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Phosphorus redistribution in acid archaeological soils from North Wales.

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INTRODUCTION

1.1 General introduction

Phosphorus (P) is widely distributed in rocks, minerals, plants and animals, being quoted by Cathcarte (1980) as the 10th most abundant element in the earth's crust at a concentration of approximately 0.12%. It is an element which is concentrated in the biosphere, up to levels which are 200× its crustal abundance, and yet because of its unique chemistry it is relatively immobile within soils and is therefore the life-limiting element in many ecosystems. In natural systems P is almost exclusively found as the tetrahedral oxy-anion PO_4^{3-}, and nearly all dissolved and particulate forms of it are combined, complexed or slightly modified forms of this ion (Jahnke, 1992). This tetrahedral structure with strongly associated oxygen atoms provides stability and prevents hydrolysis (Westheimer, 1987) which means that P tends to precipitate to form materials of low solubility, sorb onto surfaces and form complexes with metal ions. In soils, P may be divided into four general categories: P as ions and complexes in the soil solution; P adsorbed on the surfaces of inorganic soil constituents; P minerals; and P as a component of soil organic matter, (Barber, 1984). These categories are discussed in detail in section 2.2.

The immobility of P within soils is due to the low solubility products of its Al/Fe salts at a low soil *p*H and of its Ca salts at a high soil *p*H (Lindsay *et al.*, 1989) and due to the microbial fixing of P into the soil organic component. It is this immobility which leads to anomalous concentrations in the soil resulting from past biological activity. This provides archaeologists with the opportunity to undertake a P soil survey to indicate human influence on an archaeological site (*eg.* Bethel & Mate, 1989): Any inputs of P to a soil, for example, those associated with a human settlement (middens, hearths, latrine areas) will be fixed in the soil and leave a chemical trace of elevated P levels which can normally be detected for several millennia. However this trace of elevated levels can be dispersed, and the level of dispersion from any organic or mineral concentrated source of P will be dependent on the physical disturbance and the chemical regime of the soil, which will vary considerably with site conditions. The immobility of P under many soil conditions leads not only to the preservation of patterns of P distribution in archaeological sites

but also to its inherent heterogeneity of distribution at a range of scales within soil. At the smallest scale examined in this thesis; 1-100μm, this heterogeneity will be due to the variation of P content between individual mineral grains and organic particles. At 100μm-10cm, the variation within the soil fabric is important, for example, there will be differences between 'rusty' mottles and the B_g soil matrix. As the scale is increased, soil horizonation, changes in topography and changes in the management regime of a soil will produce differences in the P variation. Ultimately different parent materials and soil series will be encountered affecting the soil P content and its variation at a regional (10^2-10^3m) scale.

1.2 The need for research

There is a need for the examination of the variation of P_{tot} in the soil, to describe the inherent heterogeneity of P at the range of scales which may be encountered by archaeological field survey (10m - 0.1m), and by the micro-morphological examination of soil (0.01m - 0.00001m). The results can then be used as a comparison for any anomalous concentrations that may be measured during the course of archaeological P analysis. In a non-archaeological context the description of the natural variation of P in a soil is also useful within 'precision farming' where attempts are made to prescribe variable amounts of fertiliser to different parts of the field, streamlining the application by utilising advanced fertiliser delivery techniques. This research has developed following the growing concern regarding the environmental impact of fertilisers, especially on water quality, and to improve the efficiency of annual fertiliser additions which will have positive economic and environmental implications. Soils can be very variable, and it is a challenge to soil scientists to describe the variation present accurately, from the limited amount of data it is possible to collect. Inevitably, attempts to describe the variation present rely on accurate sampling and precise measurement with some statistical forecasting, and methods have been established to achieve these aims.

To measure the natural and anthropogenic P distribution within a soil, the choice of sampling strategy, sample preparation, method of analysis and of data presentation and interpretation is vital. The problems of sampling interval and sample size, in the design of a strategy to enable the useful interpretation of analyses, do not appear to have been fully addressed and there is a need to compare the various

procedures which are available and ascertain which provides the most suitable routine to follow. The recognition of P anomalies during the course of an archaeological survey needs to be statistically valid and some consideration should be given as to how this validity is measured.

In any P survey the movement of P within the soil before it was fixed, and of any subsequent redistribution, should be considered. The dispersion of P from isolated but potentially significant fragments of bone, and from other concentrated sources of P in the absence of plant and faunal homogenisation, is in need of clarification. This will enable the efficient sampling of archaeological features and the useful interpretation of, for example, 'body traces' of elevated P levels while taking account of the problems of P dispersion within a soil and the general background heterogeneity of P.

1.3 Strategy of study

Upland soils in North Wales commonly have *p*H values of below 5.0 and under such conditions certain archaeological artefacts, such as bone, undergo complete dissolution and will not be recoverable during excavation. Under acidic conditions a soil P survey can therefore provide useful information to support an excavation, locating these cryptic anomalous P_{tot} concentrations which could be attributed to past biological activity. Three field sites (A, B & C) were selected for this study to measure P_{tot} at a variety of scales in the soil. The selection criteria for each site were slightly different, but with this common theme of being a local acid semi-upland/upland soil. Sites A, B & C are located on map 1.1, with more detailed locations produced in maps 3.1 and 3.2, site descriptions are provided in section 3.3. Sites A & B were chosen as typical examples of acidic upland soils in North Wales for an investigation of the natural distribution of P_{tot} in the soil, with neither site being associated with any known archaeology. Site A was improved upland pasture and Site B consisted of rough unimproved grassland, with both sites presently being used as rough grazings for sheep. Archaeological features are common on land at similar altitudes to the two sites (300mOD) having generally been unaffected by land improvement and field clearance. Site C was a medieval long-hut being excavated by the Gwynedd Archaeological Trust, and was sampled to test the methodology developed at sites A & B.

Map 1.1: Location of sample sites in North Wales

The selection of an archaeological sampling strategy will always be made with regard to the constraints of available equipment, manpower, time and finances. Within these considerations however, there will always be some flexibility as to the method of sampling, either random, systematic, or some combination of the two, and the interval at which to sample. Generally, systematic grid sampling strategies are used in archaeological surveys, and are suitable for the examination of the spatial variation of soil properties: they have therefore been used as the primary sampling strategy in this thesis. The size of the sampling grid interval will vary depending on the size of area which needs to be covered and the size of the features anticipated. Phosphate surveys are commonly conducted at a range of scales (50m – 1m grid intervals) and the chances of locating a feature of 1m×1m size or a 5m×5m size vary considerably depending on the sampling grid interval used and are listed for a range of intervals in table 1.1

Table 1.1: The chance of sampling a 5m square and a 1m square anomaly at decreasing sampling intervals

Grid sampling interval	Size of feature	
	5m×5m square	**1m×1m square**
50m	1%	0.04%
20m	6.25%	0.25%
10m	25%	1%
5m	100%	4%
2m	>100%	25%
1m	>100%	100%

The larger grid intervals (50m & 20m) provide the surveyor with a less than 1% chance of collecting a sample from a feature 1m×1m in size, and if features of this size are anticipated then the survey must take place at a finer resolution, such as a 2m or 1m interval, to stand any realistic chance of sampling the feature. This thesis compares sampling intervals of 100m, 10m, 1m and 0.1m from two sites, and of 10m, 1m, 0.5m and 0.1m from a third site, to explore the background variation of P_{tot} at a wide range of sampling intervals that can be used in archaeological survey. Sampling is also continued in the laboratory at 0.01m interval, followed by 0.001m, 0.0001m and 0.00001m sampling intervals using a microprobe, to investigate the inherent variation of P_{tot} within the soil fabric.

The method of sample collection, which governs the sample size, is dependant upon site conditions (*e.g.* stoniness), the sample grid size used and the minimum amount of sample required for analysis. Commonly a soil auger (2.5cm ∅) is used. A variety of methods have been applied in this study because of the large range of scales at which P is examined (100m - 0.00001m), which means that comparisons between results collected in a different manner can only be loosely made. The methods are described in detail in the relevant sections of the thesis (3.4, 4.4).

There is a variety of analytical methods for the measurement of P in soil. A few are field based, for example the Eidt spot test (Eidt, 1977), but the majority are laboratory based and vary in their complexity and accuracy. Several methods have

been examined in this thesis (appendix II) to develop a standard protocol for analysis. Laboratory methods for soil P_{tot} were used in this study and the relationship between P_{tot} and the easily extracted P fraction was examined in some detail for selected samples. There are several techniques available for the fractionation of P_{tot}, to measure organic P, extractable (easily soluble) P, and several inorganic P components. However, due to the large number of samples measured from each site and the absence of detailed information regarding the use of P fractionation for archaeological analysis, it was not assumed that any individual P fraction could provide an appropriate measure of archaeologically derived P. Therefore no systematic fractionation of P was undertaken.

1.4 Aims and objectives

The aim of this project is to obtain a wider understanding of the distribution and variation of P in soils over a range of scales. A greater awareness of this is of fundamental relevance to, firstly, archaeological studies; where the distribution of P in the environment is examined to locate anomalies and potential archaeological features. Secondly, it is of relevance to agronomic studies; research into precision farming is advancing as techniques are sought to reduce the wastage associated with traditional agricultural practice. The objectives of this work are fivefold.

Objective one: To examine the distribution, and quantify the variation of P in the soil of an acidic upland site which has not been agriculturally improved and is not associated with any known archaeological features. These results will be compared to a second site, an acidic upland soil which had been improved, but again is not associated with any archaeology and is common to much of the North Wales. The results to these two 'background' sites can then in turn be compared to a known archaeological site on a similar soil from a similar location.

Objective two: To examine the distribution, and quantify the variation of in a soil over a 'micro' scale (<1cm), and to identify the variability of P which would be present in a single auger sample.

Objective three: As a specific illustration of objective two, the redistribution of P in the micro-fabric of sherds of Bronze Age cinerary urns has been examined. Amorphous orange-brown cutanic deposits have been observed in thin sections of these sherds, and it is assumed that the P in this material is derived from the cremated bone that was buried in the urns.

Objective four: To develop an experimental soil column system to simulate the movement of P in an acidic environment so that the diffusion of P from a concentrated source can be measured.

Objective five: To develop a suitable P sampling strategy for the detection of an archaeological grave site. This was done initially by computer modelling of data collected from a total body scan and then the results compared to those from an archaeological investigation of early Christian and Bronze Age burial cists.

1.5 Plan of the thesis

The remainder of this thesis is divided into 7 chapters. These start with a review of the literature placing the current work in context with what has been published previously, and examining the key archaeological/soil - phosphate research. The experimental work is described in the next four chapters. Each one examines a slightly different theme of research so the methods utilised are described separately, there being no comprehensive 'methods' chapter. The final two chapters discuss the results, place the work in a wider context and conclude the thesis. The first of the five appendices lists the raw data generated by this study, and the following appendices (II-V) present work related to but not directly required in the body of the thesis.

Table 1.2: Chapter and appendix headings and summary of contents

	Title	Summary
Chapter one	Introduction	General introduction, aims and plan of thesis
Chapter two	Literature review	An examination of P in soil, its measurement and variability. The development of P analysis in archaeology
Chapter three	An examination of the natural distribution of P in soil (macro level: 100m - 0.01m)	The measurement of P in soil for three sites in N. Wales at a range of sampling intervals. An examination of the variation therein.
Chapter four	An examination of the natural distribution of P in soil (micro level: 0.01m - 0.00001m)	The measurement of P in thin sections of two soils, at a micro scale. An examination of the variation therein.
Chapter five	P mobility and redistribution in the environment	An examination of P within the microfabric of cinerary urn sherds. Laboratory column experiment to examine P mobility.
Chapter six	P mobility and redistribution over grave sites	Theoretical models of distribution of P across a grave site. Practical excavation and measurement of P in a grave site.
Chapter seven	General discussion	
Chapter eight	Conclusion and further work	

Appendix one	Raw data	P analyses
Appendix two	Methods of P_{tot} analysis	Examination of three methods of total P analysis
Appendix three	The examination of rapid field tests for P	Comparison between field P tests and lab tests.
Appendix four	Flow injection analysis	Description of flow injection analysis, examination of its accuracy and precision.
Appendix five	Methods of spatial data interpolation	Examination of six methods of spatial data interpolation in the Winsurf mapping package.

LITERATURE REVIEW

2.1 Introduction

A brief overview of P in soils is provided, more detail being available in the thorough reviews by Larsen, (1967) and Stevenson, (1986). The use of soil P as an indicator of anthropomorphic activity, the measurement of available and total P in soils, and the spatial characteristics, distribution and variation of soil P are also reviewed.

Phosphorus is an element with a mass of 30.98 and is almost exclusively found as phosphate PO_4^{3-} in natural systems. Nearly all dissolved and particulate forms of P are combined, complexed or slightly modified forms of this ion, therefore in biogeochemical terms, P is synonymous with phosphate. The initial source of all P in natural ecosystems are the phosphate minerals, of which the most significant is apatite, accounting for more than 95% of all P in the earth's crust. The basic composition of apatite is

$Ca_5(PO_4)_3X$ where X = F^- in fluoroapatite

OH^- in hydroxyapatite

Cl^- in chloroapatite

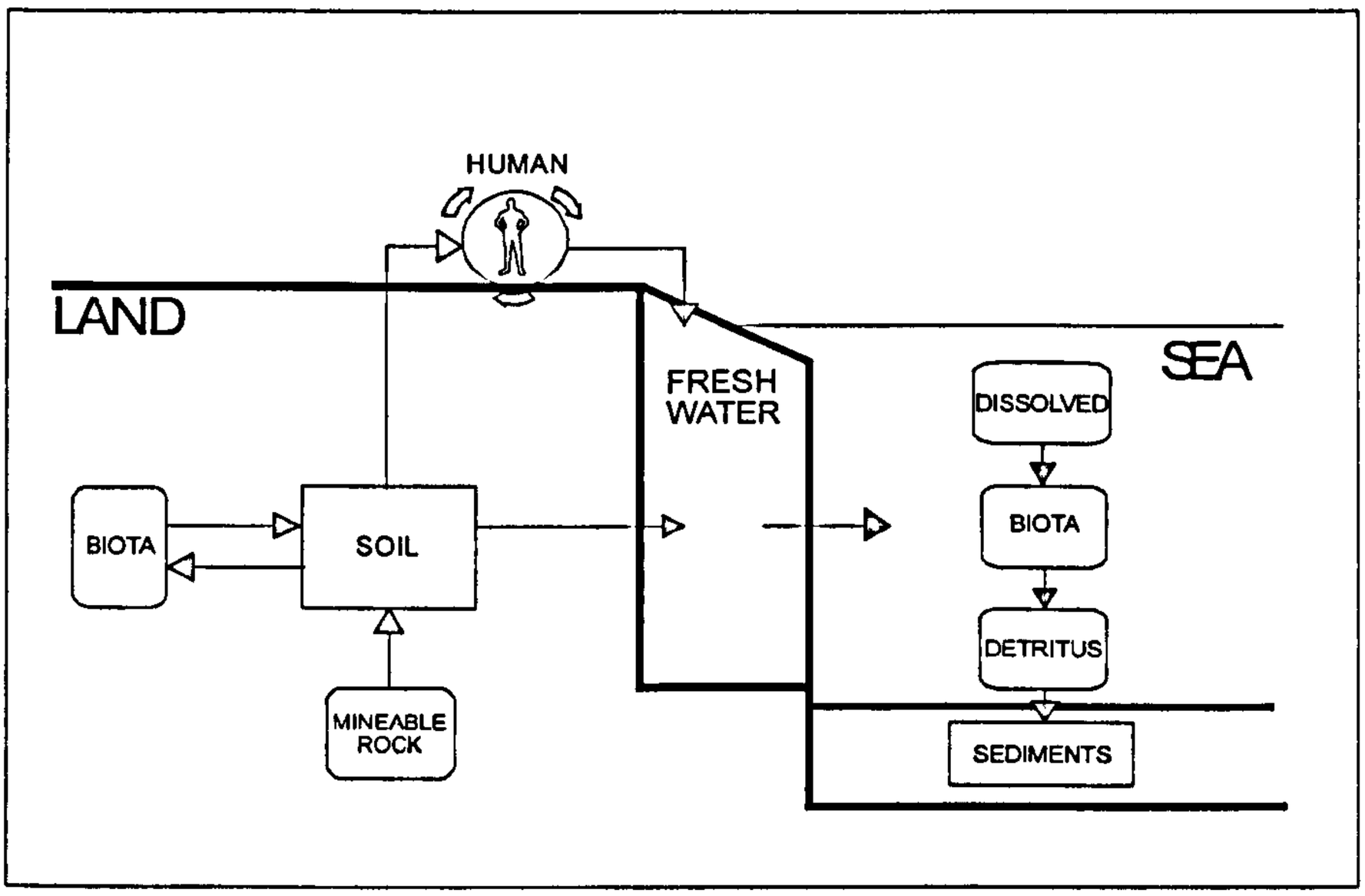
both Ca^{2+} and PO_4^{3-} can also be substituted (Jahnke, 1992). Igneous rocks contain between 0.02 and 1.2% apatite, but the largest accumulations are the massive sedimentary apatite deposits which provide 82% of the total world PO_4^{3-} production (Howard, 1979). There are over 200 phosphate minerals (classed as minerals in which PO_4^{3-} is a required structural component) which occur naturally (Larson, 1967), and phosphates are trace components in many other minerals. A comprehensive study of all these P minerals can be found in Lindsay *et. al.*, (1989).

Richey (1983) has estimated the major reservoirs of P present in the earth's crust as

	Total Phosphorus x 10^{12}kg
Ocean sediments	840 000
Soil	96-100
Dissolved (inorganic)	80
Mineable rock	19
Land Biota	2.6

These are components of a global cycle where there are fluxes between reservoirs, and these movements are represented schematically in figure 2.1

Figure 2.1 The phosphorus cycle: pools and fluxes of P (Richey, 1983)



Weathered and eroded P from terrestrial sources is transported in both dissolved and particulate form by rivers, to lakes or the sea, interacting along this pathway with biological and mineralogical systems. Phosphorus is eventually removed from the cycle when it is deposited as an ocean sediment. Man has influenced this natural cycle with large-scale mining of P reserves and the use of fertilisers, hence increasing the scale of P in, and speed of movement through, the system. Within this pathway it is the terrestrial section with which this study is primarily concerned.

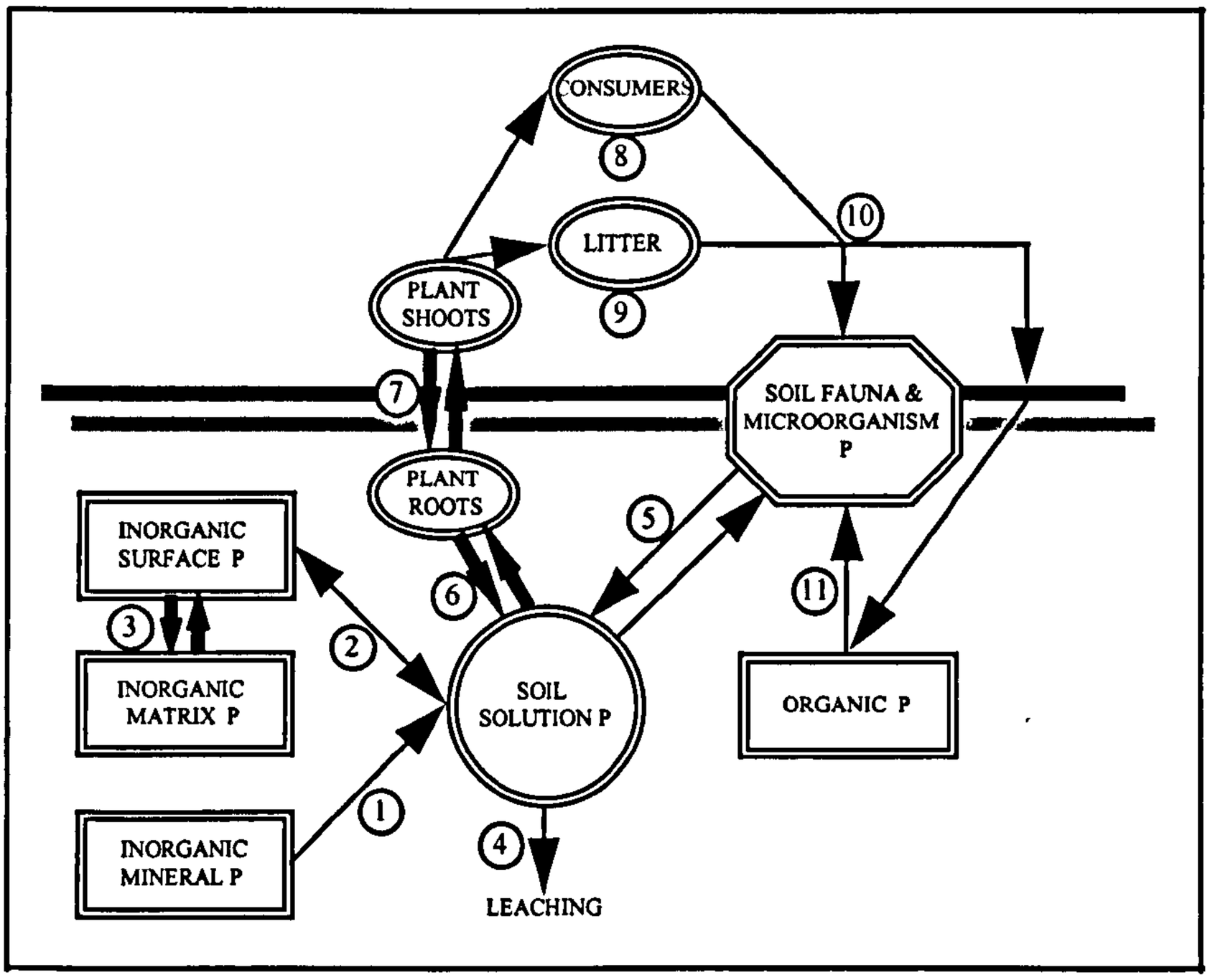
2.2 Phosphorus in soils

The primary source of soil P is from weathered apatite in the soil's parent material, so the phosphate content of 'virgin' soils is almost totally dependent on the nature of its parent material (Walker & Adams, 1958). Factors which make a large difference in the P content of soils are; the degree of weathering; the loss of phosphate through leaching and erosion; and in cultivated areas, the extent and level of fertilisation. Phosphorus levels in soils can range from 200 to 5000 $\mu g\text{-}P\ g^{-1}$ (Barber, 1984), but are generally in the region of 600 -800 $\mu g\text{-}P\ g^{-1}$ (Stevenson, 1986).

However, P accumulates close to the soil surface because it is circulated through vegetation and is deposited through leaf fall and plant decay (Anderson, 1980). In cultivated soils the surface accumulation of P can also be enhanced by the application of fertilisers.

Phosphate pools within soils and the movement between them are summarised in figure 2.2

Figure 2.2: Simplified P fractions in soil



1. Slow weathering of mineral P (mainly apatites) derived from the soil parent material releases P into solution.
2. Phosphate ions in solution are adsorbed onto mineral surfaces within the soil when the concentration of P in solution is high. The process can be reversed when the concentration of P in solution falls. This P is considered 'labile' because it is able to move into solution, so becoming available for plant uptake.

3. The gradual conversion of available P on the solid surfaces in the soil into unavailable P incorporated within the soil matrix.

This process is termed 'inorganic fixing', and will occur slowly in reverse.

4. A small amount of P in solution can be lost by leaching, if there is a net through-put of water in the system.
5. Some solution P can be used by micro-organisms, termed 'microbial fixing' or the immobilisation of solution P. Micro-organisms do return P to the soil solution through the mineralisation of organic P.
6. Solution P is taken up by plant roots. Some can return to the soil through root exudation.
7. P in plant roots is transported to the plant shoots.
8. P in plant shoots can be returned to the soil via plant consumers.
9. P in plant shoots can be returned to the soil after plant death as plant litter.
10. P from litter and in waste from consumers can enter the soil directly as a component of the inorganic pool or via micro-organisms and soil fauna.
11. Materials containing organic P are broken down by soil micro-organisms, some returning to the soil as inorganic solution P.

Soil P can be divided into organic and inorganic forms whose ratio is dependent upon soil type and land use (Haygarth & Jarvis, 1999), these pools will be discussed separately.

2.2.1 Organically bound phosphorus

The organic P fraction can constitute 20-80% of total soil P (Larson, 1967), with the exact amount being dependent on the soils organic matter (OM) content. Circumstances that lead to transformations in OM levels will lead to a subsequent change in organic soil P, however the P content of soil organic matter is variable with a C/P ratio in soil organic matter of approximately 100 (Barber, 1984). Organic P in soils is derived from plant residues, excreta and above and below ground soil organisms and while the majority of organic P is considered to be biologically stable

(Stevenson, 1986) its turnover is especially important for plant nutrition in soils with low fertility (Marschner, 1995), and for some soils in the tropics (Barber, 1984).

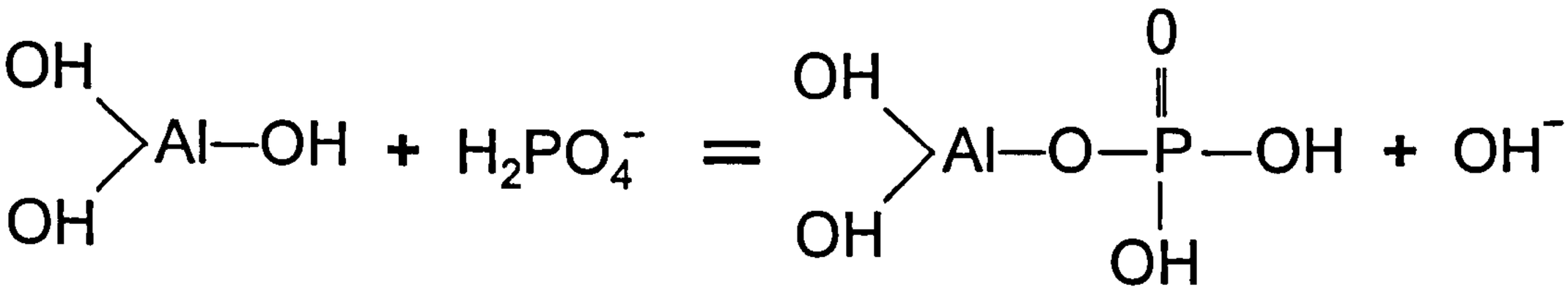
A large proportion of soil organic P remains uncharacterised (Haygarth & Jarvis, 1999), although the main forms are monoesters such as myo-inosital hexaphosphate. These 'inosital phosphates' often account for more than 50% of soil organic P and can take many years to break down. Other common organic P forms such as phospholipids and nucleic acids can add up to 5% of the total soil organic P pool and are broken down much more rapidly (Anderson, 1980).

Organic P turnover is controlled by the rates of mineralisation of organic matter and so by the activity of the soil organisms. The soil organism activity is controlled by soil temperature, moisture, oxygen, carbon, *p*H and inorganic nutrients (Tate, 1985), hence these factors control the breakdown of soil organic matter and the release of P into solution from the organic pool. More detailed reviews of organic P in soils are given by Tate, (1985) and Harrison, (1987).

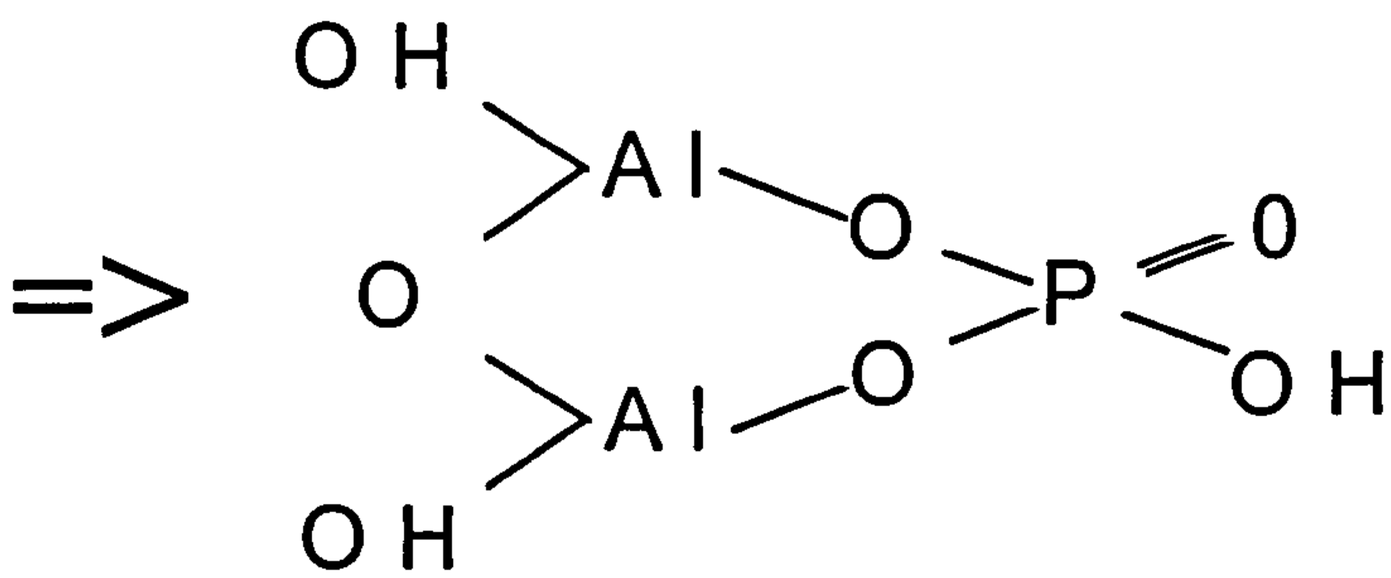
2.2.2 Inorganically bound phosphorus

Inorganically bound P in soils can be split into two fractions; those of primary minerals, which account for only a small proportion, and the 'chemical' forms, calcium, iron and aluminium phosphates, which make up the remainder. Primary P minerals such as apatite supply little P to plants due to their low solubility, however the 'chemical' forms are more important in terms of plant available P and will be discussed in more detail.

The inorganic chemical forms of P in the soil are associated with iron, aluminium and calcium ions. At a low *p*H (less than 5.5) P is adsorbed onto the surfaces of, Fe and Al hydroxy-oxides:



and absorbed into the lattices of, Fe and Al hydroxy-oxides:



It is suggested that these Al-P's and Fe-P's occur as a thin film on the surface of hydrated films of iron and aluminium oxides (Proudfoot, 1976), or on iron and aluminium ions forming part of the surface layer of clay minerals (Wild, 1988). At a higher *p*H (greater than 5.5), associations with calcium in solution, on the surface of clays, or present as calcium carbonate are important. A third less important process of holding P in soils is on the edges of clay particles through hydrogen bonding between hydroxyls in the broken edges of the clay, and oxygen in the phosphate tetrahedra (Smeck & Runge, 1971).

Inputs of P to soil are, under suitable conditions, converted to a soluble form of phosphate (P_{sol}) which is either utilised by plants and micro-organisms, or rapidly fixed. In contrast to other plant nutrients, especially nitrogen, only small amounts of P_{sol} are leached from the rooting zone of the soil (*e.g.* 7g ha^{-1} annually from a forest ecosystem, Binkley, 1986). The fixing of P depends on the specific surface area of the solid phases with which the P comes into contact, and on soil conditions. In acidic soils P becomes fixed through sorption onto insoluble Fe/Al hydrous oxides, or precipitation as insoluble salts (secondary minerals) of Fe/Al. Under neutral to alkaline conditions P fixing occurs as the precipitation of Ca phosphates or as sorption onto $CaCO_3$ surfaces (Lindsay *et al.*, 1989). In some soils the fixation of P is a major problem for crop growth, for example, lateritic soils which are rich in iron require large amounts of fertiliser to overcome a P deficiency in plants. This ability of a soil to "fix" P can be massive. Morgan & Jacobson (1942; in Black, 1957) added the equivalent of 3005lb of P per acre (3373kg ha^{-1}) to a soil throughout an eleven year period, and lost only 0.1lb of P per acre annually through an 18" depth of soil. The remainder (99.99%) was fixed.

2.3 The availability of P to plants

Phosphorus needs to be in solution before it is available to plants, however the concentration of P in the soil solution is low, between 1 and 0.01µg-P g^{-1} (Stevenson, 1986). Therefore, replenishment from the solid phase is essential if an adequate supply of P to plant roots is to be maintained. Replenishment of P in solution is dependent on the equilibria between labile inorganic P and solution P, and the mineralisation of organic P (figure 2.2).

The processes of P transport in soil are very important for plant nutrition. Replenishment of P at the root occurs mainly by mass flow and diffusion, both are slow processes: mass flow because of the low concentration of P in solution and diffusion because of the low concentration gradients (Wild, 1988). With this in mind it is vitally important that plant roots spread well through the soil to achieve close contact with P sources. Phosphate uptake by plants is discussed in detail in Wild, (1988) and Kasawneh *et al.*, (1980).

2.4 The current status of phosphorus research

Soil P has been an area of major interest throughout the history of agronomic research, however the current interest has moved away from the traditional areas of soil fertility and crop response towards the movement of P from agricultural land to surface waters. European Union initiatives express concern over water quality and the environmentally significant nutrient enrichment of surface waters (Powlson, 1998) and an understanding of P transformations and its movement are required to devise ways of minimising the problem. Recently published work includes the development of a models to upscale results from plot scale research to catchment areas (Johnes & Hodgkinson, 1998), P budget calculations for farming systems (Haygarth, et al, 1998) and lakes (Foy & Bailey-Watts, 1998), and the examination of the modes of transfer of P through soil (Haygarth & Jarvis, 1999).

2.5 The use of phosphorus as an indicator of human activity

The study of P levels in soil has become of interest to the archaeologist. As long ago as 1911 old centres of habitation in Egypt were detected through elevated P levels. Sir E J Russell (1971) mentions this;

"... The soil and plants only take up about 25 - 30 % of the quantity added even over a run of years. The rest stays in the surface soil apparently for ever: almost inert, but without losing its solubility in dilute acids which distinguishes it from the original phosphate of the soil. Sites once inhabited and now long since abandoned can still be distinguished by their higher content of this soluble phosphate compared with that of surrounding land - the residue of household waste, ordure and bones cast out before the days of the public health service existed."

Phosphorus, once added from whatever source (bones, fertiliser, manure), is fixed in the soil. This P enrichment in the soil, from the detritus associated with man, can still be seen in elevated P levels even when all the surface visible evidence of occupation has disappeared.

Since the Mesolithic period, man has progressed from the hunter-gatherer lifestyle of the pre-Neolithic and embarked on animal and crop husbandry. This era is distinguished by man building semi-permanent settlements, and starting to manage the environment for himself (Davidson, 1982). From this stage onwards the development of settlements was commonplace amongst a variety of cultures world-wide. The development of settlements led to the clearing of forests for the growing of crops and the enclosure of animals, so beginning the development of modern agricultural techniques.

Many relics of the occupation of an area by man can still be identifiable many years after the settlement was abandoned. Obvious relics are physical features such as stones and earthworks, with which may or may not be associated occupational debris such as flints, stone tools, pottery sherds and bone (Craddock *et al.*, 1985). However, the vast majority of debris associated with an early settlement would be organic and have long since decomposed (unless preserved under special conditions *i.e.* in waterlogged sites). When such debris decomposes, the chemistry of the surrounding soil will become altered, on some occasions permanently. The examination of soil P is one of the methods by which this change in the soil chemistry is discovered. Much of the material that is associated with these sites has a high level of P, for example, the refuse derived from food both from preparation and in waste, together with the remains in graves, the excreta of man and animals

and any material that may have been used as fertiliser such as animal manure (Edwards *et. al.*, 1983).

The bulk of P that enters the soil in these forms will become fixed within the soil with only very small losses, through leaching of the small proportion that goes into solution (Hammond, 1983). The addition of P to the soil from the activity of humans in a settlement - in the form of excreta, rubbish and burial, will add to the natural levels present to create areas of high phosphate content. Cook and Heizer (1965 in Proudfoot, 1976), have postulated that 100 people inhabiting a 0.81ha site would contribute a total of some 140kg of P annually per hectare. This annual increment could be as much as 10% or as little as 0.5% of the total P already present in the top one centimetre of soil. If a settlement was in use for 100 years, the total increment could be potentially significant. The location of these settlement sites is only possible if they display P levels that are much higher than background levels in the surrounding soil.

The harvesting of vegetation from a site means that the usually efficient cycling of P, with plant remains supplying the available P for the following seasons' growth, is disrupted. In tropical rainforests, this natural cycle is so well developed that the major proportion of P in the system is held in the litter and vegetation, (Wild, 1988). The plants can re-grow only by removing P from the soil solution which will need to be replenished by P fixed in the solid phase. The Rothamsted exhaustion trials (Johnston & Poulton, 1977) showed that the solid phase P present in a soil can support plant growth for a great number of years, but levels will decrease steadily. Cereals have been calculated to remove 15kg of elemental P per hectare from the top 25cm of the soil, depleting on average 4μg g^{-1} from the soil per annum (Waggaman, 1952 in Hammond, 1983). The soil P may also be subjected to solifluction or soil creep due to the effects of gravity, water and frost heaving (Bakkevig, 1980) further reducing the P content of slope or terraced soils.

The systematic approach to phosphate mapping was developed by Arrhenius in 1931 in Sweden, as he surveyed the soil of agricultural land, assessing its suitability for sugar beet growth. He discovered that soil phosphate levels were higher around occupied or deserted settlements (Bethel & Mate, 1989). His original study was

followed up by a series of papers discussing the use of enhanced soil phosphate levels to locate abandoned settlement sites where no visible remains existed. The development of soil phosphate analysis as a tool for archaeology from the early days of Arrhenius, through the sixties when it became recognised as an extremely useful technique, to the middle of the 80s, is comprehensively covered and discussed in the review by Bethel & Mate (1989).

Important developments over this time include work by Johnson (1956) who used P analysis to examine details of a smaller feature such as a soil stain at the centre of a chambered cairn in Inverness. With such a study he was able to determine that the soil stain was the result of a burial at the site. McCawley & McKerrell (1972), while working for the National Museum of Scotland's research laboratory, also found P analysis useful where little or no evidence of bodily remains or human activity was visible, when determining whether inhumation had taken place.

The development of the spot test by Eidt (1977), a rapid two stage test for P, gave archaeologists considerably more freedom. The test is qualitative, and allows the rough measurement of total P to be conducted alongside a dig, enabling the results to direct the excavation.

Sieveking's (1973) study of Grimes Graves in Norfolk used P survey to complement aerial photography, resistivity, magnetometry and field walking ground survey. Other more recent studies include Conway's investigation of a Romano-British hut circle (1983), the phosphate analysis in this case revealing the pattern of erosion of constructed floors, and the presence of features such as hearths, drains and patterns not always discernible by excavation techniques. Craddock *et al.*, (1985) surveyed sites at Fengate, Peterborough and Maxey Quarry, Cambridgeshire. These studies use the analysis of P in soil to clarify details within, and surrounding a site, aiding its interpretation. It is in these functions *i.e.* to locate ancient monuments not visible in a surface survey, to assist in the determination of site limits, and to give information about the function, activity or duration of occupation (Bakkevig, 1980) that phosphate analysis of the soil can prove itself most useful to the archaeologist.

There are three types of study of archaeological phosphate.

1. Prospection; the aim being to discover new sites previously unknown or the outer limits of sites already discovered (Balaam & Porter, 1982).

2. Intensive survey within a site to discover activity areas where the nature and limits of the site have already been discovered (Cavanagh *et al.*, 1988, Conway, 1983).

3. The investigation of a specific feature, for example, skeletal remains in a grave (McCawley & McKerrell, 1972).

The main scope of P analysis is to localise ancient monuments not visible in a surface survey, to delimit a site, and to give information about the function, activity or duration of occupation (Bakkevig, 1980). The measurement of total P in soil samples is a useful technique in the study of an archaeological site as long as local environmental conditions have been taken into account (Bakkevig, 1980). Its techniques can be applied at a variety of levels and when coupled with other studies can hugely enhance the interpretation of an excavation.

2.6 Bone in archaeology

Studies of bone within the sphere of archaeology take many forms, most of which are of little direct relevance to this study. However, of specific interest to this study is the composition of bone, its diagenesis - the complex chemical changes which usually occur after interment (Sillen, 1989), and under what soil conditions bone is preserved.

Fresh bone consists of three components, an inorganic fraction 'bone ash', an organic matrix and water, in the approximate proportions of 17 : 20 : 15 by weight (Price, 1989). The major inorganic constituents are calcium, phosphate, carbonate and magnesium, the proportions of which vary depending upon animal species, age and physiological state, though the overall composition is reasonably constant. The inorganic portion is largely mineral, in the form of hydroxy-apatite (section 2.1). Phosphorus constitutes 15.5 - 16.4% of the inorganic portion and the complete human skeleton makes up some 14.3 - 17.6% of the weight of human adults (Eastoe, 1961). From these figures a 70kg adult's skeleton would contain roughly 570g of P.

Proudfoot (1976) reports similar findings, with a 68kg adult containing 630g of P, 86% of which is found in the skeleton.

Suggested mechanisms for the breakdown of bone are described by Rottlander (1976). Bone on the surface of the ground can be broken down within a few years, assisted by the decomposition of the flesh surrounding the bone. Microorganisms breakdown the organic components of the bone and in so doing excrete organic acids which cause the dissolution of apatite minerals and the destruction of histological structure (White & Hannous, 1983). If the bone has been stripped of flesh, there is less decompositional activity and the breakdown of the inorganic bone component will be much slower. The decomposition of bone is partly governed by climatic conditions, particularly temperature and moisture, which affect the microorganisms. Good preservation of bone can be related to a cold and/or dry climate (Rottlander, 1976). Once interred in the soil, bone preservation varies according to soil conditions. Generally bone is preserved well in soils of neutral or slightly alkaline *p*H and preserved poorly in acid soils (Keeley *et al.*, 1977). Gordon & Buikstra (1981) report that bone preservation is significantly correlated to soil *p*H. Potential recovery of human bone from any archaeological site is related to the *p*H of the soil and the maturity of the person at death.

Relative ratios of Ca:P are affected by diagenesis of the bone, at first dropping from the theoretical weight ratio of 2.15 as the organic acids replace Ca^{2+} from the hydroxyapatite with protons (H^+). As the soil solution becomes less acidic, decomposition of the organic component ceases so there is no more production of organic acid from the micro-organisms. Ca^{2+} from the soil solution can replace the protons and the original mineral can be reconstituted. The ratio of Ca:P will once again increase. In more permanent acidic soil conditions, such as those involved in this study, hydrolysis of the bone will be accelerated because phosphate ions are removed by precipitation as iron and aluminium phosphates.

2.7 Measurement of phosphorus in soils

The measurement of the P content of a soil has been of great importance to the agronomist for many years, primarily due to the significance of P for soil fertility

(Khasawneh *et al.*, 1980). The chemistry of P in soil does not make its measurement simple. Phosphorus is present in the soil in a variety of compounds, listed below.

P compounds in the soil have been classed by Stevenson (1986) as

1. Soluble inorganic and organic compounds in the soil solution.
2. Weakly adsorbed (labile) inorganic phosphate.
3. Insoluble phosphates
    a. Of Ca^{2+} in calcareous and alkaline soils of arid and semi-arid regions.
    b. Of Fe and Al in acidic soils.
4. Phosphates strongly adsorbed and/or occluded by hydrous oxides of Al and Fe.
5. Fixed phosphate of silicate minerals.
6. Insoluble organic forms
    a. Of the soil biomass
    b. In undecomposed plant and animal residues
    c. As part of the soil organic matter (humus).

It is possible to measure P levels within each of these classes individually, using sequential extraction methods, described by Chang & Jackson (1957). These original methods have been updated to a more comprehensive procedure produced in Stevenson (1986).

The measurement of soil P in this study was confined to two fractions: labile or available P and total P. Methods of extraction and measurement are described below.

2.7.1 Measurement of extractable or labile P in soils

The P fraction available to plants is of primary interest to agronomists and botanists, as it is the component that is essential for plant growth. There are a large number of possible extractants for this class of P and procedures are described in Jackson (1958) and more recently in Wild (1988), but the most commonly used is the Olsen method, which employs a 0.5M sodium bicarbonate extraction (Wild, 1988). Hooper (1970) tested seven extractants for a variety of soils and rates a soil extraction with

$NaHCO_3$ as the most useful indicator of the portion of P which is considered available to plants. The Olsen method is the assay commonly used by A.D.A.S. workers when assigning soil index numbers as indicators for fertilisation (MAFF, 1986), but it was designed for neutral to high *p*H lowland agricultural soils, so is perhaps not the most suitable extractant for the low *p*H upland soils examined in this study. Rice-Williams did much work on local acidic upland soils using 0.5M acetic acid as a successful extractant of the 'available' portion of soil P (Wright, 1939), so this is the preferred method of extraction for this study.

2.7.2 Measurement of total P in soils

The measurement of total P in soils can be achieved in a variety of ways. Techniques such as x-ray fluorescence measure P_{tot} in an unprocessed sample of soil, although drying, sieving and grinding improves the accuracy and precision of the result. P_{tot} is more commonly measured using a two stage procedure. Jackson, (1958) provides four methods that can be used, of which two; a precipitation, titration method, and a digestion in HF followed by gravimetric measurement method are not suitable for routine analysis, both being too laborious. The other two methods are more commonly used. Method one, sodium carbonate fusion (SCF) is accurate, converting all the P present to orthophosphate, yet is not appropriate for large numbers of samples and requires platinum crucibles. Method two, involving digestion of soil with perchloric acid is much quicker, but can give a lower recovery of P; Muir (1952) recorded the recovery of P with the perchloric acid method as being 50 - 70 % of the amount gained by the SCF method. More recent studies seem to have had more success. Sherrell & Saunders (1966) had recoveries of 85 - 100% of the SCF method using the perchloric acid method, and Sommers & Nelson (1972), who modified the perchloric acid digestion method slightly, reported recoveries of >90%.

