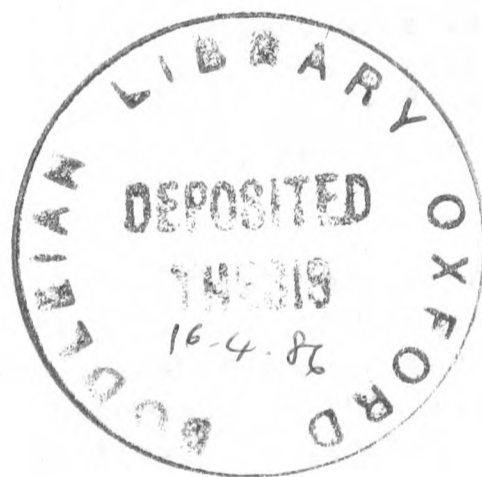


The chemical composition of soil solutions  
extracted from top soils in the Oxford  
area: the magnitude and range of variability.

Duncan J Campbell

St Cross College



Thesis submitted for the degree of

D.Phil.

Michaelmas Term, 1985

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#### Abstract

Although the soil solution lies at the centre of many of the processes which occur in soils, little information is available on the chemical composition of the soil solutions of field soils, or on the temporal and spatial variability of such solutions.

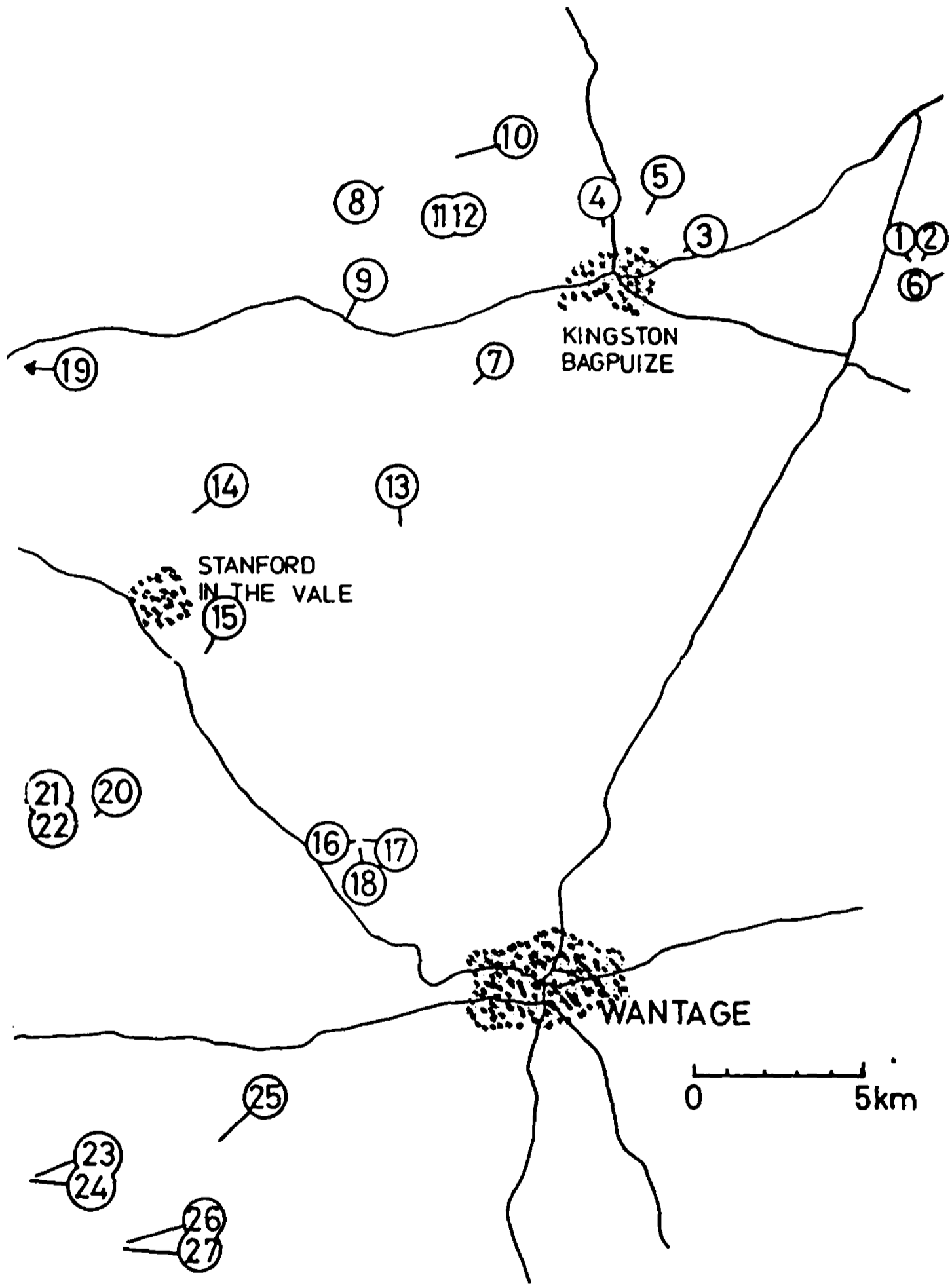
The suitability of an immiscible fluid centrifugation method for obtaining samples of the soil solution was evaluated. The method was found to be substantially free from interferences and well suited to routine use. It was adapted for use with soils of low bulk density. Yields of soil solution from soils at or near field capacity ranged from 20 to 50% of the total water present. However little or no soil solution could be extracted from dry soils. Displaced solutions were analysed for about 20 solutes principally by inductively coupled plasma spectroscopy.

Typical solute concentrations in soil solutions from six neutral and calcareous soil series in the Oxford area were in the range  $10^{-2.4}$  to  $10^{-3.4}$  M for Na, K, Ca, S, Cl,  $\text{NO}_3$ , alkalinity and dissolved organic carbon (DOC);  $10^{-3.4}$  to  $10^{-4.4}$  M for Mg, Si and P and  $<10^{-5.3}$  M for B, Li, Y, Ba, Mn, Cu, Fe, V, Zn, Al, Pb, Ni, Cd, Co, Sr and Mo.

Short-range (5-10 m) variability was significantly less, and between-soil series variability significantly more, than the variability found between grass fields on the same soil series for most solutes. The main exception to this was  $\text{NO}_3$  which exhibited a large between-field variability. In general, soil solutions from arable soils were more dilute than those from nearby pasture soils. Solutions from poorly drained sites on a heavy clay soil were more concentrated than those from freely draining sites on the same soil series.

A year-long sampling programme showed that with the exception of P and alkalinity the concentrations of solutes in the soil solution changed significantly with time. The temporal range in the concentrations of solutes was found to increase in the order Si-P<alkalinity-Fe<Na<Ca-Sr-Mg-Cu<S-DOC<K-Zn<Cl-pH<Mn.

For my mother, Annie Spiers Campbell,  
and my friend, Karen Rosemary Makings.



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### Acknowledgements

I would like to thank:-

My supervisors, Drs Philip Beckett and David Kinniburgh, for devising the project and for their help, guidance and encouragement throughout.

Rose Andrews, Jenny Cook, Doug Miles, Janice Trafford and Chris Smith of the chemistry sections of BGS and IH at Wallingford for their instruction in the use of, and help with, analytical equipment.

The many farmers and landowners who kindly allowed me to take soil samples from their land.

Jon Hoskin of IH, Wallingford, for help with the statistical analyses.

Trudy Watt and Doug Miles for reading and commenting on parts of this thesis.

My fellow travellers in 'The Department' for being themselves.

Mrs A Doyle and Gillian for their emergency typing.

And last, but by no means least, Karen Makings for her unstinting proof reading of the all-too-many drafts through which this thesis has passed.

This project was funded by an NERC 'CASE' award.

## Chapter 1

### Introduction

We are living in an age of gadgets. By all means let us take advantage of their help, but do not let them become our masters. Our knowledge ... is so fragmentary that the main problem is often to decide what to measure, not how to measure it.

R. H. Flemming, 1952

Soil forming a patchy layer usually no more than a metre in depth is the basis for nearly all forms of life on earth. The processes of soil formation are slow, and so except over periods of geological time, soil is not a renewable resource.

Soil, unlike other non-renewable resources, is not noticeably consumed but it acts as a medium for plant growth providing support, water and nutrients for vegetation.

Soils originate ultimately from the denudation and erosion of rocks. The weathering of material to form soil is the largest scale chemical change since the formation of the earth. Water plays a central role in both the physical and chemical weathering of rock to form soil. Crystals of ice expand in cracks in rocks and water transports material, abrading it as it moves. Water initiates the solution and hydrolysis of minerals and sustains primitive plant life on rock surfaces. Lichens, once established, on rocks, exude chelating agents and acids which promote chemical weathering.

As soils develop, weathering is enhanced by the presence of plants which release acids and chelates into the soil and whose roots apply stress to unbroken rock at lower levels. The physical processes of weathering reduce the size of the particles constituting soil minerals and so bring larger surface areas into contact with the soil solution. Particle size determines the rate of weathering to a certain extent, but it is chemical reactions between soil minerals

and solutes in the soil solution which largely determine the rate and direction of weathering.

Primary silicate minerals such as feldspars and micas release silicic acid and metal ions into solution as they weather. The less soluble species are often incorporated with silicates to form secondary minerals, the silicate and oxide clays, whereas the more soluble species, such as magnesium, are lost from the soil by leaching and are eventually transported to the oceans.

Because secondary minerals crystallise in solutions which contain many centres of nucleation, individual clay particles do not grow to large dimensions. The large surface area of silicate clays, together with their layer structure, makes them uniquely suitable as the sites for many soil reactions. Clays, with organic matter from decomposing plant materials, provide ion-exchange sites in the soil. The ability of soils to hold nutrients on ion-exchange sites makes an important contribution to soil fertility. Insoluble compounds do not release nutrients and soluble compounds may be leached rapidly from the soil. Ion-exchange sites, however, hold nutrients against leaching yet in forms available to plants.

Soil lies at the interface of the atmosphere and the solid earth. Rain water percolating downwards through it has its chemical composition changed by reactions with weathering minerals. These changes depend on the pathway of the water flowing through the soil and on the composition of the material through which it flows. Water flowing through highly-structured material, such as fissured clays and rocks, will have less contact with solid material and less opportunity to react with the soil: it will be less changed than water moving through poorly-structured material. Naturally, changes in the chemical composition of percolating rainwater depend on the

chemical and mineral composition of the soil. In calcareous soils the main weathering process is the dissolution of free carbonates by slightly acidic rainwater which releases bicarbonate and calcium ions into solution. The pH of water draining from such soils will be greater than 7: calcium and bicarbonate will be the dominant ions. In neutral and slightly acidic soils the chemical reactions affecting percolating water are dominated by surface exchange and adsorption processes. Protons in the incoming water are replaced by basic cations from exchange sites and the major ions in solutions draining from these soils are calcium, nitrate and chloride. The highly leached upper horizons of strongly acidic soils will have lost most of their exchangeable calcium and magnesium and are now able to retain calcium from the rain: the water becomes more acidic as it drains through the soil. Acidic precipitation falling on these soils is not neutralised and so the acidity is passed on to river systems and lakes.

In natural ecosystems soils are generally self-renewing: losses by leaching and by the removal of plant and animal materials are balanced by inputs from precipitation and from the weathering of soil minerals. The major part of nutrients are held in the biomass, and only a small fraction is present in the soil at any one time. An extreme example of this is a tropical rain forest in which the luxuriant vegetation is maintained not because of a fertile soil but because of efficient cycling of nutrients between decaying biomass and living vegetation. After removal of the vegetation, nutrients may be lost rapidly from the system by leaching. The cycling of nutrients is more apparent in grasslands where material is cycled annually.

The industrial revolution brought with it a rise in the demand for agricultural products at a time of great discoveries in chemistry

and physics. These two factors demanded, and provided the means for, increased yields and so caused innovation and change in agriculture. This resulted in a further widening of the gap between natural and agricultural ecosystems and it became increasingly necessary to add the artificial fertilizers which were then becoming available. That is to say, as more nutrients were removed, more additions were required to maintain and increase soil fertility. The urbanisation of human populations has also resulted in an increase of the removal of nutrients from the land, as less waste material is recycled. Application of fertilizers in discrete quanta, rather than continuously, means that added nutrients are more susceptible to losses by leaching. These trends have continued until the present day and agricultural ecosystems are now far removed from natural ones. Good modern agricultural practice requires a careful balance between inputs to and outputs from the soil to ensure continued fertility and to keep pollution to a minimum.

Since the industrial revolution, soils have become the recipients of a wide range of exotic inorganic and organic materials both in the form of fertilizers and pesticides, and from the disposal of domestic and industrial effluents on and in the soil. Heavy metals from sewage sludge, nitrate fertilizers and pesticides are all added to the soil and may find their way into both crops and water supplies.

The ability of soils to absorb these contaminants depends largely on the partitioning of the material between the soil solution and the soil itself. Solutes such as nitrate are not sorbed onto the soil to any extent, whereas added zinc, for example, is rapidly removed from solution onto the surface of soil colloids. Therefore an understanding of the reactions between soil and soil solution is a

vital prerequisite for the reliable prediction of the potential for the transfer of pollutants from soil into food chains.

The soil solution plays a central role in many soil processes. Adams (1971) points out that the soil solution provides the chemical environment for plant roots. It has been suggested that the ionic composition of the soil solution influences plant development directly, and that intensity factors (soil solution concentrations) are as valid as capacity factors in characterising the nutrient supply of a soil (van Praag and Weissen, 1984). The chemical composition of the soil solution is also of considerable ecological and hydrogeological significance.

However, as many authors (for example Baham, 1984; Bowen, 1979; Russell, 1973; Larsen and Widdowson, 1968) have noted, comparatively few studies of the chemical composition of the soil solution have been published. Many published studies have relied on soil suspensions or solutions from rewetted air-dried soils (for example, Brummer et al, 1983 and Larsen and Widdowson, 1968; respectively). Most studies of soils as they exist in the field have utilised ceramic cups to sample the soil solution (for example, Sears and Langmuir, 1982). However, ceramic cups may alter the concentrations of major solutes and their suitability for studying minor and trace solutes has not been assessed. As a result, there is a dearth of available data on the chemical composition of soil solutions from unadulterated soils, and even less on the variability of soil solutions extracted from different sites on the same or different soil series.

There is no universal agreement on how to obtain a representative sample of the true soil solution. Some of the many methods available are discussed in Chapter 3. However, immiscible

displacement by a heavy organic liquid, extraction of a saturation paste extract and porous ceramic cups are generally quoted as being the most popular.

### Summary

Soils, together with many other natural resources, are becoming increasingly stressed as ever more exacting demands are made of them. Removal of nutrients in crops may mean that, in the long term, soils will cease to be self-renewing, so anthropogenic inputs are required to ensure continuing fertility. Pollution from, for example, sewage sludge and acidic precipitation, may be causing further irreversible changes to the soil.

The soil solution lies at the centre of many chemical processes in the soil and so an understanding of the chemical processes occurring in the soil solution is an essential step in understanding soil processes as a whole. However, the study of the soil solution as a separate chemical phase has been hindered by the lack of a convenient method for obtaining samples representative of the true soil solution and also by preoccupation with approximations of the soil solution and with soil extracts. As a result there is little data on the chemical composition of the soil solutions of natural soils.

The purpose of this study was to find a suitable method for extracting soil solution unaltered from field soils, then to establish the normal concentration ranges of a wide range of solutes in a number of agricultural topsoils in the Oxford area, and, where possible, to gain some insight into the chemical processes occurring in those solutions.

## Chapter 2

### The Chemistry of the Soil Solution

The soil solution is ... a dynamic, open, natural water system whose composition reflects the many reactions that can proceed simultaneously between an aqueous system and a mixture of mineral and organic solids that itself varies both temporally and spatially.

Garrison Sposito, 1983

#### 2.1 Introduction

The soil solution is the principal seat of chemical reactions in soils. Its properties represent the effects of soluble complex formation, oxidation-reduction, adsorption and precipitation-dissolution reactions which proceed concurrently. Solutes in the soil solution react with other solutes to form a wide range of complexes in solution as well as reacting with the solid and gaseous phases of the soil. The formation of complexes in solution lies largely outside the scope of this study, and so the discussion below will, in the main, be limited to the chemical reactions occurring between dissolved constituents and the solid phase.

Pearson (1971) defined the soil solution as a 'quasi-equilibrium solution of electrolytes that occurs in soil under unsaturated moisture conditions'. His definition differed from that of the SSSA committee report of 1965 (SSSA Committee Report, 1965) by specifying equilibrium and unsaturated conditions. In the parlance of physical chemistry the soil solution is the aqueous phase of the soil, and from the point of view of thermodynamics it is a unique phase only if it can be isolated from the soil and studied experimentally (Sposito, 1984).

Vedy and Bruckert (1982) divided soil water into two categories, the first being free water which is drained by gravity and the second

that which is adsorbed on soil surfaces and held in small pores. This second category may be defined as the soil solution.

The soil solution interacts with percolating rain water to a varying degree. In a poorly structured soil or in a re-packed soil column (see S3.3.1) much of the soil solution will be replaced by the percolating solution. In a well-structured soil, water draining through the soil will 'bypass' the soil matrix, and hence the bulk of the soil solution, and the interaction between the soil solution and the drainage water will be reduced. The fraction of drainage water bypassing the soil matrix increases with infiltration rate (Kneale and White, 1984). This will result in a variable relationship between the chemical composition of the soil solution and that of the drainage water.

Even in a soil where the soil solution and the solid phase are in equilibrium, the composition of the soil solution will not be uniform. Water sorbed directly on the surface of soil particles and that in areas affected by the surface charges borne on soil particles (see below) will have a somewhat different chemical composition from that of the bulk solution which is free from the influence of surface charges. All of the methods for obtaining samples of the soil solution or soil water remove water from the soil up to certain limits of water tension. This limit varies from method to method, but in the more widely used methods the maximum tensions reached fall well short of those which would be required to remove water from the areas around soil particles that would be affected by surface charge.

Therefore, from an experimental point of view the portion of the soil solution which may readily be sampled does not extend into the diffuse double layer. The portion of the 'whole' soil solution,

even when the volume in the diffuse double layer is not included, which can be removed varies because different methods apply different degrees of suction or pressure to the soil. In any natural soil the bulk soil solution (that free from the direct influence of the diffuse double layer) is unlikely to be of uniform composition. Heterogeneity of the soil coupled with non-uniform biological activity will introduce concentration gradients into the soil solution. Removal of a part of the bulk soil solution will provide a possibly non-representative sample of the whole depending on the portion removed and the steepness of the concentration gradients in the bulk solution.

The fraction of the bulk soil solution removed by each method is determined by the soil moisture content, its moisture holding characteristics as well as on the method itself. At a given applied pressure or suction more solution will be removed from a moist soil than from a dry one of similar texture, and of two samples of the same gravimetric water content more solution will be removed from a more coarsely textured soil.

By definition the true soil solution cannot be isolated, but fractions of it can. The representativeness of this fraction of the true soil solution cannot be assessed. If a method can be standardised and is found to be reliable (i.e. it gives reproducible results) it will at least be internally consistent and will allow valid intracomparisons to be made.

## 2.2 Soil Charge and Ion Exchange

The soil solution, even when it is at equilibrium with the solid phases of the soil possesses an inherent microscopic heterogeneity induced by the electrical charges borne on soil particles. This charge creates nebulous zones of accumulation or depletion of ions

in the soil solution near to soil particle surfaces. Accumulation occurs for ions of charge opposite to that of the soil surface and depletion for the reverse situation. In the absence of thermal motion sufficient counter ions would adsorb onto the charged surface to neutralise the charge. Because of thermal motion this is prevented and there exists instead a diffuse double layer (ddl) in which thermal motion and electrostatic forces are balanced. In the ddl there is an excess of counter ions over coions which neutralises the charge on the soil particle.

The thickness of the ddl decreases with increasing ionic strength and with the increasing valency of the ions in solution. As soils dry by evapotranspiration, <sup>although</sup> the double layer will <sup>become</sup> thinner as the moisture films on the surface of soil particles contract the ddl may not be able to extend to its full extent and truncation will result. When such soils are rewetted a considerable swelling pressure may develop as the ddl expands. The bulk of the soil solution in moist soils, however, is not affected by the surface charges (S4.6).

A number of soil constituents carry net electrical charges. Thus isomorphous substitution of cations of lower valence (eg Al for Si) in clays creates a deficit of positive charge. Amorphous aluminosilicates also carry a net negative charge due to some aluminium being present in a 4-coordinated form. At low pH amorphous Al and Fe hydroxides become protonated, acquiring a pH-dependent positive charge.

Ionisable groups on soil organic matter result in a pH-dependent negative charge. The charge is due almost entirely to phenolic and carboxylic groups which dissociate over a range of pHs depending on the pKa of the functional group. The amount of negative charge

increases with increasing pH.

The phenomenon of ion exchange arises as a consequence of these charges on soil particles. The charges are neutralised by oppositely charged ions linked to the surface by weak electrostatic forces. The ions held on the surface can rapidly dissociate into the solution bathing the soil particle and be replaced by ions from that solution.

The amounts of ionic nutrients held by ion exchange is truly prodigious. If a cation exchange capacity (CEC) of 10 meq/100 g for calcium in a soil, and a mass of 2 106 kg/ha for the topsoil, <sup>is assumed</sup> then the amount of Ca held in readiness for plant consumption is  $\sim 4 \times 10^6$  g or 4 tonnes/ha. This compares with 0.034 tonnes/ha in the soil solution (assuming a moisture content of 200 g/kg and the concentration of Ca in the soil solution to be 2 000  $\mu\text{M}$ ). Only 0.7% of the available calcium is present in the soil solution at any one time. In neutral and calcareous soils over 80% of the exchange sites are occupied by Mg and Ca, the remainder by Na and K. As soils become more acid the fraction of the exchange sites occupied by Ca and Mg decreases and that of Al and H increases from a negligible amount in neutral soils to up to 90% of the CEC in highly acidic soils.

Highly charged ions with a small solvated radius interact most strongly with the exchange complex. The usual order of attraction for cations exchanging on clays is  $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$  (assuming equal concentrations). Irregularities on the surfaces of exchange sites may result in certain cations, when present in small quantities, being irreversibly adsorbed. The selectivity of soil organic matter to cations relates mainly to the disposition of the acidic group on the molecule. For example, two or three carboxyl

groups are more selective towards multivalent cations when they occur together on a ring structure than when they are present on a straight chain. Transition metal cations tend to be preferred to strongly basic metal cations. The formation of complexes between organic ligands and transition metal cations is a somewhat different process from that of regular Coulombic adsorption of cations in a double layer, because in principle the transition metal cation cannot be 'exchanged' against, for example, Na ions.

The anion exchange capacity of soils is considerably smaller than the CEC. Experimental evidence (Bolt, 1978) indicates the following order of preference  $\text{SiO}_4 > \text{PO}_4 \gg \text{SO}_4 > \text{NO}_3 \sim \text{Cl}$ . As a result sulphate, chloride and nitrate ions are not adsorbed even in the presence of fairly low concentrations of  $\text{PO}_4$ .

Sulphate is adsorbed as a binuclear bridging complex onto the surface of Fe and Al hydroxides, two surface hydroxyl groups being replaced by one sulphate ion. The two oxygen atoms of the sulphate ion are each coordinated to an  $\text{Fe}^{3+}$  ion (Parfitt and Smart, 1978). Phosphate, as well as forming a complex of similar structure but of greater strength to that of sulphate, can also bind strongly to the edges of clay minerals.

### 2.3 Oxidation-Reduction Reactions

A number of elements undergo oxidation-reductions in soils, the most important being C, N, O, S, Mn and Fe. Redox reactions can be slow, in part because reduction and oxidation half reactions do not couple well together. For instance, thermodynamics predicts that in a solution in equilibrium with the earth's atmosphere all of the organic carbon would be oxidised to  $\text{CO}_2$  and all atmospheric  $\text{N}_2$  to nitrate. These predictions are plainly contradicted by the presence of dissolved organic matter in soil solutions and of  $\text{N}_2$  gas in the

atmosphere.

Soil microorganisms mediate the catalysis of redox reactions in soils and allow equilibrium to be reached fairly rapidly under the right conditions. The role of microorganisms is only to accelerate the rate of redox reactions and they cannot affect the free energy changes involved. The full range of redox conditions that exist in soils can be influenced biologically in so far as microbial catalysis is concerned. (Bass Becking et al, 1960).

Redox reactions can affect the concentrations of metals in solution in a number of ways. The direct effect on the oxidation state of metals in solutions can be assessed by calculating a critical value of  $pE^*$  at which the activity of the oxidised form of the metal becomes undetectable or the reduced form just detectable in the soil solution at any given pH (Sposito, 1981). Values of the critical  $pE$  found in this way show that Mn, Cr, Hg, Fe, Cu and Mo may change their oxidation state in oxidised or moderately reduced acid soils or in moderately reduced or reduced alkaline soils. Generally the reduction of metals has an effect on their solubility (e.g. ferrous and ferric iron).

There are also three ways in which redox can indirectly produce an effect on the chemical forms of metals, including those whose oxidation state is not changed as the prevailing conditions are reached. A result of the reduction of  $SO_4^{2-}$  to  $S^{2-}$  is that the formation of metal sulphides becomes possible and the formation of insoluble sulphides of metals such as Mn, Fe and Zn limits their solubility at the low values of  $pE$  which are found in flooded soils.

Secondly, under reducing conditions soil microbial activity tends to shift from the degradation of large organic molecules to the production of organic acids which may result in the formation of

\*  $pE$  is the negative common logarithm of the free electron activity

metalo-organic complexes increasing the solubility of metals such as copper.

The third indirect effect of reduced conditions is the solubilisation of the hydroxides of Mn and Fe. This dissolution will result in the release of metals previously coprecipitated with or adsorbed on these oxides especially at low pH (Jenne, 1968).

The reduction of  $\text{NO}_3$ , denitrification, generally results from localised anaerobic sites developed because of a high rate of organic matter decomposition. If a soil becomes waterlogged by rain or sub-surface water the biological oxidation of organic matter by soil microorganisms can result in the rapid removal of oxygen from the soil. Once the oxygen is removed other reducible compounds may function as electron acceptors. The reduction of oxygen is followed by that of  $\text{NO}_3$  (mainly to  $\text{N}_2$ ) followed by Mn in neutral soils or Mn followed by  $\text{NO}_3$  in acid soils (van Breemen and Brinkman, 1978). As reduction continues, ferrous iron ( $\text{Fe}^{\text{II}}$ ) may appear if sufficient oxidisable organic material is available and if anaerobic conditions persist  $\text{SO}_4$  may be reduced.

Under temperate conditions soil horizons having a low permeability are likely to suffer from periodic water logging and exhibit a mottled appearance with orange or blue/grey mottling. These gley areas are those where reduction has occurred to produce mobile Mn and Fe species which diffuse out of the soil ped. Where conditions become aerobic the mobile reduced forms are oxidised and areas of orange mottling are produced.

#### 2.4 Dissolution and Precipitation Reactions

Dissolution and precipitation reactions largely control solubility relationships in soils. The rates at which these reactions occur

vary greatly. Some reactions attain equilibrium very rapidly while others move so slowly that in soils where there are continual fluxes of dissolved constituents through the system equilibrium is never reached. However the hypothetical state of equilibrium can provide a valuable reference point in ascertaining the direction of a chemical reaction because all reactions proceed towards equilibrium, never away from it.

Soils are generally in a state of non-equilibrium maintained in a steady state by the continual movement of energy and matter through them. The closeness of a particular reaction to equilibrium will depend on the reaction rate. More rapidly formed, less stable solids will precipitate before the more thermodynamically stable ones. Phosphate, for example, is rapidly precipitated from soil solutions as its least insoluble form which gradually changes, through a series of compounds, to the most stable and least soluble one.

In the short term soil processes in neutral and slightly acidic temperate soils are dominated by exchange and adsorption reactions. In calcareous soils and ultimately in other soils precipitation-dissolution reactions control the direction of the reactions in soil-soil solution systems. Some of the relevant precipitation-dissolution reactions are discussed in more detail in Chapter 7.

## Chapter 3

### Methods for Obtaining Samples of the Soil Solution

There does not seem to be universal agreement on how to obtain a representative sample of the soil solution that reflects its original state in the soil.

J. Baham, 1984

#### 3.1 Introduction

The problem of isolating the true soil solution from field moist soils has not yet been solved. Initially emphasis was placed on obtaining samples of soil solution unchanged by the extraction procedure, but later the emphasis shifted somewhat from examinations of the solution itself to attempts to approximate its chemical composition from measurements made on extracts (Pearson, 1971). This was largely because early methods of obtaining soil solution (reviewed by Parker in 1921) were slow and large volumes of solution were required for chemical analysis.

Early workers (Burgess, 1922) recognised the shortfalls inherent in extracting solutions from soil with water and other solvents which, at best, provided only rough approximations to the soil solution. Yet many standard procedures still use these shortcuts.

In his review, Parker classified methods for studying soil solution into three groups

a) Methods which involve extraction with comparatively large amounts of water.

b) Methods which aim to obtain the true soil solution.

c) Methods which aim to measure the concentration of solutes in the soil solution directly in the soil.

Of these a) may be discounted because there is no simple way of estimating the original concentrations in the undisturbed soil

solution. c) may be discounted because procedures such as conductivity or freezing point give only a measure of the total salt content of the soil solution. Specific ion electrodes inserted directly into the soil are unreliable because soil colloids contaminate the salt bridges.

Methods which aim to obtain true soil solution may be divided into two broad categories: suction methods and displacement methods. The most widely used suction sampler is the ceramic cup. This has been used for many years. Ceramic cups have many limitations and many variants (including hollow cellulose filters and sintered-glass filters) have been developed to try and overcome these difficulties. In displacement methods, solution is displaced from the soil in the laboratory by a miscible or immiscible fluid under the influence of gravity, pressure or centrifugal force. There are many varieties of this method, of which column displacement and centrifugal displacement are the most widely used. In column displacement the soil is packed in a cylindrical column with a bottom outlet and the soil solution is displaced by a percolating liquid (often an aqueous salt solution or ethanol) which causes the soil solution to move ahead by piston displacement and finally flow from the base of the column.

At one time centrifugation was found to be impracticable, but it has become more widely used in recent years because improvements in centrifuge design allow larger samples to be extracted. Improved analytical techniques also allow comprehensive chemical analysis of small volumes of solution. Recently a method involving centrifugation with a dense immiscible liquid has been developed. During centrifugation the dense liquid moves outwards through the soil and displaces the less dense soil solution inwards to the surface of the liquid where it can easily be removed.

Centrifugation is rapid and requires only a small amount of soil.

### 3.2 Ceramic Cups

Porous ceramic cups were first used to obtain soil solution in 1904 (Briggs and McCall, 1904). When moist, a ceramic cup is easily permeable to water but not to air and so when a cup is connected to a container at reduced pressure (normally a few mm of mercury) water from the soil flows through the walls of the cup and can be collected. This removes soil water at tensions less than 0.1 MPa. The problems associated with ceramic cups are manifold, and they are better suited to measurements of soil moisture.

Ceramic cups must be moist to remain air-tight and so may need to be primed with added water. This results in an unknown dilution of the collected solution. Also, ceramic cups do not act as passive collectors, they cause both negative and positive interferences: this was noticed many years ago by Parker (1925).

Parker noted that when solutions containing less than 1 ppm phosphate were passed through used ceramic cups, phosphate was adsorbed from solution onto (he suggested) colloidal material in the pores of the cup. Acid-washing and ignition of the cups reduced, but did not remove, this effect. He also found that new filters desorbed phosphate into the first portions of solutions passing through them. Since then many attempts have been made to avoid such contamination: none has been completely successful.

Grover and Lambourne (1970) found that ceramic cups contributed "excessive" additions of Ca, Na, and K to solutions drawn through them, and adsorbed phosphate. They found that if they leached the cups with 50 pore volumes of 1N HCl it reduced the amount of K and Na contamination to an acceptable level (less than 0.1 ppm in the

final rinsing water) but that Ca contamination, although reduced, was still significant. In contrast to Parker's findings, they found that phosphate adsorption was very low and reached equilibrium after the passage of a small volume of solution. This difference may have arisen because the cups used in each case probably had different compositions.

Hansen and Harris (1975) studied the effect of porous cups on the composition of solutes in the soil solution. The tests were designed to distinguish between the factors which combined to produce variability in the chemical composition of samples collected through commercially produced ceramic cups. They found that, under a constant vacuum, the intake rates of the cups varied by a factor of 6 and that the intake rate of solutions of 100 ppm nitrate or phosphate was greater than that of distilled water. Leaching new cups with water extracted very little phosphate (0.03 mg for 620 ml of leachate) and no nitrate. New cups were found to adsorb considerable amounts of phosphate and this was enhanced in those cups which had a slow uptake rate (as high as 110 mg for a single cup).

New cups placed in a solution containing phosphate first reduced the phosphate concentration of the ambient solution, by adsorption onto the cup surface, but then the concentration in the ambient solution increased as solution was drawn in and phosphate was screened from entering the cup. No measurable interferences with nitrate solutions were found.

When installed in the field, cups sometimes become plugged with colloidal material which reduces the uptake rate and may increase interferences. Clearly if cups with similar uptake rates are selected, interferences will be approximately the same in different

cups. However the experimenter has no control over, nor knowledge of, the amount of plugging that may occur once the cups are installed.

Barbarick et al (1979) suggested that the concentrations of Na and Ca in solutions extracted by ceramic cups do not provide a precise or accurate measure of their concentrations in the soil solution.

Cups are generally installed in slightly undersized holes in order to ensure intimate contact between the cup and the soil (Talsma et al, 1979). However, this may cause fine-textured soil to smear on the walls of the cup which could cause premature plugging. This is not found to be a problem in coarse-textured soils (Starr et al, 1978)

To overcome the interference problems inherent in ceramic cups a number of other materials have been investigated. Hollow fibres of cellulose acetate which act as molecular sieves (with a cut-off point of 30 000 molecular weight units) have been used. They are thin-walled, semi-permeable and flexible with an outside diameter of 0.25 mm. In a study on their suitability for sampling soil solution (Jackson, 1976), a bundle of 16 fibres was placed in a soil column prior to filling. They proved capable of extracting soil solution from soil at moisture levels ranging from 20 to 50% with minimal interaction between solutes and the tube material. Because of their fragility they are more suited to greenhouse studies than to use in the field.

In a comparative study of hollow fibres and ceramic cups Levin and Jackson (1977) claimed that, from a chemical point of view, both were suitable for obtaining samples for Ca, Mg and phosphate determinations, though neither was particularly suitable for nitrate. It was noted that ceramic cups were more suited to field

studies and hollow fibres to pot studies.

It is apparent that the chemical and physical properties of ceramic cups are extremely varied. This clearly limits the value of comparisons of soil solutions obtained with different types of cup.

Long (1978) designed a soil solution sampler, employing a cylindrical sintered-glass filter, which has no ion-exchange or salt-sieving properties. Its designer suggests that it should be placed in a slightly oversized hole and good contact with the soil was ensured by bedding it in a slurry made from soil removed from the hole. A pvc pipe connects the cup to the surface. This pipe is slightly oversized to prevent the channelling of surface water down the access hole.

Nielsen (1972) developed a sintered-glass suction filter with a silica-gel coating to ensure contact between soil and collector when the soil dried out. The filter plate, 90 mm in diameter, faces downwards in the soil. A 2 mm thick layer of silica-gel of low ion-retention is placed on the filter to maintain liquid contact over a range of moisture contents (up to 0.8 atmospheres tension). It was designed for pot experiments - to be placed in the soil during filling. The soil solution from soil incubated with added copper solution was isolated by the filter and analysed for copper. At concentrations of about  $10^{-7}$  M copper was not adsorbed by the filter and thermodynamic calculations showed that the concentrations of Ca and Mg ions in the soil solution were unchanged by passage through the filter. Nielsen concluded that, provided the soil-root system was at equilibrium, his suction filter extracted unchanged soil solution.

Dowdell et al (1972) used 3 cm diameter porous sintered-bronze cups to sample both soil-water and air. Clearly these cups would be

unsuitable for trace metal studies.

Shaffer et al (1979) concluded that 90% of the downward movement of water in a silt loam occurred in cracks that were drained at potentials of less than 22 cm; i.e. in cracks which could channel percolating water past porous cup collectors. This would decrease the validity of samples obtained by porous cups from wet soils.

#### Summary

Ceramic cups, although widely used, cause both negative and positive changes in the chemical composition of solutions passing through them. They are also subject to plugging which increases these interferences and decreases the rate at which they remove solution from the soil. Their suitability for trace metal work has not been investigated, but it is likely to be limited because of sorption/desorption problems. Sintered-glass or hollow fibre filters are better suited to trace element studies, but they are not suitable for installation in the field. They also require semi-permanent installation and so are not well suited for once-off sampling from several locations. As their position is fixed, it is not easy to assess how typical a sample may be. Because soil permeability changes with moisture content, solution from a varying volume of soil will be sampled. Soil water from the larger pores which may be rapidly moving through the soil will be preferentially sampled and movement of soil water to the cup will alter the local hydrology.

### 3.3 Displacement Methods

In displacement methods a fluid replaces the soil solution. This fluid may be miscible or immiscible with the displaced solution. Generally miscible displacement is carried out in columns of

repacked soil and the displacing fluid (displacent) flows through the soil under gravity and displaces soil solution by piston displacement. The term 'displacent' was first used by Whelan and Barrow (1980) to refer to the immiscible fluid and is used here for convenience. Immiscible displacement relies on an applied force to replace the soil solution by air or an immiscible liquid.

### 3.3.1 Miscible displacement

Displacement by a miscible liquid was first used to obtain soil solution by Scholesing in 1866 (Parker, 1921). Parker, however, is justly credited for developing the method. He compared water, ethanol, methanol and acetone as displacents and concluded that ethanol, which gave the highest extraction, was preferable. He argued both experimentally and theoretically that the displacing liquid should not affect the chemical composition of the soil solution which it displaced.

Parker used brass or glass columns 7.5 cm in diameter and 45 - 60 cm in length. One end of the column consisted of a supported screen with a small outlet. Soil was packed in the columns and compacted with a wooden rod. It can be difficult to estimate the optimum degree of packing and this requires considerable experience. Sandy soils may be packed firmly, as may peaty ones. It is with clays, however, that problems arise. At normal field moisture contents, packed clays are impermeable and the displacent remains on the surface. Parker overcame this problem by extracting clays at low moisture content, which imposed a severe limitation on the method.

Correct packing of the columns is essential. If the soil is too loosely packed, channelling occurs which leads to the premature appearance of the displacent at the base of the column. If the soil is too tightly packed, the displacent puddles on the surface of the

soil column and soil solution is displaced very slowly. This may allow anaerobic conditions to develop in the soil column.

Once the column has been packed with 2 kg of well-mixed, sieved soil, displacant is added to the top of the column. As it drains through the soil it displaces solution which forms a zone of saturated soil below the displacant. This zone moves slowly downwards under hydrostatic pressure from the displacant. If the column is well packed, and piston displacement occurs, then the displacant and soil solution should not mix except over a narrow band.

Clearly the first and last portions of the displaced soil solution to appear at the column base have travelled through different lengths of soil. If the soil has been well mixed, then successive aliquots of soil solution should be equivalent; all but the last portion will have been displaced by other soil solution of essentially the same composition, and the displaced solution should be truly representative of the soil solution. Parker tested this hypothesis by measuring the freezing point depression and total salt content of successive aliquots of displaced soil solution. He also tested for the appearance of the displacant (ethanol) in the displaced solutions by the iodoform reaction. He argued that if the displaced solution were the true soil solution, then each successive aliquot should be of identical chemical composition. His results were fairly conclusive and showed that, until the appearance of ethanol in the displaced solution, each aliquot had substantially the same chemical composition. Pierre (1925) labelled the aqueous displacant with potassium thiocyanate.

van Pragg and Weissen (1984) applied Adams' (1974) displacement procedure to pseudo-gleyed soils under spruce. The displacant was

an aqueous solution of saturated calcium sulphate containing both 0.4% KCNS and tritiated water as tracers. The breakthrough point of the two tracers was simultaneous. They displaced soil solution from an A horizon soil successfully, but in a mineral stony soil, the displacment immediately mixed with the soil solution and no soil solution was displaced.

Burd and Martin (1923) utilised air pressure to increase the rate of displacement of soil solution by water. By employing air pressure they were able to pack soils more closely and to obtain larger volumes of soil solution in a shorter time. Even so, it required two days to displace 60 ml of solution from 2 kg of silty loam (3 ml per 100 g), though they extracted the same volume from a sandy loam in only a few hours and obtained yields of up to 80% of the soil solution.

Burd and Martin were aware of the perils of an over-long extraction period. During two days at room temperature biological activity can cause considerable changes in the chemical composition of displaced soil solution.

More recent work (Howard and Adams, 1965; Bennett and Adams, 1970) on nutrient deficiencies in cotton plant seedlings has reinforced Parker's findings. The critical concentrations of nutrients in culture solutions were equal to their concentrations in the soil solutions displaced from soils which produced the same response as the nutrient solutions. This indicated that the soil solution obtained by miscible displacement is representative of the 'true' soil solution.

Moss (1963) mixed quartz sand (0.5-1.0 mm) with sieved and wetted air-dried soil in a 3:1 ratio before packing it in columns for displacement with ethanol. Displacement rates were increased when

necessary by the application of 0.3 atm. air pressure to the top of the column. Adding sand increased the rate of displacement and also lessened the problems of puddling in clay soils.

Larsen and Widdowson (1968) modified Moss' technique and used 50% glycerol as the displacment.

#### Summary

The column displacement method was, for a period, extensively used to provide samples of soil solution. This is no longer the case, largely because the art of column packing is not easily acquired and columns of soils of different texture and moisture content require different packing. Many fine-textured soils cannot be extracted at moisture contents near to field capacity. Also, displacing soil solution by this means takes considerable time during which bacterially induced changes may be occurring. Long extraction times and the need for considerable sample preparation would limit the number of different soils which could be studied.

#### 3.3.2 Immiscible Displacement

In immiscible displacement methods there is less risk of contaminating the soil solution with displacment. The displacment is generally air or an organic liquid and is driven into the soil by air or by centrifugal force.

#### The Pressure Membrane Method

This method was developed by Richards (1941) and Reitimeier and Richards (1944). A heavy metal cylinder is packed with soil. One end of the cylinder is closed by a cellophane membrane supported on a brass screen and a pressure of nitrogen gas is applied to the other end of the column so that soil solution is forced out of the

soil through the membrane. This continues until there is a continuous gas phase in the soil. With pressures of 1.7 MPa, yields of between 5% (clay at 23% moisture) and 30% (sandy loam at 10% moisture) were obtained over extraction periods of 20 - 70 hours.

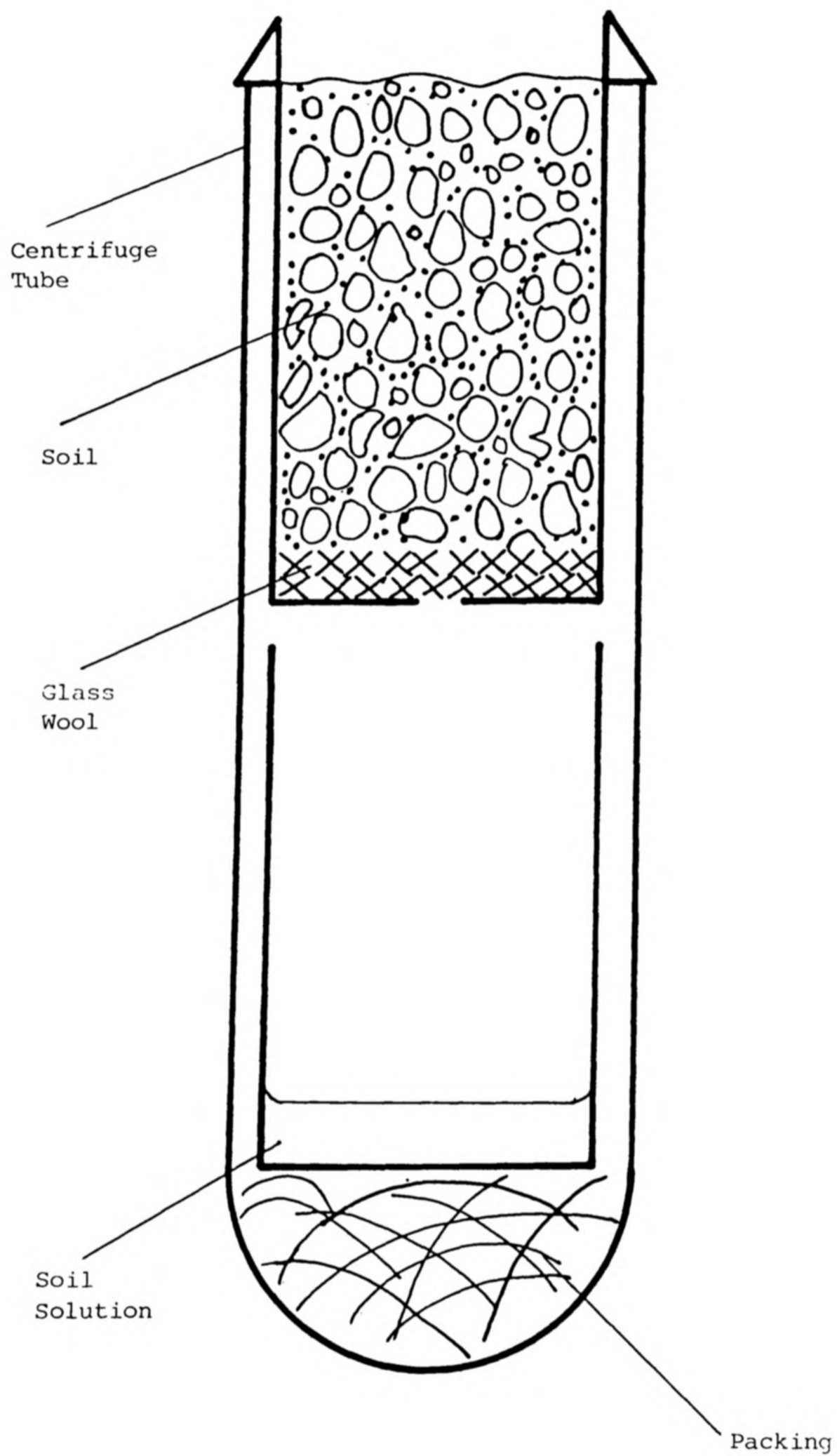
The use of cellophane membranes introduces problems of contamination and selective adsorption. Richards found that phosphate losses were considerable with new membranes. He stated that "this renders the pressure membrane method useless for this constituent".

Richards compared his method with the aqueous displacement method and found that the solutions obtained were "substantially identical" (with the exception of phosphate). However Richards' method has never been widely used.

#### Centrifugal Methods

Centrifugation was first used to dry soils to standard moisture conditions (Briggs and McLane, 1907). Because of the small volumes of water obtained and the mechanical limitations of early centrifuges the technique was dismissed as being unsuitable for obtaining soil solution as recently as 1971 (Adams). However in a more recent review (Sposito, 1984) they are quoted as being among the preferred methods. Davies and Davies (1963) developed a simple centrifuge method for extracting soil solution from small samples of brown earths. The soil was placed in a perspex bottle of 2.7 cm diameter whose base was lined with glass wool and contained a single central hole. This was placed on a similar unpunctured bottle inside a polythene centrifuge tube (Figure 3.3.1). Water was simply spun out of the soil and collected. Samples were spun at 1 200 g for one hour to extract 40 - 50% of the soil solution (around 10 ml/100 g of soil).

Figure 3.3.1



A simple centrifuge method for obtaining samples of soil solution  
(Davies and Davies, 1963).

To provide larger volumes of soil solution, and to allow more comprehensive chemical analysis of the displaced solution, Gillman (1976) modified Davies and Davies' method in order to place 250 g of soil in each centrifuge bucket. Samples were first moistened to pF 2 and were then spun at 900 g (0.5 MPa) for 45 minutes. Yields varied from 9% (clay 34% moisture) to 80% (Yellow Earth at 15% moisture). Gillman collected successive increments of solution, obtained as the centrifuge speed was increased, and tested them for electrical conductivity and Ca, Mg, K, and Na concentration. He found that successive portions were reasonably constant in composition.

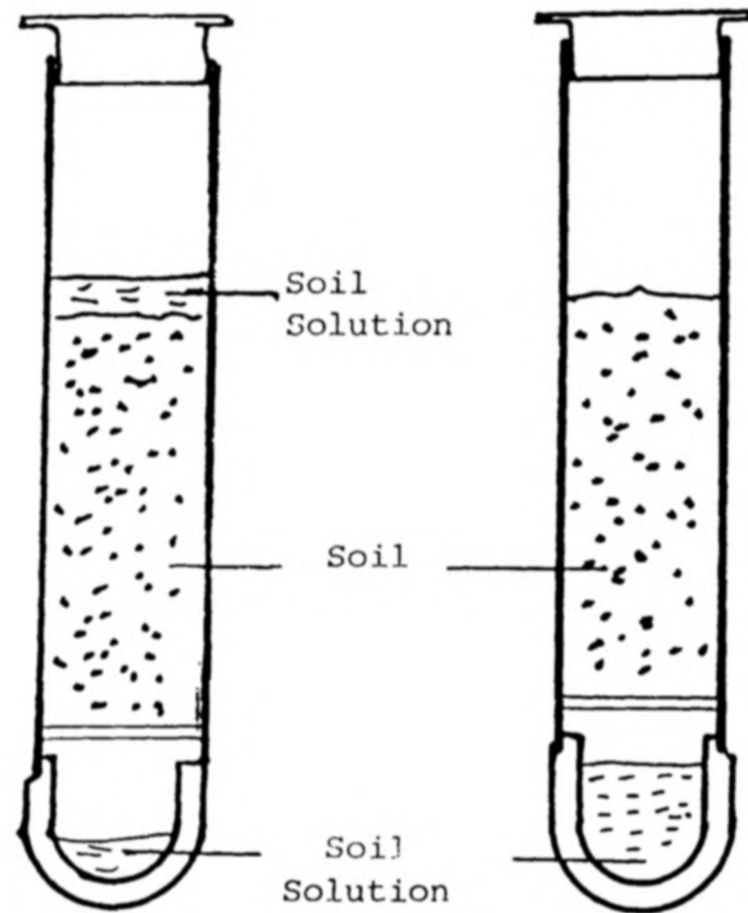
Centrifugal filtration is best suited to coarse-grained soils which do not compact to any large degree during centrifugation. Thus the soil solution may easily drain through them during spinning. Fine-grained soils become compacted during centrifugation and water is displaced from both the base and the top of the soil, rendering collection more difficult (Fig 3.3.2)

Solutions displaced by centrifugal filtration may be contaminated or altered by selective sorption by the filter through which they pass. Thus a suitable material must be chosen for the perforated plate which supports the soil sample. Metal plates are not suitable for trace element determinations.

#### Immiscible Centrifugal Displacement

Mubarak and Olsen (1976) spun soil samples in a centrifuge with a dense, water-immiscible, organic liquid to displace soil solution. A number of displacents were used including tetrachloromethane and 1,1,2-trichloroethane all of which are denser than water. This meant that the more dense displacment was driven into the soil during spinning and the soil solution, being less dense, floated to the

Figure 3.3.2



Centrifugal drainage of a) a finely textured soil and b) a coarsely textured soil. During centrifugation some solution in the finely textured soil is forced to the inner surface of the soil as it becomes compacted.

surface of the displacent.

10 g of soil was placed in a 50 ml centrifuge tube together with 10 ml of displacent. After shaking, the tube was spun at 48 300 g for various lengths of time. About half of the moisture was extracted from both clay and sandy soils at 25% moisture content. Slightly less soil solution was extracted from the clay soil.

Whelan and Barrow (1980) compared the displacents tetrachloromethane, 1,2,2-trichloroethane, dichloromethane, 1,1,2-trichloro-, 1,2,2-trifluroethane, trichloroethene, tetrachloroethene and 1,1,1-trichloroethane. They suggested that the first two were unsuitable because of their high toxicity and the next two were too volatile. Of the remainder tetrachloroethene, stabilized with thymol, was favoured as a displacent. However, it can only be used in nylon centrifuge tubes.

They extracted a range of soils at 17 000 g for 30 minutes. Varying the speed of the centrifuge had little effect on the volume of soil solution displaced from sandy soils but the volume of solution displaced from clay soils increased with increasing speed. This was attributed to the compaction of the clay soils at higher centrifugation speeds. The shaking procedure adopted by Mubarak and Olsen (1976) did not increase the yields of soil solution.

Between 4 and 10 ml of solution were displaced from a range of soils that had been drained to 100 cm water tension. The soil solution displaced from a clay soil was sampled after periods of spinning between 5 minutes and 3 hours and the aliquots were tested for ammonium, nitrate, phosphate and chloride. There were only small changes with spinning time.

Kinniburgh and Miles (1983) devised a model to describe the

processes occurring during centrifugation. They assumed that, at equilibrium, there is a network of displacent-filled cracks in the soil sample connected to the surface layer of displacent. The soil solution was considered to exist in a similar network of pores, and was only displaced from pores in which the driving pressure (arising from the density difference between the displacent and the solution) exceeded the capillary pressure tending to retain the soil solution in the soil pores. The driving pressure will vary through the sample due to differences in the radius of rotation. For soil solution to escape from the soil the uppermost layer of soil must become saturated with solution.

Their model predicts that the driving pressure depends solely on the centrifugal force and on the density difference between the displacent and the solution being displaced and so is independent of the amount of displacent used. This contrasts with the recommendation of Batley and Giles (1979) who suggested that a large displacent/soil ratio would increase the "hydrostatic pressure" on the soil and hence increase the yield.

Kinniburgh and Miles confirmed their model by extracting samples of Upper Chalk at various sample:displacent ratios. The ratios ranged from 1:5 to 1:10. There was no significant change in the yield of solution obtained.

Kinniburgh and Miles recommended 1,1,2-trichloro-1,2,2-trifluoroethane as a displacent. It has low toxicity, contains no stabilisers and can be distilled for re-use. They obtained yields of between 19 and 45% (4-22 ml/100g) of the soil solution in a range of field-moist soils.

In a comparison of column displacement and centrifugal filtration methods Adams (1980) concluded that "the soil solution composition

was not affected by the method used to separate the solution from the solid phase". He also noted that column displacement yielded the highest volume of solution.

### 3.3.3 Summary of Displacement Methods

The various displacement methods reviewed above have all been widely used to obtain soil solution. Column methods suffer from limitations imposed by soil texture and require that a large soil sample (2 kg) be sieved and carefully packed. The pressure membrane method requires expensive apparatus and the solution may be contaminated by the membrane filter. Centrifugal filtration, too, may suffer from contamination problems. Centrifugal extraction with an immiscible liquid is potentially contamination-free.

### 3.4 Other Methods.

Hinkley (1979) used specially cleaned absorbent paper to obtain small volumes of soil solution. Specially cleaned absorbent paper was used to blot up 0.3 ml of soil solution from soil in the field. The solution was then analysed for a few metals by mass spectrometric analysis following stable isotope dilution. Burgess (1922) used a similar method.

### 3.5 Soil Solution Approximations

Obtaining sufficient solution for a comprehensive analysis is often difficult especially in dry soils. A standard procedure was developed to prepare a "saturated paste extract" to provide qualitative assessments of soil salinity for management purposes. This was not intended to provide an accurate facsimile of the soil solution. However, it is often used for this purpose.

Saturation paste (Richards, 1954) and other water extracts are made

by mixing soil and distilled water in various ratios (1:1-1:10) into a slurry and removing the excess water by filtration: it is then analysed. Subsequent calculations on the results obtained generally assume that the concentrations of the various ions in the extract vary inversely with the moisture content of the soil. This is not the case. When water is added to soil two significant changes influence the concentrations of ions in the subsequent solution. Thus the amount of sparingly-soluble salts in solution increases in proportion to the volume of water added and cation exchange reactions occur because the activity ratios of cations of different valence are changed.

The Q/I (Quantity/Intensity) relations of labile potassium in certain soils (Beckett, 1964) may be used to obtain measurements of the concentration of potassium in soil solutions, but they are laborious.

Moss (1969) compared potassium concentrations measured in solutions extracted by column displacement (using ethanol) and by a full Q/I method. He found that the two methods determined the concentrations equally well. This method may only be used with exchangeable ions.

### 3.6 Summary

Of the many procedures used for obtaining soil solution outlined above, no single procedure is suitable for extracting unaltered soil solution from all types of soil. Many of them suffer from severe problems of interference and contamination which limit the range of solutes which may be studied. Others require extensive sample preparation and are, therefore, not well-suited to routine use. Immiscible centrifugal displacement would appear to be well suited to a large-scale study of a wide range of solutes in a range of soils because it is potentially contamination-free and soil solution

can be obtained rapidly with little sample preparation.

## Chapter 4

### Centrifugal Methods for Obtaining Samples of the Soil Solution

Ansi mon dessein n'est pas d'enseigner ici la méthode que chacun doit suivre pour bien conduire sa raison, mais seulement de faire voir en quelle sorte j'ai tâché de conduire la mienne.

Rene Descartes, 1637

#### 4.1 Introduction

As was outlined in the previous chapter the problem of obtaining "the true soil solution" has not yet been solved. Of the methods discussed, those involving the displacement of soil solution by centrifugation appear to offer a number of advantages over the other methods. They are swift, require minimum sample preparation and are, therefore, ideally suited to routine use. Immiscible displacement requires only very simple equipment.

Although the precise mechanism of immiscible displacement is unclear (S 3.3.2) the assumption of Kinniburgh and Miles (1983) that at equilibrium the driving pressure in the sample is balanced by a capillary pressure,  $P_c$ , is probably valid. Consequently, the capillary pressure gradient at a point P is related to the angular velocity,  $\omega$ , and the density difference between the fluid phases.

$$dp_c/dr = \Delta\rho\omega^2r \quad (1)$$

where

$$\Delta\rho = \rho_d - \rho_w \quad (2)$$

and

$$\omega = 2\pi n/60 \quad (3)$$

where  $r$  is the distance from the centre of rotation,  $\rho_d$  and  $\rho_w$  are the densities of the displacant and soil solution respectively and  $n$  is the centrifuge speed in rpm. Integrating equation 1 between the inner surface of the sample, distance  $r$  from the centre of rotation to a point P (distance  $r_2$ ) and assuming that the capillary pressure

at the inner surface is zero gives the driving pressure at P.

$$p_c(r,\omega) = \int_{r_1}^{r_2} \Delta\rho\omega^2 r \, dr = \frac{\Delta\rho\omega^2}{2} (r_2^2 - r_1^2) \quad (4)$$

Equation 4 may also be used for calculating the driving pressure with the drainage method, but here the displacment is air ( $\rho = 0$ ) and  $r$  is the distance to the outer surface of the sample.

With both of the centrifugal methods the yields of soil solution obtained increase with time of centrifugation and centrifugation speed. For sandy soils there is little increase in the volume of water extracted after a few minutes. For clay soils yields increase, albeit ever more slowly, over a period of several hours. Varying the speed of centrifugation has little effect on the volume displaced from sandy soils, but the volume of solution displaced from clay soils increases with speed (S4.6 and Whelan and Barrow, 1980). The former effect is due to the tortuosity of small diameter pores which limits the rate of replacement of soil solution with displacment. The latter effect is the result of clay soils holding soil solution at high tensions in small pores.

#### 4.2 Immiscible Liquid Displacement

Many displacments have been used with satisfactory results. The desired properties are high density, low water solubility, low volatility, low toxicity, high chemical inertness and low price.

Kinniburgh and Miles (1983) chose 1,1,2-trichloro-1,2,2-trifluroethane as a displacment. It is easily available in bulk under the trade names of Arklone P (ICI) and Freon TF (DuPont). It is compatible with polypropylene centrifuge bottles, has low toxicity and is relatively inexpensive. Arklone was therefore chosen as a displacment. The method adopted for obtaining soil solution by immiscible liquid displacement was essentially that of

Kinniburgh and Miles (1983). It is set out in detail below.

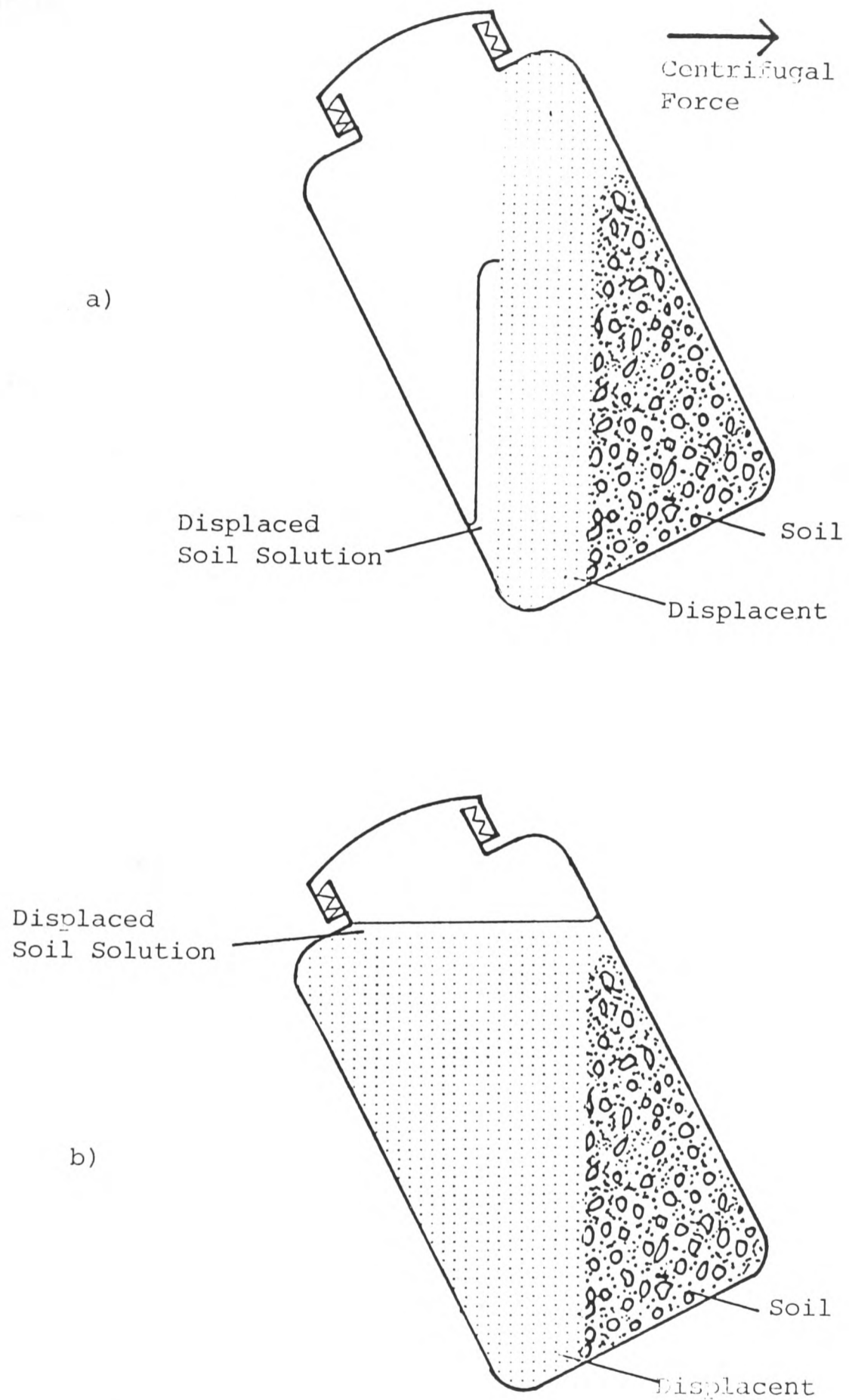
Approximately 110 g of soil was placed in a weighed 250 ml polypropylene centrifuge bottle. Arklone (about 230 g) was then added to bring the total weight <sup>(including top)</sup> up to  $380.000 \pm 0.005$  g. The bottle was then capped. A number of bottles (normally 6) were placed in a JA14 fixed angle rotor in a Beckman J21C <sup>refrigerated</sup> centrifuge.

The volume of displacant used was the minimum possible to ensure that the displaced solution did not come into contact with the soil after the centrifuge had stopped. This volume depends on the <sup>bulk</sup> density of the soil, but the proportions above were found to be acceptable for the soils that were studied (see Figure 4.2.1).

Samples were spun at 13 000 rpm for one hour. This length of time was chosen because it provided sufficient soil solution and also left enough time to process the previous set of bottles and to prepare the next batch. After one hour the bottles were taken out and the displaced soil solution removed from the surface of the Arklone with a disposable polypropylene pipette. The translucency of the pipette and the sharp interface between Arklone and soil solution meant that it was relatively straight-forward to separate solution from any displacant inadvertently drawn up into the pipette tip.

The displaced solution was transferred to a tared 7 or 30 ml polycarbonate vial and its weight recorded. If the solution contained a considerable amount of suspended solid (small amounts of clay frequently floated at the Arklone-solution interface after centrifugation) the solution was centrifuged briefly in a bench centrifuge before filtration into a clean vial through a Millex (Millipore) 0.45 micron membrane filter (see S4.5) using an acid-washed, all-glass syringe. A measured volume (2.80 ml) of

Figure 4.2.1



Immiscible liquid displacement of soil solution. a) during centrifugation and b) after centrifugation. Centrifuge bottles must contain sufficient displacant to ensure that the soil is still covered once the centrifuge has stopped.

solution was then transferred by automatic pipette to another vial and acidified with concentrated Aristar HCl to give an acid concentration of 1% by volume. The samples were stored at 5°C until analysed.

#### Notes

Centrifuge bottles were thoroughly cleaned with detergent, then soaked in 50% Analar HCl, rinsed in glass-distilled water, soaked in glass-distilled water, allowed to drain and then dried in an oven at 70°C before use. Periodically throughout the work 6 ml of MilliQ ultrapure water were shaken with approximately 230 g of Arklone in a centrifuge bottle for a few minutes. The water was then removed and treated as soil solution. Analysis of these blanks showed that contamination by any solute was almost invariably less than could be measured (see A1.11).

If less than 6 ml of solution was displaced from any one bottle and time or materials precluded the extraction of a second soil sample, then the solution was accurately weighed after filtration and diluted with an accurately weighed volume of ultra-pure water. All subsequent measurements (with the exception of pH) were corrected with the appropriate dilution factor.

Arklone was distilled for re-use. The residue remaining after large volumes had been distilled was generally straw coloured. This indicated that small amounts of dissolved organic carbon (DOC) are removed by the Arklone during centrifugation. Batley and Giles (1979) reported that FC78 removed 3% or less of the DOC from displaced solutions. They reported that the metal content of the FC78 was also small. Arklone is likely to behave in a similar fashion. Kinniburgh and Miles (1983) reported that the visible absorbance of used Arklone at 350 nm ( $A_{350}$ ) was insignificant. They

also shook organically-rich lake water with Arklone and found that the A<sub>350</sub> of the water was not measurably reduced. This would indicate that Arklone is unlikely to extract significant quantities of DOC from soils or soil solutions.

#### 4.3 Immiscible Displacement of Soils of Low Bulk Density

Kinniburgh and Miles (1983) found that clay soil with high organic matter content floated to the top of the Arklone during centrifugation so that no soil solution could be isolated. They attempted to overcome this problem by placing washed silica sand over the soil before centrifugation, but this was only partly successful. A number of soils in this study (some samples of Evesham, Denchworth and Icknield series) fell into the same category in that their bulk density at field moisture content was less than that of the Arklone (1.57 g/cm<sup>3</sup>).

This problem was overcome successfully by placing a disc of stiff nylon gauze on top of the compacted soil in the centrifuge bottle and weighing it down with glass beads. Arklone was then added and the sample spun in a swing-out bucket rotor, the gauze and beads holding the soil in place during centrifugation. The details of the method are set out below.

110 g of soil were placed in a weighed 250 ml centrifuge bottle and firmly packed down. A disc of nylon gauze was placed on top of the cylinder of soil and about 60 g of acid-washed borosilicate glass beads (2-3 mm diameter) were poured on top. Arklone was then added to bring the total weight <sup>(including top)</sup> up to 380.000 ± 0.005 g. Samples were spun in a Beckman JS7.5 rotor with four swing-out buckets at 7 500 rpm for one hour. Displaced solution was removed and treated as in Section 4.2.

In this method the driving pressure at the base of the sample is 1.5 MPa compared with 2.3 MPa for the standard Arklone method. Slightly lower yields of soil solution would be expected. The yield from an Upper Greensand soil was about 80 % of that obtained with the standard procedure. Clearly the difference in yield depends on the moisture retention characteristics of a particular soil. Blanks prepared in a similar way to that in Section 4.2 showed that there was no measurable contamination from the beads or nylon (see A1.11).

