivalent, comparing the 1.2 μm filterd and centrifuged data with the just filtered data provides some insight into the effects of centrifugation. The extra particles seem evenly distributed over the 1.2 - 0.10 μm fractions and may be small fragments of original mineral or precipitates, thereby further clouding the issue of whether this centrifugable fraction constitutes weathered enrichment or not. This problem of differential enrichment also applies to the leaf-DOC and probably the peat-DOC solutions of Chapter 3.

The 0.10 μm division forms a second boundary of enrichment. In the Fe sediment water samples 3.7% (0.36 mg/L) of the uncentrifuged Fe is <0.10 μm fraction compared to 55% or an enrichment of 9.09 mg/L in the Fe sediment leaf-DOC solution.

5.4 Discussion: apparent adsorption of inorganic complexes by DOC

In Chapter 4 it was suggested the SOILCHEM model employing Ful1 and Ful2 did not effectively model leaf-DOC because the complexation capacities were to low. The observed enrichment may have been over estimated given the effects of centrifugation. Using the figures of the <0.10 μm fraction for the uncentrifuged leaf-DOC samples, and subtracting the concentrations in the control solutions, new enrichments amounted to $2.1\mathrm{x}10^{-2}$ M of Fe in the microcline and $1.25\mathrm{x}10^{-1}$ M of Fe in the Fe sediment-based solutions. However, the complexation capacity of fulvic acid was calculated to be of the order of $1.8\mathrm{x}10^{-3}$ M for 100% of a 150 mg/L DOC concentration (found in the 300 mg/L leaf-DOC solutions of Chapter 3 after 400 hr) which is still two orders of magnitude smaller than the observed enrichment.

The o-phenanthroline study of the Fe sediment solution determined the maximum Fe bound by leaf-DOC was 2.5 mg/L, which is far short of the 9.09 mg/L of Fe present after 200 hr as demonstrated in the filtration experiment. This remaining Fe was either organically complexed by bonds that had a greater complexing capacity than o-phenanthroline or the cations were adsorbed to the surface of the DOC molecules as inorganic complexes and therefore unavailable to o-phenanthroline. In the microcline based solutions, the total Fe enrichment of 1.17 mg/L, is comparable to that of 1.0 mg/L observed in the o-phenanthroline study suggesting most of the Fe is organically bound.

Assuming the differences of Fe enrichment between DOC-rich and control solutions created by centrifugation contributed a false enrichment of about 37%, the total enrichment of Fe is within the total complexation capacity determined by Rashid (1985) of approximately 11.9 mg of metal per 150 mg/L of soil humic acid. A figure for cation exchange was also offered by Rashid (1985), but being 3 mM/g of soil humic acid, is trivial by comparison. If the Fe is at all representative of the particle size distribution of other cations, 55% being <0.10 μm, the total enrichment of all cations in this fraction is at least 21 mg/L after 400 hr (Appendix III). Therefore even compared to Rashids complexation capacity of 11.9 mg of metal per 150 ml of DOC, nearly 50% of the metals are unaccounted for. A portion of this remainder may be attributed to monovalent cation enrichment, although aided by DOC in its release, it does not complexe with it. It also may well be that leaf-DOC is well above the average ability of the soil humic acid to complex metals.

The large concentrations of Si suggest a potential for the formation of Al-Si complexes or even clay minerals to form, thereby making a portion of metals unavailable for complexation. The precipitation of complexes is known to be delayed as much as 43 times (Rashid and Leonard, 1973) and therefore seems logical that sorption of small inorganic complexes to the surfaces of larger DOC molecules is occurring. The adsorption of inorganic complexes delays or prevents thermodynamic equilibrium from being achieved. This reduces the applicabilty of thermodynamically based speciation models whose predictions are based on achieving equilibrium.