Other methods of total P conversion to orthophosphates have since been used. Anderson (1976) describes a method which involves igniting the sample at 550°C for one hour then extracting the phosphate with 1M HCl. P values of 2.7% lower than the perchloric acid method were reported for this method. Dick & Tabatabai (1977) describe, the 'alkaline oxidation' method. This involves boiling the sample

with sodium hypobromite, followed by an extraction with sulphuric acid. Phosphate returns with this method are reported as being slightly higher than the perchloric acid method and only a few percent lower than the SCF method.

The method that is most suitable for the conversion of P to orthophosphate will depend on the specifications of each particular study, the soil types examined and the equipment available. A detailed assessment of the methods of total P analysis for the soils used in this study is presented in appendix II.

2.7.3 Solution phosphate measurement

The measurement of phosphate in solution is the final stage in the measurement of available or total P. Jackson (1958) describes four methods for this purpose, of which one, the chlorostannous reduced molyphosphoric blue colour method has been widely used. Limitations of this method include a fading of the colour after 10-12 minutes, and a *p*H dependency, yet it works with few interferences. A second, more commonly used method for measuring orthophosphate is that of either Fogg & Wilkinson (1958), or Murphy & Riley (1962). These are classed together because they both use ascorbic acid to reduce the molybdo-phosphate complex, and produce a blue colour which remains stable for at least one hour. Interferences from ferric iron, silica and arsenic have been identified. Comparisons between the two ascorbic acid reduced methods suggest differences of only a few percent and Murphy & Riley's method is commonly used. The ascorbic acid reduced methods are favoured because of the stability of the colour once produced. However, the method that should be used for any particular study will depend on any expected interferences. The use of Inductively Coupled Plasma (ICP) spectrometers to measure P in solution is becoming more common, and they have the added advantage of measuring a suite of elements as well as P in solution. However, ICP analysis is expensive, and the colorimetric methods described above are still the most popular technique for P analysis.

2.7.4 Measurement of phosphorus in archaeology

A variety of tests for the measurement of phosphate in archaeological studies have been used. One of the first studies, that of Arrhenius in the early 1920s used citric acid extractant to remove P, further work by Christenson in Denmark used 1%

HNO_3 as an acid extractant. Christenson later worked with Birmingham University using 0.5% acetic acid, an extractant that was also used by Lorsch in the 1940s (Dauncey, 1952). These chemicals are part of a large list of extractants for available P which can be used. The measurement of available P is important when considering soil fertility, but is of limited use as an indicator of P associated with archaeological sites, although it has been used to help distinguish between fixed ignited forms of P in hearth features and more mobile forms in drains (Jenkins, 1994a). The success of Arrhenius, Lorsch and Christenson prove that although available P often only constitutes 1% of total P, it can be a guide of archaeologically related P, but is not as useful as total P. One of the earliest archaeological studies to compare available P with total P was by Johnson (1956) he states:

> "....it is questionable whether this particular analytical tool, applied to the predominantly acid soils of highland Britain, will contribute much to archaeology except perhaps in so far as soil fertility studies are of interest in that direction."

Since Johnson's study, the measurement of total P in the soil was considered more useful to the archaeologist. Recent studies have all measured total P, for example Conway (1983) measures total P using the perchloric acid method and Edwards *et al.*, (1983) use an ignition and extraction method.

2.7.5 Microanalysis of phosphorus

There is little evidence of work done on the measurement of P in soil on a less than 1cm scale in the literature. Traditional methods of soil sampling are designed for bulk analysis, often a 20-50g sample is collected and well mixed, before being sub-sampled for measurement. Studies of soil characteristics at a scale <1cm include the examination of diffusion of P from fertiliser granules under a variety of conditions (Lewis & Racz, 1969; Sharma *et al.*, 1985). These studies utilise the P^{32} isotope to trace the movement of P in soil columns. The measurement of P in soil at a small scale is restricted by the sampling method, and it would be difficult to sample at less than 0.5cm spacing. To measure at scales below this requires the use of specialised equipment such as the electron probe micro-analyser (microprobe). The microprobe was initially employed in the 1950s for metallurgic investigations, particularly the analysis of the surface structure of metals, but by the 1960s its use was rapidly extending to many other disciplines. The general characteristics, instrumental and theoretical aspects, potentialities and limits of electron microprobe analysis and its

use in a variety of disciplines can be found in a number of books; Birks (1963), Tousimis & Marton (1969), Anderson (1973), and Reed (1996).

The potential of the microprobe as a tool for the soil scientist is great, as it complements the petrographic examination of soil thin sections, and enables the study of the heterogeneity of composition of the soil fabric and of particle homogeneity. The use of electron microprobe analysis within the discipline of soil science is discussed by Cescas *et al.*, (1968) and Hill & Sawhney (1971).

One specific area of the use of the microprobe in soils has been the study of P. Qureshi *et al.*, (1969) studied the distribution of P in roots and the soil micro-fabric, showing the association of P with iron deposits and clay skins and with calcium in precipitates and mineral inclusions. Phosphorus was discovered uniformly distributed throughout the matrix of plagioclase feldspars, and in apatite inclusions in sand grains in a study by Cescas *et al.*, (1970). Qureshi *et al.* (1978) continued the work on P distribution within the soil micro-fabric, finding a preferential association with organic debris and iron in iron/manganese concretions, as well as in discrete grains of rare earth phosphates. A further study of calcite grains showed P uniformly distributed within the calcite rather than concentrated as discrete calcium phosphates (Qureshi & Jenkins, 1978). In an examination of the patterns of phosphate distribution within the soil micro-fabric, a seven fold concentration difference of over 100 - 200μm within a soil ped was discovered. This is important for plant nutrition as P is not mobile in soils (Qureshi & Jenkins, 1987). A further study of P using an electron microprobe, is that of the analysis of cave sediments from Pontnewydd, North Wales, a Lower Palaeolitic hominid site. These studies have shown evidence of translocated P from weathered bone-rich beds, and the redeposition of Ca - Fe phosphate cutans in the pigmented beds below (Jenkins, 1997). The distinctive nature and composition of the cutanic material opens up a new area of P geochemistry in archaeological sites (Jenkins, 1994b) and reinforces the considerable potential of the microprobe within environmental science.

2.8 Variation of soil phosphorus

Phosphorus accumulates close to the surface of both cultivated and uncultivated soil profiles (Wild, 1988), producing levels of P_{tot} that are often considerably greater in

the surface horizons than throughout the lower horizons. The variation of soil characteristics with depth is commonly recognised and discussed in standard soil science text books (*eg.* Wild, 1988, chapter 21), however the lateral variation is less studied. Beckett & Webster's review (1971) concludes that half the variance within a field may already be present within any m^2, and within-field variance often changes very little with the size of field. However, all the studies reviewed by Beckett & Webster used different sampling methods with various sized plots, so the conclusions made were tentative.

The measurement of soil P to locate abnormally high values which could represent an accumulation in P due to the activity of man has become a well established field of research within archaeology. Comparisons are made with 'background' levels of P to ascertain whether the measurements are significantly higher. Bakkevig (1982) warns of the dangers involved in taking only a few control samples and recommends taking a continuous series of samples extending away from the area of interest. Examples of earlier methods include Sieveking's P survey at Grimes Graves (1973) where probable natural background levels were estimated as the lowest repeatedly recorded concentration of P for each different soil type encountered. McCawley & McKerrell (1972) took background levels as being typically 100 - 200 $\mu g\ g^{-1}$ of P measured from control samples taken "just outside the grave site and from 15 - 30 feet away from the grave area". Sampling by Conway (1983) during his investigation of a Romano-British Hut Group included taking a set of 25 control samples and comparing them with 110 'on site' samples. The coefficient of variation was calculated and was lower for the control samples than the 'on site' samples (17% compared with 50, 23 and 52%). This is one of the few studies where background variability/natural heterogeneity of soil total P has been assessed. A study of the variation of background levels of P is essential for any study where anomalous values are being sought.

AN EXAMINATION OF THE NATURAL DISTRIBUTION OF P IN SOIL (MACRO LEVEL)

3.1 Introduction

Archaeological phosphate analyses are made to locate concentrations of P in the soil above a 'natural background' variation. The latter comprises of 'inherent' P which includes any phosphorus containing minerals together with any additions that may have occurred *i.e.* through the random manuring of animals and through the agronomic activity of humans since the beginnings of agriculture. It is important to contrast any high P level in an archaeological site with the background variation present to assess its significance. Surprisingly, the background variation of soil P does not appear to have been previously examined in any great detail. This background variation will be examined here at a range of sampling intervals, vertically down the profile and spatially over an area, and a comparison made with a P survey from an archaeological excavation.

3.2 Site selection

Locating a site which could display a 'non-managed' spatial variation of phosphorus in soil for archaeological purposes is problematic since all areas of the UK have been managed to some degree. Areas subject to prehistoric occupation and of interest to the archaeologist have either been subsequently exploited by recent agriculture (limed, ploughed, reseeded) or, if unsuited to improvement, suffered pedogenic changes due to climatic, vegetational and land-use changes. Specifically, one example is the change in climate C2500 BP, which probably caused the cessation of agricultural activity in the uplands, leaving the relict field systems and hut circles. This change to a cooler climate could be the cause of surface organic accumulation (A_h horizon) often accompanied by gleying in the horizon below which is typical of many upland soils. Two locations were chosen for sampling that were considered to be typical examples of sites where upland archaeological features in N. Wales are found, and are located on map 3.1. Site A is a podzolic brown earth on upland improved pasture. Site B is a stagno-gleyic brown earth on upland unimproved rough grassland. The two background surveys are compared to a third P survey (site C, located on map 3.2) of a shallow brown

Map 3.1: Location of site A and B

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Map 3.2: Site C

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earth on improved grassland, which formed part of an archaeological excavation, so was subject to the time and logistical constraints of an archaeological investigation. Sample soil profiles were excavated from each site and are described below.

3.3 Site locations and soil descriptions

Site A is located on the University college farm, Abergwyngregyn (GR SH65967159 - map 1.1). The site is on land at a height of 270m which was improved in the 1940-1950s (ploughed, limed, reseeded, and fertilised), but is currently used as rough grazing for sheep. The soil is a typical brown podzolic soil (*Manod* series, Rudeforth *et. al.* 1984). It would be described as a typic fragiochrept - USDA, or a Dystric cambisol - FAO (Avery, 1990)

Site A: Podzolic brown soil

Location: University college farm, Abergwyngregyn, GR SH65967159
Slope/aspect: 13° aspect E
Vegetation: grassland (improved 1950s)
Land use: rough sheep grazing
Drainage: normal

Profile

(cm)		
0-2	L	thick root mat (*festuca* spp), abrupt boundary to
2-15	A_p	reddish brown (dry 5YR 5/3) silty loam; moderate medium granular structure; abundant fine fibrous roots; few small stones; rare earthworms; smooth boundary to
15-50	B_w	reddish brown (dry 5YR 5/4) silty loam; moderate medium blocky breaking to medium granular structure; few fine fibrous roots; common medium subangular/angular shale stones, occasional rounded pebble; no earthworms; clear smooth boundary to
50-100	B_s	reddish yellow (dry 5YR 5/4-6.5) silty clay loam; moderate blocky/sub-angular structure; abundant medium-large angular shale stones; gradual irregular boundary to
100+	C	local lower Palaeozoic shattered, angular, shale

Site B is located 500m east of Bryn Hall Quarry, Llanllechid (GR SH 63656946 - map 1.1). The site is at an altitude of 305m and is above the "mountain wall", the limit of modern land improvement. It is likely never to have been intensively managed and is currently used for low intensity rough grazing for sheep and ponies. It is roughly 400 metres from a wartime mortar range. The soil is a stagno-gleyic brown soil, *Manod/Denbigh* series, *op. cit.* (typic fragiochrept - USDA; gleyic cambisol - FAO).

Site B: stagno-gleyic brown soil

Location: Bryn Hall Quarry, GR SH 63656946
Slope/aspect: 10° aspect NNW
Vegetation: unimproved grassland, occasional gorse & reeds
Land use: rough grazing (low stocking)
Drainage: receiving

Profile
(cm)

0-3	L	root mat, abrupt smooth boundary to
3-10	A_h	dark greyish brown (dry 10YR 5/2) common fine/medium fibrous roots, some woody; abrupt wavy boundary to
10-35	B_g1	very pale brown (dry 10YR 7/3) clay silty loam; moderate blocky sub-angular structure; few - 2% fine distinct mottles; few fine fibrous roots; common angular small-medium stones; gradual smooth boundary to
35-90	B_g2	light grey (dry 10YR 7/2) clay loam; moderate blocky structure; many-grading to-abundant-angular / sub-angular medium-large stones

Site C is located 1km NW of Garndolbenmaen, 18km south of Caernarfon GR SH48984455. The site is at an altitude of 140m and is improved pasture land (ploughed and reseeded 1975-79, and fertilised every spring), used for livestock grazing. The soil is a typical shallow brown soil (*East Keswick 1 association, op. cit.*). The soil analysis formed part of a one week excavation of a medieval long-hut and associated topographic features by the Gwynedd Archaeological Trust and therefore was subject to time and logistical constraints. Although the soil in the field has been much improved, the actual feature is relatively well preserved because it had been used as a dumping site for stones from historic field clearance, and therefore the chemical characteristics of the soil in the feature might be comparatively unaltered by land improvement.

Site C: typical shallow brown soil

Location: Garndolbenmaen, GR SH 48984455
Slope/aspect: level
Vegetation: improved grassland
Land use: pasture
Drainage: normal

Profile

(cm)		
0-20	A_p1	brown-grey/brown (dry 10YR 5/3-2) silty loam; moderate medium granular structure; few small sub-rounded stones; many fine fibrous roots, occasional rhizome; clear smooth boundary to
20-35	B_w1	grey/brown to yellowish/brown (dry 10YR 5/2 – 5/4) silty loam; weak sub-angular blocky breaking to moderate medium/fine granular structure; common-many sub-rounded small/medium stones; few fine fibrous roots, occasional bracken rhizome; clear smooth boundary to parent material

3.4 Sampling strategy

The variation of P down a soil profile and spatially over an area are both of interest to this study and are examined separately.

3.4.1 Profile sampling

A soil profile was excavated and examined at each site and bulked samples were collected from every 5cm down the profile to the C horizon.

The top 10cm of a soil profile is commonly collected as a bulked sample using a soil auger in many soil surveys. However, the distribution of P_{tot} over the top portion of a soil profile is often variable and requires a more thorough examination. This was done in a soil block 10cm×10cm square to 20cm depth removed from site B using a 'Kubiena tin'. A vertical plane of this block of soil was sampled with a sharp knife while the soil was still moist. Each $1cm^3$ comprised a single sample (200 samples in total) for P_{tot} analysis. A second block of soil, of similar size was removed from an area close to site B which, on examination, displayed distinctive rusty mottling just below the A_h horizon. An area of soil 5cm×5cm surrounding this mottle incorporating a portion of the A_h horizon was considered to be suitable for examination of the distribution of P_{tot} over a meso-feature in the soil, and to see

how this distribution compared to that of related soil properties. One hundred 0.5cm×0.5cm×0.5cm samples were collected from the square using a sharp knife while the sample was still moist. P_{tot}, total organic carbon, and extractable iron and extractable aluminium were measured for all these samples using the methods described in sections 3.5.2 & 3.5.3.

3.4.2 Area sampling

A number of problems arise when collecting soil samples from an area. Of primary concern is what sampling strategy to use, what sample size to take and at what depth to sample, while ensuring that the samples taken are representative of the area sampled. The sampling strategy used is dependent on the feature surveyed, the variability of the area, the manpower available, time and financial constraints, and the method of P measurement. When conducting prospective or intensive archaeological surveys over large areas, a hierarchical grid sampling system is commonly used. Samples are normally collected on a coarse grid (10-50m) initially, and field measurement techniques for phosphate are often used at this stage. The results define areas of interest which may then be sampled more intensively. Grid sampling is preferred at this stage because it provides equally spaced samples which are easy to locate, with suitable coverage of the whole area. When sampling initially on a 50×50m grid, a feature 25×25m has only a 25% chance of being identified from a single sample within a randomly located grid, and the size of the initial grid must therefore take into account a number of factors including the size of features anticipated. These can vary considerably, so the size of sampling grid interval must vary accordingly. A hearth, small midden or inhumation might only be consistently detectable using a grid interval smaller than 1m, whereas a hut circle, byre or enclosure would be detected at 5-10m interval. At larger grid intervals the chance of detecting specific features diminishes and the smallest interval should therefore be used which logistical constraints allow. Where a specific feature is being examined, a selective sampling regime is often employed to ensure relevant samples are collected, (*e.g.* the selective sampling of a darker area of soil within Corrimony Chambered cairn, Invernesshire: Johnson, 1956). For this study, samples were collected using a rigid grid sampling system over a range of sampling intervals at each site. Site A and B were sampled using a different strategy to site C, and the strategies used will therefore be described separately.

3.4.2.1 Field sampling of site A & B

A hierarchical grid sampling strategy was used; initially 9 samples were collected over a 200m square on a 100m grid interval. Within this area 25 samples were collected over a 40m square at a 10m grid interval, and within this 121 samples were collected over a 10m square at a 1m grid interval. At the next level down 121 samples were collected from two 1m squares at a 10cm interval, these 1m squares being selected at site A as the two squares which showed the largest and the smallest variation of total phosphorus across the four corners. At site B the two squares from the same relative position within the 10m square as those from site A were selected. All the field samples from sites A & B were collected using a standard 2.5cm Ø soil auger at the grid nodes or intersections. At site A samples were collected to a depth of 10cm and at site B, where a distinct A_h horizon had developed, samples were collected to a depth of 10cm below the A_h horizon to exclude all the A_h material. The inclusion of the A_h horizon, which varied in depth, to each sample would have introduced much greater variation to the sample set, P being concentrated in the A_h horizon relative to the horizons below. Samples were collected solely from the depleted B_g1 horizon as this would give a more accurate indication of the inherent variation present in the soil.

Two further blocks of soil 10cm×10cm×10cm were collected in "Kubiena" tins from within the 10cm grids from sites A & B using the method described by Fitzpatrick (1984). One block from each site was used for thin section production (section 4.1). The second block from each site was sampled on a horizontal plane at a 1cm grid interval, using a sharp knife while the soil was moist, each $1cm^3$ comprising a single sample (100 samples per site). Samples of this size are close to the minimum amount of soil needed for chemical analysis (*i.e.* the sample size is equivalent to the sample spacing). Any results from these samples cannot be compared statistically with those previously collected, as the method of sampling, the size, shape and orientation of the sample (the 'sample support') are different.

3.4.2.2 Field sampling of site C

Site C was sampled using a less rigid hierarchical grid sampling strategy. The collection of soil samples from this site was governed by the constraints of having

to be investigated during a week long archaeological excavation. Only half the suspected feature could be cleared down to the original floor level so this was all that was available to sample. Twenty-five samples were collected over a 40m square that surrounded the feature at a 10m grid interval, and within this area 169 samples were collected from a 15m×12m area on a 1m grid interval. This square was bisected by a large wall (map 3.3), so 39 samples that would have completed the sampling were not collected. This area of 1m grid interval sampling was roughly 5m west of the feature being excavated and was selected for sampling because it contained 'interesting' surface features which could have been related to the archaeology. Within the excavated feature, 46 samples were collected from a 3m square at a 0.5m spacing and within this area 164 samples were collected over a 1m×1.5m area at a 10cm grid interval. At site C the field samples at the 10cm and 1m intervals were again collected by auger to 10cm depth. However, the samples at 0.5 & 0.1m intervals, all within the long hut could not be collected by auger due to the stony nature of the floor and these samples were collected using an archaeological trowel at the grid intersections, usually to a depth of 2-3cm.

Map 3.3: Site C (GR4898 4455)

3.4.3 Summary of samples collected

		Site A	Site B	Site C
Profile Samples		20	19	7
Area Samples				
100m interval	(-100m)	9	9	0
10m interval	(-10m)	25	25	25
1m interval	(-1m)	121	121	169
50cm interval	(-0.5m)	-	-	46
10cm interval	(-0.1m)	2×121	2×121	164
1cm interval	(-0.01m)	100	100	-
Total samples		516	517	411

3.5 Methods

3.5.1 The preparation of field samples

All the samples were air-dried at 40°C and passed through a 2mm sieve yielding roughly 25g soil per auger sample, roughly 1g for 1cm grid samples and 5g for trowel collected samples. Samples were finely ground to roughly 200μm by hand, and sub-samples from each taken for analysis.

3.5.2 Analytical procedures for all the samples collected

The measurement of total phosphorus

This method was modified from Sommers & Nelson (1972) and was selected following preliminary tests with a variety of total phosphorus methods, (appendix II). 0.2g soil and 2ml of perchloric acid ($HClO_4$) are mixed in a 20ml Pyrex tube marked at 15ml (+/- 2%), and digested for 4 hours at 200°C in a driblock. Once cooled the digest is made up to 15ml with distilled water and shaken. Orthophosphate in an aliquot of the solution is measured using a Perstorp "flow solution 3000" flow injection analyser (FIA) employing the colorimetric method of Murphy and Riley (1962) by which orthophosphate can be measured over the range of 5-0.05μg g^{-1} with a 99% accuracy. Reproducibility tests in this study on 100 replicate laboratory samples produced standard errors of less than 0.5% (appendix IV).

3.5.3 Analytical procedures for selected samples

The measurement of extractable phosphorus

5g of soil is shaken with 80ml of 0.5 M acetic acid for 4 hours, and filtered through P- free filter paper (Whatman No 1). Orthophosphate in an aliquot of the solution is again measured using a Perstorp "flow solution 3000" flow injection analyser (FIA), as described above. This method is selected instead of the commonly used Olsen method (sodium bicarbonate extraction) because it has been shown to correlate well for plant utilised P in acidic upland N. Wales soils (Wright, 1939), and is compatible with the F.I.A. method used.

The measurement of soil *p*H

The *p*H was measured in distilled water using a soil:water ratio of 1:2.5 (Jackson, 1958) on an E.I.L. 7020 *p*H meter which was pre-calibrated using standard buffer solutions.

Dithionite extractable Fe and Al

2g sodium dithionite ($Na_2S_2O_4$) in 40ml citrate buffer solution at *p*H 4.8 was added to 1g of soil in a clean plastic bottle and shaken overnight (Coffin, 1963). Fe and Al in the filtered extracts and a full range of standards were measured using air/acetylene flame and nitrous oxide/acetylene flame respectively on a Varian 'Spectre-AA' (Atomic Absorption) Spectrophotometer.

Pyrophosphate extractable Fe and Al

1g soil samples were mixed with 100ml 0.1M potassium pyrophosphate ($K_4P_2O_7.2H_2O$) and shaken overnight (Bascomb, 1974). Fe and Al in the filtered extracts and a full range of standards were measured utilising air/acetylene flame and nitrous oxide/acetylene flame respectively on a Varian 'Spectre-AA' Spectrophotometer.

Loss-on-ignition

Samples of soil roughly 5g were oven dried overnight at 105°C, and the % loss-on-ignition is calculated after ashing at 500°C overnight in a muffle furnace (Ball, 1964).

Total Organic Carbon

Total organic carbon was measured using the Tinsley III method of Kalembasa & Jenkinson (1973) with reduced volumes of reagents (4ml of 0.5N potassium dichromate, 5ml sulphuric acid and 1ml phosphoric acid, titrated against 0.05N ferrous ammonium sulphate) to take into account the small sample sizes used (~0.03g).

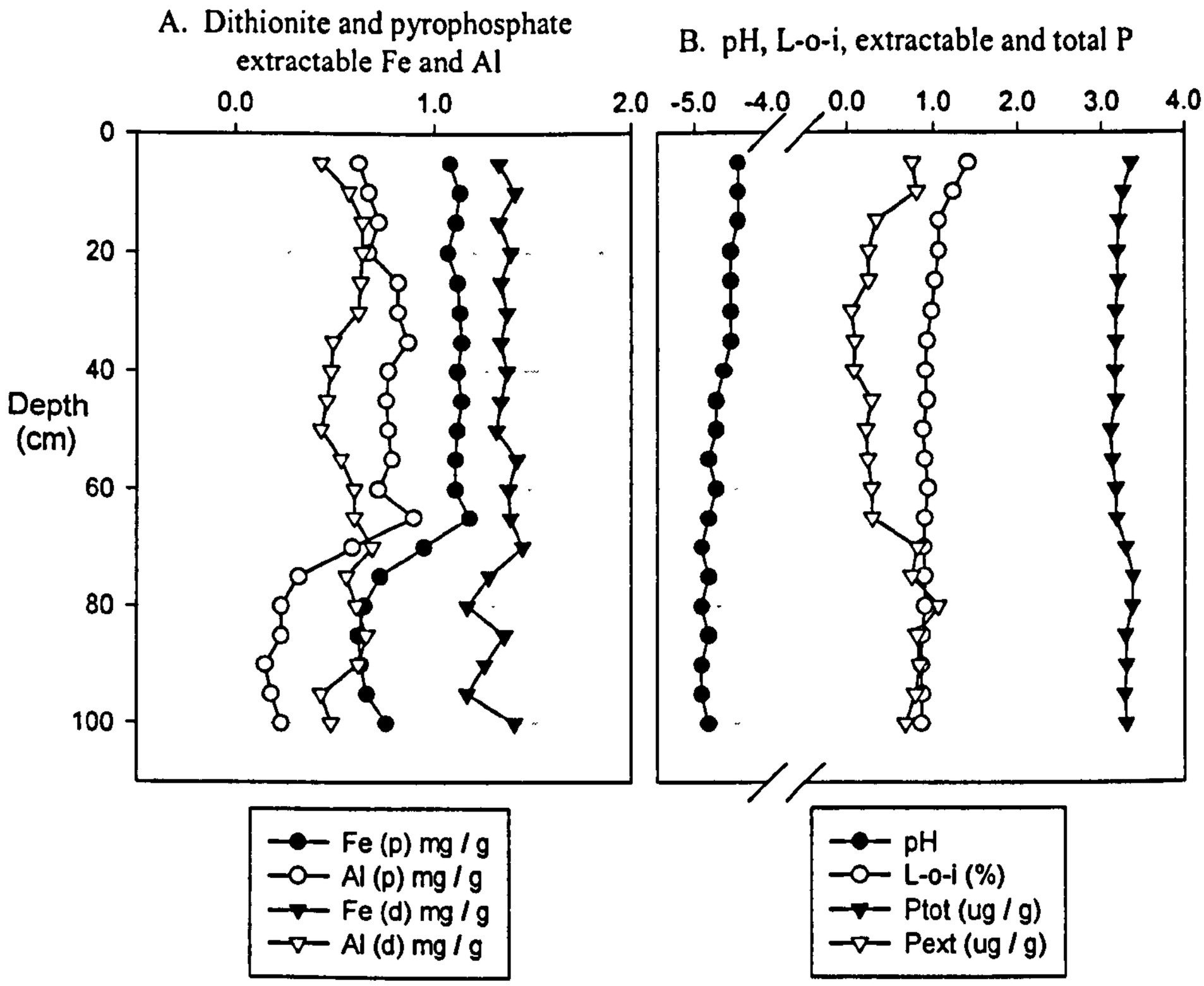
3.6 Results and discussion

The variation of soil P_{tot} will first be examined down the soil profile, followed by a detailed study of the variation of soil P_{tot} in the surface 20cm of site B, and these will be discussed separately to the work on variation of soil P_{tot} over an area which will be examined afterwards.

3.6.1 Variation with depth (complete profile)

The first consideration is how soil P_{tot} varies down the soil profile, figures 3.1, 3.2 & 3.3, and to what factors this variation can be attributed. Correlation matrices are then used to assess contributions to the variation of soil P made by the other soil characteristics. The raw data used to calculate these correlation matrices is produced in appendix I.

Figure 3.1: Variation of soil characteristics with depth for **Site A** (log scale)



The soil *p*H at site A rises from 4.2 at the surface to 4.8/4.9 in the lower horizons. The amounts of P_{tot} measured in samples collected down the profile decline until 65 cm depth where they rise slightly until 85 cm declining again afterwards. The amounts of P_{ext} measured mirror this bulge at the base of the profile. It is not surprising therefore, that P_{tot} correlates positively (P=0.01) with P_{ext}. A positive

correlation between P_{tot} and P_{ext} is expected because if the P_{tot} content of a soil horizon is high there will be more P present in a form which can replenish the labile P pool (Larson, 1967). The amounts of pyrophosphate extractable Fe and Al (p) decrease below 70cm down the profile, negatively correlating (P=0.01) with P_{tot} and P_{ext}.

Table 3.1: **Site A.** Correlation matrix: Soil characteristics with depth

	Depth	*p*H	L-o-i	P_{tot}	P_{ext}	Fe_p	Al_p	Fe_d
Depth								
*p*H	▲▲▲	1						
L-o-i	▼▼	▼▼▼	1					
P_{tot}	ns	ns	ns	1				
P_{ext}	▲	ns	ns	▲▲▲	1			
Fe_p	▼▼▼	▼▼	ns	▼▼▼	▼▼▼	1		
Al_p	▼▼	▼	ns	▼▼▼	▼▼▼	▲▲▲	1	
Fe_d	ns	ns	ns	ns	ns	▲	▲	1
Al_d	ns	ns	ns	ns	ns	ns	ns	ns

▲	Positively correlated	P= 0.5	r = 0.433
▲▲	Highly positively correlated	P = 0.1	r = 0.549
▲▲▲	Very highly positively correlated	P = 0.01	r = 0.665
▼	Negatively correlated	P = 0.5	r = -0.433
▼▼	Highly negatively correlated	P = 0.1	r = -0.549
▼▼▼	Very highly negatively correlated	P = 0.01	r = -0.665
ns	Not significantly correlated		

Figure 3.2: Variation of soil characteristics with depth for **Site B** (log scale)

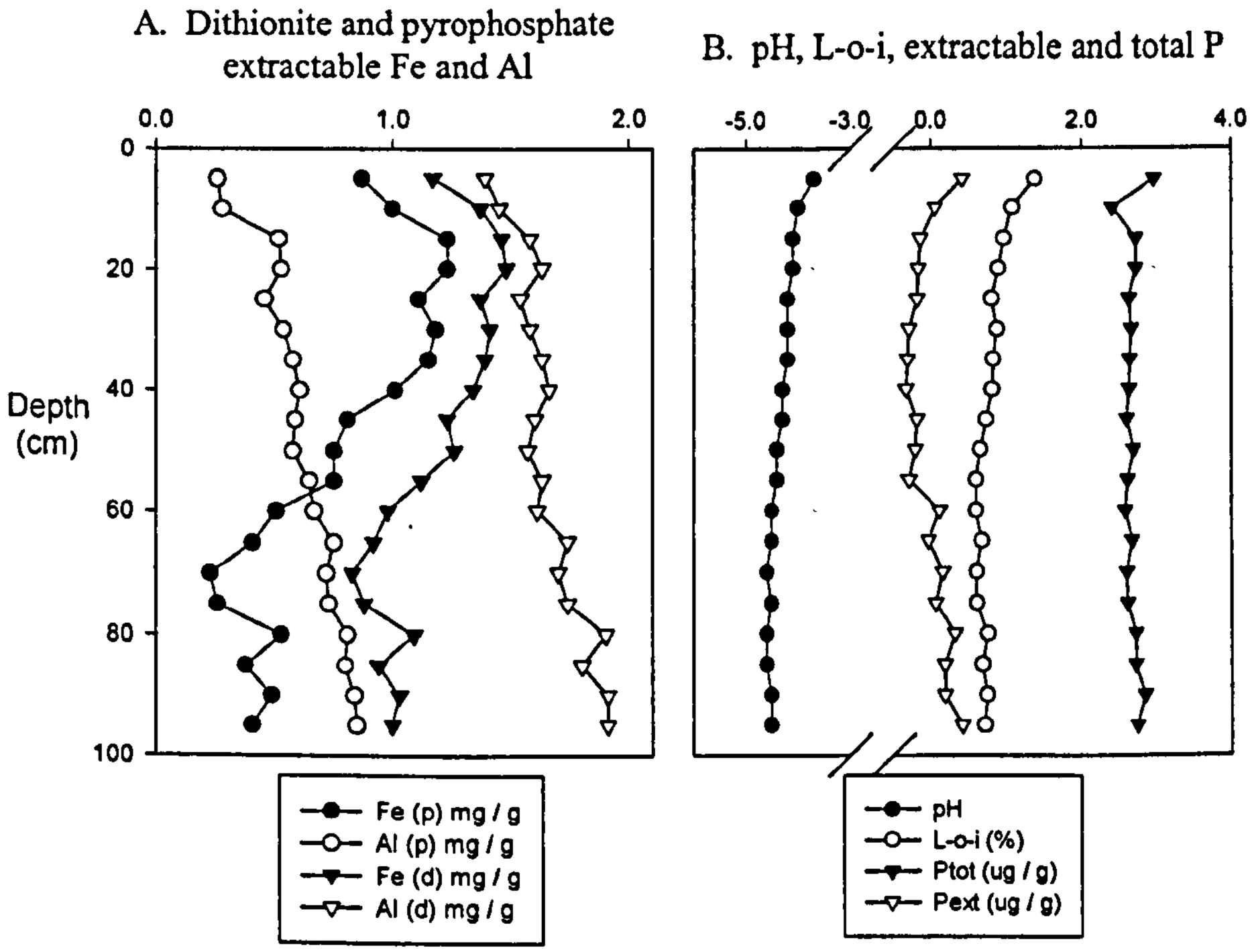


Table 3.2: Site B. Correlation matrix: Soil characteristics with depth

	Depth	*p*H	L-o-i	P_{tot}	P_{ext}	Fe_p	Al_p	Fe_d
*p*H	▲▲▲	1						
L-o-i	▼▼	▼▼▼	1					
P_{tot}	ns	ns	▲▲	1				
P_{ext}	ns	ns	ns	▲▲	1			
Fe_p	▼▼▼	▼▼▼	ns	ns	▼	1		
Al_p	▲▲▲	▲▲▲	▼▼	ns	ns	▼▼▼	1	
Fe_d	▼▼▼	▼▼▼	ns	ns	▼	▲▲▲	▼▼▼	1
Al_d	▲▲▲	▲▲▲	▼	ns	▲	▼	▲▲▲	▼

▲	Positively correlated	P= 0.5	r = 0.444
▲▲	Highly positively correlated	P = 0.1	r = 0.561
▲▲▲	Very highly positively correlated	P = 0.01	r = 0.679
▼	Negatively correlated	P = 0.5	r = -0.444
▼▼	Highly negatively correlated	P = 0.1	r = -0.561
▼▼▼	Very highly negatively correlated	P = 0.01	r = -0.679
ns	Not significantly correlated		

The soil *p*H at site B increases from 3.7 in the surface A_h horizon to 4.5/4.6 at depth. The P_{tot} content measured down the profile at site B is less than half that measured at site A. Values decline to their lowest point at 5-10cm, but are generally at an intermediate amount down the profile. There is a slight increase in P_{tot} at roughly 80cm, which is mirrored by a more obvious increase in P_{ext}. P_{tot} correlates significantly with P_{ext} and L-o-i, both at the P= 0.1 level, but not with either form of extractable Fe and Al. Al_p and Al_d both increase with an increase in sampling depth whereas Fe_d and Fe_p both decrease with sampling depth.

Figure 3.3: Variation of soil characteristics with depth for Site C (log scale)

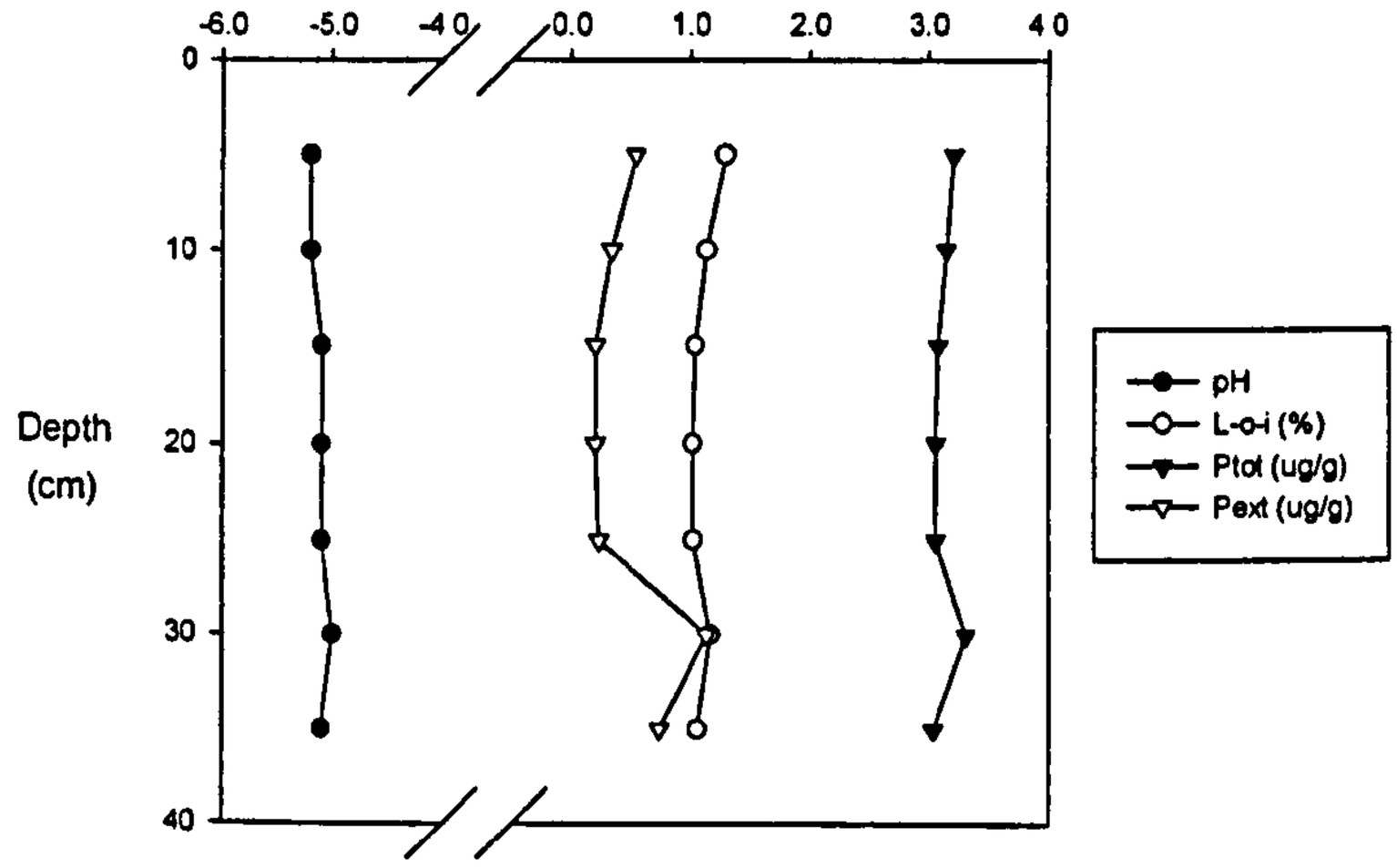


Table 3.3: **Site C.** Correlation matrix: Soil characteristics with depth

	Depth	*p*H	L-o-i	P_{tot}
*p*H	▼	1		
L-o-i	ns	ns	1	
P_{tot}	ns	ns	▲	1
P_{ext}	ns	ns	ns	▲

▲	Positively correlated	P= 0.5	r = 0.707
▼	Negatively correlated	P = 0.5	r = -0.707
ns	Not significantly correlated		

At site C the profile is much shallower (35cm), so only seven samples could be collected. The soil *p*H at site C remains around 5.0 down the soil profile, it is likely that this site was limed more recently than site A resulting in a slightly higher *p*H, site B was never limed. P_{tot} contents, although declining at first with depth, increase at 30cm, and this bulge is mirrored by a bulge in P_{ext}, and a slight increase in L-o-i. P_{tot} is correlated at site C with P_{ext} and L-o-i, (P=0.5).

3.6.2 Discussion

The distribution of P down a profile for a typical brown earth soil is well discussed in standard textbooks (*e.g.* Wild, 1988. Ch. 21). The concentration of P_{tot} in soil tends to be greater near the surface due to higher organic matter levels and agricultural inputs (fertilisers and animal manuring), and decreases down the profile. In an uncultivated upland soil a clearly defined A_h horizon can develop because there is little organic breakdown and mixing of organic inputs from litter, due to the cool, wet and acidic conditions reducing the soil organism population and their activity. Thus a very distinct P profile, that has a high P content at the surface decreasing sharply with depth, is produced, as described for site B and examined in more detail in section 3.6.3. Sites A and C are soils under agricultural use and both sites have been cultivated and limed, enhancing conditions for soil organisms, which mix the soil and increase the organic matter turnover. Consequently, the concentration of P_{tot} is greater throughout the profile at sites A and C than at site B. The amounts of P_{ext} are smaller at site B than they are at the other two sites because site B is the least well drained and poorly drained acidic soils have fewer sites on which extractable phosphates can attach because a proportion of the Fe is present as the reduced Fe^{2+}. Therefore there is less

replenishment of P which is taken up for plant growth and removed by leaching. At site B both extracted forms of Fe measured decrease down the profile because of increased gleying at depth.

The three soils sampled at sites A, B & C are brown earth variants and all show decreasing amounts of P_{tot} with depth. However in each case there is a rise of P_{tot} in the bottom quarter of the soil profile which suggests the vertical mobility of P down the soil which could be the result of the mobilisation and redistribution of iron and the P associated with it, perhaps by gleying or through the eluvial/illuvial processes described by Smeck & Runge (1971). The section of the profile with the lowest P_{tot} content, the eluvial zone, could be the result of the loss of P by the upwards recycling of plants and the downward movement in percolating water. The accumulation of P_{tot} in the lower zone of the profile, the illuvial zone, could be due to the downwards percolation of soluble P which is fixed, plus the weathering of P bearing minerals, and at this depth there would be little upwards recycling of P by plants. Runge & Riecken, (1966) reported that the immobilisation of P at depth was not due to clay content, which had been previously thought, but to the calcium carbonate levels in the soil, the soils reaching *p*H 8.0 at depth.

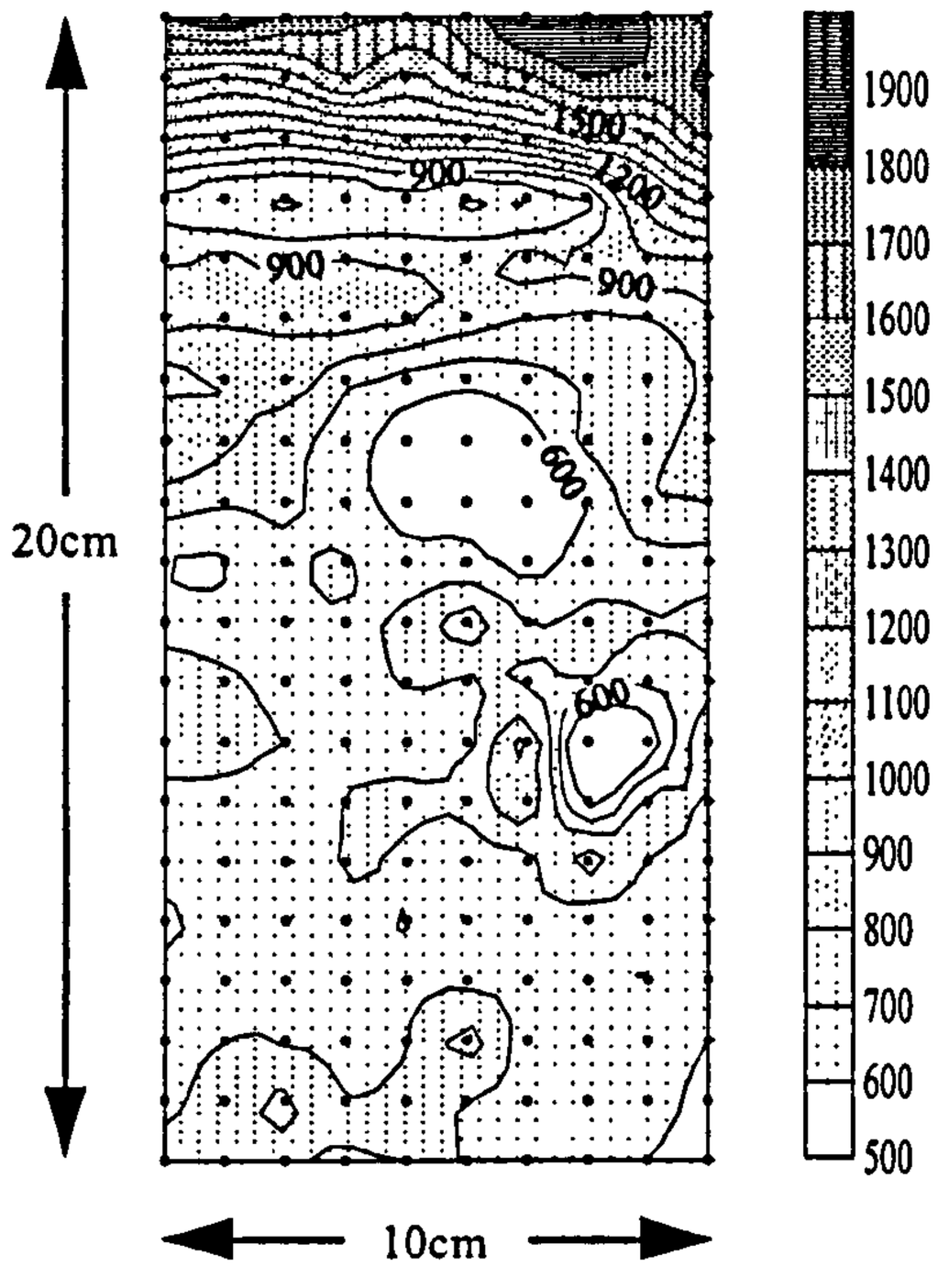
The soils from the three sites examined here are considerably more acidic with the *p*H not rising above 5.2. At this *p*H Fe and Al will play a more important role in the immobilisation of P in soil, however the P_{tot} content of the soils at Site A & B do not correlate positively with the amounts of Fe_p and Al_p and Fe_d and Al_d in the soil. It must be another more crystalline fraction of the Fe and Al present in the soil which is immobilising the P percolating through the soil profile. The correlation matrices plotted show that the P_{tot} contents of the soils at each site only consistently correlate with P_{ext}. There is a correlation between P_{tot} and L-o-i at sites B & C which might have been expected for all the sites, correlation between P_{tot} and L-o-i is unsurprising because organic forms of P in the soil can constitute 20-80% of P_{tot} (Larson, 1967). An additional factor which affects the distribution of soil parameters down a profile is the bulk density, which would be expected to increase down the profile as the percent organic matter content decreased. If soil parameters were plotted on a per volume rather than a per weight basis other trends might be illustrated.