#### 4.4 Centrifugal Drainage

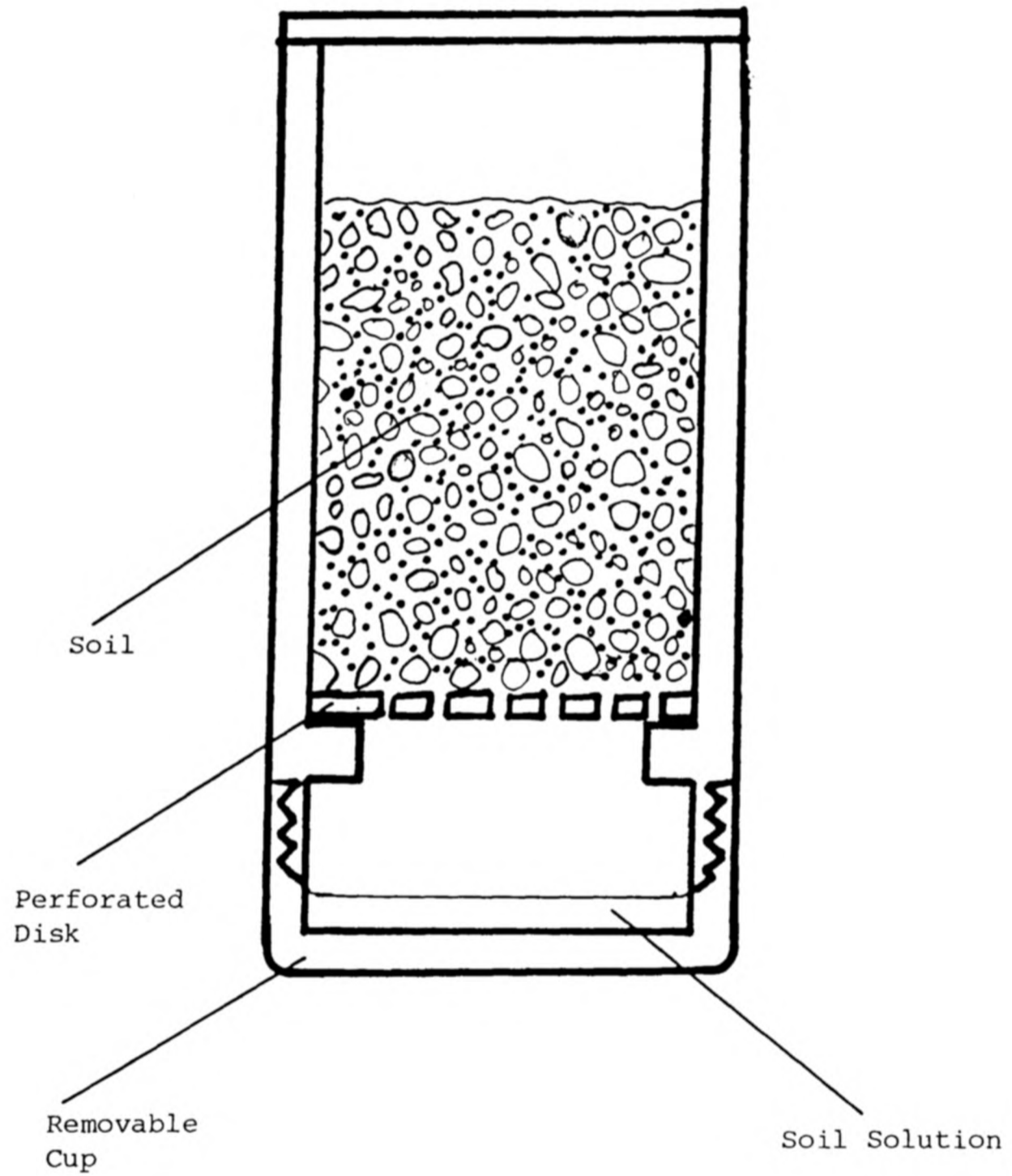
This method was not used routinely, however it was used occasionally (see Section 4.7), and is outlined below. The filter assembly was the same as that used by Edmunds and Bath (1976) (Figure 4.4.1) Soil was supported on a perforated, high-purity, alumina disc covered with a Whatman No 1 filter paper. About 100 g of soil was placed in the assembly to bring the total weight up to  $380.000 \pm 0.005$  g. Samples were spun at 7 500 rpm in the JS7.5 rotor, which produced a driving pressure of 1.8 MPa at the mid-point of the sample.

After spinning, the assemblies were removed and the basal cups unscrewed, allowing displaced solution to be removed and treated in the usual way. The filter assemblies could not be acid washed (as they were made from Delrin) and so this stage was omitted when they were cleaned.

#### 4.5 Filtration and Analysis of Displaced Solutions

The major problem facing early workers on the soil solution was that a large volume of solution (anything up to 500 ml) was required for a comprehensive analysis. With the advent of modern methods of chemical analysis many of these problems have been removed. By careful choice of methods a fairly comprehensive chemical analysis

Figure 4.4.1



Apparatus used for centrifugal drainage method. After Edmunds and Bath (1976).

can be carried out with as small a volume of solution as 6 ml. Typically this volume of solution could be obtained from a single centrifuge bottle of soil. A detailed description of the analytical methods used, together with their detection limits, precision and accuracy is given in Appendix 1.

It is customary to filter river, ground and soil waters through membrane filters with an average pore size of 0.45  $\mu\text{m}$  (Cook and Miles, 1980; Kinniburgh and Miles, 1983). The choice of 0.45  $\mu\text{m}$  filters is a compromise between efficiency of filtration and convenience. Use of smaller pore sizes is more time consuming and usually requires more equipment. The fraction retained by the filter is classed as particulate and the filtrate is said to contain the "dissolved" fraction. This distinction is purely arbitrary and reference to the contents of the filtrate as being dissolved is simply a convention.

Hem and Roberson (1967) showed that particulate aluminium could be trapped on a 0.1  $\mu\text{m}$  filter from waters previously filtered through a 0.45  $\mu\text{m}$  filter. Clay particles in the size range 0.1-0.5  $\mu\text{m}$  were thought to be responsible for errors in the determination of dissolved Al, Fe, Mn and Ti (Kennedy et al., 1974). Similar findings were obtained for iron determinations in river waters when water previously filtered through a 0.45  $\mu\text{m}$  filter was filtered through smaller pores (Boyle et al., 1977). Up to 79% of the "dissolved" iron could be collected on a 0.05  $\mu\text{m}$  filter.

Filter load influences the effective pore size of the filter. At low filter loads, Danielsson (1982) found that no iron was removed from an iron rich (4.8 mg/l) organic lake water. As the filter became clogged the effective pore size was reduced and up to 98% of the "dissolved" iron was retained. Many substances present in

natural waters stabilize fine colloidal particles of a size that will pass through a 0.45  $\mu\text{m}$  filter (Cameron and Liss, 1984). Florence and Batley (1980) concluded that most dissolved iron in oxygenated fresh waters is in the form of negatively charged colloids stabilized by organic matter.

Clearly the use of 0.45  $\mu\text{m}$  filters to distinguish between dissolved and particulate forms of material in natural waters is not valid. However, any division between particulate and dissolved fractions is likely to be purely arbitrary and filtration becomes difficult with filters of pore sizes smaller than the standard 0.45  $\mu\text{m}$ . In this study it was decided to use 0.45  $\mu\text{m}$  filters for convenience and consistency. The presence of fine colloidal matter in displaced soil solutions after filtration is reflected in the high concentrations of Al, Fe, Mn and Si found in some of the solutions analysed. Care must be taken, therefore, in interpreting the results of some of the trace element analyses.

#### 4.6 Artefacts

Apart from any contamination problems in centrifugal displacement two questions arise:

1) does the extraction procedure upset the equilibrium between the soil and the soil solution, and

2) does extraction remove soil solution from the regions near to soil particles in which the concentrations of ions are affected by surface charges?

Kittrick (1980) tested the accuracy of several displacements by displacing the equilibrium solutions from standard minerals whose solubilities are known. Equilibrium solutions were displaced from gibbsite and kaolinite using tetrachloromethane as displacant. Good agreement was found between immiscible displacement, long-term

solubility and calorimetric methods for determining gibbsite solubility. Agreement was reasonably good between immiscible displacement and long term solubility for kaolinite and kaolinite-gibbsite mixtures.

Kittrick (1983) also compared a number of displacents (tetrachloromethane, tetrachloroethene, FC70 (a fluorocarbon) and 1,1,1-trichloroethane (111,T)) by using them to displace equilibrium solutions from samples of gibbsite and calcite. All four liquids gave accurate results, except that at high pH 111,T significantly decreased the pH of solutions displaced from calcite. It would appear that, with this one exception, the displacents tested did not alter the equilibrium solutions which they displaced.

The soil solution is inherently heterogeneous because the charges on soil particle surfaces create diffuse zones of increased or decreased concentrations in the soil solution. If a centrifugal displacement method removes solution from these zones, then the concentrations of ions in the displaced solution would not be representative of those of the bulk solution. This would render comparisons of solutions obtained at different driving pressures invalid.

If we consider a heavy clay soil with a clay content of 50%, and the clay to have a specific surface area of  $100 \text{ m}^2/\text{g}$ , and assume that all of this surface has a double layer thickness of 5 nm, then the volume of solution in the diffuse double layer (ddl) would be 0.25 ml/g (dry weight), which is an over-estimate. Thus in 100 g of this soil we have 25 ml of solution in the ddl. One hundred grammes of a wet clay soil might contain about 65 g of water and so, by the estimate above, about 37% of the soil solution would be in the ddl. A typical yield from a clay soil at this moisture content, however,

is only 20%. It is clear, therefore, that ddl solution is not likely to be removed from the soil.

#### Summary

It would appear that immiscible displacement does not alter the equilibria of the solutions displaced from pure minerals.

Centrifugal methods do not extract water from the ddl, and so it is only bulk soil solution which is removed from soil samples during centrifugation. Solution influenced by the diffuse double layer is not removed.

#### 4.7 Variable Speed Experiment

The necessity to treat some soils in a different way from the standard procedure (S4.3) raises the question: can we compare soil solutions obtained at different centrifugation speeds?

It was established in the previous section that only the bulk soil solution is extracted by immiscible displacement and that solid-solution equilibria are not altered by the displacement process. However, it is improbable that any natural soil-soil solution system is ever at equilibrium and so it is likely that soil solution in pores of different size may contain solution of different composition. An experiment was designed to establish whether subjecting a soil sample to centrifugation at different speeds would displace solutions of different chemical composition.

The experiment was carried out on a well-mixed sample of Icknield series topsoil. Six subsamples of approximately 115 g were taken and extracted by the standard method (S4.2). Each sample was spun at a sequence of 8 increasing speeds, each for 20 minutes. After each period the displaced solution was removed and the yield from

the bottle recorded. The volumes of solution displaced from each sample are plotted in Figure 4.7.1.

At low speeds (5 000 and 6 000 rpm) three aliquots were obtained for analysis by combining samples from pairs of bottles. At higher speeds the solutions from three bottles were combined. The results of these analyses are shown in Table 4.7.2. There was insufficient solution for the determination of pH and alkalinity. Weighted mean concentrations were calculated for the six bottles at each centrifugation speed together with a weighted mean over all speeds. These figures were used to plot the graphs in Figures 4.7.2, 4.7.3 and 4.7.4.

The major monovalent ions (Na, K, Cl, NO<sub>3</sub>) together with Si and Mn show no pronounced trend with increasing centrifugation speed. However, the concentrations of divalent ions (Ca, Mg, Sr, Ba, SO<sub>4</sub>) together with Cu show a definite upward trend. Zinc and iron, together with phosphorus, show a marked downward trend with increasing centrifugation speed. Over the range of speeds the trend in concentration is upwards, ionic strength increasing by about 8%. These changes may possibly be the result of the pores in particles of chalk draining at higher speeds. This would explain the increase in the concentrations of Ca, Mg, Ba and Sr. The increase in these ions is balanced by the increase in bicarbonate concentration (calculated by difference).

### Conclusion

It is apparent that, for this soil at least there are small, but significant, differences between the compositions of solution displaced at different centrifugation speeds. These changes are reflected in the increase in ionic strength of the solution which increases by about 8% over the range of speeds. The change of ionic

Table 4.7.2

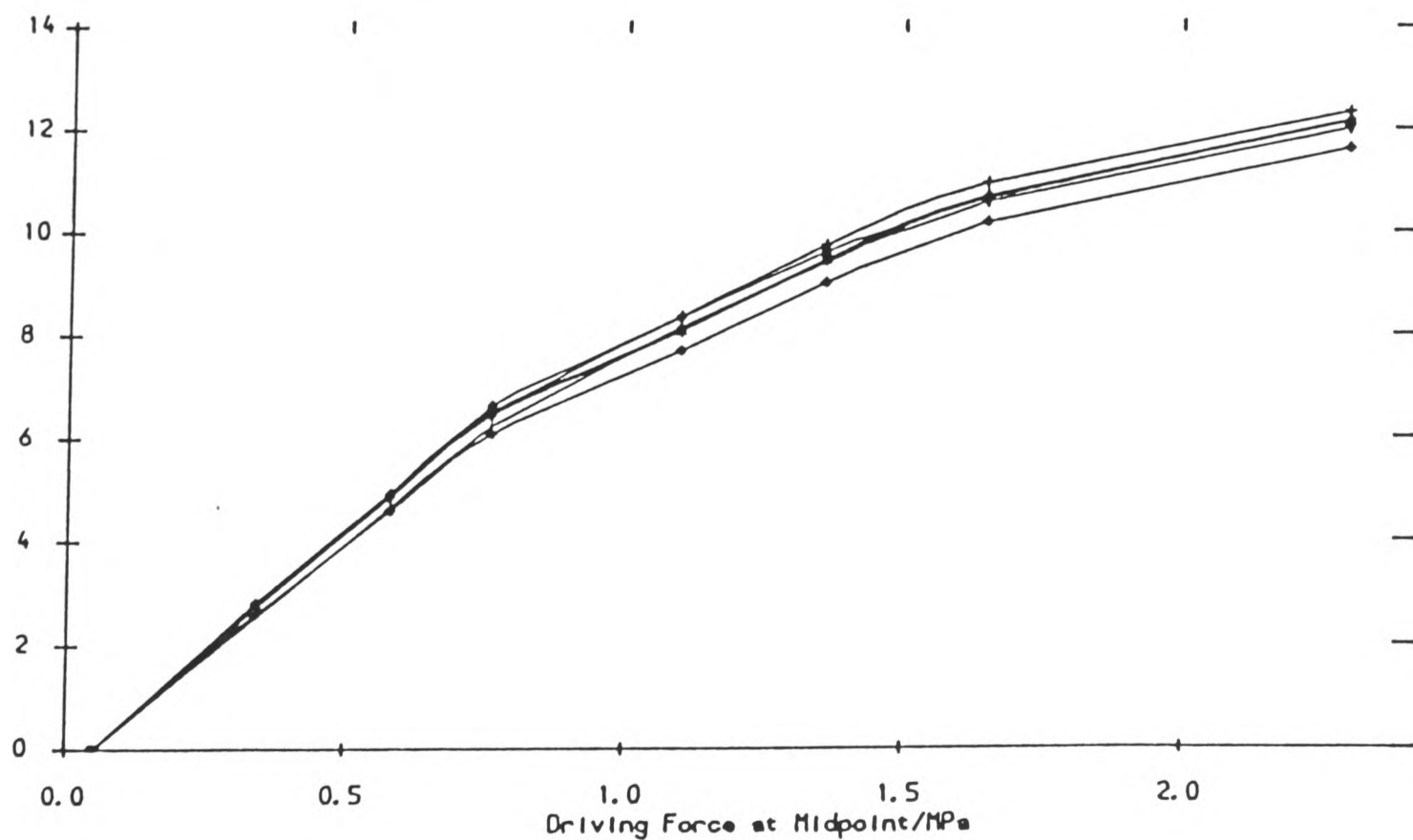
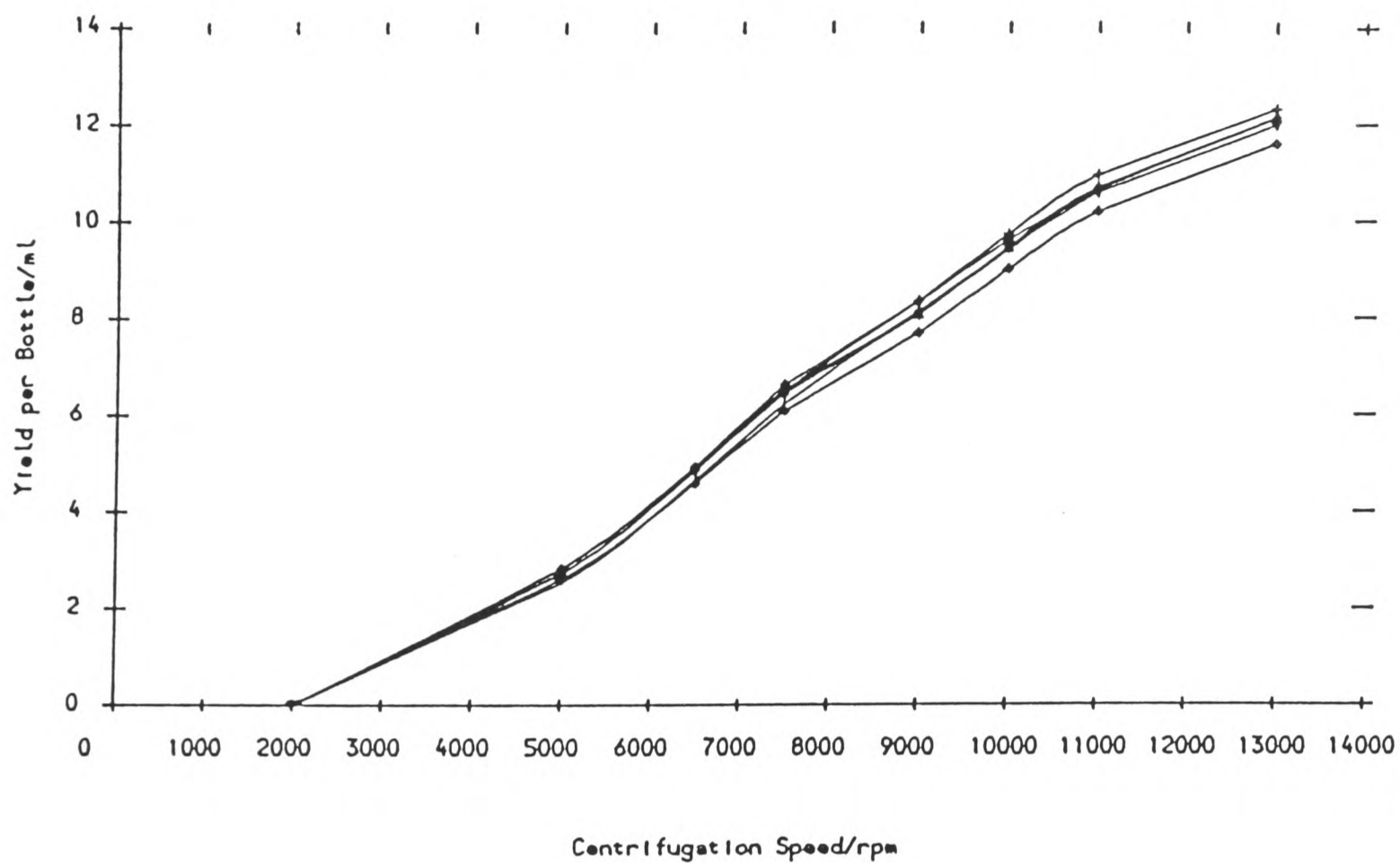
Chemical analyses of the solutions displaced by spinning samples of an Icknield soil at varying speeds. All concentrations in  $\mu\text{M}$ .

Number	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>
50/1	331	513	2830	133	380	236	60	1194	1070
50/2	301	325	2645	115	362	227	55	1090	990
50/3	338	501	2697	124	390	223	76	1228	1060
65/1	302	414	2781	122	371	229	44	1242	1090
65/2	306	322	2773	120	383	230	50	1200	1010
65/3	324	424	2656	123	379	221	81	1211	1020
75/1	305	329	2851	123	379	229	39	1206	1040
75/2	334	378	2863	133	400	232	48	1189	1100
90/1	*	*	*	*	*	*	*	1265	1040
90/2	302	335	2890	122	392	226	39	1149	1070
100/1	311	325	3017	124	396	229	34	1217	1040
100/2	296	293	2934	121	391	226	35	*	1140
110/1	311	318	3104	129	405	234	35	1194	*
110/2	294	311	2934	123	398	221	37	1155	*
130/1	341	321	3212	139	424	239	35	1254	1060
130/2	302	296	3059	126	404	225	33	1228	1040
Number	Ba	Mn	Cu	Fe	Zn	Sr	DOC		
50/1	0.240	0.68	0.38	1.26	0.70	2.02	3610		
50/2	0.207	0.30	0.34	0.89	0.48	1.84	3570		
50/3	0.238	0.87	0.42	1.49	0.89	1.81	4350		
65/1	0.230	0.53	0.41	1.09	0.54	1.94	5980		
65/2	0.223	0.28	0.38	1.04	0.54	1.94	7360		
65/3	0.251	0.70	0.40	1.55	0.73	1.83	*		
75/1	0.229	0.32	0.43	1.01	0.40	1.99	4490		
75/2	0.248	0.38	0.44	1.18	0.57	2.06	5270		
90/1	*	*	*	*	*	*	4610		
90/2	0.240	0.26	0.45	1.04	0.49	2.00	3100		
100/1	0.233	0.21	0.48	0.94	0.40	2.09	5650		
100/2	0.229	0.18	0.44	1.22	0.43	2.00	*		
110/1	0.242	0.17	0.50	1.06	0.46	2.16	3320		
100/2	0.245	0.17	0.48	1.18	0.49	2.01	3580		
130/1	0.255	0.15	0.53	0.95	0.46	2.29	*		
130/2	0.254	0.14	0.49	0.91	0.52	2.06	4860		

\* = missing value

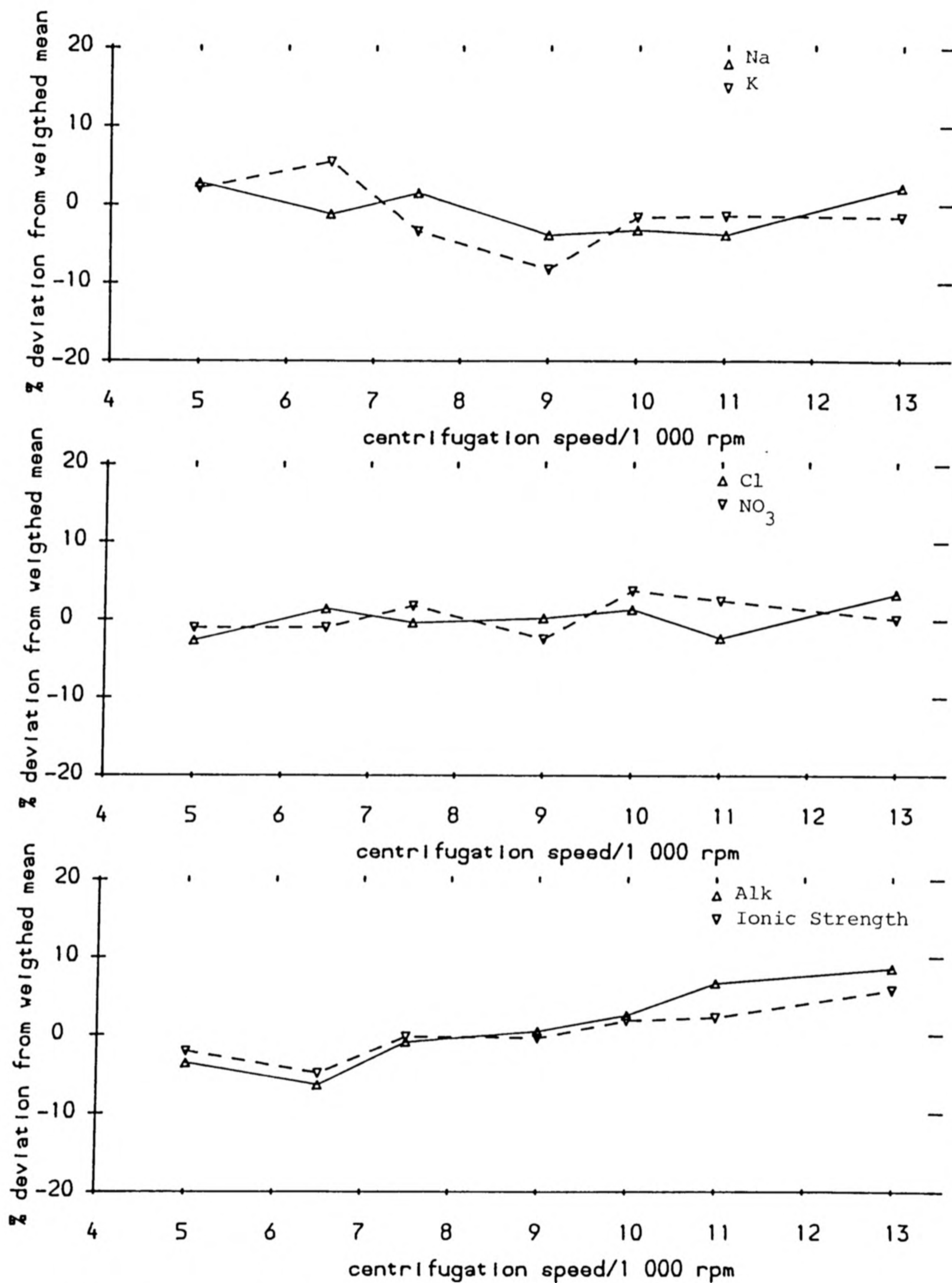
Number = centrifuge speed in 100s rpm/aliquot number

Figure 4.7.1



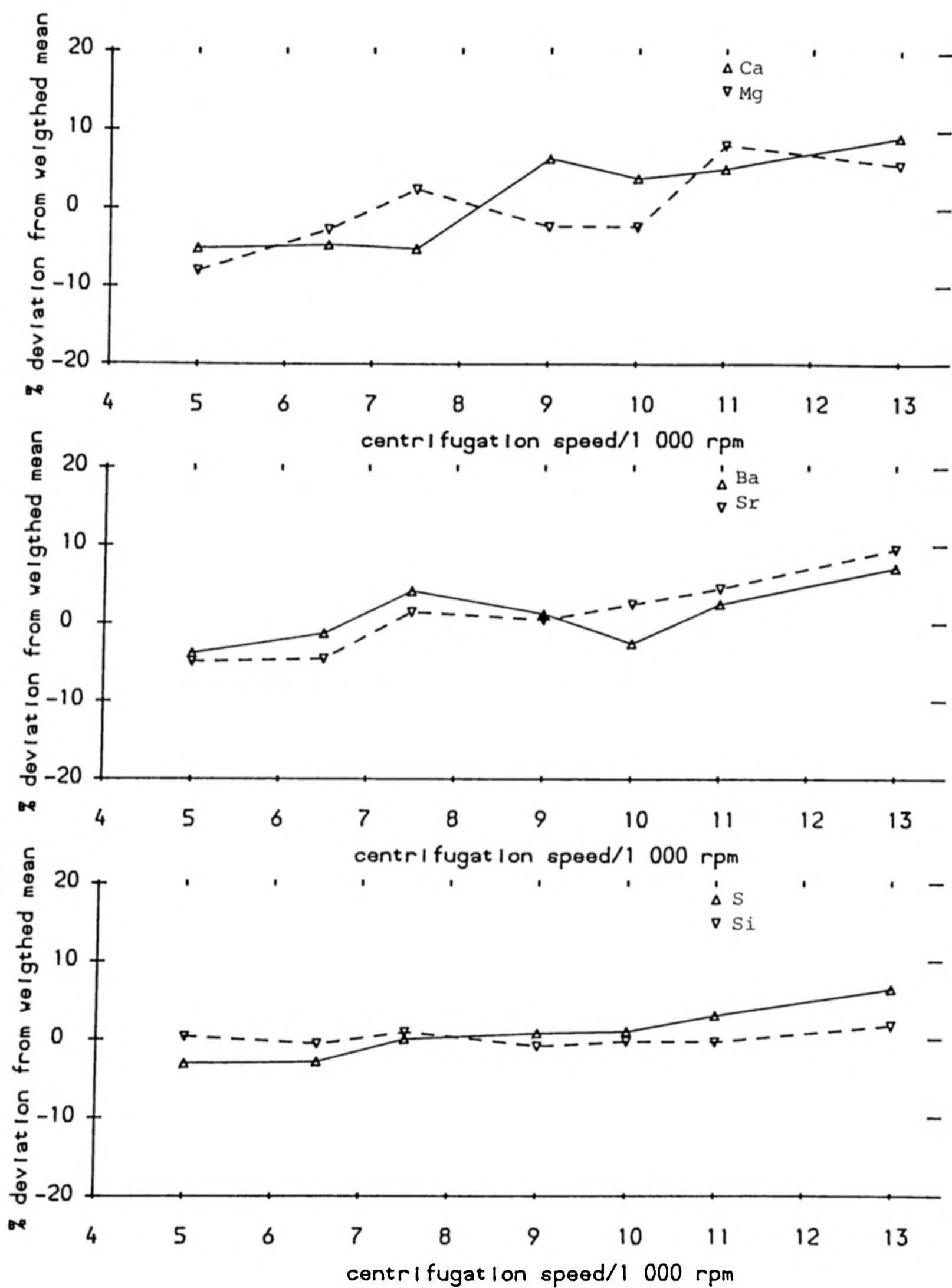
Changes in cumulative yield with increasing centrifuge speed for six samples of an Icknield soil. Changes in yield as a function of increasing driving pressure are also shown.

Figure 4.7.2



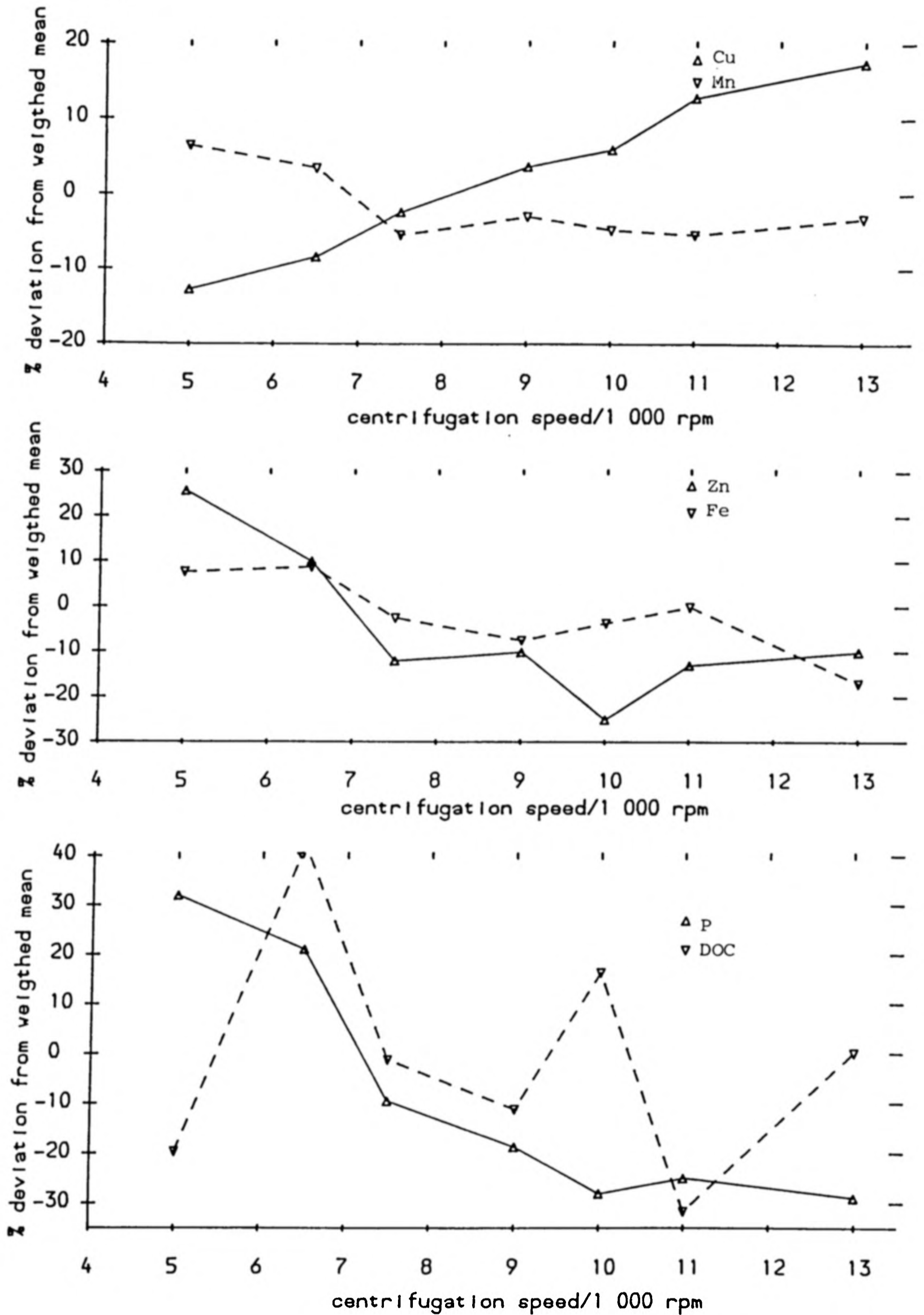
Changes in the concentrations of various solutes in solutions displaced at different centrifugation speeds. Changes are shown as the percentage deviation from the weighted mean for all speeds.

Figure 4.7.3



Changes in the concentrations of various solutes in solutions displaced at different centrifugation speeds. Changes are shown as the percentage deviation from the weighted mean for all speeds.

Figure 4.7.4



Changes in the concentrations of various solutes in solutions displaced at different centrifugation speeds. Changes are shown as the percentage deviation from the weighted mean for all speeds.

strength over the range of driving pressures used in the different methods (S4.3) is less, being about 3%. This change is not large compared to the differences between different soils, or even the differences found between different samples of the same soil (see Chapter 5) and so comparisons between solutions obtained by the different methods should be valid.

#### 4.8 Comparison of the Arklone Method with Centrifugal Filtration

It has been shown (A1.11) that displacing soil solution by Arklone does not result in any positive interferences in the chemical composition of the displaced solution. However, it is possible that Arklone might remove solutes from the solutions as they are being displaced. The solubility of water in Arklone is about 90 ppm (w/w). This means that ca 20  $\mu$ l of soil solution will dissolve in the volume of Arklone used here. Even if the chemical composition of the solution dissolving in the Arklone were markedly different from the bulk soil solution the removal of such a small volume (typically 0.3% of the volume displaced) would not cause any measurable difference in the chemical composition of the remaining solution. It is also possible that organo-metallic complexes may dissolve in the Arklone: this may result in the removal of significant amounts of metals such as copper from the displaced soil solutions. The high solubility of gases in Arklone may result in the degassing of dissolved carbon dioxide from the displaced solutions to cause an increase in pH.

In order to compare Arklone displacement with centrifugal filtration and also to test if any solutes were removed by Arklone, a number of subsamples of a soil of Icknield series (Field 25, see S6.4) were extracted in different of ways. Eight subsamples were extracted by the standard method (S4.2) save that they were centrifuged in a

swing-out rotor at 7 500 rpm and eight subsamples were extracted by the centrifugal drainage method (S4.4). A further four sub-samples were extracted by the Arklone method but re-using the Arklone used above. Displaced solutions were treated in the usual way (S4.2).

Yields of soil solution were not greatly different for any of the three methods. The higher yield from the drainage method arises from different spinning geometries.

The results of the chemical analyses (Table 4.8.1) for each of the three procedures were compared (Brownlee, 1960). The concentrations of Na, K, Mg, P, Si, Ba, B, S, and Sr were significantly<sup>1</sup> different in solutions obtained by the drainage and Arklone methods. The only determinands significantly different in a comparison of the Arklone and re-used Arklone methods were A<sub>350</sub> and Sr. It is interesting to note that certain nutrient solutes (NO<sub>3</sub>, P, K) and solutes whose concentrations are affected directly or indirectly by redox have a much higher relative standard deviation between subsamples than do solutes such as Na and Cl. This may be attributed to localised biological processes creating small pockets of nutrient and oxygen deficiency in the soil.

Compared to the standard method the solutions obtained by the drainage method contained significantly higher concentrations of Na, B, Ba, Si and Sr and lower concentrations of K, P, Mg and S.

### Conclusion

The absence of any large significant differences between the chemical compositions of the soil solutions displaced by new and re-used Arklone indicates that the differences in the chemical

<sup>1</sup> A significant difference is one which would be found by chance in less than one in ten instances if the two sets of samples being compared came from the same population.

Table 4.8.1

Chemical analyses of soil solutions displaced by different methods.

All concentrations in  $\mu\text{M}$ .

Standard Arklone method

	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	Alk	pH	DOC	A <sub>350</sub>
240	350	1851	79	363	230	48	1958	993	2470	7.950	265	0.232	
255	310	1779	77	355	224	62	1887	964	2160	7.783	335	0.218	
232	424	1964	89	376	223	53	2169	2021	2450	7.695	249	0.204	
236	329	2042	85	394	239	44	2394	1550	2440	7.626	226	0.204	
229	366	1979	84	382	232	33	2169	2829	2210	7.527	241	*	
269	316	1954	83	394	238	34	2169	2843	2140	7.753	218	0.215	
236	286	1960	82	369	230	23	2141	3836	2060	7.868	226	0.223	
236	260	2024	85	381	241	22	2197	3829	2200	7.970	210	0.235	
Mean	242	330	1944	83	377	232	40	2136	2358	2266	7.722	246	0.219
Std.Dev	13	51	88	4	14	7	14	155	1157	162	0.155	40	0.012
	B	Ba	Mn	Cu	Fe	Zn	Sr						
1.1	0.140	0.50	0.25	1.3	0.36	1.278							
0.9	0.134	0.18	0.21	0.9	0.35	1.234							
1.2	0.158	0.28	0.27	1.0	0.47	1.362							
1.1	0.147	0.17	0.27	0.7	0.35	1.411							
0.7	0.143	0.18	0.22	0.9	0.35	1.381							
0.7	0.139	0.22	0.24	1.2	0.38	1.338							
1.1	0.135	0.14	0.20	0.7	0.24	1.348							
1.4	0.142	0.09	0.27	2.3	0.30	1.375							
Mean	1.0	0.142	0.22	0.24	1.1	0.35	1.341						
Std.Dev	0.2	0.007	0.13	0.23	0.5	0.06	0.058						

Standard drainage method

	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	Alk	pH	DOC	A <sub>350</sub>
363	306	2052	80	382	269	28	2056	1279	3146	7.957	241	0.265	
340	273	2093	83	366	254	27	2197	1393	3390	8.162	218	0.227	
397	254	2105	85	379	250	25	2056	1979	2940	7.923	234	0.241	
346	219	1942	76	358	251	21	2028	1971	2690	7.830	226	0.235	
278	214	2071	74	354	243	13	1915	3171	*	*	241	0.252	
349	228	2032	75	370	245	17	1901	3021	2720	7.748	248	0.244	
334	239	2099	78	361	254	11	1859	3921	2610	7.883	241	0.239	
363	250	2061	78	384	257	13	1915	3921	2330	8.000	241	0.225	
Mean	346	248	2056	79	369	252	19	1991	2582	2832	7.929	236	0.241
Std.Dev	34	30	53	4	11	8	7	113	1067	355	0.133	10	0.013
	B	Ba	Mn	Cu	Fe	Zn	Sr						
2.5	0.165	0.09	0.38	1.0	1.08	1.494							
2.4	0.174	0.10	0.36	1.2	1.52	1.532							
1.8	0.170	0.10	0.36	1.4	1.32	1.523							
2.3	0.150	0.08	0.34	0.9	1.20	1.428							
2.3	0.163	0.07	0.23	0.9	0.52	1.504							
2.1	0.155	0.06	0.24	1.3	0.46	1.494							
2.2	0.159	0.06	0.23	0.8	0.41	1.515							
2.3	0.166	0.31	0.23	1.6	0.38	1.466							
Mean	2.3	0.163	0.11	0.30	1.1	0.86	1.494						
Std.Dev	0.2	0.007	0.08	0.07	0.3	0.47	0.034						

Standard Arklone method with used Arklone

	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	Alk	pH	DOC	A <sub>350</sub>
276	531	2197	141	399	253	39	2282	3950	2940	8.139	258	0.264	
335	578	2374	122	442	274	42	2873	3693	3020	8.084	273	0.302	
281	558	2302	103	426	257	35	2901	3914	2800	8.066	261	0.307	
373	499	2304	104	430	248	46	3014	3536	2630	8.022	304	0.301	
Mean	316	541	2294	117	424	258	40	2768	2773	2848	8.078	271	0.293
Std.Dev	46	34	73	18	18	11	5	329	195	171	0.048	21	0.019
	B	Ba	Mn	Cu	Fe	Zn	Sr						
1.3	0.161	0.09	0.25	2.4	0.47	1.462							
1.3	0.192	0.24	0.25	4.4	0.55	1.601							
1.4	0.185	0.25	0.27	1.3	0.42	1.594							
1.3	0.184	0.38	0.29	1.4	0.50	1.560							
Mean	1.3	0.180	0.24	0.26	2.4	0.48	1.554						
Std.Dev	0.1	0.135	0.12	0.02	1.4	0.05	0.064						

\* = Missing value

composition of the solutions displaced by the Arklone and drainage methods arise because of selective interferences in the drainage method. The apparent loss of P, K and Mg may be due to adsorption onto the filter paper or the alumina support. The increase in the concentrations of the other solutes probably arises from contamination from the filter paper.

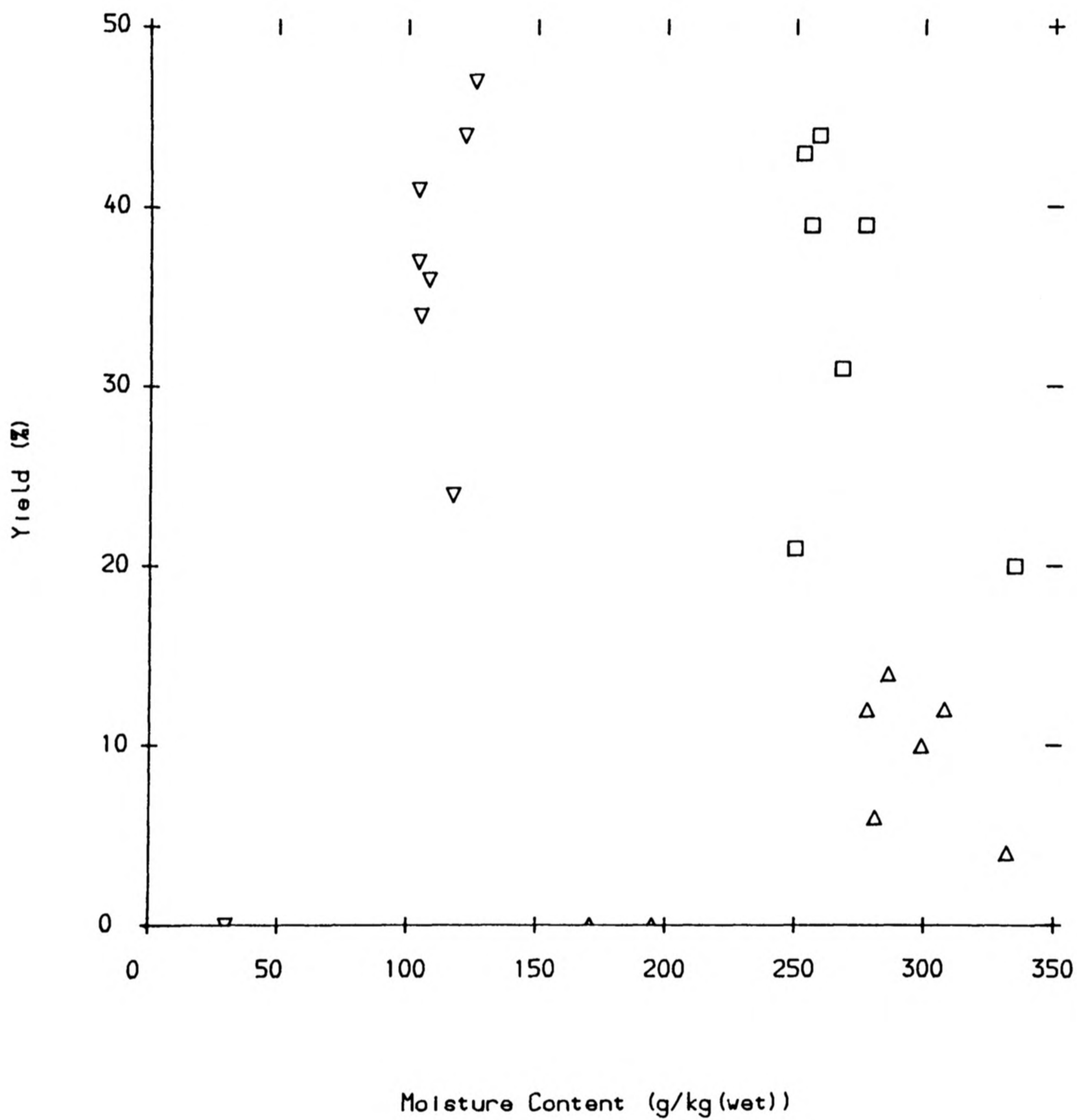
In summary: the differences found between the chemical compositions of solutions displaced by the Arklone and drainage methods can be attributed to interferences inherent in the drainage method. The Arklone method is free from any major negative interferences. The difference in the  $A_{350}$  of solutions obtained by the two Arklone methods is probably a real effect arising from partitioning of dissolved organic matter into the Arklone (see S4.2). In soil solutions with measurable amounts of trace metals bound to organic material the partitioning may result in a loss of these metals from the soil solution.

#### 4.9 Yields of Soil Solution Obtained using the Arklone Method

The fraction of the total soil solution extracted from a sample of soil is very variable and depends on soil texture, soil moisture content and whether the soil is in a wetting or drying phase. When moisture contents fall below a certain value for any one soil the innermost layer of soil in the centrifuge tube will not become saturated during centrifugation and no soil solution will be displaced from the soil.

Yields of soil solution from three pasture sites in the main experiment are shown in Figure 4.9.1. They represent three soil textures; loamy sand (Fyfield), silt loam (Icknield) and clay loam (Denchworth) at varying moisture contents. The effect of texture on the fraction of the soil solution displaced is pronounced, the

Figure 4.9.1



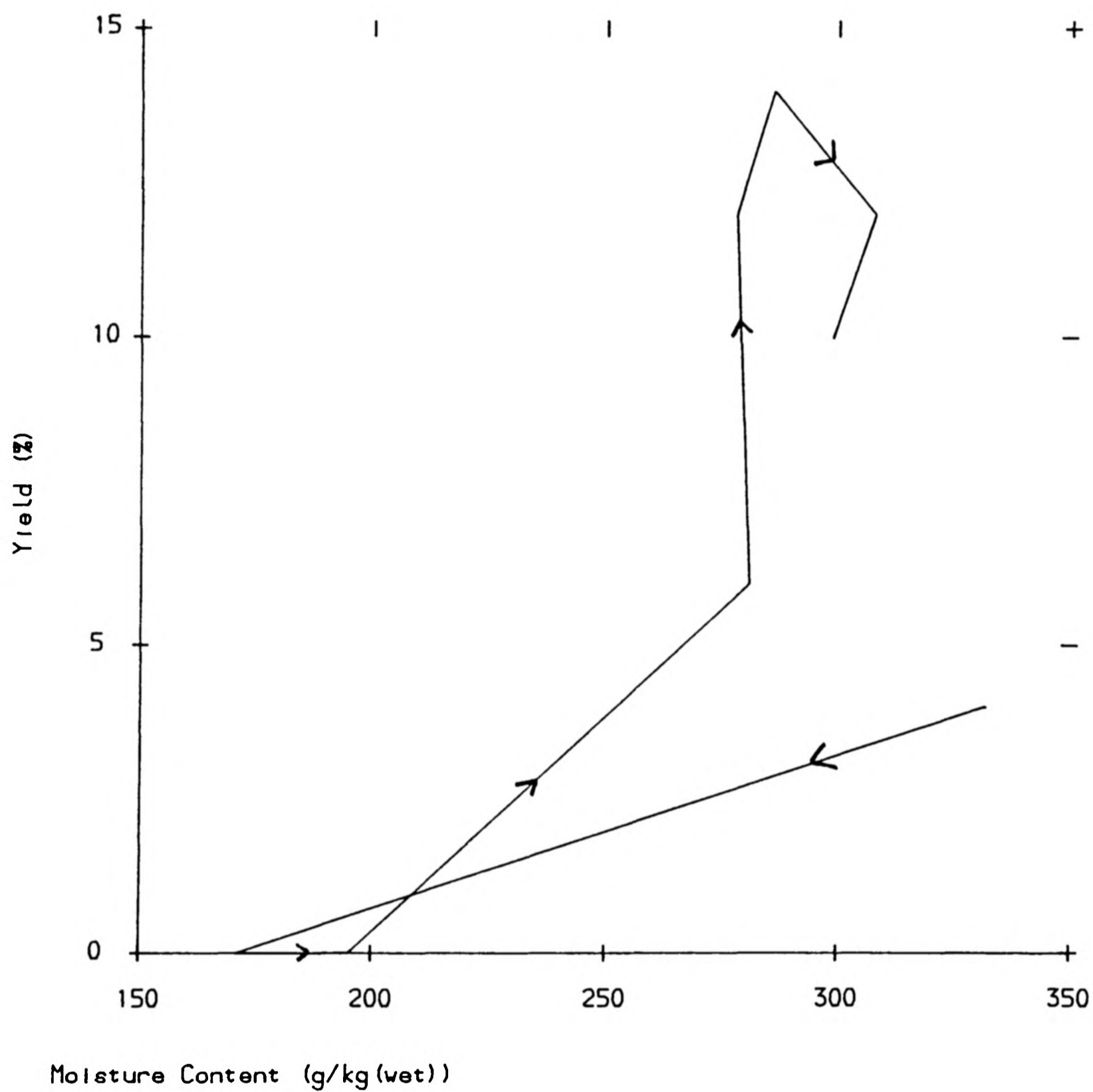
yields of soil solution obtained from three soils at different texture at various moisture contents using the standard immiscible displacement method ( $\nabla$ ) Fyfield series, ( $\square$ ) Ickniel series and ( $\blacktriangle$ ) Denchworth series.

percentage of the soil solution displaced decreasing with increasing clay content. The absence of a linear or curvilinear relationship between moisture content and yield differs from the results of Whelan and Barrow (1980) and Mubarak and Olsen (1976) respectively. In each case the soils used were moistened to varying moisture contents in the laboratory.

For a single field soil the yield does not depend solely on moisture content, but at a given moisture content, may vary depending on whether the soil is in a wetting or drying phase. The changes in yield with moisture content are shown in more detail for the Denchworth soil in Figure 4.9.2. The arrowed line follows the passage of time from June (1983), through September (two points), October, December, January, March and June (1984). The difference in yields between June and October (1983) and December and March indicates how yields vary depending on whether the soil is wetting or drying.

#### 4.10 Conclusions

The Arklone method is well suited to displacing soil solution from field-moist soils. It is largely free from both negative and positive interferences. It is not suited to displacing solutions from soils of a bulk density less than that of Arklone: however, by weighting soil with beads, and employing a swing-out rotor, solutions may be successfully extracted from such soils. The necessity of spinning such soils at a lower speed is likely to result in a small but systematic error when comparing the chemical compositions of solutions displaced by this and the standard method. The greatest practical problem likely to be encountered with the Arklone method is that frequently little or no soil solution can be isolated from dry soils. Filtered soil solutions are likely to

Figure 4.9.2

Changes in the yield of soil solution obtained from a Denchworth soil as the main experiment proceeded.

contain small, but significant, amounts of fine colloidal material, this is likely to result in elevated levels of certain "solutes" in some of the solutions.

## Chapter 5

### Preliminary Experiments

It is a capital mistake to theorise before one has data.

Sherlock Holmes

#### 5.1 Introduction

The interactions of the physical, chemical and biological factors which combine in the process of soil formation result in soil being an intrinsically heterogeneous medium, both on the micro- and macro-scopic scales. The heterogeneity of the solid phase of the soil can result in a corresponding non-uniformity in the chemical composition of the soil solution.

The chemical composition of the soil solution is also influenced by the variable fluxes of matter and energy from the atmosphere and biosphere. These result in a continual transformation of the dissolved constituents into different chemical species over a broad range of time scales.

As a result of these processes the chemical composition of the soil solution varies in both time and space. Any study of the soil solution of field soils must take these factors into account.

A large-scale study should be arranged to allow an efficient statistical interpretation of the results, to allow the partitioning of the various interacting factors into discrete categories, and to provide estimates of their magnitude.

In order to plan the large scale study (S6) to make optimum use of the time and resources available, a number of shorter investigations were carried out to provide estimates of the range and magnitude of the main components of variability and to provide a basis for planning the main sampling programme.

## 5.2 Preliminary Study

The purpose of the preliminary study was to establish the range and typical values of the concentrations of solutes in the soil solution of soils around Oxford.

Soil samples (approximately 2 kg of topsoil) were taken from ten sites on a wide range of soils on 4/10/1982 (Table 5.2.1). The samples from each site were well mixed and two subsamples of each taken for extraction. Sample 6 was extracted by centrifugal filtration (S4.4), the others by the standard immiscible displacement method (S4.2). The displaced solutions were analysed by the methods set out in Appendix 1. Phosphate and DOC were not determined.

The results of the analyses are shown in Table 5.2.2.

It is apparent from the results that the soils sampled may be divided into two broad classes:-

a) those whose soil solutions are of neutral or alkaline pH, and those of low pH. The solutions of low pH are characterised by low alkalinity and high concentrations of dissolved Mn, ~~N~~, Zn, and Al.

b) those which apparently have received high amounts of fertilizer and have high concentrations of nitrate or potassium, and those which do not.

It is apparent that land use, soil parent material and fertilizer inputs may contribute to the differences observed between different soils. It is also apparent that mixing soil samples does not remove all of the variability in the soil solution.

The differences between the chemical composition of the soil solution extracted from subsamples of a mixed soil sample indicate

Table 5.2.1

Selected properties of the ten topsoils sampled in the preliminary study.

No	Soil Series	Soil Type	Texture	National Grid Reference	Land Use	Moisture Content g/kg(wet)	Yield %
1	Rowsham	Surface Water Gley	Clay	4435 1933	Arable	280	28
2	Thames	Ground Water Gley	Clay	4432 1952	Arable	248	29
3	Fyfield	Brown Earth	Loamy Sand	4465 1993	Arable	141	51
4	Wantage	Rendzina	Silty Clay Loam	4409 1875	Arable	230	48
5	Berkhamsted/ Winchester Complex	Gleyed Brown Earth	Clay	4425 1820	Ley	163	30
6	not sur.	Podzol	Sandy Loam	4463 1720	Deciduous Woodland	426	40 <sup>@</sup>
7	Thames	Ground Water Gley	Clay	4615 1688	Arable	210	47
8	Southampton	Podzol	Sandy Loam	4635 1664	Coniferous Woodland	180	47
9	not sur.	Gley	Clay	4603 1834	Arable	195	45
10	not sur.	Gley	Clay Loam	4616 1898	Permanant Pasture	246	22

not sur. = not surveyed by the soil survey

<sup>@</sup> Extracted by centrifugal filtration

Table 5.2.2

Chemical analyses of the soil solutions displaced from soils sampled in the preliminary sampling. \* All concentrations in  $\mu\text{M}$

No	Soil Series	Na	K	Ca	Mg	S	Si	Cl	NO <sub>3</sub> -N	Alk.	pH
1	Rowsham	326	561	2069	142	292	533	685	384	3140	8.2
		309	476	2192	142	268	579	696	294	3340	8.2
2	Thames	248	302	2614	63	242	227	439	1332	2860	8.2
		254	85	2618	62	255	256	496	1340	2800	8.2
3	Fyfield	231	324	2015	209	506	168	479	2176	880	7.6
		221	306	1868	192	486	153	434	2196	640	7.3
4	Wantage	174	412	2585	68	288	284	228	1659	2780	8.1
		152	316	2220	53	186	246	197	1380	3030	8.0
5	Berkhmpst./ Winchester	246	320	1446	42	336	175	1020	326	1480	8.7
		240	223	1430	44	338	177	1110	555	*	*
6	not sur.	474	106	409	58	309	276	820	371	<10	3.7
		765	85	250	39	310	326	1040	214	<10	3.4
7	Thames	158	425	1052	65	144	310	307	2004	110	4.8
		164	378	1035	64	139	318	245	2086	40	5.0
8	Southampton	561	160	361	103	561	240	958	376	<10	3.7
		550	159	361	108	566	257	1042	*	<10	3.7
9	not sur.	964	1756	2934	123	590	220	1051	729	6160	8.6
		831	1815	3659	152	695	217	1121	671	8030	8.3
10	not sur.	367	60	2525	133	838	316	580	500	3060	8.3
		357	53	2363	126	805	327	468	400	2680	8.2
Median		282	311	2042	85	323	257	633	671	2680	8.1
logM		-3.55	-3.51	-2.69	-4.09	-3.49	-3.59	-3.20	-3.17	-2.57	

	B	Li	V	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Al	Sr	A350	
1	7.4	0.94	<0.01	0.21	0.52	0.25	1.67	0.43	<0.20	<0.38	<0.50	<4.5	2.49	0.417	
	5.8	1.10	<0.01	0.19	0.17	0.37	1.24	0.49	<0.20	<0.38	<0.50	<4.5	2.55	0.409	
2	5.7	<0.9	<0.01	0.07	0.11	<0.20	0.77	<0.23	<0.20	<0.38	<0.50	<4.5	3.49	0.207	
	6.2	<0.9	<0.01	0.08	0.18	<0.20	0.70	<0.23	<0.20	<0.38	<0.50	<4.5	3.50	0.222	
3	2.5	<0.9	<0.01	0.48	<0.11	2.24	<0.23	<0.20	<0.20	<0.38	<0.50	<4.5	1.43	0.241	
	1.9	<0.9	<0.01	0.08	0.33	<0.20	1.40	<0.23	<0.20	<0.38	<0.50	<4.5	1.28	0.233	
4	2.7	<0.9	<0.01	0.16	0.13	0.21	0.62	<0.23	<0.20	<0.38	<0.50	<4.5	2.51	0.211	
	3.0	<0.9	<0.01	0.15	0.19	<0.20	0.56	<0.23	<0.20	0.38	<0.50	<4.5	2.15	0.212	
5	3.0	<0.9	<0.01	0.12	<0.11	0.20	3.69	<0.23	<0.20	<0.38	<0.50	5.5	1.25	0.156	
	3.4	<0.9	<0.01	0.11	0.37	0.21	4.68	<0.23	<0.20	<0.38	<0.50	8.0	1.20	0.190	
6	3.5	<0.9	0.02	0.52	2.01	1.32	21.0	<0.23	<0.20	3.88	<0.50	50.0	0.64	0.203	
	4.5	<0.9	0.02	0.50	1.93	0.49	26.4	<0.23	<0.20	2.14	<0.50	61.3	0.43	0.211	
7	6.4	<0.9	<0.01	0.38	2.45	<0.20	11.9	<0.23	<0.20	<0.38	<0.50	21.6	1.27	1.40	
	7.0	<0.9	<0.01	0.41	2.48	<0.20	11.8	<0.23	<0.2	<0.38	<0.50	19.3	1.27	1.45	
8	6.9	1.4	<0.01	0.88	149	<0.20	21.6	<0.23	1.21	3.82	3.04	108	0.57	0.310	
	5.5	1.5	<0.01	0.90	159	<0.20	21.9	<0.23	1.21	3.88	3.31	106	0.58	0.385	
9	4.2	<0.9	<0.01	0.24	0.83	<0.20	1.34	<0.23	<0.2	<0.38	<0.50	<4.5	2.46	0.211	
	3.4	<0.9	<0.01	0.30	0.19	0.29	0.39	<0.23	<0.2	<0.38	<0.50	<4.5	2.99	0.204	
10	5.6	<0.9	<0.01	0.21	<0.11	<0.20	1.60	<0.23	<0.2	<0.38	<0.50	<4.5	2.04	0.287	
	4.1	<0.9	<0.01	0.20	0.11	<0.20	1.60	<0.23	<0.2	<0.38	<0.50	<4.5	1.91	0.297	
Med		4.7	<0.9	<0.01	0.20	0.33	<0.2	1.64	<0.23	<0.2	<0.38	<0.50	<4.5	1.65	0.209
Log		-5.3	<-6.0	<-8.0	-6.70	-6.48	<-6.9	-5.78	<-6.9	<-6.7	<-6.4	<-6.3	-5.35	-5.78	

\* Analyses of extractions from duplicate soil samples are given

\* = missing data

that there is heterogeneity which is not removed by mixing of the field moist soil. It is possible that more thorough mixing of the soil would reduce the magnitude of this heterogeneity. However, more complete mixing could not be carried out without resorting to a process of drying, sieving and mixing. The mixed soil would then have to be rewetted and left to re-equilibrate before extraction. This process is not only time consuming but there is ample evidence (Lahav et al, 1968; Bartlett, 1981) that such procedures greatly alter the chemical composition of the soil solution. The intrinsic heterogeneity remaining after mixing puts a limit to the resolution of any separation of the factors which contribute to differences and changes in the chemical composition of the soil solution in the field.

### 5.3 Variability Arising from Different Parent Material

The effects of parent material, land use and management were compounded in the preliminary sampling. In order to assess the possible effect of parent material alone on the chemical composition of the soil solution an area of woodland to the southwest of Oxford which covered a number of different parent materials was sampled. Samples were taken on 5/5/1985 employing the usual sampling method (S6.3) and soil solution was extracted by the standard method (S4.2). Two subsamples were taken from each bulked sample for extraction and two for moisture content determination.

Selected properties of the sampling sites are given in Table 5.3.1. The results of the chemical analyses of the displaced soil solutions are given in Table 5.3.2.

As sample B1 was taken from soil under grass its analyses are shown for interest only. The between-parent material variance (Var 1) and the between-subsample variance (Var 2) were calculated from

Table 5.3.1

Selected properties of the soils sampled in the Bagley Wood area.

S.No.	Grid Ref.	Parent Material	Vegetation	Moisture content (g/kg)	Yield (g/d)
B1	4494 2014	Lower Greensand	Pasture		
B2	4494 2014	Lower Greensand	Oak Wood	88	27
B3	4517 2028	Calcareous Grit	Bracken Scrub	77	19
B4	4513 2026	Corallian Clay	Beech/Ash Wood	150	33
B5	4512 2023	Kimmerige Clay	Oak/Hazel Wood	329	4.5 +
B6	4509 2022	Northern Drift	Beech Wood	160	31

+ Yield reduced due to part of soil floating

Yields and moisture contents are the mean of two separate determinations

Table 5.3.2

Chemical analyses of solutions displaced from the soils of Bagley Wood.

All concentrations in  $\mu\text{M}$ 

Each pair of analyses are subsamples from a mixed soil sample.

SNO	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	Alk	pH
B11	452	968	1419	211	346	109	112	1313	5057	<10	5.9
B12	498	732	1711	271	373	123	153	1437	5871	<10	5.8
B21	616	517	814	185	451	138	58	1597	2357	<10	4.7
B22	686	460	544	168	480	139	44	1631	393	<10	4.5
B31	323	1165	555	139	333	402	29	1220	3607	<10	4.7
B32	345	1078	580	151	328	406	24	1220	4171	<10	4.6
B41	228	197	1693	81	323	144	14	521	3607	1650	7.5
B42	212	91	1906	68	323	90	12	383	3607	1480	7.5
B51	219	148	307	78	383	334	6	338	443	<10	3.9
B52	219	152	327	81	405	335	7	346	307	<10	*
B61	407	167	339	81	508	506	11	772	200	<10	3.4
B62	402	173	340	84	517	499	11	792	186	<10	3.4
Var 1	704	2988	1672	1977	141	1537	2111	1453	6734	*	25998
Var 2	4	116	34	9	1	42	28	18	685	11@	62
SNO	B	Ba	Mn	Cu	Fe	Zn	Al	Sr	DOC	Abs <sub>350</sub>	
B11	3.6	0.325	20.8	0.41	27.7	0.40	21.9	1.015	*	0.465	
B12	3.5	0.338	17.9	0.59	29.0	0.66	21.0	1.144	701	0.581	
B21	7.3	0.465	209.3	0.19	22.5	2.77	51.3	0.792	732	0.354	
B22	8.3	0.519	303.3	0.15	20.4	3.94	56.7	0.638	1433	0.282	
B31	9.5	0.658	133.8	0.19	32.8	1.24	66.1	0.547	678	0.469	
B32	9.0	0.824	217.0	0.19	31.0	1.96	71.6	0.588	576	0.432	
B41	5.3	0.271	42.0	0.15	18.2	0.72	20.8	1.328	86	0.177	
B42	5.4	0.151	8.8	0.14	2.2	0.38	5.2	1.488	86	0.133	
B51	6.0	0.310	92.5	0.09	33.2	1.80	70.1	0.332	569	0.365	
B52	5.9	0.316	87.4	0.09	36.9	1.82	81.5	0.353	724	0.413	
B61	5.8	0.539	21.6	0.11	55.8	3.62	96.1	0.532	732	0.654	
B62	5.4	0.533	20.8	0.15	51.9	3.81	92.9	0.510	950	0.620	
Var 1	184	937	5286	77236	3247	2457	3063	917	347		
Var 2	4	76	71	40	861	198	375	13	113		

Variances are calculated from the log-transformed data and relate only to the last five pairs of subsamples.

Var 1 is the between-soil type variance for the last 5 sets of data  $\times 10\ 000$ Var 2 is the pooled subsample variance for the last 5 pairs of subsamples  $\times 10\ 000$ 

variances are multiplied by 10 000 to remove confusing decimal places.

\* not calculated, @ calculated from sample B4 only.

log-transformed data.

There is good agreement between subsamples with the exception of  $\text{NO}_3$  in sample B2 and K, Mn, Fe and Al in sample B4. This could be due to large differences between the two subsamples, for example widely different amounts of mobile and immobile soil water.

Differences in pH arising from different parent materials lead to the different concentrations of Al and Fe in different samples, and are inversely correlated with pH. Ca concentrations are linearly correlated with pH. The high pH and alkalinity of sample B4 is due to the presence of free carbonate in the soil. Other marked differences in the chemical composition of the soil solutions, for example in P, Zn and Cl concentrations are not directly related to soil pH.

These data demonstrate how when the possible effects of land use and management are reduced, differences due to different parent materials become apparent.

#### 5.4 Short-range Spatial and Temporal Variability

It is apparent from the two sections above that different parent materials give rise to soils whose soil solutions have differing chemical compositions. Also the soil solution may vary considerably over short distances.

If the majority of this variability were present over distances of less than ca 1 cm because of differences between the exterior and interior of single soil peds then the simple mixing and subsampling which it is reasonable to perform may not significantly reduce the magnitude of the variability. If, on the other hand, most of the variability arises mainly from heterogeneity over distances of one metre or more, then bulking and subsampling should significantly

reduce the variability.

The experiment set out below was designed to compare the variability over a few metres with that remaining after bulking and subsampling, and to assess the magnitude of short term temporal changes.

Two contrasting grassland sites were chosen, one on a clay soil (Evesham series) on the University Field Station near Wytham, the other in a clearing between mature trees on an Upper Greensand soil from the University Arboretum near Nuneham Courtenay. Both sites were under permanent grass, the former grazed and the latter mown. The former but not the latter had received regular applications of fertilizer.

At each site three sampling areas of approximately  $0.25 \text{ m}^2$  were chosen such that they lay on the circumference of a circle (6 m radius at Wytham, 5 m radius at Nuneham Courtenay). On successive visits the sampling triangle was rotated so that new ground was covered each time.

During the sampling period (17/11-9/12/1982) each site was visited twice each week. Samples to a depth of 20 cm were taken with a 2 cm diameter coring auger. 8-10 cores were taken from each sampling area and bulked to produce 3 bulked samples from each site at each visit.

The bulking of samples from each area was achieved by shaking the soil vigorously in a polythene bag which was sealed and contained about twice as much air (by volume) as soil. The soil was mixed by shaking the bag with a circular motion. The degree of mixing depends on texture, coarse-textured soils mixing more completely than fine-textured soils. This method allowed mixing with a minimum amount of contamination and moisture loss.

Soil solution was extracted from the sandy soil by the standard method (S4.2) and from the clay soil by the alternative method (S4.3), which was first developed for the Wytham soil since the standard method used for the first two sets of samples yielded no soil solution.

Rainfall during the period was slight and frequent. During the sampling period there was no pronounced change in soil moisture contents.

Insufficient soil solution was isolated for the determination of alkalinity and pH on every sample so a number of samples were bulked to give an 'average' analysis for each soil. The pH of solution from the clay soil was pH 8.4 and from the sandy soil pH 6.7.