There have been numerous theories put forth concerning mechanisms for organic:mineral sorption such as Coulombic interactions (which involve anion or cation exchange), hydrogen bonding, and London dispersion forces (Greenland, 1971). The most important mechanism, may in fact, be just the attraction of opposite charges. The polarization of molecules results in a negative end and a positive end therefore allowing molecules to align themselves against a larger surface of one type of charge. Although the bonds are weak, the amounts of complexes held in solution by such forces maybe substantial considering that layers may develop as a second series of molecules may align themselves at the outside of the first layer.

The role of sorption, cation exchange and complexation (chelation) will vary from case to case. An in depth study of such phenomena would be require the characterization of all the components of the system with regard to surface area, charge, available sites, and composition. This is indeed a monumental task that is far beyond the scope of this work. The conditions in experiment chambers and likewise those of the natural environment will affect the relative importance of sorption, exchange, and complexation. For example, the most important means of mobilizing metals in fens or lakes by DOC maybe adsorption, where bond strength may not be as important. But complexation is more likely to be the most effective of the phenomena in soils, where potentially more bonding sites are present, physical abrasion occurs and the DOC is subjected to constantly changing chemical conditions.

The peat and leaf-DOC solutions appear to bring different total amounts and distributions of available cations into solution. This may not only be a result of differences in composition and structure, relating to the number of exchange or complexation sites, but also the surface area and charge affecting adsorption properties. Since the distribution of metals between DOC-adsorbed and DOC-complexed fractions and the strength of the associated bonds varries with the type of DOC, the environmental conditions can play an important role in what type of DOC is the most effective in mobilizing metals.

5.5 Conclusions

Centrifugation at 4500 rpm extracted 37% more Fe from the <1.2 μm fraction of the control solutions. The differential effect of centrifugation between the DOC-rich and control solutions has potentially biased the results of Chapter 3. The majority of the Fe enrichment from weathering Fe sediment and microcline in DOC-rich solutions, compared to control solutions, occurred in the <0.10 μm fraction after 200 hr where >80% of the DOC fraction was located. This implies the Fe enrichment resulted directly from the presence of DOC through complexation, exchange or adsorption reactions.

Chapter 6

Conclusions and Areas For Future Research

6.1 Conclusions

The study of the Schefferville fens revealed no visual evidence of preferential weathering in the underlying sediment, nor any evidence for an association between high concentrations of DOC and dissolved cation. The main obstacle in studying the activity of DOC was the complicated hydrology of the fens, especially the potential influence of ground water. High concentrations of cations related to preferred ground water paths masked potential relationship between element accumulation and migration with areas of high DOC concentration.

In laboratory studies, solutions containing DOC-rich leachate from leaf litter and peat were 1.5 to 3 times more effective in weathering clinochlore and microcline and an Fe rich sediment, obtained from one of the Schefferville fens, than waters of near neutral pH, (5 to 7) at an Eh of +600 mV. The Fe sediment was the most easily weathered material, probably because of the presence of more easily soluble oxides. The concentrations of di and trivalent cations in all the aerobic DOC-rich solutions, particularly Fe and Mg, were far in excess of mineral stoichiometry. Filtration experiments revealed that the degree of weathering might not be as high as first indicated, the DOC keeping large particles or colloids in solution which otherwise would have been removed by centrifugation at 4500 rpm. The type and concentration of DOC affected the degree of weathering. Increasing the DOC concentration 6 times resulted in only a doubling of the weathering rate after 400 hr. The non- linear response suggests dissolution is still primarily controlled by the rates of surface reactions. Under anaerobic conditions (Eh of +200 mV) the peat-DOC solutions were only as effective at weathering as the control solutions of the same pH after 400 hr.

Adsorption of DOC by the minerals and sediment was substantial at an Eh of +600 mV, being 50% of the original concentration after 400 hr. The Fe sediment was slightly more effective in adsorbing DOC than the pure minerals clinochlore and microcline. In anaerobic solutions, DOC adsorption by the minerals and sediment were negligible and remained small (<20%) even after the solutions were oxidized to an Eh of +600 mv.