3.6.3 Variation with depth (top 20cm)

It is common practice for soil samples to be collected using a soil auger to a depth of 10–20 cm. This sample is then bulked and processed (dried, sieved) ready for analysis, where a sub-sample of less than 1g may be used to measure P_{tot}. There is however, inherent variation in P_{tot} within the sample collected, and over the top 10cm of a soil profile. This has been examined for a block of soil removed from site B.

The variation of P_{tot} over the top 20cm of the soil profile is most conveniently examined as a P_{tot} distribution map plotted using surface mapping for windows and a minimum curvature interpolation, see figure 3.4.

Figure 3.4 P_{tot} ($\mu g\ g^{-1}$) distribution over 10cm×20cm square at site B



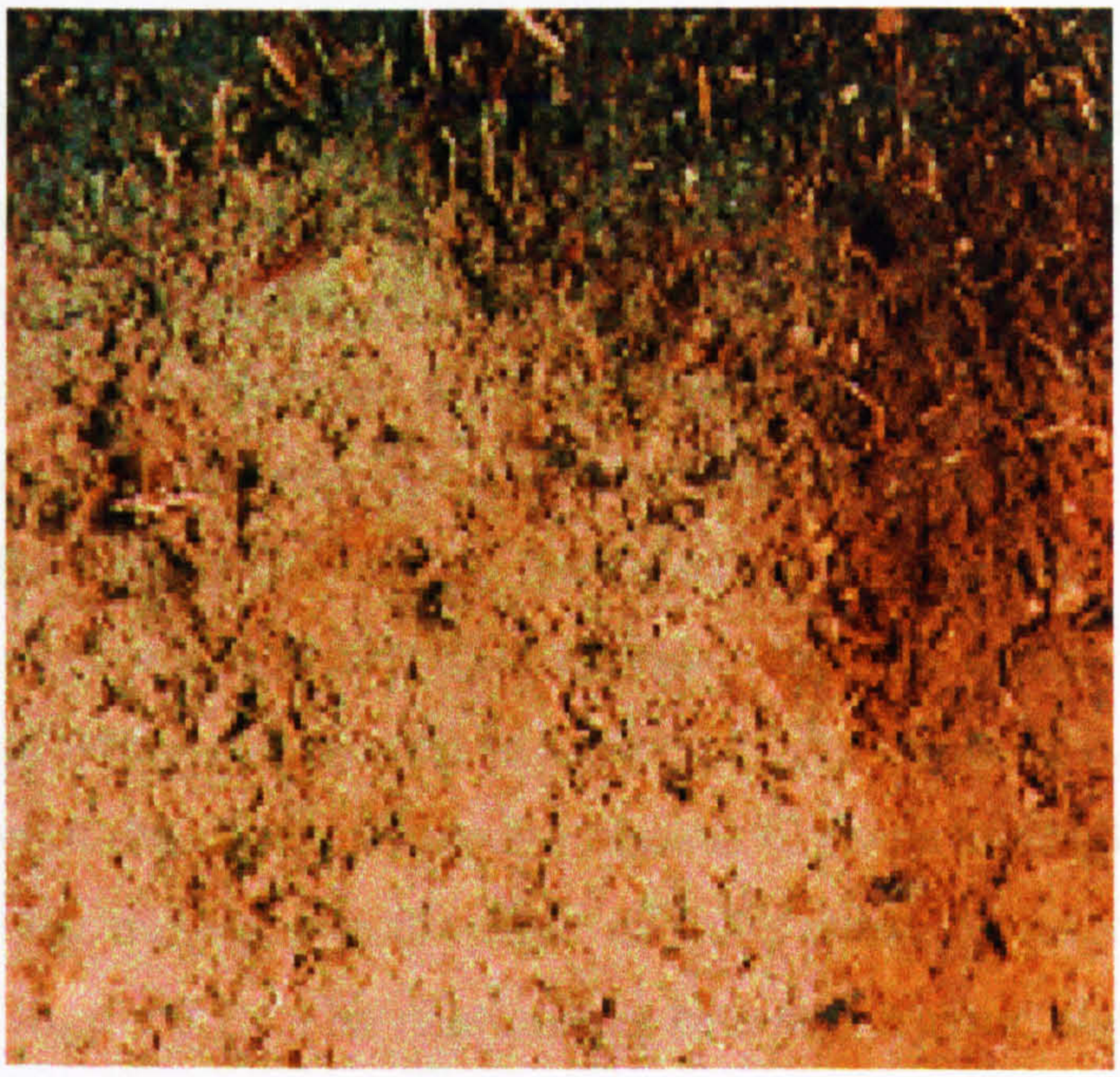
The soil at site B is a stagnogleyic brown earth which has an A_h horizon of varying depth. This is clearly seen on the distribution map, which reveals a P_{tot} gradient of 1900 to 500 $\mu g\ g^{-1}$ over 20cm, but more particularly 1900 - 1000$\mu g\ g^{-1}$ over the top 3cm. Any sampling by soil auger from the surface of this soil will include some of the organic A_h horizon which has accumulated a greater P_{tot} content than the B horizon below, so the P_{tot} content measured will depend on the depth of the A_h

horizon at the point of sampling. The variation of P_{tot} calculated from a stagnogleyic soil is therefore dependent on the method of sampling and the depth of soil taken for each sample. To avoid this additional factor when considering the variation of P_{tot} in stagnogleyic soils, samples can be collected from below any well defined A_h horizon, so an auger sample is taken from roughly 10 – 20cm. This was the method used to sample the soils at site B in this study, but obviously it does not address the problem of sampling a poorly defined A_h horizon. Therefore the sampling strategy to be used should be selected only after an examination has been made of the soil profile.

3.6.4 Variation of P_{tot} with depth (0.5cm level) within a stagnogleyic soil

The distribution of P_{tot} over an area of a stagnogley is examined and compared to the distribution of total organic C, and dithionite extractable iron and aluminium (Fe_d & Al_d). The area of soil was selected to include a prominent rusty mottle and a section of the A_h horizon (figure 3.5)

Figure 3.5 Area of soil sampled (5cm×5cm)



Descriptive statistics for the results from the 100 samples (0.5cm×0.5cm×0.5cm) collected over the sample area are produced in table 3.4.

Table 3.4: Statistics for the measured soil characteristics

	Total P (mg g^{-1})	Total organic C (mg g^{-1})	Fe_d (mg g^{-1})	Al_d (mg g^{-1})
Mean	0.69	76.40	11.60	0.70
Std error	0.03	3.00	1.50	0.04
Median	0.60	66.65	4.00	0.65
Std deviation	0.30	30.30	15.20	0.44
Range	0.35-1.65	36-193	1-56	0.36-3.35
Coeff. var	44%	40%	131%	62%

The variation of the four chemical properties is large; the coefficient of variation is above 40% for each characteristic. However this is a soil selected for its visible variability over a small area (figure 3.5). The colour is a useful indicator of the variation of organic matter and iron in the sample and there are colour changes from the upper to lower portion of the square. The "value" as denoted by the Munsell colour system (1975) drops from 7 in the A_h horizon to 4 in the B_g horizon and from the left to the right of the sample square, the "chroma" increases from 2 in the grey B_g matrix (ferrous iron) to 4 in the rusty mottle (ferric iron). The pattern of P distribution corresponds to these colour changes and can be clearly seen when the distribution maps are plotted, see figures 3.6 – 3.9

An area of obvious visual heterogeneity will contain greater variability in many soil characteristics. P_{tot} amounts would be expected to be greater in areas of increased organic matter, illustrated by the example in section 3.6.3, but is the variability of P_{tot} greater in an area of gleyed soil with large rusty mottles? It could be postulated that the iron associated with a rusty mottle (ferric) will have a greater P content relative to the ferrous iron in the surrounding soil matrix. The pattern of P_{tot} distribution (figure 3.6) clearly corresponds with the colour changes across the sample square which can be seen in figure 3.5. Amounts of P_{tot} are highest in the upper portion of the square where the organic C levels are highest (figure 3.7), the P_{tot} content also increases to the right of the square, corresponding with higher levels of Fe_d (figure 3.9). The relationship between organic matter content and P_{tot} in soil has been well established; between 20% and 80% of P in the surface horizons of a soil are in the form of organic P (Barber, 1984). P absorption in acidic soil is related to amounts of amorphous Fe and Al (Freese *et.al.*, 1992), however under gleyed soil conditions the more soluble reduced Fe phosphates could be leached out, or redeposited on the ferric Fe of the mottles, which would make a difference in

Figure 3.6: Total P distribution (mg/g) over a 5cm x 5cm square

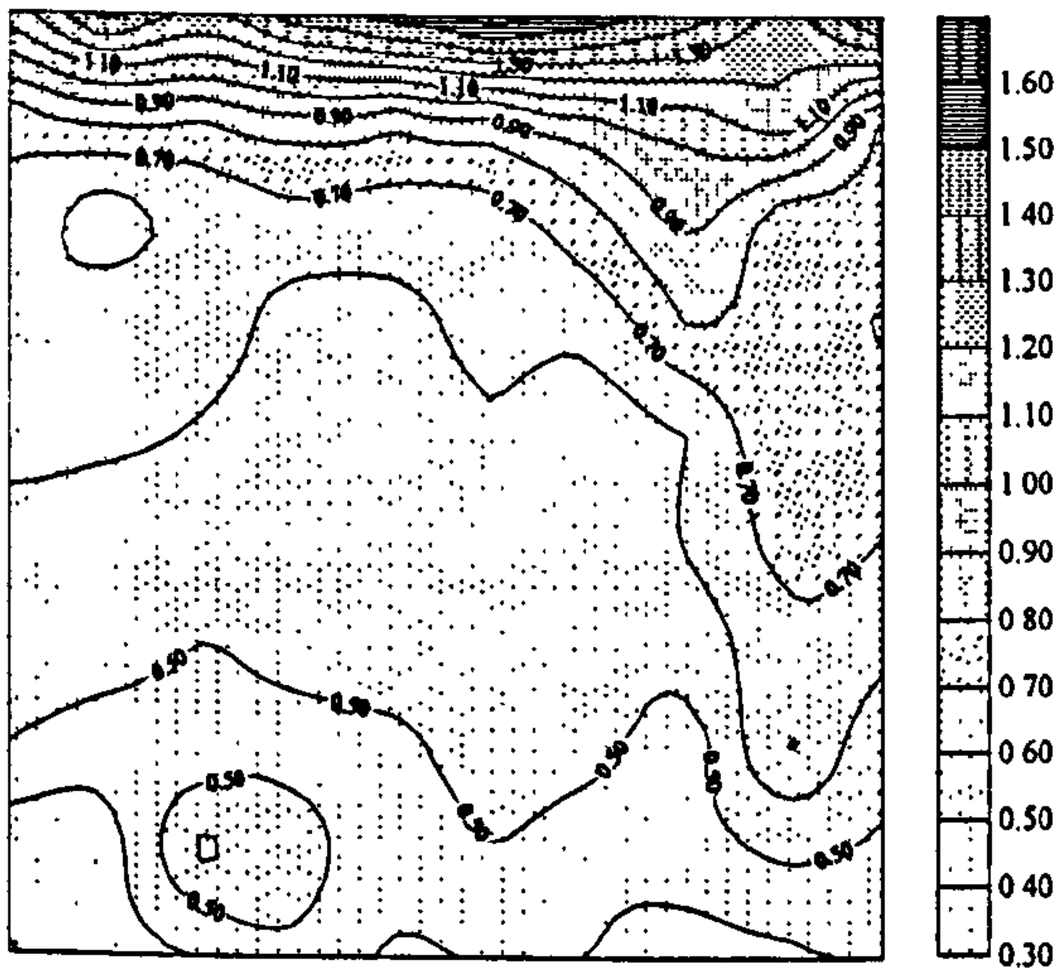


Figure 3.7: Total organic C distribution (mg/g) over a 5cm x 5cm square

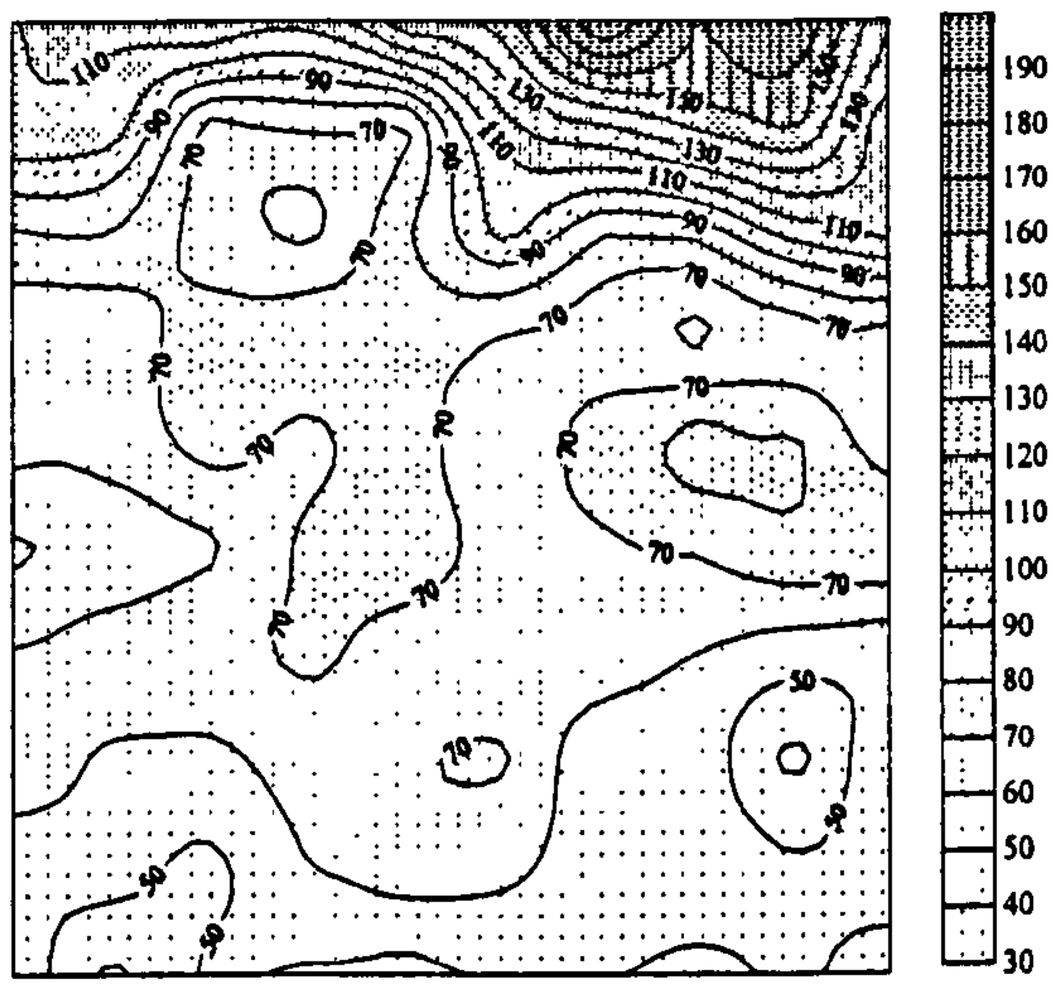


Figure 3.8: Dithionite extractable Al distribution (mg/g) over a 5cm x 5cm square

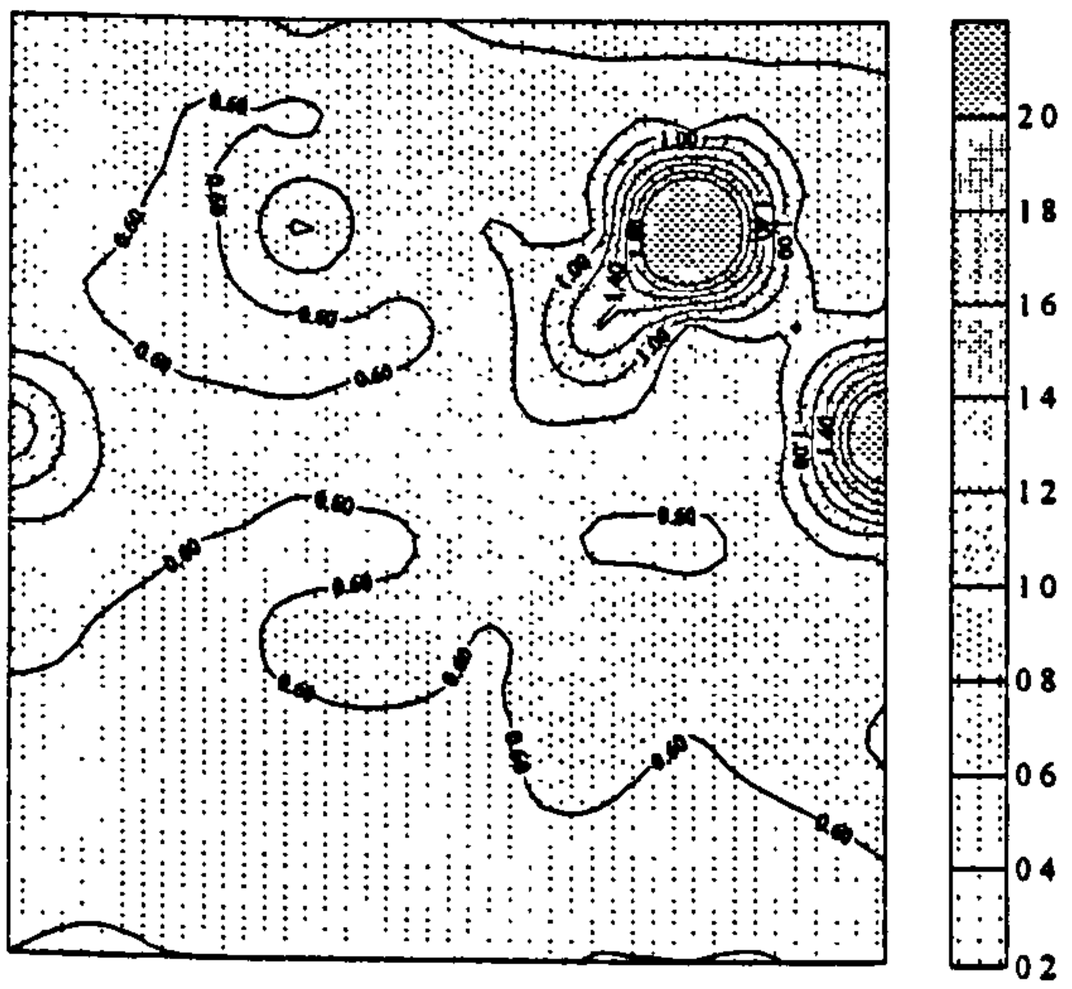
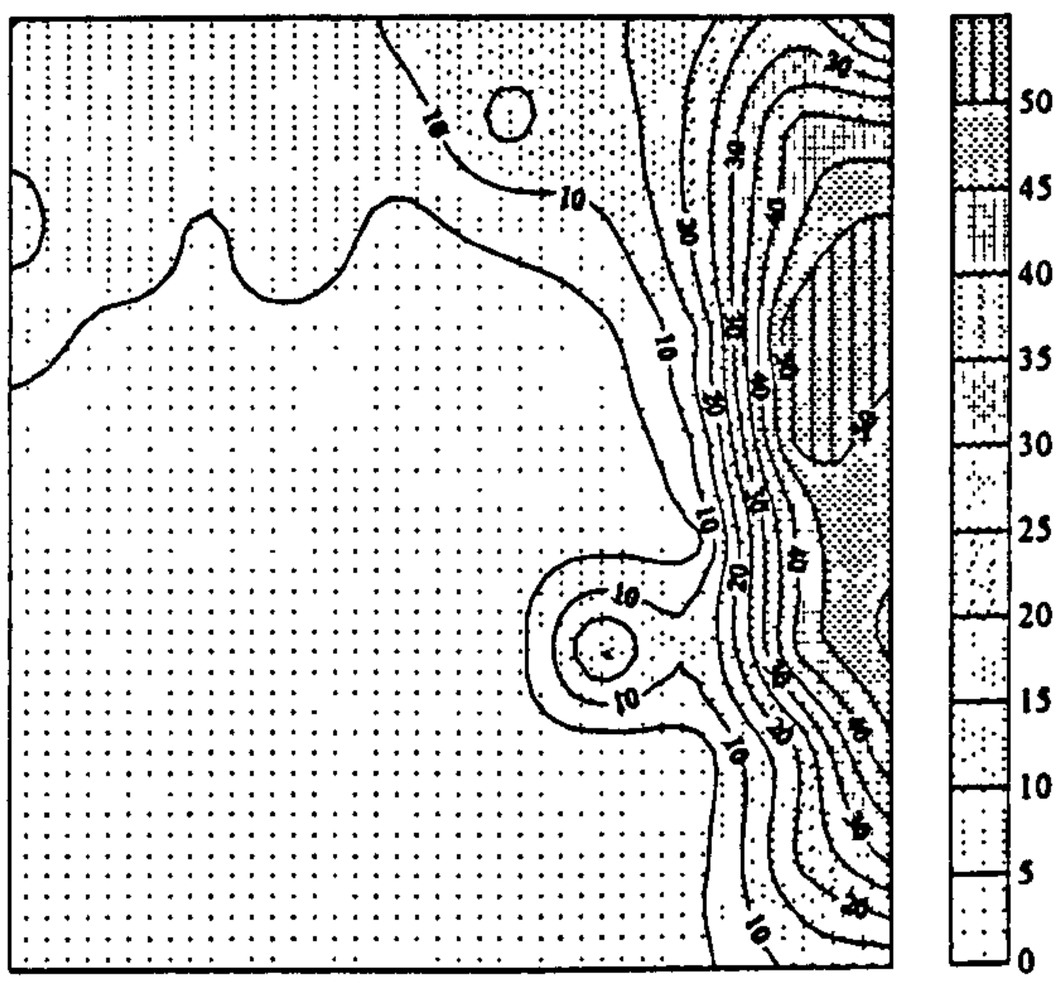


Figure 3.9: Dithionite extractable Fe distribution (mg/g) over a 5cm x 5cm square



P_{tot} levels between the two areas of Fe oxidation within the B_g matrix. A visual examination of the spatial distribution of P_{tot} over the 5cm square suggests it is closely allied to the distribution of Fe_d, with levels of P being 10% greater in the B_g mottle than in the reduced B_g matrix.

A correlation matrix (table 3.5) calculated for the 4 soil characteristics reveals that while there is a significant correlation (P=0.01) between P_{tot} and organic C, the correlation between Fe_d and P_{tot} is weaker (P=0.5) whilst the correlation between Al_d and P_{tot} is more significant (P=0.1), even though the distribution of P_{tot} and Al_d do not appear to be closely connected on the distribution maps. In this acidic upland soil, dithionite extractable aluminium appears to play a greater role in P fixation than the extractable iron. There is a surprising difference between the visual distributions and the statistical analyses.

Table 3.5: Correlation matrix, selected soil characteristics over a 5cm×5cm square

	P_{tot}	Organic C	Iron (d)
Organic C	▲▲▲		
Iron (d)	▲	▲	
Aluminium (d)	▲▲	ns	▲▲

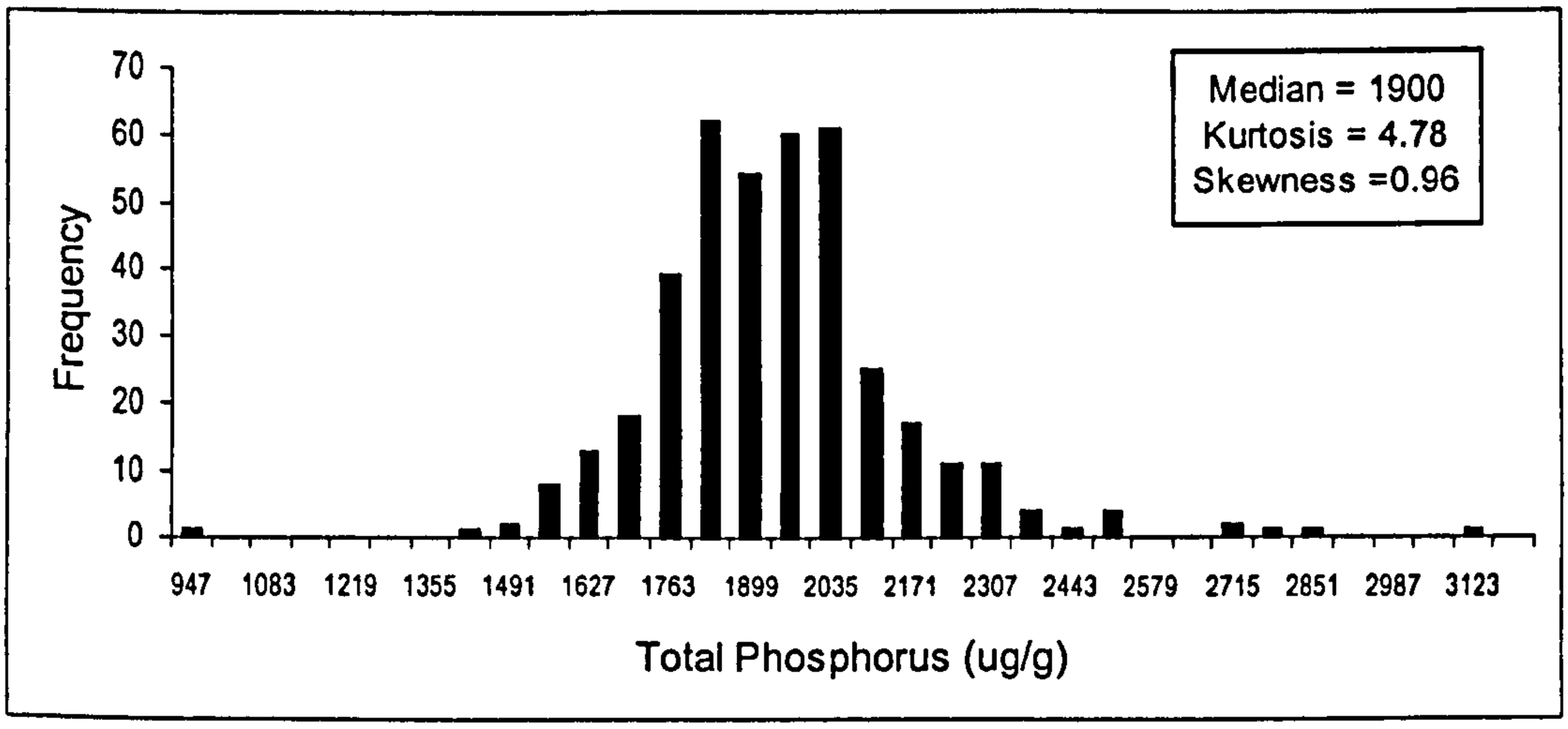
ns	Not significantly correlated		
▲	Positively correlated	P=0.5	r=0.195
▲▲	Highly positively correlated	P=0.1	r=0.254
▲▲▲	Very highly positively correlated	P=0.01	r=0.321

3.6.5 Variation with area

This study yielded over 2500 total phosphorus results, the raw data being presented in appendix 1. The variation of P_{tot} across the sampling grids will be examined in a number of ways. The data will be inspected statistically using standard procedures of exploratory data analysis, including means, variances, standard deviations, coefficients of variances and ranges. A histogram is presented initially for all of the field data collected at each site, further histograms being used for each sampling grid to describe the population parameters median, skewness, kurtosis and range. To aid the visualisation of the distribution of P_{tot}, 2D interpolated maps will also be plotted for each sampling interval.

3.6.5.1 Variation within site A

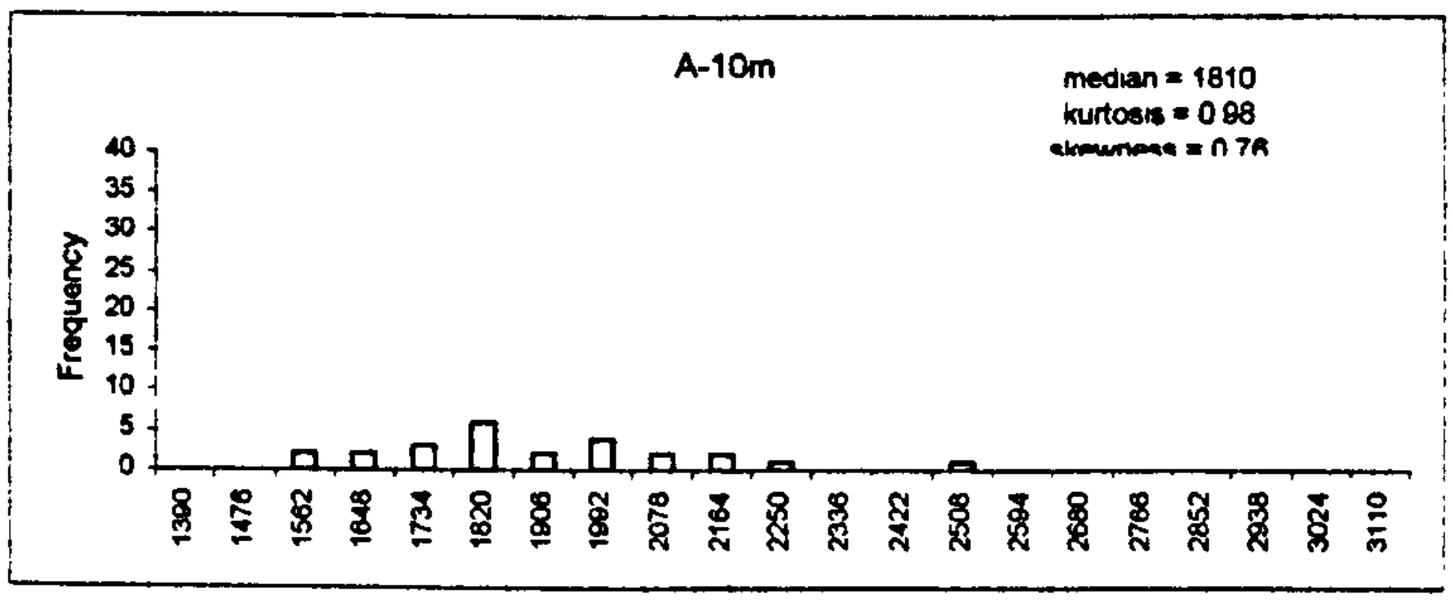
Figure 3.10: Distribution of Site A field data down to a 10cm sampling grid (n=397)

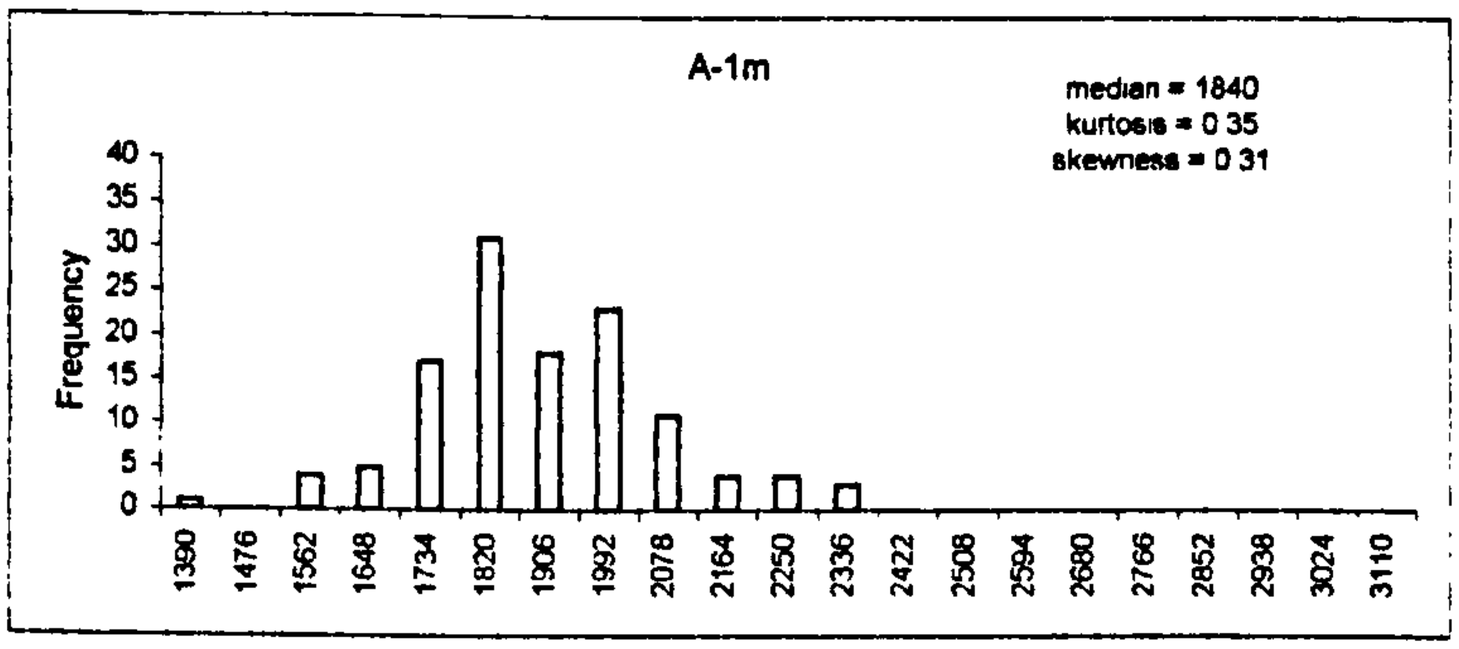


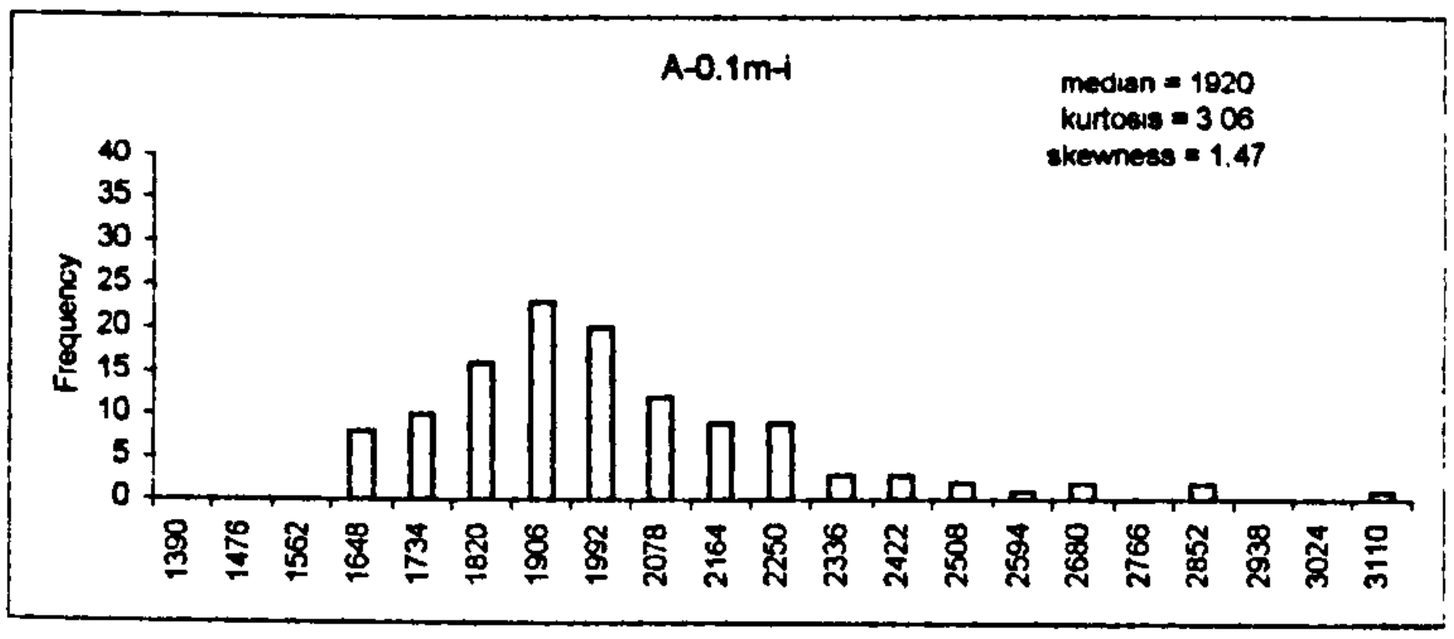
The histogram for all the site A field data reveals a number of features of the data set. P_{tot} ranges from 947 - 3100+ $\mu g\ g^{-1}$; however, the majority (96%) of data points fall in the much narrower range of 1500 - 2300 $\mu g\ g^{-1}$ (2×sd), and 77% of the data falls between 1720 - 2110$\mu g\ g^{-1}$ (1×sd). Individual points some way from the data median make the data appear peaked, *i.e.* have a high positive kurtosis (4.78). If a few outliers were removed the data would appear much more normally distributed.

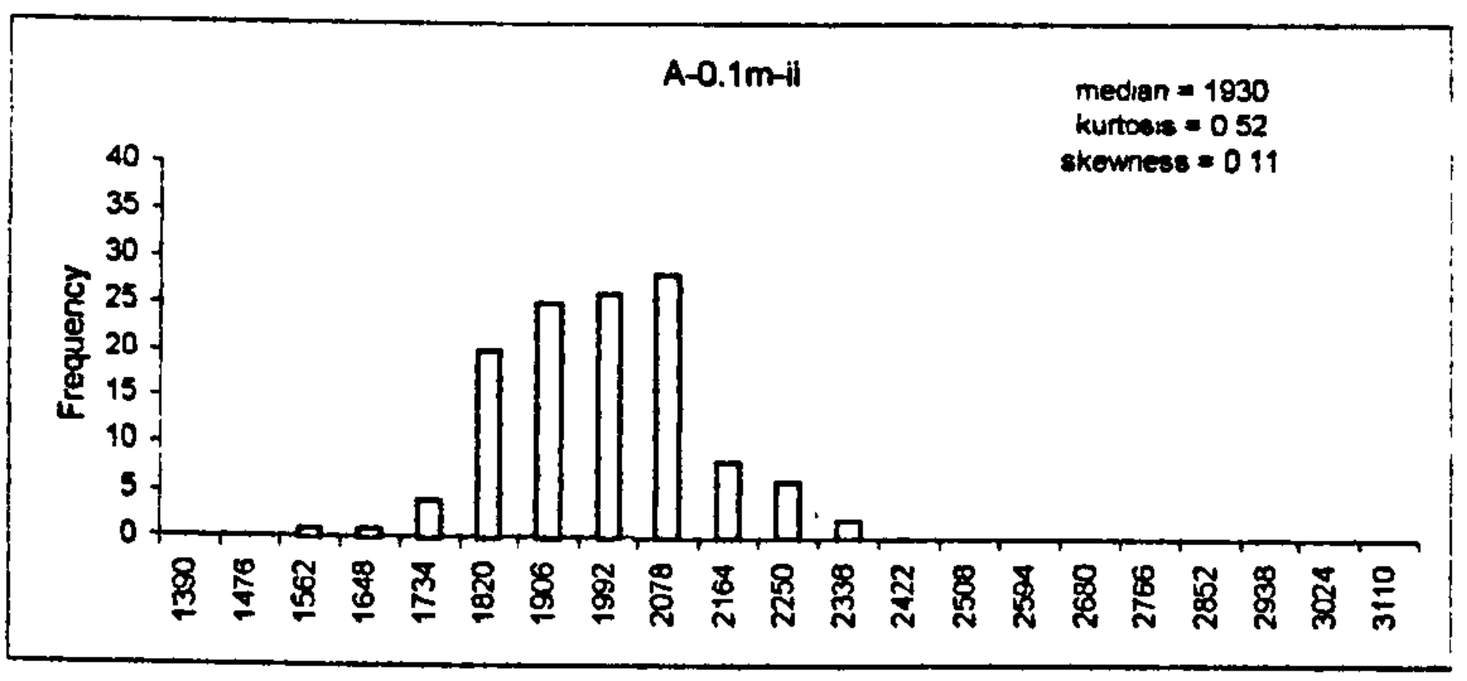
Histograms are also plotted for all the individual sampling grids, figure 3.11, and are a useful method of examining the distribution of the data. The spread of the data for all the sampling intervals is easily compared: the data for A-0.01m displays the least spread, whereas A-0.1m-i has a much greater spread of data, reaching

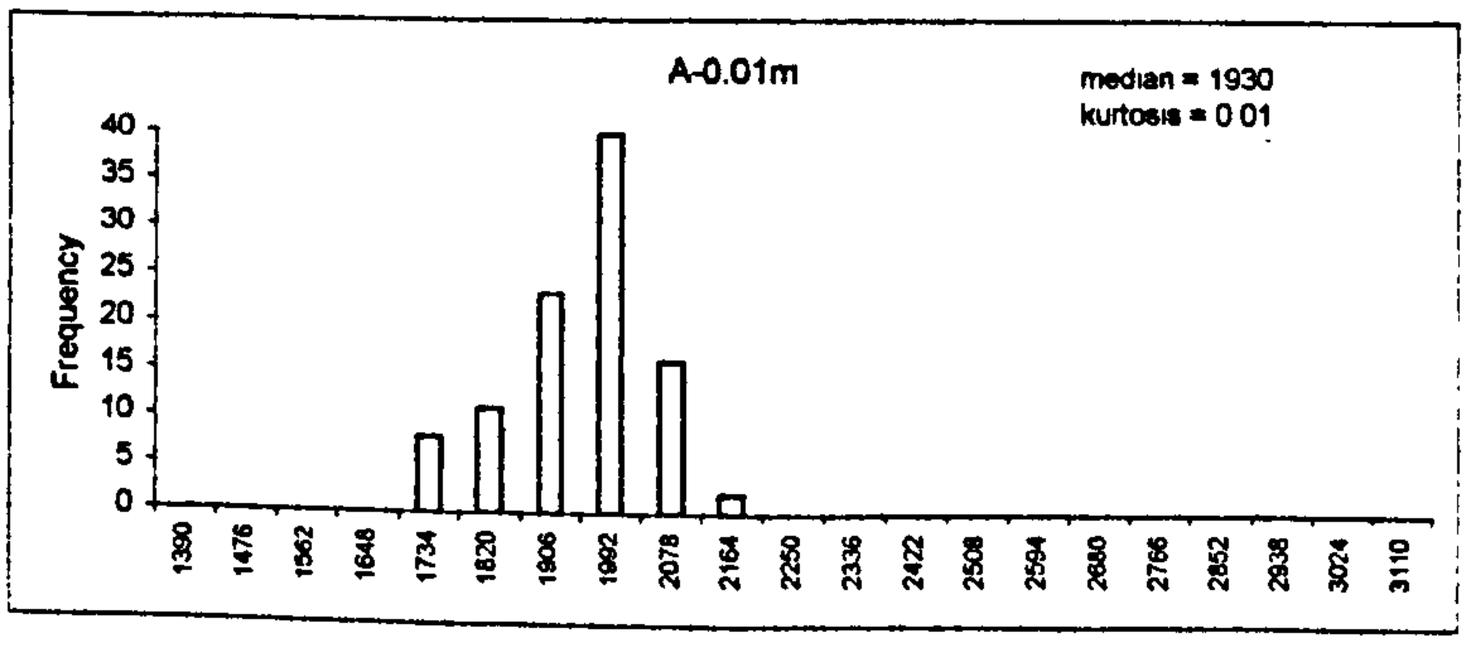
Figure 3.11: Histograms of Ptot values (ug/g) for all Site A sampling grids











3100μg g^{-1}. The majority of values for P_{tot} are within the same range and the mean values for the sampling intervals from A-10m to A-0.01m displayed in table 3.6 are close (1860-1970μg g^{-1}). The examination of the distribution of data is important because, in an archaeological context, samples collected from an area of elevated P would be represented as a number of large values, such as the value at 3110μg g^{-1}, on the A-0.1m-i histogram. Statisticians often replace outlying values (those greater than 3× the standard deviation of the mean) with mean or median values to improve the validity of their data set. However for the archaeologist these outliers are an important and significant indicator.

