

*Thesis
2351*

Rock, soil and soil water chemistry in the Loch Dee Catchment, S.W. Scotland:
Implications for the release of Al.

Submitted for the degree of
Doctor of Philosophy

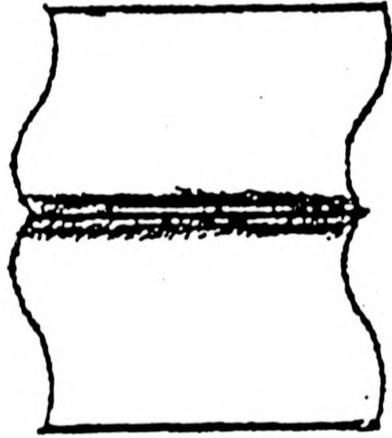
Rachel Louise Marsden B.A. Hons (Oxon)

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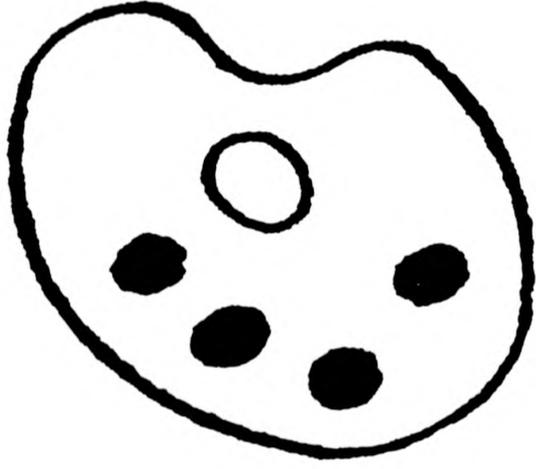
Department of Environmental Science,

University of Stirling.

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ABSTRACT

The solid geology of the Loch Dee catchment was characterised according to chemistry and mineralogy. The chemistry of weathered and unweathered rock samples were compared. Differences noted did not conform to the weathering scenarios of Goldich. The results, which were explained with reference to weathering rates, supported previous observations on base flow water quality in the area.

The drift geology of the area was characterised chemically and texturally and found to be of mixed local origin. Soils in the area were sampled and analysed. They exhibited some chemical differences due to soil profile type. The lack of soil chemical variation due to geology was explained by the mixed drift component of the soil parent material. Soil thin sections highlighted the heterogeneity of drift material in the soil and indicated drift cover was not uniform. Movement of organic material through the soil profile was identified and considered important in the transport of Al within the catchment.

Soil waters were sampled at monthly intervals over a 15 month period. Chemical analyses indicated a strong maritime influence that gave rise to seasonal variations. Other patterns in the soil water chemistry were explained by changing temperature and biological uptake throughout the year. Solutions extracted from soils overlying diorites and granodiorites were found to be relatively enriched in Al. Other chemical differences identified were thought to be related to soil site distinctions.

Soil waters extracted from soils overlying diorites had greater concentrations of Si than those extracted from soils over granodiorites. Concentrations of Al in these soil waters were related to soil water DOC concentration. This masked the role of Si in influencing Al form and further work is required to determine this relationship. DOC appeared to control the form of Al in solution - dialysed fractions of Al (potentially toxic) were less concentrated where solution DOC was greater. The presence of this and other ions in solution caused Al solubility to deviate from standard $\text{Al}(\text{OH})_3$ controls. Fractions of Al < 2.4 nm conformed to reversible non-ideal aluminosilicate mineral solubility controls.

The possible presence of hydroxyaluminosilicate species in the soil waters was identified. These were disordered, probably in the form of proto-imogolite allophane. The presence of such species indicated an alternative mechanism for the movement of Al through the soil profile. XRD work on the soils in the area would be useful to positively identify the presence of imogolite or proto-imogolite.

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This thesis is dedicated to Sandy.....

'Shine on.....'

CHAPTER 1 :Introduction

1.1 Acidification of the environment.

Acid rain has been suggested as the cause of much environmental damage within the Western world e.g. the decline of Germany's Black Forest, loss of fish stocks in Sweden, Norway and Scotland and the destruction and decay of many architectural masterpieces. Rain water is naturally acidic with a pH of 5.6, the theoretical pH of 'pure' water in equilibrium with dissolved CO_2 at atmospheric conditions. It is only described as acidic, however, when its $\text{pH} < 5.6$ implying the presence of more than CO_2 as impurities in the water. Acidifying compounds included in acid rain may vary but the most important are SO_2 , NO and NO_2 , (collectively referred to as NO_x) together with their reaction products. Oxidation and acid/base reactions convert these gases to acids and airborne particles or aerosols e.g. HNO_3 , H_2SO_4 , SO_4^{2-} and NO_3^- (Fowler et al 1985, Kennedy 1986). In this way, the 'acidity' of rain water is dependent on its proximity to pollutive sources.

Acid rain is a collective term encompassing all possible routes for the deposition of acidifying pollutants from the atmosphere. These include wet deposition, (deposition of pollutants dissolved in precipitation either as rain or snow), dry deposition, (the adsorption of gases and/or aerosols directly from the atmosphere) and occult deposition (deposition of pollutants in fog and dew). These forms of 'acid rain' affect areas exhibiting specific natural and anthropogenic features to different degrees. Wet deposition is most important in areas of high rain and/or snowfall. Since these typically increase with altitude, upland areas are often most prone to deposition in this form. Forested areas are prone to acid rain mostly through dry and occult deposition.

A recent study by Nisbet et al (1992) suggested occult deposition in a forested upland area could be as much as 180% of that in a similar moorland area due to the increased scavenging ability of forested areas for pollutants. Conifers have a greater capacity than most broadleaves for scavenging pollutants from the atmosphere because of the high surface area of their needles, Stokes Law, (Mayer and Ulrich 1983, Miller 1984). Sitka spruce was shown by Miller et al (1991) to especially enhance the interception and subsequent cycling of anthropogenically deposited sulphur. Coniferous plantations generally tend to exhibit the effects of acidification more rapidly than broadleaved plantations although in the absence of pollution, forested zones need not necessarily increase environmental acidification (Miller 1985). In addition to forested zones any area susceptible to fogs and low lying clouds will be affected by occult deposition (Dollard et al 1983).

Research concerned with the causes and effects of acidification has been executed at an individual scale and by large teams of workers. The Surface Water Acidification Programme (SWAP) involved the collaboration of some 30 research groups and a wide variety of institutions and disciplines within Britain, Norway and Sweden. It was designed to study the main physical, chemical and biological processes involved in acidification of surface waters, (Mason 1990). Other smaller scale ventures have been of great importance e.g. Loch Fleet and nearby Loch Dee projects. The Loch Fleet project assumed the loss of fish from this loch in SW Scotland was caused by a change in water quality (Howells and Brown 1987). The project explored the potential of a variety of ameliorative techniques including the liming of both land and surface waters and found short term solutions for the fish survival (Howells and Dalziel 1992).

1.2 Natural versus anthropogenic acidification.

There has been considerable disparity in the literature concerning the importance of acid rain as a cause of environmental acidification. Many authors have stressed the natural acidification of soils and subsequently waters through time (Krug and Frink 1983, Cresser and Edwards 1987). Krug and Frink (1983) denied the necessity of atmospheric input into the ecosystem to cause the current level of acidification. These authors suggested acidification could be brought about by a greater quantity of raw humus in surface waters caused by changing land use practices and/or from the biological oxidation of C,N and S. Kennedy (1986) and Cresser and Edwards (1987) also indicated the possible importance of isolated events such as volcanic activity, thunderstorms and wildfires in the addition of acidifying compounds to the environment. Johnson et al (1984) accepted the existence of natural acidification but refuted the thesis proposing the insignificance of atmospheric acidic input to the problem. Rowell and Wild (1985) also stressed a combination of natural and anthropogenic acidic sources as the causes of soil acidification. Jones et al (1989) used paleolimnological techniques to show the acidification of non-afforested lochs in the Galloway region of Scotland could only be explained by acid rain. Other workers also concluded that long term acidification of the environment resulted mainly from an increase in sulphate in atmospheric deposition, (Skartveit 1981 and Van Breeman et al 1984).

1.3 Response of systems to acidic input - role of the soil.

The response of a system to an input of H^+ ions from the atmosphere varies and depends, to a great extent, on the nature and properties of the soil within that system.

Soil may act as a buffer to neutralise incoming acidity by ion exchange mechanisms (Kennedy 1986). Soils can undergo ion exchange if they possess colloidal clay and/or organic matter. These substances possess a net negative charge arising in the clays because of either isomorphous substitution or clay lattice edges (Krauskopf 1979). These negatively charged particles attract cations to their surfaces in order to retain electrostatic neutrality. Basic cations are more usually found on clays whereas organic matter tends to attract H ions and organic soils are thus more acidic. For ion exchange to occur within a system Bache (1984) outlined the following constraints:

1. There must be excess salt present.
2. Charge balance in solution must be maintained.

Bache also stressed that reactions between acid waters and soils would be more rapid when there was a considerable disequilibrium between the H ion concentrations of the solution and the soil.

The availability of base cations on the soil exchange complex (base saturation), is the principal determinant in the acid neutralising capacity (ANC) of a soil. This presence of cations within the soil environment is principally determined by weathering rate and potential of soil parent material. Primary minerals are decomposed by slow acid hydrolysis reactions (Carroll 1970, Hunt, 1972) releasing cations into the soil where they are available for exchange. If the soil parent material has abundant and easily accessible base cations resultant soils will have a greater base saturation. Therefore, soils derived from basalts usually have a good base saturation and will be able to neutralise most incoming acidity, hence the persistence of small farming communities on fertile slopes of basaltic volcanoes. In contrast, soils formed on highly siliceous

rocks of low weatherability will be base poor and more prone to early acidification.

1.4 The importance of aluminium within the acidification problem.

The association of acid rain with fish decline is proposed by increased mobilisation of aluminium from acid soils. Although the base status of acid soils, by definition, is very low there are typically large amounts of aluminium present on the exchange complex. The form of aluminium on release determines its level of toxicity to fish. Van Breeman et al (1984) looked at the internal proton sources within soil systems and showed that acidic soils impacted by atmospherically deposited sulphate would release inorganic monomeric forms of aluminium. These are toxic to fish (Birchall et al 1989). However, aluminium released from soils may be complexed by ligands that render it non-toxic to fish e.g. aluminium released in storm waters is often associated with organic complexes (Giusti 1991) and is non-toxic. Other complexing ligands that have the effect of decreasing the toxicity of soluble aluminium include fluoride (Moore and Ritchie 1988) and silicic acid (Exley 1989). It is therefore important to determine the form of aluminium in any soil and/or water acidification studies. Many different methods have been proposed in the literature for the determination of the toxic fraction of aluminium (Chapter 6). Exley and Birchall (1992b) tested a number of fractionation methods for the identification of hydroxyaluminosilicate species within synthetic solutions containing aluminium. They proposed that although the formation of such species increased aluminium solubility it actually decreased the toxicity of Al to fish. This link between aluminium and silicic acid was deemed very important in the context of this thesis, since silicic acid is released on rock weathering (Carroll 1970, van Breeman and Brinkman 1976, Johnson 1984).

1.5 Other factors in acidification

Burt (1979) investigated the effect of hydrological pathway on the chemistry of rainwater en route to a stream or loch. He found that if waters entered a soil profile they were buffered relative to those flowing overland. The length of retention time of waters within soils also influences the buffering of acidic components. Thicker and lower angled soil patches lead to greater retention times and better buffering of any acidity, (Cozzarelli et al 1983, Bache 1984).

The susceptibility of a catchment area to the inputs of acid rain will also be determined by seasonal and temporal factors such as the proximity of the coast e.g. sea salt events (Wilklander 1975) and frequency of storm events. Langan (1986) looked into the acid surge effects in streamwater associated with the input of large quantities of seasalts from coastal rains. He found that the greater concentrations of sodium in coastal rain led to the release of H^+ ions into the aquatic system by exchange between the rain and the acidified soil exchange complex. This resulted in a decrease in streamwater pH leading to an 'acid surge'. These sea-salt events can be beneficial in the short term to the base status of soils with Na^+ being retained on the release of H^+ . However, these cations will typically be exchanged for H^+ through time leading to the re-acidification of the soils. Acid surges can also occur following snowmelt (Drablos and Tolland 1980). Ionic impurities in snow tend to fractionate into early melts resulting in large concentrations of pollutants, especially nitrates, being released and causing acidification.

The frequency and impact of storm events has been considered by many workers (Burt

1979, Reid et al 1981a, Skartveit 1981). These have shown storm events to result in an increase in stream flow accompanied by increases in acidity, concentration of Al and dissolved organic carbon (DOC). The concentration of base cations usually decreases at these times due to both dilution and the source of most surface storm waters being from the organic horizons of soils. These responses, however, are dependent on antecedent soil moisture conditions. If a storm follows another storm this response is unlikely whereas if a storm follows a dry period these features can usually be noted (Walling and Foster 1975).

1.6 Sensitivity of catchments to acidification and predicting responses.

The sensitivity of a catchment to acidification is thus very complex involving at least two scales of time and many interacting variables. The Department of the Environment has recently used the Critical Loads system, originally used by the Canadian government in the 70's, to determine the sensitivity of areas to acid input. This data thirsty system can be applied to soil and/or water quality parameters and the results used to suggest whether or not a particular system is prone to acidification and also for future predictions to determine whether planned decreases in emissions would improve the lot of currently sensitive areas. The critical loads approach, however, uses mean data and does not recognise short term fluctuations like low the pH events associated with the increased solubility of aluminium. Application of the critical loads system to the soils and waters of the same catchment produced some contrasting results, (Langan and Harriman 1992) and highlighted the poor definition of the system as a whole when viewed for a small catchment.

The desire to predict the responses of the environment to both changing and constant deposition pollutant levels has led to the production of many chemical models working at both a long and short (episodic) time scale. Long term models take account of current deposition levels and estimates of how they have varied historically. They also involve estimates for weathering which are extremely difficult to obtain; much research has gone into this problem alone (Reid et al 1981b, Wilson 1986, Jacks 1990, van Grinsven and van Riemsdijk 1992).

The MAGIC (Model of Acidification of Ground-water in Catchments) model of Cosby et al (1985, 1986) was explicitly designed to perform long term simulations of changes in streamwater chemistry in response to changes in acid deposition. It is basically a chemical model driven mainly by changes in sulphate inputs. The Birkenes Model of Christopherson et al (1982) is a hydrochemical model designed to simulate short period changes in stream-flow and chemistry and to account for the episodic and seasonal variations within the chemistry. The ILWAS (Integrated Lake Watershed Acidification Study) model of Gherini et al (1985) is a more sophisticated and data intensive short term hydrological response model that pays particular attention to chemical changes due to water routing.

These models have been applied to many catchment sized studies throughout Britain and Norway (Whitehead et al 1986, Whitehead and Neal 1987, Whitehead et al 1988, Jenkins et al 1988, Stone et al 1990). However none of them successfully account for dual time nature of the acid sensitivity problem. Robson et al (1991) suggested a way towards predicting the future episodic changes in stream chemistry using a

combination of a long term model (MAGIC) and an end member chemical mixing approach. This was applied to the Afon Gwy catchment at Plymlimon in Wales and the model produced a good fit to observed present day stream, soil and baseflow chemistry.

1.7 Current aims: the problem outlined.

Theoretical considerations outlined in this section indicate that variation within the solid geology of a catchment area may be reflected in soil chemical characteristics such as soil base status and ANC. Additionally, differences in soil parent materials may result in a variable input of aluminium in both form and amount to the aqueous environment. This project aimed to see if these hypotheses could be supported by work at Loch Dee.

The study area: The Loch Dee basin, S.W. Scotland.

The area chosen for the study was Loch Dee situated in the Galloway hills in SW Scotland, (see inset of Figure 1.7A for location details). Loch Dee forms the head-water of the Kirkcudbrightshire River Dee. The Loch has a surface area of 1km² and a total catchment area of 15.6 km². The area has been the focus of an investigation into the effects of acidification on forestry and fisheries since 1979. This project is coordinated by the Solway River Purification Board (SRPB), the Forestry Commission and the Scottish Office Agriculture and Fisheries Department (SOAFD).

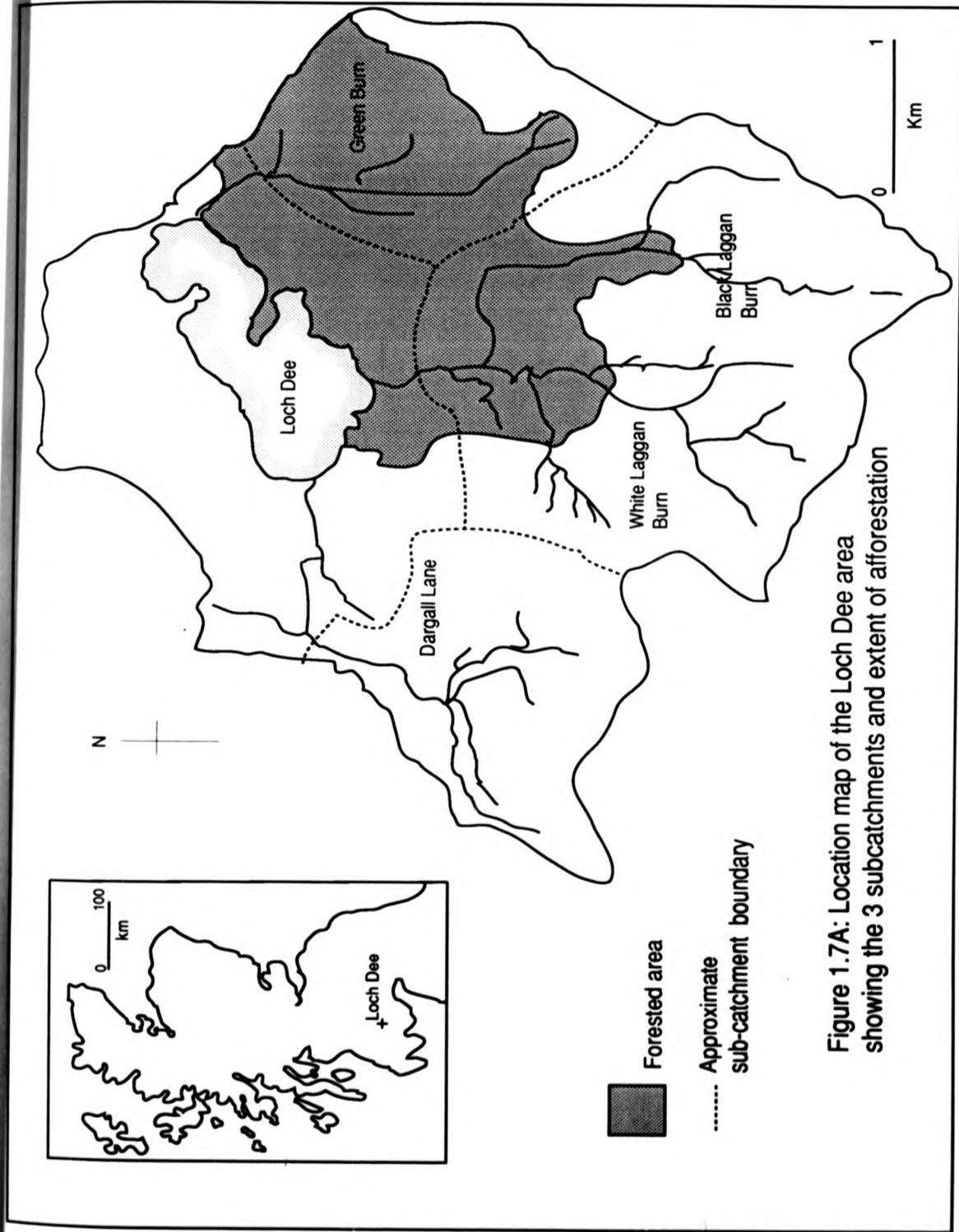


Figure 1.7A: Location map of the Loch Dee area showing the 3 subcatchments and extent of afforestation

The catchment area is subdivided into 3 sub-catchments, shown in figure 1.7A, which show different characteristics:

1. The Dargall Lane sub-catchment is not afforested, has a high mean angle of slope and typically a poor water quality.
2. The White/Black Laggan sub-catchment is partially afforested (c.30%) has a gentle slope and typically good water quality.
3. The Green Burn sub-catchment shows the highest degree of afforestation (c.70%), a moderate to low slope and variable surface water quality.

For further details of water quality see Burns and Lees (1987) and Lees (1988, 1989, 1990, 1991, 1992).

In the Loch Dee area the soil parent material is a combination of solid and drift geology. The solid geology is split into two main types: relatively base rich and more weatherable diorite and granodiorite and relatively base poor and less weatherable greywackes and shales. The drift geology of boulder clays and morainic gravels appears to be widespread throughout the catchment. Despite the local derivation of the drift its presence could cause problems in defining soil parent materials and hence could confuse chemical inputs to the soil system.

Despite the presence of this drift material, work by Welsh and Burns (1987) suggested a geological control over water quality in the Loch Dee catchment. They indicated this was best noted at baseflow conditions where the contrast in water quality between the Dargall Lane and the White Laggan burns was most obvious. A later review paper by

Burns and Lees (1987) further stressed that the pH difference in the streams was primarily due to catchment geology. Following this Grieve (1990b) attempted a systematic comparison of soil water chemistry on different parent materials within the Green Burn sub-catchment. The results of this study led to the conclusion that soil solution chemistry within the Green Burn catchment displayed significant variations that could be related to a number of factors. The parent material control however, was slightly obscured by differences in the depth of organic horizons but the distinct patterns of neutralisation of acidity in 3 plots of different parent material were related to soil variation greater than could be explained by the organic discrepancy alone. The present thesis is an extension of the work of Grieve aiming to determine the reality of a parent material control on the stream water and thus loch water quality in the Loch Dee basin.

In an attempt to decrease the variables affecting soils and their solutions work mainly focused in the White/Black Laggan and Green Burn sub-catchments, south of the afforestation. However, in order to sample particular lithologies, e.g granodiorite, it was sometimes necessary to enter the afforested limits. Giusti had already begun work on a similar theme in the Dargall Lane sub-catchment (1991) so this sub-catchment was not included. In addition, to ensure no confusion with past liming experiments in the White Laggan sub-catchment, the area of application of the lime was avoided for the purposes of soil sampling.

In conclusion an outline of the specific project aims and objectives:

1. To identify geological controls on the soil chemistry in the Loch Dee catchment.
2. To determine in more detail the input of drift material to the soils and the nature of this drift.
3. To ascertain the relationship between soil water chemistry and both soil profile type and solid geology.
4. To test the methods of Al fractionation and speciation of Exley and Birchall (1992) on soil waters and determine if natural soil water silicon was:
 - a. determined by geology,
 - b. capable of controlling the release of toxic Al fractions.

Chapter 2: The solid geology of the Loch Dee area.

2:1 INTRODUCTION

Loch Dee is situated within the Southern Uplands of Scotland. The overall geology of the Southern Uplands region is typified by Ordovician and Silurian sediments and meta-sediments with a few granitic intrusions (figure 2.1). To the north of the Southern Upland fault the region is juxtaposed against igneous and sedimentary rocks of the Scottish Midland Valley. Further north still passing the Highland Boundary Fault metamorphic rocks are most common. Crossing the Scottish Border into the English lake District to the south similar Ordovician and Silurian sediments and meta-sediments are found to outcrop. These generate a topography not dissimilar from the Southern Uplands themselves.

Loch Dee is located on the southern margin of the Loch Doon pluton (fig 2.1A) one of three major Devonian (Old Red Sandstone-ORS) intrusions in the Galloway area. The pluton is a steep sided body extending from Loch Doon in the North to Loch Dee in the south, c. 12 miles. The date of intrusion into the already altered country rocks was estimated by Halliday et al (1979) using Rb/Sr whole rock and U/Pb zircon analyses at some 408 Ma. This corresponded to the end of the Caledonian orogeny following the suture of the Iapetus ocean, (Brown et al 1979).

The geomorphology of the area (plate 2.1A) reflects the susceptibility of the solid geology types to weathering and glacier action. The loch, a topographic depression, is located on weatherable intermediate igneous rocks, plate 2.1A1. High ground south

Figure 2.1 Simplified geological map of southern Scotland

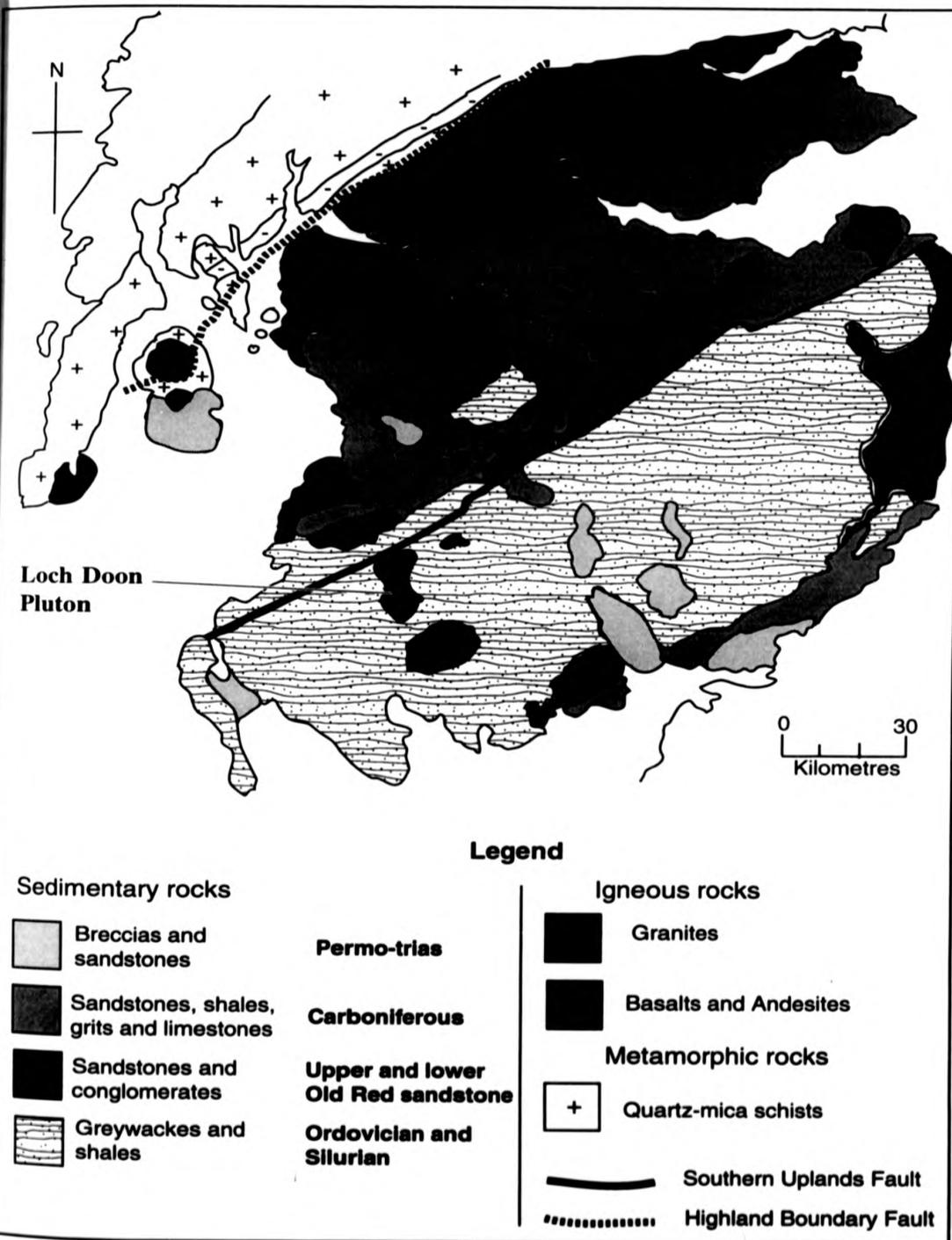


Figure 2.1A Igneous petrology of the Loch Doon pluton

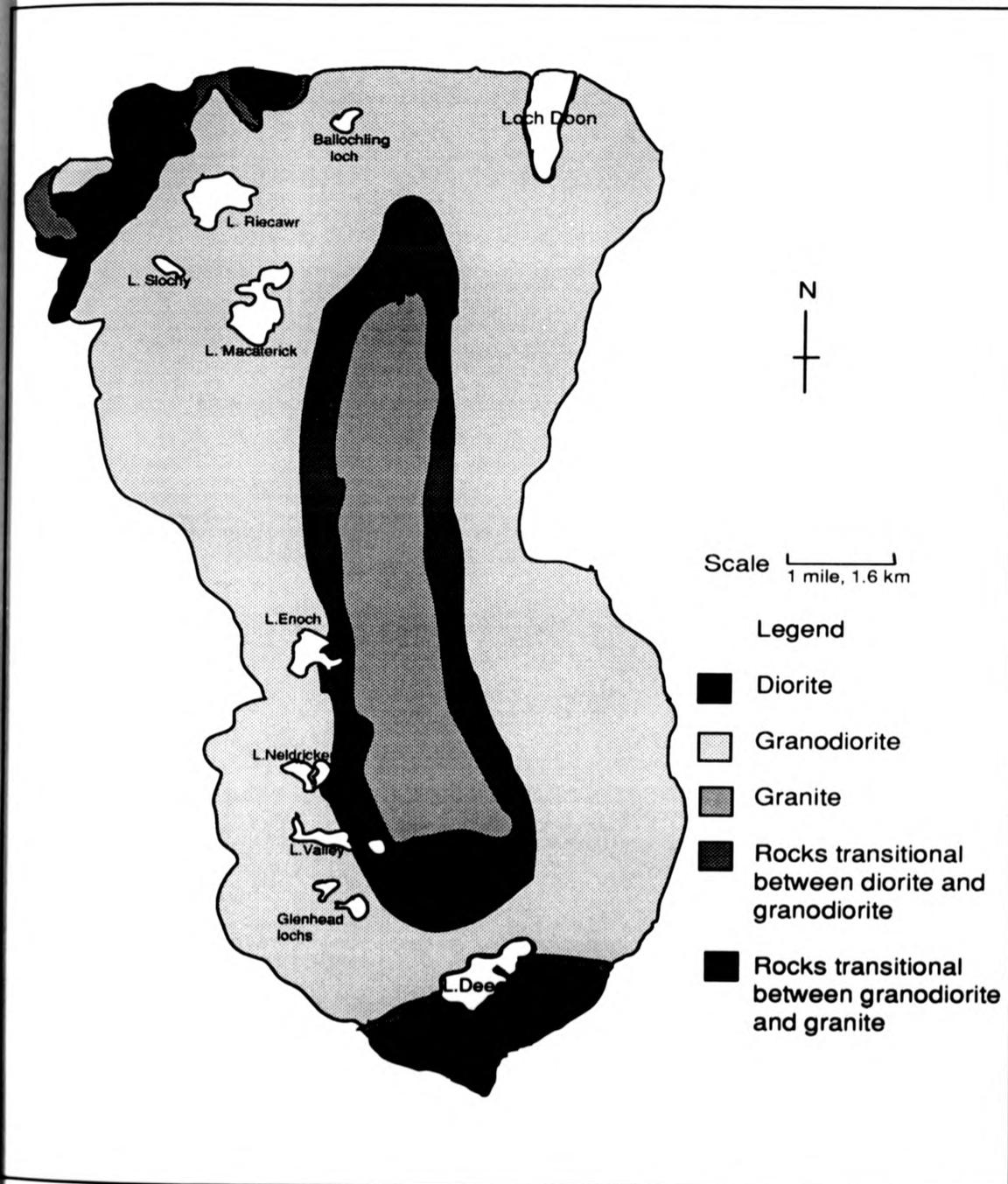




Plate 2.1A: Digitised contours at 10m intervals for the Loch Dee area and the corresponding 3-D map showing the topography of the Loch and surrounding hills.

Geological map of the Loch Dee area :
 Isometric view from the north (x1.5)
 (PLATE 2.1A1)



GEOLOGY
 ORDOVICIAN / SILURIAN
 B4 SHALES AND
 GREYWACKES



B9 BLACK SHALES



B3 SHALES AND
 GREYWACKES



IGNEOUS ROCKS
 MAJOR :



GRANDIORITY



DIORITE SUITE



MINOR :



MINOR DYKES OF
 VARIABLE COMPOSITION
 (LAMPORPHYRES,
 PORPHYRYTES, FELSITES)

of the loch is formed by highly siliceous Ordovician and Silurian meta-sediments. North of the loch resistant granite constitutes the central belt of the Loch Doon intrusion forming spectacular mountainous areas including Craiglee at 1741ft, Mullwharcher at 2270 ft and Hoodens Hill at 1790 ft (plate 2.1B).

2:11 The meta-sediments

The sedimentary sequences found in the Loch Dee area were formed in marine conditions possibly on a continental slope. During the Ordovician, marine incursions resulted in the deposition of some deeper water deposits i.e. the black shales. These outcrop as highly folded beds on both the Curleywee and White Hill summits, (fig 2.1B). The sediments show a prevalent NE to SW strike which was imparted on the rocks of SW Scotland during Caledonian earth movements, (Gardiner and Reynolds 1932). Minor faulting within the area (plate 2.1C) can also be attributed to the same source.

2:12 The Loch Doon Pluton

Figure 2.1A (page 16) based on an original from Gardiner and Reynolds (1932), illustrates the petrology of the Loch Doon pluton. The diagram shows the pluton's concentricity in terms of 'acidity'. Granite occupies the central zone of the pluton with an outer zone composed of more basic granodiorite. Diorite outcrops in the SE and NW corners of the pluton. The boundaries between the different rock types are diffuse. Nomenclature of the rocks within the Loch Doon pluton varies throughout the literature and no single piece of work is in agreement with the terminology adopted on figure 2.1A. Relationships between the nomenclature used in the literature and that

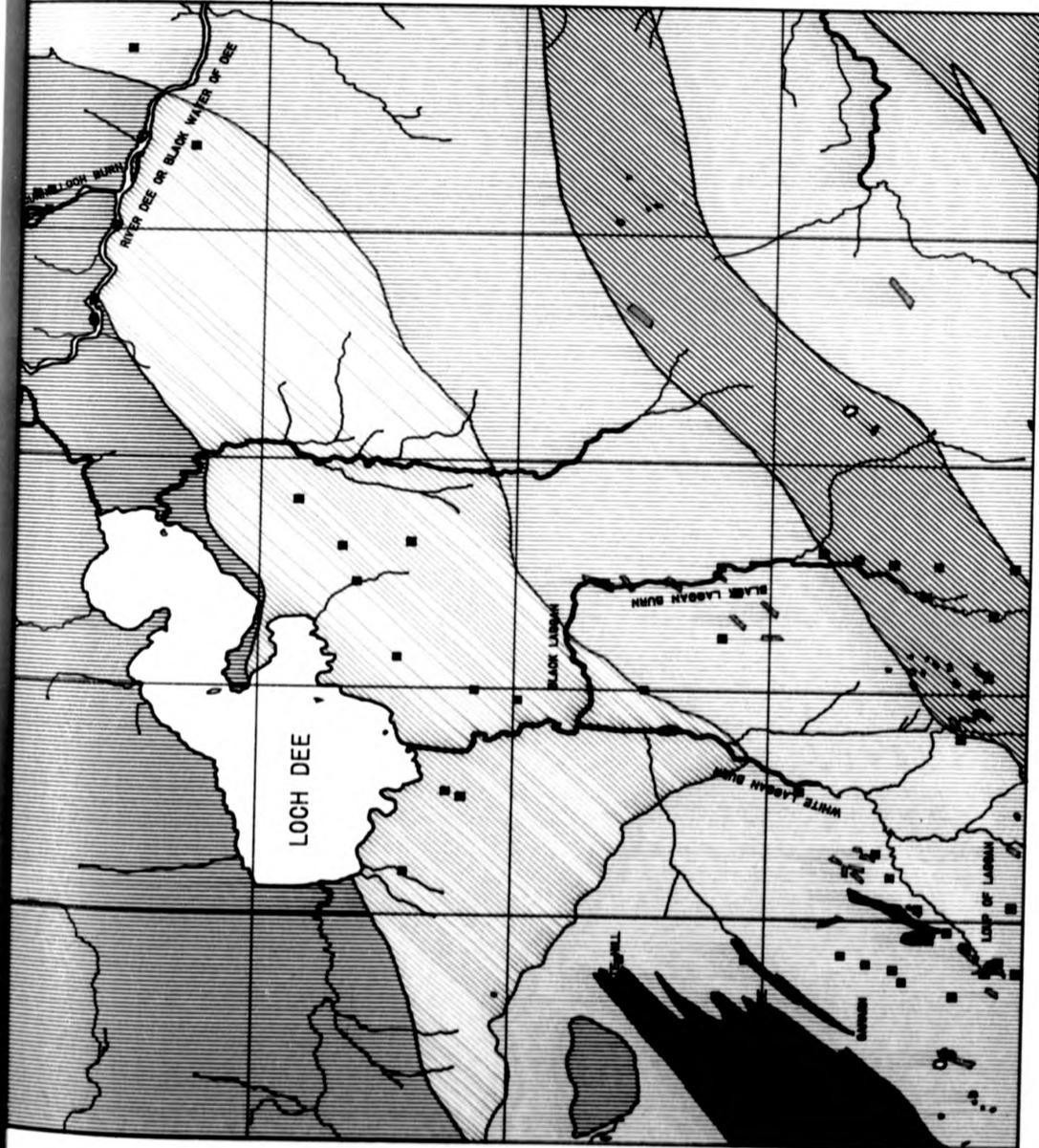


Plate 2.1B: Photograph looking north up the central granite ridge from Loch Dee.



Plate 2.1C: Minor faulting within the Loch Dee area.

FIG. 2.1B :
GEOLOGICAL MAP
OF THE LOCH DEE
AREA



LEGEND

GEOLOGY

ORDOVICIAN / SILURIAN



S4 SHALES AND GREYWACKES



S3 BLACK SHALES



S2 SHALES AND GREYWACKES

igneous rocks

MAJOR-

GRANODIORITE



DIORITE SUITE

MINOR-

GRANODIORITE



MINOR DYKES OF
VARIABLE COMPOSITION
(LAMPROPHYRES,
PORPHYRYTES,
FELTSITES)



RIVERS

GEOLOGICAL SAMPLING POINTS



adopted throughout this study, chosen to reflect both the literature and the results from the classification of geological samples (section 5.2), are given on table 2.1A.

Table 2.1A: Nomenclature of the igneous rocks of the Loch Doon pluton from the literature.

	Granite	Granodiorite	Diorite
Teall 1899	Hornblende granitite	Qtz diorite or tonalite	Hyperite or norite
Gardiner and Reynolds 1932	Granite	Tonalite	Norite
Ruddock 1969	Admellites	Granodiorite	Hypersthene rocks -diorites
Brown et al 1979	Granites	Qtz monzonites	Diorites

2.13 Pluton formation

The geological history of the Loch Doon pluton has been debated. Gardiner and Reynolds (1932) suggested the pluton formed as a result of three separate intrusions the first and most basic intrusion gradually being split apart by more acidic and successively later intrusions. Ruddock (1969) showed differentiation trends within the chemistry of the rocks that suggested the magma for all three rock types originated from one source. He used Mg:Fe ratios and Cr content of the rocks to suggest an association with gabbroic material during petrogenesis. Brown et al (1979) produced the most plausible account of the pluton history. They concluded that the form of the pluton resulted from a parental monzodioritic magma generated from meta-basaltic crust which rose and fractionated progressive skins of diorite, quartz monzodiorite and monzonite leaving granitic residual liquids. They suggested this included the assimilation of country rocks which explained some of the petrographical variations

noted within the intrusion, (Higazy 1954, MacIntyre 1947, Rutledge 1950).

2.14 Contact metamorphism within the area

The intrusion of the Loch Doon pluton altered the complex Lower Palaeozoic country rocks. Teall (1899) noted an increasing presence of biotite mica and loss of quartz grain boundaries in the sediments closer to the pluton. Typical metamorphic minerals e.g. andalusite and sillimanite were rarely reported. Garnet, however, was said to be characteristic of contact metamorphic rocks of the Loch Dee area, (Teall 1899).

2.15 Minor igneous intrusions

Dykes were intruded into both the country rock and the igneous mass. Ruddock (1969) studied the dykes 'within' the pluton. He proposed the dykes were of two different phases one pre pluton injection of 'lamprophyre' dykes and one post pluton of a variable composition including both acidic (porphyritic, microgranodiorite, microadmellite and microgranite) and basic (lamprophyre and microdiorite) dykes. Gardiner and Reynolds (1932) suggested most of the dykes intruded into the meta-sediment mass were post pluton as they showed no metamorphic alteration. The characteristics of post-pluton dykes are presented in table 2.1B.

Teall (1899) indicated a few differences:

1. Porphyritic dykes included plagioclase, hornblende and biotite as phenocrysts.
2. Diorite dykes hornblende was deep brown, the presence of biotite was not stressed.
3. Lamprophyres included hornblende as slender prisms.

Table 2.1B: Characteristics of post-pluton dykes according to Gardiner and Reynolds (1932).

Classification	Main mineralogy	Features
Felsites and quartz porphyries	Orthoclase + qz + chloritised biotite + sodic plagioclase	Grey to pinkish rocks with phenocrysts not conspicuous.
Porphyrites	Biotite, hornblende, augite (in samples from Loup of Laggan),	Microcrystalline groundmass. Ferromagnesian minerals g/m or phenocrysts.
Diorites	Qz + biot + hbl (green); this may be most dominant.	Occur as dykes and larger intrusions. Coarse.
Lamprophyres - mica or hornblende	Plag and biot and hbl. Occasional kspar in g/m.	Plag and biot/hbl in laths. Few phenocrysts.

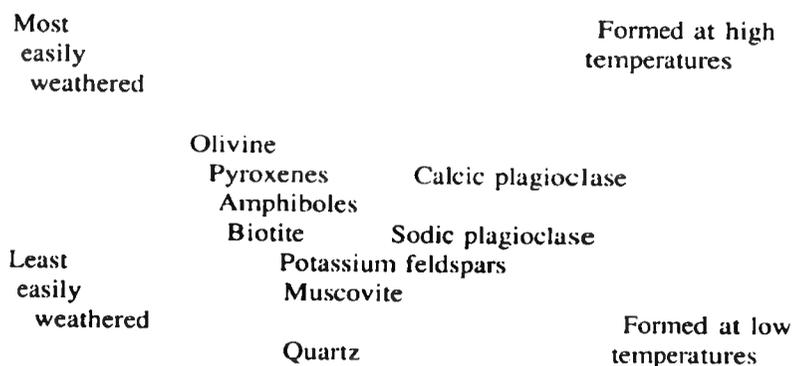
2.16 Rock weathering

Weathering of rocks occurs because of the instability of many common rock forming minerals at earth surface pressure and temperature conditions (Boul et al 1973, Johnson 1984). Goldich (1938) described the weathering of the common silicate minerals in terms of structural complexity, fig 2.16A. This figure corresponds to Bowen's Reaction series which describes the cooling and crystallisation of silicate minerals from a magma.

Silicate mineral structure is based on the arrangement of 4 oxygens around 1 silicon in a tetrahedral arrangement forming the silicon tetrahedron. The degree of linkage between adjacent tetrahedra determines a minerals' structural strength and subsequent susceptibility to weathering. Olivine which crystallises at high temperatures from an igneous melt, is an orthosilicate. Structurally, olivine involves isolated silicon tetrahedra linked only by cations (Fe and/or Mg). This 'weak' structure is prone to weathering. Pyroxene minerals crystallise at lower temperatures and share one oxygen

between adjacent silicon tetrahedra linking them in chains. Cations lie between the chains. Amphibole minerals, which form at lower temperatures, involve more oxygen sharing and form double chains. Micas are formed by the interlink of Si tetrahedra to form sheets. Finally, at the base of the temperature scale, quartz represents a tectosilicate where silicon tetrahedra are linked to form a 3 dimensional framework. This type of structure is very resistant to weathering.

Figure 2.16A Stability of common silicate minerals according to Goldich (1938)



The right hand side of the diagram involves the continuous solid solution series of the plagioclase feldspars. The calcic members of the series e.g. anorthite, bytownite, labradorite are more susceptible to weathering. These members include a greater level of Al substitution for Si within the Si tetrahedron. Each substituted Al provides a weak link and makes a mineral more susceptible to weathering (Johnson 1984).

2.2 AIMS

The main aims of this chapter were:

1. To establish chemical and mineralogical characteristics of the solid geology from the Loch Dee area.
2. To produce a database against which to compare soil chemistry.
3. To determine the likely effects of weathering on the different rock types and compare these with measured findings and literature predictions.

2.3 MATERIALS AND METHODS

2.31 Sampling

The rocks of the Loch Dee area were sampled in November 1989 at locations shown in figure 2.1B. The grid references for these sample points are given in appendix A with sample names and rock types. The material sampled was as 'fresh' as possible; weathered rocks were sampled at 14 of the points. These were collected for comparison of analytical results between weathered and un-weathered samples.

The number of samples taken from each rock type was assessed according to the following factors:

1. The areal outcrop of a particular rock type according to previous geological maps - these indicated diorites and Ordovician meta-sediments to be most common.
2. Variability within a single rock type as identified by previous authors. Gardiner and Reynolds (1932) and Ruddock (1969) suggested greater variability in the diorites than granodiorites. In addition, the meta-sediments were termed complex by many authors, (Teall 1899).
3. Although dyke rocks are only minor occurrences they were sampled thoroughly. It

has often been found that dyke material can drastically influence soil and stream-water chemistry. This was the case at the Loch Chon catchment in central Scotland where the presence of a dolerite dyke increased soil water Ca by a factor of 5 compared with soils in the rest of the catchment (Miller et al 1990). This increased Ca was also noted in stream-waters and highlighted the way geology could contribute significantly to stream water chemistry.

Using these as guidelines the number of samples taken for each rock type was:

Granodiorite (Major)	= 3 + 2 weathered
Diorite	= 12 + 5 weathered
b3 (Ordovician) meta-sediments (mixture of coarse and fine)	= 17 + 3 weathered
b4 (Silurian) meta-sediments (mixture of coarse and fine)	= 8 + 1 weathered
Black shales	= 4
Dyke rocks	= 6 + 2 weathered
Granodiorite (minor)	= 2 + 1 weathered
Others	= 2

2.32 Methods

The rocks were tested for:

1. Major oxide content by X-ray fluorescence (XRF).
2. Trace element content by XRF.
3. Mineralogy by thin section description of the coarse meta-sediments and the igneous material from the area.

2.33 Chemical analytical methods

A representative sample of each rock type, (2 fist sizes for coarse samples and 1 for fine samples - Batcheolar 1980) was transferred to the Grant Institute at Edinburgh University for chemical analysis of major oxides and trace metals by XRF methods. Initial preparation of rock samples included crushing and grinding to a fine powder using a combination of hydraulic rock splitters, jaw crushers and a tungsten carbide tema mill. All equipment was cleaned between samples to avoid cross contamination; this was especially important at the powder stage in the tema pot. Once a rock had been powdered two different routes were followed; one method for major oxides another for trace metals.

Major oxide preparatory procedure.

Major oxide preparation procedure was complex:

1. Rock powder samples were dried by placing a sub-sample into a glass jar at 110°C for at least 2 hours.
2. Once dried a known weight (c.0.9g) of dry rock powder was added to a pre-weighed and clean platinum crucible. 5 x the exact weight of rock powder was the amount of flux (Spectroflux 105) necessary for addition at later stage.
3. The crucible was covered with a lid and placed on a silica tray in a furnace at 1100°C for at least 20 minutes.
4. After heating sample was removed from the furnace and placed on a steel cooling block for 1 minute then in a desiccator before reweighing and calculating the loss on ignition of the sample.
5. The predetermined weight of flux was added to the sample and it was returned to

the furnace for 20 minutes.

6. The sample was retrieved and placed on a cooling block for 20 minutes prior to adding a further small amount of flux.

7. Finally the sample was heated over a bunsen flame and cast by pouring into a steel cylinder. A steel plunger was pressed down on top of the 'glass discs' which were then removed. Each disc was loaded onto an XRF machine, sample number and LOI value input to the computer and analysis made.

Trace metal powder preparation procedure

For trace element analysis of a rock sample a small portion of rock powder was added to 'Miowol' (2% PVA) and Boric acid powder. These were then crushed to form a pellet using a tungsten carbide weight system and finally pressed together using a 8 tonne hydraulic pressure jack for 1 minute. The pellet was analysed in this form. Between samples the tungsten carbide weight system was cleaned to avoid cross contamination.

2.34 Thin sectioning procedure

Thin sections were made in the Department of Environmental Science at the University of Stirling. They were made using Logitech equipment, (Vacuum assisted saw and lapping machine), and affixed to glass slides using 'epofix' resin and hardener. Any specimens too weathered to remain intact at the lapping stage were impregnated with epoxy resin under vacuum (see chapter 4 for more detail of impregnation method). Once made the thin sections were examined with the aid of an optical microscope using both plane and cross polarised light.

2.4 RESULTS

2.41 Major oxide analysis

Table 2.4A shows the mean results for the major weight % oxides of the different rock types in the area. Meta-sediments were split into coarse and fine meta-sediments rather than B3 and B4 greywacke and shale mapped units as illustrated in figure 2.1B, page 21. This was due to the chemical differences between the coarse and fine rock types. Full major oxide results for the unweathered specimens are presented in Appendix B, pages 270-276.

SiO₂

The black shales had the highest mean silica with a value of 84.8%. This mean did not include one of the samples given in the appendix (6b3). Use of this more transitional sample would have decreased the mean and increased the standard error. This value was closely followed by the coarse meta-sediments which had 77.6% silica on average. The fine meta-sediments, granodiorites, diorites and dykes showed lower mean weight % silica at 57.2%, 63.4%, 60.1% and 58.4% respectively. In all cases the degree of variation within a single group was low e.g. standard deviation ranged between 0.47 for the diorites and 4.54 for the black shales.

Al₂O₃

Alumina was low in coarse meta-sediments and in the black shales. The fine meta-sediments showed the highest mean alumina content at 17.7%. The igneous rocks all showed similar levels of alumina at 15.5% for the diorites, 16.0% for the granodiorites and 16.9% for the dyke rocks. The within group variation was low for most rock types with standard deviation ranging from 0.12 in the diorites to 2.15 in the black shales.

Table 2.4A: Mean major oxide weight % analyses for the different rock types, (unweathered samples only), standard deviation given in italics.

Mean weight %	Diorite n = 12	G/dior Major + minor n = 5	Dykes n = 6	Coarse m/seds n = 17	Fine m/seds n = 8	Black shale n = 3
SiO ₂	60.1 <i>0.47</i>	63.4 <i>0.70</i>	58.4 <i>1.65</i>	77.6 <i>0.73</i>	57.2 <i>1.84</i>	84.8 <i>4.54</i>
Al ₂ O ₃	15.5 <i>0.12</i>	16.0 <i>1.00</i>	16.9 <i>1.16</i>	9.35 <i>0.46</i>	17.7 <i>1.06</i>	6.46 <i>2.15</i>
Fe ₂ O ₃	5.74 <i>0.24</i>	4.60 <i>0.30</i>	5.62 <i>1.13</i>	4.12 <i>0.31</i>	8.50 <i>0.57</i>	2.13 <i>1.01</i>
MgO	5.58 <i>0.30</i>	3.70 <i>0.40</i>	4.69 <i>1.42</i>	1.88 <i>0.29</i>	6.00 <i>0.85</i>	0.96 <i>0.57</i>
CaO	4.94 <i>0.54</i>	3.50 <i>1.40</i>	5.54 <i>0.95</i>	1.10 <i>0.19</i>	1.20 <i>0.57</i>	0.50 <i>0.38</i>
Na ₂ O	3.53 <i>0.18</i>	3.70 <i>0.30</i>	3.47 <i>0.54</i>	1.96 <i>0.27</i>	1.90 <i>0.28</i>	0.47 <i>0.53</i>
K ₂ O	2.59 <i>0.36</i>	2.80 <i>0.70</i>	2.44 <i>0.48</i>	1.45 <i>0.24</i>	3.40 <i>0.28</i>	1.91 <i>0.26</i>

Fe₂O₃

Fe₂O₃ was lowest in the black shales at 2.13% and highest in the fine meta-sediments at 8.50%. Most of the other rock types fell between the range of 4-6% mean weight % Fe₂O₃ with the coarse meta-sediments at 4.12%, the granodiorites at 4.60%, the diorites at 5.74% and the dykes at 5.62%. The variation in the Fe content within individual rock type groups was low except in the case of the dyke rocks where standard deviation was 1.13.

MgO

MgO was lowest in the black shales and coarse meta-sediments at 0.96% and 1.88%. The fine meta-sediments showed greater weight % MgO at 6.00%. The results for the igneous rocks were similar to those for the weight % Fe with the granodiorite least enriched at 3.70%, the dykes next at 4.69% and the diorites most enriched at 5.58%. Within group variation was low for the granodiorites and the diorites as shown by the

standard deviations of 0.40 and 0.30 respectively. However, for all the other rock types it was significant especially for the dykes and the black shales where standard deviation rose to 1.42 and 0.57.

CaO

CaO was variable in all rocks although to a lesser degree in the diorites. The highest mean weight % of CaO was in the dyke rocks at 5.54%. Diorites showed the next highest CaO result at 4.94% then granodiorites at 3.50%. The fine meta-sediments and the coarse meta-sediments were very similar in terms of CaO content at 1.20% and 1.10% respectively although variation was much greater in the fine meta-sediments. The black shales contained minimum CaO (0.50%) and a high internal variation with a standard deviation of 0.38.

Na₂O

Results were higher in the igneous rocks than the meta-sediments 3.47% for the dykes, 3.53% for the diorite and 3.70% for the granodiorites. Variation within the group was low for the diorites and granodiorites (standard deviations 0.18, 0.30 respectively) but again, in the case of the dykes it was high (standard deviation 0.54). The coarse meta-sediments had 1.96% of this oxide on average and the fine meta-sediments 1.90%. In both cases the degree of within group variability was moderate. The results for the black shales averaged at 0.47% with high variation.

K₂O

K₂O was highest for the fine meta-sediments at 3.40%, the internal variation was very low (standard deviation 0.28). The granodiorites demonstrated the next largest result at 2.80%; the within group variation, however, was high (standard deviation 0.70). The mean for the diorites was 2.59% with a moderate degree of variation within the group

(standard deviation 0.36). The dykes gave a mean result of 2.44% with a moderate degree of variation (standard deviation 0.48). The coarse meta-sediments exhibited an average of 1.45% with moderate variation (standard deviation 0.24). Finally the black shales gave the lowest result for this weight % oxide at 1.91%. The internal variation was high with standard deviation of 0.26.

2.42 Trace element analysis

The results for the trace element analysis of all the rock samples are presented in Appendix B. The mean trace element results, however, are given in table 2.4B along with standard deviation to give an indication of variability.

Table 2.4B: Trace element results for the different rock types given as a mean value in $\mu\text{g/g}$, standard deviation is given in italics.

	Diorite n = 12	G/dior n = 5	Coarse M/seds n = 17	Dykes n = 6	Black shales n = 4	Fine m/seds n = 8
Ni	132 <i>14</i>	64 <i>15</i>	45 <i>31</i>	91 <i>79</i>	18 <i>15</i>	171 <i>47</i>
Cr	251 <i>34</i>	156 <i>12</i>	88 <i>66</i>	171 <i>235</i>	61 <i>16</i>	248 <i>42</i>
V	124 <i>10</i>	100 <i>6</i>	79 <i>10</i>	121 <i>46</i>	265 <i>54</i>	159 <i>15</i>
Sc	19 <i>2</i>	16 <i>2</i>	13 <i>2</i>	20 <i>8</i>	11 <i>3</i>	26 <i>2</i>
Cu	23 <i>7</i>	12 <i>3</i>	6 <i>4</i>	13 <i>13</i>	25 <i>14</i>	41 <i>9</i>
Zn	55 <i>4</i>	51 <i>7</i>	50 <i>8</i>	58 <i>10</i>	32 <i>10</i>	110 <i>21</i>
Sr	632 <i>66</i>	533 <i>106</i>	89 <i>25</i>	778 <i>204</i>	70 <i>29</i>	113 <i>29</i>
Rb	76 <i>11</i>	84 <i>25</i>	52 <i>10</i>	65 <i>15</i>	60 <i>10</i>	125 <i>15</i>
Zr	184 <i>21</i>	196 <i>11</i>	279 <i>84</i>	203 <i>20</i>	68 <i>23</i>	183 <i>20</i>
Nb	10 <i>1</i>	11 <i>2</i>	15 <i>2</i>	9 <i>1</i>	7 <i>2</i>	16 <i>2</i>
Ba	969 <i>76</i>	891 <i>131</i>	299 <i>44</i>	963 <i>416</i>	259 <i>68</i>	522 <i>109</i>
Pb	15 <i>2</i>	13 <i>5</i>	12 <i>3</i>	9 <i>4</i>	30 <i>9</i>	20 <i>7</i>
Th	8 <i>2</i>	10 <i>4</i>	11 <i>1</i>	6 <i>3</i>	8 <i>1</i>	13 <i>2</i>
La	27 <i>2</i>	26 <i>3</i>	29 <i>4</i>	28 <i>11</i>	15 <i>5</i>	34 <i>3</i>
Ce	60 <i>5</i>	59 <i>7</i>	64 <i>8</i>	50 <i>16</i>	35 <i>9</i>	72 <i>5</i>
Nd	26 <i>2</i>	25 <i>2</i>	27 <i>3</i>	24 <i>4</i>	17 <i>4</i>	29 <i>2</i>
Y	20 <i>2</i>	19 <i>1</i>	22 <i>3</i>	19 <i>2</i>	18 <i>5</i>	27 <i>2</i>

Rock trace element results show a number of striking features:

1. Low variability within the diorites and many of the granodiorite readings.
2. Very high variability in the dykes and some of the meta-sediment results.
3. Very much higher Sr and Ba values in igneous rocks.

2.43 Mineralogical analysis

All coarse rock types were subjected to thin section description. The full results of the individual samples are tabulated in Appendix C, pages 277-279. The results presented here draw out the common features of the groups. Alteration class is as used by Bullock et al (1985) in the Handbook for Soil Thin Section Description. The relative amounts of different minerals was also estimated with reference to Bullock et al.

Diorites

The diorites varied in grainsize from coarse to medium (Plates 2.4A and 2.4B). The diorites were also diverse in the relative amounts of minerals present and their level of alteration. They typically consisted of 35 - 55% plagioclase feldspar, 5 - 10% potassium feldspar, 5 - 10% Quartz, 10 - 15% biotite (occasionally up to 30%), 20 - 35% pyroxenes. Minor minerals included apatite and opaque oxides. The plagioclase, typically andesine, showed multiple twinning, compositionally zoned crystals were rare. Plagioclase was highly altered, usually internally and sericitically, alteration class 1 to class 3. Mymerkitic intergrowths with quartz were very rare. Potassium feldspar was typically interstitial and alteration was scarce, class 0. Quartz was typically unaltered. Ferromagnesian minerals tended to clump together, plate 2.4C. Two forms of biotite occurred, a well cleaved variety and an amorphous form associated with pleochroic haloes around zircons. Biotite showed only minor alteration, < class 1. Both

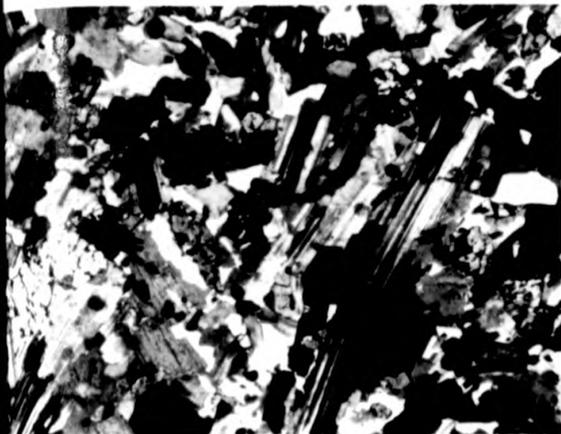


Plate 2.4A: Medium grainsize in diorites. Sample = 4HR x 1. PPL.



Plate 2.4B: Coarse grainsize in diorites. 3HR x 1. XPL.



Plate 2.4C: Ferromagnesian clumps in diorites. 1HR x 4. XPL.

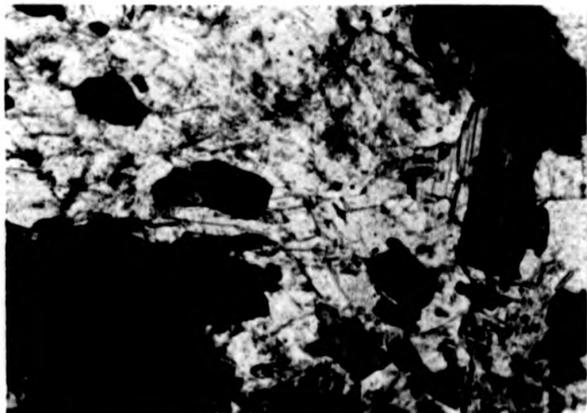


Plate 2.4D: Altered pyroxene in diorites. 8HR x 2. PPL.



Plate 2.4E: Sample 5/1 x 4. PPL.

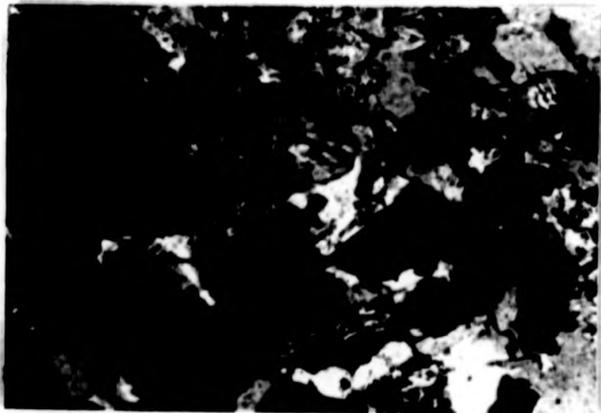


Plate 2.4F: Sample 5/1 x 4. XPL.

orthopyroxenes (OPX) and clinopyroxenes (CPX) appeared, opx was the dominant type. The pyroxenes exhibited the highest degree of alteration ranging from class 1-4, plate 2.4D, and often showed a mosaic texture and alteration at the edges to chlorite and/or hornblende.

Sample 5/1 was dissimilar to the other diorites in mineralogical terms. It had a finer grain size and pyroxene minerals were almost totally replaced, plates 2.4E and F.

Granodiorites

The granodiorites within the Loch Doon pluton exhibited some variability. All three samples contained 30 - 45% plagioclase in the range andesine to oligoclase. Only 2 samples included biotite (c.20%), plates 2.4 G and H, while the other sample was deplete of biotite. Green hornblende was the other ferromagnesian mineral and made up between 15 - 25% of all three samples. Potassium feldspar and quartz constituted c.30% of all samples. Plagioclase was multiple twinned and often highly altered, class 2 - 3. Biotite was present in both cleaved and uncleaved forms and often clumped with the hornblende. The potassium feldspar was altered between classes 1 - 2 whilst the quartz was unaltered.

Samples from the minor granodioritic intrusion in the south of the area were different from the main granodiorite mass. They exhibited 30 - 45% plagioclase, 10% biotite, 15 - 25% green hornblende and 20 - 30% potassium feldspar + quartz.

Plagioclase showed multiple twinning and occasional zoning. It was typically andesine although some crystals were more complex showing occasional X-hatching in addition to twinning. Alteration was internal and up to class 3. The ferromagnesian minerals

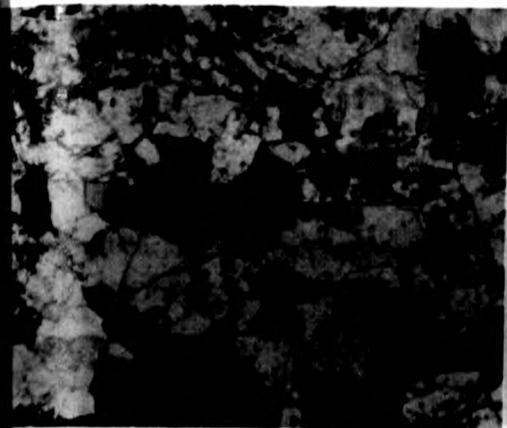


Plate 2.4G: Granodiorite.
4GD x 1. PPL.

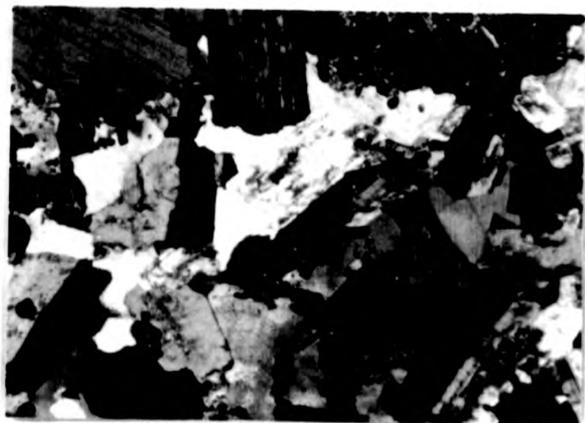


Plate 2.4H: Granodiorite.
2GD x 1. XPL.



Plate 2.4I: Porphyrite dyke.
1PD x 1. PPL.

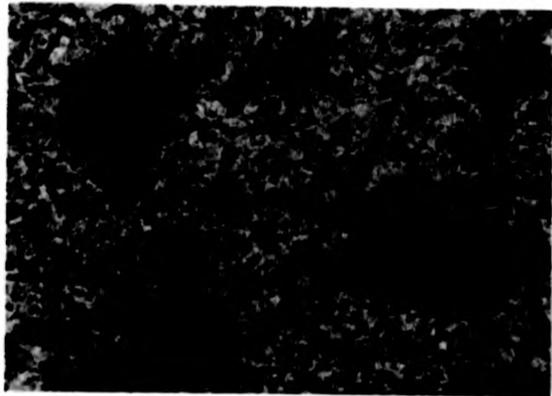


Plate 2.4J: Lamprophyre dyke.
9b3 x 2. PPL.

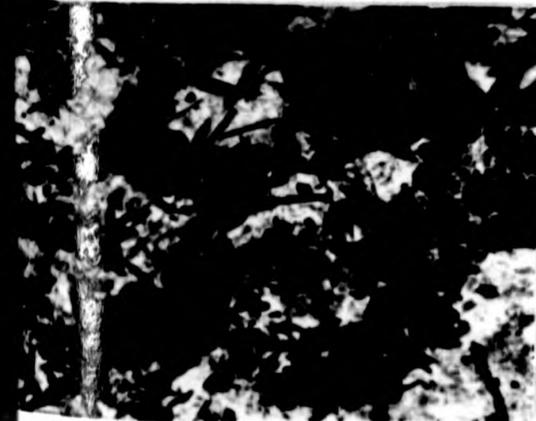


Plate 2.4K: Basic Dyke.
1LD x 2. PPL.



Plate 2.4L: Acidic dyke.
7LD x 2. XPL.

tended to clump together. Minor pyroxenes were identified altering at the edges to green hornblende. The potassium feldspar was altered up to class 2, whilst the quartz remained unaltered.

Dyke rocks

The dyke rocks sampled were of 4 different types; they were typically highly altered and mineralogy was often difficult to determine.

1.Porphyrite dykes

1 sample was taken from two different dykes. They both contained c.50% phenocrysts and 50% groundmass. The phenocrysts were made up of plagioclase and altered pyroxenes. The plagioclase was more abundant and showed multiple twinning within the andesine range; it was altered to class 1 - 2. The 'pyroxenes' were altered up to class 3 and barely recognisable as pyroxene minerals. The groundmass was fine and glassy and the mineralogy was difficult to determine, plate 2.4I.

2.Lamprophyre dykes

2 samples were identified. Plate 2.4J shows a representative photomicrograph. Mineralogy was difficult to determine.

3.Basic dyke

One basic dyke was sampled, plate 2.4K.

4.Acid dyke

This dyke had 50% plagioclase which exhibited multiple twinning identifying it as andesine. Occasional zoned crystals were present as were intergrowths with quartz. Plagioclase was highly altered - up to class 2. Biotite was the main ferromagnesian mineral - up to 20% of the rock. It was altered to class 1 and had pleochroic haloes

around zircon. Potassium feldspar and quartz made up 30% of the rock. Minor opaques minerals were present. See plate 2.4L.

Coarse meta-sediments

The coarse meta-sediments varied in grain size, plates 2.4M and 2.4N. Plate 2.4M shows a typical greywacke including a variety of grainsizes and plate 2.4N shows a more uniformly finer grained gritstone with a metamorphic fabric.

The clasts within the coarse meta-sediments were typically subangular and usually quartzose in nature, plate 2.4O. The quartz was mono and polycrystalline and often had undulose extinction. Rock fragments were rare but did occur, plate 2.4P. Clasts outlines were not always totally visible indicating contact metamorphism.

Greywackes were typically clast supported; the matrix composition was difficult to determine because of its fine nature but it appeared to be made up of a mixture of finer quartz grains and clay minerals, in some cases biotite could be identified.

Fine meta-sediments

No mineralogical data was collated for the fine meta-sediments. However, on a gross scale they varied from mudstones to shales.

Black shales

The black shales were very fine grained, mineralogy was not easily identified. However sample 6b3 in plate 2.4Q shows both its quartzose nature and metamorphic fabric.

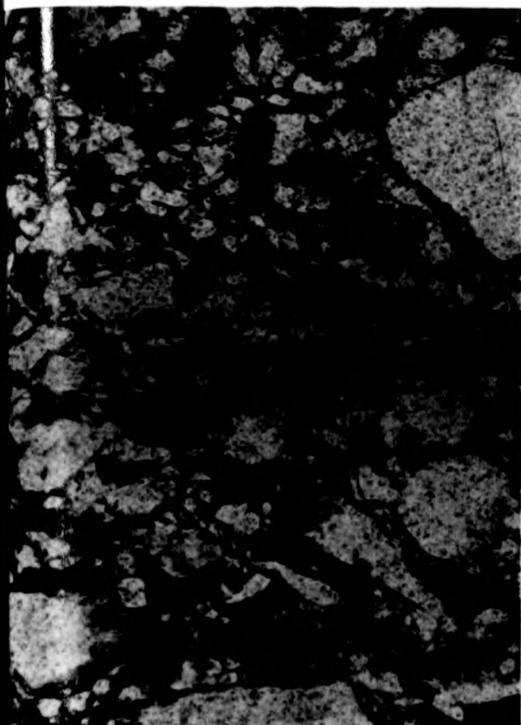


Plate 2.4M: Greywacke.
1GR/b3 x 2. PPL.



Plate 2.4N: Gritstone.
2GR/b3 x 2. PPL.



Plate 2.4O: Quartzose clasts in
greywacke. 4b4 x 2. XPL.



Plate 2.4P: Rock fragments
in greywacke. 8b4 x 2. PPL.

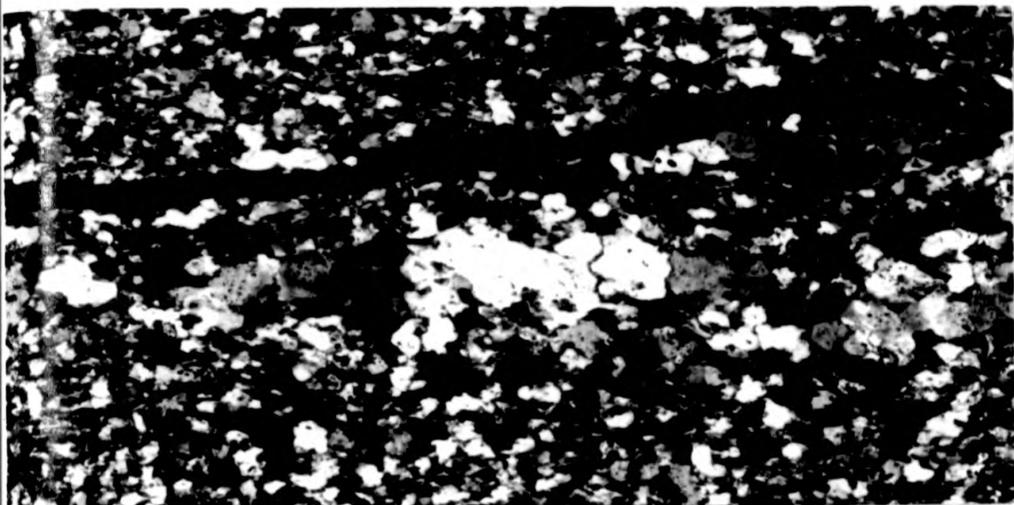


Plate 2.4Q: Black shale showing banding. 6b3/BS x 4. XPL.

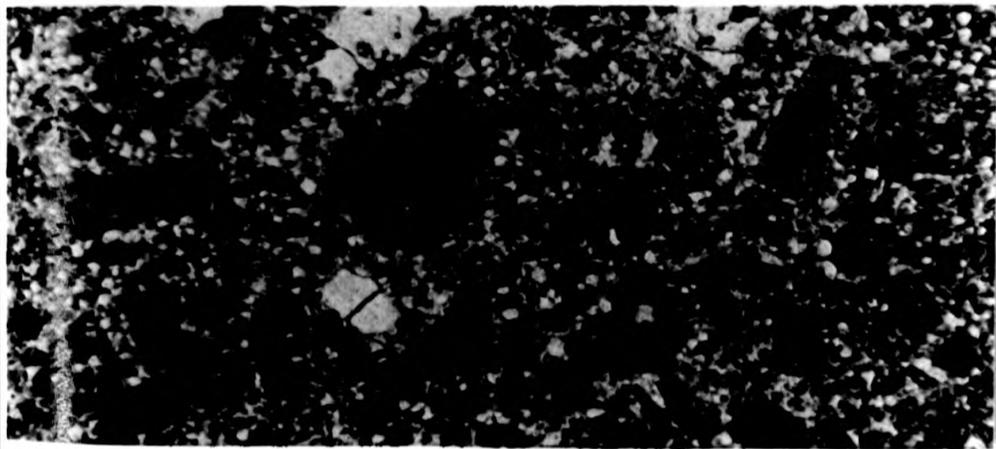


Plate 2.4R: 3PDB - Mixed character rock. x1. PPL.

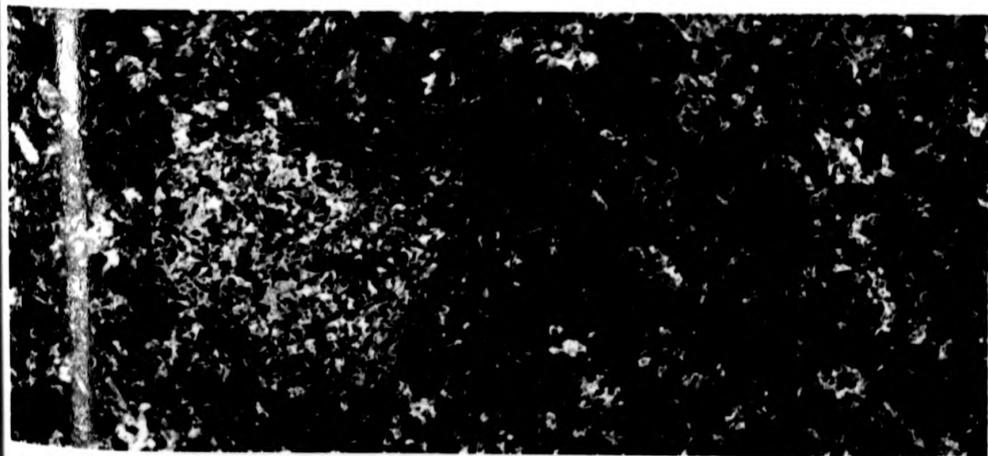


Plate 2.4S: MS1 - Mixed character rock. x 4. XPL.