The results from the chemical analyses are shown in Table 5.4.1. The pH difference is reflected in the concentrations of Mn, Fe, Zn and Al in the solutions.

#### Interpretation

The statistical analysis of the results was based on the possible factors outlined above. A log-normal distribution of solute concentrations was assumed and so the results were log-transformed before the analysis. Because there was no equivalent Wytham data the first two sets of results from the Nuneham Courtenay site were not included in the analysis. Therefore for each solute there were 72 values: two subsamples from each of three sampling areas from each of two sites from each of six visits.

The concentration of a solute in the  $l$ th sample from the  $k$ th sampling area from the  $j$ th soil at the  $i$ th time can be given by:-

Table 5.4.1

Solute concentrations of the soil solutions displaced from the

Wytham and Nuneham Courtenay sites.

All concentrations in  $\mu\text{M}$ . Moisture contents g/kg wet weight.

Each successive pair are subsamples from mixed soil from each sampling area.

Date 1982	Site	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	B	Ba	Mn	Fe	Zn	Al	Sr	mc
22.11	Wyt1	705	288	2482	213	470	228	16	1577	2186	8.0	0.185	0.48	2.00	2.62	<4.5	2.81	399
22.11	Wyt2	689	337	2271	207	506	228	110	1510	2236	7.7	0.233	1.67	3.13	2.98	<4.5	2.64	399
22.11	Wyt3	583	339	2289	183	413	236	113	1020	2486	6.6	0.164	0.24	5.96	1.37	<4.5	2.44	381
22.11	Wyt4	628	403	2488	198	284	220	59	1079	2550	7.5	0.193	0.10	1.67	2.37	<4.5	2.62	381
22.11	Wyt5	518	855	3051	249	489	168	130	2008	2557	5.1	0.199	0.37	1.07	0.58	<4.5	3.25	388
22.11	Wyt6	506	665	2902	231	464	159	48	1687	2486	4.7	0.179	0.36	1.49	0.69	<4.5	3.03	388
22.11	Nun1	576	228	994	269	603	255	94	1715	535	17.5	0.724	20.70	8.56	4.02	38.7	1.57	245
22.11	Nun2	581	214	975	274	536	267	55	1575	409	18.3	0.760	22.70	9.79	4.13	41.3	1.55	245
22.11	Nun3	458	268	495	211	318	145	25	1051	189	9.3	0.723	21.70	8.69	2.79	39.4	0.78	269
22.11	Nun4	464	314	484	200	318	168	21	1248	197	8.8	0.897	22.40	9.49	3.33	45.8	0.83	269
22.11	Nun5	377	284	760	211	351	173	18	1738	201	11.3	0.735	17.90	5.94	22.10	30.4	1.07	214
22.11	Nun6	394	318	815	222	351	161	21	1859	194	9.7	0.714	20.60	6.39	27.70	32.0	1.14	214
25.11	W1	1114	230	2615	210	360	186	23	1983	268	10.8	0.178	0.52	1.58	0.38	<4.5	3.38	390
25.11	Wyt2	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
25.11	Wyt3	795	782	1382	207	427	211	37	1859	1721	6.0	0.240	1.80	2.53	1.58	<4.5	2.48	375
25.11	Wyt4	565	256	2115	179	369	172	24	1166	1429	7.4	0.237	2.00	4.43	1.97	6.7	2.39	375
25.11	Wyt5	793	504	2233	189	361	183	19	1594	230	5.8	0.258	1.48	1.92	1.74	1.0	2.36	412
25.11	Wyt6	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
25.11	Nun1	504	576	745	222	428	182	35	2268	208	10.3	0.598	17.70	8.03	19.90	37.3	0.97	211
25.11	Nun2	538	937	882	254	470	188	39	2355	289	8.9	0.700	16.90	11.30	25.20	47.8	1.17	211
25.11	Nun3	503	788	540	265	280	225	33	1555	51	9.1	1.050	29.30	22.50	4.85	114.0	0.99	278
25.11	Nun4	439	620	399	202	255	225	14	1425	80	5.9	0.769	23.60	12.80	2.99	53.0	0.73	278
25.11	Nun5	509	397	731	238	288	250	25	1403	144	15.0	0.698	20.10	13.10	3.35	44.0	1.32	282
25.11	Nun6	501	355	707	240	405	203	16	1696	162	15.7	0.750	19.10	15.40	2.61	45.7	1.20	282
29.11	Wyt1	653	291	1935	175	443	266	57	1710	675	10.3	0.122	2.22	2.41	1.01	<4.5	2.46	*
29.11	Wyt2	626	167	2141	186	427	251	33	2485	1185	10.1	0.120	1.11	2.65	0.64	<4.5	2.69	*
29.11	Wyt3	497	757	2536	220	515	251	21	2239	1264	7.7	0.208	1.52	3.76	1.81	<4.5	2.58	399
29.11	Wyt4	466	684	2159	179	498	252	21	1918	465	6.1	0.177	1.25	3.11	1.25	<4.5	2.18	399
29.11	Wyt5	560	206	2172	168	331	179	15	2220	270	9.2	0.170	0.84	1.89	1.38	<4.5	2.07	431
29.11	Wyt6	694	154	2602	193	294	184	14	2865	1064	10.4	0.185	0.84	3.53	1.51	<4.5	2.67	431
29.11	Nun1	635	621	1043	341	337	270	48	2245	139	17.3	1.070	30.70	16.80	4.12	63.7	1.90	252
29.11	Nun2	580	401	951	312	331	221	29	2152	139	14.3	0.862	28.00	14.30	4.01	54.1	1.68	252
29.11	Nun3	452	515	494	247	387	188	26	1524	52	8.4	0.604	26.20	22.60	2.68	41.1	0.73	258
29.11	Nun4	434	411	393	306	410	212	48	1403	50	8.8	0.681	29.40	9.83	3.22	62.8	0.69	258
29.11	Nun5	335	297	539	178	594	264	70	1423	124	8.9	0.615	22.10	10.20	18.70	50.1	0.81	204
29.11	Nun6	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
2.12	Wyt1	560	366	2739	248	589	264	47	2141	836	12.1	0.218	1.28	2.13	1.76	<4.5	3.50	396
2.12	Wyt2	454	312	2552	213	434	199	50	1910	900	11.7	0.463	0.73	1.81	1.84	<4.5	3.38	396
2.12	Wyt3	571	653	2734	225	387	186	37	1992	1329	9.1	0.256	1.06	2.87	2.88	<4.5	2.74	456
2.12	Wyt4	583	563	2256	179	278	225	43	1797	393	5.1	0.135	0.89	2.20	2.36	<4.5	2.33	456
2.12	Wyt5	588	136	2169	150	354	190	16	1820	109	3.4	0.084	0.50	2.50	0.91	<4.5	2.23	407
2.12	Wyt6	631	168	2240	161	349	169	19	1997	43	4.1	0.126	0.94	1.56	0.52	<4.5	2.32	407
2.12	Nun1	567	880	749	233	410	279	49	2501	145	9.8	0.786	28.70	8.75	3.70	45.6	1.42	266
2.12	Nun2	544	1178	745	264	383	210	31	2228	136	10.0	0.694	24.30	7.34	2.55	38.2	1.35	266
2.12	Nun3	602	361	609	215	584	243	43	1648	93	10.4	0.686	23.40	6.33	3.38	46.3	1.05	223
2.12	Nun4	567	406	517	208	675	283	87	1558	94	9.4	0.618	28.30	6.27	4.99	47.4	0.87	223
2.12	Nun5	357	792	605	190	470	151	28	1794	237	8.4	0.507	18.10	6.83	10.89	40.4	0.89	203
2.12	Nun6	352	411	605	189	414	162	31	1648	205	8.1	0.449	16.80	6.66	10.74	33.7	0.87	203
6.12	Wyt1	620	245	2436	214	441	149	21	1972	140	12.0	0.176	1.21	2.22	0.93	<4.5	3.40	397
6.12	Wyt2	679	266	2524	217	432	149	19	1952	213	21.8	0.154	0.44	1.85	1.30	<4.5	3.54	397
6.12	Wyt3	727	1177	3025	242	582	319	26	3085	471	7.7	0.262	0.63	3.06	1.82	<4.5	3.34	387
6.12	Wyt4	610	524	2714	183	617	342	30	2392	575	3.9	0.135	0.43	5.31	1.08	<4.5	2.77	387
6.12	Wyt5	613	297	2283	167	381	202	43	2101	90	13.7	0.136	0.18	3.65	0.52	<4.5	2.29	370
6.12	Wyt6	606	350	2394	185	379	196	45	2270	56	6.2	0.128	0.17	2.38	0.75	<4.5	2.41	370
6.12	Nun1	517	913	828	260	533	171	16	1896	229	11.4	0.524	22.70	8.80	8.60	39.3	1.30	210
6.12	Nun2	418	509	749	199	574	175	17	1825	246	24.0	0.519	15.00	5.57	7.88	36.7	1.20	210
6.12	Nun3	664	1182	828	293	348	209	20	2535	89	12.6	0.749	25.70	11.60	2.98	52.3	1.35	264
6.12	Nun4	604	596	736	233	339	207	29	2056	86	12.1	0.590	15.60	6.68	2.57	37.4	1.23	264
6.12	Nun5	636	539	772	270	353	203	22	1932	101	18.0	0.741	28.40	9.01	3.44	48.6	1.42	233
6.12	Nun6	556	311	815	238	373	231	19	1645	104	13.1	0.701	22.60	9.59	3.07	44.8	1.59	233
9.12	Wyt1	528	179	2835	236	342	272	50	2634	431	25.4	0.144	0.72	2.24	2.57	<4.5	3.71	358
9.12	Wyt2	437	193	2072	167	347	232	33	946	526	17.6	0.116	0.11	1.53	0.95	<4.5	2.82	358
9.12	Wyt3	566	401	2653	166	557	285	16	1462	1164	13.9	0.169	0.09	1.12	1.46	<4.5	2.81	332
9.12	Wyt4	501	441	2871	164	564	292	25	1732	1385	13.0	0.151	0.09	1.46	1.09	<4.5	2.88	332
9.12	Wyt5	494	206	2005	137	450	243	59	1600	253	13.9	0.133	*	2.04	1.36	<4.5	1.96	338
9.12	Wyt6	562	193	2623	177	428	243	23	2814	121	18.9	0.180	0.44	5.25	1.30	<4.5	2.68	338
9.12	Nun1	432	143	642	155	332	194	11	1332	90	12.3	0.392	8.47	10.80	2.05	28.5	1.08	235
9.12	Nun2	428	226	612	153	342	191	37	1380	84	15.8	0.435	9.94	14.10	2.46	31.6	1.12	235
9.12	Nun3	448	337	571	183	441	206	33	1434	102	14.6	0.562	13.60	9.53	2.32	40.0	0.98	264
9.12	Nun4	487	305	641	195	357	252	60	1307	102	24.7	0.701	25.30	13.80	2.71	51.9	1.39	264
9.12	Nun5	340	204	620	164	301	246	18	1332	205	16.1	0.534	11.90	10.10	4.08	46.4	1.07	250
9.12	Nun6	274	118	455	122	443	221	70	952	203	12.3	0.368	12.20	8.56	2.83	29.7	0.74	250

\* = missing data

Moisture contents were not determined in duplicate.

$$C_{ijkl} = \mu + T_i + S_j + H_k + (H.S)_{kl} + \sum_{ijkl}$$

where  $\mu$  is the grand mean.

- 1)  $T_i$  = time effect
- 2)  $S_j$  = soil effect
- 3)  $H_k$  = between-sampling area effect
- 4)  $(H.S)_{kl}$  = sample-within-sampling area effect
- 5)  $\sum_{ijkl}$  = error term

The last three terms were lumped together into the residual term against which the significance of the time and soil effects were assessed.

A GENSTAT program was written to carry out the ANOVAR (see Appendix 2.2) In the program the sample-within-sampling area effect is nested within the sampling area effect in the BLOCK term. This results in the sample error being placed in a separate stratum which allows the subsampling variance to be recorded separately and the between-sampling area variance to be used as the test of the significance of the time and soil effects. The ANOVAR is summarised in the plan below.

Hole Stratum	DofF
Time	5
Soil	1
Residual	29
Total	35
Hole.Sample Stratum	36
Grand Total	71

Within the Hole stratum, the variance was partitioned into a time effect, a soil effect and a residual term (the between-sampling area variance). The within-sampling area (subsampling) variance was

used to test the significance of the between-sampling area variance. (That is:- compared to the variability between subsamples, is the variability between sampling areas significant ?)

If this term was significant it was then used to test the soil and time effects for significance. If it was not then it was pooled with the between-sampling area variance and the pooled variance was used to test the two higher terms. The variance ratios calculated by the procedures outlined above are shown in Table 5.4.3.

It is interesting to note that the between-sampling area variance is very highly significant for most solutes. This indicates that, compared to the variability remaining after mixing, there is considerable variability over a range of a few metres. It is also notable that for a number of solutes (S, Si, P) the difference between areas a few metres apart is greater than that between solute concentrations on different parent materials and under different managements.

The significant differences between the two soils can be attributed to two factors; fertilizer applications ( $\text{NO}_3$  and Ca) and soil solution pH (Al, Fe and Mn). The concentration of barium in the soil solutions from Nuneham Courtenay was higher than in solution from Wytham. This may have been due to the presence of barytes cements in the Upper Greensand (see S7.4). There were no highly significant ( $\underline{p} < 0.01$ ) changes with time.

#### 5.5 Short Range Spatial Variability

The results from S5.4 indicated that there was considerable variability over a range of a few metres, some of which was still present after mixing the soil samples. The variance between subsamples is a crucial factor in determining the significance of

Table 5.4.2

Variances for each level in the ANOVAR of the Wytham/Nuneham Courtenay experiment. Variances are calculated from the log-transformed data of Table 5.4.1 using the GENSTAT program in Appendix A2.1.

Solute	Factor			
	Time	Soil	Between-Hole	Sample within-hole
Na	0.0370	0.2308	0.0127	0.0014
K	0.1847	0.1205	0.0912	0.0152
Ca	0.0120	5.7615	0.0134	0.0020
Mg	0.0278	0.0617	0.0082	0.0024
S	0.0116	0.0038	0.0110	0.0023
Si	0.0154	0.0008	0.0139	0.0015
P	0.1324	0.0009	0.0793	0.0384
Cl	0.0479	0.0684	0.0131	0.0196
NO <sub>3</sub>	0.6932	0.1704	0.2259	0.4625
B	0.1531	0.3127	0.0403	0.1010
Ba	0.0488	5.8488	0.01947	0.0069
Mn	0.0456	42.6825	0.1020	0.0276
Fe	0.0636	7.0169	0.0353	0.2388
Zn	0.0823	6.4817	0.304	0.0106
Sr	0.0137	2.7817	0.0960	0.0024
D of F	5	1	29	33

Table 5.4.3

Variance ratios and significant sources of variation calculated from the variances in Table 5.4.2.

Solute	Source of Variation		
	Time	Soil	Between-Hole
Na	2.91 *	18.13 ***	8.95 ***
K	2.03 ns	1.32 ns	6.00 ***
Ca	0.89 ns	430.95 ***	6.80 ***
Mg	3.39 *	7.53 *	3.36 **
S	0.61 ns	0.20 ns	8.38 ***
Si	1.11 ns	0.05 ns	9.30 ***
P	1.67 ns	0.01 ns	2.06 **
Cl	3.66 *	5.22 *	1.96 *
NO <sub>3</sub>	3.07 *	27.31 ***	11.6 ***
B	3.80 *	7.77 **	3.97 ***
Ba	2.51 **	300.39 ***	2.82 **
Mn	4.49 **	418.36 ***	3.70 ***
Fe	1.46 ns	161.67 ***	1.87 ns
Zn	0.45 ns	35.41 ***	17.33 ***
Sr	0.78 ns	158.48 ***	7.25 ***

ns not significant at 95 %

\* significant at 95 %

\*\* significant at 99 %

\*\*\* significant at 99.9 %

the variances attributed to effects such as soil type and land use. The experimental design for the main survey will have to ensure that differences between and within land use and soil type are not obscured by noise from short range spatial variability.

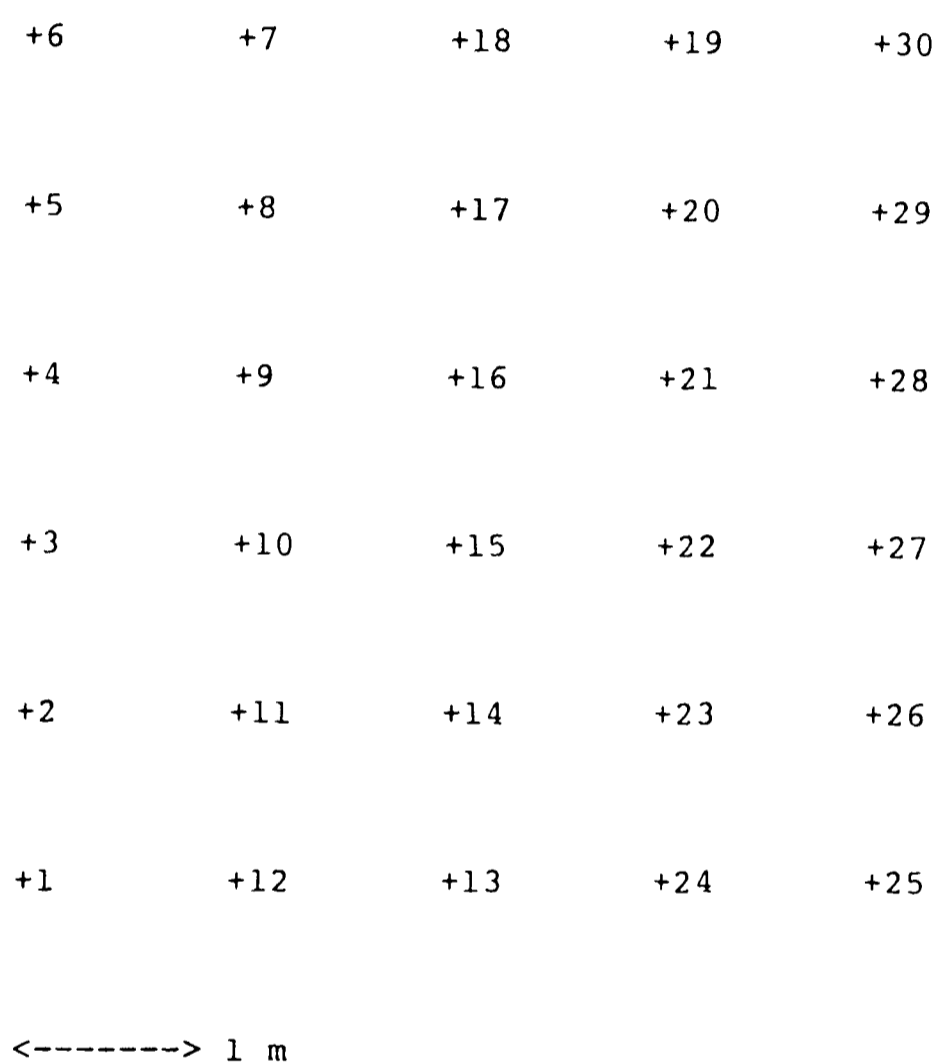
A further experiment was designed to estimate the variability present over a range of a few metres in a pasture field, and the reduction of that variability by bulking and subsampling. A field site on Kingston series was chosen from the main field experiment (Field No 5, see S6.2). A 5 X 4 m grid was marked out near the centre of the field and thirty samples were taken at the intersections of the grid lines. A 2 cm coring auger was used to provide samples to a depth of 20 cm. Fifteen of these cores were bulked and mixed, the remainder were kept separate. The nearest neighbours of each unbulked core were cores which were bulked and vice versa. The sampling grid and numbering system is shown in Figure 5.5.1. A number of other cores were taken from within the sampling area for moisture content determination. The bulked and mixed, soil sample was divided into 15 subsamples which were extracted, as were the separate cores, by the standard Arklone method (S4.2).

The results of the chemical analyses are shown in Table 5.5.1. Alkalinity and pH were not determined. Li, Y, V, Cd, Co, Ni, Mo, Al and Pb were present at concentrations below their detection limits. Some of the concentrations of Cu and Zn in the table are lower than the normal six  $\sigma$  detection limit (0.20 and 0.38  $\mu\text{M}$ , respectively).

A comparison of the variances of the unbulked and bulked solutions shows that, with the exception of copper, the variances of subsamples from 15 bulked cores were less than those from the separate, unbulked samples. The variance is significantly reduced

Figure 5.5.1

The diagram below shows the sampling grid used in the spatial variability experiment. Even numbers correspond to cores which were extracted separately and correspond to the sample numbers in Table 5.4.1.



Moisture content (mean of 4) 207.2 g/kg on a wet-weight basis (rsd 4.4 %)

Mean yield from the separate cores 27.5 % (rsd 11.0 %)

Mean yield from the bulked cores 29.9 % (rsd 5.8 %)

Table 5.5.1

Chemical analyses of soil solutions from unbulked soil samples  
See Fig. 5.5.1 for sampling grid. All concentrations are in  $\mu\text{M}$   
variances calculated from the log-transformed data

No	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	DOC
2	760	678	3123	246	580	148	108	4900	1171	2733
4	858	1822	2920	365	495	225	239	4170	1786	3283
6	2330	1449	5002	501	758	305	307	6560	4886	5233
8	1110	191	4040	305	853	146	45	5630	1843	1808
10	692	304	2378	164	519	163	43	3490	1286	1525
12	1055	1265	3466	451	527	180	148	5010	2143	2867
14	925	1151	2961	232	505	127	120	4080	1843	2133
16	591	564	3115	150	393	111	34	4390	1207	1667
18	547	235	1721	91	383	131	47	2370	2	4117
20	767	601	3727	203	1019	149	81	4820	593	2133
22	1055	1210	6403	437	645	209	126	5830	7429	1900
24	736	720	9524	463	462	169	40	8700	10214	1250
26	1019	281	4991	339	583	144	47	4820	6071	1342
28	700	454	4703	277	385	178	84	4280	6143	1200
30	636	992	2008	134	457	121	129	2930	664	2058
Mean	919	794	4005	291	571	167	106	4799	3152	2350
Variance x 10 000	221	944	305	457	147	121	819	176	1696	329

No	B	Ba	Mn	Cu	Fe	Zn	Sr
2	2.5	0.23	1.42	0.19	1.81	0.52	1.57
4	3.5	0.27	6.86	0.35	4.59	1.06	1.51
6	3.0	0.33	6.15	0.29	3.60	1.22	2.51
8	1.8	0.17	0.78	0.12	0.83	0.18	1.88
10	4.9	0.16	0.98	0.12	1.92	0.22	1.18
12	2.9	0.26	4.48	0.28	3.94	0.79	1.78
14	2.7	0.25	4.69	0.21	3.50	0.70	1.45
16	1.7	0.17	1.12	0.18	1.17	0.33	1.44
18	2.7	0.11	0.81	0.14	3.41	0.29	0.82
20	2.2	0.21	1.67	0.22	1.59	0.39	1.73
22	3.6	0.41	2.75	0.16	1.28	0.60	3.05
24	3.0	0.56	0.91	0.13	0.74	0.23	4.40
26	3.6	0.28	1.12	0.12	1.00	0.27	2.29
28	4.7	0.36	1.41	0.11	1.03	0.32	2.24
30	2.7	0.17	1.60	0.12	1.56	0.49	0.96
Mean	3.0	0.26	2.45	0.18	2.13	0.51	1.92
variance x 10 000	159	7883	2122	248	655	604	330

Chemical analyses of the bulked and sub-sampled cores  
Sample numbers do not refer to the core numbers in Fig 5.3.1

No	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	DOC
1	696	413	2824	178	482	123	35	3460	1764	1900
3	756	314	3169	215	689	158	80	3660	1643	1992
5	797	865	3737	245	512	142	101	4590	2800	2642
7	908	997	3087	217	535	128	80	5150	2086	*
9	1112	2081	3121	259	586	139	124	3770	2500	*
11	812	766	3110	218	582	133	97	3970	2043	*
13	1238	1244	5382	402	1260	205	256	4080	3971	2358
15	770	558	3214	203	527	126	73	5010	2286	2917
17	936	956	3577	298	557	140	89	3660	3643	1850
19	749	531	3017	195	492	125	91	3490	2080	4442
21	784	946	2922	209	501	119	85	4080	2121	1900
23	694	476	2885	188	496	117	58	3410	2121	2083
25	696	274	2765	169	491	114	19	3300	2100	1942
27	658	399	2854	185	451	111	34	3460	3429	1942
29	806	636	3222	236	504	145	109	3550	3086	2058
Mean	827	764	3259	278	578	135	89	3909	2512	2336
Variance x 10 000	56	533	48	87	108	42	667	35	125	114

No	B	Ba	Mn	Cu	Fe	Zn	Sr
1	3.8	0.22	1.35	0.14	1.36	0.33	1.36
3	4.6	0.24	2.69	0.20	1.32	0.35	1.52
5	3.1	0.27	2.56	0.23	1.53	0.50	1.81
7	2.0	0.24	2.94	0.20	2.13	0.49	1.58
9	3.1	0.40	3.51	0.34	8.65	0.80	1.61
11	2.5	0.26	1.68	0.16	2.08	0.49	1.57
13	5.1	0.41	2.82	0.24	2.80	1.63	2.71
15	3.2	0.23	1.44	0.13	1.22	0.71	1.57
17	2.9	0.32	1.66	0.21	2.73	0.69	1.79
19	2.7	0.20	0.96	0.12	1.02	0.35	1.49
21	3.6	0.26	1.52	0.13	1.11	0.54	1.42
23	3.6	0.21	1.98	0.11	1.24	0.40	1.37
25	64.7	0.18	0.79	0.09	1.67	0.26	1.33
27	2.8	0.20	1.63	0.10	1.25	0.39	1.35
29	3.8	0.25	1.07	0.12	1.40	0.56	1.54
Mean	7.4	0.26	1.91	0.17	2.10	0.57	1.60
variance x 10 000	250	101	339	249	517	355	55

\* = missing values

( $P < 0.02$ ) for Na, Ca, Mg, Cl,  $\text{NO}_3$ , Ba, Mn, and Sr.

Comparing the means of the (log-transformed) data (by the procedure outlined by Brownlee, 1960) the values of  $t$  obtained are below the 5% significance level for all solutes except silicon whose value is 2.424 (5% level 2.05). It can be concluded that at the 95% probability level ( $P < 0.05$ ) the bulked and unbulked samples come from the same population of samples.

### 5.6 Conclusions

The experiments outlined above indicate that:-

1) Soil solutions displaced from different types of soil and/or different land use can be markedly different. Large differences may be attributed to factors such as pH and fertilizer applications.

2) Sampling soil solutions from soils derived from different parent materials under the same land use and management showed that there are differences in the chemical compositions of their soil solutions, some of which can be attributed to soil pH.

3) Sampling soil solution from two contrasting soils over a short period showed that the differences found in 1) above are significant compared to short range heterogeneity over a range of a few metres for some solutes. For other solutes short range variability may mask these differences. The variance between subsamples from the same bulked sample from a small ( $0.25 \text{ m}^2$ ) area is significantly less than the variance between sites a few metres apart. Over a period of a few weeks there were no significant changes. Thus a sampling frequency of more than one per month would not be necessary.

4) By comparing bulked and separate samples from within the same area it was shown that bulking significantly reduces the variance. The variances for major non-nutrient solutes were reduced

by at least 80% by bulking, and that of the nutrient solutes by between 20 and 50%. The two types of sample were shown to come from the same population. Thus, if only a limited number of soil samples can be extracted, taking subsamples from a bulked sample will give rise to a smaller spread of values and will result in a better estimate of the mean.

The variances calculated from the results above may be conveniently grouped into three categories:

a) subsampling variance, i.e. the variability between subsamples from one mixed sample;

b) short range variability, i.e. the variability between separate samples taken from a small area (less than 10 m between samples);

c) longer range variance, i.e. the variability between samples of different soils on different parent materials (distances of 0.1-10 km).

As these variances came from data pertaining to different populations it is not possible to compare them quantitatively. However, it is instructive to compare them qualitatively. The variances in Table 5.6.1 are calculated from the results so far; variances are grouped into three categories; a) between soil series, b) short range spatial variability and c) variability between subsamples.

The initial ANOVAR of the data from S5.4 combined the between-sampling-area variance and the subsampling variance into one term. By altering the ANOVAR to separate these two terms a measure of the between-sampling-area variance may be obtained. The GENSTAT program written to do this is shown in Appendix 2.3.

The inter-soil variances are from S5.3 and S5.4, the intra-soil

variances are from S5.4 and S5.5 and the subsampling variances are from S5.2-S5.5 inclusive. By comparing the variances at different levels the solutes may be placed into one of two categories:-

i) those with distance-dependent variability, i.e. the further apart two samples are the greater the difference between them, Na, K, Ca, Cl, NO<sub>3</sub> and Mn; and

ii) the remainder which do not exhibit any clear distance dependent variability.

The variability over short distances is likely to limit the interpretation of the results from any large scale study: it is the yardstick against which the significance of all other variability must be assessed. From the results presented above it is clear that the short-range variability for some solutes may be as large as that found over large distances. With few exceptions (Mg, Zn, Fe) the two measures of short-range variability in Table 5.6.1 are of a similar magnitude for each solute. It is reasonable, then, to assume that they provide a fairly accurate measure of variability over short distances. The larger of these two variances was taken as the 'baseline variance' which was compared with variances at other levels in the main experiment.

Table 5.6.1

A comparison of variances at different distances calculated from the data in the introductory studies.

All variances are multiplied by 10 000

Solute	Between Soil Series Variability		Short Range Variability		Subsampling Variability			
	A	B	C	D	E	F	G	H
Na	704	2308	127	221	45	4	13	56
K	2988	1205	903	944	181	116	133	533
Ca	1672	57615	164	346	34	34	20	48
Mg	1977	617	82	457	162	9	23	87
S	141	38	205	147	28	4	23	108
Si	1537	8	149	121	7	42	66	42
P	2111	9	694	819	*	28	535	667
Cl	1453	684	134	176	87	18	67	35
NO <sub>3</sub>	6743	61704	2173	1696	78	685	208	125
Alk	*	*	*	26	11	*	*	*
pH	25998	*	*	*	183	62	*	*
DUC	347	*	*	329	*	113	*	114
B	184	3127	423	159	41	4	101	250
Ba	937	58488	2177	7883	312	76	125	101
Mn	5268	426825	941	2122	58	71	267	339
Cu	7236	*	*	248	1494	40	*	249
Fe	3247	70169	3243	650	467	861	194	517
Zn	2475	64817	3503	660	*	198	372	371
Al	3063	*	*	*	46	375	*	*
Sr	917	27817	797	330	226	13	69	55
DF	5	1	35	14	5	5	71	14

\* Not calculated.

#### Between soil variability

A Variability between soil types in Bagley Wood.

B Variability between Wytham and Nuneham Courtenay sites

#### Short range spatial variability

C Variability within Wytham and Nuneham Courtenay sites

D Variability between unbulked cores in S5.5

#### Subsampling Variance

E Preliminary Study

F Bagley Wood

G Wytham and Nuneham Courtenay

H Bulked samples from S5.5

## Chapter 6

### The Main Field Sampling Experiment

We see that the theory of probabilities is at bottom only common sense reduced to calculation: it makes us appreciate with exactitude what reasonable minds feel by a sort of instinct.

P.S. Laplace

#### 6.1 Introduction

The large differences between the chemical compositions of soil solutions from different soils are the product of a number of interacting processes (Chapter 2). In field soils these processes and their interactions are complex. However, it is possible that a small number of these factors may be predominant. Conversely, random spatial variations may be so great that the effects of these processes are completely obscured.

It is apparent that, at any one time, soil type, land-use, topography and management (Chapters 2 and 5) are likely to affect the chemical composition of the soil solution. Together with the time-dependent phenomena of rainfall and evapotranspiration they will interact to produce temporal changes. The main experiment outlined below was designed to estimate the significance and magnitude of these effects.

The findings of the preliminary studies indicated that for some solutes, the short-range spatial variability (s.r.s.v.) was of a similar magnitude to the variability between different soil types. However, the s.r.s.v. could be reduced by bulking soil samples from a sampling area and taking subsamples of the bulked sample for extraction. In view of this it was decided to choose three separate fields on each soil series and take samples from a site of an area of approximately 5 x 5 m. By choosing three fields on each soil

series an estimate of the within-soil series variability can be obtained. The results from S5.4 indicated that changes over a one month period were not significant when compared to the s.r.s.v. Thus, sampling intervals of less than one month would not increase the resolution of temporal changes.

The main part of the experiment focussed on grass sites on a number of different soil series and temporal changes over a one year period. Concurrently with this sampling, a number of arable and wet pasture sites were also sampled to allow comparisons to be made between them and the pasture sites. Pasture fields were chosen for the majority of sites for a number of reasons. They are more numerous than arable fields, access is easier and they are unlikely to suffer from extremes of agricultural practice.

The sampling framework was designed to allow differences between measurements at different times and on different soils to be partitioned between different possible contributing factors and to allow the significance of these factors to be estimated. Seven sets of samples were taken at approximately six week intervals over a one year period from June 1983. The dry summer of 1983 precluded soil solution samples being extracted between June and September (December in some cases).

## 6.2 Description of the Sampling Sites

The choice of sites was based largely on information in the memoir of the soil survey of the Wantage and Abingdon District (Jarvis, 1973). After an initial reconnaissance, suitable areas were chosen, then further visits were made to choose sites within particular fields.

Sites were chosen on six soil series which, between them, comprise

37% of the area of soils mapped in the survey of the area. They covered a wide range of soil textures and profile drainage. The characteristics of the six soil series are set out in Table 6.2.1.

On each of the six soil series, three pasture sites were chosen. These 18 sites provide the basis for the main ANOVAR. Comparison between the sites on each series allowed intra-soil series differences to be estimated. Two of the sites on each of Fyfield, Denchworth and Icknield series were chosen such that there were arable fields nearby to allow a comparison between different landuses to be made. Two sites on Denchworth series and one on Fyfield series were chosen with adjacent wet sites for a wet/dry pasture comparison. A description of the sites is given in Table 6.2.2.

### 6.3 Sampling

At each of the sites an area of approximately 5 X 5m was chosen and cores were taken to a depth of 20 cm with a 2 cm diameter coring auger. Between 20 and 25 cores were taken at approximately 1 m intervals on an imaginary grid. On successive visits the grid was displaced slightly to sample new ground over the same area. On each sampling visit the cores were bulked and mixed (S5.3), two or more subsamples being taken for extraction and a further two for moisture content determination. Pasture sites were visited seven times over a one year period: (6-10 June, 22-28 Sept, 18-26 Oct, 5-6,12-15 Dec 1983, 16-20 Jan, 26-30 March, 1-7 June 1984).

Two or more subsamples from each mixed sample from each site were extracted by the standard method (with the exception of sites 16, 17, 18, 21, 26 and 27 which were extracted by the low bulk density method, S4.3). Extracted soil solution was treated as in S4.2.

Table 6.2.1

Characteristics of the soil series sampled in the main experiment  
(from Jarvis, 1973)

Soil Series	Soil Sub-Group	Parent Material	Principal Texture
Fyfield	Brown Earth (lessive)	Jurassic and Cretaceous Sands	Loamy Sand
Kingston	Surface-water Gley	Jurassic and Cretaceous Sands	Fine Sandy Loam
Sherborne	Brown Earth (calcareous)	Jurassic Limestone	Stony Loam
Evesham	Gleyed Calcareous	Jurassic Stony Limestone	Loam
Denchworth	Surface Water Gley	Jurassic Calc. Clays	Clay Loam
Icknield	Rendzina	Chalk	Silt Loam

## Selected properties of the sites sampled in the main field experiment

Site No	Soil Series	Landuse	National Grid Ref	Relief (slope)	O.M (%)	C.E.C. meq/100g	Free CaCO <sub>3</sub>
<b>Grass Sites</b>							
2	Fyfield	Grass (grazed)	4452 1985	Gentle	1.8	33.3	
3	Fyfield	Grass (ley)	4418 1987	Gentle	1.6	11.1	
11	Fyfield	Grass (grazed)	4383 1988	Gentle	1.7	9.6	
4	Kingston	Grass (grazed)	4406 1992	Gentle	2.0	20.1	
5	Kingston	Grass (silage)	4414 1992	Gentle	6.5	47.6	+
9	Kingston	Grass (ley)	4367 1978	Gentle	1.2	14.0	
7	Sherborne	Grass (grazed)	4386 1965	Gentle	4.0	40.2	+
13	Sherborne	Grass (grazed)	4377 1946	Gentle	2.6	24.7	+
14	Sherborne	Grass (silage)	4346 1947	Gentle	6.9	45.5	+
8	Evesham	Grass (silage)	4372 1994	Gentle	4.4	41.9	+
10	Evesham	Grass (grazed)	4386 1997	Gentle	4.6	35.8	
19	Evesham	Grass (grazed)	4273 1962	Gentle	5.5	33.3	
15	Denchworth	Grass (hay)	4348 1928	Gentle	7.4	36.4	+
17	Denchworth	Grass (grazed)	4369 1898	Gentle	9.9	47.1	
22	Denchworth	Grass (grazed)	4328 1903	Gentle	3.4	34.2	
23	Icknield	Grass (gallops)	4323 1852	Moderate	8.3	46.0	+
25	Icknield	Grass (grazed)	4352 1856	Moderate	6.7	28.4	+
26	Icknield	Grass (gallops)	4338 1842	Moderate	10.5	62.2	+
<b>Arable Sites</b>							
1	Fyfield	Arable (barley)	4452 1985	Gentle	1.0	8.7	
12	Fyfield	Arable (barley)	4384 1988	Gentle	1.2	10.6	
18	Denchworth	Arable (barley)	4373 1896	Gentle	8.7	50.3	+
20	Denchworth	Arable (barley)	4333 1905	Gentle	3.8	29.7	
24	Icknield	Arable (barley)	4323 1852	Moderate	6.0	37.7	+
27	Icknield	Arable (barley)	4338 1842	Moderate	17.0	59.1	+
<b>Wet Grass Sites</b>							
6	Fyfield	Grass (grazed)	4455 1984	Gentle	4.0	26.7	
16	Denchworth	Grass (grazed)	4368 1897	Gentle	8.7	42.1	+
21	Denchworth	Grass (grazed)	4330 1905	Gentle	9.3	44.8	+

#### 6.4 Results of the Chemical Analyses

The results are shown in full in Appendix 3. A summary of the results is set out below. Medians and ranges of concentration, which treat all of the samples as coming from the same population, are shown in Table 6.4.1.

An inspection of the data showed that the concentrations were approximately log-normally distributed (with the exception of pH and alkalinity) <sup>(See Appendix 3)</sup> so all subsequent statistical analyses were executed on the log-transformed data (with the exception of pH values).

#### 6.5 Comparison of Soil Solution Composition with Other Published Data

As was mentioned in Chapter 1 relatively few comprehensive studies of the chemical composition of the soil solution have been published, especially in recent years. Bowen (1979) was content to describe the soil solution as having a similar composition to river waters. Reisenauer (1966) found less than a thousand measurements of the concentrations of even major solutes of the soil solutions in his review of the literature. Even then, most of the data was published before 1940.

Direct comparisons between data from different studies is difficult because the soils were often treated in some way before extraction, and solutions were extracted in different ways. Of the data presented in Table 6.5.1 only that from this study and that of Kinniburgh and Miles (1983) relate to soil solutions obtained by immiscible displacement of unaltered field soils. The remaining data relate to solutions obtained by a number of techniques, generally miscible displacement of one sort or another. Some data from saturation paste extracts is also included (C, D and F). The

Table 6.4.1

Statistical summary of the results from the main experiment.  
All concentrations in  $\mu\text{M}$ .

Solute	N	N<D.L	Median	Range
Na	337	0	465	126 - 4250
K	337	0	390	10 - 4627
Ca	337	0	2119	417 -17272
Mg	337	0	135	13 - 1904
S	337	0	327	70 - 5572
Si	337	0	220	25 - 1340
P	337	11	64	<13 - 810
Cl	329	0	1587	71 -11025
NO <sub>3</sub>	327	0	857	1 -36429
Alk	314	-	1810	<10 -13570
pH	327	-	7.7	5.0- 8.5
DOC	322	0	4246	750 -22600
Abs <sub>350</sub>	306	-	0.323	0.043-1.158
B	337	27	5.1	<1.7- 36
Li	337	217	<0.9	<0.9- 7.7
Y	337	182	<0.01	<0.01- 0.06
Ba	337	0	0.16	0.03- 1.96
Mn	337	47	0.52	<0.1 - 105
Cu	337	130	0.25	<0.2 - 2.8
Fe	337	0	3.4	0.1 -1070
V	337	317	<0.23	<0.23- 0.55
Cd	337	337	<0.16	- -
Co	337	332	<0.2	<0.2 - 6.3
Zn	337	186	<0.38	<0.38- 150
Ni	336	295	<0.5	<0.5 - 9.1
Mo	337	309	<0.4	<0.4 - 8.6
Al	335	212	<4.5	<4.5 -2200
Pb	336	336	<0.4	- -
Sr	337	0	1.9	0.5 - 20.4

N = number of analyses, N<D.L - number of these where the solution concentration was less than could be detected.

A more detailed summary, including histograms and time and soil means where appropriate is given in Appendix 8.

Table 6.5.1

A comparison of the soil solution data from this study with that from other published sources. The numbers are the median concentrations in log M for each set of data.

Soil Types	Neutral and Calcareous	A Range of Californian		Slightly Acidic Agricultural	Acidic Woodland	
Solute						
Major Solutes						
Na	-3.3	-3.6	-	-2.7	-3.3	-3.5
K	-3.4	-3.5	-2.9	-3.0	-4.2	-3.8
Ca	-2.7	-2.9	-2.7	-2.6	-2.9	-3.3
Mg	-3.8	-4.1	-2.6	-2.3	-3.6	-3.4
S	-3.4	-3.5	-2.9	-2.4	-3.6	-3.4
Si	-3.7	-3.5	-	-	-3.7	-3.5
P	-4.2	-	-5.5	-	-5.2	-4.9
Cl	-2.9	-3.3	-	-2.6	-	-3.1
NO <sub>3</sub>	-3.1	-3.3	-	-2.0	-3.3	-2.9
Alk.	-2.7	-	-	-2.7	-	<-5.0
pH	7.7	7.8	-	7.3	5.5	4.7
DOC	-2.4	-2.4	-	-	-	-
Abs <sub>350</sub>	0.322	0.246	-	-	-	-
Source	A	B	C	D	E	A
Minor Solutes						
B	-5.3	-5.0	-	-	-	-5.2
Li	<-6.0	<-6.5	-	-	-	<-6.0
Y	<-8.0	<-8.5	-	-	-	<-8.0
Ba	-6.8	-7.0	-	-	-	-6.3
Mn	-6.3	-6.5	-7.0	-	-	-4.0
Cu	-6.6	-6.6	-6.9	-	-6.5	-6.8
Fe	-5.5	-5.4	-6.6	-	-5.3	-4.5
V	<-6.6	-7.7	-	-	-	<-6.6
Zn	<-6.4	-6.6	-6.6	-	-6.5	-5.7
Al	<-5.3	-5.0	-	-	-4.9	-4.3
Pb	<-6.4	<-6.7	<-7.3	-	-	<-6.4
Ni	<-6.3	<-6.7	<-6.7	-	-	<-6.3
Cd	<-6.8	<-8.0	-	-	-	<-6.8
Co	<-6.7	<-7.3	<-8.0	-	-	<-6.7
Sr	-5.9	-5.9	-	-	-	-6.3
Mo	<-6.4	<-6.7	-	-	-	<-6.4
Y	<-8.0	<-8.5	-	-	-	<-8.0
Source	A	B	F	E	A	

## Sources:-

A) This study (170 and 5); B) Kinniburgh and Miles, 1983 (10);

C) Reisenauer, 1966 (149-979); D) Eaton et al, 1960 (10);

E) Bennias et al, 1977 (7); F) Jarvis and Jones, 1981 (14).

Figures in parentheses are the number of soil samples in each study.

somewhat limited data from Bagley Wood is included to extend the range of pH over acid soils.

If we take the figures of the first two columns of Table 6.5.1 as representing the 'norm', then the concentrations of Na, K, Mg,  $\text{SO}_4$ , and Cl are higher in the solutions of the American soils, probably as a result of higher salinity. Concentrations of Si,  $\text{SO}_4$  and Cu are similar in all of the British soils, whereas concentrations of Al, Fe, Zn and Mn are higher in the soils of low pH; K, Ca, and alkalinity being lower.

It would appear that the results of this study are broadly in agreement with those from other studies. Differences between the concentrations of some solutions in this study and other data may be attributed to differences in salinity and pH. The concentrations of Na, S, Si, Cl,  $\text{NO}_3$ , and Cu seem to be independent of solution pH.

Table 6.5.2 compares the median soil solution concentrations from the main experiment with typical rain and fresh water concentrations from other sources. To some extent the data illustrate the different processes which influence the chemical composition of the soil solution. Concentrations of Cl, S and Na are similar in all of the waters, indicating that the soil neither releases these elements nor accumulates them. Magnesium, which is more strongly leached than calcium, is present at similar concentrations in the soil solution and fresh water. Both are lost from the soil as carbonate minerals dissolve. Potassium is not readily leached because it is incorporated into secondary minerals and is efficiently recycled in vegetation. Concentrations of DOC are much higher in the soil solution than in rain or river waters, which highlights the importance of the cycling of organic C in soils. It would appear from the limited data available that trace metals, such as iron and

Table 6.5.2

A comparison of median solute concentrations in the soil solution and in typical rain and fresh waters.

Solute	Rain Water	Soil Solution	Fresh-water
Na	-3.80	-3.33	-3.58
K	-4.51	-3.41	-5.25
Ca	-4.32	-3.42	-3.94
Mg	-6.73	-3.82	-3.78
S	-4.23	-3.42	-3.94
Si	-	-3.66	-3.60
P	-	-4.19	-6.19
Cl	-3.79	-2.93	-3.71
NO <sub>3</sub>	-3.95	-3.07	-5.45
DOC	-4.54*	-2.40	-4.12\$
B	-	-5.30	-5.87
Li	-	<-6.05	-6.54
Mn	-	-6.28	-6.84
Cu	-6.00	-6.60	-7.33
Fe	-4.11	-5.47	-
V	-	<-6.64	-9.05
Cd	-7.46	<-6.80	-9.05
Co	-6.60	-6.70	-8.47
Zn	-5.89	<-6.64	-6.64
Ni	-7.09	<-6.30	-8.07
Mo	-	<-6.39	-8.28
Al	-5.42	<-5.35	-4.95
Pb	-6.94	<-6.39	-7.84
Sr	-	-5.27	-6.10

Rain data are average concentrations over the period 1975-1981 at Harwell, Oxfordshire. Soil solution data are the median concentrations from the main experiment. Fresh water data, representing global median concentrations, from Bowen, 1979. Except for, \* Plynlimon, Wales (C Neal and C J Smith, private communication) and \$ River Dorn, Oxfordshire median of three samples taken January - March 1984.

copper are accumulating in soils, though this is only likely to occur in non-acid soils.

### 6.6 Pasture site ANOVAR

The ANOVAR of the data from the pasture sites is essentially an incomplete three factor analysis with duplication. In the analysis we have two subsamples from each of three fields from each of six soil series at each of seven times. The concentration of a solute in the  $l^{\text{th}}$  sample from the  $k^{\text{th}}$  field of the  $j^{\text{th}}$  soil series at the  $i^{\text{th}}$  time can be expressed by :-

$$C_{ijkl} = \mu + T_i + S_j + (S.F)_{jk} + (T.S)_i + (T.S.F)_{ijk} + \sum_{ijkl}$$

Where  $\mu$  is the grand mean.

1)  $T_i$  = time effect

2)  $S_j$  = soil effect

3)  $(S.F)_{jk}$  = field within soil interaction

4)  $(T.S)_i$  = time \* soil interaction

5)  $(T.S.F)_{ijk}$  = field-within-soil-within-time interaction

6)  $\sum_{ijkl}$  = error term

1, 2 and 3 are likely to be the main effects. Effects 4 and 5 (4 being the effect of time on different soils and 5 being the effect of time on different fields within the same series) are likely to be less pronounced. The error term (term 6) includes analytical error and the short range heterogeneity in the soil which is not removed by bulking.

The numbers which are actually compared in the statistical analysis are set out below.

1) Time: for each of the seven sampling times all of the

values are averaged. So the values for all six soil series (eighteen fields) are averaged to give a mean value for that time. These means are then compared.

2)Soil: for each of the six soil series all of the values are averaged over the three fields and seven times to give a mean value for each soil series. These means are then compared.

3)Field-within-soil:For each of the three fields (on each of the six soil series) all of the values are averaged over time to give a mean value for each field. These means are then compared with the other two for that soil and the six variances pooled.

4)Time-within-soil: For each of the six soil series at each of the seven sampling times the values of the three fields are averaged to give a mean for each soil at each time. These means are then compared.

5)Field-within-soil-within-time:Three field means for each soil at each time are compared and the variances pooled. This value is compared with the other two for that soil and the variances pooled.

To examine effects 1 to 3, only, the GENSTAT statements :-

```
'TREAT' TIMES + (SOILS/FIELDS) (1)
```

```
'BLOCK' SAMPLES
```

are used.

To examine the effects 1 to 5 the statements :-

```
'TREAT' TIMES * (SOILS/FIELDS) (2)
```

```
'BLOCK' SAMPLES
```

are used.

Three solutes chosen to represent major, minor and trace solutes were analysed using both analyses above and the results compared (a listing of the GENSTAT program is shown in Appendix 2.3). The table below shows the total and residual SS% values for each of the two analyses

Element	Na		Si		Ba	
	1	2	1	2	1	2
Prog.						
Total	113.18	115.99	110.96	112.38	104.47	105.97
SS %						
Res	36.69	5.92	23.78	2.06	38.76	3.83

The analysis which separates time-within-soil and time-field (within soil) interactions (program 2) has a far lower residual SS% term, this model was used.

The model outlined above has three levels. The main effects are time (T) and soil series (S). The secondary effects are the interactions between time and soil series (T.S) and the field-within-soil effect (S.F). There is also a tertiary interaction, the time-field (within soil) interaction (T.S.F).

If there were a relationship between the equivalent fields on each of the soil series (e.g. if all of the fields numbered '1' were unfertilized) then the ANOVAR would be complete. However there is not, so the time-field interaction and the field effect are not real and there are only two interactions.

The rest of the residual variance is made up of variability which is not accounted for in the model. It consists of a combination of analytical error, which is likely to be small, and soil heterogeneity which is not removed by bulking. This variability was separated into the error term, thus the between-subsample variance is removed from the ANOVAR. The ANOVAR may be summarised by

Factor	DF	
Sample Stratum	1	Error Term
Unit Stratum		
7 Times	6	Time Factor
6 Soils	5	Soil Factor
Time.Soil	30	Time-within-Soil Interaction
Soil.Field	12	Field-within-Soil Interaction
Time.Soil.Field	72	F-within-S-within-T "
Residual	125	
Total	250	
Grand Total	251	

In calculating the significance of the variance ratios in the analysis of variance it would be valid, statistically, to test the significance of the lowest stratum (the T.S.F interaction) against the residual variance. However, the results from the preliminary studies indicate that the residual (subsampling) variance is small when compared to the s.r.s.v. If the residual variance were so used, the question which it would ask would be:- compared with the variance not accounted for in the model, is the difference between separate fields on the same soil series significant? Clearly it would be for most solutes.

Ideally it would be possible to take further samples to measure the spatial variability in each field sampled. This would allow the

inclusion of an extra stratum in the ANOVAR which would ask the question:- compared to the variability found in a single field are separate fields on the same soil series different? To measure the within-field variability for each field would have entailed considerably more field and laboratory work. However, we have some estimates of the short-range variability from three sites (Table 5.6.1). With some reservations and given that they are of the same order of magnitude, we may use them as a measure of the 'baseline variance' against which to test the significance of the T.S.F. interaction. It was decided to use the larger of the two estimates for each solute as the denominator in the variance ratio for the lowest stratum of the ANOVAR. This test gives a qualitative measure of the significance of the T.S.F. interaction.

The GENSTAT program developed above (A2.3) was used to perform an ANOVAR of the log-transformed data from the pasture sites and the variance was partitioned into the strata outlined above. The estimate of within-sampling area variance (W.S.A.V.) or baseline variance was used as a starting point to test the significance of the T.S.F. interaction.

The estimate of the within sampling area variance (W.S.A.V.) was used to test the field-within-soil-within-time (T.S.F) interaction for significance. The T.S.F. variance was used as a test of the significance of the field-within soil and the soil-within-time interaction. If the T.S interaction was significant it was then used to test the time and soil strata.

If the variance of the T.S interaction was not significant it was pooled with that of the T.S.F interaction and this pooled variance was used to test the soil and time strata.

In effect, the tests of significance arising from the ANOVAR are

designed to answer the following questions: compared to the variations found in a single field are the differences between different fields on the same soil series at the same time significant? Compared to the differences between different fields on the same soil at any one time, are the differences between different fields on the same soil averaged over time significant and does time have a significantly different effect on different soils? Compared to the variability within one soil series at any one time: a) is the variability between different soils (when averaged over time) significant; and, b) is the variability between times (averaged over all soils) significant?

#### 6.7 Pasture./Arable ANOVAR

On each of the Fyfield, Denchworth and Icknield series two locations were chosen at which there were adjacent pasture and arable fields. The arable sites were sampled six times during the sampling period.

An appropriate statistical analysis similar to the one in the previous section was devised and a GENSTAT program written to perform an ANOVAR (A2.4). The analysis of variance is in effect a complete three factor analysis with duplication, thus there are three factors, three secondary interactions and one tertiary interaction. They are:- time (T), soil (S), and Landuse (L); soil-within-time (T.S), landuse-within-time (T.L) and landuse-within-soil (S.L); landuse-within-soil-within-time (T.S.L). The ANOVAR may be summarised by

Factor	DF	
Locns. Stratum	1	Error Term
Locns.Samples Stratum	2	"
Units Stratum		
6 Times	5	
3 Soils	2	
2 Land Uses	1	Land Use Factor
Time.Soil	10	
Time.Land Use	5	
Soil.Land Use	10	Land Use-within-Soil Interaction
T.Soil.Land Use	2	
Residual	105	L-within-S-within-T "
Total	140	
Grand Total	143	

The terms which are of interest are L, L.T and L.S.T. The other terms are largely redundant as they have been more fully examined in the preceding analysis. Because the analysis is complete, the interpretation of the variances calculated by the GENSTAT program is somewhat more complex (the full method is set out in Brownlee, 1960), yet essentially the same as the one for the pasture ANOVAR. The variance between locations is included in the error term.

At the lowest level the ANOVAR should ask the question:- is there greater variability between adjacent pasture and arable fields than would be found between two adjacent pasture or arable fields. Strictly, to effect this it would be necessary, at each location, to sample from at least two pasture and one arable fields. This would have been impractical. A measure of the variability between non-adjacent fields can be obtained from the data relating to the pasture sites (in effect the T.S.F. term). By limiting the ANOVAR of the pasture sites to three soil series and six times corresponding to the arable site samplings a more relevant measure of the T.S.F. term may be obtained. This T.S.F term relates to the variability between fields on the soil series which were included in the arable site sampling. This restricted T.S.F. term was used to test the L.S.T. term (qualitatively) in the ANOVAR. The L.S.T. factor was then used

as the denominator to test the secondary interactions for significance.

### 6.8 Pasture/Wet Pasture Comparisons

Originally three wet pasture sites were chosen (two Denchworth and one Fyfield). However because of the distance between the Fyfield wet site and its neighbour it was decided to limit the statistical analysis to a comparison of the sites on Denchworth series soils. The wet pasture sites were visited six times during the sampling period. Thus there are two samples from each of two pairs of locations (a wet and dry site) on one soil series sampled at each of six times.

The ANOVAR (GENSTAT program A2.5) is a two factor analysis with duplication. The ANOVAR may be summarised by

Factor	DF	
Locns. Stratum	1	Error Term
Locns.Sample Stratum	2	"
Units Stratum		
6 Times	5	
2 Topographies	1	Topography Factor
Time.Topog	5	Topog-within-Time Interact.
Residual	33	
Total	44	
Grand Total	47	

T.S.F. variance was estimated by restricting the pasture ANOVAR to the Denchworth series and six sampling times and was used to test (qualitatively) the significance of the lowest term (topography-within-time (T.Top)). The T.Top term was then used to test the time and topography factors for significance. Again the T term is redundant.

### 6.9 Significant Factors

The procedures outlined in the three sections above produced a series of variance ratios whose significance was determined by referring to

statistical tables. GENSTAT programs allow for missing data by estimating their value and then using them in the calculations. It is prudent, none the less, to regard conclusions drawn from an experiment with missing observations with rather more caution than if the data had been complete. Only very highly significant ( $P < 0.001$ ) factors and interactions are quoted. The factors which were found to be significant are shown in Tables 6.9.1 and 6.9.2 for the pasture and pasture/arable ANOVARS. Only alkalinity and Sr showed significant differences in the pasture/wet pasture comparison, in the Topography stratum.

The factors of time and soil series are significant for most solutes as is the S.F interaction, whereas the T.S. interaction is not significant. That is to say, the chemical composition of the soil solution in pasture fields varies with time and between soil series, and within each soil series fields are different from one another.

The solutes which do not exhibit significant temporal changes are P and alkalinity both of which are well buffered in the soil, the former by adsorbed phosphate and the latter by free carbonates and soil organic matter.

Only three solutes show no significant differences between soil series; nitrate, which shows high variability between fields on the same soil series, copper and zinc.

There are fewer significant differences when different landuses are compared (Table 6.9.2) only Na, Mg, S, P, Cl, Ba, K, alkalinity and pH show significant differences between pasture and arable sites. In general, solutes which are significantly different between landuses or between landuse within soil series have lower concentrations in the arable fields than in the pasture ones. Concentrations are between 40 and 90% higher in solutions from the pasture fields.

Table 6.9.1

Factors affecting solute concentrations in the Pasture sites

Solute	Factor				
	Time	Soil	T.S	S.F	T.S.F
Na	***	***		***	***
K	***	***		***	
Ca	***	***			
Mg	***	***			
S	***	***		***	***
Si	***	***		***	
P		***		***	
Cl	***	***			***
NO <sub>3</sub>	***			***	***
Alk		***		***	@
pH	***	***		***	@
DOC	***	***		***	
Ba	***	***		***	
Mn	***	***		***	
Cu	***			***	***
Fe	***	***		***	
Zn	***			***	
Sr	***	***		***	

\*\*\* = Significant at  $\underline{P}$ <0.001

@ no data to test this stratum

Table 6.9.2

Comparison between adjacent pasture and arable sites

Solute	Factor	
	Landuse	Landuse- within- Soil
Na	***	
K		***
Ca		
Mg	***	
S	***	
Si		
P	***	
Cl	***	
NO <sub>3</sub>		
Alk		***
pH		***
DOC		
B		
Ba	***	
Fe		
Mn		
Sr		

The Landuse-within-Time and the Landuse-within-Soil  
-within-Time factors were not significant for any solute.

\*\*\* = significant at P<0.001.

When different degrees of wetness are compared the only significant differences found were for alkalinity and Sr.

#### 6.10 Conclusions

By careful design and appropriate statistical analysis of a year-long sampling programme the significance of the variability in the chemical composition of the soil solutions of a number of field soils has been estimated. An overview of the results shows that they are in accordance with the findings of other published soil solution data. The concentrations of most solutes varies temporally, and generally there are significant differences between soil series and between different fields on the same soil series. The factors of landuse and drainage are significant for some solutes but statistical analysis of these comparisons was limited by the limited amount of data available.

In the two chapters which follow the solutes are discussed in turn to try to establish which soil-constituents, if any, control their concentrations in different soil types and a broader study is made of the factors causing temporal changes.

## Chapter 7

### The Role of Soil Class in Soil Solution Composition

Thermodynamics tells us that the existence of soils is precarious - like that of people. But experience tells us that soils and people are wonderfully resilient to disintegration.

Richmond Bartlett , 1981

#### 7.1 Introduction

The statistical analysis of the main field study shows that for many of the solutes studied there is a significant soil-type effect on the composition of the soil solution. These differences may derive from several factors, but it is likely that soil parent material and soil texture play a large part. Parent material contributes to the mineral phase of the soil and its component soil minerals may determine the concentrations of certain solutes in the soil solution. Soil texture influences the moisture-holding properties of soil and the way in which rain water percolates through the soil. In coarsely-textured soils water movement by piston displacement means that the soil solution is more fully replaced by percolating water than in more finely-textured soils where a larger portion of the flow is concentrated in macropores and flows past micropores.

The sections below discuss possible controlling factors for each solute.

#### 7.2 Calcium

The calcium content of soils is largely influenced by soil parent material and rainfall. Soils developed from calcareous parent materials often have calcium carbonate somewhere in the profile. With advanced weathering and high rainfall calcium carbonate and most other calcium minerals disappear. So, apart from its presence in alumino-silicates or in organic combination, calcium exists in

soils in one or both of two forms:-

- i)calcium carbonates,
- ii)exchangeable calcium.

In calcareous soils calcium carbonate minerals, the most stable of which is calcite (Lindsay, 1979), buffer calcium concentrations in the soil solution . In acid and neutral soils soluble calcium is buffered largely by exchangeable calcium.

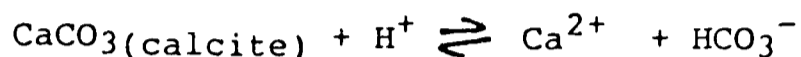
Of the soils studied in the main experiment (S6) those of the Evesham, Sherborne and Ickniel series would be expected to contain calcareous A horizons. By comparing the amount of calcium found in each soil digest (Appendix 5) with the corresponding cation exchange capacities (CEC), (Table 6.2.2), the amount of non-exchangeable calcium can be estimated. Estimated in this way, non-exchangeable calcium will comprise calcium incorporated in soil organic matter, calcium salts precipitated from the soil solution on drying, and calcium in the form of free carbonate. Of these three only the last is likely to be of any magnitude. From these estimates, soils with more than 1.5% (15 000 mg/kg) of digest soluble calcium would be expected to contain some free carbonate.

If so, all of the soils of the Ickniel series and some of the the Denchworth, Evesham and Sherborne soils contain free carbonate. With one or two exceptions, this division matched the assessment of free carbonate obtained by treating the air-dried soils with dilute HCl and noting the evolution of carbon dioxide (Table 6.2.2.).

The presence of calcium carbonate in soils has a dominating influence on many soil properties. Calcite dissolution and precipitation are rapid, and so may be expected to buffer pH and the concentrations of calcium and bicarbonate ions in the soil solutions of calcareous soils.

Of the 378 samples of soil solution from the main experiment 154 were from calcareous soils and 224 from non-calcareous soils (including missing values). The distribution of calcium concentrations, alkalinity and pH, are shown in Figure 7.2.1. Clearly the presence of calcite in the topsoil does influence the range of these solutes.

If the reaction



$$pK_a = 1.92$$

is controlling the calcium concentration in the soil solution of calcareous soils, then the equation

$$\log[\text{Alk}] + \log[\text{Ca}^{2+}] + \text{pH} = 1.92$$

(from Lindsay, 1979) may be used to calculate the extent of calcite saturation in the soil solution, according to the calcite saturation index (SI)

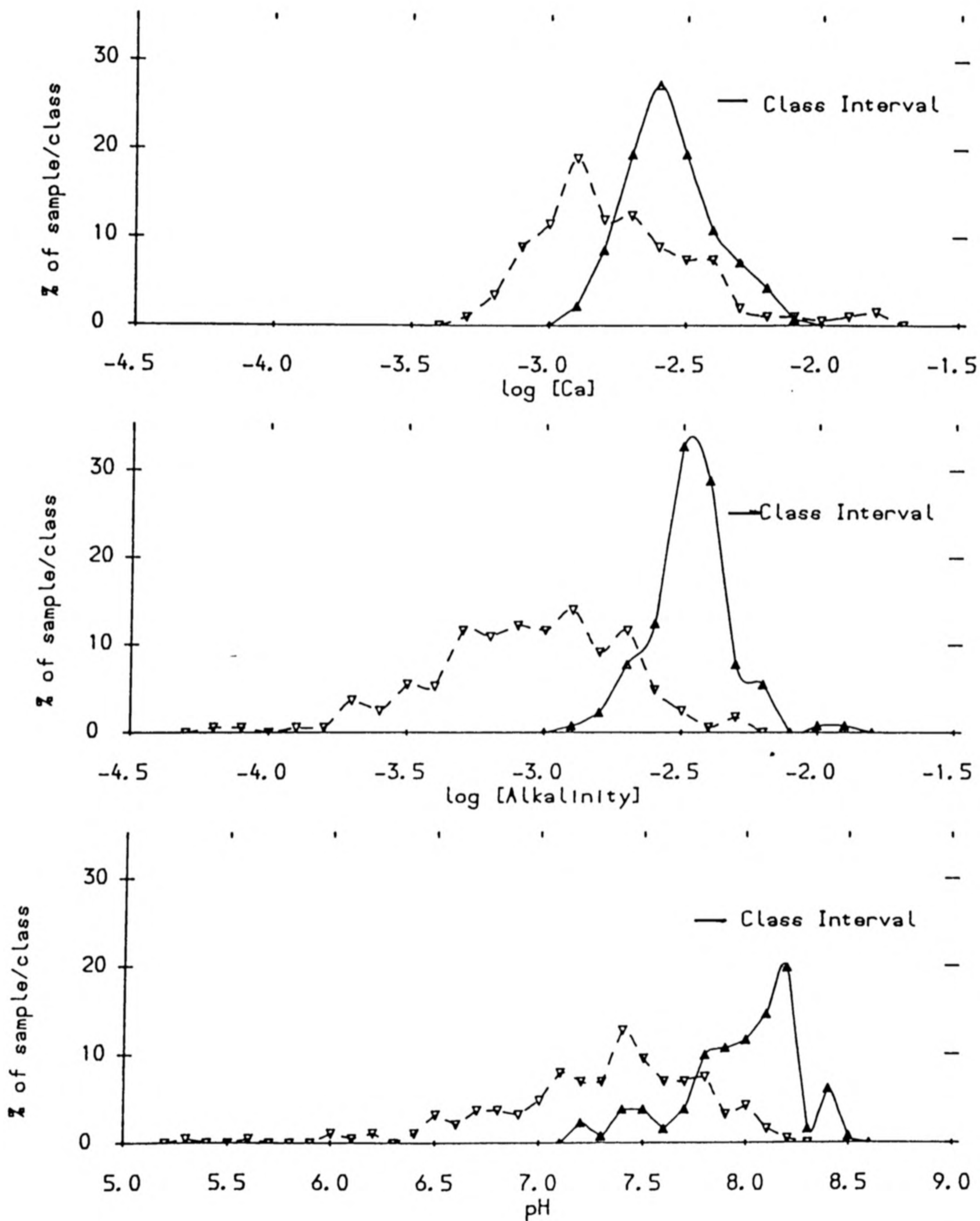
$$\text{SI} = \log\text{IAP} - \log K_{\text{sp}}$$

where IAP is the ion activity product,  $[\text{Alk}][\text{Ca}]/[\text{H}^+]$ , and  $K_{\text{sp}}$  is the solubility product of calcite. A negative value indicates under-saturation and vice versa.

The values of pH used in the calculations which follow have been corrected to soil  $\text{pCO}_2$  because the pH measurements were made on solutions in equilibrium with atmospheric concentrations of carbon dioxide. This means that the measured pH is elevated by approximately one pH unit over that of the soil solution in situ. The correction calculations are set out in full in Appendix 6.