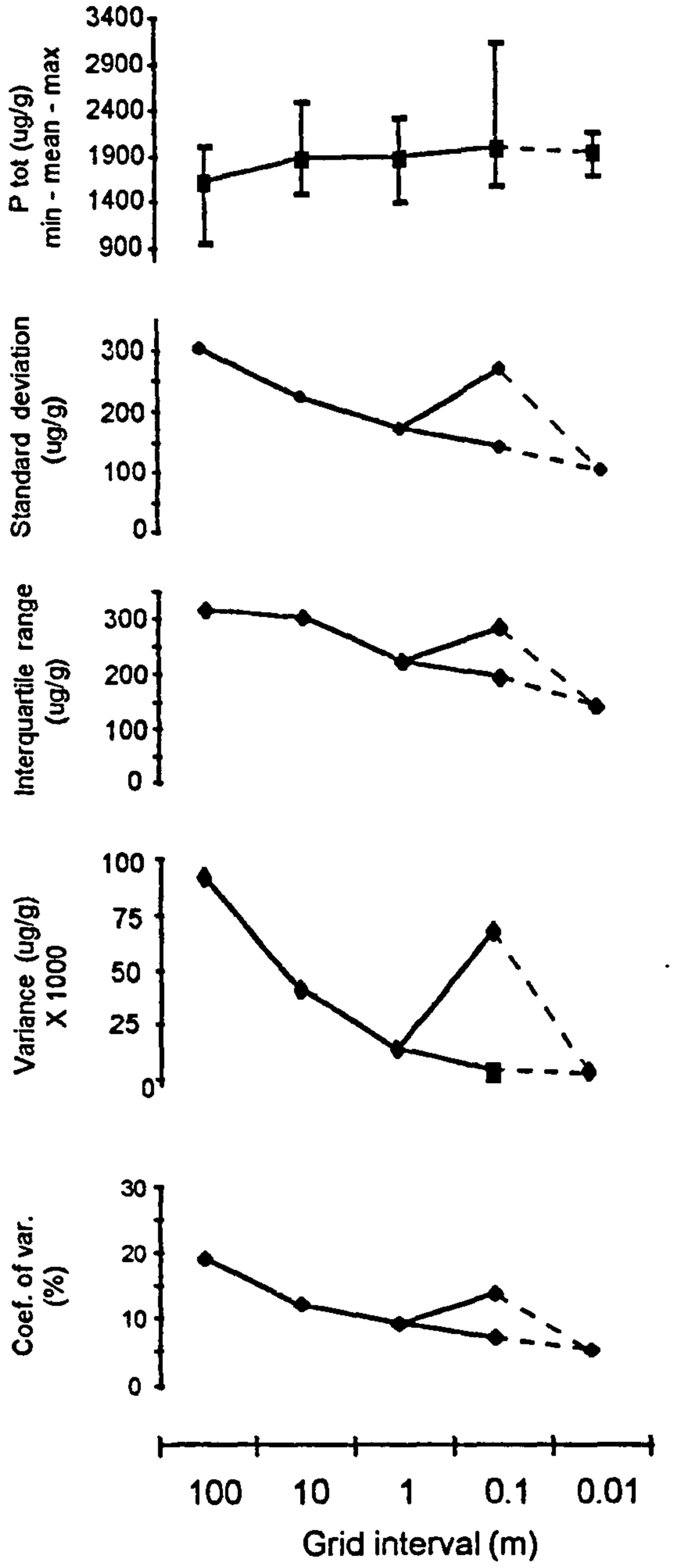
To describe the data and assess their variation, statistics are listed in table 3.6 and plotted for increasing grid size in figure 3.12. The 0.01m points are connected to the larger sampling intervals with a dotted line in figure 3.12 because these samples were not collected using the same method as the others, (section 3.4.2).

Table 3.6: Descriptive statistics for field data from Site A (μg g^{-1})

	100m	10m	1m	0.1m-i	0.1m-ii	0.01m
Mean	1614	1861	1857	1974	1935	1913
Std. Error	101	45	15	24	13	10
Std. Deviation	304	224	169	268	138	99
Sample variance	92309	50249	28417	71919	18977	9845
Range	1060	990	920	1570	760	470
Min. - Max.	947 - 2007	1490 - 2480	1390 - 2310	1570 - 3110	1540 - 2300	1660 - 2130
Count	9	25	121	121	121	100
Coef. of var. (%)	18.8	12.0	9.1	13.6	7.1	5.1

The mean P_{tot} results for the 10m - 0.01m sampling grids only range from 1860-1970 $\mu g^{-1}g$. This suggests that P_{tot} contents of soil at this site are normally distributed as long as sufficient samples are collected. Outliers at the upper and lower end of the distribution cancel each other out. The mean for the 100m sampling grid is calculated from 9 data points so is not a statistically viable result. There are noticeable differences between grid interval sizes for the other calculated statistics which are apparent when the data is plotted (figure 3.12), with a distinct downward trend as the grid sampling interval is reduced. As the area sampled is reduced, less variation in P_{tot} is encountered. There is a large difference in the P_{tot} value from the two 0.1m sampling grids chosen because they had the largest and smallest variation in P_{tot} across their 4 corners. As would be expected, the square

Figure 3.12: Variation in P_{tot} at site A College farm



which had the largest variation across its 4 corners displays a greater range of P_{tot} values and greater variation in soil P: two 1m×1m squares, only 2 metres apart, can apparently display a large difference in the variation of P_{tot}.

Since the variation of the data has a spatial element, it is convenient to present it as interpolated 2D distribution maps for a number of the sampling grids (10m, 1m, 0.1m-i, 0.1m-ii & 0.01m), to enable the discussion of the spatial spread of P_{tot}, and to check for any regularity or patterns in the data, (figures 3.13 - 3.17). The use of distribution maps to aid in the visualisation of data sets is common practice in many studies and a variety of mapping packages can be used. The maps are produced here using the surface mapping for windows package *'Winsurf'* (Golden Software, 1993) using the 'minimum curvature' interpolation method. A full discussion on the interpolating techniques within the *'winsurf'* mapping package is produced in appendix V.

The maps show the grid sampling points and the location of any further sampling grids within them. At the 10m sampling interval the P_{tot} distribution may have a general North/South trend running across the slope. There are no visible surface features in the field to explain this, but as the distribution map is correlated from only 25 sample points, the trend cannot be described as significant. The distribution at the 1m sampling interval is more complex. A banded pattern can be observed running up/down the slope roughly 3m apart. This could be attributed to the application of P fertiliser - basic slag - to the area in the 1940-50s. The applications would be made using a tractor-pulled, rear-spreading trailer, moving up/down the slope. If the applications overlapped or left bare strips then this banding pattern could occur.

The distribution map for the A-1m-i grid is dominated by an area of high P in the N corner of the grid, which can be seen on the coarser grid A-1m, and is part of the banding pattern. The previous management practice of the site has had a definite effect on the P distribution over a 1m×1m square. There is a second high spot on this map, in the S corner of the grid, but this is only a single point which has a larger P_{tot} content than the surrounding points, so the interpolation method has had to 'bullseye' the pattern around it, so drawing attention to it. This high spot is not

Figure 3.13: A-10m

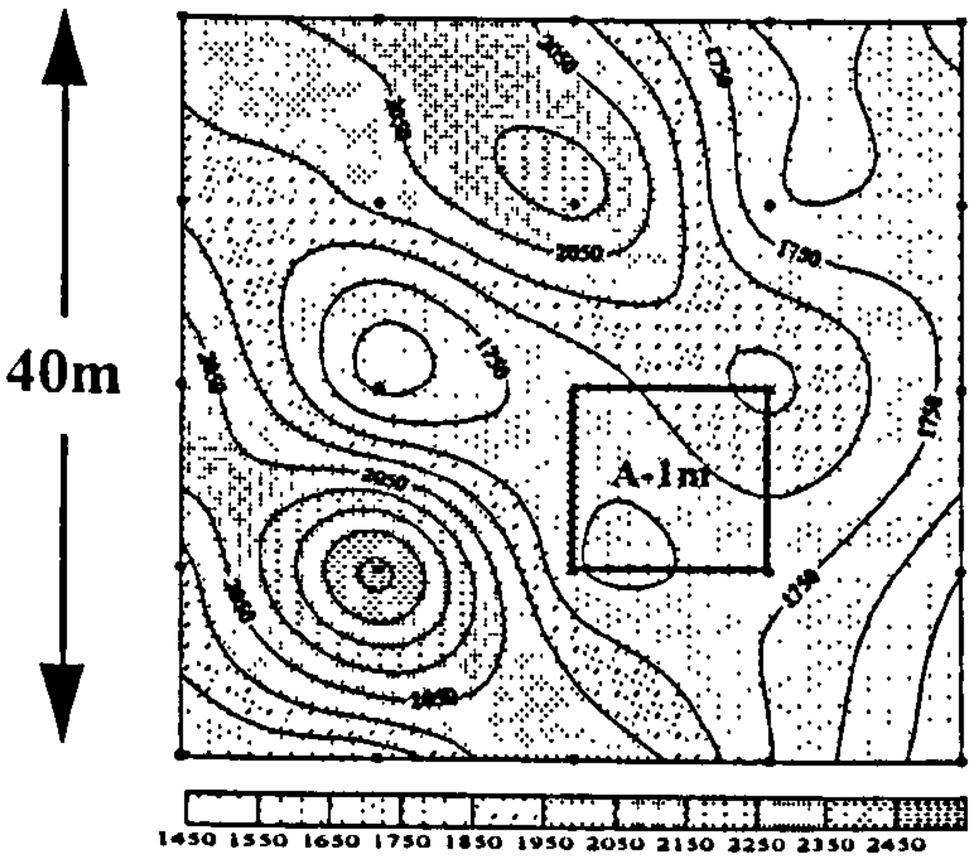
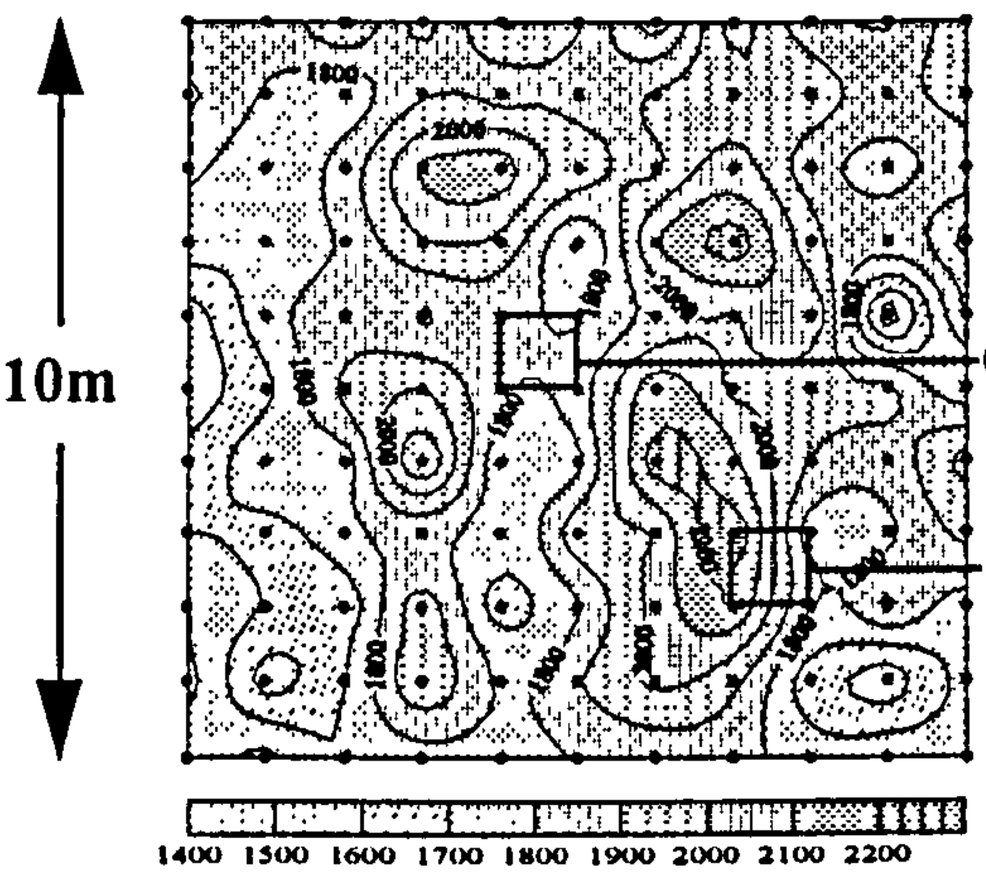


Figure 3.14: A-1m



N

Figure 3.15: A-0.1m-i

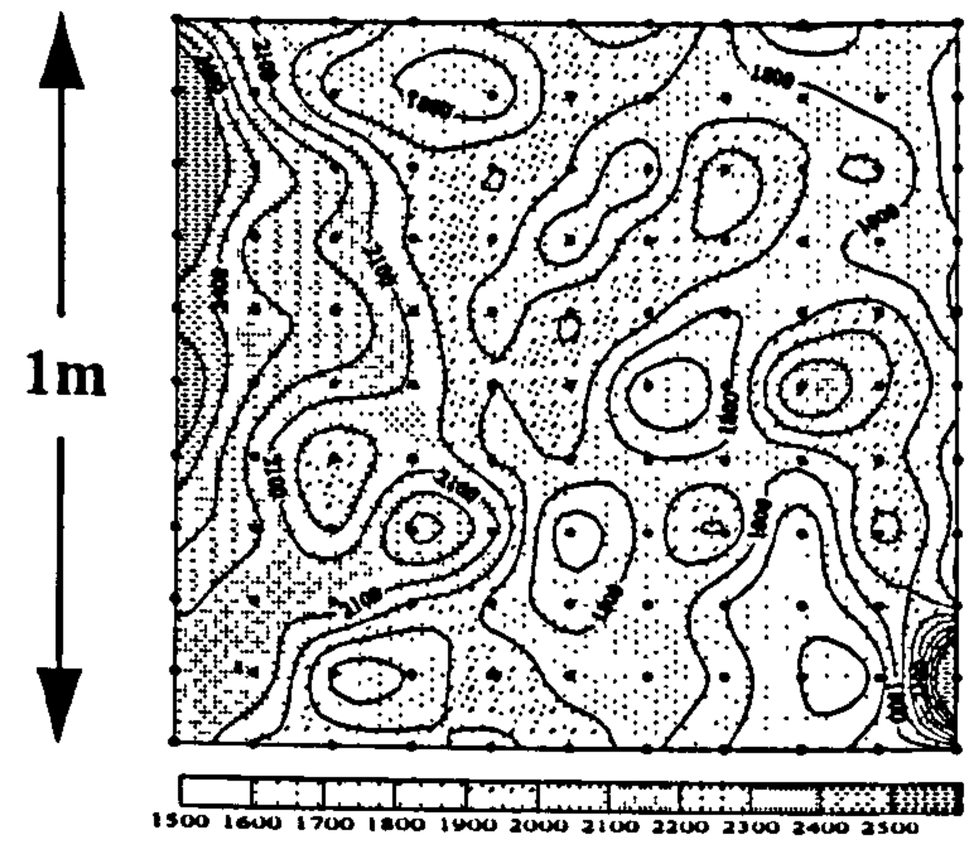


Figure 3.16: A-0.1m-ii

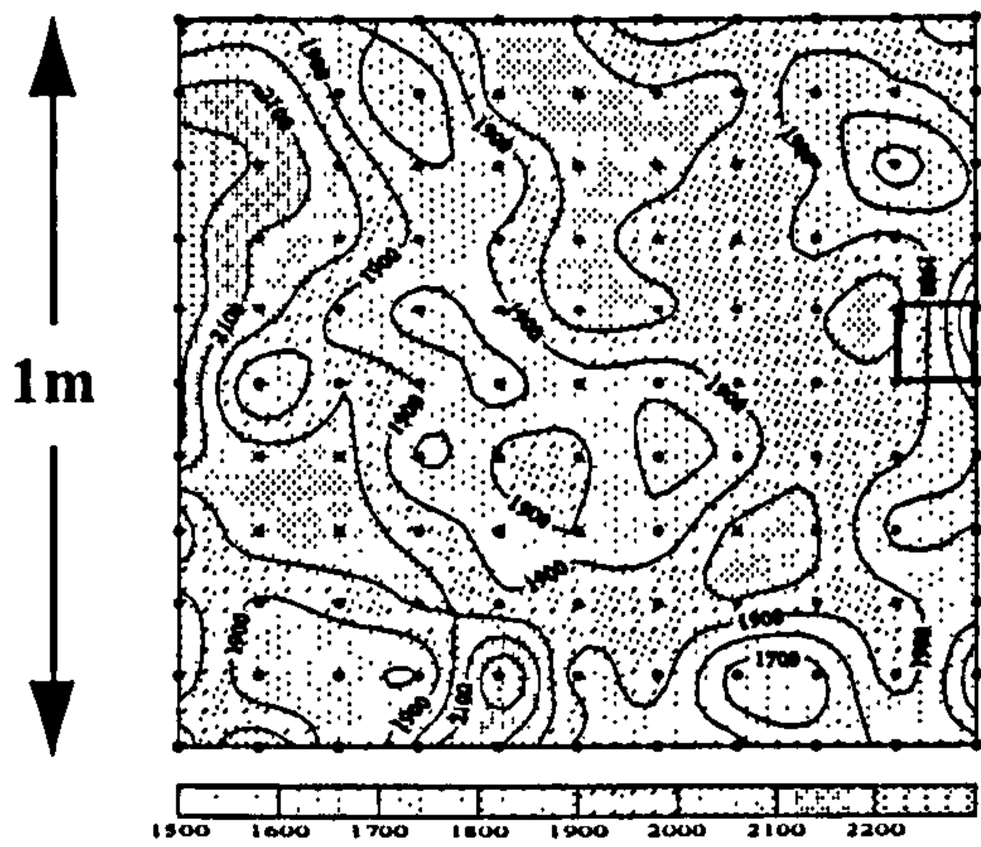
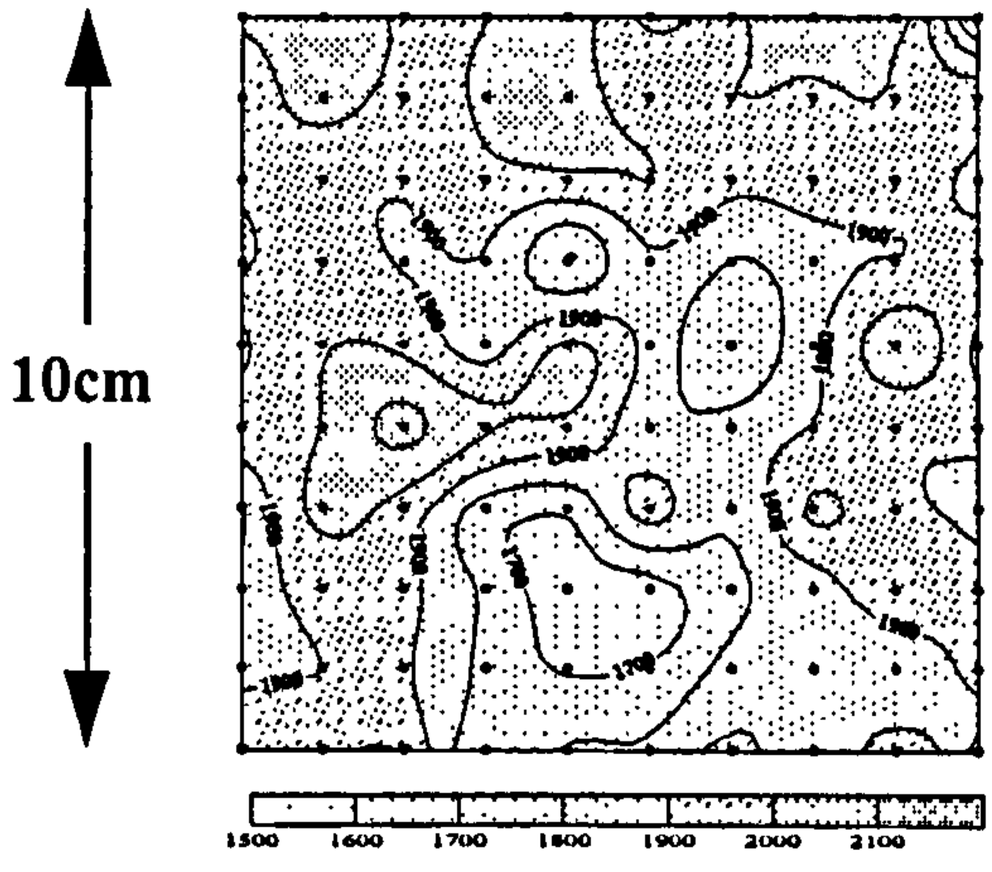


Figure 3.17: A-0.01m

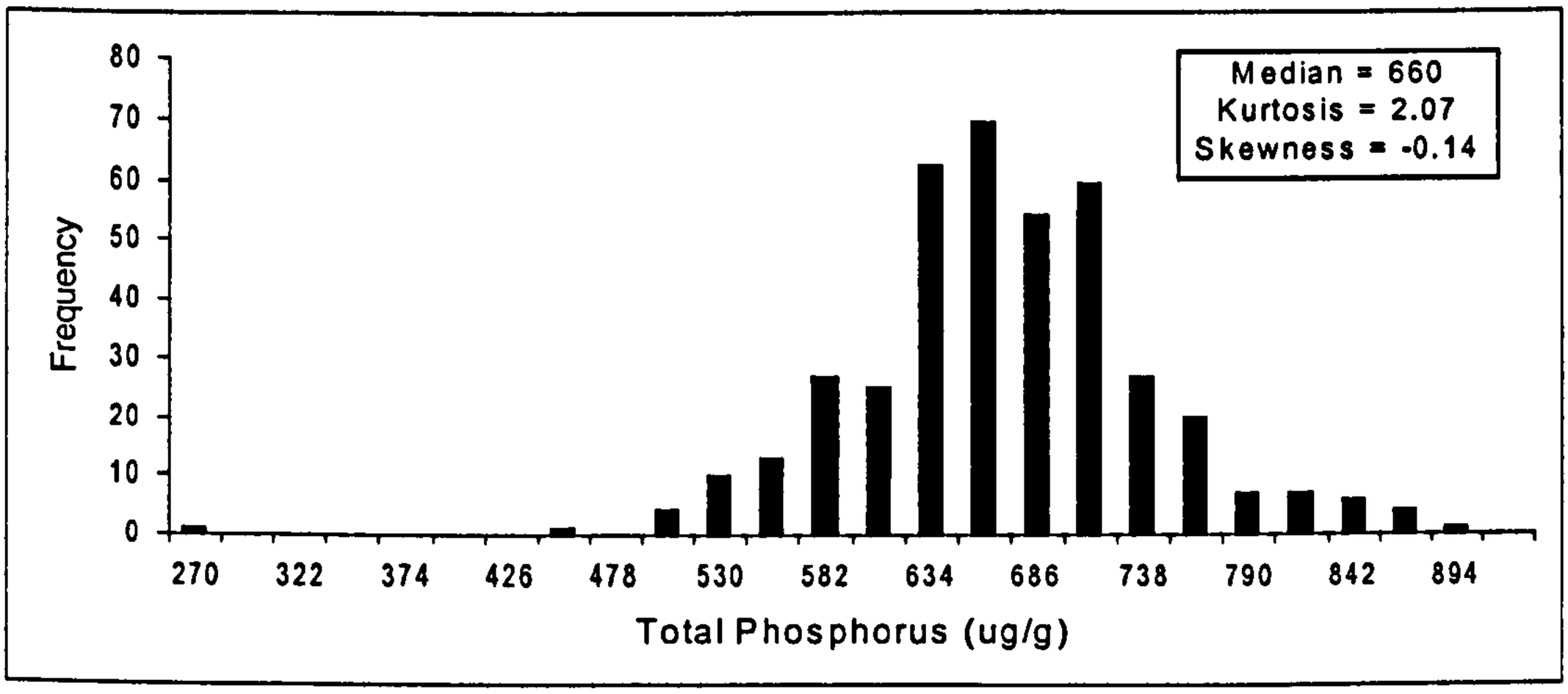


apparent on the more coarse scale distribution map A-1m, demonstrating how potential features are easily missed at a coarse sampling resolution. There are several interpolation methods which can smooth out single points like this, but from an archaeological perspective it is important that these points remain because they could indicate potential features.

The A-0.1m-ii map displays a more random P_{tot} distribution, with no dominating feature and no pattern. Similarly the A-0.01m map displays a random P_{tot} distribution, although it is less variable than the larger grid sampling intervals. Its location on A-0.1m-ii shows a banded distribution pattern which is not apparent at a greater resolution of sampling. The distribution of P_{tot} over a high resolution sampling grid will often bear little or no resemblance to its interpolated distribution from a coarser sampling grid.

3.6.5.2 *Variation within site B*

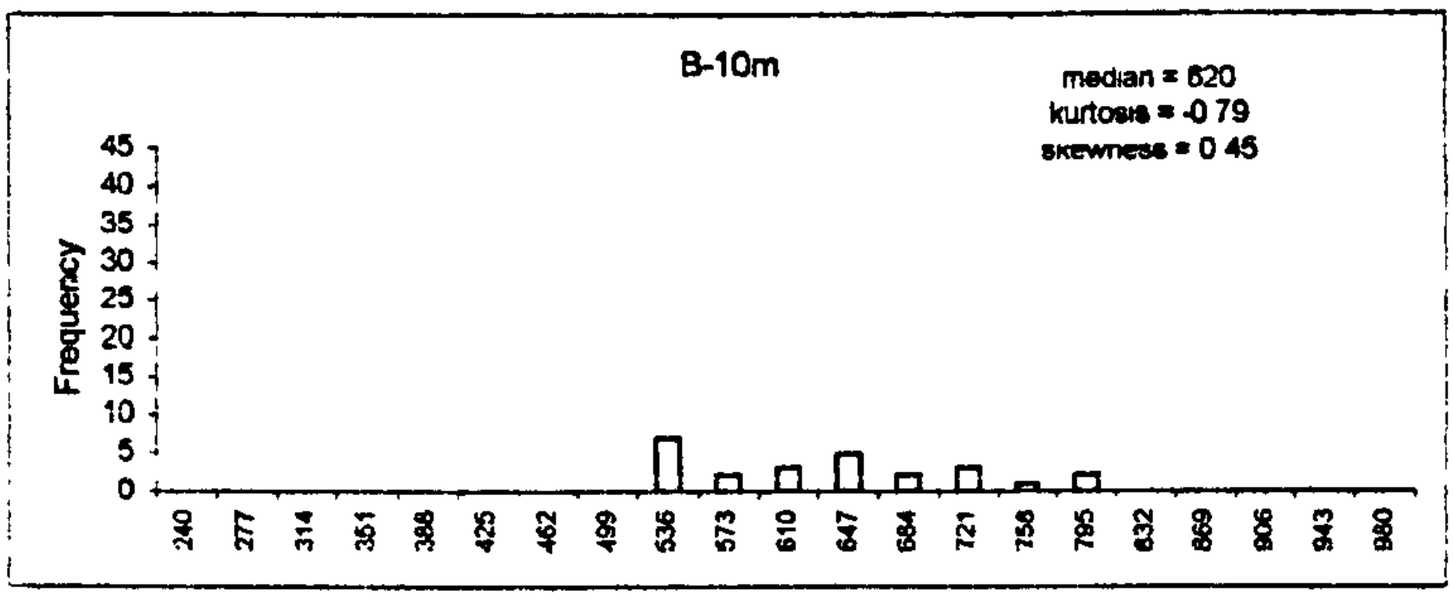
Figure 3.18: Distribution of site B field data down to a 10cm sampling grid (n=397)

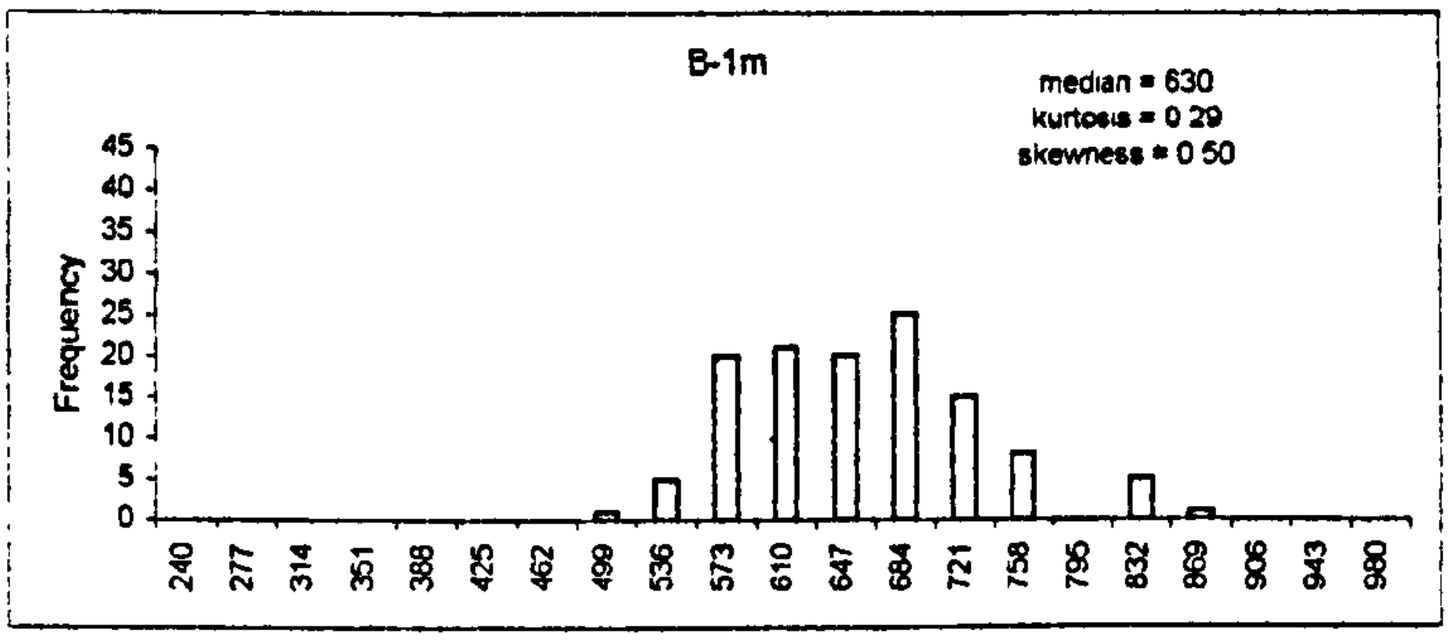


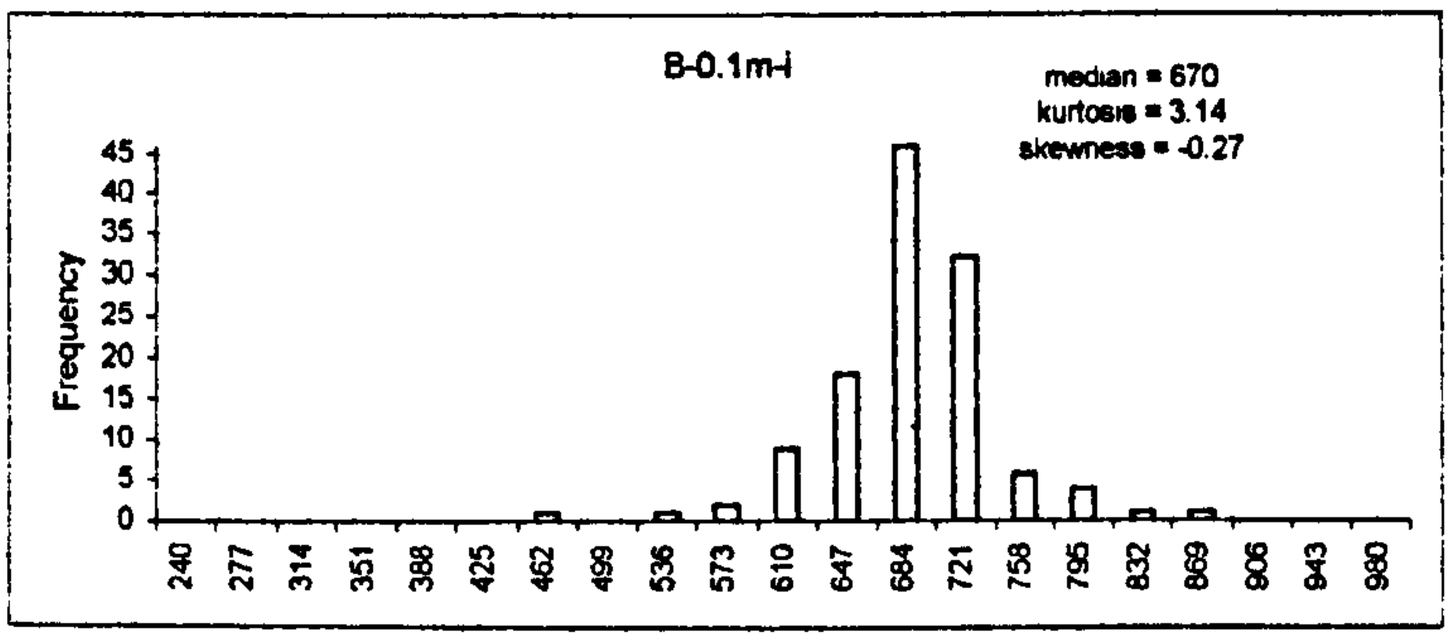
The histogram calculated for all the field data from site B reveals a single relatively low value and a peaked (kurtosis = 2.07) data distribution. If this single outlier were removed the histogram would appear much more normally distributed. P_{tot} values range from 270 - 890μg g^{-1}, but 94% of the values are between 513 - 805μg g^{-1} (2×sd) and 75% of the values are between 586 - 732μg g^{-1} (1×sd). These ranges and the data distribution are similar to those for site A.

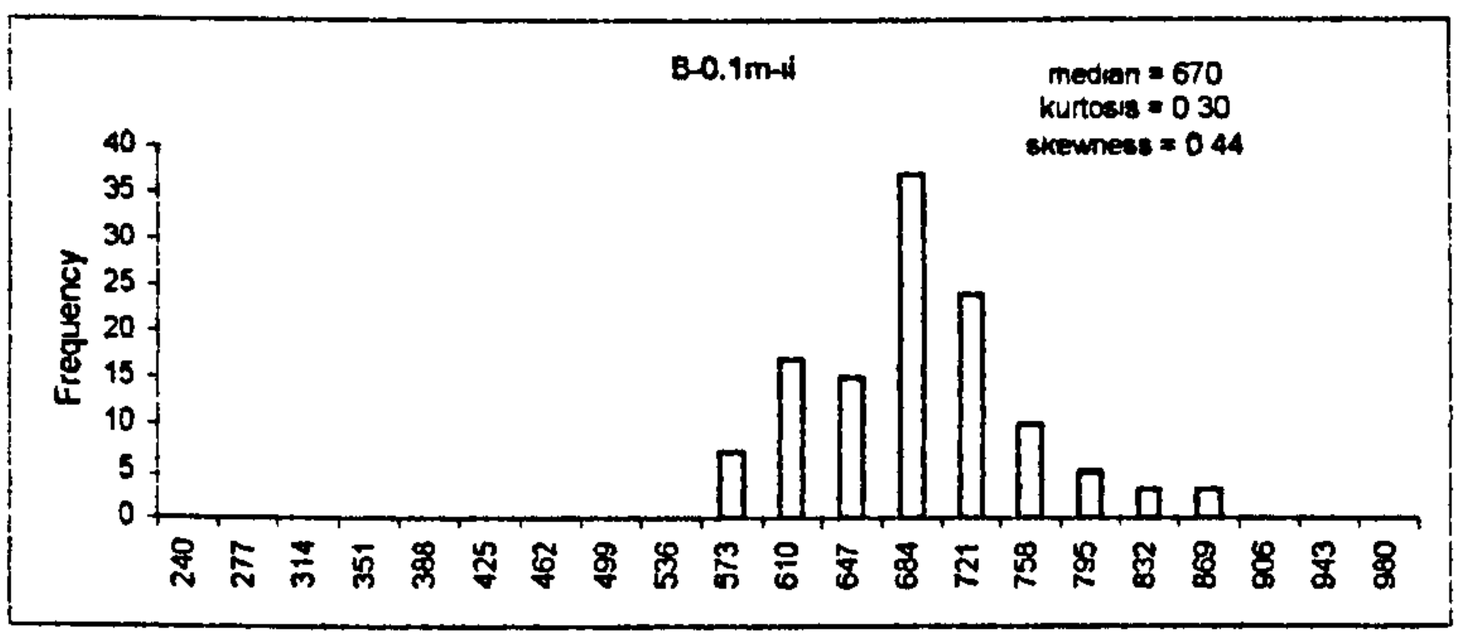
Histograms are plotted for all the sampling grids in figure 3.19. B-0.01m displays the greatest spread of P_{tot} concentrations, with a peaked distribution, which is the

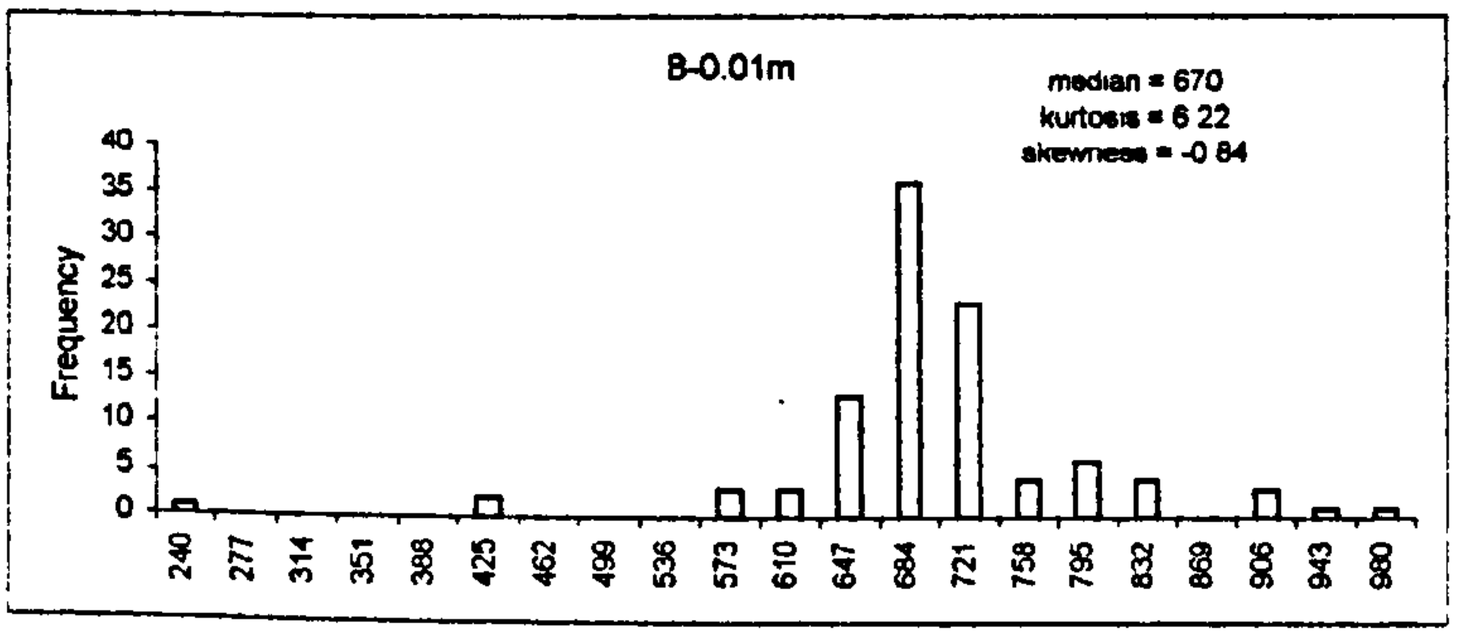
Figure 3.19: Histograms of Ptot values (ug/g) for all Site B sampling grids











result of three low values. The set of histograms show that a large proportion of all the samples from all the sampling grids have similar P_{tot} contents and the B-0.1m-i, B-0.1m-ii and B-0.01m sampling intervals have the same median value (670µg g^{-1}).

To describe the data and assess its variation, statistics are listed in table 3.7, and plotted for increasing grid size in figure 3.20.

Table 3.7: Descriptive statistics for the field data from Site B (µg g^{-1})

	100m	10m	1m	0.1m-i	0.1m-ii	0.01m
Mean	732	615	639	669	672	683
Std. error	64	18	7	5	6	9
Std..Dev.	192	91	72	53	64	94
Sample var.	36994	8251	5184	2849	4119	8781
Range	620	290	350	410	310	720
Min. - Max.	270 - 890	500 - 790	490 - 840	450 - 860	550 - 860	240 - 960
Count	9	25	121	121	121	100
CV (%)	26.2	14.8	11.3	7.9	9.5	13.8

The mean P_{tot} values over all the grid sizes do not vary greatly (615-732µg g^{-1}). Two from a total 497 samples measured from this site are very low (240 & 270µg g^{-1}), one collected from the 100m interval sampling grid and the other from the 0.01m interval sampling grid. The measures of variation plotted in figure 3.20 all generally decline with decreasing grid size to 0.1m. However, from 0.1m to 0.01m there is an increase in standard deviation (sd); variance (V) and coefficient of variation (CV), so there appears to be a greater variation in P_{tot} values over the smallest grid sampling interval. These are not strictly statistically comparable due to the differences in sampling methods used. The two 1m grid sampling intervals display very similar values for sd; IqR; V and CV.