Other samples

Two rock specimens were sectioned that were not categorised because of mixed character. Specimen 3PDB is shown in plate 2.5R. This rock exhibited a mass of subrounded quartz grains and also elements of an igneous nature. It was sampled from the ordovician meta-sediments south of the igneous/sediment boundary close to the position where a porphyrite dyke had been reported. Plate 2.4T shows a rock sampled from much further south; it was highly altered but again showed both igneous and sedimentary features.

Major and trace metal analytical results for these two samples can be found in appendix B, tables B:31 - B:35. Trace element results also indicated mixed characteristics with Sr results of 179 and 268 mg/L and Ba measurements of 525 and 672 mg/L. In terms of major oxides, these rocks exhibited higher silica than the other igneous rocks of the area but had typical igneous alumina values and higher Na and K than was reported in any of the other meta-sediments.

2.5 DISCUSSION

2.5.1 Variation within the Igneous rocks.

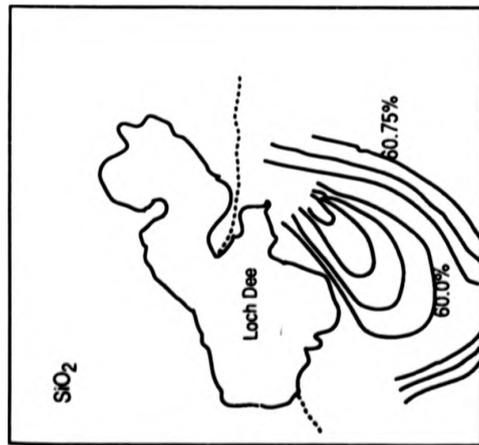
Diorites

Diorites were typified by moderate silica, high alumina and high base oxides. The results were comparable with the norites of Gardiner and Reynolds (1932), the hypersthene diorites of Ruddock (1969) and the diorites of Brown et al (1979). The results supported the suggestion by Ruddock of little chemical variation except in the

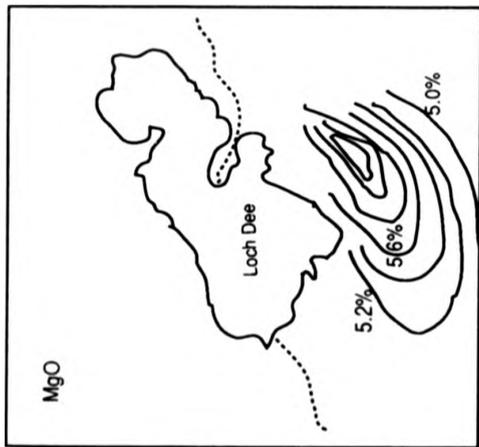
case of CaO and K₂O where the removal of sample 5/1 from the calculations considerably decreased the internal variation. This sample exhibited a much lower CaO content and higher K₂O content than the other members of the diorite group. The diorite major oxide results were used to interpolate contours of oxide distribution on maps shown in figure 2.5A. These indicated the southern zone of the Loch Doon pluton mapped as diorite (figure 2.1A) had a central basic zone with lower SiO₂ and total alkalis and higher MgO, CaO and Fe₂O₃. These oxide distribution maps were not consistent with similar whole pluton maps presented by Ruddock (1969) but it is possible they showed the presence of a smaller scale feature. The results of interpolation are, however, difficult to explain but appear to be 'real' because of the repetition of trends for different oxides within the area. However, since the feature is only small scale both in terms of area and 'contour' interval it may not be of great significance.

Mineralogical investigation of the diorites also indicated a significant difference in sample 5/1 (plates 2.4E and F) despite the overall diorite mineralogical variation being greater than the chemical. Thin section analysis also provided a plausible mechanism for the chemical differences noted in sample 5/1. The replacement of the pyroxene minerals from sample 5/1 was by a greenish yellow mineral of low birefringence. If this mineral was K enriched its presence could explain the lower CaO and greater K₂O within this sample.

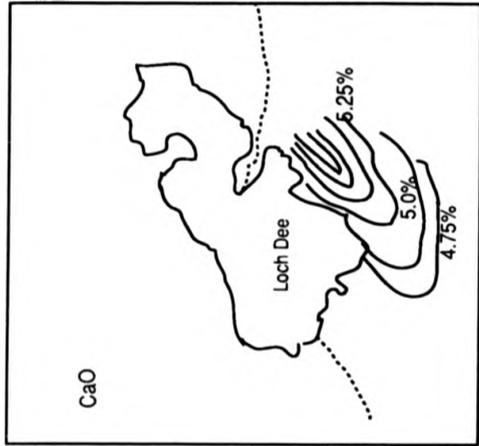
The diorites also varied in grain-size although the samples collected did not agree with the suggestions of Gardiner and Reynolds (1932) that finer grained varieties were



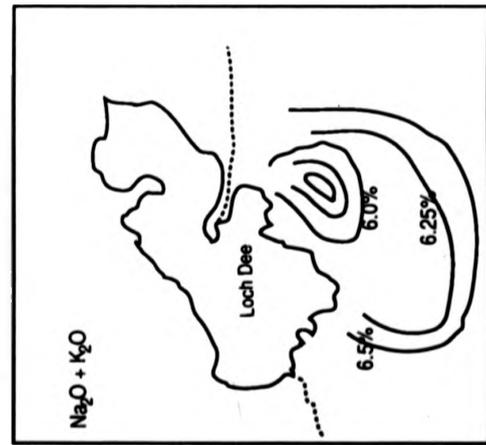
SiO₂ weight % contours
59 - 61% (interval = 0.25%)



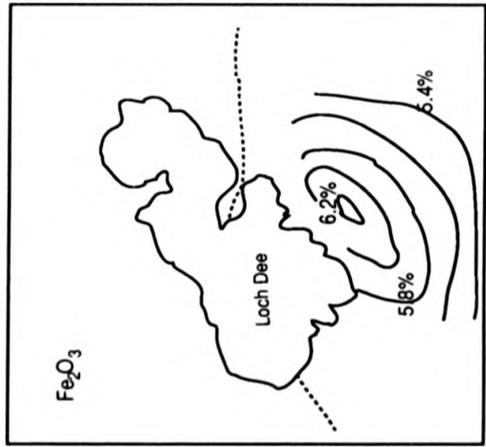
MgO weight % contours
5 - 6.2% (interval = 0.2)



CaO weight % contours
4.75 - 6.0% (interval = 0.25)



Total alkali weight % contours
5.5 - 6.5% (interval = 0.25)



Fe₂O₃ weight % contours
5.4 - 6.2% (interval = 0.2)



Legend

— Weight % oxide
'contour'

..... Approximate
diorite/granodiorite
boundary

Figure 2.5A Diagrams illustrating the chemical variation within the diorites.

concentrated in the south of the area.

Granodiorites

Granodiorites were typified by moderate silica, high alumina and slightly less base oxides than the diorites. The chemical analyses were similar to the tonalites of Gardiner and Reynolds (1932), intrusives of Giusti (1991) and quartz monzodiorites and monzonites of Brown et al (1979). The variation in the CaO and the K₂O for the granodiorites was explained by grouping of two different phases of granodiorite in one category. CaO was higher and K₂O lower in the minor granodiorite than the granodiorite which formed part of the Loch Doon pluton. This also explained mineralogical differences between the granodiorites.

The internal variation noted in the mineralogy of the major granodiorite was not indicated by the work of previous authors. If the granodiorite was as mineralogically uniform as the literature suggests it is possible that the sample lacking biotite was one of the acidic post pluton intrusions into the pluton itself reported by Ruddock (1969).

Dykes

The dykes were chemically and mineralogically variable since 4 different igneous rock types were grouped together. Porphyritic dykes had 6.28 and 6.32% Fe₂O₃, 6.39 and 6.40% MgO, 5.72 and 5.91% CaO, 3.30 and 3.51% Na₂O and 2.30% and 2.16% K₂O. These were not consistent with the analyses of porphyrite dykes given by Ruddock (1963). Lamprophyre dykes had 4.74 and 4.79% Fe₂O₃, 1.73 and 1.75% MgO, 4.17% and 4.09% CaO, 4.01 and 3.70% Na₂O and 2.93% and 2.68% K₂O. The other two members of the dyke suite were both chemically different and had 7.93 and 3.67%

Fe₂O₃, 9.33% and 2.52% MgO, 7.33 and 6.00% CaO, 2.80 and 3.50% Na₂O and 2.15% and 2.42% K₂O. The more basic dyke had a comparable silica content to a hornblende lamprophyre reported from the Gaham swarm of dykes at Loch Dee by Gardiner and Reynolds (1932). The dyke results confirmed the chemical and mineralogical variability of the dyke rocks within the area.

2.52 Classification of the igneous rocks

The plutonic rocks are referred to as granodiorites and diorites throughout the text. However, these classifications and those suggested for the minor igneous bodies did not always apply when results were tested using the TAS (Total alkalis vs silica) and the QAP classificatory systems (Cox, Bell and Pankhurst 1979). The results are presented in table 2.52A. For full details of the individual samples see appendix C.

Table 2.52A Classification of the different rock types according to mineralogical and chemical analyses.

Classification used in text.	Classification according to TAS.	Classification according to QAP.
Diorites	Mostly classed as qz monzodiorites with a few granodiorites and qz diorites.	Split between qz monzodiorite, qz diorite and diorite.
Granodiorites (major)	Granodiorite	Granodiorite
Porphyrite dykes	Qz monzodiorite	*
Lamprophyre dykes	Granodiorite	*
Acid dyke	Qz monzodiorite	Qz monzodiorite
Basic dyke	Qz Diorite	*
Granodiorite (minor)	Granodiorite	Granodiorite

* In these cases the QAP system was not used as the samples either contained a basic plagioclase or it was difficult to breakdown the mineralogy.

2.53: Variation within the sediments and meta-sediments.

Coarse meta-sediments

The results from this study highlighted the chemical, mineralogical and textural variability within the coarse meta-sediments which included matrix supported greywackes and gritstones. The gritstones showed variable grainsize which was often reflected by the manifestation of metamorphic fabrics, finer grained gritstones typically showed metamorphic fabrics more definitely. Despite the suggestions of Teall (1899) the metamorphic mineral garnet was not found in any of the thin sections taken.

Coarse meta-sediments had high silica content and low alumina and base/alkali metals. Giusti (1991) used similar chemical methods in the analysis of his greywackes yet his results indicated lower silica and higher alumina than those tested for this thesis. Giusti also found oxides of magnesium, iron, calcium and sodium to be higher in the Dargall lane sub-catchment meta-sediments than those measured here in the White Laggan sub-catchment.

Some samples were chemically very different e.g. 2GR(b3), MS2. None of the differences in these cases were explainable in terms of either textural variability or proximity to the Loch Doon pluton and thereby greater chances of contact metamorphic chemical changes. The chemical differences noted within these two samples was taken to indicate the degree of variation within the coarse meta-sediments caused by differences in both the source of the original sediments and the superimposed effects of regional and contact metamorphism. The previously reported differences in analytical results for the greywackes of Giusti support this idea of great

variability within the coarse meta-sediments.

Fine meta-sediments

The fine meta-sediments had low silica content, high alumina, Fe and Mg oxides and low Ca, Na and K. The results contrasted greatly with those collated by Giusti (1991). He suggested mudstones from the Dargall lane had c.72% silica, similar alumina levels and lower base metal.

The fine meta-sediments reported here showed textural and chemical variations that could not be explained in terms of textural differences or proximity to the pluton. It was concluded that the chemical variations apparent within the meta-sediments were related to different depositional circumstances e.g. source material, setting etc. combined with contrasting effects of regional metamorphism. This also explained the difference in results reported by Giusti (1991).

Black shales

The black shales had the highest silica content and typically all other oxides were depleted within this group. This agreed with the analyses of Giusti (1991). Variability was high in all oxide categories except silica. This variability was again explained by reference to differences in source material and metamorphic response.

2.54 Analysis of variance

The major oxide chemical analyses indicated chemical differences in the rocks from the Loch Dee area.

Analysis of variance demonstrated the chemical variability within the different rock types to be less than that between the different groups of rocks. It was concluded there were significant differences in the major oxide chemistry of the different rocks at the 95% level of confidence.

The trace element results for the rock types were often similar except in the cases of Sr and Ba. In the igneous rocks Sr was greater and ranged between 463 - 1112 $\mu\text{g/g}$ whilst the range in the meta-sediments was 70 - 113 $\mu\text{g/g}$. The Ba results were also higher in the igneous rocks ranging between 698 and 1848 $\mu\text{g/g}$ against 259 - 522 $\mu\text{g/g}$ in the meta-sediments.

2.55 Mineralogical implications for the weathering of rocks from the Loch Dee area.

Diorites from the Loch Doon pluton contained the highest proportions of unstable minerals with respect to earth surface conditions of all the rocks in the area. Granodiorites embraced slightly greater proportions of K feldspar and quartz indicating, in theory, a greater resistance to weathering. The coarse meta-sediments were quartz-rich again suggesting a resistance to weathering; there was no mineralogical data relating to the fine meta-sediments in the area. The chemical data pertaining to the fine meta-sediments, however, indicated the importance of Al_2O_3 within these rock types. This together with the fine nature of the rocks signifies the importance of clay minerals within this rock class. This being the case weathering

potential should be reduced since clay minerals are typically viewed as the close to the end product of weathering in a temperate climate i.e. relatively adjusted to earth surface conditions. The coarse and fine meta-sediments together made up the high ground in the south of the area,(fig 2.1B) supporting the notion of lower susceptibility to weathering.

2.56 Weathering of the rocks as indicated by chemical comparison.

Birkeland (1984) suggested that SiO_2 , CaO , MgO , K_2O and Na_2O commonly decreased during the weathering of rocks. He considered Al_2O_3 to be relatively conservative during weathering explaining this by the insolubility of Al at 'normal pH' and its presence in clay mineral weathering products. Using this assumption, the author compared results between weathered and unweathered samples by using:

$$\% \text{Al}_2\text{O}_3 \text{ freshrock} / \% \text{Al}_2\text{O}_3 \text{ weathered rock}$$

as a multiplication factor to recalculate weathered rock oxide contents. Changes were reported as the difference between this recalculated value and the fresh rock sample. Birkeland indicated this method was limited as Al_2O_3 was not totally conservative; pH values experienced by weathering can lead to an increase in the solubility and therefore mobility of aluminium. Given the nature of the thesis it seemed inappropriate to employ a method based on the assumption of the conservation of alumina throughout weathering. Birkeland suggested another and more accurate way to determine chemical differences between weathered and unweathered samples would

involve comparing the gains and losses in weights of material on a volume basis. It was not possible to attempt this using the data collected in this exercise. Evans and Adams (1975 a + b) compared the use of quartz content, TiO_2 , ZrO_2 and soil residue after acid digestion as internal chemical standards to assess chemical changes related to soil horizons. All these methods showed good results but the acid residue method appeared to be marginally the best using subjective criteria. However, again this data was not available. Of the other 3 methods quartz content would have been difficult to employ as the SiO_2 values given for the rocks were not wholly in the form of quartz. Muir and Logan (1982) stressed the possibility of problems with the use of titania as an internal standard because it was typically minimal in rocks highlighting the possibility of uneven distribution within rocks and the significance of any analytical discrepancies. Despite this TiO_2 was used as the internal standard using a calculation similar to the one suggested for alumina by Birkeland. In addition and as a check, oxide values were also recalculated using zircon values, table 2.56A. However, because zircon was measured as a trace element rather than an oxide it was first necessary to express them as a % of the total trace element content. The ratio of this for the fresh rock sample to the weathered rock sample was used as the multiplication factor. Because the trace element content is not finite there are possible problems with this methodology.

Table 2.56A: Differences between weathered and unweathered samples of rock from Loch Dee. Plain print indicates values for titania, italics for zircon.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O
5/1 Diorite	+0.86 <i>-0.07</i>	-0.27 <i>-0.51</i>	+0.28 <i>+0.20</i>	+0.29 <i>+0.20</i>	-0.17 <i>-0.21</i>	-0.07 <i>-0.11</i>	+0.09 <i>+0.02</i>
4/1 Diorite	+1.71 <i>+2.30</i>	+0.25 <i>+0.41</i>	+0.30 <i>+0.35</i>	+0.42 <i>+0.47</i>	+0.07 <i>+0.12</i>	+0.08 <i>+0.12</i>	+0.21 <i>+0.23</i>
4HR Diorite	+1.53 <i>+1.52</i>	+0.48 <i>+0.48</i>	+0.10 <i>+0.11</i>	+0.14 <i>+0.14</i>	+0.08 <i>+0.08</i>	+0.17 <i>+0.17</i>	+0.04 <i>+0.04</i>
7HR Diorite	-0.27 <i>+0.58</i>	+0.06 <i>+0.27</i>	-0.02 <i>+0.05</i>	0.00 <i>+0.08</i>	-0.07 <i>0.00</i>	+0.02 <i>+0.07</i>	-0.03 <i>0.00</i>
8HR Diorite	-0.53 <i>-1.38</i>	-0.07 <i>-0.29</i>	-0.29 <i>-0.37</i>	-0.19 <i>-0.27</i>	-0.16 <i>-0.23</i>	-0.01 <i>-0.06</i>	+0.06 <i>+0.02</i>
1b3 C. M/sed	-0.41 <i>+2.76</i>	-0.27 <i>+0.14</i>	-0.03 <i>0.15</i>	0.00 <i>+0.08</i>	-0.66 <i>-0.58</i>	-0.05 <i>+0.04</i>	-0.02 <i>+0.07</i>
3b3 C. M/sed	-0.76 <i>-2.54</i>	-0.09 <i>-0.29</i>	+0.06 <i>-0.02</i>	+0.09 <i>+0.04</i>	+0.44 <i>+0.27</i>	-0.61 <i>-0.64</i>	+0.06 <i>+0.03</i>
9b3 Dyke	+0.41 <i>+0.70</i>	+0.08 <i>+0.16</i>	-0.07 <i>-0.05</i>	+0.02 <i>+0.03</i>	-0.80 <i>-0.79</i>	-0.08 <i>-0.06</i>	+0.50 <i>+0.52</i>
3b4 F. M/sed	-0.58 <i>-0.23</i>	+0.02 <i>+0.12</i>	-0.03 <i>+0.02</i>	-0.06 <i>-0.03</i>	+0.29 <i>+0.30</i>	-0.03 <i>-0.01</i>	+0.11 <i>+0.13</i>
2GD Major G/dior	-0.83 <i>-4.56</i>	-0.05 <i>-0.96</i>	-0.07 <i>-0.35</i>	-0.03 <i>-0.25</i>	-0.16 <i>-0.36</i>	-0.03 <i>-0.24</i>	-0.02 <i>-0.21</i>
3GD Major G/dior	-2.33 <i>-7.18</i>	-1.31 <i>-2.46</i>	-0.06 <i>-0.41</i>	-0.19 <i>-0.44</i>	-0.13 <i>-0.20</i>	-0.04 <i>-0.30</i>	-0.57 <i>-0.78</i>
4GR Minor G/dior	+0.10 <i>-0.05</i>	+0.15 <i>+0.11</i>	-0.03 <i>-0.04</i>	-0.13 <i>-0.14</i>	-0.10 <i>-0.11</i>	0.00 <i>0.00</i>	-0.03 <i>-0.03</i>
1LD Dyke	+0.61 <i>-2.21</i>	+0.21 <i>-0.58</i>	-0.12 <i>-0.31</i>	+0.22 <i>-0.29</i>	+0.18 <i>-0.22</i>	+0.03 <i>-0.12</i>	-0.06 <i>-0.17</i>
1PD Dyke	-0.18 <i>+0.19</i>	0.00 <i>+0.10</i>	-0.07 <i>-0.03</i>	-0.12 <i>-0.08</i>	-0.32 <i>-0.28</i>	-0.03 <i>-0.01</i>	0.00 <i>+0.02</i>

The summed numerical losses for the different rock types on weathering are given in table 2.56B.

Table 2.56B: Summed losses on weathering

	Diorite	G/dior	Dykes	Coarse m/seds	Fine m/seds
Losses using titania	5/1 0.51 4/1 0.00 4HR 0.00 7HR 0.39 8HR 1.25	Major 2GD 1.46 3GD 4.63 Minor 4GR 0.29	Lam'yre 9b3 0.95 Basic 1LD 0.18 Por'tic 1PD 0.69	1b3 1.44 3b3 1.46	3b4 0.70
Losses using Zr	5/1 0.90 4/1 0.00 4HR 0.00 7HR 0.00 8HR 2.60	Major 2GD 6.89 3GD 11.9 Minor 4GR 0.37	Lam'yre 9b3 0.90 Basic 1LD 3.33 Por'tic 1PD 0.40	1b3 0.58 3b3 3.49	3b4 0.27

The two different internal standards gave similar results on most occasions although there were a few discrepancies. However, the results indicated:

Diorites - Using both methods there was an apparent variability in the losses on weathering for samples within this group which is consistent with variations reported in the mineralogical analysis of the diorites including differences in the alteration class of minerals for different rock samples. In addition to this, disparity of results found in any rock division could also be caused by volumetric differences in the ratio of weathered to fresh material crushed and prepared for analysis.

Samples 8HR and 5/1 experienced the greatest losses (silica, alumina, Fe_2O_3 , MgO , CaO and Na_2O_3) and appeared to be the most easily weathered.

Granodiorites - There were two samples of the major granodiorite. Both experienced losses in all oxides on weathering according to the titania and Zr methods although losses were greater for Zr. Harriss and Adams (1966) suggested Ca and Na would be

lost first in the weathering of granitic rock types because of the decomposition of plagioclase feldspar. Although the order of elemental loss is not known in this case, volumetrically silica and alumina were the most important losses. The minor granodiorites from the south of the catchment were represented by one sample. This showed losses in Fe_2O_3 , MgO , CaO and K_2O by both methods although the losses were much less than recorded in the case of the major granodiorites. There was no obvious mineralogical distinction between these two granodiorites that could explain the severe difference in weathering losses.

Dykes - The lamprophyre dyke tested showed substantial losses in CaO on weathering by both methods of estimation and more minor losses in Fe_2O_3 and Na_2O . The data for the basic dyke was very different using the two different methods. Titania indicated very few losses on weathering. However, Zr indicated substantial losses in all oxides on weathering. Finally the porphyrite dyke lost Fe_2O_3 , MgO , CaO and Na_2O on weathering when tested by both methods. Losses in CaO were the most important.

Coarse meta-sediments - The coarse meta-sediments in the area experienced losses on weathering of silica, alumina and Na_2O . Most losses identified by the Zr method were from the sample 3b3. However, using titania the losses from both 1b3 and 3b3 were approximately the same.

Fine meta-sediments - Only one sample was tested but showed losses in SiO_2 on weathering and less substantial losses in MgO and Na_2O using both methods. With the titania method there was also a small loss in Fe_2O_3 .

Total Losses

The summed losses for the different samples contrasted with theoretical predictions. The diorites according to Goldich (1938) should be the most weatherable rocks in the area yet their summed losses using this method ranged between 0.00 and 0.90 (table 2.56B). The coarse meta-sediments represented the most quartz rich rocks tested by this method from the area; summed losses predicted using this method ranged between 0.58 and 3.49 considerably more than theoretically susceptible diorites. The highest summed losses shown in table 2.66B were for the major granodiorites. These experienced losses up to 4 times higher than the highest loss from a diorite sample. These results are difficult to explain in terms of the weathering scenario proposed by Goldich and indicate the presence of some other factor influencing the weathering of the rocks of the Loch Dee area. However, the results could indicate a decrease in the weathering rate of the more basic igneous rocks after having weathered substantially in the past. The metasediments in the area would have started weathering more slowly and possibly are now weathering at a greater rate than the diorites.

Implications of results for long term water quality analysis within the area.

Welsh and Burns (1987) suggested baseflow waters within the Loch Dee catchment reflected a geological input. They suggested that in the White Laggan sub-catchment Ordovician rocks provided better buffering conditions than the granites. This conflicts with theoretical mineralogical principles but corresponds to the measured weathering changes using both titania and Zr as internal standards in assessing chemical changes on the weathering of rocks.

2.6 CONCLUSIONS:

Rocks of the Loch Dee area were chemically distinct, a feature that may be related to soils with these rock types as parent materials. Igneous rocks were enriched in bases with respect to the sediments and meta-sediments while the diorites had a greater supply of bases than the granodiorites within the large intrusive mass. The dykes were chemically highly variable. Black shales had the lowest base content and highest silica content and coarse meta-sediments were similarly enriched in silica. Both of these rock types were depleted in alumina. On the other hand fine meta-sediments had alumina content akin to that from the igneous rocks in the area.

The diorites of the Loch Doon pluton demonstrated minor chemical variations that were mapped on a small scale. Mineralogical variations were greater within the diorite group. Granodiorites from the pluton were less variable in terms of chemistry. Mineralogical variations noted were explained in terms of the presence of an acidic dyke within the pluton.

The meta-sediments of the area were variable in texture, mineralogy and chemistry. Coarse meta-sediments included greywackes and gritstones which showed a variable degree of metamorphic influence not related to the proximity of the pluton. Fine meta-sediments included shales and mudstones. Chemical and textural variability was not related to pluton proximity. The black shales were chemically distinct but internally variable.

Minor intrusions in the area varied from granodiorites in a boss or stock like form to

dykes of porphyritic, basic, lamprophyric and acidic nature. All minor intrusion types were chemically and mineralogically very different from one another. The main concentration of dykes was situated in the south of the catchment within the meta-sediment mass.

Studies into the nature of weathering within these rock types gave results contrary to the theoretical suggestions of Goldich. The results, however, supported chemical analytical data of water quality within the area explained by the weathering of bedrock geology. Baseflow stream water quality analyses indicated waters draining the sediments and meta-sediments of the White Laggan sub-catchment had the highest pH. The coarse metasediments herein experienced one of the greatest total losses on weathering in the form of silica, alumina and CaO or Na₂O. This may account for the improved water quality experienced draining the coarse sediments and meta-sediments in the area and was explained in terms of the variable nature of the rate of weathering.

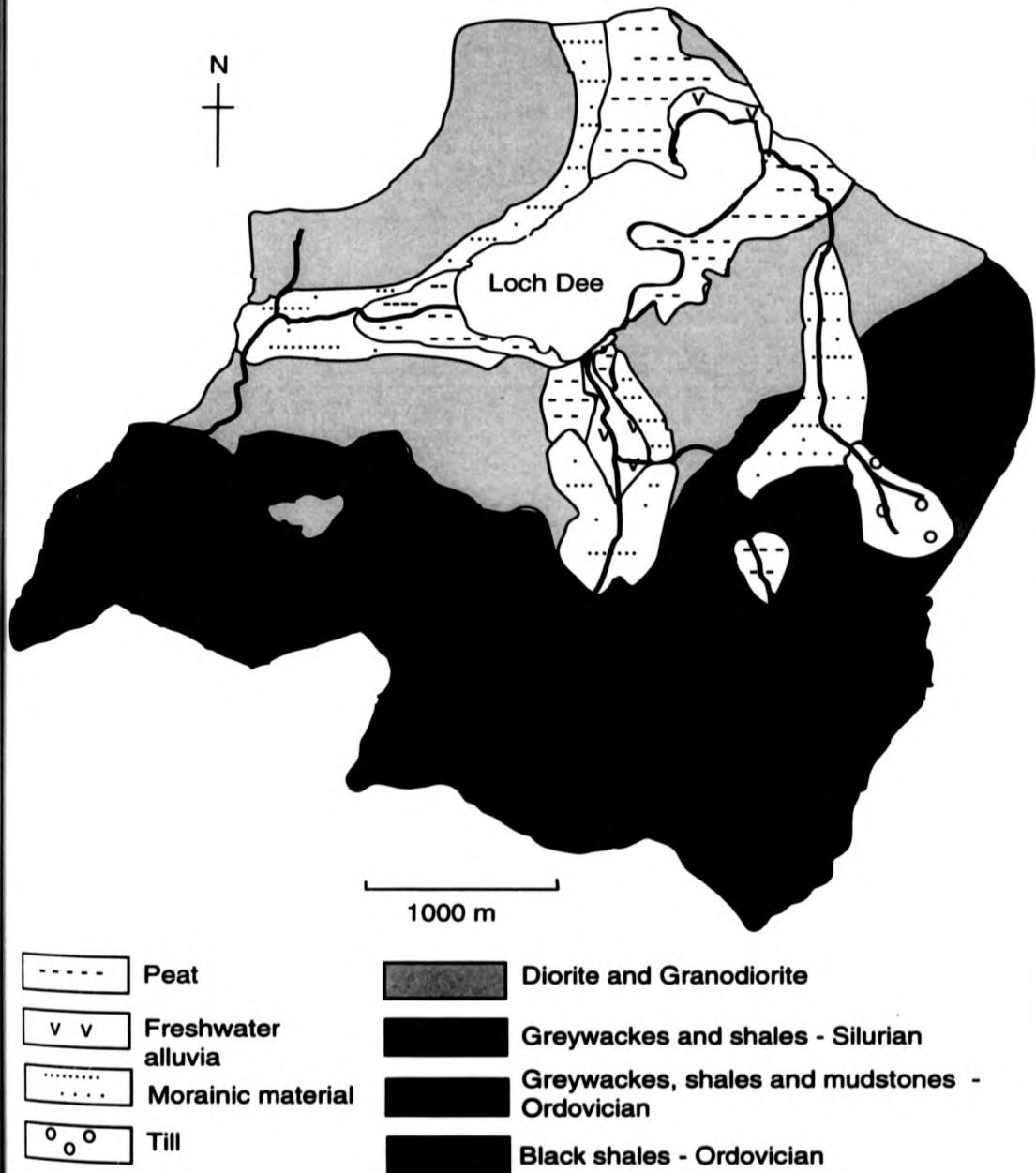
Chapter 3: Drift Geology of the Loch Dee area.

3.1 INTRODUCTION

During the last glaciation of Scotland the Loch Dee area was covered by part of the Southern Upland ice sheet. This formed an independent centre for dispersion of the southern component of the Scottish ice sheet, (Geikie 1863). Striae, cut into rock faces by glacial action, are abundant in the area and show a radial pattern (Geological Survey 1980) with a focal point SW of Loch Doon. These striae indicate a thick mass of ice 'flowed' northward into Ayrshire while a still thicker mass of ice moved southward to the Solway Firth and Irish sea, (Slater 1929, Charlesworth 1957).

The influence of this glacial activity is manifested in the Loch Dee area both in geomorphology and drift deposits. The White Laggan sub-catchment is a broad low sloped U-shaped valley bounded on either side by craggy rock faces. Hummocky terrain is common in the low lying land. The topography of the Dargall Lane sub-catchment is striking in its contrast; it has a steep gradient and includes an armchair shaped corrie face. Most of the drift deposits in the area are of glacial origin and range from firm boulder clay to unconsolidated moraine (Greig 1971). Farley and Werritty (1989) indicated drift deposits in the catchment were as shown in figure 3.1A, taken from the Geological Survey drift map of 1977, sheet 8E. This map highlights the relative insignificance of drift deposits in the area and splits any present into small expanses of morainic material in all three sub-catchments and minor till in the Green Burn sub-catchment.

**Figure 3.1A : Solid and drift geology of the Loch Dee catchment
(after Farley and Werritty 1989)**



Other literature implies drift deposits were more widespread. Gregory (1925) reported the Loch Doon pluton was surrounded by a band of moraines generally between 800 and 600ft above sea level but dipping down to 225ft near the confluence of the Trool and Minnoch waters. Geikie (1863) and Gregory (1925) both indicated the presence of boulder clay in great thicknesses along valley bottoms in the Southern Upland region. This boulder clay was split into an upper and lower clay and in some localities separated by sands and gravels (Eckford 1932). The lower boulder clay was described as firm and tenacious while the upper one was more sandy with large angular boulders (Geological Survey of Great Britain 1980). Giusti (1991) found evidence of these boulder clays within the Dargall lane sub-catchment. These had not previously been reported and are not illustrated on figure 3.1A. They were poorly exposed and often mixed with morainic material. He proposed the lower boulder clay was deposited some 12000 years before present (BP) during glacial advance, corresponding to dates given by Bishop and Coope (1977). Giusti suggested the lower boulder clay included a greater quantity of intensely weathered boulders than the upper variety, a description that deviates from that given by the Geological Survey (1980). The later boulder clay was suggested to represent ablation tillites deposited during and after the melting of the ice. Giusti (1991) also indicated a limited re-advance of ice, between 11800 and 11300 years ago, left behind additional morainic ridges of poorly consolidated gravel, sand, silt and clay.

3.2 AIMS:

The main aims of this chapter were:

1. To characterise some of the drift deposits in terms of particle size distribution and chemistry.
2. To determine if the deposits were locally derived and the degree of mixing of solid geology types.

3.3 MATERIALS AND METHODS

The drift material was not implied to be of great areal importance on figure 3.1A, therefore only 6 samples were collected to represent the drift deposits of the area. They were collected from the points illustrated on figure 3.3A. Most of these points corresponded to mapped positions of morainic material.

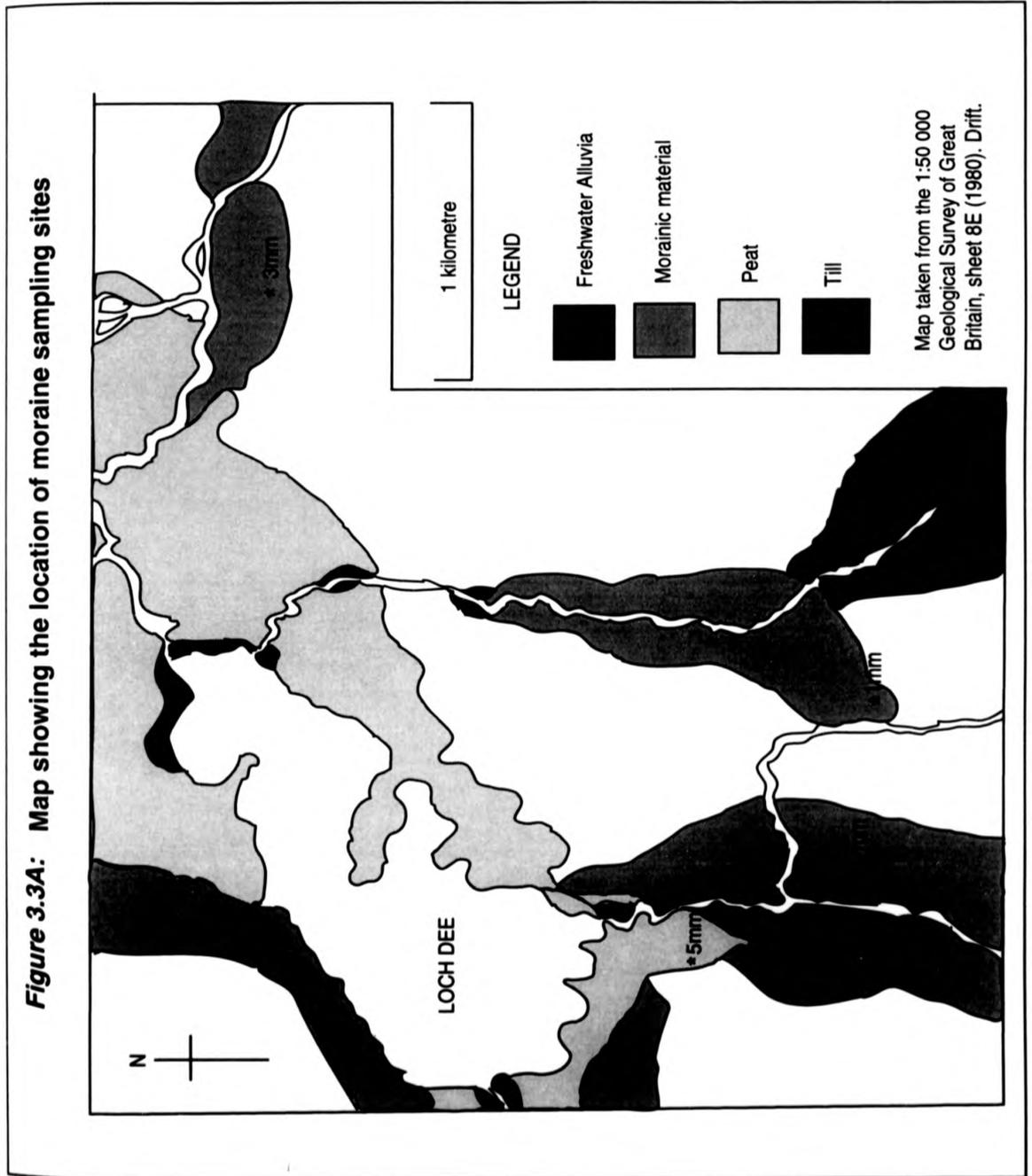
Prior to particle size analysis samples were air dried for a couple of days and any aggregated material was broken down using a rubber pestle and mortar (chapter 4).

3.31 Particle size analysis

Particle size analysis included two parts:

1. A stack of sieves with mesh sizes ranging between 63 μ m and 16mm was set over a collecting pan. A known weight of a sample was put into the top sieve and closed off by a lid. The equipment + sample was moved to a mechanical shaker and jolted for 10 minutes. After this time the material in the collecting pan and each individual sieve was weighed and expressed as a % of the total sample.

Figure 3.3A: Map showing the location of moraine sampling sites



Particles > 2mm were also classed for their origin, as far as was possible. Particles < 2mm in size were thoroughly remixed for further particle size and chemical analysis.

2. The sample was split into sand, silt and clay sized particles by a sieving/sedimentation method. The procedure was standard (Avery and Bascomb 1974) and follows:

A. 10g of material <2mm in size was weighed and placed into a 500ml conical flask, 10ml of hydrogen peroxide was added to the flask and the reaction observed for 30 minutes. The peroxide destroyed any organic matter present. If reaction was vigorous further H_2O_2 was added. After reaction had ceased the contents of the flask were diluted to 40ml and heated at 90° C for 1 hour. When cooled, the contents of the flask were added to a 250ml plastic bottle and 10ml of dispersing agent (sodium hexametaphosphate) added. At the same time 10ml of dispersing agent was also added to a dry, clean, weighed watchglass. This was evaporated to dryness overnight and the weight of the residue (R) noted for future calculation. Meanwhile, the volume of the bottle was made up to 150ml with distilled water, the bottles were capped and moved to a mechanical shaker where the contents of the bottle were agitated overnight.

B. The contents of the bottle were put through a 63 μ m sieve into a 500ml measuring cylinder. Any material left on the sieve was washed into a weighed beaker with distilled water and the beaker was evaporated to dryness overnight. This fraction was weighed (S) and expressed as a % of the original 10g of sample. This was the sand fraction.

C. The volume in the cylinder was made up to 500ml, stirred then 25ml of sample was taken by pipette from a 20cm depth and emptied into a dry weighed beaker which

3.32 Chemical analysis

The drift material < 2mm in size was tested by standard wet chemical methods for a number of its chemical properties.

i. Exchangeable cations

Exchangeable cations were measured by leaching a known weight of sample with excess ammonium ions in the form of ammonium acetate at pH 7. In theory the cations become replaced by ammonium and can be measured in the leachate. Exchangeable calcium and magnesium were measured in the leachate by flame atomic absorption spectrophotometry (AAS) using an oxyacetylene flame and sodium and potassium by flame photometry. Exchangeable hydrogen was measured by reference to the pH change of the ammonium acetate solution after passage through the samples. This pH change was compared with a graph given in Hesse (1971) which converted this value to exchangeable hydrogen. Further details of these standard methods can be found in Hesse.

ii. Exchangeable Aluminium

Exchangeable aluminium was measured by a standard method reported in Hesse (1971). A known weight of sample was leached with unbuffered 1M KCl solution and leaching time was kept to a minimum to avoid dissolution of non-exchangeable aluminium (Pratt and Bair 1961 in Hesse 1971). The KCl was in considerable excess because aluminium is firmly held by exchange sites. McClean (1965) suggested the need to maintain a low pH throughout the leaching but indicated sufficient acidity was formed during leaching to maintain the solubility of the aluminium during the extraction. Aluminium was measured in resultant leachates by flame AAS using a

nitrous oxide flame.

iii. Cation exchange capacity

Cation exchange capacity was tested by two methods:

- a. Summation of mean exchangeable cations
- b. Saturation of a known weight of sample with Ba ions in the form of a buffered (at pH 8.2) BaCl₂ solution. This method is reported by Avery and Bascomb (1974). The sample and solution were separated after overnight shaking by centrifuging at 2500 rev/min for 15 minutes. The supernatant liquid was discarded. Following this the sample was shaken with distilled water and the sample and solution again separated by centrifuging and the washing discarded. Finally the sample was saturated with magnesium ions by addition of MgSO₄, capping and shaking for two hours on a mechanical shaker. The solution and sample were finally separated using centrifugation. This time the supernatant liquid was measured for its magnesium content by flame AAS. The amount of magnesium adsorbed by the exchange complex was calculated by:

Concentration of magnesium in the MgSO₄ solution - magnesium in Supernatant

This represented a measure of the exchange capacity of the sample. Other methods of CEC measurement were explored by Chapman (1965), and Bache (1976). Chapman suggested cation exchange capacity was operationally defined with each method giving a result of the correct order of magnitude but not an accurate result. He indicated particular failings of methods on samples with low pH since most methods involved measurement at neutral or alkaline pH. In this study summation was proposed to be the only feasible procedure to follow.

3.4 RESULTS

3.41 Sample description

The samples were described for colour and physical appearance.

1MM = Light coloured material typically fine grained and often clay rich. Coarser inclusions limited in both size and number.

2MM = Medium brown in colour, including a number of coarse particles of sedimentary origin.

3MM = Medium brown in colouration, including a number of coarse particles greater than 2cm in diameter.

4MM = Light to medium brown in colour. Includes extremes of very coarse and very fine material.

5MM = Medium brown coloration, including numerous very coarse pebbles.

6MM = Light to med brown in colour. Inclusions of coarse size common.

3.42 Particle size analysis

The results for the first part of the particle size analysis are presented in table 3.42A. Samples 3-6 included fragments over 16mm in size. Samples 1MM and 6MM included the least coarse grained material and sample 1MM had by far the greatest fine fraction. Samples 3MM and 5MM included the greatest fraction of coarse fragments. All of these results supported the initial visual descriptions of the material.

Table 3.42A Results for the sieving of samples expressed as a weight % of the total sample in each sieve.

Sieve Mesh	1MM	2MM	3MM	4MM	5MM	6MM
16mm -4Ø	0.00%	0.00%	4.96%	5.68%	14.9%	2.28%
8mm -3Ø	1.10%	6.03%	12.0%	2.05%	9.42%	4.08%
4mm -2Ø	1.98%	9.66%	12.2%	7.16%	10.4%	3.50%
2mm -1Ø	4.29%	7.98%	26.0%	19.2%	17.8%	8.95%
1mm 0Ø	7.41%	10.8%	15.4%	17.9%	13.1%	17.3%
0.5mm 1Ø	10.9%	12.2%	12.6%	14.2%	12.3%	16.5%
0.25mm 2Ø	14.7%	15.1%	7.80%	12.4%	10.2%	13.7%
0.125 mm 3Ø	16.6%	17.1%	4.93%	10.0%	7.06%	11.0%
63µm 4Ø	18.6%	13.9%	3.10%	6.73%	3.24%	9.92%
< 63µm	24.1%	7.19%	2.14%	4.70%	1.53%	12.8%

The tabulated results indicated 1MM included mostly fine particles whereas 5MM had the greatest quantity of coarse fragments.

The nature of all coarse fragments (> 2mm) was also noted and the results are given in table 3.42B.

Table 3.42B: Nature and origin of the coarse fraction.

Sample	Clast angularity *	Clast type
1MM	Subangular to angular	Mixed; Sed and ig rocks found locally.
2MM	Angular	Mostly ig with minor sed found locally
3MM	Subrounded to angular	Mostly ig with minor sed found locally
4MM	Angular to subangular	Ig rocks found locally
5MM	Angular	Mostly ig with minor sed found locally
6MM	Subangular to subrounded	Mixed; Sed and ig rocks found locally.

* Angularity estimated from figure 2.5, Tucker (1981) after Pettijohn et al (1973).

The table indicated most of the drift coarse fractions could have been of local origin; however, there did appear to be some mixing of these local rock types.

Results for the sample % clay, silt and sand by the settling column experiments detailed in section 3.31:2 are given in table 3.42C.

3MM and 5MM were mostly made up of fine sand. 1MM displayed the greatest weight % of clay minerals and was also relatively enriched in silt. Sample 2MM encompassed the highest proportion of silt. Replication of results was good for the sand sized particles of the fine fraction, good for the silt sized particles but generally poor for the smallest fraction. Loss of this clay sized fraction is much easier throughout the method.

Table 3.42C: Particle size analysis in terms of sand, silt and clay - results are given as mean % of the initial 10g weight. Standard deviation is given in italics, n = 3.

Sample	% sand (> 63 µm)	% silt (2-63 µm)	% clay (< 2µm)
1MM	65.7 <i>2.98</i>	22.6 <i>4.03</i>	11.6 <i>2.65</i>
2MM	67.4 <i>1.16</i>	24.9 <i>2.11</i>	7.72 <i>1.57</i>
3MM	82.8 <i>2.16</i>	9.81 <i>0.35</i>	7.36 <i>2.47</i>
4MM	77.4 <i>0.76</i>	16.4 <i>0.85</i>	6.18 <i>0.92</i>
5MM	79.9 <i>0.71</i>	15.2 <i>0.70</i>	5.57 <i>0.09</i>
6MM	70.6 <i>3.38</i>	20.3 <i>3.05</i>	7.02 <i>0.84</i>

3.43 Chemical analyses

Exchangeable cation results are given in table 3.43A

Table 3.43A - Exchangeable cation results given as mean values. Standard deviation is given in italics, n=3. Where no standard deviation result is given one result was much different from the other two and discarded. The result given is then a mean of the two similar values.

	Exch Ca meq/kg	Exch Mg meq/kg	Exch Na meq/kg	Exch K meq/kg
1MM	6.98 <i>0.28</i>	5.77	3.66 <i>1.86</i>	1.34
2MM	2.24	1.53 <i>0.66</i>	1.59 <i>0.12</i>	0.84 <i>0.08</i>
3MM	1.43 <i>0.76</i>	0.79 <i>0.54</i>	1.50 <i>0.07</i>	0.52 <i>0.19</i>
4MM	1.88	0.97 <i>0.68</i>	1.40 <i>0.15</i>	0.62
5MM	2.45 <i>1.41</i>	1.35 <i>0.71</i>	1.21 <i>0.07</i>	0.48 <i>0.21</i>
6MM	1.70	0.90 <i>0.58</i>	1.38 <i>0.06</i>	0.31 <i>0.11</i>

1MM had higher concentrations of exchangeable base cations than the other samples. 2MM and 5MM involved the next highest exchangeable calcium and magnesium. Variability within results was high except in the case of sodium measurements which were similar for each sample.

Exchangeable aluminium, exchangeable hydrogen and CEC results are given in table 3.43B.

Table 3.43B: Exchangeable Al, H and CEC results. Al results expressed as a mean value with standard deviation in italics. Where no standard deviation is given one result was very different from the other two and was disregarded. and the results are mean values. Exchangeable H and CEC results are mean values.

	Exch Al meq/kg	Exch H meq/kg	CEC measured meq/kg	summed CEC meq/kg
1MM	0.61 <i>0.37</i>	64.6	64.5	83.0
2MM	13.0 <i>1.37</i>	160	260	179
3MM	3.29 <i>0.67</i>	103	73.6	111
4MM	12.4	131	98.3	148
5MM	11.7 <i>1.26</i>	218	150	235
6MM	33.7 <i>7.45</i>	127	213	165

Tests were triplicated for aluminium. Exchangeable hydrogen and summed CEC were only tested in duplicate for each sample. Summed CEC values represents the sum of mean exchangeable cations. Replication was moderate in the exchangeable aluminium samples. Replication was poor in the CEC tests. 6MM had the highest level of exchangeable aluminium, 1MM the lowest. 5MM had the highest level of exchangeable hydrogen, 1MM the lowest. Summed CEC was higher than measured CEC in the case of 1MM, 3MM, 4MM and 5MM. Summed CEC < measured for 2MM and 6MM. In all cases most of the CEC was due to hydrogen and problems in measurement could lead to differences between measured and summed CEC.

3.5 DISCUSSION

3.51 Particle size analysis

The samples taken all varied in their particle size distribution. Figure 3.5A shows the cumulative % oversize curves for each of the drift samples. The horizontal scale is represented by phi units which are based on a \log_2 size scale. The phi units ran from -4 which is a 16mm sieve to >4 which represents the pan below a 63 μ m sieve. Use of this scale enables the direct comparison of class % for both coarse and fine particles. This is achieved by compensation for the lighter weight of the smaller sized grains since the physical difference between the positive phi units is smaller. Using these diagrams it was possible to characterise each sample in terms of:

a. Median grainsize = 50% ϕ value.

b. Graphic mean by i. $\phi_{16} + \phi_{50} + \phi_{84}$

$$\frac{\phi_{16} + \phi_{50} + \phi_{84}}{3}$$

Folk and Ward (1957)

ii. $\phi_{10} + \phi_{30} + \phi_{50} + \phi_{70} + \phi_{90}$

$$\frac{\phi_{10} + \phi_{30} + \phi_{50} + \phi_{70} + \phi_{90}}{5}$$

McCammon (1962)

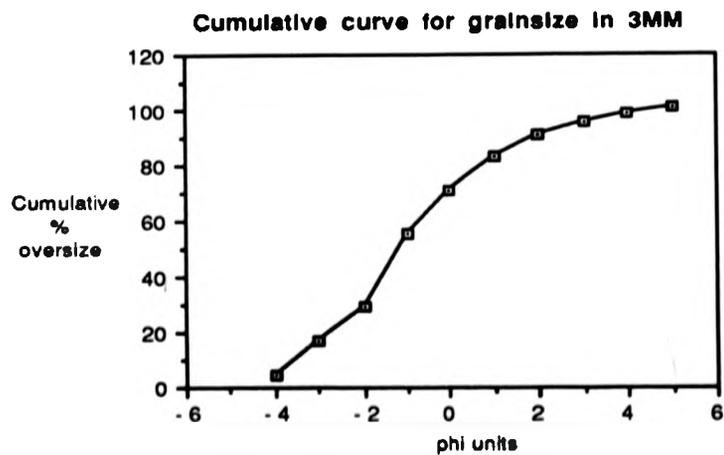
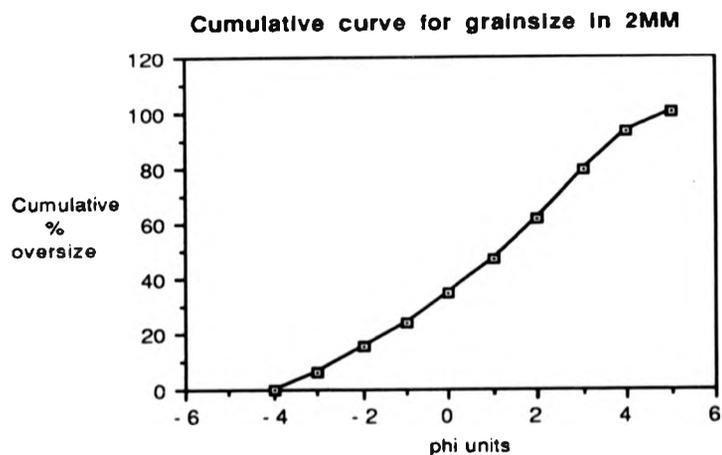
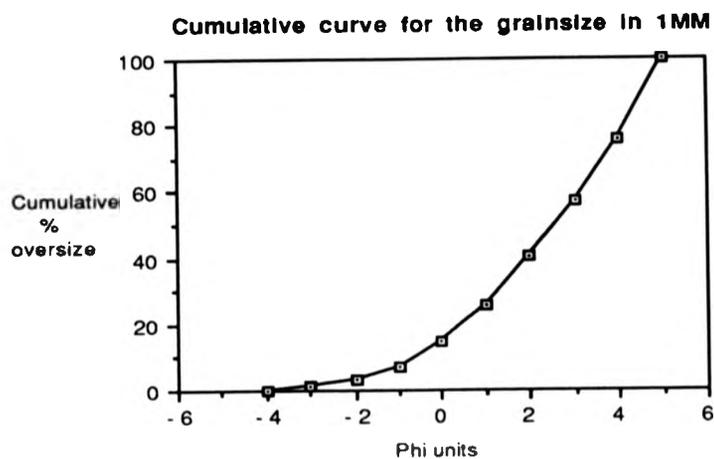
c. Inclusive graphic standard deviation which gives an indication of sorting using:

$$\frac{\phi_{84} - \phi_{16}}{4} + \frac{\phi_{95} - \phi_5}{6.6}$$

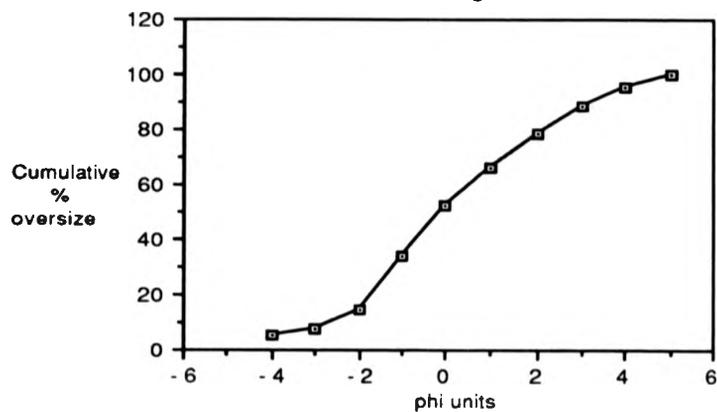
This equation was also taken from Folk and Ward (1957).

These values are given in table 3.5A.

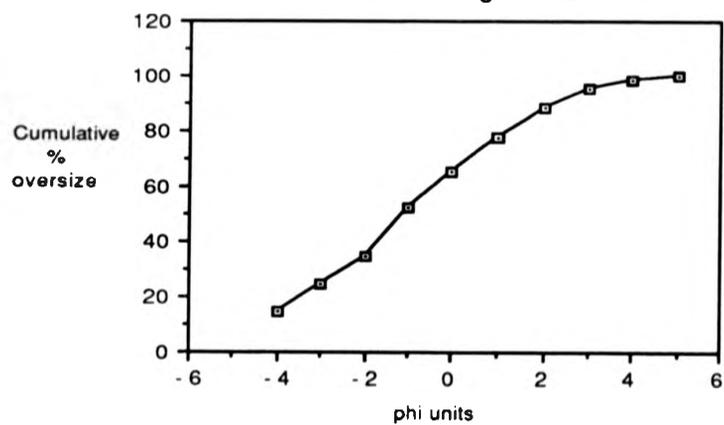
Figure 3.5A: Cumulative curves for the drift samples from Loch Dee



Cumulative curve for grainsize in 4MM



Cumulative curve for grainsize in 5MM



Cumulative curve for grainsize in 6MM

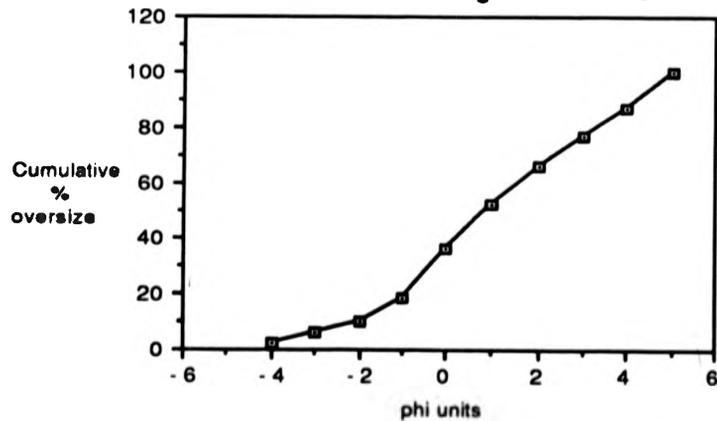


Table 3.5A: Table giving the descriptive statistical parameters for the drift samples from Loch Dee calculated using the % oversize cumulative curve.

	Median	Mean (i)	Mean (ii)	S.D.
1MM	2.6Ø	2.36Ø	2.34Ø	2.03
2MM	1.3Ø	0.90Ø	0.95Ø	2.43
3MM	-0.10Ø	0.17Ø	0.14Ø	2.33
4MM	-0.10Ø	0.27Ø	0.14Ø	2.39
5MM	-1.1Ø	-1.1Ø	-1.08Ø	2.56
6MM	1.10Ø	1.10Ø	1.80Ø	2.40

The descriptive statistical values indicated:

- a. Sample 1MM had a much finer average grainsize than the other samples.
- b. Sample 5MM had the most coarse average grainsize.
- c. All samples were very poorly sorted according to the scheme of Folk and Ward (1957); 1MM showed the lowest standard deviation and hence a better degree of sorting than sample 5MM which had the highest standard deviation.

Poor sorting would be anticipated for samples of glacial origin.

Coarse fraction of the drifts

The coarse fraction in all samples was made up of a mixture of both sedimentary and igneous rocks of possible local derivation. The samples taken above igneous solid geology (2-6MM) were typically dominated by igneous coarse fractions. Bown (1979) indicated that drift materials from the igneous part of the catchment were derived from igneous rock types and were potentially part of the Dalbeattie soil parent materials. Although igneous clasts dominated the coarse fraction of the Dalbeattie drifts collected in this study the presence of some sedimentary material e.g. sample 6MM indicated

some mixing of solid geology types in the drift formation.

Sample 1MM was the only sample taken from the meta-sedimentary part of the catchment and included a mixture of both igneous and sedimentary coarse fragments with no rock type demonstrating obvious dominance. Further samples would have been useful to determine the extent of mixing. Bown (1979) indicated drift materials overlying the 'country rocks' would be derived from these rocks and potentially form part of the Etrick Association soil parent material. Results from this study appeared to deviate from this definition since the drift coarse fraction was of mixed origin. However, drift formed in the south of the catchment would have a number of different solid geology types to draw from which could explain the mixed nature of the sample taken.

The possibility of mixing of igneous and sedimentary material in the coarse fraction of drift samples highlighted the unlikely situation of soils derived from these drifts displaying the chemical characteristics of a single solid geological parent material; i.e any solid geological control on soil chemical properties would become obscured due to mixing of drift types.

3.52: Analysis of variance according to texture.

The soil textural characteristics of % sand, silt and clay were analysed according to the different soil parent material classes (Bown 1979). Samples 2-6MM (potential parent material for the Dalbeattie soils) were similar in % sand and silt contents to sample 1MM (potential parent material for the Etrick Association soils). However, as indicated in section 3.51, % clay content was much greater in the sample 1MM.

Analysis of variance indicated this difference was significant at the 95 percentile level of certainty. This greater clay content in the drift materials overlying the sediments and meta-sediments was in agreement with the work of Bown (1979) and highlighted a difference in the two drift types explainable in terms of solid geology. Drifts derived from the sediments and meta-sediments included a significantly higher clay content than those derived from rocks of the Loch Doon Pluton. Shales and mudstones are both aggregates of numerous clay sized particles and both rock types only occur in the southern half of the catchment and according to Bown, should only contribute to the 'Etrick' drifts.

3.53 Chemical analysis

Sample 1MM exhibited the highest concentration of exchangeable bases and the highest clay content. The CEC in this sample (both measured and summed) was much lower than any other sample; it is likely that bases were retained in an exchangeable form on the clays and that very little other material capable of cation exchange e.g. organic matter, was present in this sample. Acidic cations typically held by organic matter for ion exchange were noticeably lower in this sample than any other. Samples 2MM and 5MM had the next highest exchangeable calcium and magnesium; these did not correspond to high clay contents. These two samples also exhibited the greatest exchangeable hydrogen and correspondingly the greatest CEC. Since this could not be explained with reference to clay content, it was assumed these samples were associated with limited organic matter. However, organic matter appeared to be low or absent in all samples when tested with H_2O_2 . Exchangeable aluminium was constantly greater in sample 6MM despite poor replication of results. This was

reflected in a high CEC. Sample 3MM had lower exchangeable aluminium than all samples except 1MM.

3.54 Analysis of variance of drift chemical data

The chemical data derived from the drift material <2mm in size was analysed according to the two soil parent material classes which defined the Dalbeattie and Ettrick Associations of Bown (1979), see chapter 4. Table 3.54A gives the chemical differences between these two classes at the 95 percentile level of certainty.

Table 3.54A: Chemical differences between the Dalbeattie and Ettrick drifts at the 95 percentile level of certainty.

	P value	Ettrick	Dalbeattie
Exch Ca (meq/kg)	0.00	6.98 (0.00)	1.94 (0.41)
Exch Mg (meq/kg)	0.00	5.77 (0.00)	1.11 (0.32)
Exch Na (meq/kg)	0.00	3.66 (0.00)	1.42 (0.14)
Exch K (meq/kg)	0.02	1.34 (0.00)	0.55 (0.20)

Analysis of variance indicated some strong chemical differences between the drifts from the south of the catchment and those from the north. Dalbeattie drifts (those associated with the igneous rocks) were much lower in all exchangeable cations than the Ettrick drifts. This appeared to be a reflection of the clay content of the drifts. Ettrick drifts were richer in both exchangeable bases and clay than the Dalbeattie drifts. However, this apparently strong difference in the <2mm fraction between the two drift types should be approached with caution because of the small population size of both classes.

3.6 CONCLUSIONS

Drift material was both chemically and texturally diverse. Chemical features of some samples were explained by clay content. Others chemical features appeared to be explained by the presence of organic matter. Since the organic matter content of the samples had not been measured this could not be confirmed.

The samples chosen exhibited a range of mean grainsizes from 2.4 ϕ to -1.1 ϕ or approximately 0.125 - 0.25 mm to 2mm. All samples were poorly sorted as would be expected for drift materials.

The coarse fraction of all drift samples indicated a mixing of solid geology types of local derivation. That sampled from the drift over the igneous rock types (Dalbeattie drift) was dominantly igneous although occasional significant inputs from coarse sedimentary fractions did occur. The sample population, however, was not large enough to be certain of the degree of mixing and whether or not it was commonplace. One sample taken from the meta-sedimentary solid geology realm (Ettrick Drift) exhibited a strong mixing of rock types in its coarse fraction.

The two different classes of drift exhibited some chemical differences in the > 2mm fraction that appeared to be related to sample clay content. Textural differences in this size class could have been related to geology. However, the population size of both drift classes was too small to be certain of any strong differences.

Merging of solid geology types in drift materials would be significant for the identification of a geological control on the chemistry of soils in the area. If a mixed drift was a significant component of soil parent material any geological controls on soil chemistry would become obscured. Soil chemical data would not be expected to express clear differences due to input from different solid geology types. Data collected in this chapter illustrated the importance of the mixing of solid geology types in drift coarse fractions. This would also be expected in the finer fraction of the drift material. However drift material < 2mm in size exhibited some significant chemical and textural differences between 'Dalbeattie' and 'Ettrick' samples. This apparent difference between the two drift types could just be a reflection of the small sample population - much more work would need to be carried out to confirm the reality of such a difference.

Chapter 4: Soils of the Loch Dee area.

4.1 INTRODUCTION

Soils are the result of complex interactions between physical, chemical and biological agents through time. They are inherently dynamic systems even when developed under stable conditions (Pearsall 1950). During soil formation animal and plant organic residues are broken down and mixed with decaying inorganic and mineral materials. Degradation products are redistributed or removed to form layers of soil with contrasting physical and chemical properties (Krauskopf 1979). A collection of such soil horizons makes up a soil profile; the horizon characteristics and ordering within the profile determines the classification of the soil (Avery 1980).

Soil forming factors:

5 main factors contribute to the formation of a soil:

1. **Climate** - External conditions influence the processes that operate in a soil e.g high leaching occurs in tropical climates whereas waterlogging and gleying are more common in temperate climates with high rainfall. Such contrasts in climate can lead to major differences in the degree and type of mineral weathering that occurs. On a smaller scale microclimatic variations can introduce soil heterogeneity.
2. **Parent material** - This helps to determine the base saturation of a soil and influences drainage patterns through textural variability.
3. **Relief** - Affects pedogenesis by controlling water flow within a soil body. It can also affect microclimate since temperature and precipitation typically increase with altitude.
4. **Biological agencies** - Fauna and flora influence soils in many different ways. Earthworms mix soil material, plant communities feed on nutrients in the soil which

are returned to the soil on their death; man affects soil formation through management techniques such as conifer afforestation, clearfelling of plantations, catchment liming and crop rotation.

5. Time - The soil changes through time in response to changing external and internal conditions. The age of a soil is reflected in its chemical proximity to its parent materials.

4.11 Soil forming factors at Loch Dee

Loch Dee is situated in a wet, upland area in the south west of Scotland. Two processes commonly occur in the soils developed in the area:

- i. Leaching
- ii. Gleying

Leaching is common in well aerated freely drained soils. Non-exchangeable bases are removed from the soil imparting a buff coloration. Less mobile elements, e.g. iron and aluminium may be leached out of both eluvial and surface mineral soil horizons and may accumulate to form an iron pan. Alternatively the two elements may be concentrated over a wider zone (Farmer 1986). Soils with these characteristics are termed podzols. In contrast, gleying occurs in soils with impeded drainage and poor aeration where chemical reactions include the 'reduction' of Fe^{3+} , manganese, NO_3^- and SO_4^{2-} . Such anaerobic conditions and subsequent chemical reactions bestow a grey/blue hue to soils, termed gleys. Organic matter decay is typically checked under such conditions and accumulation of peaty surface horizons is not uncommon. Mineral horizons may become mottled with peaty material which decreases the influence of minerogenic material on soil water chemistry.

Soil parent materials are local bedrock and/or drift derived from it (Bown 1979). The solid geology either belongs to the Loch Doon pluton suite to the north or the complex meta-sediments in the south of the area (chapter 2). Glacial deposits analysed in chapter 3 highlighted a mixing of these solid geology types. Soils involving a major drift component in their parent materials may, therefore, have similar chemical properties.

Changes in relief are important in the area, with the rocky microrelief causing the development of many minor and irregular pockets of soil. On a larger scale a 100m rise in altitude has been reported to impart a 5-6% increase in rainfall (Welsh and Burns 1987) in the area thereby causing significant changes to microclimate.

Vegetation around Loch Dee is variable including conifer plantation, grasses, heather and mosses. The wild flowers Birdsfoot trefoil, Tormentil and the common spotted orchid all occur along the banks of the White Laggan Burn. Fauna is also heterogeneous and includes wild deer and goats, sheep, adders and a wide variety of birdlife. Man has been active in the area for many years with more recent managerial implementations including soil liming (Tervet and Harriman 1988), planting of Sitka spruce and Lodgepole pine plantations and their subsequent upkeep including fertiliser applications (Lees 1992).

All the soils date from the end of the glacial period (Bown et al 1982) and are of a similar age C. 10,000 years old. Earlier soils would have been eroded or reworked by glacier action.

4.12 Loch Dee soils

The soils in the Loch Dee area are highly irregular having developed in little pockets with limited areal extent (Bown 1979, Bown et al 1982). Mapping of these soils has been based, in the past, on recognition of soil patterns and groupings related to landform rather than soil profile types. Figure 4.1A illustrates the soils of the area according to Bown (1979) and includes the positions of sampling sites (see later).

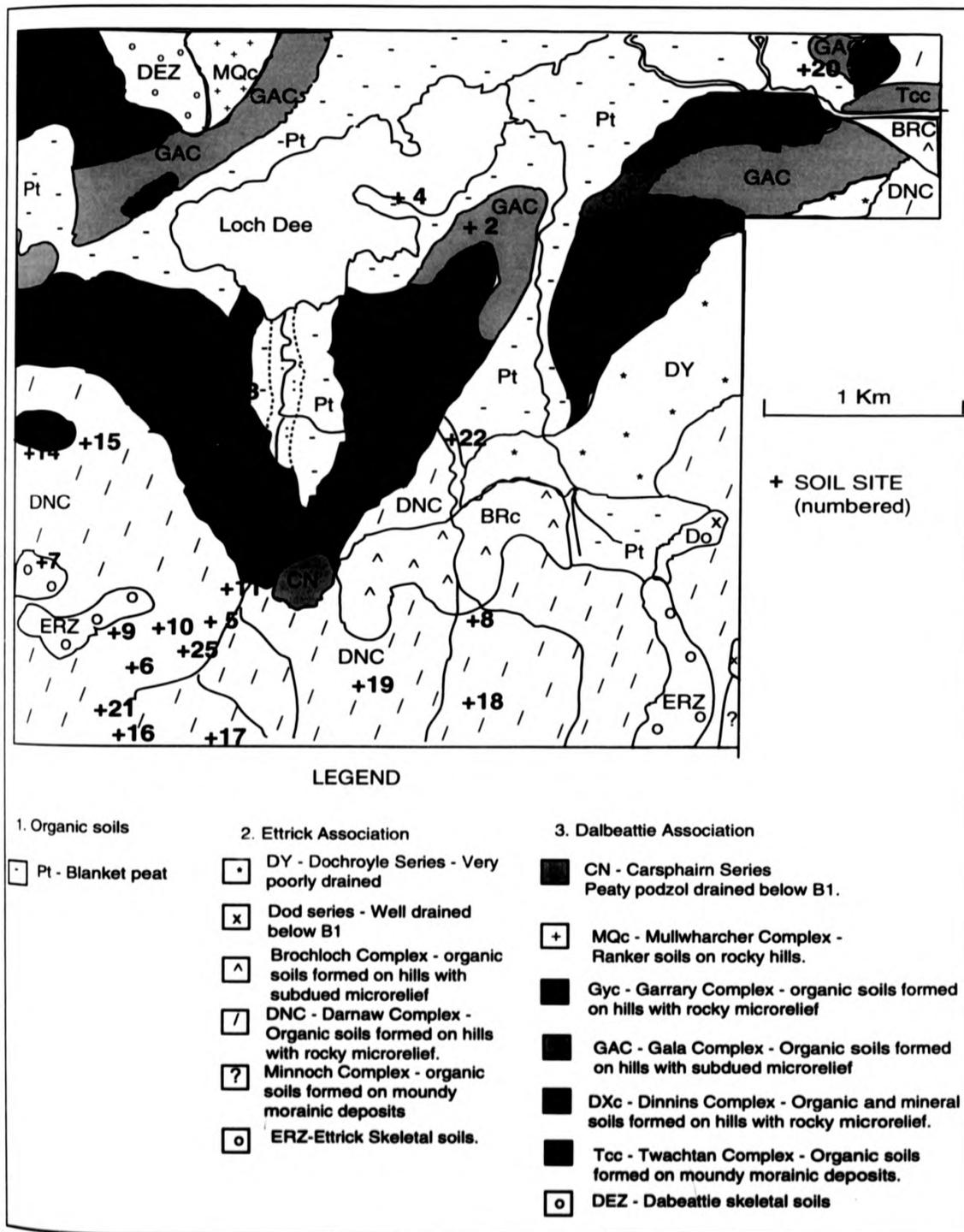
The soils are differentiated according to the dominant parent materials into organic soil profiles and mineral soil profiles of the Etrick and the Dalbeattie Associations, although it is not uncommon for organic soil profiles to occur within the realm of Etrick and Dalbeattie soils. These two mainly mineral soil associations are subdivided into small series or complexes according to relief and drainage patterns. Organic soils are divided according to thickness and topographic situation.

Etrick Association

The Etrick Association soils are developed on Ordovician and Silurian sediments and meta-sediments and drift material derived from these rock types. Giusti (1991) split this association into 3 categories according to whether the soils were developed on bare rock, stony drift or fine textured till. Bown (1979) separated the Etrick Association into 9 series and 10 complexes. Two of these series, 3 complexes and some skeletal soils are developed in the Loch Dee area. The main features of these latter soil units are given below.

Dod series - Peaty podzols generally found on moderate/steep slopes or morainic mounds and drumlins.

FIGURE 4.1A - SOIL MAP OF THE LOCH DEE AREA INCLUDING SAMPLING SITES
AFTER C.J. BOWN (1979).



Dochroyle series - Peaty gleys with varied topographic associations. Peaty surface horizons are well developed and act as sponges absorbing water and maintaining intense gleying conditions even in dry periods.

Brochloch Complex - Found on uneven hills with little or no outcropping rock. Includes podzol rankers, peaty podzols, peaty gleys and peat soils. Parent materials are typically thin stony drifts. All soils have a well developed raw humus or peaty surface horizon.

Darnaw complex - Found on rugged hilly sites at high altitude (> 800 ft). Includes rankers, podzols, peaty gleys and peat.

Minnoch Complex - Developed on moundy topography of morainic hummocks and intervening hollows. Includes peaty podzols (Dod series), peat soils and occasional brown forest soil on the slopes of mounds.

Ettrick Skeletal soils - Shallow soils (15 - 20cm), often tinned rankers commonly found on high ridges or corrie faces.

Dalbeattie Association

The Dalbeattie Association soils are developed on the rocks of the Loch Doon intrusion and drifts formed from these rocks. Bown (1979) split the association into 3 soil series and 7 soil complexes. 1 series, 5 complexes and some skeletal soils are developed in the area. The main features of these series and complexes are:

Carsphairn Series - Peaty podzols found on steep slopes with coarse textured stony drift or moraine as parent materials.

Dinnins Complex - Found < 800 ft on short uneven slopes with variable microrelief. Soils are typically freely drained and shallow and include peaty podzols, brown forest

soils but minor peaty gleys and peats occur in depressed areas.

Gala Complex - Mapped along the lower slopes of hills where rock outcrops are few. Soils all have raw humus surface horizons and are typically in the form of peaty gleys although peaty podzols are also common.

Garrary Complex - Associated with hilly microrelief and prominent rock outcrops. Between outcrops a thin cover of eroded granitic material is common. All soils have raw humus surface horizon but otherwise are variable. Includes peaty podzols and peaty gleys, peat soils and ranker profiles.

Mullwharther Complex - Formed on high hills where bare rock is common. Soils formed between outcrops are typically rankers although frequently raw humus develops on rock.

Twachtan Complex - Developed on mounded topography of morainic humps and hollows occurring on lower, hill slopes or valley bottoms. Soils are typically peaty with occasional patches of brown forest soil.

Dalbeattie skeletal soils - Typically occur on the central ridge of the Loch Dee-Loch Doon basin. Soil formation typically restricted to humus accumulation on bare rock.

Organic soils

Organic soils have > 60% organic matter content for a thickness exceeding 50cm (Avery 1980). Two types of organic soil are present in the Southern Upland district (Bown et al 1982). These are basin and valley peat 1-5m thick and blanket peat 0.5-1m thick but locally deeper. Only the latter organic soil type occurs within the immediate vicinity of Loch Dee although local pockets of organic soils are developed as part of both the Ettrick and Dalbeattie Associations (Bown 1979, Bown et al 1982).

4.2 AIMS:

The aims of this chapter were:

1. To sample soils from both the Ettrick and Dalbeattie associations and characterise these both chemically and texturally.
2. To determine the extent of geological (both drift and solid) input on the texture and chemistry of the minerals soils.
3. To use micromorphological thin sections to view the minerogenic fraction of the soil and determine its source.