The thermodynamic model SOILCHEM (Sposito et al., 1988) can be effectively used to predict inorganic speciation. However, the accompanying stability constants, in conjunction with the complexation capacity formula for fulvic acid, greatly under predict the number of cations bound by DOC as determined in the o-phenanthroline method. The program can be modified by adding new and more applicable stability constants and has the provision for exploring adsorption phenomena. Most of the 300 mg/L leaf-DOC was in the <0.10 µm fraction, where the majority of Fe enrichment occurred, compared to the control solutions. If complexation capacities offered by Rashid (1985) are used, most of the discrepancy between the complexation determined by o-phenanthroline (which probably includes cation exchange, being difficult to separate from complexation), and SOILCHEM would be eliminated. Adsorption of complexes and metals onto the surface of the DOC would account for the remaining enrichment.

The presence of inorganic colloids and particles makes predicting the effects of DOC, both on metal transport and mineral weathering, based solely on thermodynamic models most difficult. Artifacts of the employed methodologies (e.g. centrifugation) can greatly influence the data, making it important to clearly state the methods used. Since the SOILCHEM program assumes a thermodynamic equilibrium state will be achieved, something that probably does not occur in the fragments of natural systems that are studied. The value of models based solely on thermodynamics are therfore greatly reduced. SOILCHEM does contain the means for entering adsorption data, however, determining meaningful data for input is a difficult task.

Although the experiments provided useful information concerning the ability of DOC to weather minerals under different conditions, little new can be added to the theories of Weber (1988) and, Zutic and Stumm (1984) about the mechanisms whereby organic acids increase the rate of mineral weathering. It may be the result of: complexation forcing thermodynamic balancing of solubilities as Weber (1988) suggests; through direct surface interactions between organic acids promoting preferential weathering as Zutic and Stumm suggest (1984); as a positive feedback between weathering, which promotes an increase in pH, and the organic acids which respond by releasing more H^+ ions to promote weathering. Not only does it appear that all three mechanisms contribute to organic acids being more effective in weathering minerals than strong inorganic acids of the same measured pH, but the organic acids serve as adsorption sites for inorganic complexes, further promoting dissolution and increasing the total mobile metal fraction.

In the Schefferville fens it is possible that the lower Eh at the base of the fens aids in keeping the DOC in solution, preventing it from adsorbing onto mineral surfaces, even when the DOC percolates below the sediment boundary.

However, the lower Eh also nullifies the complexation and adsorption ability of the DOC. Therefore, in this environment where the mobility of cations is normally enhanced by reduction weathering, it is not further exaggerated by the presence of DOC. In fact the weathering of minerals may occur at a slower rate than in the oxidized terrestrial environment were DOC can be more active.

6.2 Areas for Future Research

The most important, yet difficult, area for future research lies in understanding the properties of DOC or organic acids in general. The key as indicated by Ziechmann (1988), probably lies in understanding the functional groups and the internal bonding patterns of DOC molecules. A natural off shoot of such research will be the determination the ability of organic acids structures to cope with environmental changes, particularly Eh and pH. However, the structures of the organic acids that make up DOC of natural waters may prove to be random, or at least extremely variable, therefore a statistical modelling approach maybe more useful for studies involving natural solutions. The determination of complexation capacities for different types of DOC under varying environmental conditions, perhaps derived in a manner similar to Sposito et al. (1981), are therefore required. Breaking the

DOC down into components as described by Bracewell et al. (1988) maybe used to identify the "active fraction or fractions" of DOC, thereby simplifying and improving the accuracy of the models. An understanding of how the DOC competes for metals with inorganic ligands is required to in turn understand possible kinetic factors.