Interpolated maps for sampling grids 10m, 1m, 0.1m-i, 0.1m-ii & 0.01m are produced in figures 3.21- 3.25, and indicate the sampling points over each square and the location of any further sampling grids within them. In general, all the maps show a random distribution of P_{tot} values, though there is perhaps a band of high values running across the slope across the B-1m grid. Such banding could for example be attributed to the increased dunging along a previously used sheep track; however, there was no visible evidence of any track running across the square, either in erosion or vegetation features. The track would not be connecting

Figure 3.20: Variation in P_{tot} at site B Bryn Hall

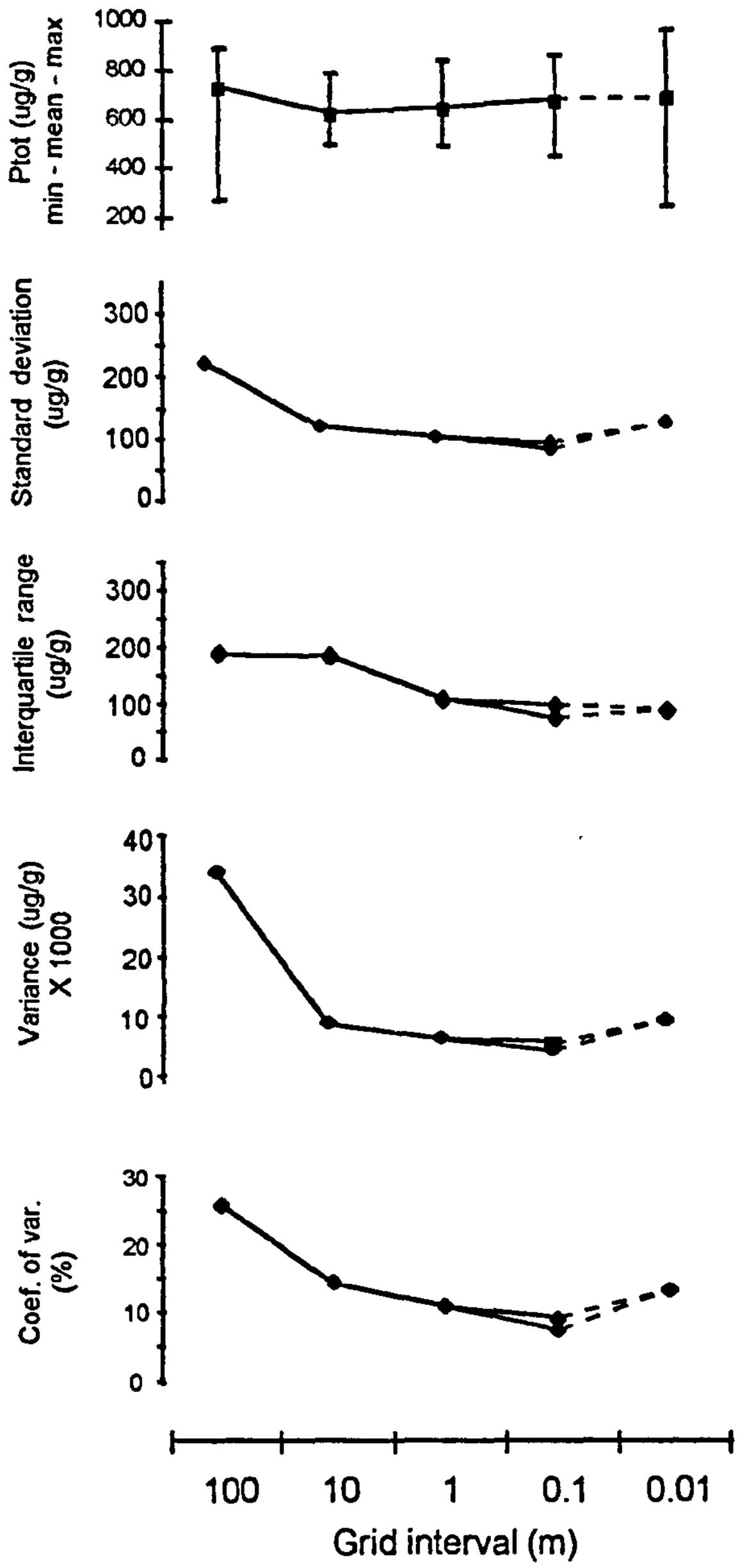


Figure 3.21: B-10m

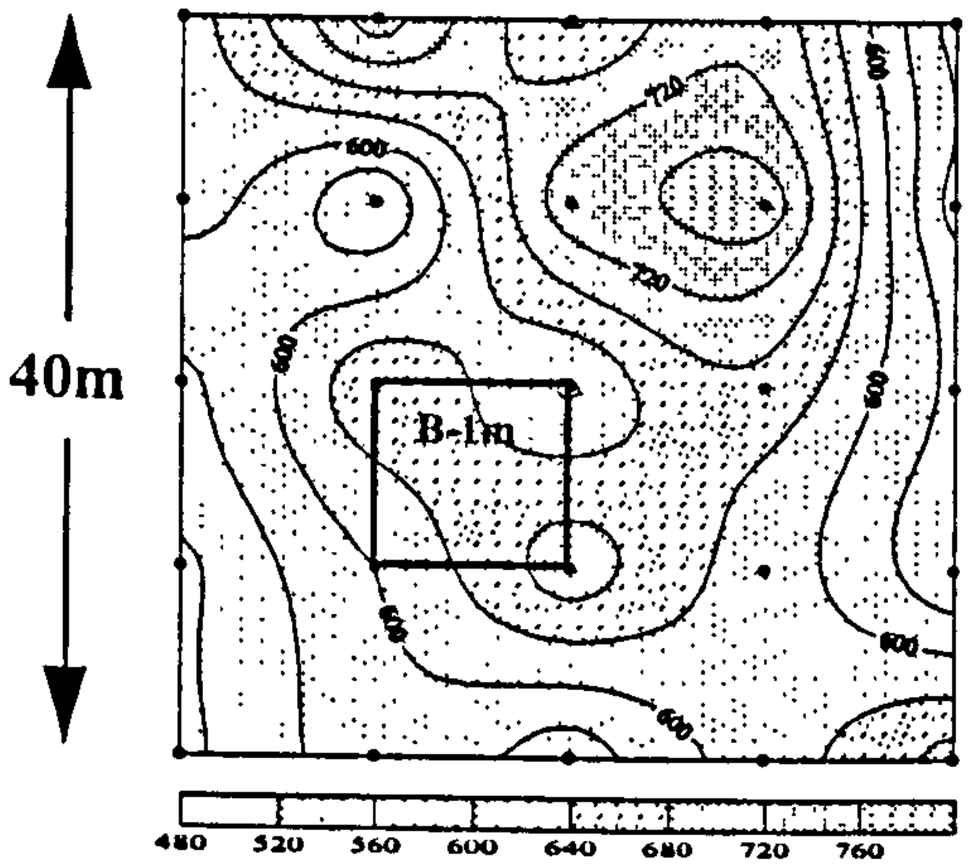
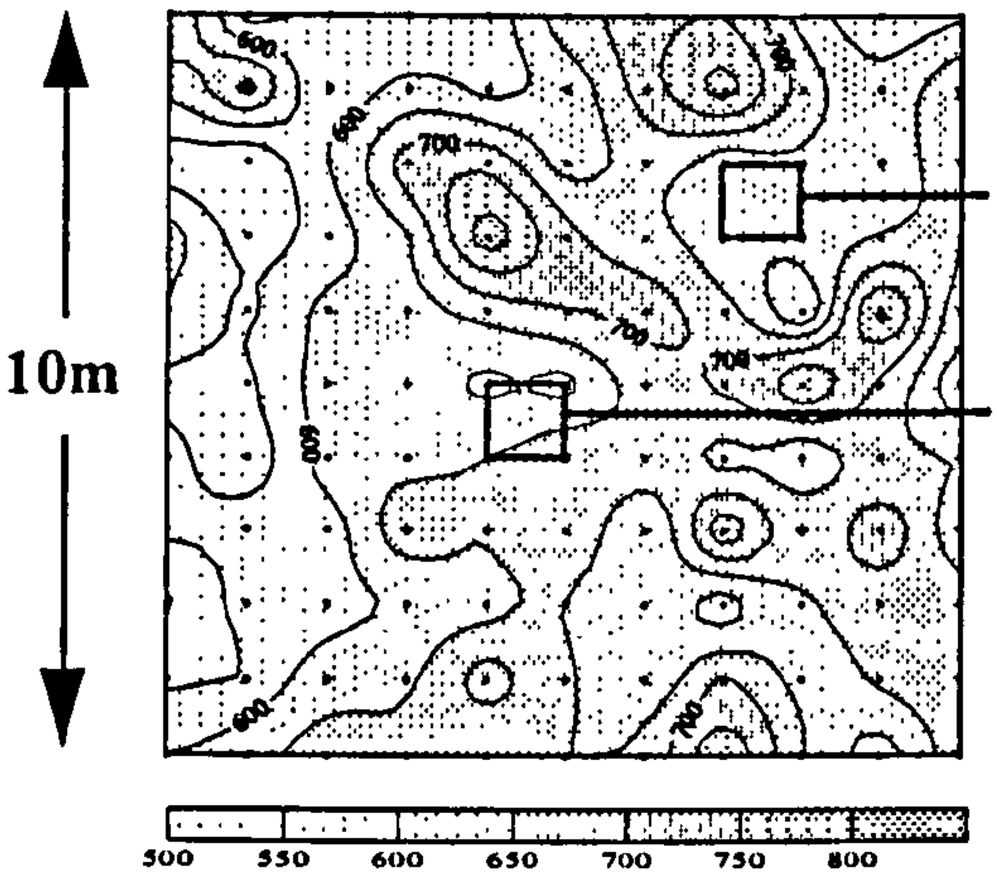


Figure 3.22: B-1m



N

Figure 3.23: B-0.1m-i

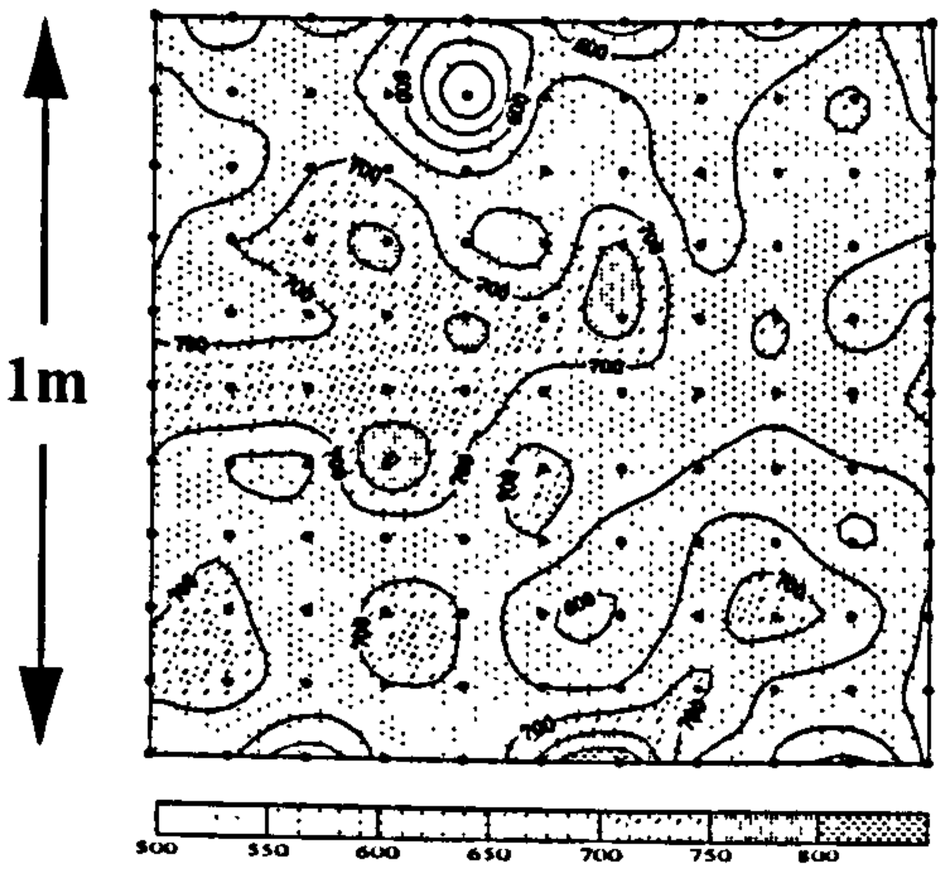


Figure 3.24: B-0.1m-ii

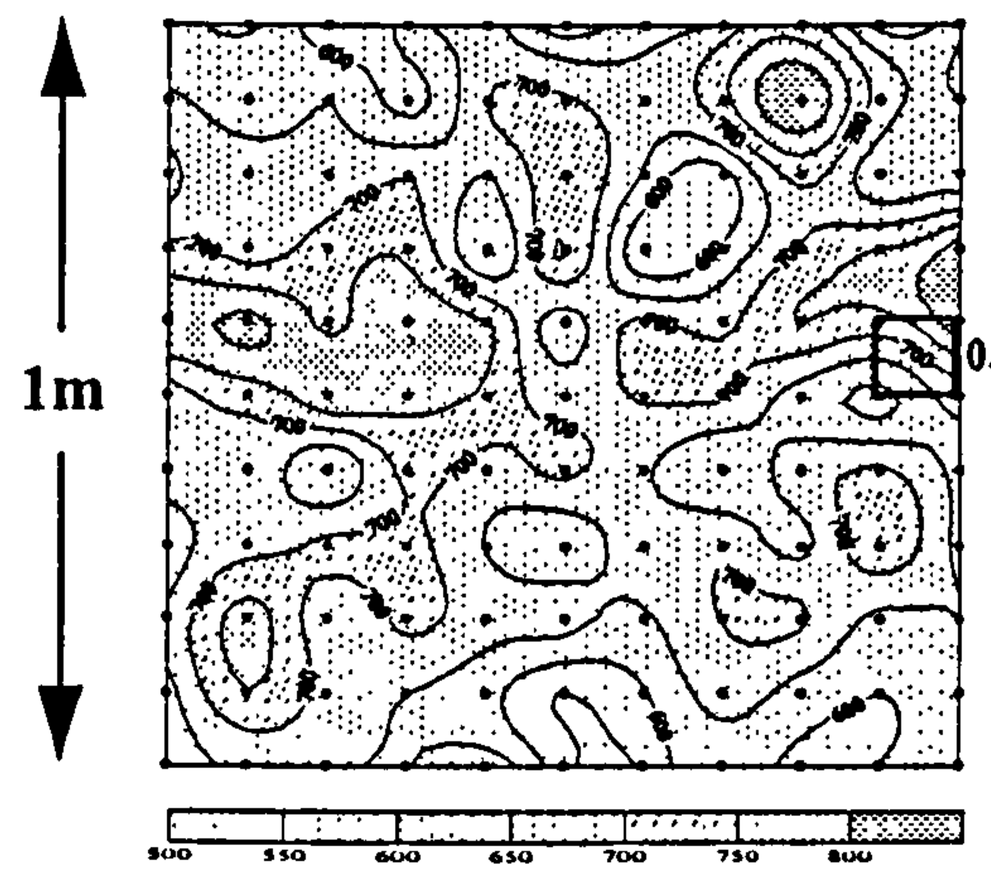
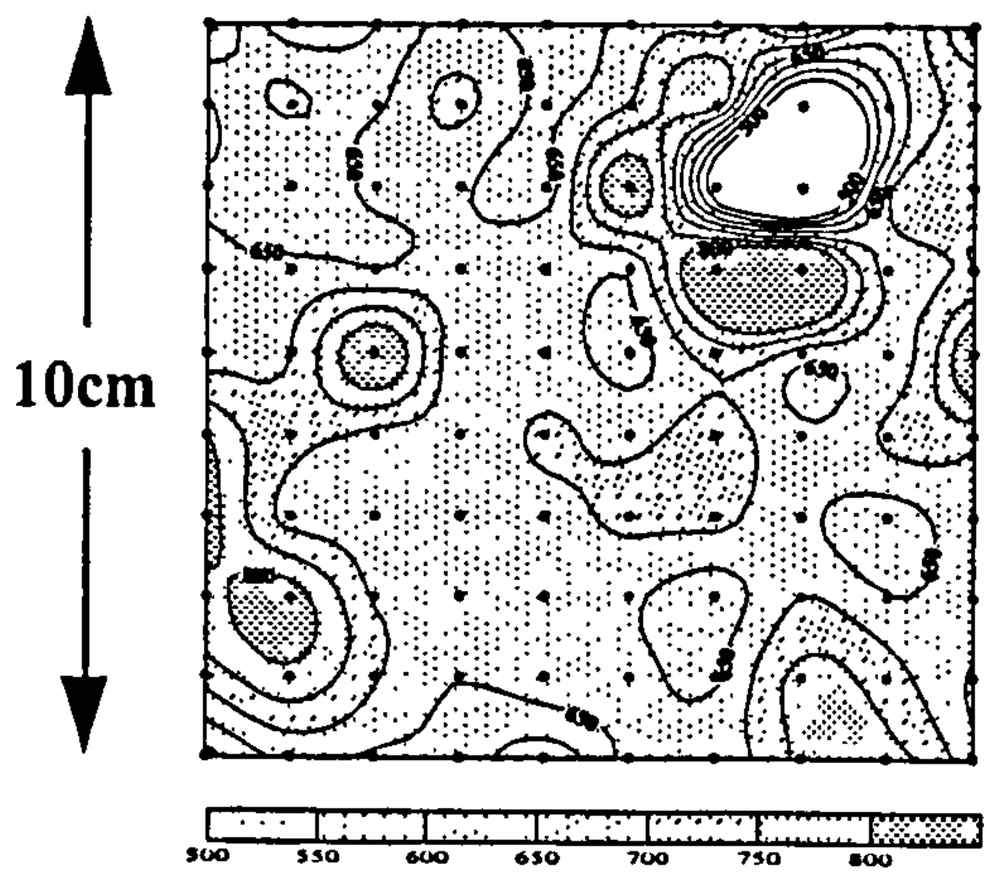


Figure 3.25: B-0.01m



any particular features in the landscape either, so the possibility of a track is unlikely, and there is not a large drop in amounts of P_{tot} to the up-slope side of the track as might be expected. The B-0.1m-i square is located on the B-1m distribution map in an area of uniform P_{tot} levels (600-650μg g^{-1}), however when the resolution of the grid is increased to sampling every 10cm, considerable variation in soil P_{tot} appears (500-800μg g^{-1}). The B-0.01m distribution map is dominated by a low area to the E corner of the square, made up of three sampling points <500μg g^{-1} P_{tot}. This area only represents 1cm×1cm and so the low values could be due to a stony area of the soil containing less P rich components.

3.6.5.3 *Variation within site C*

Two initial histograms have been plotted for the P_{tot} data from site C, because the samples from the 10m & 5m sampling intervals were collected by soil auger to a depth of 10cm, and the samples from the 0.5m & 0.1m sampling intervals were collected by trowel to a depth of 3cm.

Figure 3.26: Distribution of data collected at site C from the 10m & 1m grids

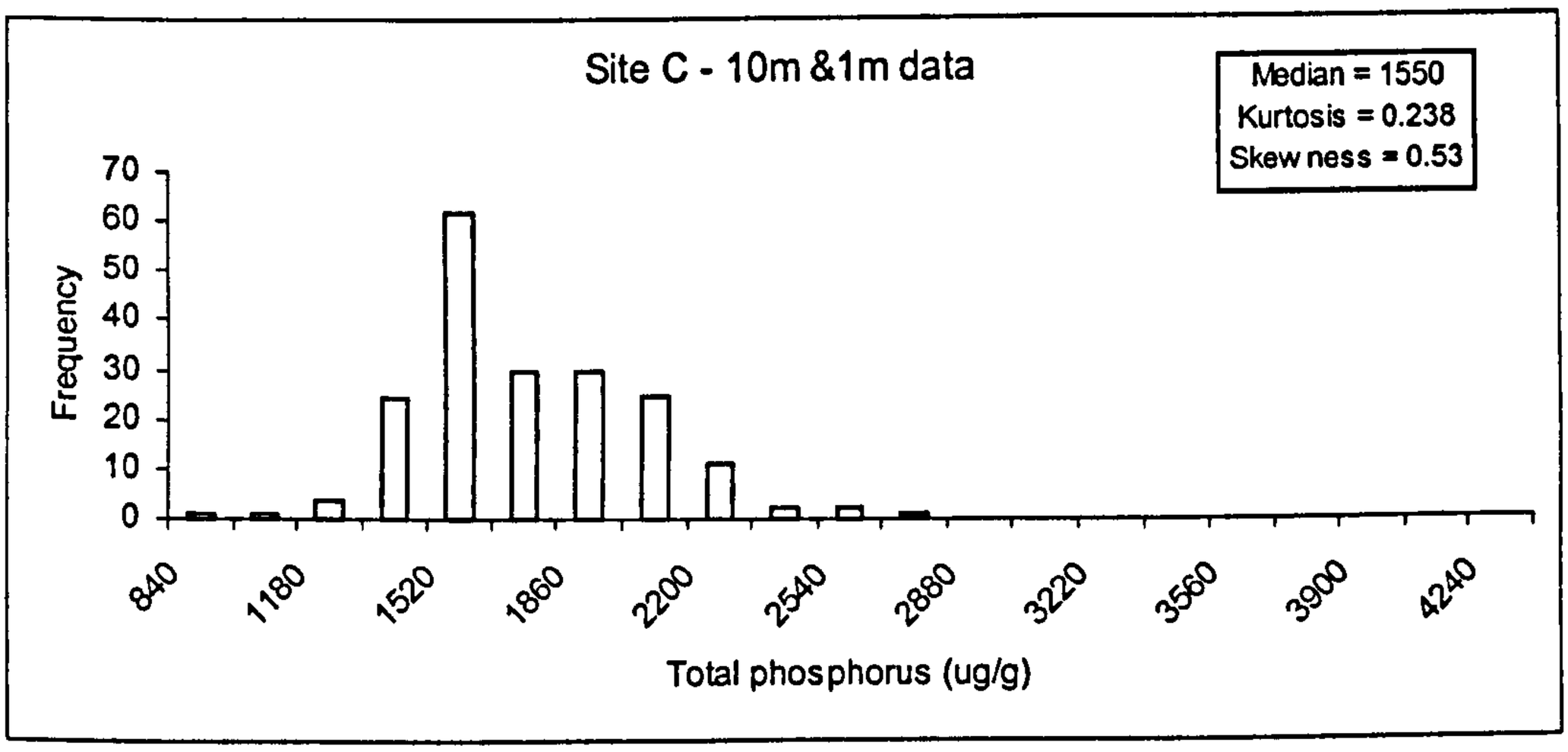
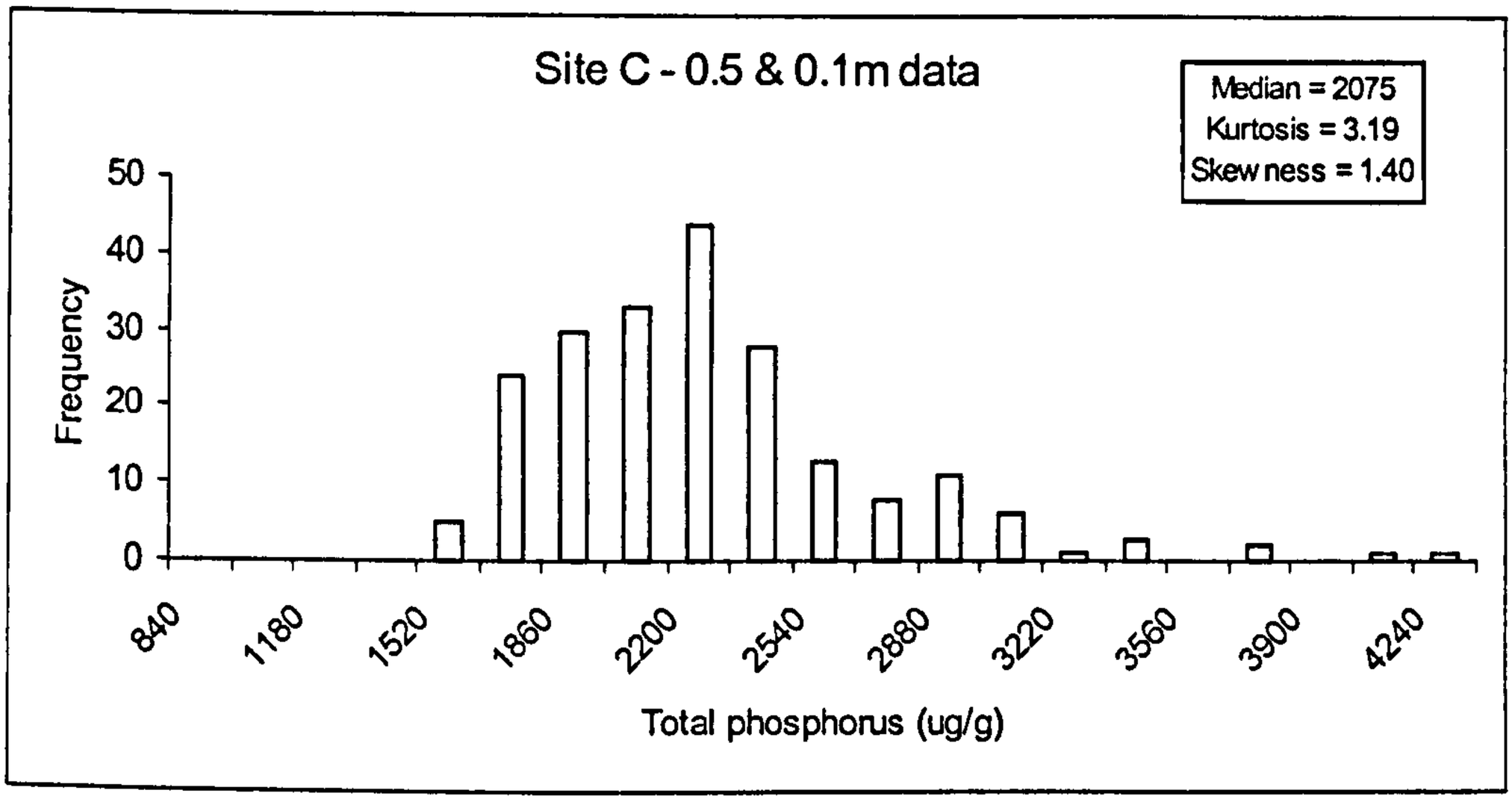


Figure 3.27: Distribution of data collected at site C from the 0.5m & 0.1m grids

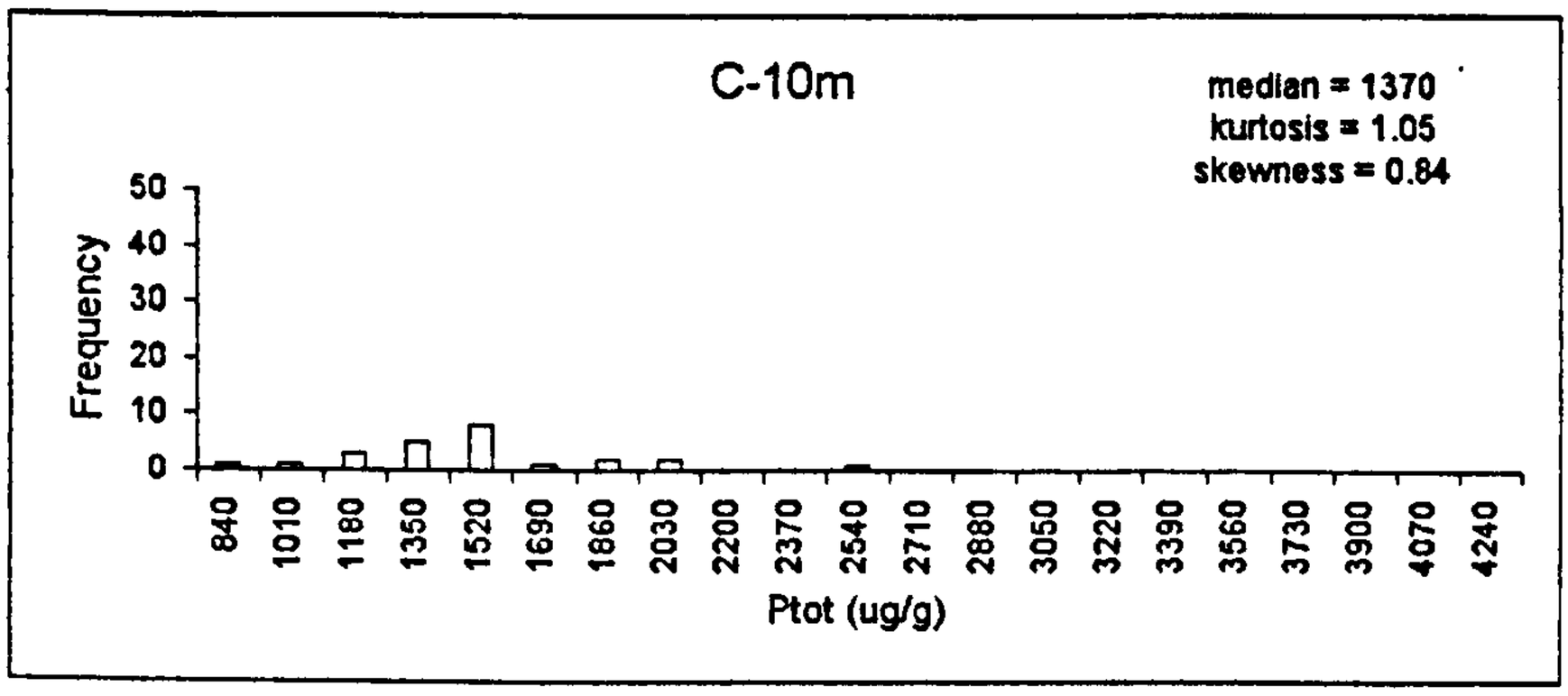


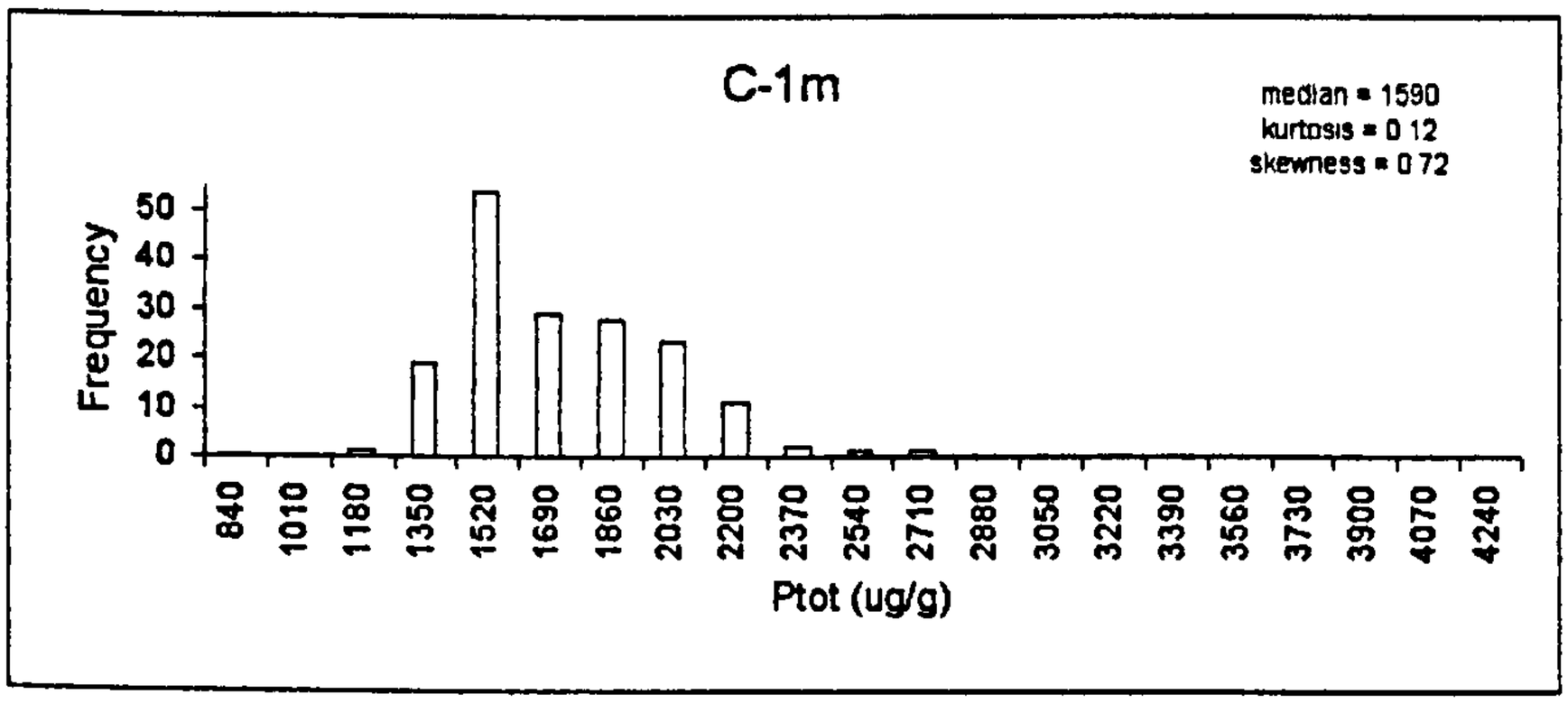
Both histograms show a degree of positive skewness (0.53 & 1.4), which indicates that there are a number of samples with much larger P_{tot} values than the majority of the data. This sort of distribution can be an indicator that there has been some influence on the site to increase P_{tot} levels in the soil, which could be historic/archaeological, agricultural or artificial. The median for the 0.5m & 0.1m data (2075) is greater than the 10m & 1m data (1550) indicating the higher P_{tot} values measured over the 0.5m & 0.1m grids.

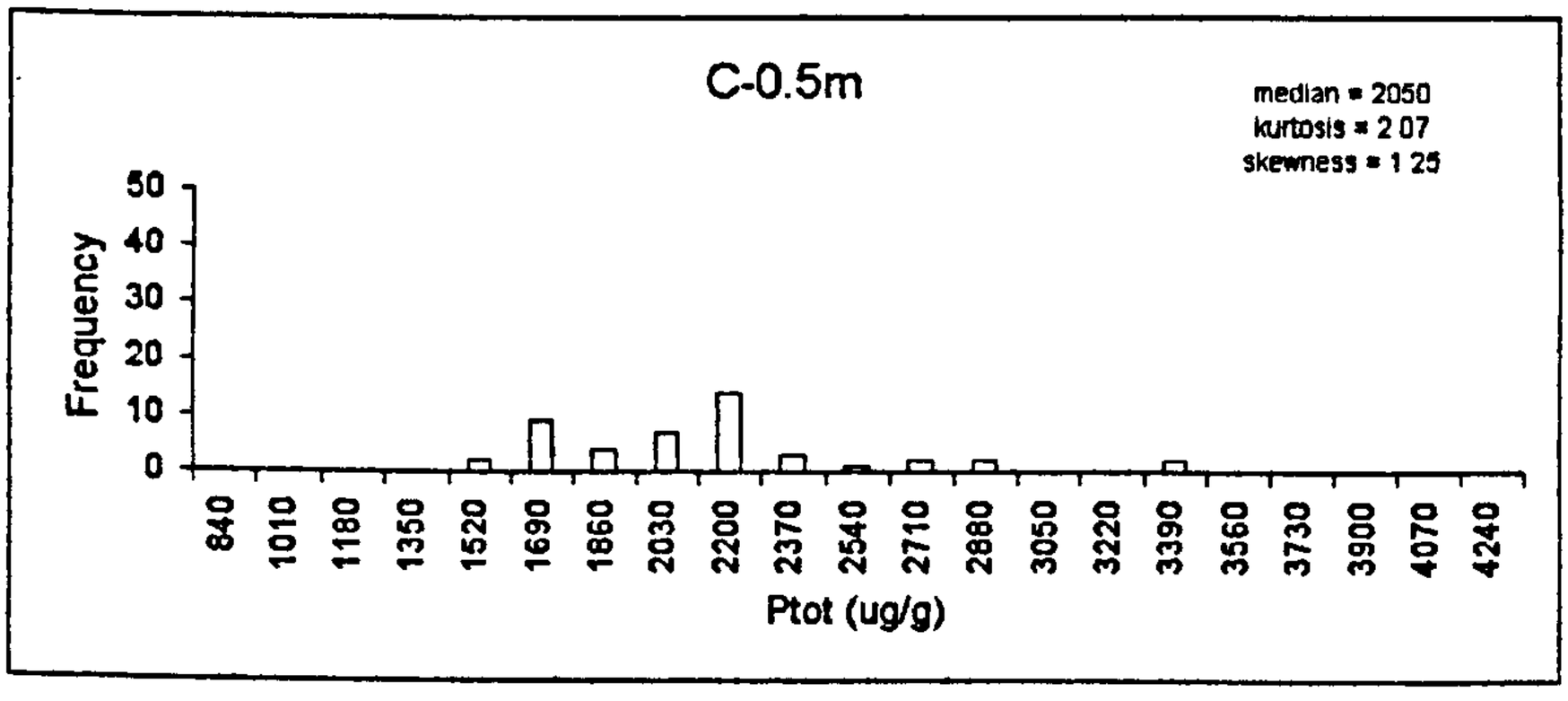
Histograms for each sampling interval grid are plotted in figure 3.28. The four data sets show distributions which are all positively skewed (skewness = 0.84, 0.72, 1.25 & 1.43), which could be indicative of a number of samples collected from enhanced archaeological contexts within the sampling areas, and thus having elevated P_{tot} levels. The histogram for C-0.1m data shows the largest spread of data, and as the sampling interval decreases, the median value increases (1370 - 1590 - 2050 - 2110). The 0.5m and 0.1m histograms show small separate populations of high values associated with the anomalous results, and as all site C sampling grids are located on or close to a medieval long-hut, the high values could be locating hearths, middens or other archaeological features with elevated P_{tot} levels.

To describe the data and assess their variation, statistics are listed in table 3.8 and

Figure 3.28: Histograms for all Site C sample grids







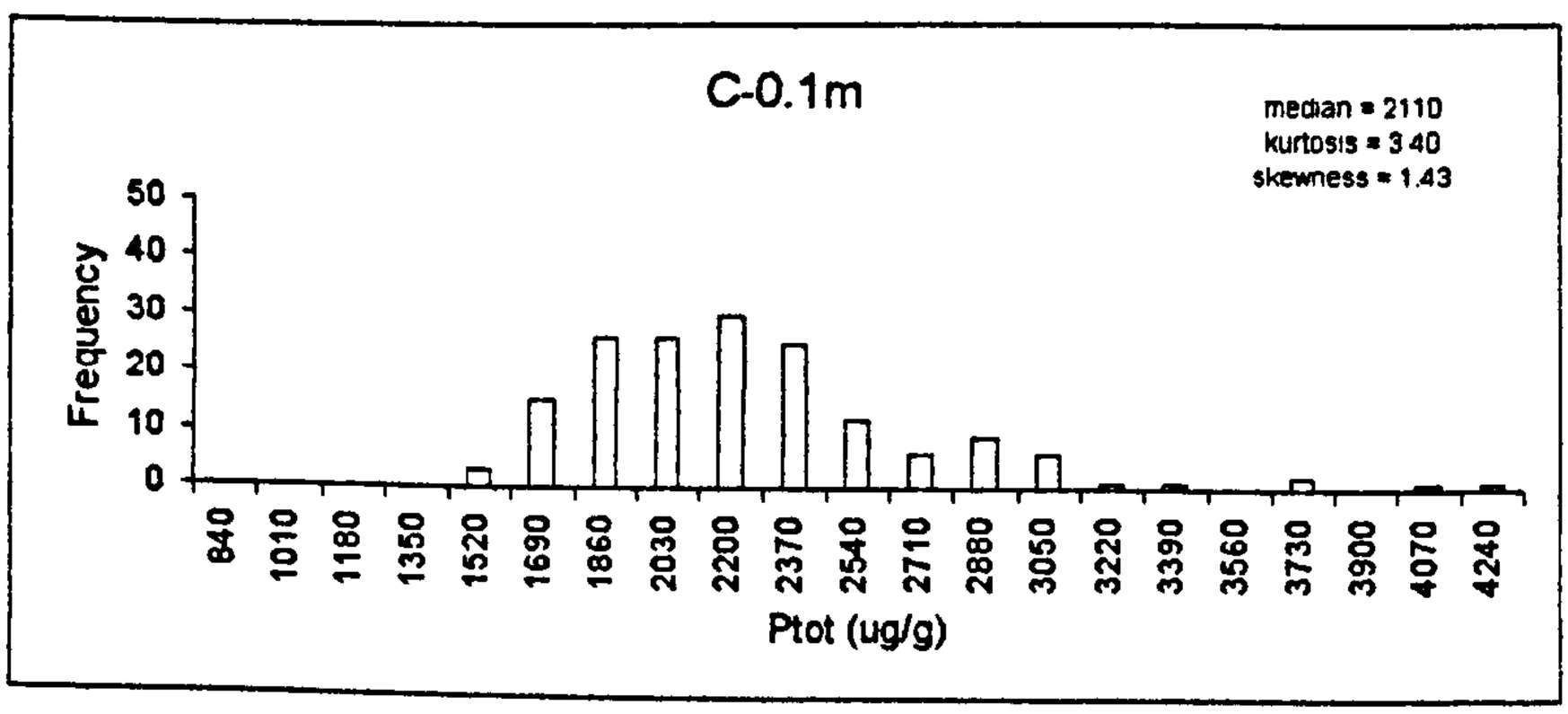
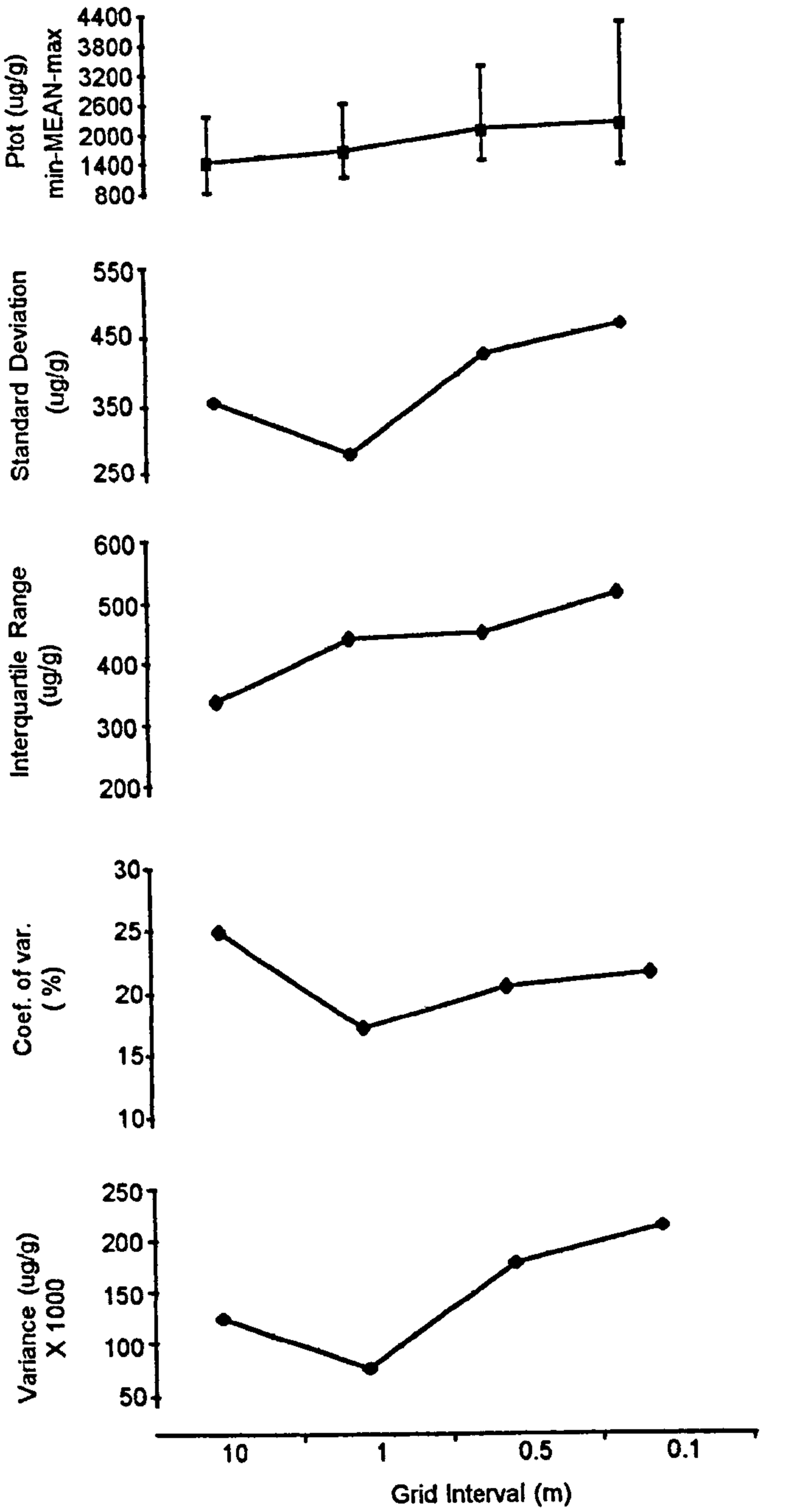


Figure 3.29: Variation in P_{tot} at site C Garnodolbenmaen



plotted for decreasing grid size in figure 3.29.

Table 3.8: Descriptive statistics for all Site C data (μg g^{-1})

	10m	1m	0.5m	0.1m
Mean	1429	1642	2067	2171
Std. error	73	21	62	36
Std. deviation	355	279	423	465
Sample var.	126203	78025	178808	215887
Range	1540	1490	1900	2860
Min. - Max.	840 - 2380	1140 - 2630	1460 - 3360	1360 - 4220
Count	25	169	46	164
CV. (%)	24.8	17.0	20.5	21.4

The means of each grid size vary much more than at site A and B (1429-2171μg g^{-1}). As the grid size reduces, the mean increases, and the range of the P_{tot} values measured increases because the situating of the smaller grids on the archaeological features has allowed more samples to be collected from actual archaeological anomalies, hence increasing the variation encountered. The sd, IqR & V all increase to a maximum at the smallest sampling interval, suggesting that the variation in P_{tot} values is greater at the smallest interval at this site. This trend is the opposite of what was encountered at site A & B, the two 'background' sites.