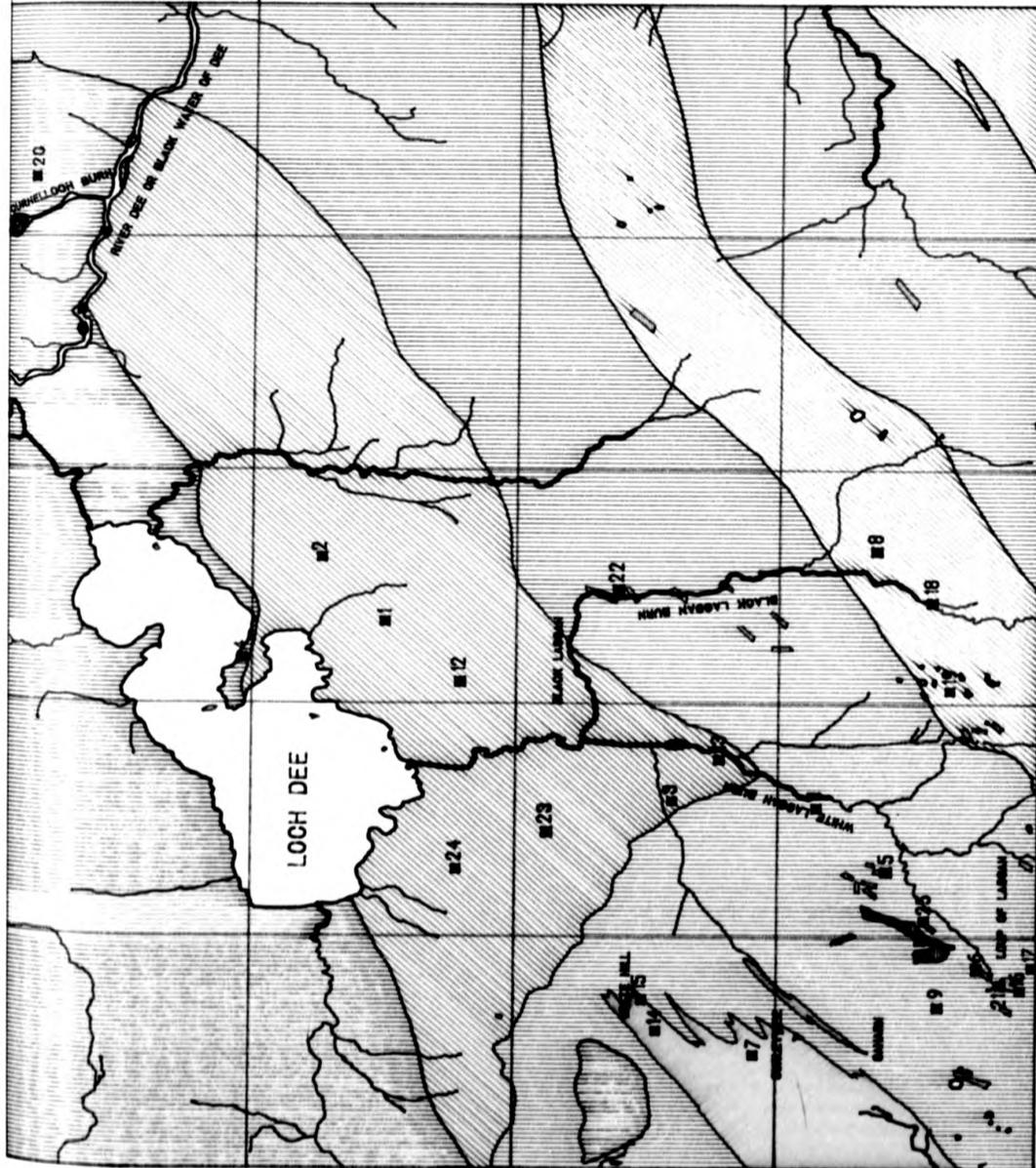
4.3 MATERIALS AND METHODS: Chemistry and texture of the soil.

4.31 Sampling procedure

A sampling scheme was devised including 25 sites chosen according to the mapped positions of solid geology types (Chapter 2) as indicated in figure 4.3A. 7 soil sites were located over diorites, 2 over granodiorite from the Loch Doon pluton and 1 over a minor granodioritic intrusion in the south of the catchment. 6 soil sites were over dykes within meta-sediments, 4 over coarse meta-sediments, 2 over fine meta-sediments and 3 over the black shales. The dykes were strongly represented because small geological bodies have been reported as strongly influencing the chemistry of nearby soils and soil waters e.g. increased Ca within the Loch Chon catchment close to a dolerite dyke (Miller et al 1990).

The soil sites are shown in relation to the soil associations, series and complexes in figure 4.1A. 15 soil sites were located as part of the Darnaw Complex (Ettrick Association) while 5 soil sites were positioned as members of the Garrary Complex

FIGURE 4.3A : SOIL SITE
POSITIONS IN RELATION
TO SOLID GEOLOGY
TYPES



LEGEND

GEOLOGY

84 SHALES AND GREYWACKES

88 BLACK SHALES

86 SHALES AND GREYWACKES

82

IRREGULAR ROCKS

MAJOR-

GRANODIORITE

DIORITE SUITE

MINOR-

GRANODIORITE

MINOR DYKES OF
VARIABLE COMPOSITION
(CLAPPHOPHITES,
PORPHYRITES,
FELSITES)

RIVERS

CONTOURS AT 5m INTERVALS

SOIL SAMPLING POINTS

(Dalbeattie Association). The Etrick skeletal soils and the Gala and Dinnins Complexes (Dalbeattie Association) were all represented by one soil site. Two soil sites were within the Organic soil zone.

The soil sites were described in terms of their slope, elevation and vegetation patterns, appendix D, pages 280-290. At each site between 2 and 5 soil samples, (typically 4, one from the upper and lower parts of organic and mineral horizons) were taken for analysis. At sites 1-11 soil pits were dug and the soil profile was characterised (appendix D). At sites 12-25 samples were taken by auger and depths of samples noted. The original aim of the project was to extract samples for soil thin section analysis from the first 11 sites which were thus excavated in the form of a pit. However, once the pits had been dug the mineral soils were often too stony or poorly developed to extract material from them for thin section analysis and so fewer soil thin sections were actually collected.

Samples were split analytically into organic and mineral soil horizons by reference to their carbon content. All samples were analysed for field moisture content, particle size, texture, colour, pH, organic carbon content, moisture content, exchangeable cations including Al and H, pyrophosphate extractable Fe and Al and cation exchange capacity.

4.32 Methods of soil chemical and particle size analysis

(i) Soil field moisture content

This was measured on field wet samples prior to drying. A known weight of soil (40 - 50g) was placed in a weighed beaker and left in an oven at 105°C overnight. The difference in weight produced on drying was expressed as a % of the initial soil weight. Single determinations were made on each sample.

(ii) Sample preparation

Soil samples were air dried on shallow trays for up to two weeks. Soils were dried at room temperature to decrease both chemical and physical changes reported by Hesse (1971). Drying involves the destruction of micro-organisms and liberation of soluble organic matter; oven drying can result in loss of carbon by oxidation. Physically the soil becomes dehydrated and clay particles may cement together giving the impression of a sandy texture to the soil. Special attention was paid to breaking up the soils daily to ensure both thorough drying and minimal clay clotting.

When dry the soils were passed through a 2 mm sieve; this size is used for most routine analyses (Hesse 1971). Any soil not passing through this sieve was weighed and expressed as a % of the total soil sample. The origin of these larger fractions was also noted.

(iii) Soil air dried moisture content

Air dry moisture content of the soil was measured to convert chemical analytical results to an oven dried soil basis, the conventional way to present soil chemical results. Moisture content was determined on 1 sample of each soil by placing a known weight of soil in an oven at 105° C for 4 hours, allowing to cool in a desiccator and then reweighing. Chemical analytical results were converted to an oven dried basis by multiplying by $(1 + 0.01m)$ where m = air dried moisture content.

(iv) Soil organic matter content

Soils were tested for their organic matter content by loss on ignition. This method was chosen as the soils were non-calcareous and sandy (Ball 1964). A known weight of sample was placed into a dry, weighed crucible and heated in a furnace at 850°C for 4 hours. Samples were then removed to a desiccator for 20 minutes to cool before reweighing. Triplicate determinations were made for each soil and the results used to split samples into mineral and organic soils, see later.

(v) Particle size analysis

Samples from mineral soil horizons (identified by LOI) were tested for particle size distribution by the second part of the sieving/sedimentation method discussed in chapter 3 (Avery and Bascomb 1974).

(vi) pH of the organic soil

Organic soils were tested for pH as fresh samples. The results from the field moisture content were utilised to determine a mass of soil equivalent to 2.5g dry weight. This was added to 50ml of distilled water and 4ml 0.125M CaCl₂ solution. This was stirred and the pH of the soil solution determined after a 30 minute period using a Corning pH meter calibrated at pH 4. When soil pH is measured in the presence of CaCl₂ solution the results are more consistent (Schofield and Taylor 1955).

(vii) pH of the mineral soils

pH was tested in CaCl₂ solution. 10g of air dried soil was weighed into a clean 50ml beaker and 25ml distilled water was added. The beaker contents were stirred and left for 30 minutes. The solution was then restirred and 2ml of 0.125M CaCl₂ solution added. This was measured by Corning pH meter against pH 4 and pH 7 buffers.

(viii) Soil exchangeable cations

Exchangeable cations were measured in all soils by standard methods set out in chapter 3. Exchangeable Mg and Ca were measured in leachates by flame AAS using an oxyacetylene flame. Na and K were measured by flame photometry. Al was measured by AAS using a nitrous oxide flame. Exchangeable H was estimated by the change in pH of the leachate solution and cross reference to a graph from Hesse (1971). Triplicate determinations were made for each soil sample.

(ix) Cation exchange capacity

Cation exchange capacity (CEC) of the soils was tested using the Bascomb Ba method buffered at pH 8.2 (Avery and Bascomb 1974) outlined in chapter 3 and also by summation of mean exchangeable cations.

(x) Pyrophosphate extractable Fe

The soils were measured for their pyrophosphate extractable Fe content. Pyrophosphate extracts Fe bound in amorphous and organic forms (Bascomb 1968). The method used was standard and is as given in Avery and Bascomb (1974). Approximately 0.40g (W) of air dry soil was poured into a 50 ml centrifuge tube containing 40 ml potassium pyrophosphate solution. These tubes were then capped and put onto mechanical shakers for 16 hours. A reagent blank was also prepared. After this time the tubes were placed into a centrifuge and spun for 15 minutes at 2000 r.p.m.. The supernatant liquid was decanted for analysis. Fe was measured by flame AAS against known standards made up in pyrophosphate solution. Sample concentration (C) and blank concentration (B) results were plugged into the following equation to give a result of the samples extractable Fe:

$$\% \text{ Fe} = \frac{C - B}{200 \times W}$$

4.4 RESULTS

Full results are given in appendix E, pages 291-297.

4.41 Organic content of the soil horizons.

LOI results (table E4) were used assign soil horizons to the classes of organic and mineral soils. Avery (1980) indicated organic soil horizons contained at least 20% organic matter. This figure, however, was dependent on the clay mineral content of the soil increasing to 30% in a soil with 50% or more clay content. Loss on ignition on the soil samples highlighted two general clusters of organic matter results:

25 - 70% - organic soil horizons 0 - 15% - mineral soil horizons.

Samples 3A, 5B, 6A, 7B and 13D fell outwith these limits.

All of these samples, except 6A, were close to the lower limit of the organic soil horizon cluster. They were classed as organic soil horizons and 23% organic matter was chosen as the cut off point for organic soil in this study.

Replication was good throughout the measurement of LOI.

Mean mineral soil horizon LOI was 10.9% (S.D. 4.87). The LOI values ranged between 0.01% for soil 4C and 22.9% for 6A. The result for 4C was exceptional with sample 24B closest at 4.33%. Organic soil horizon LOI was, by definition, greater with a mean value of 47.6% (S.D. 17.7). LOI values ranged from 23.7% for soil 22A to 84.8% for 8A. The results were evenly spread between these limits.

4.42 Field moisture and air dry moisture

Organic soil horizons held greater amounts of moisture in the field than the mineral soil horizons (table E1). Mean organic horizon field moisture was 72.9% (S.D. 11.9) compared with 40.6% (S.D. 14.4) for the mineral horizons. This was expected since organic horizons contain more fibres which are capable of trapping moisture between them and thus have a greater water holding capacity. Organic samples retaining minimal field moisture e.g. samples 16A and 3A were typically low in organic C. Mean air dry moisture (table E3) was also greater in the organic soil horizons at 10.9% (S.D. 3.01) compared with 4.04 (S.D. 2.39) for the mineral horizons.

4.43 pH of the soil horizons.

Mean organic soil horizon pH was 3.6 (table E2), less than the mean mineral horizon pH of 4.1 (table E8). The maximum organic and mineral horizon pH values were similar at 4.5 (7A) and 4.7 (7D) respectively. The minimum organic horizon pH was much lower at 2.9 (4A) than the minimum value for the mineral soils 3.5 (14B).

4.44 Particle size analysis of the mineral soil horizons.

Samples 6A, 4C, 14C, 15B, 19C, 25B, 7D, 7C, 18C, 14B and 6B were described as stony having substantial weight % > 2mm in size (table E5). In many cases this coarse fraction of the soil included rocks not indicated by Bown (1979) as parent material. At sites 5, 7, 8, 9, 11, 18, 19, 22 and 25, all from the south of the catchment, the coarse fraction included igneous material foreign to the solid geology specified for that site. At sites 12 and 13 (both diorite sites) shales were present. Table E6 gives the origin of these coarse particles in full.

One measurement was made of each sample for particle size distribution in terms of clay, silt and sand (table E7). For all samples the lack of reaction of the soil with H₂O₂ supported their classification as mineral soil horizons. Mean clay content was 4.81% (S.D. 3.86) with a range of values from 0.00% (11C) to 21.4% (14B). Both of these values were exceptional with most results falling between 1 and 11% clay. Mean silt content was 12.7% (S.D. 8.27) with a range of values between 0.00% (4D) and 44.4% (16B). Again both these limits were exceptional with the majority of samples falling between 3 and 25% silt. Mean sand content was 82.6% (S.D. 8.54) with a range between 54.3% (16B) and 95.4% (23B).

4.45 Exchangeable Cations

Triplicate determinations were made on soil samples for exchangeable cations. Success in replication was variable. Mean results with standard deviation for the mineral and organic horizons are given in table 4.45A.

Table 4.45A: Mean exchangeable cation results for organic and mineral soil horizons. Results are given in meq/kg, standard deviation in italics.

	Organic horizons	Mineral horizons
Exch Ca	11.1 <i>11.6</i>	2.87 <i>3.12</i>
Exch Mg	13.1 <i>18.6</i>	1.70 <i>1.52</i>
Exch Na	3.65 <i>2.58</i>	1.07 <i>0.84</i>
Exch K	3.53 <i>2.90</i>	0.69 <i>0.69</i>
Exch H	294 <i>68.1</i>	150 <i>41.2</i>
Exch Al	43.1 <i>34.1</i>	22.8 <i>13.4</i>

Most exchangeable cations were more concentrated in the organic soil horizons. Mean exchangeable Ca was greater in the organic samples at 11.1 meq/kg (table E10) compared with 2.87 meq/kg (table E9) for the mineral samples. Both soil types varied considerably as indicated by standard deviations. The range of exchangeable Ca concentrations recorded in the organic horizons was 1.42 - 57.7 meq /kg greater than the range of 0.55 - 14.5 meq /kg in the mineral horizons. Maximum values for both soil groups were recorded from site 25.

Mean exchangeable Mg in the organic horizons was 13.1 meq/kg (table E10), much higher than 1.67 meq/kg (table E9) for the mineral horizons. Variability indicated by standard deviation was high in both soil groups. The range of exchangeable Mg values recorded in the organic horizons was 1.92 - 91.5 meq /kg. This was much greater than the range of 0.27 - 7.16 meq /kg found in the mineral horizons.

Mean exchangeable Na was greater in the organic horizons at 3.65 meq /kg (table E12) than for the mineral horizons at 1.07 meq /kg (table E11). Standard deviation indicated variability was high in both soil horizon types. The range of exchangeable Na results of 0.80 -11.8 meq /kg for the organic horizons was greater than the range of 0.07 - 4.84 meq/kg for the mineralic horizons. Maximum exchangeable Na and Mg were both recorded from the organic sample at site 4. The mineral horizon at this site had the minimum exchangeable Na.

Mean exchangeable K was greater in the organic horizons at 3.53 meq/kg (table E12) than the mineral horizons at 0.69 meq/kg (table E11). Within this group variability

indicated by the standard deviations was slightly greater in the mineral horizons. The range of exchangeable K results was 0.17 - 11.9 meq/kg in the organic soils. This was much greater than the range of 0.00 - 2.98 meq/kg in the mineral horizons. Minimum exchangeable K was found at site 4 for both the mineral and organic soils.

Mean exchangeable H was greater in the organic horizons at 294 meq/kg (table E16) than 150 meq /kg (table E15) in the mineral horizons. Variability indicated by standard deviation was moderate in both soil horizon types. The range of exchangeable H results in the organic horizons was 176 - 453 meq /kg, greater than that of 59.6 - 249 meq /kg in the mineral soils.

Exchangeable Al was measured by a different method. However, the replication of results remained variable. Mean exchangeable Al was greater at 43.1 meq/kg (table E14) in the organic horizons than 22.8 meq/kg (table E13) in the mineral soils. Variation was high in both soil groups as indicated by standard deviation. The maximum result of 133 meq/kg (21B) in the organic horizons was greater than the result of 59.6 meq /kg (21C) in the mineral soils. In contrast the minimum value of 2.79 meq/kg (4B) in the organic soils was lower than the result of 4.06 meq/kg (20D) recorded in the mineral horizons.

4.46 Pyrophosphate extractable Fe

Mean extractable Fe was similar in the organic horizons at 0.57% (S.D. 0.47) and the mineral horizons at 0.49% (S.D. 0.57). Within this group variation indicated by standard deviations was slightly greater in the mineral soils. The maximum reading

in the organic soils (2.25% - 14A) was lower than the highest result in the mineral horizons (2.66% -10C). The minimum readings in the organic and mineral horizons were very similar at 0.02% (4A, 4B) and 0.01% (4C, 4D) respectively, (tables E19 and E20).

4.47 Cation Exchange capacity

Full results for the CEC by measurement and by summation are given in tables E17 and E18. There were many discrepancies between the two values. More than half of the organic samples gave a measured value lower than the summed value. Only 7A gave a measured result greater than the summed value. The mineral horizon results from both methods were slightly better matched with only a quarter of the samples having a measured value greater than the summation result. Sample 4C had summed value > measured result.

4.48 Base saturation

Base saturation was calculated as the sum of the base cations (Ca, Mg, Na, K) expressed as a % of the summed CEC (tables E21 and E22). Base saturation was typically greater in the organic horizons with a mean value of 7.64% (S.D. 6.15) compared with 3.73% (S.D. 3.20) for the mineral horizons. The range of results recorded for the organic horizons was 2.19% -25.4% base saturation. This was slightly greater than the range of 0.80% - 18.0% for the mineral horizon. Maximum base saturation was found at site 25 for both soil types.

4.49 Correlation among soil properties

Table 4.49A shows the correlation among the chemical properties for the organic soil horizons.

Table 4.49A: Correlation among the organic soil horizon chemical properties.

	Ex Ca	Ex Mg	Ex Na	Ex K	Ex H	Ex Al	LOI	Ext Fe	pH
Mg	0.65								
Na	0.66	0.85							
K	0.47	0.19	0.46						
H	0.36	0.57	0.66	0.30					
Al	-0.44	-0.41	-0.35	0.00	0.24				
LOI	0.54	0.57	0.76	0.54	0.65	-0.13			
Fe	-0.18	-0.53	-0.55	-0.26	-0.64	-0.15	-0.58		
pH	-0.20	-0.55	-0.57	-0.26	-0.63	-0.12	-0.57	-1.00	
CEC	0.40	0.58	0.65	0.38	0.92	0.34	0.66	-0.65	-0.64
%BS	0.85	0.77	0.70	0.30	0.25	-0.48	0.49	-0.23	-0.28

Organic matter content (determined by LOI) was correlated with exchangeable Na, H and CEC (summed). Extractable Fe was strongly and inversely correlated with soil pH. The strong correlation found between CEC and exchangeable H was anticipated since this cation accounts for a large proportion of the positive charge on the cation exchange complex. CEC was also strongly inversely correlated with extractable Fe and soil pH. Ca, Mg and Na were closely intercorrelated.

Correlation of soil chemical properties among the mineral soil horizons are presented in table 4.49B.

Table 4.49B: Correlation among the mineral soil horizon properties

	Ex Ca	Ex Mg	Ex Na	Ex K	Ex H	Ex Al	LOI	Ext Fe	pH
Mg	0.82								
Na	0.29	0.36							
K	0.22	0.40	0.52						
H	-0.01	0.20	0.30	0.19					
Al	-0.25	0.03	0.20	0.20	0.81				
LOI	0.41	0.35	0.27	0.31	0.53	0.37			
Fe	-0.09	-0.05	0.24	0.29	0.43	0.28	0.38		
pH	0.10	-0.07	-0.12	-0.07	-0.23	-0.25	0.05	0.20	
CEC	-0.06	0.14	0.33	0.23	0.90	0.87	0.62	0.38	-0.22
%BS	0.85	0.77	0.70	0.30	0.25	-0.48	0.49	-0.23	-0.28

As in the organic soils there was a correlation between CEC and LOI. Exchangeable Ca and Mg were strongly correlated a feature typical of many igneous rocks. Exchangeable H and Al were strongly correlated with each other and CEC. This was anticipated since H and Al constitute the bulk of the CEC.

4.5 DISCUSSION: Chemical and textural soil features.

All soils representing the Darnaw Complex (Etrick Association), figure 4.1A, fitted the descriptions of this variable soil class. The profiles sampled ranged from peaty podzols to peaty gleys, peat and ranker soils. The profile sampled at site 7 was too deep to belong to the Etrick Skeletal soils and was re-assigned to the spatially proximal Darnaw Complex. The Dalbeattie Association soils involved a greater variety of map classifications. 4 of the 5 soil sites (1, 3, 12, 13) assigned to the Garrary Complex complied with the description of the group. However, the profile at site 24 did not include a raw humus surface horizon and was similar to the profile found at site 23 (Dinnins Complex). Both soils may represent brown forest soils belonging to the Dinnins Complex although both were c. 1m in depth, a feature atypical of this complex. Soils from site 2 fitted their assignation to the Gala Complex. Soils at sites 4 and 20 were described as organic soils. This served for site 4 but the profile at site 20 had only 20 cm of peat and was not an organic soil. It was mapped in close spatial proximity to the Gala complex and was re-assigned to this group.

4.51: Reliability of results.

LOI results were well replicated. Only single determinations were made on soil pH therefore reliability of the results could not be ascertained. Replication of exchangeable cation results was variable. Reproduction of exchangeable calcium results was diverse for the mineral horizons; sample 16B gave a mean result of 1.02 meq/kg (S.D. 0.04) yet the mean result for sample 3B was 0.66 meq/kg (S.D. 0.52). Variation was most marked in the numerically lower results. Organic horizon

exchangeable calcium was better replicated probably because of higher concentrations. Replication of exchangeable magnesium was improved relative to calcium in the mineral horizons and was good in the organic horizons. Exchangeable sodium replication was poor in the mineral horizons and only slightly better in the organic horizons. Exchangeable potassium results were typically low and the replication correspondingly poor; where potassium > 1.5 meq/kg replication was improved. Replication of exchangeable potassium was also poor in the organic soils despite higher values. Exchangeable hydrogen was moderately well replicated in the mineral horizons except in a few cases e.g. soils 3C, 8C and 23B. Exchangeable hydrogen was less well replicated in the organic horizons despite the higher concentrations. Replication of exchangeable aluminium was poor in most soils.

This consistent poor to variable replication in the results indicated:

- i) Operator error
- ii) Within sample variability (physical and chemical) or
- iii) a combination of the above.

Operator error could explain some of the poor replication in:

1. The organic soils - if the soils were not totally saturated on the initial addition of ammonium acetate or KCl solution during the leaching process this could affect the concentrations of exchangeable ions. This was especially difficult to achieve in the case of the organic soils.
2. The exchangeable hydrogen results - if the change in ammonium acetate pH after passage through the soil was not properly observed this could make significant differences when translated to exchangeable hydrogen concentrations by reference to Hesse (1971).

Textural variability could have affected results by:

1. Producing diverse leaching rates which would allow a variation in leaching time to creep in and consequently time for cation exchange to be variable.
2. A greater adsorption of the leachate resulting in differences in the amount of pure ammonium acetate/KCl needed to top up the sample leachate to 100 ml.

CEC by measurement replicated at varying levels of success. The differences encountered in the cation exchange capacity results between measured and summed methods were explained by:

- a. Discrepancies in the measurement technique introduced during the 'washing' step employed in this method (Hesse 1971).
- b. The presence of soil organic matter with strongly and preferentially held polyvalent cations. These could only be replaced by other polyvalent cations capable of forming stronger bonds with the organic matter (Giusti 1991). If aluminium were a prominent cation on the exchange resin, as was the case for many of the soils, this would result in an underestimation of CEC.
- c. Chapman (1965) advised the use of summation for estimation of CEC in distinctly acid soils since the Bascomb method used is typically buffered at pH 8.2 and CEC is related to pH.
- d. Poor replication of the results for individual cations could affect the accuracy of the summed results.

4.52 Comparison of results

Organic horizon pH was similar to the results of Little (1985), Grieve (1990), Giusti (1991) and MacIntyre (1991) all from the Loch Dee catchment. The mean value of pH 3.6 was very similar to that suggested by Bache (1984) as typical of a podzol humic horizon. This mean value, however, was lower than those quoted by Walker et al (1990) for the catchment studies at Hoylandet in Norway, Mharcaidh in the Scottish Cairngorms, Chon and Kelty, both from the Loch Ard Forest in Central Scotland. However, pH readings in these cases were measured in water only. If pH is measured

in CaCl_2 it is typically lower (Kennedy 1986). This is explained by the displacement of protons from colloids or, in the case of acid soils, by the release of trivalent Al from exchange sites. Soil pH reported by Anderson et al (1993) for the Balquhider catchment in central Scotland were also measured in CaCl_2 and gave a range of values similar to those reported for Loch Dee.

The two extremes of pH (2.9, 4.5) represented limits of site height (the lowest pH at the lowest altitude) but this feature did not hold for the group as a whole, ($r = 0.553$). Little (1985) stressed the importance of vegetation in the variability of organic soil pH. He indicated moorland peat pH < forest peat pH. Vegetation at soil site 4 was dominated by heather and classed as moorland. The peats from this site had the lowest reported pH values at 2.9 and 3.0 i.e. this was in agreement with the findings of Little.

Mineral soil pH was lower than results reported by Little but similar to those recorded by Grieve (1990), MacIntyre (1991) and Giusti (1991). The mean value of pH 4.1 was in between the values of 3.8 and 4.5 suggested by Bache (1984) to be typical of the bleached and the underlying enriched horizons of podzolic soils. Mean pH values were again lower than those given for Hoylandet, Mharcaidh, Chon and Kelty but these soil pH values were again measured without CaCl_2 . The mean mineral soil pH, however, was similar to those reported for the Bs horizons of iron humus podzols and the Eg and Bg horizon of surface water gleys from the Balquhider catchment (Anderson et al 1993).

Loss on ignition results were within a similar range to those of Grieve (1990),

MacIntyre (1991) and Giusti (1991) all from the Loch Dee catchment. Giusti reported a relationship between LOI in top soils and the site slope (low slope = high LOI) and direction (facing S and E = higher LOI, facing W = lower LOI) in the Dargall Lane sub-catchment. This relationship was not obvious for the White Laggan sub-catchment soils. However, peat development was limited at site with a high gradient e.g. sites 23 and 24 and greater topsoil LOI (c. 70%) was often found in sites with a negligible gradient. The highest LOI value was found at site 8 where there was a 5° slope to the north.

Exchangeable cation results were compared with the results from other studies in the area, see tables 4.52A and 4.52B. Organic horizon exchangeable cations were similar to those reported by the other authors working in the Loch Dee area. The apparent differences highlighted the variable nature of the soils from the area. Exchangeable calcium results were more variable than the soils of Grieve (1990), but less than those of Giusti (1991). Exchangeable magnesium had a greater range than all authors. Both these ions were of a similar level to those reported to those of Bache (1984) as typical of podzol humic horizons. Mean exchangeable sodium and potassium were similar to the results of Grieve (1990) and Giusti (1991). Mean exchangeable aluminium was much greater in the Loch Dee soils than the value of 5 meq/kg suggested by Bache as typical of podzol humic horizons.

Table 4.52A: Comparison of organic soil exchangeable cations with data from other work at Loch Dee. Units are meq/kg.

	Results - mean and range	Results from Grieve (1990) Range.	Results from Giusti (1991) Range
Exch Ca	11.1 1.42 - 57.7	6 - 35	19.7 - 150
Exch Mg	13.1 1.92 - 91.5	5 - 34	2.30 - 60.2
Exch Na	3.65 0.80 - 11.8	7 - 8	2.70 - 30.8
Exch K	3.53 0.17 - 11.9	2 - 9	1.8 - 13.8
Exch H	294 176 - 453	283 - 567	105 - 359
Exch Al	43.1 2.79 - 133	28 - 82	67.4 - 570

Exchangeable calcium, potassium and aluminium were in a similar range to these ions reported for surface water gleys and humus iron podzols from the Balquhiddy Catchment (Anderson 1993). However exchangeable sodium, magnesium and hydrogen were typically lower in the surface soils from the Balquhiddy catchment. Lower sodium and magnesium values at these sites may reflect a lower input from coastal rains although there are inputs of these elements from marine sources (Anderson et al 1993). Lower exchangeable hydrogen values in the Balquhiddy soils are more difficult to explain. It is possible the soils at Balquhiddy were less acidified due to the presence of a band of Loch Tay limestone in the area. However, this was not reflected in higher calcium content of the soils and possibly reflects either elevated acidification of the Loch Dee surface soils or the presence of greater quantities of organic matter in the soils.

Soil exchangeable cations from the Llyn Brienne catchment (Whitehead et al 1988) were typically within the range of results found for the Loch Dee soils although they were usually at the lower end of the scale.

Walker et al (1990) presented data for exchangeable acidity and exchangeable aluminium for the Mharcaidh Catchment, Hoylandet Catchment and the Chon and Kelty Catchments. All of these are within upland areas, have podsollic soils and are acidified to different degrees. Exchangeable acidity was much greater in the surface soils of all these catchments when compared with the Loch Dee organic horizons. Exchangeable aluminium, however, was noticeably lower than the Loch Dee soils in the Hoylandet and Chon surface soils, similar in the Mharcaidh organic horizons and much higher in the surface soils of the Kelty catchment. Hoylandet was designated a 'pristine' site by the Surface Water Acidification Programme (Mason 1990) and lower concentrations of acidic cations might be anticipated in its soils. Loch Chon was designated an 'acidified' site by the SWAP study and yet had lower exchangeable aluminium in its organic horizons than soils from Loch Dee. Mharcaidh was designated a 'transitional' site by SWAP and the Kelty Catchment 'acidified'. Comparison of Loch Dee surface soils with those from SWAP sites thus indicates the area to be 'transitional' in terms of acidification.

Exchangeable cations in the mineral soil horizons were also compatible with those of other authors working in the Loch Dee area (table 4.52B) and again any differences served to highlight the variability of the mineral soils in this area.

Table 4.52 B: Comparison of mineral soil exchangeable cations with those from other work at Loch Dee. Units are meq /kg

meq/kg	Results mean and range	Results of Grieve - Range	Results of Giusti - Range
Ex Ca	2.87 0.55 - 14.5	2 - 11	17.6 - 41.0
Ex Mg	1.70 0.27 - 7.16	2 - 4	1.1 - 32.2
Ex Na	1.07 0.07 - 4.84	0 - 4	1.70 - 21.5
Ex K	0.69 0.00 - 2.98	0 - 0	1.0 - 4.0
Ex H	150 73.1 - 249	110 - 259	125 - 269
Ex Al	22.8 4.06 - 59.6	12 - 29	18.4 - 138

Exchangeable calcium, magnesium, sodium and aluminium had a range of results lower than those of Giusti from the Dargall Lane. The range of exchangeable aluminium, however, was greater than those of Grieve from the Green Burn sub-catchment.

Mean exchangeable calcium, magnesium and aluminium from the soils of the Loch Dee area were typically greater than those quoted by Bache (1984) as typical of podzolic bleached and enriched horizons. Exchangeable calcium, potassium and aluminium were within a similar range to Mharcaidh (Jenkins et al), Llyn Brianne (Whitehead et al 1988) and Balquhiddy soils (Anderson et al 1993). Exchangeable sodium, magnesium and hydrogen were much lower in the Balquhiddy soils but similar in the Llyn Brianne mineral horizons.

Exchangeable acidity in the Loch Dee mineral horizons was similar to the results for the Hoylandet and Loch Chon mineral soils, higher than those in the Mharcaidh catchment and lower than the exchangeable acidity found in the Kelty Catchment (Walker et al 1990). The latter result was anticipated because of the SWAP designation of Kelty as an acidified site. Exchangeable aluminium from the mineral soils at Loch Dee was similar to Hoylandet, Chon and Mharcaidh but often lower than that at Kelty again because Kelty is a relatively acidified site compared with Dee. The similarity in mineral horizon exchangeable hydrogen and aluminium between Loch Dee and Loch Chon soils was interesting since Chon was also designated an acidified site. However, the presence of a base rich dolerite dyke at this site may have allowed the soils some buffering capacity and kept concentrations of acidic cations down to a level similar to those in Loch Dee mineral horizons.

Summed CEC results were compared with the results from other work within the Loch Dee catchment. The results of this comparison are given in 4.52C.

Table 4.52C: Comparison of summed CEC results from other studies in the Loch Dee area. Standard deviations are given in italics for the results from this study.

	Organic horizons (meq/kg)	Mineral horizons (meq/kg)
Grieve (1990)	303 - 647	120 - 278
Giusti (1991)	236 - 919	204 - 462
This study	379 <i>91.6</i>	179 <i>51.7</i>

Mineral soil horizon CEC results were comparable with those of other authors working in the Loch Dee area. Sample 4C from this study was lower than any other reported values but was a beach sediment rather than a soil per se. The organic soil results

were within the range given by Grieve (1990) but lower than those of Giusti.

Loch Dee organic soils had lower CEC than those reported by Jenkins et al (1988) for the Mharcaidh Catchment but greater CEC than those reported by Whitehead et al (1988) for the Llyn Brienne Catchment and summed organic soil CEC calculated for the Balquhiddy Catchment (Anderson et al 1993) and the Birkenes Catchment (Seip et al 1990). This probably reflects a higher organic matter content in the Loch Dee organic soil horizons than found at Balquhiddy and Birkenes since organic matter and CEC are closely related.

Loch Dee mineral soil CEC was greater than for Mharcaidh (Jenkins et al 1988), Birkenes (Seip et al 1990) and Llyn Brienne (Whitehead et al 1988) but similar to concentrations reported for the Balquhiddy soils (Anderson et al 1993).

Organic soil base saturation results from this study were of a similar range to those of Giusti (1991) from the Dargall Lane sub-catchment (10.1 - 28.0%) but were within a slightly lower numerical bracket (2.40 - 25.4%).

Loch Dee organic soil horizon base saturation was also lower than those reported by Seip et al (1990) for Birkenes and Ingabekken (Hoylandet) but similar to results in the Mharcaidh and Llyn Brienne Catchments (Jenkins et al 1988, Whitehead et al 1988) and some Dutch woodland soils reported by Mulder et al (1987). Base saturation results calculated from the data of Walker et al (1990) and Anderson et al (1993) for the Chon and Balquhiddy catchments were also similar to those at Loch Dee. Kelty

soils had typically lower base saturation in the organic soils as would be expected in soils from a relatively acidified catchment.

Mineral soil base saturation at Loch Dee (0.80 - 18.0%) was again in a numerically lower bracket than those of Giusti (1991) from the Dargall Lane (9.30 - 27.4%).

Base saturation at Birkenes 1 (Seip et al 1990), Llyn Brianne (Whitehead et al 1988) and Mharcaidh (Jenkins et al 1988) was within a similar range to the Loch Dee mineral horizons. However, Birkenes 2 and the Ingabekken sites of Seip et al (1990) and some of the mineral soils reported by Mulder et al (1987) from the Netherlands typically had greater base saturation and probably therefore represent less acidified sites. Base saturation results were calculated from the data of Walker et al (1990) and Anderson et al (1993). Chon, Kelty, Mharcaidh and the humic podzols of Balquhidder were similar to the results at Dee. However, the surface water gleys from Balquhidder were typically more base enriched. The similarity between the base saturation of the mineral soil horizons from both the Loch Dee and Loch Kelty catchments gives an insight into the degree of acidification in the Loch Dee area.

Soil exchangeable aluminium was expressed as a % of CEC (summed). The organic horizons of Loch Dee gave a mean result of 12.8% (S.D. 6.61) exchangeable aluminium but the range was 0.50 - 26.6%. These results were similar to those of Grieve (1990) for the Green Burn sub-catchment at Loch Dee but lower than those from the Dargall Lane sub-catchment (Giusti 1991).

Concentrations of exchangeable aluminium compared with CEC from this study were also similar to those from the surface water gleys of Balquhiddar but lower than the humus iron podzols at the same site (Anderson et al 1993). Chon, Kelty and Mharcaidh had similar levels of aluminium enrichment on the soil exchange sites (Walker et al 1990). Mulder et al (1987), however, indicated aluminium concentrations were slightly greater in some woodlands soils from the Netherlands than the Loch Dee soils. Again the similarity between the aluminium saturation of the exchange complex in the soils of Loch Dee and Kelty indicate the level of acidification reached by the soils at Loch Dee.

The Loch Dee mineral soil exchange complex was slightly more enriched in aluminium than in the case of the organic soils. On average the aluminium saturation was 13.6% (S.D. 4.38) with a range of values between 5.42% and 24.0%. These values were analogous to the results of Grieve (1990) but again, much lower than those of Giusti (1991) for the Dargall Lane soils.

Loch Dee mineral soil aluminium saturation was also similar to the Balquhiddar (Anderson et al 1993), Hoylandet and Chon catchments (Walker et al 1990). However, Kelty and Mharcaidh (Walker et al 1990) and some Dutch soils (Mulder et al 1987) were all reported to have greater saturation of the soil exchange complex with aluminium than the Loch Dee mineral soil horizons in this study.

4.53 Variability of soil chemistry and texture:

Ai. Chemical variability on the site scale.

Chemical components often varied systematically throughout the soil profile and reflected changes in CEC through the soil horizons. Soil profiles were distinguished according to the pattern of changes in the concentrations of 4 components throughout the soil profile:

i). Base cations typically decreased in concentration in one of three ways down the soil profile, figure 4.53A.

1. Decrease was greatest in the organic soil e.g. soil profile 1, 2, 4, 8, 10, 12, 20, 21 and 22.

2. Similar to 3 but with a slight increase in the base of the mineral horizon e.g. 3, 9, 17, 23, 24

3. Decrease was steady throughout the soil profile e.g. profiles 5, 11 and 19.

Soil profiles at sites 7, 13, 14, 16 and 18 did not have comparable results for all base cations but showed some similarities with the above three patterns.

ii) Acidic cations typically followed one of four patterns fig 4.53B.

1. Decreased down profile with maximum decrease in the mineral soil e.g. site 1, 7, 11, 16 20.

2. Increased to a maximum in the upper soil then decreased rapidly e.g. soil 5, 21.

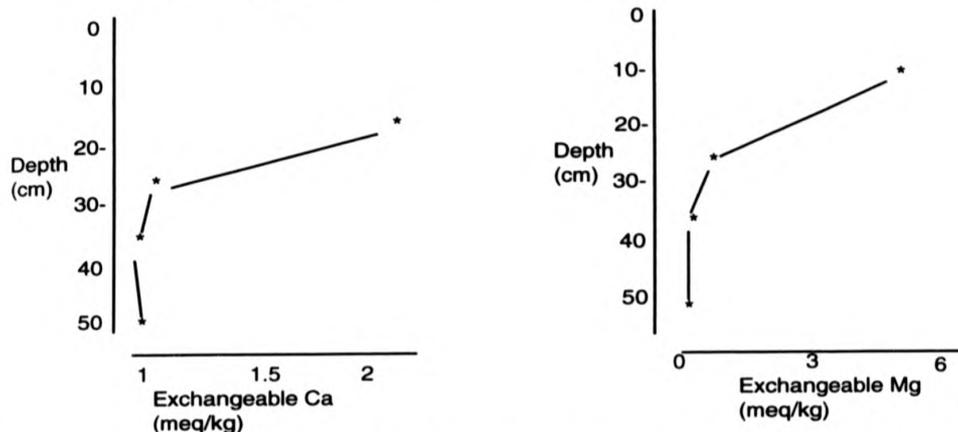
3. Decreased steadily throughout the profile e.g. soil 10, 12, 13, 17, 18, 19, 22.

4. Decreased in the organic soil then increased in the mineral soil e.g. site 23, 24.

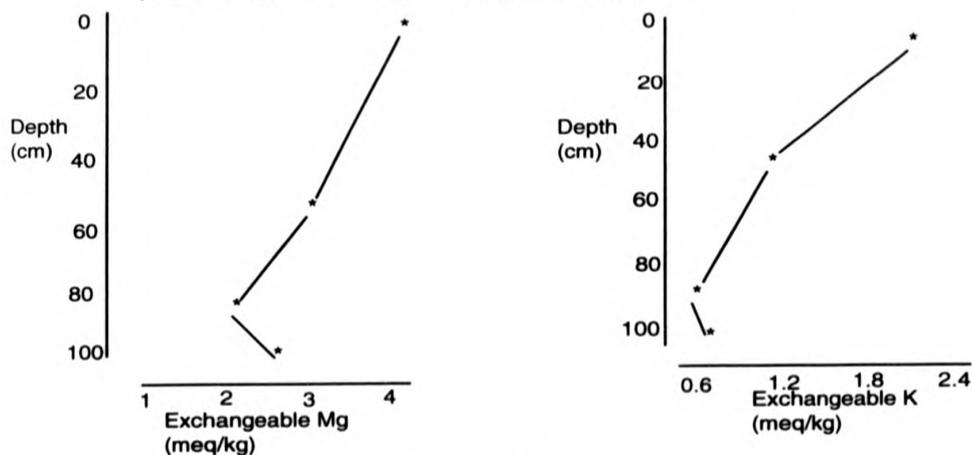
In a few cases the distribution of Al and H throughout the soil profile were not related e.g. sites 2, 3, 4, 8, 9, 14.

Figure 4.53A: Patterns of soil exchangeable bases throughout profiles.

a. Where decrease in exchangeable cations was greatest in the upper soil e.g. soil site 10.



b. where the decrease in exchangeable cations was steady throughout the soil profile but there was a slight increase in the lower soil.



c. where the decrease in exchangeable cations was steady throughout the soil profile e.g. site 5

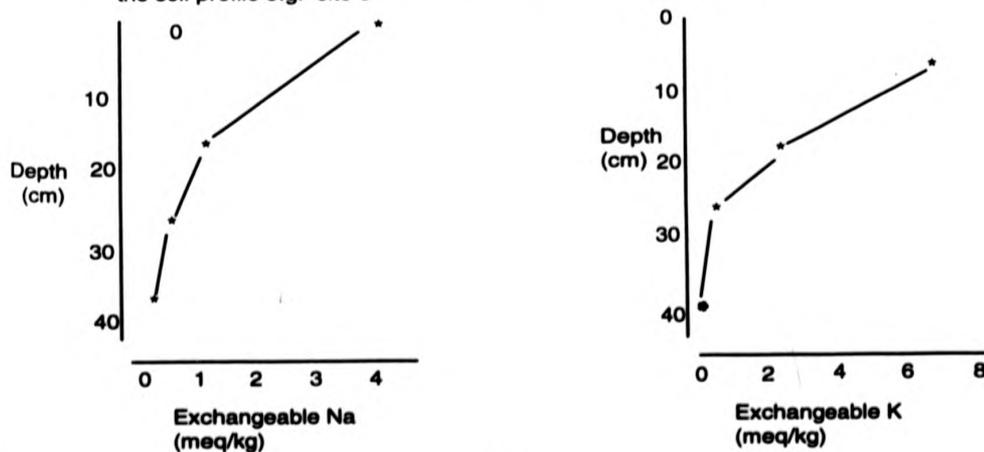
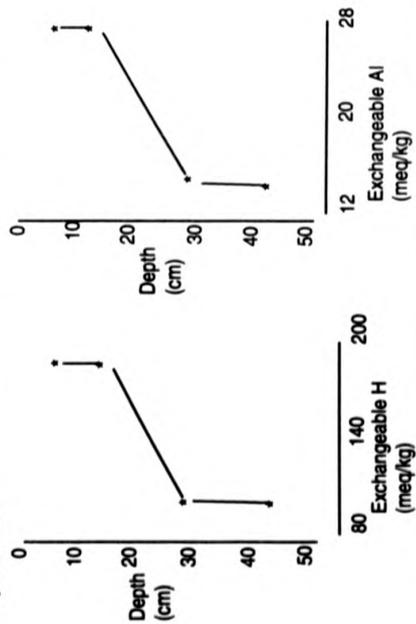
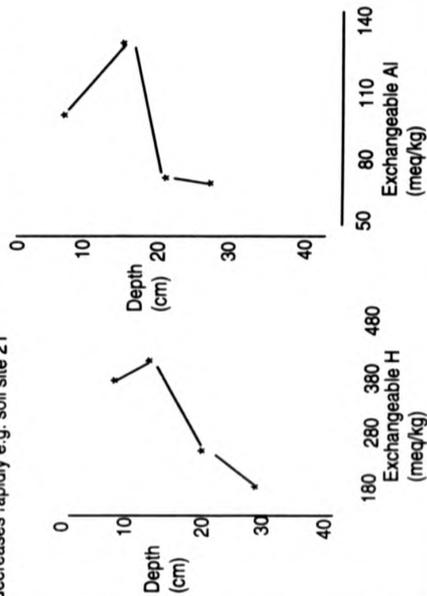


Figure 4.53B: Patterns of exchangeable acidity throughout soil profiles

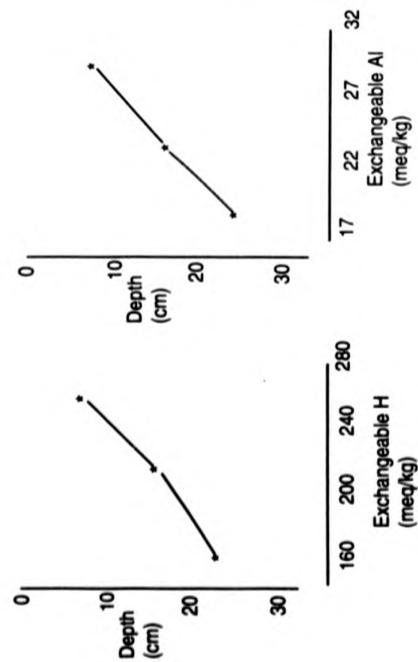
a. Where maximum decrease in exchangeable acidity is in the lower or middle soil e.g. soil site 7



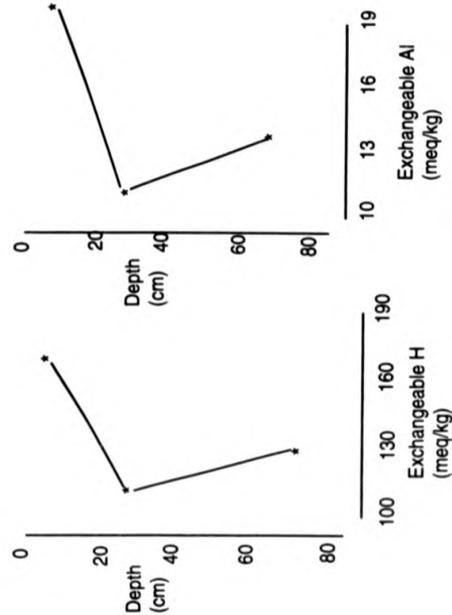
b. Where exchangeable acidity increases to a maximum in the upper soil then decreases rapidly e.g. soil site 21



c. Where exchangeable acidity decreases steadily throughout the soil profile e.g. soil site 18



d. Where exchangeable acidity decreases then increases in the base of the profile e.g. soil site 24



iii) Distribution of pyrophosphate extractable iron throughout the profile was described as:

1. Following the exchangeable bases e.g. sites 1, 4, 9, 12, 14, 18, 23, 24.
2. Decreasing then increasing to a maximum in the mineral soil e.g. profile 2,10,13,17.
3. Increasing to a maximum in the upper soil profile then decreasing e.g. soil 3, 5, 7, 8, 21.
4. Following exchangeable acidity e.g. soil site 11, 16, 19, 20, 22, 23, 24.

iv) Soil LOI either:

1. Followed the pattern of exchangeable hydrogen and 0 - 3 exchangeable bases e.g. sites 1, 3, 9, 12, 13, 14, 16, 17, 18, 20, 22, 23, 24.
2. Followed the pattern of two or more of the bases but not hydrogen e.g. soil 4, 5, 7, 8, 10, 11, 19, 21.

In one case, soil LOI did not follow any patterns at all e.g. site 2.

Aii. Correlation among soil properties.

Organic matter content was important in controlling the cation exchange properties of the organic soils. It was correlated with exchangeable sodium, hydrogen and CEC (summed). This feature may dominate the chemistry of soil solutions associated with these soils.

Extractable iron was strongly and inversely correlated with soil pH in the organic soils. In acidic soil conditions pyrophosphate extractable iron was often more abundant. Since iron extracted by pyrophosphate is typically in an organic or amorphous form and organic rich soils often have a low pH this relationship is sensible.

There was a correlation between CEC and LOI in the mineral soils again indicating a control of organic material over soil chemical processes. However, because organic matter is less prominent in the mineral soils any control should be less obvious and soil organic matter may not substantially affect the chemistry of soil solutions.

The correlation of soil exchangeable calcium and magnesium was strong and could be ascribed to input from geological source; such a correlation is typical of many igneous rocks. There was not any apparent relationship between the extractable iron component of the soils and organic matter contained within the soils. Extractable iron was also not related to soil pH.

Aiii. Analysis of variance according to soil profile type:

Chemical and textural data for both the organic and mineral soil horizons were assessed for variability due to soil profile types. Tables 4.53A and B indicate the chemical features ascribed to soil profile differences at the 95% confidence level for both soil horizon types.

Table 4.53A: Analysis of variance for organic soil data due to soil profile type. Table gives mean values with standard deviations in italics.

	P value	Peat soils	Podzols	Gleys	Rankers	Other
Ex H	0.04	317 <i>72.7</i>	317 <i>50.2</i>	269 <i>44.7</i>	299 <i>60.9</i>	185 <i>1.41</i>

There was a considerable difference in the exchangeable hydrogen content of the organic soil horizons from the 'other' category. This included only organic soils from site 7 which were lower in exchangeable H than all other soil profile types. However, this is more likely to be a feature of altitude rather than the profile type and related

to the low organic matter content of the organic horizons from this site.

Table 4.53B: Differences shown up by the analysis of variance in the mineral soil horizons based on soil profile type. Table reports mean values with standard deviations in italics.

	P value	Peat soil	Podzol	Gley	Ranker	Other
% ADM	0.03	4.36 <i>2.44</i>	6.22 <i>3.39</i>	4.22 <i>2.06</i>	3.53 <i>0.77</i>	2.92 <i>1.01</i>
Ex Al meq/kg	0.01	21.5 <i>11.4</i>	37.9 <i>15.0</i>	24.9 <i>14.2</i>	26.9 <i>10.7</i>	16.1 <i>7.01</i>
Ex H meq/kg	0.01	151 <i>38.6</i>	176 <i>38.2</i>	139 <i>33.4</i>	151 <i>34.3</i>	116 <i>33.0</i>
CEC summed meq/kg	0.02	180 <i>50.6</i>	217 <i>51.6</i>	171 <i>43.8</i>	183 <i>45.2</i>	139 <i>42.3</i>
% Ext Fe	0.00	0.30 <i>0.33</i>	1.13 <i>0.86</i>	0.18 <i>0.16</i>	0.45 <i>0.43</i>	0.42 <i>0.27</i>

Mineral soil horizons from podzolic profiles had greater air dry moisture content, exchangeable aluminium and hydrogen and extractable iron than mineral soils from other profile types. Higher exchangeable aluminium and hydrogen was also reported for the humus iron podzol soils than the surface water gleys in the Balquhiddar Catchment in Central Scotland (Anderson et al 1993). Mineral soils from the 'other' category had lower CEC by the summed method. This class also included the soils from sites 23 and 24. Soil site 7 was high in altitude and soil sites 23 and 24 were of high gradient. These features may explain the low CEC of these soil horizons rather than it reflecting soil profile type.

Aiv. Analysis of variance according to rock type:

Variability of the chemical features within the different soil horizon types was also determined according to the solid geology underlying the soil sites. Variability in parent material input controlled by the solid geology should be reflected in the mineral soil horizons but not the organic horizons. Table 4.53C gives the important results for the mineralic horizons.

Table 4.53C: Mineral soil horizon differences due to input from different rock types. Results given as mean values with standard deviation in italics.

	P value	Dior	G/dior	dykes	Black shale	C. M/sed	Fine M/sed
% Silt	0.05	12.4 <i>5.54</i>	6.57 <i>4.52</i>	18.9 <i>12.9</i>	14.4 <i>6.39</i>	10.7 <i>4.60</i>	7.93 <i>7.17</i>
% Sand	0.01	83.4 <i>6.50</i>	89.8 <i>5.03</i>	76.5 <i>12.1</i>	75.2 <i>4.51</i>	85.5 <i>2.99</i>	86.9 <i>0.21</i>

The mineral soils had only textural and no discernable chemical differences between the 6 rock classes when tested for one-way analysis of variance. These results were not found in the organic soils. Mineral soils developed over dykes carried a signature of greater silt content while those developed over granodiorite were more likely to be coarse. This latter observation is easy to understand in terms of geological input since the granodiorite was one of the most coarse grained igneous rocks sampled within the area. However, the relationship between the dykes and the silt is more difficult.

4.54 Textural Classification of the soils

% clay, silt and sand results for the mineral soils (Table E7) were plotted onto a triangular diagram forming a textural classification, figure 4.54A, after Avery (1980). Despite the differences indicated by analysis of variance of the mineral soil results, once these soils were texturally classified all but one of the mineral soils was described by just 3 soil types irrespective of underlying geology. 24 samples were sands, 13 samples sandy loams and 9 samples loamy sands. Sample 14B had a higher clay content and was classed as a sandy clay loam.

4.55 Evidence for drift input to the soils

The coarse fraction (> 2mm) of the soils (Table E6) indicated the presence of drift material at many sites e.g. 7, 8, 9, 11, 12, 13 etc. (section 4.44A). It appeared that this drift was of mixed origin. This was very similar to the situation reported in the coarse fraction of the drift samples reported in chapter 3.

A comparison of the mineral soil mean chemical data and the drift mean chemical data (chapter 3) is presented in table 4.55A. Despite the differences observed in the drift data in chapter 3 when split according to Etrick and Dalbeattie Associations mean drift results were used in a comparison here since the drift sample population was too small to be sure if the contrast noted was real.

Table 4.55A: Comparison of drift and mineralic horizon chemistry. Data given are mean results with standard deviations in italics.

	Drift samples	Mineral soils
Exchangeable Ca	2.78 <i>1.82</i>	2.87 <i>3.12</i>
Exchangeable Mg	1.89 <i>1.72</i>	1.70 <i>1.52</i>
Exchangeable Na	1.79 <i>0.84</i>	1.07 <i>0.72</i>
Exchangeable K	0.69 <i>0.33</i>	0.64 <i>0.48</i>
Exchangeable H	134 <i>47.6</i>	150 <i>41.2</i>
Exchangeable Al	12.5 <i>10.6</i>	22.8 <i>13.4</i>

The results in the table highlight the similarity between the drift and mineralic horizon chemistry. Main similarities were in the case of calcium, magnesium, potassium and hydrogen. Aluminium, however, was typically greater in the soil samples and exchangeable sodium greater in the drift.

There were also textural similarities between the drift and mineralic horizon samples, table 4.55B.

Table 4.55B: Comparison of the textural components of the mineral soil horizons and the drift samples. Results given as mean values with standard deviations in italics.

	Drift	Mineral soil horizons
% sand	74.0 <i>6.43</i>	82.6 <i>8.54</i>
% silt	18.2 <i>5.02</i>	12.7 <i>8.27</i>
% clay	7.58 <i>1.68</i>	4.81 <i>3.86</i>

The table illustrates the textural similarity between the soils and the drift. The soils were, however, typically enriched in sand relative to the drifts.

Chemical and textural similarities between the drift samples from chapter 3 and the mineral soil results reported in this chapter indicated significant input from the drift materials to the soils as a parent material component. Coarse soil fractions indicated input from a source of mixed origin. Soil thin sections were analysed in order gain a clearer picture on the frequency of the input of drift to the soil parent material and the nature of this drift.

4.6 MATERIALS AND METHODS: Soil Thin Sections

4.6.1: Soil sampling for thin section

At soil sites 1, 2, 3, 5, 6, 7 and 10 samples from mineral soil horizons were extracted in Kubierna tins for thin section analysis. Two tins were taken at different depths at sites 2 and 10. The soils were collected according to the procedure of Murphy (1986) which is set out below:

1. Soil pit face was cleaned and sketched. A kubierna tin was placed onto face with one lid on and pushed in squarely until the tin was full. Care was taken to avoid overfilling and compaction.
2. When the tin was full it was levered out any unnecessary soil sliced off.
3. A second lid was located on the tin and the sample number, date, depth and orientation were marked and recorded.
4. The tin was taped up with masking tape and labelled on the outside and finally placed into a plastic bag and stored.

4.62 Thin section preparation:

Soil thin sections were produced in the Department of Environmental Science using standard methods produced there (Muriel Macleod pers comm.) after Fitzpatrick (1984) and Murphy (1986). The procedure was as follows:

Drying:

Air drying produces shrinkage especially in clayey soils where clay minerals with expandable lattices contract on water loss (Jongorius and Heintzberger 1975). Organic soils are also prone to shrinkage. Water was replaced and the soil effectively dried using pure acetone. This was achieved by the following procedure, after Murphy (1986):

1. Soil samples were unwrapped, orientations noted and the basal kubiena lid replaced with a similar perforated lid.
2. The tin was placed perforated lid down onto a grill in the base of a large bowl. The top lid of the kubiena tin was removed. Orientation of the sample was recorded.
3. The bowl was filled with acetone to half the level of the tins. Bowls were set left in a fume cupboard.
4. The acetone was changed every 3-4 days until 8-10 changes had been made. The soils were then ready for impregnation.

Impregnation:

The soils were impregnated with a polyester resin mixed with thinner and catalyst; this mixture seeps into voids and solidifies retaining soil structure and enabling the soil to be cut as a block into a thin section. 180ml of polyester (crystic) resin was used to every 25ml of acetone (thinner) and 1.8ml of catalyst. Acetone was used as a thinner

since the sample was already 'familiar' with this medium. The thinner works to allow the resin to penetrate the pores of the soil more quickly and successfully. The catalyst promoted polymerisation in the resin helping the block to harden. The impregnation process is outlined below.

1. The resin, thinner and catalyst were mixed in a beaker in a fume cupboard using magnetic stirrers.
2. The soils in their kubiena tins (no lids) were placed into hardened tinfoil casings and orientations noted. The tin foil casings were taller than the actual kubiena tins.
3. These heightened containers were then placed into a desiccator fixed with a vacuum pump and the resin mixture was poured into each container.
4. When the containers were at capacity volume the desiccator lid was replaced and a vacuum created. This caused the resin to bubble.
5. Gaseous material given off in this process was collected as a solid. It was piped into a flask cooled externally by liquid nitrogen.
6. The resin was topped up three times during the 8 hour impregnation time and the level of liquid nitrogen was kept high -usually by refilling every hour.
7. When this 8 hour process was complete the soils were removed from the desiccator and left to cure in the fume cupboard. This takes a minimum of 28 days.

When the impregnated soils were hardened thin sections were taken by exactly the same method as rock thin sections and orientation etched onto the glass slide.

Once prepared the thin sections were assessed for void content, organic and mineral components and the relationship between the coarse and fine fractions determined with reference to a diagram from Bullock et al (1985) reproduced in figure 4.6A.

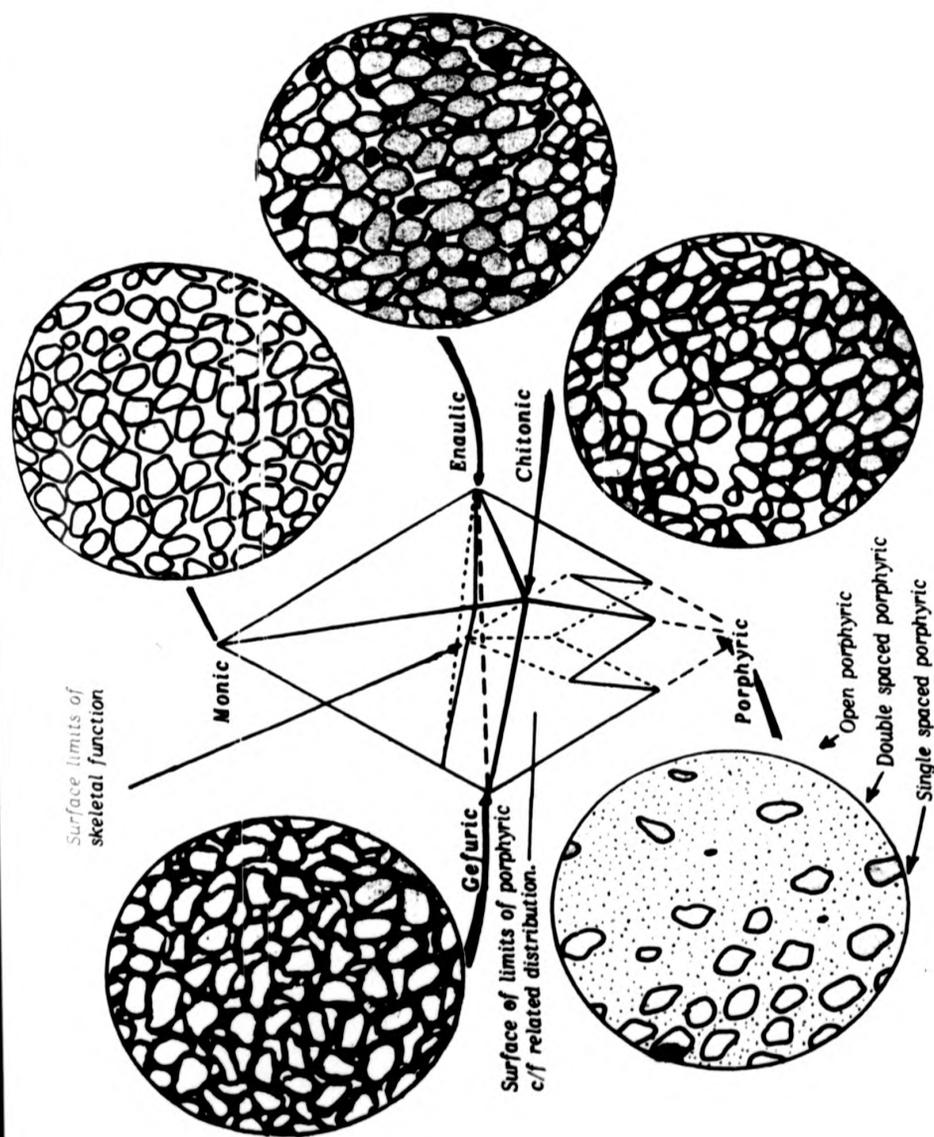


Fig. 4.6A RELATIONSHIPS BETWEEN THE 5 BASIC TYPES OF COARSE/FINE SOIL MATERIAL DISTRIBUTIONS (From Bullock et al - 1985. After Stoops and Jongerius - 1975)

4.7 Thin section results and discussion

Thin sections were analysed primarily with respect to their mineralogy to test the hypothesis that soil parent material was a mixture of locally derived drift, of mixed origin and solid geology underlying a particular soil site. Main soil features are given in tables F1, F2, F3 and F4 in Appendix F, pages 298-299. Coarse and fine material were separated throughout the descriptions by a size margin of 5 μ m.

Site 1:

Voids were often associated with decaying organic matter. They ran perpendicular to the soil surface and probably represented old root channels. The fine fraction of the soil was especially rich in organics but included some mineralic fragments. It was brown and speckled and had an open porphyric relationship (Figure 4.6A) with the coarse fraction (plate 4.7A) i.e. large fabric units occurred within a groundmass of smaller units. Coarse fraction organic components retained cell structures. The mineral fraction corresponded almost exclusively to a dioritic parent material. However, the presence of strained quartz fragments in the sample indicated an influx of material from meta-sediments to the south. This highlighted the likelihood of mixed parent material at this site.

Site 2:

Two samples were taken from site 2. The shallow soil was apedal with coarse and fine fraction related by a porphyric structure. The deep soil had more coarse material the majority of which was mineralic and the coarse fine relationship was described as porphyric tending to enaulic (Figure 4.6A) i.e. coarse fabric units were within a fine groundmass but were tending towards supporting themselves in a network. Soil voids

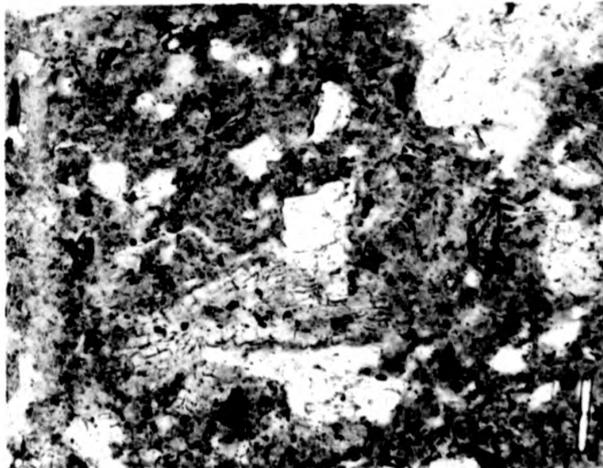


Plate 4.7A: Soil 1; Porphyritic relationship. X4, PPL.



Plate 4.7B: Soil 2, Root Channels. X2, PPL.

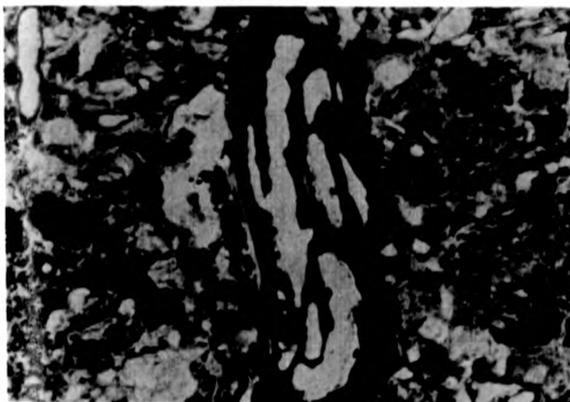


Plate 4.7C: Soil 2; Coarse fraction organics. X2, PPL.

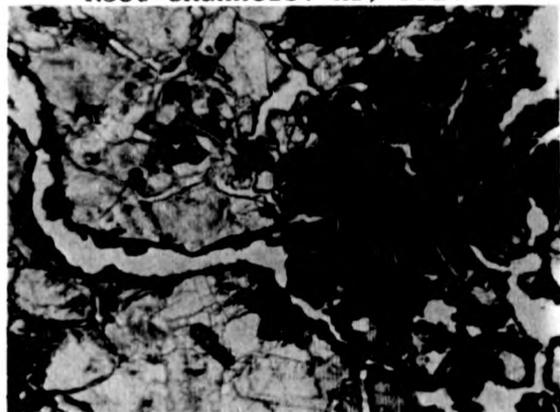


Plate 4.7D: Soil 2; Decay of diorite. X2, PPL.

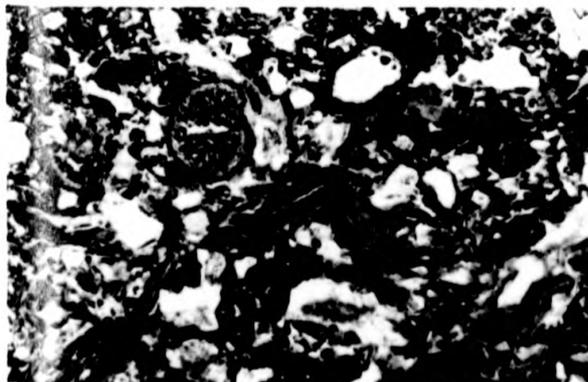


Plate 4.7E: Soil 3; Junction of upper and lower soil. X1, PPL.



Plate 4.7F: Soil 3; Biotite rich lower soil. X2, PPL.

were more abundant in the upper soil and were dominated by root channels, plate 4.7B, and ovate chambers. Plate 4.7C shows a piece of organic material from the upper part of the soil assumed to be of vegetable origin. Voids were occasionally infilled with organic rich, isotropic material. In the lower soil voids were more commonly filled with amorphous, isotropic yellow material assumed to be of organic origin. Together, these two observations could indicate translocation of organic matter through the soil profile. The soil mineral fraction was entirely dioritic; the lower soil contained a piece of diorite weathering in situ. The rock was riddled with isotropic planar cracks partly infilled with an uneven globular non-reflective red material, probably of organic origin, occasionally associated with Fe oxides and decaying biotite, plate 4.7D. Drift material was not necessary to explain any of the features in the soils taken from site 2.

Site 3:

The soil from site 3 was zoned. Plate 4.7E shows the junction of two of the zones. The upper zone had less coarse material and was apedal. Void space was uncommon (7-10%) and typically took the form of planar cracks. The lower zone was almost entirely mineralic made up of disintegrating rock fragments, rich in biotite (plate 4.7F) with minor fine fraction material and a greater proportion of voids. The coarse/fine relationship was porphyric in the upper zone but tending towards enaulic in the lower zone, figure 4.6A. In between the two zones was a large sub-rounded pebble of lamprophyric dyke material (plate 4.7G). The presence of this and other minor rock fragments in the soil profile indicated input of drift material of mixed origin to the soil parent material.

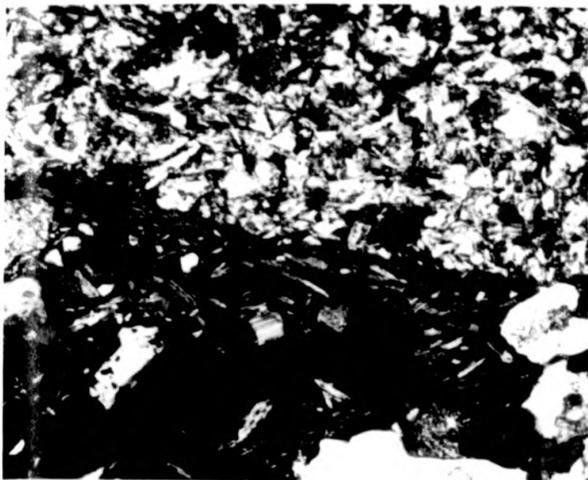


Plate 4.7G: Soil 3; Junction
of pebble and lower soil. X2, XPL.

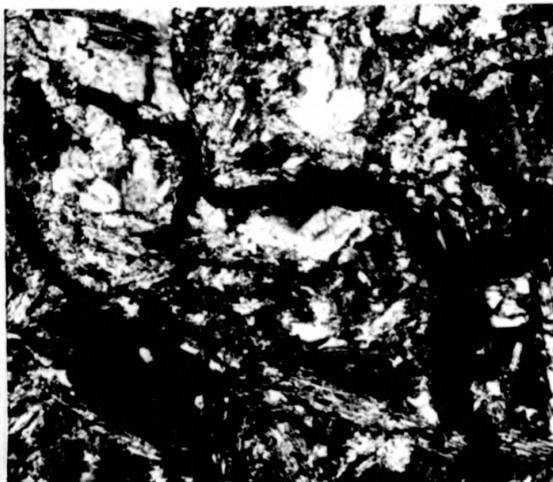


Plate 4.7H: Soil 5; Void
structure. X4, XPL.

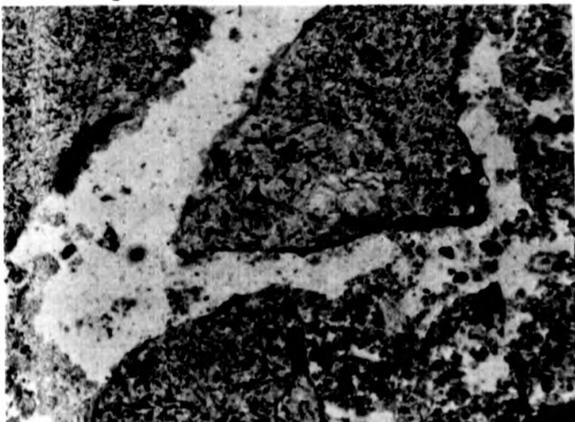


Plate 4.7I: Soil 6; Void
structure. X1, PPL.

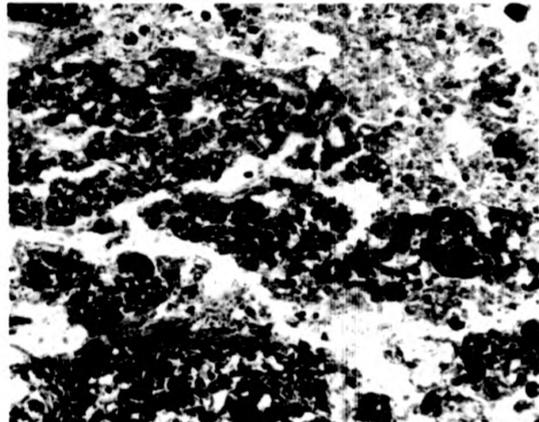


Plate 4.7J: Soil 6;
Pedality. X1, PPL.



Plate 4.7K: Soil 7; Granite
pebble. X2, XPL.

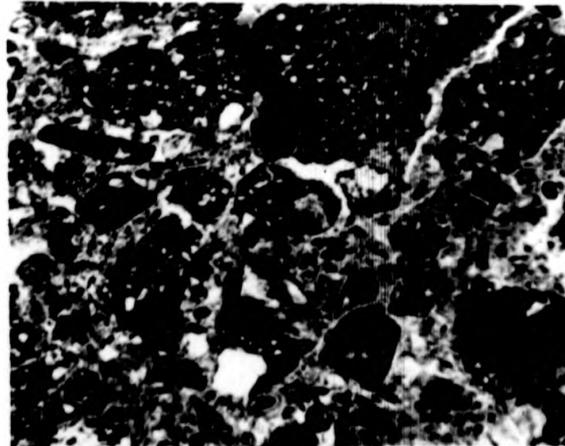


Plate 4.7L: Soil 7;
Pedality. X1, PPL.

Site 5

Soil from site 5 was very stony. The coarse fine relationship was gefuric, figure 4.6A i.e. coarse fabric units were linked by braces of finer material. Groundmass was rare. Voids formed a network of planar cracks throughout the soil (plate 4.7H). Organics were not prominent. Mineralic material was mainly of basic dyke origin (plate 4.7H) although there were large pieces of strained quartz present that could have been derived from meta-sediments surrounding the dyke. The thin section evidence in this soil, therefore, did not point to an input from locally derived yet 'foreign' drift but did involve a mixture of solid geology types in the parent material.

Site 6

Soil from site 6 was also stony. Voids again appeared to form a planar network throughout (plate 4.7I). Organics were a minor part of the coarse fraction and the coarse/fine relationship was gefuric, figure 4.6A. Fine fraction material showed some pedality (plate 4.7J). The mineralic material was typically angular (plate 4.7I) and exclusively porphyritic in origin. There was no evidence of locally derived yet foreign drift material in the material for the soil at site 6.