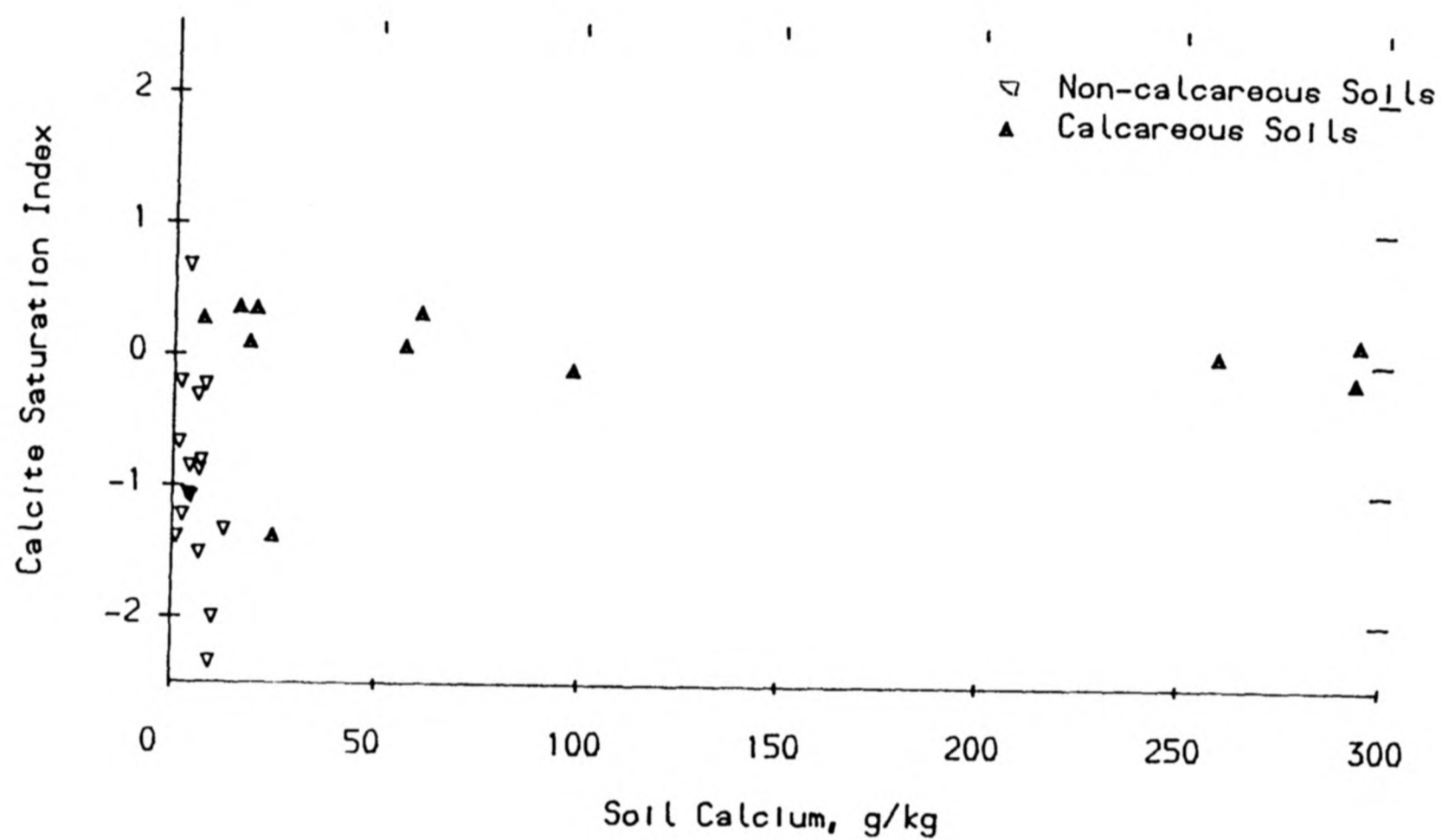
A plot of the geometric mean SI for each field in the main study against acid digestible calcium content is shown in Figure 7.2.2. With one or two exceptions, soils with free calcium carbonate maintain soil solution calcium concentrations near to calcite

Figure 7.2.1



Range of [Ca], alkalinity and pH found in soil solutions of calcareous and non-calcareous soils in the main experiment.

Figure 7.2.2



(Field) mean calcite saturation index against soil calcium  
concent for calcareous and non-calcareous soils.

saturation.

In non-calcareous soils exchangeable calcium is the main source of soluble calcium. Lindsay (1979) states a reference concentration of Ca in the soil solution of  $10^{-2.5}$  M for near neutral non-calcareous soils. The geometric mean (i.e. the mean of the log-transformed data) for this study is  $10^{-2.9}$  M, which is only 40% of Lindsay's 'reference' value.

Thus, the range of calcium concentrations in the soils studied is not large, because the soil exchange complex maintains concentrations near to those which are in equilibrium with free calcite. Variability between soil series, which was approximately two fold (2.2 times<sup>1</sup>), is only slightly greater than that between fields on the same soil series (1.7 fold) which reflects the impact of liming on the concentration of calcium in the soil solution. The lowest concentrations were found in soil of the Fyfield series probably because of their low cation exchange capacity and low pH.

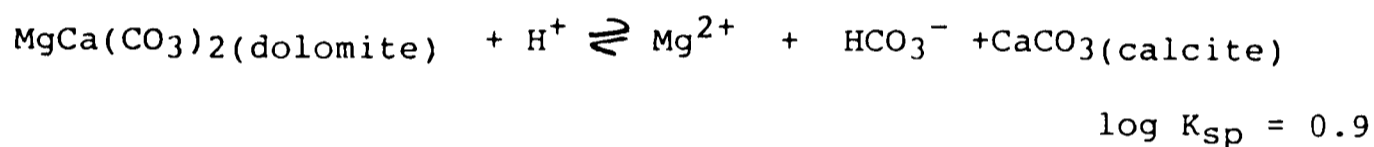
### 7.3 Magnesium

Magnesium is present in soils in similar forms to calcium. During the geochemical cycle magnesium, unlike calcium, is maintained in silicates and may also be present with calcium in dolomite. Magnesium is the more strongly leached. In calcareous soils the proportion of calcium to magnesium held on soil exchange sites is similar to that of the parent rock. In chalk soils the exchangeable magnesium is generally less than 1 meq/100 g compared to as much as 20% of the CEC in non-calcareous soils.

<sup>1</sup> The range between soils is the range of the means for each soil series averaged over time and fields. They are calculated from the log-transformed data. The range between fields is the average range of the mean for each field on each soil series averaged over time (again calculated from the log-transformed data).

In calcareous soils, Lindsay (1979) states that the controlling minerals for Mg may be dolomite in equilibrium with calcite, talc, or Mg-montmorillonite. The relative stabilities of these solids depend on the partial pressure of CO<sub>2</sub> in the soil air and the Si concentrations in the soil solution. The Si concentrations of the solutions studied were too low to allow talc as a stable solid and the kinetics of montmorillonite formation are so slow compared to other soil processes that it is unlikely to play any role in determining soil solution composition except over periods of geological time. This is reflected in the composition of the soil solutions studied, almost all of which were highly supersaturated with respect to Mg-montmorillonite.

The dolomite-calcite equilibrium:



$$\log[\text{Mg}^{2+}] + \log[\text{Alk}] + \text{pH} = 0.9$$

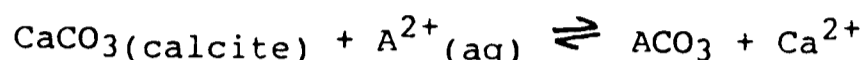
might control the Mg concentration in the solution of calcareous soils. The SI calculated from the above equation gave similar results to calcite. However, it is likely that the concentrations of Mg (and Sr and Ba) in the solutions of calcareous soils are controlled by their presence as impurities in calcite.

#### 7.4 Magnesium, Strontium, and Barium

The relationship between Ba or Sr and soil calcium content is similar to that of Ca and Mg, that is calcareous soils show fairly constant values of  $\log[A] + \log[\text{Alk}] + \text{pH}$  ( $A = \text{Mg, Ba or Sr}$ ). However their IAPs are about 100 times less than the K<sub>sp</sub>s for pure Mg, Ba and Sr carbonates would require, possibly because these elements are present mainly as impurities in calcite and so their activities in solution are reduced compared to that expected if they

were in equilibrium with their pure carbonate (Sposito, 1981, 1983).

The mole fractions of Ca, Mg, Sr and Ba in the Upper Chalk rocks are typically 0.99,  $8.33 \times 10^{-3}$ ,  $7.99 \times 10^{-4}$  and  $3.64 \times 10^{-5}$  respectively (W.M. Edmunds, private communication). If the concentration of a divalent trace metal cation (A) in solution is governed by the exchange reaction



then the equilibrium for the exchange constant, K, is;

$$K = f_{\text{A}}N_{\text{A}}(\text{Ca}^{2+})/f_{\text{Ca}}N_{\text{Ca}}(\text{A}^{2+})$$

$$= K_{\text{CaCO}_3}/K_{\text{ACO}_3} \quad (\text{Sposito, 1981})$$

The ratio <sup>nal</sup> activity coefficient of a trace divalent metal, A, may be expressed as

$$f_{\text{A}}/f_{\text{Ca}} = \frac{K_{\text{CaCO}_3} [N_{\text{Ca}}(\text{A}^{2+})/N_{\text{A}}(\text{Ca}^{2+})]}{K_{\text{ACO}_3}}$$

Where N is its mole fraction in the solid, f is its ratio activity coefficient, K is its solubility product and ( ) denotes activities in solution. Since  $N_{\text{Ca}} = 0.99$  in the Upper Chalk, it is reasonable to assume that  $f_{\text{Ca}} \sim 1.0$  and therefore

$$f_{\text{A}} = K[(\text{A}^{2+})/N_{\text{A}}(\text{Ca}^{2+})]$$

$$\approx K([\text{A}]/N_{\text{A}}[\text{Ca}])$$

where [ ] denotes a concentration in M. This is a reasonable approximation in view of the low ionic strength of the solutions and the high proportion of the metals present as their free divalent cations (>93%).

The soils of the Icknield series contain fragments of Upper Chalk and so their solutions are in contact with calcite containing known fractions of impurities. Table 7.3.1 below shows the time- and field-averages of log-transformed soil solution concentrations in the Icknield pasture sites (S6.2.2). Together with their mole fractions, N, and the relevant solubility products these were used

to calculate  $f_A$ .

Table 7.3.1

	N	Mean concentration in soil solution	log $K_{sp}$ of carbonate	K	$f_A$
Ca	0.99	$2.69 \times 10^{-3}$	-8.53		
Mg	$8.33 \times 10^{-3}$	$1.08 \times 10^{-4}$	-7.93	0.25	1.21
Sr	$7.99 \times 10^{-4}$	$1.94 \times 10^{-6}$	-9.0	2.95	2.66
Ba	$3.64 \times 10^{-5}$	$1.42 \times 10^{-7}$	-8.3	0.59	0.89

The reduction in the activity of  $A^{2+}(aq)$  is given by

$$(A^{2+})/(A^{2+})_O = f_A N_A$$

where  $(A^{2+})_O$  is the activity of  $A^{2+}$  in equilibrium with pure  $ACO_3$ : this approximates to the reduction in [A] from the expected value. The predicted and measured depressions in the concentrations of Mg, Sr, and Ba are shown below

Solute	Depression (log M)	
	Measured	Predicted
Mg	2.4	2.0
Sr	2.5	2.7
Ba	4.4	4.5

The ranges of Mg, Sr, and Ba in the soil solution are similar to those of calcium, reflecting their similar chemistry. The lowest magnesium concentrations are found in soils of Fyfield and Icknield series.

The concentrations of barium in the soil solutions from Bagley Wood showed a different trend from that of the other group 2 cations (Table 5.4.1). Also the concentrations of barium in the solutions from the Nuneham Courtenay site were significantly higher than those at Wytham (Table 5.4.1). This would suggest that the concentration of barium in the solutions of non-calcareous soils is being

controlled by processes other than those which control the concentrations of the other group 2 cations.

The most common barium mineral in soils is barytes,  $\text{BaSO}_4$ , which is often found as a cement in sandstones and in glaebules in clays. It is likely that this mineral is present in some of the soils, and is controlling the concentration of Ba in the soil solutions of these soils.

### 7.5 Sodium

The main input of sodium to the soil comes from rain which typically contains  $160 \mu\text{M}$  of Na (S6.5.2). This may be compared with a typical soil solution concentration in unfertilised fields of  $230\text{--}300 \mu\text{M}$ . In the short term, variations in the concentration of sodium in the soil solution will be buffered by cation exchange. It would be expected that the less well-drained soils, where the flux of sodium from the soil is less, would have higher Na concentrations in the soil solution and this is indeed the case. The geometric mean sodium concentration in the wet Denchworth sites was twice that at the well-drained sites.

The range of concentrations for sodium is somewhat greater than for chloride. This is probably because, although the input levels are similar, the concentration of sodium is influenced not only by the ratio of evapotranspiration to rainfall but also by cation exchange. Presumably the effects of water-holding capacity and CEC are compounded in heavy-textured soils where the highest Na concentrations are found.

### 7.6 Potassium

Primary alumino-silicate minerals contain large amounts of potassium, which is released during primary weathering. It may not

be strongly leached because of 'refixing' in the inter-lamellar spaces of secondary 2/1 clay minerals (e.g. vermiculite). In temperate soils a steady state is established between the release from primary minerals and refixation by secondary minerals. K is also strongly held on exchange sites.

Most potassium salts are too soluble to exist in soils, and the concentration of K in rain is too low (ca 30  $\mu\text{M}$ ) to maintain potassium at the concentrations found in soil solutions (300-1 000  $\mu\text{M}$ ). So in the long-term K must be supplied by the weathering of primary minerals, with short-term buffering by cation exchange.

The range of concentrations between soil series is quite large (4 fold), as is the between-field range (2.6 times) which may be attributed to different management practices. Potassium is one of the three most commonly applied fertilizer nutrients (see Appendix 7). Concentrations are highest in Fyfield series soils.

#### 7.7 pH

The range of pH in the soils studied was not large, the time-averaged range was only one pH unit, which represents a ten-fold range in concentration. The range of pH in non-calcareous soils was four times greater than that within the Icknield series. This is another indication of the dominating influence that free carbonates have on the chemical composition of the soil solution. The lowest pHs were found in Fyfield soils.

#### 7.8 Alkalinity

The factor which most affects alkalinity is the absence or presence of free calcite which releases bicarbonate ions on dissolution (S7.2). In neutral and calcareous soils the main contribution to the alkalinity of the soil solution is the bicarbonate anion.

Alkalinity is higher by a factor of 6 in calcareous soils than in non-calcareous soils. As with pH, the range found within one soil series is much greater in those series which lack free calcite. The range within the Icknield series is only one fifth that in the other soils. Fyfield soils have the lowest alkalinity.

Alkalinity was one of the few determinands which differed significantly ( $P < 0.001$ ) between the wet and dry Denchworth sites under grass. At each sampling time, the alkalinity in solution was lower at the dry sites by, on average, 50% than that at the wet sites.

#### 7.9 Chloride

The major source of chloride in soil solutions is rain (mean concentration 160  $\mu\text{M}$ ). It may also be applied in the form of potassium chloride in fertilizers: an application of 60 units (30 kg/ha) KCl adds as much chloride to the soil as a year's rainfall. The range of concentrations between soil series is only slightly higher than that between fields (factors of 1.7 and 1.5 fold respectively) indicating the large influence of fertilizer additions.

#### 7.10 Phosphorus

Phosphorus occurs in soil in three forms; adsorbed on the surface of soil particles, as sparingly soluble minerals, and incorporated in soil organic matter. The first two of these are likely to buffer the soil solution concentration in the short and long term respectively. Organic P is released into the soil as organic matter is mineralised. P is very dilute in the soil solution, which is the immediate source of phosphate to plants and contains only a small fraction of the phosphate needed by plants in a single growing

season. Burd and Martin (1923) observed that there was little change in the concentration of phosphate in the soil solution throughout the growing season and attributed this to rapid renewal of P in the soil solution from the solid phase.

The range of P concentrations (between soil series) in the soil solutions studied was slightly less than three fold, compared to a between-field range of two fold (2.3 times). This is consistent with the high short-range spatial variability found in the preliminary experiments (S5.4). Concentrations are lowest in Icknield soils and highest in Fyfield and Sherborne series indicating a degree of pH-dependence.

Earlier soil solution data (Larsen, 1967; Wild, 1954) showed no agreement between the concentrations of P in the soil solution and those predicted by solubility products. This was taken to indicate that the concentration of P in the soil solution is governed by reactions involving adsorbed phosphate species: kinetic factors may limit the dissolution and precipitation of phosphate minerals. Calculation showed that the soil solutions in this study were highly supersaturated with respect to hydroxyapatite, the most thermodynamically stable phosphate mineral in soils, and undersaturated with respect to di-calcium phosphate (DCP). However, the DCP saturation index (SI) was near to zero for some of the soil solutions, particularly for the September samples which may indicate that DCP controls the maximum concentration ( $\sim 10^{-3.8}$  M) of phosphate in the soil solution. SIs for octa-calcium phosphate (OCP) ranged from +3 to -6 (-3 for calcareous soils) suggesting, again, that kinetic factors limit precipitation/dissolution reactions.

Rapid replenishment of dissolved phosphate is provided by desorption

of adsorbed phosphate. DCP may be controlling the background P levels about which soil solution P concentrations oscillate.

### 7.11 Silicon

Soils contain silicon either in combined states (silicates and aluminosilicates) or in the free state as amorphous or crystalline oxides. Weathering releases soluble silicon in the form of monosilicic acid which may precipitate as amorphous forms at varying rates. A significant part of the silicon content of soils is cycled by vegetation

Dissolved silicon is present in the soil solution almost entirely as protonated monosilicic acid: silicon concentrations usually lie between that expected for equilibrium with amorphous silica ( $10^{-2.7}$  M) and that of quartz ( $10^{-3.7}$  M).

Elgawhary and Lindsay (1972) postulated that silicon concentrations in the soil solution were controlled by a range of silicate matrices ranging from newly precipitated amorphous silica to quartz. However, as Yariv (1973) pointed out, even a small amount of amorphous silica should maintain silicon concentrations in solution at  $10^{-2.7}$  M (2000  $\mu$ M). It seems likely that the activity of amorphous silica may be reduced by polyvalent metal ions (Al and Fe) and organic material on its surface. If as little as 5% of the surface is covered by Al then the concentration of Si in solution is reduced to  $10^{-3}$  M (Iler, 1973).

There is also evidence to suggest that silicon is adsorbed onto the surface of iron and aluminium sesquioxides. Jones and Handreck (1965) found that the addition of ferric and aluminium hydroxides to soils maintained at constant pH and pF reduced the concentration of Si in soil solutions. Aluminium oxides had the more marked effect.

There is also evidence that calcite may absorb silicon from solution (Beckwith and Reeve, 1965). The sorption of Al, Fe or organic matter onto the surface of amorphous silica will decrease silica dissolution whereas the sorption of monosilicic acid onto sesquioxides may increase the dissolution of amorphous silica into solution.

The position is made more complicated by the cycling of silica in vegetation and the tendency of amorphous silica to disperse on dilution (Elgawhary and Lindsay, 1972). This may lead to artificially high levels of 'dissolved' silicon in samples of soil solution taken after rain.

The range of Si concentrations found in this study ( $10^{-4.6}$  to  $10^{-2.9}$  M) is of the same order as those found by Guillet and Souchier, (1982) of  $10^{-5.1}$  to  $10^{-3.5}$ , and Kinniburgh and Miles (1983) of  $10^{-4.6}$  to  $10^{-3.1}$  M.

The range of concentrations between soils is three fold (2.6), that between fields two fold (2.1). The highest concentrations are found in Denchworth soils and the lowest in Icknield series. The high montmorillonite content of Denchworth soils would explain the high Si concentration in these solutions. The minimum Si concentrations were found at pH(corr) 7 but fairly high concentrations were found at this pH also. The low concentrations in Icknield soils may be associated with low levels of sesquioxides, or the presence of large amounts of calcite. The concentrations are less than they would be if the solutions were in equilibrium with quartz, however the dissolution of quartz in soils is hindered by adsorbed species on the surface of the quartz grains. High values of Abs<sub>350</sub> are associated with high silicon concentration in the soil solution. This may indicate the stabilization of the high concentrations of Si

in solution by humic substances. Acquaye and Tinsley (1965) found that dilute solutions of humus extracted from the Ao horizon of a podzol supported Si concentrations of  $10^{-3.4}$  M (400  $\mu$ M). This does not explain why, in this study, equally high Si concentrations are found in solutions with a very low Abs<sub>350</sub>. It may be that in solutions with a high Abs<sub>350</sub>, amorphous silica surfaces are coated with humic substances from solution which prevent the adsorption of newly dissolved Si released into solution by weathering.

Many different processes appear to be affecting the concentration of Si in the soil solution.

#### 7.12 Sulphur

Sulphur occurs as sulphide in many igneous rocks and is released as sulphate on weathering. Sulphate is also present as an impurity in some limestones and chalks. The principal reservoir of soil sulphur is soil organic matter. Inputs from rain vary greatly depending on distance from the sea, and from industrial sources of SO<sub>2</sub>. The mean concentration in rain (Harwell) is 60  $\mu$ M. Together with dry deposition this is the main source of sulphur to unfertilized soils.

In non-flooded soils sulphur in the soil solution is present mainly as sulphate with some sulphur incorporated in dissolved organic matter. The main buffering agent is sulphate adsorbed on the surface of soil colloids, especially on iron and aluminium hydroxides (Harward and Reisenauer, 1966). There are no insoluble sulphates present in the soils of humid areas.

A two fold range of sulphur concentrations between soil series was found, which was only slightly more than that found between fields (within series). Sulphur concentrations in the solutions from arable fields were significantly ( $P < 0.001$ ) lower than those found

in neighbouring pasture fields. This reflects the lower reservoir of organic matter in the arable fields (T6.2.2) and a higher uptake of sulphate by cereal crops.

Sulphur concentrations in the solutions of acid woodland soils (T5.3.2) were similar to those found in unfertilized pasture sites (around  $10^{-4.3}$  M), this indicates that the concentration of S in the soil solution is independent of soil pH, at least in the soils studied.

### 7.13 Dissolved Organic Carbon (DOC)

The time-averaged dissolved organic carbon (DOC) concentrations in the soil solutions for each field are significantly ( $\underline{p} < 0.01$ ) correlated with the organic matter content of the soils studied in the main field sampling experiment (Table 6.2.2). The range found between different soil series was not great (1.6 times) and was of a similar magnitude to that found between fields (within soil series). This may reflect the influence of different agricultural practices (e.g. application of dung) on the organic matter status of the individual fields.

The mean Abs<sub>350</sub> for each field, although significantly correlated ( $\underline{p} < 0.001$ ) with its DOC, is not correlated with the organic matter content of the soil.

The relationship between DOC and Abs<sub>350</sub> is not a simple one because simple organic molecules such as sugars and amino-acids, contribute to the DOC but not to the Abs<sub>350</sub> which gives a semi-qualitative measure of the humic substances present in solution.

A number of workers have sought a relationship between UV-visible absorbance and DOC in natural and polluted waters (e.g. Dobbs et al, 1972). It is generally accepted that there is no unique

relation between DOC and absorbance at any given wavelength. The poor association found between DOC and absorption measurements for waters of similar composition has led to some doubt being cast on the validity of these assumptions even for such waters.

Kinniburgh and Miles (1983) found only a poor correlation between Abs<sub>350</sub> and DOC for the soil solutions which they studied, as did Truitt and Weber (1981) for lake waters. Seasonal variations in the relationship between the Abs<sub>275</sub> and DOC in water reservoirs were noted by van Steenderen and van Rossum (1985) who found closer correlations if readings were separated into four seasonal classes. If the soil solution data from the main study is divided into seven consecutive periods the correlation coefficients between DOC and Abs<sub>350</sub> are 0.560, 0.581, 0.741, 0.244, 0.508, 0.704 and 0.776 respectively, compared with 0.556 for the whole data set. The correlation is very significant ( $\underline{P} < 0.001$ ) for the October, March and June 1984 samplings.

Since the relationship between absorbance and DOC depends on the fraction of the DOC which contains chromophores, we may define a relationship between DOC and Abs<sub>350</sub> by

$$[\text{DOC}] = c + m(\text{Abs}_{350})$$

where  $c$  = concentration of DOC which does not absorb and  $m$  is the average number of carbon atoms per chromophore in the organic molecules in the soil solution. The non-absorbing portion of the DOC will be made up of small molecules such as sugars, amino-acids (both free and combined) and fatty acids. The concentrations of these compounds will vary according to current biological activity. The value of  $m$  will change as absorbing substances in the soil solution such as fulvic acids are built up and degraded.

If the composition of chromophores remains constant and the

proportion of non-absorbing molecules varies with time, then a linear regression of DOC against Abs<sub>350</sub> would always have the same gradient but the value of  $c$  would vary. Linear regressions at different times give values of  $m$  from 4000 to 20 000 and values of  $c$  from 1 000 to 4 000. This indicates that the nature of the chromophores is changing as well as their relative fraction of the total DOC.

#### 7.14 Iron and Aluminium

In studies of the dissolved constituents of natural waters it is often difficult to distinguish between forms which are truly dissolved and material which is present as a fine colloidal dispersion (see S4.5). The majority of 'dissolved' iron in oxygenated fresh waters is in the form of negatively charged colloids stabilized by organic matter (Florence and Batley, 1980). A casual inspection of the data from the main field sampling experiment shows that some of the solutions, at least, (e.g. samples 611021 and 611111, Appendix 3) must contain particulate iron and aluminium fine enough to pass through a 0.45  $\mu\text{m}$  filter. These two samples were taken after heavy rain and probably contain dispersed sesquioxides. Many of the samples may have contained some particulate material. This renders the interpretation of the data and the identification of possible controlling phases difficult.

#### Iron

Iron is present in the reduced state in primary silicate minerals in soils and is released as  $\text{Fe}^{2+}$  on weathering. Ferrous iron released in this way may be precipitated and oxidised or oxidised and precipitated. Oxidation followed by precipitation, which occurs in most temperate soils, leads to the formation of goethite ( $\alpha\text{-FeOOH}$ ) and haematite ( $\text{Fe}_2\text{O}_3$ ). Only a small fraction of the iron released

from primary minerals is incorporated into secondary minerals and organic matter. The majority is precipitated as poorly crystalline solids.

In temperate regions iron is cycled biologically and microbial activity is an essential factor in the mobilization of iron from primary minerals (Aristovskaya, 1974). Soil microorganisms excrete mineral and organic acids, enzymes and complexing agents into the soil and bring iron into solution. The mobilized forms are mobile over a wide pH range. Rapid mineralisation of soluble iron complexes of low molecular weight leads to the precipitation of loose deposits of iron hydroxides which may be then converted to goethite by non-biological processes.

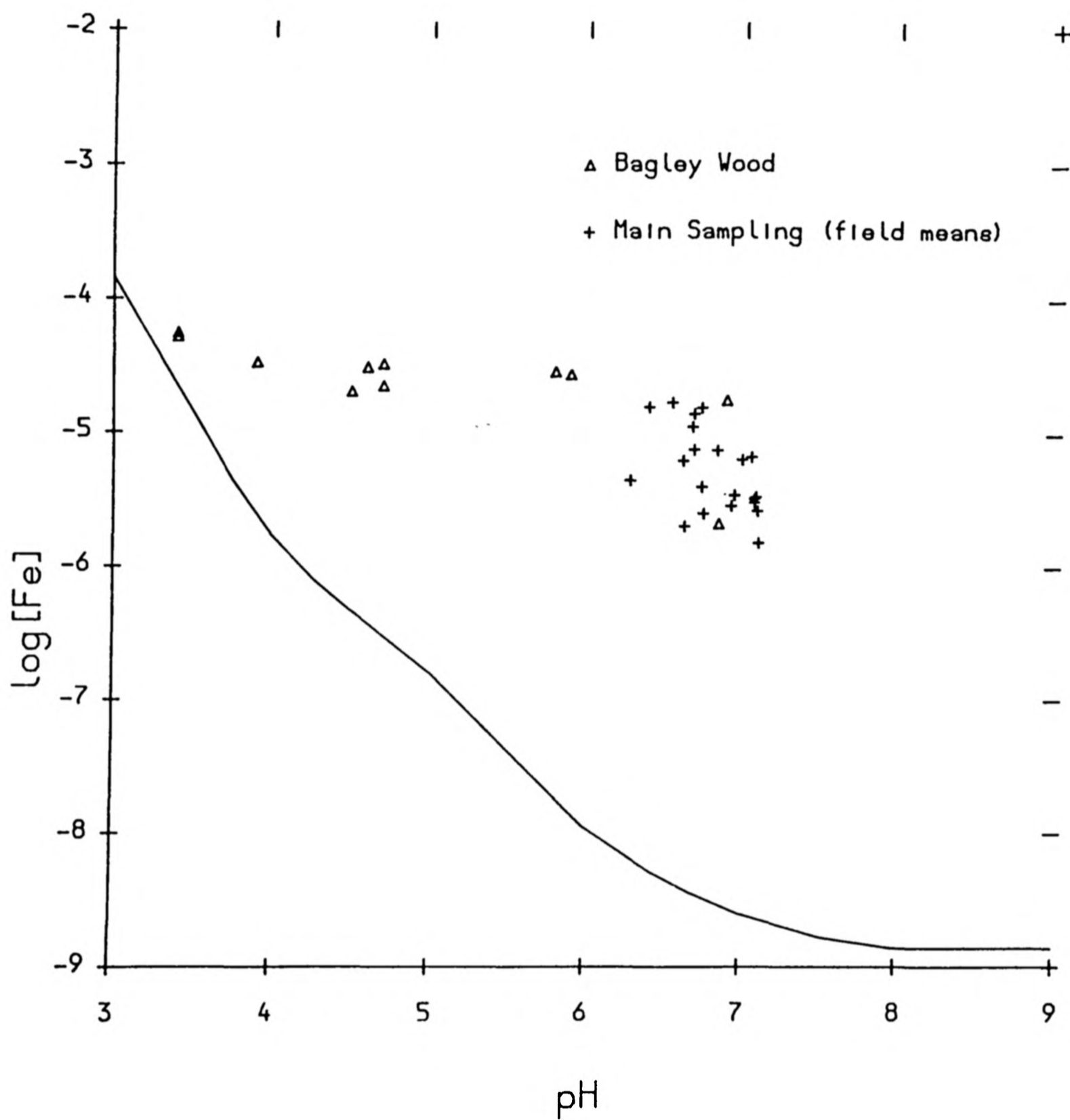
The transformation of newly precipitated hydroxides to more stable states is slow (years) compared to the rate of turnover of iron in the soil and so active iron hydroxides are likely to be present in most soils.

Bohn (1967) reports that the values of  $(\text{Fe})(\text{OH})_3$  ion products for amorphous Fe hydroxides lie between 1 and  $6 \times 10^{-39}$  compared to  $5 \times 10^{-42}$  for finely-crystalline goethite. This suggests that the concentrations of Fe in solution might be controlled by amorphous iron hydroxides.

A graph of the total dissolved Fe in a solution that is in equilibrium with amorphous  $\text{Fe}(\text{OH})_3$  ( $\log K_{\text{sp}} 6 \times 10^{-39}$ ) against pH is shown in Figure 7.14.1. The soil-solution data from Bagley Wood are shown together with field means (log transformed data) from the main experiment.

Except in the most acid soils the concentration of Fe in the solutions is greater than would be expected from equilibration with

Figure 7.14.1



Graph of  $\log [Fe]$  against pH for i) a solution in equilibrium with amorphous  $Fe(OH)_3$  (line), ii) soil solutions from Bagleywood and iii) field means from the main experiment.

amorphous iron hydroxides. This is in agreement with Benians et al (1977) who reported concentrations greatly in excess of ferric hydroxide solubility in a number of slightly acidic basaltic soils. It suggests that other soluble (probably complexed) iron species are contributing to the total concentration of iron in the soil solution. In acid woodland soils a correlation was found between visible absorbance (350 nm) and Fe concentration (see below). In the main experiment  $\log[\text{Fe}]$  was significantly correlated ( $P < 0.001$ ) with absorbance and  $\log[\text{Si}]$  and negatively correlated with pH. In the main experiment the solutions show a large range in  $[\text{Fe}]$  over a relatively small pH range. These concentrations are greater by a factor of up to 1000 than those expected if the solutions were in equilibrium with amorphous iron hydroxides; this may be due to one or a combination of factors. For example, inorganic complexes and free iron will be present in only very low concentrations ( $\ll 10^{-6}$  M) with the majority of dissolved iron present in complexes with microbial exudates and organic acids.

Fine colloidal iron, stabilized by adsorbed organic acids or silicic acid, (Taylor et al, 1983) will form a variable fraction of the 'dissolved' iron.

The negative correlation of iron concentration with pH, which is exemplified in the soil solutions of the Icknield series is due, at least in part, to the increased adsorption of iron by sesquioxides at high pH (Jenne, 1968).

Statistical analysis of the iron concentrations of the soil solutions of the pasture sites showed that the between-soils range is 9 times when the very high Fyfield concentrations are included. The between-field (within soil series) range is 2 times. The highest concentrations are found in Fyfield soils (see below) and

the lowest concentrations in the Icknield soils. This may be because of stronger adsorption of Fe by sesquioxides at the high pH of these soil solutions.

### Aluminium

Aluminium occurs in soils in a number of forms; in aluminosilicate clay minerals, Al of short-range order and Fe silicates and sesquioxides. In soils of pH <5.5 Al begins to be present as an exchangeable cation. In acid soils, aluminium from the weathering of clays replaces part of the Ca, Mg, K, and Na on exchange sites and at pH <4 Al ions replace  $\text{Ca}^{2+}$  on carboxylic sites on soil organic material.

It is most likely that the controlling mineral phase is amorphous aluminium hydroxide, except in soils of pH <4 and where sulphate is the dominant anion of the soil solution, where aluminium sulphates may control the concentrations of Al in solution (Wilson and Bergkvist, 1983). The concentrations of sulphate in the soil solutions studied were too low to suggest that aluminium sulphates may be present as a stable phase.

In the short term, control of Al concentration in the soil solution is likely to be by cation exchange in acid soils and by sorption/desorption reactions of adsorbed Al species together with dissolution of precipitated aluminium hydroxides in neutral and alkaline soils. The identification of possible controlling phases is made more difficult by the presence of organically complexed aluminium species in solutions as well as fine colloidal Al from the dispersion of colloidal sesquioxides and silicates. There is also some evidence for the formation of poly-nuclear hydroxy-Al ions in solutions containing as little as 0.05 M Al (Aveston, 1965) and in soil suspensions (10 mM  $\text{CaCl}_2$  1:5 soil:solution ratio; Bache and

Sharp, 1976). However the solutions studied were too dilute and of too high a pH to allow the formation of even  $\text{Al}_2(\text{OH})_4^{2+}$ .

Pierre et al (1932) reported a wide range of Al concentrations in the soil solution of a range of soils of the same pH. This may be due to the presence of varying amounts of organically complexed and colloidal Al in their soil solutions.

The master variable controlling the dissolution of Al, and hence its concentration in solution, is pH. The influence of pH on the total concentration of Al in a solution in equilibrium with gibbsite is given in Figure 7.14.2 (from data in Lindsay, 1979). From this it would be expected that all of the soil solutions in the main study would contain Al at concentrations lower than could be detected by ICP-OES ( $4.5 \mu\text{M}$ ,  $10^{-5.3} \text{ M}$ ). However only 56% of the solutions had concentrations less than this value. This indicates that organically complexed forms of Al or, more likely, colloidal Al is present in many of the solutions.

The soil solutions from the soils of Bagley Wood (Table 5.3.2) were sufficiently acid to contain measurable concentrations of Al. A plot of  $\log[\text{Al}]$  vs pH is shown in Figure 7.14.2. A linear regression through the points has the form

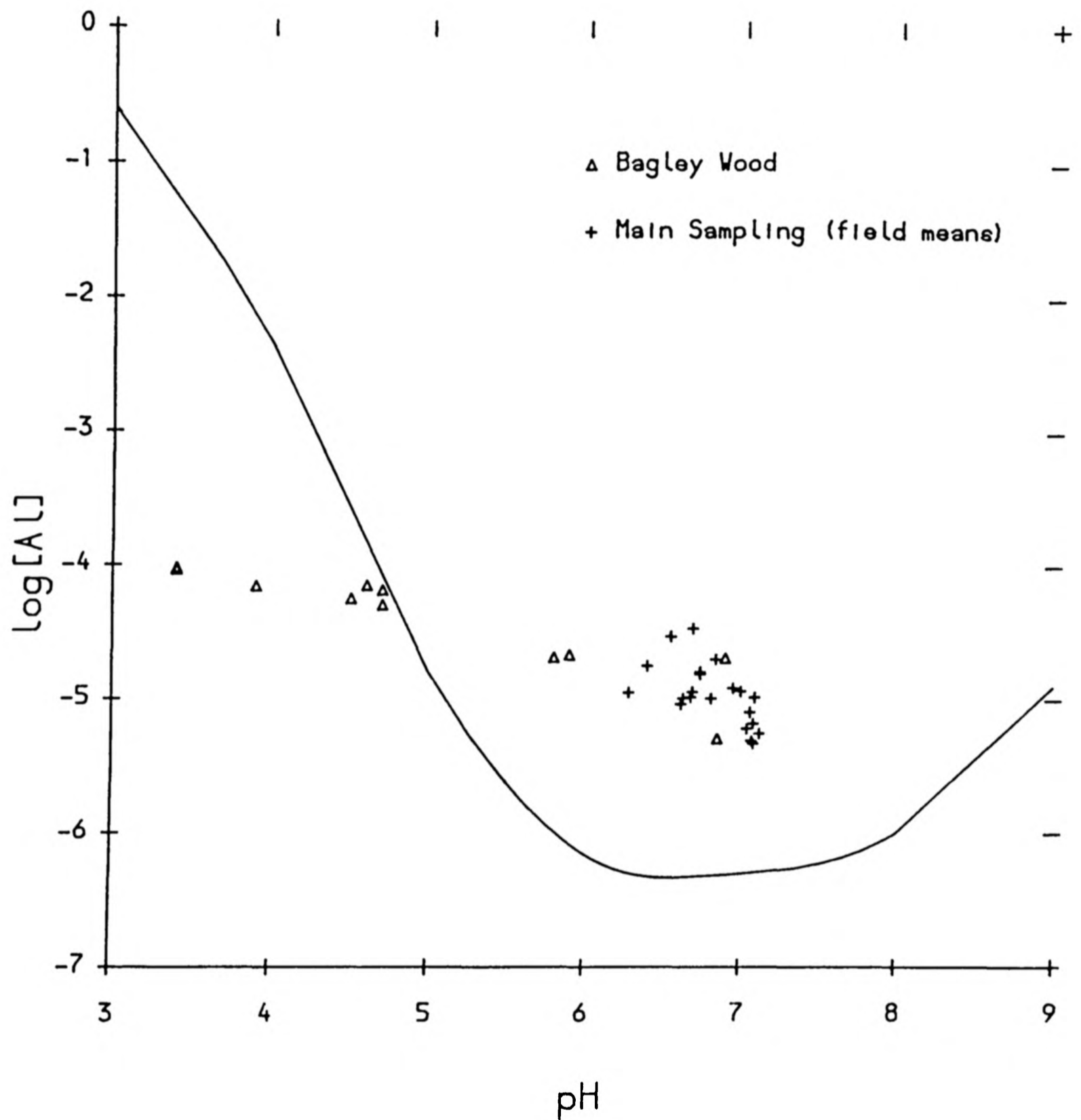
$$\log[\text{Al}] = -2.89 - 0.305\text{pH}$$

The curve superimposed on this graph is that of the total Al concentration of a solution in equilibrium with Gibbsite which does not correspond to the points very well. Bache (1985) states that at pH 4.7 amorphous  $\text{Al}(\text{OH})_3$  appears to control  $[\text{Al}]$  and gives the equation

$$\text{pH} - (1/3)\text{pAl} = 3.2$$

Solutions from Bagley Wood with pH in the range 4.5 to 4.7 give an average value of  $\text{pH} - (1/3)\text{pAl}$  of 3.21. This indicates that over

Figure 7.14.2



Graph of  $\log [Al]$  against pH for i) a solution in equilibrium with  $Al(OH)_3$  (line), ii) soil solutions from Bagley Wood and iii) field means from the main experiment.

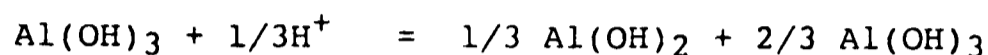
this small pH range the dissolution/precipitation of amorphous  $\text{Al(OH)}_3$  may be controlling the Al concentration.

A regression through all of the Bagley Wood data gives the line:

$$\log[\text{Al}] = -2.89 - 0.305\text{pH}$$

$$r^2 = 0.93$$

The dissolution of amorphous aluminium hydroxide to give both  $\text{Al(OH)}_3$  and  $\text{Al(OH)}_2^+$ , that is



$$\log K = -3.43$$

would give a line of the form

$$\log[\text{Al}] = -3.43 - 0.333\text{pH}$$

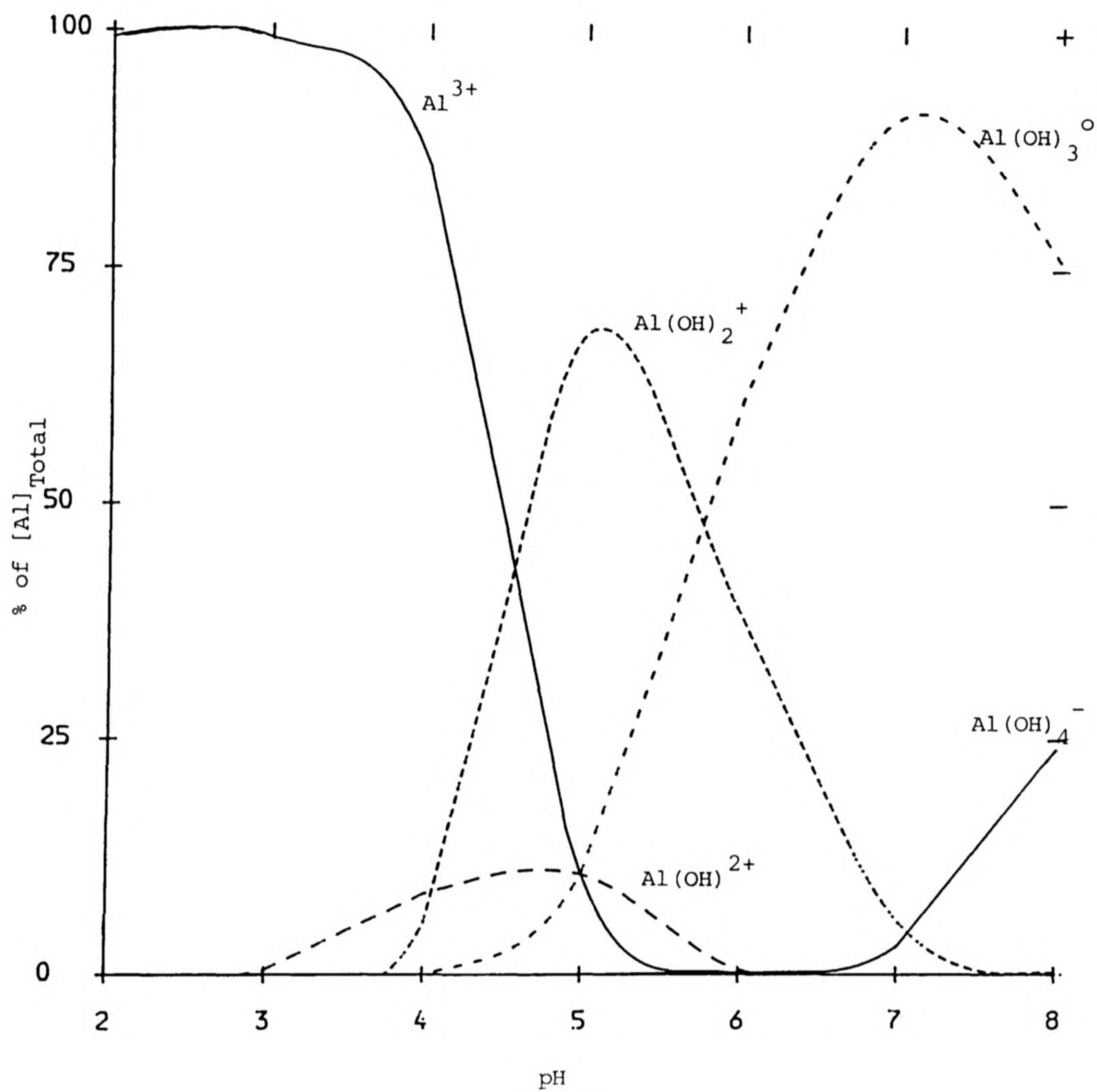
However, the proportions of these two hydroxy species would not remain constant over the range of pHs of the solutions (see Figure 7.14.3).

#### Correlations Between DOC, Abs<sub>350</sub> Al and Fe

Organic complexation may account for a large fraction of the Al and Fe present in some soil solutions. The relationship between dissolved organic carbon, absorbance at 350 nm, and the concentrations of metal species in solution is not a simple one because metal-complexing organic matter forms a variable fraction of the total dissolved organic matter and of that fraction of the DOC which absorbs light at any given wavelength. From their study of copper-complexing capacities of DOC in river waters Longford et al (1979) found that the dominant organic fraction responsible for  $\text{Cu}^{2+}$  binding was the hydrophobic (fulvic) acid fraction which was the only fraction of the DOC to have a strong absorbance at 254nm. Truitt and Weber (1981), on the other hand, found that colour was not a good indicator of metal-binding capacity.

The interaction of the many processes which combine to produce the

Figure 7.14.3



Monomeric aluminium species in a solution in equilibrium with gibbsite at different pHs.

mixture of organic compounds which make up the DOC in the soil solution results in no clear relationship between DOC, absorbance and metal binding capacity.

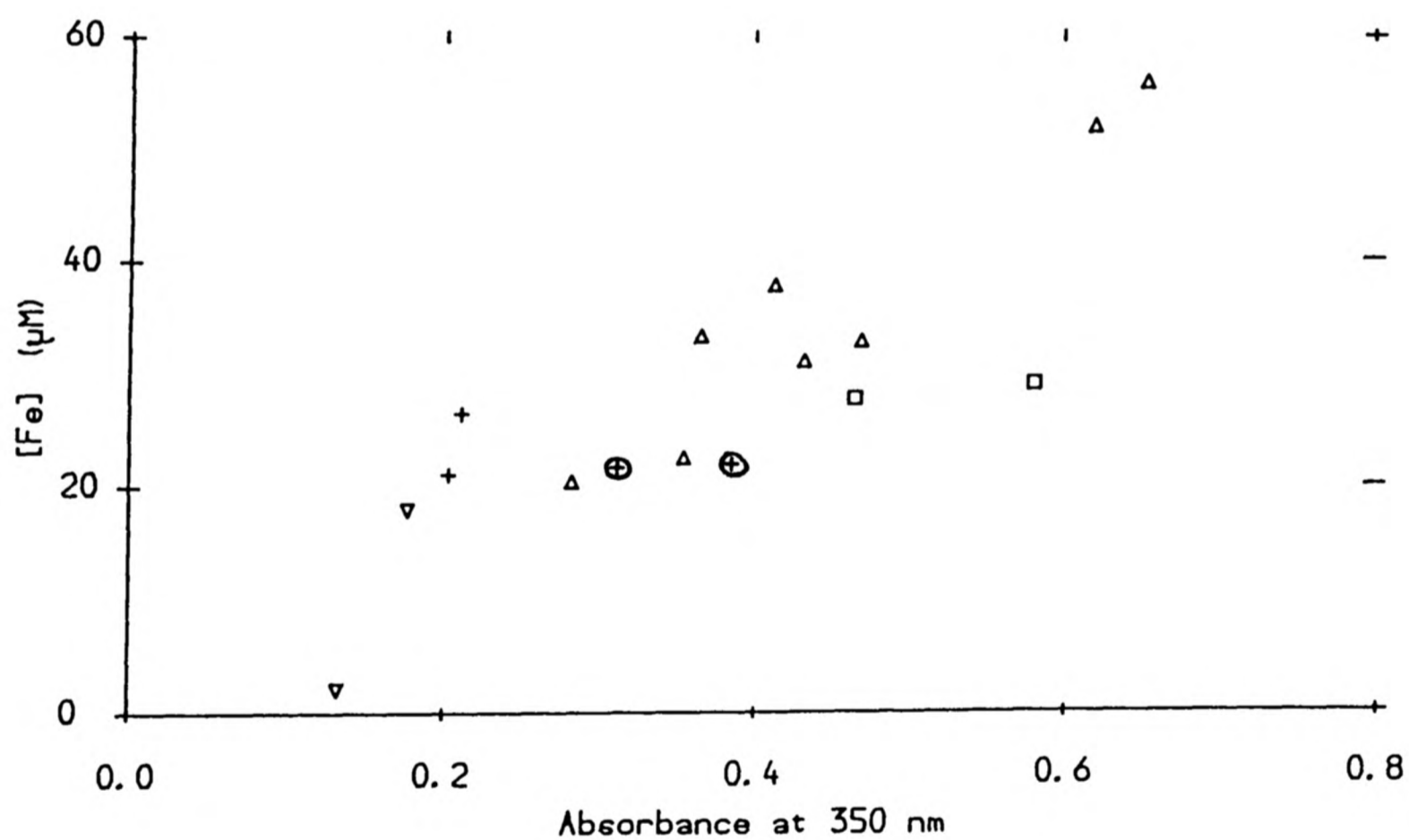
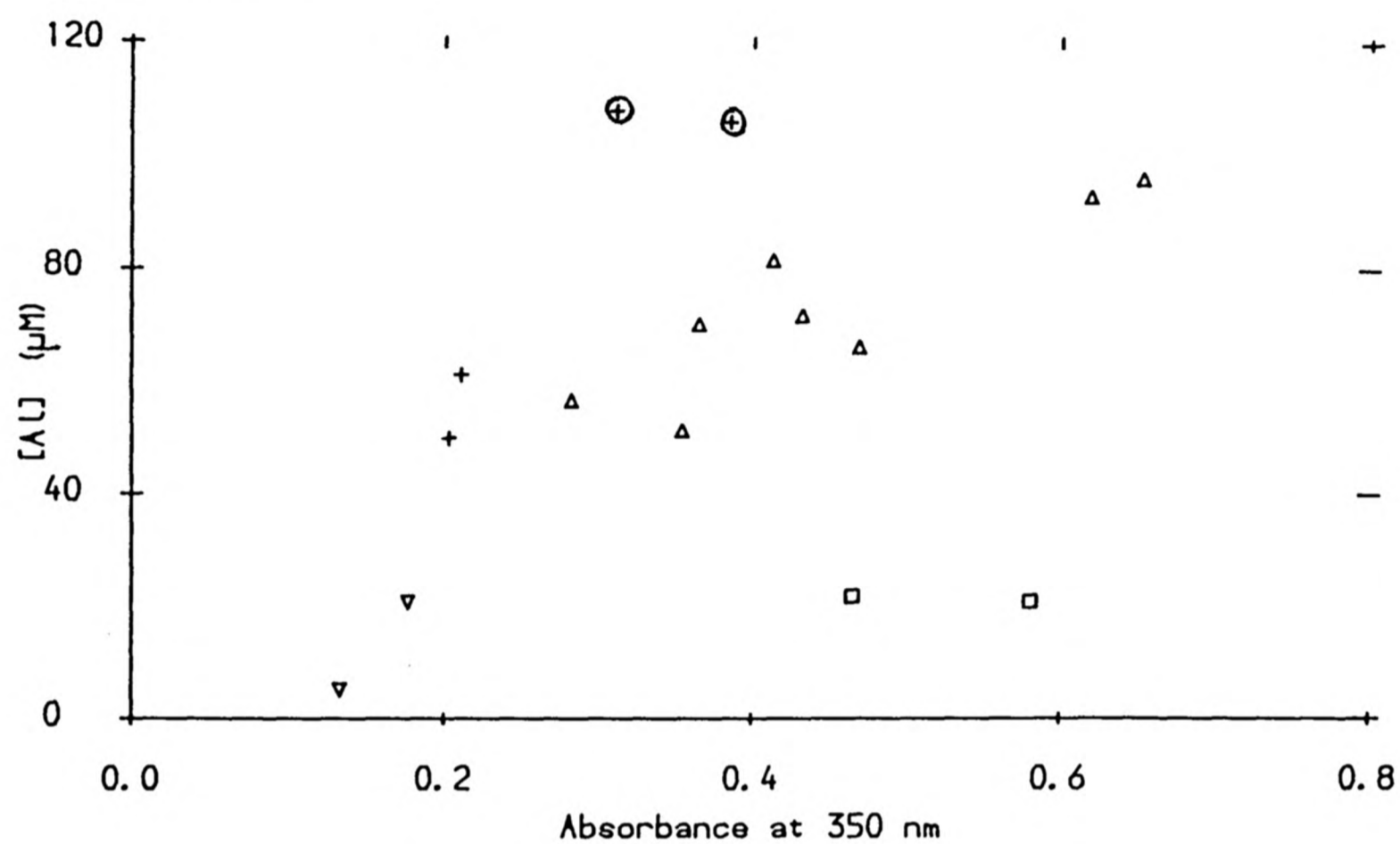
Within a more narrowly defined range of soils, relationships may become apparent. With the exception of two grassland samples the soil solutions from acid soils (S5.3) are from soils under the same vegetation and were taken on the same day, so the composition of the DOC in the different samples might be similar. The samples from acid woodland in the preliminary sampling (samples 6 and 8, S5.2) may also contain similar DOC.

Figure 7.14.4 shows the relationship between [Al], [Fe] and Abs<sub>350</sub> for these samples. It is clear, at least for the acid woodland sites that there is a relationship between Abs<sub>350</sub> and the concentrations of Al and Fe in the soil solution. No similar relationship was found between Zn, Mn, Ni, Co or pH and Abs<sub>350</sub> nor between DOC and any metals in solution. The graphs show that there is a difference in the Al-complexing capacity of the coloured fraction of the DOC in the solutions from the pasture site and in the solutions from a soil under coniferous woodland. The complexing capacity is reduced at pH > 6 for both Al and Fe.

### 7.15 Manganese

The main forms of manganese present in soils are divalent Mn ions held by clay and organic matter and the much less soluble MnIV present in oxide concretions and surface coatings. These oxides are practically universal in soils with pH >6. The large surface area of the coatings give them a far larger role in soil chemistry than would be expected from the amounts present. They have a high CEC and appear to act as scavenging agents for heavy metals.

Figure 7.14.4



Relationship between [Al], [Fe] and  $Abs_{350}$  for a number of soil solutions. a) Bagley Wood; ▽ neutral, △ acidic. b) □ acidic grassland soil c) ⊕ acidic woodland soil (coniferous acidic woodland soil).

Manganese is less abundant in soils than aluminium or iron. The soils in the main study contained between 110 and 1650 mg/kg acid-digestible Mn.

The most stable mineral in aerobic soils is pyrolusite ( $\text{MnO}_2$ ). The solubility of this mineral is such that in aerated conditions neutral and alkaline solutions in equilibrium with it will contain less than  $10^{-10}$  M of  $\text{Mn}^{2+}$ . In the soil solutions in the main study concentrations of Mn ranged from less than 0.01  $\mu\text{M}$  to 104  $\mu\text{M}$  in solutions where colloidal material was suspected. A normal upper limit is ca 16  $\mu\text{M}$ . There was no systematic dependence on pH, although the lowest concentrations were found in Icknield soils and the highest in acid woodland soils (300  $\mu\text{M}$ ).

The range between soils was large because of occasional high concentrations in Fyfield and Kingston series where the large within-soil variability (10 times) was high compared to that in the other soil series (4 times). The range of concentrations found in the main field study was similar to that found by Ceering et al (1969) for a range of New York and Wisconsin soils of 0.2 to 68  $\mu\text{M}$ . As in this study, they found that the range of Mn concentrations was much greater than for Cu and Zn.

The difference in Mn concentrations between the wet and dry Denchworth sites was not significant ( $P < 0.001$ ) because the concentrations in October, March and December were similar. At the times of both June samplings and in January the concentrations in solution at the wet sites were higher by between 3 and 8 times. This is consistent with microbial reduction of  $\text{Mn}^{\text{IV}}$  to  $\text{Mn}^{\text{II}}$  during periods of water-logging.

#### 7.16 Solutes Showing no Significant Between-Soil Variability

The only major solute not to show significant differences between different soil series was nitrate. The lack of significance was due to the high intra-series variability which (at 6.2 times) was almost double that found between soil series. These large differences arose because large amounts of nitrate fertilizers are applied to some fields and  $\text{NO}_3^-$  is not buffered at all by the soil.

Copper and zinc, too, showed no significant difference between soil series.

### 7.17 Solutes with Many Values Less Than the Detection Limit

In some or all of the soil solutions studied a number of the trace metals were present at concentrations lower than could be detected by ICP-OES. Lead and cadmium concentrations were always less than could be detected. A large fraction of the concentrations of Li, V, Ni, Mo and Al were less than could be detected, as were some of the concentrations of B, Y, Mn, Cu and Zn. The presence of a large number of essentially unknown concentrations rendered statistical analysis for these solutes impossible. In the case of Cu and Zn all of the positive concentrations were used in the statistical analysis. In the case of B, Mn and P all values less than the detection limit were treated as missing values. Some of these solutes are discussed below.

#### Boron

Boron occurs in a number of ill-defined soil silicates (for example, tourmaline) which yield boric acid on weathering. The nature of borate adsorption on soil materials is not well understood: adsorption capacity seems to be determined by clay minerals, sesquioxide impurities on their surfaces, or by free sesquioxides.

The major adsorbing species are iron and aluminium sesquioxides (Sims and Bingham, 1968). Borate ions may be adsorbed by simple exchange with hydroxyl ions or by a reaction analogous to the formation of a borate-diol complex. Both of these reactions are favoured by increases in pH up to pH 8-9 when hydroxyl ions begin to compete for sites and hydrous oxides begin to acquire a negative charge. Since adsorption increases with pH, soil solution concentrations of boron might be expected to be low in calcareous soils. However, the boron analyses showed no direct pH-dependence over a wide pH range; even in very acid soils (Table 5.3.2) the

maximum B concentration is around  $10^{-5}$  M. The lowest B concentrations were found in solutions of pH  $\sim 8$  where they are less than  $10^{-5.7}$  M. However, fairly high B concentrations ( $10^{-5}$  M) were also found at this pH. This indicates that factors other than adsorption on sesquioxides are controlling the boron concentration, in the solutions of some of the soils at least.

#### Yttrium

The yttrium content of the soil solutions in the main field sampling experiment were very low, never exceeding  $0.06 \mu\text{M}$ , and frequently less than  $0.01 \mu\text{M}$ . It is present at total concentrations of 2-40 ppm in the soils studied and is thought to occur with other lanthanide elements in the mineral monazite.

#### Lithium

The concentration of lithium in the soil solutions of the main study were generally less than  $10^{-6}$  M except in Denchworth and Icknield series soils which contain relatively high levels of lithium in the solid phase.

#### Nickel

With very few exceptions Ni in the solutions of the main field experiment was present at concentrations of less than  $0.5 \mu\text{M}$  ( $10^{-6.3}$  M). Even in the acid woodland soils concentrations were less than could be detected. These findings agree with those of Mattigod et al (1980) who quote Ni concentrations of  $< 10^{-7}$  M.

### 7.18 Moisture Content

In an area of fairly uniform rainfall and similar crops, soil moisture content will depend on soil texture, clay content and organic matter content together with drainage.

The range of moisture contents between soil series was fairly small (2.6 times), the lowest being on sandy soils and the highest on soils with a high clay content and high organic matter. The range of moisture contents between fields (within soils) was small (1.4 times) and the values significantly ( $P < 0.001$ ) correlated with soil organic matter content.

### 7.19 Differences Between Arable and Pasture Sites

For a number of solutes there were significant differences between arable and pasture sites (Table 6.9.2). These significant differences correspond to a pattern that soil solutions of the arable sites are generally more dilute than their pasture neighbours. Of the solutes which showed a significant difference, the concentrations in the pasture solutions were between 40 and 90% higher than in the arable ones. For some solutes this pattern was reversed. For example, K concentrations in the solutions of Icknield arable soils were higher than the pasture ones (see Ap. 8).

The reason for these differences is not immediately apparent. Overall, the moisture contents of the arable soils are lower than those of the ones under grass by about 20%. However this average is misleading because it conceals the fact that the moisture contents of the arable and pasture Fyfield soils are about the same, the pasture fields of the Denchworth series are 20% dryer than their arable neighbours, whereas the arable Icknield soils are 47% dryer than their grass neighbours. There is no systematic difference

between cation exchange capacities of the two landuses. In all but one grass and arable pair the organic matter (OM) content of the grass soil was greater. The relationship between OM and moisture content (S7.18) suggests that in the same soil series, under the same crop, the moisture content is related to the OM content and so, ignoring any cropping demands, the moisture holding capacity of the arable soils would be less. Therefore more drainage, and hence a high flux of solutes, would be expected in soils of lower OM. The soil structure in arable fields is likely to be poorer than in neighbouring grass fields and so at each location the proportion of drainage water flowing in macropores would be greater in a grass soil. These two factors together would result in the soil solutions of the arable soils being more dilute than in the corresponding pasture soil. That is; the soil solution in an arable soil may be more fully replaced by percolating rain water than the soil solution in a nearby soil under grass.

#### 7.20.1 Summary and Conclusions

The results discussed above indicate that a number of chemical processes appear to be controlling the chemical composition of the soil solution.

##### Equilibrium with crystalline solids

In calcareous soils the concentrations of Ca, Mg, Ba, Sr and possibly trace metals such as zinc are controlled by the presence of free calcite in the soil. Reactions of phosphate in the soil solution with OCP and DCP may control the concentrations about which P concentrations fluctuate and the maximum soil solution concentration respectively.

##### Equilibrium with amorphous solids

It is likely that the dissolution and precipitation of amorphous solids controls the concentrations of Si, Al, Fe and to some extent

Mn in the soil solution. The activity of these solid phases is very variable, however, due to the adsorption of material onto their surfaces. Dispersion of these colloids on sudden increase of moisture content may result in high concentrations of fine (<0.45  $\mu\text{m}$ ) material containing Al, Fe, Si, Mn and Co in a stable colloidal dispersion.

#### Ion exchange

The concentrations of Na and K in all of the soil solutions and those of Ca and Mg in the non-calcareous soils are apparently buffered by cation exchange. Sulphate concentrations, even in acid soils, are likely to be buffered by ion-exchange.

#### Other factors

The concentration of DOC in the soil solution (and to some extent moisture content) are related to the organic matter content of the soil.

The range of Mn concentrations is so large that it is likely that, in certain conditions, reduction of  $\text{Mn}^{\text{IV}}$  occurs, enhancing Mn concentration in solution.

#### Inputs

The concentrations of Na, Cl,  $\text{NO}_3$  and S are controlled by both natural and anthropogenic inputs to the soil. When the holding power, and losses from the soil are similar, then the concentrations in the solutions of different soils are comparable.

#### Comparisons of pasture and arable fields

The soil solutions of pasture fields are generally more concentrated than those of similar soils under cereal crops. This difference may arise because of the different water-holding capacities and drainage patterns under the different landuses.

#### Comparison of Ranges

The range of concentrations over the different soil series varies

from solute to solute. A summary is given in Table 7.20.1; ranges are calculated from the soil means for the pasture sites. The range is the ratio of the largest to the smallest of the six soil means. Range\*\* is the range if the median concentrations from the Bagley Wood sampling are added to give a seventh number for comparison. Thus, the first column gives the approximate range found in neutral and calcareous soils, and the second the range found in acid, neutral and calcareous soils.

For most soils the range between different soil series is not very large. The exceptions are alkalinity, pH, Fe and Mn. The presence or absence of carbonates is the major factor influencing the first pair, and the dispersion of soil colloids and solubilisation of reduced forms the second pair.

If the comparison is extended to cover acid soils, the range is increased for many solutes. Where soil solution concentrations are governed mainly by inputs, for example Na, S, NO<sub>3</sub>, the range is not increased. Chloride might be expected to behave similarly, however the higher rate of evapotranspiration under trees results in higher chloride concentrations in the solutions of woodland soils. Concentrations of Mg, Ca, K, Sr, and Cu are lower in the solutions of acid soils, whereas the concentrations of Mn, Fe, Al, Zn, and Ba are increased. The largest increase in ranges are in those of pH and alkalinity.

Comparison of soil-dependent variability for different solutes. Ranges are calculated from the time and field averaged means (of the log-transformed data) for each soil series. The range is the ratio of the largest to the smallest of these means. Range\*\* is the range found if the median concentration from the Bagley Wood sampling is included with the six soil means.

Solute	Range	Range**
Na	2.6	2.6
K	3.9	5.0
Ca	2.2	6.3
Mg	2.8	3.6
S	1.9	1.9
Si	2.6	10.7
P	2.8	11.8
Cl	1.7	2.2
NO <sub>3</sub>	3.8	3.8
Alk	5.9	>300
pH	10.5	1840
Ba	2.3	3.1
Mn	11.0	350
Cu	2.0	2.8
Fe	9.1	29
Zn	1.7	4.9
Sr	3.7	7.9

## Chapter 8

### Temporal Changes in the Chemical Composition of the Soil Solution

The soil exists in a state of constant change, taking part in cycles that have no beginning and no end.

Rachel Carson, 1963

#### 8.1 Introduction

The time scales of chemical reactions in the soil-soil solution system vary from those of soil formation over periods of thousands of years to those of exchange between the ions in the soil solution and those adsorbed on the surface of exchange sites which have half lives of the order of a few seconds. Thus the chemical composition of the soil solution is changing via reactions which proceed simultaneously at differing rates. Changes at the extremes of this range of time scales lie outside the scope of this project. Even to cover seasonal changes would have entailed a sampling programme extending over a number of years, so this chapter is concerned with changes occurring over periods of weeks and months.

Over such periods changes in the chemical composition of the soil solution can occur as a result of one or more different processes. For example, dilution by rain, concentration by evapotranspiration, or losses of solutes by leaching or plant uptake. Dilution and concentration will lead to changes in the ratios of mono- and di-valent ions due to cation exchange. The magnitude of the change in concentration of any one solute in the soil solution in response to, say plant uptake from that solution will vary greatly depending on the solute and its distribution between the soil solution and labile solid phases.

Addition of pure water to soil generally results in a proportional decrease in the concentrations of Na, Cl, and NO<sub>3</sub> in solution, whereas the concentrations of K, HCO<sub>3</sub>, and P remain relatively

constant (Russell, 1973). The behaviour of sulphate is intermediate. Thus, on the addition of water to a moist soil the mass of solutes, such as nitrate, in solution remains constant, whereas the mass of a solute such as phosphate in solution will increase.

There is little published data on seasonal changes in the composition of the soil solution. Tan and Smillie (1981) reported that major ions are most concentrated in the winter, low in spring and autumn and intermediate in summer. Iron and manganese were found to have maxima in the spring and autumn, with minima in winter and summer. Greive et al (1984) found that chloride concentrations were highest in the autumn with a decline into spring followed by a gradual rise over the summer. Magnesium showed an autumnal maximum, potassium a spring maximum. These results suggest that seasonal changes depend on the chemical characteristics of the individual solute. For instance, the concentration of solutes whose solubility is affected by redox will behave differently from a solute such as chloride which does not interact to any extent with the soil.

## 8.2 General Trends

During the main experiment the differences in moisture content from one sampling time to the next were not great, the maximum deviation of the time means from the grand mean being  $\pm 8\%$ . This does not mean that there were no large changes in moisture content in the intervals between sampling times: clearly moisture contents did fall to low levels during the summer months. In the extreme case of the Fyfield soils the moisture content was less than  $5\%$  for much of this period. However, the small range of moisture contents results in the changes in concentration of any one solute being directly related to the changes of the mass of that solute in the soil

solution. Discussion will be limited to changes in concentration over the sampling period rather than changes in amounts in solution on a mol/kg basis.

Comparing the geometric means of all of the soil solution concentrations of the pasture sites for each of the seven sampling times (time means) shows that solutes may be grouped into three broad classes:

i) those showing a small or insignificant change in concentration with time, (less than two fold),

ii) those showing an intermediate variability with time, (2-3 fold) and

iii) those exhibiting large temporal variability (> 3 fold).

The range for each solute is shown in Table 8.2.1.

It must be stressed that these ranges represent the range in the concentrations of the times sampled. They do not represent the maximum annual range which might have been found if it had been possible to extract soil solution when the soils were very dry during the summer. It is reasonable to regard them as the likely range in concentrations between the months from September to June. In the summer months soil moisture contents fall well below those encountered in these samples.

The anions showed the largest spread in ranges of concentrations, the range increasing in the order  $P \sim Si < Alk < S < Cl < NO_3$ . This conforms to the picture of P and Si being in rapid equilibrium with amorphous solids, alkalinity with carbonates and organic matter. Sulphate is buffered by anion exchange more than chloride which is not adsorbed onto the soil to any great extent. Changes in the concentration of nitrate are greater than those of chloride because of biological reactions.

Table 8.2.1

Comparisons of temporal variability in soil solution concentration.

The ranges given are those between the minimum and maximum Time Means

for the 18 pasture sites. Range = max/min.

	Solute	Range	Time of Max.	Time of Min.
Small range				
	Alk	1.94	*	*
	P	1.57	*	*
	Si	1.54	Sept	Dec
	Fe	1.93	Sept	Jan
	MCwet	1.10	March	Sept
Medium Range				
	Na	2.12	Sept	Jan
	Ca	2.64	Sept	Jan
	Mg	2.74	Sept	Jan
	Ba	2.88	Sept	Jan
	Sr	2.61	Sept	Jan
	Cu	2.77	Sept	Jan
	S	2.95	Sept	Jan
Large Range				
	DOC	3.04	June '83	Jan
	K	3.14	Sept	Jan
	Zn	3.17	Sept	Jan
	Cl	3.62	Sept	June '84
	pH	3.68	June '83	March
	NO <sub>3</sub>	5.50	Sept	June '84
	Mn	7.01	June '83	Jan

\* no significant temporal change

All of the metal ions for which there was sufficient data manifested significant changes with time, the order being  $\text{Fe} \sim \text{Na} < \text{Ca} \sim \text{Sr} \sim \text{Mg} \sim \text{Cu}$   $\text{Ba} < \text{K} \sim \text{Zn} \ll \text{Mn}$ . Ranges of metals in group two of the periodic table are similar, reflecting their similar sources and chemistries. Iron, whose solution concentration is controlled by equilibrium with amorphous hydroxides shows only a small temporal range, contrast this with the changes in the concentration of Mn which are far greater. This indicates that at least some of the soils become sufficiently anaerobic to allow the presence of  $\text{Mn}^{\text{II}}$  but not of  $\text{Fe}^{\text{II}}$ .