Information concerning the adsorption ability of organic acids is lacking. Little is known about the physical properties (ie available surface area, shape, charge, strength of charge etc.) that are required to create adsorption models. Studies using a multi technique approach of exchange resins, XRD (Thurman et al., 1982) or SEM could be used to separate adsorbed and bound metals as well as determining if inorganic complexes are adsorbed. Every analytical technique has at least one flow that creates estimation errors, therefore more than one method of investigation is needed (Weber, 1988). More information is required concerning the limitations of these methods and ways of minimizing associated problems. Finally, the stability constants and adsorption data need to be correlated and translated into a model similar to that of SOILCHEM.

All the laboratory investigations mentioned above will provide a better understanding of DOC and its ability to enrich solutions with metals under varying conditions.

However, in the end, all these studies must be corroborated by field observations. How much metal is DOC actually moving in the environment and what are the fluxes, forms and sinks of DOC? What other factors such as speed of water flow, dilution, temperature, freeze thaw cycles, and the activity of inorganic ligands, are important in affecting the activity of DOC? How does DOC change in its ability to weather and transport metals in its progression from source to sink? The best initial source for this data is the environment itself, therefore measurements need to be accurate and numerous in order that simpler models can be developed to understand the processes involved.

Appendix I

The modified Walkley Black method of determining DOC concentrations.

Chemicals

H_2SO_4, H_3PO_4
Ag_2SO_4, $K_2Cr_2O_7$, NH_4FeSO_4, Barium diphenylamine Sulphonate.

Reagents

Acid - a 2:1 ratio of $H_2SO_4:H_3PO_4$ and 0.5 g/100ml of Ag_2SO_4

Dichromate - 0.00864 M $K_2Cr_2O_7$ in distilled H_2O (2.542 g/L)

Titrant - 0.02448 M NH_4FeSO_4 (9.6 g/L) and 5 ml/L of H_2SO_4

Indicator - Barium diphenylamine sulphonate

Procedure

1) Measure the absorbancy of the sample to determine the amount of sample needed, or if dilutions are required. Recommended concentrations for absorbancies measured at 330 nm in 1 cm^3 cells are:

100 ml	0-0.1
50 ml	0.1-0.2
25 ml	0.2-0.3
15 ml	0.3-0.4
10 ml	0.4-0.6
5 ml	>0.6.

2) Evaporate 25-250 ml of DOC solution to dryness at 105°C.

3) Pipette 10 ml of dichromate solution into flask. Add 25 ml of acid and swill flask to dissolve all the residue. Transfer all the solution, rinsing flask with distilled water, into a heating tube, and heat for 3 hr at 100°C. Make 4-5 blanks.

4) Dilute the solution to 200 ml with distilled water, add 1 ml of indicator and titrate with titrant.

Calculations

$$\text{DOC} = \frac{\text{V. tit. for Blk} - \text{V. tit for samp.}}{\text{V. tit. for blank}} \times \text{size corr.} \times 1.28$$

Size corrections based on volume of sample.

250 ml - 6
150 ml - 12
100 ml - 15
75 ml - 22.5
50 ml - 30
25 ml - 60
15 ml - 120
10 ml - 150
5 ml - 300
2.5 ml - 600

Appendix II

Composition of the minerals used in the dissolution experiment of Chapter 3, presented as oxide ratios.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3*	MnO	MgO	CaO	NaO	K_2O
					%				
Clin.	30.63	0.17	25.40	7.35	0.09	24.41	0.18	<0.01	0.47
Mic.	66.40	0.01	19.03	0.13	0.02	<0.01	0.02	2.48	12.27
Fe Sed.	62.83	0.51	10.14	18.72	0.19	0.90	0.27	0.42	2.42

	P_2O_5	V	Cr_2O_3	Ni	BaO	LOI	Total	FeO	Fe_2O_3
	%	ppm	ppm	ppm	ppm	%	%	%	%
Clin.	0.02	116	40	34	810	12.01	100.84	4.81	2.01
Mic.	0.01	<10	<15	29	<10	0.05	100.40	0.05	0.07
Fe Sed.	0.10	77	91	37	575	4.18	100.76	0.61	18.05