Site 7

Two slides were taken from the soil at site 7. The shallower soil had a greater proportion of voids than the deep soil but organics were minimal in both soils. Pedality was strongly developed in the upper soil, the peds were granular. The coarse fine relationship within these peds was porphyric, figure 4.6A. The mineral fraction in the upper soil included black shale rock fragments with porphyry and 'granite' (plate 4.7K). The lower level soil had a less well developed pedality, especially in its lower reaches (plate 4.7L). It contained a greater variety of rock types including

greywacke (plate 4.7M), black shale (plate 4.7N) and igneous material. Drift of mixed yet local origin was very important within the parent material at this particular site.

Site 10

Soil from site 10 was apedal. Coarse and fine fraction showed a porphyric relationship, figure 4.6A. The upper 2cm of the soil had a deep red coloration and voids were often filled with yellow amorphous material of partly organic origin (plates 4.7O and P). This isotropic amorphous organic rich material was often mixed with plant material. The material also appeared further down the profile (see plate 4.7Q) and may have indicated the down profile movement of organics. The soil mineralogy was consistent with a granodioritic geology although the presence of strained quartz (plate 4.7R) indicated an input from surrounding meta-sediments. It again seemed that a mixed origin drift component of soil parent material was not necessary to explain the features found in soil thin section at site 10.

Soil thin sections therefore gave further evidence of the mixing of drift materials at sites 1, 3 and 7. This mixing was not a feature of the whole area but appeared to be localised being especially prominent on high ground and in the north of the area. The results of the soil thin section work together with that of the nature of the coarse fraction of the soil strongly suggested drift material in the area could be made up of mixed solid geology types and that such drift was a prominent input to soil parent materials.

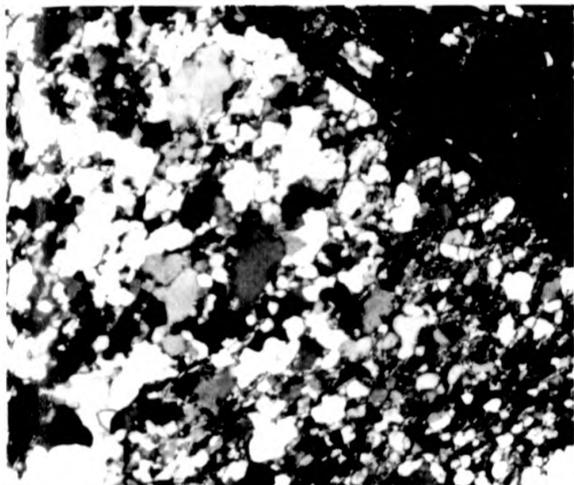


Plate 4.7M: Soil 7; Greywacke pebble. X2, XPL.



Plate 4.7N: Soil 7; Black shale pebble. X1, PPL.



Plate 4.7O: Soil 10; Red colour of upper soil. X2, PPL.

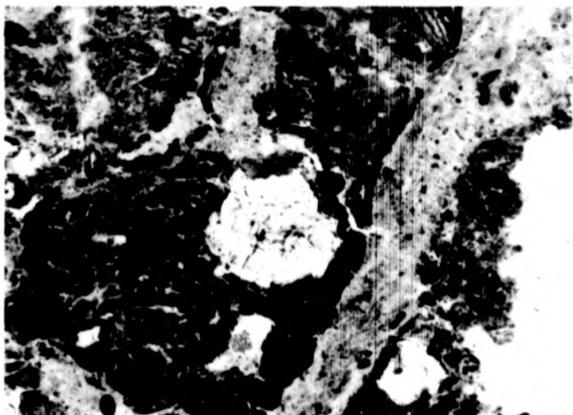


Plate 4.7P: Soil 10, Yellow void infill. X2, PPL.

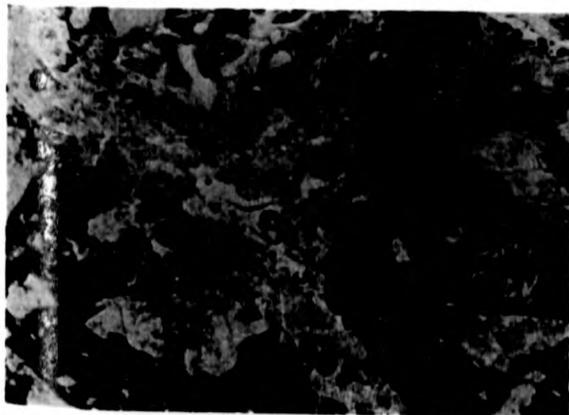


Plate 4.7Q: Soil 10; Void fill in deeper soil. X2, PPL.

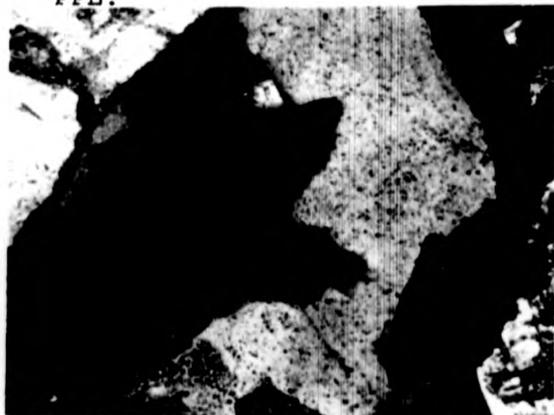


Plate 4.7R: Soil 10; Strained Qtz. X4, XPL.

4.8 CONCLUSIONS

The soils of the Loch Dee area were of short spatial range typically developed within small pockets, changing chemically within fractions of metres. The soils were adequately described by the mapping categories assigned by Bown (1979) and included peat soils, peaty podzols, peaty gleys, ranker soils and podzol rankers.

Soil pH showed some variation with vegetation. The organic soil horizons had greater exchangeable cations than the mineral horizons, reflected in much greater cation exchange capacity. Base saturation was higher in the organic soils. The organic matter was the key to the chemical exchange properties of the organic soils. Organic matter was less abundant in the mineral soils (by definition) yet maintained a control on the cation exchange process within these soils.

Soil chemical properties measured were within a similar range to results from previous studies in the area. A notable difference was lower Al concentrations in both organic and mineral horizons in the White Laggan sub-catchment compared to the Dargall Lane described by Giusti. This and other differences served to highlight the variable nature of the soils in the area.

The chemistry of the soils of the area showed some resemblance to the results from Balquhiddy, Chon, Kelty and Mharcaidh in Scotland, Llyn Brianne in Wales and Hoylandet and Birkenes in Norway. Relative base and aluminium saturation of the soil exchange complex indicated most similarities between the soil data of Loch Dee and Lochs Kelty and Chon in Central Scotland. These were both designated acidified sites

by the Surface Waters Acidification programme. The lack of any base rich geology in both the Dee and Kelty catchments makes their similarities even more striking and highlights the level of acidification that has been reached in the Loch Dee area.

The mineral horizons had greater mean extractable Fe than the organic horizons. This was often expressed as a podzolic iron pan as at sites 2 and 10. In the case these sites this richness in organic iron correlated with an 'orange' coloration in the soil thin sections. Voids in these soils were filled with amorphous, non-reflective material of assumed organic origin which may have included iron rich organic complexes. In the soil from site two this material was more abundant in a lower soil and indicated the translocation of organic material through the soil profile. This is important with respect to transportation of both iron and aluminium in the soil profile (Farmer 1985).

Extractable iron was also enriched in some organic soil horizons e.g. site 14, site 15, site 17 and site 21. Sites 15 and 17 had limited mineral soil development. High concentrations of extractable iron in the organic soils from sites 14 and 21 may have indicated incomplete downwashing of iron with organic matter to the mineral horizons. This was in direct contrast to the results from sites 2 and 10.

Variability in soil chemical properties was partly explained by soil profile type. Podzolic soils had greater exchangeable hydrogen and aluminium and pyrophosphate extractable iron than any other soil type. None of the soil chemical variability could be explained in terms of solid geology. This lack of geological influence was explained with reference to a drift component of soil parent materials. Soil thin section

evidence also indicated the mixing of solid geology types at small igneous intrusions. Drift was also sometimes of a mixed origin rather than derived directly from any one solid geology type. Input of this drift to the parent material component of the soils in the area and solid geology mixing at small igneous intrusions obscured the strong chemical differences noted in chapter 2 of the geology types in the area. Soil chemical and textural evidence clearly showed the similarities between the mineral soils and the drifts.

The results from this section highlight the low pH, base poor nature of the Loch Dee soils and the high concentrations of aluminium on the soil exchange complex. All of this indicates low buffering capacity for the neutralisation of incoming acidity. In addition, the levels of aluminium in the soils in an exchangeable form could signify problems in terms of future water quality and fish survival in the area.

Chapter 5: Spatial and temporal variations in soil water chemistry.

5.1 INTRODUCTION

Soil water is comprised of two physically distinct components. Firstly 'free water' including that drained by gravity through the soil profile and involved with the transport of material in solution and suspension. Secondly 'capillary water' which is adsorbed on to soil micelle surfaces (holding cations in an exchangeable form) or held in small pores and involved in weathering reactions (Vedy and Bruckert 1979). The soil fluid component is assumed to be in equilibrium with the soil solid component. However, this equilibrium is very complex (Bruce et al 1989). The chemistry and quantity of both integral soil water components are affected by input from sources both internal e.g. mineral weathering and external, e.g. wet, dry and occult deposition, tree bark and leaf litter leachate, to the soil.

Soil waters are the 'soil reactive medium' responsible for buffering acidic inputs to the ecosystem or sometimes releasing 'stored' acidity into the environment. Langan (1989) used soil column leaching experiments to mimic an influx of seasalts to an ecosystem during a storm. The seasalt rich solution was acidified on its passage through a H⁺ rich podzolic soil - the soil retained the salts in exchange for its H⁺. On a catchment scale this would have resulted in an acidification of surface waters that could have had disastrous effects on fish populations. The work of Langan highlighted one possible short term influence of atmospheric deposition on the chemistry of soil water. Further leaching of the same soil column with an acidic rainwater solution reflected the more usual and long term effect of atmospheric input on the soil system. The soils buffered the incoming acidity by exchanging seasalt ions on its exchange

complex for the H^+ of the incoming rain. In this case the effluent was less acidic than the input but the soil exchange complex was reacidified. If base cations are not replaced on the soil exchange complex through the actions of weathering, acidic inputs from the atmosphere are not buffered by the soil and consequently surface waters become more acidic.

Buffering of acidic inputs was identified by Welsh and Burns (1987) in the Loch Dee area. The buffering capacity of the soil appeared to be related to lithological controls and was reflected in the variability of surface water chemistry. Waters draining non-metamorphosed country rock were the most highly buffered with respect to rainfall chemistry closely followed by waters draining metamorphosed country rock and then granite. Waters draining black shales were the most acidic. The authors suggested these results were caused by increased weathering reactions within the soils overlying the non-metamorphosed country rocks giving these soils a greater base saturation and therefore greater buffering capacity. Reid et al (1981a + b) came to similar conclusions in the Glendye catchment in Aberdeenshire where they found a strong relationship between surface water chemistry and soil weathering reactions.

A complicating factor in defining the geological controls on soil water chemistry is soil water retention time. The greater length of time water is retained by a soil the greater are its chances of participation in slow weathering reactions releasing ions for cation exchange. A soil with a high buffering capacity increased through weathering will improve the quality of acidic waters passing through it. The retention time is influenced by slope of the area, thickness of a soil and soil texture. In the case of the

Loch Dee catchment waters draining black shales run into the Dargall Lane sub-catchment which has a steep slope and thin mineral soils. Surface runoff is typical in the steep parts of the sub-catchment giving little opportunity for the neutralisation of the any acidic components. When this runoff reaches the valley floor it meets highly acidic deep peats which decrease the likelihood of acidity neutralisation in the runoff (Langan 1986). The White Laggan / Black Laggan sub-catchment is associated with both contact metamorphosed and non-contact metamorphosed rock types. This sub-catchment has a much shallower slope and the likelihood of throughflow is increased. This intensifies the chances of neutralisation of acidic waters by cation exchange processes within the soil provided the soil has the chemical capacity to buffer.

Monitoring of the changes in soil water chemistry through time gives an insight into the processes occurring within the soil in response to seasonal fluctuations in atmospherically derived inputs, changes during the course of a complete vegetational cycle and of course, input by weathering. An overall picture can help to clarify questions concerning the source and sinks of elements within the soil water system and provide a perspective on the potential damage of short term events. A thorough understanding of the soil water buffer system is a necessity for realistic catchment modelling studies.

Previous studies into seasonality have helped to define features of soil water chemistry that are not typically related to geological controls. Seasonality in nitrate content, typified by a summer low, was noted in surface water chemistry at Glendye (Reid et al 1981) and in some Norwegian soils (Skartveit 1981). In the Norwegian case

potassium also showed the same seasonality and in neither case was this reflected by atmospheric inputs. Burns and Lees (1987) reported some seasonality in the Loch Dee surface waters - summer lows in potassium and nitrate were explained by biological uptake. Skartveit (1981) indicated seasonality in chloride and sulphate that was reflected in soil and surface water chemistry and indicated the ease of movement of these anions through a catchment. Lees (1989) suggested chloride and sulphate dominated both the chemistry of the rainwater and runoff at Loch Dee and were considered mobile within the catchment. This was supported by soil water chemical analyses of Grieve (1990a). Johnson and Reuss (1984) found a negative correlation between soil organic matter and sulphate adsorption. This helped to explain the mobility of sulphate in the Loch Dee catchment because of the highly organic nature of the soils. It has proved more difficult to ascertain solid facts concerning the input of geology to the soil water system. Farley and Werritty (1989) used a budget approach to suggest the catchment was a source of sodium, potassium, calcium, magnesium, aluminium, sulphate, nitrate and silica. Some of these could be input by the processes of rock weathering. This chapter aims to use the knowledge of the chemistry of the rocks in the Loch Dee area and the chemistry of atmospheric inputs in an attempt to decipher more concerning the geological inputs to the Loch Dee system.

5.2 AIMS

The aims of this chapter were:

1. To determine the nature of any seasonality within the soil water chemistry.
2. To determine the relationship between chemical components of the soil waters and attempt to define their source.
3. To test the findings of Welsh and Burns in terms of geological controls on the chemistry of surface waters in the light of findings from earlier chapters.

5.3 MATERIALS AND METHODS

5.3.1: Soils and soil sites

25 soil sites had been characterised according to soil chemistry and texture in chapter

4. Of these 25 sites, 20 were maintained within the monitoring procedure. This was the maximum number of soil profiles envisaged within the scope of the project. The sites were selected on a basis of:

1. Solid geology type
2. Soil type

The 20 sites aimed to cover both podzolic and gleyed soil profiles for each solid geology type. However, because of the amount of peaty or ranker soils within the area it was inevitable that some of these were chosen.

Table 5.3A gives the breakdown of sites, soil types and geology types; site positions are indicated on figures 4.1A and 4.3A in chapter 4.

Table 5.3A: Solid geology and soil profile relationships within the soil sites chosen for monitoring.

Solid geology type	Soil profile type		
	Podzol site	Gley site	Other (peat soils or rankers)
Diorite	2,	3, 12	1, 23
Coarse meta-sediment	8		9, 19, 22
Dykes	16, 21	5, 6, 25	
Black shales	14		7
Fine meta-sediments	11		18
Granodiorite (M+m)	10	20	

5.32 Method of soil water extraction

Methods available for the extraction of soil waters were investigated. They were of two main types:

1. Extraction in-situ including the use of suction free lysimeters and porous pot suction lysimeters. Barbee and Brown (1986), Grieve (1990a and b).
2. Extraction from a soil sample - by displacement.

Rauland - Rassmassen (1989) highlighted the possibility of Al contamination in soil waters extracted using porous pots. Hughes and Reynolds (1990) suggested this would be eliminated given sufficient field equilibration periods for the pots. However, in reply, Rauland - Rasmassen (1991) indicated this equilibration time would necessarily be greater than 1 year for this method to be used. Because time was finite in this study and Al an important component of the soil acidification problem, plans for in-situ extraction were abandoned. Furthermore, most of these techniques extracted only 'gravitational' waters.

Extraction of waters from soils within the laboratory included such methods as displacement columns, centrifugation and mechanical squeezing. These all extract gravitational and capillary waters. Vedy and Bruckert (1979) highlighted the possibility of reaction between a displacing liquid and the soil. Adams et al (1980) suggested displacement columns were time consuming and required operator skill when compared with centrifugation techniques. Wolt and Graveel (1986) discussed a column displacement method that reduced extraction time but had the disadvantage of still requiring operator skill. Chemical analyses of soil waters tested using column displacement and centrifugation were found by Adams et al to be comparable therefore centrifugation was determined as the most appropriate method to extract soil waters. Adams et al (1980) highlighted the problem of extraction of water using this method from soils of a high clay content. This was resolved by Elkhatib et al (1986) by the use of centrifugation with immiscible liquids. This method also increased the amount of recoverable moisture in all soil types. Menzies and Bell (1988) indicated that both of these centrifugal methods produced solutions of comparable chemistry from the soils. However, the toxicity of some of these immiscible liquids (e.g. Carbon tetrachloride) and the cost of others (e.g. ethylbenzoylacetate) meant they were inappropriate for general use in this project. In addition, the majority of soils tested for particle size analysis in chapter 4 were low in clay content so use of immiscible liquids would not have substantially improved the amount of soil water recoverable. A standard procedure of two-way centrifugation was adopted.

200ml two-way polypropylene centrifuge tubes with a small piece of glass wool in the base of the upper chamber were employed to extract the soil waters. 100ml tubes had

been tested initially to extract soil solutions but this smaller tube volume meant the number of extractions required to obtain at least 25ml of sample was increased and extraction was more time consuming. The glass wool in the base of the upper tube acted as a filter. A small scale investigation was made to determine the most appropriate centrifuge speed and time of centrifugation for a peaty soil (Table 5.32A).

Table 5.32A: Determination of centrifuge time and speed.

Time (minutes)	Speed (rpm)	Vol of soil water (ml)
15	3900	27
20	3900	30
25	3900	30
20	4100	32
20	4300	32
25	4100	33

These investigations indicated a centrifuge speed of 4100 rpm for a time of 20 minutes was the most productive combination.

5.33 Sampling procedure

Soils were sampled by auger from the organic and mineral horizons at the 20 sites chosen. One sample was taken from each horizon at three points within the immediate vicinity of the original soil site. The depth of the sample was approximate. Every effort was made to sample the same soil horizons and given the variable nature of the soils in the area these often varied in depth. At sites 12 and 16, chemical analytical work in chapter 4 had indicated the presence of an intermediate humic mineral

horizon. These were sampled in addition to the organic and mineral soils but were notably more difficult to discern. The three sub-samples extracted from each horizon at each site were mixed thoroughly prior to extraction of their waters.

The sites chosen for monitoring were split into two and sampled at approximately monthly intervals over a 15 month period. This time period was split into days - day one represented 1st November 1990 and each day counted on from this one. One sampling group included sites 1, 2, 3, 7, 12, 14, 20, 23. The other included sites 5, 6, 8, 9, 10, 11, 16, 18, 19, 21, 22, 25.

In the initial stages of sampling these two groups were sampled at approximately monthly intervals, a fortnight apart. However, latterly the samples were collected on one day or two consecutive days.

5.34 Analysis of waters

When the soil waters had been extracted from the soils they were shaken to mix and then analysed for:

- a. Cation content
- b. pH
- c. DOC content
- d. Anion content.

Soil waters were not filtered prior to analysis except where this is stated in methods. Cations were measured directly from the soil water. Calcium was measured by flame atomic absorption spectrophotometry (AAS) against fresh 10mg/L and 20mg/L standards treated with SrNO₃/HCl solution. All standards were made up in distilled water unless otherwise indicated. Samples were also treated with SrNO₃/HCl solution which masked interferences from other chemical constituents during the measurement

of calcium. Magnesium was measured by AAS against 2.5mg/L and 5mg/L standards. Aluminium (total) and iron were also measured directly from the soil water by AAS. Aluminium measurement employed 10mg/L and 20mg/L standards, iron 2.5mg/L and 5mg/L standards.

Sodium and potassium were measured by flame photometry directly from the soil water samples and compared with calibration curves compiled from the measurement of blanks, 25mg/L and 50mg/L standards for sodium and 5mg/L and 10mg/L standards for potassium. Where the sample had >50mg/L sodium or >10mg/L potassium an aliquot of the soil water was diluted and the sample remeasured. This value was then read off from the calibration curve and the result in mg/L multiplied by the dilution factor.

pH of the soil water was measured on an aliquot of sample immediately after extraction. Storage of the samples prior to other chemical measurements produced fluctuations in pH.

Dissolved organic carbon (DOC) was measured using a TOCSIN II Aqueous Carbon analyser. The samples were diluted 10 - fold prior to measurement and tested in triplicate. The machine was calibrated using three blanks and three 10mg/L standards. Mean blank and standard values were used to convert sample readings to mg/L values prior to multiplication of results to account for dilution.

Anions were measured by ion chromatographic methods using a Dionex ion chromatograph. Soil waters were tested for fluoride, chloride, nitrate and sulphate.

Samples were measured against a standard solution containing 1mg/L fluoride, 2mg/L chloride, 10mg/L nitrate and 20mg/L sulphate in deionised water. Samples were diluted 10 fold prior to measurement with deionised waters and tested in triplicate. Samples were manually injected into the ion chromatograph through a 0.2µm filter. This minimised blockages within the chromatograph but had no chemical effect on the anions to be measured (Menzies et al 1991). Mg/L conversions on the Dionex readouts were multiplied by the dilution factor (i.e.10). Mean values were then registered for the triplicated readings. Where one of the three values was significantly different from the other, two more replicates were tested until three similar values were found. If this had not occurred within 6 replicates this was taken as an indication of sample heterogeneity and a mean value recorded of all measurements. If diluted samples exceeded the chloride content of the standard (2ppm) they were diluted by a greater factor and retested.

5.4 RESULTS

Full soil water results for the different soil sites are presented graphically in Appendix G, pages 300-320. However, mean properties of the organic and mineral soil waters together with their combined ranges for the whole sampling period are given below in table 5.4A.

The chemistry of both organic and mineral soil solutions was dominated by sodium chloride, sulphate, nitrate and dissolved organic carbon. Sodium and chloride can be attributed to maritime inputs that dominate rainfall in the area. The high concentrations of DOC highlight the importance of organic matter throughout the catchment.

Table 5.4A: Mean and range of chemical properties for the organic and mineral horizon soil waters throughout the monitoring period. Results, except pH, are given in mg/L.

mg/L	Range of mean values calculated for any one sampling period.	Organic soil horizon waters	Mineral soil horizon waters
Ca	0.58 - 7.29	3.21	2.30
Na	2.52 - 36.0	15.3	15.0
Mg	0.52 - 1.40	1.14	0.75
K	1.38 - 8.03	3.99	1.83
Fe	0.40 - 3.20	1.21	0.92
Al	0.58 - 3.21	1.15	1.77
Cl ⁻	10.8 - 30.1	18.5	15.6
SO ₄ ²⁻	7.27 - 35.3	13.2	9.73
NO ₃ ⁻	3.74 - 54.0	13.1	9.09
F	0.00 - 7.93	1.54	1.40
pH	4.83 - 5.95	5.32	5.61
DOC	0.67 - 108	59.8	40.6

Organic soil waters were typically enriched in calcium, magnesium, potassium, iron, chloride, sulphate, nitrate and DOC compared with mineral soil waters. Waters extracted from both organic and mineral soil horizons tended to be similar in concentrations of sodium and fluoride. Waters extracted from the mineral soil horizons appeared to have greater concentrations of aluminium than those extracted from the organic soil horizons.

5.41 Trends within the data

Calcium concentration peaked in organic and mineral soil waters at all sites in December 1991 (c.day 400) and was also enriched between April and August 1991 (days 150 - 300). This is illustrated for site 1 in figure 5.4A.1. This diagram also demonstrates a calcium peak limited to the organic soil waters of sites 1 and 6 in January 1991 (day 100). In general soil water calcium was limited between September and October 1991 (days 300 -350) and prior to April 1991 (days 1-150) except at sites 1 and 6 where a concentration peak has been identified.

Maximum soil water sodium was found at many sites in January 1991 (day 100) although the organic soil water peaks from sites 1, 2 and 8 were unusually low at this time. Sodium concentration decreased to a minimum in June 1991 (day 220) but after this increased again and fluctuated around this lower peak for the remaining monitoring period. This pattern is illustrated for the soil waters from site 3 in figure 5.4A.2.

Soil water magnesium showed on average 3 distinctive peaks - January 1991 (day 100), April 1991-September 1991 (days 150 - 300) and again in October 1991 (day 350) and was often at a minimum between the July and October peaks (c. days 280 - 350). These patterns are shown for soil site 21 in figure 5.5A.3. However, soil water magnesium varied considerably for the different soil sites, see figures 1-20 appendix G.

Soil water potassium displayed two main concentration peaks. The first appeared in

Fig 5.4A.1 Mean concentration of Ca through time in soil waters from site 1

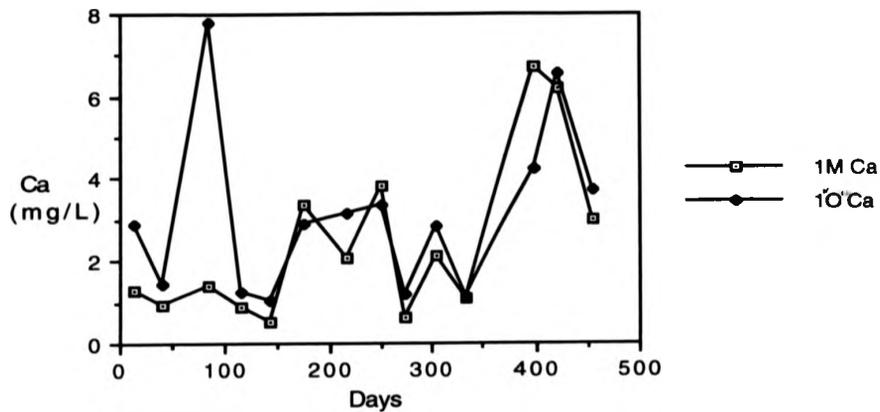


Fig 5.4A.2 Mean concentration of Na through time in soil waters from site 3.

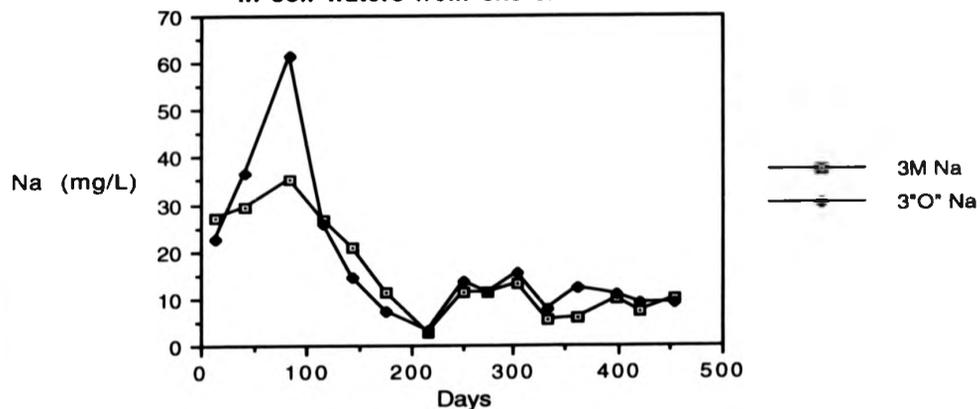
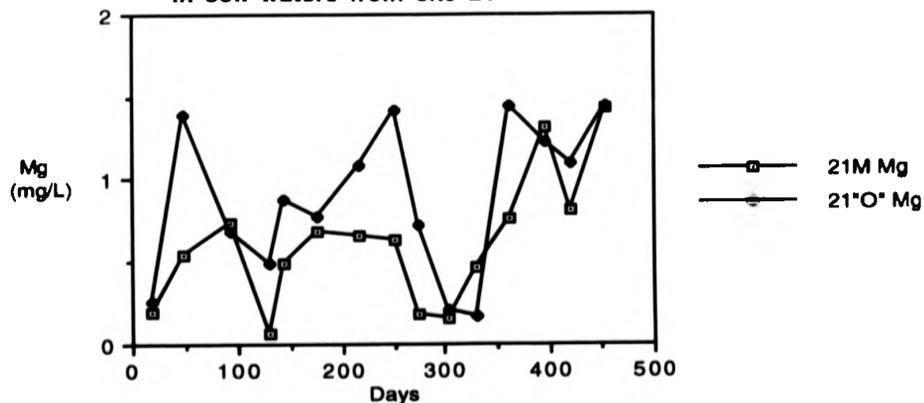


Fig.5.4A.3 Mean concentration of Mg through time in soil waters from site 21



both organic (except site 1) and mineral (except sites 5 and 6) soil waters in winter 90/91; the second was a prominently organic soil water peak in late summer 1991 (days 250 - 300). These configurations are presented for soil site 6 in figure 5.4A.4. There was an additional peak in winter 91/92 (days 400 - 450) in mineral soil waters from site 9 and organic soil waters from sites 10, 14, 18, 19, 22. The humic mineral soil waters from site 23 were unusually and consistently high in potassium.

Soil water iron was highly variable through time and between soil sites. Extremes are illustrated for sites 2 and 14 in figures 5.4A.5 and 6. Iron concentrations in soil waters from sites 2, 5, 10, 20, 21, 22 and 25 peaked >5mg/L at least once during the monitoring period. At sites 2, 5, 10 and 21 these peaks were in mineral soil waters. All these profiles except site 5 were classed as podzolic. Concentrations of iron in soil waters from sites 7 and 14 were consistently lower than at other soil sites.

Soil water aluminium often had two concentration peaks, a maximum winter/spring 1991 (c.day 100) peak and a second lower peak in late summer 1991 (c.day 250 -300). This is demonstrated for the soil waters from site 25 in figure 5.4A.7.

Soil water chloride peaked twice within the monitoring programme, once early in 1991 (c. day 100 - 150) and for a second time around mid October 1991 (day 350). Chloride was low throughout the summer except at site 23 where chloride was greatest in early July. These trends are illustrated for site 9 in figure 5.4A.8.

Results for individual sites indicated a high degree of variation of soil water sulphate

Fig5.4A.4 Mean concentration of K through time in soil waters from site 6

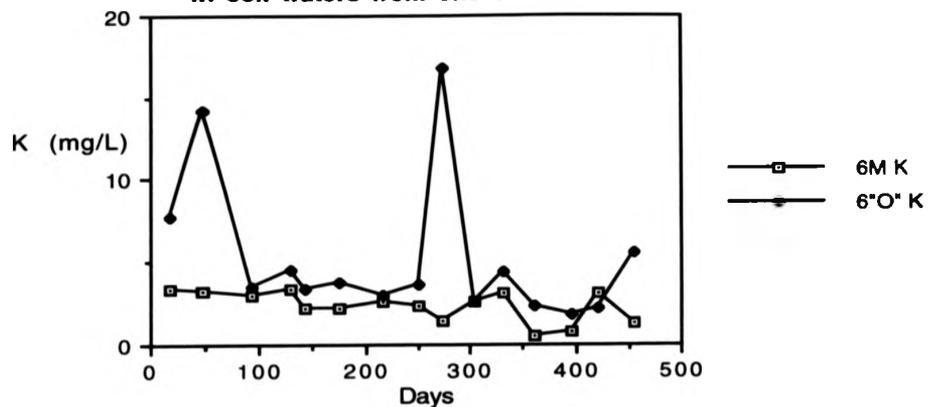


Fig 5.4.A.5 Mean concentration of Fe through time in soil waters from site 2

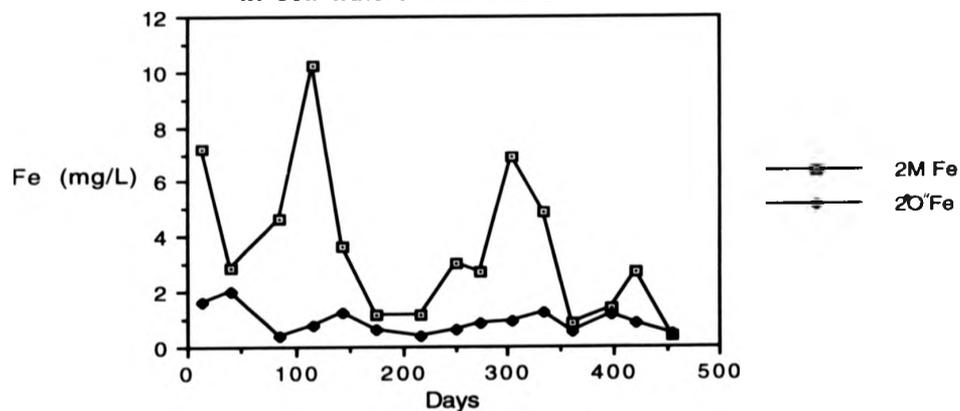


Fig 5.4.A.6 Mean concentration of Fe through time in soil waters from site 14

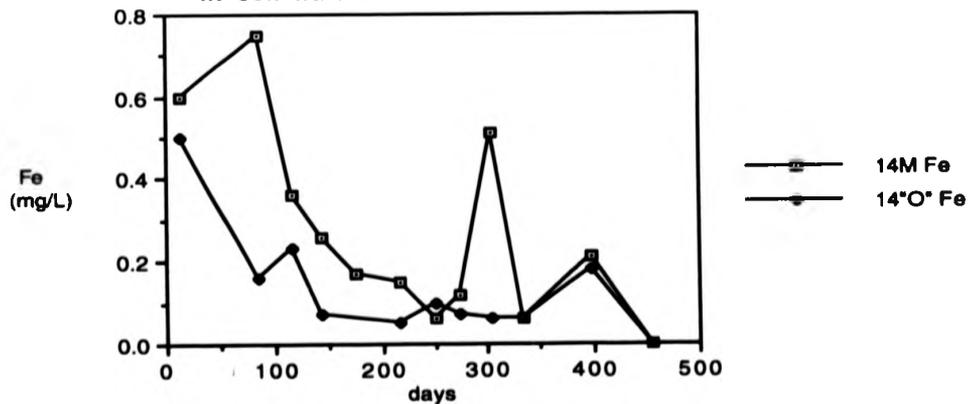


Fig 5.4A.7 Mean concentration of Al through time in soil waters from site 25

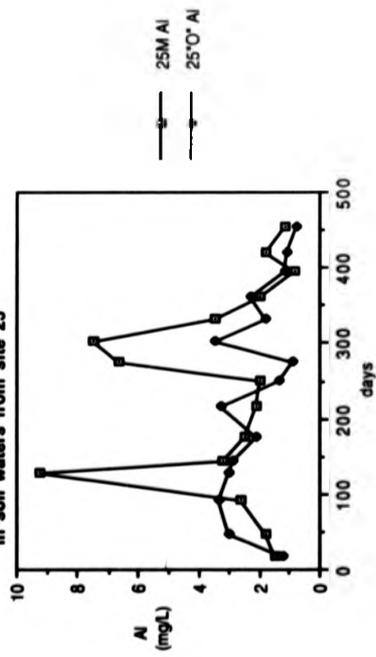


Fig 5.4A.8 Mean concentration of chloride through time in soil waters from site 9

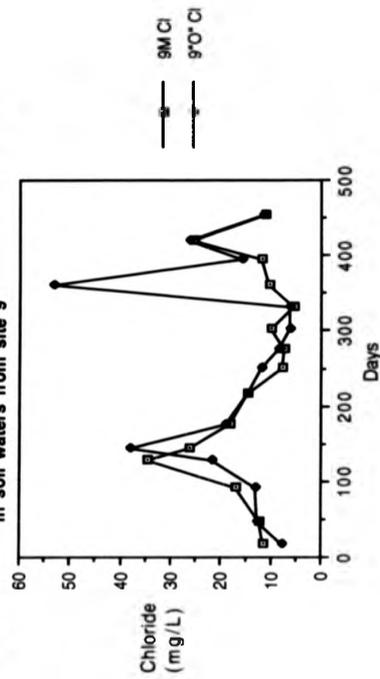


Fig 5.4A.9 Mean concentration of sulphate through time in soil waters from site 20

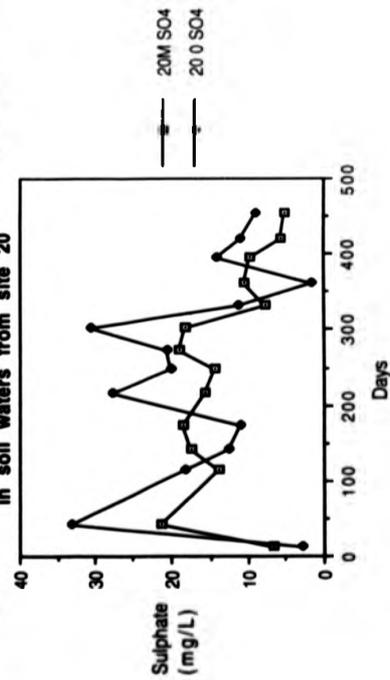
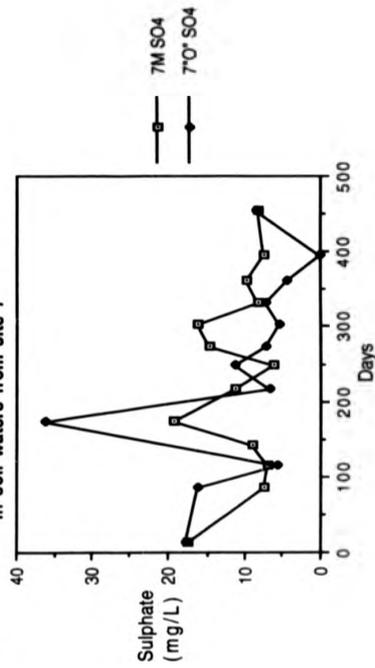


Fig 5.4A.10 Mean concentration of sulphate through time in soil waters from site 7



although there was a common peak around March - April 1991. Both this and the variability between sites is exemplified for sites 7 and 18 in figures 5.4A.9 and 10. However, in order to fully comprehend the variation refer to Appendix G.

Soil water nitrate varied between sites. However, there were two commonly occurring concentration peaks, one in spring 1991 (c. days 150 - 200) the other late summer to autumn 1991 (days 280 - 350), although this later peak did not occur at sites 8, 11, 16 and 18. These are depicted for site 10 in figure 5.4A.11. As for K the humic mineral soils from site 23 remained high in nitrate throughout the summer.

Maximum concentrations of fluoride in soil waters were commonly found in winter/spring 1991 (days 20 - 150) and exhibited a lower peak in autumn/winter 1991 (days 280 - 450). Between these times fluoride was often negligible. This pattern is illustrated for site 16 in figure 5.4A. 12.

Soil water pH fluctuated throughout the monitoring period but was typically lower in the summer months. This trend was weak but is characterised for site 11 in figure 5.4A.13.

DOC concentrations showed two peaks in concentration, one in January 1991 (c. day 50), the other late August 1991 (c.day 280). DOC was typically minimal around April 1991. These trends are illustrated for soil site 18 in figure 5.4A.14.

Fig 5.4A.11 Mean concentration of nitrate through time in soil waters from site 10

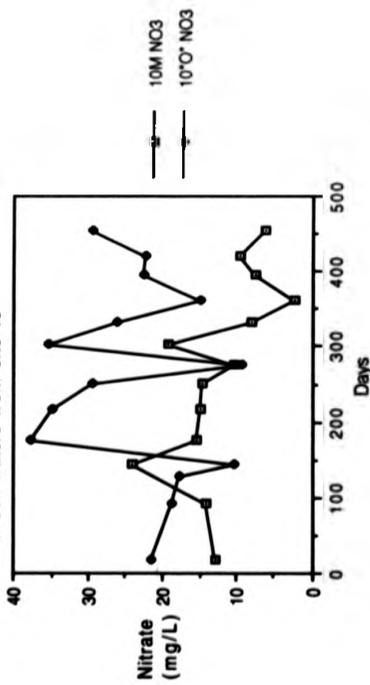


Fig 5.4A.12 Mean concentration of fluoride through time in soil waters from site 16

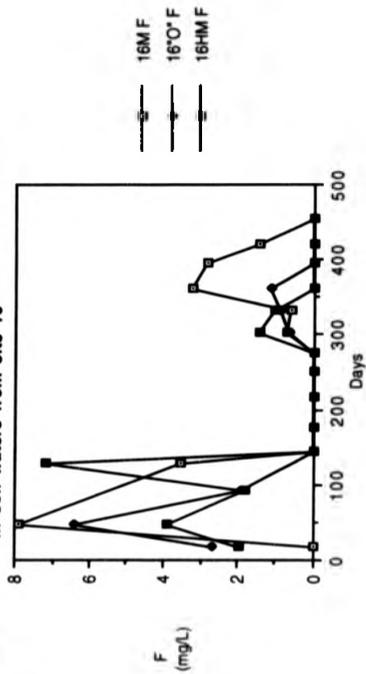


Fig 5.4A.13 Mean pH through time in soil waters from site 11

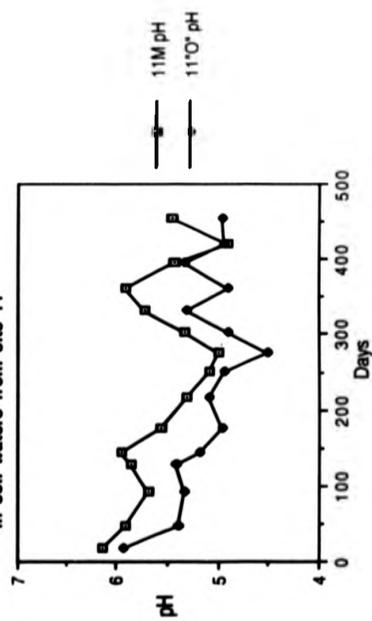
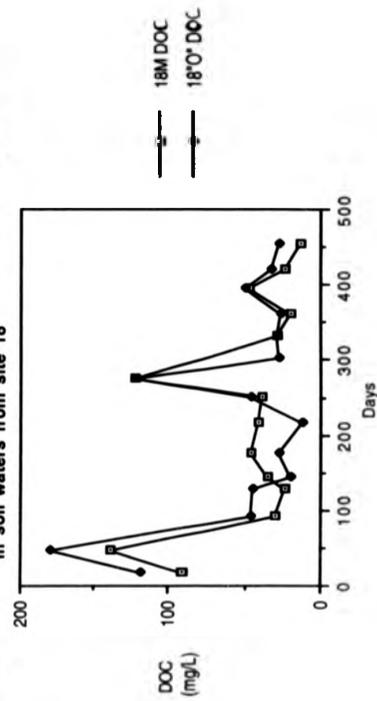


Fig 5.4A.14 Mean concentration of soil water DOC through time in soil waters from site 18



5.5 DISCUSSION

5.51. Reliability of results:

Analysis of soil water cations was by a single measurement where dilution was not stated in the method. Results therefore gave no indication of within sample variability. Soil water anions and DOC were measured with a dilution factor and therefore replicated. This replication ranged from very good indicating sample homogeneity and method reliability to poor. In these cases, despite numerous attempts to find a single characteristic concentration, poor replication was thought to indicate heterogeneity within the soil water.

5.52 Comparisons and explanations

All results were within the ranges of previous studies on soil water chemistry in the Loch Dee area and showed the high spatial variability in chemistry indicated by Grieve (1990a). The range of results for soil water calcium, sodium, potassium, aluminium and nitrate was greater than those of Grieve (1990a) for the Green Burn sub-catchment at Loch Dee. However, magnesium, chloride, sulphate, iron and DOC displayed similar concentrations. The frequency of large DOC concentrations in soil waters was, however, much greater in this study than found by Grieve in the Green Burn.

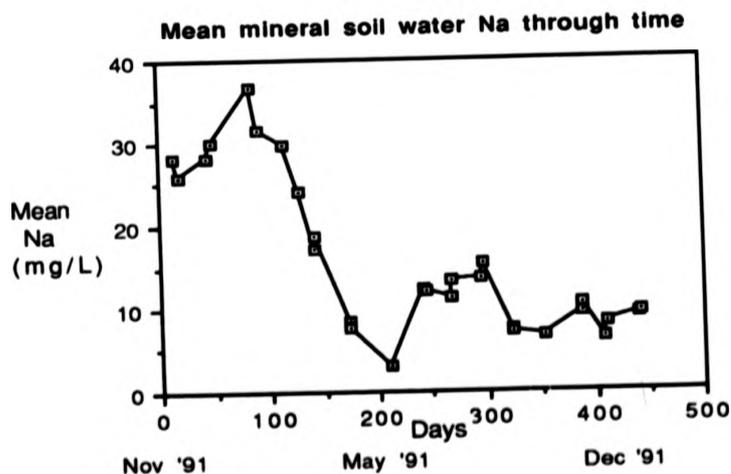
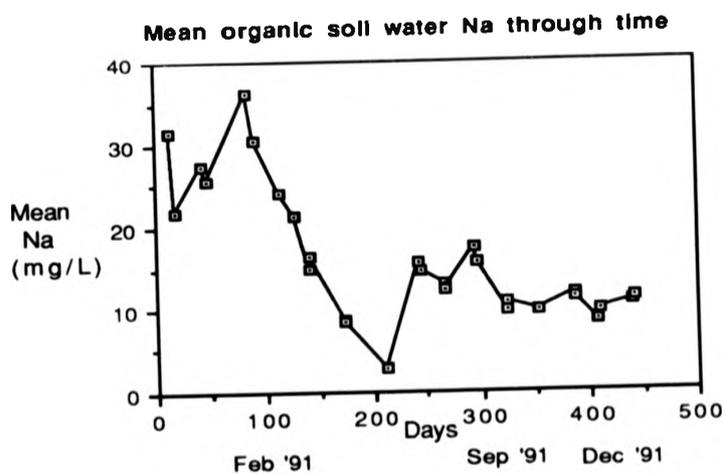
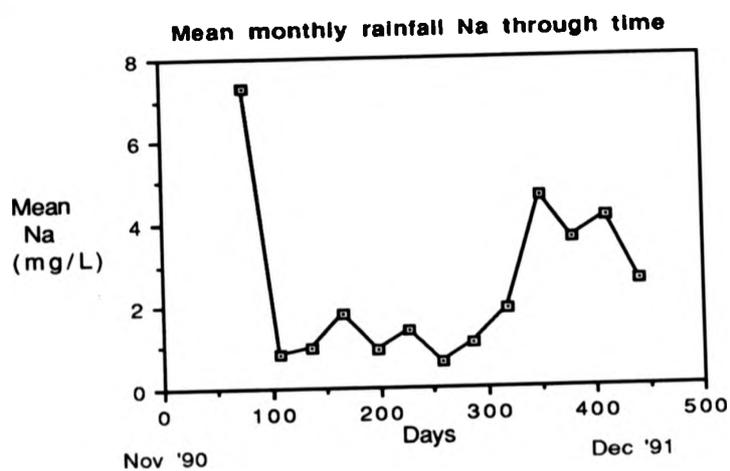
Soil water calcium, magnesium, potassium, aluminium and pH results were greater than those reported by Hornung et al (1986) for Welsh stagnopodzols and potassium and DOC were typically greater than the results given by Ferrier et al (1990) for soil water leachates from the Chon and Kelty catchment soils. Soil water pH was also

typically greater than reported by Mulder et al (1987) for atmospherically impacted woodland soils from the Netherlands. However, calcium, magnesium and sulphate concentrations from this study were much lower than those reported by Nilsson and Bergkvist (1983) for some Swedish soil waters. Iron and DOC were comparable with those of Nilsson and Bergkvist.

The pattern of results found for soil water calcium concentrations was similar in some respects to the results of Grieve (1990a) in that soil waters showed a winter peak. A similar winter calcium concentration peak was common in graphical results of Hultberg et al (1990) for soils from the Lake Gardsjon project in S.W. Sweden. In this project soils had been treated with acid sulphate and calcium increased gradually in soil waters through time but also exhibited the winter peak. The peak in the Loch Dee data did not correspond to any peaks in rainfall calcium concentration and was difficult to explain.

Soil waters reported by Grieve and the results from this study exhibited winter peaks and summer lows in sodium concentrations. This was explained by Grieve with reference to atmospheric inputs. Figure 5.52A shows the pattern of mean monthly rainfall sodium concentrations in the Loch Dee area compared with mean organic and mineral soil water sodium concentrations. Rainfall showed corresponding winter concentration peaks and can thus be used to explain high soil water sodium at this time. The results differed from those of Grieve since both the organic and the mineral soil waters reflected the chemistry of the precipitation. The late summer peak in soil water sodium concentrations, however, did not correspond to atmospheric input and

Figure 5.52A : Mean monthly rainfall Na compared with mean organic and mineral soil water Na through time



was explained by a concentration effect on drying of the soils through the summer period. Miller et al (1990) reported a slightly different response in the Chon and Kelty catchments in central Scotland. Although similar seasonal variations were apparent in the input of this element to these catchments seasonality did not show through in the soil water chemistry. Autumn/winter soil water maxima were, however, reported by Hornung et al (1990) for the Plynlimon site in Wales.

Soil water magnesium concentrations peaked three times once in winter, once in summer and then a final peak in the autumn 1991. Grieve (1990a) also reported strong autumn/winter soil water magnesium peaks. The first and third peak corresponded with peaks in rainfall magnesium concentration as illustrated in figure 5.52B. As with Na the summer peak did not correspond to atmospheric input and was again explained in terms of a drying and concentration effect. In contrast to Grieve (1990a) and Grieve et al (1984) both organic and mineral soil waters exhibited these peaks in magnesium concentrations. Different extremes of climate can be cited to explain this, i.e. a drier summer when samples were extracted for work herein than experienced by Grieve (1990a) would have meant drying and concentration affected mineral soils too. Results illustrated graphically by Hultberg et al (1990) showed corresponding soil water chemical peaks in the year 1987. Prior to this acid sulphate had not been added to the catchment soils and a peaky response was not observed. After 1987, this peaky response became less obvious and soil water magnesium concentrations remained high.

Soil water potassium winter peaks compared favourably with those found in rainfall as indicated in figure 5.52C. There was a late summer peak in potassium but this time

Figure 5.52B : Mean monthly rainfall Mg compared with mean organic and mineral soil water Mg through time

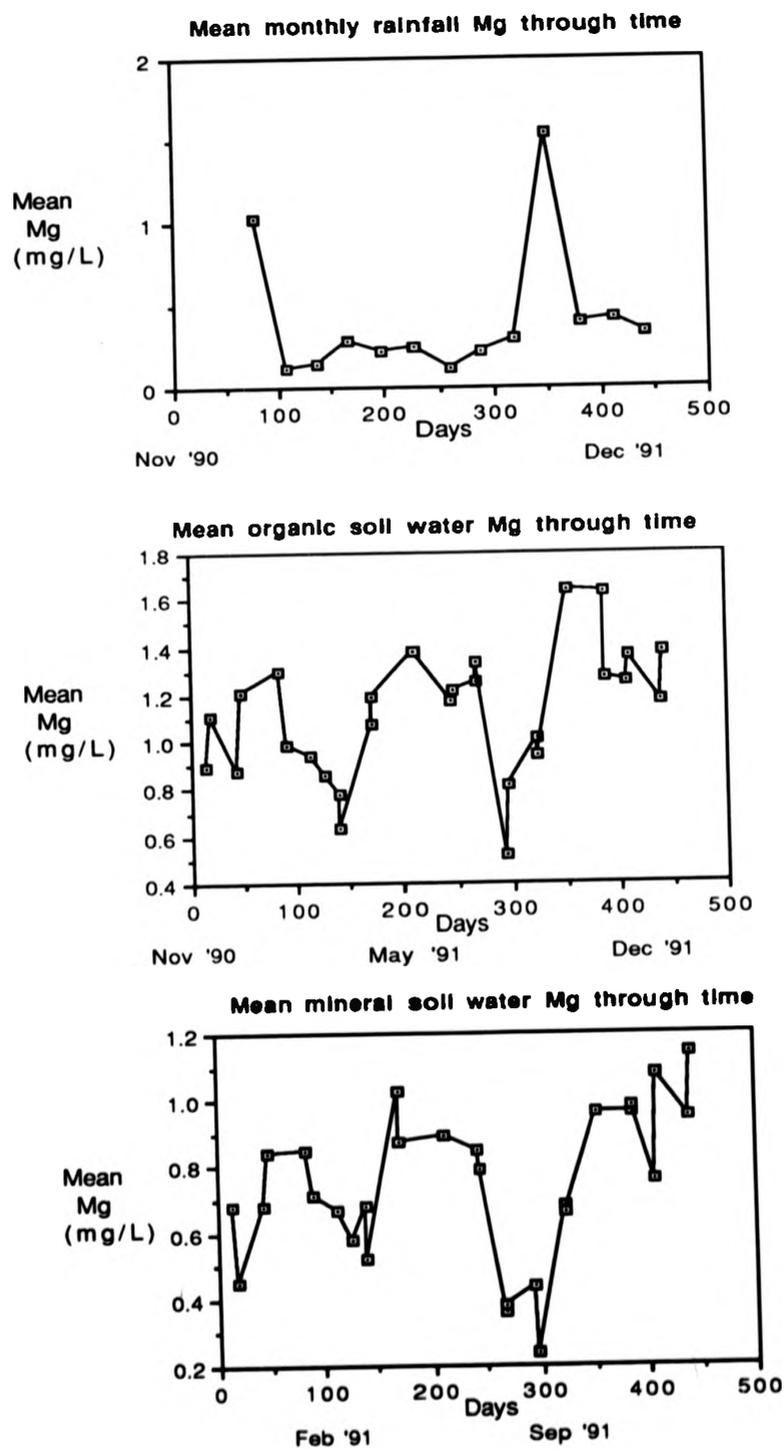
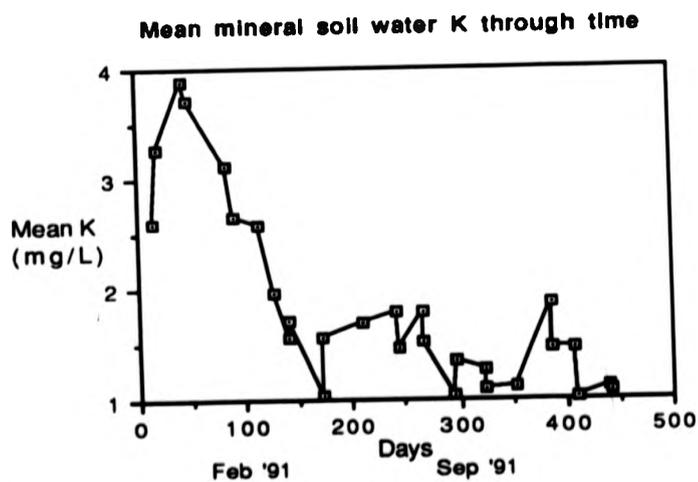
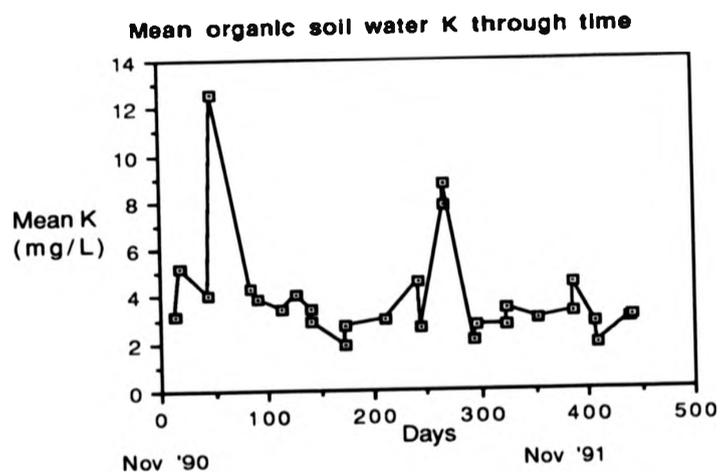
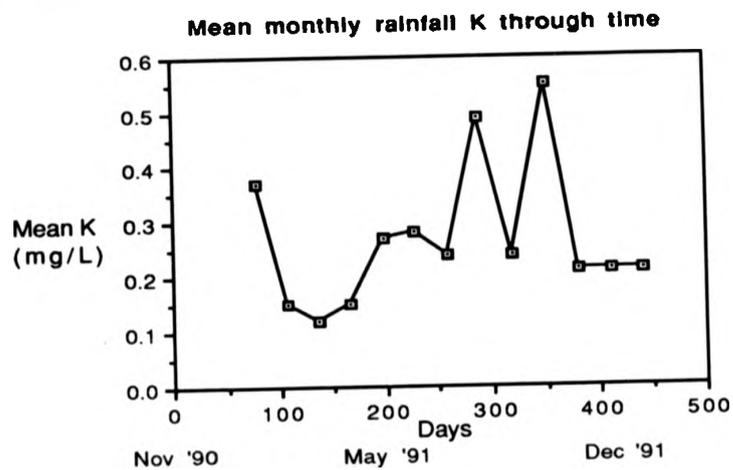


Figure 5.52C : Mean monthly rainfall K compared with mean organic and mineral soil water K through time



it was restricted to the organic soil waters. This was again explained by summer drying and concentration effects. The absence of this late potassium peak in the mineral soil waters and the lower variability in potassium concentrations in the mineral soils was consistent with the work of Grieve et al (1984) where it was explained with reference to soil cation exchange processes maintaining the potassium at a relatively constant level. The consistently high potassium from the soils at site 23 was more difficult to explain. Unusual features at this site included bracken vegetation and a high slope. During sampling of the surface soils at this site it was common to find thick oozing decaying root material within the soils. It is possible that this was related to the high potassium content.

Grieve et al (1984), Grieve (1990a), Hornung et al (1986) and Hornung et al (1990) reported seasonality in soil water chloride similar to the results in this study. Both Grieve (1990a) and Hornung et al (1990) found strong relationships between soil water chloride and atmospherically deposited chloride. Soil water chloride concentration peaks compared favourably with atmospheric inputs as shown in figure 5.52D. Soil water fluoride concentration peaks were very similar to those for chloride and were assumed to be similarly related to atmospheric inputs although there was not any data available on fluoride content of rainfall. Chloride results supported indications of the anions' mobility within the soil system made by Skartveit (1981) and Johnson and Reuss (1984).

Spatial variability was paramount in the soil water sulphate concentrations and was difficult to explain. The only common feature was a concentration peak in March -

Figure 5.52D : Mean monthly rainfall chloride compared with mean organic and mineral soil water chloride through time

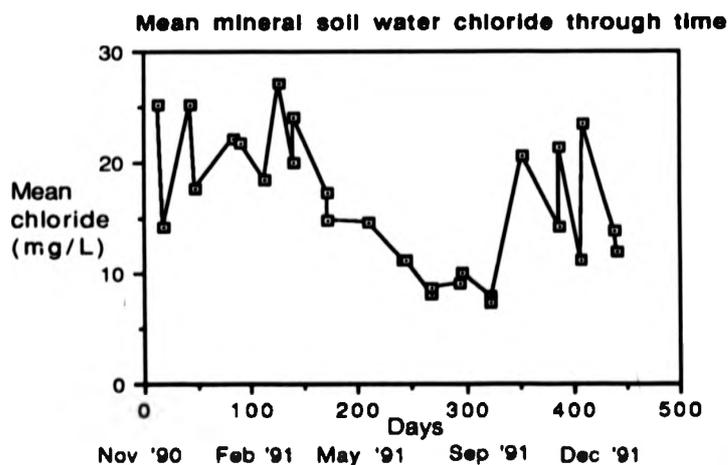
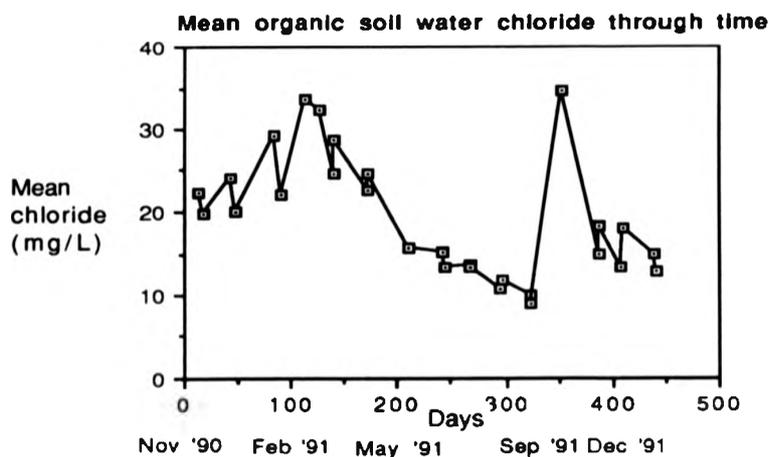
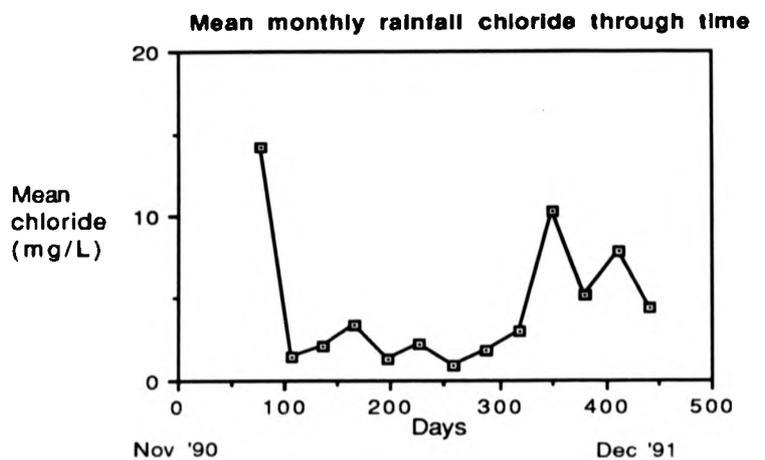
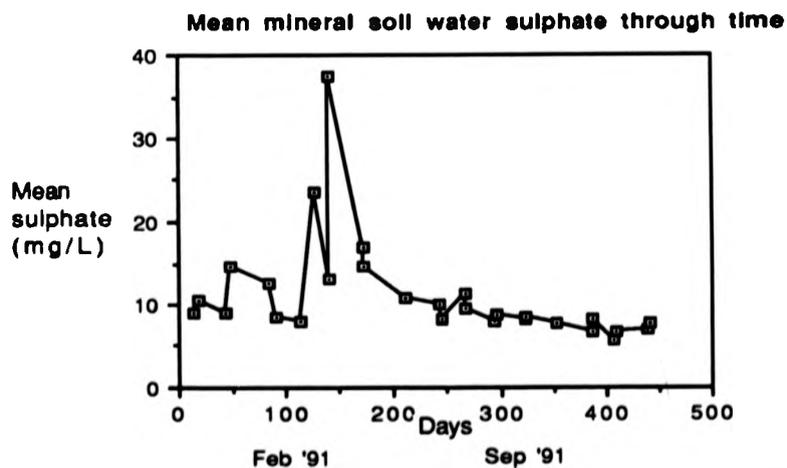
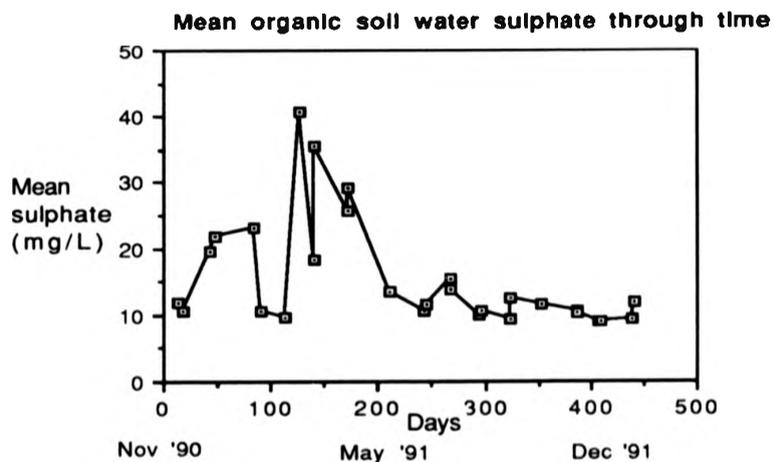
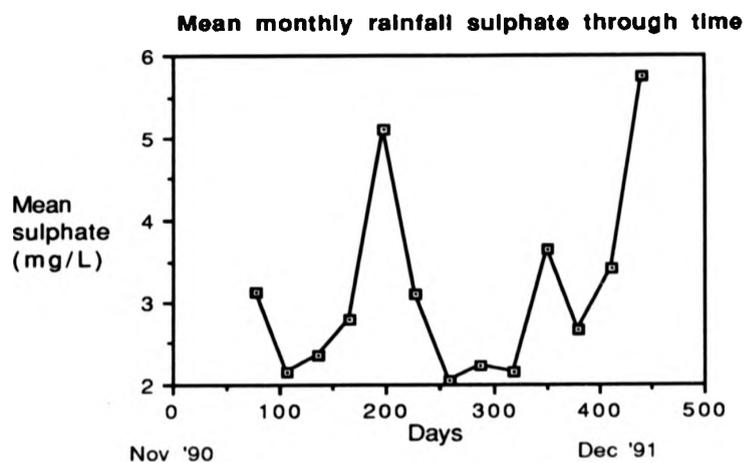


Figure 5.52E : Mean monthly rainfall sulphate compared with mean organic and mineral soil water sulphate through time

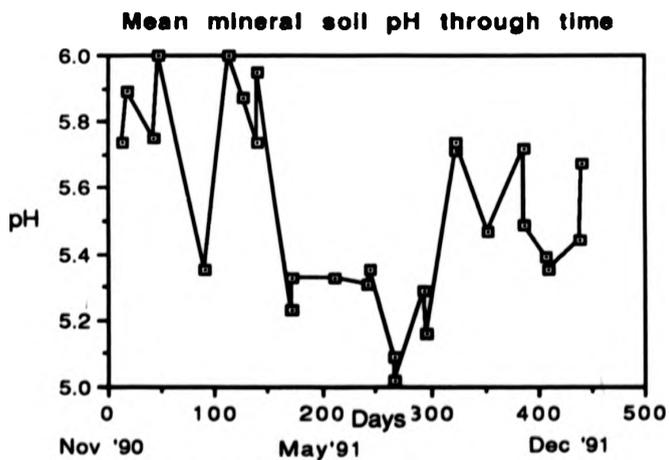
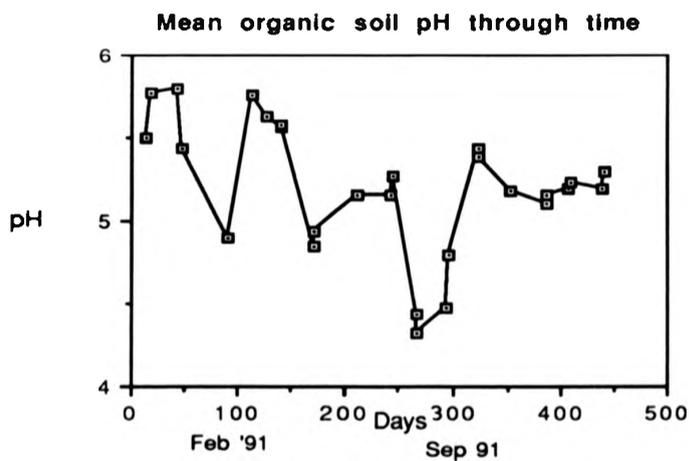
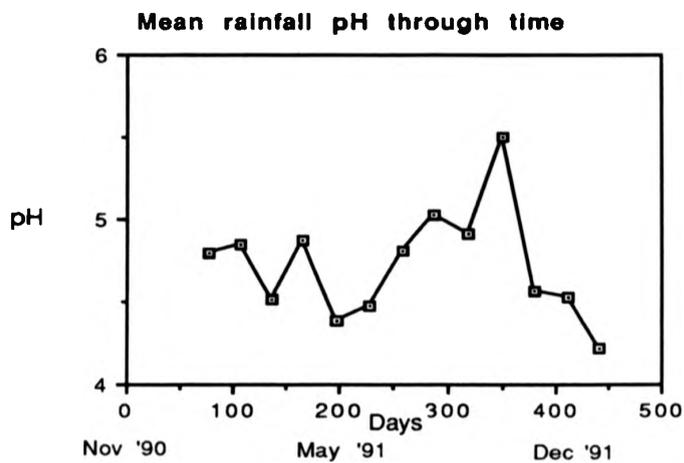


April 1991 which did not correlate with atmospheric input by rainfall as indicated in figure 5.52E. These findings opposed the suggestions of Lees (1989) who stressed sulphate mobility within the Loch Dee catchment. Johnson and Reuss (1984) suggested soil sulphate adsorption was positively correlated with iron and aluminium oxide content but negatively correlated with organic matter. Grieve (1990a) indicated that in the case of the Loch Dee soils this would result in a lack of sulphate retention.. However, variability in the soil water sulphate results herein suggest maybe this was not the case. It is possible that the soil iron and aluminium oxide contents offset the organic nature of the soils and caused some sulphate retention. However, there is no information available for the aluminium and iron oxide content of these soils. Miller et al (1990) found that soil water sulphate concentrations at the Chon and Kelty catchments reflected results in tree throughfall. In this case, however, this would not be a factor affecting most of the soil sites which were chosen to be, in the majority, outwith the limits of afforestation.

Higher concentrations of nitrate, potassium and DOC were found in organic soil waters than mineral soil waters. This was also noted by Grieve (1990a) and Hornung et al (1986). These authors explained this in terms of increased biological activity in the surface horizons.

Grieve (1990a) found higher pH in the mineral soil waters than organic soil waters. He also indicated surface soil solutions were acidic with a mean pH lower than in coming rain. This was not the case in this study - surface soil waters were acidic but typically less so than incoming rain. This must have been due to cation exchange

Figure 5.52F : Mean monthly rainfall pH compared with mean organic and mineral soil water pH through time



processes within the soils buffering some of the acidity of the atmospheric inputs. Grieve (1990a) did not record any obvious decrease in soil water pH for the summer season. This pattern was not explained by variations in rainfall pH - see fig 5.52F. Miller et al (1990) indicated the H^+ ion concentrations in soil waters at the Chon and Kely catchments in the Loch Ard Forest area reflected throughfall chemistry. These typically had lower H^+ concentrations in the summer which would correspond to higher pH, i.e. Miller et al's results were opposed to the observation in the Loch Dee soil waters. However, as noted in the section on sulphates, afforestation was a less prominent factor in the determination of soil water chemistry at the sites in this study. The mean mineral soil water pH (figure 5.52F) rose rapidly after this summer low period. This sudden increase in soil water pH corresponded to samples collected from a particularly strong storm in October 1991. The increase in soil water pH observed corresponded with an increase in rainwater pH; it is likely that the rainfall was enriched in seasalts and this was what was sampled in the soils prior to exchange occurring.

Increases of soil water pH with depth were sometimes accompanied by increases in aluminium concentrations. This is contrary to aluminium-pH solubility relationships given by Martin (1986). However, similar relationships were noted by Mulder et al (1987) in some Dutch woodland soils. Here the phenomenon was attributed to the extreme rate of acid addition to the soils and the relatively slow dissolution of aluminium minerals resulting in incomplete neutralisation in surface soil layers.

The results of this study indicated summer peaks in soil water iron, aluminium and

DOC concentrations similar to those reported by Grieve (1990a). He explained DOC peaks with reference to both summer temperatures promoting the formation of water soluble organic compounds and flushing effects when relatively dry soils were rewetted. Hornung et al (1990) also suggested concentration peaks in soil water DOC were driven by temperature interacting with biological processes. Mulder et al (1987) also reported late summer peaks in soil water aluminium concentration. In the case of these Dutch soil waters the observations were correlated with nitrate peaks and explained by reference to evaporative concentration effects. Since nitrate peaks were also commonly found in many of the Loch Dee soils this gives further evidence of concentration/ flushing effects indicated by Grieve (1990a). Aluminium, iron and DOC also showed winter peaks which were more difficult to explain. Similar movement of aluminium, iron, DOC and manganese were found by Reid et al (1981) at Glendye - these were explained in relation to high rainfall and were subsequently discharged into streams.

5.53 Correlation between soil water components

Tables 5.53A and 5.53B contain the correlation coefficients for the organic soil water and mineral soil waters throughout the monitoring period.

Table 5.53A: Organic soil water correlation

	Ca	Na	Mg	K	Fe	Al	Cl	SO ₄	NO ₃	F	pH
Na	-0.32										
Mg	0.48	-0.16									
K	-0.17	0.33	0.28								
Fe	-0.17	0.13	-0.17	0.10							
Al	-0.32	0.25	-0.23	0.20	0.56						
Cl	0.11	0.22	0.15	0.09	-0.01	0.04					
SO ₄	0.02	-0.01	0.13	0.20	0.06	0.11	0.30				
NO ₃	0.01	0.01	0.01	-0.08	-0.19	-0.18	0.18	0.35			
F	-0.19	0.50	-0.16	0.19	0.09	0.30	0.55	0.12	0.14		
pH	-0.03	0.30	-0.18	-0.08	0.11	-0.05	0.08	-0.15	-0.07	0.12	
DO C	-0.30	0.14	-0.04	0.45	0.26	0.48	0.10	0.21	-0.17	0.07	- 0.24

Table 5.53B: Mineral soil water correlation

	Ca	Na	Mg	K	Fe	Al	Cl	SO ₄	NO ₃	F	pH
Na	-0.40										
Mg	0.56	-0.19									
K	-0.17	0.62	0.11								
Fe	-0.30	0.34	-0.33	0.19							
Al	-0.37	0.36	-0.30	0.08	0.48						
Cl	0.18	0.25	0.21	0.21	0.08	0.04					
SO ₄	-0.19	0.07	-0.12	0.12	0.03	0.06	0.10				
NO ₃	-0.23	0.16	0.05	0.13	0.11	0.12	0.19	0.32			
F	-0.22	0.55	-0.08	0.24	0.22	0.27	0.50	0.17	0.26		
pH	-0.09	0.33	-0.11	0.17	0.18	0.13	0.15	0.06	0.01	0.21	
DO C	-0.30	0.28	-0.19	0.33	0.22	0.34	0.00	0.20	0.00	0.17	0.05

Table 5.53A illustrates the lack of correlation between chemical properties within the organic soil waters. This was in disagreement with the findings of Grieve (1990a)

where results indicated correlation between pH, calcium and sulphate and sodium, magnesium and chloride. The best correlations in the data were between calcium and magnesium, sodium and fluoride, potassium and DOC, iron and aluminium, aluminium and DOC and chloride and fluoride. Table 5.53B indicated slightly greater correlation between mineral soil water chemical components and illustrated a significant relationship between sodium and potassium. Soil water calcium and magnesium were significantly correlated (0.71) in the mineral soil waters reported by Grieve (1990a). Results here indicated this relationship existed but it was less significant. Correlation between iron and aluminium (0.64) reported by Grieve was not so strong in the results from this study (0.48). In this study the strongest additional correlations were between sodium, fluoride and chloride - i.e. typically atmospherically controlled ions. These were similar to the results of the organic soil waters. Iron distribution within the soils was related to DOC content of the soils and also soil type.

Despite the lack of significant correlation between soil water iron, aluminium and DOC throughout the whole monitoring period these three parameters were related. Both the soils and soil waters from the heights of Curleywee and White Hill had limited iron, DOC and to a lesser extent aluminium. Grieve (1985) noted such a relationship between iron and DOC in stream waters from the Ochils and also in the soil waters of the Greenburn sub-catchment (1990a and b). Such a relationship was explained by Duchafour (1982) with reference to the mobilisation of iron and aluminium by the translocation of organic material through the soil profile. This was shown to be a predominant feature of some of the soils in this area by micromorphological soil thin section examination presented in chapter 4.