Interpolated maps for sampling grids 10m, 1m, 0.5m, 0.1m, are produced in figures 3.30 – 3.33, and indicate the sampling points over each square and the location of any further sampling areas within them. The position of the sampling squares relative to each other are located on the map 3.3. At this site sampling was still carried out on a regular grid but the presence of obstructions (mainly large stones) meant that not all the samples within each grid could be collected. The interpolated distribution map C-10m is dominated by three central high P_{tot} sample points, these having considerably higher P_{tot} amounts than the surrounding samples, producing a distinctive 'bullseye' distribution pattern. At this coarse level of sampling the archaeological site is accurately located as an area 20m×20m to the centre of the whole square, though features smaller than this grid interval are missed. The 1m sampling grid was located to the east of the long-hut because the area showed the remnant of a structure (a possible platform or yard) obscured by ploughing. Any such P anomaly associated with this structure is not apparent at the 10m sampling interval level, although at the 1m interval sampling level areas of raised P levels are

Figure 3.30: Site C - 10m

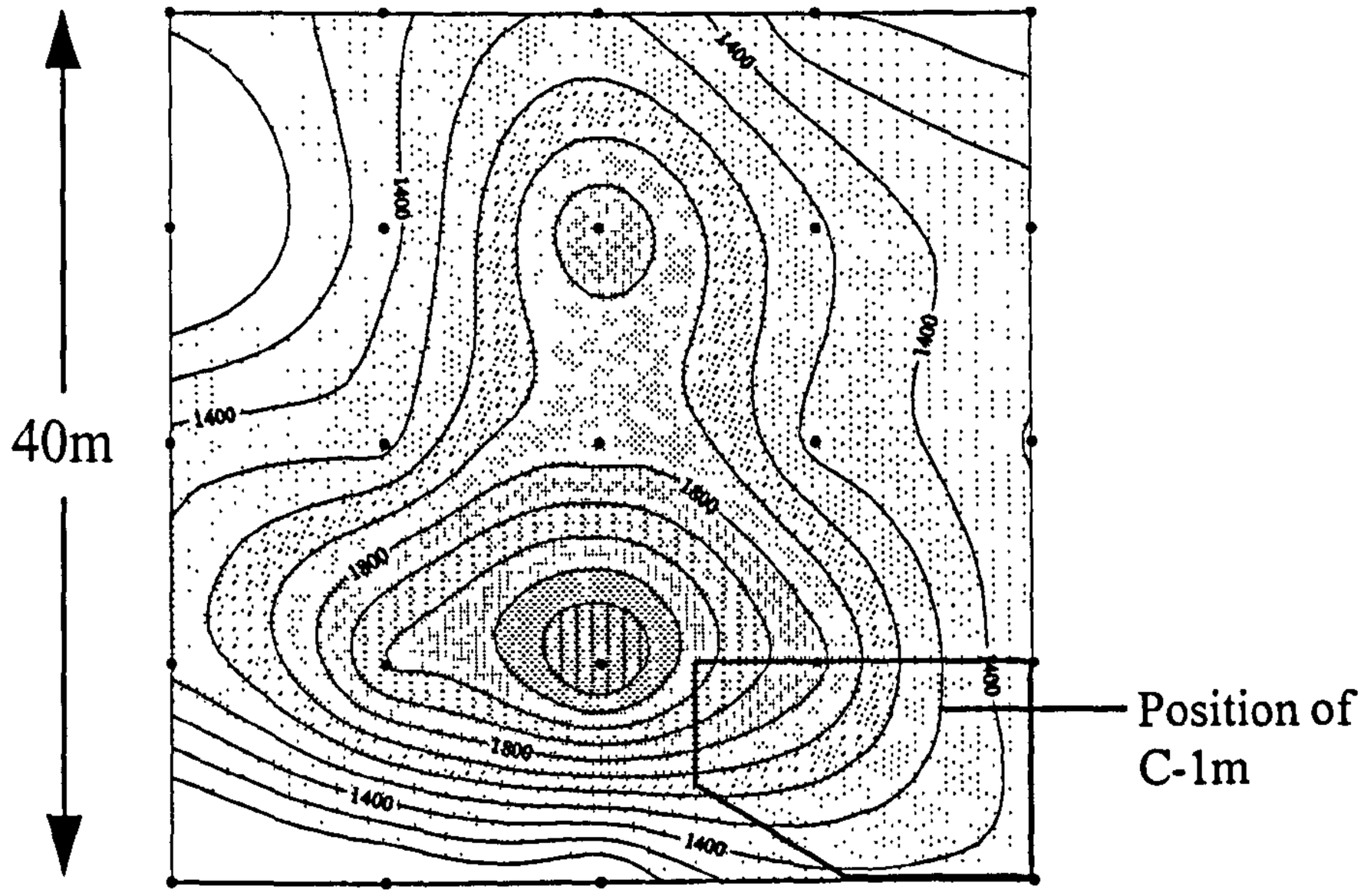


Figure 3.31: Site C - 1m

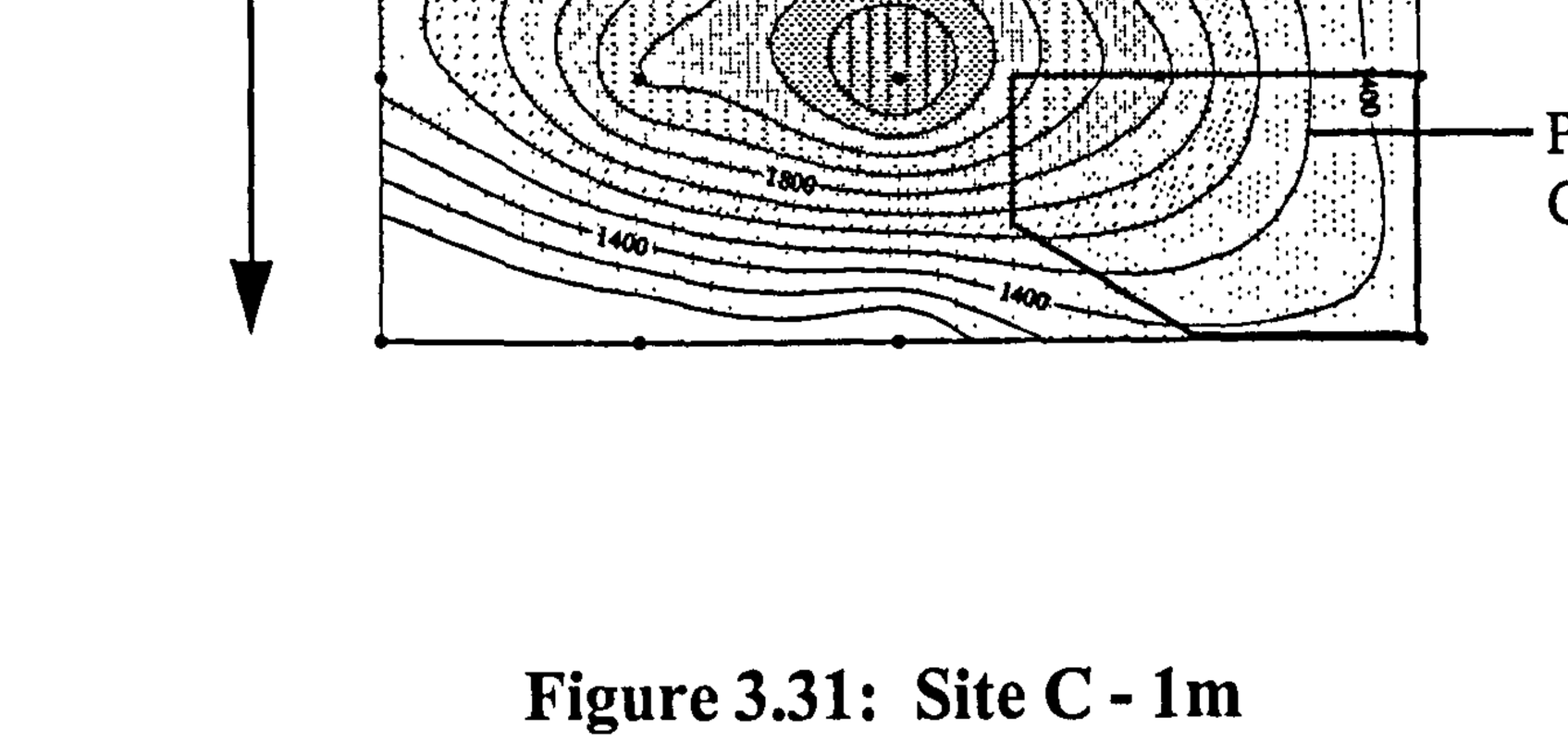


Figure 3.32: Site C - 0.5m

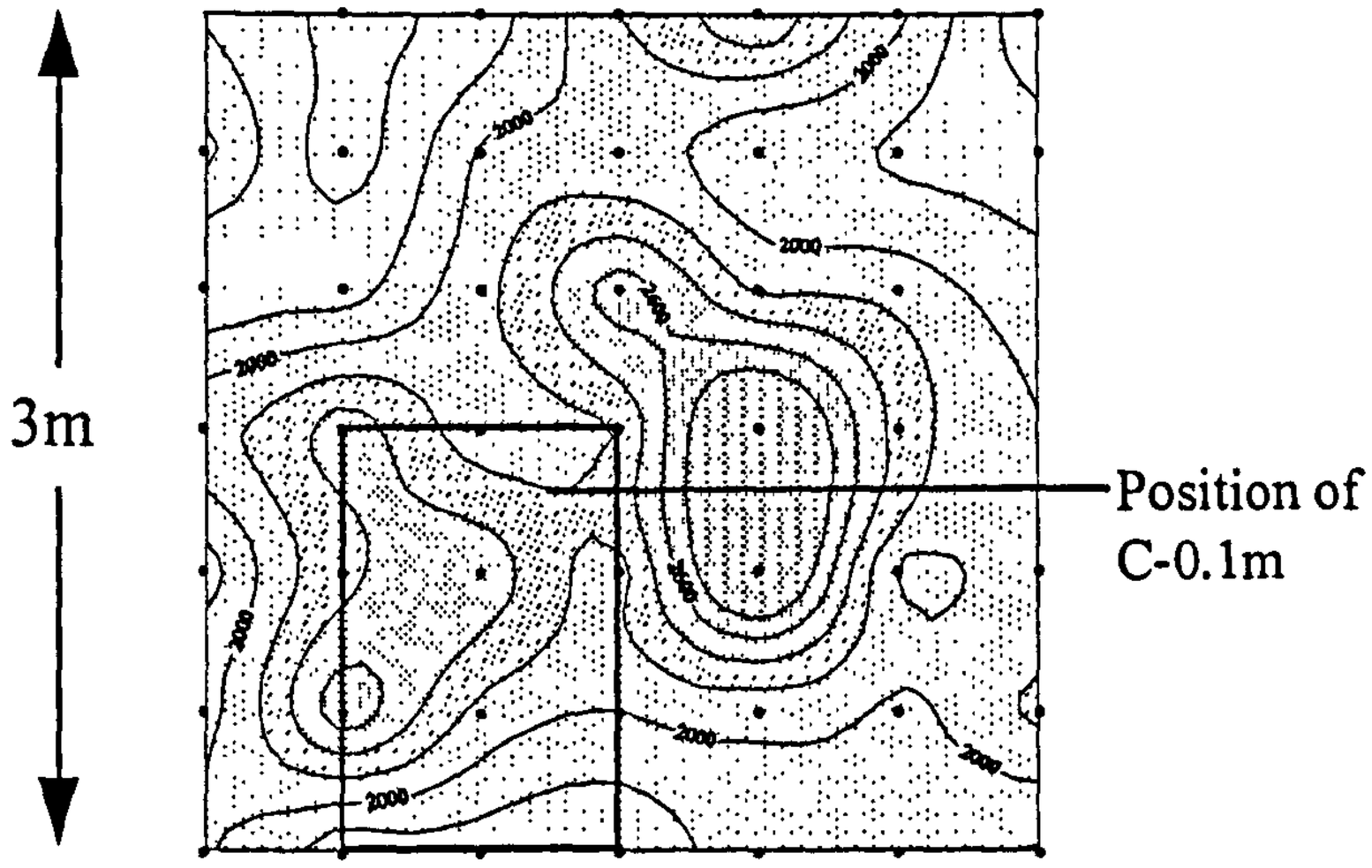
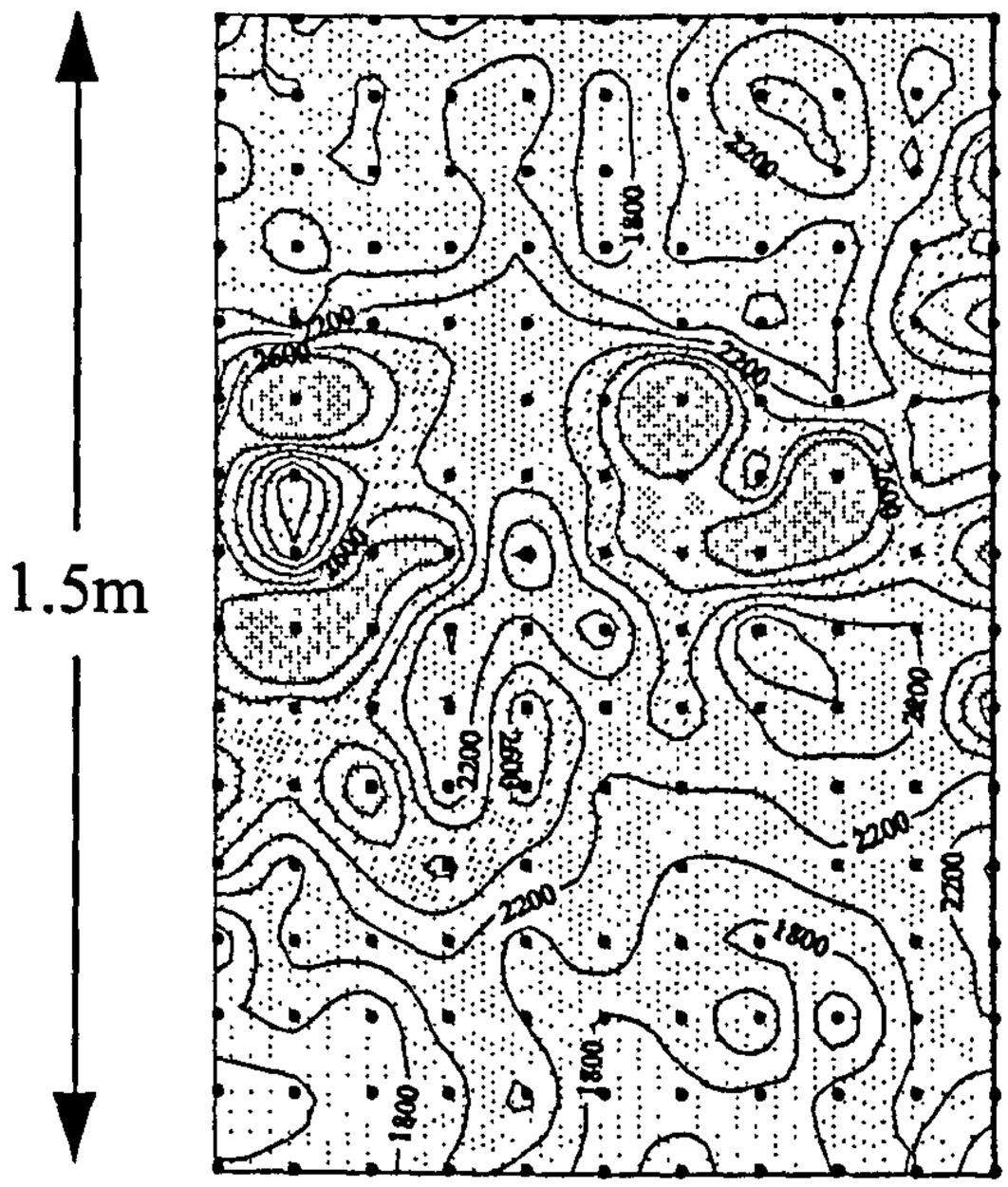


Figure 3.33: Site C - 0.1m

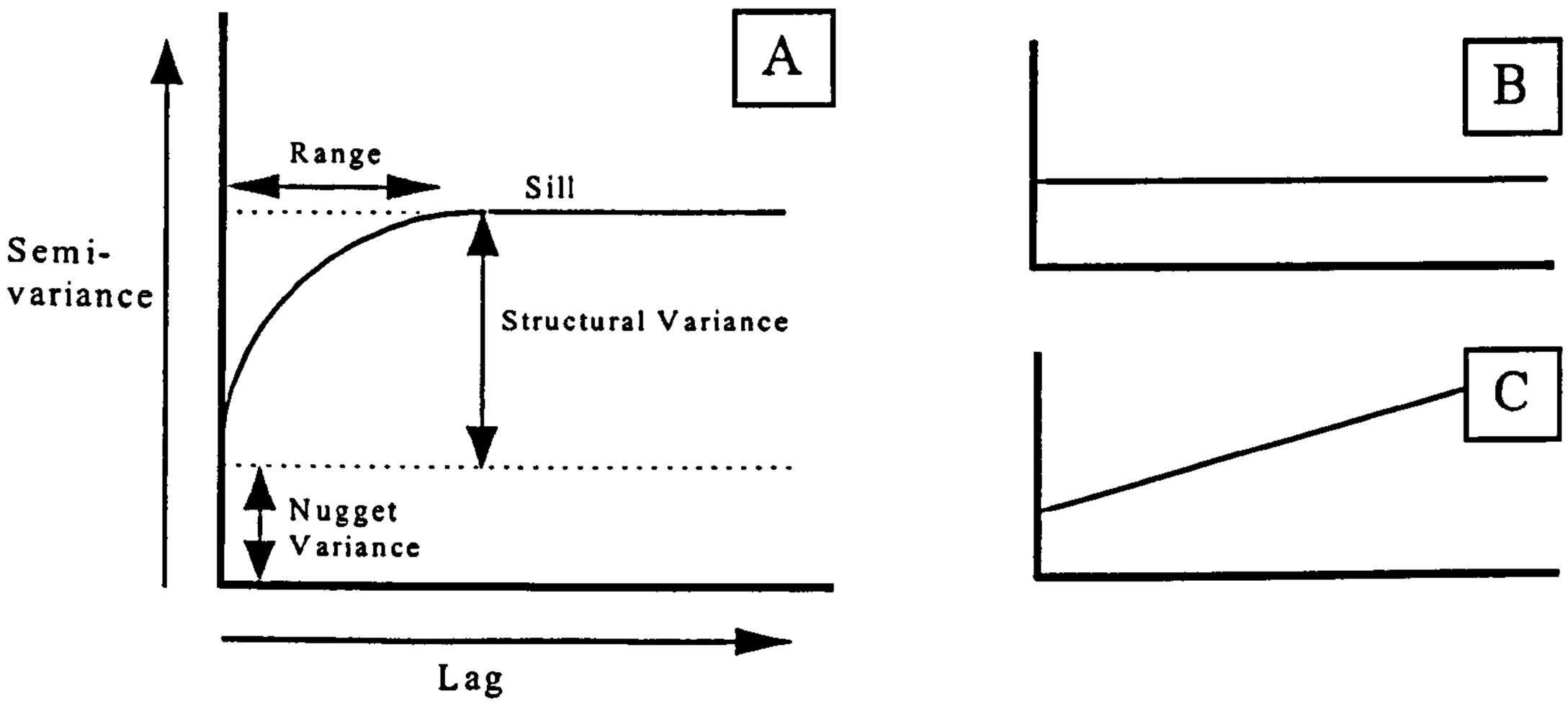


indicated, which have a P_{tot} content of 2600µg g^{-1} (60% greater than the mean). High P_{tot} values are mainly concentrated to the west of the sampled area and correlate reasonably well with the suspected structure. The 1m grid was sampled in this shape because a large wall ran along the southern edge of the feature, veering northwards, and it was decided not to sample to the south of this wall. The 0.5m & 0.1m sampling grids were not located within the 1m sampling area, but actually on the excavated floor of the long-hut, and a number of samples at these levels could not be collected because of its stony nature. The 0.5m distribution map displays an area of elevated P_{tot} levels to the east of centre of the area sampled, defined by three high results. The 0.1m distribution map shows two main areas of elevated P levels within the sampled rectangle. The P_{tot} distribution over figure 3.33 is more detailed than that over the coarser grid, figure 3.32, but the general pattern displayed is similar.

3.6.6 The use of Semi-Variograms to examine variation

The final way in which the variation in P_{tot} within each data set will be examined is with the use of semi-variograms (often called variograms). Variograms are models used to summarise the variation of a property within a region (Webster & Oliver, 1990) and enable spatial trends to be identified. The variogram is the central component in any geostatistical analysis working on the assumption that while most soil properties vary continuously in space, the values at sites close together are more similar than those further apart. They are not independent of one another and the data is therefore spatially dependent. Variograms are plots of the change in variance between sampling points at different distances apart (the distance between two sample points is called the "lag"). The properties commonly described from variograms include; the "range"; the "sill"; the "structural variance" and the "nugget variance". These are identified on the theoretical variogram below (figure 3.34), and are discussed in a number of textbooks with chapters on spatial data analysis (*e.g.* Bailey & Gatrell, 1995).

Figure 3.34: Theoretical variograms



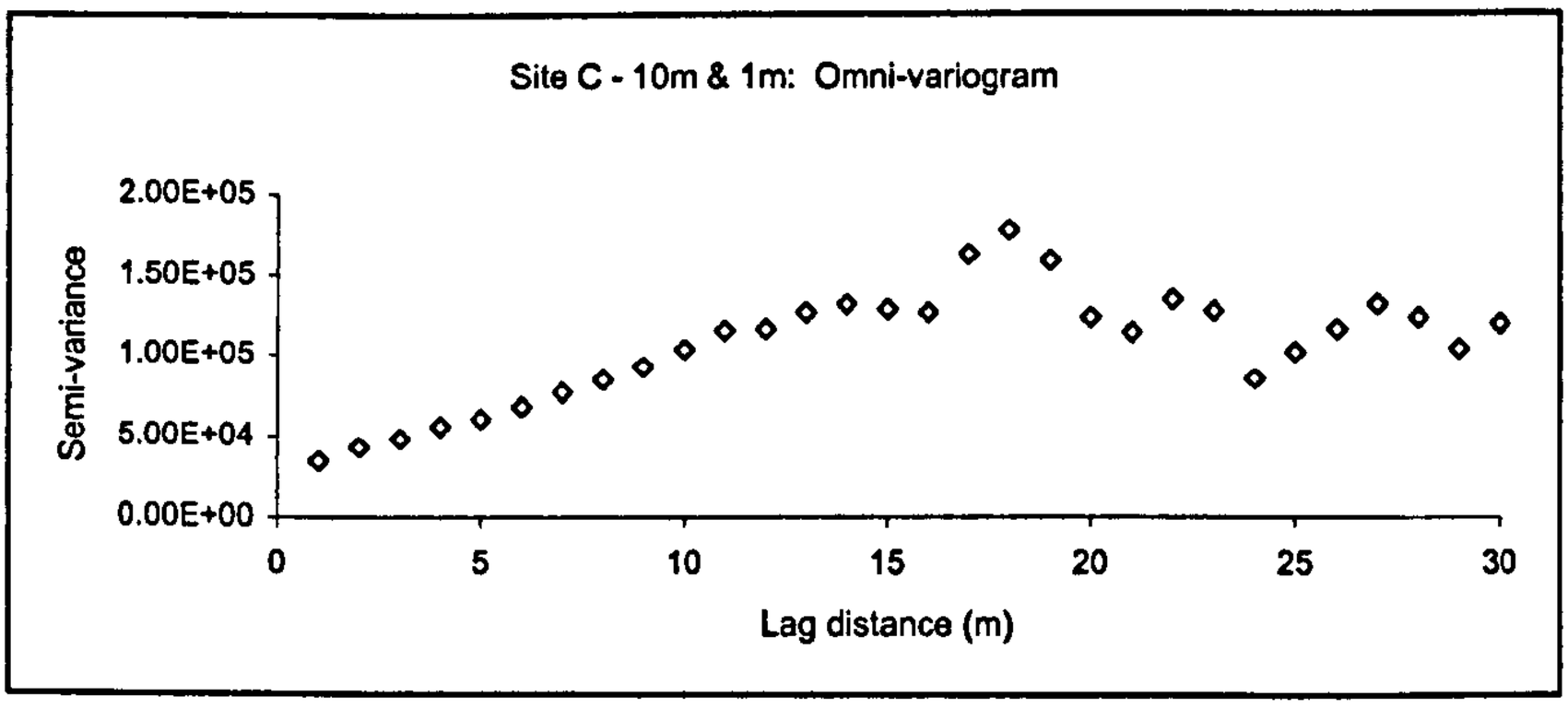
Variogram A (figure 3.34) shows a semi-variance which increases as the lag distance gets larger, but reaches a maximum where the graph flattens out, known as the "sill". The lag distance at which the variogram reaches the sill is the "range". Beyond the range the semi-variance bears no relation to the lag distance. The semi-variance commonly crosses the y axis at a positive value, which is known as the "nugget variance". A positive nugget variance shows that variation exists below

the smallest lag (sampling distance). The amount of semi-variance between the sill and the nugget point is the structural variance. Variogram B shows a semi-variance which does not change with lag distance, producing a horizontal variogram, which is described as a pure nugget variogram. This implies that the heterogeneity of the soil property is the same at all spatial scales, *i.e.* the data has no spatial dependence. Variogram C shows a semi-variance which rises steadily with increasing lag distance and does not reach a sill, the data being spatially dependent over all lag distances. This situation is not unusual because often as a larger area is sampled more sources of variation are encountered.

The examination of data using variograms will proceed in a number of stages; first an "isotropic" omni-variogram will be estimated which incorporates all the data collected from all the field samples, that have the same sample support (100m, 10m, 1m, & 0.1m sample squares for site A & B and separate 10m & 1m, and 0.5m & 0.1m variograms for site C). These initial omni- (*i.e.* not directional) variograms (figure 3.35) for each site will be based on the maximum number of sample pairs so the resulting variogram should be less erratic and have a more interpretable structure than variograms based on fewer sampling pairs. Secondly, variograms will be plotted for the individual sampling grids for each site, (figures 3.36 – 3.38). The 10m sampling grid at each site and the 0.5m sampling grid at site C have too few sampling points (<100) to plot reliable variograms, so are not used. Webster & Oliver (1992) suggest this minimum and recommend over 225 to produce a reliable variogram. The sample grids examined at sites A, B & C have from 100 – 170 sample points, therefore only the general shape of them will be discussed, individual features will be described but are not considered reliable.

The omni-variogram for site A is nearly pure nugget from a lag distance of only 2m. The semi-variance hardly rises at all with increasing lag to 26m, after this distance the points become erratic and it is likely that these are calculated from too few sample points. A variogram of this shape indicates that the largest variation in P_{tot} between two sample points occurs at a separation of about two metres and at a greater separation there will be little added variation. The omni-variogram for site B rises steadily, at a steeper angle than that for site A, until a lag separation of 15m where a sill is reached and the semi-variance levels off. At greater lags than this

Figure 3.35: Omni-variograms from Site A, B & C



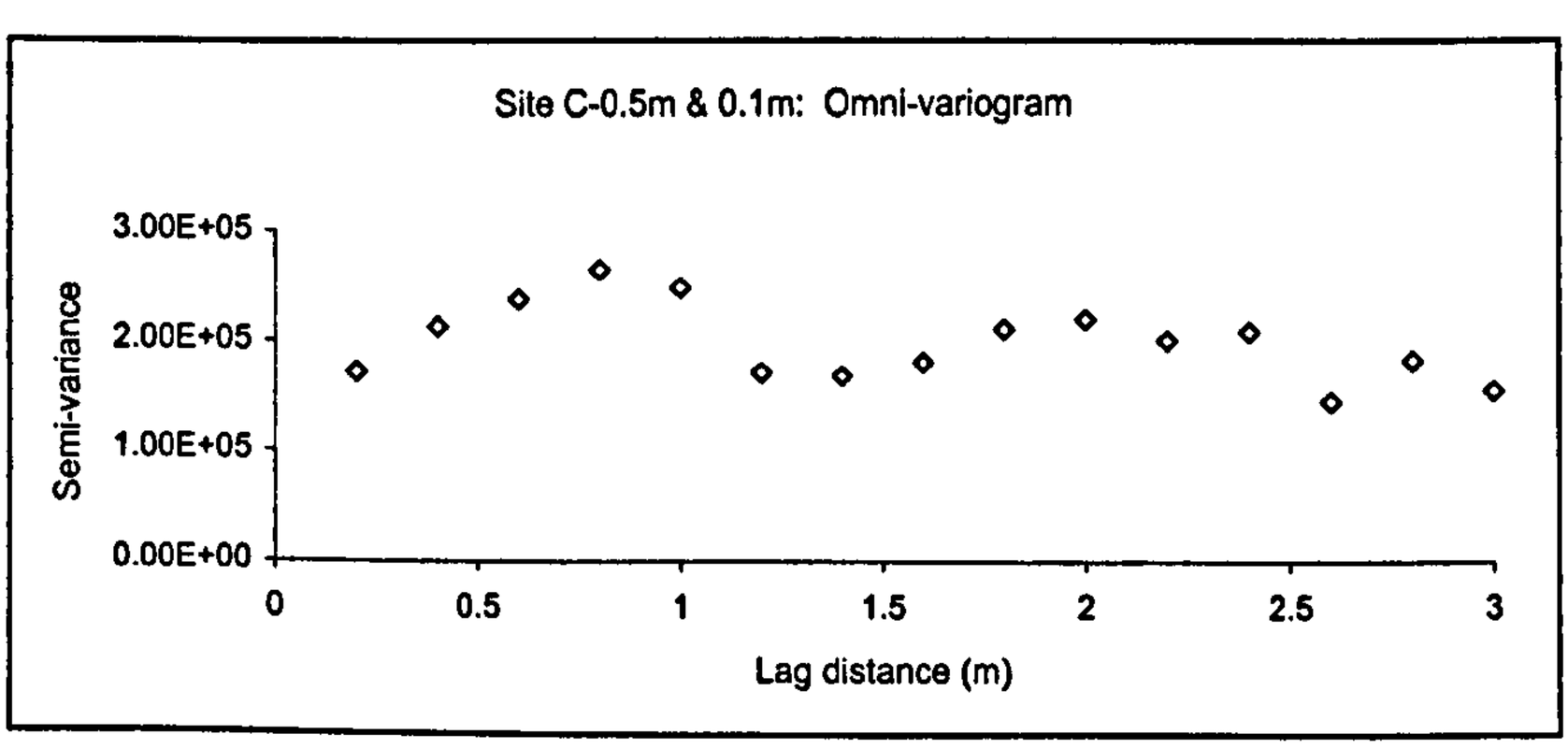
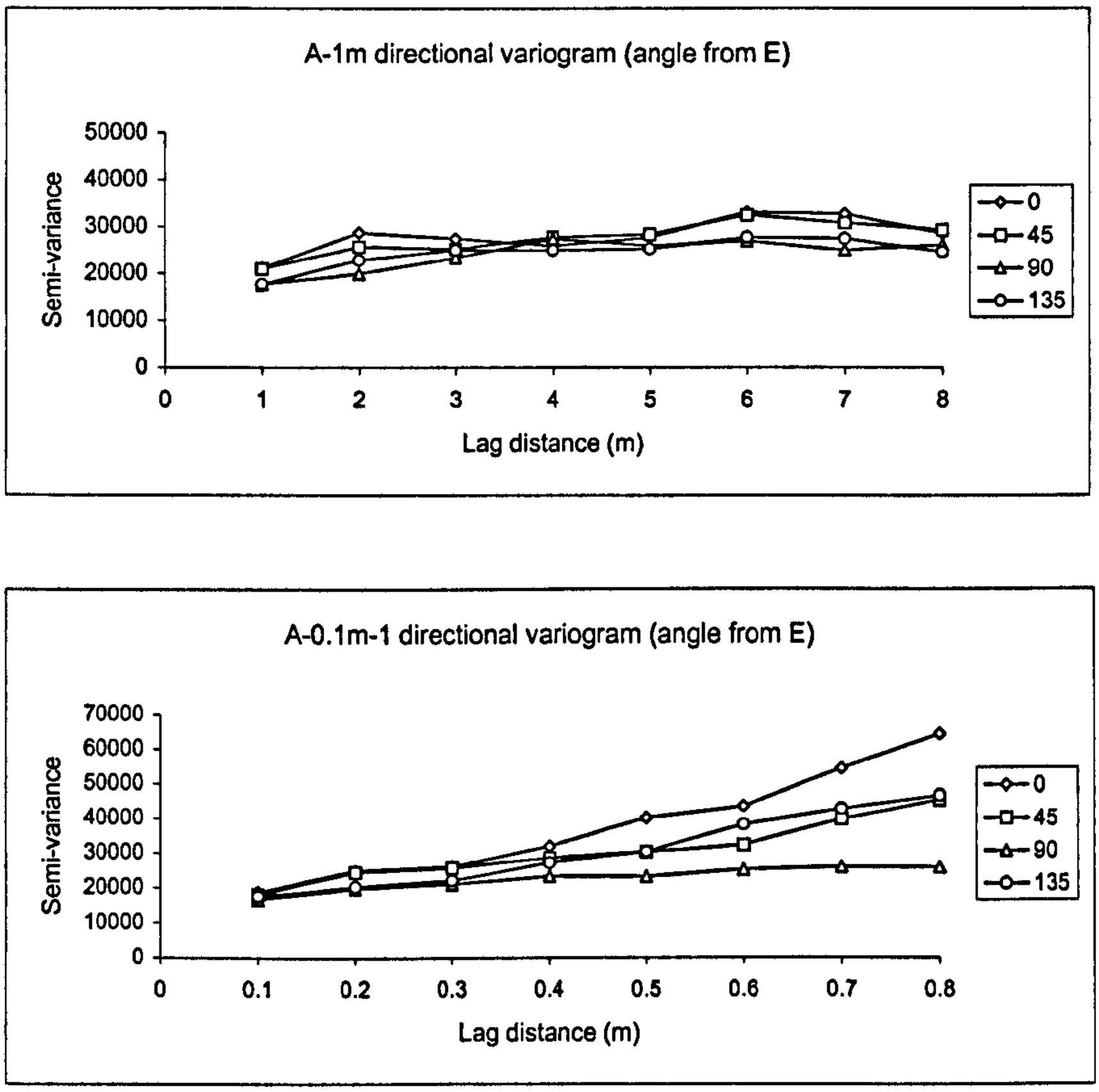
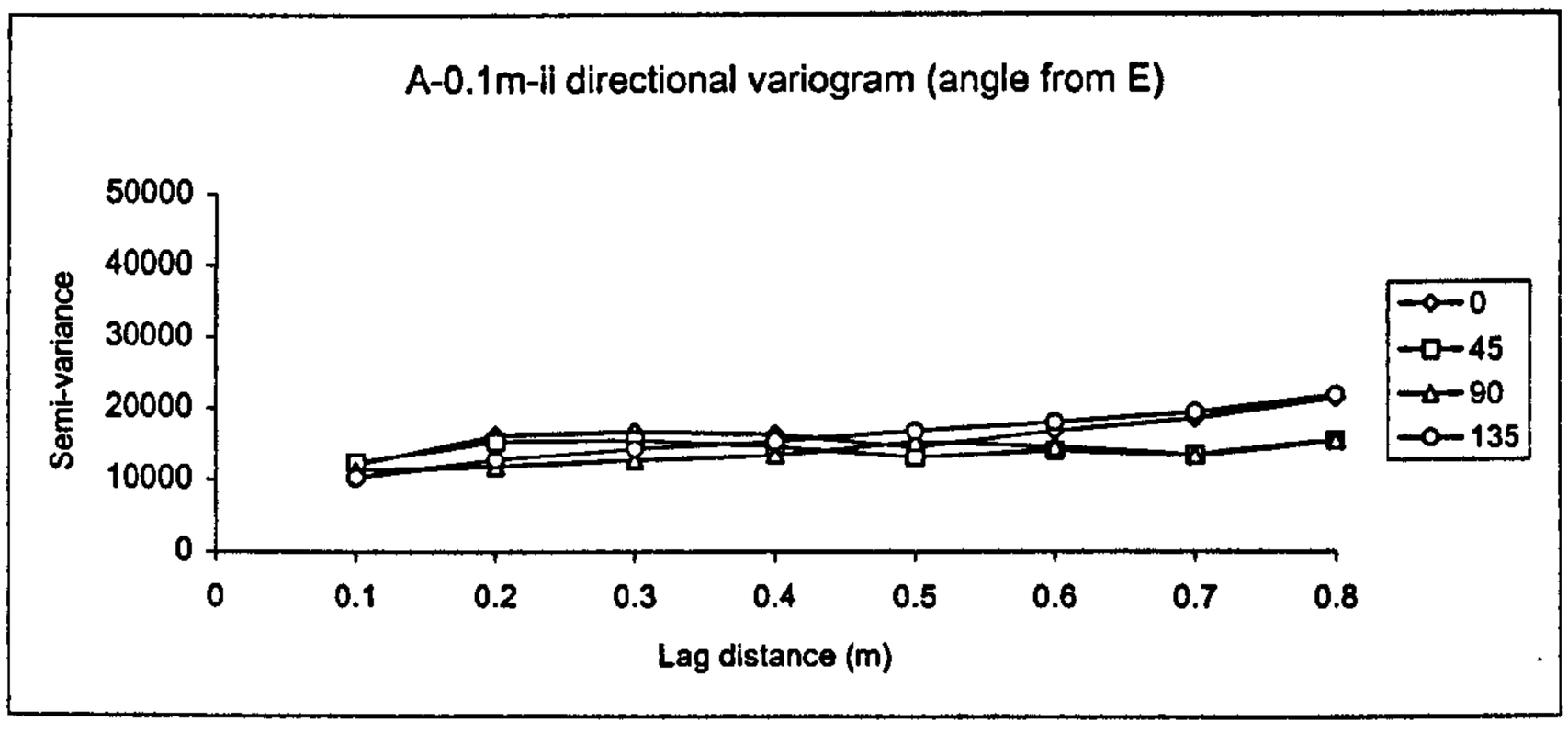


Figure 3.36: Directional variograms for Site A





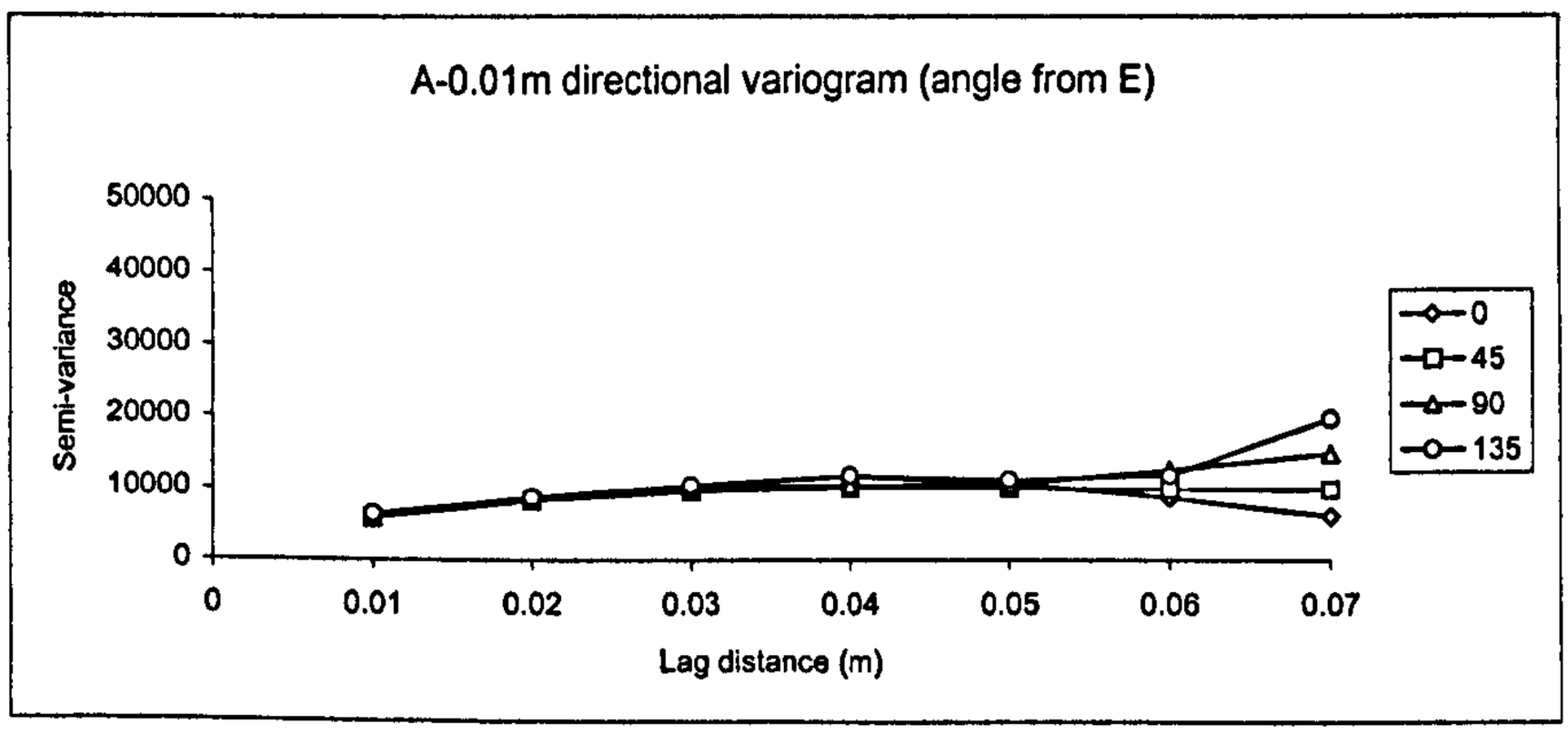
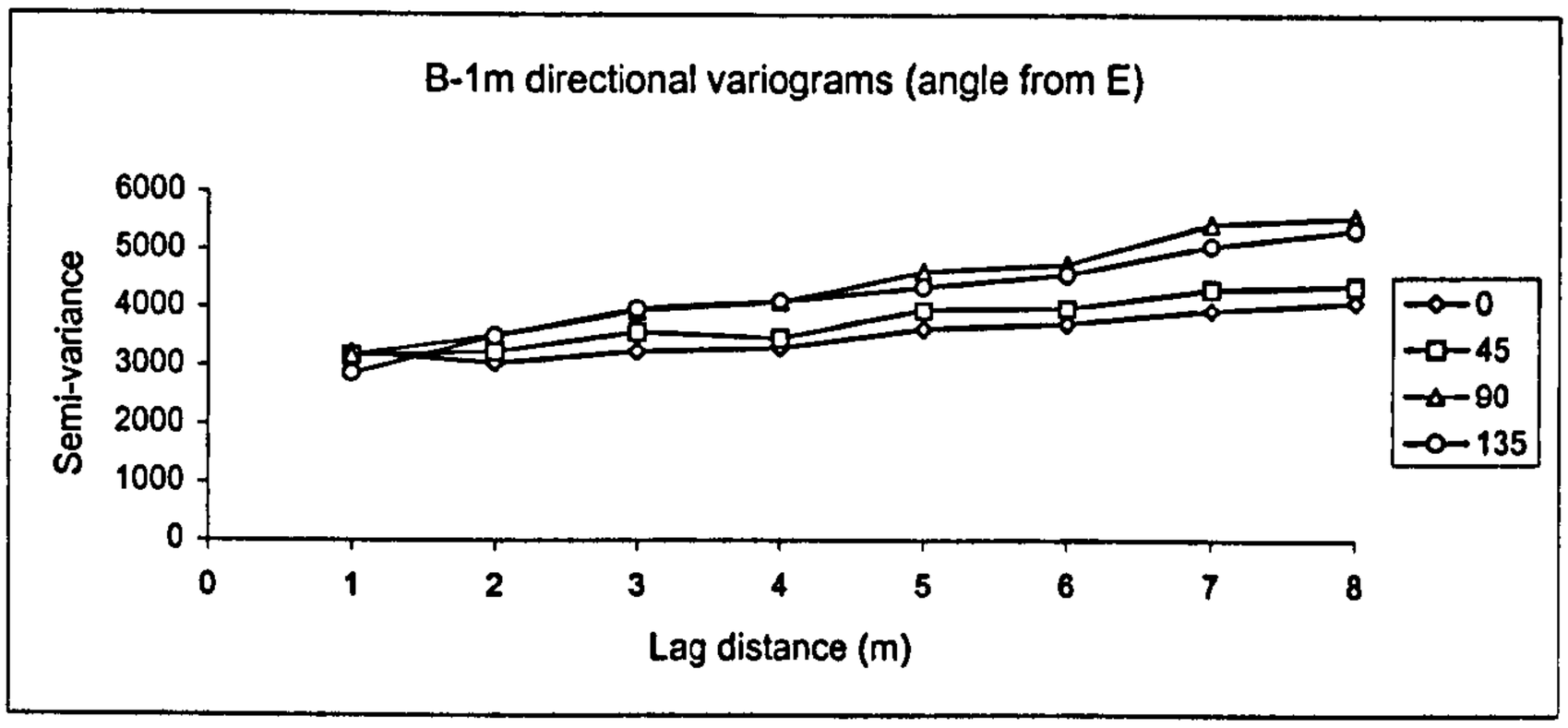
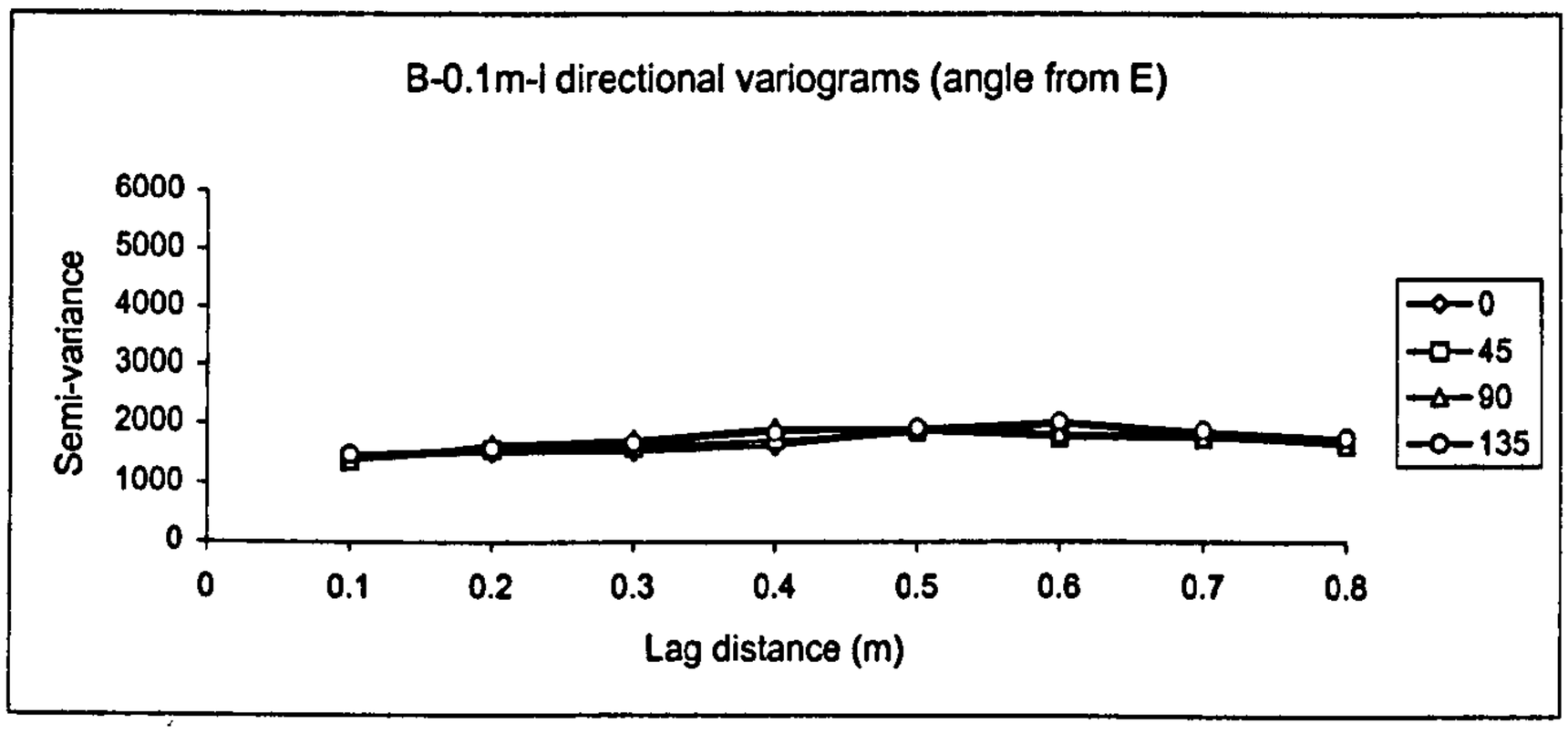
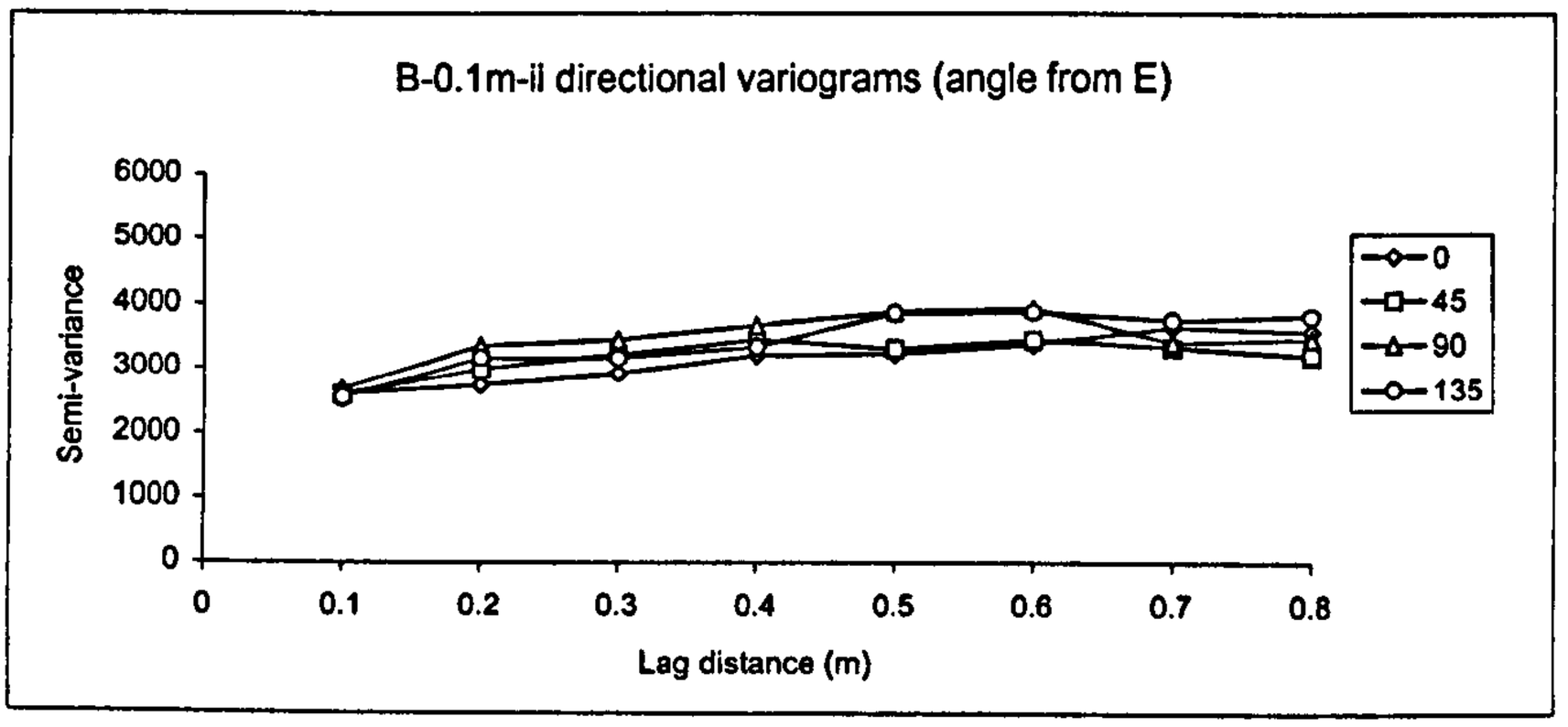