Clin=Clinochlore; Mic=Microcline; Fe Sed=Fe sediment

X-ray fluorescence of the rock powder was conducted by the Geochemical Laboratories, Dept. of Geology, McGill University. Detection limit of major elements was 0.01%, for Cr_2O_3: 15 ppm, rest: 10 ppm. * Total iron present was recalculated as Fe_2O_3. Ferrous iron, FeO(%), was determined using ammonium metavanadate titration and Fe_2O_3 by subtracting from total iron determined by x-ray fluorescence. Detection limit was 0.01 %

Appendix III

Dissolution Data From Weathering Experiment

Clinochlore in 50 mg/L Peat DOC

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.9	-
10	0.0*	0.8	1.3	1.5	0.4*	0.0*	0.0*	4.0	7.2	11
20	0.0*	1.8	1.1	1.3	0.5*	0.0*	0.0*	4.7	7.0	14
50	0.0*	5.7	1.8	2.7	0.3*	0.0*	0.0*	10.6	7.0	33
100	0.0*	8.2	1.9	3.1	1.9*	0.0*	2.2	17.3	7.3	28
400	0.0*	5.5	1.3	7.0	1.0*	0.0*	1.8	16.5	7.2	34

Clinochlore in 50 mg/L Leaf DOC

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.9	-
10	0.4	3.5	0.9	2.9	0.9*	0.0*	0.8*	8.9	6.6	7
20	1.0	5.7	0.8	2.8	2.2	0.0*	3.1	15.7	6.7	9
50	0.4	7.3	1.8	3.6	0.9*	0.0*	2.2	16.2	7.2	27
100	0.8	7.9	1.2	3.6	1.8	0.0*	3.5	18.9	6.7	21
400	1.6	14.9	1.6	5.3	2.8	0.0*	4.8	30.9	7.3	33

Clinochlore in 300 mg/L Leaf DOC

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.0	-
10	1.4	10.0	1.5	10.4	2.3	0.0*	0.0*	25.6	6.4	28
20	1.6	9.9	1.6	9.9	2.3	0.0*	0.0*	25.3	6.7	31
50	1.9	12.2	2.5	11.0	3.6	0.0*	0.2*	31.3	7.0	38
100	2.6	18.7	2.1	11.8	3.9	0.0*	0.7*	39.3	7.3	42
400	5.3	25.4	2.1	13.8	5.6	0.0*	3.5	55.7	7.4	64

Clinochlore in Water

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.7	-
10	Tr*	1.6	1.3	1.7	0.1*	0.0*	1.0*	5.7	6.8	5
20	Tr*	1.8	0.9	1.8	0.1*	0.0*	0.9*	5.6	6.8	6
50	Tr*	2.9	1.8	2.3	0.1*	0.5*	1.1*	8.8	7.0	6
100	Tr*	4.8	0.6	2.6	0.1*	0.7*	1.3*	10.1	7.1	12
400	0.0*	6.3	1.9	5.1	0.1*	1.4	1.1*	15.9	7.5	14

Clinochlore in Anaerobic 50 mg/L Peat DOC

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-
10	0.0*	9.0	1.2	5.8	0.0*	0.0*	1.7	17.7	6.1	1
20	0.0*	9.2	1.1	6.0	0.0*	0.0*	2.1	18.4	6.0	2
50	0.0*	6.6	0.7	2.1	0.0*	0.0*	1.7	11.1	6.1	2
100	0.0*	7.7	1.0	2.7	0.0*	0.0*	2.5	13.9	6.0	1
400	0.0*	8.5	1.7	6.6	0.3*	0.0*	5.2	22.3	6.5	2