5.54 Analysis of variance according to soil profile type

Table 5.54A indicates the significant results from analysis of variance of soil chemical properties with soil profile types.

Table 5.54A: Significant soil water chemical differences related to soil profile type.

	Podzols	Rankers	Gleys	Peat soils	Other
Mg mean and s.d.	0.91 <i>0.56</i>	1.00 <i>0.45</i>	0.89 <i>0.44</i>	0.82 <i>0.31</i>	1.46 <i>1.09</i>
K Mean and s.d.	3.00 <i>2.69</i>	3.21 <i>3.25</i>	2.64 <i>2.75</i>	1.50 <i>1.05</i>	6.61 <i>8.14</i>
Fe Mean and s.d.	1.49 <i>1.64</i>	0.88 <i>1.03</i>	1.20 <i>1.25</i>	0.55 <i>0.80</i>	0.28 <i>0.32</i>
Al mean and s.d.	1.38 <i>1.33</i>	1.26 <i>1.65</i>	2.03 <i>1.74</i>	0.95 <i>0.82</i>	0.62 <i>0.55</i>
Cl Mean and s.d.	17.7 <i>9.89</i>	17.0 <i>7.72</i>	16.8 <i>9.50</i>	16.6 <i>10.8</i>	19.9 <i>13.2</i>
SO ₄ Mean and s.d.	11.5 <i>6.14</i>	11.3 <i>7.49</i>	12.0 <i>6.10</i>	9.65 <i>4.95</i>	9.09 <i>5.66</i>
NO ₃ Mean and s.d.	11.0 <i>10.5</i>	10.7 <i>10.4</i>	9.72 <i>10.0</i>	10.9 <i>7.38</i>	18.3 <i>14.9</i>
DOC Mean and s.d.	48.7 <i>37.4</i>	50.4 <i>39.1</i>	57.4 <i>40.0</i>	46.5 <i>42.0</i>	19.4 <i>16.3</i>

The results from one-way analysis of variance of the complete data set according to soil profile type indicated:

1. Soil waters from the profiles classed as 'other' had significantly higher potassium, magnesium, chloride and nitrate but lower iron, DOC than the soil waters from all other groups. Results from chapter 4 indicated similar differences within the soils from this grouping. In that case and this, these differences were thought to reflect features of the sites included within the group. Soil at site 23 was responsible for the high

potassium readings; this was explained earlier with reference to vegetation/ slope features that contrast strongly with other soil sites. Soil waters from site 7 had very low iron and DOC readings and high nitrate throughout the monitoring period; this site is at a higher altitude than all other soil sites.

2. Soil waters extracted from soils classed as podzols had higher iron concentrations. This corresponds with results from chapter 4 where mineral soils from podzolic profiles were shown to include greater extractable iron.

3. Soils classed as gleys had soil waters with significantly higher aluminium concentrations than all other soil profile types. This was correlated with higher Fe than most soil profile types. These features were similar to those in chapter 4 for the soil chemistry. However, in the case of soils it was typically podzols that were associated with the greater aluminium concentrations.

5.55 Analysis of variance according to bedrock

The data set was split into organic and mineral soils then tested by one-way analysis of variance for the different lithology types. Significant results for the mineral soil waters are given in table 5.55A.

Table 5.55A: Significant analysis of variance results for the mineral soil waters.

	P value	Dior	Grano - dior	shales	grits	dykes	Black shale
Mg Mean + s.d	0.026	0.78 0.34	0.57 0.32	0.77 0.38	0.82 0.39	0.69 0.39	0.84 0.33
Fe Mean + s.d	0.000	1.02 1.83	1.82 1.63	0.64 0.70	0.67 0.95	1.00 1.03	0.25 0.29
Al Mean + s.d.	0.000	2.38 2.08	2.85 2.28	0.94 0.59	1.68 2.68	1.52 1.68	0.64 0.66
DOC Mean + s.d.	0.000	41.6 24.1	42.0 29.9	46.7 30.5	42.2 42.0	42.4 29.2	19.3 14.8

The p values in the table indicated the mineral soil waters overlying the different solid geology types showed some chemical differentiation for at least one of the rock types at the 95 percentile level of certainty.

1. Soil waters from the soils overlying the granodiorites were significantly lower in magnesium and higher in aluminium and iron. However, this can be explained partly in terms of soil profile type. Two soil sites were situated over granodioritic geology; one soil site had a podzolic profile whereas the other had a gleyed profile. These two profile types were found to be associated with soil waters rich in iron and aluminium respectively. The lower magnesium content, however, may well be a reflection of geology.

2. Soil waters from the soils overlying the diorites were also enriched in aluminium.

3. Soil waters from soils overlying the black shales were lower in both iron and DOC concentrations. However, these features could be explained in terms of altitude. All black shale soil sites (7, 14) were situated at greater heights than other soil sites.

Any of these features that were caused by geological controls should not also be present in the soil waters extracted from the organic soils.

Table 5.55B shows the results from oneway analysis of variance on the organic soils indicated to be of significance at the 95 percentile level by p values.

1. Soil waters overlying the diorites were significantly lower in potassium. The relationship between diorites and aluminium was not repeated in the organic soils and could have been a true feature of geology.

2. Soil waters overlying the black shales were significantly lower in iron, aluminium and DOC whereas they were typically enriched in nitrate. Because these features had also been present in the mineral soils it was assumed the altitudinal explanation was most likely. This would have led to an extreme of climatic conditions and typically much heavier rainfall; Welsh and Burns (1987) reported an increase in rainfall of 5 to 6% per 100m in height.

Table 5.55B: Organic soil water chemical variance according to underlying geology.

	P value	Dior	Grano - dior	Shales	Grits	Dykes	Black shale
K Mean and s.d.	0.003	2.83 2.57	4.58 4.17	5.17 5.67	3.28 2.73	4.21 3.61	5.68 3.29
Fe Mean + s.d	0.000	1.02 0.70	1.53 1.64	0.92 0.81	1.15 1.30	1.70 1.40	0.24 0.26
Al Mean + s.d	0.000	1.24 0.59	1.28 0.85	1.20 0.57	0.89 0.55	1.37 0.73	0.67 0.65
NO ₃ Mean + s.d	0.000	15.9 13.9	15.0 11.8	7.87 6.44	13.3 12.5	9.73 9.61	20.7 15.2
DOC Mean + s.d.	0.000	71.6 47.0	48.1 34.6	63.5 42.5	47.3 38.1	72.8 51.3	30.4 20.2

Because the analysis of variance on the whole data set had proved fruitless in terms of geological controls one data set was singled out to be further tested. Welsh and Burns (1987) highlighted the relationship between stream water quality and lithology in the Loch Dee area from chemical measurements made on stream water samples at base flow conditions. Oneway analysis of variance was therefore tested on the data from the soils collected when stream flow was at its lowest; this was at May 31st

1991. In the case of the mineral soils this analysis of variance indicated significantly higher aluminium in soil waters overlying both diorites and granodiorites. This feature was not reproduced when the organic soils were tested and was assumed to be real. There was not any obvious variation in calcium as was indicated for the stream waters at base flow condition by Welsh and Burns.

It was concluded that the following features were likely to be geologically controlled:

1. High concentrations of aluminium in mineral soil waters overlying diorites and granodiorites.
2. Low concentrations of magnesium in soils overlying granodiorites.

High aluminium concentrations can be explained in terms of a geological control. Diorites and granodiorites have high Al_2O_3 (chapter 2) when compared with the black shales and the coarse meta-sediments. However, the concentration of aluminium was similar to that found in the dykes and lower than the fine meta-sediments. The form of the aluminium in these four rock types can be utilised to explain the increased presence of this element in mineral soil waters related to diorites and granodiorites. In these two rock types aluminium was present in aluminosilicate minerals such as pyroxenes, amphiboles, micas and feldspars which would have been weatherable and have the potential to release aluminium into the soil water environment.. However, in the case of the shales, aluminium was primarily in the form of clay minerals. These are typically envisaged as one of the end products in the weathering scenario in temperate climates, being relatively stable at Earth surface conditions. Aluminium in the dykes would also be in the form of weatherable aluminosilicate minerals. Lower

concentrations of aluminium in soil waters associated with this mixture of rock types can be partially explained by two factors:

1. Soils would also be affected by the chemistry of the country rocks e.g. soil thin section evidence from chapter 4 indicated the minor igneous intrusion from site 5 included mineralic input from the surrounding meta-sediments.
2. Because of the presence of drift in the soil parent material subtleties of chemistry formed by minor dykes would be even less likely to be evident.

The low concentrations of magnesium from soil waters at granodioritic sites was, however, difficult to explain in geological terms; MgO concentrations in granodiorite was lower than dykes, diorites and fine meta-sediments but higher than coarse meta-sediments and black shales (Chapter 2, table 2.4A). Oneway analysis of variance on the soil water data according to soil profile type, however, indicated that both podzols and gley soils included soil waters of low magnesium concentrations. As with the high Fe associated with granodiorites it is possible that this low magnesium concentration resulted from the soil profile type rather than the underlying geology.

5.6 CONCLUSIONS

Results from the monitoring of soil waters indicated a strong influence of the chemistry of precipitation over the chemistry of soil waters. Organic soil water chemistry trends mimicked trends in rainfall of chloride, sodium, magnesium and potassium. Mineral soil waters also followed these trends although to a lesser extent in the case of potassium. Further peaks in soil water sodium, magnesium and potassium were explained with reference to a drying and concentration effect within

soils over the summer period. Smaller responses in mineral soil water potassium through time were explained by cation exchange buffering processes although the lower potassium in mineral soil waters was thought to reflect greater biological activity in the upper soil horizons. This same explanation was given for the decrease in soil water nitrate with depth. Soil water iron, aluminium and DOC were not highly correlated but did show great similarities in patterns with winter and late summer concentration peaks. The relationship between the three quantities tied in with evidence of organic matter translocation down the soil profile from chapter 4.

The geological controls defined by Welsh and Burns (1987) were difficult to determine even at base-flow conditions. The data set suggested a possible geological control on soil water aluminium with this being typically greater in soils developed over diorites and granodiorites. It is likely that the presence of drift material within the area prevented a more clear view of geological controls. Other strong relationships found within the data set were thought more likely to be related to different chemical processes acting in different soil profile types or more harsh weather conditions promoting differences within soils at higher altitudes.

CHAPTER 6: Soil water Aluminium: Extraction, form and relation to geology.

6.1 INTRODUCTION

Aluminium is the third most abundant element in the earth's crust and the most abundant metal. It is mainly present in rocks and soils bound in complex mineral structures including framework or 'tectosilicates' such as feldspars. In this form it is insoluble and largely innocuous.

Breakdown of the primary minerals by weathering can lead to the release of soluble cations, including aluminium, into the soil environment. These cations are adsorbed on to negatively charged clay mineral or organic particles and are termed 'exchangeable'. The strength with which the exchangeable cations are held is a function of both charge density and concentration. If aluminium is present on exchange sites it is typically held very tightly. It is a trivalent ion with a large charge density and is more strongly adsorbed than most other cations in solution. Low base status within soils can often be identified by the release of aluminium from exchange sites into the aquatic environment. Base rich soils can neutralise small highly charged H^+ ions by ion exchange.

One of the major problems highlighted by the release of aluminium into the environment has been a decline of indigenous fish populations from waters draining catchments susceptible to acidification. The Loch Dee and Loch Fleet catchments in SW Scotland have both been affected in this way (Welsh 1992, Howells and Dalziel 1992). Recent articles have not only linked fish death with aluminium release (Baker and Schofield 1982; Driscoll et al 1980), but have also attempted to suggest a

mechanism by which the increased mortality rate can be explained in terms of toxicity of aluminium (Booth et al 1988, Exley et al 1991). The toxicity of aluminium is strongly influenced by the form in which it is present in solution (Dobbs et al 1988). This is intrinsically linked to the 'bioavailability' of aluminium or the measure of its potential to interact within a biological system (Exley and Birchall 1992a). Typically the inorganic monomeric fraction of aluminium (i.e. free, uncomplexed Al^{3+} , $\text{Al}(\text{OH})^{2+}$ ions in solution) is cited as the 'toxic entity' (Martin 1986). Aluminium has also been linked with toxicity in higher vertebrates including man. Here research has mainly focused on the problems related to neurodegenerative disorders such as Alzheimers disease, (Birchall and Chappell 1988).

Positive action towards the restoration of the aquatic environment to its natural 'pre-industrialised' state has involved strategies aimed to ameliorate the toxic effect of aluminium. Lake liming was first tested in Sweden in 1976 (McCormick 1985) with encouraging results; the lake liming programme, however, was less successful in Norway where lakes tended to have a shorter turnover time (McCormick 1985). Under these circumstances sustained improvements in water quality by lake liming would be too short lived to be economically viable. Closer to home the Loch Dee project situated in SW Scotland also investigated loch liming. Both pH and the quality of the water within the Loch were increased on the addition of lime (Tervert and Harriman 1988). However, like Norwegian lakes, Loch Dee has a short turnover time (< 0.15 years) and the effects of liming were short lived. Alternative strategies investigated during the course of the nearby Loch Fleet project included catchment liming. In this approach lime was spread onto the catchment soil surfaces (Howells and Dalziel 1992). This improved the base status of the catchment soils increasing mean pH of

limed sites to 3.48 compared with 3.08 in control sites (Howells and Brown 1987). Increased soil base saturation was also reflected by a decrease of aluminium in the aquatic environment. The benefits of this strategy were longer-lasting but the dosage rates were greater and more expensive. Additionally catchment liming caused the loss of flora such as sphagnum moss which naturally flourish in acidic environments (Clymo 1984, Clymo et al 1992).

The potential of a further ameliorative strategy was examined under laboratory conditions by Exley (1989). He investigated the solubility and toxicity of aluminium and examined the possible role of silicon in the treatment of toxicity. Following this Birchall et al (1989) reported that although the fraction of aluminium termed 'exchangeable' in experimental waters increased with increasing silicon concentration, the survival rate of fish also increased indicating that the toxicity of the aluminium was ameliorated. Birchall et al (1989) postulated that silicon in the form of silicic acid affected the biological availability of aluminium by interacting with hydroxy-aluminium species to form hydroxyaluminosilicate (HAS) species. The formation of HAS prevented aluminium from exchanging at anionic sites on gill epithelia. Huang (1991) suggested that such HAS formation would be dependent on other environmental factors such as the presence of humic compounds which could also affect the form of aluminium in solution.

6.11 Aluminium chemistry

The aqueous chemistry of aluminium is complex (Birchall and Espie 1986), and has attracted much interest in the recent past (Hem and Robertson 1967, Lindsay 1979,

Martin 1986). Martin (1986) investigated solutions of aluminium ions in pure water, free from ligators other than hydroxide. The results indicated that in solutions with a pH < 5, aluminium existed as the octahedral hexahydrate ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$. With an increase in pH this trivalent species was successively deprotonated to yield $[\text{AlOH}]^{2+}$ and $[\text{Al}(\text{OH})_2]^+$. In basic solutions $[\text{Al}(\text{OH})_4]^-$ was found to be the most common ion, see fig 6.1A.

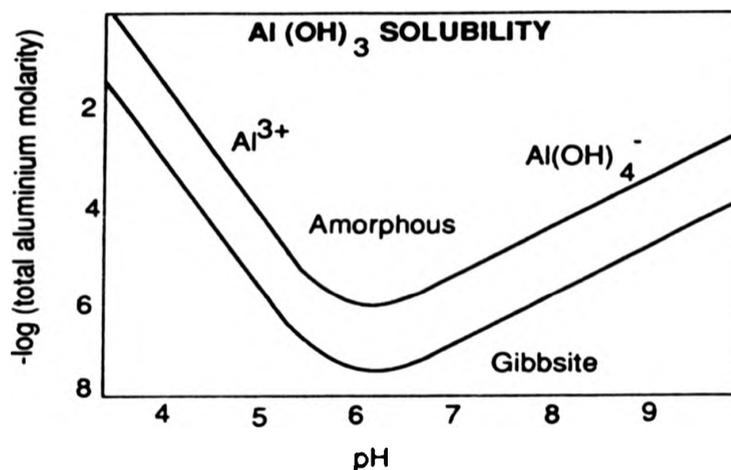


Figure 6.1A - Negative logarithim of total molar concentration of aluminium allowed by $\text{Al}(\text{OH})_3$ solubility vs pH, (Martin 1986 after Hem and Robertson 1967).

Gibbsite is a naturally occurring solid crystalline phase of $\text{Al}(\text{OH})_3$, that can be theoretically linked with the deprotonation series of Martin. The solubility of gibbsite has been extensively investigated and the concentrations of aluminium in equilibrium with gibbsite as a function of pH have been calculated (Bache 1986). However, the solubility of gibbsite is limited and naturally occurring amorphous forms of $\text{Al}(\text{OH})_3$ are more than one order of magnitude more soluble (fig 6.1A).

The solubility of $\text{Al}(\text{OH})_3$ has been compared with experimental results from the natural environment (Driscoll et al 1984, Burns 1989) and used in short and long term modelling of acidic deposition (Christopherson et al 1982, Cosby et al 1985). However, the concentration of aluminium in natural solutions was not always as predicted by $\text{Al}(\text{OH})_3$ solubility curves i.e. aluminium solubility is not simply controlled by gibbsite in crystalline or amorphous forms. Neal (1988) tested stream water data from the Plynlimon catchment in Wales and found simple $\text{Al}(\text{OH})_3$ and aluminium hydroxy sulphate solubility controls to be inappropriate. However, he indicated the data suggested an alternative and unknown simple mechanism operated probably based on two component mixing reactions. In a later paper, Neal et al (1989) explained the hydrochemical behaviour of inorganic aluminium at Plynlimon and a further Welsh site, Beddgelert, using a combination of ion exchange, weathering, water mixing and aluminium precipitation reactions. This highlighted the inappropriate use of gibbsitic solubility controls in long and short term acidification models to describe the behaviour of inorganic aluminium.

Bache (1986) outlined other possible explanations for the deviation of aqueous inorganic aluminium from gibbsitic solubility controls. These included:

1. The presence of complexing ligands that can increase or decrease the solubility of aluminium within a solution relative to gibbsite.
2. The possibility of other mineralogical controls on the solubility of aluminium.
3. Equilibrium between the solution and the solid phase not reached.

Organic acids such as fulvic and humic acids are proposed to increase the solubility

of aluminium in waters high in dissolved organic carbon (DOC) relative to an $\text{Al}(\text{OH})_3$ solubility control. LaZerte (1988) suggested that waters high in organics would not show a mineralogical solubility control of the aluminium; Schecher and Driscoll (1987) suggested aluminium in waters draining organic soils or wetlands was complexed with naturally occurring organic solutes and thus deviated from proposed mineral phase solubility.

Inorganic ligands of aluminium can also result in a deviation of experimental results from a gibbsite solubility control. Fluoride has a strong affinity for aluminium in soils and can compete with exchange sites for the cation. If displaced, the resultant aluminium - fluoride complexes formed are more soluble than gibbsite (Moore and Ritchie 1988). Silicic acid may react with hydroxyaluminium species to form HAS (Birchall et al 1989); these are typically less soluble than gibbsite (Farmer et al 1980). Lou and Huang (1988) suggested that HAS was one of the major forms of soluble aluminium within the acidic environment.

Lindsay (1979) reported data for the solubilities of aluminosilicate mineral species common to the soil environment and highlighted their possible importance in controlling aluminium solubility. Litaor (1987), after Hutton (1982), related the solubility of different minerals to aluminium, pH and silicic acid concentrations (fig 6.1B) and compared experimental results with resultant diagrams.

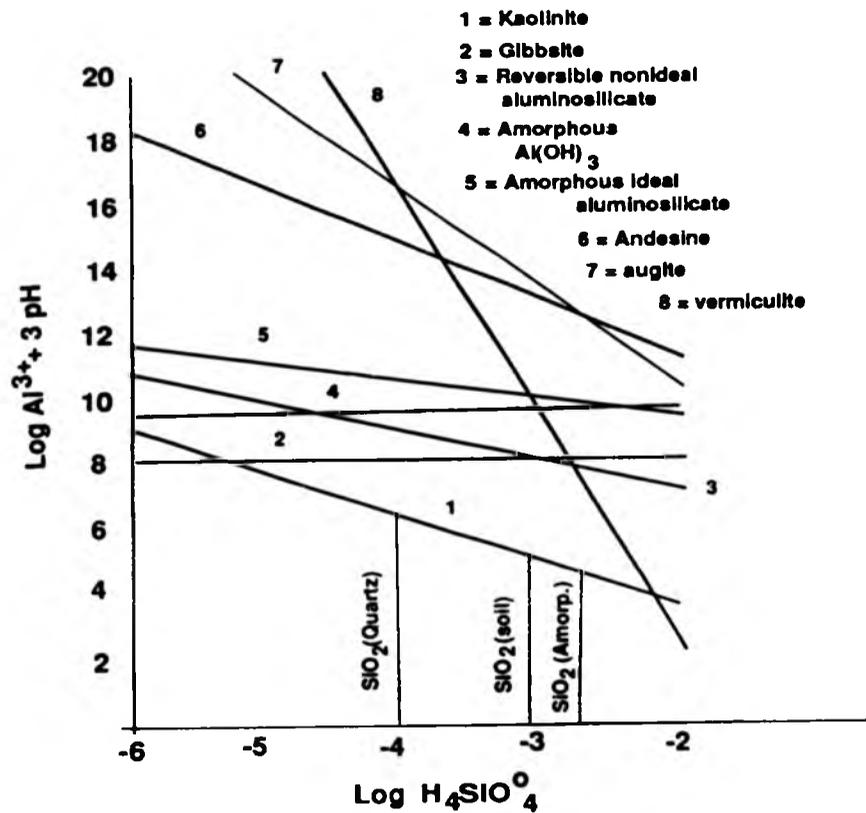


Fig 6.1 B The solubility of different minerals (Litaor 1987) after Hutton (1982).

Conclusions from these comparisons were supported with soil thin section and XRD analysis. These included the probable importance of a reversible ideal aluminosilicate discussed by Páces (1978) in aluminium solubility control in the results of Litaor.

6.2 AIMS

The aims of the work reported in this chapter were two fold.

(i) An experimental procedure was designed to test the discriminatory powers of dialysis, ion exchange and membrane filtration mechanisms to fractionate aluminium in natural soil solutions according to size and reactivity. Exley and Birchall (1992b) tested these methods on synthetic solutions and were able to recognise the formation of HAS species in waters of low aluminium concentration. The results of the study suggested the identification of these species was dependent on both the pH and the concentration of silicic acid in the synthetic solution. This study aimed to test the use of these methods in natural soil solutions.

(ii) It was postulated that release of silicon by weathering may influence the biological availability of aluminium - a prerequisite to toxicity. Geological controls on the concentration of silicic acid and aluminium in soil waters were investigated. The primary source of silicic acid in soils is from the weathering of silicate minerals (Bricker and Garrels 1967). Sites were chosen to reflect differences in weathering ability using Bowens Reaction Series which relates this to the structure of common minerals (Chapter 2). Orthosilicate minerals, e.g. olivine, have single silica tetrahedra linked by non-framework cations and are more easily weathered than tectosilicates, e.g. quartz and feldspar, where silica tetrahedra are linked in a continuous framework. When aluminium is incorporated into the silicate mineral structure by substitution for silicon in tetrahedra minerals are more easily weathered (Johnson 1984), thus feldspars weather more easily than quartz.

6.3 MATERIALS AND METHODS

6.31 Soils and sites

The results of the monitoring data presented in chapter 5 indicated six sites with mineral soil waters that showed high concentrations of total aluminium measured using flame atomic absorption spectrophotometry (AAS); these were sites 2, 5, 8, 10, 12 and 20.

Sites adjacent to 2 and 10 from the monitoring programme were identified as those best fitting the aims of the study. Soil water monitoring work had indicated the possibility of a geological control over aluminium concentration in soil waters at sites overlying diorites and granodiorites. Sites 2 and 10 were over diorite and granodiorite respectively. Diorite is an intermediate to basic rock type and contains 10 - 15% of quartz + potassium feldspar. Granodiorite is an intermediate to acid rock type and contains 25 - 35% quartz + potassium feldspar. This mineralogical difference should, in theory, result in the release of silicon in greater quantities at site 2 which may influence the form of aluminium at this site. Investigations into weathering rates in chapter 2 supported this theory to a small extent revealing a greater summed loss on weathering in the diorite samples (between 0 and 1.25 units using titania as an internal standard and 0 - 2.60 units using zircon as an internal standard) than for the minor granodiorites (0.29 and 0.37 units respectively). However, actual silica loss on weathering only occurred in 20% of the diorite samples tested (0.53 units). This was still greater than the only minor granodiorite sample tested which indicated a loss of silica on weathering of 0.05 units.

Other controlling factors were kept as similar as possible. Both sites chosen had a podzolic soil profile at least partially developed and had similar vegetation patterns. However, the elevation of the two soil sites was different at 260 m and 400 m respectively. Such a difference in elevation can affect temperature and alter the amount of rainfall a site receives increasing with altitude between 5-6% per 100m Welsh and Burns (1987). This could affect the rates of weathering and peat formation at the two sites.

6.32 Sampling times

Two sampling periods were selected. These were designed to include the extremes of a wet and dry period. From the experience of monthly monitoring (chapter 5) and data produced by the Solway River Purification Board (Burns and Lees 1987, Lees 1990), March was identified as a period of high rainfall and May/June as typically dry.

The first sampling period was in March 1992 on a cold day where precipitation fell in the form of snow and hail rather than rain (March 1992, total rain = 335.6 mm). Snow completely covered site 10 but there was no snow at site 2. The second sampling period was in May 1992, (May 1992, total rain = 112.8 mm). Samples were taken on a damp day. Soils, however, were very dry due to dry antecedent conditions. Figures given refer to the Lower Black Laggan tipping bucket gauge.

The contrast in weather conditions for the two sampling days can be illustrated in terms of stream discharge. For sampling period 1 the discharge of the White Laggan

was c.122 m³s⁻¹ this had been preceded by 4 days of higher flow. For sampling period 2 flow was much less at 6.6 m³s⁻¹. The flow had been below 40 m³s⁻¹ for 1 week prior to sampling.

6.33 Sample collection and preparation

Two soil pits, (to account for within site variability), were dug at each site and the mineral horizons sampled. 3 sub-samples of soil were collected from each mineral horizon and subsequently bulked and mixed. The bulked soils were separated into two portions; one was air dried, the other centrifuged in two-way tubes (Chapter 5) to extract waters. A known weight of air dried sample was passed through a 2mm sieve. The amount of material >2mm was weighed and expressed as a % weight of the total soil, see table 6.41A. Soils were then stored in polythene bags prior to chemical analysis, see section 6.34.

The soil waters were filtered through a 5 µm membrane filter, (Whatman cellulose nitrate WCN type), using a closed polycarbonate vessel reduced pressure system (Sterifil 47mm millipore) prior to storage in acid washed polypropylene bottles at temperatures below 4°C prior to chemical analysis. Previous investigative work had suggested the total aluminium content of soil waters could fluctuate without this filtration step which removed fine sediment particles. During filtration any changes in the appearance of the soil waters were noted.

6.34 Analysis of soils

Soils were tested for exchangeable cations, pH, organic matter content (LOI), moisture content and pyrophosphate extractable iron and aluminium (amorphous and organic-bound forms). The methods used were standard and the same as presented in chapters 3 and 4. In addition dithionite extractable iron and aluminium (crystalline oxides and hydroxides) were also measured using standard methods outlined by Avery and Bascomb (1974). Dithionite extractions were made on separate samples.

6.35 Soil water chemistry - major components

The soil waters were tested for their gross chemistry. Calcium, magnesium and iron were measured directly using flame AAS, sodium and potassium measured using flame photometric methods. Anions were measured using the Dionex ion chromatograph; each sample was diluted 10 fold and because of this a three way replication was adopted. DOC was measured using the TOCSIN II aqueous carbon analyser; again the samples were diluted (10 fold) prior to measurement and at least three replicates were tested.

6.36 Aluminium fractionation methods

Major analytical techniques of aluminium fractionation are based on:

1. The rate of reaction of Al^{3+} with a specific analytical complexing agent.
2. The removal of inorganic charged species by their sorption on cation exchange resins.
3. Size exclusion of large complexes.
4. The use of a fluoride electrode and calculations.

Dobbs et al (1988) stressed that all of these separation procedures were operationally defined and results achieved from their use depended entirely on the way in which the experiments were conducted.

Ferron (FOP) (Driscoll 1984), aluminon (Wright et al 1987) hydroxyquinoline (Driscoll 1984, Kerven et al 1989) and pyrocatechol violet (PCV) (Dougan and Wilson 1974) are all examples of reaction rate procedures. Seip et al (1984) compared FOP with PCV and found the latter to be more sensitive and less susceptible to interference from organics or fluoride. Hodges (1987) suggested that hydroxyquinoline and ferron procedures were of limited use in the analysis of samples high in DOC. Kerven et al (1989) found all commonly used colourimetric methods failed to discriminate effectively between inorganic monomeric and organically complexed forms of aluminium when tested with an organic ligand of natural origin. Wright et al (1987) highlighted the thoughts of Dobbs suggesting these techniques in particular to be limited because the forms of aluminium found were operationally defined and the specific reacting species of aluminium not well known.

Driscoll (1984), used a cation exchange column to separate non-labile monomeric and labile monomeric fractions of aluminium and found the measurement of non-labile monomeric aluminium to be dependent on the flow rate of solution through the column. Difficulty arose in the control pH of solutions on passage through the column. Campbell et al (1983) suggested the use of these resins in a stirred batch process whereby pH was much easier to control. However, Hodges (1987) suggested the ion exchange column and chelating resins were both unable to distinguish inorganic forms

of aluminium from one another.

LaZerte (1984) used equilibrium dialysis to separate organic aluminium from inorganic monomeric aluminium and compared his results with computed estimates involving fluoride measurements. He found the results to be comparable. Membrane filtration and dialysis were both used by Exley and Birchall (1992b) to discriminate aluminium species according to a variety of sizes. They tested these methods and cation exchange resins to see which best defined the formation of HAS species in dilute solutions and found membrane filtration to be most effective.

Hodges (1987) used fluoride sensitive electrode and thermodynamic calculations to obtain aluminium activities equal to theoretical predictions in solutions without fulvic acid.

Problems associated with interference from organics using colorimetric methods for aluminium determination were important since the soil waters from Loch Dee had often been highly coloured when sampled throughout the monitoring exercise. Driscoll et al (1984) checked total aluminium measurement using FOP by those determined directly using Graphite Furnace AAS and found close agreement in results. GFAAS has also been used effectively by Exley and Birchall (1992b) in the measurement of aluminium and this method was chosen for the present study. The methods of dialysis, membrane filtration and cation exchange tested by Exley and Birchall were also adopted here.

6.37 Size Fractionation

Dialysis:

La Zerte (1984) discussed the method used. Viskin tubing (Medicell) was used as the dialysis membrane. This has a size exclusion of 2.4nm and Molecular Weight Cut Off (MWCO) 12-14000 and should allow only the movement of very small species of Al from the soil water outside the dialysis bag to the double deionised water (DDW) inside the bag. This small fraction was found by LaZerte (when using 1000 MWCO membrane) to be comparable to that found using fluoride based calculations i.e. the inorganic monomeric fraction. However, for present experiments this fraction could include any aluminium species less than 2.4 nm in size e.g. small organic complexes.

Exploratory investigations using viskin tubing had indicated considerable problems with sample replication; this was attributed to contamination and therefore a more thorough preparatory procedure was used:

1. 20 x 10cm lengths of viskin tubing were cut then added to a dilute solution (0.01M) EDTA. This was heated (not greater than 50 °C) for 1 hour .
2. Viskin tubing was washed with DDW and immersed in 5% v/v HNO₃ (aristar) which was agitated using magnetic stirrers for at least 24 hours.
3. The tubing was rinsed thoroughly in DDW before being immersed in DDW and left to stir for 12 hours.
4. Step 3 was repeated.
5. The water surrounding the tubing was tested for conductivity. Any water registering more than 2 μScm^{-1} was rejected and step 4 repeated until the conductivity of the DDW + dialysis bags equalled the conductivity of water alone. At this stage the tubing

was ready to use for aluminium fractionation according to the following procedure:

2.5ml of DDW was added to the dialysis bag. It was clipped shut and immersed in 22.5ml of soil water contained within a small Nalgene Centrifuge tube. This was then sealed and left to shake for 24 hours. After 24 hours the waters inside the bag were extracted for analysis of silicon and aluminium. Samples were stored in acid washed polypropylene containers below 4°C. 5 replicates were made for each bulked soil water. Prior to use all equipment was acid washed and thoroughly rinsed in DDW to minimise the risk from contamination.

Equilibration time:

Exley and Birchall (1992b) found 3 hours sufficient for the equilibration of dialysis experiments with synthetic solutions. LaZerte (1984) looked at natural waters and suggested minimising equilibration time to prevent the entry of smaller fulvics and reduce the overestimation of inorganic monomeric fractions of aluminium. LaZerte used a 24 hour equilibration period in his experiments. Exploratory work using soil solutions from the Loch Dee catchment had suggested that 12 hours was enough time for silicon to equilibrate. However, concentrations of aluminium were not stabilised in this time so the 24 hour period of LaZerte was adopted for this experiment.

Membrane filtration

Larger sized aluminium fractions can be split using a series of membrane filters of different pore sizes. In view of the small size of the dialysis membrane and the very large pore size of the initial filtration membrane (5 µm), 0.45 µm filters (Whatman

Cellulose nitrate WCN type) were chosen for use in this study. This had been previously used to indicate the cut off point for soluble fractions of aluminium (Neal et al 1989). Menzies et al (1991) stressed that this was an arbitrarily chosen point, however, rather than a strict definition.

Filters were prepared by immersion in DDW for up to 3 hours and the soil solution to be tested for a minimum of 1 hour. This procedure was an attempt to reduce the effects of aluminium retention on the membrane through adsorption of charged species. All equipment was acid washed and rinsed thoroughly in DDW and finally soil water prior to use.

Filtration was carried out using disposable syringes with filter attachment. This method was relatively rapid to perform and no sample storage was necessary. The procedure was replicated 4 - 5 times for each soil water.

6.38 Cation Exchange Methods

Cation exchange methods fractionate aluminium according to both size and reactivity. The methods used were outlined by Exley and Birchall (1992b) based on a stirred resin, (Campbell et al 1983). This method was chosen for the ease of pH control throughout the experiment. A micro pH electrode (Russell) was immersed in the polypropylene experimental vessel for the duration of the tests and any pH changes controlled by the addition of dilute (0.01M) NaOH or (0.01M) HNO₃.

The resins used were Amberlite 200 and IRC 50, (Sigma Chemical Co.). Amberlite 200 has a strongly acidic sulphonic acid grouping and the IRC 50 a weakly acidic carboxylic acid grouping.

Resins were prepared by methods outlined by Exley and Birchall (1992b). To ensure directly comparable starting points with respect to charge 2g of the amberlite 200 and 0.84g of the amberlite IRC 50 were used. The strongly acidic resin has 4.2 meq of charge per g whilst the weakly acidic resin has 10 meq of charge per g. These weights resulted in a starting charge of 8.4 meq on both resins which was calculated to be in excess of the greatest soil water aluminium total.

After preparation the resin was equilibrated with a synthetic solution containing all the soil water major ions, except aluminium, previously determined in the soil solution (tables 6.42B and C). This equilibration exercise ensured minimal pH change on the addition of the soil solution to the resin. Large changes in pH affect the form of the aqueous aluminium. The soil solution DOC was not accounted for in the buffer solutions.

A 25ml sub-sample of bulked soil water was in contact with a pre-equilibrated resin for one hour (Exley and Birchall 1992b). After this time the soil solution was filtered through a 5 μ m membrane filter in a closed polycarbonate filtration vessel (Sterifil, 47mm millipore) to rescue the resin for elution. The filtered liquids were stored prior to analysis in acid washed polypropylene containers below 4°C. Aluminium and silicon measured in these samples was either in a form stable with respect to the resin

functional group or too large to enter the resin mesh.

For aluminium, subtraction of this 'inert' fraction from the total aluminium gave an estimate of 'exchangeable aluminium' small enough to enter the resin mesh. This might be expected to include the free aquo ion, exchangeable complexes, aluminium in monomeric complexes weaker than the resin functional group plus cationic poly nuclear species of low molecular weight. In addition, Campbell et al (1983) suggested labile complexes stronger than the aluminium functional group complex may contribute to the exchangeable fraction if the resin was concentrated relative to aluminium; in this case the resin was in excess.

Elution

Recovered resins were rinsed with DDW, filtered to dryness and then eluted with 20ml 10% v/v HNO₃ for 10 minutes. The acid was decanted from the resin and stored prior to analysis in acid washed polypropylene containers below 4°C. These eluted samples represent relative values used in the identification of matter left on the resin by inspection of molar Si:Al ratios.

The procedure was replicated 3-5 times for both resin types and all soil water samples.

6.39 Measurement of aluminium and silicon.

Aluminium and silicon were measured by GFAAS (Perkin Elmer 2280 Atomic Absorption Spectrophotometer) using programmes previously developed by Exley (1989), tables 6.39A and 6.39B.

Aluminium was measured in a matrix of HNO₃ (1% v/v acid). 3 - 6 standards were

used and made up using a 10 mg/L stock solution. Dilution of samples (maximum of 10 fold) was usually necessary; calibration was only linear up to 300 µg/L.

Table 6.39A Al programme:

Wavelength = 309.3 - 309.6 Coated graphite tube Spectral Bandwidth = 0.7 Å 30 µL sample aliquot
 Current = 40 mA 3 replicates
 Background correction - yes Tube prepared using instructions
 Peak height time - 3 seconds provided by Perkin Elmer.

Step	1	2	3	4	5	6	7
Temp (°C)	80	130	500	1500	1500	2650	2700
Ramp (s)	5	10	10	10	1	0	1
Hold (s)	5	30	10	15	5	5	5
read						yes	
Rec						yes	
Base line					yes		
flow						stop flow	

Silicon was measured without the addition of HNO₃. 3 - 6 standards were used for calibration. Standards were made using a 10 mg/L stock solution. Dilution was not necessary for silicon; calibration was virtually linear up to 3000 µg/L.

Table 6.3B Si programme:

Wavelength = 252 Uncoated graphite tube Spectral Bandwidth = 0.2 Å 30 µL sample aliquot
 Current = 40 mA 3 replicates
 Background correction - yes Tubes prepared according to
 Peak height time - 3 seconds manufacturers instructions.

Step	1	2	3	4	5	6	7
Temp (°C)	80	130	500	1150	1150	2600	2700
Ramp (s)	5	10	10	10	1	0	1
Hold (s)	5	30	10	15	5	5	3
Read						yes	
Rec						yes	
Base line					yes		
flow						stop flow	

6.4 RESULTS

6.41 SOILS

The results presented in this section refer to bulked soils. Two pits were dug at each site and 3 bags of soil taken from each pit. Bulking involved mixing the three bags of soil from each individual pit together.

In March soils from site 2 were reddish brown and loamy with occasional gritty patches. Soils from site 10 were more gritty with a reddish speckled coloration. In May soils from site 2 were reddish brown and loamy although gritty patches were more abundant; the soils from site 10 were gritty but and included peat.

Table 6.41A shows the results from the sieving of air dried samples of the bulked soils.

Table 6.41A The relative proportions of the fine and the coarse fractions within the soil samples expressed as the weight % of the total fraction coarser than 2mm, standard deviation is given in italics, n = 3.

Soil/site March	Mean % >2mm	Soil/site May	Mean % >2mm
2M1	3.96 <i>1.29</i>	2M1	2.40 <i>0.86</i>
2M2	1.14 <i>0.79</i>	2M2	2.06 <i>0.58</i>
10M1	7.99 <i>3.00</i>	10M1	10.81 <i>1.58</i>
10M2	15.53 <i>1.56</i>	10M2	11.90 <i>3.08</i>

The results confirmed the visual impression that the soils from site 10 had a greater proportion of coarse fragments and confirmed observations in chapter 4 that soils associated with granodioritic geology typically had greater proportions of sand sized particles.

Results from the chemical analysis of the soils are given in tables 6.41B and 6.41C

Table 6.41B - Soil exchangeable cations - all results are expressed as mean values in meq/kg, standard deviation is given in italics, n = 3.

Soil	Exch Ca meq/kg	Exch Mg meq/kg	Exch Na meq/kg	Exch K meq/kg	Exch H meq/kg	Exch Al meq/kg
2M1 March	1.73 <i>0.09</i>	0.90 <i>0.16</i>	2.84 <i>1.09</i>	0.26 <i>0.00</i>	223 <i>8.34</i>	145 <i>34.9</i>
2M2 March	1.63 <i>0.33</i>	0.77 <i>0.16</i>	2.54 <i>0.82</i>	0.13	177 <i>8.06</i>	83.4 <i>1.56</i>
10M1 March	1.05 <i>0.16</i>	0.82 <i>0.11</i>	2.06 <i>0.49</i>	0.28 <i>0.02</i>	223 <i>8.34</i>	136 <i>2.69</i>
10M2 March	0.88 <i>0.16</i>	0.55 <i>0.08</i>	2.31 <i>0.34</i>	0.26 <i>0.00</i>	203 <i>6.58</i>	94.2 <i>11.0</i>
2M1 May	0.25 <i>0.16</i>	0.44 <i>0.23</i>	0.65 <i>0.05</i>	0.71 <i>0.41</i>	107 <i>16.5</i>	108 <i>4.88</i>
2M2 May	0.60 <i>0.07</i>	0.58 <i>0.16</i>	0.41 <i>0.06</i>	0.32 <i>0.08</i>	100 <i>28.5</i>	96.0 <i>3.46</i>
10M1 May	0.20 <i>0.09</i>	0.41 <i>0.04</i>	0.61 <i>0.14</i>	0.28 <i>0.04</i>	164 <i>23.6</i>	58.6 <i>4.45</i>
10M2 May	0.12 <i>0.05</i>	0.63 <i>0.08</i>	0.29 <i>0.00</i>	0.26 <i>0.00</i>	142 <i>33.8</i>	47.9 <i>3.25</i>

Soil exchange sites were enriched in hydrogen and aluminium at both sites and at both sampling times. In March, site 2 soils had greater exchangeable calcium and sodium than site 10 and approximately the same magnesium and potassium. In May, exchangeable cations were less abundant. The two sites showed marked differences in the acidic cations with site 2 having greater exchangeable aluminium and site 10 greater exchangeable hydrogen. Base cations were typically similar although internal variation was high in the case of calcium and potassium at site 2 and sodium at site 10. Because the soils were bulked variations in results reflected the precision of the techniques employed.

Table 6.41C Soil chemical properties. All results are expressed as a mean value, standard deviation is given in italics, n = 3.

Soil	pH In CaCl ₂	% airdry Moist.	% LOI	P-extr Fe %	P-extr Al %	D-extr Fe %	D-extr Al %
2M1 Mar	4.10	4.60 <i>0.59</i>	10.2 <i>0.86</i>	1.43 <i>0.23</i>	0.74 <i>0.11</i>	2.15 <i>0.16</i>	0.74 <i>0.11</i>
2M2 Mar	4.1	6.50 <i>1.32</i>	6.0 <i>1.56</i>	0.13 <i>0.06</i>	0.34 <i>0.03</i>	1.72 <i>0.13</i>	0.43 <i>0.01</i>
10M1 Mar	4.0	27.1 <i>2.79</i>	12.6 <i>0.89</i>	1.17 <i>0.31</i>	1.01 <i>0.06</i>	1.74 <i>0.33</i>	0.62 <i>0.08</i>
10M2 Mar	4.30	14.3 <i>0.40</i>	11.1 <i>2.16</i>	0.78 <i>0.33</i>	0.88 <i>0.16</i>	1.28 <i>0.33</i>	0.71 <i>0.06</i>
2M1 May	3.90	7.25 <i>1.30</i>	11.7 <i>1.09</i>	0.87 <i>0.06</i>	0.69 <i>0.07</i>	0.84 <i>0.01</i>	1.02 <i>0.04</i>
2M2 May	3.90	19.2 <i>10.1</i>	10.2 <i>1.53</i>	0.65 <i>0.09</i>	0.65 <i>0.07</i>	0.81 <i>0.03</i>	0.95 <i>0.07</i>
10M1 May	3.85	10.2 <i>2.93</i>	13.5 <i>1.99</i>	1.12 <i>0.08</i>	0.77 <i>0.13</i>	0.82 <i>0.03</i>	0.88 <i>0.13</i>
10M2 May	3.95	5.88 <i>1.12</i>	11.4 <i>1.17</i>	0.96 <i>0.22</i>	0.77 <i>0.08</i>	0.87 <i>0.03</i>	1.04 <i>0.10</i>

The soils in May had a slightly lower pH than those at the same sites in March. Soils from site 10 had greater organic matter content than soils from site 2 in March but very similar concentrations in May. Dithionite extractable iron i.e. organically bound, amorphous and that in the form of crystalline oxide and hydroxides (Bascomb 1968) was always greater than pyrophosphate extractable iron (in an amorphous or organically bound form) as would be anticipated. The results indicated that iron extracted from the soils at both sites in March was in both organically bound and crystalline forms. However, in May all iron extracted from the soils at both sites was in an organic form only. Shuman (1990) extended these definitions to extractable aluminium and again indicated the overlap in type of aluminium extracted. Pyrophosphate extractable aluminium was greater at site 10 than dithionite extractable

aluminium for both samples in March indicating the possibility of poor sample mixing leading to this variability at site 10. Dithionite extractable aluminium was greater than pyrophosphate extractable aluminium, as would be anticipated, at both sites in May. These results suggested that aluminium extracted from the soils in March was more likely to be in a purely organic form whereas in May, aluminium also occurred in the form of crystalline oxides and hydroxides.

6.42 SOIL WATERS

Results presented refer to bulked soil waters. All waters extracted from the soils of a single pit were bulked and mixed thoroughly prior to analysis. Table 6.42A gives the observations recorded on the filtration of whole samples through a 5µm membrane. This filtration was purely to remove particulate material prior to analysis.

Table 6.42A: Observations on the filtration of soil waters.

	Water Colour prior to and after filtration	paper colour after filtration	Particle size on filter paper (mm)	% covering of filter paper
2M1 March	Light brown - no change	Brown	< 1mm	5-10%
2M2 March	Brown - no change	Dark brown	< 1mm	5-10%
10M1 March	Light brown - no change	Brown	< 2.5mm	10-15%
10M2 March	Not coloured - no change	Very light brown	< 1.5mm	10-12%
2M1 May	Light brown - to lighter brown	Brown	< 0.5 mm	5%
2M2 May	Very light brown to brown - no change	Very light brown	< 1.5mm	5-10%
10M1 May	Light brown to brown - no change	light brown to brown	< 1mm	5%
10M2 May	Brown - change to lighter brown	dark brown	<1.5mm	5-10%

Most soil waters remained the same colour on filtration through a 5 µm membrane. However, colour intensity in waters extracted from pit 2 at site 10 in May decreased considerably after filtration.

The results for the chemical analysis of the bulked soil waters are presented in tables 6.42B and 6.42C.

Table 6.42B - Major ion analysis for the March soil waters: All results are in mg/L. All results represent one bulked measurement except for anions and DOC where mean results are given, n = 3.

	2M1	2M2	10M1	10M2
Ca ⁺⁺	0.90	1.18	1.23	1.42
Mg ⁺⁺	0.24	0.41	0.24	0.33
Na ⁺	14.50	13.50	14.00	15.30
K ⁺	2.03	1.30	1.23	1.30
Fe ⁺⁺	2.12	0.53	0.74	0.17
DOC	24.00	18.80	13.20	11.90
NO ₃ ⁻	8.49	6.97	6.81	6.53
Cl ⁻	12.90	12.20	12.50	12.70
SO ₄ ²⁻	7.96	6.52	7.32	6.13
F ⁻	0.00	0.00	0.00	0.00

The soil waters from the two sites were very similar in magnesium, sodium, nitrate, chloride, sulphate and fluoride. Calcium was slightly greater in the soil waters from site 10 and potassium, iron, DOC were less in the soil waters from site 10.

Table 6.42C - Major ion analysis for the soil waters in May: All results are in mg/L. All results are from one bulk soil water reading except for anions and DOC where mean results are given, n = 3.

	2M1	2M2	10M1	10M2
Ca ⁺⁺	0.64	1.52	0.54	1.73
Mg ⁺⁺	0.16	0.56	0.06	0.14
Na ⁺	27.50	33.50	23.0	35.0
K ⁺	1.80	2.20	0.90	1.57
Fe ⁺⁺⁺	2.46	0.63	1.35	3.04
DOC	17.30	13.30	21.30	17.70
NO ₃ ⁻	10.09	24.30	4.08	6.19
Cl ⁻	9.59	9.85	11.48	11.86
SO ₄ ⁻⁻	7.18	10.23	7.56	8.45
F	1.19	0.00	0.62	0.50

The soil waters from the two sites were similar in calcium, sodium, sulphate and fluoride content but site 10 soil waters contained lower concentrations of magnesium, potassium, and nitrate and greater iron, DOC and chloride than the soil waters at site 2.

6.43 SOIL WATER - EXTENDED ANALYSIS

(i) pH - pH of bulked soil waters are given in table 6.43A.

Table 6.43A - pH results for the bulked soil waters. pH was only measured once for each soil water.

March Site/soil	March samples pH	May Samples pH	May site / soil
2M1	6.02	5.82	2M1
2M2	5.87	5.61	2M2
10M1	5.64	6.00	10M1
10M2	5.55	6.41	10M2

In March site 10 soil waters were slightly more acidic than those at site 2. This relationship reversed for the soil waters in May.

(ii) Total aluminium and silicon (filtered through 5µm membrane filter).

5 replicates of each bulked soil water were measured for 'total' (filtered through 5µm membrane) aluminium and silicon. Additionally, when evaluations were made of fractionated samples one sample of 'total' aluminium or silicon was also included. All totals were used to calculate the mean result expressed in table 6.43B.

Table 6.43B Total Al and Si in soil waters; results are given as a mean value in µg/L, standard deviations are given in italics, n = 7+

March soil / site	March Total Al	March Total Si	May Soil / Site	May Total Al	May Total Si
2M1	1242 <i>139</i>	1886 <i>94.0</i>	2M1	641 <i>75.8</i>	2217 <i>135</i>
2M2	2375 <i>111</i>	3590 <i>108</i>	2M2	231 <i>22.3</i>	2730 <i>144</i>
10M1	390 <i>89.6</i>	1227 <i>83.7</i>	10M1	1282 <i>77.2</i>	1579 <i>40.0</i>
10M2	293 <i>45.0</i>	1225 <i>83.7</i>	10M2	1620 <i>180</i>	1245 <i>51.0</i>

Total aluminium replicated well. In March site 2 soil waters had higher concentrations of Al; in May greater aluminium concentrations were found in site 10 soil waters.

At both sampling periods the highest concentration of total silicon was in site 2 soil waters. Total silicon from both pits at both sites were consistent except at site 2 in March when total silicon contrasted for the two pits.

(iii) Filtration through a 0.45µm membrane filter: soluble aluminium and silicon.

Table 6.43C gives the analytical results from the soil waters after a second filtration through a 0.45µm filter.

Table 6.43C Soluble aluminium and silicon. Results are given as mean values in µg/L, standard deviation given in italics, n=5.

	0.45 µm filtered Al	% < 0.45 micrometer	0.45 µm filtered Si	% < 0.45 micrometer
2M1 March	1058 <i>58.9</i>	85.2 %	1831 <i>13.0</i>	97 %
2M2 March	1765 <i>61.0</i>	74.3 %	2933 <i>104</i>	81.7%
10M1 March	375 <i>40.8</i>	96.1%	1063 <i>9.00</i>	86.6%
10M2 March	218 <i>51.8</i>	74.4%	772 <i>21.0</i>	63%
2M1 May	600 <i>24.0</i>	93.6%	2225 <i>17.7</i>	100%
2M2 May	220	95.7%	2580 <i>44.0</i>	94.5%
10M1 May	485 <i>27.0</i>	37.8%	1380 <i>24.0</i>	92.9%
10M2 May	1567 <i>126</i>	96.7%	1169 <i>24.0</i>	93.9%

Replication of results was variable. In March site 2 aluminium < 0.45µm replicated well. However, replication was poor for site 10 aluminium < 0.45µm indicated by the standard deviations. In May replication of results was poor at site 2 but good at site 10. aluminium < 0.45µm was greater at site 2 than site 10 in March but the reverse was true in May. Aluminium < 0.45µm accounted for between 74 and 96% of the total aluminium at both sites in March and 93 - 96% at both sites in May. One soil water at site 10 in May was the exception where only 37.8% of the total aluminium was < 0.45µm.

All 0.45µm filtered samples replicated well when tested for silicon. In March at site 2, 97.0% and 81.7% of the total silicon passed through a 0.45 µm membrane. In May at the same site 100% and 94.5% of the total silicon was < 0.45µm. At site 10, 86.6% and 63% of the total silicon passed through a 0.45 µm membrane in March whereas in May the results were higher at 92.9% and 93.9%.

(iv) Dialysis

Dialysed aluminium and silicon in the soil waters are given in table 6.43D.

Table 6.43D - Dialysed aluminium and silicon. The results are reported as mean values in µg/L, standard deviation is given in italics, n = 4. No S.D. value indicates poor replication of results i.e. only 2 out of a possible 4-5 results showed similarity and the result given is the mean of these.

	Dialysed Al	% < 2.4 nm	Dialysed Si	% < 2.4nm
2M1 March	147 <i>14.5</i>	11.8%	925	49.0%
2M2 March	337	14.2%	1338	37.3%
10M1 March	69.0	22.0%	607	49.5%
10M2 March	61.0	19.4%	412 <i>10.0</i>	33.6%
2M1 May	67.0	10.5%	1825 <i>129</i>	82.3%
2M2 May	43.8 <i>2.54</i>	18.4%	2563 <i>59.8</i>	93.9%
10M1 May	24.0	1.9%	1100 <i>20.4</i>	69.7%
10M2 May	18.0 <i>3.06</i>	1.3%	750	60.2%

The small fraction of aluminium able to pass through the dialysis membrane was not often well replicated. At site 2 in March between 11.8% and 14.2% of the total aluminium was small enough to pass through the dialysis membrane. In May the results were similar with 10.5% to 18.4% of the total aluminium dialysable; on average this was slightly higher in May. At site 10 in March 22.0% and 19.4% of the total aluminium was able to pass through the dialysis membrane but in May only 1.9%

and 1.3% of the total aluminium was smaller than 2.4 nm.

Silicon dialysis results were better replicated. At site 2, 49.0% and 37.3% of the total silicon passed through the dialysis membrane in March and in May this had increased to 82.3% and 93.9%. At site 10, 49.5% and 33.6% of the total silicon was smaller than the 2.4 nm mesh in March. In May this had increased to 69.7% and 60.2% of the total silicon. This increase, however, was not as great as was found at site 2.

(V) Cation exchange experiments

Amberlite 200

The amberlite 200 resins were easily equilibrated with the buffer solutions and pH was regulated throughout the experiments. On addition of the soil water there was always a noticeable pH rise presumably because the buffer solution did not account for all the species present in the natural soil waters. The rise was probably indicative of a release of base cations into solution.

Exchangeable aluminium was defined as that which was not retained by the ion exchange resin subtracted from the total aluminium. This exchangeable fraction must be smaller than approximately 100 nm (Exley and Birchall 1992b) to be able to enter the resin initially.

Table 6.43E Results for the soil waters that had reacted with amberlite 200 resin. All results are mean values in $\mu\text{g/L}$, standard deviation is given in italics, $n = 3$. Where no SD reading is given, replication was poor.

	Al in soil water after 1 hour resin contact ($\mu\text{g/L}$) = X	Exchangeable Al (5 μm filtered - X) = C.	% Exch Al (C/5 μm filt x 100).	Resin eluted Al ($\mu\text{g/L}$).
2M1 March	473 <i>49.1</i>	769	61.9	378
2M2 March	1287 <i>78.2</i>	1088	45.8	1332
10M1 March	215	175	44.9	137
10M2 March	118 <i>9.11</i>	175	59.7	83.0
2M1 May	460 <i>9.50</i>	181	28.2	138 <i>2.83</i>
2M2 May	144 +/- 14	109	47.2	86.0 <i>4.61</i>
10M1 May	224	1058	82.5	326
10M2 May	479	1141	70.4	481 <i>35.4</i>

Replication of results from the solutions in contact with the Am 200 cation exchange resin was variable. Non-exchangeable aluminium was replicated reasonably well but results following acid elution of the resins proved more difficult to repeat. At site 2, 61.9% and 45.8% of the total aluminium was exchangeable in March, an average of 53.8%. At site 10 at this time, 44.9% and 59.7% of the total aluminium was exchangeable an average of 52.3%, which was very similar to the result from site 2. At site 2 in May only 28.2% and 47.2% of the total aluminium was exchangeable, an average of 37.7%. At site 10, however, exchangeable aluminium increased to 82.5% and 70.4% of the total, an average of 76.5%.

Silicon measured from the soil waters after reaction with the resins are given in table 6.43F.

Table 6.43F - Silicon results for the soil waters after reaction with Am 200. All results are given as mean values, standard deviations are given in italics, n = 3. No SD result indicates poor replication.

	Soil water Si after 1 hour contact with resin ($\mu\text{g/L}$).	% of total Si	Eluted resin Si ($\mu\text{g/L}$)
2M1 March	750	39.8%	140
2M2 March	1685 <i>68.0</i>	46.9%	234 <i>10.8</i>
10M1 March	617 <i>12.0</i>	50.3%	75 <i>2.83</i>
10M2 March	319	26%	45
2M1 May	1443 <i>93.3</i>	65.1%	62
2M2 May	2118 <i>81.0</i>	77.6%	37 <i>2.12</i>
10M1 May	858	54.3%	59
10M2 May	575	46.2	33

The replication of the results for silicon remaining in the soil water after reaction with the Am 200 resin was variable. As with aluminium the resin elution sample replication was especially poor. At site 2 in March, 39.8% and 46.9% of the total silicon was not retained by the exchange resin whereas at site 10 the amount of inert silicon was 50.3% and 26% of the total silicon. In May at site 2 inert silicon increased to 65.1% and 77.6% of the total silicon and at site 10 54.3% and 46.2 % of total silicon was found.

The results indicated the presence of silicon in some form retainable by the resin. This conclusion was supported by resin elution.

Amberlite IRC 50

This resin took a greater time for equilibration with buffer solutions and required constant attention and addition of dilute HNO₃ throughout the hour of exchange. The pH increases experienced after the addition of the soil waters were usually much less than had been found for the Am 200 resins. Sigma chemical company were approached for a cut off point for the size of species able to enter this resin type but no data was available.

Table 6.43G - Aluminium results for the soil waters after reaction with Am IRC 50 resins. All results given are mean values in µg/L, standard deviations are given in italics, n = 3. No SD data indicates poor replication.

	Solution Al after 1 hour contact with resin (µg/L) = X.	Exchangeable Al (5µm filtered - X). (µg/L) = C	% Exch Al (C/5µm filt x 100)	Resin eluted Al (µg/L).
2M1 March	521 <i>21.2</i>	721	58.1	349 <i>35.7</i>
2M2 March	1028 <i>21.2</i>	1347	56.7	600
10M1 March	99 <i>6.24</i>	291	74.6	120 <i>12.7</i>
10M2 March	137 <i>2.04</i>	156	53.2	75
2M1 May	468 <i>26.7</i>	173	27.0	149 <i>6.56</i>
2M2 May	67	164	71.0	142 <i>5.97</i>
10M1 May	653	629	49.1	507
10M2 May	953	667	41.2	713

Replication of aluminium results using Am IRC 50 resin was variable. Non-exchangeable aluminium results replicated well in March; however, only one set of soil water samples from the May group showed internal consistency. The resin elution

samples replicated less well.

At site 2 in March, 58.1% and 56.7% of the total aluminium was exchangeable, an average of 57.4%. Site 10 at this time had 74.6% and 53.2% of the total aluminium in an exchangeable form, an average of 63.9%. In May exchangeable aluminium contrasted greatly in the two samples from site 2; in one case 27% of the total aluminium was exchangeable and in the other 71% was retained by the resin, giving an average of 49.0% for the site. In May at site 10 49.1% and 41.2% of the total aluminium was exchangeable, an average of 45.2%.

Table 6.43H - Silicon measurements for the soil waters that had been in contact with Am IRC 50 resin. Results given are mean values given in $\mu\text{g/L}$, standard deviation is given in italics, $n = 3$. No SD indicates poor replication.

	Soil water Si after 1 hour contact with resin ($\mu\text{g/L}$).	% of total Si	Resin eluted Si ($\mu\text{g/L}$)
2M1 March	850 <i>20.4</i>	45.1%	193
2M2 March	2250	62.7%	98
10M1 March	807 <i>40.3</i>	65.8%	75
10M2 March	563 <i>9.40</i>	46.0%	52 <i>6.36</i>
2M1 May	1480 <i>84.9</i>	66.8%	32 <i>0.58</i>
2M2 May	1780 <i>28.3</i>	65.2%	35 <i>3.70</i>
10M1 May	860 <i>28.3</i>	54.5%	40 <i>1.90</i>
10M2 May	603 <i>31.0</i>	48.4%	31 <i>3.60</i>

Replication of silicon results using Am IRC 50 was better than with the Am 200. However, this resin type also indicated retention of silicon. At site 2 in March 45.1% and 62.7% of the total silicon was found in the soil solutions after reaction with the resin. At site 10 at this time, 65.8% and 46.0% of the total silicon escaped attachment to the resin. In May the results for site 2 were similar at 66.8% and 65.2%. At site 10 the results were again similar at 54.5% and 48.4%.

6.44 Summary of results:

Bulk soil analysis:

- i. Soils from site 10 were slightly more gritty than those from site 2.
- ii. Greater exchangeable calcium, sodium, hydrogen and aluminium in the March soils at both sites than in the samples taken in May.
- iii. Greater soil exchangeable calcium and sodium at site 2 in March than site 10.
- iv. Greater soil exchangeable hydrogen at site 10 in May than site 2.
- v. Greater soil exchangeable aluminium at site 2 in May than site 10.
- vi. Soil pH, on average, was slightly lower in March than in May.
- vii. Soil % LOI typically fell between 10 - 12%.
- viii. Soil extractable aluminium was all organically bound or amorphous at both soil sites in March. In May, some crystalline oxides or hydroxides of aluminium were detected by dithionite extraction.
- ix. Soil extractable iron was completely in organic or amorphous forms in the May but the March soils had some crystalline oxides and hydroxides of iron present.

Gross chemical analysis of bulked soil water samples:

- i. Potassium, iron and DOC were greater in the soil waters from site 2 in March than those from site 10.
- ii. DOC and chloride were more concentrated in soil waters from site 10 in May than site 2.
- iii. Soil solution pH was lower at site 10 in March and site 2 in May.

Extended analytical work:

- i. Total aluminium (after 5 μ m filtration) was greater at site 2 than site 10 in March; in May the reverse was true.
- ii. Greatest total silicon (again after 5 μ m filtration) was always found in soil waters from site 2.
- iii. Aluminium species < 0.45 μ m were 74 - 96% of the total aluminium in March compared with 38 - 97% in May.
- iv. Silicon species < 0.45 μ m were 63 - 97% of the total silicon in March compared with 93 - 100% in May.
- v. Only small amounts of the total aluminium could pass through the dialysis membrane. In March 10 - 20% of the total aluminium from the soil samples were small enough. At site 10 the proportion was slightly greater than at site 2. In May between 1 and 20% of the total aluminium passed through the dialysis membrane. At this time proportionally more aluminium from site 2 was small enough to enter the dialysis membrane.
- vi. Silicon small enough to be dialysed was 30 - 50% of the total silicon in the March samples but 60 - 95% in May. In May, silicon dialysis was most successful at site 10.
- vii. In March there were similar proportions of exchangeable aluminium in both soil waters when mixed with a strongly acidic resin (Amberlite 200). In May, however, there was proportionally less exchangeable aluminium at site 2 (45 - 65%) than at site 10 (70 - 83%).
- viii. Using a weaker acidic resin proportions of exchangeable aluminium remained similar at both sites in March. However, in May, results were highly contrasted at site 2, but but much less variable at site 10.

ix. Silicon was retained by both resin types.

6.5 DISCUSSION

6.51 Soils

The more gritty and coarse nature of the soils from site 10 (table 6.41A) can be explained by geological input; site 10 was situated above a coarse granodiorite and site 2 a medium grained diorite. Analysis of variance on soil textural data from chapter 4 indicated soils developed over granodiorites included a greater % of sand sized particles.

Soils at both sites were acid and the saturation of the exchange complexes on both sampling occasions with hydrogen and aluminium was symptomatic of their base deficiency and indicated sensitivity to acid inputs. Lower concentrations of exchangeable acid and base cations were found in samples taken in May at both sites. Mean soil exchangeable calcium at site 2 was 1.68 meq/kg in March but down to 0.42 meq/kg in May. At site 10 the contrast was also strong with mean soil exchangeable calcium at 0.97 meq/kg in March compared with 0.16 meq/kg in May. This was explained by release of base cations for the requirements of vegetation.

Dithionite extractable iron was greater or similar to pyrophosphate extractable Fe in all soils; this is consistent with Bascomb (1968) who indicated pyrophosphate extracted organically bound and amorphous forms of iron and dithionite extracted both of these and crystalline oxides and hydroxides. The soils in March had both forms of iron; however, the May soils contained only organically bound iron. Dithionite

extractable aluminium was greater than pyrophosphate extractable aluminium at both sites in May indicating the presence of soil aluminium in a crystalline form (Shuman 1990). In March, pyrophosphate extractable aluminium was greater than dithionite extractable aluminium at site 10 but similar to dithionite extractable aluminium at site 2 and indicated aluminium was typically organically bound or amorphous at this time. These contrasting results for iron and aluminium strongly suggest any relationship between these two parameters in these soils to be weak or inverse.

6.52 Soil waters: relationship with soils

A comparison of the results from tables 6.41B,C and 6.42B and C indicated a strong negative correlation (-0.927) between soil and soil water sodium. Soil solution total silicon was negatively correlated with pyrophosphate extractable aluminium (-0.924) and iron (-0.742). This indicated lower soil water silicon concentrations could be expected from soils where aluminium and iron was bound principally in organic and amorphous forms. Where silicon concentrations were greater pyrophosphate extractable iron and aluminium were typically less obvious. No other chemical components seemed to be related.

Bruce et al (1989) indicated that soil solid phase was in equilibrium with the soil solution phase but that many factors determined this equilibrium. In this study, the soil waters and the soils from which they were extracted showed very little similarity. However, Bruce et al (1989) showed that although calcium concentration or calcium activity increased with exchangeable calcium or calcium saturation that regression between these components was poor with $r^2 < 0.3$ and relationships between the two were complex.

The apparent lack of relationship between the soils and soil waters in this study need not be due to a lack of equilibration between the two components but could indicate relationships are more complex than can be identified with simple correlation (Bruce et al 1989). However, it is also possible that the soil solutions did not have time to equilibrate with the soils due to recent washing with rain-water. These differences could also be explained by the small concentrations of chemical components in both soils and waters exacerbating any variability present within the experimental techniques.

6.53 Soil waters - main features.

The lack of colour change in the soil waters on filtration indicated very large (> 5 μm) particles were rare. However, in the soil waters from pit 2 at site 10 in May there was a great change in coloration after filtration (table 6.42A). This indicated the presence of some very large organic species.

In March the soil waters from both sites exhibited similar concentrations of atmospherically deposited ions e.g. magnesium, sodium, nitrate, chloride, fluoride and sulphate. Many of these ions also positively correlated with one another. Calcium concentrations in the soil waters from site 10 was greater than at site 2 but this could not be explained by geological input.

In May trends were more difficult to explain in terms of atmospheric inputs as anticipated during this drier period. The results were also not entirely reconcilable in terms of geological input. Calcium concentrations were variable at both sites but

greater magnesium from the soil waters at the geologically base rich site 2 indicated a possible geological influence. Large sodium concentrations at both sites at this time probably indicated a similar drying and concentration effect that had been noted in most soils in the previous summer period, chapter 5.

6.54 Soil water pH

In March site 2 soil waters had the higher pH whilst those at site 10 were higher in May. These higher pH results corresponded with greater soil water DOC concentrations suggesting a possible control of soil water pH by organic acids.

Organic acids can act as buffers in the pH regime; they are weak acids and are much less likely to give up hydrogen ions and contribute to pH. Calcium and magnesium may act to displace H^+ - at site 2 the soil water with the greatest sum of calcium and magnesium had the lowest pH. The strongly acidic anion component (nitrate + sulphate) was also highest at site 2 for the lowest reported pH. However, at site 10 the soil water with the highest pH corresponded to the greatest sum of calcium and magnesium and the greatest strongly acidic anion component. The two soil sites thus gave very different responses to investigation of pH control.

6.55 Soil water total aluminium and silicon.

Giusti (1991) reported total aluminium concentrations from stream waters within the Dargall lane sub-catchment at Loch Dee of between 50 and 200 $\mu\text{g/L}$; these were much smaller than the total aluminium concentrations found in soil waters sampled in the adjacent White Laggan sub-catchment in the present study.

At both sampling periods highly coloured, DOC rich waters were associated with the greatest concentrations of total aluminium. This relationship was often noted throughout the monitoring exercise (chapter 5) but differs from the findings of David and Driscoll (1984) where higher total aluminium was not always related to higher DOC.

The higher concentrations of total aluminium also corresponded to higher pH values in the soil waters although the relationship was not linear. David and Driscoll indicated a poor negative correlation between soil water pH and total aluminium content and suggested that pH, DOC and total aluminium were all interrelated factors, a conclusion also indicated from the monitoring data in chapter 5. Driscoll et al (1984) also indicated little correlation between total aluminium and pH attributing this to variability in the levels of organically complexed aluminium. Because of the relationship between total aluminium and DOC, this explanation would seem to be most appropriate here.

The total aluminium concentration was not controlled simply by geology. A purely geological control would have resulted in consistently greater aluminium concentrations at site 2 where the aluminium should be more easily released from mineral weathering. However, mineral weathering at this site should also consume more H^+ ions and therefore possibly reduce aluminium concentration due to greater pH.

Farmer (1986) suggested silicon in soil solutions ranged from 1-40 mg/L. The total

silicon found in soil waters from the Loch Dee catchment were within the lower half of this range. The silicon results were related to geology. Soil water silicon was always greater at site 2 which was situated above diorite where silicon was in a more easily weathered form than in the granodiorite at site 10. However, total silicon from site 2 in May was not internally consistent, (see table 6.43B). This can be explained by:

1. Samples extracted from the same horizon but at different depths within this horizon. The soil water with higher silicon concentration was extracted from soils with a slightly greater % of coarse grains (see table 6.42B); this may indicate a greater geological influence. The soil pit with higher silicon also had greater exchangeable bases which may also indicate a greater geological control.
2. The presence of foreign drift material that altered the availability of silicon to the soil waters. However, there was no field evidence of drift material at site 2 and soil thin section examination, chapter 4, implied a purely dioritic parent material.
3. Silicon concentration also controlled by none geological factors e.g. phytoliths. However, thin section examination had not indicated the presence of phytoliths.

6.56 Fractionation Methodology - reliability for use with soil waters.

Filtration was reliable in terms of replication of silicon results but less so in the case of aluminium as indicated by standard deviation. It was commonplace for large quantities of aluminium and silicon to be lost on filtration through a 0.45µm filter. Exley and Birchall (1992b) indicated that loss of silicon at least, on filtration, should be minimal. Possible improvements therefore suggested to improve the accuracy of this method were:

- a. Soaking of filters in the soil waters over a greater time period to decrease the chances of adsorption.
- b. Increase in the number of sample replicates to quantify the precision of this method more precisely.

The dialysis method gave less consistent results. Small concentrations of small sized Al fractions within the soil waters could have been the main source of discrepancy. Increasing the number of replicates could have given a better idea of the precision of these results. Decreasing the volume of DDW within the dialysis bag would not have resulted in any differences in results since the dialysable fraction of aluminium and silicon formed an equilibrium between the soil solution outwith the dialysis bag and the DDW within the dialysis bag.

The cation exchange experimental results showed variable replication. Greater caution in the following may have decreased the chances of error:

- a. Ensuring the resin was properly equilibrated with buffer solution prior to use.
- b. More care on the addition of dilute alkali/acid to the experimental solution to counteract any pH changes.

Despite the problems encountered with the experimental methods there were some significant trends within the data. These will be discussed.

6.57 Size fractionation - main trends.

Aluminium 0.45 - 5.00 μm in size.

At site 2 there was a greater fraction of aluminium $> 0.45 \mu\text{m}$ in March than in May; there was also higher concentrations of soil water DOC in March at this site. At site 10 in March aluminium $< 0.45 \mu\text{m}$ in size was poorly replicated from both soil pits. This fraction was numerically small and this alone could have caused the problems with replication. In May, at site 10 soil water aluminium $< 0.45 \mu\text{m}$ in size was

contrasting at the two pits sampled. Both pits soil waters, however, were enriched in DOC. Table 6.42A indicated soil water 10M2 had already lost much of its large organic complexes on filtration through a 5µm membrane. Virtually all the aluminium remaining in this sample passed through a 0.45 µm filter. However, soil water 10M1 lost very little colour on 5µm filtration. This observation can explain the contrast in 0.45µm filterable aluminium at this site if the large volume of aluminium > 0.45µm in size for 10M1 was in an organic form between 0.45 and 5 µm in size.

In both cases the concentration of aluminium > 0.45µm in size seemed to be related to soil water DOC content - where DOC was greatest there was a tendency for the soil waters to contain larger fractions of aluminium. Menzies et al (1991) found a decrease in soil water aluminium content on passage through a 0.45µm filter that was sometimes but not always associated with a decrease in soil water coloration and was also explainable in terms of DOC content.

Dialysed Aluminium

In March the small sized aluminium determined by dialysis was numerically greater at site 2 than site 10 but made up a smaller fraction of the total aluminium (5µm filtered) at site 2 where DOC was more concentrated. In May small sized aluminium fractions determined by dialysis were strikingly less at site 10 where the DOC content was highest than at site 2 where DOC was lower. This association of soil waters rich in DOC with less aluminium in a small and potentially toxic form was assumed to result from complexation by organic compounds. The concentrations of small and potentially toxic aluminium separated by this dialysis method were in a similar range

to those found by LaZerte (1984) for lakes and streams of Muskoka-Haliburton region of central Ontario during Spring snowmelt.

Silicon in solution

Farmer (1986) suggested that silicon in natural waters occurred entirely as monosilicic acid. Exley (pers comm.) indicated this should pass through a dialysis membrane. In both filtration and dialysis, however, the fractionated sample was less than total (5µm filtered) silicon. This was explained by:

1. Silicon adsorbed by the filter and/or dialysis membrane.
2. Silicon present in forms other than silicic acid i.e. particulate material including Si between 0.45 µm and 5 µm in size. Silicon present in particulate form could be as silicate and/or aluminosilicate minerals. There was no correlation between large sized silicon particles and iron concentrations therefore the formation of iron gels could not be cited to explain the results.