Potassium shows a fairly large temporal range indicating that processes other than simple dilution and concentration are influencing its concentration in the soil solution. The large range, is most likely to be due to a combination of plant uptake and fertilizer applications (Appendix 7).

As would be expected, the concentrations of the major ions are lowest in the spring after winter leaching. If the solute content of the soil solution is summarised in one term, that of ionic strength, approximated by

$$1/2 \sum 4[\text{Ca}] + 4[\text{Mg}] + [\text{Na}] + [\text{K}] + 4[\text{S}] + [\text{P}] + [\text{NO}_3] + [\text{Cl}] + [\text{Alk}]$$

it is possible to look at the overall temporal trend in soil solution concentration. The temporal range for individual pasture fields lies between two- and ten-fold, most lying between two- and four-fold. The magnitude of the temporal range is not directly linked to mean moisture content, CEC, soil organic matter or soil texture. This may be because of fertilizer additions upsetting any natural relationship. The lowest temporal range was in Icknield soils, and the highest in Sherborne soils. Of the times at which samples were taken the soil solutions were most concentrated in September and most dilute in January, with the average range for the

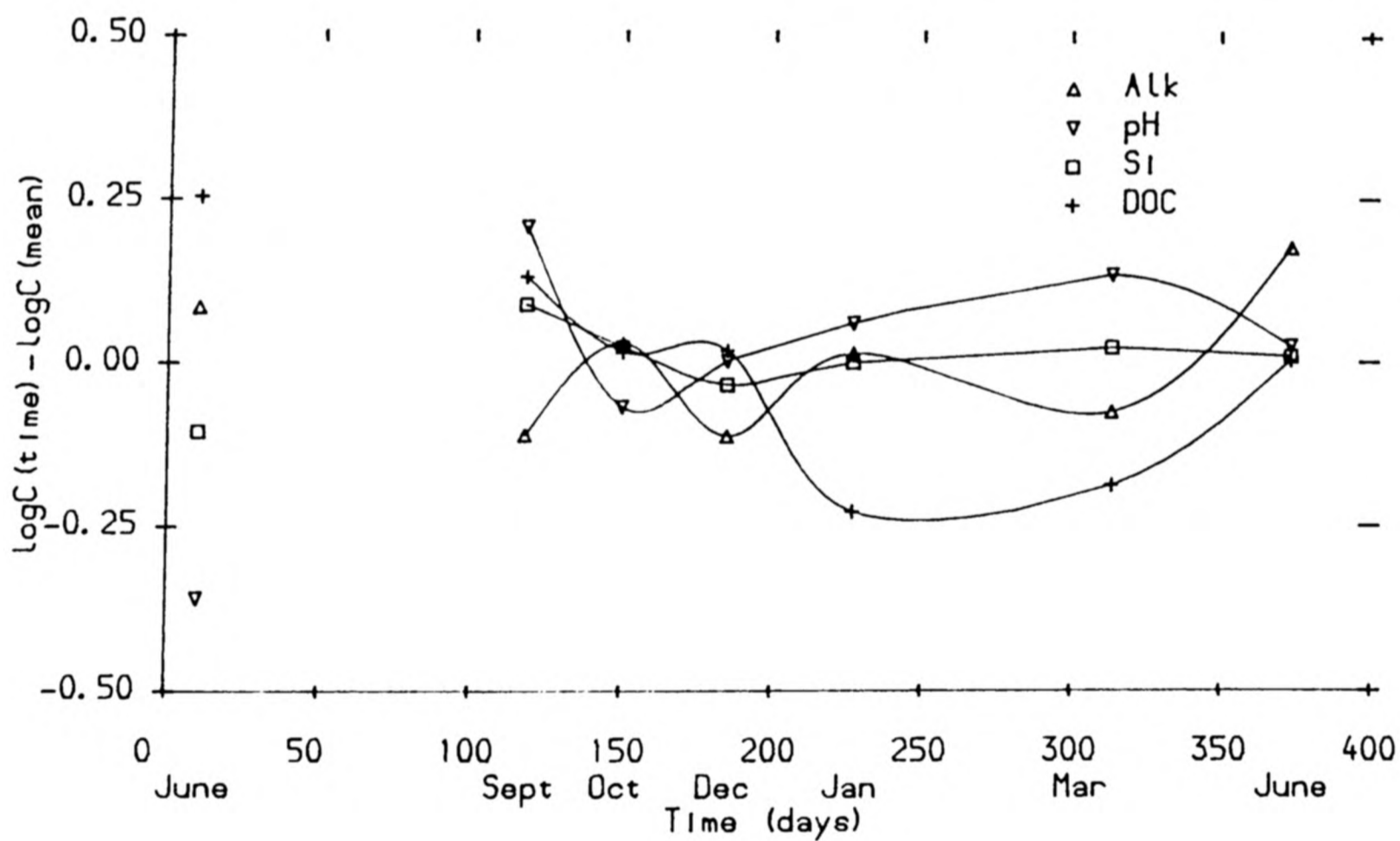
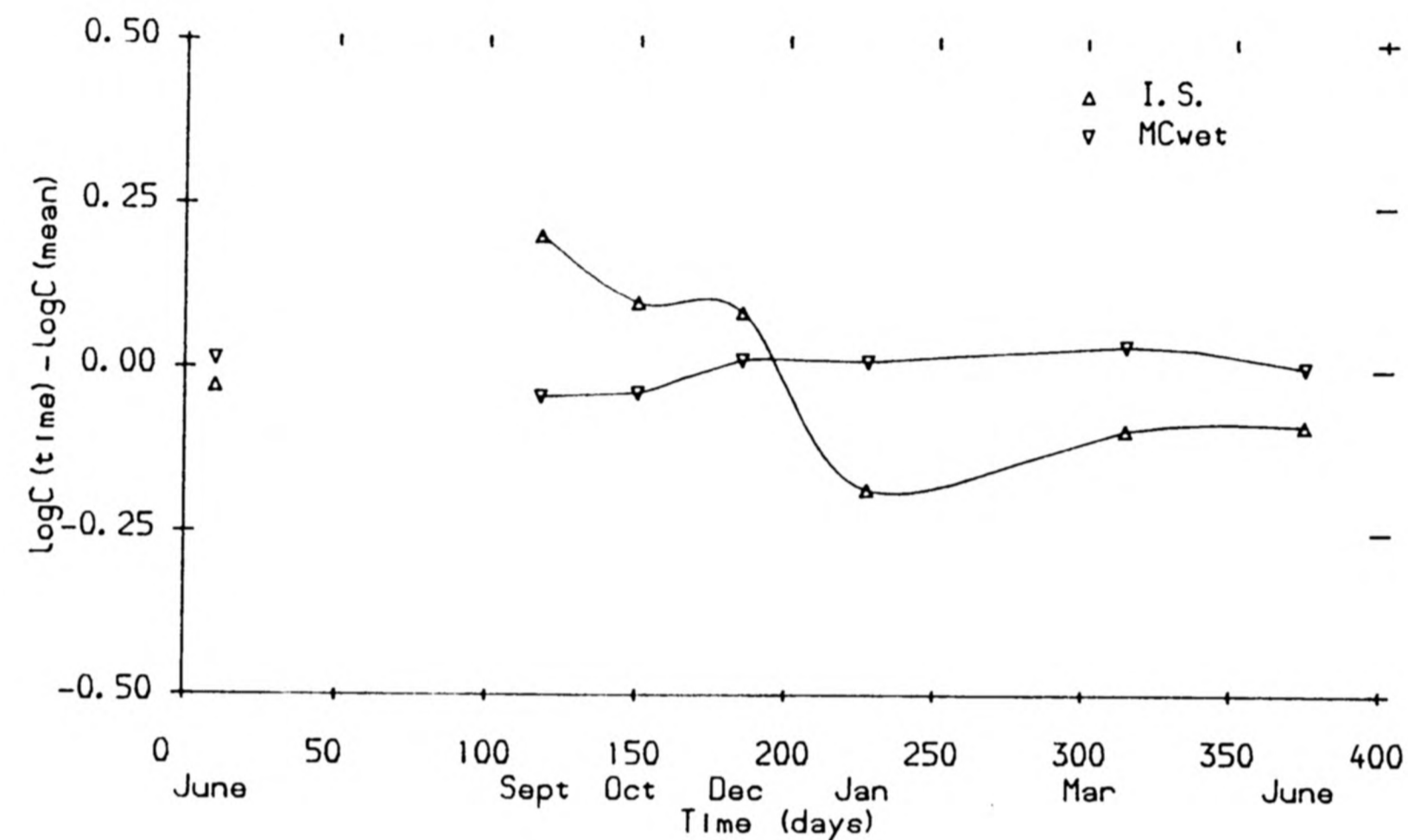
pasture fields being slightly less than two and a half times.

Temporal changes averaged over the pasture sites (calculated from the log-transformed data) are shown for a number of solutes in Figure 8.2.1. The eighteen pasture sites may be grouped together in this way because no solute showed a significant variance in the T.S stratum of the pasture site ANOVAR (Table 6.9.1); in other words the temporal changes in each of the six soil series followed a similar pattern.

The ordinate on each of the graphs shows the difference between the grand mean for all of the pasture sites (two samples from each of eighteen sites at each of seven sampling times, excluding missing values) and the geometric mean for each of the seven individual times (time means). The difference between the means is a difference between logs and so a value of +0.3 is one where the concentration is approximately double that of the mean. The graphs illustrate the similarities found in Table 8.2.1; that is that Mg, Ca, Na, K, Ba, Sr, Cu and Fe show similar trends with a greater temporal range than Si, P and alkalinity. Potassium shows a similar pattern to the other major metals, but with a more pronounced January minimum. The trace metals, with the exception of Mn follow the changes in the concentrations of the major metals. Mn, being more susceptible than Fe to reduction to more soluble forms in the soil, has a maximum in June 1983 during conditions of water logging in warm weather.

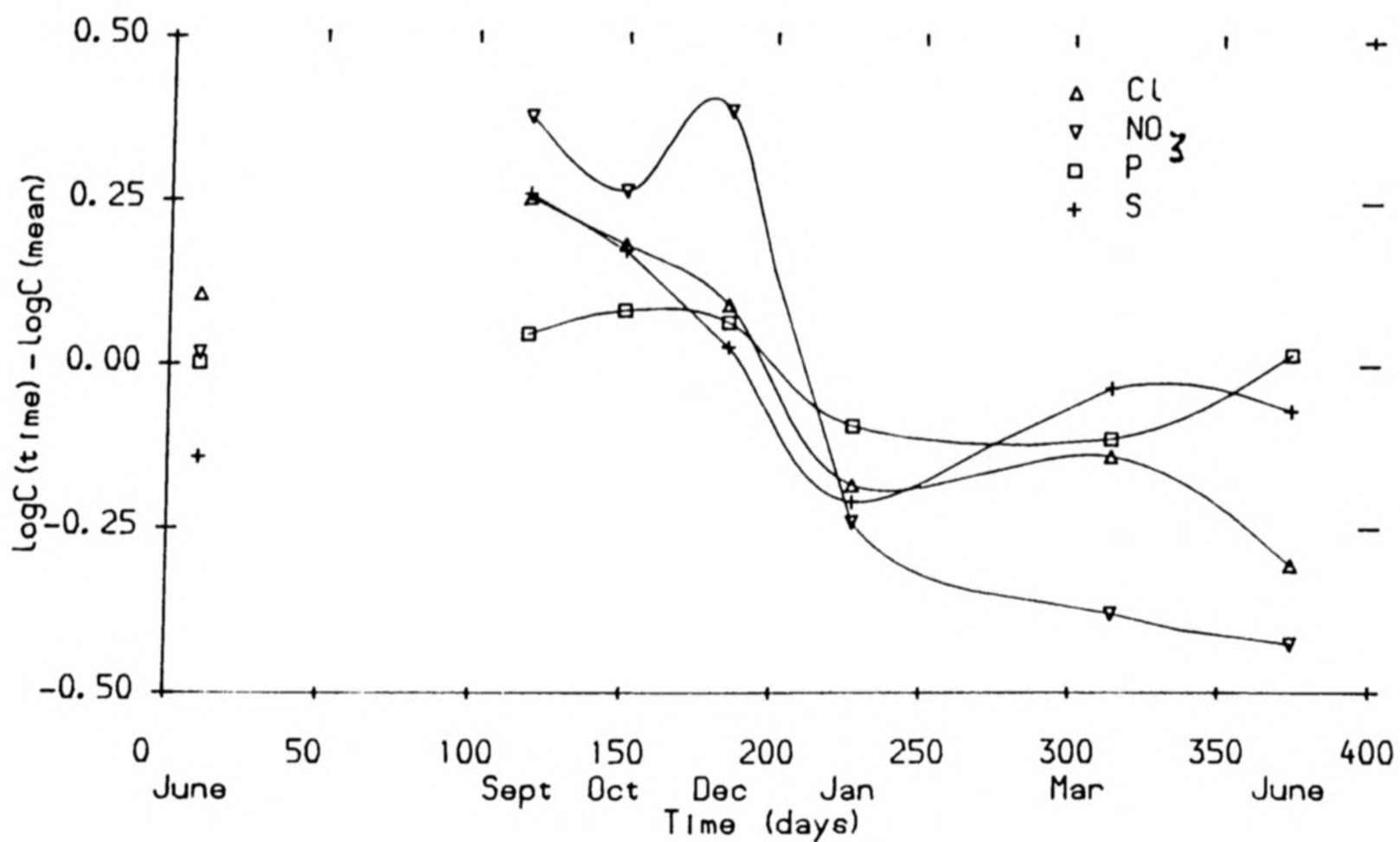
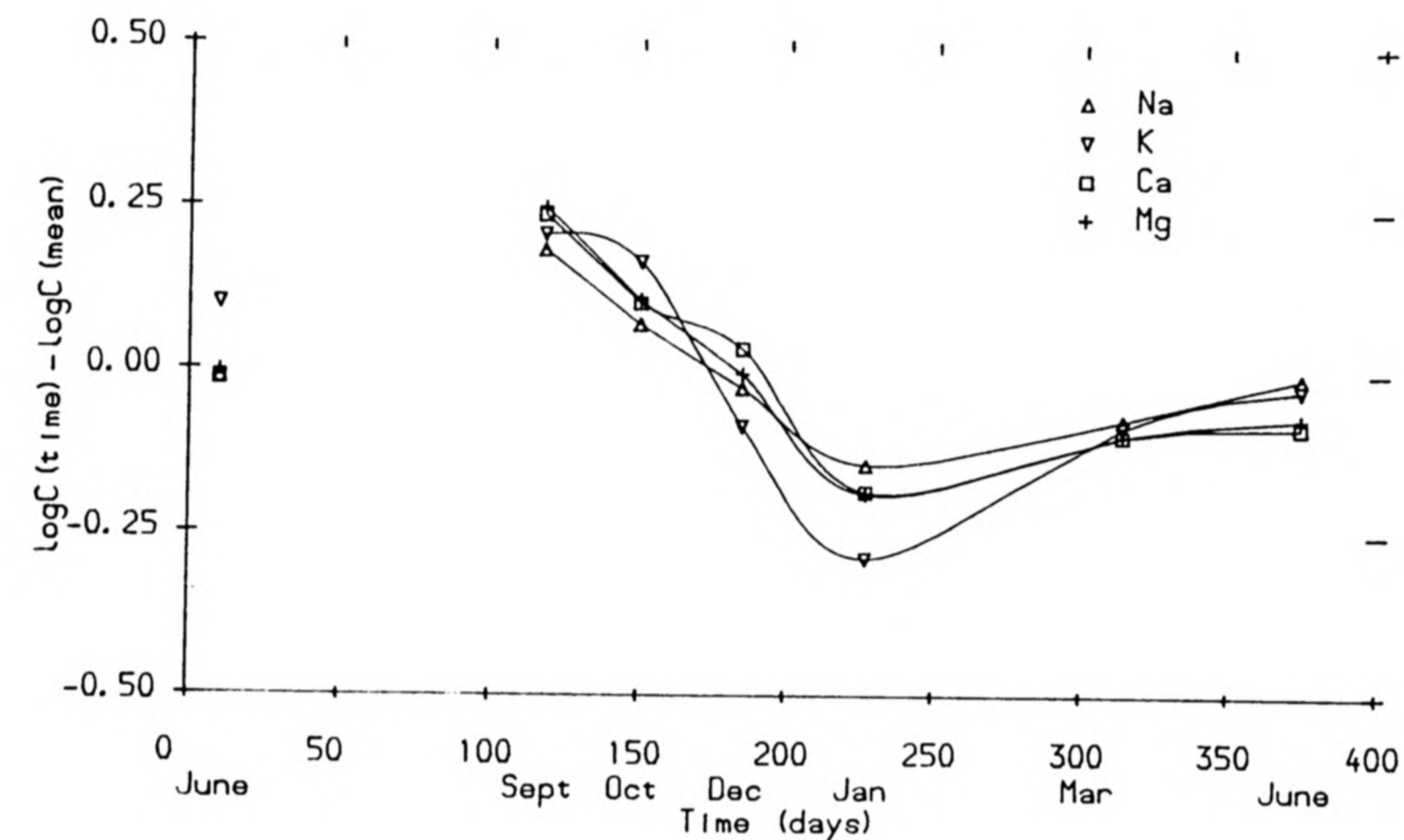
Of the anions, P and Si follow the general trend, with the amplitude of changes in P concentrations being much reduced. NO<sub>3</sub> and Cl do not follow a cyclic trend, but are much more dilute at the end of the sampling period than at the beginning. This downturn is mirrored by an increase in alkalinity over the period March to June

Figure 8.2.1



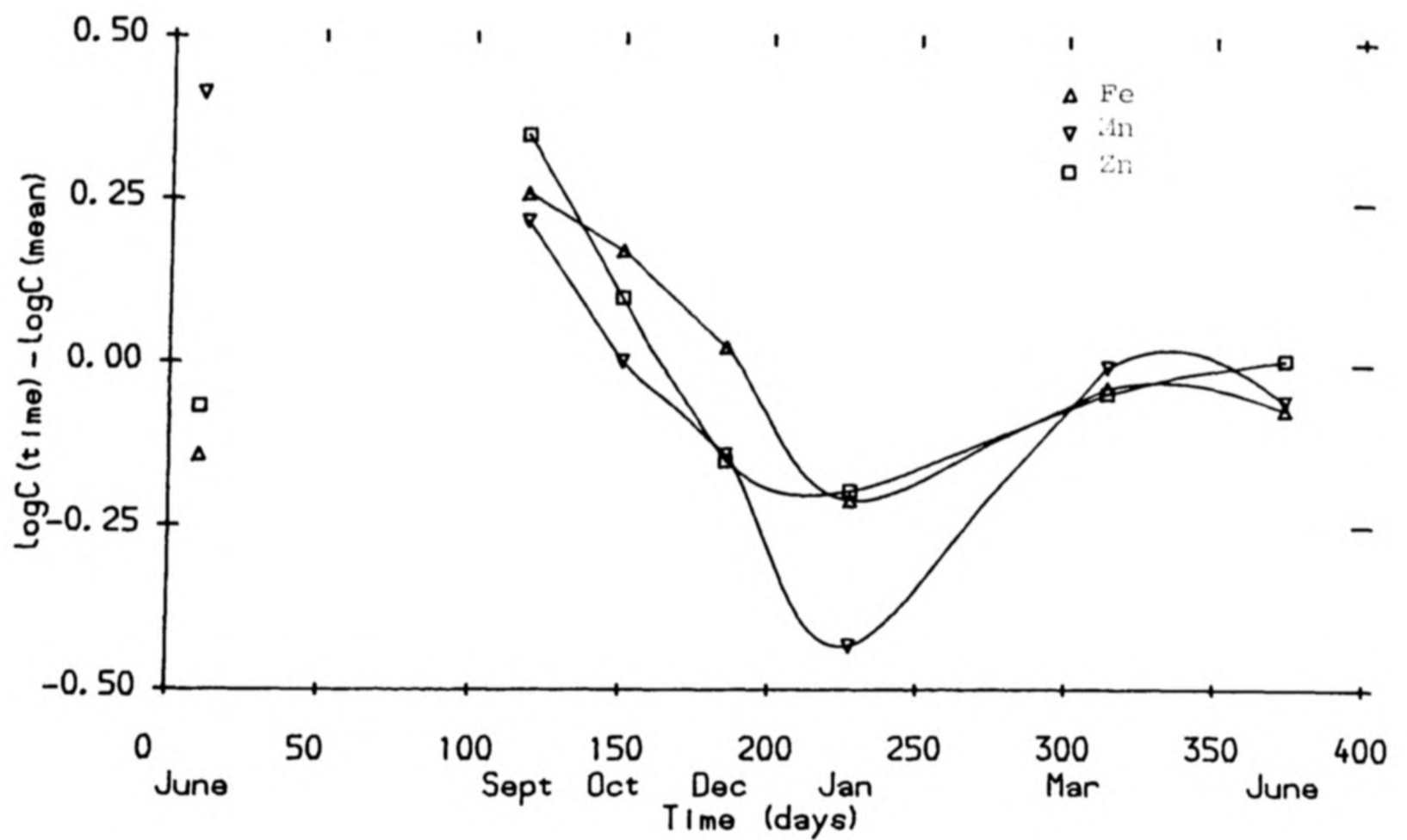
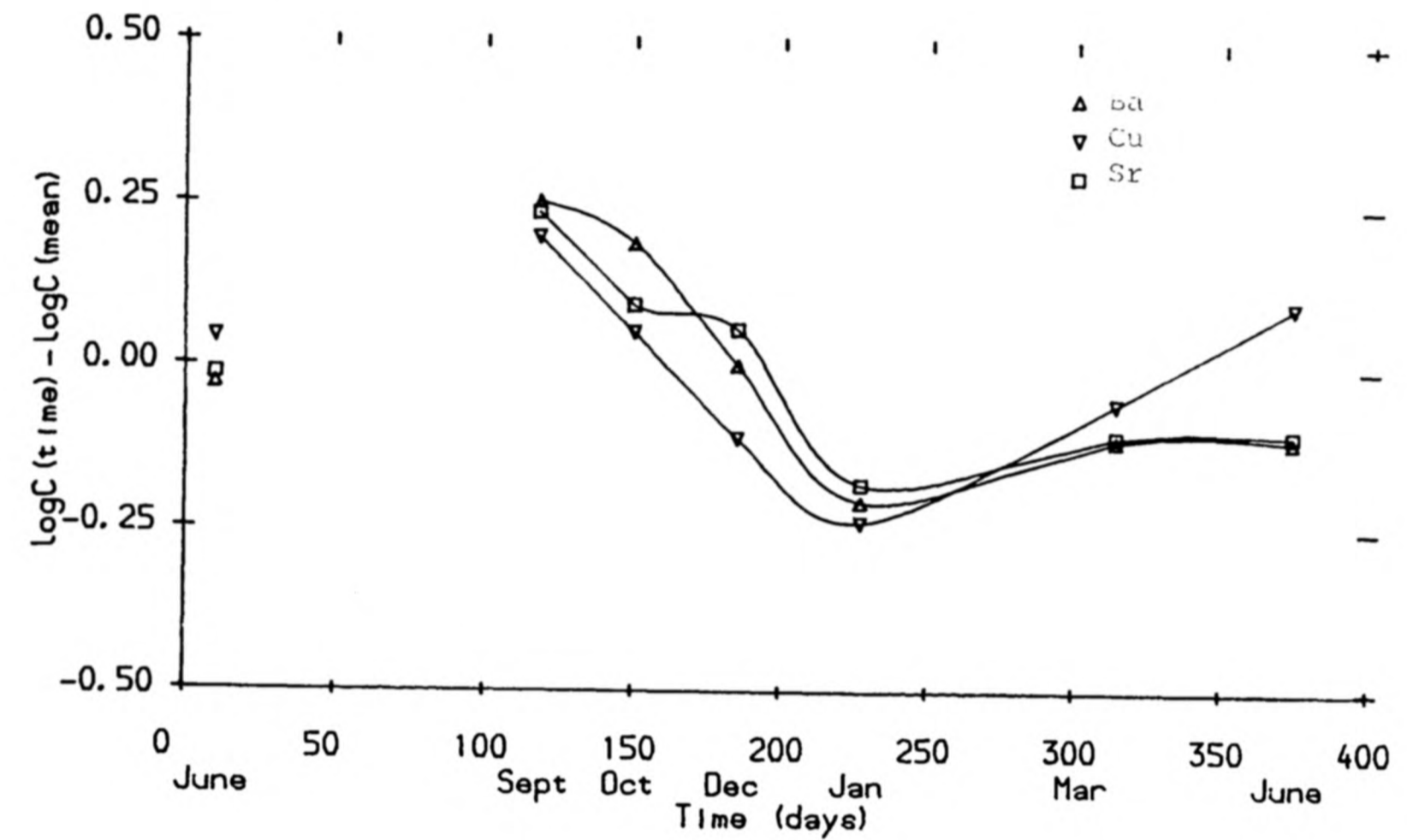
Temporal changes in the concentrations of solutes in the soil solutions from pasture sites relative to the grand geometric mean for each determinand.

Figure 8.2.1 cont.



Temporal changes in the concentrations of solutes in the soil solutions from pasture sites relative to the grand geometric mean for each determinand.

Figure 8.2.1 contd.



Temporal changes in the concentrations of solutes in the soil solutions from pasture sites relative to the grand geometric mean for each determinand.

1984. DOC, too, is more dilute in the soil solution at the end of the sampling period than at the beginning.

### 8.3 Winter Leaching

The data from the main field experiment is most complete for the late autumn and winter of 1983/84 when all of the solutes studied became less concentrated in the soil solution. Over the winter period rainfall exceeds evapotranspiration and so field capacity is reached and drainage occurs once soils have replenished the moisture deficit built up over the summer. Rainwater displaces the soil solution and mixes with it as it moves through the soil. The amount of piston displacement and mixing depends on the texture of the soil and the hydraulic conductivity of the soil peds. As, for most solutes, rain water is more dilute than the soil solution the soil solution tends to become less concentrated over the winter period and solutes are leached from the soil in the drainage water. The extent to which the leaching of any one solute takes place depends on the partitioning of that solute between the soil solution and labile solid phases. Solute such as chloride, which are present almost entirely in the soil solution, are more strongly leached than solutes such as phosphate.

Taking the period between September and January as the period of winter leaching and defining chloride as having a leaching index of 100% (that is  $[Cl]_{Sept}/[Cl]_{Jan} = 100$ ) we may look at the relative losses of other solutes (Table 8.3.1). Ca, Mg, Ba and Sr are leached to a similar extent and their losses are higher than those of sodium. Anion losses decrease in the order  $NO_3 > Cl > S > Alk > P$ , whilst pH, alkalinity, Si and DOC show similar changes over the period. Of the major solutes K and  $NO_3$  are much more strongly leached than chloride: in the case of nitrate this may be explained

Table 8.3.1

The reduction in the concentrations of a range of solutes in the solutions from the main experiment over the winter period relative to that of chloride.

Solute	Leaching Index
Na	77
K	115
Ca	96
Mg	100
S	108
Si	45
P	40
Cl	100
NO <sub>3</sub>	152
Alk	51
pH	51
DOC	84
Ba	105
Mn	163
Cu	101
Fe	46
Zn	128
Sr	95

in terms of denitrification in addition to leaching losses and in the case of K in the concentration in the soil solution may have been artificially high in the autumn because of fertilizer applications (Appendix 7). Mn and Zn are also strongly leached.

At first sight, the fact that of sodium is less diluted than the divalent cations seem to contradict the expected trend (Russell, 1973), however the ratio of concentrations in the soil solution compared to that in the rain for sodium is about 3 compared to 45 for calcium. As leaching continues the concentration of sodium in the soil solution will fall near to that in the rain far in advance of the same occurring for calcium. In January the geometric mean sodium concentration in the solutions from the pasture sites was 380  $\mu\text{M}$  compared with a mean rainfall concentration of 160  $\mu\text{M}$ .

Although the statistical analysis of the main experiment demonstrated that all of the solutes showed similar temporal trends in the different soils, the magnitude of the changes in the different soil series might be expected to differ. The decrease in the ionic strengths of the solutes in the different soil series between September and January was least in Icknield soils and greatest in the Sherborne series. The other series showed a similar, intermediate, dilution. This pattern is different from that expected from simple textural considerations, which would suggest that the solutions of Fyfield soils would be more susceptible to losses from leaching.

Soils under grass are generally more structured than similar soils under cereal crops which are ploughed annually. Crumb structure and macropores are usually better developed in grassland soils, and the mixing of percolating rainwater and the soil solution is likely to be slower. Over the winter, therefore, higher dilution of the soil

solution would be expected in arable soils and leaching losses might be expected to be greater.

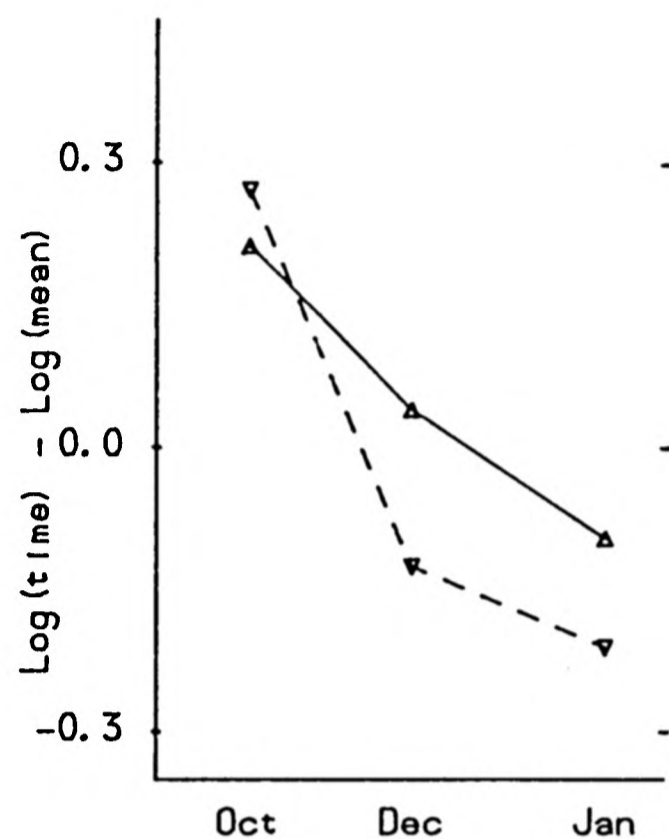
This is indeed the case, and the graphs in Figure 8.2.1 show the fluctuations in ionic strength about their grand geometric mean (over 12 sites and six times) for a) all soils, b) Fyfield soils, c) Ickniel soils and d) Denchworth soils. For each soil series there were two pasture and two arable sites (see S6.2), and so each point on the last three graphs is the mean of two samples from each of two sites at each time. The different degree of leaching between the two land uses is most pronounced in Denchworth soils, but in all cases dilution of the soil solution is more rapid and occurs to a greater extent in the arable soils.

As only a few poorly drained sites were sampled, the statistical analysis of this comparison was somewhat limited. However, inspection of the data shows that there are some, at least qualitative, differences between the two drainage types. Figure 8.2 shows the changes in the ionic strengths of the solutions at the different types of site over the winter period. The points were calculated in a similar way to those in the previous figure. After an initial rapid phase, leaching from the sites with poor drainage was delayed relative to that from the more freely draining sites. A similar dilution resulted by January, with the solutions at both types of site being about half as concentrated at the end of the winter. Both are at minimum concentration in March, which is later than in Ickniel and Fyfield soils.

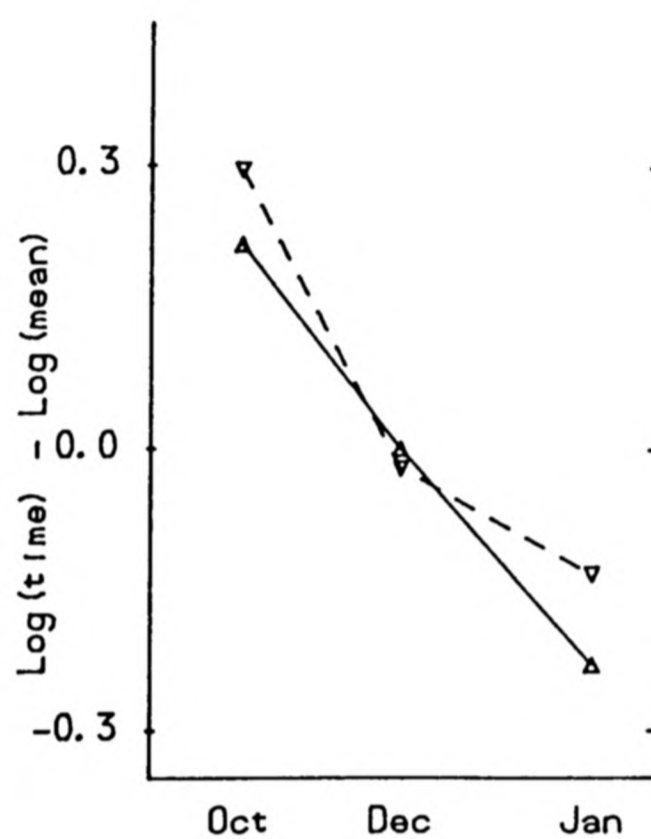
#### 8.4 Anaerobic Conditions

The anomalous pattern of temporal changes in the concentration of manganese in the soil solutions of the pasture sites (Figure 8.2.1) suggested that anaerobic soil conditions were prevailing in June of

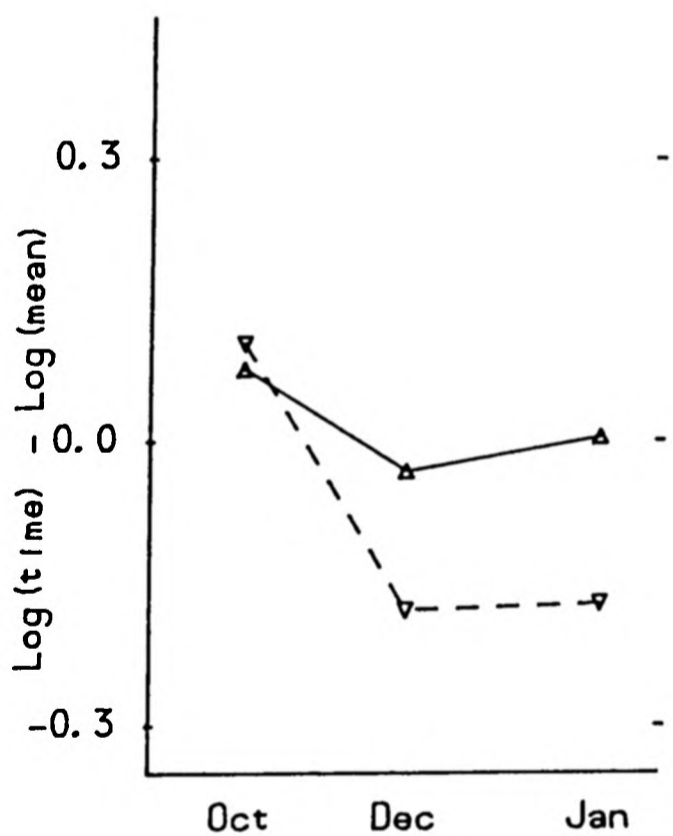
Figure 8.2.1



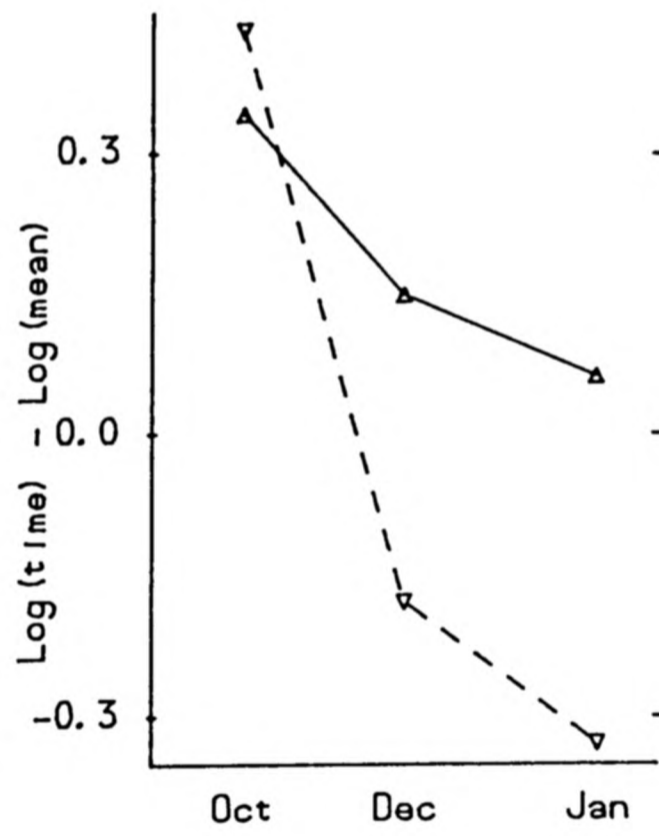
a) All Soils



b) Fyfield Soils



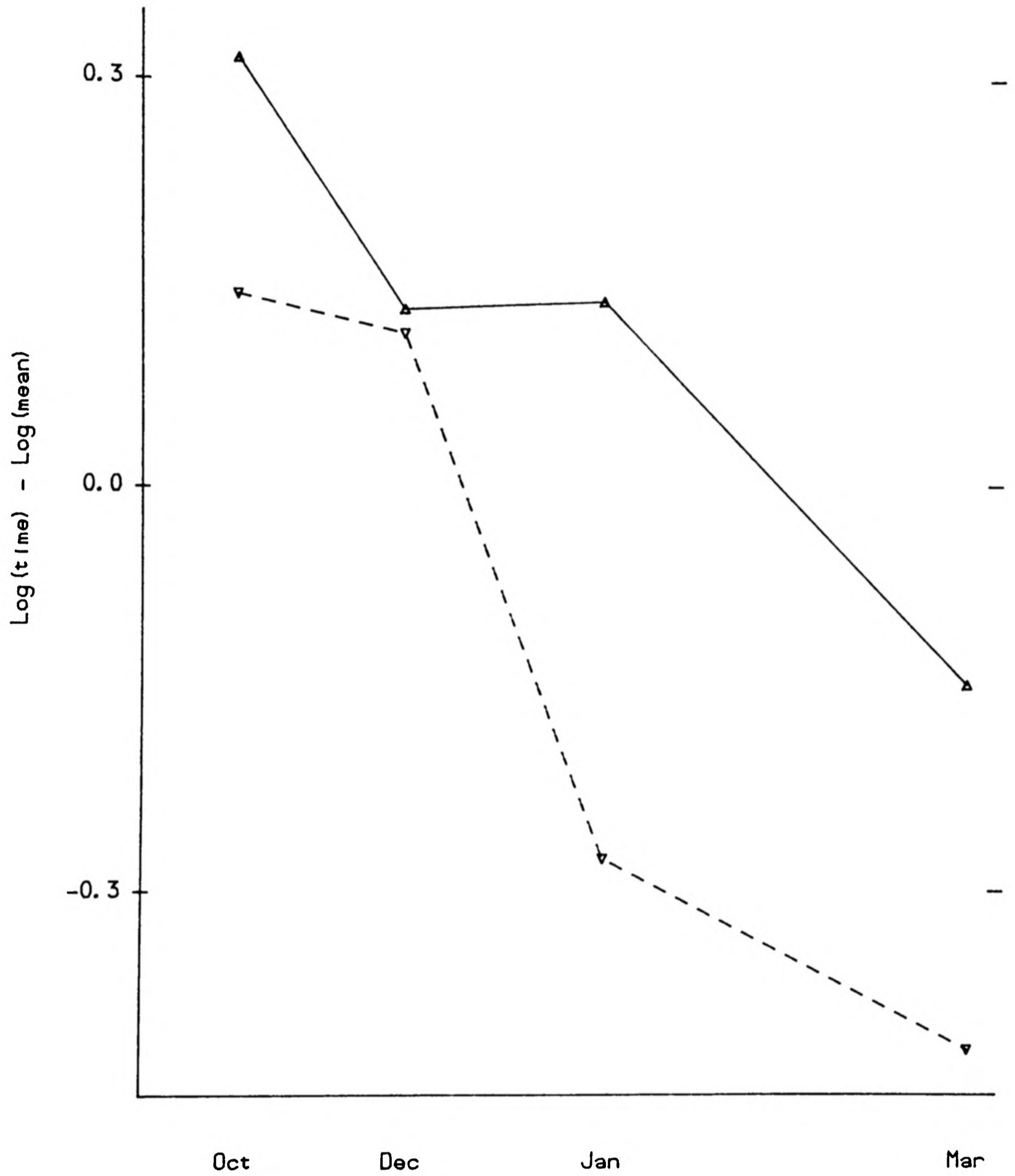
c) Icknield Soils



d) Denchworth Soils

A comparison of the reduction in ionic strength in arable (∇) and pasture (Δ) sites for a) 3 soils b) Fyfield soils c) Icknield soils and d) Denchworth soils.

Figure 8.3.2



A comparison of the reduction in ionic strength in the freely ( $\blacktriangledown$ ) and poorly ( $\blacktriangle$ ) draining pasture sites over the winter period.

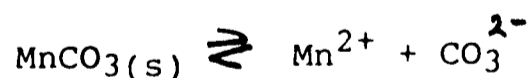
1983. These conditions might be expected to be most pronounced in the wet Denchworth soils which were heavily waterlogged at this time. A comparison of the solutions from the wet and neighbouring dry sites shows a large difference in the concentrations of some solutes. Nitrate concentrations in solutions from the wet sites were only  $10^{-5}$  M, about 100 times less than in those from the dry ones. Mn and Fe concentrations were about  $10^{-4.7}$  M in the solutions from the wete sites, both about 6 times higher than in solutions from the dry sites.

Under an atmosphere of 5%  $\text{CO}_2$  the  $\text{Mn}^{2+}$  activity in soil suspensions maintained at  $\text{pH} + \text{pe} = 15$  is controlled by the solubility of  $\text{MnCO}_3$  (Schwab and Lindsay, 1983) such that

$$\log \text{Mn}^{2+} + 2\text{pH} = 9.5$$

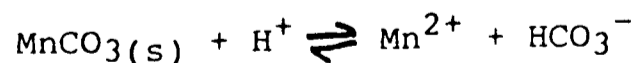
If the mean pH for the solutions from the wet sites for June 1983 is corrected to that expected at this partial pressure of  $\text{CO}_2$ , then the estimated pH will be 6.6. A solution containing  $10^{-4.7}$  M  $\text{Mn}^{2+}$  in equilibrium with  $\text{MnCO}_3$  under a partial  $\text{CO}_2$  pressure of 5% would have a pH of 7.1.

Sposito and Mattigod (1980) used a solubility product for  $\text{MnCO}_3$  of  $10^{-10.4}$  in the GEOCHEM data base.



$$\log K_{\text{sp}} = -10.4$$

which gives,



$$\log K_{\text{sp}} = -0.07$$

Substituting values from the wet Denchworth solutions of  $\text{pH}_{\text{corr}} = 6.6$ ,  $\log \text{Mn} = -4.72$  and  $\log \text{alkalinity} = -2.06$  (approximating bicarbonate for alkalinity) gives an ion activity product of  $-0.18$ , which is in fairly close agreement with the one quoted above.

These findings suggest that in anaerobic soil conditions  $\text{MnCO}_3$  does control the concentration of Mn in the soil solutions of Denchworth soils.

### 8.5 Fertilizer Applications

Appendix 7 presents the available information on the fertilizer histories of the sampling sites. Much of this information was too general to be of use in investigating the effects of fertilizer applications on the chemical compositions of the soils studied, but some was sufficiently detailed to be of interest.

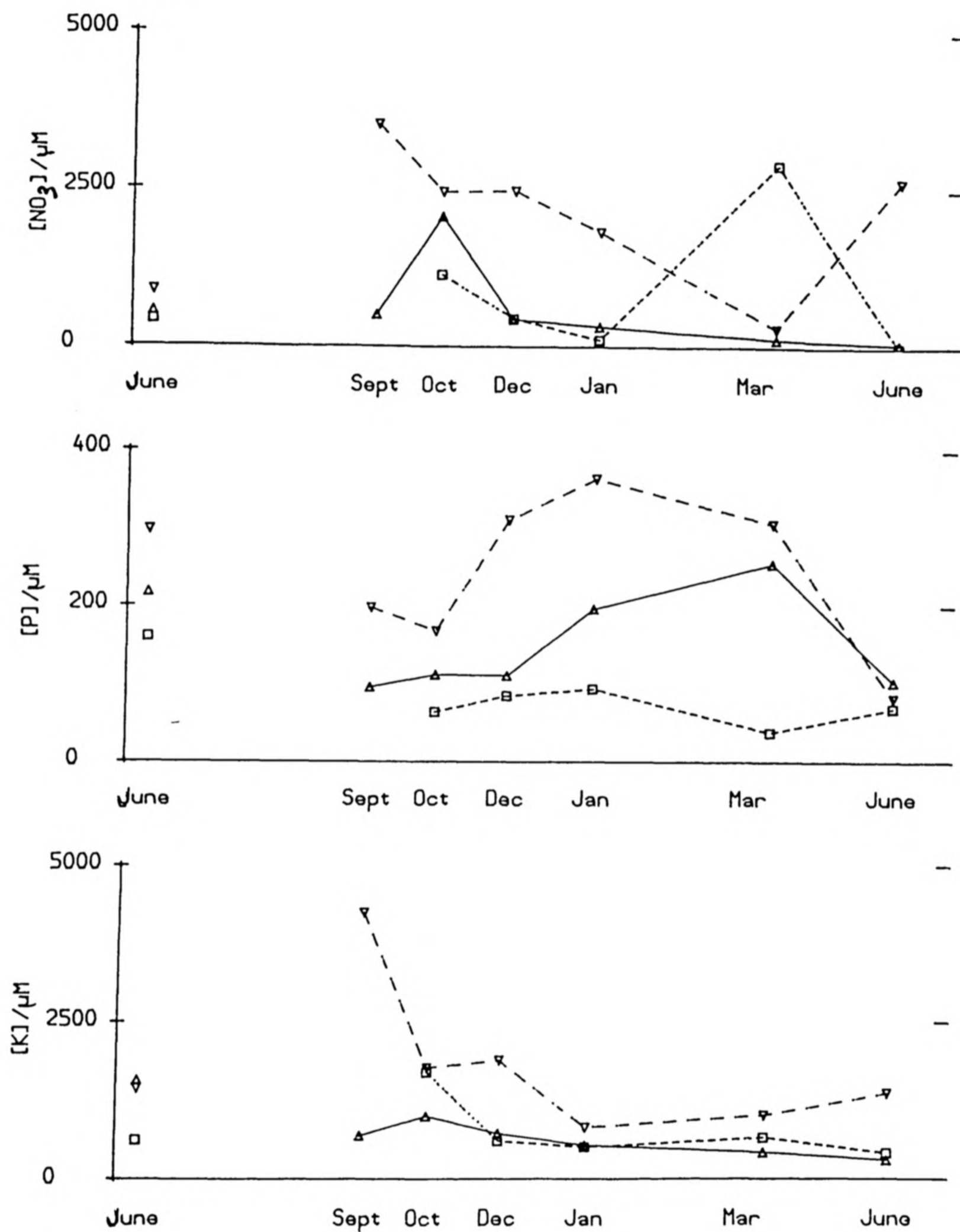
#### Fyfield Soils

Figure 8.5.1 shows temporal changes in the chemical composition of the soil solutions from three Fyfield soils; a) pasture receiving no fertilizer, b) pasture receiving fertilizer and c) arable receiving fertilizer. The fertilized pasture field received an autumn application of 50 kg/ha 5.24.24 NPK and a spring application of 30 kg ha<sup>-1</sup> N. The arable field received 4 kg ha<sup>-1</sup> N, 14 of P and 25 of K in the autumn and 55 kg ha<sup>-1</sup> N in March 1984. The graphs illustrate the rapid release of N and K from the fertilisers and a much slower release of P. They also illustrate the more rapid loss of nitrate from the soil solution following the March application to the arable field in contrast to that of K.

#### Slurry Application

One of the fields on Kingston series (Field 4) received an application of slurry between October and December 1983, and 28 kg ha<sup>-1</sup> N on 5/3/84. Temporal changes in the DOC, Abs<sub>350</sub> and nitrate in the soil solution from this field are shown in Figure 8.5.2 and are compared with another Kingston soil (Field 9) which was receiving only inorganic fertilizers. Decomposition of the slurry

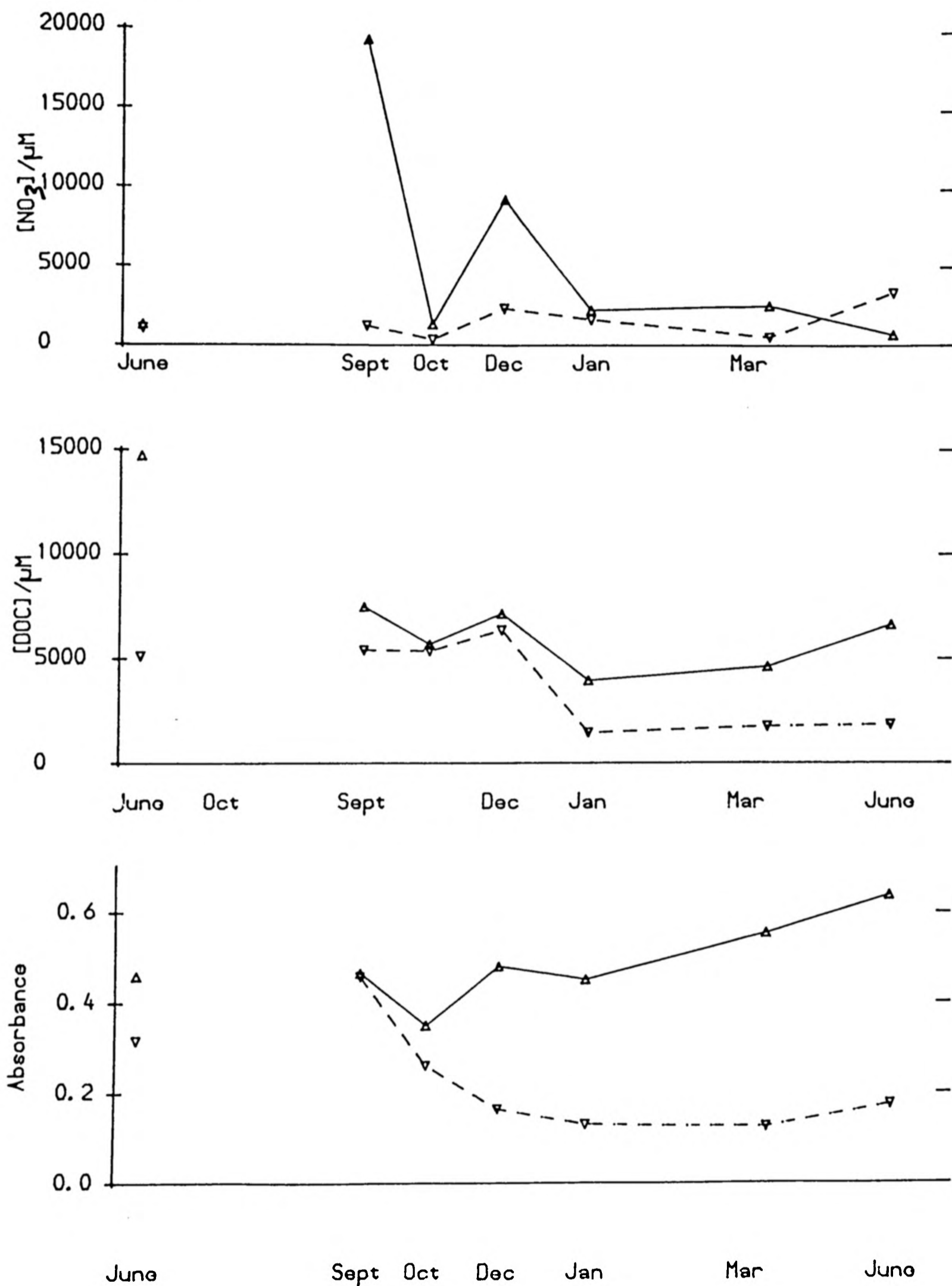
Figure 8.5.1



Changes in the concentrations of  $\text{NO}_3$ , P and K in the soil solutions of three Fyfield soils in response to fertilizer applications.

( $\blacktriangle$ ) unfertilized pasture, ( $\nabla$ ) fertilized pasture, ( $\square$ ) fertilized arable.

Figure 8.5.2



Changes in the concentrations of  $NO_3^-$  and DOC and  $Abs_{350}$  in the solutions of two Kingston soils in response to fertilizer and slurry applications. (▽) inorganic fertilizer only. (△) both inorganic fertilizer and slurry.

reversed the general decrease in DOC and Abs<sub>350</sub> over the winter. The spring N application was just before the March sampling. It would appear that the fertilizer had not dissolved by the time of sampling. By the June sampling apparently all of the nitrate applied had been lost from the soil solution. This soil also exhibited the Birch effect on rewetting after the dry summer period.

#### 8.5 Summary and Conclusions

Concentrations of most of the solutes studied showed significant temporal changes over the sampling period. These changes are almost certainly less than the maximum possible range for these soils because no soil solution samples were obtained during the dry summer months. The ranges in concentration were greatest for those solutes which do not interact strongly with the soil and those whose solubility is affected by redox reactions. The changes in concentration were not precisely those that would have been expected had pure water been added to the soil because the rain inputs a considerable amount of certain solutes, notably sodium and chloride.

The dilution of the soil solution over the winter period was similar in soils with different freedom of drainage. In the Denchworth series dilution of the soil solution in the arable fields over winter was much greater than in neighbouring pasture sites. This effect was also found, to a lesser degree in the other soils. Anaerobic conditions resulting in denitrification and reduction of manganese were present in some of the soils at the start of the sampling period and at the wet sites at other times.

The chemical composition of the soil solution may be used to monitor the dissolution and removal of added fertilizers.

## Chapter 9

### Conclusions

Life is the art of drawing sufficient conclusions from insufficient premises.

Samuel Butler, 1835-1902

The soil solution plays a central role in the many chemical reactions which occur in soils. As increasing demands are made on the soil, a greater understanding of the chemical processes which occur in soils is necessary to ensure that the nature and magnitude of the changes incurred in the soil can be assessed.

Although the importance of the soil solution is acknowledged, its study as a separate phase of the soil has been hindered by the lack of a convenient method for obtaining representative samples of the soil solution. Much of the available data relates to soils which have been amended in some way. The soil solutions of unaltered field soils have rarely been studied, nor has the magnitude of the variability of these solutions been estimated.

The aim of the work undertaken was to find a suitable method for extracting samples of soil solution from unaltered field soils and then to establish the normal concentration ranges of a number of solutes in the soil solution.

Immiscible displacement of the soil solution by centrifuging a soil sample with a dense, water-immiscible liquid was considered the most suitable method for routinely obtaining samples of the soil solution. The method was found to be swift, free from interferences and required minimal sample preparation. Although good yields of soil solution were obtained from soils at or near field capacity, little or no soil solution could be extracted from soils sampled during the summer months. Plasma emission spectrometry was used to

determine a wide range of solutes, and was well suited for routine use. However, the concentrations of a number of trace solutes were too low to be determined by this method.

Initial studies showed that the chemical composition of the soil solution was very variable over both large and small distances. Frequently quite large differences were found between solutions extracted from subsamples of a mixed soil sample. This variability was largest for nutrient solutes (K,  $\text{NO}_3$ , P) and solutes whose solubility might be expected to be dependent (directly or indirectly) on redox (Fe, Mn, Cu). When bulked and unbulked samples were compared it was found that bulking and subsampling reduced the variability of non-nutrient solutes more than that of nutrient solutes, indicating that the latter were more heterogeneous over short distances.

Over larger distances, the two main factors influencing variability were found to be soil pH and fertilizer applications. The soil solutions of acid soils contained more Al, Fe etc. and less Mg and Ca than neutral and calcareous soils. Solutions from fertilized soils contained higher concentrations of  $\text{NO}_3$  and K than those from unfertilized soils.

In view of the large differences found between, in effect, agricultural and non-agricultural soils it was decided to limit more detailed study to agricultural soils. The major constraints in designing the main experiment were the limited time and resources available, and so the study was limited to a one year period and covered, in the main, only grassland sites. The sampling programme was designed to allow the factors contributing to the variability in the chemical composition of agricultural soils to be separated and their significance assessed. A small number of arable and wet

pasture sites were also sampled to allow a semi-quantitative comparison to be made between them and neighbouring grass sites.

The findings of the main experiment demonstrated that a combination of natural within-soil series variability and management practices resulted in the concentrations of most solutes being significantly different in different fields on the same series, compared to an estimated short-range variability. Only in the case of nitrate did fertilizer applications swamp the significant differences found between different soil series.

The comparisons between grass sites, arable sites and wet pasture site, although of limited statistical value, illustrate that the way in which rain water percolates through a soil profile has considerable influence on the chemical composition of the soil solution. Where drainage is inhibited and fluxes of solutes from the topsoil are reduced the soil solution tends to be more concentrated. When the degree of soil structure is reduced by ploughing the soil solution is more fully replaced by percolating rainwater and so soil solution concentrations are lower. In arable soils structure loss is compounded with a lower organic matter content which results in a lower water holding capacity and so there is a greater flux of solutes from the topsoil.

Most of the solutes studied were found to follow a similar temporal trend. Concentrations fell from a maximum in late summer to a minimum in late winter. The magnitude of the temporal changes varies from solute to solute and was found to depend not only on the partitioning of the solute between the soil solution and labile solid phases but on the relative concentration of the solute in the soil solution and in rain water.

From the results discussed in Chapters 6 and 7 it is possible to

estimate the likely errors that might be encountered if generalisations were made from a limited set of samples of the soil solution. Consider a set of data consisting of subsamples from bulked samples taken from within each of three pasture fields on a single soil series. The mean concentration of each solute from this set is likely to agree to within a factor of two for S, Cl, Zn and Cu and four for Na, K, Ca, Mg, Si, P, NO<sub>3</sub>, Ba and Sr with the concentrations found in other neutral or calcareous soils in that area.

Similarly, if we wish to estimate the concentration of a solute at a different season then the mean will provide an estimate to within a factor of two for alkalinity, P, Si and Fe and to within a factor of three for Na, Ca, Mg, Ba, Sr, Cu and S.

The work reported above deals only with the concentrations of solutes in the soil solution from the topsoil and could readily be expanded into two areas. Firstly a study of the speciation of solutes in the soil solution both by experiment and computation. Secondly an extension of the study to cover lower soil horizons and to relate the chemical composition of the soil solution to that of water draining through different soil horizons.

## Appendix 1

### Analytical Methods

#### Al.1 Introduction

The choice of analytical methods for the chemical analyses of the displaced soil solutions was governed largely by the need for sensitive methods which could be used with small volumes of soil solution. A typical volume of solution displaced from a single centrifuge bottle containing 110 g of soil was 6 ml.

Duplicate analyses of the same soil solution showed that analytical error was small compared to the variability between solutions displaced from subsamples of the same soil. In view of this it was decided to run duplicate analyses only occasionally to check the precision of the method.

The small volumes of soil solution which could easily be obtained also placed logistic constraints on the range of analyses which could be carried out. Also the desire to cover as wide a range of soil solutions as was possible limited the time available to perform analyses on the displaced solutions. For example, because many of the trace metals in soil solutions are present at concentrations below those which can be detected by ICP-OES it would have been profitable to use flameless atomic absorption or polarographic techniques for their determination. However, this would have involved spending considerable time in both obtaining and analysing large volumes of soil solution.

#### Al.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

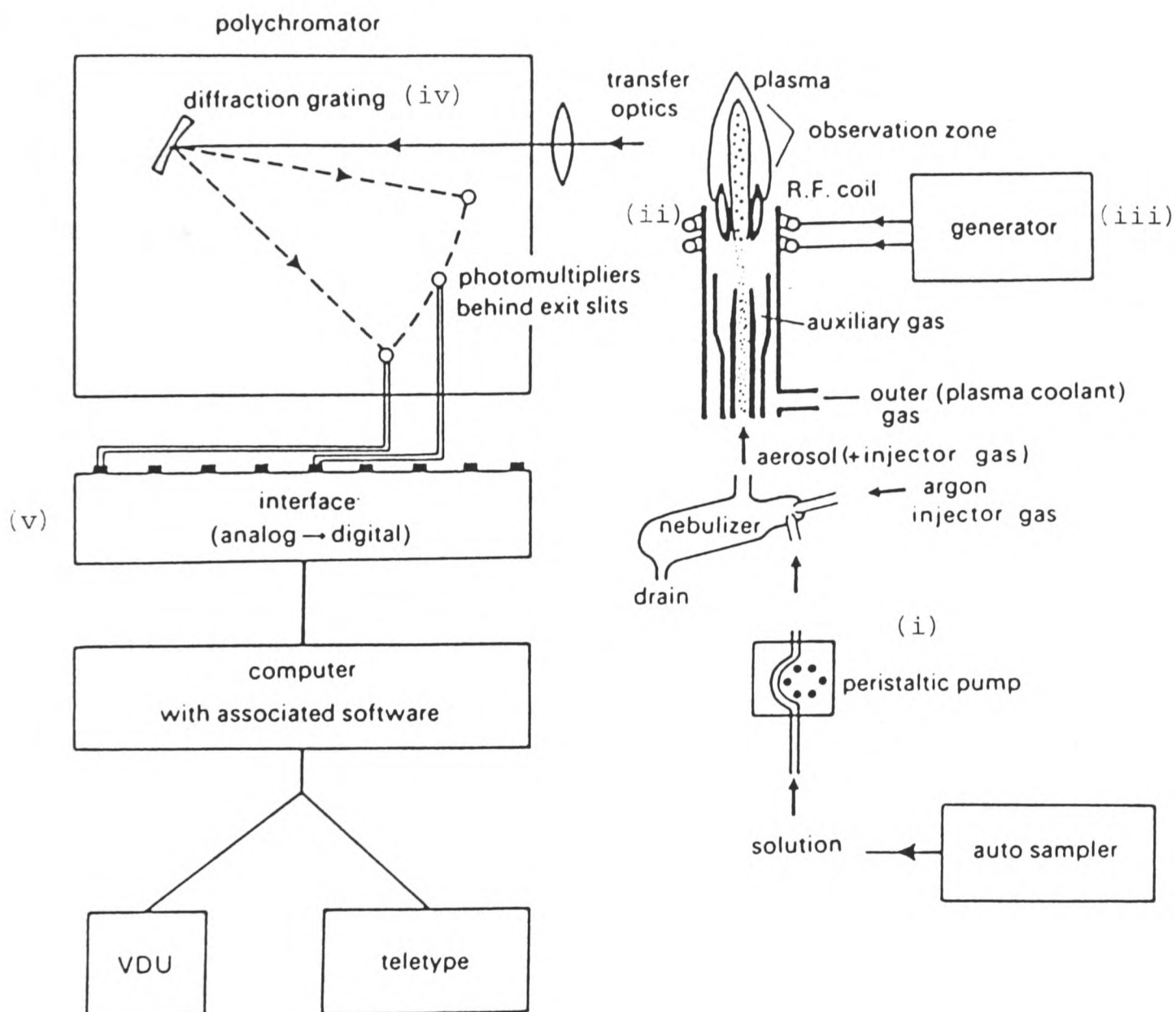
Most of the solutes were determined by ICP-OES. Conceived in the early 1960s, ICP-OES is a method of extraordinary capability. It was developed to overcome the interference problems arising because of the formation of stable compounds in the flames of flame photometric and atomic absorption methods of analysis (Greenfield et al., 1964). The inductively coupled argon plasma is an effective emission source which can be used in conjunction with a suitable spectrometer for the simultaneous determination of a large number of elements. Calibration curves are generally linear over several orders of magnitude. Detection limits are low: for most elements they are in the range 1 - 100 micro grammes per litre. Short term precision is of the order of 1% rsd and accuracy can be made equally good through appropriate calibration with suitable standards.

A schematic diagram of a simultaneous ICP system is set out in Fig. A1.2.1 (from Thompson and Walsh, 1983). The major constituent parts are (i) the sample introduction system (nebuliser), (ii) the ICP torch, (iii) the high frequency generator, (iv) the transfer optics and spectrophotometer and (v) the interface and computer.

A solution of the elements whose concentrations are to be determined is introduced into the ICP torch as an aerosol. The light emitted by the excited atoms or ions in the ICP is converted to an electrical signal by the photomultipliers in the spectrophotometer. The intensities of these signals are compared to those of previously measured standards and the concentrations are computed.

Sample is introduced into a concentric glass Meinhard nebuliser by

Figure A1.2.1



Schematic diagram of a simultaneous ICP system; (i) sample introduction system (nebulizer), (ii) the ICP torch, (iii) the high frequency generator, (iv) the transfer optics and spectrometer, (v) the interface and computer. After Thompson and Walsh, 1983.

a flexible capillary tube. The nebuliser generates fine droplets, which are transported into the axial channel of the plasma. Droplets of greater than 10 microns diameter are removed by an impactor bead. A large proportion of the solution goes to waste with less than 2% of that introduced reaching the plasma torch (this compares with 10% for many atomic absorption nebuliser systems). The equilibration time between the start of a sample introduction and taking a measurement is of the order of 20 seconds compared with a few seconds for an AA system.

Electrical conductivity is initiated in the normally non-conducting Argon gas by a tesla discharge. The plasma is maintained by a high frequency current (27.12 MHz, 1 100 W) flowing in a three-turn induction coil surrounding the tip of the plasma torch which is then inductively coupled to the flowing gas stream and the resultant high temperature plasma (6 000-10 000 K) is maintained by ohmic heating. The cooler "tail flame" above the bright plasma is the region used for spectroscopic measurement.

Introduction of the samples aerosol into the axial channel of the ICP results in very efficient heating and excitation and avoids self absorption which occurs with flame and arc sources

Self-absorption and self-reversal arise when emitted photons are absorbed by the ground state atoms or ions of the same element and so the overall observed radiation is reduced, destroying the proportionality between element concentration and light emitted. The extent to which the ICP succeeds in avoiding these effects is reflected in the very wide range over which linear calibration graphs are obtained.

In the system used for this project light emitted by the ICP is focused on the entrance slit of a Paschen-Runge type spectrometer fitted with a 1080 lines/mm ruled diffraction grating. The intensities of the diffracted radiation at specific analyte wavelengths is measured simultaneously by photomultiplier tubes mounted around the Rowland circle.

The signal produced by the photomultiplier tube is used to charge a microfarad capacitor. By allowing the capacitor to be charged for a specific period (10 s) the signal is "integrated" and the precision is improved. At the end of the analytical cycle the capacitor is discharged and the charge converted to a digital signal before being fed to the computer.

The dedicated minicomputer attached to the ICP-OES stores calibration data, and so converts the measured intensity to a concentration. Computer software allowed for the correction of interferences, for example that of calcium with sulphur (Miles and Cook, 1982). During the analyses, blanks and standards were run at intervals between samples and so correction for instrumental drift could be made to the raw data.

### Calibration

An ARL 34000C ICP-OES linked to a PDP-11/03 minicomputer was used routinely for the analysis of the following 23 elements: Na, K, Ca, Mg, B, Li, Y, Ba, Mn, Cu, Fe, V, Cd, Co, Zn, Mo, Al, Pb, Sr, S, Si, P<sup>1</sup> (the emission lines for each element are shown in Table A1.2.1).

The instrument was calibrated using multi-element and single element standards. The standards were grouped into:- major

metals, trace metals, silicon, sulphur and phosphorus. In all, there were 36 standards. The calibration range for the standards is shown in Table A1.2.1. Generally, calibrations were carried out before each batch of analyses, however the calibration is stable over a period of weeks. A standard of each group (chosen to have concentrations in the range of the solutions being analysed <sup>2</sup>)(see Table A1.2.1) was run after every 12 sample analyses. 1% HCl blanks were run after every 6 analyses (including standards).

Measured concentrations were based on the average of three 10 second integrations, which with preflush required less than 2.8 ml of sample at an uptake rate of 2.4 ml/min.