Figure 3.37: Directional variograms for Site B







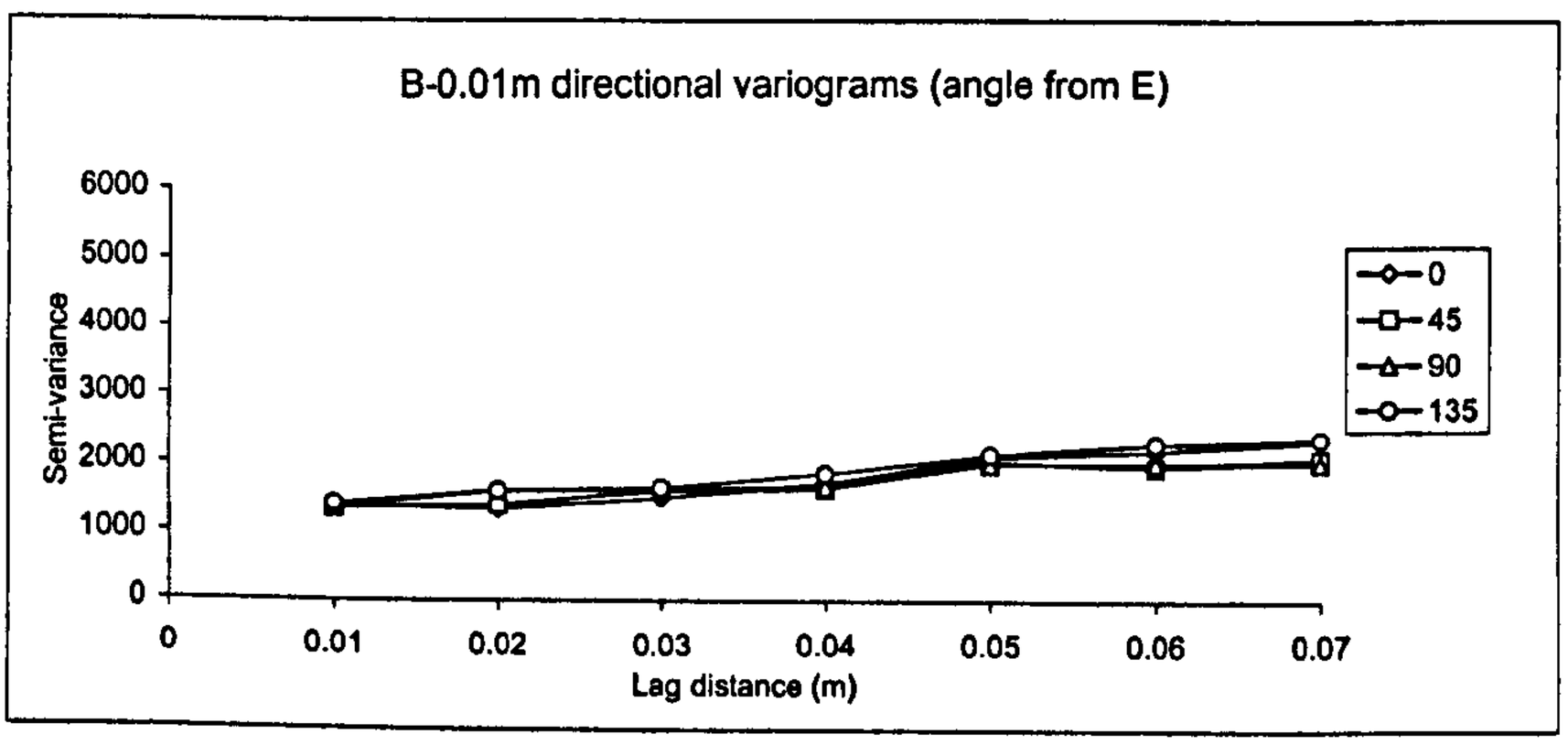
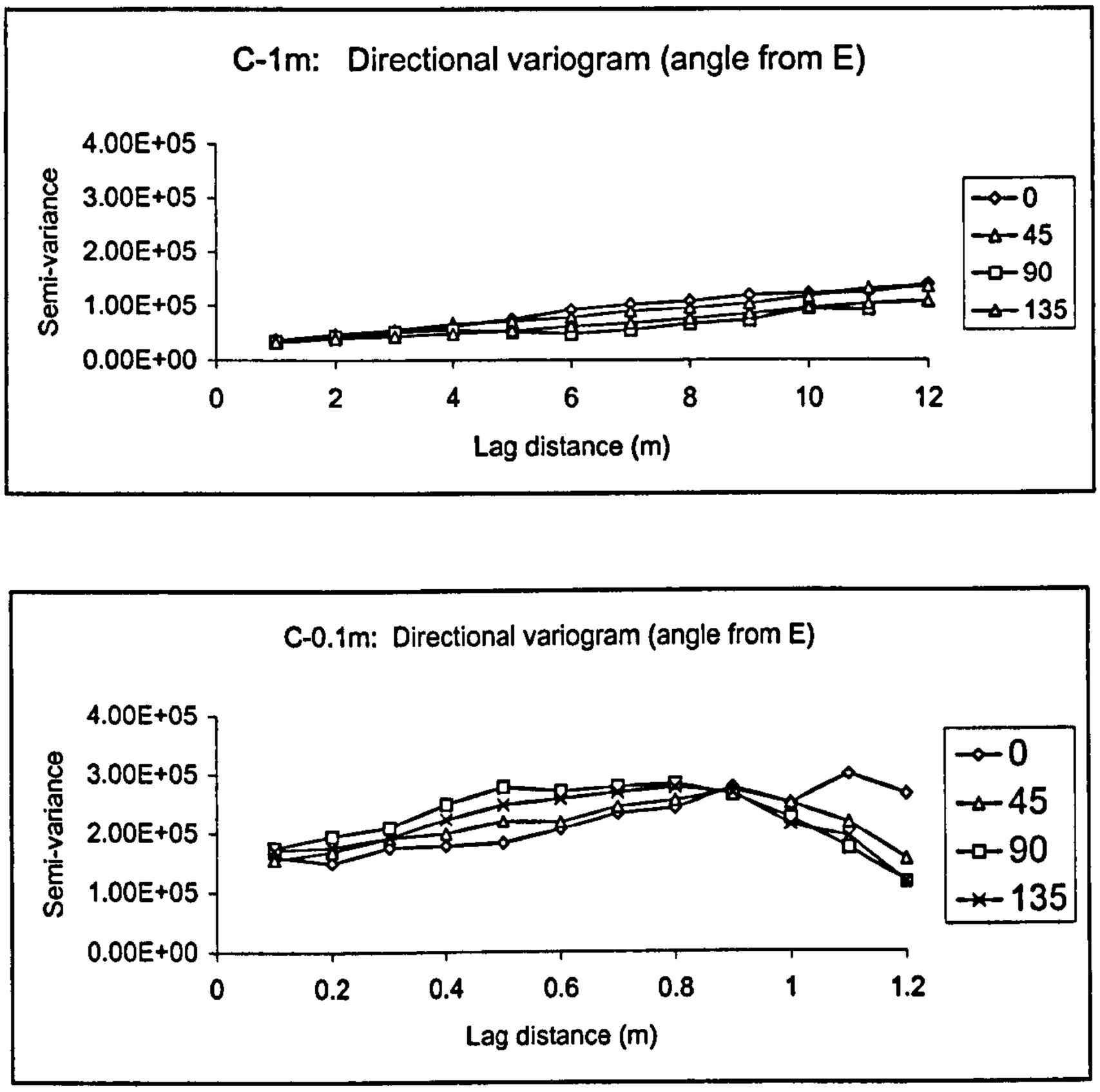


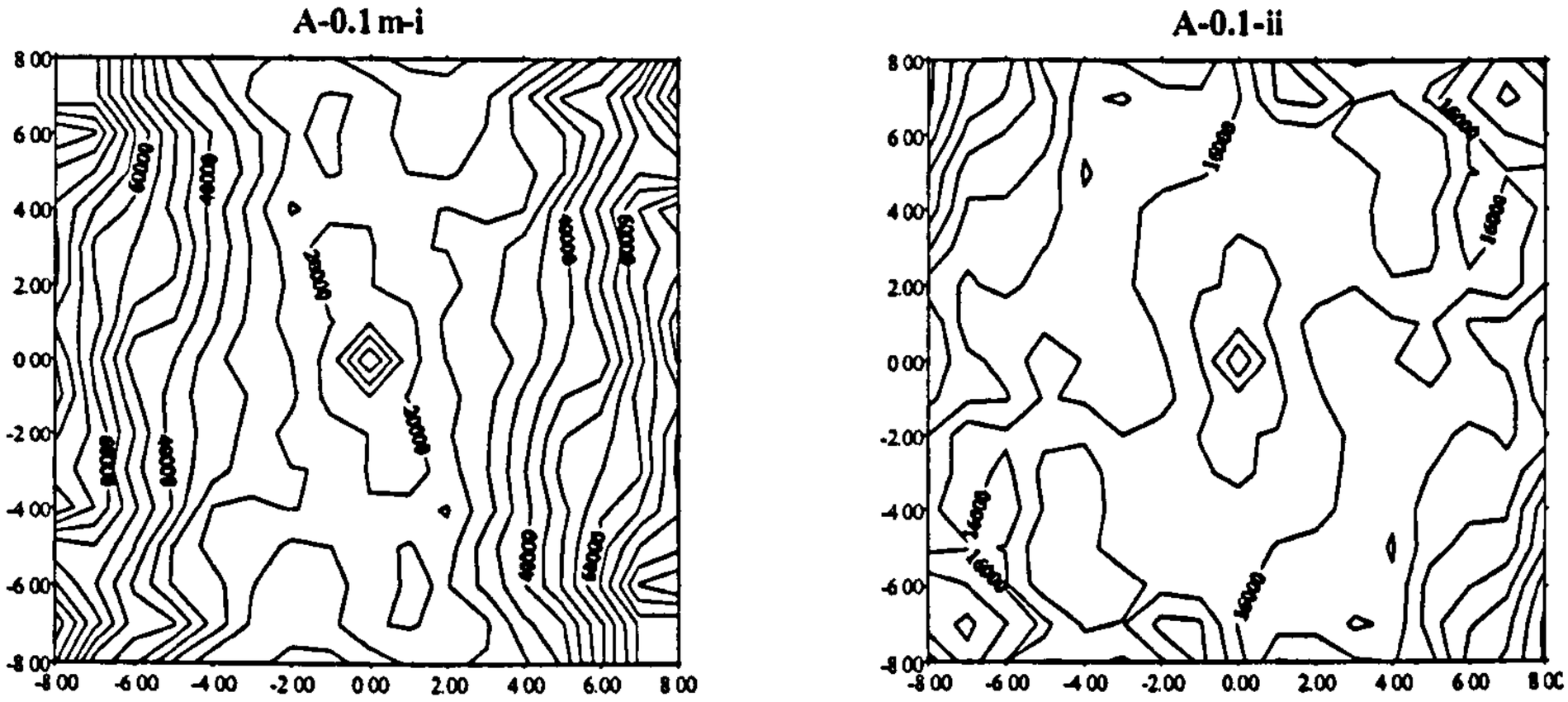
Figure 3.38: Directional variograms for Site C



there is no real change in the variation of the P_{tot} measured. The first omni-variogram for site C (10m & 1m) rises gradually to 15m but reaches a sill beyond this point, similarly the second omni-variogram from this site for the 0.5 & 0.1m sampling grid appears to reach a maximum at around a lag of 0.4m, before tailing off as the lag increases. Both the variograms for site C reach a sill so defining the sampling interval where the maximum variation in P_{tot} is reached. In general the omni-variograms show that the semi-variance is greater at site C than at site A which is greater than site B, this sequence indicates the scales of variation encountered in each data set, and similar results are reported using descriptive statistics (section 3.7).

Variograms are also plotted for the individual sampling grids from each site (figures 3.36 - 3.38). When plotting variograms the directional variation of each sampling grid can also be examined, as some soil characteristics can vary quite drastically in just one direction, perhaps relating to the topography of the landscape or the previous management practice. To check for such anisotropy of spatial continuity a "variogram surface" can be plotted. A variogram surface plots semi-variance with orientation for increasing lag distance from a point at the centre of the square. For example, the variogram surfaces of A-0.1m-i and A-0.1m-ii sampling grids are plotted in figure 3.39. The more circular the appearance of the variogram surface the more isotropic the directional variograms will be. The structure of the surface for A-1m-ii is more rounded than the other, and if the directional variograms are examined (figure 3.36), they are more isotropic for the A-1m-ii data set. The variogram surfaces are not shown for all the sampling grids at each site because directional variograms, rather than omni-variograms, will be plotted and described.

Figure 3.39: Variogram surfaces plotted for two sample grids from Site A (lag spacing (m) in x axis direction plotted against lag spacing (m) in y axis direction)



The variogram for the A-1m sampling grid rises to a lag of about 6m where the semi-variance tails off. If the line were projected back to a zero lag there is a large potential nugget, so a large amount of the variation in P_{tot} at this site is at a scale smaller than the 1m sampling interval used here. There is little difference between the semi-variance in all directions at this scale. The two A-0.1m variograms display a rising semi-variance, although the 0.1m-i variogram rises at a greater rate than the 0.1m-ii variogram, and both display a large potential nugget variance. A-0.1m-i is more anisotropic than A-0.1m-ii having a greater difference in directional variances as shown in the variogram surfaces (figure 3.39). The A-0.01m variogram reaches a sill at around 0.04m, with all four directions showing a similar variogram structure diverging at the last lag interval which will be calculated from too few sample pairs so can effectively be ignored. At this scale of sampling the potential nugget semi-variance is much smaller than at the other scales, however it would still not reach zero, so some nugget variation in P_{tot} remains at a smaller sampling interval than 1cm.

At site B the variograms have a similar structure to those at site A, showing even less anisotropy between the direction of sampling. B-1m shows a rising semi-variance with increasing lag and no sill is reached by the largest lag interval of 8m. The two B-0.1m variograms are a similar shape, a very slight increase in semi-variance to about 0.5m, after which it tails off. They both have a small structural variance and could almost be described as pure nugget variograms. The B-0.1m-ii

sampling grid has roughly twice as much variance as the B-0.1m-i . The B-0.01m variogram shows a slight rise to the largest lag at 0.07m, the semi-variance is still increasing at this sampling interval.

The two directional variograms from site C are quite different from each other (figure 3.38); the 1m variogram displays an increasing semi-variance with increasing lag interval and no sill is reached, and the 0.1m variogram reaches a sill at roughly 0.5m where the semi-variance then tails off. The semi-variance from the 0.1m grid is double that at the 1m scale, so there is much larger variation in P_{tot} results from the smaller sampling interval. The nugget variance is large so there is still considerable variation in P_{tot} over a lag of less than 10cm.

The main features of the directional variograms (figures 3.36 – 3.38) are summarised in table 3.9

Table 3.9 Summary of features from directional variograms

	Nugget variance ($\mu g\ g^{-1}$)	Structural variance ($\mu g\ g^{-1}$)	Range (lag distance)	Directional Isotropy
A-1m	15 000	28 000	2m	✓
A-0.1m-i	12 000	-	no sill	×
A-0.1m-ii	9 000	15 000	0.2m	✓✓
A-0.01m	3 000	10 000	0.04m	✓✓
B-1m	2 800	-	no sill	✓
B-0.1m-i	1 200	1 800	0.5m	✓✓✓
B-0.1m-ii	2 200	3 400	0.5m	✓✓
B-0.01m	1 200	-	no sill	✓✓✓
C-1m	20 000	-	no sill	✓✓
C-0.1m	150 000	220 000	0.5m	✓

The directional variograms from the three sites (figures 3.36 – 3.38) can be divided into two 'types', a few have a definite 'sill' and so can be described in terms of a structural variance and a range *e.g.* B-0.1m-ii and C-0.1m. The variance of these

data sets reaches a maximum at a certain lag spacing after which there is no increase. The others *e.g.* A-0.1m-i and B-1m do not reach a sill and at the largest lag distance the variance is still increasing. From this limited study there does not appear to be a pattern between sites as to which grid sizes are 'bounded', *i.e.* reach a sill, and which continue to increase. All but one example are isotropic, the variograms calculated are similar no matter which way the grids are sampled, and a completely random distribution produces a set of isotropic variograms, so P_{tot} in the soils examined here is randomly distributed. The variograms for site C, the archaeological site, show a greater level of variation in P_{tot} than the variograms for the two 'background' sites. The semi-variances are higher and have a greater range for site C. The archaeological site has a greater variation in P_{tot} which is apparent in the structure of the variograms plotted.

3.6.7 A comparison between P_{tot} and extractable P (P_{ext}) across the 10m sampling square

The early studies which linked soil phosphorus with 'archaeologically' derived phosphorus all measured 'extractable' phosphate in the soil (Bethel & Mate, 1989). The extractable P fraction is often only a few percent of soil P_{tot}, but levels are still sufficiently elevated in areas of archaeological activity for anomalies to be detected, although not as clearly, (Conway, 1983). The extractable phosphorus content present in the soil over the 1m sampling grids, as compared to the amounts of total phosphorus from site A and site B, can be seen in table 3.10. P_{ext} amounts are less than 0.1% of the mean P_{tot} content of these soils and just within the range of 0.1-10$\mu g\ g^{-1}$ for P_{ext} in soil provided by Wild, (1988).

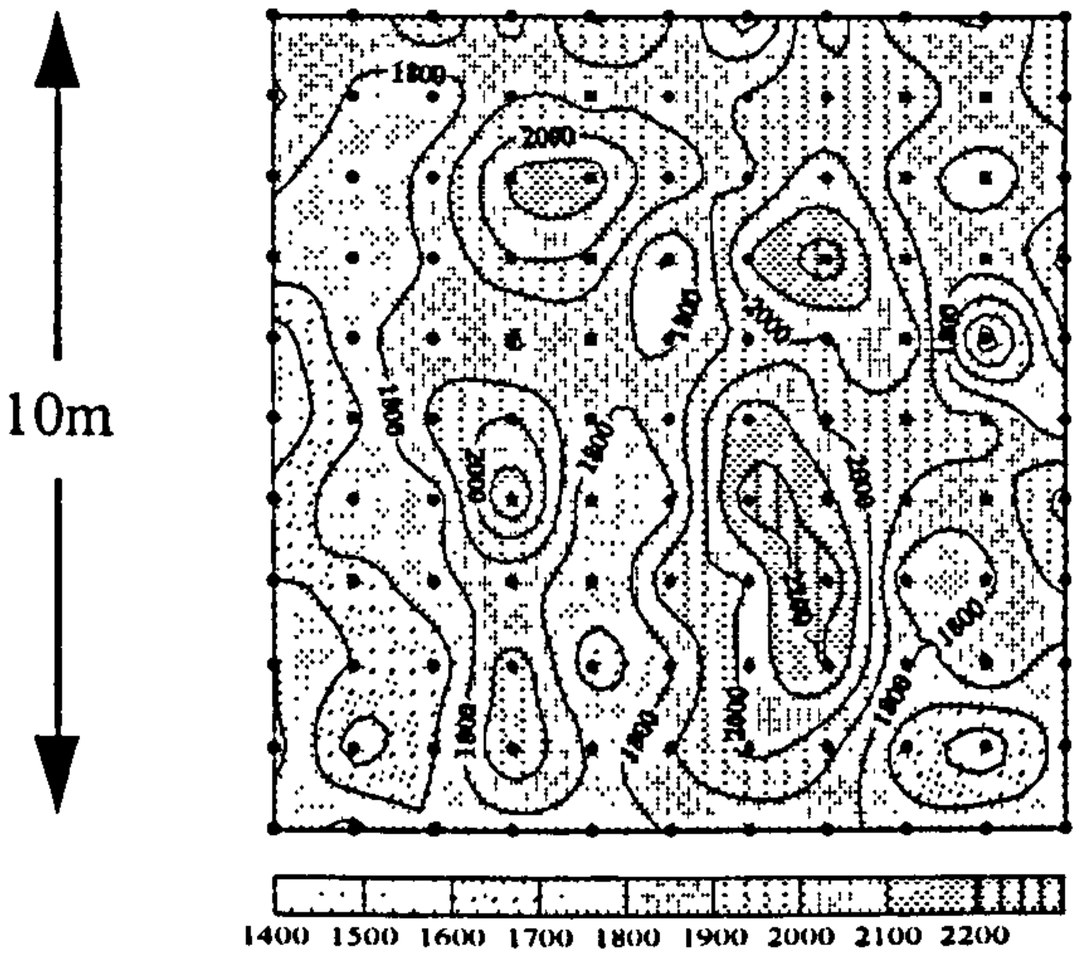
Table 3.10. Descriptive statistics for P_{tot} & P_{ext} ($\mu g\ g^{-1}$) results from site A and site B

	Site A		Site B	
	P_{tot}	P_{ext}	P_{tot}	P_{ext}
Mean	1857	1.74	639	0.34
Std. Deviation	169	1.78	72	0.1
Min - Max	1390 - 2310	0.24 - 10.72	490 - 840	0.20 - 0.69
Coef. Of Var (%)	9.1	102.3	11.3	29.4
Count	121	121	121	121

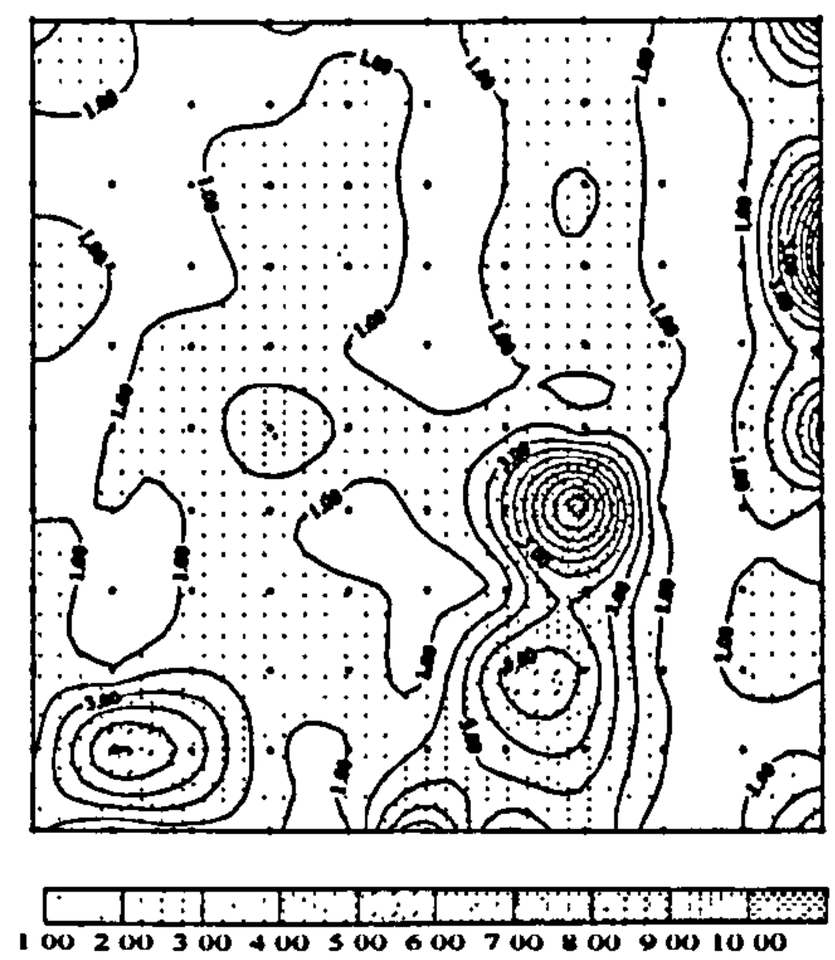
The majority of P present in these soils is in a form immediately unavailable to plants. The P_{ext} results are displayed as interpolated 2D distribution maps (figure

3.40; site A and figure 3.41; site B), showing the spatial distribution of P_{ext} in comparison with that of P_{tot}, and in comparison with the P_{ext} results expressed as a percentage of P_{tot}. The distribution of P_{ext} at site A is similar to the distribution of P_{tot}, there appear to be two stripes of higher values running down over the square at roughly a 2m separation. It is suggested that these stripes are a relic from a previous land management practice; the application of basic slag by tractor pulled rear-spreading trailer. The raised levels of the stripes which are evident as P_{tot} are also evident in the P_{ext} fraction in the soil. The distribution of P_{ext} at site B is dissimilar to the distribution of P_{tot} at site B. The random location of areas of higher P_{tot} values over the 10m square do not have associated higher levels of P_{ext}. The variation of P_{ext} over the 10m square is much greater for site A (CV%=102.3) than site B (CV%=29.4), the input of P from the addition of basic slag has had the effect of increasing P_{ext} levels in the soil giving rise to a banded pattern of P_{ext} distribution. At site B where there has been no known additions of P to the soil, the distribution of P_{ext} is more random, but less variable, and not allied closely to the distribution of P_{tot}. Where P_{ext} is expressed as a percentage of P_{tot}, the distribution maps appear to be similar in pattern to the P_{ext} maps for both sites. The P_{ext} results are therefore not independent of the P_{tot} results and where P_{tot} results are high, P_{ext} results rise similarly, with both P fractions correlating at each site ($r^2 = 0.214$*; site A, and $r^2 = 0.554$ ***; site B). This suggests that, although not ideal, the measurement of the extractable portion of P in the soil can be a good indication of the variation of P_{tot}. However, neither of the soils tested were from an archaeological site and the results may differ in archaeological P anomalies.

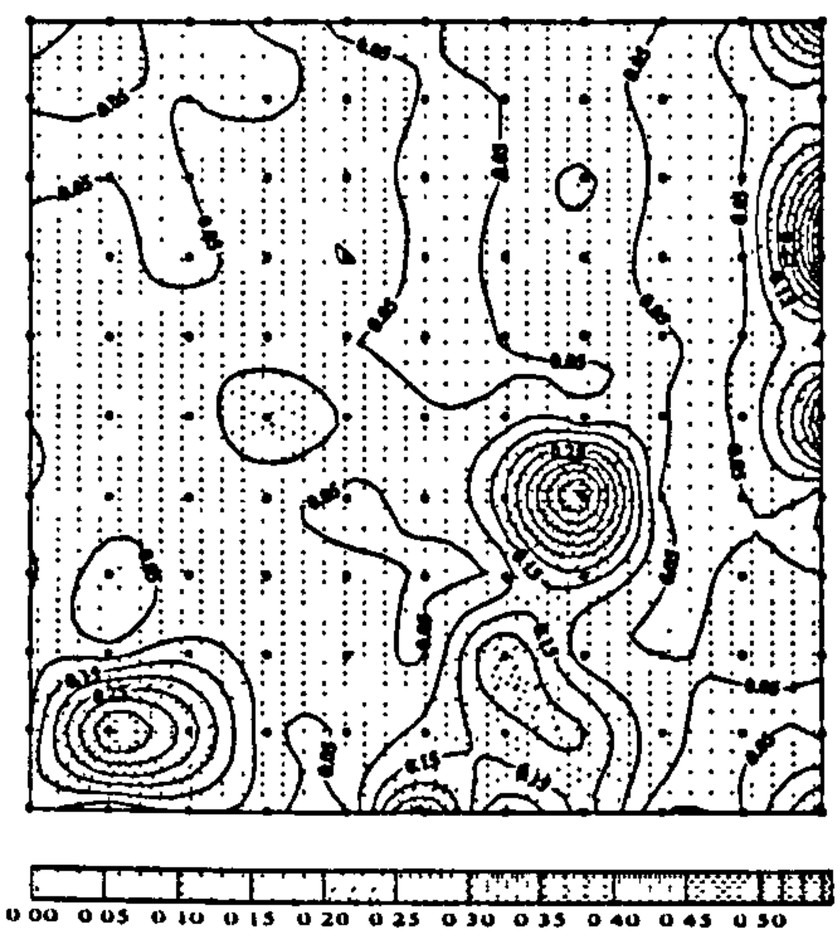
Figure 3.40: Comparison between the distribution of P_{tot} and P_{ext} over a 10m x 10m square at Site A



Total P (ug/g)

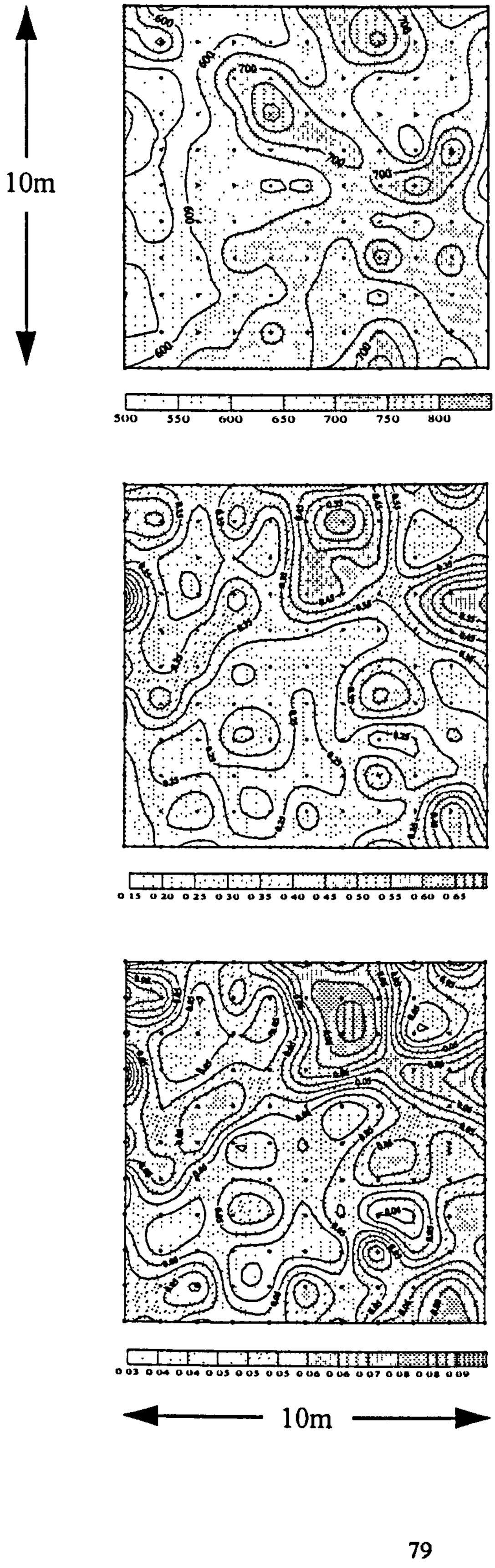


Extractable P (ug/g)



P_{ext} as a % of P_{tot}

Figure 3.41: Comparison between the distribution of P_{tot} and P_{ext} over a 10m x 10m square at Site B



Total P (ug/g)

Extractable P (ug/g)

P_{ext} as a % of P_{tot}

3.7 Variation between sites

Initial comparisons between the field data collected at each site are given below in table 3.11 which shows the general differences present between each site

Table 3.11: Descriptive statistics for P_{tot} results down to a 10cm sampling interval from each site (samples collected using a soil auger)

	Site A	Site B	Site C
Mean (μg g^{-1})	1911	659	1615
Standard deviation	213	73	297
Variance	45466	5389	88349
Min. – Max.	950 - 3110	270 – 890	840 – 2630
Coef. of variation (%)	11	11	18
Count	397	397	193

The range and means of P_{tot} values from site A & C are similar, but vary from those of site B. Both site A & C have been agriculturally improved (ploughed and fertilised), whereas site B remains unimproved so P_{tot} values at site B are roughly a third of those at site A & C. The lowest P_{tot} result at site B (270μg g^{-1}) was measured from a sample collected on the B-100m grid; at this grid interval an area of gleyed soil was sampled which had a low P_{tot} content. The variation within each site is different, the variance being greater at site C than site A, even though the mean is lower. The variance is lower still at site B but this is partly because the mean is lower. Where the means vary, the coefficient of variation (CV) can be used to compare the variation. The CV at sites A and B are lower than that at site C. The differences between the three sites are not significant, and although site C is an archaeological site, the P anomalies that were measured at the smaller sampling intervals collected by trowel (section 3.6.5.3), do not show up distinctly at the larger scale. If the results were being examined for P_{tot} anomalies to locate potential archaeological sites, the results from site C appear not significantly different to the results from site A. If descriptive statistics such as these are viewed in isolation then it would be easy to miss potential sites.

3.8 Discussion

There are three main considerations for any archaeological phosphate survey: a, the sampling; the selection of the most appropriate sampling strategy, and method of sample collection; b, the manner of preparation of the samples collected and the method of phosphorus measurement; c, the analysis of the results and the presentation of the data for interpretation. These three stages will be discussed separately and considered in terms of the data that has been collected for the three sites presented in this chapter.

3.8.1 Sampling strategies

The sampling strategy to be used will be dependent on a number of factors. These include the feature or site to be surveyed, the variability of the area, the manpower available, time and financial constraints, and the method of P analysis, as discussed in chapter one. Two sampling procedures are commonly used within archaeology, the first being systematic grid sampling, where the nodes of a grid are sampled over the survey area. The size of the grid interval will again be dependent on a number of factors, the most important being the size of the features expected, or of interest. The grid interval has to be small enough to ensure that if such a feature is present it will be sampled. If the survey is a prospective one, then the smallest grid interval that logistics will allow should be used to obtain as much detail as possible. Over large survey areas sampling intervals of 10m-50m may have to be used to cover the whole area economically, but within a defined area an interval of at least 1m is needed to get a more detailed distribution, many features only becoming apparent if sampling is conducted on an even finer grid interval. The second sampling strategy used is a selective system where samples are collected from points of interest over the site. This strategy is most often used when only a limited number of samples can be collected, and while pin-pointing sampling data to areas of interest, statistical considerations are limited and any distribution maps produced from such limited data are likely to be inaccurate.

The collection of control samples

It is important when using any sampling strategy to collect control samples to provide comparative information on the amounts and 'natural' variation of P present in the soil. Ideally, the control samples should be collected from a position

where no features can be observed, to assess background levels of P, but often if samples are collected on a large grid it is assumed that a proportion of the samples collected will be from an area with no archaeological inputs of P therefore, no separate background samples are collected. Both methods of control sampling are common within archaeological soil studies.

In this study samples were collected from the nodes of a grid at a range of sampling intervals (10m, 1m, 0.5m, 0.1m, 0.01m). This systematic strategy was chosen because it provides a good coverage of area and the samples are easy to locate. For these reasons it is the most common strategy used for collecting soil samples in archaeology, and provides the simplest method for this study to assess the background variation of soil P. Three sites were sampled in order to compare results from an archaeological site with those from two background sites.

A soil auger was used to collect most of the samples, giving roughly 25g soil from each point, and this technique is commonly used in most soil survey. It is important that all the soils collected for P measurement are sampled in the same manner if statistical comparisons between samples are to be made. This is problematic where soil material is limited or very stony, for example, within an archaeological feature such as a buried cobbled floor (as in site C). In these cases samples may have to be collected using a trowel, so the sample support "the size, shape and orientation of the sample", is different. Any statistical comparisons made between samples with a different support are tentative and the methods of sampling used should be described. The depth of sampling is important and a soil profile should be examined and described to assess the appropriate sample depth. When sampling with a soil auger, a depth of 10cm is often taken, but consideration has to be made of any horizonation of the soil. For example, if a soil has a surface A_h horizon, samples containing a greater proportion of A_h material will have a greater P_{tot} content, and positively skew the results. Brown earth agricultural soils which have been ploughed will tend to have a well homogenised surface soil horizon, with a relatively uniform P profile, so sampling with a soil auger is acceptable. In other soils, the method and depth of soil collection should only be decided after the soil profile has been considered. When sampling an archaeological site the P_{tot} contents of samples collected sequentially down a soil

profile can be measured initially to detect vertical variation in P_{tot} content. The results can then guide the survey as to the most suitable depth at which samples should be taken to detect archaeological anomalies.

3.8.2. Sample preparation and method of P measurement

In this study, samples were air dried and sieved <2mm, a sub-sample was further ground in a ball mill <200μm, and a second sub-sample taken from this for digestion prior to P measurement using flow injection analysis. The method of measurement used can only be decided by the facilities locally available and the level of precision and accuracy required for the survey. An examination of methods used for the measurement of P_{tot} in soil in the laboratory is presented in appendix 2, and methods of measurement of P_{tot} in the field are examined in appendix 3. By grinding a sub-sample of the soil before digestion, the soil is homogenised to decrease the variation of P_{tot} within each sample. If the results for P_{tot} contents are examined in soils that have been sieved to <2mm and soils which have been further ground to <200μm, the range narrows from 127–40 μg g^{-1} and the standard deviation reduces by two thirds, although the mean is not significantly different (table 3.12).

Table 3.12: P_{tot} content of a Bs soil (μg g^{-1}) with two levels of preparation

	Air-dried, sieved <2mm	Air-dried, milled <200μm
Mean	490	470
Standard deviation	34	10
Range	437 - 534	451 – 491
Count	12	12

The level of precision obtained for any measurement will be increased the greater the sample preparation. Measurements conducted in the field are less accurate and precise than laboratory measurements because of the moisture and stone content of the soil. In the field sample measurement is more often done by a set volume of soil; a scoop or spatula, and this can vary in weight by ~ 10% from soil to soil. Field methods of P_{tot} measurement are a useful guide to P_{tot} contents and two methods are compared to laboratory methods in appendix III. If field measurement of P_{tot} is to be done then a proportion of samples must be taken to a laboratory and re-measured. The accuracy and precision of any field method used can then be

assessed and errors can be given when the results are quoted. For this study all the samples were ground to achieve good homogenisation before a sub-sample was taken for P_{tot} measurement. The variation of P_{tot} present within a sample was assessed (coefficient of variation = 7% before, & 2% after, grinding: table 3.12). This level of sample preparation was important because the variation in P in three sites at a variety of sampling intervals was being examined, so the variation present within each sample had to be reduced to a minimum. In studies where the examination of variation is not so important then such rigorous sample preparation is not essential.

3.8.3 Analysis and interpretation of results

Once the results are calculated the techniques of data analysis to be used must be considered. This is only possible if there is a clear conception of what needs to be achieved. In this study the primary aims and objectives are set out in section 1.4, and for this the variation of P_{tot} in the soil from three sites is measured and compared, and the P_{tot} distribution examined. This should clarify what differences there are between local welsh upland soils which have had no anthropogenic inputs of P, soils which have been recently modified by agricultural practices (ploughed, limed and fertilised), and soils collected from a known archaeological site. The standard procedure to be used in any such comparative studies is to produce summary/descriptive statistics and histograms for each set of results. The results can then be described in terms of the spread of data about the mean, and with the interquartile ranges, the number of outlying data points. This is important from an archaeological perspective because the outliers which are larger than the mean could signal the presence of a separate population of results with higher P_{tot} amounts. Outliers can be considered significantly different to the main population if they are three times the standard deviation greater than the mean (Hammond, 1983). At this stage the outliers should be identified and their locations noted. If they are grouped in a particular area then reasons can be considered for the existence of an anomoly. For example, the samples are collected from a different field which has had a different management regime, or the samples are collected from an area of suspected archaeological activity. The variation in the data is considered using the standard deviations, the ranges, the variances and the coefficients of variation. These calculations for the three sites considered here can

be seen in table 3.11. Site C has the greatest standard deviation, variance and coefficient of variation, even though its mean is lower than site A. The range is greater for site A and the coefficient of variation is high for site B. The results are therefore far from conclusive in showing the differences which may be present in an archaeological site, when compared with a background site, and there is always the possibility that a 'background' site has in fact unrecognised archaeological features. The variation of data in a site and the spatial dependence of a particular soil characteristic can be examined using semi-variograms which are discussed in section 3.6.6. Plotted variograms display the amount of variation present over increasing sampling distances so comparisons between sites can be easily made. They can also be used to display directional variation so, for example, differences down and across a slope can be examined. The variograms calculated for site C show greater variance than those at sites A & B, a consequence of the archaeologically enhanced P_{tot} measurements at this site. The majority of sample grids display directional isotropy, and the variograms do not show a uniform structure either between, or within sites; four being 'unbounded' and the remainder reaching a maximum variance at an intermediate lag interval. Generally there is a large nugget variance, and the variograms do not rise greatly, showing the large proportion of the total variation of P_{tot} which is present over the smallest sampling interval.

The distribution of the data and its spatial arrangement is important for identifying anomalies over an area, so 2D interpolated distribution maps should be plotted. There are a number of computer mapping packages to achieve this, all offering a range of interpolation methods (*e.g.* appendix 5 for the 'Winsurf' package) which should be carefully considered, and the method chosen quoted with the maps produced. These interpolated maps are a guide to the distribution of P_{tot}, but are only as accurate as the data points allow, because any large gaps in the data are filled in by interpolation which can be inaccurate. The sampling points should be shown on the distribution maps, or a separate map showing the sample points should be attached, so that the spread of sampling points and their density can be examined. The maps enable trends and hotspots in the data to be identified.

Through the use of descriptive statistics, histograms, semi-variograms and distribution maps, the variation present in a set of data can be assessed, and consideration given to the presence of archaeological anomalies. In this study, site C, surrounding a medieval long-hut showed slightly greater variation in P_{tot} than the other two background sites, the histograms displaying a positively skewed distribution to the data; the effect of archaeological P inputs to the system, and the distribution maps showed high regions of P in the areas surrounding the surface archaeological features. Site A, the agriculturally improved site, displayed suspected anisotropic features resulting from the application of basic slag in the 1950s, and the distribution maps for site B showed no pattern, just a random P distribution. The methods described could therefore distinguish between the three sites examined, but it is important to consider all the methods of examining the P_{tot} variation and distribution together, as no individual method would have sufficed in this case.

AN EXAMINATION OF THE NATURAL DISTRIBUTION OF P AT A SCALE BELOW 1CM² IN SOIL

4.1 Introduction

Phosphorus was measured over a 1cm square; a 1mm square; and a 100μm square, in thin sections prepared from soil blocks taken from sites A & B. This augments the 'macro' sampling over the range of 100m-0.01m, which has been described and discussed in chapter 3, and extends down to the scale of individual soil components. In this study the chemical examination of soil thin sections was made by electron microprobe analysis, using a Cameca 'Camebax Microprobe' with a Link analytical AN10000 (10/85s) analysis system, using Link Spectra microprobe automation software and Link ZAF4 FLS data correction software at the Electron Probe Unit, Manchester University.

4.2 Thin section production

A section of a soil block was separated while field moist with a sharp knife, air-dried at 35°C in a drying cabinet, and carefully placed into glass containers with labels written using permanent Indian ink in preparation for impregnation. To impregnate the sample, a mixture of equal amounts of unsaturated polyester resin in styrene monomer (crystic, B&K Resins Ltd.) and acetone was used, with 1.25% of a catalyst (ethyl methyl ketone peroxide) added (Fitzpatrick, 1984). It is important to impregnate a soil sample slowly, so only a little of the resin mixture was added at first to cover the bottom of the sample, in a fume chamber. The resin soaks through the sample by capillary action and was frequently added over a few days. Once resin had reached the top surface of the sample, the soil block was immersed in resin and kept at room temperature to cure (4-6 weeks). The resin was occasionally topped up with the original impregnating mixture (extra was prepared initially) as the acetone, used as a solvent, evaporated off. Once cured thin sections were made from each block on 26mm×76mm glass slides. The process of thin section production is explained in detail by Fitzpatrick (1984) and Murphy (1986), and will not be reproduced here. The finished soil thin sections, roughly 25-30μm thick were polished using 6μm & 3μm diamond pastes in preparation for analysis.