6.58 Cation exchange

All ions in a solution in contact with a cation exchange resin and small enough to enter the mesh of the resin compete for exchange sites. Analyses of the soil waters (tables 6.42B and C) indicated that only iron (also a trivalent ion), fluoride (capable of forming very stable compounds with Al^{3+}) (Moore and Ritchie 1988) and DOC (also capable of forming very stable compounds with Al^{3+}) (Inoue and Huang 1990) were concentrated enough in some or all cases to influence aluminium in solution when in contact with a cation exchange resin. Fluoride and DOC would compete with resin functional groups for the aluminium and iron would compete with the aluminium for attachment to the functional groups. The level of interference of iron with aluminium chemistry was illustrated by Henmi and Huang (1985b) in relation to the

formation of imogolite. They showed that if a solution contained an Fe:Al ratio > 0.5 imogolite formation would be impeded because of the affinity of iron for silicic acid. Calcium, magnesium and potassium were not present in great enough relative concentrations to compete with greater binding strengths of Al^{3+} present in larger concentrations, for sites on the cation exchange resins. Henmi and Huang (1985a) also indicated that for sodium to compete with aluminium for silicic acid sites and perturb the formation of imogolite sodium would need to be present in a ratio Na:Al > 60 . Although attraction to silicic species is not the same as cation exchange resin species this example serves to illustrate the relative concentrations of sodium necessary to compete with aluminium. Although sodium was concentrated in the soil waters it was not concentrated enough to substantially influence the chemistry of aluminium.

The two resin types reacted differently with respect to the proportion of Al defined as exchangeable. At site 10 in May exchangeable aluminium (identified by the Am 200 resin) was greater relative to total aluminium ($5\mu m$ filtered) than in March. At site 2 the reverse was true. DOC was higher at site 2 in March and at site 10 in May. This indicated soil waters rich in DOC the fraction of total aluminium that was exchangeable (identified using the Am 200 resin) was increased. This can be explained if the resin functional group had a greater affinity for the organically bound aluminium than the organic particles themselves. This relationship was not identified for Am IRC 50 resin where the weaker functional group probably could not compete with strongly bound aluminium-organic complexes.

In May at site 2 there was a contrast in the exchangeable aluminium identified by both

resin types in the two soil waters. In both cases there was a lower amount of exchangeable aluminium reported at pit 1. In these waters, fluoride was present at 1.19 mg/L and iron at 2.46 mg/L. Fluoride forms very strong complexes with Al^{3+} (Moore and Ritchie 1988). The results suggest these were able to remain intact on passage through the exchange resin. In addition, Fe^{3+} would have competed with Al^{3+} for exchange sites releasing more aluminium into solution and resulting in lower estimates for exchangeable aluminium. Soil waters from the other pit had no fluoride and lower iron concentrations resulting in greater proportions of exchangeable aluminium.

The exceptionally high value for exchangeable aluminium at site 10 in May identified by Am 200 corresponded with very low fractions of small sized aluminium separated by dialysis. It has been suggested that this high value was caused by the ability of the strongly acidic functional group to compete with organic ligands for aluminium; this presence of organic ligands would also decrease the likelihood of the presence of small and potentially toxic forms of aluminium in the soil water.

Any influence of silicon concentration on potentially toxic aluminium in soil waters was obscured by the presence of DOC. The dialysis results from the soil waters at both sites with lower DOC concentrations were compared. This indicated on average less (< 15% as compared with 20.7%) of the total aluminium was in a potentially toxic form at site 2 compared with site 10. This was the site where total silicon was highest. The results, however, were too unreliable in terms of replication and the data set too small for any more than a tenuous link to be drawn; much more work would be necessary to support the theory that soil water Si concentration affects the amount

of aluminium in a small and potentially toxic form.

Tables 6.43 F and 6.43 H indicated that silicon from the soil waters was retained after reaction with the cation exchange resins. Further investigation of the cation exchange results should indicate more clearly the form of some of the silicon in solution.

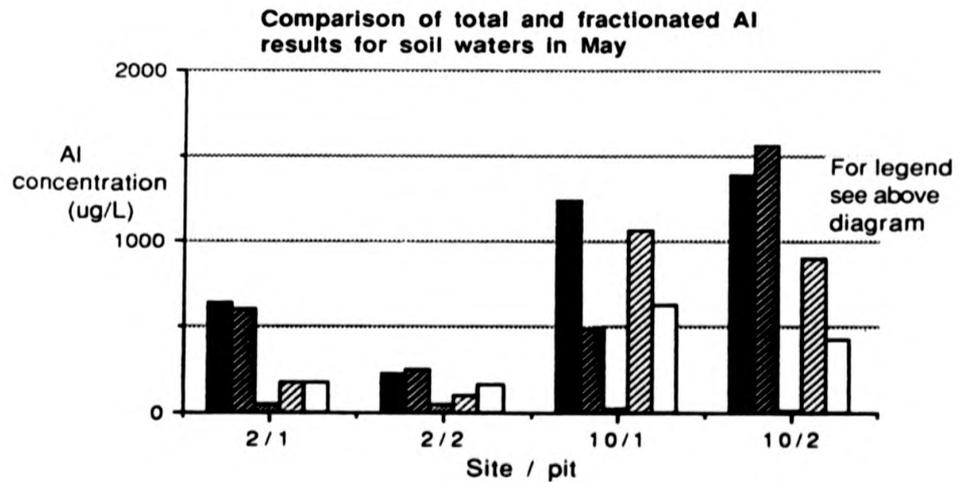
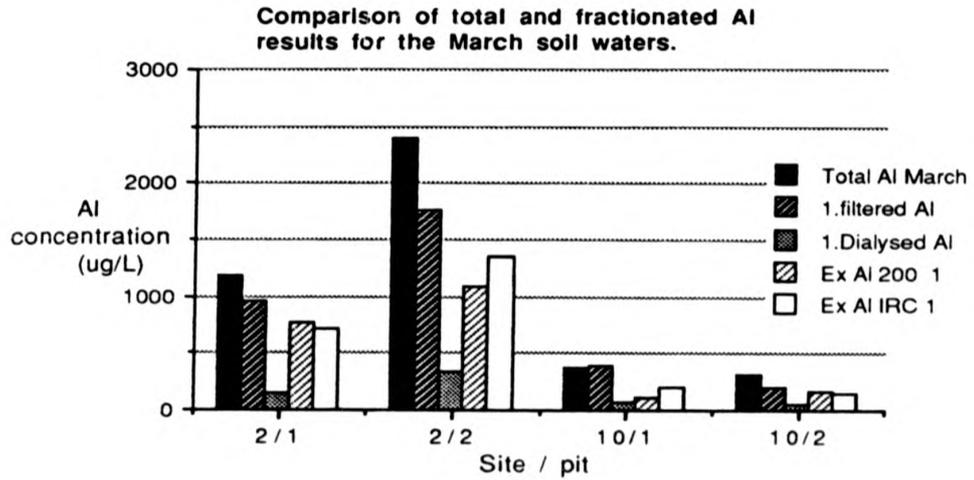
6.59 Comparisons between results of experimental work.

The results from the fractionation of the aluminium species according to size are presented in figure 6.59A. The column graphs present a comparison of the measured concentrations of aluminium according to the different methods used; i.e. $< 5\mu\text{m}$ (Total), $< 0.45\mu\text{m}$ (filtered) and $< 2.4 \text{ nm}$ (dialysed) fractions plus the results for exchangeable aluminium using 2 different CE resins. The results for the Am 200 were a minimum estimate of the fraction of aluminium that was $< 100 \text{ nm}$ in size (Exley and Birchall 1992b). No data was available for the Am IRC 50 resin; however, like the Am 200 resin the 'wet mesh' was rated at 16 - 50, it was assumed that this indicated a similar exclusion size for the Am IRC 50 resin.

The column graphs indicated splitting aluminium according to size by different methods yielded consistent results except in the following cases:

1. 10/1 in May had a greater fraction of exchangeable aluminium separated using both resins than by simple filtration; the Am 200 resin result was especially high. The exchangeable aluminium results were poorly replicated and probably represented overestimates. The filtered result, however, was well replicated and the low filtered result was explained in terms of organic particles between 0.45 and $5\mu\text{m}$ in size.
2. The filtered results at 2/2 and 10/2 in May were higher than the total aluminium. This was explained by the use of mean values in presentation of results. When the filtered samples were measured a 'total' aluminium sample was also measured; this was always higher than the filtered results.

Figure 6.59A: Comparisons of total Al and that fractionated by different techniques in soil waters.



6.60 Cation exchange implications

HAS species are retained by cation exchange resins because they are stable with respect to the functional group on the resin and carry a positive charge. Farmer et al (1986) suggested that imogolite was a pure aluminosilicate with essentially no cation exchange capacity and capable of carrying only a small positive charge. Protoimogolite and allophane are hydroxyaluminosilicates that are less well ordered and may represent precursors to imogolite (Farmer et al 1980, Farmer and Fraser 1982). They possess many broken edges and show a much greater capacity for the adsorption of anions. Because of greater charge these poorly ordered species are more likely to remain attached to a cation exchange resin.

In experimental work by Exley and Birchall (1992b) the presence of HAS species in a solution was identified with reference to molar Si:Al ratios of species retained by a cation exchange resin. Birchall et al (1989) also used this procedure. Silicon retention by the cation exchange resins was implicated by resin elution of the Am 200 and IRC 50 resins (Tables 6.43 F and H). These resin elution results were therefore examined in terms of their molar Si:Al ratios.

Elution of both resin types after reaction with soil solutions produced concentrations of aluminium and silicon that were poorly replicated. However, because the results are only used in a relative sense this poor replication was of little consequence. The molar Si:Al for the two resin types are given in the following two tables.

Table 6.60A Si:Al for Am 200

Soil/site	March Si:Al (M)	Soil/site	May Si:Al (M)
2M2	0.36	2M1	0.43
2M3	0.17	2M2	0.41
10M2	0.53	10M1	0.17
10M3	0.52	10M3	0.07

In March at site 10 the species left on the Am 200 resin showed a Si:Al ratio similar to that of 0.5 indicated by Farmer (1980) as typical of protoimogolite.. The values for site 2 were much lower. It is possible that HAS species were present on this resin in addition to other species involving aluminium resulting in a lower Si:Al ratio.

In May Si:Al ratios for site 10 were very much smaller than 0.5 and could not be reconciled without the presence of large amounts of aluminium on the resin not in the form of HAS. The Si:Al ratios of 0.41 and 0.43 for site 2 were lower than would be anticipated to identify protoimogolite but much closer than the site 10 values.

Table 6.60B Si:Al for Am IRC 50

soil/site	Si:Al March	soil/site	Si:Al May
2M2	0.53	2M1	0.20
2M3	0.15	2M2	0.24
10M2	0.61	10M1	0.08
10M3	0.66	10M3	0.04

The results for March indicated a possibility of HAS species presence in the soil waters from one pit at site 2 and from both pits at site 10 although silicon would need to be present in a form other than HAS for ratios of 0.61 and 0.66 to support the

presence of HAS. In May, none of the Si:Al ratios for the Am IRC 50 resin indicated the presence of HAS species.

There was an apparent difference in the ability of the resins to identify HAS species. It was anticipated that carboxylate resins would suffer greater interference from other soil solution components because of its weaker functional group. It follows that it should be less reliable in the identification of HAS species.

The formation of HAS species is influenced by a number of factors. These are outlined below.

1. The presence of fulvic and humic acids substantially perturbs the genesis of allophane and imogolite (Inoue and Huang 1990).
2. The formation of imogolite is impeded by an increase in molar ratio of Fe(III)/ Al from 0.01 to 0.025. Imogolite formation is completely inhibited at Fe(III)/Al ratio >0.5 . (Henmi and Huang 1985b).
3. The presence of increasing concentrations of nitrate and chloride can affect the formation of allophane (Huang 1991).
4. The presence of magnesium and sodium at great concentrations can impede the formation of imogolite (Henmi and Huang 1985a).

These constraints on the formation of HAS species were examined in conjunction with the Si:Al ratios. Am 200 resins identified a low possibility of HAS in solutions from site 2 in March and site 10 in May. These soil waters had higher DOC content therefore allophane and imogolite formation would be perturbed.

Henmi and Huang (1985b) suggested molar Fe:Al ratios >0.5 would be important in the perturbation of imogolite formation. Table 6.60C shows the molar ratios for the total aluminium and total iron in the bulked soil waters.

Table 6.60C Fe(III):Al ratios for 'total' solutions

Total Al ($\mu\text{g/L}$)	Al (M) $\times 10^{-5}$	Total Fe ($\mu\text{g/L}$)	Fe (M) $\times 10^{-5}$	Fe (III): Al (M)
1242	4.60	2120	3.80	0.83
2375	8.80	530	0.95	0.11
390	1.40	740	1.32	0.94
293	1.10	170	0.30	0.28
641	2.40	2460	4.40	1.83
231	0.86	630	1.13	1.31
1282	4.80	1350	2.42	0.50
1620	6.00	3040	5.44	0.91

This suggested the formation of imogolite would be completely impeded in most of the soil waters tested because of the presence of relatively high concentrations of iron. The inhibition of imogolite formation at Fe:Al ratios >0.5 was attributed to the perturbation of interaction of hydroxy - aluminium ions with orthosilicic acid preventing the formation of imogolite. These results suggest that imogolite could only be present in the soil waters extracted from one pit at site 2 and site 10 in March and site 10 in May. However, the concentration of DOC at site 2 in March and site 10 in May would disturb the formation of HAS species.

By perturbing hydroxy-aluminium ions and orthosilicic acid interaction poorly ordered mineral colloids e.g. protoimogolite allophane are typically formed. Therefore at one pit from site 10 in March and at both pits from site 2 in May any HAS species within the soil waters would be in a poorly ordered form.

Concentration of sodium and magnesium in solution relative to aluminium can also impede the ordering of any aluminosilicate species. Henmi and Huang (1985a) found that precipitates formed with Mg:Al of 15 and Na:Al of 60 were poorly ordered. These conditions were applied to the soil waters.

Table 6.60D Mg:Al and Na:Al results for bulked solutions.

Total Mg (µg/L)	Mg (M) x 10 ⁶	Mg:Al (M)	Total Na (µg/L)	Na (M) x 10 ⁴	Na:Al (M)
240	9.87	0.21	14500	6.30	13.71
410	16.90	0.19	13500	5.87	6.67
240	9.87	0.71	14000	6.09	43.50
330	1.36	1.23	15300	6.66	60.50
160	6.58	0.27	27500	12.00	49.84
560	23.00	2.68	33500	14.60	169.40
60	2.47	0.05	23000	10.00	20.84
140	5.76	0.10	35000	15.20	25.37

These results suggest that:

1. Magnesium concentration in the soil solutions was never great enough to impede the ordering of any aluminosilicates.
2. Sodium was only concentrated enough in the soil solutions from one pit at site 10 in March and one pit at site 2 in May to disrupt the ordering of any HAS species present.

Overall HAS species were identified in terms of Si:Al ratios of c0.5 from the soil waters at site 10 in March and the soil waters at site 2 in May. The concentration of DOC in the soil waters from site 2 in March and site 10 in May were presumably too high for the formation of HAS species. HAS species present at site 10 in March could

not have an ordered structure because of the concentrations of iron in one soil water and high concentrations of sodium in the other. HAS species formed at site 2 in May would not have an ordered structure because of high concentrations of iron and sodium in one soil water and just iron in the other. Thus if any HAS species were present on the CE resins they would be poorly ordered species, typically like protoimogolite or protoimogolite allophane.

6.61 Solubility controls of aluminium in solution

1. Solubility control by $\text{Al}(\text{OH})_3$

The fraction of aluminium conventionally termed soluble ($< 0.45\mu\text{m}$) (Neal 1988) in the soil waters were compared with curves from Martin (1986) that represented the solubility of gibbsite and amorphous $\text{Al}(\text{OH})_3$, fig 6.61A. Neal (1988) indicated that the analytical evaluation of the presence or absence of aluminium mineral solubility controls by visual means was at best, qualitative. He argued that the inaccuracy of inorganic aluminium analysis coupled with the importance of organic and fluoride complexation of aluminium and also the inability of $0.45\mu\text{m}$ filtration to delineate dissolved and particulate aluminium (Goenaga and Williams 1988) all obscured any solubility relationships. He suggested that all these points could cause experimental results to deviate from solubility controls that may actually be present. However, despite Neal's comments this comparison was still made mainly in the interest of identifying the deviations. The conversion of the soluble fraction of aluminium from $\mu\text{g/L}$ to the molar concentrations are presented in table H1, appendix H, pages 321-324.

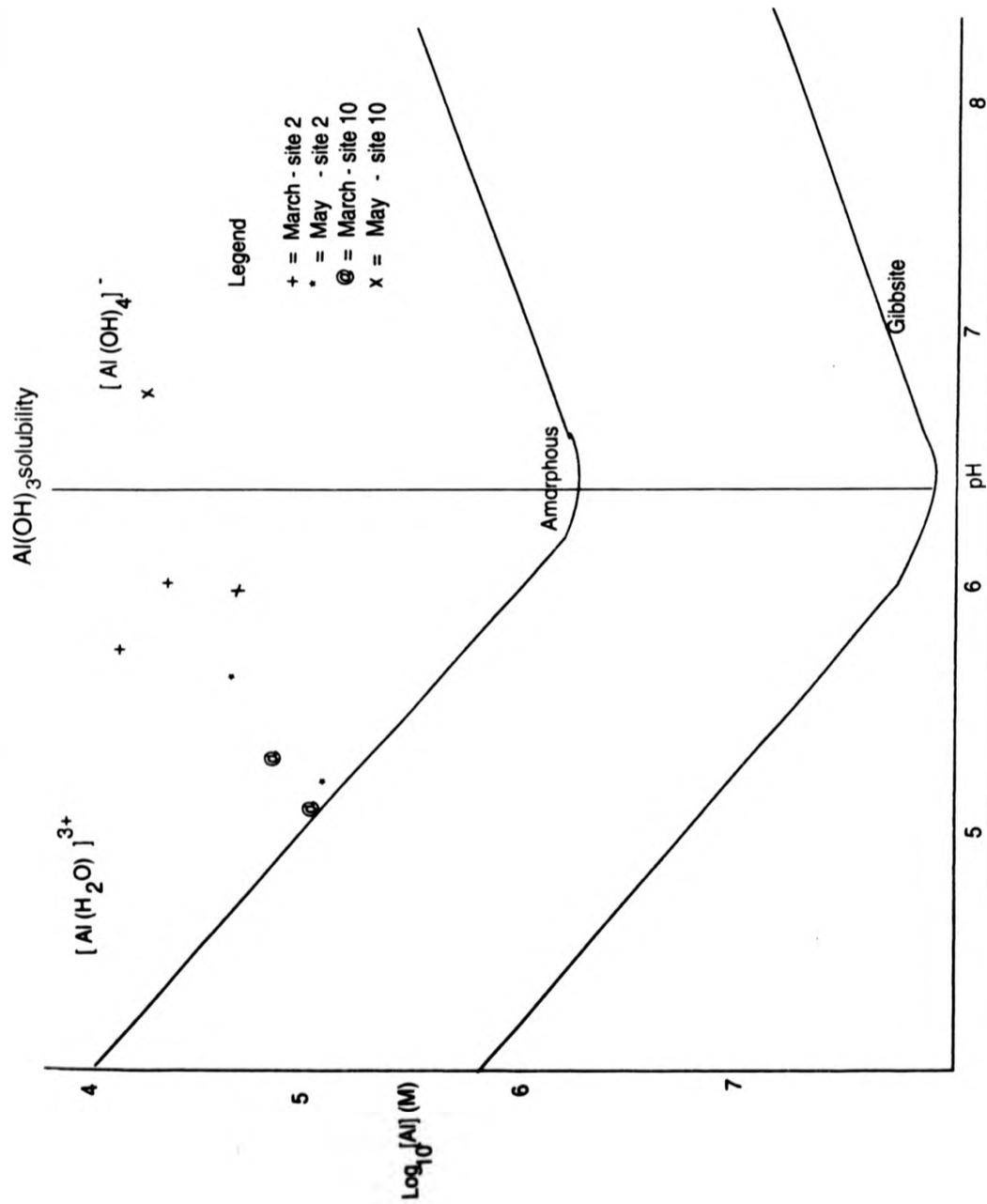


Figure 6.61A - comparison of soluble Al fractions with Al(OH)₃ solubility curves.

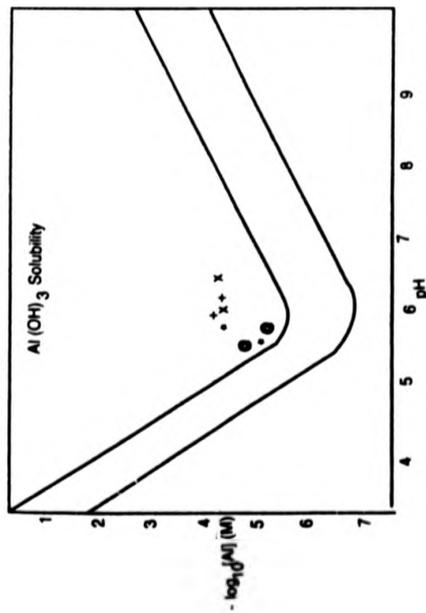
The diagram indicates that concentration of aluminium in all the soil waters (assuming that fraction $< 0.45\mu\text{m}$ in size represents the soluble fraction) was greater than that if aluminium solubility was controlled by gibbsite alone. In most cases the concentration of aluminium was not explained either by an amorphous form of $\text{Al}(\text{OH})_3$ controlling solubility. This indicated either a control by another mineral species or that the solubility of aluminium was partially controlled by the presence of complexing ligands (Neal 1988). The results which showed the highest deviation from $\text{Al}(\text{OH})_3$ solubility control were enriched in DOC and could therefore involve aluminium-organic complexes. However, soil water soluble aluminium from site 10 in March and from one soil pit at site 2 in May plotted close to the theoretical amorphous $\text{Al}(\text{OH})_3$ and could in principal have been controlled by it.

Goenaga and Williams (1988) indicated that this fraction ($< 0.45 \mu\text{m}$) may not satisfactorily define the soluble portion of aluminium. Because of this, all aluminium fractionation results were compared with $\text{Al}(\text{OH})_3$ solubility control see fig 6.61B 1-4. The conversion data for the diagrams are presented in tables H2-5, appendix H.

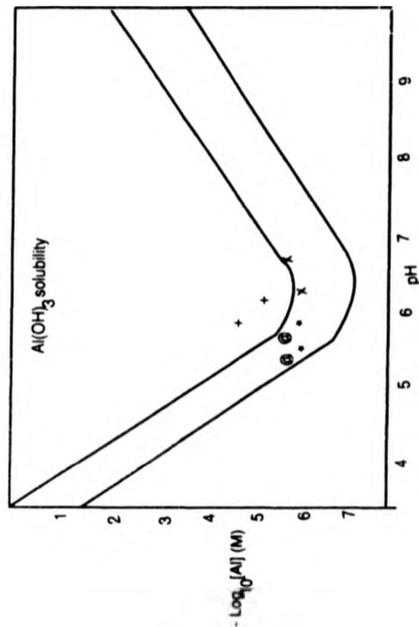
These diagrams indicated:

1. Total aluminium was greater in all samples than controlled by $\text{Al}(\text{OH})_3$ in crystalline or amorphous forms alone.
2. Dialysed aluminium in all samples, except those from site 2 in March, could be explained in terms of control by an amorphous form of $\text{Al}(\text{OH})_3$.
3. The exchangeable fraction of aluminium with respect to Am 200 resin was usually too high to be controlled by $\text{Al}(\text{OH})_3$. However, results from site 10 in March and site

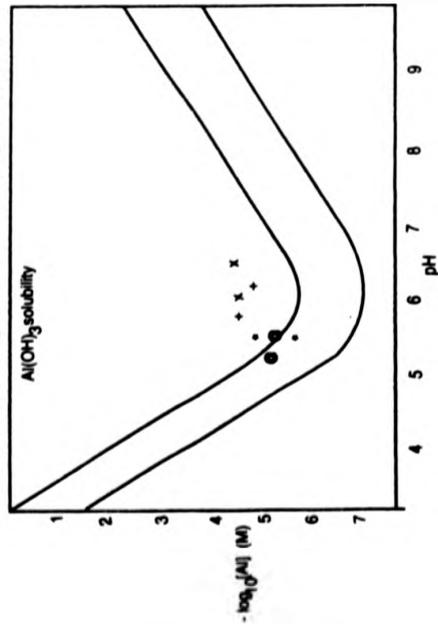
1. Plots of total aluminium



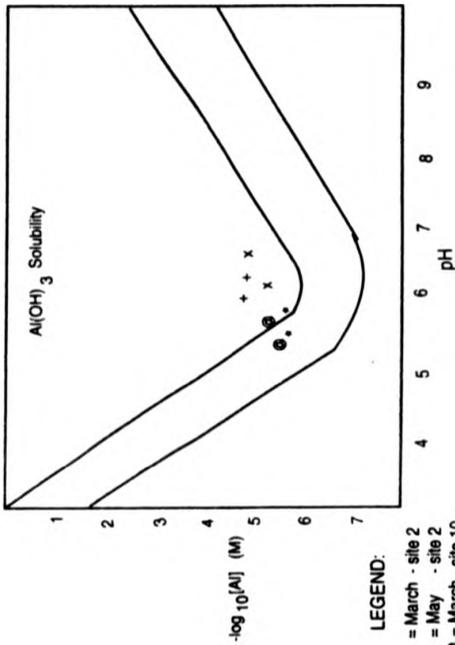
2... Plots of small sized Al identified using dialysis



3. Plots of exchangeable Al identified using Am 200 resin



4. Plots of exchangeable Al identified using Am IRC 50 resin.



LEGEND:

- + = March - site 2
- = May - site 2
- = March - site 10
- x = May - site 10

Figure 6.61B Comparison of total Al and fractionation results with Al(OH)₃ solubility curves

2 in May indicated the possibility of some degree of control by an amorphous form of $\text{Al}(\text{OH})_3$. These were the soil waters low in DOC.

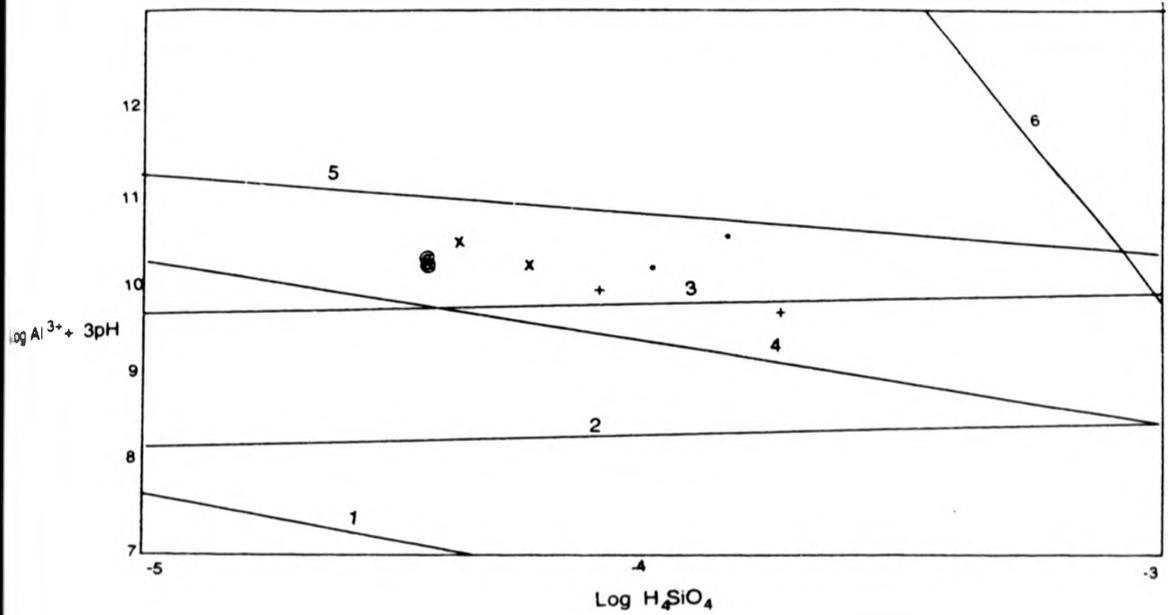
4. The results for the exchangeable fraction of aluminium tested using the Am IRC 50 resin also indicated this result.

2. Solubility control by aluminosilicate minerals

Litaor (1987), viewed the solubility of aluminium in soil waters in terms of a control by aluminosilicate minerals. He produced a diagram after Hutton (1982) of the stability of several minerals in terms of concentration of silicic acid, aluminium and pH. He plotted on to this diagram the results for soil water parameters that he had measured using methods similar to those detailed in this chapter. The results suggested his soil interstitial waters were supersaturated with respect to gibbsite and kaolinite; XRD analysis also failed to determine the presence of these minerals. Litaor found that most of his soil water analyses plotted along the line for an ideal aluminosilicate mineral proposed by Páces (1978) and suggested an amorphous ideal aluminosilicate mineral of formula $\text{Al}(\text{OH})_{x(1-x)} \text{SiO}_{2x}$ limited the solubility of aluminium in the soils he had tested.

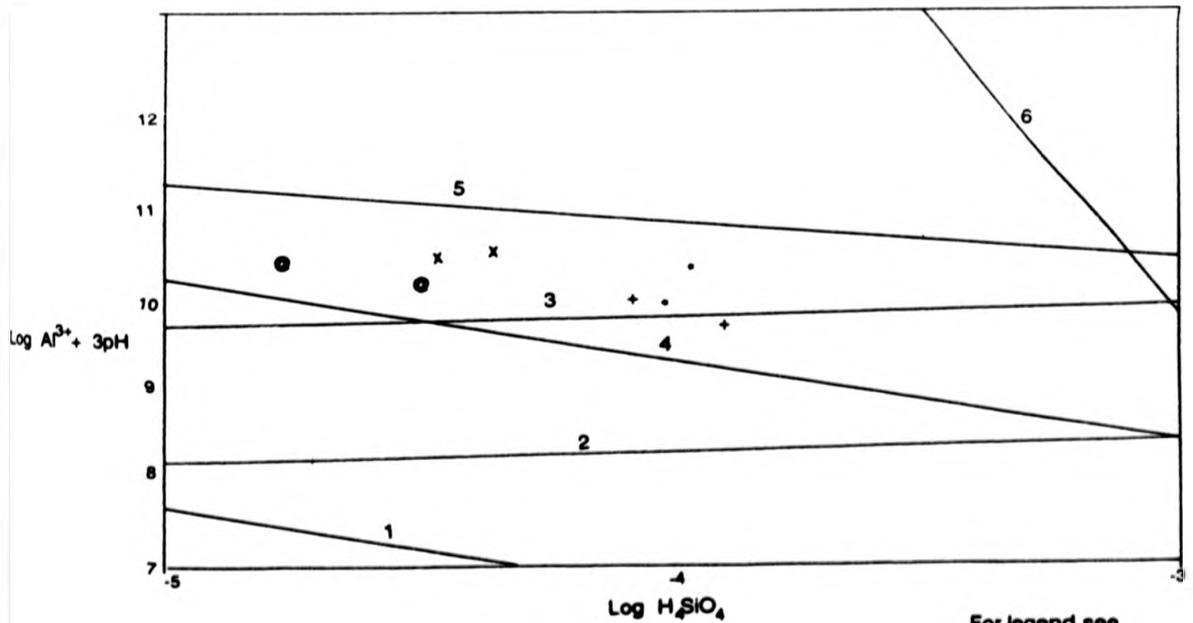
The results from this study were plotted on a similar diagram. Although the results had indicated that not all of the soil water silicon was in the form of silicic acid some of it undoubtedly was and therefore aluminosilicate solubility controls were possible. Figures 6.61 C,D and E show the plots; the data for the plots are presented in tables H6, H7 and H8, appendix H.

Fig 6.61C Total Al and Si data compared with aluminosilicate solubility data



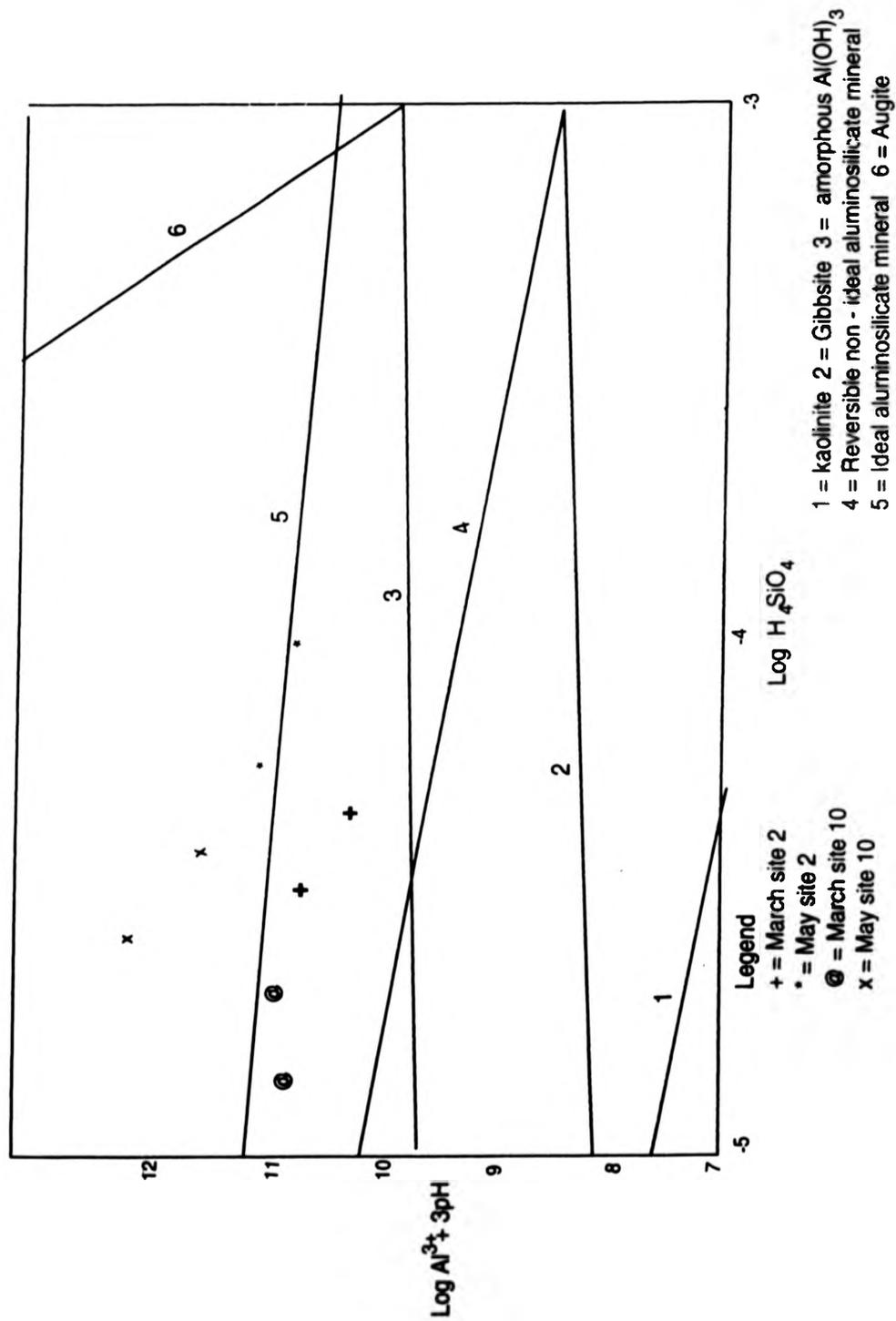
For legend see figure 6.61E.

Fig 6.61D: 0.45 μm filtered Al and Si data compared with aluminosilicate solubility data.



For legend see figure 6.61 E.

Fig 6.61 E Dialysed Al and Si data compared with aluminosilicate mineral solubility curves.



The total Al/Si data (see fig 6.61C) and the filtered Al/Si data (see fig 6.61D) corroborated the results from comparison of just the aluminium data with curves after Martin i.e. soil waters were oversaturated in aluminium with respect to an amorphous Al(OH)_3 solubility control. However, total and filtered results from one pit at site 2 in March indicated the possibility of an amorphous Al(OH)_3 solubility control that had not been recognised with the plot involving just Al. This confusion could have arisen because of the silicon not being in the form of silicic acid and also adds to the conclusions of Neal (1988) about the purely qualitative results achievable on the visual comparison of soil water data with mineral solubility controls.

Figure 6.61E presents the plot for dialysed aluminium and silicon. In this case Si was assumed to be in the form of silicic acid because of its size. The plot indicated an oversaturation of all results with respect to Al(OH)_3 (amorphous). However, the equilibrium dialysis results from the soil waters less enriched in organics plotted close to the line of the amorphous ideal aluminosilicate mineral of Páces (1978) i.e. similar to the results achieved by Litaor (1987).

The findings from these solubility diagrams were supported by reference to soil micromorphological thin sections. Plates 6.61 1,2,3 and 4 show mineral fractions from soils at sites 10 and 2. They indicate the instability of aluminosilicate minerals in the soil conditions and their subsequent breakdown to amorphous aluminosilicate minerals. This would necessarily involve the release of aluminium. Use of XRD experimental techniques would also have been useful in identifying the actual mineralogy of these alteration products and may have been able to provide evidence to back up a



Plate 6.61.1: Instability of feldspar in a soil thin section from site 10. XPL, x4 Mag.



Plate 6.61.2: Instability of biotite from a soil thin section from site 2.. PPL, x4 Mag.



Plate 6.61.3: Alteration of a ferromagnesian mineral from a soil thin section from site 2. PPL, x2 Mag.



Plate 6.61.4: Crossed polarised view of above.

mineralogical control on the solubility of aluminium in soil solutions. The results also find agreement with McMahon and Neal (1990) who suggested that the regulation of aluminium in both stream and soil waters from 3 Scottish catchments was controlled by non-equilibrium weathering reactions rather than expected mineral equilibrium solubility processes.

6.7 CONCLUSIONS

Aluminium in soil waters was greatly affected by the presence of organic compounds. DOC affected both the amount of aluminium in soil solutions and the form in which it was present.

1. Total aluminium concentrations were greater in solutions with higher DOC.
2. A smaller proportion of total aluminium was filterable (soluble) in solutions with a higher DOC content.
3. Potentially toxic aluminium identified using dialysis made up a lower proportion of total aluminium where soil solution DOC was higher.
4. In DOC rich waters greater proportions of aluminium were found to be exchangeable with respect to a strongly acidic cation exchange resin.
5. High DOC concentrations were shown to decrease the likelihood of the formation of HAS species in soil waters.
6. Finally DOC was shown to cause 'soluble' aluminium results to deviate from suggested solubility controls.

Geological controls on the concentration of aluminium within the soil waters were obscured by high concentrations of DOC within the waters. The total silicon results,

however, suggested a relationship with mineral weathering potential i.e the form of silicon in the two different rock types tested. This result is important but in no way conclusive. Much greater sampling of soil water silicon associated with other parent materials would be necessary before any strong link was confirmed.

Silicon in soil waters did not appear to be exclusively in the form of silicic acid. Dialysis, filtration and retention of silicic acid on exchange resins suggested the presence of silicon in other forms.

Any effects of silicon on soil water aluminium was difficult to distinguish because of the nature of the waters. The presence of DOC in high concentrations in all samples obscured the chance of discovering any relationship. Further work on soil solutions with low DOC would be required before any relationship could be defined.

The deviation of results from $\text{Al}(\text{OH})_3$ solubility controls gives further evidence to the need of future acidification models to resist in relying on $\text{Al}(\text{OH})_3$ as a control of Al in solution. The importance of the organic component in these soil waters clearly caused deviation from mineralic solubility controls although as this section evidence showed, the dissolution of minerals within the soil zone was important. Further attempts at modelling the effects of acid deposition must surely take these factors into account.

Chapter 7: Conclusions

7.1 Overview of aims

Welsh and Burns (1987) reported a geological control on surface water chemistry in the Loch Dee area at stream baseflow conditions. They indicated that waters draining sediments and meta-sediments of the White Laggan sub-catchment were of a better water quality than those draining the rocks of the Loch Doon pluton. The black shales in the Dargall Lane sub-catchment gave rise to the most acidic, poor quality waters. This project aimed to determine how real this control was, whether the geology of the catchment influenced the soil and soil water chemistry and if there was any link between catchment geology and the release of potentially toxic aluminium to the aquatic environment.

7.2 Geology

The solid geology of the Loch Dee area is dominated to the north by rocks of the Loch Doon pluton and Ordovician / Silurian sediments and meta-sediments to the south. The plutonic rocks include granodiorites and diorites; the diorites represent the southern most extension of the pluton. Mineralogical variations not previously registered in the granodiorites were accounted for by the presence of acidic dykes in the plutonic mass. The chemistry of the diorites was found to vary systematically on a small scale of observation; mineralogy also differed between specimens. The meta-sediments to the south were split into coarse and fine meta-sediments on chemical grounds. Coarse meta-sediments included greywackes and gritstones whilst fine meta-sediments included shales and mudstones. The sediments and meta-sediments exhibited

varying degrees of metamorphism which was often more clearly manifested in fine grained rocks by the formation of a fabric. The degree of metamorphism did not appear to be related to the proximity of the pluton which was explained by a pre-pluton regional phase of metamorphism . A swarm of highly variable dykes including porphyrites, lamprophyres, acid and basic dykes intrude the meta-sediments. These were found to be especially common to the south of the catchment. On the heights of Curleywee to the west and to a lesser extent on the White Hill black shales were present. These were typically tightly folded and of limited outcrop. All sediments and meta-sediments (including the black shales) included chemical variations that were explained by source variability and metamorphic changes.

All rock types sampled were chemically different. The igneous rocks were enriched in bases relative to the meta-sediments. Sums of basic oxides (calcium, magnesium, sodium and potassium) in the igneous rocks ranged between 13.7 and 16.6 weight % whilst in the sediments the range was 3.84 - 12.5%. The black shales and coarse meta-sediments were especially rich in silica, 84.8% and 77.6% respectively and deplete in bases, 3.84% and 6.39% respectively. Greatest Al_2O_3 concentrations were found in the shales at 17.7%, similar to 15-17% found in the range of igneous rock types. These shales were also enriched in Fe_2O_3 and MgO. Chemical differences in the rocks were expected to be relayed to soils forming from them.

Weathered samples of these rock types were analysed. Losses on weathering relative to fresh samples were assessed using zircon and TiO_2 as internal standards. This indicated greatest losses from granodiorites and coarse meta-sediments which

supported to a certain extent the proposed geological control of Welsh and Burns (1987). Initially these results appeared to conflict with theoretical mineral weathering implications of Goldich (1938). Weathering according to the Goldich scheme would have released greater quantities of bases from minerals that were more unstable at earth surface conditions. These minerals include those formed at higher temperatures e.g. olivines, pyroxenes and calcic plagioclase which were concentrated in the dioritic rocks. The results of the study, however, were reconciled with the work of Goldich through the concept of weathering rate. The dioritic rocks were initially more susceptible to weathering and form the low lying land in the area. However, now the initial rate of weathering has decreased and originally less susceptible sediments and meta-sediments are the source of base materials to the area.

Drift geology in the vicinity of Loch Dee area was reported to include boulder clay and moraines. Only morainic material was sampled. Textural investigations on the coarse fraction of this drift indicated a mixing of solid geological components. Drift material < 2mm in size appeared to show some spatial differences in chemistry and texture. However, the sample population was too small to be certain of this feature.

7.3 Soil studies and implications

The soils studied in the area included peaty podzols, peaty gleys, peats and ranker soils. Ranker soils were sampled most frequently and probably represented the most commonly occurring soil type. Soils in general were poorly differentiated into horizons although there was usually a distinct organic and mineral horizon.

Organic matter was important in the control of cation exchange reactions in the organic soils. Organic matter in these soils ranged between 23% and 80% with the organic rich soils typically retaining more moisture in the field. Organic soils also typically contained greater exchangeable bases and acidity than the mineral soils probably due to this greater organic component. Exchangeable aluminium, however, was often greater in mineral soil horizons. Organic matter also appeared to have some influence on cation exchange reactions in the mineral horizons. However, in the case of these soils organic matter was not the sole influence. Mineral soil exchangeable calcium was correlated with exchangeable magnesium. This feature is common in igneous rocks.

Generally the soils were of low pH and base saturation and included high concentrations of aluminium on the exchange complex. These features highlighted the acidified nature of the catchment and indicated low potential for the neutralisation of inputs of H^+ ions from the atmosphere.

Chemical analysis of soil horizons indicated some chemical differences due to soil profile type. These included greater concentrations of exchangeable hydrogen and aluminium and pyrophosphate extractable iron in podzolic profiles. Other soil chemical features appeared to be more related to site specific controls. Organic soils formed at site 7, were typified by low LOI and exchangeable hydrogen concentrations whilst the mineral soils had low CEC and exchangeable aluminium. Some of these features may have been related to the high altitude of this soil site e.g. low LOI and exchangeable hydrogen in the organic soils due to the severity of weather conditions.

The mineral soils were not chemically differentiated in terms of geological input. However, textural differences were noted according to rock type. These highlighted the importance of the coarse fraction in soils associated with granodioritic geology. However, textural classification of the soils was not affected by geology types with most mineral soils tested falling into the category of sand, sandy loams and loamy sands.

The absence of chemical differences in the soils associated with contrasting rock types was explained by the presence of drift material of mixed composition. The importance of this morainic drift component in the soil parent material was highlighted by the chemical proximity of mean mineral soil and mean drift exchangeable calcium, magnesium, potassium and hydrogen. The mineral soils and drift samples also appeared to be related in terms of texture.

Soil thin section evidence, however, indicated that this drift material was not uniformly present. Soils from sites 1, 3 and 7 included mineralic fragments of both igneous and sedimentary origin that were present in different areas of the catchment. This mixing of solid geology types was most pronounced in the soils from site 7, the site at the greatest altitude. Mineral soils from site 2 and 6 involved only mineralic fractions from their respective solid geologies and included no evidence for the input of drift material. Soils from site 5 and 10 included mineralogic components that indicated a mixed geological input. However, it was possible to explain this in terms of mixing of two proximal geology types at sites where minor igneous intrusions invaded meta-sediments.

Soil micromorphological thin section analysis also highlighted the process of organic matter movement down the soil profile at podzol sites. It was postulated that this movement may have been associated with the movement of iron and/or aluminium through the soil profile.

7.4 Soil water studies

Soil solutions were extracted from organic and mineral soils by centrifuge methods. Organic soil waters often showed greater concentrations of many chemical components than the mineral soils. Greater organic soil potassium, nitrate and DOC were ascribed to greater biological activity in the surface horizons.

The chemistry of the soil solutions was monitored through time and found to be greatly affected by atmospheric inputs. Soil water sodium, magnesium, chloride and potassium were all, at least partly, determined by fluctuations in the concentrations present in atmospheric precipitation and also by the amount of precipitation the catchment received. Sodium and chloride were especially important in the soil waters because of the strong maritime influence the catchment receives. Consequently soil waters had winter peaks in sodium, chloride, magnesium and potassium when rainfall was most common. However, sodium and chloride were typically low throughout the drier summer months but tended to increase to a lesser concentration peak at the end of summer due to an evaporative concentration effect. This was also true for potassium. Fluoride showed a similar response to chloride but there was no data available to compare this with rainwater chemistry. Magnesium typically had an additional peak in summer related to this concentration and drying effect but also

possibly weathering. Most of these atmospherically induced chemical effects were found in both the organic and mineral soil waters. Potassium peaks, however, were less well defined in the case of the mineral soil waters.

Soil water pH was typically lower throughout the summer period. In most of the soil waters this increased sharply after a severe storm in mid October 1991. This pH increase corresponded to a similar peak in rainfall and was explained by the soil water sampled reflecting sea salts in the rainfall before exchange had chance to occur.

Aluminium, iron and DOC were related in terms of seasonal response in the soil waters at many sites, all peaking in late summer due to a temperature related concentration and flushing effect. Despite this common peak, however, iron was typically highly variable among the soil sites. Soil water sulphate was also typically variable among the soil sites and it was difficult to determine any common responses. This anion did not appear to be mobile in the catchment as a whole which was opposed to the typically organic nature of many of the soils in the catchment. However, it has been suggested that the presence of iron and aluminium oxides may promote the retention of sulphate and it is possible that this is what happens in some of the soils at Loch Dee. However, data was not available to support or deny this process.

The chemistry of the soil waters showed some variability related to soil profile type. This included higher iron contents in soil waters from podzolic profiles and higher aluminium content in soil waters from gleyed profiles.

Soil water chemistry also appeared to be related, to some degree, to geological inputs. Waters extracted from soils overlying black shales were low in DOC, exchangeable hydrogen and iron. These features, however, were common to both organic and mineral horizons and were better explained by soil site altitude rather than the presence of the black shales. Soil waters extracted from soils overlying diorites had greater concentrations of aluminium throughout the monitoring period. At base flow conditions this feature of high aluminium concentration was also found in soil waters related to granodiorites and both were investigated in greater detail.

7.5 Soil water aluminium form and relationships.

Soil waters extracted from soils overlying diorites had greater silicon concentrations than those from soils overlying granodiorites. This was consistent with a geological influence implicated by a Goldich style weathering scenario. The amount of total aluminium present in soil waters did not appear to be affected by the presence of this silicon.

Soil water aluminium concentration appeared to be closely related to the presence of organic compounds. Soil waters with higher DOC concentrations were typically richer in total aluminium which can be explained in two ways. Firstly, the presence of organic acids in soils can significantly increase the rate of mineral weathering. Secondly, organic compounds have a great affinity for aluminium tending to retain it in solution.

The presence of organic compounds influenced the form of aluminium in the soil

waters. In some cases large fractions of aluminium was removed by a 0.45µm filter in waters associated with high DOC concentrations. Also the fraction of aluminium small enough to pass through a dialysis membrane (estimated at 2.4 nm, MWCO 12000) decreased in the presence of high concentrations of DOC. Cation exchange resins with strongly acidic functional groups extracted a larger quantity of exchangeable aluminium where soil water DOC concentrations were greater. This implied a greater attraction of the resin bound sulphonic acid groupings for the trivalent alumino ion than was offered by the organic complexes. This was not the case when the same soil waters were tested with cation exchange resins with a weaker functional group.

Soil waters with lower concentrations of DOC may have experienced some control on the form of aluminium present by silicon. It appeared that soil waters with greater silicon concentrations and low DOC were associated with lower amounts of small and potentially toxic aluminium extracted by methods of dialysis; this could have been accounted for by the formation of hydroxyaluminosilicate species which has been suggested as a mechanism for the amelioration of the toxicity of aluminium to fish (Exley and Birchall 1991). However, the data set was too small to be conclusive and much more work would be necessary to establish the validity of such a statement.

The formation of HAS species such as proto-imogolite or allophane was reported by Farmer et al (1980) as a method of aluminium mobilisation within the soil profile leading ultimately to podsolisation. Resin elution indicated the possible occurrence of HAS species with Si:Al of 0.5 (i.e. similar to imogolite) in the soil waters at Loch

Dee, although the evidence was not conclusive. Other soil water chemical parameters including DOC, sodium concentration and iron concentration, however, indicated that if HAS species were present in the soil water they would probably be poorly ordered species similar to proto-imogolite or proto-imogolite allophane. Although imogolite has not been reported from the soil profiles at Loch Dee it is possible that in addition to the transport of aluminium and iron through the soil profile in association with organic matter (as seen in thin section) proto-imogolite allophane acts to move aluminium through the soil profile and promote podsolisation.

Solubility controls on the aluminium in the soil waters tended to deviate from common $\text{Al}(\text{OH})_3$ models. This was explained by the presence of organic complexes and also the fluoride component of some of the soil waters was great enough to elevate solubility from that controlled by crystalline or amorphous gibbsite alone. The fraction of aluminium small enough to enter a dialysis membrane corresponded to solubility control dictated by an amorphous form of $\text{Al}(\text{OH})_3$.

The aluminium and silicon present in soil waters were also tested against graphical data for aluminosilicate mineral solubility controls. In this case the dialysis results corresponded to solubility controlled by an amorphous ideal aluminosilicate mineral. Thin section evidence indicated the weathering of mineral material in the soil which may have had an influence on the solubility of aluminium present in the soil solution. However, this comparison of data with two types of mineral solubility controls served to highlight the weakness of such approaches. The aluminium present in the soil solutions appeared to be a function of mineral weathering although because of the presence of organic and inorganic complexes it was difficult to determine the exact

source of this aluminium.

7.6 Overview

Baseflow surface water chemistry described by Welsh and Burns as ascribable to catchment geology was difficult to reconcile. Rock weathering investigations were in support of the findings of these authors. However, geological characteristics were typically not related to soils due to a large and variable drift component in the area. This, in itself, indicated the use of a selective catchment liming programme based on solid geology would be difficult to implement. Higher soil water aluminium concentrations were associated with the diorites and granodiorites of the area which could account for the relationship of these rock types with poorer water qualities. The poorest water qualities associated by Welsh and Burns with the black shales may be more directly related to sub-catchment topography than geology.

Methods devised for the recognition of hydroxyaluminosilicate silicate species in synthetic solutions were less conclusive in soil solutions due to the presence of many interfering ions. However, the presence of unordered HAS species like proto-imogolite and proto-imogolite allophane could not be ruled out in the Loch Dee catchment. Their presence could be important in the transfer of aluminium through the soil profile in the process of podsolisation.

Soil thin sections indicated the presence of decaying aluminosilicate minerals which presumably provided some sort of solubility control for aluminium. However, most of the work on the aluminium species in the soil waters highlighted the strong association between aluminium and organic compounds, a feature which masked any geological influence.

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Appendix A

The table shows the grid reference, sample name and rock type for the solid geology.

Sample no.	Grid ref.	Rock type	Sample no.	Grid ref.	Rock type
7/1	46377784	Diorite	1b3	47327614	Greywacke
5/1	46837726		2b3	47337608	Shale
4/1	46817720	Diorite	3b3	47387717	Greywacke
9/1	46487832	Diorite	4b3	46507680	Shale
1HR	47097845	Diorite	5b3	46167651	mudstone
2HR	47847883	Diorite	6b3	45817767	blackshale
3HR	46847816	Diorite	7b3	49817950	Greywacke
4HR	46957799	Diorite	8b3	47127719	Greywacke
5HR	47237861	Diorite	9b3	45837610	Dyke
6HR	47697845	Diorite	10b3	45787602	Mudstone
7HR	46507767	Q/diorite	11b3	45787612	Mudstone
8HR	47687868	Q/diorite	1BS	45727728	Blackshale
MS1	46937621		2BS	45727771	Blackshale
MS2	46937621	Greywacke	3BS	45737716	Blackshale
2GD	49147989	G/diorite	1b4	47427640	Greywacke
3GD	49157984	G/diorite	2b4	47417640	Greywacke
4GD	49077987	G/diorite	3b4	47577682	Shale
1LD	46307659	Dyke	4b4	47547662	Greywacke
5LD/pd	45897625	Porphyry	5b4	47517655	Mudstone
6LD	46077641	Dyke rock	6b4	46717632	Shale
7LD	45827611	Acid dyke	7b4	47007624	Greywacke
1PD	45927628	Porphyry	8b4	46877624	Greywacke
3GR	46037648	G/diorite	2LD/b3	45717649	Greywacke
4GR	45947638	G/diorite	3LD/b3	45667642	Greywacke
2PD/b3	46077605	Greywacke	4LD/b3	45627629	Greywacke
3PDA	47417767	Greywacke	1GR/b3	45747660	Greywacke
3PDB	47417767		2GR/b3	45767669	Greywacke

Appendix B

The following tables show the results for the major and trace oxides for the different rock types. Tables B:1 and B:2 show the major weight % oxide results for the diorite samples.

Table B:1

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
7/1	59.89	15.76	6.00	5.74	5.45
4/1	60.42	16.14	5.16	4.78	5.19
9/1	59.49	15.76	5.96	5.33	5.29
1HR	59.66	15.64	6.11	5.57	5.26
2HR	61.34	15.38	5.33	4.54	4.38
3HR	59.03	15.60	6.18	6.38	5.64
4HR	59.86	15.33	6.01	5.78	5.26
5HR	58.75	15.43	6.12	6.29	5.33
6HR	60.51	15.65	5.83	5.41	5.10
7HR	61.72	15.03	5.45	5.52	4.85
8HR	59.91	15.30	5.74	5.50	5.09
5/1	59.79	15.93	5.03	6.06	2.4

Table B:2

	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
7/1	3.72	2.36	0.87	0.10	0.24
4/1	3.84	2.35	0.88	0.08	0.25
9/1	3.56	2.58	0.92	0.09	0.27
1HR	3.53	2.52	0.96	0.10	0.23
2HR	3.61	3.03	0.89	0.08	0.23
3HR	3.49	2.17	0.81	0.11	0.24
4HR	3.51	2.54	0.96	0.10	0.25
5HR	3.46	2.16	0.81	0.10	0.22
6HR	3.69	2.12	0.81	0.10	0.20
7HR	3.59	2.46	0.80	0.09	0.20
8HR	3.59	2.61	0.88	0.09	0.24
5/1	2.77	4.23	0.88	0.05	0.22

Tables B:3, B:4 and B:5 give the trace element results for the diorite rocks in mg/L.

Table B:3

	Ni	Cr	V	Sc	Cu	Zn
Mean	132	243	124	19	24	55
7/1	125	223	119	18	19	57
4/1	129	248	129	19	19	60
9/1	127	265	137	21	35	61
1HR	119	218	121	17	16	55
2HR	108	209	120	18	25	58
3HR	147	273	117	21	22	56
4HR	126	232	120	18	34	54
5HR	156	285	115	17	21	54
6HR	114	216	117	19	23	55
7HR	145	247	110	16	16	53
8HR	135	253	132	18	26	58
5/1	155	334*	146	23	14	43

*not included in mean calculation.

Table B:4

	Sr	Rb	Zr	Nb	Ba	Pb
Mean	601	75	183	10	970	15
7/1	696	70	187	10	1050	18
4/1	629	65	175	8	886	13
9/1	699	82	186	10	1092	15
1HR	649	78	187	11	1015	15
2HR	566	99	230	13	968	19
3HR	712	59	154	9	950	13
4HR	657	76	213	10	1049	17
5HR	701	61	152	8	957	14
6HR	599	60	156	9	856	13
7HR	564	75	190	10	873	15
8HR	641	83	179	11	1038	17
5/1	474*	97	191	9	900	11

* not included in the mean calculation

Table B:5

	Th	La	Ce	Nd	Y
Mean	8	27	60	26	20
7/1	7	29	61	26	20
4/1	6	28	61	26	19
9/1	9	27	65	28	21
1HR	8	27	62	27	21
2HR	12	31	68	28	22
3HR	5	24	54	25	19
4HR	8	27	65	28	21
5HR	6	24	52	23	17
6HR	6	25	52	23	19
7HR	8	28	55	24	20
8HR	10	26	61	27	20
5/1	7	26	59	25	17

Tables B:6 and B:7 show the results for the major weight % oxides in the granodiorites (both the major and minor intrusions).

Table B:6

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
2GD	63.25	15.27	4.74	3.78	3.63
3GD	64.63	16.10	4.64	3.40	1.07
4GD	63.37	15.20	3.73	3.56	3.56
3GR	62.36	17.59	4.05	3.23	4.59
4GR	63.35	15.67	4.92	4.24	4.43

Table B:7

	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
2GD	3.61	3.19	0.74	0.08	0.19
3GD	3.38	3.21	0.74	0.02	0.19
4GD	3.52	3.39	0.74	0.08	0.19
3GR	4.08	1.99	0.59	0.06	0.14
4GR	3.91	2.19	0.70	0.09	0.18

Tables B:8, B:9 and B:10 give the results for the trace element content of the granodioritic rocks in mg/L.

Table B:8

	Ni	Cr	V	Sc	Cu	Zn
Mean M	75	159	100	15	13	53
Mean m	47	153	100	17	12	48
2GD	77	175	107	17	10	56
3GD	72	157	102	13	10	53
4GD	76	145	90	16	16	50
3GR	39	143	96	17	9	39
4GR	54	162	104	17	14	56

M = Major (GD) m = minor (GR).

Table B:9

	Sr	Rb	Zr	Nb	Ba	Pb
Mean M	463	104	204	12	975	16
Mean m	639	54	185	12	766	8
2GD	516	101	197	12	937	16
3GD	383	99	205	12	1114	13
4GD	489	111	209	13	875	18
3GR	705	52	181	7	736	5
4GR	572	55	188	9	795	11

M = Major (GD) m = minor (GR).

Table B:10

	Th	La	Ce	Nd	Y
Mean M	13	28	65	27	20
Mean m	6	23	51	23	18
2GD	10	26	61	25	20
3GD	14	28	63	27	20
4GD	16	30	70	28	20
3GR	5	22	51	23	17
4GR	7	23	51	22	18

M = Major (GD) m = minor (GR).

Tables B:11 and B:12 give the major weight % oxide content of the coarse metasediments.

Table B:11

	SiO ₂	Al ₂ O ₃	FeO ₂	MgO	CaO
1b3	74.34	9.80	4.18	2.01	2.50
1b3	78.77	8.80	3.78	1.83	1.14
7b3	77.17	9.63	4.04	2.09	1.02
8b3	77.94	9.53	3.83	1.70	0.68
1b4	77.73	9.04	4.09	1.87	1.29
2b4	78.71	8.84	4.03	1.46	0.80
4b4	81.41	7.80	3.66	1.70	0.22
7b4	76.32	9.99	4.56	1.73	0.80
8b4	77.91	9.30	4.28	1.70	0.82
MS2	79.30	8.93	3.98	1.71	0.26
2LD(b3)	78.66	9.06	4.06	1.82	0.85
3LD(b3)	74.66	10.93	4.65	1.95	1.43
4LD(b3)	79.09	9.06	4.07	1.73	0.93
1GR(b3)	77.74	9.47	4.18	1.81	0.87
2GR(b3)	72.03	11.39	5.15	3.05	1.43
3PD(b3)	78.72	8.26	3.49	1.93	2.43
3PD(b3)	78.34	9.20	3.93	2.05	1.01

Table B:12

	MnO	P ₂ O ₅	TiO ₂	MgO	F ₂ O ₃
1b3	2.12	1.34	0.81	0.06	0.14
1b3	2.14	1.38	0.84	0.05	0.12
7b3	2.02	1.21	0.80	0.05	0.11
8b3	2.24	1.62	0.86	0.03	0.12
1b4	1.97	1.16	1.10	0.07	0.22
2b4	2.01	1.42	1.14	0.04	0.18
4b4	1.16	1.64	0.54	0.04	0.10
7b4	2.14	1.46	0.94	0.05	0.15
8b4	1.88	1.45	0.85	0.04	0.12
MS2	1.49	1.57	0.90	0.03	0.13
2LD(b3)	2.09	1.40	0.86	0.04	0.12
3LD(b3)	2.26	1.86	0.89	0.07	0.14
4LD(b3)	2.12	1.22	0.89	0.04	0.12
1GR(b3)	2.14	1.44	0.85	0.05	0.13
2GR(b3)	2.27	2.00	0.90	0.06	0.16
3PD(b3)	1.31	1.01	0.73	0.09	0.11
3PD(b3)	2.03	1.43	0.80	0.04	0.13

Tables B:13, B:14 and B:15 show the results for the trace element analyses for the coarse metasediments in mg/L.

Table B:13

	Ni	Cr	V	Sc	Cu	Zn
Mean	38	67	74	13	6	50
1b3	42	71	75	13	9	53
3b3	39	62	67	11	14	48
7b3	39	73	75	12	0	48
8b3	36	63	75	11	0	42
1b4	33	64	73	13	7	50
2b4	31	80	72	12	7	37
4b4	31	66	82	11	8	37
7b4	34	67	82	12	7	56
8b4	35	65	75	11	8	55
2LD(b3)	34	62	74	11	3	50
3LD(b3)	38	71	86	15	6	54
4LD(b3)	33	75	76	11	6	45
1GR(b3)	36	65	73	11	9	54
2GR(b3)	65	113	96	16	13	67
2PD(b3)	167*	348*	110	20	3	66
3PD(b3)	44	71	73	12	10	52
MS2	36	72	75	11	0	42

* not used in mean calculation

Table B:14

	Sr	Rb	Zr	Nb	Ba	Pb
Mean	95	52	279	13	299	12
1b3	132	54	252	14	275	10
3b3	106	55	284	15	258	12
7b3	84	42	232	15	243	11
8b3	85	52	254	16	302	14
1b4	97	44	413	18	238	14
2b4	90	47	539	18	286	10
4b4	37*	54	139	9	296	16
7b4	95	53	303	17	343	14
8b4	95	48	253	14	355	10
MS2	43*	46	300	15	261	5
2LD(b3)	73	46	247	15	334	11
3LD(b3)	127	66	248	16	361	14
4LD(b3)	91	41	286	14	303	10
1GR(b3)	75	48	276	16	307	12
2GR(b3)	104	70	267	17	400	14
2PD(b3)	77	77	190	11	265	15
3PDA(b3)	100	48	254	14	262	9

* Not used in mean calculation

Table B:15

	Th	La	Ce	Nd	Y
Mean	10	29	61	27	21
1b3	11	27	66	29	22
3b3	10	25	56	25	21
7b3	11	31	62	24	21
8b3	11	28	68	28	21
1b4	12	41	83	36	29
2b4	11	31	75	31	28
4b4	7	25	50	23	15
7b4	12	29	71	29	25
8b4	10	32	62	29	24
MS2	12	26	59	24	20
2LD(b3)	9	27	59	26	21
3LD(b3)	9	32	69	29	26
4LD(b3)	11	28	59	26	21
1GR(b3)	11	29	65	28	21
2GR(b3)	13	34	75	31	26
2PD(b3)	10	24	53	23	19
3PDA(b3)	10	27	60	25	20

Tables B:16 and B:17 contain the results for the major weight % oxides of the dyke rocks.

Table B:16

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
9b3	61.57	18.29	4.74	1.73	4.17
1LD	52.34	14.55	7.93	9.33	7.33
5LD(PD)	57.97	15.04	6.32	6.39	5.72
6LD	61.63	18.42	4.79	1.75	4.09
7LD	59.38	19.85	3.67	2.52	6.00
1PD	57.56	15.02	6.28	6.40	5.91

Table B:17

	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
9b3	4.01	2.93	0.55	0.13	0.23
1LD	2.80	2.15	1.07	0.14	0.32
5LD(PD)	3.30	2.30	1.00	0.11	0.22
6LD	3.70	2.68	0.55	0.12	0.24
7LD	3.50	2.42	0.62	0.07	0.15
1PD	3.51	2.16	1.00	0.11	0.22

Tables B:18, B:19 and B:20 give the trace element analysis of the dyke rocks in mg/L. In these tables the mean results for the dyke rocks are not given due to the number of different dyke types.

Table B:18

	Ni	Cr	V	Sc	Cu	Zn
9b3	14	7	71	12	0	65
1LD	215	630	196	33	22	72
5LD(PD)	142	325	145	24	28	61
6LD	12	6	74	10	0	53
7LD	21	27	93	18	0	39
1PD	141	321	148	24	27	59

Table B:19

	Sr	Rb	Zr	Nb	Ba	Pb
9b3	863	82	220	9	1002	13
1LD	1112	38	218	9	1848	1
5LD/PD	528	62	207	11	695	9
6LD	790	66	210	8	899	11
7LD	850	81	159	8	632	6
1PD	526	59	205	11	701	11

Table B:20

	Th	La	Ce	Nd	Y
9b3	7	34	72	30	19
1LD	0	16	40	20	20
5LD(PD)	7	48	23	22	21
6LD	6	28	66	28	19
7LD	5	17	47	19	16
1PD	8	23	51	23	21

Tables B:21 and B:22 exhibit the major weight % oxide content of the black shales.

Table B:21

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
6b3	78.59	9.35	3.64	1.72	0.90
1BS	84.34	6.52	1.74	1.06	0.74
2BS	88.72	4.40	1.67	0.44	0.19
3BS	87.60	5.56	1.48	0.60	0.15

Table B:22

	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
6b3	1.26	1.89	0.45	0.02	0.04
1BS	0.20	1.68	0.31	0.02	0.20
2BS	0.20	1.79	0.23	0.01	0.02
3BS	0.23	2.28	0.28	0.03	0.03

Tables B:23, B:24 and B:25 gives the trace element content of the black shales in mg/L.

Table B:23

	Ni	Cr	V	Sc	Cu	Zn
Mean	26	61	265	11	25	32
6b3	13	83	202	15	16	47
1BS	34	66	239	11	39	25
2BS	15	38	348	8	7	21
3BS	42	55	271	9	38	33

Table B:24

	Sr	Rb	Zr	Nb	Ba	Pb
Mean	70	60	68	7	259	30
6b3	106	55	104	10	354	22
1BS	91	65	69	7	202	24
2BS	49	47	44	5	186	44
3BS	35	74	53	6	292	29

Table B:25

	Th	La	Ce	Nd	Y
Mean	8	15	35	17	18
6b3	8	21	46	21	17
1BS	9	18	41	21	26
2BS	6	9	23	12	14
3BS	7	13	31	14	16

Tables B:26 and B:27 give the major weight % oxide results for the fine metasediments.

Table B:26

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
2b3	57.29	18.08	8.78	5.25	0.32
4b3	57.29	18.89	9.58	6.73	0.86
5b3	61.15	15.13	7.31	5.56	2.51
10b3	56.53	17.80	8.31	6.56	0.77
11b3	57.83	16.43	8.42	6.14	1.76
3b4	58.83	16.65	7.86	5.83	1.82
5b4	56.71	19.89	8.38	3.73	0.60
6b4	52.06	18.92	9.64	7.77	0.78

Table B:27

	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
2b3	2.01	3.18	0.95	0.07	0.18
4b3	1.00	3.04	0.89	0.06	0.15
5b3	1.91	3.14	0.86	0.10	0.15
10b3	1.95	3.71	0.90	0.10	0.16
11b3	2.03	3.13	0.88	0.08	0.17
3b4	2.63	3.20	0.87	0.08	0.16
5b4	1.78	4.12	0.88	0.09	0.13
6b4	1.81	3.79	0.91	0.09	0.14

Tables B:28, B:29 and B:30 give the trace element measurements of the fine metasediments in mg/L.

Table B:28

	Ni	Cr	V	Sc	Cu	Zn
Mean	186	248	159	26	41	110
2b3	133	218	157	23	28	90
4b3	216	256	178	29	52	120
5b3	176	307	138	23	43	92
10b3	178	272	158	26	40	120
11b3	188	253	146	25	40	102
3b4	186	253	146	25	34	82
5b4	67*	153	162	25	33	120
6b4	225	269	183	28	58	151

* Not included in the mean calculation

Table B:29

	Sr	Rb	Zr	Nb	Ba	Pb
Mean	113	125	183	15	522	20
2b3	113	114	199	16	548	6
4b3	94	117	156	16	597	16
5b3	133	122	217	14	360	19
10b3	58	130	176	16	643	19
11b3	109	116	174	14	398	20
3b4	140	112	185	14	482	18
5b4	157	163	200	20	686	31
6b4	96	123	158	16	464	27

Table B:30

	Th	La	Ce	Nd	Y
Mean	13	34	72	29	27
2b3	13	37	81	32	27
4b3	14	36	75	30	26
5b3	13	34	69	29	26
10b3	13	34	69	28	25
11b3	13	29	65	27	27
3b4	12	34	69	27	25
5b4	17	38	79	33	31
6b4	12	29	71	29	25

Tables B:31 and B:32 give the major weight % oxides for the none classed samples.

Table B:31

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO
3PDB	69.26	15.23	2.47	0.72	1.97
MS1	72.31	15.56	1.60	0.67	0.26

Table B:32

	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅
3PDB	3.73	2.92	0.35	0.07	0.09
MS1	3.13	3.62	0.31	0.03	0.05

Tables B:33, B:34 and B:35 give the trace element concentrations in mg/L for the samples that remain 'unclassified'.

Table B:33

	Ni	Cr	V	Sc	Cu	Zn
3PDB	17	17	44	7	0	26
MS1	12	14	40	5	0	18

Table B:34

	Sr	Rb	Zr	Nb	Ba	Pb
3PDB	268	101	161	9	672	16
MS1	179	123	146	10	525	24

Table B:35

	Th	La	Ce	Nd	Y
3PDB	17	24	51	18	14
MS1	17	25	49	17	11

Appendix C - Mineralogy and classification

The mineralogy and classification of the igneous rocks can be tabulated to give a better idea of constituents.

Table C:1 shows the main mineralogy of the dioritic rocks and the degree of alteration.

Table C:1

	Comments	Mineralogy	Abundance	Alterati on class
9/ 1	Plagioclase at sodic end of andesine.	Andesine Pyroxenes Biotite Kspar and Quartz	45 - 50% 30 % 10 - 15% 10%	1 1 0 0
7/ 1	Plag often forms mymerkytic intergrowths with Qtz. Opx typically mosaiced. Px altered at edges to chlorite. Common exsolution textures in px.	Andesine Pyroxenes Biotite Kspar + Quartz	50 - 55% c. 25% c. 15% 5-10%	1 1 0 0
4/ 1	Alteration in px obviously chloritic. Occasional zoned feldspar crystals.	Andesine Pyroxenes Biotite Kspar + Quartz	50% 30% 10 - 15% 5 - 10%	<2 2 0 0
1H R	Pyroxenes lack exsolution textures and twinning. Plag twinning poorly defined; some oscillatory zonation apparent.	Andesine Pyroxenes Biotite Kspar + Quartz Minors	45 - 50 % 20 - 25% 10 - 15% 10 - 15% 2 - 5%	<2 <1 0 0 -
2H R	Biotite present in greater abundance. Pyroxenes heavily altered possibly to chlorite and green hornblende in the form of a corona texture. Feldspar laths typically smaller than ferromag minerals.	Andesine Pyroxenes Biotite Kspar + Quartz Px alteration	35 - 40% 10 - 15% 25% 15% 5 - 15%	<3 <4 0 0 -
3H R	Occasional overgrowth of green hornblende on opx.	Andesine Pyroxenes Biotite Kspar + Quartz	40 - 45% 25 - 30% 10 - 15% 15%	<2 <2 0 0
4H R	Pyroxenes occasionally show exsolution features and twinning. Hbl overgrowth apparent.	Andesine Pyroxenes Biotite Kspar + Quartz	45% 30% 10% 15%	<2 <1 0 0
5H R	Pyroxenes more abundant than in previous samples.	Andesine Pyroxenes Biotite Kspar + Quartz Opaques and apatite	42 - 45% 30 - 35% 10% 10% 3%	1 2 0 0 -
6H R		Andesine Pyroxenes Biotite Kspar + Quartz Opaques	45 - 50% 25 - 30% 15% 5 - 10% 2%	2 1-2 0 0 -
7H R	Plag shows compositional zoning in addition to multiple twinning.	Andesine Pyroxenes Biotite Kspar + Quartz	45% 20 - 25% 15 - 20% 10 - 15%	1 1-2 0 0
8H R	Cpx often twinned and small in size. Biotite associated with pleochroic haloes. Andesine at more calcic end.	Andesine Pyroxenes Biotite Kspar + Quartz Opaques	40% 25% 20 - 25% 10% 3%	2 2-3 0-1 0 -
5/ 1	Heavily altered - possible original pyroxene mineral replaced by chlorite.	Biotite Plagioclase Chlorite Pyroxenes Quartz Hornblende	Difficult to determine;	All mins alter- ed.

Table C:2 shows the main type, abundance and degree of alteration of the minerals in the granodiorites associated with both the Loch Doon pluton and those from a minor intrusion in the south.

Table C:2

	Comments	minerals	Abundance	Alteration class
2GD	Quartz very prominent. Amphibole probably hornblende. Plag zoned in range andesine to oligoclase.	Oligoclase Biotite Amphibole Kspar + Quartz	35% 18% 18% 27%	>2 0 1-2 <2 0
3GD	Composition of plag indeterminate due to alteration. Amphibole mineral is green.	Plagioclase Amphibole Kspar + Quartz	45% 25% 30%	<3 1 <2 0
4GD	Plag in the range andesine to oligoclase. Amphibole shows pleochroism in shades of green.	Oligoclase Biotite Amphibole Kspar + Quartz	30% 20% 16% 34%	<2 0 1 1 0
3GR	Plag is typically twinned although can show zoning - alteration is very great. Amphibole is green.	Andesine Amphibole Biotite Kspar + Quartz	45% 25% 10% 20%	<3 <3 1 <2 0
4GR	Plag appears to be complex including andesines and possible anorthoclase (x hatched laths).	Andesine Hornblende Biotite Opx Kspar + Quartz.		