### Precision

Published data (Thompson and Walsh, 1983) of a survey of typical application studies of ICP-OES shows that precision is of the order of 1% rsd. In trace element analysis, precision is

<sup>1</sup> In the introductory work  $PO_4-P$  was determined by the standard autoanalyser method (Cook and Miles, 1982), whereby orthophosphate reacts with ammonium molybdate in acid solution to form 12-molybdophosphoric acid which is reduced by ascorbic acid to form a blue complex. This method proved to be unsatisfactory for the determination of the phosphate in soil solutions. The results produced were very unreliable. It is thought that this was due to a combination of two factors. Firstly, the high concentration of calcium in many of the soil solutions led to the formation of a precipitate of calcium sulphate. Secondly, that there was unreproducible breakdown of soil solution organo- and poly-phosphates in the heating coil of the auto analyser cartridge.

For these reasons the ICP-OES was calibrated for phosphorus and subsequently total P was determined. The 178.29 nm emission line was used because of its high sensitivity and freedom from interferences (Cook and Miles, 1985).

<sup>2</sup> Trace metal standards of 1.0 mg/l were chosen because standards of very low concentration would have resulted in lower precision.

Table A1.2.1

Emission wavelength, calibration range, standards and detection limits for the solutes determined by ICP-OES.

Element	Wavelength nm	Calibration Range (approx)		Cal. Std.	6 $\sigma$ d.l.	6 $\sigma$ d.l. (logM)
		$\mu\text{M}$				
Na	589.00	220	-87 000	4300	23	-4.638
K	766.49	125	- 2 500	125	31	-4.509
Ca	315.89	30	-12 500	625	0.3	-6.523
Mg	279.08	50	- 4 000	2000	5	-5.301
B	249.68	10	- 900	50	1.7	-5.770
Li	676.78	20	- 1 400	70	0.9	-6.046
Y	371.03	0.06-	110	10	0.01	-8.000
Ba	455.40	0.04-	70	7	0.01	-8.000
Mn	257.61	0.09-	180	20	0.11	-6.959
Cu	324.75	0.16-	160	15	0.20	-6.950
Fe	259.94	1.80-	180	18	0.11	-6.959
V	311.07	0.20-	200	20	0.23	-6.950
Cd	226.50	0.45-	90	10	0.16	-6.796
Co	228.62	0.84-	170	17	0.20	-6.699
Zn	202.55	1.5 -	150	15	0.38	-6.420
Ni	231.60	3.4 -	170	15	0.50	-6.301
Mo	203.03	2.1 -	104	10	0.41	-6.387
Al	308.21	7 -	370	40	4.5	-5.347
Pb	220.35	1.9 -	95	5	1.2	-5.921
Sr	407.77	0.06-	115	11	0.01	-8.000
S	178.73	260	-21 000	3125	19	-4.721
Si	288.16	36	-36 000	1800	7.1	-6.149
P	178.20	16	- 320	160	13	-4.886

significantly reduced as the detection limit is approached.

Precision both within and between batches was estimated by analysing duplicate samples of soil solution in a routine way. The results from these analyses are shown in Table Al.2.2 (within batch) and Table Al.2.3 (between batch).

Table Al.2.4 shows the calculated median relative standard deviations (rsd) both within and between batches. Rsds were not calculated for Li, Y, V, Co, Cd, Ni, Mo, Al, or Pb because the concentrations of these solutes in the solutions analysed were less than could be detected. The same day reproducibility is generally better than 3% for major solutes and better than 10% for minor solutes. Considering the closeness of the concentrations of the minor solutes to the detection limit, these figures are quite acceptable.

Precision over longer periods (5 - 7 months) is poorer: about 5% for major solutes and 10% for trace solutes.

#### Data Correction and Manipulation

The only test of accuracy possible is to compare the corrected values for the standards with their actual values. This is in fact a test of the quality of the correction programme.

Raw analytical data may be corrected by the computer in one of two ways:-

a) by calculating a mean value for each standard and calculating the correction factor needed to bring this mean to the actual value for each standard: sample concentrations are then

Table A1.2.2

Comparison of duplicate analyses carried out on the same day  
All concentrations in  $\mu\text{M}$

Sample Number	Date of Analysis	Na	K	Ca	Mg	B	Li	Y	Ba	Mn	Cu	Fe
111111	16.6.83	287	1450	1020	228	8.6	<0.9	0.02	0.24	16.05	0.20	23.10
11111A	16.6.83	275	1532	1248	292	8.6	<0.9	0.02	0.26	12.70	<0.20	21.31
153213	16.6.83	735	46	3892	328	9.4	5.0	0.02	0.27	14.94	<0.20	4.73
15321C	16.6.83	726	47	3824	326	9.6	5.0	0.02	0.30	16.65	<0.20	4.78
42105Q	19.2.83	853	568	3924	220	4.7	<0.9	0.02	0.04	<5.0	<0.20	4.93
42105R	19.2.83	853	555	3917	219	3.6	<0.9	0.02	0.04	<5.0	<0.20	1.51
562241	06.02.84	129	127	1689	22	2.7	<0.9	<0.01	0.06	<5.0	<0.20	0.56
56224A	06.02.84	128	128	1667	20	2.8	<0.9	<0.01	0.06	<5.0	<0.20	2.18
561252	06.02.84	223	181	1662	70	<1.7	<0.9	<0.01	0.12	<5.0	<0.20	0.81
56125B	06.02.84	271	185	1664	70	<1.7	<0.9	<0.01	0.13	<5.0	<0.20	0.63
766262	11.07.84	704	50	3887	185	3.3	<0.9	0.02	0.12	<5.0	0.35	1.32
76626B	11.07.84	677	50	3884	181	3.2	<0.9	0.02	0.12	<5.0	0.35	1.33
762272	11.07.84	303	190	2249	71	5.1	<0.9	0.02	0.09	<5.0	0.38	1.65
76227B	11.07.84	300	190	2241	71	4.2	<0.9	0.01	0.09	<5.0	0.32	1.61

Sample Number	Sr	S	Si	P
111111	0.95	854	240	309
11111A	1.13	1108	310	300
153213	7.51	349	662	14
15321C	6.80	345	659	13
42105Q	1.99	650	141	21
42105R	1.96	639	138	20
562241	1.20	142	78	16
56224A	1.19	144	78	15
561252	1.16	215	254	49
56125B	1.15	211	250	43
766262	2.40	394	125	33
76626B	2.33	387	123	32
762272	1.53	179	118	37
76227B	1.53	181	118	38

Table A1.2.3

Comparison of plasma analyses carried out on different days on duplicate samples. All concentrations in  $\mu\text{M}$ .

Sample Number	Date of Analysis	Na	K	Ca	Mg	B	Ba	Mn	Cu	Fe
662252	11.05.85	304	387	2299	83	0.8	0.186	0.14	<0.20	0.83
662252	12.12.84	318	422	2547	89	0.9	0.208	0.15	<0.20	0.97
662271	11.05.85	335	382	2132	78	4.2	0.085	0.08	0.25	2.15
662271	12.12.84	354	418	2346	82	4.6	0.005	0.09	0.26	2.19
766261	11.07.85	664	86	3999	197	3.3	0.133	0.32	0.33	2.00
766261	12.12.84	733	98	4463	217	3.4	0.148	0.37	0.34	2.13
772271	11.07.85	304	187	2066	66	4.7	0.082	0.27	0.35	1.52
762271	12.12.84	319	194	2424	75	4.1	0.085	0.05	0.34	1.37
Sample Number	Zn	Sr	S	Si	P					
662252	0.28	1.68	335	211	29					
662252	0.38	1.75	329	237	34					
662271	0.38	1.47	208	157	38					
662271	0.42	1.56	220	181	43					
766261	0.56	2.44	449	146	40					
766261	0.75	2.62	481	169	41					
762271	0.38	1.40	165	109	34					
762271	0.32	1.58	187	120	32					

multiplied by this factor; or

b) by assuming a linear drift between two chosen standards and calculating a correction factor for each sample by interpolation. As the instrument was stable the former of these two methods was used. The rsds of the standards used for a typical batch of analyses is shown in Table A1.2.4. The rsds for all of the solutes are better than 2% (except for lead which was always below the detection limit in the soil solutions analysed.)

The dedicated minicomputer was used extensively for manipulating the data. It was used to correct the results for the effects of dilution due to, for example, acidification, and also to convert the concentrations from  $\mu\text{g/l}$  to  $\mu\text{M}$  and log molar units.

Other software allowed flexibility in the presentation and storage of the data and its conversion into a format suitable for transfer to a mainframe computer via a floppy disk.

#### Detection limits

Because ICP-OES is an emission method of analysis the noise level of the signal is much greater than that of the background. When a 1% HCl blank is being aspirated the background is very stable as all the noise is simply the noise from the plasma background plus that from the photomultipliers and electronics.

For these reasons a detection limit based on six times the standard deviation of the blank measurements is quoted and used as a criterion for most of the analyses. These six detection limits are shown in Table A1.2.1.

Table A1.2.4

Element	Precision		Correction
	Within	Between	Error
	Batch	Batch	
	rsd(%)	rsd(%)	rsd(%)
Na	2.8	3.6	0.8
K	1.6	6.2	1.9
Ca	0.8	7.4	1.9
Mg	0.4	5.8	1.7
B	2.4	7.3	0.8
Li			1.6
Y			0.5
Ba	1.8	7.7	1.3
Mn	12.0	9.2	0.9
Cu	6.1	2.1	0.8
Fe	6.8	5.8	1.3
V			0.9
Cd			0.4
Co			0.3
Zn	13.0	11.3	0.9
Ni			0.9
Mo			1.2
Al			0.9
Pb			3.7
Sr	1.1	4.6	0.6
S	1.2	3.0	0.3
Si	1.2	9.1	0.5
P	2.0	6.4	0.9

Detection limits for each batch of analyses were calculated from the standard deviations of the blanks run during the analyses. Blank correction by the computer subtracted the mean blank reading for each element from all of the analyses prior to standard corrections. The maximum six<sup>σ</sup>detection limits are shown in Table A1.2.4. Unless otherwise stated these detection limits were used as a criterion for the exclusion of results below those values from any discussion or statistical analysis.

### Summary

The ICP-OES was used for the routine analysis of displaced soil solutions. It allowed the accurate and swift determination of a large number of solutes from a small volume (2.8 ml) of solution and was ideally suited to the chemical analyses of displaced soil solutions.

### A1.3 Chloride

Chloride was determined by an automated colorimetric method (Cook and Miles, 1980) using a Technicon Autoanalyser II fitted with a chloride cartridge. Chloride reacts with mercuric thiocyanate, releasing the thiocyanate ion. In the presence of ferric ions a highly coloured thiocyanate complex is formed, the absorbance of which is proportional to the chloride concentration. Absorbance is measured at 480 nm in a 2 cm flow cell.

A modified sample tray was used which allowed the storage vials to be sampled directly without having to decant them into special cups. This eliminated any wastage of sample as only the solution drawn into the machine (0.1 ml) was lost.

Samples were run at 50 per hour with a 4:1 sample:wash ratio.

### Standards

Standards were prepared in the range 0 - 100 mg/l (0 - 28 000  $\mu\text{M}$ ) Concentrations were recorded in mg/l and later converted to  $\mu\text{M}$ . The calibration graph was approximately linear over this range. The detection limit was 0.5 mg/l (14  $\mu\text{M}$ ). RSDs were typically around 1%. Accuracy in calibration was better than 2%.

### Al.4 Nitrate

Combined nitrate and nitrite nitrogen was determined in the displaced solutions using the automated colorimetric method of Henricksen and Selme-Olsen (1970).

Nitrate is reduced to nitrite by a copper-cadmium reductor column. The nitrite ions then react with sulphanilamide under acidic conditions to form a diazo compound which complexes with N-1-naphthylethylenediamine dihydrochloride to form a reddish purple azo dye. The absorbance of this dye is measured at 550 nm in a 2 cm flow cell.

This method was chosen rather than the alternative nitrate method, (Henricksen, 1965) where the nitrate is reduced by hydroxylamine in solution, because it does not suffer from interference from dissolved organic matter and has greater sensitivity (10 times). The greater sensitivity allowed a fifteen fold dilution of the sample in the autoanalyser cup by automatic pipette. This meant that only 50  $\mu\text{l}$  of sample was used instead of 0.3 ml.

Standards in the range 0 - 60 mg/l  $\text{NO}_3\text{-N}$  (0 - 4 300  $\mu\text{M}$  N) were prepared and were diluted in the same way as the samples. The calibration graph was essentially linear over this range. The rsd of the standards for this method was  $\pm 2\%$ .

#### Al.5 Alkalinity and pH

Alkalinity and pH were measured on a 1.00 ml sample of solution. A Radiometer pH meter fitted with pH and calomel reference electrodes was used to measure pH. The electrodes were standardised with pH 7.00 and pH 4.01 buffers.

Samples were stirred for 30 seconds, then the pH was allowed to stabilise before a reading was taken.

The total alkalinity of the solution was determined by titrating the 1.00 ml sample with 0.02 N sulphuric acid (standardised against 0.020 N sodium hydrogen carbonate) using a Radiometer titrimeter fitted with a 2.5 ml digital burette. The burette was operated at one tenth volume to give an effective volume of 0.25 ml. The titration curve was plotted directly onto a chart recorder and the end point estimated by a Gran plot.

The total alkalinity is the sum of the bicarbonate alkalinity and the buffering capacity of weak acid groups on the dissolved organic matter in the solution. The titration was continued to pH 2.5 to ensure that all of these groups were protonated.

#### Accuracy

Because of the large volume of solution required for the

titration, duplicate analyses were not routinely carried out. However the accuracy can be estimated from the standardisation titrations. The error arises mainly because a graphical method is used to estimate the end point. The limit of the resolution of this method is about  $\pm 50$  micro equivalents/l. This represents a potential error of between 1 and 10% depending on the alkalinity of the sample.

#### The Effect of Storage on pH

Rainwater samples, which are very poorly buffered, become alkaline if stored in polycarbonate vials for some time (D Kinniburgh, private communication). Polycarbonate ( $-\text{[-OCOORO-]}_n-$ ) is essentially the polyester derived from 'carbonic acid'. Gradual degradation of the polymer may release small amounts of carbonate into solutions during storage causing a subsequent rise in the pH of poorly buffered solutions.

To test if this is the case with soil solutions a number of samples with low alkalinity were titrated both before and after storage for some weeks. The results of these titrations are shown in Table A1.5.1.

The changes in alkalinity are within the errors estimated above. However, the pH has in all cases increased by about 0.1 pH units. This may well be due to degassing of carbon dioxide from the solutions, or it may be due to a reaction with the storage vials. For this reason it was felt that to quote solution pHs to any more than one decimal place would be misleading.

#### A1.6 Dissolved Organic Carbon

Table A1.5.1

Duplicate determinations of alkalinity and pH

Sample	Date Ext.	Date Anal.	Alkalinity ( $\mu$ equiv/l)	pH
01	21.11.84	29.11.84	275	6.232
01	"	07.02.85	284	7.023
11	28.11.84	29.11.84	235	6.829
11	"	07.02.85	216	6.970
21	6.12.84	10.1.85	40	5.480
21	"	01.02.85	80	5.550

Dissolved organic carbon (DOC) in the displaced soil solutions was determined automatically by a TOCSIN (Phase Separation Ltd., Wales) aqueous carbon analyser.

This method is essentially an automated version of the method of Cropper et al. (1967).

Briefly, sample is pumped from an auto sampler, through a sparging system into an oxidation furnace, where, over a reduction column, carbon dioxide from the DOC is reduced to methane which is then burnt in a standard flame ionisation detector (FID).

Dissolved inorganic carbon is removed in the sparging system by acidification with dilute nitric acid which liberates inorganic carbon as carbon dioxide. The carbon dioxide produced is removed from solution in a mixing coil by a stream of carbon dioxide free air, which is then removed in a debubbler.

The solution is then pumped through a ceramic bead oxidation furnace at 900°C. High temperature steam is produced which acts as a carrier gas. Organic carbon is quantitatively converted to carbon dioxide. The outflow from the furnace is mixed with nitrogen before the steam is removed by condensation and passage through a phase separator. The gas stream is then mixed with hydrogen and passes over a nickel catalyst at 450 °C where the carbon dioxide is reduced to methane.

The methane is burned in a conventional FID. The signal produced is directly proportional to the DOC concentration.

Standards were prepared from stock potassium hydrogen phthalate solution in the range 0 - 20 mg/l (0 - 1700 µM) carbon. Four ml

of solution is required per analysis, so soil solutions were generally diluted by a factor of ten by automatic pipette. Samples of very high or very low DOC content were diluted accordingly. Standards were diluted in exactly the same way. This also brought the solutions within the optimum operating range of the machine. Samples were run at a rate of one every seven minutes with a sample:wash ratio of 6:1. Output was recorded both digitally and on a chart recorder.

The precision of the method was estimated at  $\pm 4\%$ .

#### A1.7 Visible Absorption

The displaced soil solutions were generally found to be straw coloured. The 'colour' of the solutions was quantified by measuring their absorbance at 350 nm wavelength. 350 nm is close to the UV-visible boundary, and is a convenient wavelength at which to record the absorbance. It was chosen as a reference because it usually gave an absorbance reading of between 0.1 and 0.5 in a 10 mm cell. The shape of the UV-visible absorption spectra of a number of soil solutions have been found to be similar (Kinniburgh and Miles, 1983).

The absorbance was measured in 1 cm silica cells at 350 nm in a Pye-Unicam UV-Visible spectrophotometer.

#### A1.8 Charge Balance

The chemical analyses, for the most part, have been shown to be fairly precise. Accuracy, however is much more difficult to estimate.

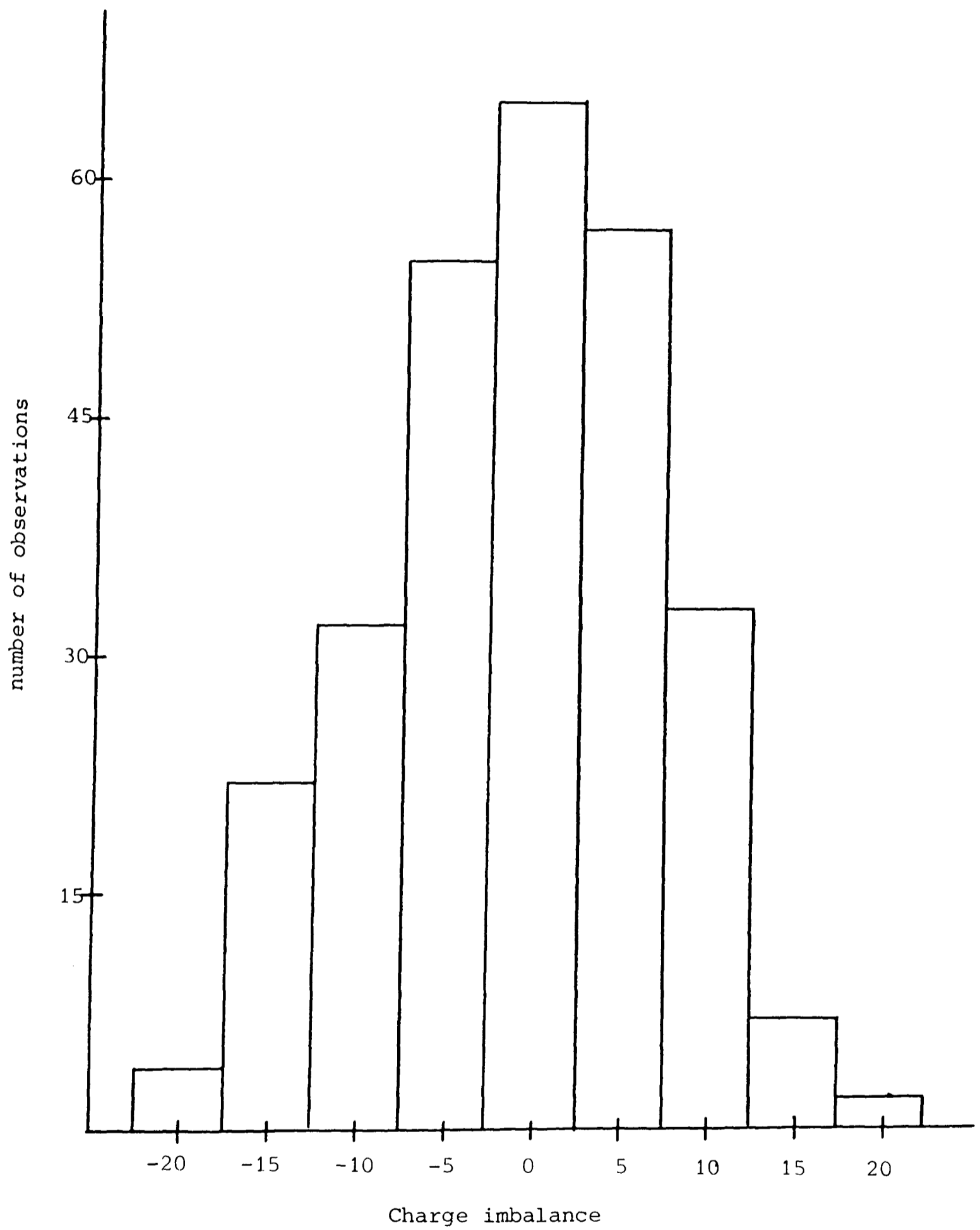
As all of the major solutes of the solutions were measured it is possible to use a calculation of charge balance as a test of the overall accuracy of the individual analyses. The results from the main experiment were chosen for this test. The solute concentrations incorporated in the charge balance calculation were: Na, K, Ca, Mg, S, P, Cl, NO<sub>3</sub> and alkalinity. Na and K were assigned a charge of +1, Ca and Mg a charge of +2, S was assumed to be all sulphate and assigned a charge of -2, P was assumed to be all orthophosphate and assigned a charge of -1. Cl and NO<sub>3</sub> were each assigned a charge of -1, as was the alkalinity. In solutions of the pH range encountered in these soil solutions all of the silicic acid would be uncharged.

The ions above account for more than 99% of the ionic species in the solutions. A histogram of the charge imbalance expressed as a percentage of the total cationic charge is shown in Figure A1.8.1. More than 95% of the analyses lie within a range of  $\pm 15\%$  and the distribution is centred on zero. Considering the large number of separate analyses combined in the charge balance this is very satisfactory.

There is no correlation between charge imbalance and DOC or visible absorbance, however, analyses with a high charge imbalance have a high DOC concentration. This might indicate that DOC with variable charge is causing some of the discrepancy in the charge balance calculation.

#### A1.9 Summary of Soil Solution Analyses

The chemical analytical methods were chosen because of their sensitivity, swiftness and precision. They were shown to be

Figure A1.8.1

Histogram of charge imbalance (expressed as a % of the total cation charge) for soil solutions from the main experiment.

accurate within prescribed limits, and when tested together in the form of a charge balance are quite acceptable.

#### Al.10 Soil Analyses

A number of analyses were carried out on whole soil samples.

The gravimetric moisture contents of soil samples were determined from approximately 70 g subsamples of soil. These were dried in an oven at 110°C for 24 hours and the weight change recorded.

#### Organic Carbon

The organic content of some of the soil samples was determined by the modified Tinsley method proposed by Kalembasa and Jenkinson (1973).

A sample of air dried soil containing between 5 and 15 mg of organic carbon was refluxed in acidic potassium dichromate for 20 minutes. The amount of dichromate consumed was determined by titrating the suspension with acidic ferrous ammonium sulphate. The results obtained were expressed as a percentage of the air-dried soil weight in terms of oxidisable organic matter.

#### Soil Digests

Acid digests were performed on a subsample of some of the soil samples. Subsamples were air dried, disaggregated, and sieved through a 2 mm sieve before being oven dried at 105°C. Samples of 0.250 g were heated in a thick-walled 15 cm pyrex test tube with 1 ml of concentrated nitric acid for 75 minutes. After cooling, 9

ml of glass-distilled water were added and the samples thoroughly mixed. <sup>(Kinniburgh and Beckett, 1983)</sup> After settling, the supernatant solution was removed and analysed by ICP-OES. Twenty-fold dilutions were carried out for the separate determination of Ca, Mn, Al, S and P by ICP-OES.

Blank digests were run and analysed, but the level of possible reagent contamination was so low that blank values were not subtracted from the results. The results of the chemical analyses of the blank digests are shown in A1.11, below.

The precision and accuracy of these results was the same as that of the routine soil solution analyses for the major solutes, but is likely to be far better for the trace metals as their concentrations were much higher.

#### Cation Exchange Capacity

The cation exchange capacity (CEC) of the soils in the main field experiment was determined on air dried, sieved (2 mm) subsamples from the first sampling. A scaled-down version of Bascomb's (1964) method was used.

Cations are displaced from the soil by barium chloride solution buffered at pH 8.1 with triethanolamine to prevent the dissolution of soil carbonates. After washing, the barium is displaced by the addition of magnesium sulphate (compulsive displacement). Barium sulphate is precipitated and magnesium ions replace barium ions on the exchange sites. The amount of magnesium removed from solution is determined by difference. The magnesium concentration remaining after exchange was determined by ICP-OES.

## A1.11 Chemical Analyses of 'Blanks'

Chemical analyses of MilliQ water shaken with Arklone or Arklone, glass beads and nylon gauze; also a chemical analysis of the acid blank from the soil digests. The six  $\sigma$  detection limits are shown in the first column for comparison. All concentrations are in  $\mu\text{M}$ .

Solute	6 $\sigma$ d.l	Arklone Blanks				With Beads	Acid Blank
		A	B	C	D		
Na	23	1.5	0.4	0.5	1.5	22	7.3
K	31	0.1	2	1	1	2	3
Ca	0.3	0.6	0.0	0.6	5.9	3.8	1.7
Mg	5.0	0.4	0.8	1.8	0.2	0.3	2.0
S	19	5	2	3	3	5	11
Si	7.1	0.3	0.6	0.3	0.1	2.5	0.1
P	13	1	1	3	0	7	0
Cl	14	0	5	8	11	0	-
NO <sub>3</sub>	1.5	0	-	0.7	0.7	0.5	-
DOC	250	93	23	5	191	-	-
B	1.7	0.2	1.2	0.8	0.1	0.2	0.4
Li	0.9	0.1	0.0	0.4	0.0	0.2	0.4
Y	0.01	0.002	0.002	0.008	0.003	0.001	0.01
Ba	0.01	0.006	0.006	0.009	0.000	0.003	0.000
Mn	0.11	0.01	0.04	0.06	0.01	0.06	3.43
Cu	0.20	0.06	0.05	0.02	0.03	0.01	0.09
Fe	0.11	0.12	0.09	0.07	0.02	0.57	0.07
V	0.23	0.02	0.02	0.05	0.00	0.02	-
Cd	0.16	0.00	0.02	0.01	0.00	0.01	0.03
Co	0.02	0.04	-	0.02	0.02	0.02	0.03
Zn	0.38	0.08	0.01	0.01	0.08	0.08	0.20
Ni	0.50	0.00	0.29	0.00	0.10	0.50	0.22
Mo	0.41	0.10	0.00	0.00	0.00	0.00	0.11
Al	4.5	0.6	0.0	1.8	0.1	0.1	0.37
Pb	1.2	0.1	0.3	0.2	0.0	0.1	0.0
Sr	0.01	0.00	0.01	0.00	0.00	0.00	0.00

Dates on which Arklone blanks were obtained: A 11/5/84, B 19/02/83, C 16/6/83, D 25/06/85.

## Appendix 2

### Statistical Analyses

#### A2.1 Introduction

The major part of the statistical analyses consisted of multi-level analyses of variance of large sets of data to enable the significance of several interacting factors to be determined. The analyses were carried out using GENSTAT, a general statistical program, (Alvey et al, 1983) which enabled rapid statistical analyses of large volumes of data.

Care was taken to ensure that the basis of the programs was statistically rigorous and gave the appropriate form of analysis.

Split plot analyses are commonly applied to experimental results where several successive observations of the same variable have been recorded on each experimental unit, for example measurements of a variable repeated a number of times. The assumptions required for such an analysis are rarely satisfied in experimental situations (Rowell and Walters, 1976).

Contrasts over time may be made by analysing the data for each time separately and performing orthogonal contrasts between pairs of observations taken at different times (Yates, 1982). The investigation of repeated observation data may also be considered as a multivariate analysis which is as valid but computationally more complex (Cole and Grizzel, 1966).

The use of a computer program such as GENSTAT renders multilevel analyses of variance no more difficult than repeated uni-variate analyses and removes the need for a second analysis to test for

significant temporal changes. Multi-variate analyses were performed by means of GENSTAT programs.

#### A2.2 ANOVAR of the data from the Wytham/Nuneham Courtenay experiment

Programme for the initial ANOVAR of the results from the Wytham/Nuneham Courtenay experiment. The program reads in values from a file which contains the data for a single solute. The file has the same sequence of numbers as Table 5.4.1. The GENE statement instructs the program to read the data into the different FACTORS. The last factor in the list is the one which changes most frequently. The first factor changes least frequently.

```
'REFERENCE' SODIUMNC
'UNIT' $96
'OUTPUT' 2
'INTEGER' NTIME =1...8
'NAME' SOIL =CLAY,SANDY
'FACT' TIME$NTIME
      : MATERIAL$SOIL
      : TMHOLE$3
      : SAMPLE$2
      : HOLE$36=2(1...36)
'GENE' TIME, MATERIAL , TMHOLE,SAMPLE
'INPUT' 2
'READ/NUN=V' NA
'INPUT' 1
'BLOCK' SAMPLE
'TREAT' TIME *MATERIAL + TIME.MATERIAL.HOLE
'ANOVA' NA
'RUN'
'CLOSE'
'STOP'
```

This program separates the between-hole and the within-hole variances to allow an estimate of short range variability.

```
'REFERENCE' WYTHAMNUNEHAM
'UNIT' $72
'OUTPUT' 2
'INTEGER' NTIME =1...6
'NAME' SOIL =CLAY,SANDY
'FACT' TIME$NTIME
      : MATERIAL$SOIL
      : TMHOLE$3
      : SAMPLE$2
      : HOLE$36=2(1...36)
'GENE' TIME, MATERIAL , TMHOLE,SAMPLE
'INPUT' 2
'READ/NUN=V' NA
'INPUT' 1
'BLOCK' SAMPLE/HOLE
'TREAT' TIME *MATERIAL
'ANOVA' NA
'RUN'
'CLOSE'
'STOP'
```

A2.3 ANOVAR of the data from pasture sites

The GENSTAT program used for multi-level analysis of variance of the pasture fields.

```
'REFERENCE' ANOVAR
'UNITS'    $252
'OUTPUT' 2
'FACTORS' TIMES $ 7
           : SOILS $ 6
           : FIELDS $ 3
           : SAMPLES $ 2
'GENERATE' TIMES,SOILS,FIELDS,SAMPLES
'INPUT' 2
'READ' CONCS
'INPUT' 1
'BLOCKS' SAMPLES
'TREATMENTS' TIMES*(SOILS/FIELDS)
'ANOVAR' CONCS
'RUN'
'CLOSE'
'STOP'
```

A2.4 ANOVAR of the data in the pasture/arable comparison

The GENSTAT program . which was written to  
execute the ANOVAR to compare pasture and arable sites

```
'REFERENCE' PARR
'UNITS' $ 144
'OUTPUT' 2
'FACTORS' SOILS $ 3
      :   LOCNS $ 2
      :   LANDU $ 2
      :   TIMES $ 6
      :   SAMPLES $ 2
'GENERATE' SOILS,LOCNS,LANDU,TIMES,SAMPLES
'INPUT' 2
'READ' CONCS
'INPUT' 1
'BLOCKS' LOCNS/SAMPLES
'TREATMENTS' TIMES * (SOILS/LANDU)
'ANOVAR' CONCS
'RUN'
'CLOSE'
'STOP'
```

A2.5 ANOVAR of the data in the pasture/wet pasture comparison

The GENSTAT program to execute the ANOVAR to compare the wet and dry pasture sites.

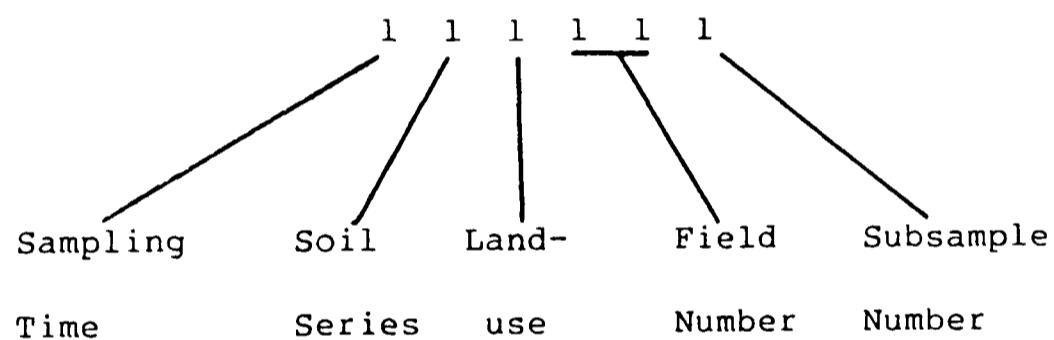
```
'REFERENCE' TOPOGRARHYANOVAR
'UNITS' $ 48
'OUTPUT' 2
'FACTORS' TIMES $6
      :      LOCNS $2
      :      TOPOG $2
      :      SAMPLES $2
'GENERATE' TIMES,LOCNS,TOPOG,SAMPLES
'INPUT' 2
'READ' CONCS
'INPUT' 1
'BLOCKS' LOCNS/SAMPLES
'TREAT' TIMES*TOPOG
'ANOVAR' CONCS
'RUN'
'CLOSE'
'STOP'
```

Appendix 3

Results From the Main Experiment

A3.1 Introduction

The results from the main experiment are set out in the following pages. The results for each field are contained on a single page. The order is the same as that for Table 6.2.2. Each sample has a unique number which enables the soil series, sampling time, etc. to be determined. The key to the sample numbering is set out below.



Sampling Times	Soil Series	Landuse
1    June '83	1    Fyfield	1    Pasture
2    Sept "	2    Kingston	2    Arable
3    Oct "	3    Sherbourne	3    Wet Pasture
4    Dec "	4    Evesham	4    Silage
5    Jan '84	5    Denchworth	5    Hay
6    March "	6    Icknield	6    Gallops
7    June "		

Field No. 2, Fyfield Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	C1	NO3	A1k	pH	DOC	Abs350	MCwet	% Yld
111021	259	1698	1583	118	244	303.0	234	1268	569	*	*	*	0.453	115	23
111022	171	1447	1471	96	203	198.1	200	1239	521	1870	7.0	*	0.294	120	25
211021	333	521	1124	51	453	196.3	91	1183	564	440	7.4	4750	0.442	112	35
211022	336	834	1259	57	441	215.9	99	1437	443	460	7.7	4250	0.453	106	38
311021	556	1132	1852	107	323	155.4	86	1577	2571	750	6.9	3833	0.306	104	41
311022	535	844	1166	84	295	163.5	156	1493	1571	320	7.1	3417	0.338	87	45
411021	345	825	795	60	261	192.9	123	1070	410	860	7.5	*	*	102	39
411022	248	603	685	51	255	169.8	99	775	460	*	7.5	*	*	107	35
511021	371	374	666	48	196	212.9	112	855	330	800	7.1	2583	0.643	104	35
511022	665	693	727	53	333	167.0	282	1070	310	1060	7.0	4833	0.605	106	33
611021	500	488	772	59	304	155.5	162	893	140	840	7.4	2750	*	127	46
611022	251	343	830	42	281	220.9	93	994	110	290	6.1	2917	*	126	48
711021	341	297	1158	59	327	214.2	103	958	55	1020	7.2	3583	0.400	122	47
711022	*	*	*	*	*	*	*	1150	52	1240	7.6	3583	0.271	109	42

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
111021	3.3	<0.9	<0.010	0.041	7.64	0.38	3.01	<0.2	<0.2	0.66	<0.5	<0.4	4.6	0.955
111022	3.4	<0.9	<0.010	0.047	6.40	0.39	5.72	<0.2	<0.2	0.56	<0.5	<0.4	11.0	0.892
211021	7.0	<0.9	<0.010	0.142	1.53	0.39	7.49	<0.2	<0.2	<0.38	<0.5	<0.4	11.2	0.815
211022	6.4	<0.9	<0.010	0.136	1.88	0.42	10.97	<0.2	<0.2	<0.38	0.7	*	20.3	0.885
311021	6.4	<0.9	0.018	0.251	0.98	0.34	1.35	<0.2	<0.2	1.08	0.6	<0.4	<4.5	1.483
311022	6.7	<0.9	0.015	0.184	1.72	0.26	2.73	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.873
411021	8.3	<0.9	<0.010	0.150	1.81	0.28	12.64	<0.2	<0.2	<0.38	<0.5	<0.4	21.9	0.580
411022	7.0	<0.9	<0.010	0.141	2.06	0.26	11.03	<0.2	<0.2	<0.38	<0.5	<0.4	19.4	0.512
511021	10.9	<0.9	0.025	0.223	4.89	0.31	33.71	<0.2	<0.2	0.57	<0.5	<0.4	60.0	0.503
511022	6.5	<0.9	<0.010	0.162	2.48	0.25	12.64	<0.2	<0.2	0.53	<0.5	<0.4	17.6	0.558
611021	4.8	<0.9	<0.010	0.145	7.20	0.60	307.00	<0.2	<0.2	1.82	<0.5	<0.4	540.0	0.591
611022	4.9	<0.9	0.028	0.225	6.94	0.28	478.00	<0.2	<0.2	1.81	<0.5	8.1	850.0	0.581
711021	5.1	<0.9	0.012	0.110	3.64	0.27	20.85	<0.2	<0.2	0.42	<0.5	<0.4	36.2	0.727
711022	*	*	*	*	*	*	*	*	*	*	*	*	*	*

Field No. 3, Fyfield Series, Grass Ley

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	Alk	pH	DOC	Abs350	MCwet	% Yld
111031	397	1357	1463	112	387	141.1	206	1577	673	700	5.2	9083	0.469	106	28
111032	405	1011	1337	92	344	135.0	181	1662	195	2120	7.9	22250	0.506	108	30
211031	179	431	1015	58	401	381.5	67	845	371	650	7.5	3250	0.331	127	33
211032	182	373	1117	52	478	305.1	61	930	371	440	7.2	2750	0.252	114	35
311031	333	589	1133	64	298	273.1	95	1293	643	910	7.5	2750	0.242	111	22
311032	216	256	1020	44	236	252.1	53	789	643	690	7.4	2167	0.227	*	24
411031	351	1319	2833	172	367	253.3	157	2910	3020	1290	7.6	2000	0.271	133	36
411032	304	1362	2994	177	366	269.1	166	2980	3490	1840	7.8	1667	*	136	42
511031	149	230	856	46	140	356.9	80	500	680	960	7.1	1250	0.199	129	38
511032	161	396	870	48	141	282.4	77	475	680	1060	7.0	833	0.226	130	42
611031	252	430	2440	113	398	256.1	47	476	3660	550	7.4	1083	0.129	146	49
611032	278	422	2340	111	331	248.2	51	465	3870	510	7.4	917	0.114	142	38
711031	161	412	1938	175	166	269.9	141	208	2960	1000	7.6	2750	0.265	108	40
711032	164	411	1899	184	143	270.0	130	175	3070	980	7.7	2500	0.205	144	40

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
111031	5.5	<0.9	0.014	0.183	10.11	0.49	10.66	<0.2	<0.2	0.51	<0.5	<0.4	17.2	1.022
111032	5.0	<0.9	<0.010	0.149	7.18	0.47	9.16	<0.2	<0.2	0.42	<0.5	<0.4	14.5	0.959
211031	4.6	<0.9	<0.010	0.053	1.28	0.23	18.63	<0.2	<0.2	<0.38	<0.5	<0.4	40.9	0.761
211032	4.9	<0.9	<0.010	0.038	0.77	0.21	4.62	<0.2	<0.2	<0.38	<0.5	<0.4	8.6	0.819
311031	3.2	<0.9	<0.010	0.083	1.31	0.29	10.35	<0.2	<0.2	0.46	0.8	<0.4	19.3	0.748
311032	3.8	<0.9	<0.010	0.071	0.64	<0.2	4.47	<0.2	<0.2	<0.38	0.8	<0.4	8.2	0.628
411031	3.7	<0.9	<0.010	0.095	1.86	<0.2	0.47	<0.2	<0.2	0.49	<0.5	<0.4	<4.5	1.734
411032	3.9	<0.9	0.013	0.080	2.20	0.23	0.64	<0.2	<0.2	0.50	<0.5	<0.4	<4.5	1.793
511031	2.9	<0.9	<0.010	0.042	0.92	<0.2	26.24	<0.2	<0.2	<0.38	<0.5	<0.4	51.0	0.525
511032	2.4	<0.9	<0.010	0.031	0.73	<0.2	8.58	<0.2	<0.2	<0.38	<0.5	<0.4	15.8	0.552
611031	2.3	<0.9	<0.010	0.047	0.25	<0.2	1.80	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.406
611032	1.9	<0.9	0.011	0.037	0.19	<0.2	0.95	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.351
711031	4.6	<0.9	0.011	0.059	0.35	0.29	4.02	<0.2	<0.2	<0.38	<0.5	<0.4	5.3	1.057
711032	4.4	<0.9	0.011	0.057	0.31	0.30	1.63	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.031

Field No. 11, Fyfield Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
111111	287	1452	1021	226	855	240.2	309	1155	458	520	5.6	5250	0.497	138	34
111112	264	1422	1213	266	1109	246.6	286	1042	418	*	*	5250	*	137	34
211111	757	3859	4266	797	3134	603.8	220	4620	3000	1010	6.5	7333	0.640	142	29
211112	756	4672	4340	755	2900	651.2	176	4620	4071	360	6.2	10000	0.597	144	28
311111	554	1755	2309	360	1418	486.1	194	2366	2000	350	6.7	5417	0.452	141	21
311112	536	1752	4025	575	2453	483.1	153	2873	2929	280	6.6	6167	0.340	119	30
411111	787	1981	1828	341	1038	486.7	414	*	2140	1140	7.4	10583	0.503	139	42
411112	463	1827	1861	324	777	464.2	209	1630	2810	0	5.2	7667	0.525	143	44
511111	232	815	653	123	251	439.1	372	690	880	*	6.5	3667	0.616	152	43
511112	255	816	614	111	230	372.2	357	640	950	450	6.7	4750	0.615	155	40
611111	284	1048	621	105	390	572.9	297	572	180	650	7.4	3500	0.102	205	35
611112	275	962	477	97	347	594.8	315	428	410	80	6.4	3833	*	156	32
711111	345	1263	1301	152	429	421.9	86	493	2250	590	7.6	2667	0.279	283	33
711112	337	1455	1246	164	429	489.7	79	439	3028	820	7.2	2583	0.310	157	44

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
111111	8.6	<0.9	0.018	0.257	16.07	1.71	23.12	<0.2	<0.2	1.98	<0.5	<0.4	20.5	0.940
111112	8.1	<0.9	0.015	0.216	11.79	1.53	14.82	<0.2	<0.2	1.60	<0.5	<0.4	15.0	1.076
211111	15.1	2.7	0.049	0.911	77.77	1.22	12.51	<0.2	<0.2	4.86	1.6	<0.4	18.6	3.736
211112	13.8	3.0	0.031	1.167	104.82	1.10	7.97	<0.2	<0.2	4.97	2.0	4.7	15.7	3.862
311111	10.2	1.8	0.031	0.550	40.66	0.97	10.30	<0.2	<0.2	2.52	1.0	<0.4	15.0	2.050
311112	11.5	2.5	0.027	0.774	72.65	0.77	4.99	<0.2	<0.2	3.89	1.5	<0.4	10.8	3.475
411111	10.6	1.2	<0.010	0.356	8.40	0.74	2.26	<0.2	<0.2	1.33	<0.5	<0.4	<4.5	1.729
411112	10.8	1.7	<0.010	0.524	14.13	0.91	4.07	<0.2	<0.2	1.69	<0.5	<0.4	5.9	1.764
511111	8.0	<0.9	<0.010	0.216	4.35	0.91	24.22	<0.2	<0.2	0.99	<0.5	<0.4	31.6	0.640
511112	8.0	<0.9	<0.010	0.202	3.61	0.84	12.76	<0.2	<0.2	0.67	<0.5	<0.4	12.7	0.705
611111	8.1	<0.9	0.035	0.288	7.90	2.10	1072.00	0.31	<0.2	4.94	<0.5	<0.4	2220.0	0.615
611112	8.6	<0.9	0.034	0.308	6.20	1.90	970.00	0.30	<0.2	4.56	<0.5	<0.4	2111.0	0.495
711111	7.0	<0.9	<0.010	0.185	0.46	0.48	5.56	<0.2	<0.2	<0.38	<0.5	<0.4	8.5	1.060
711112	5.6	<0.9	<0.010	0.175	0.41	0.48	7.18	<0.2	<0.2	<0.38	<0.5	<0.4	12.0	1.056

Field No. 4, Kingston Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO <sub>3</sub>	Alk	pH	DOC	Abs350	MCwet	% Yld
121041	708	881	1958	247	223	207.1	74	4648	1325	*	*	15167	0.485	183	28
121042	593	826	1881	208	192	187.8	76	2130	1300	1260	6.9	14250	0.445	222	20
221041	2794	2492	17259	1904	1422	682.0	174	702	22857	*	*	*	1.158	186	13
221042	1404	2209	10587	1071	823	287.8	84	9270	15929	*	*	7500	0.465	*	*
321041	1159	1813	8625	834	913	290.4	96	*	1200	1380	7.1	4583	0.349	158	17
321042	1205	2557	8076	815	912	300.2	150	*	1429	1980	7.5	6833	*	206	14
421041	972	2029	5476	797	802	344.4	123	3320	9070	1660	7.8	6083	0.460	265	25
421042	972	1442	5428	848	806	361.2	114	3320	9500	1420	7.7	8250	0.501	254	26
521041	650	964	2514	243	375	308.1	110	1270	2240	2430	8.0	4167	0.457	218	25
521042	634	875	2561	237	375	308.0	75	1225	2240	2700	7.2	3750	0.443	221	29
621041	574	1086	2279	228	394	258.2	123	1398	2590	2160	7.8	4833	0.613	232	30
621042	497	657	2314	221	342	248.5	75	1346	2500	1820	8.0	4417	0.496	227	25
721041	505	544	1342	117	377	255.5	80	834	117	1800	8.0	6167	0.700	138	44
721042	508	745	1851	171	382	267.5	101	527	560	3140	7.9	7083	0.576	211	31

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
121041	2.7	<0.9	<0.010	0.145	9.80	0.35	5.82	<0.2	<0.2	0.45	<0.5	<0.4	<4.5	1.169
121042	3.2	<0.9	<0.010	0.142	<0.59	0.36	4.93	<0.2	<0.2	0.40	<0.5	<0.4	<4.5	1.139
221041	10.9	1.2	0.051	0.899	2.27	1.11	17.89	0.33	<0.2	1.20	4.0	<0.4	<4.5	<0.957
221042	3.4	<0.9	0.029	0.553	0.88	0.53	1.67	<0.2	<0.2	0.59	<0.5	<0.4	<4.5	6.163
321041	4.2	<0.9	0.023	0.490	0.76	0.41	0.98	<0.2	<0.2	0.69	<0.5	<0.4	<4.5	4.939
321042	2.7	<0.9	0.021	0.447	1.44	0.48	1.40	<0.2	<0.2	1.13	<0.5	<0.4	<4.5	4.641
421041	4.7	<0.9	0.014	0.287	0.60	0.52	2.60	<0.2	<0.2	0.87	0.6	<0.4	<4.5	3.133
421042	4.4	<0.9	0.012	0.261	0.28	0.50	1.06	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	3.181
521041	2.3	<0.9	<0.010	0.130	0.33	0.40	1.10	<0.2	<0.2	0.72	<0.5	<0.4	<4.5	1.487
521042	2.5	<0.9	<0.010	0.131	0.15	0.33	1.34	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.489
621041	4.1	<0.9	<0.010	0.146	0.91	0.72	3.12	<0.2	<0.2	0.99	<0.5	<0.4	<4.5	1.330
621042	3.7	<0.9	<0.010	0.126	0.82	0.51	2.50	<0.2	<0.2	0.69	<0.5	<0.4	<4.5	1.312
721041	4.5	<0.9	0.011	0.084	0.36	0.70	13.08	<0.2	<0.2	0.42	<0.5	<0.4	7.0	0.792
721042	4.6	<0.9	0.012	0.100	0.40	0.76	6.20	<0.2	<0.2	0.60	<0.5	<0.4	<4.5	1.055

Field No. 5, Kingston Series, Silage

Sample	Na	K	Ca	Mg	S	Si	P	C1	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
121051	510	167	1688	103	141	110.5	19	2324	410	1020	7.5	8583	0.177	196	26
121052	790	485	2008	145	171	111.9	60	4817	357	620	6.5	5667	0.188	200	24
221051	850	298	2839	210	436	144.8	40	*	2286	690	7.4	*	0.222	183	9
221052	1187	321	4612	347	481	156.4	39	4676	4500	810	7.4	*	0.293	172	15
321051	595	436	1471	108	378	132.8	127	1690	714	870	7.2	3250	0.215	189	21
321052	548	296	1661	109	357	133.2	50	2225	714	870	7.4	2833	0.210	192	20
421051	1079	551	4129	289	777	220.0	42	3150	4790	640	7.2	3750	0.197	223	32
421052	990	905	3769	224	671	157.7	62	3080	4360	150	7.1	4000	0.188	237	31
521051	438	151	1289	82	288	142.1	29	1025	270	1530	8.1	1833	0.236	233	27
521052	441	86	1139	69	284	126.4	19	880	150	1230	8.1	2667	0.185	236	23
621051	632	384	2796	156	384	138.7	35	3200	840	2200	8.0	2417	0.224	210	27
621052	441	569	2297	126	443	140.0	43	2913	1040	1550	7.9	1750	0.293	193	31
721051	530	320	1721	118	626	161.9	72	1524	171	1370	7.4	4083	0.237	186	26
721052	478	266	1769	121	889	162.1	90	1327	179	1260	7.4	6250	0.202	203	30

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
121051	3.5	<0.9	<0.010	0.118	5.10	<0.2	3.35	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.867
121052	2.9	<0.9	<0.010	0.167	8.48	<0.2	2.49	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.059
221051	4.6	<0.9	<0.010	0.220	0.54	<0.2	1.55	<0.2	<0.2	<0.38	<0.5	<0.4	*	1.504
221052	4.4	<0.9	0.017	0.370	1.12	0.21	2.68	<0.2	<0.2	0.52	<0.5	<0.4	<4.5	2.408
321051	4.9	<0.9	<0.010	0.194	0.39	<0.2	2.15	<0.2	<0.2	<0.38	0.7	<0.4	<4.5	0.761
321052	4.3	<0.9	0.015	0.182	1.40	0.21	1.60	<0.2	<0.2	<0.38	0.6	<0.4	<4.5	0.842
421051	6.7	<0.9	0.024	0.371	2.77	0.21	3.38	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.157
421052	5.2	<0.9	0.011	0.343	0.90	<0.2	1.29	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.986
521051	2.4	<0.9	<0.010	0.073	0.30	<0.2	3.66	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.654
521052	2.0	<0.9	<0.010	0.064	0.14	<0.2	2.00	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.569
621051	2.7	<0.9	0.012	0.152	0.79	<0.2	1.35	<0.2	<0.2	0.45	<0.5	<0.4	<4.5	1.319
621052	3.7	<0.9	<0.010	0.170	0.85	<0.2	1.45	<0.2	<0.2	0.41	<0.5	<0.4	<4.5	1.098
721051	6.1	<0.9	0.014	0.137	1.35	0.27	7.67	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.882
721052	5.1	<0.9	<0.010	0.123	1.05	0.25	8.13	<0.2	<0.2	0.45	<0.5	<0.4	<4.5	0.955

Field No. 9, Kingston Series, Grass Ley

Sample	Na	K	Ca	Mg	S	Si	P	C1	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
121091	273	657	1016	77	133	197.1	104	1380	1022	420	5.3	4917	0.271	138	19
121092	237	690	824	72	116	212.2	96	592	1125	*	*	5333	0.364	133	19
221091	655	617	2803	197	661	316.6	186	4873	1679	*	*	5083	0.508	111	7
221092	467	665	2436	203	705	305.6	100	3268	807	1130	8.0	5750	0.406	114	9
321091	224	352	894	64	521	320.4	54	1155	*	220	7.0	7167	0.251	133	20
321092	245	353	1002	76	500	376.7	66	1127	357	240	6.9	3583	0.268	127	21
421091	334	213	1877	86	390	207.9	123	2670	2760	*	6.8	7667	0.192	135	26
421092	300	172	1767	79	386	203.8	103	2590	2090	*	6.8	5083	0.133	140	29
521091	234	172	1206	78	223	281.0	41	945	1640	430	6.7	1833	0.129	146	29
521092	242	173	1222	78	234	294.5	42	945	1600	390	7.1	1083	0.129	140	34
621091	384	535	2274	163	1296	299.7	34	2825	770	0	5.0	2583	0.128	145	32
621092	366	524	2147	150	1268	315.4	34	2569	280	<10	6.0	917	0.120	146	33
721091	465	315	1508	104	751	315.6	43	361	1620	570	6.7	2000	0.221	197	25
721092	386	212	2059	128	1010	304.0	25	417	1943	200	7.0	1667	0.130	149	31

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
121091	8.2	<0.9	0.022	0.308	17.11	0.29	18.36	<0.2	<0.2	0.60	<0.5	<0.4	22.4	0.926
121092	6.3	<0.9	0.031	0.172	8.96	0.35	19.11	<0.2	<0.2	0.50	0.8	<0.4	19.0	0.774
221091	8.0	1.5	0.026	0.594	15.78	0.28	4.63	<0.2	<0.2	1.77	0.8	<0.4	12.9	2.089
221092	6.8	1.3	0.016	0.397	10.01	0.44	4.87	<0.2	<0.2	1.07	<0.5	<0.4	7.8	1.873
321091	7.4	1.1	0.021	0.189	7.43	0.21	9.59	<0.2	<0.2	<0.38	<0.5	<0.4	17.0	0.656
321092	6.4	1.1	0.025	0.186	8.29	0.23	19.86	<0.2	<0.2	<0.38	<0.5	<0.4	28.2	0.766
421091	5.5	<0.9	<0.010	0.271	11.43	<0.2	0.22	<0.2	<0.2	0.44	<0.5	1.0	<4.5	1.817
421092	5.0	<0.9	<0.010	0.271	12.49	<0.2	0.11	<0.2	<0.2	0.47	<0.5	1.1	<4.5	1.674
521091	6.8	<0.9	<0.010	0.204	4.77	<0.2	2.36	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.963
521092	6.4	<0.9	<0.010	0.232	5.09	<0.2	3.99	<0.2	<0.2	<0.38	<0.5	<0.4	6.5	0.947
621091	7.7	1.5	0.015	0.424	14.68	<0.2	1.40	<0.2	<0.2	<0.38	<0.5	<0.4	6.5	1.728
621092	8.2	1.4	0.013	0.405	14.24	<0.2	1.78	<0.2	<0.2	<0.38	<0.5	<0.4	4.6	1.582
721091	10.2	1.3	0.018	0.204	7.08	<0.2	10.45	<0.2	<0.2	<0.38	<0.5	<0.4	9.6	1.069
721092	10.0	1.3	0.013	0.231	5.64	<0.2	3.69	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.440

Field No. 7, Sherborne Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
131071	1335	2146	3441	221	244	121.6	185	2676	1046	4560	7.8	9167	0.478	247	7
131072	1076	1542	2827	168	196	119.2	154	2169	800	4400	7.9	10417	0.442	251	7
231071	1211	952	17272	1457	403	273.5	107	3493	36429	0	7.2	11000	0.372	266	4
231072	1291	820	14898	1321	451	309.5	61	283	31786	0	7.4	12833	0.543	268	3
331071	1061	992	11524	1038	428	266.9	107	6062	22570	730	7.3	13000	0.550	251	6
331072	940	654	12084	1017	273	257.1	44	9012	20000	390	6.7	5417	0.301	263	8
431071	586	273	4366	404	293	279.7	71	1240	8866	800	7.1	6000	0.475	314	9
431072	525	139	4542	404	250	278.0	59	1230	9726	550	6.0	4083	0.343	303	6
531071	339	94	1528	144	205	240.8	57	640	2240	820	6.9	3000	0.327	304	13
531072	394	64	1442	145	191	258.4	51	645	2220	550	7.5	3833	0.345	229	12
631071	378	192	1117	119	360	362.1	85	586	430	1230	7.7	5667	*	306	13
631072	444	134	1231	124	371	295.5	79	541	550	1320	7.7	4417	*	306	14
731071	681	807	1264	154	435	295.5	98	546	1040	1450	7.4	7083	0.882	145	29
731072	642	807	1089	135	415	286.8	104	482	1214	1100	7.5	8667	0.915	276	10

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
131071	4.8	<0.9	0.014	0.414	3.21	0.84	8.17	<0.2	<0.2	1.33	<0.5	<0.4	5.6	3.181
131072	5.4	<0.9	<0.010	0.333	2.34	0.69	10.89	<0.2	<0.2	1.09	<0.5	<0.4	9.4	2.674
231071	12.7	<0.9	0.058	1.962	6.69	0.41	4.75	<0.2	<0.2	1.13	<0.5	0.5	<4.5	14.060
231072	14.4	<0.9	0.051	1.776	4.94	0.47	5.01	<0.2	<0.2	0.86	<0.5	<0.4	<4.5	12.415
331071	10.4	1.4	0.049	1.285	3.60	0.25	2.91	<0.2	<0.2	0.59	<0.5	<0.4	<4.5	9.362
331072	12.1	1.3	0.047	1.240	2.70	<0.2	1.51	<0.2	<0.2	0.42	<0.5	<0.4	<4.5	9.364
431071	10.6	<0.9	<0.010	0.581	2.48	<0.2	5.67	<0.2	<0.2	<0.38	<0.5	<0.4	4.6	4.165
431072	10.4	<0.9	<0.010	0.562	1.90	<0.2	2.98	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	4.150
531071	7.8	<0.9	<0.010	0.194	0.87	<0.2	5.17	<0.2	1.23	<0.38	3.5	<0.4	5.0	1.349
531072	7.7	<0.9	<0.010	0.176	0.69	<0.2	6.92	<0.2	<0.2	<0.38	<0.5	<0.4	6.5	1.291
631071	9.7	<0.9	0.021	0.168	1.25	0.40	27.94	<0.2	<0.2	<0.38	<0.5	<0.4	36.7	0.969
631072	9.3	<0.9	0.020	0.151	0.95	0.73	11.60	<0.2	<0.2	<0.38	<0.5	<0.4	11.3	1.034
731071	9.4	<0.9	0.026	0.201	0.97	0.68	33.66	<0.2	<0.2	<0.38	<0.5	<0.4	32.4	1.094
731072	9.2	<0.9	0.027	0.177	0.70	0.72	38.03	<0.2	<0.2	0.40	<0.5	<0.4	36.8	0.937

Field No.13, Sherborne Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	C1	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
131131	418	1595	2925	349	436	406.0	279	2113	1342	2920	7.3	7583	0.448	160	10
131132	309	1870	2637	335	454	349.7	304	2000	1364	2800	7.4	14167	0.554	163	12
231131	1638	1861	3219	359	1540	333.1	807	3127	786	2090	8.0	*	1.040	137	6
231132	615	1547	4233	485	923	325.3	259	4366	929	4140	8.0	*	*	137	6
331131	252	634	2207	231	305	232.9	134	*	*	*	*	3750	0.447	160	9
331132	200	612	1365	170	351	232.6	117	*	*	*	*	5417	0.486	154	10
431131	240	510	2248	221	425	337.2	146	1040	740	3530	8.2	3000	0.254	162	19
431132	365	831	2381	309	560	387.2	255	1170	770	3840	8.2	3917	0.321	181	26
531131	229	374	1741	217	230	337.1	160	630	190	3410	7.9	2917	0.225	182	21
531132	180	315	1585	180	166	305.6	158	775	110	3030	8.2	2083	0.184	179	16
631131	352	619	2291	289	362	354.7	211	1175	7	4250	8.2	*	*	188	22
631132	385	1151	2550	347	470	377.6	319	1276	3	3920	8.0	*	*	182	21
731131	244	793	2031	201	315	334.4	152	580	*	3670	7.8	5167	0.452	200	17
731132	284	778	1935	198	325	344.9	164	591	26	3770	8.1	6750	0.490	181	19

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
131131	7.8	1.8	<0.010	0.326	3.84	0.83	5.00	<0.2	<0.2	0.74	<0.5	<0.4	<4.5	2.701
131132	7.6	1.4	<0.010	0.311	4.47	0.81	5.95	<0.2	<0.2	0.74	<0.5	<0.4	<4.5	2.282
231131	7.3	<0.9	<0.010	0.445	10.53	0.80	7.61	<0.2	<0.2	2.29	<0.5	<0.4	5.2	2.676
231132	6.6	<0.9	<0.010	0.457	2.93	1.17	5.14	<0.2	<0.2	1.90	0.6	<0.4	<4.5	3.326
331131	4.9	<0.9	0.014	0.261	1.32	0.31	2.73	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.759
331132	4.6	<0.9	<0.010	0.190	0.93	0.30	2.89	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.106
431131	6.8	<0.9	<0.010	0.196	<0.11	0.28	2.94	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.923
431132	7.2	1.0	<0.010	0.266	0.17	0.33	0.83	<0.2	<0.2	0.40	<0.5	<0.4	<4.5	2.080
531131	4.1	<0.9	<0.010	0.127	0.41	0.25	1.73	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.505
531132	3.1	<0.9	<0.010	0.099	0.52	0.21	2.81	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.311
631131	4.3	<0.9	<0.010	0.201	1.56	0.29	2.38	<0.2	<0.2	0.48	<0.5	<0.4	<4.5	1.849
631132	5.3	<0.9	<0.010	0.242	2.40	0.40	1.86	<0.2	<0.2	0.91	<0.5	<0.4	<4.5	2.048
731131	7.1	1.1	<0.010	0.219	2.66	0.41	4.12	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.633
731132	6.4	1.1	<0.010	0.212	2.69	0.38	8.34	<0.2	<0.2	<0.38	<0.5	<0.4	8.7	1.552

Field No.14, Sherborne Series, Silage

Sample	Na	K	Ca	Mg	S	Si	P	Cl	N03	Alk	pH	DOC	Abs350	MCwet	% Yld
134141	668	918	5714	398	503	183.0	155	5549	3751	2040	7.4	4167	0.338	285	5
134142	697	646	3379	282	437	183.0	144	1643	3357	1980	7.8	6917	0.328	310	6
231141	514	1984	5237	416	948	258.5	227	2282	6000	4220	8.1	11750	*	189	6
231142	634	1257	4761	382	824	317.0	219	2141	5071	4790	8.0	10250	*	218	6
334141	625	1882	3074	293	728	271.3	458	1915	929	4930	7.8	8667	1.057	236	8
334142	416	1285	2901	256	566	268.4	255	1211	857	4530	8.0	8333	0.772	240	8
434141	474	1854	2755	222	506	227.7	299	2270	260	4800	8.2	11500	0.452	249	18
434142	304	463	2163	163	393	180.7	97	*	250	4430	8.0	5167	0.344	259	18
534141	347	425	2119	131	241	173.3	136	845	290	4020	7.8	4167	0.324	272	15
534142	361	734	2135	228	253	227.9	239	1200	250	4120	7.8	14750	0.423	275	15
631141	457	397	3717	245	291	206.9	71	769	4260	3700	8.3	3750	*	273	14
631142	496	1251	3390	267	327	283.1	162	1175	4200	4100	8.3	4750	*	276	12
731141	262	656	2683	195	249	173.6	60	285	114	5040	8.1	4917	0.403	244	20
731142	247	936	2914	244	287	266.9	96	668	295	*	*	6500	*	270	14

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
134141	2.3	<0.9	<0.010	0.425	0.18	0.48	0.76	<0.2	<0.2	0.64	<0.5	<0.4	<4.5	5.441
134142	4.0	<0.9	<0.010	0.285	0.14	0.37	1.42	0.28	<0.2	<0.38	<0.5	<0.4	<4.5	3.359
231141	4.8	<0.9	0.018	0.628	1.57	2.76	4.34	<0.2	<0.2	2.36	0.8	<0.4	<4.5	5.035
231142	9.2	<0.9	0.014	0.627	1.33	1.35	9.07	<0.2	<0.2	3.09	<0.5	<0.4	<4.5	4.588
334141	4.4	<0.9	<0.010	0.470	0.49	0.74	5.15	<0.2	<0.2	1.53	<0.5	<0.4	<4.5	3.015
334142	4.2	<0.9	0.012	0.384	0.60	0.61	1.36	<0.2	<0.2	0.90	<0.5	<0.4	<4.5	2.745
434141	5.1	<0.9	<0.010	0.396	0.92	0.65	1.82	<0.2	<0.2	1.71	<0.5	<0.4	<4.5	2.728
434142	5.4	<0.9	<0.010	0.220	<0.11	0.31	0.88	<0.2	<0.2	1.12	<0.5	<0.4	<4.5	2.136
534141	2.1	<0.9	<0.010	0.192	0.21	0.34	2.41	<0.2	<0.2	0.67	<0.5	<0.4	<4.5	2.146
534142	1.8	<0.9	<0.010	0.233	0.46	0.33	4.82	<0.2	<0.2	1.02	<0.5	<0.4	<4.5	2.193
631141	2.6	<0.9	<0.010	0.308	1.04	0.69	2.64	<0.2	<0.2	1.26	<0.5	<0.4	<4.5	3.543
631142	3.3	<0.9	<0.010	0.391	1.16	0.99	2.99	<0.2	<0.2	1.56	<0.5	<0.4	<4.5	3.197
731141	4.1	<0.9	<0.010	0.237	0.70	0.40	3.33	<0.2	<0.2	0.44	<0.5	<0.4	<4.5	2.513
731142	3.7	<0.9	0.012	0.294	2.47	0.57	6.10	0.27	<0.2	0.61	<0.5	<0.4	<4.5	2.653

Field No.8, Evesham Series, Silage

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
144082	952	627	4595	540	363	131.5	148	2690	3643	3580	8.0	7000	0.318	288	13
144081	901	660	4587	533	338	136.3	108	3456	3714	2980	7.8	4417	0.259	289	13
244081	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
244082	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
344081	1084	989	5035	555	1351	151.4	56	2338	5929	3130	7.9	5833	0.428	258	5
344082	1068	896	5664	619	1435	149.9	54	2535	6214	3190	8.0	3917	0.435	244	6
444081	701	454	3224	282	716	136.9	135	1810	2940	2760	7.6	9917	0.380	252	10
444082	671	420	2856	240	659	118.9	109	1540	2671	2160	8.1	6667	0.351	259	15
544081	525	377	2109	193	347	142.8	60	780	590	4130	8.1	3167	0.250	260	13
544082	661	349	2734	248	474	124.0	54	945	860	4590	7.9	3000	0.259	272	16
644081	719	666	4000	390	604	148.6	47	899	2460	4900	8.4	3083	0.532	330	13
644082	826	805	4381	436	670	176.5	55	1020	2830	5900	8.4	3417	0.614	332	15
744081	2166	1525	3035	343	606	193.5	203	1370	1390	7000	7.6	7500	0.563	252	9
744082	2235	2261	3655	444	828	216.7	403	1653	1680	6900	7.2	10333	0.680	267	11

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
144082	4.5	2.1	<0.010	0.254	1.01	0.25	0.69	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	6.579
144081	6.5	2.1	<0.010	0.266	1.08	0.24	1.16	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	6.527
244081	*	*	*	*	*	*	*	*	*	*	*	*	*	*
244082	*	*	*	*	*	*	*	*	*	*	*	*	*	*
344081	4.7	1.7	0.024	0.341	0.23	0.49	1.12	<0.2	<0.2	2.22	0.6	<0.4	<4.5	6.748
344082	4.6	1.9	0.025	0.376	0.20	0.36	1.14	<0.2	<0.2	1.16	<0.5	<0.4	<4.5	7.505
444081	2.6	<0.9	<0.010	0.194	<0.11	<0.2	0.44	<0.2	<0.2	0.65	<0.5	1.0	<4.5	5.086
444082	2.5	<0.9	<0.010	0.166	<0.11	<0.2	0.89	<0.2	<0.2	0.58	*	1.1	<4.5	4.557
544081	2.8	<0.9	<0.010	0.105	<0.11	<0.2	1.71	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.791
544082	2.7	<0.9	<0.010	0.127	<0.11	<0.2	1.20	<0.2	<0.2	<0.38	0.7	<0.4	<4.5	3.537
644081	4.4	1.9	0.013	0.184	0.17	0.31	1.67	<0.2	<0.2	0.53	4.4	<0.4	<4.5	4.769
644082	4.5	2.0	0.016	0.209	0.19	0.34	2.72	<0.2	<0.2	0.70	<0.5	<0.4	<4.5	5.234
744081	5.8	<0.9	<0.010	0.233	0.57	0.99	5.05	<0.2	<0.2	1.79	0.8	<0.4	<4.5	3.749
744082	4.4	1.0	<0.010	0.285	1.15	1.07	8.69	<0.2	<0.2	2.25	<0.5	<0.4	<4.5	4.471