Clinochlore in $1x10^{-5}$ M HCl

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-
10	0.2	1.6	1.6	1.5	0.2*	0.4*	0.3*	5.7	6.4	0
20	0.1	1.6	1.4	1.5	Tr*	0.4*	0.6*	5.7	6.6	1
50	Tr*	2.1	1.6	2.2	Tr*	0.5*	0.8	7.2	6.9	1
100	0.0*	3.1	1.5	2.4	Tr*	0.7	1.1	8.8	7.1	2
400	0.0*	6.2	2.3	5.2	Tr*	1.4	1.1	16.3	7.2	2

Microcline in 50 mg/L Peat DOC

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.9	-
10	0.1*	0.1	1.2	1.7	0.2*	0.0*	0.3*	3.5	7.6	17
20	0.0*	0.0*	1.2	1.9	0.3*	0.0*	0.4*	3.8	7.2	20
50	0.0*	0.0*	2.6	3.3	0.2*	0.0*	0.0*	6.1	7.2	22
100	1.2	0.0*	2.1	4.4	0.5*	0.0*	1.2*	8.9	7.3	18
400	6.0	0.0*	2.3	3.6	1.0*	0.0*	3.0*	15.9	6.9	18

Microcline in 50 mg/L Leaf DOC

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.3	-
10	0.3	0.4	1.1	3.9	0.5*	0.6*	0.1*	6.9	6.1	5
20	0.3	0.5	1.2	4.2	0.6*	0.7*	0.2*	7.7	6.6	6
50	0.9	0.4	2.3	4.6	0.7*	0.4*	0.4*	9.5	6.4	5
100	1.1	0.4	1.0	4.8	0.9*	0.1*	1.0*	9.2	6.1	6
400	2.0	0.8	2.1	6.4	1.0*	0.5*	2.7	15.5	6.1	4

Microcline in 300 mg/L Leaf-DOC

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.0	-
10	0.6	2.6	1.6	11.3	0.7*	4.1	0.0*	20.8	5.7	10
20	0.6	2.1	1.7	10.9	0.6*	3.5	0.0*	19.5	5.75	6
50	1.0	2.4	2.7	11.3	0.6*	3.8	0.0*	21.8	5.5	9
100	1.6	2.7	1.5	12.4	0.9*	4.0	0.0*	23.0	5.6	8
400	3.8	2.8	3.0	15.5	1.4*	3.4	0.0*	29.9	6.1	6

Microcline in Water

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.7	-
10	Tr*	0.3	0.8	1.8	0.1*	0.0*	0.5*	3.4	6.8	4
20	Tr*	0.4	1.3	2.0	0.2*	0.0*	0.6*	4.5	6.4	3
50	Tr*	0.1	2.2	3.2	0.1*	0.6	0.8*	7.1	6.6	7
100	0.1	0.1	1.0	3.7	0.3*	0.1	1.3*	6.5	6.7	7
400	0.1	0.3	2.5	5.7	0.3*	0.6	2.3	11.8	6.5	5

Microcline in Anaerobic 50 mg/L peat-DOC

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-
10	Tr*	0.7	1.3	3.9	0.1*	0.5*	1.1*	6.6	6.2	1
20	Tr*	0.7	1.3	4.2	0.1*	0.5*	1.0*	8.0	6.3	2
50	0.1	1.2	1.1	4.9	0.0*	0.4*	0.7*	8.4	6.4	2
100	0.4	1.3	1.6	5.5	0.2*	0.0*	1.7*	10.9	6.5	2
400	0.9	0.5	0.8	6.8	0.2*	0.0*	1.8*	11.1	6.4	2

Microcline in 10^{-5} M HCl

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-
10	0.0*	0.1	1.6	2.1	0.1*	0.2*	0.2*	4.4	6.5	0
20	0.0*	0.1	1.9	2.5	0.1*	0.3*	0 2*	5.1	6.0	0
50	0.0*	0.1	1.9	3.0	0.1*	0.3*	0.5*	6.0	6.1	0
100	0.0*	0.1	1.9	3.5	0.2*	0.2*	1.1*	7.0	6.5	0
400	0.0*	0.2	2.5	6.4	0.3*	0.3*	2.7	9.7	6.5	0