Table C:3 gives the type, abundance and alteration class of the minerals in the dyke rocks.

Table C:3

	Comments	Minerals	Abundance	Alteration class
9b3	Highly altered - difficult to identify minerals. Laths common.			
1LD	Fine grained. Acicular needles of amphibole invade feldspar.	Plagioclase Amphibole Kspar + minor quartz	Difficult to determine	
5LD	Porphyritic with phenocrysts of plag and an altered mineral in a weathered red/brown matrix. Multiple and compositional zoning in the plag - ranging labradorite to andesine.	Plagioclase Altered pyroxene (?)mineral. Groundmass.	25% 25% 50%	1-2 3 ?
6LD	Difficult to positively identify any minerals because the amount of alteration blurs everything.	Minerals that are possible are: Opagues Quartz Altered plag.	?	High amount of alteration throughout the slide
7LD	Biotite shows pleochroic haloes. Plag shows multiple twinning and compositional zoning. Occasionally intergrown with quartz.	Andesine Biotite Kspar + Quartz Opagues + apatite Alteration products	50% 20% 20% 5% 5%	<3 1 1 0 -
1PD	Porphyritic with phenocrysts of felspar and altered pyroxenes - very similar to 5LD. Plag is typically multiple twinned with range andesine to oligoclase.	Plagioclase Altered pyroxene Groundmass	25% 25% 50%	2 3 -

Classification of the igneous rocks

The following tables show the TAS and QAP classification results for the igneous rocks of the area. Where no QAP result is given this is either due to the plagioclase being of too basic a composition or the mineralogy being difficult to determine.

Table:1

Sample	TAS classification	QAP classification
9/1	Quartz monzodiorite	Quartz diorite
7/1	Quartz monzodiorite	Quartz diorite
4/1	Quartz monzodiorite	Quartz diorite
5/1	Quartz monzodiorite	-
1HR	Quartz monzodiorite	Quartz monzodiorite
2HR	Granodiorite	Quartz monzodiorite
3HR	Quartz monzodiorite	Quartz monzodiorite
4HR	Granodiorite	Quartz monzodiorite
5HR	Quartz diorite	Quartz diorite
6HR	Granodiorite	Quartz diorite
7HR	Granodiorite	Quartz diorite
8HR	Quartz monzodiorite	Quartz diorite

Table 2 contains the classification for both the major and the minor granodiorites.

Table 2

Sample	TAS classification	QAP classification
2GD	Granodiorite	Granodiorite
3GD	Granodiorite	Granodiorite
4GD	Granodiorite	Granodiorite
3GR	Granodiorite	Granodiorite
4GR	Granodiorite	Granodiorite

Finally table 3 shows the classification for the minor intrusives.

Table 3

Sample	TAS classification	QAP classification
5LD/PD	Quartz monzodiorite	-
1PD	Quartz monzodiorite	-
6LD	Granodiorite	-
9b3/LD	Granodiorite	-
7LD	Quartz monzodiorite	Quartz monzodiorite
1LD	Quartz diorite	Diorite

Appendix D

site 1: G.R. 47427857

see Plate D1 a

Elevation: 250m slope: 5° to SW Solid geology = diorites

Presence of drift = None found in pit

Vegetation = 80% grasses, 20% heather + mosses + flowers

Soil class = peat soil

Drainage: Drainage ditches adjacent, soils dry but sticky.

Number of samples taken = 5

Sample depths - 1A - 5-10cm 1D - 50-55cm

1B - 25-28cm 1E - 60-65cm

1C - 40-50cm

Soil colours and textures:

1A - 10YR2/1 Black - sticky and plastic - peat soil

1B - 10YR2/1 Black - sticky and plastic - peat soil

1C - 10YR2/2 Very dark brown - sticky and plastic - peat soil

1D - 10YR2/2 Very dark brown - sticky and gritty - sandy loam

1E - 10YR2/2 Very dark brown - sticky and gritty - sandy loam

site 2 G.R. 47697882 see plate D1 b

Elevation = 260m Slope = flat Solid geology = diorites

Presence of drift = None in soil pit

Vegetation = 70% grasses

30% heather + flowers + mosses

Soil class = Peaty podzol

Drainage = good, soils dry

Number of samples taken = 5

Sample depths - 2A - 5-7cm

2D - 30-35cm

2B - 10-15cm

2E - 45-50cm

2C - 23-26cm

see plate D2 a

Soil colours and textures:

2A: 10YR2/1 Black - sticky and plastic - peaty

2B: 10YR2/1 Black - sticky and plastic - peaty

2C: 10YR2/1 Black - sticky and plastic - peaty

2D: 10YR3/2 Very dark greyish brown - sticky and gritty - loamy

2E: 10YR2/2 to 10YR5/8 Very dark brown to yellowish - gritty - sand

Site 3 G.R. 46627742

Elevation = 260m Slope = 15° North Solid geology = diorites

Presence of drift = None in pit

Vegetation = 85% grasses

15% flowers

Soil class = Peaty gley

Drainage: poor, damp soils and common waterlogging.

Number of samples taken = 4

Sample depths = 3A - 2-8cm

3C 30-35cm

3B 15-20cm

3D 40-50cm

Soil colours and textures:

3A: 10YR2/1 Black - sticky and gritty - loamy

3B: 10YR2/1 Black - sticky and gritty - loamy

3C: 10YR2/2 to 10YR5/8 Very dark brown to yellowish brown - gritty - sand

3D: 5YR3/4 Dark reddish brown - gritty - sand.

Site 4 G.R. 47197908

Elevation = 230m Slope = none Solid geology = Granodiorites (M)

Presence of drift = Difficult to tell, beach site.

Vegetation = Mainly heather

Soil class = peat soil

Drainage = good, soils dry.

Number of samples taken = 4

Soil depths - 4A - 40-50cm

4C - 110-120cm*

4B - 90-100cm

4D - 130-140cm

Sample 4C was not from this soil profile but from where the peat soil met the beach.

Soil colours and textures:

10YR2/1 Black - sticky and plastic - peaty

10YR2/1 Black - sticky and plastic - peaty

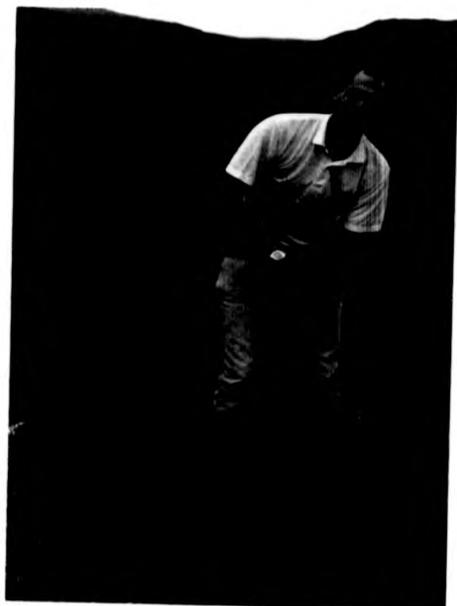
10YR6/4 Light yellowish brown - Gritty - sand

10YR2/2 Very dark brown - sticky and gritty - peaty

PLATE D1: SOIL SITE PHOTOGRAPHS



a. Soil site 1



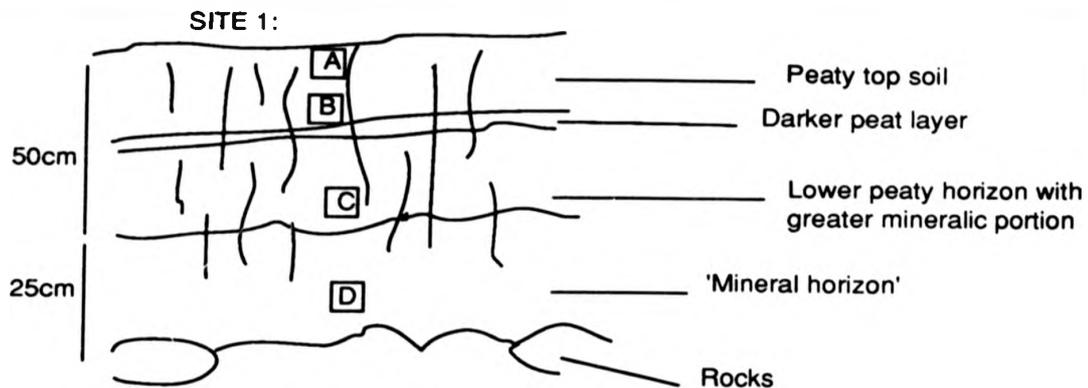
b. Soil site 2



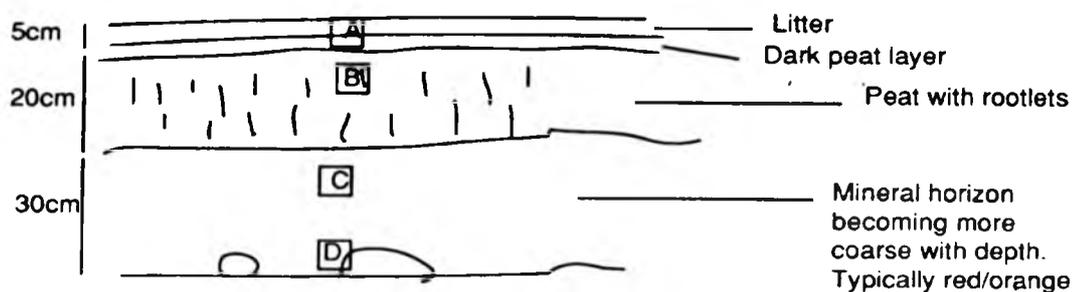
c. Soil site 12



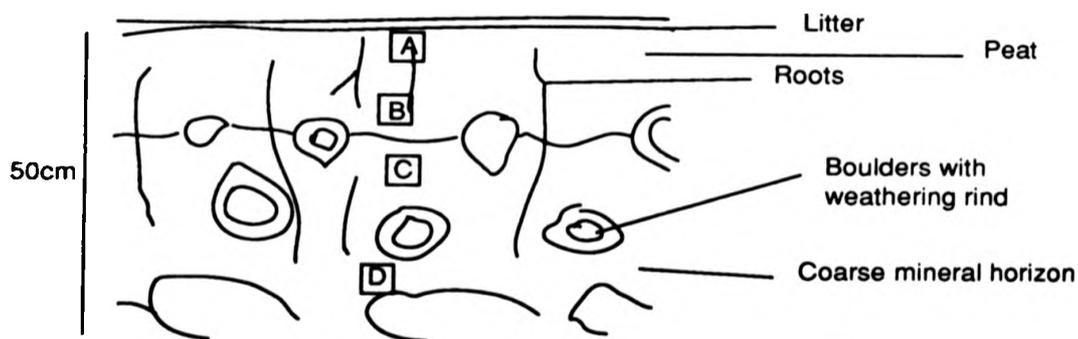
d. Soil site 19



SITE 2: (see plate D2 a)



SITE 3:



SITE 4:

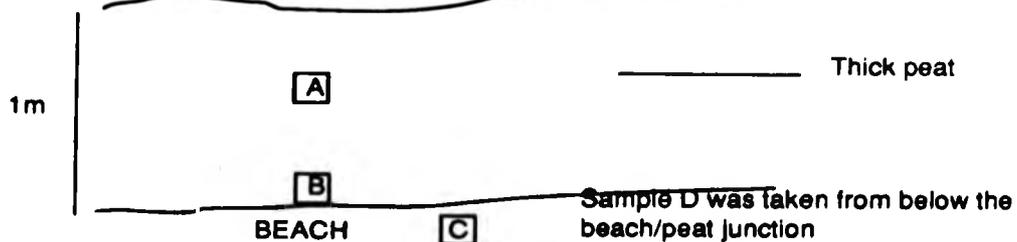


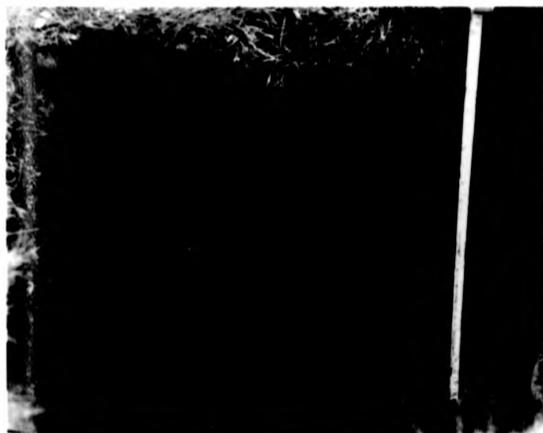
PLATE D2: SOIL PIT PROFILES



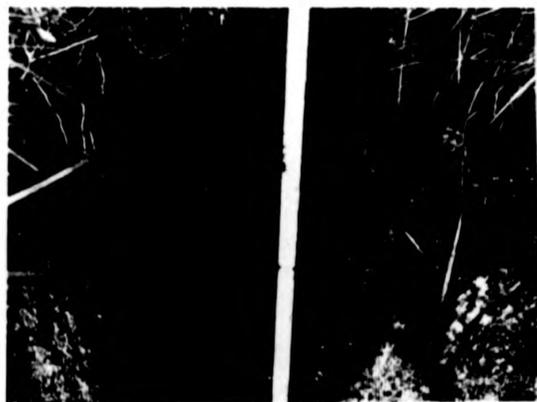
a. Soil pit at site 2



b. Soil pit at site 5



c. Soil pit at site 7.



d. Soil pit at site 10.

Site 5 G.R. 46297661

Elevation = 355m Slope = flat Solid geology = Basic dyke in sediments.
Presence of drift = Presence of coarse igneous material in soils
Vegetation = 85% grasses
15% heather

Soil class = Peaty gley
Drainage = good, soils usually dry
Number of samples taken = 4
Soil depths - 5A - 5-10cm 5C - 25-30cm
5B - 15-20cm 5D - 35-40cm
see plate D2 b

Soil colours and textures:

5A: 10YR2/1 Black - sticky and plastic - peaty
5B: 10YR2/1 Black - sticky and plastic - peaty
5C: 10YR3/3 Dark brown - Gritty - sand
5D: 10YR5/3 Brown - gritty - sand.

Site 6 G.R.45847624

Elevation = 390m Slope = 15° to West Solid Geology = Porphyritic dyke within sediments
Presence of drift = None obvious in pit but site close to distinctive grassy mound

Vegetation = Mixture of heather, grasses and flowers

Soil class = Peaty gley
Drainage: poor, soils wet, common waterlogging
Number of samples taken = 2

Soil depths - 6A - 5-10cm 6B - 15-17cm

Soil colours and textures:

6A: 10YR2/1 Black - sticky and plastic - peaty
6B: 10YR2/2 Very dark brown - sticky and gritty - sand.

Site 7 G.R.45507710

Elevation = 630m Slope = 10° to north Solid Geology Black shales

Presence of drift = Presence of igneous material within the soils

Vegetation: Sparse grasses with minor heather. Occasional moss.

Soil class =

Drainage: good, soils dry, waterlogging within 10m.

Number of samples taken = 4

Soil depths - 7A - 5-10cm 7C - 26-33cm

7B - 12-18cm 7D - 41-48cm

see plate D2 c

Soil colours and textures:

7A: 10YR3/1 Very dark grey - sticky and plastic - peaty

7B: 10YR2/1 Black - sticky and plastic - peaty

7C: 10YR5/3 Brown - sticky and gritty - loam

7D: 10YR5/3 Brown - sticky and plastic - clay loam

Site 8 G.R.47637660

Elevation = 450m Slope = 5° to north Solid geology - greywackes

Presence of drift = Yes, granitic boulders found within pit

Vegetation = south of the afforestation limit, grasses and heather with minor flax.

Soil class = Podzol ranker

Drainage = variable, peats often wet but mineral soils dry.

Number of samples taken = 3

Soil depths - 8A - 5-10cm 8C - 45-50cm

8B - 15-20cm

Soil colours and textures:

8A: 10YR2/1 Black - sticky and plastic peaty

8B: 10YR2/1 Black - sticky and plastic peaty

8C: 10YR3/3 Dark brown sticky and gritty loam

Site 9 G.R.45657640

Elevation = 440m Slope = none Solid geology - grits

Presence of drift = Yes, granite and shale boulders occurred within the pit.

Vegetation = Mainly grasses, rare heather and flowers

Soil class = peat soil.

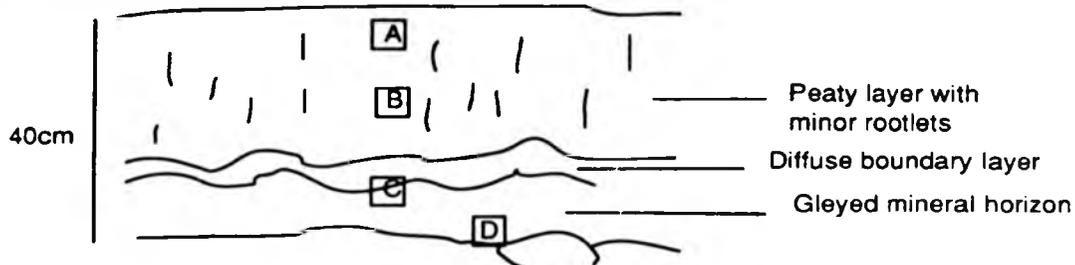
Drainage: reasonable, soils dry but sticky.

Number of samples taken = 4

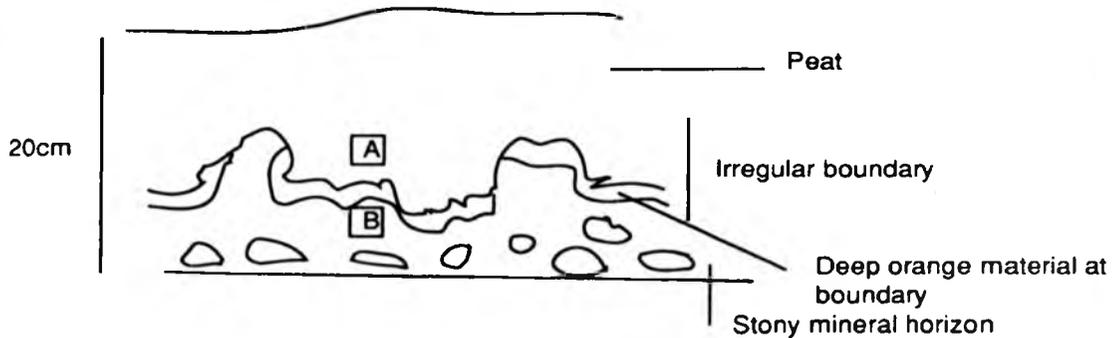
Soil depths - 9A - 5-10cm 9C - 45cm associated with granite

9B - 40-45cm 9D - 60cm associated with shale

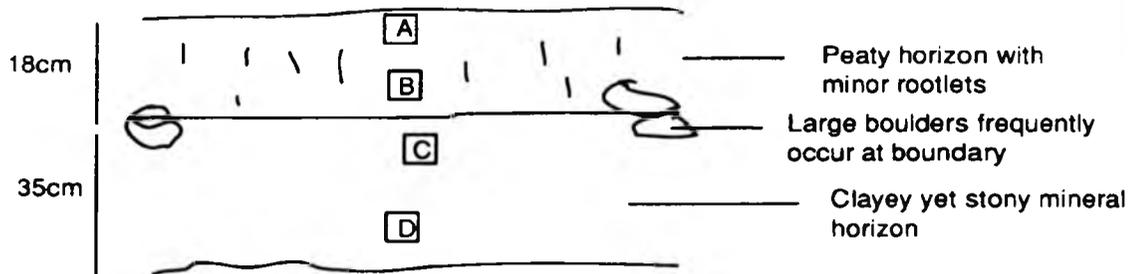
SITE 5: (see plate D2 b)



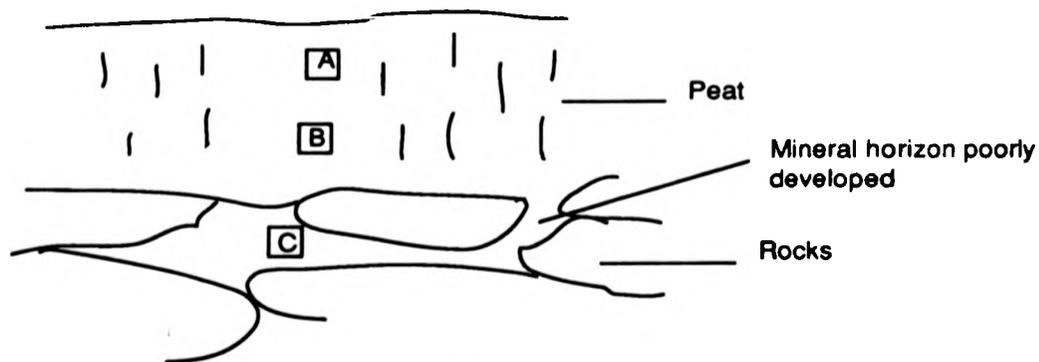
SITE 6:



SITE 7: (see plate D2 c)



SITE 8:



Soil colours and textures:

9A:10YR2/1 Black - sticky and plastic - peaty
9B:10YR2/2 Very dark brown - sticky and plastic - peaty.
9C:10YR2/2 Very dark brown - sticky and gritty - loamy.
9D:10YR2/2 Very dark brown - sticky and plastic - peaty.

Site 10 G.R.45957649

Elevation = 410m Slope = none Solid geology = granodiorite (m)
Presence of drift = None in pit but some shaley boulders found at later sampling.
Vegetation = Grasses and heather
Soil class = peaty podzol
Drainage = good but soils occasionally damp
Number of samples taken = 4
Soil depths - 10A - 10-20cm 10C - 33-40cm
10B - 22-33cm 10D - 47-57cm
see plate D2 d

Soil colours and textures:

10A: 10YR2/1 Black - sticky but crumbly - loamy peat
10B: 10YR2/2 Very dark brown - sticky and gritty - loamy peat
10C: 7.5YR3/2 to 10YR6/6 Dark brown to brownish yellow - gritty - sandy loam
10D: 7.5YR3/2 to 10YR6/6 Dark brown to brownish yellow - gritty - sandy loam

Site 11 G.R.46637682

Elevation = 330m Slope = none Solid geology = shales
Presence of drift = yes, 'granitic' material found at this site.
Vegetation = grasses with minor heather
Soil class = Podzol ranker
Drainage = good, soils dry
Number of samples taken = 3
Soil depths - 11A - 5-10cm 11C - 22-25cm
11B - 15-20cm

Soil colour and texture:

11A: 10YR2/1 Black - sticky and plastic - peaty
11B: 10YR2/1 Black - sticky and plastic - peaty
11C: 10YR3/2 Very dark greyish brown - sticky and plastic with stones - clay loam.

Site 12 G.R. 47127824 see plate D1 c

Elevation = 260m Slope = 10° to west Solid geology = diorites
Presence of drift = presence of coarse shale material within the soils
Vegetation = mainly grasses, within firebreak of afforested area.
Soil class = Peaty gley
Drainage = poor, permanently waterlogged
Number of samples taken = 3
Sample depths - 12A - 5-15cm 12C - 55-75cm
12B - 45-60cm

Soil colours and textures:

12A: 10YR2/1 Black - sticky and plastic - peaty
12B: 10YR2/2 Very dark brown - sticky and gritty - loamy peat
12C: 10YR2/2 Very dark brown - sticky and gritty - loamy peat

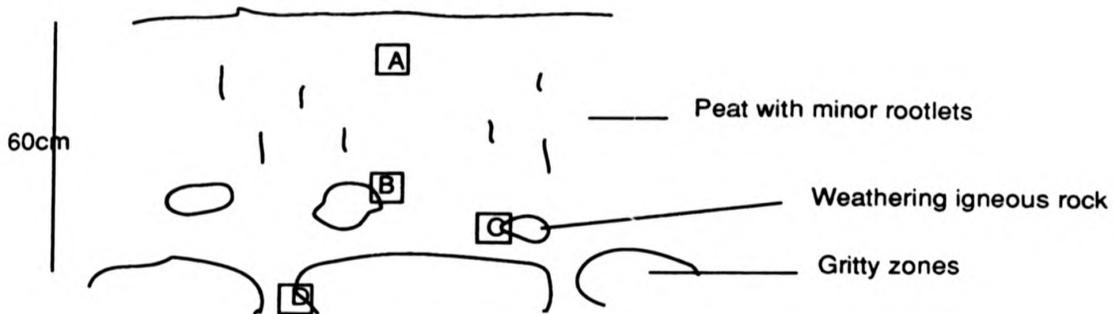
Site 13 G.R. 46697718

Elevation = 280m Slope = 5° to east Solid geology = diorites
Presence of drift = shales apparent within the soils
Vegetation = Grasses, out of limit of afforestation
Soil class = peat soil
Drainage = variable, soils wet
Number of samples taken = 5
Soil depths - 13A - 0-15cm 13C - 0-15cm
13B - 30-45cm 13D - 40-55cm
13E - 50-65cm

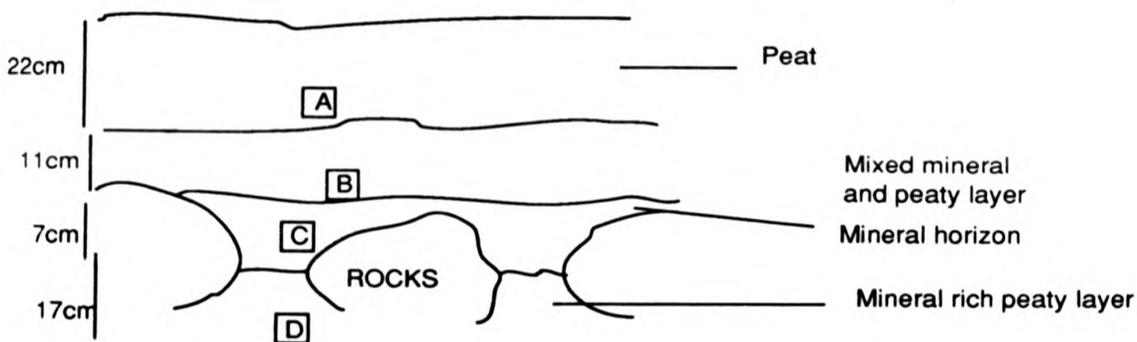
Soil colours and textures:

13A: 10YR2/1 Black - sticky and plastic - peaty
13B: 10YR2/2 Very dark brown - sticky and gritty - loamy peat
13C: 10YR2/1 Black - sticky and plastic - peaty
13D: 10YR2/1 Black - sticky and plastic - peaty
13E: 10YR2/2 Very dark brown - sticky and gritty - loamy peat.

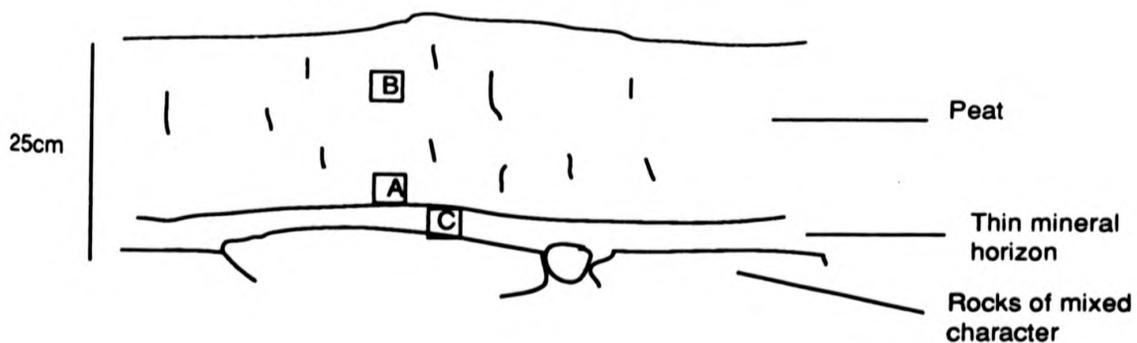
SITE 9:



SITE 10: (see plate D2 d)



SITE 11:



site 14 G.R. 45527765

Elevation = 570m Slope = 5° to south Solid geology = black shales
 Presence of drift = difficult to tell, soil was full of rocks.

Vegetation = grasses and mosses

Soil class = Ranker soil

Drainage = poor, soils wet, occasional waterlogging

Number of samples taken = 3

Soil depths - 14A - 5-10cm 14C - 30-40cm

14B - 12-18cm

Soil colours and textures:

14A: 10YR2/1 Black - sticky and plastic - peaty

14B: 10YR2/1 to 10YR5/4 Black with yellowish brown mottles - sticky and slightly gritty - loamy peat

14C: 10YR2/2 to 10YR5/4 Very dark brown with yellowish brown mottles - sticky and gritty - loam

Site 15 G.R. 45707760

Elevation = 590m Slope = 30° to southeast Solid geology = black shales

Presence of drift = soil rich in boulders

Vegetation = Grasses, mosses and flowers.

Soil class = Ranker soil

Drainage = good, soils dry

Number of samples taken = 2

Soil depths 15A - 0-15cm 15B - 20-25cm

Soil colours and textures:

15A: 10YR2/1 Black - sticky and plastic - peaty

15B: 10YR2/1 Black - sticky and plastic with stones - loamy peat

Site 16 G.R. 45787609

Elevation = 360m Slope = 5° to east Solid geology - acid dyke within greywackes

Presence of drift = none seen

Vegetation = Grasses

Soil class = Peaty podzol

Drainage = very good, soils very dry

Number of samples taken = 4

Soil depths - 16A - 0-10cm 16C - 20-30cm

16B - 15-25cm 16D - 30-40cm

Soil colours and textures:

16A: 10YR2/1 Black - crumbly and gritty - sandy peat

16B: 10YR2/2 Very dark brown - crumbly - sandy loam

16C: 10YR4/3 Brown - gritty - sand

16D: 10YR4/3 Brown - gritty - sand

Site 17 G.R. 46057601

Elevation = 440m Slope = 5° to west Solid geology - shales

Presence of drift = none obvious

Vegetation = Grasses

Soil class = peat soil

Drainage = poor, soils wet, waterlogging

Number of samples taken = 3

Soil depths - 17A - 5-20cm 17C - 40-45cm

17B - 30-45cm

Soil colours and textures:

17A: 10YR2/1 Black - sticky and plastic - peaty

17B: 10YR2/1 Black - sticky and plastic - peaty

17C: 10YR2/2 Very dark brown - sticky and plastic - peaty

Site 18 G.R. 47427640

Elevation = 460m Slope = 10° to west Solid geology = shales

Presence of drift = presence of igneous material within the soils

Vegetation = sparse grasses, heather and flax.

Soil class = Ranker soil

Drainage = good, soils dry

Number of samples taken = 3

Soil depths - 18A - 5-10cm 18C - 20-25cm

18B - 10-20cm

Soil colours and textures:

18A: 10YR2/1 Black - sticky and plastic - peaty

18B: 10YR3/1 Very dark grey - sticky and plastic - peaty

18C: 10YR3/2 Very dark greyish brown - sticky and gritty - loam

Site 19 G.R.47127608 see plate D1 d
Elevation = 520m Slope = none Solid geology = greywackes shales
Presence of drift = Igneous material seen within the soils
Vegetation = heather and grasses
Soil class: Ranker
Drainage = variable, wet soils, occasional waterlogging
Number of samples taken = 3
Soil depths - 19A - 2-8cm 19C - 20-25cm
 19B - 10-20cm
Soil colours and textures:
19A: 10YR2/1 Black - sticky but crumbly loamy peat
19B: 10YR2/1 Black - sticky but crumbly - loamy peat
19C: 10YR4/3 Dark Brown - sticky and gritty - loam

Site 20 G.R. 49077987
Elevation = 220m Slope = none Solid geology = Granodiorite (M)
Presence of drift = none seen
Vegetation = grassy firebreak within afforested zone
Soil class = peaty gley
Drainage = poor, wet soils, waterlogging
Number of samples taken = 4
Soil depths - 20A - 5-10cm 20C - 20-30cm
 20B - 10-20cm 20D - 30-40cm
Soil colours and textures:
20A: 10YR2/1 Black - sticky and plastic - peaty
20B: 10YR2/1 Black - sticky and plastic - peaty
20C: 10YR3/4 Dark yellowish Brown - sticky and gritty - sandy loam
20D: 10YR3/3 Dark brown - sticky and gritty - sandy loam

Site 21 G.R. 45727615
Elevation = 450m Slope = on top and around steeply sloping edges of mound Solid geology = acid dyke within greywackes
Presence of drift = none seen
Vegetation = Grasses
Soil class = peaty podzol
Drainage = very good, soils very dry
Number of samples taken = 4
Soil depths - 21A - 5-10cm 21C - 17-24cm
 21B - 10-17cm 21D - 24-30cm
Soil colours and textures:
21A: 10YR2/1 Black - sticky and gritty - loamy peat
21B: 10YR2/1 Black - sticky and plastic - peaty
21C: 10YR5/4 to 10YR2/1 Yellowish brown to black - sticky and gritty - sandy loam
21D: 10YR5/3 Brown - crumbly - sand.

Site 22 G.R.47507769
Elevation = 320m Slope = none Solid geology = possible dyke within greywackes
Presence of drift = igneous material within the soils
Vegetation = mainly heather with grasses
Soil class = Ranker soil
Drainage = variable, soils usually dry
Number of samples taken = 4
Soil depths - 22A - 2-7cm 22C - 10-15cm
 22B - 0-2cm 22D - 15-20cm
Soil colours and textures:
22A: 10YR2/1 Black - sticky and plastic - peaty
22B: 10YR2/2 Very dark brown - sticky and plastic - peaty
22C: 10YR3/2 Very dark greyish brown - sticky and gritty - loam
22D: 10YR3/2 Very dark greyish brown - sticky and gritty - loam

Site 23 G.R. 46497788
Elevation = 300m Slope = 40° to east Solid geology = diorites
Presence of drift = none seen
Vegetation = Grasses and bracken above conifer plantation
Soil class = peaty podzol
Drainage = good at surface, poor in mineral horizons
Number of samples taken = 4
Soil depths - 23A - 0-10cm 23C - 80-95cm
 23B - 40-55cm 23D - 95-105cm

Soil colours and textures:

23A: 10YR3/2 Very dark greyish brown - sticky and plastic peaty
23B: 10YR3/2 Very dark greyish brown - sticky and plastic peaty
23C: 10YR3/3 Dark brown - sticky and gritty - sandy loam
23D: 10YR3/3 Dark brown - sticky and gritty - sandy loam

Site 24 G.R. 46197831

Elevation = 300m Slope = 40-50° to east Solid geology = diorites
Presence of drift = none seen
Vegetation = Grasses, ferns, flowers.
Soil class = peaty podzol
Drainage = variable, good in surface but poor in mineral horizons
Number of samples taken = 3
Soil depths - 24A - 0-10cm 24C - 60-75cm
24B - 15-30cm

Soil colours and textures:

24A: 10YR2/1 Black - sticky and plastic - peaty
24B: 10YR3/2 Very dark greyish brown - sticky and gritty - sandy loam
24C: 10YR3/2 Very dark greyish brown - sticky and gritty - sandy loam

Site 25 G.R. 46157647

Elevation = 350m Slope = 5° to east Solid geology = lamprophyre dyke within
greywackes
Presence of drift = igneous material within the soils
Vegetation = grassy with minor heather
Soil class = peaty gley
Drainage = poor, permanent waterlogging
Number of samples taken = 2
Soil depths - 25A - 5-10cm 25B - 35-40cm

Soil colours and textures:

25A: 10YR2/1 Black - sticky and plastic peaty
25B: 10YR2/2 Very dark brown - sticky and plastic with stones - loamy peat.

Appendix B

Table E1: soil field moisture expressed as % of total soil mass. All results represent one single measurement.

soil	% fm						
1A	79.8	6B	16.2	13B	66.1	20B	64.8
1B	80.0	7A	55.4	13C	76.0	20C	47.1
1C	79.5	7B	57.9	13D	75.0	20D	39.1
1D	52.4	7C	23.6	13E	36.6	21A	80.5
1E	46.3	7D	24.0	14A	58.5	21B	70.2
2A	79.5	8A	85.5	14B	34.8	21C	46.5
2B	82.6	8B	74.0	14C	69.4	21D	27.7
2C	77.0	8C	28.1	15A	58.0	22A	55.1
2D	44.0	9A	66.8	15B	53.0	22B	88.5
2E	40.7	9B	61.6	16A	45.5	22C	33.8
3A	49.6	9C	61.8	16B	44.1	22D	34.2
3B	44.0	9D	54.9	16C	19.3	23A	53.6
3C	23.9	10A	75.5	16D	19.9	23B	47.7
3D	40.0	10B	47.9	17A	89.2	23C	41.9
4A	84.1	10C	43.9	17B	78.3	23D	38.8
4B	86.9	10D	43.4	17C	72.4	24A	56.3
4C	6.35	11A	71.7	18A	79.5	24B	39.7
4D	30.8	11B	83.2	18B	67.5	24C	36.2
5A	72.4	11C	33.7	18C	54.9	25A	90.1
5B	57.6	12A	86.8	19A	67.7	25B	67.0
5C	25.7	12B	54.4	19B	66.7		
5D	21.5	12C	39.9	19C	24.3		
6A	58.2	13A	82.6	20A	82.6		

Table E2: Organic soil pH - results represent one single reading

soil	pH	soil	pH	soil	pH	soil	pH
1A	3.5	4B	3.0	10A	3.7	15A	4.0
1B	3.6	5A	3.6	11A	3.8	15B	4.3
1C	3.7	5B	3.7	11B	3.6	16A	4.0
2A	3.2	7A	4.5	12A	3.8	17A	4.1
2B	3.4	7B	4.5	13A	3.5	17B	4.3
2C	3.6	8A	3.2	13C	3.1	17C	4.3
3A	3.8	8B	3.6	13D	3.3	18A	4.1
4A	2.9	9A	4.4	14A	3.5	18B	4.2
						25A	3.5

Table E3: Soil air-dried moisture content expressed as a weight % of total soil. Only 1 sample was tested for each soil.

soil	%dm	soil	%dm	soil	%dm	soil	%dm
1A	12.9	5A	12.4	10B	14.0	15B	8.89
1B	8.16	5B	8.88	10C	9.74	16A	6.78
1C	8.63	5C	3.96	10D	7.30	16B	4.56
1D	2.98	5D	3.61	11A	9.98	16C	3.10
1E	3.30	6A	5.60	11B	12.5	16D	3.20
2A	20.6	6B	4.88	11C	3.89	17A	13.8
2B	13.0	7A	10.7	12A	13.2	17B	9.45
2C	12.2	7B	8.53	12B	4.27	17C	11.4
2D	5.79	7C	3.27	12C	2.13	18A	10.6
2E	5.26	7D	3.31	13A	11.9	18B	8.55
3A	11.4	8A	13.3	13B	4.39	18C	4.18
3B	9.80	8B	9.19	13C	13.0	19A	15.7
3C	3.35	8C	2.74	13D	5.47	19B	7.31
4A	5.01	9A	9.91	13E	3.32	19C	3.85
4B	15.0	9B	7.42	14A	8.04	20A	11.0
4C	14.6	9C	7.12	14B	4.38	20B	5.94
4D	0.83	9D	7.53	14C	3.89	20C	2.62
4E	2.39	10A	14.4	15A	9.83	20D	2.45

Table 84. Organic matter content of soils expressed as weight % lost on ignition of the sample at 850° C for 30 minutes. Results are expressed as mean values with 1 standard deviation in brackets, n = 3.

soil	NLOI	soil	NLOI	soil	NLOI
1A	56.1 (2.69)	8C	6.31 (1.35)	17A	58.8
1B	47.3 (1.81)	9A	40.8 (0.06)	17B	40.9
1C	40.8 (2.83)	9B	19.2 (2.21)	17C	42.0
1D	14.5 (1.80)	9C	18.9 (0.50)	18A	39.0 (2.70)
1E	12.3 (0.49)	9D	20.0 (0.83)	18B	30.8 (2.83)
2A	74.0 (1.72)	10A	60.9 (2.46)	18C	19.9 (2.60)
2B	83.7 (0.45)	10B	15.4 (0.60)	19A	36.9 (0.80)
2C	43.5 (0.64)	10C	18.1 (0.17)	19B	28.2 (1.55)
2D	11.4 (0.72)	10D	15.1 (1.50)	19C	11.8 (0.18)
2E	10.6 (0.31)	11A	44.1 (0.68)	20A	56.2 (7.02)
3A	24.1 (0.02)	11B	67.7 (0.42)	20B	32.4 (2.12)
3B	15.7 (0.29)	11C	9.35 (0.04)	20C	9.95 (0.53)
3C	7.42 (0.15)	12A	68.8 (2.92)	20D	8.42 (0.25)
3D	10.8 (0.14)	12B	15.7 (0.47)	21A	55.2 (1.86)
4A	70.4	12C	6.40 (0.16)	21B	40.3 (0.50)
4B	67.8	13A	54.3	21C	14.2 (0.19)
4C	0.01	13B	13.1	21D	8.86 (0.46)
4D	7.10	13C	65.2	22A	23.7 (2.37)
5A	69.3 (4.71)	13D	24.5	22B	57.0 (0.53)
5B	24.8 (1.26)	13E	9.43	22C	12.5 (0.71)
5C	7.69 (0.09)	14A	46.3 (0.69)	22D	7.48 (0.31)
5D	6.57 (0.47)	14B	14.2 (3.40)	23A	12.8 (0.04)
6A	22.9 (1.71)	14C	11.5 (0.06)	23B	8.33 (0.71)
6B	9.31 (0.36)	15A	30.1	23C	5.18 (0.24)
7A	36.6 (2.26)	15B	26.4	23D	5.73 (0.36)
7B	26.0 (1.11)	16A	27.0 (1.64)	24A	12.3
7C	6.85 (0.09)	16B	10.5 (3.47)	24B	4.33
7D	5.82 (0.02)	16C	5.91 (0.31)	24C	5.46
8A	84.8 (2.15)	16D	5.24 (1.00)	25A	69.8
8B	34.8 (1.76)	17A		25B	12.4

Table 85. Soil material > 2mm expressed as a weight % of the total sample. Results represent single readings.

Soil	Weight % of total sample	Soil	Weight % of total sample	Soil	Weight % of total sample
1D	0.05	9D	2.25	18B	0.01
1E	0.05	10B	2.77	18C	41.1
2D	1.32	10C	8.72	19A	0.08
2E	2.58	10D	13.2	19B	17.0
3A	2.06	11A	0.03	19C	31.5
3B	2.42	11C	17.1	20A	0.02
3C	14.1	12B	2.71	20B	0.01
3D	12.3	12C	16.5	20C	2.39
4C	20.7	13A	1.14	20D	3.91
4D	7.87	13B	10.2	21A	2.58
5B	9.23	13D	2.24	21B	2.16
5C	1.40	13E	8.39	21C	2.76
5D	0.01	14A	18.4	21D	1.24
6A	20.5	14B	41.2	22A	4.56
6B	66.2	14C	22.3	22B	0.06
7A	11.8	15A	9.77	22C	4.61
7B	16.6	15B	27.0	22D	1.78
7C	39.7	16A	1.79	23B	1.45
7D	35.4	16B	1.04	23C	1.68
8B	0.03	16C	0.08	23D	4.23
8C	11.2	16D	0.08	24B	3.01
9C	0.02	17B	0.06	24C	2.85
				25B	12.8

Table 86: Description of fraction of soil > 2mm for each soil site.

Site	Coarse fraction	site	Coarse fraction	site	Coarse fraction
1.	Diorites	10	Granodiorite	19	Ig rx + shale
2.	Diorites	11	Qtz, shale + igrx.	20	Granodiorite
3.	Diorites	12	Diorite + shale	21	Ig rx
4.	G/diorites + qtz	13	Diorite + shale	22	Ig rx + shale
5.	qtz + mixed ig rx	14	Black shale	23	Diorite
6.	Porphyry	15	Shale	24	Diorite
7.	Black shale, grit + ig rx	16	Ig rx + shale	25	Ig rx + shale
8.	Igneous rx	17	Shale		
9.	Ig rx + shales	18	Shale + Ig rx		

Table 87 gives the minerals' soil particle size distributions in terms of clay, silt and sand expressed as weight % of the total sample. The results given represent single measurements. Sample 10B was not tested.

soil	wclay	wsilt	wsand	soil	wclay	wsilt	wsand
1D	4.16	5.03	90.8	13B	1.43	17.7	80.9
1E	6.02	18.3	75.7	13E	1.37	12.7	85.0
2D	8.74	4.79	86.5	14B	21.4	7.58	71.0
2E	8.60	22.7	68.7	14C	5.42	23.0	71.6
3B	5.98	20.3	73.7	16B	1.31	44.4	54.3
3C	4.27	15.6	80.2	16C	1.78	11.0	87.3
3D	3.75	13.7	82.6	16D	7.58	2.86	89.6
4C	1.26	3.88	94.8	18C	10.4	2.86	86.7
4D	6.30	0.00	93.7	19C	9.83	3.71	86.5
5C	2.81	25.9	71.3	20C	7.08	2.67	89.6
5D	4.63	5.62	89.8	20D	7.82	12.9	79.3
6A	1.47	29.4	69.1	21C	12.6	14.3	73.2
6B	8.66	26.1	65.2	21D	2.26	20.9	76.9
7C	7.50	13.6	78.9	22C	1.41	10.9	87.7
7D	7.33	13.3	79.3	22D	3.65	11.1	85.3
8C	1.81	8.37	89.8	23A	5.83	15.4	78.8
9B	6.43	11.7	81.9	23B	1.83	2.82	95.4
9C	5.23	17.9	82.1	23C	3.43	6.43	90.3
9D	1.66	9.34	90.7	23D	1.40	13.0	85.6
10C	1.31	8.05	90.6	24A	3.54	8.58	87.9
10D	1.49	9.18	89.3	24B	3.50	10.6	85.9
11C	0.00	13.0	87.0	24C	3.15	9.55	87.3
12B	3.57	13.00	83.4	25B	3.42	8.29	88.3
12C	1.44	14.1	82.2				

Table 88: Mineral soil pH. Results are for single measurements.

soil	pH	Soil	pH	soil	pH	soil	pH
1D	4.1	5D	4.5	10C	4.3	16D	4.4
1E	4.2	6A	3.7	10D	4.5	18C	4.2
2D	4.3	6B	4.5	11C	4.3	19C	4.0
2E	4.2	7C	4.6	12B	4.0	20C	3.7
3B	4.4	7D	4.7	13B	3.9	20D	3.8
3C	4.4	8C	4.3	13E	3.8	21C	3.7
3D	4.4	9B	4.6	14B	3.5	21D	4.1
4C	4.2	9C	4.6	14C	4.0	22C	3.7
4D	3.6	9D	4.6	16B	4.0	22D	4.0
5C	4.3	10B	4.0	16C	4.3	23A	4.0

Table 89: Mineral soil exchangeable Ca and Mg results are given as mean Value with 1 standard deviation in brackets, n=3. Results are reported in meq/kg.

Soil	Exch Ca	Exch Mg	Soil	Exch Ca	Exch Mg
1D	2.02(0.33)	0.86(0.02)	12C	5.89(0.85)	4.48(0.27)
1E	1.80(0.37)	0.57(0.04)	13B	3.32	1.91
2D	1.00(0.43)	0.83(0.09)	13E	3.78	1.73
2E	0.94(0.46)	0.67(0.10)	14B	1.23(0.14)	1.81(0.04)
3B	0.66(0.52)	1.03(0.04)	14C	1.46	0.96
3C	0.55(0.40)	0.45(0.06)	16B	1.02(0.04)	1.17(0.05)
3D	0.66	0.36(0.07)	16C	0.86(0.10)	1.91(0.12)
4C	1.66	1.04	16D	0.72(0.04)	0.79(0.04)
4D	1.83	0.93	18C	9.99(0.42)	4.61(0.17)
5C	1.68(0.70)	0.97(0.09)	19C	0.99(0.09)	1.00(0.07)
5D	1.05(0.32)	0.60(0.08)	20C	2.25(0.12)	1.54(0.11)
6A	1.98(0.44)	2.22(0.33)	20D	1.92(0.07)	1.33(0.11)
6B	1.18(0.25)	0.27(0.07)	21C	1.28(0.09)	2.88(0.09)
7C	1.06(0.35)	0.33(0.08)	22C	0.75(0.09)	1.04(0.14)
7D	1.02(0.33)	0.33(0.08)	22D	1.98(0.19)	2.10(0.16)
8C	1.10(0.42)	0.45(0.07)	23A	1.55(0.10)	1.27(0.15)
9B	10.2(0.60)	3.18(0.05)	23B	6.25(0.14)	4.34(0.14)
9C	6.92(0.20)	2.15(0.06)	23C	3.42(0.04)	1.81(0.18)
9D	10.7(0.77)	2.96(0.10)	23D	2.33(0.07)	1.16(0.17)
10B	1.10(0.47)	0.74(0.09)	24A	2.66(0.05)	1.44(0.17)
10C	1.06(0.57)	0.60(0.09)	24B	4.16	3.18
10D	1.05(0.50)	0.46(0.09)	24C	1.78	1.56
11C	0.99(0.67)	0.60(0.22)	24C	5.52	1.78
12B	6.95(0.32)	5.89(0.85)	25B	14.5	7.16

Table #10: Organic soil exchangeable Ca and Mg; results are given as mean values with 1 standard deviation in brackets. Results are reported in meq/kg.

soil	Ex Ca	Ex Mg	soil	Ex Ca	Ex Mg
1A	15.7(0.06)	11.9(0.1)	13D	7.08	4.02
1B	6.33(1.4)	3.88(0.3)	14A	1.70(0.17)	4.61(0.16)
1C	4.61(1.0)	2.17(0.3)	15A	2.16	5.02
2A	25.1(1.8)	31.3(1.5)	15B	1.72	2.35
2B	8.62(0.6)	5.3(0.1)	16A	2.22(0.14)	3.33(0.12)
2C	5.13(0.1)	2.40(0.1)	17A	20.8	15.0
3A	1.44(0.5)	2.14(0.0)	17B	19.2	6.13
4A	24.7	91.5	17C	20.8	6.94
4B	23.5	69.6	18A	24.1(1.39)	13.0(0.15)
5A	4.14(0.2)	8.09(0.4)	18B	21.2(0.93)	12.6(0.21)
5B	1.77(0.4)	3.17(0.2)	19A	1.89(0.07)	4.52(0.06)
7A	1.42(0.5)	1.92(0.1)	19B	1.62(0.09)	3.29(0.03)
7B	1.42(0.53)	1.92(0.05)	20A	9.32(0.48)	9.73(0.36)
8A	28.0(2.45)	47.3(1.37)	20B	5.14(0.18)	4.05(0.14)
8B	4.12(0.54)	5.33(0.14)	21A	10.6(0.62)	16.6(0.80)
9A	9.87(1.19)	5.12(0.18)	21B	3.03(0.15)	6.60(0.23)
10A	2.25(0.73)	5.23(0.39)	22A	5.28(0.11)	6.03(0.14)
11A	1.91(0.74)	3.59(0.21)	22B	17.7(0.64)	20.0(0.50)
11B	3.36(1.09)	7.74(0.71)	25A	57.6	38.2
12A	30.0(7.03)	27.5(2.81)			
13A	9.22	10.5			
13C	9.65	8.77			

Table #11: Exchangeable Na and K for mineral soils. Results are expressed as a mean value +/- 1 standard deviation, n = 3. Results are expressed in meq/kg.

Soil	Ex Na	Ex K	Soil	Ex Na	Ex K
1D	0.43(0.26)	0.23(0.16)	12C	0.77(0.29)	0.45(0.55)
1E	0.31(0.16)	0.10(0.13)	13B	4.84	0.08
2D	3.04(1.99)	2.47(0.85)	13E	0.29	0.00
2E	0.34(0.14)	0.14(0.23)	14B	1.57(0.23)	1.45(0.17)
3B	0.53(0.08)	0.58(0.21)	14C	1.59	0.68
3C	0.19(0.22)	0.11(0.06)	16B	1.35(0.32)	0.97(0.21)
3D	0.29(0.13)	0.11(0.16)	16C	1.04(0.25)	0.35(0.03)
4C	0.07	0.00	16D	1.18(0.42)	0.48(0.06)
4D	0.43	0.00	18C	1.47(0.26)	0.68(0.15)
5C	0.43(0.17)	0.23(0.14)	19C	1.04(0.18)	0.68(0.17)
5D	0.34(0.06)	0.20(0.20)	20C	0.99(0.19)	0.61(0.08)
6A	1.06(0.23)	2.71(0.23)	20D	0.84(0.19)	0.46(0.03)
6B	0.24(0.03)	0.33(0.20)	21C	1.15(0.26)	0.91(0.06)
7C	0.70(0.08)	0.67(0.08)	21D	0.92(0.10)	0.52(0.20)
7D	0.53(0.15)	0.48(0.23)	22C	1.50(0.25)	1.45(0.30)
8C	0.43(0.17)	0.33(0.25)	22D	0.91(0.13)	0.45(0.13)
9B	1.45(0.05)	0.57(0.32)	23A	1.64(0.49)	2.24(0.13)
9C	1.18(0.17)	0.40(0.32)	23B	1.16(0.10)	1.15(0.23)
9D	1.50(0.06)	0.68(0.26)	23C	0.99(0.19)	0.59(0.17)
10B	0.82(0.23)	0.40(0.32)	23D	0.92(0.14)	0.68(0.17)
10C	0.96(0.06)	0.37(0.06)	24A	3.19	2.98
10D	0.68(0.23)	0.23(0.23)	24B	1.37	0.51
11C	0.53(0.51)	0.31(0.51)	24C	1.16	0.85
12B	0.94(0.22)	0.37(0.40)	25B	1.87	1.69

Table B12: Soil exchangeable Na and K for the organic soils. Results given are mean values with 1 standard deviation in brackets, n = 3. Results are expressed in meq/kg.

Soil	Exch Na	Exch K	Soil	Exch Na	Exch K
1A	6.52(1.14)	4.06(2.70)	13C	3.41	1.15
1B	1.71(0.79)	0.73(0.40)	13D	1.15	1.27
1C	1.05(0.58)	0.26(0.17)	14A	2.54(0.32)	4.58(1.46)
2A	9.47(5.54)	11.6(1.76)	15A	3.04	3.96
2B	6.07(2.20)	4.43(0.52)	15B	2.87	2.49
2C	4.15(2.66)	3.38(0.52)	16A	1.88(0.35)	2.81(0.00)
3A	0.96(0.49)	1.76(0.38)	17A	5.47	4.23
4A	11.8	0.34	17B	3.46	1.44
4B	8.48	0.17	17C	3.32	1.75
5A	3.25(0.57)	6.43(1.26)	18A	4.56(0.35)	2.87(0.45)
5B	1.20(0.49)	2.13(0.00)	18B	2.03(0.26)	1.72(0.56)
7A	0.80(0.13)	1.93(0.32)	19A	2.22(0.32)	2.61(0.23)
7B	1.09(0.05)	1.77(0.38)	19B	1.69(0.20)	1.61(0.74)
8A	9.75(0.85)	9.50(5.05)	20A	3.85(0.55)	5.47(0.57)
8B	1.98(0.06)	1.46(0.30)	20B	1.94(0.31)	1.86(0.33)
9A	2.02(0.20)	1.91(0.18)	21A	4.36(0.77)	5.58(0.45)
10A	2.85(0.38)	4.24(0.12)	21B	2.56(0.46)	3.07(0.17)
11A	1.81(0.13)	3.31(0.58)	22A	1.69(0.20)	2.41(0.06)
11B	3.65(0.59)	5.74(0.75)	22B	4.48(0.36)	10.6(0.76)
12A	3.85(0.81)	2.80(0.26)	25A	6.63	11.9
13A	4.02	3.21			

Table B13: Mineral soil exchangeable Al. Results represent a mean value where standard deviation is given in brackets, n = 3. Others were from one single reading. Units are meq/kg.

Soil	Exch Al	Soil	Exch Al	Soil	Exch Al
1D	18.7 (3.92)	9B	16.8 (1.13)	18C	18.5
1E	22.5 (4.36)	9C	18.6 (1.91)	19C	28.2
2D	27.8 (6.55)	9D	16.2 (1.11)	20C	14.7
2E	32.8 (7.27)	10B	54.3 (1.15)	20D	4.06
3B	24.8 (10.9)	10C	29.7 (0.87)	21C	59.6
3C	23.1 (9.96)	10D	25.0 (1.62)	21D	57.9
3D	20.1 (7.24)	11C	25.2	22C	37.5
4C	4.35	12B	25.4	22D	31.4
4D	21.0	12C	16.9	23A	33.4
5C	45.0 (18.4)	13B	46.5	23B	15.1
5D	34.4 (13.0)	13E	29.1	23C	11.1
6A	56.0 (24.5)	14B	39.9	23D	13.0
6B	19.2 (7.49)	14C	28.4	24A	20.0
7C	14.5 (6.14)	16B	46.3	24B	11.0
7D	13.2 (4.65)	16C	24.1	24C	13.6
8C	6.38	16D	21.4	25B	15.5

Table B14: Exchangeable Al in organic soils. Results are means where standard deviation is given in brackets, n = 3. Others represent single readings. Results are given in meq/kg.

S	Exch Al	S	Exch Al	S	Exch Al	S	Exch Al
1A	22.7(12)	7A	27.0(12)	13D	48.9	19B	92.2
1B	27.5	7B	27.3(11)	14A	33.3	20A	42.7
1C	19.7(13)	8A	12.1	15A	49.1	20B	38.9
2A	22.9	8B	65.6(31)	15B	37.0	21A	94.8
2B	36.8(16)	9A	19.8(9)	16A	46.3	21B	133
2C	62.4(20)	10A	83.8(18)	17A	61.1	22A	57.9
3A	28.6(15)	11A	56.9(5)	17B	38.7	22B	80.0
4A	3.89	11B	57.7	17C	31.8	25A	10.7
4B	2.79	12A	27.7	18A	30.1		
5A	53.8(17)	13A	59.2	18B	22.8		
5B	86.3(54)	13C	123	19A	107		

Table E15: Exchangeable H in mineral soils. Results expressed as a mean value with standard deviation given in brackets, n = 3. Other results are single readings. Units are meq/kg.

Soil ID	Exch H	Soil	Exch H	Soil	Exch H
1D	159 (8)	9B	134 (34)	18C	163 (20)
1E	158 (4)	9C	131 (36)	19C	131 (59)
2D	169	9D	160 (18)	20C	107 (46)
2E	173 (9)	10B	225 (20)	20D	109 (21)
3B	177 (6)	10C	185 (22)	21C	249 (4)
3C	128 (56)	10D	157 (32)	21D	180 (17)
3D	156 (7)	11C	127 (32)	22C	175 (5)
4C	73.1	12B	164 (12)	22D	151 (10)
4D	150	12C	92 (37)	23A	157 (4)
5C	157 (17)	13B	216	23B	114 (50)
5D	156 (12)	13E	178	23C	81 (31)
6A	197	14B	193 (35)	23D	92 (27)
6B	130 (31)	14C	177	24A	180
7C	97.0 (29)	16B	167 (47)	24B	107
7D	91.0 (18)	16C	125 (47)	24C	124
8C	87.0 (35)	16D	129 (35)	25B	99.3

Table E16: Exchangeable H for organic soils. Results are given as mean values with standard deviation is given in brackets, n = 3. Other results were single measurements. Units are meq/kg.

Soil	Exch H	Soil	Exch H	Soil	Ex H
1A	272	7A	186(10)	13D	234
1B	292 (47)	7B	184 (7)	14A	286(32)
1C	279 (35)	8A	453(81)	15A	300
2A	323	8B	326(17)	15B	253
2B	304	9A	176(29)	16A	243(15)
2C	306	10A	341(15)	17A	391
3A	227 (45)	11A	259(13)	17B	315
4A	422	11B	280(15)	17C	316
4B	387	12A	302(11)	18A	268 (29)
5A	229	13A	323	18B	216(15)
5B	278 (42)	13C	393	19A	308(57)

Table E17: Cation exchange capacity of mineral soils, added and measured. Results given are single values. Units are meq/kg.

	CEC (S)	CEC (M)	CEC (S)	CEC (M)	CEC (A)	CEC (M)	CEC (A)	CEC (M)
1D	181	202	9B	166	207	18C	198	231
1E	183	201	9C	160	202	19C	163	221
2D	204	191	9D	192	214	20C	127	249
2E	208	173	10B	282	252	20D	118	207
3B	205	235	10C	218	208	21C	315	281
3C	152	166	10D	184	257	21D	241	206
3D	177	163	11C	155	137	22C	220	216
4C	80.2	46.0	12B	204	246	22D	187	159
4D	174	171	12C	120	176	23A	205	268
5C	205	217	13B	273	271	23B	137	181
5D	193	161	13E	213	186	23C	97	18
6A	261	280	14B	239	203	23D	111	176
6B	151	150	14C	210	180	24A	213	258
7C	114	191	16B	209	209	24B	123	182
7D	107	130	16C	152	131	24C	346	166
8C	95.7	188	16D	154	161	25B	140	182

Table E18: Cation exchange capacity of organic soils, added and measured. All values are singular. Units are meq/kg.

Soil	CEC (A)	CEC (M)	Soil	CEC (A)	CEC (M)	Soil	CEC (A)	CEC (M)
1A	333	395	8B	404	370	17B	384	228
1B	330	222	9A	215	179	17C	380	200
1C	307	217	10A	436	142	18A	343	221
2A	423	333	11A	327	227	18B	276	271
2B	365	279	11B	483	125	19A	426	196
2C	384	375	12A	394	208	19B	375	194
3A	262	255	13A	410	236	20A	392	215
4A	555	157	13C	540	134	20B	298	318
4B	491	384	13D	297	255	21A	512	335
5A	305	247	14A	333	334	21B	534	599
5B	324	213	15A	363	288	22A	307	140
7A	219	345	15B	299	273	22B	483	169
7B	217	236	16A	300	281	25B	450	188
9A	560	281	17A	497	65			

Table E19. Soil pyrophosphate extractable Fe from mineral soils. All readings are singular. Expressed as a % of the original 0.50g of soil.

Soil	Ext. Fe						
1D	0.02	6B	0.09	12C	0.04	21C	1.39
1E	0.02	7C	0.20	13B	0.05	21D	0.26
2D	2.20	7D	0.16	13E	0.56	22C	0.32
2E	1.70	9C	0.04	14B	1.22	22D	0.27
3B	0.61	9B	0.70	14C	0.99	23A	0.78
3C	0.35	9C	0.61	16B	0.71	23B	0.51
3D	0.29	9D	0.70	16C	0.21	23C	0.16
4C	0.01	10B	0.86	16D	0.19	23D	0.28
4D	0.01	10C	2.66	18C	0.44	24A	0.90
5C	0.19	10D	1.12	19C	0.26	24B	0.34
5D	0.08	11C	0.07	20C	0.12	24C	0.43
6A	0.18	12B	0.05	20D	0.13	25B	0.08

Table E20. Soil pyrophosphate extractable Fe for organic soils. Results are all singular, expressed as a % of the 0.5g soil used.

Soil	Ext. Fe						
1A	0.33	7A	0.28	13D	0.15	19B	0.54
1B	0.15	7B	0.51	14A	2.25	20A	0.52
1C	0.05	8A	0.06	15A	1.25	20B	0.29
2A	0.5B	8B	0.28	15B	1.42	21A	0.41
2B	0.31	9A	1.10	16A	0.81	21B	1.31
2C	0.38	10A	0.87	17A	0.67	22A	0.40
3A	0.19	11A	0.39	17B	0.44	22B	0.45
4A	0.02	11B	0.41	17C	1.34	22C	0.10
4B	0.02	12A	0.78	18A	1.18		
5A	0.35	13A	0.29	18B	0.91		
5B	0.39	13C	0.30	19A	0.53		

Table E21. Mineral soil base saturation expressed as a % of summed base cations of summed CEC.

Soil	% B.S.						
1D	1.96	6B	1.34	12C	9.66	21C	1.97
1E	1.52	7C	2.42	13B	3.72	21D	1.34
2D	3.60	7D	2.21	13E	2.72	22C	3.20
2E	1.00	8C	2.41	14B	1.55	22D	2.24
3B	1.37	9B	9.28	14C	2.23	23A	7.09
3C	0.86	9C	6.66	16B	2.16	23B	5.19
4D	0.80	9D	8.25	16C	2.14	23C	5.23
4C	3.45	10B	1.09	16D	2.06	23D	5.14
4D	1.83	10C	1.37	18C	8.46	24A	6.34
5C	1.55	10D	1.32	19C	2.28	24B	4.24
5D	1.13	11C	1.57	20C	4.24	24C	6.38
6A	3.05	12B	6.94	20D	4.14	25B	18.0

Table E22. Base saturation in the organic soils given as summed base cations expressed as a % of summed CEC.

Soil	% B.S.						
1A	11.5	7A	2.77	13D	4.55	19B	2.19
1B	3.80	7B	2.86	14A	4.03	20A	7.23
1C	2.60	8A	16.9	15A	3.91	20B	4.36
2A	18.3	8B	3.19	15B	3.15	21A	7.25
2B	6.60	9A	8.80	16A	3.41	21B	2.86
2C	2.78	10A	3.34	17A	9.15	22A	5.02
3A	2.40	11A	3.25	17B	7.88	22B	10.9
4A	23.1	11B	4.24	17C	8.63	22C	25.4
4B	20.7	12A	16.3	18A	13.0		
5A	7.18	13A	6.57	18B	13.6		
5B	2.55	13C	4.26	19A	2.64		

Appendix F

Table F:1 Soil void content.

Soil site and depth	Voids by volume	Detail of voids.
Site 1 45-55cm	30%	Typically channel structures running C. perpendicular to surface. Includes decaying rootlets. Also minor planar zigzag voids.
Site 2 25-35cm	25%	15% Root channels perpendicular to ground surface, 1.5% planar zigzag voids, 7% ovate chambers with decaying plant material, 1.5% channel structures with amorphous, isotropic yellow infill.
Site 2 45-55cm	20%	Both channel and planar void types occur. Channels show no obvious preferred orientation. Associated larger sized chamber like voids concentrated in lower half of slide. Voids occasionally infilled with amorphous yellow none reflective material seen in higher soil.
Site 3	upper zone - 10% lower zone - 15%	Voids mainly planar cracks rather than channels in both zones.
Site 5	30-40%	Mainly planar voids forming a network throughout the soil. Occasional channels including decaying organic material.
Site 6	10-15%	Large channels of x-cutting nature and minor planar voids.
Site 7	30% in upper soil 15% in lower soil	Planar cracks and channels without preferred orientation. Channels less apparent in the lower slide.
Site 10 30-40cm	20% by volume	Includes both channel and chamber voids and planar zigzag voids. Typically infilled in top part of soil with yellow amorphous material of organic origin with minor Fe oxides. Some voids perpendicular to ground surface and associated with decaying organic matter.

Table F:2 Soil coarse fraction: Mineralic portion.

Soil site and depth	Soil mineralogic fraction: rock fragments.	Soil single mineral(s), alteration class
Site 1 45-55cm	40% of soil by volume. Rk frags and min grains. Rx typically acidic with high qz/fsp content. Angular.	Much unweathered Qtz, often strained. Feldspat (3), pyroxenes (3), biotite (2) and amphibole (2).
Site 2 25-35cm	45% of soil by volume. Rock and single mineral grains. Rock fragments included associations of Qtz and feldspar with occasional biotite and cpx. Up to 4mm in size. Subangular.	Qtz (-) and feldspat most common. Plag (2) in andesite range. Kspat (2). Biotite rare. Cpx present. Fractured to mosaic. Colourless amphibole mineral altering to chlorite.
Site 2 45-55cm	60% of the soil by volume. Single mineral grains <2.4 mm. Whilst the rock fragments <5cm. Rock fragments dioritic.	Biotite (2), Cpx and opx (2), K (2) and plag (3) feldspars. Plag most abundant. Quartz (-) common, augit.
Site 3	Upper zone - 40% by volume, lower zone - 80% by volume. Both rx and sgl mins. Dioritic and other Rk fragments occur. Includes large pebble of lamprophyre dyke material.	Qtz (-), fsp (3), Biotite (1), esp. common close to alien pebble, other f.m. mins and opaques less common.
Site 5	50% of slide by volume. Rk fragments and sgl minerals. Typically similar to basic dyke although occasional large strained quartzose pebbles occur.	Pyroxenes (x4), plag (2), Qtz pebbles - strained.
Site 6	40-60% of slide by volume. Rk ranged 1mm to 1cm. Porphyritic in nature.	No single mineral grains. Rk phenocryst (3).
Site 7	40% by vol. Rk frags include black shales, porphyry, diorite, greywacke etc. Black shale abundant in upper soil. In lower soil highly quartzose metasediments most common.	Only strained Qtz apparent as single mineral grains.
Site 10 30-40cm	30-35% of the soil. Rk frags and sgl mins. Rk frags more abundant and larger than sgl mins, <3mm. Rx subrounded to angular, randomly distributed. Qtz and fsp rich with minor f.m. mins and opaques.	Biotite, plag (x4), twinning obscured, Quartz (1) commonly angular, strained internally. Fibrous amphibole mineral (3), altered along cleavage. Rare green hornblende and K feldspat (3).

Table F:3: Coarse fraction : organic component

Soil site and depth	Soil organic components
Site 1 45-55cm	Mainly rootlets in voids perpendicular to the surface. With cellular structure and occasional birefringent central portion.
Site 2 25-35cm	10% of soil by volume. Includes decaying root material and large rounded reddish areas with a central void including mineralic material.
Site 2 45-55cm	5% of soil by volume. No obvious root structures. Amorphous, associated with Fe oxides.
Site 3	Very few in upper soil- c.5% by volume. More common in lower soil especially related to voids. Cell structures apparent.
Site 5	Decaying plant material within voids. Maximum 10% volume.
Site 6	Rootlets within voids - groundmass typically reddened if associated with organics.
Site 7	Organic material rare throughout - maximum of 5% of soil by volume.
Site 10 30-40cm	Abundant organics include remnant plant pieces with decaying cell walls, coarse organic material with small voids, accumulations of small rounded organic particles - possible fungal material.

Table F:4: Soil fine fraction.

Soil site and depth	Soil fine fraction
Site 1 45-55cm	40% of soil. Organomineralic - mainly organic. Brown, speckled. Colouration variable.
Site 2 25-35cm	20-25% of soil. Organomineralic. Light brown, speckled with patches of redness. Mainly isotropic.
Site 2 45-55cm	15% of soil. Organomineralic. Variable in shades of brown. Speckled. Patches of more reddish material.
Site 3	Upper zone - 40%, lower zone - 10%. Organomineralic. Brown. Speckled.
Site 5	Groundmass rare 15-20%. Brown and speckled. Organomineralic. Some zones more organically enriched
Site 6	Groundmass rare - 15-20%. Typically organomineralic. Brown.
Site 7	Groundmass 25% upper and 15% lower soil by volume. Yellow colour. Speckled.
Site 10 30-40cm	50% of soil by volume. Mainly organic. Brown with a dotted texture.

APPENDIX G.