## Field No.10, Evesham Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
141101	492	50	1182	109	330	199.0	23	1521	214	320	6.5	8167	0.310	383	10
141102	494	73	1619	146	286	238.0	15	2169	107	640	7.3	8417	0.269	452	10
244101	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
244102	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
341101	*	*	*	*	*	*	*	*	*	*	*	*	*	320	0
341102	*	*	*	*	*	*	*	*	*	*	*	*	*	324	0
441101	937	115	2077	209	1103	207.2	101	2816	600	450	7.4	7583	0.372	298	1
441102	2891	1126	3057	424	2697	262.7	741	*	1290	1160	7.6	*	*	343	1
544101	570	52	1300	145	841	184.7	30	975	310	510	7.5	2667	0.163	364	18
544102	601	25	1259	149	930	171.4	23	930	400	320	7.1	2333	0.119	354	17
644101	867	61	1504	194	1021	204.3	20	1842	*	820	7.7	*	*	399	13
644102	989	132	1752	235	1070	214.7	33	2513	*	790	7.4	*	*	378	8
744101	1894	362	1921	241	655	170.2	43	2850	111	1400	6.9	5167	0.245	335	6
744102	1776	456	2992	412	1034	173.7	156	5000	309	2840	7.8	8833	0.262	319	3
Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	A1	Sr	
141101	9.7	1.0	<0.01	0.100	1.77	<0.2	14.16	<0.2	<0.2	0.40	<0.5	<0.4	<4.5	1.865	
141102	7.0	1.3	<0.01	0.130	2.38	<0.2	14.63	<0.2	<0.2	<0.38	<0.5	<0.4	6.9	2.427	
244101	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
244102	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
341101	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
341102	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
441101	12.1	<0.9	<0.01	0.201	0.34	<0.2	6.56	<0.2	<0.2	0.82	<0.5	0.8	<4.5	4.310	
441102	28.6	<0.9	<0.01	0.562	2.81	0.66	33.94	<0.2	<0.2	5.58	0.8	<0.4	<4.5	6.586	
544101	7.3	<0.9	<0.01	0.087	0.16	<0.2	3.53	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.440	
544102	8.3	<0.9	<0.01	0.112	0.18	<0.2	5.91	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.550	
644101	11.4	1.7	<0.01	0.144	2.86	<0.2	11.14	<0.2	<0.2	<0.38	<0.5	<0.4	5.3	2.892	
644102	11.8	1.7	<0.01	0.184	4.28	0.23	15.34	<0.2	<0.2	<0.38	<0.5	<0.4	5.3	3.363	
744101	23.8	2.1	<0.01	0.208	5.09	0.24	14.10	<0.2	<0.2	7.65	<0.5	<0.4	21.1	3.535	
744102	35.8	3.1	<0.01	0.483	12.92	0.31	15.17	<0.2	<0.2	18.87	1.3	<0.4	33.0	5.670	

Field No.19, Evesham Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
141191	335	221	1684	186	278	133.4	41	1831	114	1380	7.3	15167	0.325	239	12
141192	565	235	1827	216	272	134.9	36	1662	114	2080	7.8	15750	0.353	254	8
241191	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
241192	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
341191	1258	1112	3400	485	1266	217.8	223	3042	3286	*	7.5	9417	0.448	208	2
341192	1004	955	3534	508	957	234.9	136	2873	4357	1380	7.0	8500	0.707	194	4
441191	371	238	1631	194	410	187.7	59	1115	2070	610	7.3	5083	0.281	241	12
441192	366	194	1386	167	325	162.7	66	1195	1928	300	7.0	15250	0.251	248	18
541191	330	99	1222	138	430	165.2	18	940	1021	410	7.1	3333	0.230	270	14
541192	256	100	1244	134	410	171.3	21	915	1060	390	7.4	4167	0.316	233	4
641191	370	289	1013	136	326	143.9	35	873	590	1200	7.3	*	*	294	21
641192	333	459	1120	158	314	169.1	44	1085	260	1650	8.0	3583	*	272	20
741191	424	402	985	143	337	194.1	103	*	261	1110	7.5	6167	0.525	259	18
741192	401	281	1018	125	409	190.3	101	570	291	1160	7.5	9750	0.590	237	15

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
141191	5.8	1.7	<0.010	0.144	<0.94	0.26	17.39	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.019
141192	5.6	1.8	<0.010	0.178	9.47	0.32	14.12	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.224
241191	*	*	*	*	*	*	*	*	*	*	*	*	*	*
241192	*	*	*	*	*	*	*	*	*	*	*	*	*	*
341191	7.0	2.3	0.013	0.521	1.90	0.92	16.52	<0.2	<0.2	1.13	<0.5	<0.4	<4.5	4.488
341192	7.7	2.2	<0.010	0.614	2.09	0.82	15.25	<0.2	<0.2	0.71	<0.5	<0.4	<4.5	4.752
441191	6.7	<0.9	<0.010	0.164	0.55	<0.2	8.63	<0.2	<0.2	<0.38	<0.5	<0.4	8.7	2.348
441192	6.2	<0.9	<0.010	0.146	0.63	<0.2	6.50	<0.2	<0.2	<0.38	<0.5	0.5	<4.5	2.070
541191	6.7	1.2	<0.010	0.095	0.32	<0.2	9.57	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.553
541192	7.2	1.2	<0.010	0.104	0.28	<0.2	7.64	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.554
641191	6.6	1.0	<0.010	0.115	2.07	0.38	22.92	<0.2	<0.2	<0.38	<0.5	<0.4	11.0	1.303
641192	7.3	1.1	<0.010	0.151	3.09	0.44	35.49	<0.2	<0.2	0.55	<0.5	<0.4	18.9	1.412
741191	9.1	1.0	<0.010	0.143	0.60	1.15	31.90	<0.2	<0.2	0.56	<0.5	<0.4	26.7	1.346
741192	6.6	1.1	0.011	0.142	0.73	1.31	36.40	<0.2	<0.2	0.86	<0.5	<0.4	24.5	1.451

Field No.15, Denchworth Series, Hay

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
155151	827	641	2993	322	493	318.5	113	1915	1464	3780	7.7	8167	0.559	301	4
155152	636	374	2210	230	358	164.4	149	1468	770	2860	7.7	6583	0.592	363	4
255151	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
255152	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
355151	895	856	2725	293	984	176.5	167	2732	71	3370	7.9	5167	0.647	282	5
355152	1000	1121	2560	288	958	192.9	156	2817	143	3130	7.9	6167	0.603	280	7
455151	*	*	*	*	*	*	*	3085	560	2410	7.7	3750	0.263	288	12
455152	663	171	3135	242	707	109.9	37	*	560	2330	8.1	4250	0.237	296	12
555151	858	343	2017	195	399	143.3	60	1490	240	3400	8.2	3417	0.415	283	14
555152	820	282	2810	263	554	125.7	58	2705	120	3710	8.3	4583	0.389	290	13
655151	792	464	1965	241	380	230.4	87	969	3	3940	8.1	5250	*	364	11
655152	865	518	2275	277	395	209.8	84	1166	7	3990	8.2	*	0.043	353	13
755151	951	316	2304	256	365	174.8	69	690	52	4300	8.2	5083	0.386	323	10
755152	1217	298	2259	232	327	144.6	62	745	68	4200	8.2	4667	0.359	275	10

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
155151	4.1	2.1	<0.010	0.249	2.17	0.38	7.50	0.29	<0.2	<0.38	<0.5	<0.4	<4.5	3.548
155152	3.8	2.5	<0.010	0.176	0.14	0.27	3.55	0.35	<0.2	<0.38	<0.5	<0.4	4.8	2.303
255151	*	*	*	*	*	*	*	*	*	*	*	*	*	*
255152	*	*	*	*	*	*	*	*	*	*	*	*	*	*
355151	5.6	2.1	0.015	0.294	0.23	0.47	2.37	<0.2	<0.2	0.96	<0.5	<0.4	<4.5	2.991
355152	12.3	2.5	0.013	0.258	0.16	0.48	2.27	<0.2	<0.2	0.80	<0.5	<0.4	<4.5	2.823
455151	*	*	*	*	*	*	*	*	*	*	*	*	*	*
455152	<1.7	1.1	<0.010	0.161	<0.11	<0.2	1.26	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	3.227
555151	3.1	2.0	<0.010	0.133	<0.11	0.27	1.87	<0.2	<0.2	0.42	<0.5	<0.4	<4.5	2.249
555152	3.1	2.1	<0.010	0.157	<0.11	0.28	1.58	<0.2	<0.2	0.47	<0.5	<0.4	<4.5	3.039
655151	3.5	1.8	<0.010	0.180	0.15	0.30	4.81	<0.2	<0.2	0.41	<0.5	<0.4	<4.5	2.303
655152	2.8	1.9	<0.010	0.140	0.19	0.28	5.46	<0.2	<0.2	<0.38	<0.5	<0.4	4.6	2.539
755151	3.6	2.1	<0.010	0.149	<0.11	0.39	4.42	<0.2	<0.2	<0.38	<0.5	<0.4	4.8	2.543
755152	3.2	2.0	<0.010	0.146	<0.11	0.37	3.82	<0.2	<0.2	0.55	<0.5	<0.4	4.7	2.495

Field No.17, Denchworth Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
151171	1335	566	3858	554	520	927.1	73	3352	1643	4820	7.8	17333	0.635	458	11
151172	2323	1072	6414	872	1147	1033.8	74	8845	1000	5160	7.8	15750	0.564	414	11
251171	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
251172	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
351171	*	*	*	*	*	*	*	*	*	*	*	*	*	276	0
351172	*	*	*	*	*	*	*	*	*	*	*	*	*	266	0
451171	482	106	1774	159	292	471.3	86	1740	*	1670	6.8	5833	0.414	369	16
451172	568	117	1518	157	297	475.2	95	1200	*	1610	7.2	4583	0.463	561	16
551171	627	719	1085	195	153	749.6	425	1205	140	2230	7.9	4333	0.926	387	26
551172	770	737	1218	217	166	824.3	320	1585	550	1960	7.4	3167	0.744	394	24
651171	702	467	1400	164	372	778.1	163	642	950	2040	8.1	4417	0.604	415	26
651172	630	390	1247	151	289	755.1	156	451	*	2580	7.6	2833	*	414	22
751171	816	252	2008	237	352	752.2	262	460	1143	2750	7.6	10000	0.902	349	12
751172	788	246	1928	229	334	780.6	266	455	1286	2550	7.3	9667	0.950	309	12

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
151171	10.3	4.8	<0.010	0.274	3.22	0.28	3.19	0.24	<0.2	0.89	<0.5	<0.4	<4.5	6.389
151172	8.0	<0.4	0.014	0.475	6.03	0.27	1.94	<0.2	<0.2	0.49	<0.5	<0.4	<4.5	10.332
251171	*	*	*	*	*	*	*	*	*	*	*	*	*	*
251172	*	*	*	*	*	*	*	*	*	*	*	*	*	*
351171	*	*	*	*	*	*	*	*	*	*	*	*	*	*
351172	*	*	*	*	*	*	*	*	*	*	*	*	*	*
451171	4.1	1.0	<0.010	0.145	0.45	<0.2	6.13	<0.2	<0.2	0.61	<0.5	0.7	6.2	3.179
451172	2.7	<0.9	<0.010	0.093	<0.11	<0.2	3.25	<0.2	<0.2	<0.38	<0.5	0.6	<4.5	2.821
551171	8.1	1.1	<0.010	0.193	0.15	0.21	7.43	0.29	<0.2	4.21	<0.5	<0.4	5.4	1.883
551172	7.8	1.6	0.011	0.164	<0.11	0.26	7.15	0.40	<0.2	4.25	<0.5	<0.4	7.5	2.017
651171	5.8	1.5	<0.010	0.109	<0.11	<0.2	12.83	0.30	<0.2	<0.38	<0.5	<0.4	21.2	2.275
651172	4.5	1.4	<0.010	0.093	<0.11	<0.2	12.91	0.27	<0.2	<0.38	<0.5	<0.4	23.5	2.049
751171	9.5	1.7	0.012	0.132	0.17	0.71	9.77	0.55	<0.2	2.14	<0.5	<0.4	14.5	3.027
751172	11.0	1.8	0.013	0.146	0.19	0.69	11.35	0.55	<0.2	2.52	<0.5	<0.4	16.9	2.894

Field No.22, Denchworth Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	N03	Alk	pH	DOC	Abs350	MCwet	% Yld
151221	516	479	1483	199	514	233.9	48	*	643	1240	7.4	7500	0.296	286	20
151222	516	238	1342	141	409	231.2	48	1211	500	1080	7.4	7667	0.275	252	20
251221	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
251222	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
351221	1088	756	3189	463	1858	322.8	184	2366	1043	2000	7.6	6417	0.540	234	8
351222	1096	621	3681	477	2112	318.5	186	2338	2429	1580	7.5	5667	0.536	236	6
451221	994	388	3262	354	1327	260.8	55	2705	2770	670	7.5	6500	0.300	273	6
451222	1062	525	3221	385	1346	266.8	69	2040	2710	2420	7.7	<0.4	2750	0.310	300
551221	485	243	1463	180	498	215.2	34	1165	1355	*	7.3	2167	0.240	297	14
551222	516	140	1319	149	441	237.3	28	1090	1156	510	7.4	2500	0.386	239	14
651221	330	105	847	97	371	253.1	35	628	4	980	7.6	3250	*	283	16
651222	355	114	762	93	341	220.1	32	479	1	820	7.5	3833	*	255	12
751221	1143	321	1174	188	380	330.8	152	990	124	1990	7.2	6750	0.620	269	12
751222	379	246	818	109	217	265.9	55	350	98	1380	7.6	3667	0.401	296	13

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
151221	4.4	1.6	<0.010	0.215	2.69	0.23	9.11	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.175
151222	4.9	1.5	<0.010	0.157	0.74	0.26	5.93	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.947
251221	*	*	*	*	*	*	*	*	*	*	*	*	*	*
251222	*	*	*	*	*	*	*	*	*	*	*	*	*	*
351221	6.9	2.4	0.018	0.489	0.45	0.59	2.53	<0.2	<0.2	0.59	<0.5	<0.4	<4.5	4.302
351222	7.2	2.2	0.017	0.539	0.60	0.65	2.33	<0.2	<0.2	0.59	<0.5	<0.4	<4.5	4.772
451221	5.4	2.0	<0.010	0.388	0.46	<0.2	1.53	<0.2	<0.2	<0.38	<0.5	7.9	<4.5	4.464
451222	4.8	2.0	<0.010	0.406	0.36	<0.2	1.63	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	4.337
551221	4.7	1.1	<0.010	0.186	0.16	<0.2	4.13	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.230
551222	4.8	1.2	<0.010	0.157	0.13	<0.2	4.36	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.920
651221	5.1	<0.9	<0.010	0.095	0.51	0.25	13.80	<0.2	<0.2	<0.38	<0.5	<0.4	<0.9	1.299
651222	4.8	<0.9	<0.010	0.094	0.27	0.25	9.89	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.162
751221	5.7	1.2	0.025	0.212	1.02	0.45	24.94	<0.2	<0.2	0.74	<0.5	<0.4	15.7	1.866
751222	7.2	1.5	0.023	0.135	0.31	0.41	13.82	<0.2	<0.2	0.46	<0.5	<0.4	7.1	1.208

Field No.23, Icknield Series, Gallops

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
166231	357	340	2431	97	369	47.7	42	1127	143	3080	8.1	10250	0.243	343	10
166232	326	169	2412	91	387	50.1	36	1042	143	2960	7.9	8417	0.231	271	10
266231	418	429	3433	141	621	158.3	57	2133	314	4240	8.0	6083	0.437	276	10
266232	331	234	2745	104	509	99.8	38	1746	286	3500	8.0	8538	0.441	295	12
366231	281	225	3000	74	529	82.3	28	1662	1286	2870	8.1	2667	0.291	364	12
366232	262	202	2881	70	535	67.7	22	1549	1429	2710	8.1	2250	0.280	354	11
466231	203	122	2014	61	321	72.4	61	950	220	3350	7.8	15250	0.253	316	35
466232	190	151	2047	65	325	81.3	73	1040	240	3490	8.3	2833	0.235	289	35
566231	249	113	2000	67	293	84.4	39	930	7	3080	8.4	3417	0.379	312	21
566232	243	95	1925	59	242	79.8	35	820	7	2920	8.2	1833	0.214	325	22
666231	308	178	2669	94	610	109.4	30	1194	110	3000	8.1	4000	*	325	21
666232	325	127	2515	87	622	98.1	34	1149	40	2800	8.0	3750	*	320	22
766231	310	228	2514	95	374	69.9	40	843	81	3730	7.2	4000	0.304	319	20
766232	413	238	2644	99	432	72.0	39	*	*	3880	7.2	*	*	318	18

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
166231	<1.7	<0.9	<0.010	0.110	0.40	<0.2	0.76	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.900
166232	<1.7	<0.9	<0.010	0.102	0.15	<0.2	0.81	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.855
266231	2.5	<0.9	0.017	0.163	0.24	0.38	1.31	<0.2	<0.2	0.69	<0.5	<0.4	<4.5	2.618
266232	2.0	<0.9	0.012	0.116	0.16	0.24	0.94	<0.2	<0.2	0.45	<0.5	<0.4	<4.5	2.128
366231	3.2	<0.9	0.015	0.137	0.22	<0.2	0.65	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.233
366232	3.1	<0.9	0.016	0.133	0.12	<0.2	0.51	<0.2	<0.2	<0.38	<0.5	<0.4	*	2.157
466231	<1.7	<0.9	<0.010	0.063	<0.11	<0.2	0.44	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.684
466232	<1.7	<0.9	<0.010	0.081	<0.11	<0.2	0.46	<0.2	<0.2	<0.38	<0.5	0.5	<4.5	1.754
566231	<1.7	<0.9	<0.010	0.072	0.16	<0.2	1.03	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.533
566232	<1.7	<0.9	0.012	0.071	0.12	<0.2	1.43	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.395
666231	<1.7	<0.9	<0.010	0.107	0.15	<0.2	1.46	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.008
666232	<1.7	<0.9	<0.010	0.092	0.18	<0.2	2.16	<0.2	1.52	0.40	<0.5	<0.4	5.4	1.938
766231	<1.7	<0.9	0.013	0.096	0.35	<0.2	1.70	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.953
766232	<1.7	<0.9	0.015	0.104	0.62	<0.2	2.24	<0.2	<0.2	<0.38	<0.5	<0.4	4.6	2.010

Field No.25, Icknield Series, Pasture

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
161251	360	886	3611	167	520	133.0	126	1014	3000	3000	8.0	15583	0.361	375	18
161252	289	1031	3099	156	306	121.7	68	915	2429	3200	7.9	8667	0.411	295	22
261251	383	571	3235	152	642	201.5	65	1549	1057	4260	8.2	4500	0.508	250	21
261252	409	822	3158	148	688	199.9	83	1740	1286	4140	7.8	5833	0.495	251	22
361251	341	468	2687	114	398	191.7	60	1183	1071	3780	8.1	6167	0.332	289	32
361252	409	1113	3170	156	608	209.5	102	1690	1429	3540	7.5	5250	0.425	248	31
461251	218	263	2365	65	267	132.7	67	775	1980	*	8.1	3833	0.314	257	45
461252	245	428	2448	68	280	140.0	62	820	2440	*	8.1	3000	0.259	261	42
561251	256	200	1601	68	197	269.3	59	585	140	2820	8.0	2500	0.298	258	39
561252	227	190	1691	70	219	258.0	50	570	140	2840	7.9	2500	0.300	254	38
661251	308	621	2325	94	332	198.4	67	899	1410	3270	8.1	3333	*	246	48
661252	304	387	2299	83	335	210.5	29	870	1240	3020	8.2	3167	*	261	38
761251	270	623	2392	111	287	176.4	59	723	*	4120	7.5	4500	0.438	284	39
761252	592	744	2335	108	377	174.7	130	767	104	4020	8.0	5583	0.460	270	39

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
161251	<1.7	<0.9	<0.010	0.350	1.02	0.31	2.74	<0.2	<0.2	1.79	0.7	<0.4	<4.5	2.670
161252	<1.7	<0.9	<0.010	0.353	1.29	0.49	3.34	<0.2	<0.2	0.82	0.7	<0.4	<4.5	2.188
261251	1.9	<0.9	<0.010	0.287	0.39	0.38	0.84	<0.2	<0.2	0.75	<0.5	<0.4	<4.5	2.386
261252	1.8	<0.9	<0.010	0.314	0.36	0.42	0.91	<0.2	<0.2	0.79	<0.5	<0.4	<4.5	2.356
361251	<1.7	<0.9	<0.010	0.233	0.16	0.28	0.69	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.933
361252	<1.7	<0.9	0.012	0.371	0.74	0.39	1.03	<0.2	<0.2	0.81	<0.5	<0.4	<4.5	2.275
461251	<1.7	<0.9	<0.010	0.170	<0.11	<0.2	0.13	<0.2	<0.2	<0.38	<0.5	0.5	<4.5	1.919
461252	<1.7	<0.9	<0.010	0.180	<0.11	<0.2	0.15	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.985
561251	<1.7	<0.9	<0.010	0.121	<0.11	<0.2	0.55	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.161
561252	<1.7	<0.9	<0.010	0.126	<0.11	<0.2	0.82	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.187
661251	<1.7	<0.9	<0.010	0.214	0.34	<0.2	1.54	<0.2	<0.2	0.49	<0.5	<0.4	<4.5	1.704
661252	<1.7	<0.9	<0.010	0.186	0.14	<0.2	0.83	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.683
761251	2.3	<0.9	0.013	0.213	0.76	0.37	1.61	<0.2	<0.2	0.59	<0.5	<0.4	<4.5	1.671
761252	<1.7	<0.9	<0.010	0.230	0.62	0.27	2.14	<0.2	<0.2	0.56	<0.5	<0.4	<4.5	1.732

Field No.26, Icknield Series, Gallops

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
166261	506	45	2424	97	350	83.3	19	1014	929	*	*	12083	0.320	451	8
166262	570	91	2385	103	454	83.8	36	1746	857	1960	8.1	9333	0.386	430	7
266261	1067	318	4881	320	942	196.2	58	4423	286	5250	7.8	14167	0.469	390	15
266262	876	230	4800	268	807	138.5	37	4450	279	4530	7.8	12250	0.689	373	14
366261	490	95	2791	132	539	159.3	49	1684	429	3170	8.0	6833	0.422	421	15
366262	468	147	2809	139	488	204.6	62	1606	357	3600	7.4	6250	0.509	429	16
466261	467	32	2721	100	328	111.5	74	1690	720	*	8.4	4917	0.338	428	27
466262	418	23	2275	74	304	86.2	81	1215	610	*	8.3	*	0.304	467	26
566261	452	93	2991	133	363	184.0	50	1340	360	4290	8.2	4333	*	460	26
566262	476	114	3012	132	379	218.1	70	1550	460	4610	8.2	5083	*	451	27
666261	609	101	3157	164	460	139.2	41	1487	740	3940	8.0	7833	0.404	274	39
666262	545	161	2899	150	441	122.6	46	1763	770	3510	8.2	5417	0.354	457	24
766261	664	86	3999	197	449	145.7	40	893	40	5800	7.4	5083	0.230	449	24
766262	646	46	3571	170	362	114.6	30	1161	38	6300	7.8	7417	0.313	422	23

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
166261	9.3	<0.9	<0.010	0.123	0.12	0.36	1.07	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.619
166262	8.1	<0.9	<0.010	0.111	0.55	0.43	2.46	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.583
266261	6.7	<0.9	0.022	0.251	0.81	0.60	1.83	<0.2	<0.2	15.38	<0.5	<0.4	<4.5	3.113
266262	6.5	<0.9	0.018	0.247	0.34	0.51	1.25	<0.2	<0.2	12.33	<0.5	<0.4	<4.5	3.021
366261	9.4	<0.9	0.015	0.263	0.13	0.27	1.75	<0.2	<0.2	0.47	<0.5	<0.4	4.7	1.800
366262	3.3	<0.9	0.015	0.123	0.16	0.23	1.11	<0.2	<0.2	0.70	<0.5	2.2	<4.5	1.808
466261	<1.7	<0.9	<0.010	0.079	<0.11	<0.2	0.49	<0.2	<0.2	<0.38	<0.5	0.5	<4.5	1.925
466262	<1.7	<0.9	<0.010	0.065	<0.11	<0.2	0.68	<0.2	<0.2	<0.38	<0.5	0.6	<4.5	1.693
566261	6.5	<0.9	<0.010	0.105	0.14	<0.2	1.85	<0.2	<0.2	0.83	<0.5	<0.4	<4.5	1.945
566262	5.9	<0.9	0.011	0.111	0.19	<0.2	2.91	<0.2	<0.2	1.04	<0.5	<0.4	6.3	1.961
666261	4.2	<0.9	<0.010	0.102	0.52	<0.2	2.31	<0.2	<0.2	0.57	<0.5	<0.4	5.4	20.478
666262	4.4	<0.9	0.017	0.105	0.56	<0.2	2.48	<0.2	<0.2	0.60	<0.5	<0.4	6.3	1.853
766261	3.3	<0.9	0.019	0.133	0.32	0.33	2.00	<0.2	<0.2	0.56	<0.5	<0.4	<4.5	2.439
766262	3.0	<0.9	0.015	0.107	<0.11	0.32	1.21	<0.2	<0.2	0.50	<0.5	<0.4	<4.5	2.202

Field No.1, Fyfield Series, Arable

Sample	Na	K	Ca	Mg	S	Si	P	C1	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
112011	170	145	971	35	115	165.4	195	269	1107	*	*	3583	0.239	105	37
112012	212	488	1127	45	132	182.5	231	276	1324	640	6.2	4167	0.248	113	34
212011	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
212012	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
312011	295	1014	3079	98	182	358.3	321	1690	4770	300	6.4	2167	0.206	127	25
312012	295	846	3227	98	188	358.6	243	1746	4770	*	*	2333	0.187	103	29
412011	256	664	1911	55	276	252.8	188	550	3090	590	7.2	2750	0.270	95	34
412012	238	566	1850	49	250	244.3	162	520	3270	650	7.3	2417	0.229	96	31
512011	346	411	1663	45	279	230.0	149	1835	1436	820	6.6	3000	0.234	101	34
512012	*	*	*	*	*	*	*	2216	1420	780	7.4	4083	0.284	106	37
612011	556	779	2604	74	352	159.9	69	682	4200	730	7.6	1750	0.192	130	50
612012	497	778	2531	72	329	173.5	111	693	4230	550	7.4	1583	0.193	129	50
712011	243	239	2064	51	284	237.9	60	197	3430	750	7.3	1500	0.142	416	29
712012	235	279	1950	47	262	229.0	66	191	3180	450	7.1	1500	0.161	122	46

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
112011	9.2	<0.9	<0.010	0.102	2.16	0.35	<0.46	<0.2	<0.2	<0.38	<0.5	<0.4	12.5	0.688
112012	8.3	<0.9	<0.010	0.111	2.79	0.38	9.63	<0.2	<0.2	<0.38	<0.5	<0.4	18.0	0.801
212011	*	*	*	*	*	*	*	*	*	*	*	*	*	*
212012	*	*	*	*	*	*	*	*	*	*	*	*	*	*
312011	11.9	<0.9	0.017	0.250	0.93	0.22	1.16	<0.2	<0.2	<0.38	0.8	<0.4	<4.5	2.156
312012	12.1	<0.9	0.018	0.241	0.98	0.21	1.24	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.192
412011	7.4	<0.9	<0.010	0.109	0.45	<0.2	0.86	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.228
412012	6.5	<0.9	<0.010	0.087	0.26	<0.2	0.85	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.177
512011	7.4	<0.9	<0.010	0.081	0.31	<0.2	2.59	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.094
512012	*	*	*	*	*	*	*	*	*	*	*	*	*	*
612011	4.2	<0.9	<0.010	0.082	0.20	<0.2	1.23	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.583
612012	4.7	<0.9	<0.010	0.091	0.28	<0.2	3.33	<0.2	<0.2	<0.38	<0.5	<0.4	5.0	1.545
712011	6.3	<0.9	0.014	0.098	0.46	<0.2	1.92	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.197
712012	5.9	<0.9	0.012	0.086	0.37	<0.2	1.60	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.128

## Field No.12, Fyfield Series, Arable

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	A1k	pH	DOC	Abs350	MCwet	% Yld
112121	156	658	1216	130	506	208.9	172	1296	442	560	7.1	3583	0.418	116	12
112122	159	577	952	95	364	188.6	149	394	386	900	7.2	3500	0.403	116	23
212121	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
212122	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
312121	287	1777	2525	151	491	473.9	84	3352	1143	1290	7.7	2250	0.227	128	30
312122	283	1583	2633	146	453	462.6	44	3166	1143	1600	7.8	2250	0.227	130	39
412121	167	627	1048	57	203	375.4	84	840	490	1110	7.8	2167	0.250	132	44
412122	145	566	958	48	181	361.8	86	673	410	1080	7.6	1833	0.238	132	44
512121	132	486	801	48	99	414.8	97	640	110	1330	7.7	1833	0.214	150	45
512122	134	523	851	44	97	307.4	92	670	110	1760	7.6	4917	0.253	149	42
612121	223	671	2398	107	195	262.2	42	828	3130	1780	7.8	1000	0.117	147	47
612122	207	630	2133	89	203	257.2	35	693	2700	1690	8.0	1083	0.122	146	46
712121	138	409	1003	57	214	272.7	64	417	1	1670	7.9	2250	0.214	162	44
712122	126	402	921	53	130	313.8	75	394	1	1530	7.8	2250	0.233	140	45

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	MO	Al	Sr
112121	5.9	<0.9	0.013	0.154	4.94	0.70	11.70	<0.2	<0.2	0.65	<0.5	<0.4	17.3	0.860
112122	4.8	<0.9	<0.010	0.090	3.40	0.55	8.34	<0.2	<0.2	0.48	<0.5	<0.4	9.7	0.661
212121	*	*	*	*	*	*	*	*	*	*	*	*	*	*
212122	*	*	*	*	*	*	*	*	*	*	*	*	*	*
312121	4.3	<0.9	<0.010	0.196	0.52	0.31	4.48	<0.2	<0.2	<0.38	<0.5	<0.4	8.1	1.444
312122	3.4	<0.9	<0.010	0.214	0.40	0.31	5.30	<0.2	<0.2	<0.38	<0.5	<0.4	9.2	1.431
412121	3.9	<0.9	0.013	0.075	0.46	<0.2	18.64	<0.2	<0.2	<0.38	<0.5	<0.4	38.7	0.615
412122	3.7	<0.9	0.012	0.087	0.63	<0.2	19.35	<0.2	<0.2	<0.38	<0.5	<0.4	35.8	0.569
512121	3.9	<0.9	<0.010	0.092	0.43	<0.2	26.30	<0.2	<0.2	<0.38	<0.5	8.6	50.6	0.529
512122	1.9	<0.9	<0.010	0.044	0.17	<0.2	9.81	<0.2	6.27	<0.38	<0.5	<0.4	17.1	0.535
612121	2.7	<0.9	<0.010	0.109	<0.11	<0.2	0.68	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.399
612122	2.9	<0.9	<0.010	0.088	<0.11	<0.2	0.80	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.231
712121	4.3	<0.9	<0.010	0.068	0.23	0.27	13.61	<0.2	<0.2	<0.38	<0.5	<0.4	23.3	0.579
712122	4.7	<0.9	<0.010	0.061	0.29	0.25	21.53	<0.2	<0.2	<0.38	<0.5	<0.4	36.2	0.537

Field No.18, Denchworth Series, Arable

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
152181	551	32	894	127	242	477.9	17.0	873	1000	660	7.1	5500	0.396	417	9
152182	545	14	873	116	242	322.3	<13	930	857	220	6.6	4417	0.363	414	9
252181	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
252182	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
352181	829	131	4254	550	961	377.4	45.0	2620	6071	260	7.0	3250	0.183	321	4
352182	930	243	4378	574	1096	396.8	95.0	2761	6000	970	7.4	4333	0.247	321	5
452181	300	10	1034	108	148	199.4	47.0	1745	*	120	6.7	*	0.199	394	23
452182	229	19	702	73	134	243.0	61.0	800	*	490	7.1	14833	0.280	398	24
552181	381	*	875	118	156	340.1	30.0	1105	570	460	7.3	4917	0.367	404	14
552182	354	11	806	102	141	386.7	32.0	1075	740	200	6.5	*	0.288	400	16
652181	414	26	1180	151	317	289.5	16.0	358	2030	240	6.8	3167	0.334	413	26
652182	377	14	1287	161	365	275.4	<13	304	2300	60	6.7	2750	0.191	406	19
752181	264	17	709	88	204	318.4	23.0	614	233	330	7.1	3083	0.340	385	13
752182	323	13	1008	119	194	259.8	14.0	1414	189	200	6.6	2833	0.204	380	*

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
152181	10.0	1.9	0.018	0.106	0.50	<0.2	71.37	0.24	<0.2	<0.38	<0.5	<0.4	85.3	2.132
152182	10.1	1.6	0.016	0.097	0.60	<0.2	47.69	<0.2	<0.2	<0.38	<0.5	<0.4	39.7	2.134
252181	*	*	*	*	*	*	*	*	*	*	*	*	*	*
252182	*	*	*	*	*	*	*	*	*	*	*	*	*	*
352181	9.0	3.9	0.025	0.365	0.83	0.23	1.94	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	9.823
352182	10.1	4.0	0.022	0.427	2.07	0.31	2.65	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	10.399
452181	7.9	<0.9	<0.010	0.079	0.31	<0.2	9.44	<0.2	<0.2	0.55	<0.5	0.5	<4.5	2.784
452182	4.7	<0.9	<0.010	0.082	0.17	<0.2	20.14	<0.2	<0.2	<0.38	<0.5	0.6	18.7	2.061
552181	15.1	1.3	<0.010	0.102	0.28	<0.2	18.33	<0.2	<0.2	1.70	<0.5	<0.4	<0.5	2.000
552182	13.8	1.1	<0.010	0.075	0.21	<0.2	21.57	<0.2	<0.2	0.59	<0.5	<0.4	22.4	1.975
652181	11.1	1.8	0.011	0.089	0.18	<0.2	15.15	<0.2	<0.2	<0.38	<0.5	<0.4	<0.5	2.725
652182	8.9	1.9	0.012	0.091	0.22	<0.2	10.11	<0.2	<0.2	<0.38	<0.5	1.8	5.8	2.940
752181	13.1	1.6	0.026	0.085	0.19	0.21	52.88	0.29	<0.2	<0.38	<0.5	<0.4	30.5	1.584
752182	13.6	1.7	0.020	0.090	0.22	<0.2	23.67	<0.2	<0.2	<0.38	<0.5	<0.4	10.8	2.347

Field No.20, Denchworth Series, Arable

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
152201	*	*	*	*	*	*	*	479	1286	540	7.2	5333	*	220	9
152202	383	394	881	175	233	210.3	41	394	1357	520	6.8	5500	0.325	218	10
252201	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
252202	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
332201	597	1002	4294	771	943	417.9	22	4282	5429	320	6.8	2750	0.239	234	17
332202	588	1019	4410	817	855	420.2	16	4817	5500	220	6.5	3000	0.217	*	13
452201	338	445	1261	213	435	343.7	22	1130	1590	530	7.3	2833	0.312	370	23
452202	348	589	1292	230	442	391.6	28	1165	1610	730	6.8	3750	0.392	346	31
552201	275	379	679	120	308	277.6	22	466	780	630	7.5	3667	0.434	269	22
552202	216	291	471	87	175	277.4	19	240	560	510	7.3	2750	0.460	256	20
652201	342	447	844	153	181	253.9	46	394	1150	960	7.7	2583	0.379	279	23
652202	281	404	1213	219	149	250.0	32	310	2430	780	7.7	2333	0.259	277	26
752201	559	524	2785	538	145	227.8	25	444	6136	610	7.0	3083	0.222	196	8
752202	539	626	2842	550	153	221.6	47	513	6015	1040	7.5	2750	0.257	205	11

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	A1	Sr
152201	*	*	*	*	*	*	*	*	*	*	*	*	*	*
152202	10.5	1.5	<0.010	0.129	0.72	<0.2	11.24	<0.2	<0.2	<0.38	<0.5	<0.4	<0.4	1.834
252201	*	*	*	*	*	*	*	*	*	*	*	*	*	*
252202	*	*	*	*	*	*	*	*	*	*	*	*	*	*
332201	10.8	4.0	0.021	0.563	0.63	0.25	0.85	<0.2	<0.2	0.42	<0.5	<0.4	<4.5	8.697
332202	11.0	4.1	0.022	0.590	0.98	0.26	1.19	<0.2	<0.2	0.46	<0.5	<0.4	<4.5	<0.501
452201	10.3	1.8	<0.010	0.143	0.13	<0.2	11.81	<0.2	<0.2	<0.38	<0.5	<0.4	7.1	2.717
452202	11.2	2.0	<0.010	0.205	0.39	<0.2	23.91	<0.2	<0.2	<0.38	<0.5	<0.4	29.6	2.790
552201	10.2	2.0	<0.010	0.100	0.31	0.26	14.41	<0.2	<0.2	<0.38	<0.5	<0.4	10.1	1.436
552202	9.1	2.0	0.013	0.070	0.18	0.21	14.83	<0.2	<0.2	<0.38	<0.5	<0.4	<0.5	0.986
652201	7.2	1.3	<0.010	0.096	0.28	<0.2	9.20	<0.2	<0.2	<0.38	2.4	<0.4	<4.5	1.658
652202	7.5	1.5	<0.010	0.125	0.29	<0.2	3.23	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.489
752201	11.5	3.9	0.037	0.332	2.91	0.24	5.16	<0.2	<0.2	0.40	<0.5	<0.4	4.8	5.514
752202	10.8	3.1	0.022	0.331	2.42	0.23	5.99	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	5.459

Field No.24, Icknield Series, Arable

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
162241	254	198	3615	53	72	25.8	26.0	225	4786	2000	7.9	1833	0.089	198	22
162242	211	186	3866	55	70	25.4	24.0	141	5500	1900	7.9	1750	0.081	200	12
262241	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
262242	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
362241	273	256	4778	71	790	55.8	19.0	2761	3857	1630	7.9	1500	0.155	207	35
362242	235	223	4401	53	731	54.5	<13	2423	3429	1710	8.0	1167	0.094	219	36
462241	137	131	2037	17	327	46.2	47.0	770	1150	2390	8.0	12583	0.081	308	42
462242	130	122	2032	13	286	39.4	46.0	795	1240	2370	8.2	13583	0.078	266	43
562241	131	129	1719	22	144	79.7	16.0	310	290	3060	8.1	2750	0.092	257	46
562242	138	140	1840	23	138	80.8	<13	275	390	3060	8.2	1000	0.096	254	47
662241	168	122	2229	29	218	43.6	<13	434	1500	2670	8.3	833	0.109	259	48
662242	165	134	2305	28	217	46.6	<13	386	1640	2900	8.2	750	0.106	259	48
762241	155	119	1977	27	202	36.4	<13	100	413	3330	7.8	1500	0.089	240	33
762242	135	239	1904	24	193	33.2	<13	71	479	3080	7.7	1250	0.079	237	32

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
162241	2.4	<0.9	<0.010	0.112	0.17	<0.2	0.65	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.460
162242	2.2	<0.9	<0.010	0.114	0.18	<0.2	0.70	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.606
262241	*	*	*	*	*	*	*	*	*	*	*	*	*	*
262242	*	*	*	*	*	*	*	*	*	*	*	*	*	*
362241	3.8	<0.9	0.022	0.193	0.16	<0.2	0.19	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	3.326
362242	3.8	<0.9	0.023	0.191	0.46	<0.2	10.80	<0.2	<0.2	<0.38	3.6	<0.4	<4.5	2.998
462241	1.8	<0.9	<0.010	0.067	<0.11	<0.2	0.11	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.595
462242	<1.7	<0.9	<0.010	0.050	<0.11	<0.2	0.11	<0.2	<0.2	<0.38	<0.5	0.5	<4.5	1.518
562241	2.8	<0.9	<0.010	0.059	<0.11	<0.2	0.57	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.214
562242	2.8	<0.9	<0.010	0.063	<0.11	<0.2	0.33	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.263
662241	3.1	<0.9	<0.010	0.067	<0.11	<0.2	0.30	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.557
662242	3.3	<0.9	0.011	0.069	<0.11	<0.2	0.34	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.586
762241	3.7	<0.9	<0.010	0.063	<0.11	<0.2	0.48	<0.2	<0.2	<0.38	1.3	<0.4	<4.5	1.340
762242	3.8	<0.9	0.012	0.059	<0.11	<0.2	0.41	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.255

Field No.27, Icknield Series, Arable

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
162271	502	39	2633	104	378	83.1	19	817	929	3080	8.2	11167	0.331	406	11
162272	506	79	2761	111	499	82.7	47	1296	1000	2800	8.1	13417	*	393	9
262271	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
262272	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
362271	415	339	2059	74	274	174.3	48	845	1000	2490	8.2	6333	0.298	316	19
362272	402	352	2014	70	272	168.0	46	817	1000	2490	8.2	6000	0.312	341	18
462271	216	295	1304	31	136	172.5	88	480	900	*	7.9	3500	0.288	402	31
462272	197	306	1213	26	127	150.0	86	365	910	*	7.7	2833	0.258	373	32
562271	272	256	1431	48	125	142.2	38	560	460	2940	8.0	2000	0.174	352	32
562272	317	302	1487	54	139	147.9	51	700	440	2940	8.2	1667	0.210	363	33
662271	335	382	2132	78	222	160.0	37	710	1210	3190	8.2	2667	0.198	469	24
662272	324	381	2105	75	218	157.0	38	685	1220	3080	8.3	2833	0.213	402	29
762271	304	187	2246	71	186	109.9	34	255	650	3590	7.9	2667	0.194	369	26
762272	278	169	2066	66	165	108.5	34	241	645	3220	8.2	2750	0.159	317	24
Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr	
162271	6.3	<0.9	<0.010	0.182	0.21	0.51	2.28	<0.2	<0.2	0.89	<0.5	<0.4	<4.5	1.734	
162272	5.0	<0.9	<0.010	0.119	<0.11	0.32	1.01	<0.2	<0.2	0.65	<0.5	<0.4	<4.5	1.859	
262271	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
262272	*	*	*	*	*	*	*	*	*	*	*	*	*	*	
362271	6.9	<0.9	0.012	0.098	<0.11	0.34	1.54	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.436	
362272	6.6	<0.9	0.014	0.099	<0.11	0.28	0.86	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.391	
462271	2.7	<0.9	<0.010	0.062	0.29	<0.2	6.60	<0.2	<0.2	<0.38	0.9	0.5	5.0	1.092	
462272	2.7	<0.9	<0.010	0.043	<0.11	<0.2	0.81	<0.2	<0.2	<0.38	0.8	0.5	<4.5	1.032	
562271	7.9	<0.9	<0.010	0.065	<0.11	<0.2	0.83	<0.2	<0.2	1.00	<0.5	<0.4	<4.5	1.019	
562272	10.2	<0.9	<0.010	0.063	0.13	<0.2	3.05	<0.2	<0.2	1.09	<0.5	<0.4	7.0	1.070	
662271	4.2	<0.9	<0.010	0.085	<0.11	0.25	2.15	<0.2	<0.2	<0.38	<0.5	<0.4	6.0	1.505	
662272	4.0	<0.9	0.013	0.080	<0.11	0.24	2.41	<0.2	<0.2	<0.38	<0.5	<0.4	6.8	1.474	
762271	3.7	<0.9	<0.010	0.079	<0.11	0.34	1.31	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.581	
762272	4.7	<0.9	0.014	0.082	0.27	0.35	1.52	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.401	

Field No.6, Fyfield Series, Pasture (wet)

Sample	Na	K	Ca	Mg	S	Si	P	C1	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
113061	906	356	1802	157	412	95.4	46.0	*	673	*	*	4583	0.498	313	22
113062	890	338	1728	139	413	85.7	40.0	1690	211	2060	7.1	6667	0.415	295	36
213061	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
213062	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
313061	4126	149	6144	290	3175	77.2	14.0	8648	214	2240	7.3	3167	0.204	287	39
313062	3335	79	4229	252	1985	127.2	<13	6535	214	1860	7.7	2917	0.241	305	40
413061	3572	117	4097	227	1541	98.3	15.0	5860	1030	1920	7.8	3000	0.233	412	28
413062	3439	36	3589	213	1362	104.1	<13	5660	930	1630	7.7	3167	0.213	397	33
513061	1527	101	1273	97	547	143.6	31.0	1475	430	1290	7.5	2083	0.293	394	32
513062	1688	98	1380	96	662	97.0	17.0	1525	460	1330	7.8	2000	0.235	379	31
613061	1526	176	1837	162	513	161.5	<13	1634	*	2840	8.2	2667	0.382	321	28
613062	1674	77	1927	118	502	91.4	<13	1583	260	2980	8.0	1917	0.454	330	38
713061	2020	124	1641	112	543	133.9	37.0	1445	180	2260	6.9	5833	0.448	147	39
713062	1756	51	1360	93	475	122.3	28.0	1270	100	1900	7.2	3250	0.320	267	36

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
113061	6.4	<0.9	<0.010	0.165	1.36	0.24	2.57	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.996
113062	7.2	<0.9	<0.010	0.180	3.90	0.37	6.62	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.091
213061	*	*	*	*	*	*	*	*	*	*	*	*	*	*
213062	*	*	*	*	*	*	*	*	*	*	*	*	*	*
313061	3.2	<0.9	0.023	0.451	0.18	0.24	0.53	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	2.633
313062	3.2	<0.9	0.019	0.283	<0.11	<0.2	0.89	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.866
413061	4.3	<0.9	0.013	0.297	0.29	<0.2	0.79	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.885
413062	5.0	<0.9	0.011	0.248	0.14	<0.2	0.89	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	1.723
513061	3.9	<0.9	<0.010	0.117	0.47	<0.2	18.72	<0.2	<0.2	<0.38	<0.5	<0.4	18.4	0.635
513062	3.6	<0.9	<0.010	0.117	0.30	<0.2	5.68	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.681
613061	3.6	<0.9	<0.010	0.138	1.05	0.27	4.98	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	0.873
613062	2.4	<0.9	<0.010	0.125	0.38	0.28	3.59	<0.2	4.88	<0.38	<0.5	<0.4	9.1	0.880
713061	31.8	<0.9	0.012	0.154	0.54	0.27	16.52	<0.2	<0.2	<0.38	<0.5	<0.4	11.7	0.811
713062	4.0	<0.9	0.015	0.122	0.39	0.21	18.42	<0.2	<0.2	<0.38	<0.5	<0.4	12.1	0.649

Field No.16, Denchworth Series, Pasture (wet)

Sample	Na	K	Ca	Mg	S	Si	P	C1	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
153161	3343	574	6499	796	213	1311.8	65.0	5972	21	10740	8.2	13417	0.371	437	21
153162	2994	633	7639	942	184	1338.5	49.0	4592	7	13750	8.5	22583	0.681	434	21
253161	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
253162	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
353161	*	*	*	*	*	*	*	*	*	*	*	*	*	259	0
353162	*	*	*	*	*	*	*	*	*	*	*	*	*	*	0
453161	989	169	1549	165	302	389.5	68.0	1430	910	1960	7.5	4917	0.589	379	25
453162	1088	153	1529	160	346	292.2	69.0	1555	*	1960	7.5	22000	0.528	413	21
553161	3735	457	4100	775	452	302.6	<13	9135	2250	2720	7.9	4083	0.382	354	17
553162	4251	513	4564	972	508	288.4	<13	11025	2260	1140	7.8	3583	0.293	355	18
653161	834	160	1719	170	305	342.9	20.0	507	1800	1840	8.0	3583	0.544	435	22
653162	841	100	1683	165	328	351.5	15.0	546	1880	1610	8.0	4167	0.542	468	23
753161	2100	53	2098	206	445	227.3	24.0	887	246	4290	8.3	5750	0.450	347	15
753162	1882	89	2187	215	447	252.7	37.0	969	343	4060	8.3	5417	0.481	401	14

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
153161	10.6	5.6	0.020	0.624	12.66	<0.2	20.56	0.29	<0.2	<0.38	<0.5	<0.4	<4.5	9.438
153162	9.5	6.1	0.020	0.591	15.76	<0.2	14.26	0.31	<0.2	<0.38	<0.5	<0.4	<4.5	10.867
253161	*	*	*	*	*	*	*	*	*	*	*	*	*	*
253162	*	*	*	*	*	*	*	*	*	*	*	*	*	*
353161	*	*	*	*	*	*	*	*	*	*	*	*	*	*
353162	*	*	*	*	*	*	*	*	*	*	*	*	*	*
453161	<1.7	<0.9	<0.010	0.150	0.46	<0.2	7.89	<0.2	<0.2	0.44	<0.5	0.5	<4.5	2.618
453162	<1.7	<0.9	<0.010	0.093	<0.11	<0.2	5.25	<0.2	<0.2	<0.38	<0.5	0.6	<4.5	2.725
553161	16.6	4.2	0.016	0.826	0.56	0.37	1.65	<0.2	<0.2	79.36	<0.5	<0.4	<4.5	4.905
553162	30.8	4.8	0.017	1.209	1.41	0.44	2.11	<0.2	<0.2	130.82	<0.5	<0.4	<4.5	5.239
653161	4.3	2.4	0.011	0.116	0.33	0.21	16.85	<0.2	<0.2	<0.38	<0.5	<0.4	7.5	2.222
653162	4.2	2.4	0.012	0.102	0.14	<0.2	15.49	<0.2	<0.2	<0.38	<0.5	<0.4	8.9	2.261
753161	9.7	3.1	<0.010	0.109	<0.11	0.40	5.22	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	3.165
753162	9.7	3.4	0.019	0.128	<0.11	0.46	3.47	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	3.180

Field No.21, Denchworth Series, Pasture (wet)

Sample	Na	K	Ca	Mg	S	Si	P	Cl	NO3	Alk	pH	DOC	Abs350	MCwet	% Yld
153211	814	50	3565	538	622	871.3	23.0	1746	7	6100	8.4	10833	0.452	408	14
153212	820	54	3691	305	445	588.6	15.0	1718	7	6600	8.4	10000	0.387	442	20
253211	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
253212	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
353211	1501	192	6655	495	5572	262.9	26.0	2479	786	3040	7.5	6750	0.466	307	7
353212	*	*	*	*	*	*	*	2563	929	*	*	8167	0.590	*	9
453211	1638	196	6084	472	4387	340.2	52.0	2810	550	2840	8.0	7250	0.407	452	7
453212	1515	170	5973	429	4188	375.2	36.0	2505	510	2670	8.1	5333	0.371	477	8
553211	1115	98	3658	277	2077	264.2	15.0	1475	430	2740	8.2	4250	0.283	389	17
553212	963	140	3223	235	1598	375.7	14.0	1355	430	2740	8.3	3583	0.317	344	6
653211	816	42	3446	262	1239	405.8	<13	1648	250	3760	8.4	3750	0.314	476	26
653212	652	32	3161	241	835	494.4	17.0	1659	90	4140	8.4	3417	0.325	413	27
753211	1441	110	4944	401	2273	245.5	15.0	2930	239	3800	8.0	4750	0.239	371	10
753212	3770	366	2853	333	639	193.6	53.0	3740	193	*	7.4	5750	0.351	381	7

Sample	B	Li	Y	Ba	Mn	Cu	Fe	V	Co	Zn	Ni	Mo	Al	Sr
153211	10.6	5.8	0.019	0.400	34.75	<0.2	15.67	<0.2	<0.2	<0.38	1.5	<0.4	<4.5	12.390
153212	14.5	4.7	0.019	0.303	18.02	<0.2	64.63	0.29	0.27	<0.38	9.2	<0.4	<4.5	6.930
253211	*	*	*	*	*	*	*	*	*	*	*	*	*	*
253212	*	*	*	*	*	*	*	*	*	*	*	*	*	*
353211	7.3	3.5	0.025	0.526	0.27	0.61	1.64	<0.2	<0.2	1.00	0.7	<0.4	<4.5	13.635
353212	*	*	*	*	*	*	*	*	*	*	*	*	*	*
453211	7.9	3.7	<0.010	0.520	<0.11	0.25	1.19	<0.2	<0.2	0.56	<0.5	<0.4	<4.5	12.510
453212	6.7	3.6	0.017	0.488	<0.11	0.25	1.22	<0.2	<0.2	0.46	<0.5	<0.4	<4.5	11.543
553211	5.0	2.6	<0.010	0.284	0.57	<0.2	0.77	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	6.985
553212	6.0	2.9	0.011	0.270	1.27	<0.2	1.00	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	6.000
653211	5.6	2.4	0.013	0.235	0.23	<0.2	1.77	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	5.879
653212	5.8	3.0	0.013	0.212	0.22	<0.2	2.26	<0.2	<0.2	<0.38	<0.5	<0.4	<4.5	5.072
753211	10.1	3.7	0.021	0.381	1.62	0.25	4.32	<0.2	<0.2	2.00	<0.5	<0.4	4.8	8.683
753212	22.6	3.1	0.011	0.296	5.21	0.34	21.22	<0.2	<0.2	4.55	<0.5	<0.4	23.1	4.393

Appendix 4

Partitioning of variances in the main field study based log transformed variables.

All variances are multiplied by 10 000

Denom. = estimated variance used to qualitatively test the lowest stratum; see Chapter 6 for details.

A4.1 Pasture ANOVAR

Partitioning of variance in the Pasture ANOVAR

Strat	DF	Na	K	Ca	Mg	S	Si
T	6	3917	10535	7137	7416	10089	1263
S	5	12239	19906	6394	15791	4541	9708
T.S	28	573	1659	553	697	109	207
S.F	12	3349	10568	2433	5230	2771	5065
T.S.F	66	465	1132	747	844	546	113
Resid	115	675	196	32	44	51	27
Denom		221	944	345	457	205	149

Strat	DF	P	Cl	NO <sub>3</sub>	Alk	pH	DOC
T	6	2086	15840	44895	4192	11916	10192
S	5	14921	4065	20652	36903	57400	2877
T.S	28	1531	1208	7339	3447	4954	405
S.F	12	4798	1336	27034	21789	18211	2047
T.S.F	66	880	772	5718	3714	2936	468
Resid	115	202	209	191	633	941	161
Denom		819	176	2173	*	*	329

Strat	DF	Ba	Fe	Zn	Cu	Sr
T	6	10054	19087	12033	7700	7293
S	5	7559	45504	2382	550	19442
T.S	28	662	2986	3716	1062	478
S.F	12	4736	12151	9500	5249	2407
T.S.F	66	694	2764	1924	604	663
Resid	115	66	313	208	61	319
Denom		2177	3243	3503	250	797

A4.2 Partitioning of variance in the Pasture/Arable ANOVAR

Strat	DF	Na	K	Ca	Mg	S	Si
T	5	1403	4212	4685	4701	7174	697
S	2	12233	66361	8893	32943	1881	50019
L	1	18354	8664	245	17904	27625	2468
T.S	10	678	964	720	872	1010	523
T.L	5	416	2429	948	1184	127	651
S.L	2	68	14245	3070	2941	2	268
T.S.L	9	197	371	751	694	304	102
Resid	88	246	1348	185	276	414	363
Denom		504	1151	689	828	583	196

Strat	DF	P	Cl	NO <sub>3</sub>	Alk	pH	DOC
T	5	1113	11974	28868	1966	3122	4914
S	2	38897	2292	10102	63549	114248	2431
L	1	29100	21861	69726	8075	581	20890
T.S	10	1572	1268	5969	975	4169	514
T.L	5	555	2462	13367	1119	454	5923
S.L	2	6394	2488	12012	26452	28565	667
T.S.L	9	604	1115	5310	961	1266	835
Resid	88	551	358	3528	1206	1539	393
Denom		756	781	6298	893	1429	558

Strat	DF	B	Ba	Fe	Mn
T	5	1010	6024	10899	10804
S	2	9161	8996	114722	88211
L	1	62	11455	483	44792
T.S	10	6553	969	3546	4326
T.L	5	163	572	16673	2624
S.L	2	5494	1357	25416	30893
T.S.L	9	584	511	6160	2959
Resid	88	225	212	1611	966
Denom		384	753	3618	3295

A4.3 Partitioning of variance in the Pasture/Wet Pasture ANOVAR

Strat	DF	Na	K	Ca	Mg	S	Si
Time	5	1523	3598	2405	3393	5269	
Top	1	11034	15854	10983	3891	7593	
T.Top	5	526	635	288	465	624	
Resid	28	411	1035	422	465	569	
Denom		590	1366	709	832	805	

Strat	DF	P	Cl	NO <sub>3</sub>	Alk	pH	DOC
Time	5	2532	5161	30736	2174	3202	3545
Top	1	40510	5237	8242	10265	26760	631
T.Top	5	1830	1229	25767	359	1492	263
Resid	28	522	754	2388	461	850	183
Denom		1207	716	9744	470	1237	2398

Strat	DF	Ba	Fe	Sr
Time	5	3393	7281	2708
Top	1	3906	1529	14747
T.Top	5	626	4469	172
Resid	28	533	912	451
Denom		555	1055	590

Appendix 5Acid digests of the Soils from the Main Experiment

Subsamples of the soils from the first sampling of the main experiment were digested in acid (A1.10) and the digest solutions analysed by ICP-OES. The results are shown overleaf, and are expressed in ppm of the ~~CCA~~-dry soil weight.

Field Number	Na	K	Ca	Mg	B	Li	V	Ba	Mn	Cu	Fe	V
1	37	545	2442	326	4.5	2.1	3.9	33	768	7	9845	12
2	14	275	941	160	2.7	1.0	2.2	18	474	3	6007	7
3	28	628	3638	418	6.6	2.0	5.9	38	1544	9	14719	22
6	27	741	1794	461	4.0	2.0	5.3	18	526	15	10289	16
11	31	743	1400	409	4.5	1.7	3.8	23	503	20	10047	12
12	18	601	4067	424	4.3	1.9	4.4	17	532	9	9939	14
4	50	581	3722	573	4.6	2.1	5.7	20	509	16	13009	12
5	57	820	6466	1050	5.0	4.5	5.5	29	302	18	12136	18
9	64	334	5972	560	5.1	2.8	6.6	34	788	12	13728	16
7	78	1047	12601	1432	8.7	7.2	15.0	53	493	31	26866	28
13	54	2013	20027	1473	8.0	5.5	13.5	70	809	23	20833	22
14	79	2243	69651	1904	8.9	6.7	10.2	65	915	34	26416	31
8	71	1786	18441	2011	11.4	7.5	10.8	80	1512	31	28616	36
10	63	777	9502	1108	6.1	9.7	5.6	47	221	26	19108	16
19	59	1228	6573	1387	8.2	12.1	7.3	45	375	23	26338	25
15	101	2178	24520	1898	7.7	14.6	8.5	47	331	16	21322	30
16	247	1120	56700	2104	3.0	18.1	5.5	66	169	20	8848	14
17	119	1285	7796	1823	6.1	20.1	9.1	45	221	27	17809	27
18	130	750	10111	1657	4.6	19.6	11.1	68	114	28	15760	17
20	40	1165	4517	1004	9.3	7.8	7.9	28	363	23	26885	22
21	111	1031	15863	1433	5.0	12.9	8.4	63	293	26	13401	12
22	72	806	6854	1193	6.9	11.3	6.8	57	234	9	23240	14
23	187	384	259370	1342	5.3	3.5	22.3	49	742	8	6357	10
24	170	515	293420	1424	6.0	3.4	20.3	43	710	8	6512	13
25	165	503	294290	1429	7.5	1.9	10.3	27	440	9	3963	12
26	83	849	60511	1961	7.7	9.5	39.8	106	1648	16	16089	22
27	127	561	97925	1806	7.9	8.1	29.2	81	1249	13	13062	20

Field Number	Cu	Co	Zn	Ni	Mo	Al	Pb	Sr	S	Si	P
1	2.3	3.6	32	20	2.2	2436	25	6	570	49	601
2	1.4	2.2	18	13	0.7	1242	13	3	334	31	292
3	3.7	5.8	41	38	2.3	2889	22	9	586	47	766
6	2.5	4.5	36	18	1.8	2945	19	4	587	56	357
11	2.3	5.2	51	17	2.2	2287	25	5	667	62	807
12	2.4	4.8	41	17	1.8	2633	20	7	525	70	528
4	3.1	4.1	39	22	3.1	3512	26	7	1191	59	504
5	3.0	4.3	53	16	3.2	5309	25	24	1647	87	476
9	3.4	4.6	39	25	2.7	4201	29	9	1561	75	455
7	6.5	7.7	58	28	6.7	11175	37	29	1921	107	910
13	5.2	10.0	71	35	4.3	5781	37	32	1239	139	1736
14	6.7	12.8	108	44	5.2	9824	50	120	3270	134	1687
8	7.0	16.3	67	55	5.7	7799	40	41	2172	126	1092
10	4.3	4.2	38	12	4.3	6607	37	25	1206	88	416
19	6.3	9.9	60	29	4.2	7397	33	21	1724	95	577
15	5.1	8.5	64	27	5.4	8797	32	48	2820	123	1151
16	2.2	3.6	87	12	3.3	4997	32	102	3246	93	1170
17	4.2	6.6	55	18	5.4	9572	35	46	2641	119	681
18	3.7	5.4	43	16	5.0	9753	32	65	2775	138	769
20	6.5	8.5	48	22	4.1	4979	28	24	1210	81	911
21	3.3	4.9	56	16	3.5	6499	31	63	3143	118	819
22	5.3	6.1	33	19	4.2	7142	40	28	1048	86	409
23	2.4	4.1	38	20	5.5	6806	33	257	4423	153	1144
24	2.3	3.9	34	18	5.2	6940	30	266	3903	150	1170
25	1.6	3.1	28	13	4.1	2543	29	269	3994	117	993
26	5.2	9.4	84	47	7.7	14069	56	75	5065	120	2146
27	4.2	7.2	66	36	6.9	11317	46	95	6066	124	1660

## Appendix 6

### Measurement of pH

Many equilibria in the soil-soil solution system are directly influenced by the pH of the soil solution, for example, dissolution of minerals and binding of metals to organic matter. The measurement of the pH of the soil solution in situ is, however, difficult. Direct measurements made by placing electrodes into the soil are subject to errors arising from junction potentials at the soil-electrode interface.

Determinations of pH made from soil pastes and soil suspensions, commonly used in soil testing laboratories, are not free from errors. The addition of water or salt solution to soil samples in excess of that occurring naturally induces dilution effects which arise from exchange reactions (Russell, 1973; Pierre, 1925) and may cause large changes in the activity of ions in the soil paste or suspension.

It is possible to remove the soil solution from the soil without dilution effects (Chapter 23). Separation removes the buffering effect of the soil and allows the soil solution to come into intimate contact with the external atmosphere which generally has a much lower partial pressure of  $\text{CO}_2$  than soil air. Contamination of soil solution with atmospheric concentrations of  $\text{CO}_2$  results in degassing of dissolved  $\text{CO}_2$  and a subsequent rise in pH. The care taken to free soil solution extraction procedures from contamination is rarely extended to contamination with atmospheric air. Pierre (1925) modified Parker's (Parker, 1921; S3.3.1) miscible displacement method to protect displaced soil solution from laboratory air. Mubarak and Olsen (1976a) modified their immiscible displacement method (Mubarak and Olsen, 1976; S3.3.2) to enable pH

measurements to be made without removing the displaced solution from a sealed centrifuge tube. By keeping the system closed, changes in pH caused by the loss of CO<sub>2</sub> were avoided.

The problems of preventing contact with the atmosphere are compounded when dealing with samples of field soil. Both of the above techniques were developed for use with laboratory amended soils which were under close control. When dealing with field soils, unless the soil solution is extracted immediately and pH measurements made under sealed conditions, loss of CO<sub>2</sub> from the soil atmosphere and a subsequent rise in soil solution pH is unavoidable.

Thus, to obtain accurate measurements of the true pH of the soil solution would require that solutions be extracted and their pH measured in the field. This would have been very difficult given the time and resources available. Soil solution pHs were measured at equilibrium with normal atmospheric levels of CO<sub>2</sub>. In solutions with negative alkalinity, that is those from acidic soils, degassing on equilibration with atmospheric CO<sub>2</sub> levels does not increase the pH (Reuss and Johnson, 1985). In those solutions with a positive alkalinity pHs are systematically elevated by an unknown amount above their true in situ value. The in situ pH will be determined, to an extent, by the partial pressure of CO<sub>2</sub> in soil air. This is very variable and depends on a number of factors such as microbial activity and soil porosity. A partial pressure of 0.3% is widely regarded as the norm for a typical topsoil, though the normal range is 0.03 to 3%.

Discussion of soil solution equilibria based on pH measurements made in this study will be severely limited by the lack of accurate pH data and the total lack of measurements of the partial pressure of CO<sub>2</sub> in the soil atmosphere.

Whilst estimates of in situ soil solution pH based on simple assumptions are likely to be inaccurate, accurate methods are likely to be involved and require extensive calculations. In view of the precision of the original pH measurements (A1.6) rigorous calculations would be futile. The method set out below was deemed to be sufficiently accurate.

#### Neutral and Alkaline soil solutions

The alkalinity of a solution is conservative with changing partial pressures of CO<sub>2</sub> provided that no heterogenous carbonate reactions are involved. If it is assumed that the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in contact with the soil solution remains constant in the samples until they are extracted then the change in pH arising from re-equilibration with an atmospheric pCO<sub>2</sub> can be calculated from the alkalinity.

In neutral and alkaline soil solutions the main contribution to alkalinity are the aqueous carbonate species. The concentrations of hydroxide, protons, boron and silica are so much lower than those of the carbonate species that they will make a negligible contribution to the alkalinity.

The equation

$$[\text{Alk}] = \frac{K_{\text{H}} p\text{CO}_2 (a_1 + 2a_2)}{a_0}$$

where  $a_0$ ,  $a_1$ , and  $a_2$  are the ionisation fractions of H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> respectively and  $K_{\text{H}}$  is the Henry's law constant and pCO<sub>2</sub> is the partial pressure of CO<sub>2</sub> may be used to calculate the pH of a solution at equilibrium with a given pCO<sub>2</sub>.

Where

$$a_0 = \left( 1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right)^{-1}$$

$$a_1 = \left( \frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} \right)^{-1}$$

$$a_2 = \left( \frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1 \right)^{-1}$$

Where  $pK_H = 1.269$ ,  $pK_1 = 6.464$ ,  $pK_2 = 10.490$  (corrected to an ionic strength of  $10^{-3}$  M,  $T = 10^\circ\text{C}$ ) and  $pCO_2$  is the partial pressure of carbon dioxide in atmospheres.

The above equation was incorporated into a simple iterative computer program to enable an estimate of the in situ pH of the displaced soil solutions to be made. A  $pCO_2$  of 0.3% was assumed.

#### Acidic Soil Solutions

In solutions of pH less than 6 the bicarbonate concentration becomes vanishingly small, and is far less than  $10\ \mu\text{M}$  which is the minimum that can be measured by titration (Al.5). In such solutions the major carbon species is  $CO_2(\text{aq})$ . Degassing of  $CO_2$  due to a decrease in  $pCO_2$  will not result in an increase in soil solution pH. And so no pH correction is necessary when using pH in calculations concerning solutions from acidic soils.

Appendix 7Fertilizer Histories of the Fields in the Main Experiment

Information on the fertilizer histories of some of the sites in the main

experiment was made available by the owners of the fields concerned.

Field 1, Arable; no information.

Field 2, Grass; no fertilizer applications in recent years.

Field 3, Grass; 4.7 tonnes/ha ground limestone in autumn 1983.

Field 4, Grass; 56 units N on 5/3/1984, pig slurry in the winter of 83/84

Field 5, Grass; no information.

Field 6, Grass; no fertilizer applications in recent years.

Field 7, Grass; no information.

Field 8, Grass; no information.

Field 9, Grass; 2.5 cwts/a 5.24.24 NPK plus 60 units N in 1984.

Field 10, Grass; no information.

Field 11, Grass; as Field 9.

Field 12, Arable; 8N.28P.56K in autumn 1983, 110 units N in March 1984.

Field 13, Grass; no information.

Field 14, Grass; no information.

Field 15, Grass; FYM and a light application of NPK in 83/84.

Field 16/17, Grass; 80 kg/ha N as urea in 1984, same plus 24 tonnes/ha FYM in 1983

Field 18, Arable; 80N(urea).30P.30K in 1984, same in 1983.

Field 19, Grass; 200-250 units N in 83/84

Field 20, Arable; no information.

Field 21/22, Grass; no information.

Field 23, Grass; occasional light dressings of P.

Field 24, Arable; 3 cwt/a ICI No 11, 3 cwt/a Nitram and 1.5 cwt/a Key Nitro during 83/84

Field 25, Grass; no information.

Field 26, Grass; no information.

Field 27, Arable; 140.72.104 NPK during 83/84.