Fe Sediment in 50 mg/L Peat-DOC

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.0	-
10	4.7	0.0*	1.0	0.5	1.7*	0.0*	4.0	12.0	6.6	9
20	7.7	0.0*	1.2	0.5	2.3	0.0*	4.8	16.6	6.4	9
50	29.8	0.0*	1.9	1.7	5.3	0.0*	10.3	49.0	6.5	10
100	53.9	0.0*	1.7	5.2	21.0	0.0*	37.9	119.8	6.4	9
400	67.3	0.0*	1.1	7.3	32.5	0.0*	55.9	164.1	6.6	7

Fe Sediment in 50 mg/L Leaf-DOC

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.3	-
10	6.8	0.5	0.9	1.8	2.8	0.0*	5.1	17.8	5.8	1
20	6.3	0.5	0.9	1.8	2.8	0.0*	5.0	17.3	5.8	1
50	7.6	0.6	1.8	2.2	3.0	0.0*	5.7	21.0	6.5	3
100	18.2	0.7	1.5	3.2	7.0	0.0*	13.3	43.9	5.9	3
400	47.7	1.6	1.5	6.2	18.5	0.0*	32.6	108.1	6.4	3

Fe Sediment in 300 mg/L Leaf-DOC

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	5.0	-
10	2.8	1.7	1.1	5.6	1.5	0.0*	0.0*	12.8	5.7	5
20	2.5	1.3	1.0	5.3	1.5	0.0*	0.0*	11.6	5.8	6
50	28.6	4.1	2.3	9.8	14.2	0.0*	20.0	79.0	5.9	7
100	37.8	5.1	0.0*	10.9	19.6	0.0*	29.5	103.0	5.8	7
400	41.2	3.9	2.4	12.7	25.6	0.0*	37.6	123.0	6.7	16

Fe Sediment in Water

Time	Fe	Mg	Na	K	Al	Ca	Si	Total	pH	Alk
(hours)					ppm					
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.7	-
10	4.4	0.3	0.6	1.1	2.0	0.0*	4.2	12.6	5.8	0
20	4.0	0.3	0.6	1.0	2.0	0.0*	4.5	12.2	5.8	0
50	5.3	0.4	1.6	1.4	3.2	0.0*	8.0	19.8	5.9	0
100	0.3	0.3	0.6	0.7	0.3*	0.0*	3.4	5.7	5.3	1
400	20.0	1.6	2.0	5.8	15.7	Tr *	35.8	80.9	5.6	0

Fe Sediment in Anaerobic 50 mg/L Peat-DOC

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-
10	0.0*	0.9	1.4	3.5	0.1*	1.0	1.6	8.4	6.8	5
20	0.0*	0.5	1.5	3.5	0.2*	0.7	2.0	8.4	6.9	5
50	1.7	0.0*	1.2	2.2	1.1*	0.0*	3.8	9.9	6.5	2
100	2.5	0.0*	1.5	2.3	1.5*	0.0*	4.8	12.5	7.3	7
400	5.5	1.4	1.6	4.2	2.6	0.0*	8.2	23.4	7.4	13

Fe Sediment in 10^{-5} M HCl

Time (hours)	Fe	Mg	Na	K	Al ppm	Ca	Si	Total	pH	Alk
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-	-
10	0.0*	0.4	1.6	0.7	0.2*	0.5*	0.9	4.2	6.0	0
20	0.0*	0.4	1.5	0.6	0.1*	0.5*	1.1	4.3	6.1	0
50	2.5	0.4	1.5	1.2	1.7*	0.2*	6.0	13.5	5.7	0
100	2.2	0.4	1.6	1.4	1.6*	0.2*	6.6	14.0	5.5	0
400	2.7	0.6	1.8	2.3	2.1	0.2*	10.4	20.1	5.5	0

* Concentrations were below accurate detection levels but the value is considered a good approximation.
Tr = Trace.
\- = no measurement taken.

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