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Figure 1 : Site 1 soil water monitoring results

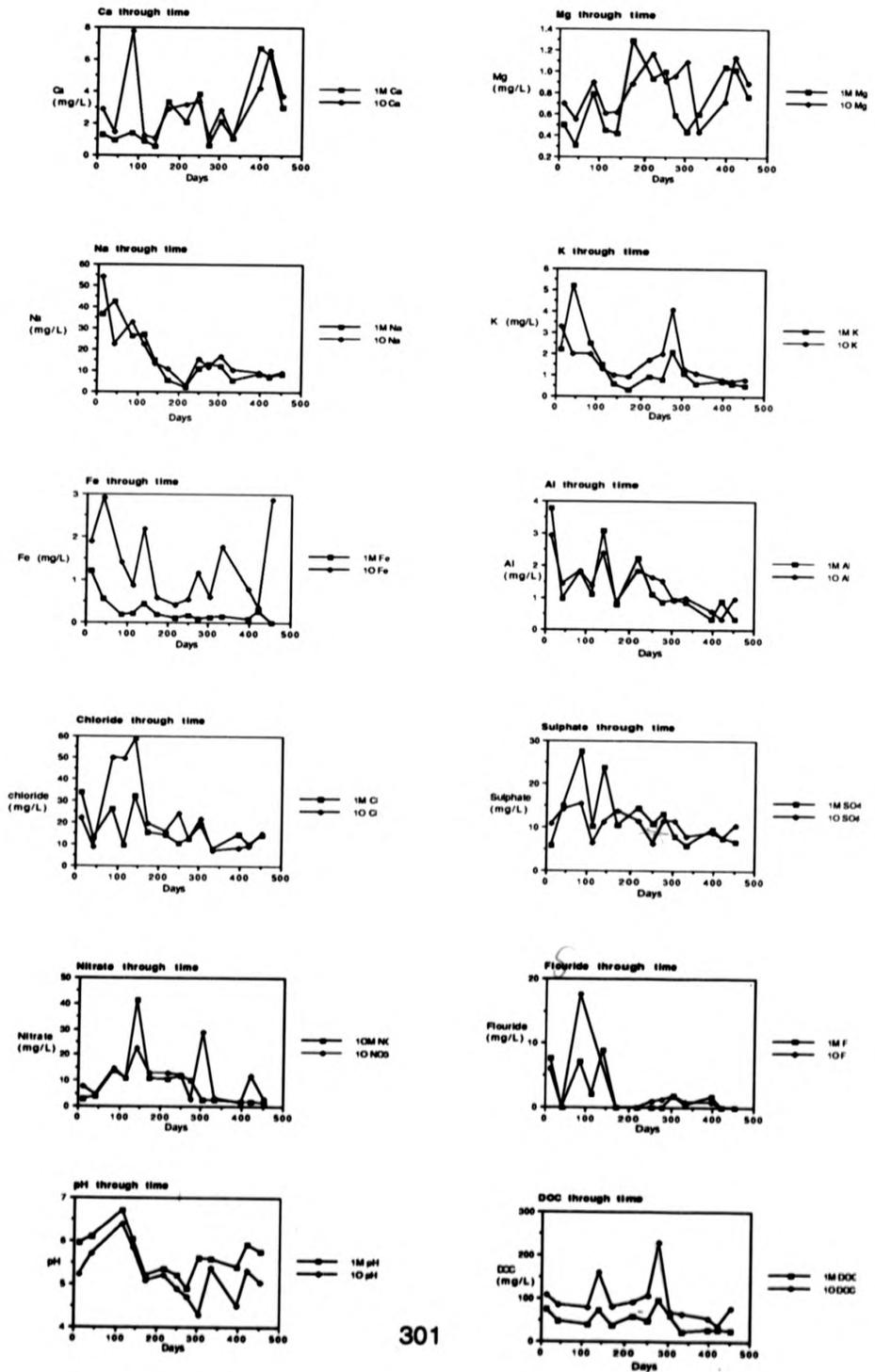


Figure 2 : Site 2 soil water monitoring results

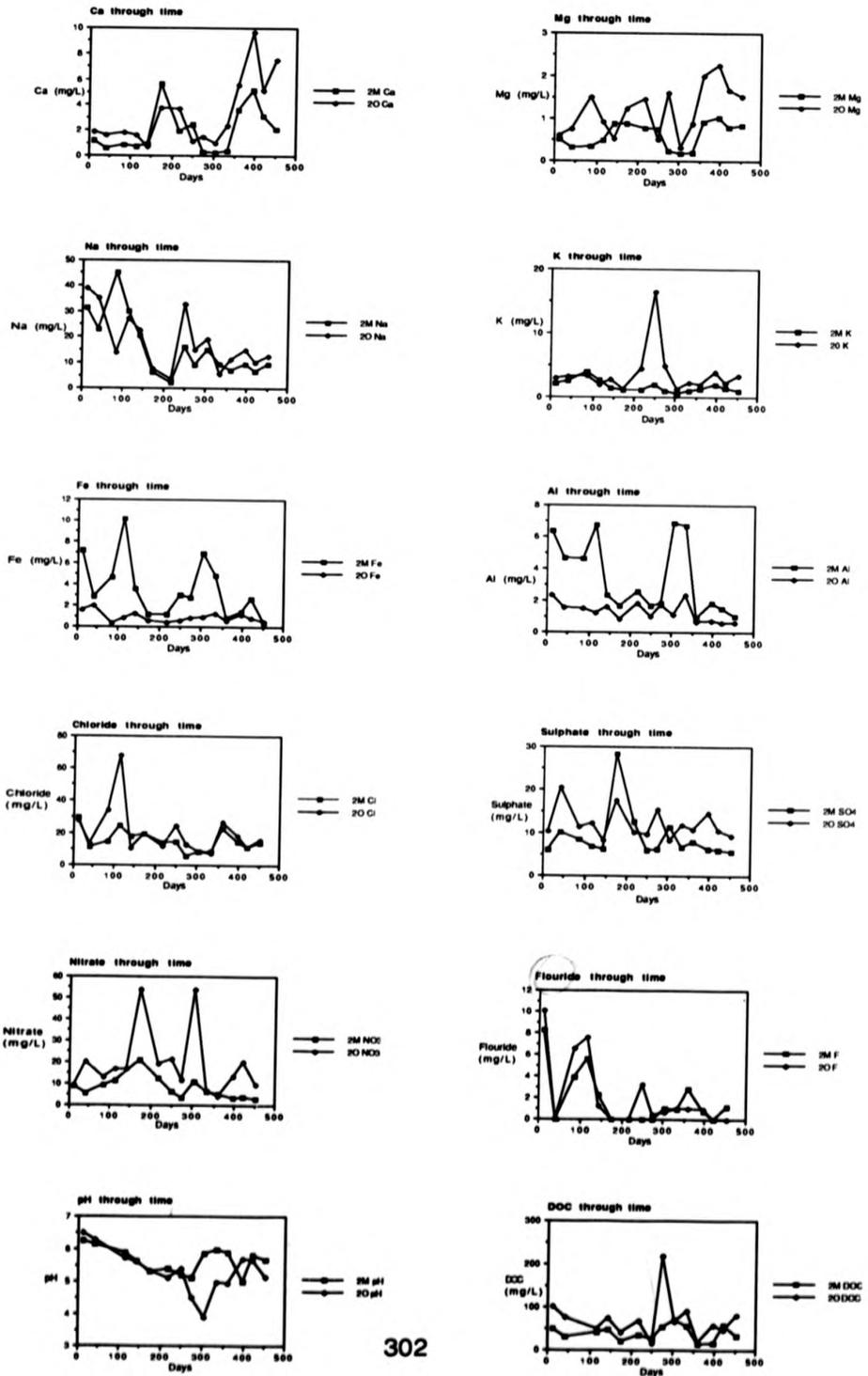


Figure 3 : Site 3 soil water monitoring results

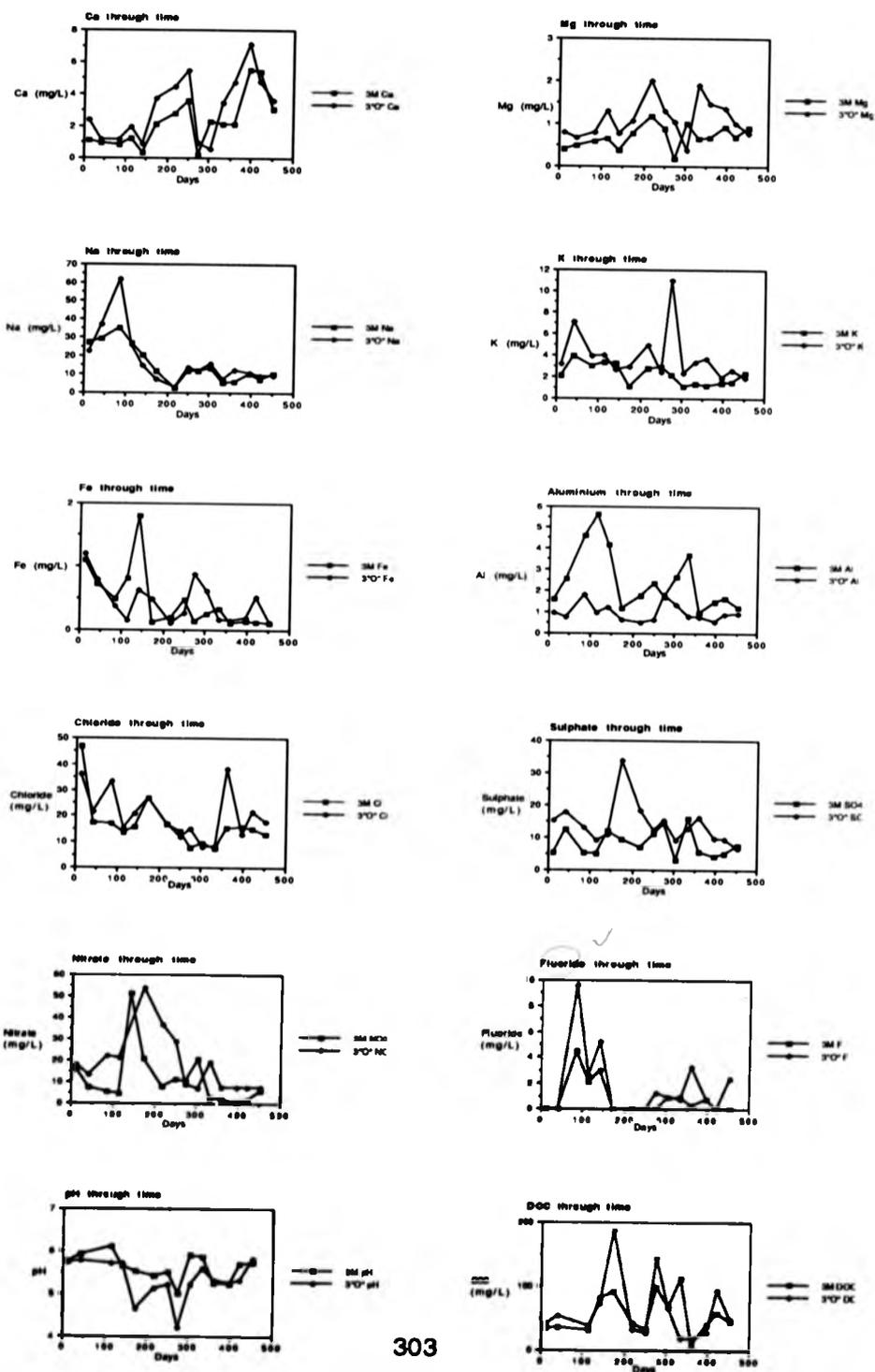


Figure 4 : Site 5 soil water monitoring results

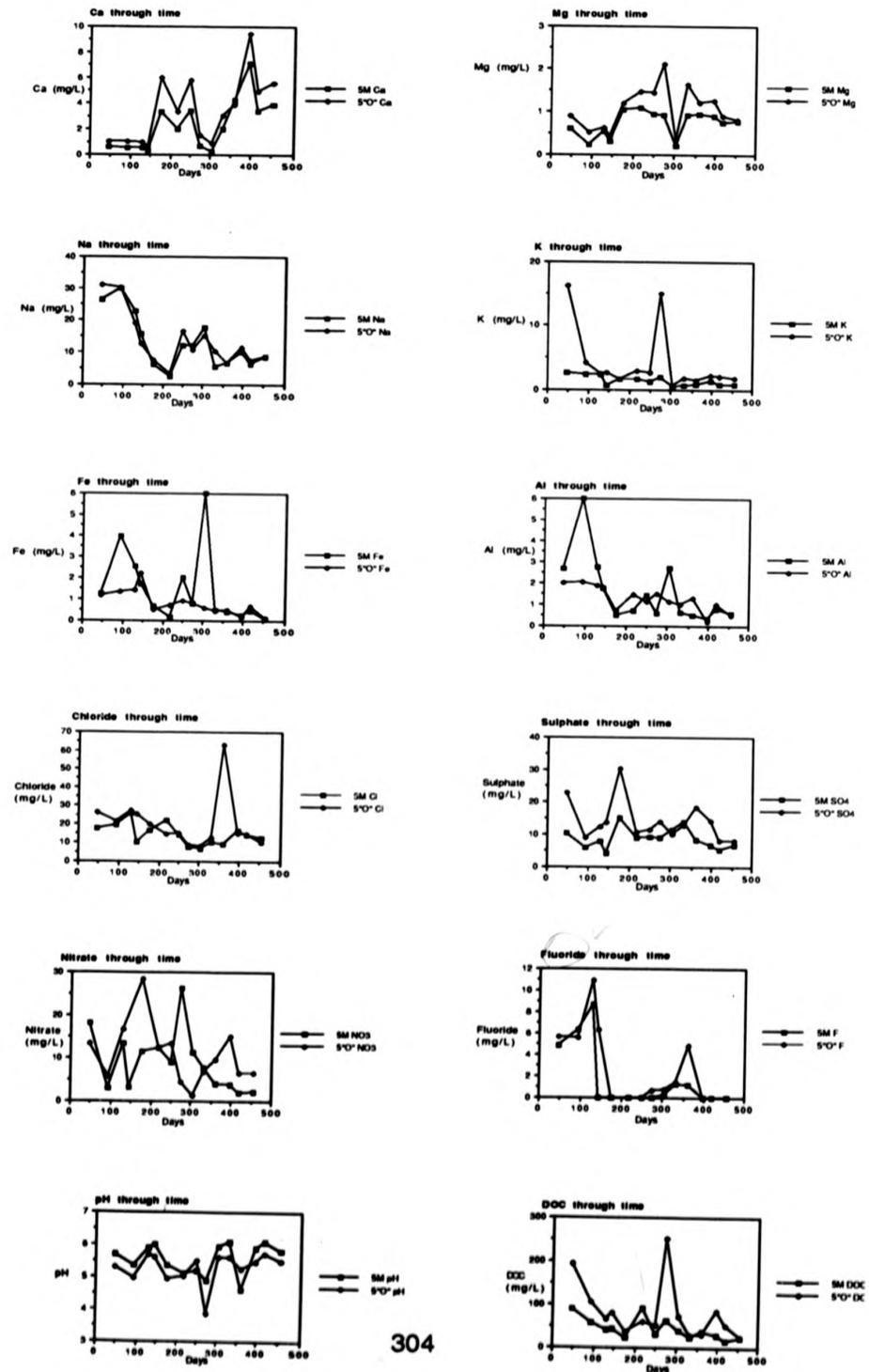


Figure 5 : Site 6 soil water monitoring results

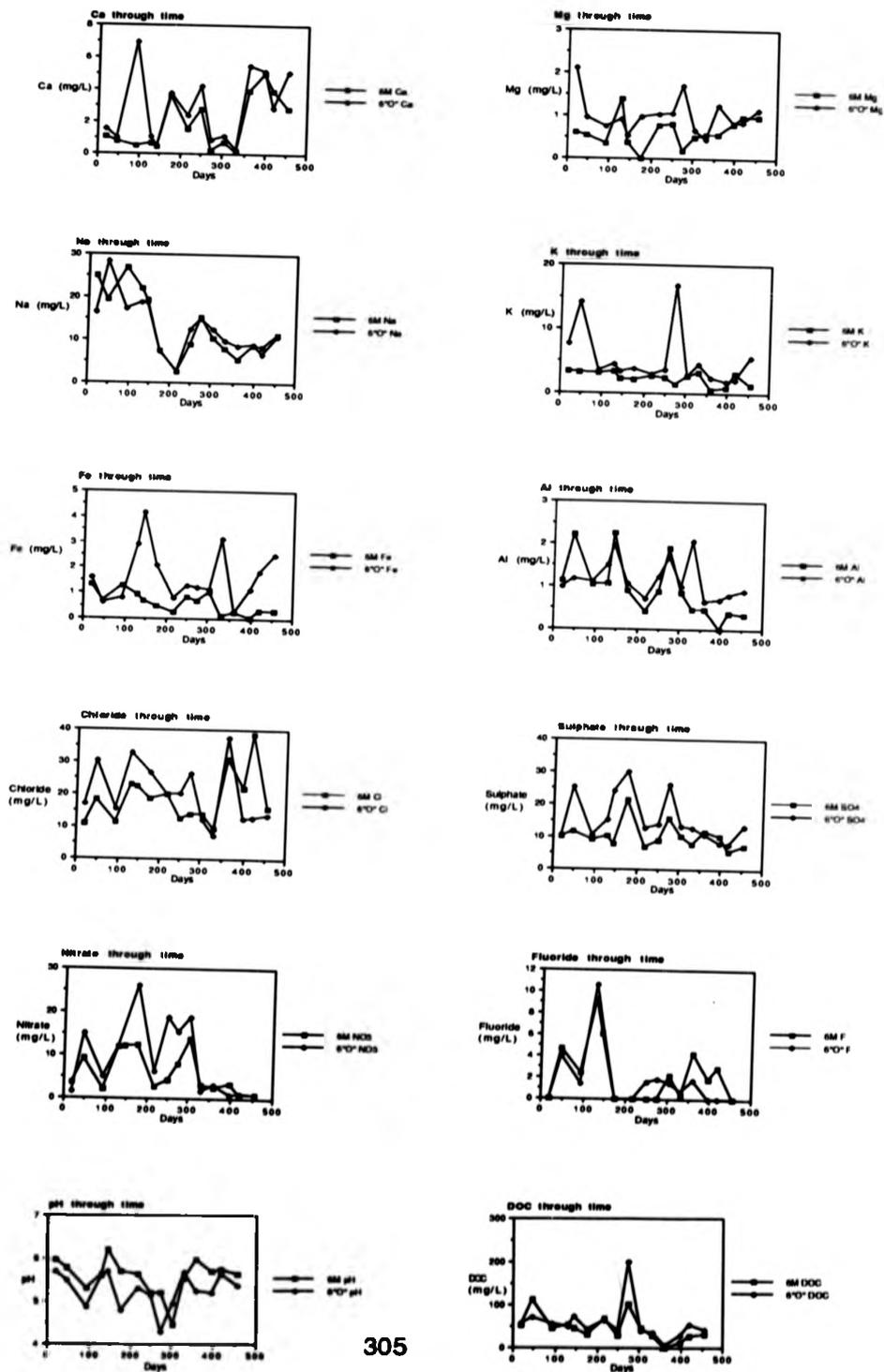


Figure 6 : Site 7 soil water monitoring results

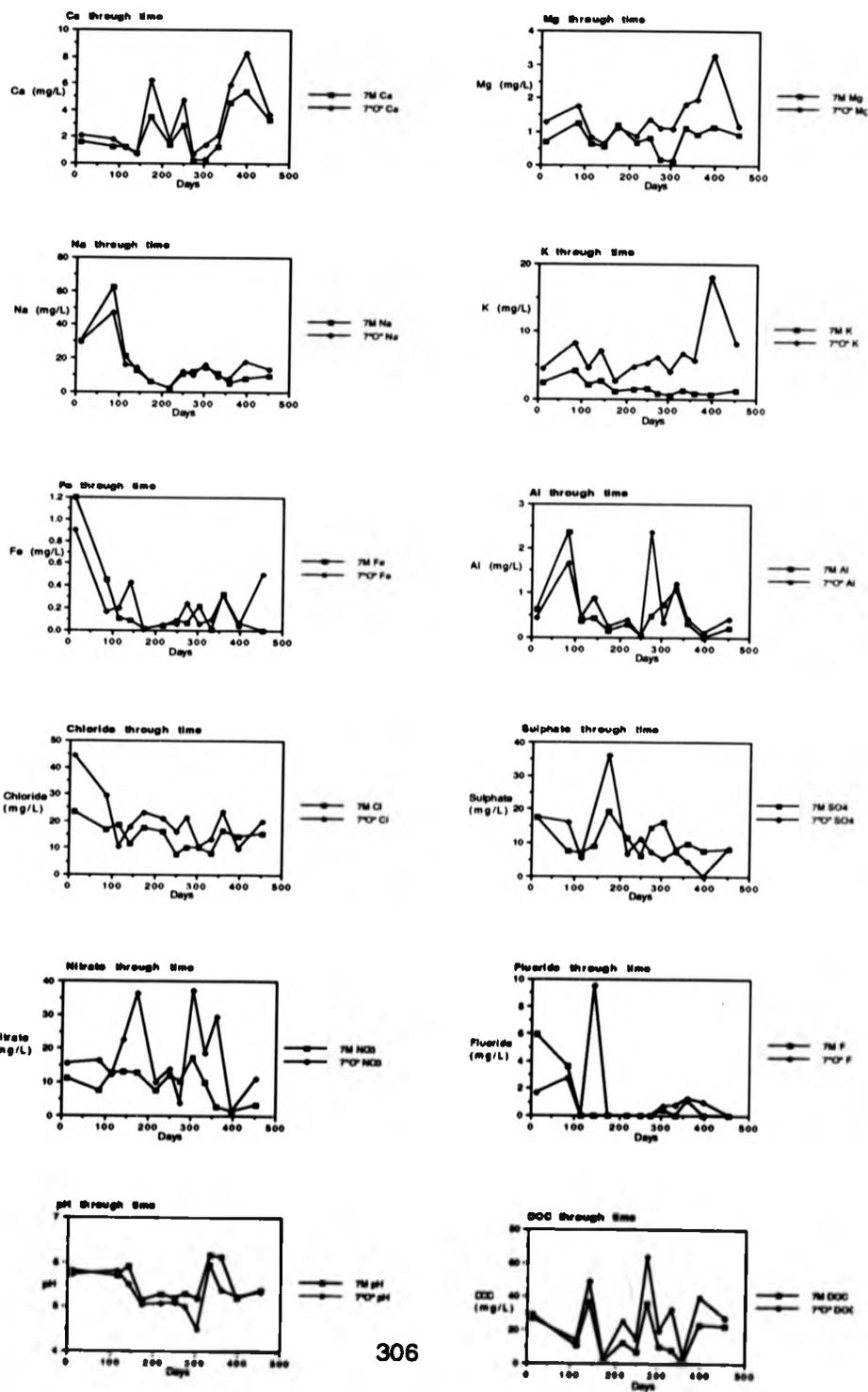


Figure 7 : Site 8 soil water monitoring results

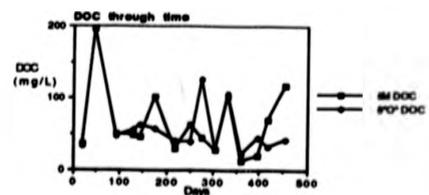
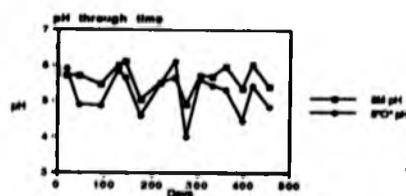
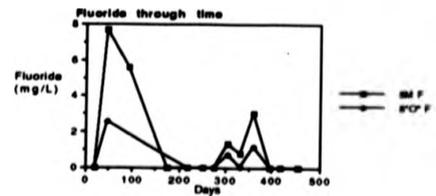
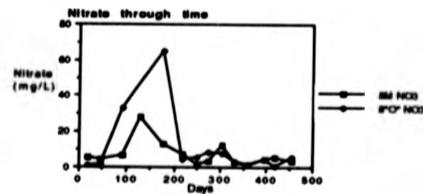
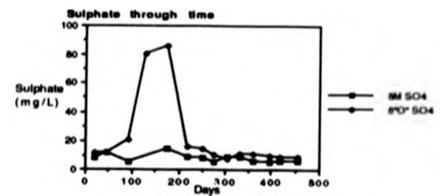
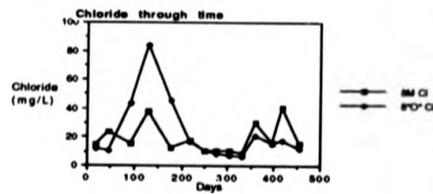
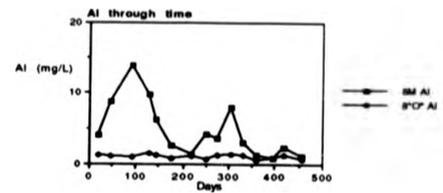
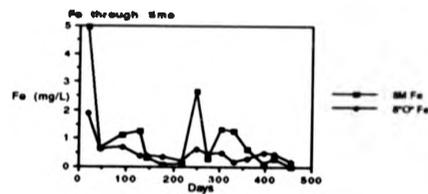
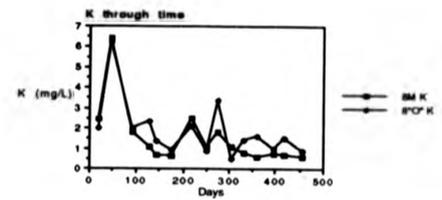
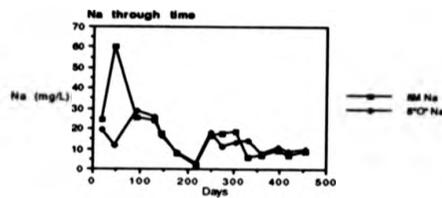
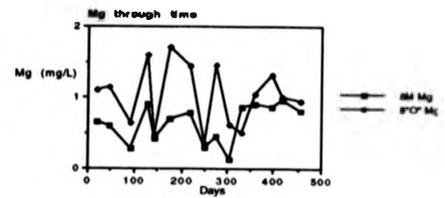
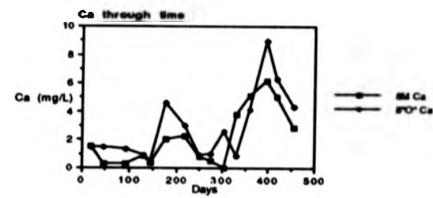


Figure 8 : Site 9 soil water monitoring results

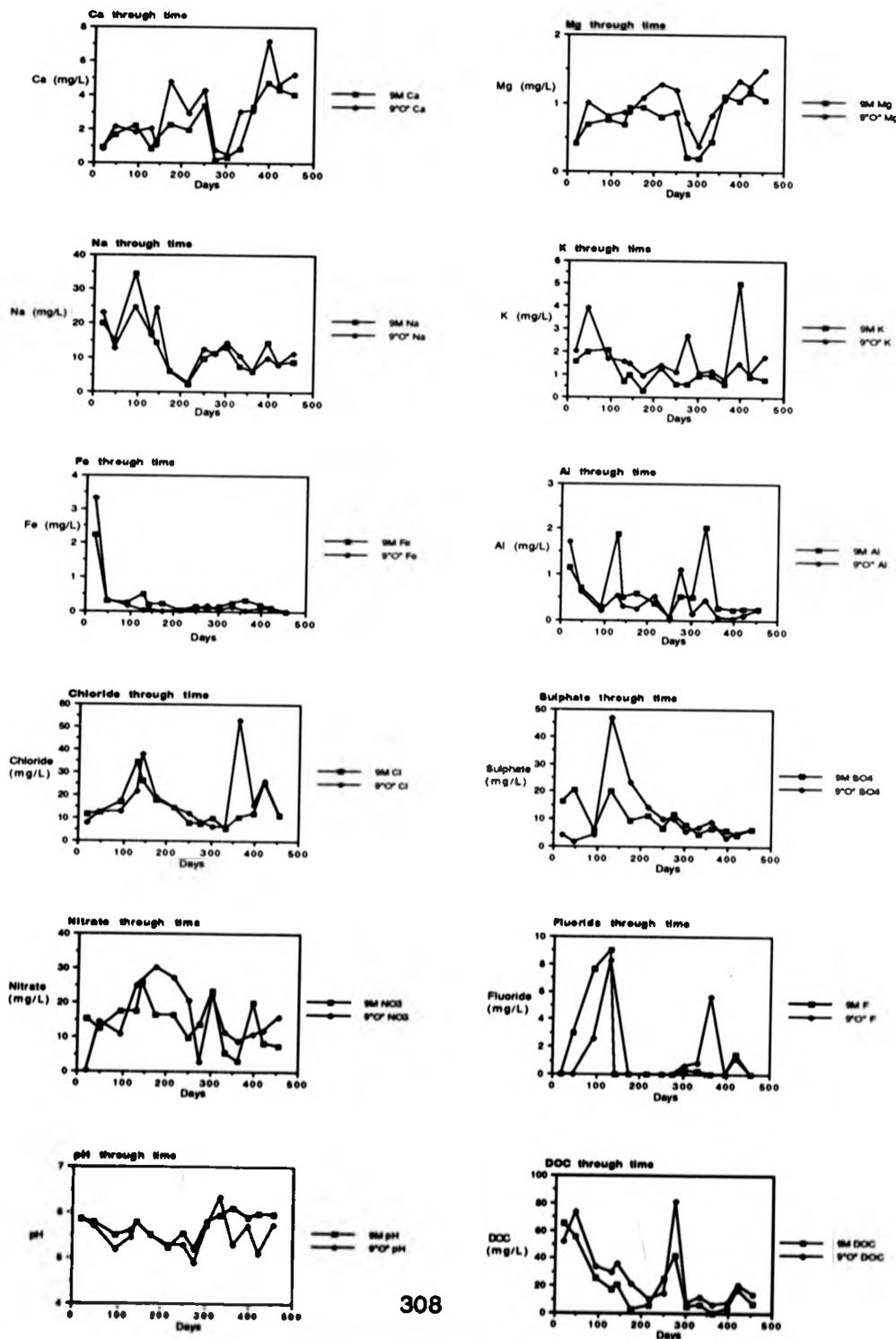


Figure 9 : Site 10 soil water monitoring results

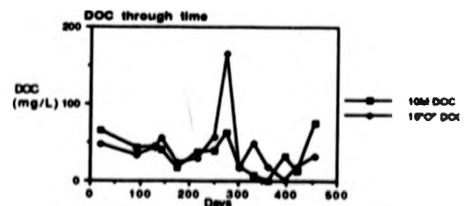
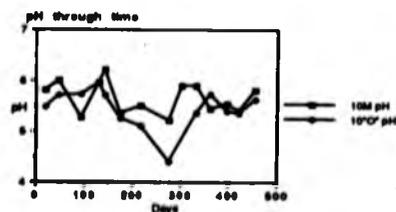
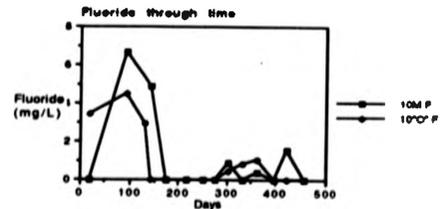
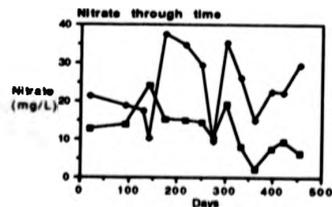
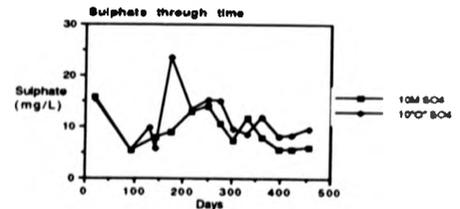
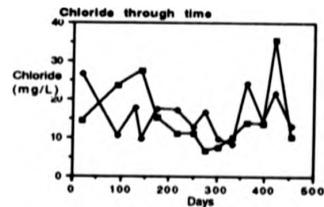
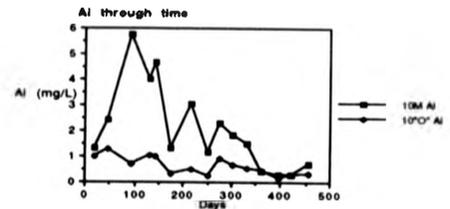
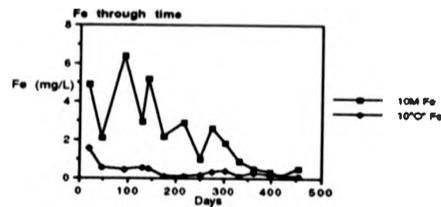
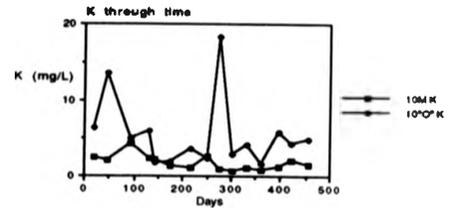
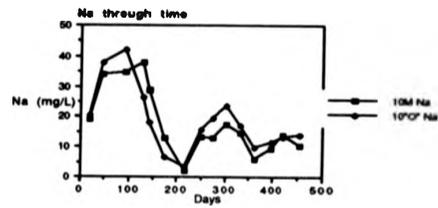
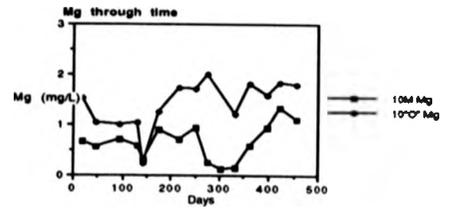
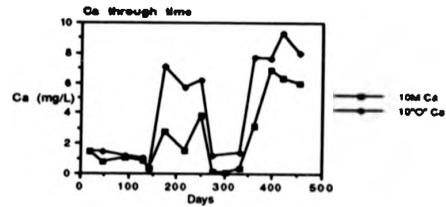


Figure 10 : Site 11 soil water monitoring results

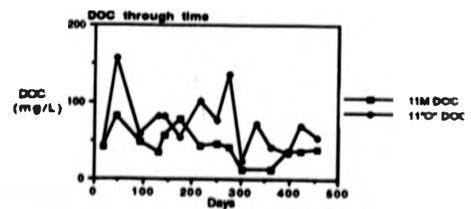
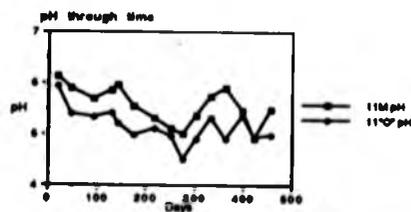
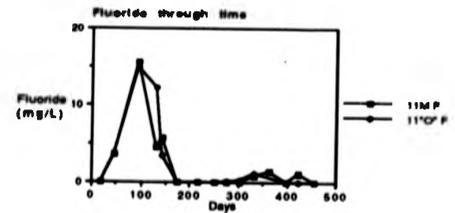
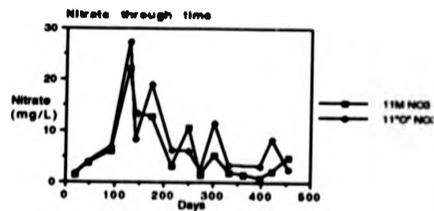
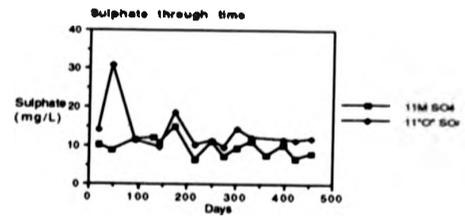
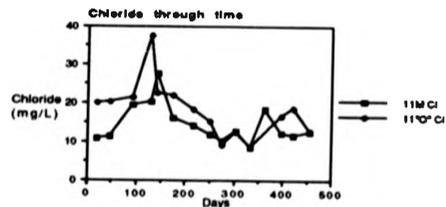
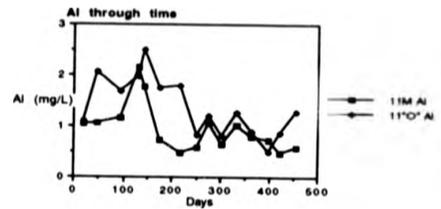
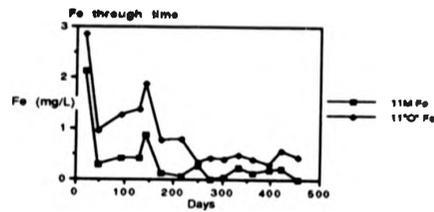
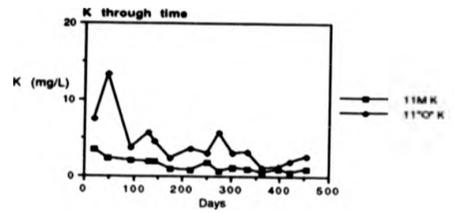
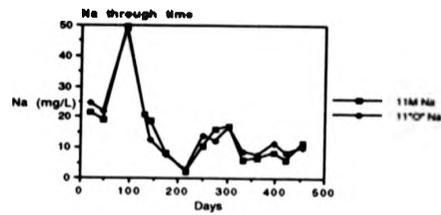
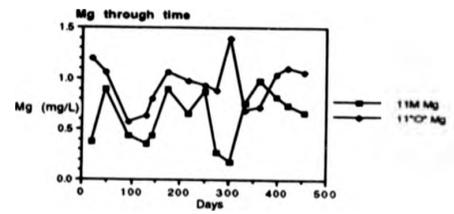
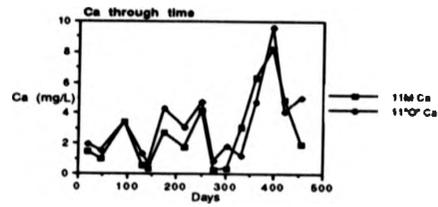


Figure 11 : Site 12 soil water monitoring results

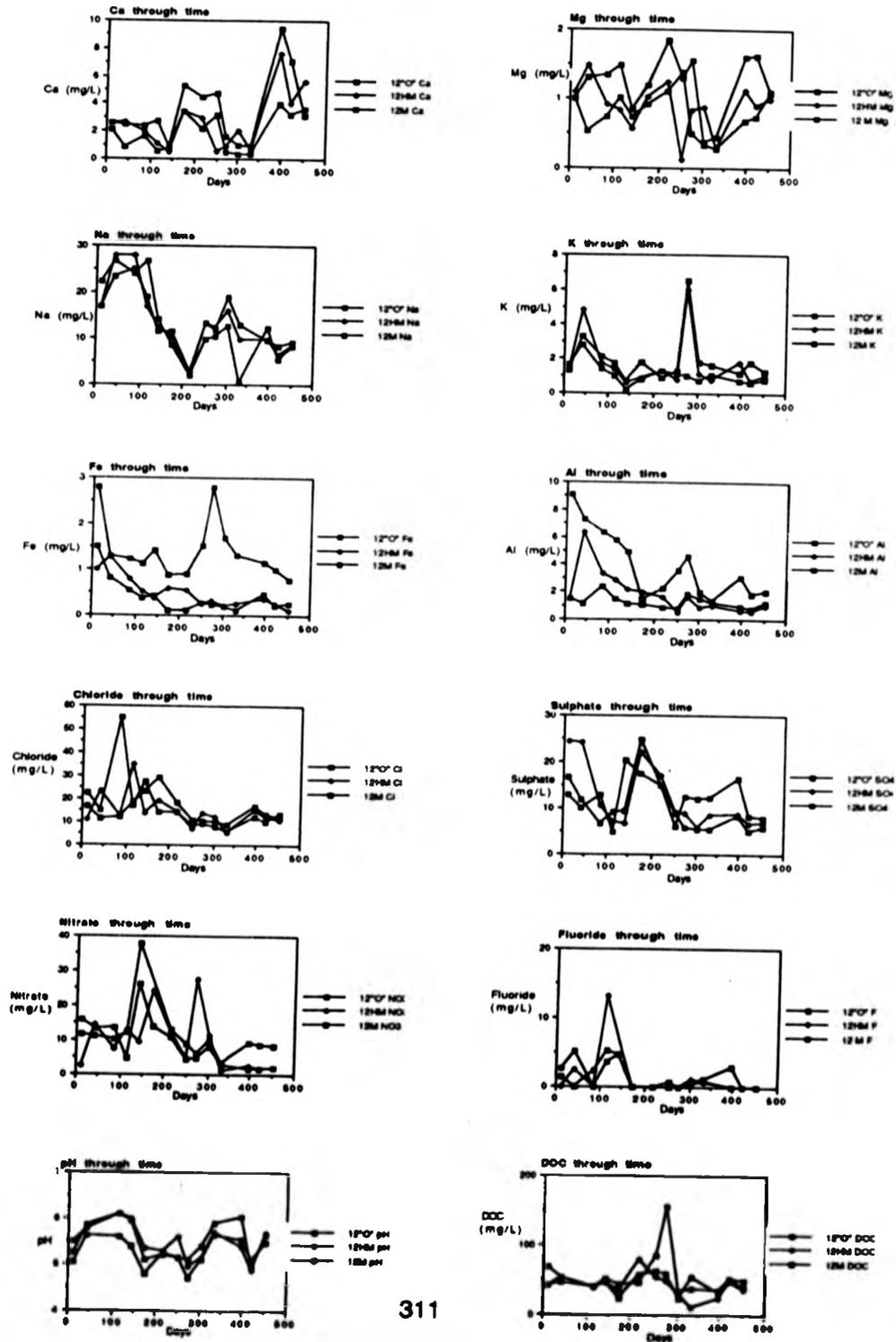


Figure 12 : Site 14 soil water monitoring results

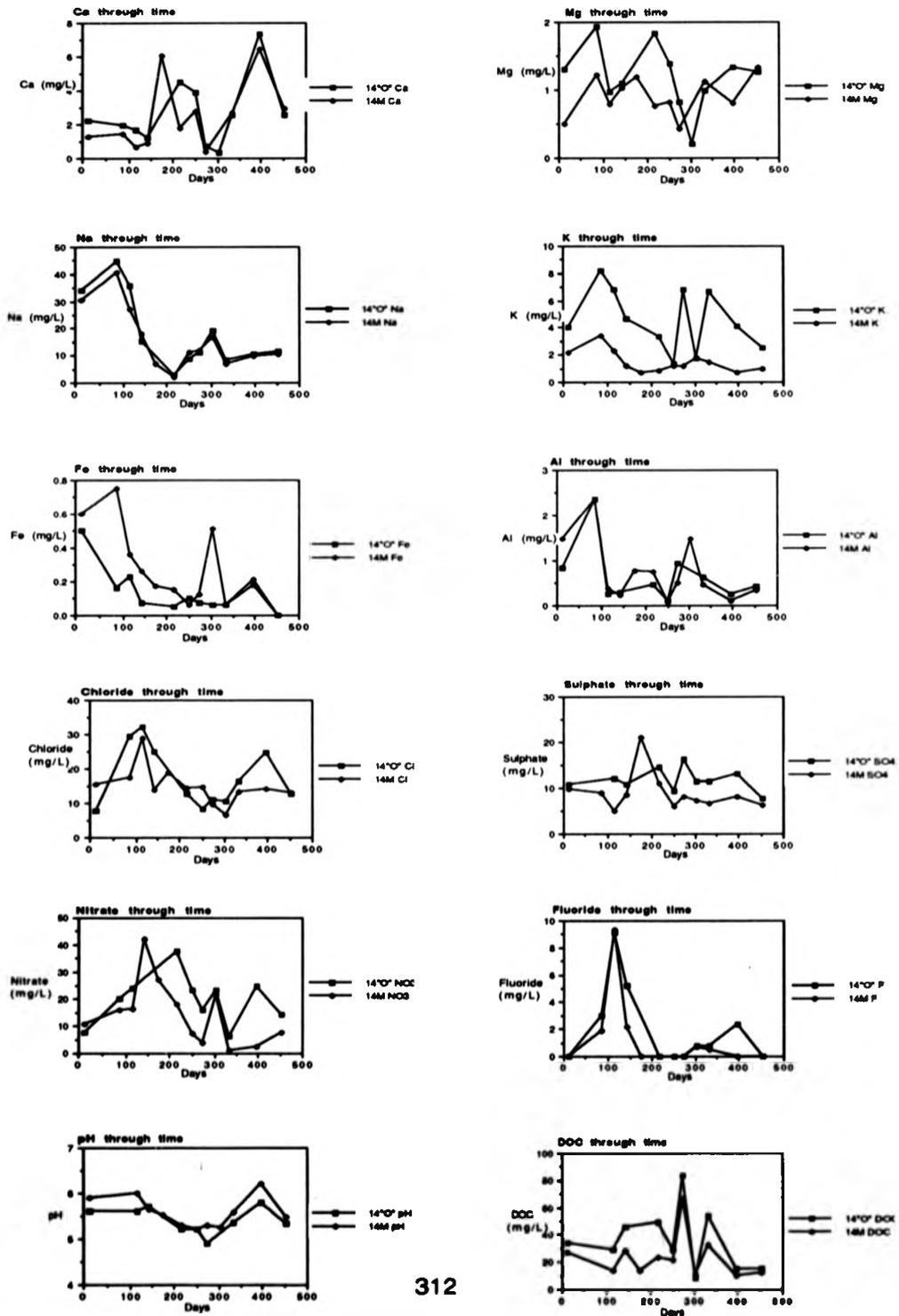


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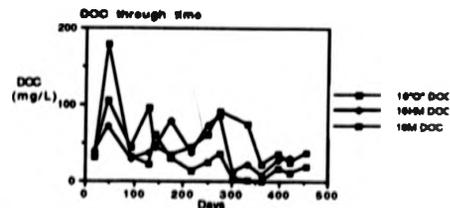
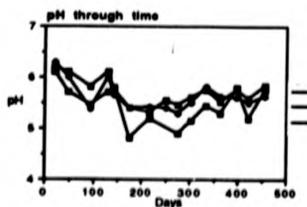
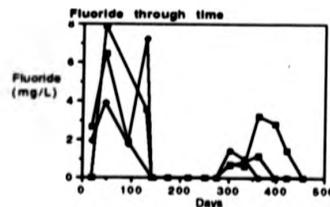
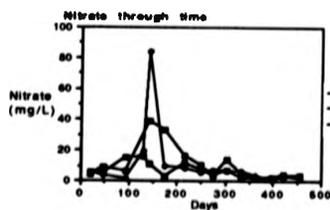
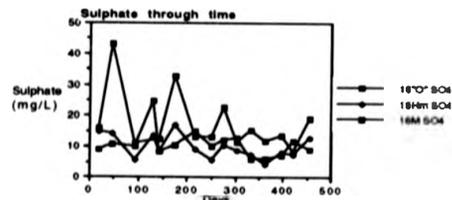
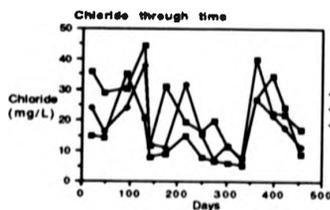
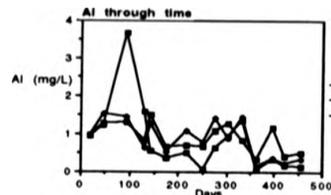
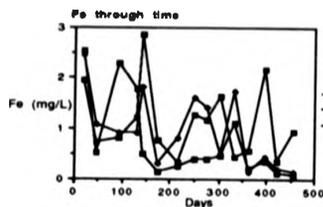
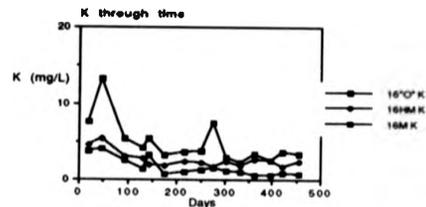
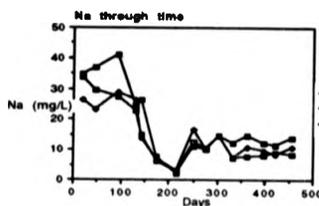
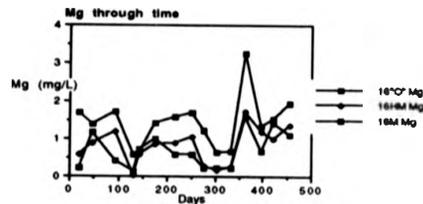
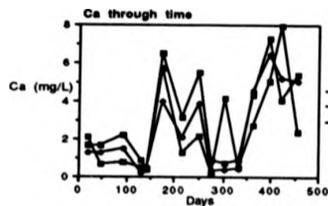


Figure 14 : Site 18 soil water monitoring results

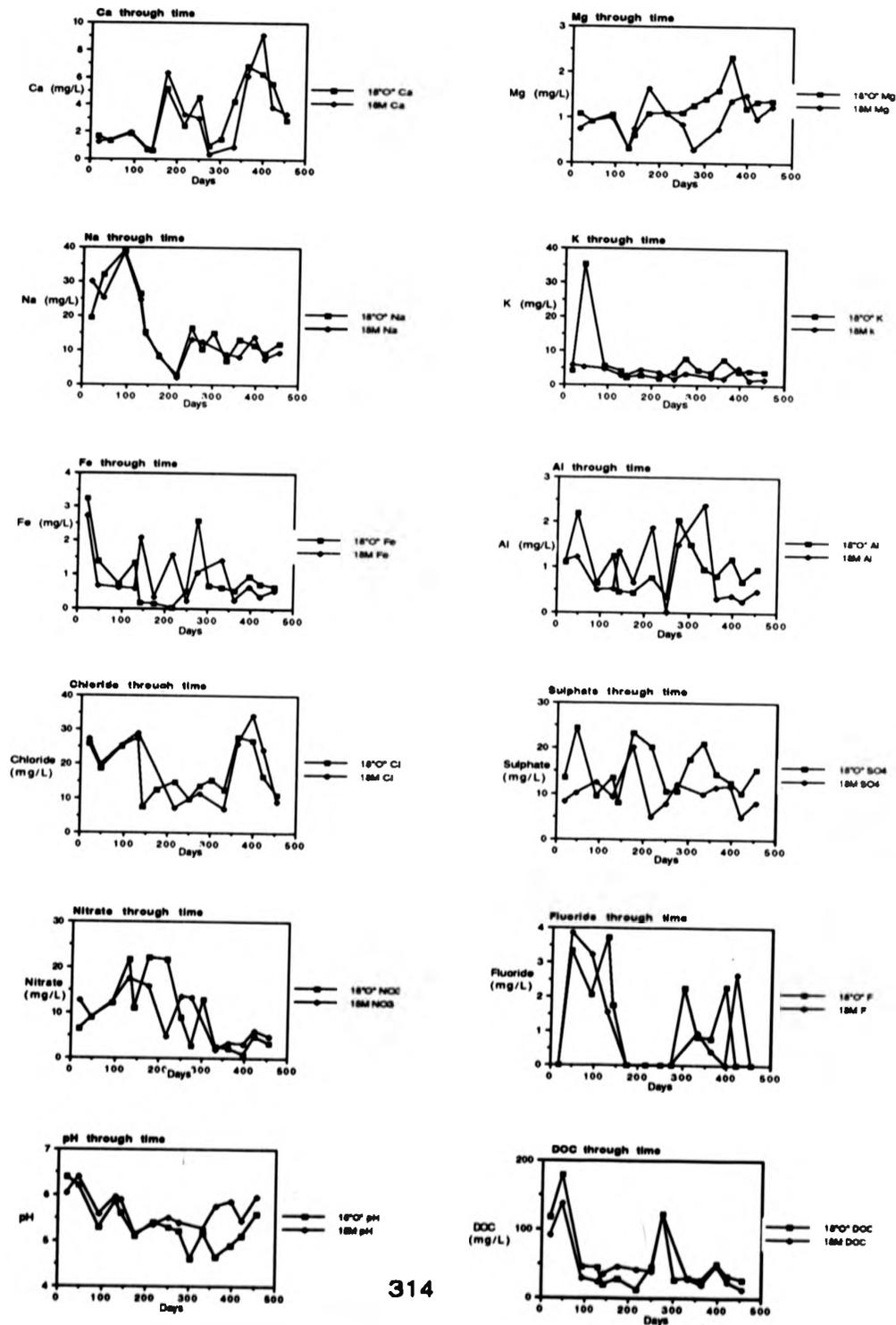


Figure 15 : Site 19 soil water monitoring results

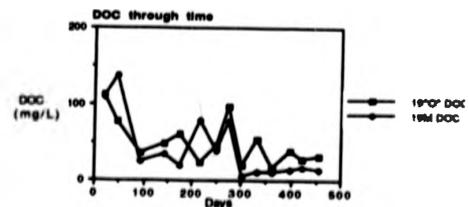
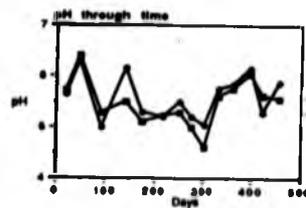
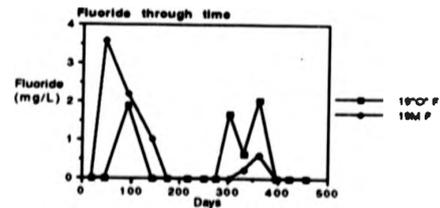
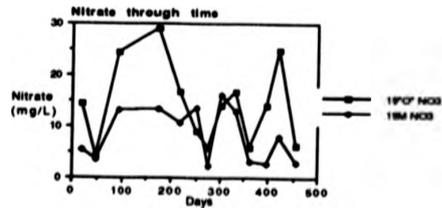
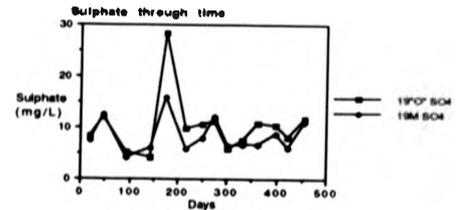
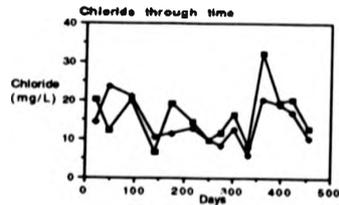
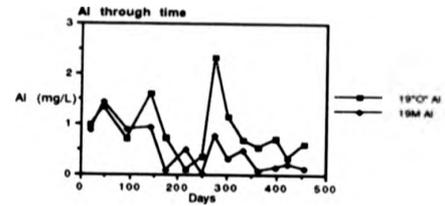
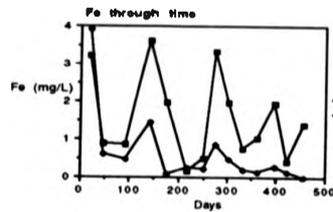
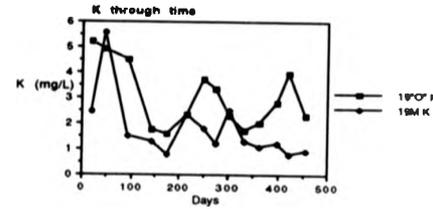
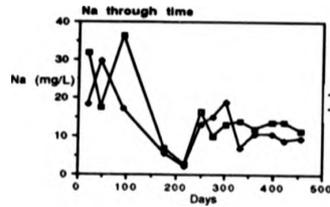
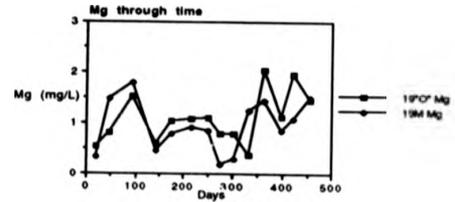
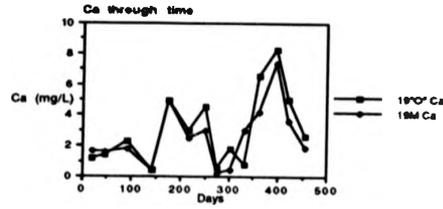


Figure 16 : Site 20 soil water monitoring results

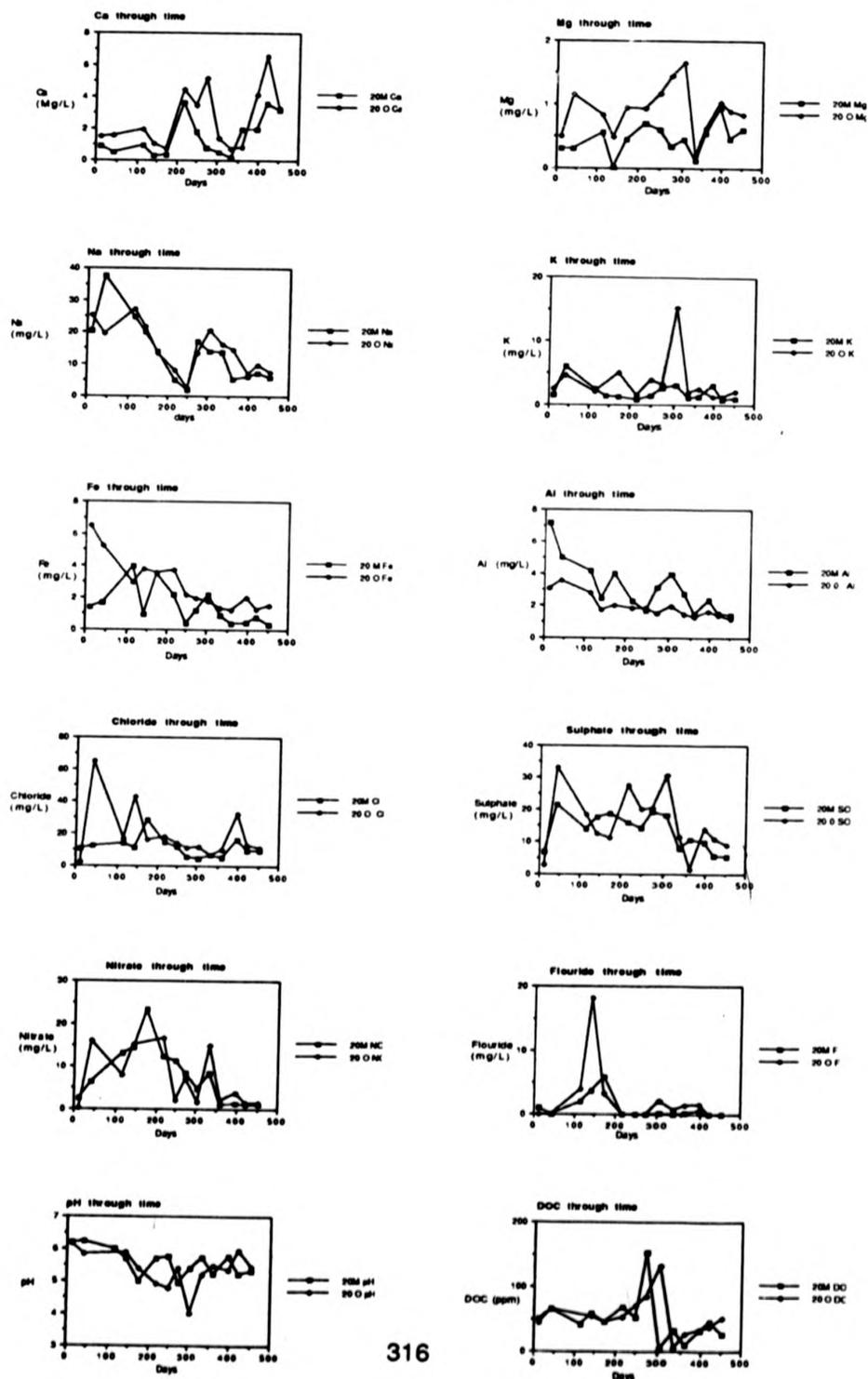


Figure 17 : Site 21 soil water monitoring results

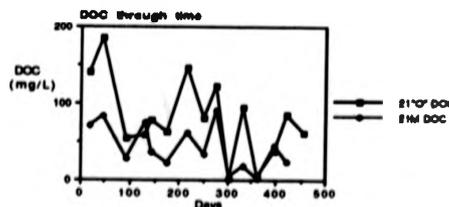
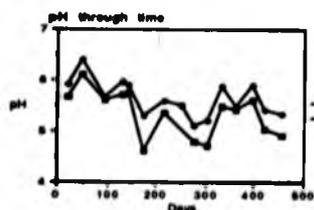
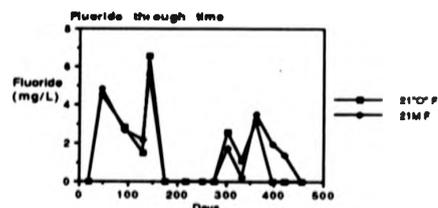
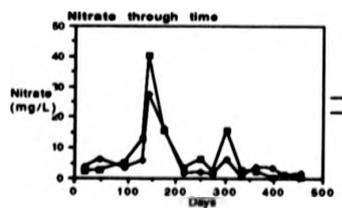
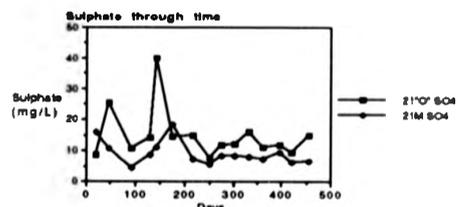
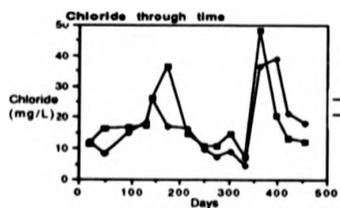
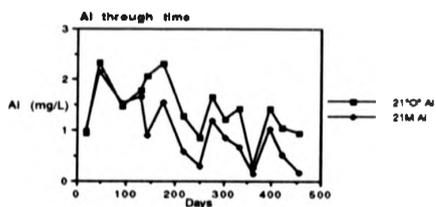
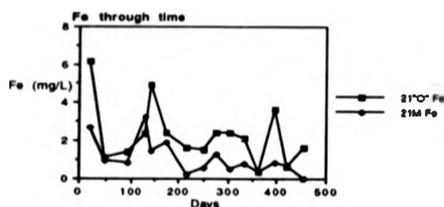
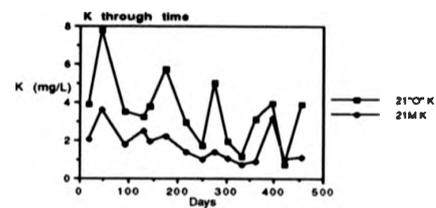
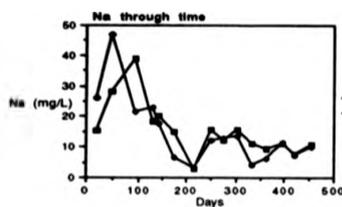
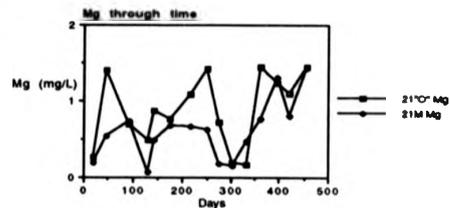
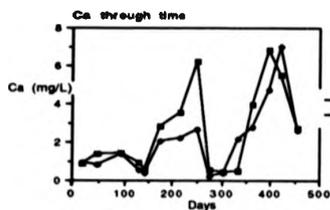


Figure 18 : Site 22 soil water monitoring results

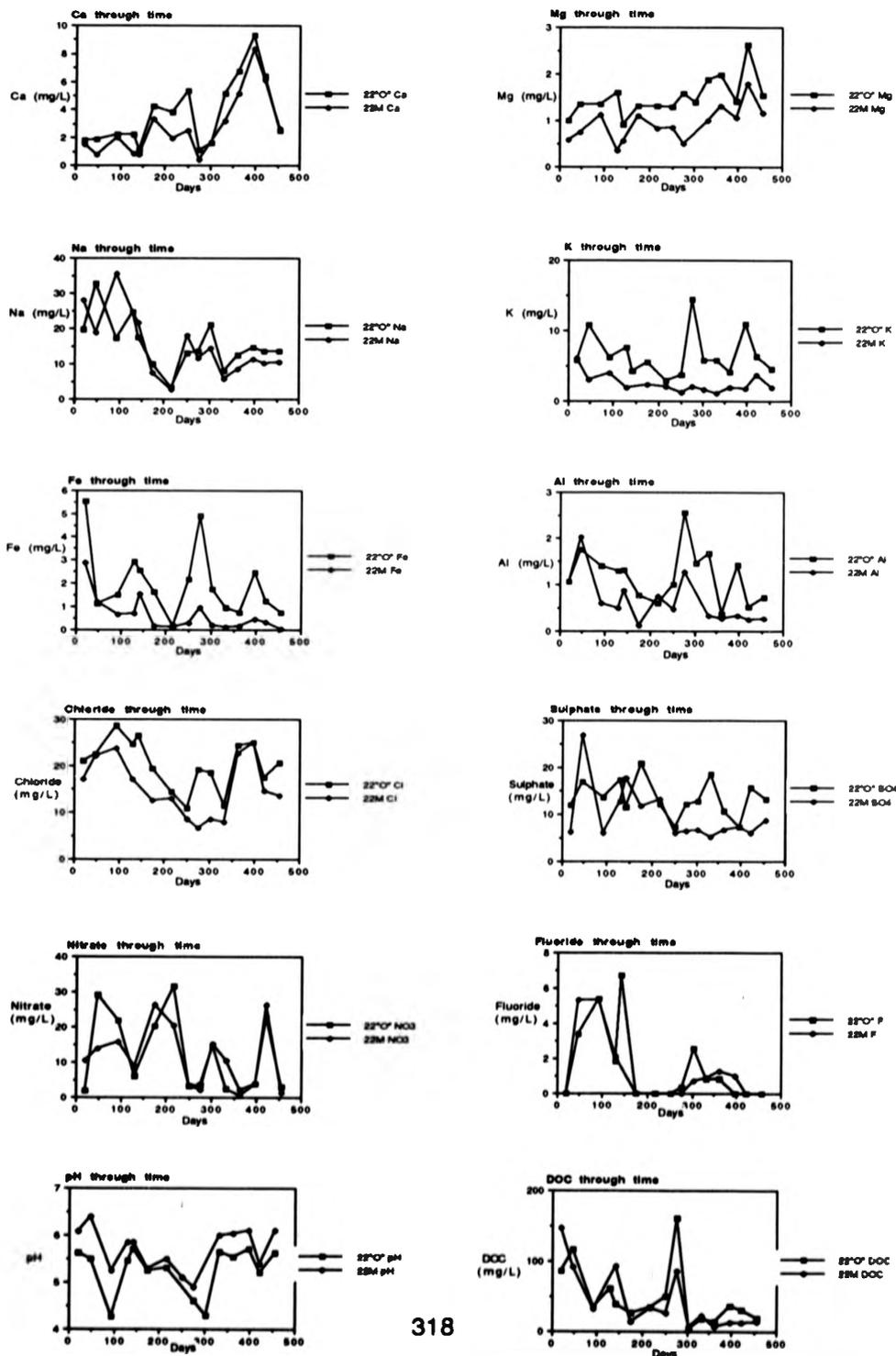


Figure 19 : Site 23 soil water monitoring results

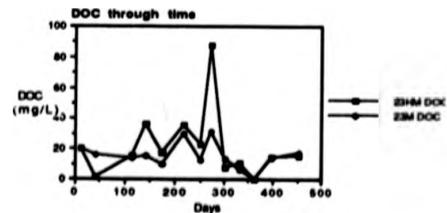
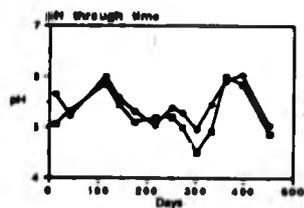
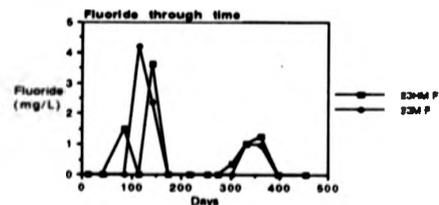
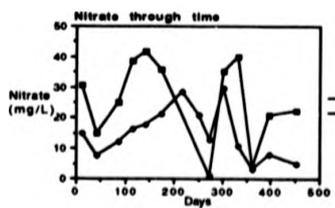
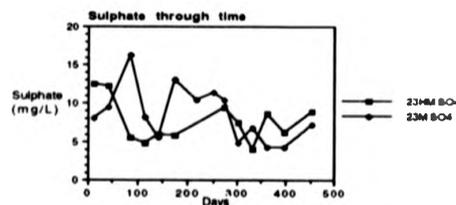
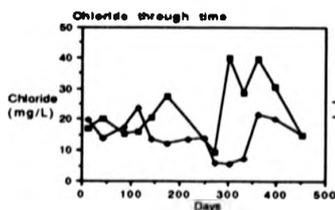
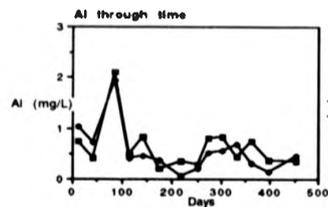
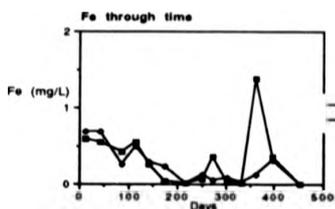
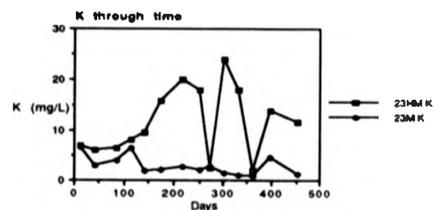
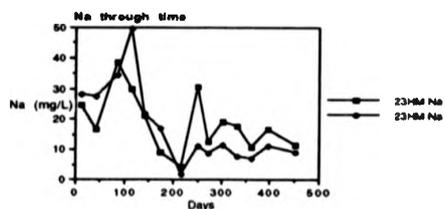
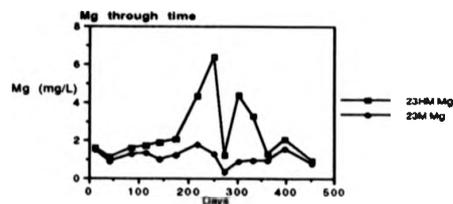
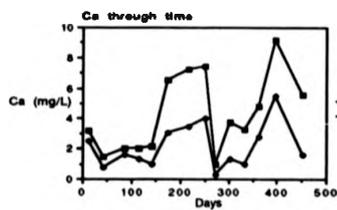
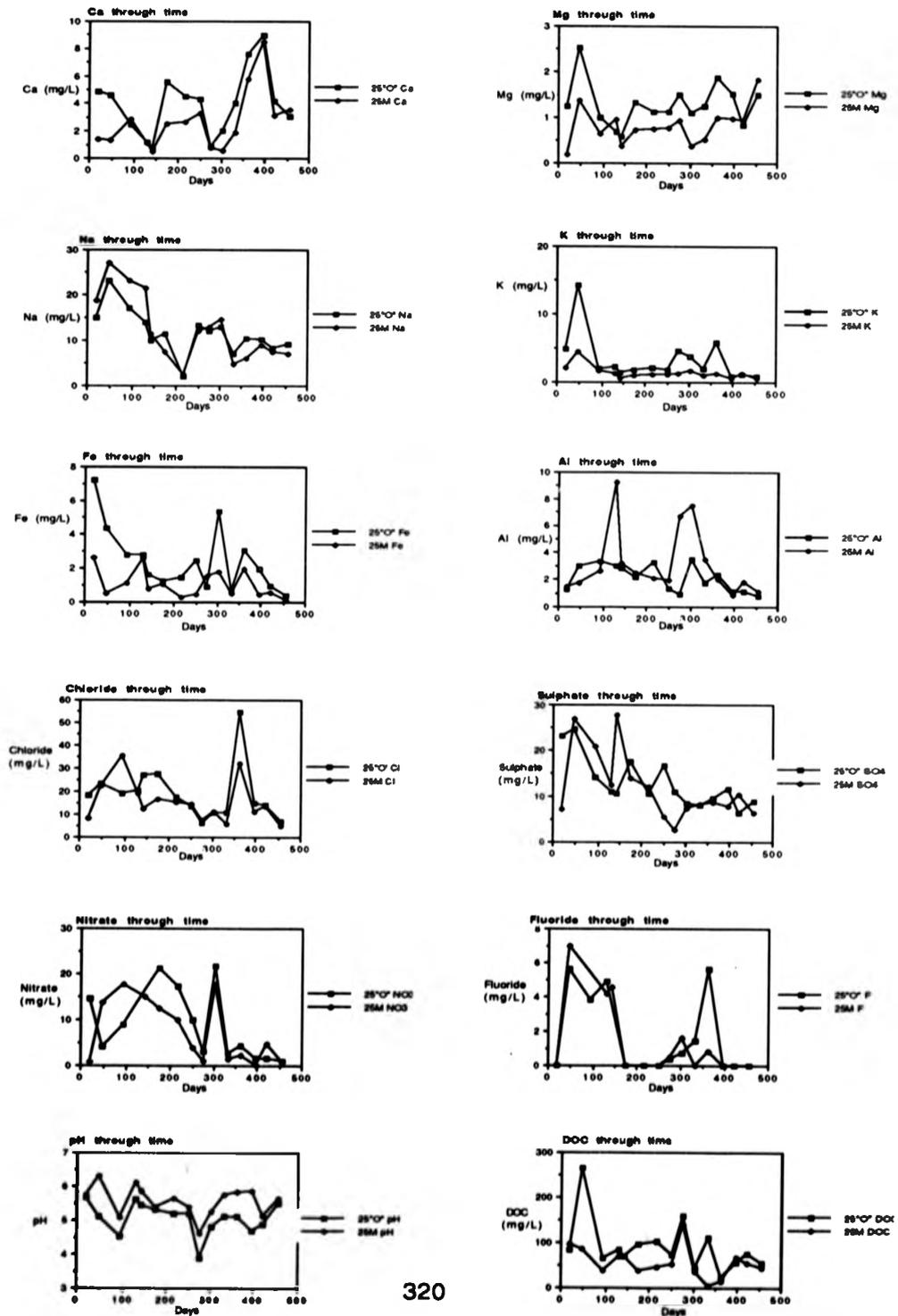


Figure 20 : Site 25 soil water monitoring results



Appendix H

Table H1: Conversion of Al < 0.45µm in size to molar concentrations.

	Al < 0.45 µm (µg/L)	Al < 0.45 µm (M)	-log ₁₀ M
2M1 March	1058	3.9 x 10 ⁻⁵	4.41
2M2 March	1765	6.5 x 10 ⁻⁵	4.18
10M1 March	375	1.4 x 10 ⁻⁵	4.86
10M2 March	218	8.1 x 10 ⁻⁶	5.09
2M1 May	600	2.2 x 10 ⁻⁵	4.65
2M2 May	220	8.2 x 10 ⁻⁶	5.09
10M1 May	485	1.8 x 10 ⁻⁵	4.75
10M2 May	1567	5.8 x 10 ⁻⁵	4.24

Table H2: Conversion of 'total' Al data to Molar concentrations

	'Total' Al (µg/L)	'Total' Al (M)	-log ₁₀ M
2M1 March	1242	4.6 x 10 ⁻⁵	4.34
2M2 March	2375	8.8 x 10 ⁻⁵	4.06
10M1 March	386	1.4 x 10 ⁻⁵	4.84
10M2 March	302	1.1 x 10 ⁻⁵	4.96
2M1 May	641	2.4 x 10 ⁻⁵	4.62
2M2 May	231	8.6 x 10 ⁻⁶	5.07
10M1 May	1282	4.8 x 10 ⁻⁵	4.32
10M2 May	1620	6.0 x 10 ⁻⁵	4.22

Table H3: Conversion of dialysed Al data to molar concentrations

	Dialysed Al ($\mu\text{g/L}$)	Dialysed Al (M)	$-\log_{10} M$
2M1 March	147	5.4×10^{-6}	5.26
2M2 March	337	1.2×10^{-5}	4.90
10M1 March	69	2.6×10^{-6}	
10M2 March	61	3.2×10^{-6}	5.65
2M1 May	67	2.5×10^{-6}	5.60
2M2 May	44	1.7×10^{-6}	5.78
10M1 May	24	8.9×10^{-7}	6.05
10M2 May	18	6.7×10^{-7}	6.17

Table H4: Conversion of exchangeable Al identified by Am 200 to molar concentrations.

	Exch Al ($\mu\text{g/L}$) Am 200	Exch Al (M) Am 200	$-\log_{10} M$
2M1 March	769	2.9×10^{-5}	4.54
2M2 March	1088	4.0×10^{-5}	4.39
10M1 March	175	6.5×10^{-6}	5.19
10M2 March	175	6.5×10^{-6}	5.19
2M1 May	181	6.7×10^{-6}	5.17
2M2 May	109	4.0×10^{-6}	5.39
10M1 May	1058	3.9×10^{-5}	4.41
10M2 May	1141	4.2×10^{-5}	4.37

Table H5: Conversion of exchangeable Al identified by Am IRC 50 results to molar concentrations.

	Exch Al ($\mu\text{g/L}$) IRC 50	Exch Al (M) IRC 50	$-\log_{10} \text{M}$
2M1 March	721	2.7×10^{-5}	4.57
2M2 March	1347	5.0×10^{-5}	4.30
10M1 March	291	1.1×10^{-5}	4.97
10M2 March	156	5.8×10^{-6}	5.24
2M1 May	173	6.4×10^{-6}	5.19
2M2 May	164	6.1×10^{-6}	5.21
10M1 May	629	2.3×10^{-5}	4.63
10M2 May	667	2.5×10^{-5}	4.61

Table 6H: Conversion of 'total' Si data to molar concentrations and Al data for use in figure 6.61C.

Si ($\mu\text{g/L}$)	Si (M) $\times 10^3$	$-\log_{10} \text{Si (M)}$	Al ($\mu\text{g/L}$)	$-\log_{10} \text{Al (M)}$	pH	$-\log_{10} \text{Al (M)}$ $+ 3\text{pH}$
1886	6.71	4.17	1242	4.34	6.02	9.88
3590	12.8	3.89	2375	4.06	5.87	9.45
1227	4.37	4.36	386	4.84	5.64	10.0
1225	4.36	4.36	302	4.96	5.55	10.0
2217	7.89	4.10	641	4.62	5.82	9.96
2730	9.72	4.01	231	5.07	5.61	10.2
1570	5.62	4.25	1282	4.32	6.00	9.84
1245	4.43	4.35	1620	4.22	6.41	10.2

Table H7: Conversion of 0.45 μ m filtered Si data to molar concentrations and Al data for use on figure 6.61D.

Si (μ g/L)	Si (M) $\times 10^3$	$-\log_{10}$ Si (M)	Al (μ g/L)	$-\log_{10}$ Al (M)	pH	$-\log_{10}$ Al + 3pH
1831	6.71	4.17	1058	4.41	6.02	9.95
2933	10.4	3.98	1765	4.18	5.87	9.57
1063	3.78	4.42	375	4.86	5.64	10.0
772	2.75	4.56	218	5.09	5.55	10.2
2225	7.92	4.10	600	4.65	5.82	9.99
2580	9.18	4.04	220	5.09	5.61	10.2
1380	4.91	4.31	485	4.75	6.00	10.3
1169	4.16	4.38	1567	4.24	6.42	10.1

Table H8: Conversion of dialysed Si data to molar concentrations and Al for use on figure 6.61E.

Si (μ g/L)	Si (M) $\times 10^3$	$-\log_{10}$ Si (M)	Al (μ g/L)	$-\log_{10}$ Al (M)	pH	$-\log_{10}$ Al + 3pH
925	3.29	4.48	147	5.26	6.02	10.8
1338	4.76	4.32	337	4.90	5.87	10.3
607	2.16	4.67	69	5.59	5.64	10.8
412	1.47	4.83	61	5.65	5.55	10.7
1825	6.50	4.19	67	5.60	5.82	11.1
2563	9.12	4.04	44	5.78	5.61	10.9
1100	3.92	4.41	24	6.05	6.00	11.6
750	2.67	4.57	18	6.17	6.41	12.1