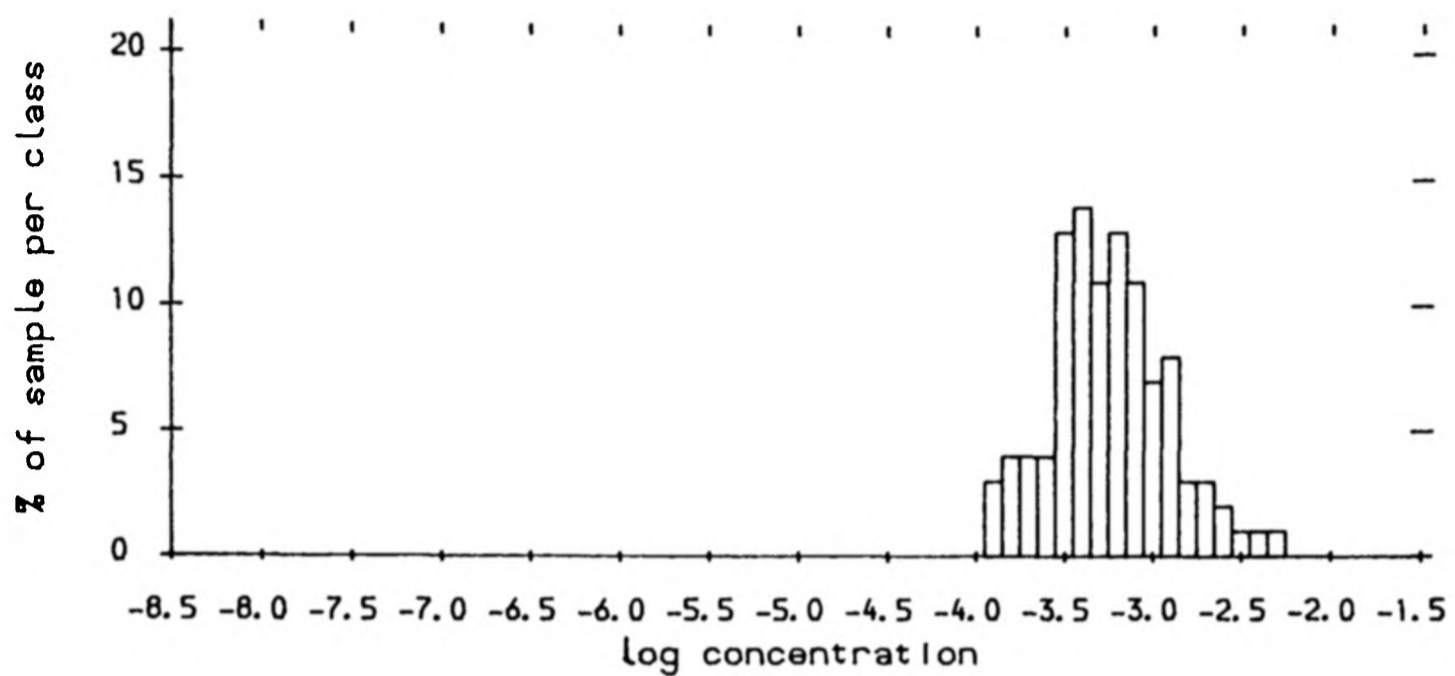
One unit is approximately 0.5 kg/ha

Appendix 8A Summary of the Results from the Main Experiment

The results from the main experiment are summarised in a number of ways on the following pages. All of the concentrations are log M. A number of different means are quoted, all of which are geometric means. The grand mean is the mean of all of the pasture samples. Each of the soil means is the mean for the three pasture sites on that soil, averaged over the seven sampling visits. Each of the time means is the average over all of the pasture sites at each of the sampling times. Where a single figure is given for the arable soils, this is the average for all of the arable sites over all of the sampling times. Where three figures are given they refer to the three soils separately. Similarly for the wet sites.

Na

Grand Mean -3.278



## Soil Means

Fy -3.493

Kg -3.255

Si -3.329

Ea -3.087

Da -3.082

Ia -3.425

## Time Means

Ju -3.292

S -3.094

O -3.207

D -3.304

Ja -3.421

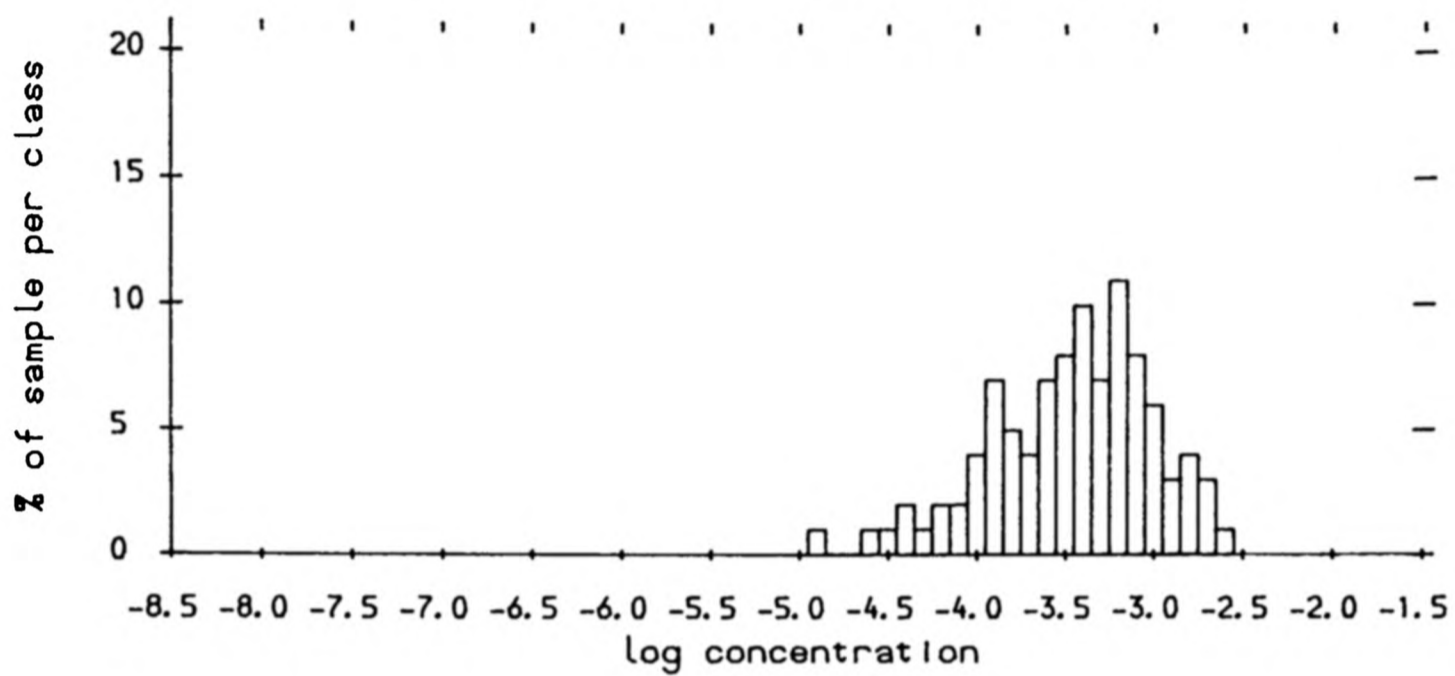
M -3.349

Ju -3.284

Arable Soils -3.560

K

Grand Mean -3.350



## Soil Means

Fy -3.090

Kg -3.287

Si -3.164

Ea -3.472

Da -3.397

Ia -3.687

## Time Means

Ju -3.264

S -3.138

O -3.180

D -3.431

Ja -3.635

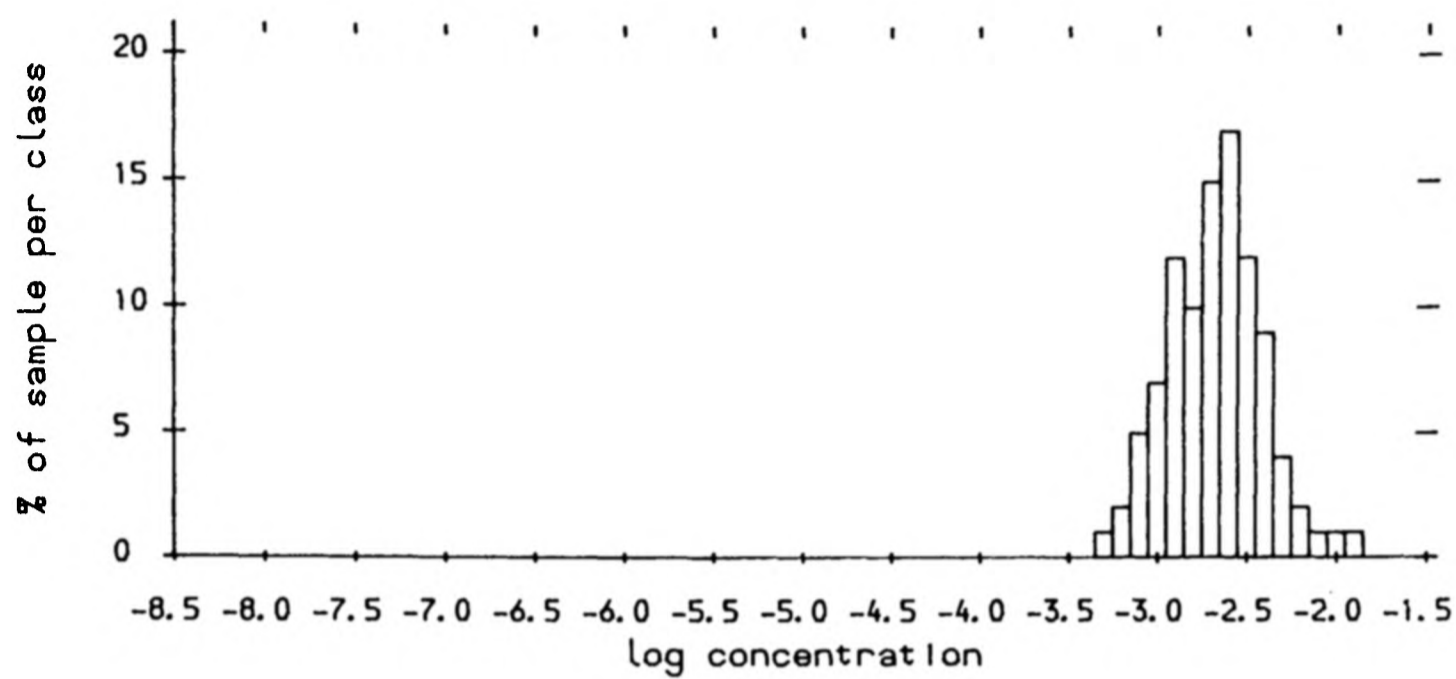
M -3.430

Ju -3.370

Arable Soils Fy -3.254 Da -3.939 Ia -3.728

Ca

Grand Mean -2.648



## Soil Means

Fy -2.884

Kg -2.635

Si -2.535

Ea -2.612

Da -2.655

Ia -2.570

## Time Means

Ju -2.663

S -2.410

O -2.544

D -2.613

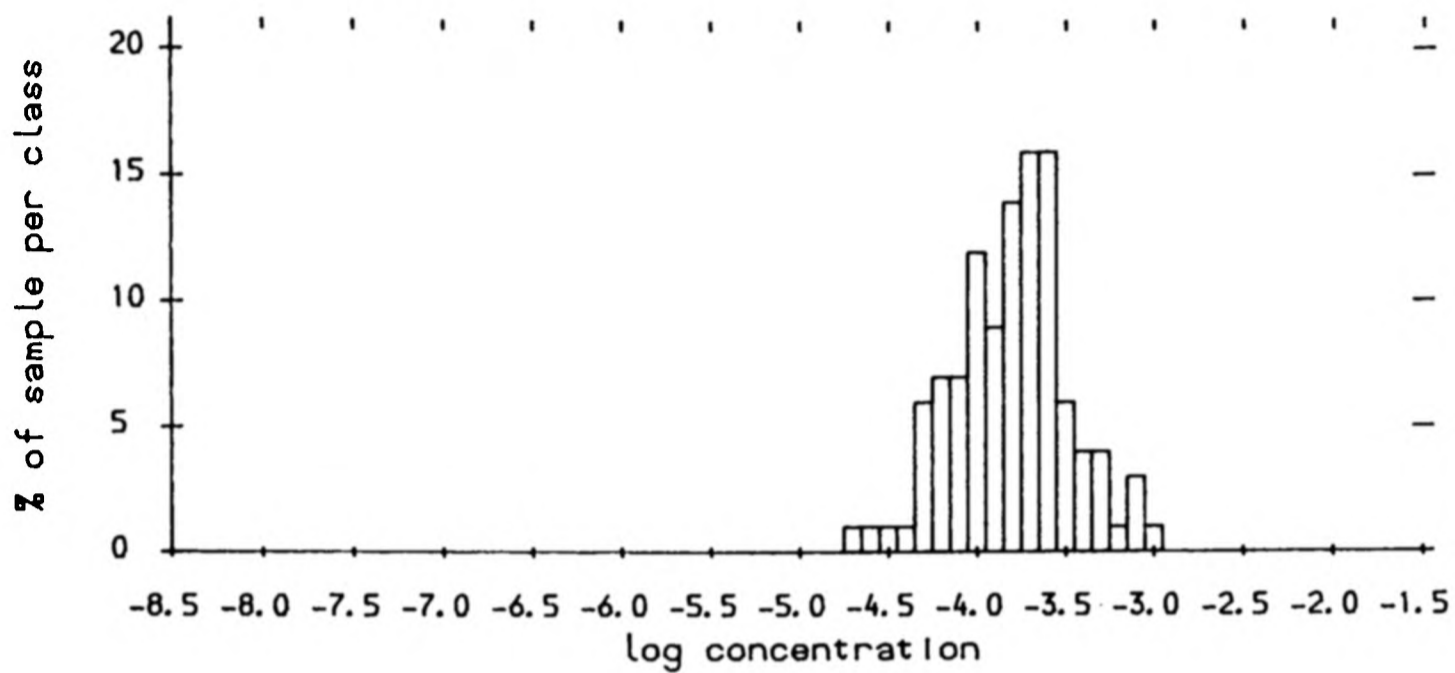
Ja -2.832

M -2.745

Ju -2.730

Mg

Grand Mean -3.725



## Soil Means

Fy -3.949

Kg -3.744

Si -3.560

Ea -3.548

Da -3.508

Ia -3.966

## Time Means

Ju -3.728

S -3.475

O -3.615

D -3.728

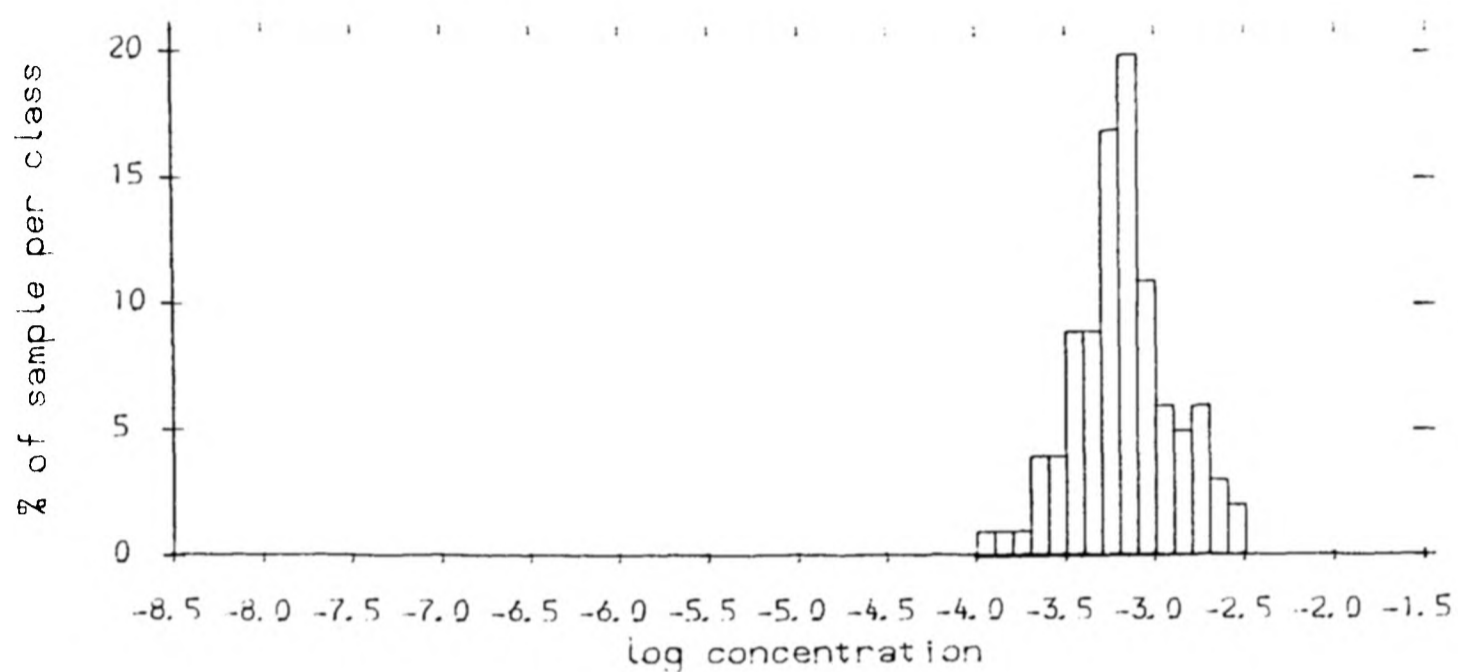
Ja -3.913

M -3.820

Ju -3.973

Arable Soils -4.084

Grand Mean -3.326



Soil Means

Fy -3.398

Kg -3.344

Si -3.422

Ea -3.151

Da -3.256

Ia -3.387

Time Means

Ju -3.468

S -3.066

O -3.154

D -3.301

Ja -3.537

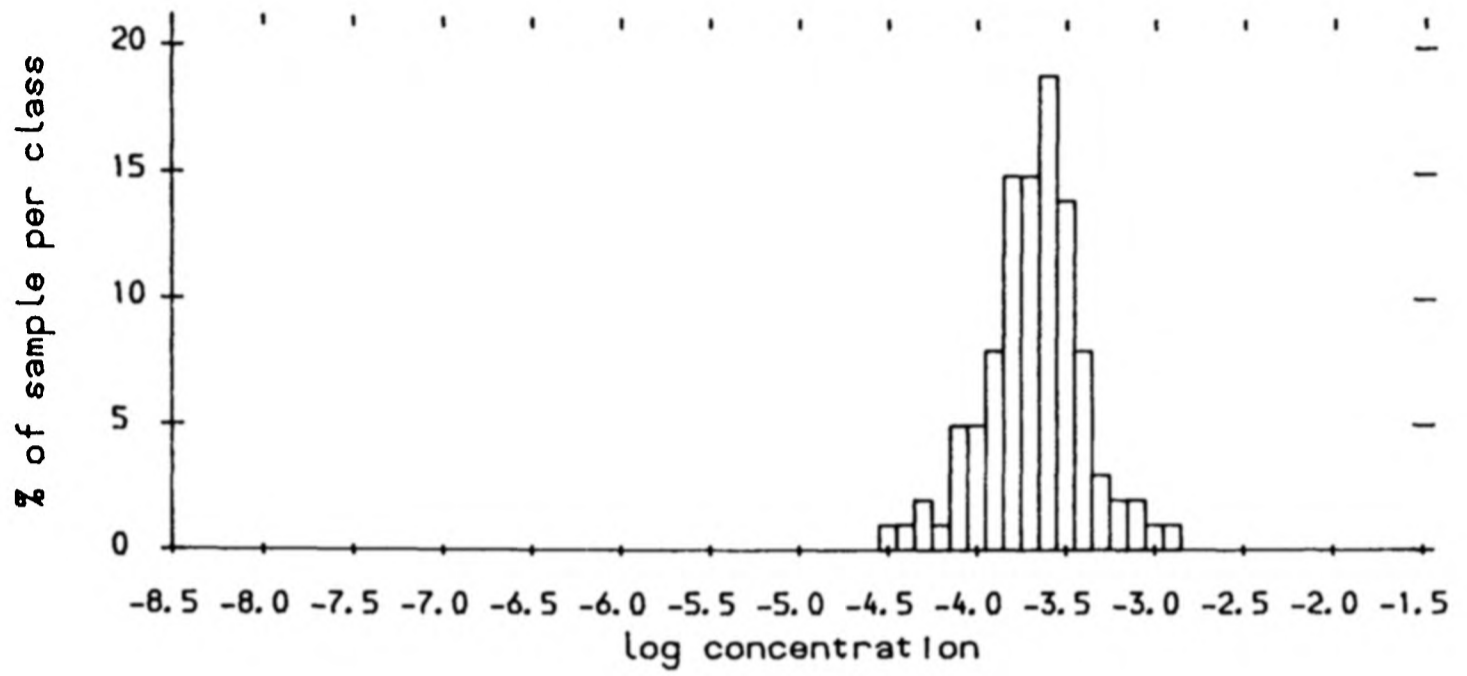
M -3.361

Ju -3.396

Arable Fields -3.360

Si

Grand Mean -3.650



## Soil Means

Fy -3.555

Kg -3.645

Si -3.577

Ea -3.743

Da -3.479

Ia -3.902

## Time Means

Ju -3.755

S -3.562

O -3.627

D -3.585

Ja -3.651

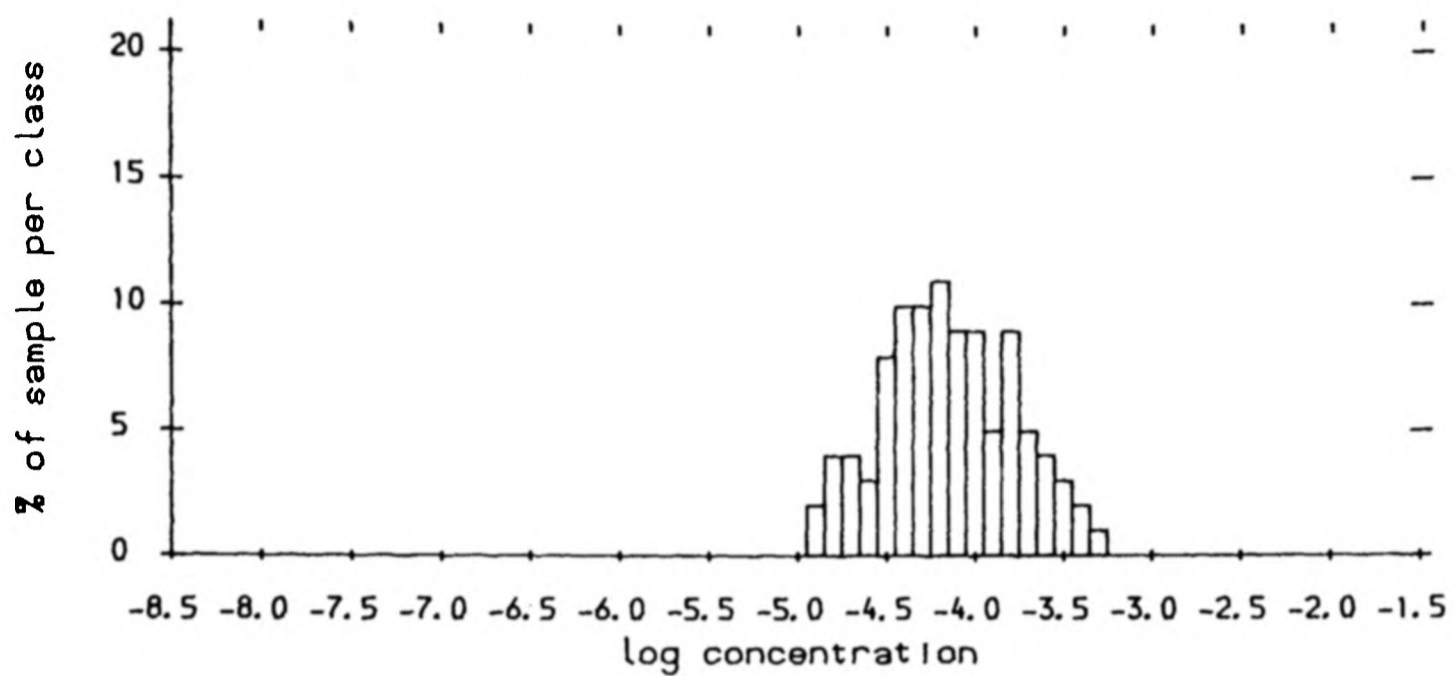
M -3.628

Ju -3.641

Arable Fields -3.733

P

Grand Mean -4.061



3% of values below the first class

Soil Means

Fy -3.854

Kg -4.179

Si -3.847

Ea -4.179

Da -4.003

Ia -4.302

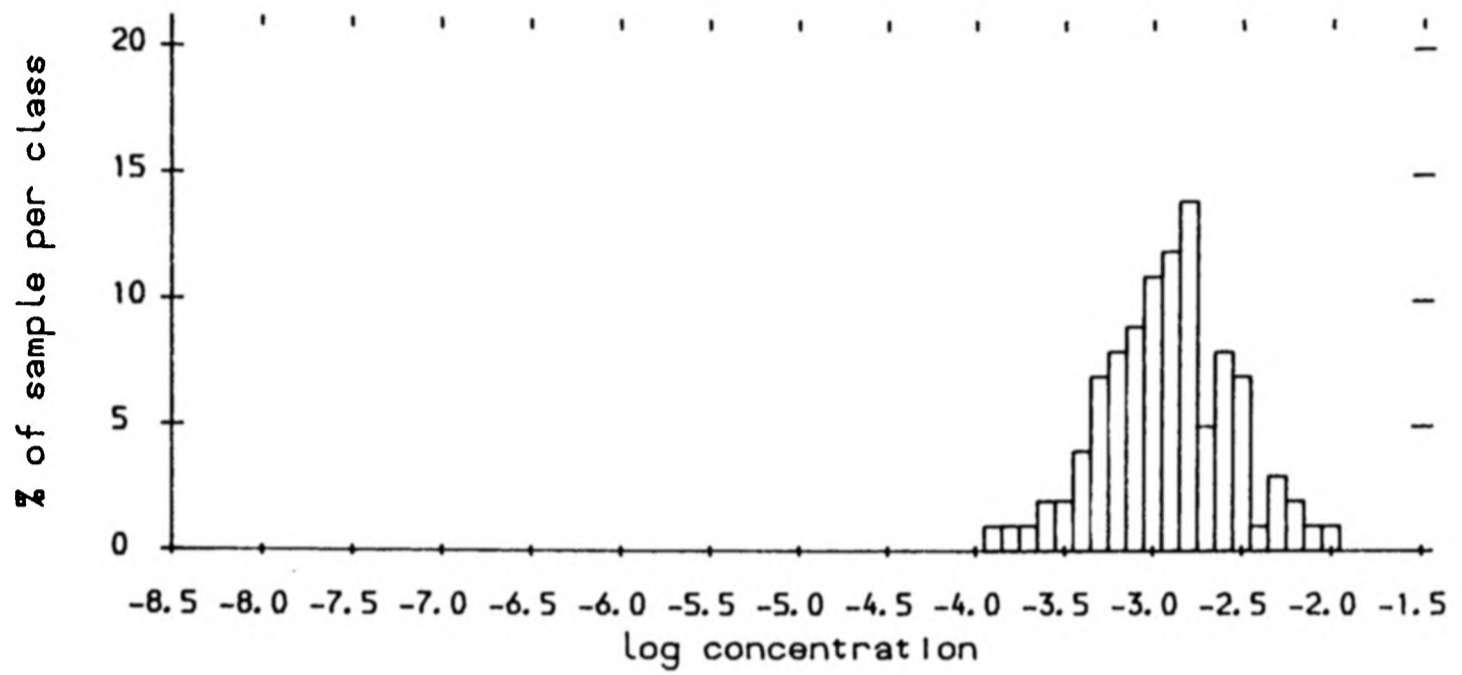
Time Means

No significant temporal change

Arable Soils -4.328

Cl<sup>-</sup>

Grand Mean -2.847



## Soil Means

Fy -2.994

Kg -2.750

Si -2.867

Ea -2.739

Da -2.816

Ia -2.914

## Time Means

Ju -2.740

S -2.594

O -2.664

D -2.757

Ja -3.032

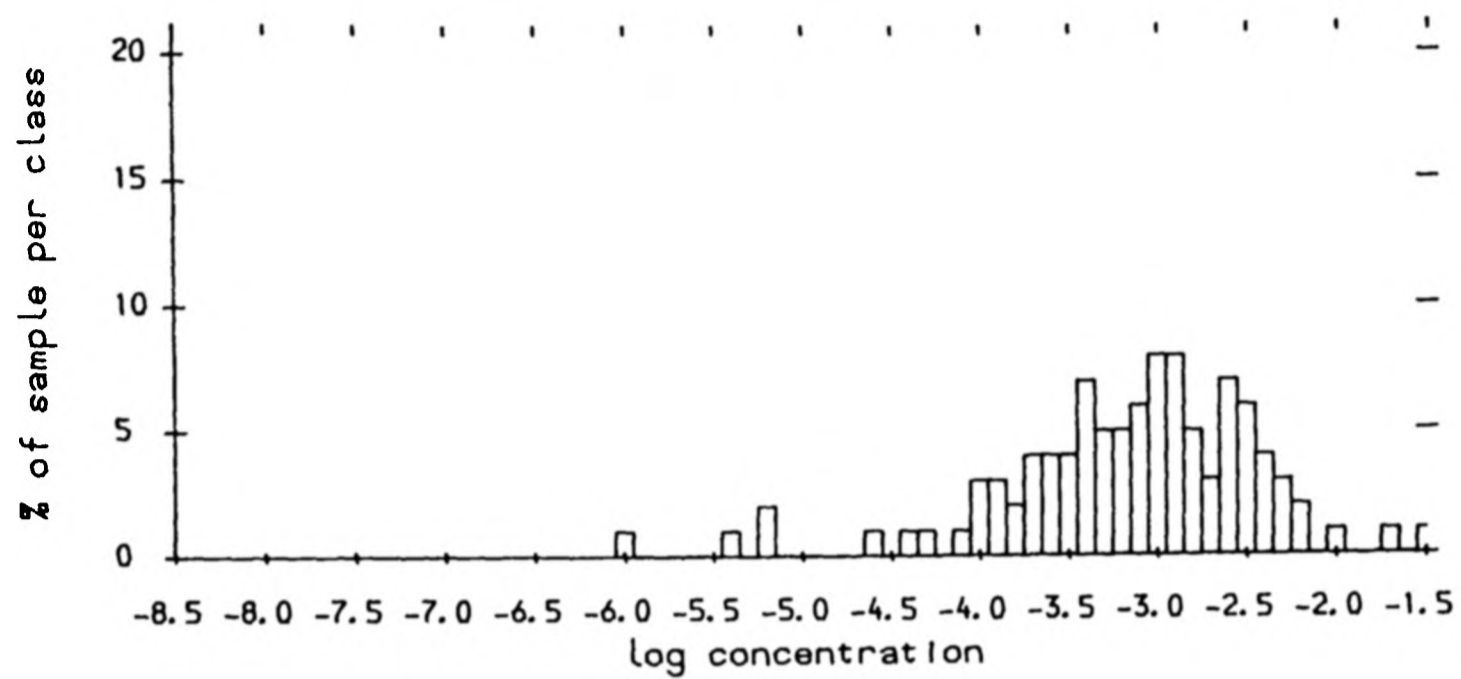
M -2.987

Ju -3.153

Arable Soils -3.178

NO<sub>3</sub><sup>-</sup>

Grand Mean -3.154



Soil Means

No significant between-series difference

Time Means

Ju -3.154

S -2.775

O -2.889

D -2.766

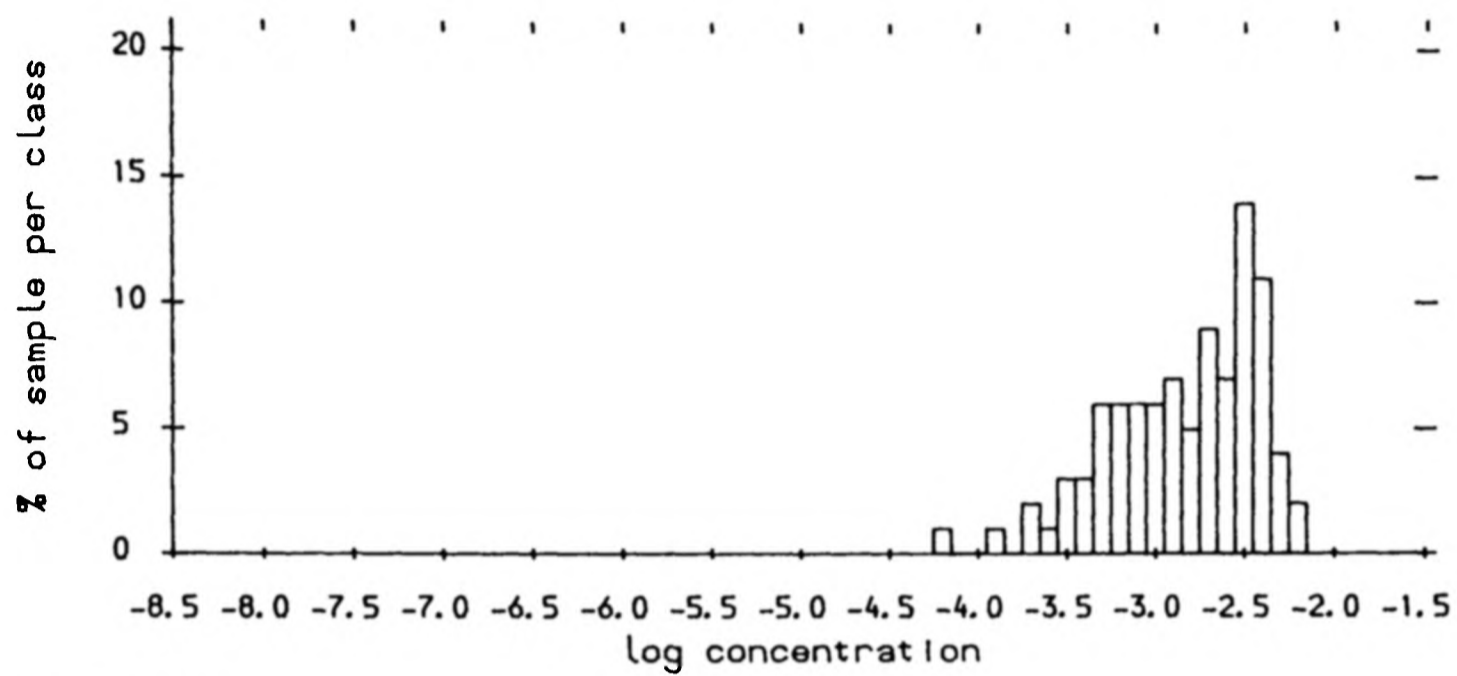
Ja -3.395

M -3.534

Ju -3.580

## Alkalinity

Grand Mean -2.859



## Soil Means

Fy -3.226

Kg -3.170

Si -2.751

Ea -2.869

Da -2.683

Ia -2.452

## Time Means

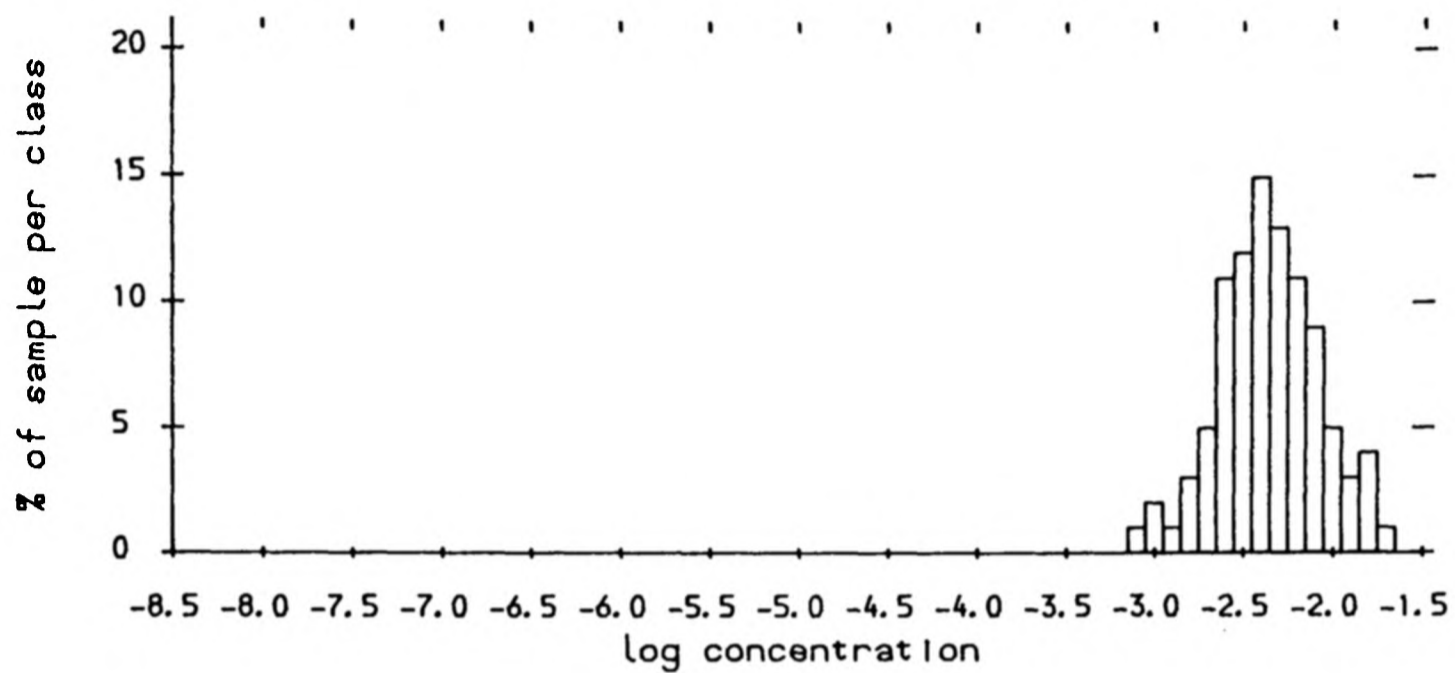
No significant temporal change

Arable Soils Fy -3.047 Da -3.043 Ia -2.576

Wet Sites -2.761

DOC

Grand Mean -2.296



## Soil Means

Fy -2.420

Kg -2.368

Si -2.216

Ea -2.223

Da -2.252

Ia -2.298

## Time Means

Ju -2.042

S -2.166

O -2.282

D -2.280

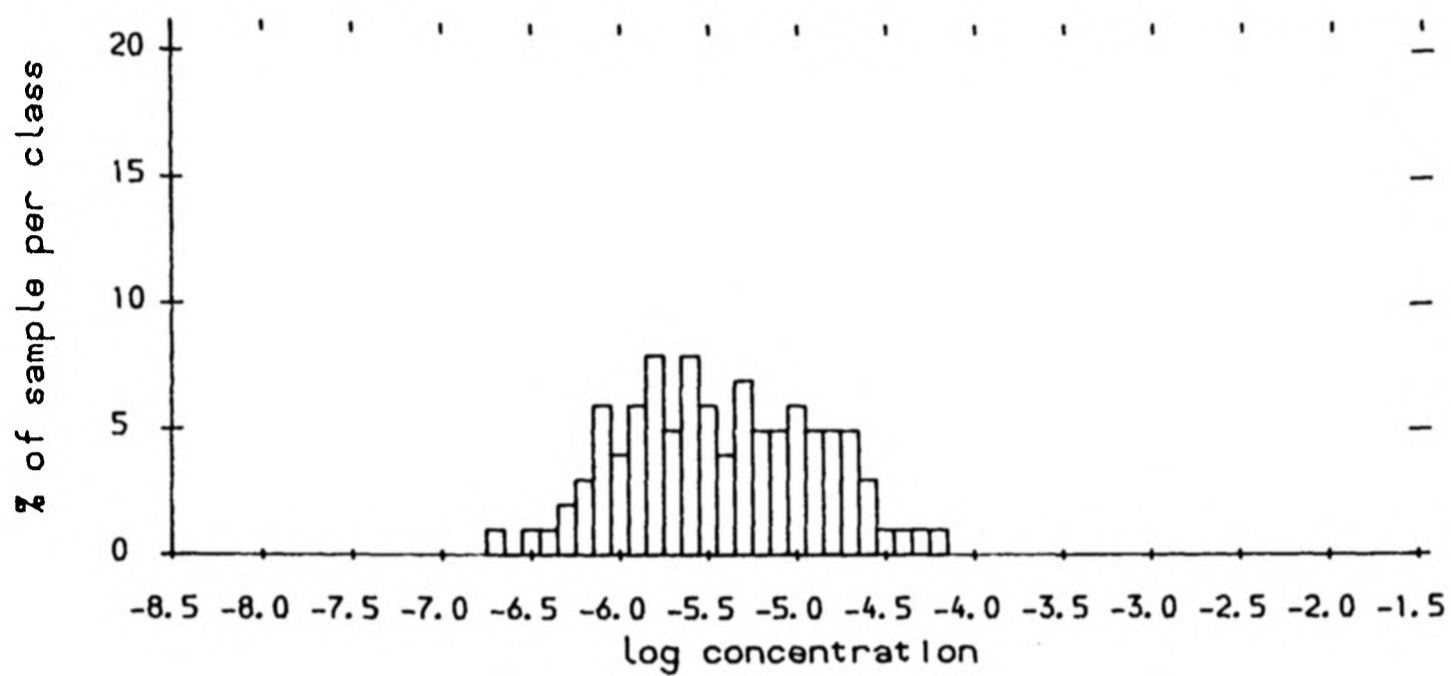
Ja -2.525

M -2.485

Ju -2.293

Fe

Grand Mean -5.399



## Soil Means

Fy -4.999

Kg -5.525

Si -5.392

Ea -5.182

Da -5.337

Ia -5.960

## Time Means

Ju -5.337

S -5.339

O -5.556

D -5.810

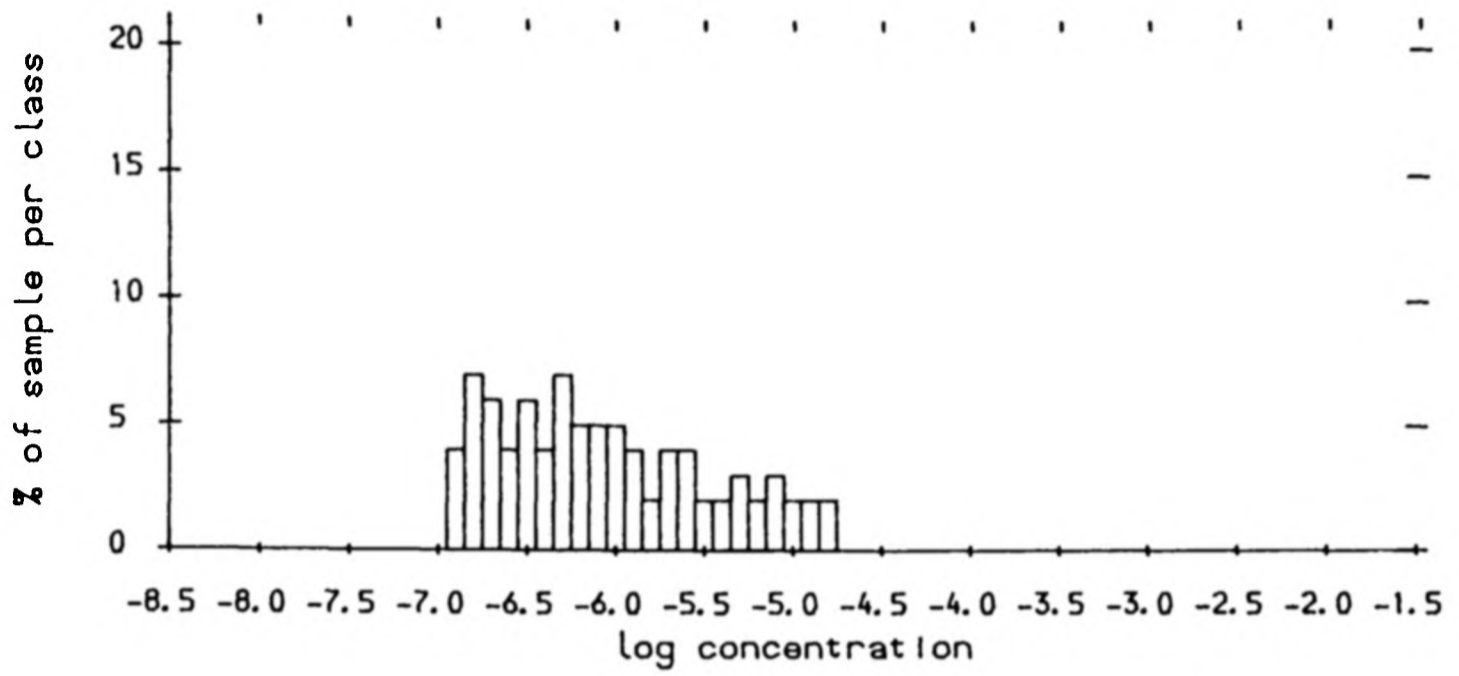
Ja -5.436

M -5.167

Ju -5.150

Mn

Grand Mean -6.037



14% of values below the first class

Soil Means

Fy -5.508

Kg -5.690

Si -5.923

Ea -6.067

Da -6.482

Ia -6.553

Time Means

Ju -5.624

S -5.820

O -6.035

D -6.178

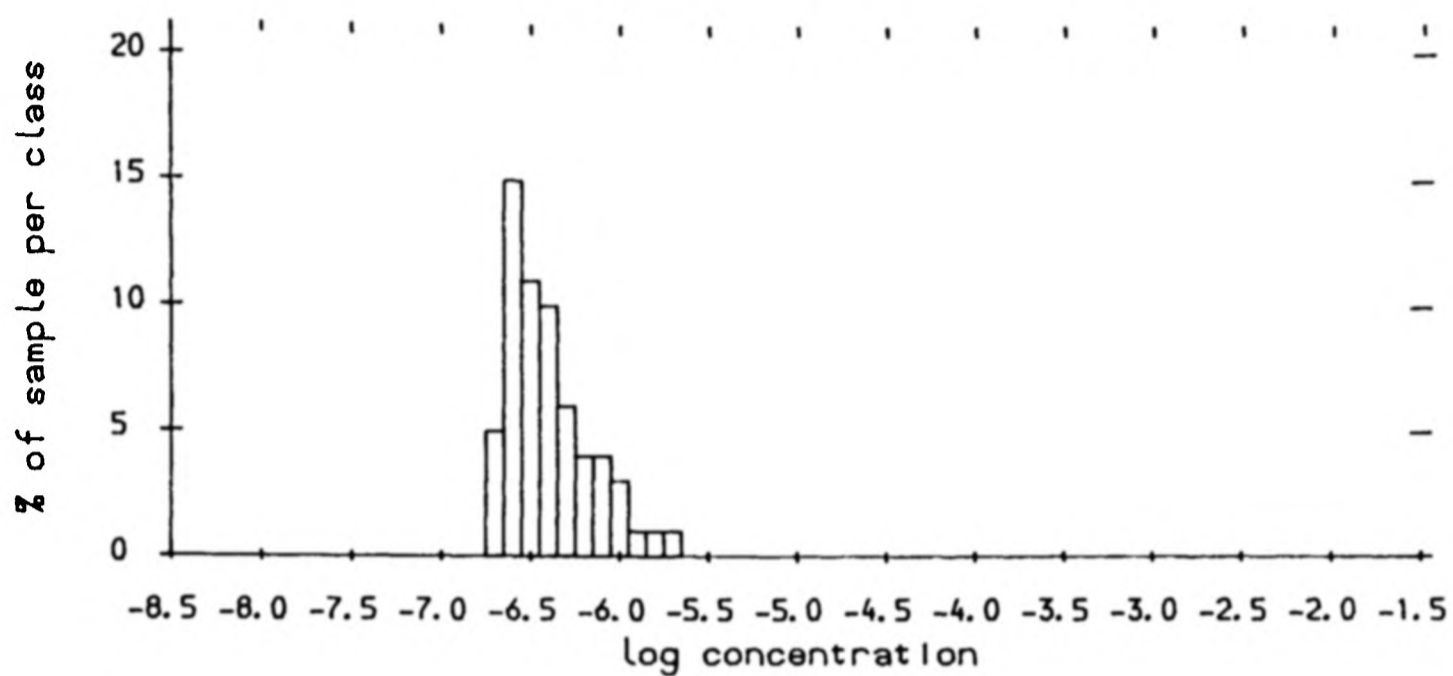
Ja -6.470

M -6.041

Ju -6.094

Cu

Grand Mean -6.487



38% of values below the first class

## Soil Means

Fy -6.384

Kg -6.576

Si -6.356

Ea -6.454

Da -6.496

Ia -6.656

## Time Means

Ju -6.443

S -6.286

O -6.433

D -6.595

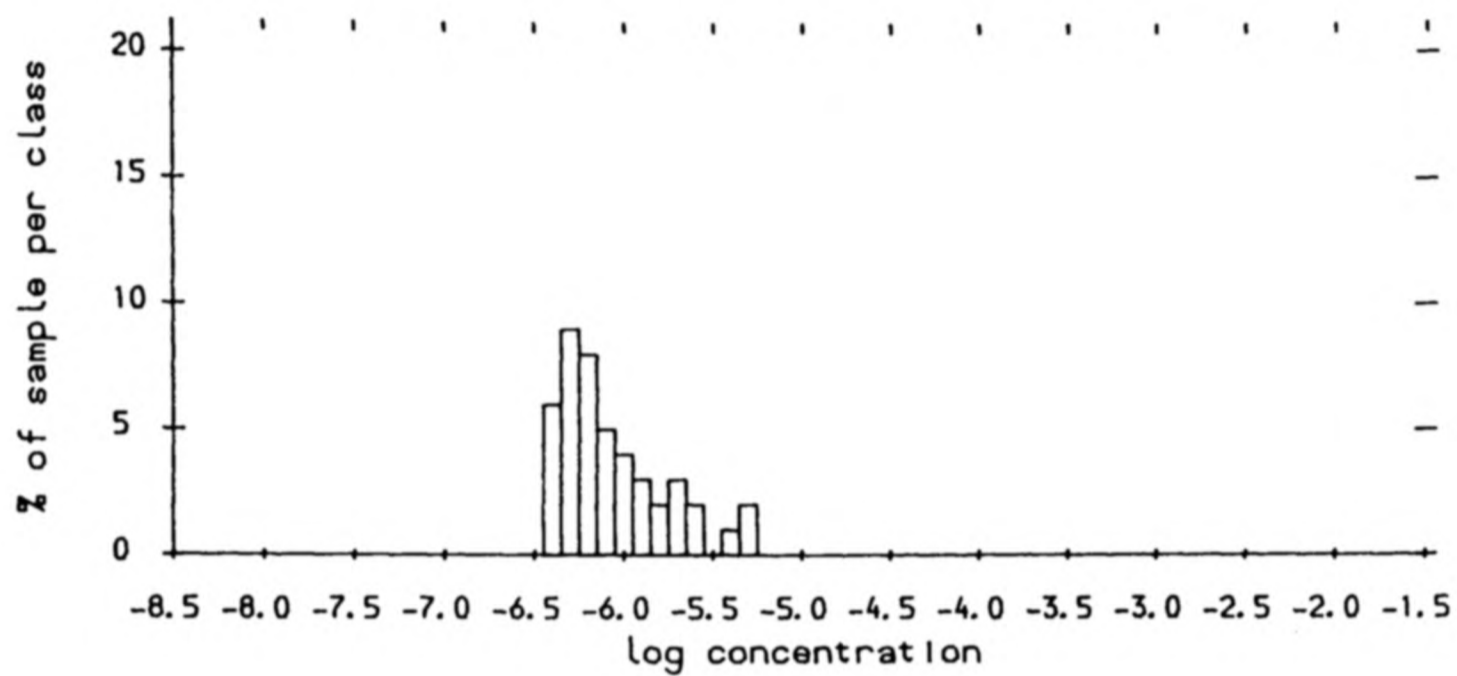
Ja -6.728

M -6.539

Ju -6.386

Zn

Grand Mean -6.218



55% of values below the first class

## Soil Means

Fy -6.249

Kg -6.393

Si -6.257

Ea -6.167

Da -6.251

Ia -6.313

## Time Means

Ju -6.339

S -5.921

O -6.172

D -6.422

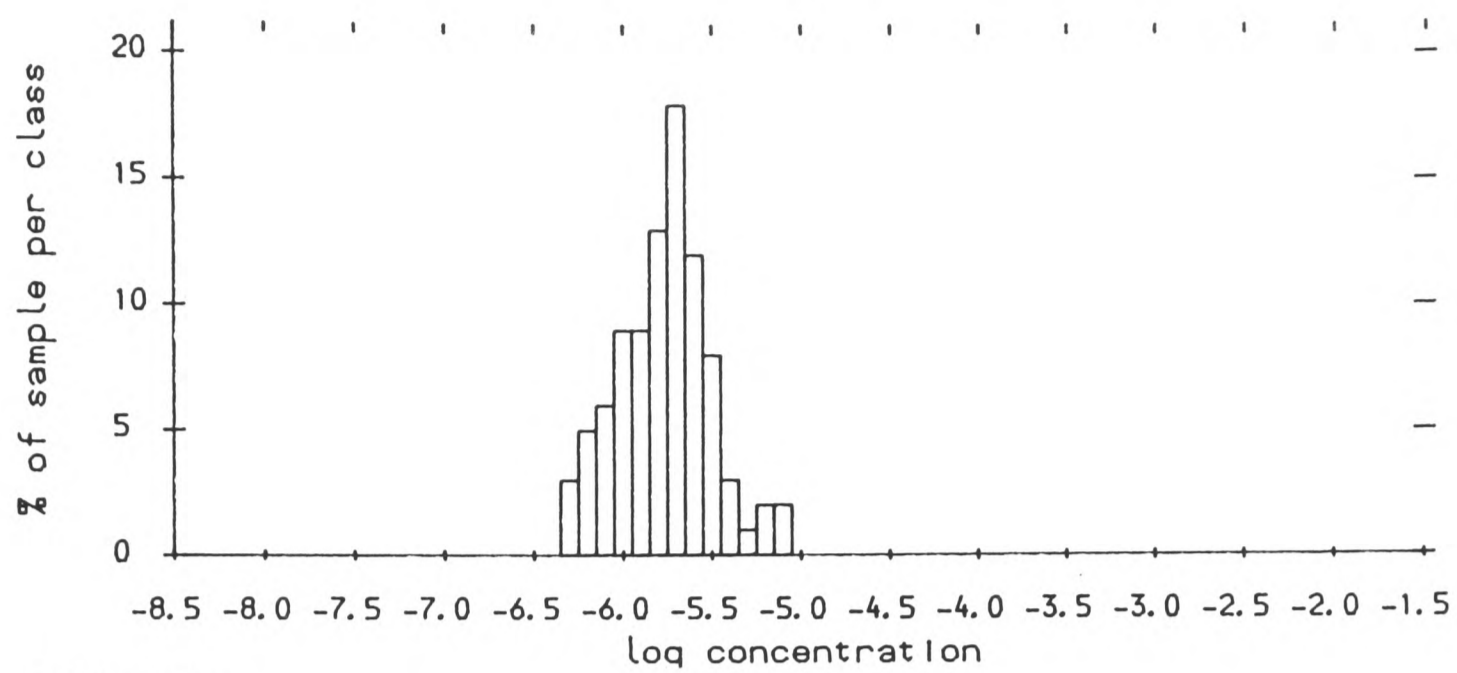
Ja -6.467

M -6.317

Ju -6.264

Sr

Grand Mean -5.685



## Soil Means

Fy -6.012

Kg -5.843

Si -5.586

Ea -5.439

Da -5.516

Ia -5.713

## Time Means

Ju -5.698

S -5.447

O -5.589

D -5.625

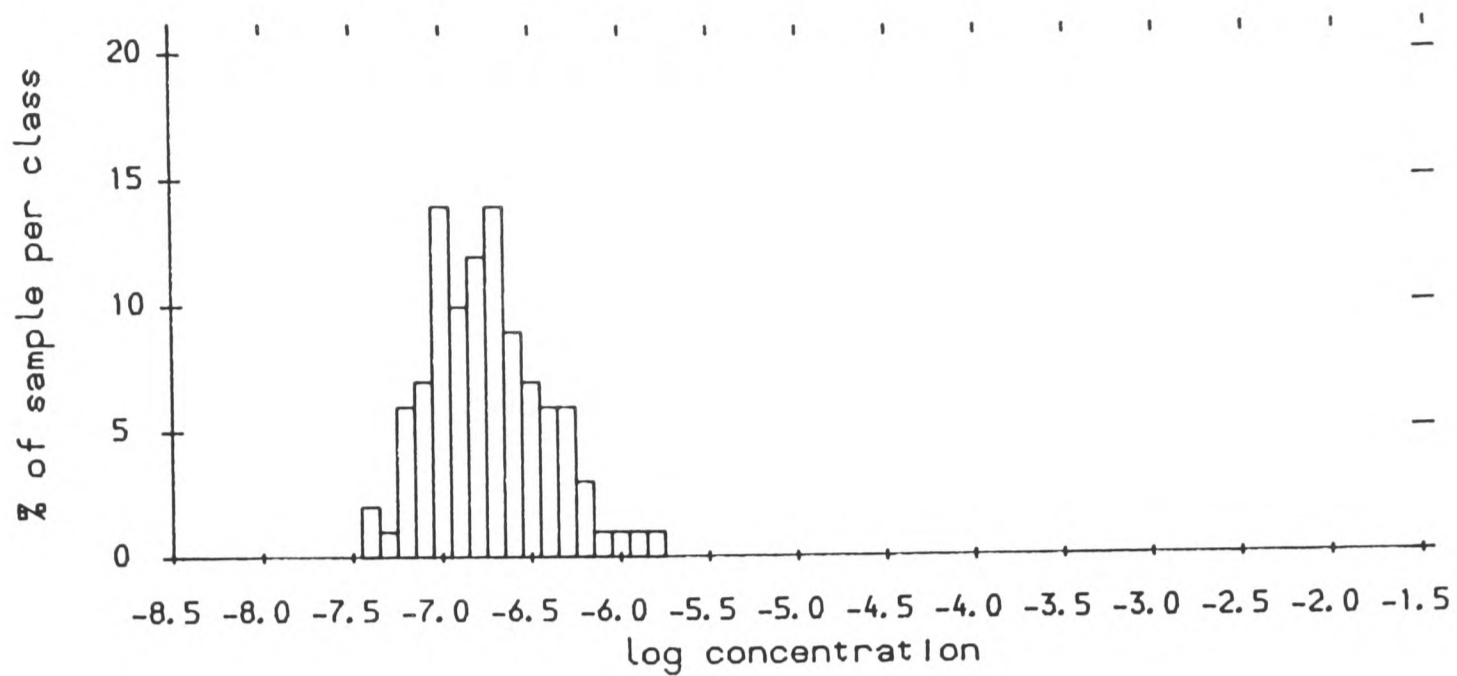
Ja -5.863

M -5.787

Ju -5.784

Ba

Grand Mean -6.697



## Soil Means

Fy -6.839

Kg -6.669

Si -6.488

Ea -6.658

Da -6.676

Ia -6.849

## Time Means

Ju -6.724

S -6.442

O -6.506

D -6.692

Ja -6.902

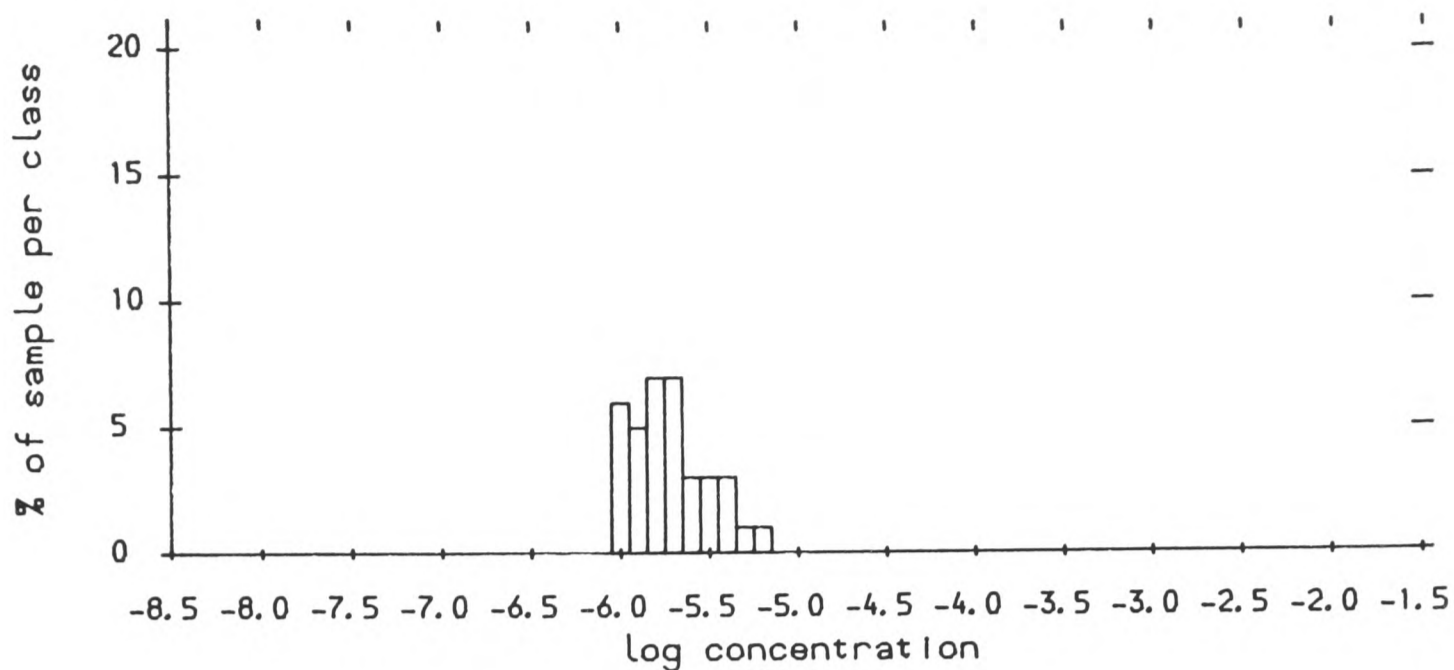
M -6.805

Ju -6.804

Arable Soils -6.973

Li

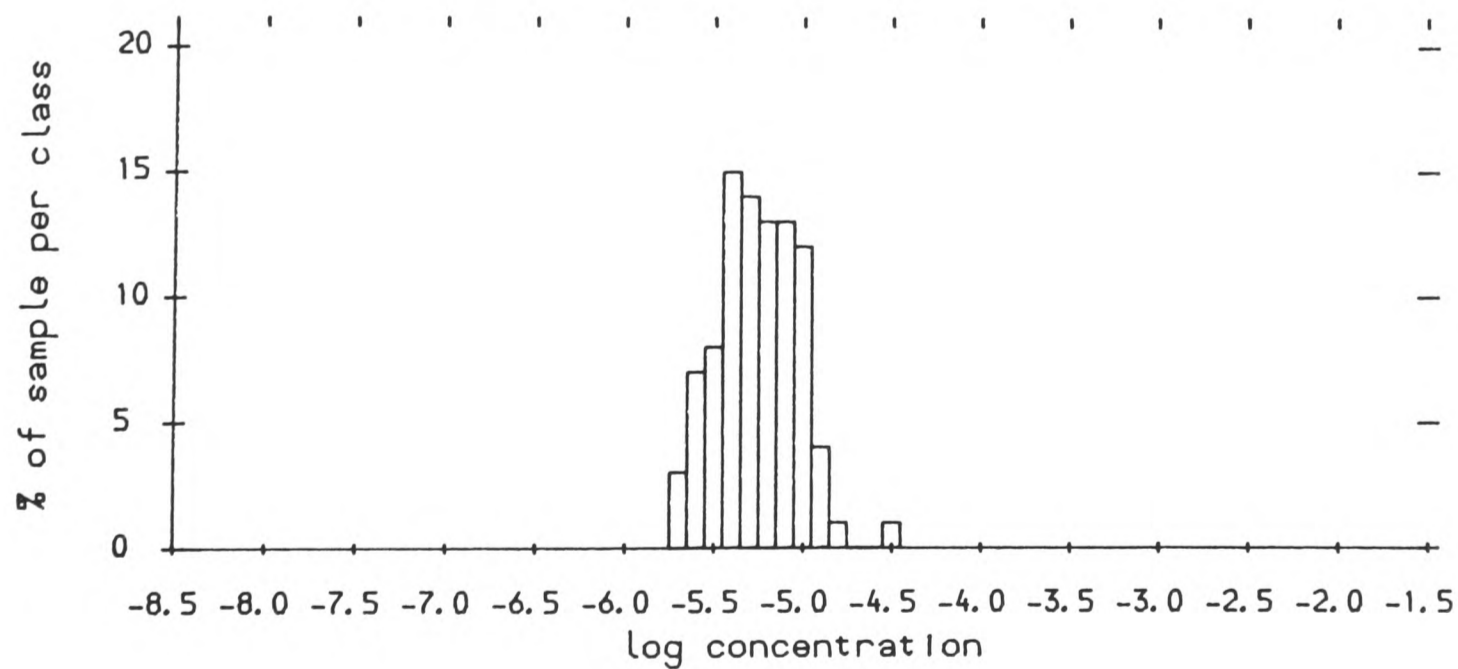
Median <-6.06



64% of values below the first class

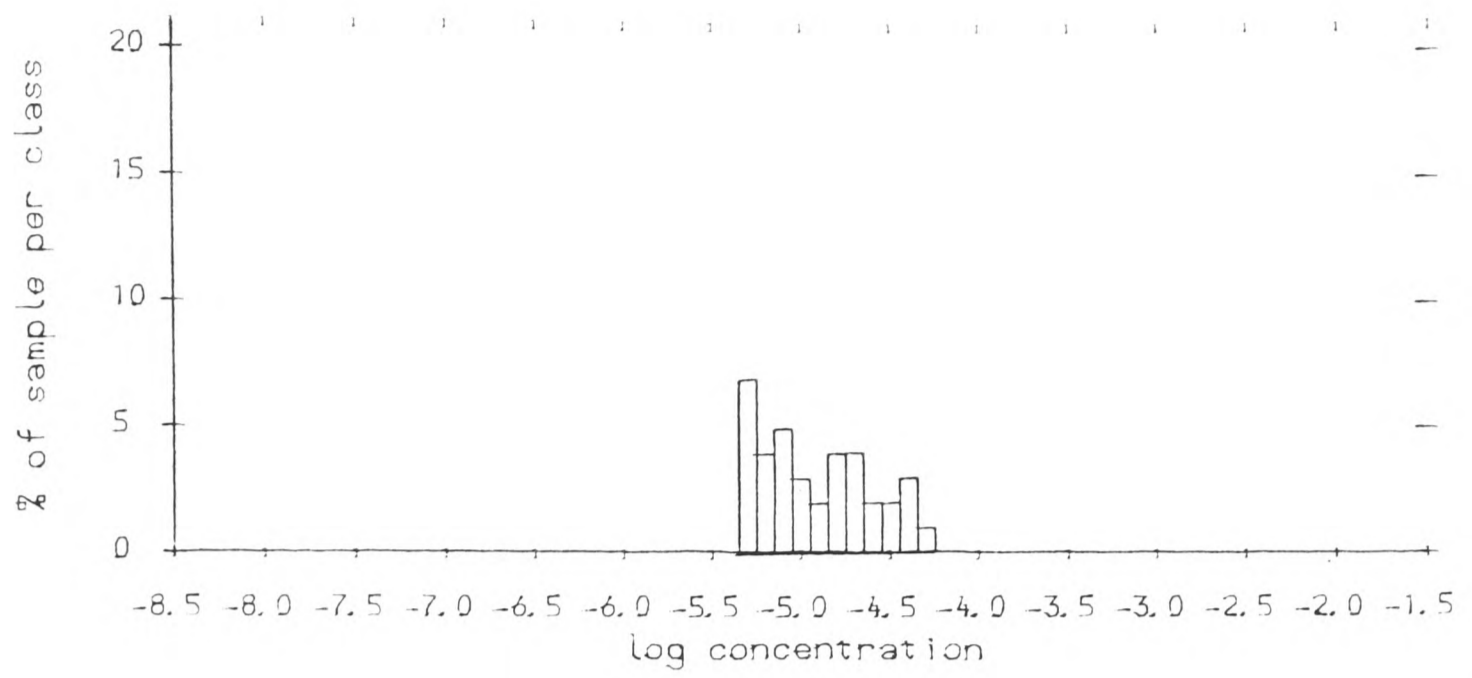
B

Median -5.292



8% of values below the first class

Median <-5.347



64% of values below the first class

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