4.3 Microprobe analysis

Electron microprobe analysis is a technique for chemically analysing small areas of solid samples to a minimum spatial resolution of roughly 1μm by exciting a selected area using a focussed electron beam, generated with an electron gun. The x-ray spectrum emitted contains lines which are characteristic of the elements present, and by comparing the intensities of these lines with those emitted from standards, elemental concentrations can be calculated. Information on, and applications of, microprobe analysis can be found in Anderson (1973), and Reed (1996). The X-ray photon energies from the sample are analysed by spectrometers, either wavelength dispersive (WD) or energy dispersive (ED). WD-type analysis has greater resolution but is tuned to detect only one wavelength at a time, whereas the ED-type analysis can record the whole spectrum simultaneously so is faster and more convenient but is less sensitive. For this study natural and synthetic standards were used as listed in table 4.1:

Table 4.1 Standards used to calibrate the microprobe and method of detection

Element	Standard	Detector type
Si & Ca	Wollastonite	ED
Al	Corrundum	ED
Fe	Fayalite	ED
Mn	Tephroite	ED
Mg	Periclase	ED
Na	Jadeite	ED
K	Orthoclase	ED
Cl	Halite	ED
S	Gypsum	ED
P	Fluor-apatite	WD

The element suite included Cl to give an estimate of the amount of impregnating resin present, since Cl is not normally detectable in the soils used, measurements with high Cl readings indicate large proportions of impregnating resin *i.e.* a void or partial void area. The other elements were selected because they are common in soil. Completed thin sections roughly 30μm thick were cut down to 26mm×48mm, to fit into a sample holder for a CAMECA microprobe, and coated under vacuum

with carbon (C) to provide a path for the current in the electron beam to discharge itself. C is generally used because it has a minimal effect on the x-ray spectrum.

4.4 Sampling strategy

Phosphorus was measured in thin sections prepared from blocks of soils collected from site A & B (figure 4.1) which display obvious structural differences. The thin section from site A was more structurally organised, with definite peds roughly 5mm across, surrounded by cracks/voids which are roughly 0.5mm across. Site B was less organised with obscure weak peds containing fine disorganised scattered voids. Stone fragments contribute roughly 2% of the site B thin section. Samples were collected from each thin section over a grid interval range of 1mm - 10μm (table 4.2) and each 121 grid samples were collected during an automated overnight run using a mechanical stage programmed to move between each count. Due to the presence of up to 50% void space within soil (White, 1997), the data at each location was collected by scanning the electron beam over a 50μm × 50μm square raster, the central part of the raster correlating with the grid node. The analysis would therefore produce a mean result for the whole raster and so be less sensitive to the numerous small voids in soil. Each raster was scanned for 200 seconds so a full run of 121 points lasted 6.7 hours. At site B a further two sets of data were collected using a defocused 5μm point rather than a 50μm raster for comparative purposes. This data was collected over a 1mm × 1mm square at a 100μm grid interval, and over a 100μm × 100μm square at a 10μm grid interval, these analyses were not done at site A due to time constraints. When dealing with such a small sampling area the location of the starting point is important as some areas of a thin section may contain many more voids within the soil fabric than others. The starting point for all the grid analyses was located at a point which would enable the most complete area of the thin section to be analysed.

Figure 4.1: Soil thin sections for site A & B

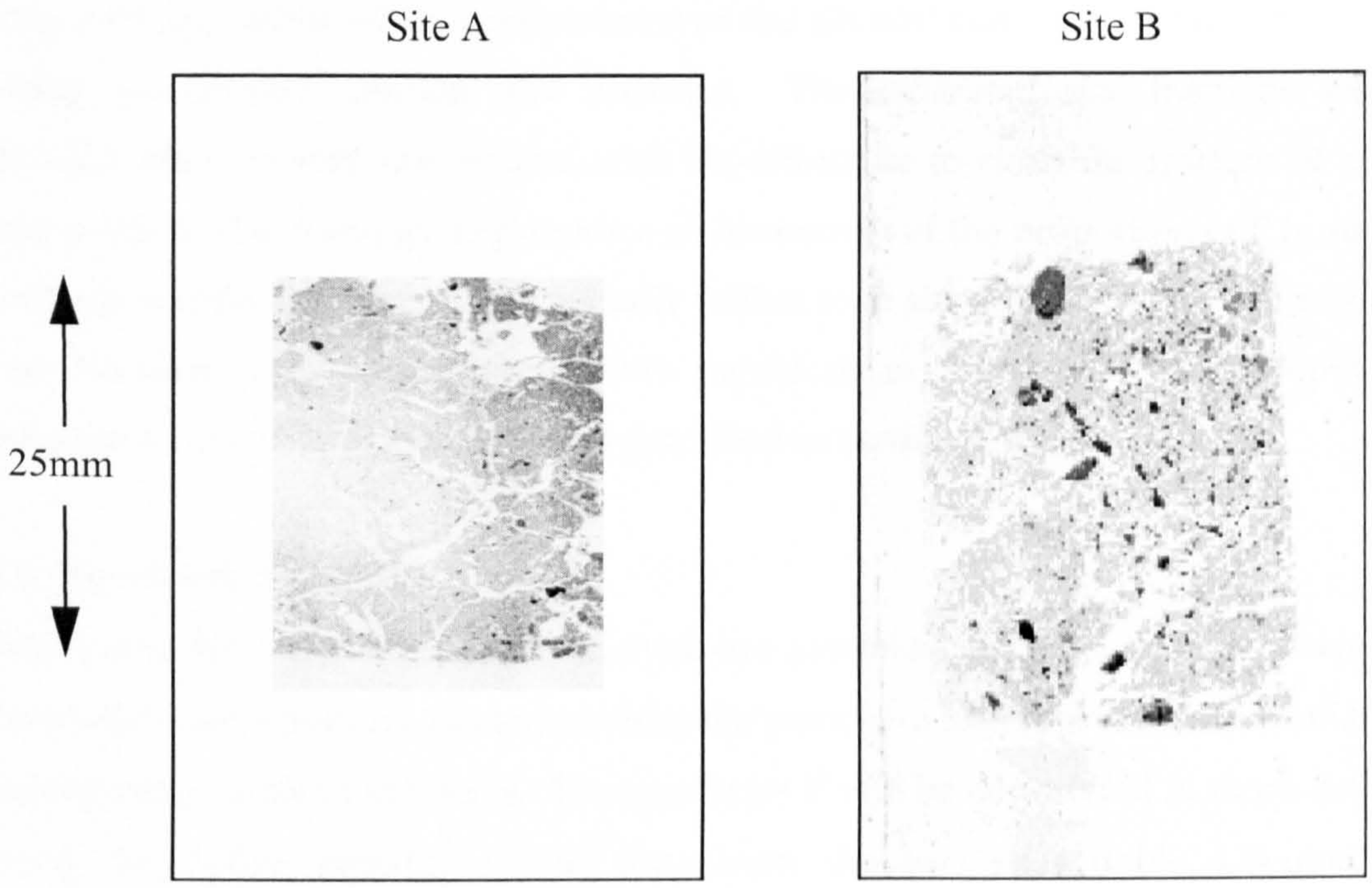


Table 4.2 Summary of analyses by microprobe

Grid interval	Grid area	Raster size	No of sample points	
			Site A	Site B
1mm (0.001m)	1cm×1cm	50μm square	121	121
100μm (0.0001m)	1mm×1mm	50μm square	121	121
100μm (0.0001m)	1mm×1mm	5μm point	-	121
10μm (0.00001m)	100μm×100μm	5μm point	-	121

4.5 Textural analysis

When considering the distribution of P in a soil the texture of that soil (the proportion of sand; 2mm-63μm, silt; 63μm-2μm and clay; <2μm Hodgson, 1976) is important. In many soils the P present will be mainly associated with the silt and the clay fraction (Williams & Saunders, 1956), unless the parent material has a detrital apatite component, when higher P contents may be measured in the coarser size fractions. Apatite is the commonest P mineral, accounting for 95% of P in the earths crust (Larson, 1967), however, other P minerals such as monazite and xenotime have been identified locally in the Irish sea till (Qureshi *et. al.* 1978). The texture of the air-dried, sieved <2mm soils from site A and site B was measured

using wet sieving, to separate the three sand fractions (2mm-630μm; 630μm-200μm; 200μm-63μm), followed by measurement of the silt and clay using a Micromeritics 'Sedigraph 5000ET' particle size analyser. The separated size fractions were divided, and one half was treated with Na-dithionite to clean the fraction of any iron oxide or clay coatings, to provide a measurement of the proportion of P in such coatings and the proportion of P actually within each size fraction. The two sets of size fractions were then digested with perchloric acid and the orthophosphate measured in each digest using FIA as described in section 3.5.

4.6 Results & discussion

The results from the microprobe analysis are produced in appendix 1 as percent elemental concentrations, calculated from the percent oxides (the raw data from the microprobe) for all 11 elements. The results for P will be considered in more detail using descriptive statistics of the data from the two sites (table 4.4) and a comparison of descriptive statistics for P_{tot} results from each sampling interval at each site (table 4.6). These results cannot be directly compared to the field results for P because, although the field and microprobe samples are both measured over a rigid grid interval system, the actual sample size and so the 'sample support' is different (the penetration of the electron beam is only 1μm deep over the area of the raster). These results are therefore examined separately to the field data. The initial problem with the analysis of these results is whether analysis of areas of no soil material *i.e.* soil voids, which result in measurements with very low total oxide percentages, should be considered. These vary in number between soil type and between the grid interval size, so affect the statistical calculations considerably, and direct comparisons between the soil types and the grid interval sizes are therefore more useful after they have been removed. Histograms of the total oxide data from site A and site B (figure 4.2 and 4.3) show the proportion of samples from each site which have a very low total oxide percentage. While there is a continuum of data, the smallest category (up to 5% total oxides) is five times larger at site A, and three times larger at site B than the next category (up to 15%). An arbitrary figure of up to 5% total oxides has been used to indicate an area of void and these void results have been removed from each sampling grid data set.

Figure 4.2: Histogram of total oxide percentages from site A

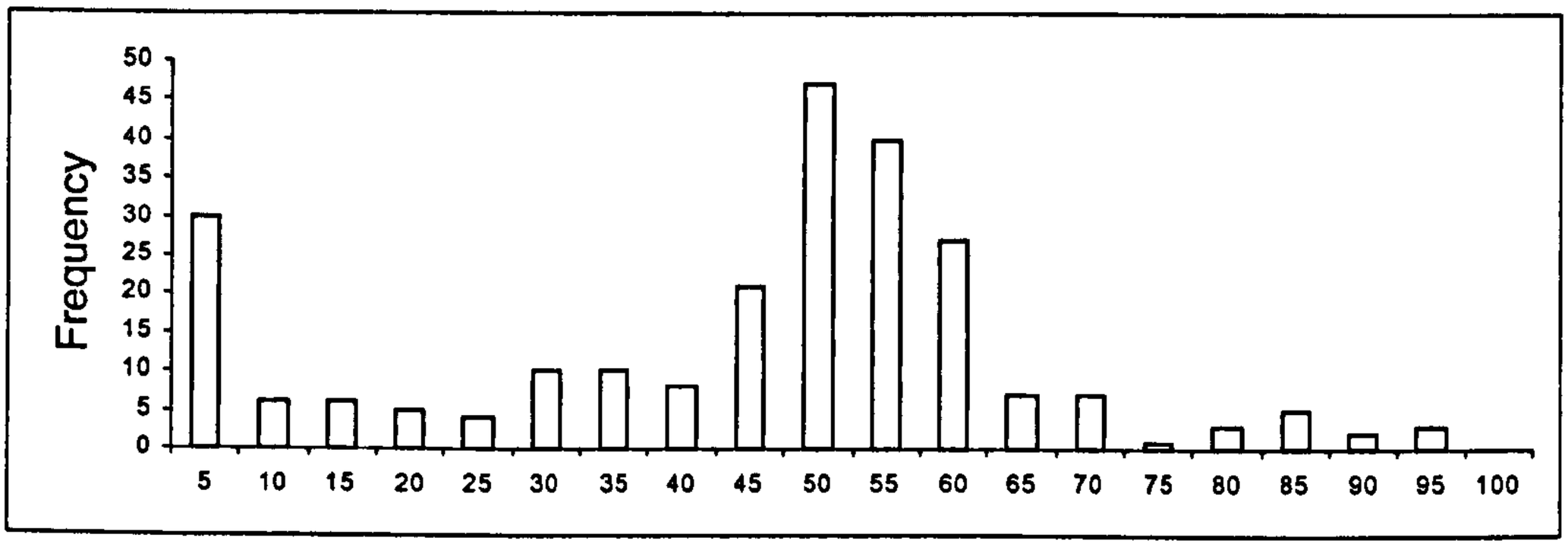
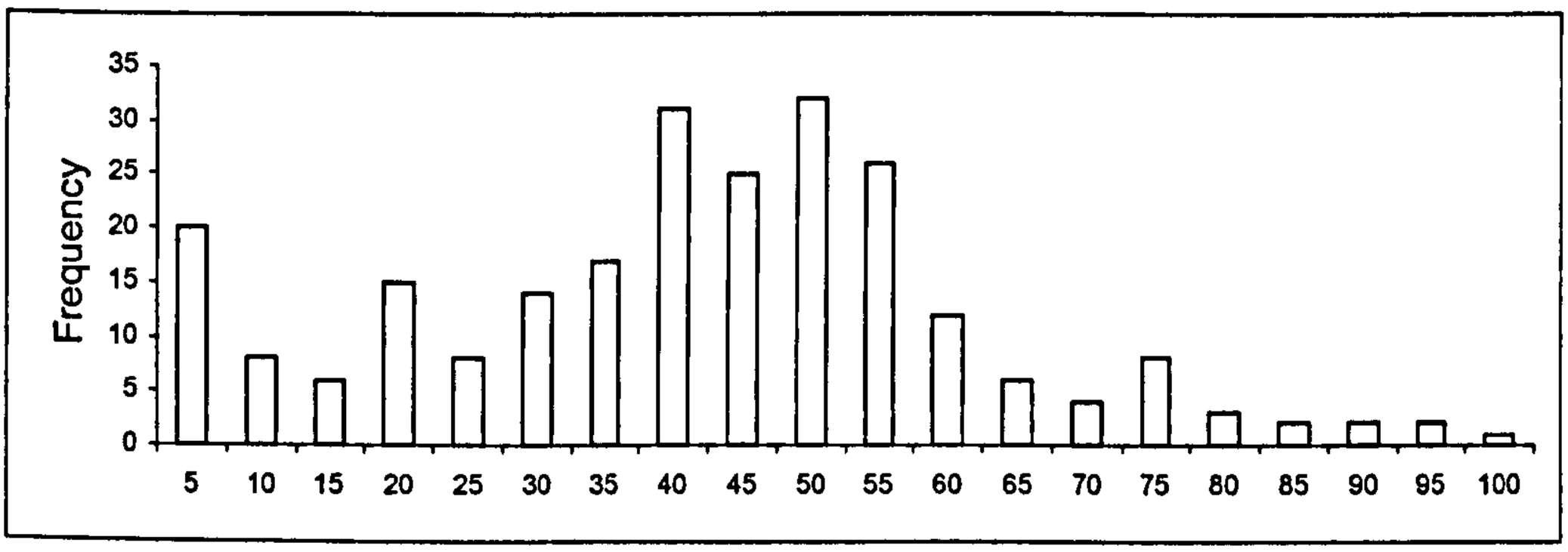


Figure 4.3: Histogram of total oxide percentages from site B



The total number of analyses with greater than 5% total oxides is presented in table 4.3. The number of excluded void results ranges from 3 – 26% and is not consistent for site or sampling interval. The amount of void space varies between soil types, an effect of the soil structure, and it could be argued that the soil voids are inherent and so will form part of the natural variation. However, all other analyses are on a weight basis, not a volume basis, and the number of void samples affects the correlations and description of variation of P in the soil, so the void results are discounted here.

Table 4.3 Microprobe analyses for each site at each sampling interval (minus void results)

Grid interval	Grid area	Raster size	No of results (minus voids)	
			Site A	Site B
1mm (0.001m)	1cm×1cm	50μm square	121 (89)	121 (116)
100μm (0.0001m)	1mm×1mm	50μm square	121 (117)	121 (98)
100μm (0.0001m)	1mm×1mm	5μm point	-	121 (101)
10μm (0.00001m)	100μm×100μm	5μm point	-	121 (113)

4.6.1 Comparison between site A and site B

The results at the two sampling intervals (0.001m & 0.0001m) for the 50μm raster analyses are grouped for each site and described in table 4.4.

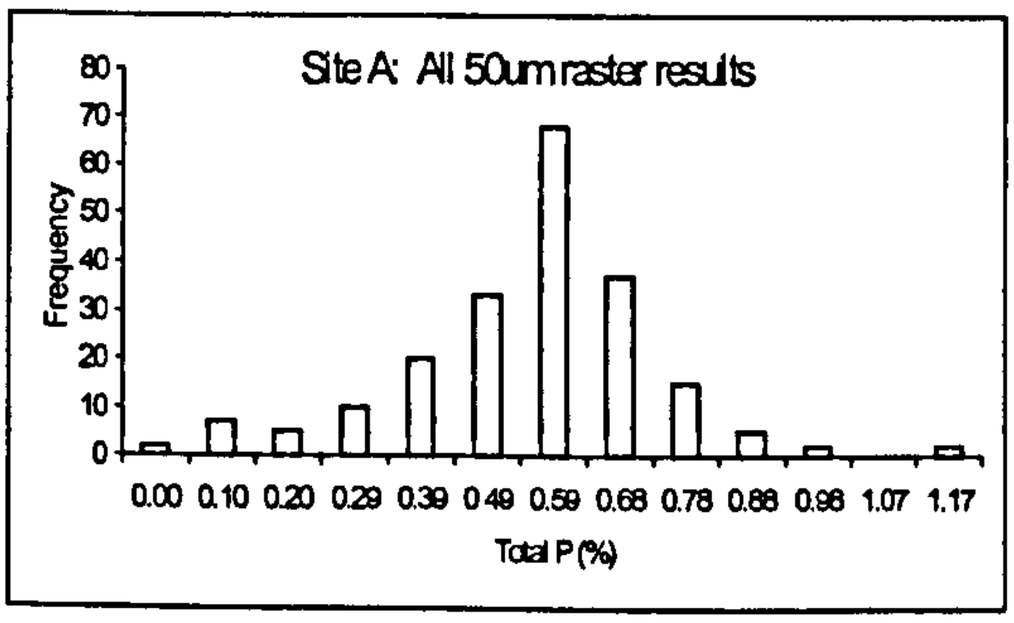
Table 4.4 Descriptive statistics for the microprobe data for the two sites

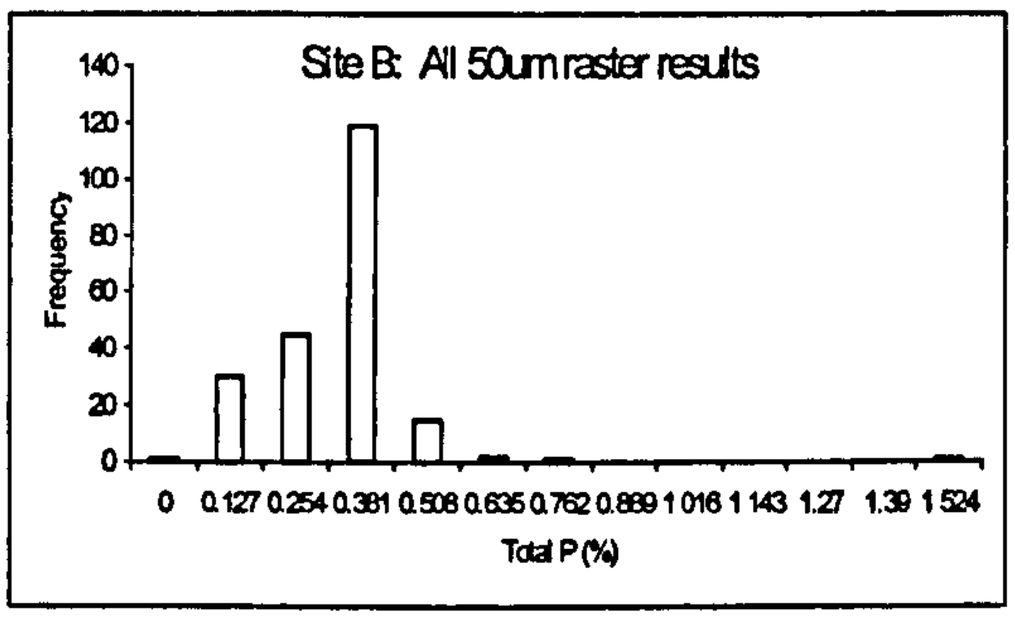
	Site A	Site B
Mean	5036	2724
Standard deviation	1831	1400
Sample variance	3.3×10^6	1.9×10^6
Min - max	0 – 11690	0 – 15222
Coefficient of Variation (%)	36.3	51.4
Count	206	214

The mean P_{tot} values, as measured by the microprobe, are roughly twice as great at site A than site B. This trend in P_{tot} is similar to that measured in the field samples at the macro scale. However the actual amounts measured by microprobe are close to double the amounts measured from the field samples using standard wet chemical techniques. Values of P_{tot} measured over a 50 μm raster are as high as 1.5% at site B, ten times greater than the highest P_{tot} amount measured in the field samples at that site. The reason for this anomaly is not clear and will be considered in more detail in section 4.6.2.

The standard deviation and the sample variance of P_{tot} are higher at site A than at site B, however, the range and the coefficient of variation are greater for site B. This apparent contradiction is because the mean P_{tot} values are quite different and the standard deviation and the sample variance are greater for site A because the mean is twice as high as site B. The CV is a better indication of variation where means differ, and this shows a greater variation at site B. An examination of the histograms (figure 4.4) reveals a close to normal distribution for Site A, and a very peaked distribution for site B, a consequence of there being one very high P_{tot} result (1.52%) from this sampling grid.

Figure 4.4 Histograms of all the 50µm raster data collected by microprobe from each site.



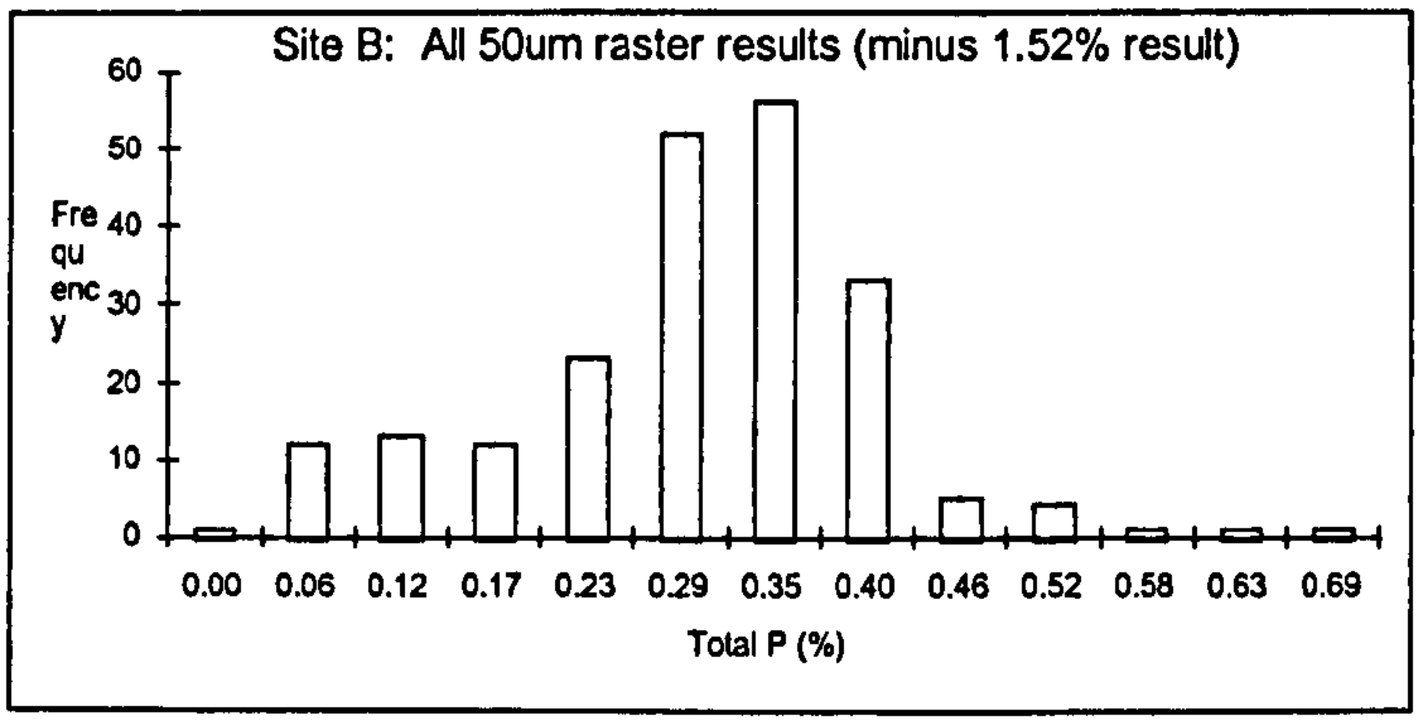


If the one anomalous result is removed the distribution for site B is much closer to normal and the variation of the results is much less, see figure 4.5

Figure 4.5: Histogram and descriptive statistics for site B 50µm raster data, minus one outlier.

Descriptive statistics for all 50 um raster data from site B

Mean	2666
Standard Error	76
Median	2823
Standard Deviation	1106
Sample Variance	1223366
Kurtosis	1.03
Skewness	-0.16
Range	6893
Minimum	0
Maximum	6893
Count	214
CV	41.5



The variation present in the results for site B minus the single anomalous high result is much closer to that of site A, however the CV is still greater even though the mean, variance and range are smaller. There is greater variation in P_{tot} at site B than at site A at sampling intervals smaller than 1cm.

4.6.2 Testing the microprobe by analysis of prepared standards

The results from the microprobe analyses of thin sections from site A and site B are much higher than wet chemical P_{tot} results on soil from the two sites. The wet chemical results have been repeated many times, using a number of methods on soil samples collected from the two sites, all of which produce results for P_{tot} in the same

range (0.05-0.3%). The results from microprobe analyses are up to 5× higher with a range of 0.01-1.5%. To test the microprobe results, a number of standards were made up by mixing powdered Al_2O_3, $FePO_4$, Fe_2O_3, Mn_3O_4, SiO_2, $CaCO_3$ & $CaHPO_4$ in different proportions (reported in appendix I), and pressing out standards which could be mounted on a slide and measured. The theoretical actual elemental proportions (%) and proportions measured by the microprobe (%) are presented in table 4.5. The measured percentage results from the microprobe are all means of between 5-7 replicate analyses.

Table 4.5 Mixed elemental proportions (%) compared with measured microprobe results (%) *ital.*

		Si	Al	Fe	Ca	Mn	P
Std A	mixed %	11.2	18.4	12.0	1.2	4.1	3.0
	measured %	*11.7*	*23.5*	*11.9*	*0.9*	*4.3*	*3.3*
Std B	mixed %	7.5	27.6	8.0	1.4	2.7	2.0
	measured %	*6.3*	*34.7*	*7.8*	*0.8*	*3.2*	*2.2*
Std C	mixed %	16.0	4.6	18.0	1.8	6.2	4.5
	measured %	*15.0*	*6.7*	*21.2*	*2.6*	*7.8*	*5.6*
Std D	mixed %	3.7	6.1	28.2	4.2	16.9	1.0
	measured %	*3.8*	*8.2*	*30.6*	*6.3*	*18.9*	*1.3*
Std E	mixed %	0	0	30.0	0	0	17.0
	measured %	*0*	*0*	*39.1*	*0*	*0*	*20.0*
Std F	mixed %	0	0	0	29.2	0	23.4
	measured %	*0*	*0*	*0*	*34.1*	*0*	*22.6*

The microprobe results are on average 14% different to the mixed elemental proportions, and are not consistently greater or smaller than the theoretical actual values. This is an acceptable result because the consistency of mixing to produce homogenous standards cannot be guaranteed. The microprobe is therefore not over estimating the levels of P in these standards so is unlikely to be over estimating the levels of P in the soil thin sections. The 100%+ difference between microprobe results and wet chemical total P results is not due to the calibration of the probe.

4.6.3 Comparison of sampling intervals

4.6.3.1 A comparison of 0.001m (1mm) and 0.0001m (100μm) sampling intervals

Descriptive statistics have been used (table 4.6) to examine the variation of P_{tot} from both sites at a 1mm and a 100μm sampling grid interval. There are 2 sets of statistics for the smallest sampling interval at site B because the data has been re-examined with the removal of a single outlier which was 5× greater than the mean.

Table 4.6: Descriptive statistics for microprobe data (50μm raster analyses)

	Site A		Site B		
	0.001m	0.0001m	0.001m	0.0001m - 1	0.0001m - 2 (minus outlier)
Mean	4677	5309	2585	2890	2758
Std. error	195	165	86	182	130
Std. deviation	1839	1784	922	1801	1289
Sample variance	3.3×10^6	3.1×10^6	8.5×10^5	3.2×10^6	1.6×10^6
Range	8796	11352	5653	15222	6892
Min. – Max.	0 - 8796	338 - 11690	177 - 5830	0 - 15222	0 – 6892
Coef of variation	39.3	33.6	35.7	62.3	46.7
Count	89	117	116	98	98

At both site A & site B, the mean P_{tot} value increased as the sampling grid interval decreased, however the statistical parameters which are used to describe variation were different at the two sites. At site A the standard deviation, the sample variance and the coefficient of variation are similar at both grid intervals, being slightly greater at the 1mm sampling interval than at the 100μm interval. At site B the standard deviation, the sample variance and the coefficient of variation all increase as the sampling grid interval decreases. There are large differences between the two sets of results for the 0.0001m sampling grid interval at site B, which shows that a single outlying result can have a significant effect on any consideration of variation within a data set.

When examining soil characteristics, it is often found that when the area sampled is increased, the variation present also increases. The greater diversity of soil type and soil conditions encountered within the larger area sampled increase the variability of the characteristics measured. Any soil characteristic which displays this

phenomenon is said to be 'spatially dependent', meaning samples located closer together are more alike than samples collected from positions further apart. At this level of analysis within the soil microfabric, the samples collected from the smallest grid interval (0.0001m) at site B show greater variation than samples collected from the larger grid interval (0.001m). At site A there appears to be little difference in the variation of P_{tot} measured between both sampling grid intervals, therefore P_{tot} does not display spatial dependence at this level of sampling in the soil microfabric.

Correlation matrices for all the elements have been calculated from the results to clarify the variation in P_{tot} discussed above, and are displayed in figures 4.6 – 4.9

Figure 4.6 Site A–0.001m (1mm spacing over 1cm square)

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲▲									
Ca	ns	▼▼▼	▼								
K	▼▼▼	▲▲▲	▲	▼▼							
Mg	ns	▼▼▼	ns	▲▲▲	ns						
Mn	▼▼▼	ns	▲▲▲	ns	ns	ns					
Na	ns	▼▼▼	▼▼	▲▲▲	▼	▲▲▲	ns				
P	▼▼▼	▲▲▲	▲▲▲	ns	▲▲▲	ns	ns	▼			
S	▼▼▼	ns	ns	ns	▲▲▲	▲	ns	ns	▲▲▲		
Cl	▼▼▼	ns	ns	ns	▲▲	▲▲	ns	▲	▲▲▲	▲▲▲	
Total ox	▲▲▲	▼▼▼	▼	ns	▼▼▼	ns	ns	ns	▼▼▼	▼▼▼	▼▼▼

Figure 4.7 Site A– 0.0001m (100μm spacing over 1mm square)

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲									
Ca	▼▼▼	▲▲▲	▲								
K	▼▼▼	▲▲▲	ns	▲▲							
Mg	▼▼▼	▲▲▲	▲▲	▲▲▲	▲						
Mn	▼▼▼	ns	▲▲▲	ns	ns	ns					
Na	▼	▲▲	ns	▲▲	ns	▲	ns				
P	▼▼▼	▲▲▲	▲▲▲	▲▲▲	▲▲▲	▲▲▲	ns	ns			
S	▼▼▼	▲▲▲	ns	▲▲▲	▲▲	▲▲▲	ns	▲	▲▲▲		
Cl	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	
Total ox	▲▲	▼▼▼	ns	▼▼▼	▼▼	▼▼	ns	ns	▼▼▼	▼▼▼	ns

Figure 4.8 Site B-0.001m (1mm spacing over 1cm square)

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲									
Ca	ns	ns	ns								
K	▼▼	▲▲▲	ns	ns							
Mg	▼▼▼	▲▲▲	ns	▲▲	ns						
Mn	▼▼	ns	ns	ns	ns	ns					
Na	▼▼	▲▲	ns	ns	ns	▲▲	ns				
P	▼▼▼	▲▲▲	▲▲	ns	▲	ns	ns	ns			
S	ns	ns	ns	▲▲▲	ns	ns	ns	ns	▲▲		
Cl	ns	ns	ns	▲▲	ns	ns	ns	ns	ns	▲	
Total ox	▲▲	▼▼	▼	ns	ns	ns	ns	ns	▼▼▼	▼▼▼	▼

Figure 4.9 Site B-0.0001m (100μm spacing over 1mm square)

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲									
Ca	ns	ns	ns								
K	▼▼▼	▲▲▲	ns	ns							
Mg	▼▼▼	▲▲▲	▲▲	ns	▲▲						
Mn	▼▼▼	▲	ns	ns	ns	ns					
Na	▼▼	▲▲▲	ns	ns	ns	ns	ns				
P	▼▼▼	▲▲▲	▲▲	▲	▲▲	▲▲▲	ns	ns			
S	▼	ns	ns	▲▲	ns	ns	ns	ns	▲▲▲		
Cl	ns	ns	ns	ns	ns	▲▲	ns	ns	▲▲	▲▲	
Total ox	▲▲▲	▼▼▼	ns	▼	▼	▼▼▼	ns	ns	▼▼▼	▼▼	▼▼▼

Key to symbols			Fig 4.6	Figs 4.7, 4.8 & 4.9
▲	Positively correlated	P= 0.5	r = 0.205	r = 0.195
▲▲	Highly positively correlated	P = 0.1	r = 0.267	r = 0.254
▲▲▲	Very highly positively correlated	P = 0.01	r = 0.338	r = 0.321
▼	Negatively correlated	P = 0.5	r = -0.205	r = -0.195
▼▼	Highly negatively correlated	P = 0.1	r = -0.267	r = -0.254
▼▼▼	Very highly negatively correlated	P = 0.01	r = -0.338	r = -0.321
ns	Not significantly correlated			

A number of points can be highlighted from the four correlation matrices.

1. Si consistently, very significantly, correlates negatively with many of the other elements, and very significantly, positively correlates with total oxides. This is because the mineral quartz (SiO_2) is a common component (~30% of the 2mm-2μm fraction) in these two soils. The samples measured in areas with little void space, *i.e.* high total oxides, are likely to be dominated by quartz grains, and therefore the amount of Si measured will be high while all the other element oxides will be lower.
2. Phosphorus consistently, very significantly, correlates positively with Fe and Al. In these acidic soils P is commonly associated with aluminium and iron oxy and hydroxy ions.

3. Phosphorus also consistently, very significantly, correlates negatively with total oxides as does Al and S, so when the percent total oxides is low, the percentages of these elements is high. This suggests that commonly these elements are associated with the surfaces of the solid phases in soils and so samples with high proportions of these elements will also contain a high proportion of void area, so total oxide levels will be low.
4. There is a significant negative correlation between Cl and total oxides, twice in four sets of analyses, and between Cl and Si once in four sets of analyses. If Cl were a good indicator of resin, and therefore void content, it should consistently, significantly correlate negatively with both these. Cl therefore, does not offer an accurate method of recording the amount of resin measured in each raster.

4.6.3.2 A comparison of 0.0001m (100μn) and 0.00001m (10μn) sampling interval

A 1mm square grid at a 100μm sampling interval, and a 100μm square grid at a 10μm sampling interval were examined at site B using a defocused 5μm beam. Descriptive statistics (table 4.7) have been applied to examine the variation in P_{tot} over these two squares. These results cannot be compared to the previous ones over a larger sampling interval because the size of the analysis area is different, so the method of data collection does not have the same sample 'support'. The raster size had to be reduced tenfold to a defocused beam because the 10μm sampling interval was too small to allow analysis with a 50μm × 50μm square raster.

Table 4.7 Descriptive statistics for two sampling intervals from site B

Descriptive statistics for microprobe data (defocused 5μm beam analyses)

	0.0001m	0.00001m
Mean	2799	1834
Std. error	230	100
Std. deviation	2309	1062
Sample variance	5.3×10^6	1.1×10^6
Min. - Max.	0 - 17026	0 - 5178
Coef of variation	82.5	57.9
Count	101	113

The results from the two sampling intervals are quite different. At the larger sampling interval, the mean and coefficient of variation are roughly 1.5× greater than at the smaller sampling interval, the standard deviation is 2× and the variance nearly 5× as great. As the sampling interval increases from 10μm to 100μm the variation in P_{tot} measured at site B increases. As a smaller area of soil is examined from a 1mm square to a 100μm square, the constituent components of the soil could share a closer derivation, and hence a more similar P content. A smaller area of soil would also have experienced the same pedogenic conditions of P mobilisation and leaching and so be more uniform. These factors could account for the lower variation over the smaller sampling square, so at this level, P at this site displays some spatial dependence.

At this resolution of sampling the correlation of P_{tot} with the other elements analysed can be examined and compared for each sampling interval (figure 4.10 & 4.11)

Figure 4.10: Site B–0.0001m (100μm spacing over 1mm square, defocused beam analyses)

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲▲									
Ca	ns	ns	ns								
K	▼▼▼	▲▲▲	▲▲	ns							
Mg	▼▼▼	▲▲▲	▲▲▲	ns	▲▲▲						
Mn	▼▼▼	ns	ns	ns	ns	ns					
Na	▼▼▼	▲▲▲	▲▲▲	ns	▲▲▲	▲▲▲	ns				
P	▼▼▼	▲▲▲	▲▲▲	ns	▲▲▲	▲▲▲	ns	▲▲▲			
S	▼▼▼	▲▲	ns	▲▲▲	▲▲▲	▲▲▲	ns	▲▲▲	▲▲▲		
Cl	ns	ns	ns	▲	ns	ns	ns	ns	ns	▲▲▲	
total ox	▲▲▲	▼▼▼	▼▼▼	ns	▼▼▼	▼▼▼	ns	▼▼▼	▼▼▼	▼▼▼	▼▼

Figure 4.11: Site B-0.00001m (10μm spacing over 100μm square, defocused beam analyses)

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲▲									
Ca	ns	ns	ns								
K	▼▼▼	▲▲▲	▲▲	ns							
Mg	▼▼▼	▲▲▲	▲▲▲	ns	▲▲▲						
Mn	▼▼	▲	▲▲▲	ns	ns	ns					
Na	▼▼▼	▲▲▲	▲▲	ns	▲▲▲	▲▲	ns				
P	▼▼▼	▲▲▲	▲▲▲	▲▲▲	▲	▲▲▲	▲	▲▲▲			
S	▼▼	ns	▲▲▲	▲▲▲	ns	▲	ns	▲▲	▲▲▲		
Cl	ns	ns	ns	▲▲▲	ns	ns	ns	ns	▲▲▲	▲▲▲	
total ox	ns	ns	ns	▼	ns	ns	ns	ns	▼▼	▼▼▼	▼▼

Key for figure 4.10 & 4.11

▲	Positively correlated	P= 0.5	r = 0.195
▲▲	Highly positively correlated	P = 0.1	r = 0.254
▲▲▲	Very highly positively correlated	P = 0.01	r = 0.321
▼	Negatively correlated	P = 0.5	r = -0.195
▼▼	Highly negatively correlated	P = 0.1	r = -0.254
▼▼▼	Very highly negatively correlated	P = 0.01	r = -0.321
ns	Not significantly correlated		

There is little difference between the associations of the elements measured over these two sampling intervals. Most elements significantly correlate negatively with Si, which is likely to be due to the predominance of quartz in the >2μm fraction, and P significantly positively correlates with Al, Fe, K, Mg, Na and S at a 100μm sampling interval and with Al, Fe, Ca, Mg, Na and S at a 10μm sampling interval. Few elements correlate with total oxides at the smallest (0.00001m) sampling interval, which could indicate that the defocused beam analyses measured few voids over this sample square.

4.6.4 Comparison of analysis area size

Two sizes of analyses were conducted at site B; the standard 50μm square raster analysis with the centre of the square corresponding to each grid node, and a smaller 5μm defocused beam analysis on each grid node, both sizes of analysis being made at a 100μm grid interval. Comparisons are made between the two analysis sizes (table 4.8) but these can only be considered very generally because differences are to be expected with the variation in size of area analysed.

Table 4.8 Descriptive statistics for two analysis sizes from site B

	50μm raster analysis	5μm point analysis
	0.0001m	0.0001m
Mean	2890	2799
Std. error	182	230
Std. Dev.	1801	2309
Sample var.	3.2×10^6	5.3×10^6
Min. – Max.	0 - 15222	0 - 17026
Coef. of var.	62.3	82.5
Count	98	101

When the size of an analysis area is decreased from a 50μm raster to a 5μm diffuse point, the mean P_{tot} measured is hardly altered (2890 – 2799 μg g^{-1}), however the variation in P_{tot} measured over the sampling grid increases, the standard deviation (1801 – 2309), sample variance (3.2×10^6 – 5.3×10^6) and the CV% (62 – 82) all increase significantly. The variation in P_{tot} measured surrounding the mean has increased because the 5μm point is more likely to measure whole areas or individual mineral grains within the sample area, which could have high or low P values. Most 50μm raster analyses will have some void areas within them, but probably cover areas of high and low P so amounts measured will even out, producing less variation in P results.

4.6.5 Textural analysis

The soil texture is important when considering the distribution of P within the soil, because P is reported to be mainly associated with the silt and clay size fractions, although this is dependent on the soil type (Williams & Saunders, 1956). The amounts of each size fraction within the soil will have a bearing on the total P concentration and its distribution. The texture of the soil from site A & B has been measured (table 4.9), and the P_{tot} content of each fraction measured before and after 'cleaning' with dithionite, to remove any Fe oxide/clay coatings.

Table 4.9 Proportions of sand, silt and clay with P_{tot} contents before and after treatment with dithionite in the soils from site A & B (textural classes calculated from triangular diagram, pp24. Hodgson, 1976).

		Site A			Site B		
		%	P_{tot} ($\mu g\ g^{-1}$)		%	P_{tot} ($\mu g\ g^{-1}$)	
				+ dithionite			+ dithionite
Sand	(2mm-63µm)	**16**			**41**		
	(2mm-630µm)		*1180*	*190*		*480*	*80*
	(630µm-200µm)		*1170*	*180*		*300*	*70*
	(200µm-63µm)		*830*	*150*		*250*	*90*
Silt	(63µm-2µm)	**54**	*1120*	*140*	**27**	*140*	*80*
Clay	(<2µm)	**30**	*5840*	*320*	**32**	*1930*	*210*
Textural class		Silty clay loam			Clay loam		

The soil from site A has a lower proportion of sand, but much more silt than site B, amounts of clay for both soils are similar. The P_{tot} contents for each size fraction vary between the two sites but in a similar order. Most noticeable is the large P_{tot} content within the clay fraction of each site, being 4-5 times greater than the P_{tot} content of the other size fractions. However, once each size fraction is 'cleaned' with dithionite to remove the iron oxide and clay coatings the P_{tot} contents, while remaining in a similar order, are much lower. This is a clear demonstration of the association of P in the soil with the surface coatings of sand, silt and clay, this fraction of P accounting for between 2 to 18 times more than the 'component' P within these constituents.

4.7 Discussion

The majority of published work on the variation and distribution of soil properties has been at the field level (1 hectare or greater), the early work having been reviewed by Beckett & Webster (1971). The advancement of fertiliser delivery technology means that work on the distribution of soil properties at a field level is becoming more important, in an attempt to streamline the costs of agronomic practices. However, work on the distribution of soil properties over a 'micro' scale is rare. The elemental composition and distribution of soil properties at a 'micro' scale can be examined with a microprobe, which incorporates either energy

dispersive X-ray analysis, or wavelength dispersive X-ray analysis. The limitations are that only a small area of the soil, commonly less than 2cm×4cm on a thin section can be analysed, and the production of soil thin sections is a lengthy process. Any such analyses can only provide a 'window' into the characteristics of a particular soil because only one small section of the soil is examined. The examination of the distribution of P in a soil thin section is useful because the soil micro-structure remains intact, and it is within this structure at the scales examined using a microprobe (1cm - 1μm) that the fine plant roots and root hairs spread through the soil, the proximity of the roots to the soil material being of primary importance to nutrient uptake. The distribution of P in the soil at this scale is dependent on the soil textural class and the arrangement of these soil constituents (sand, silt and clay) as well as organic matter. The variation present will be dependent on the composition and homogeneity of the parent material and subsequent pedogenic and environmental factors acting on the soil (*e.g.* Qureshi & Jenkins, 1987) .

An unresolved problem with the use of the microprobe for the measurement of the % elemental composition of soils is that, in this study, it appears to have over-estimated the P content. The results are often more than double those obtained by standard wet chemical and X-ray fluorescence (XRF) techniques. Tests of the microprobe method have shown that a set of standards pressed from well homogenised AnalaR chemicals are not overestimated (section 4.6.2) and the P and Ca content of bone in thin section is measured accurately by the microprobe (section 5.5.3). If the actual values measured by the microprobe are not correct, the method cannot be used quantitatively for soils in thin section, however they can be used with a semi-quantitative proviso and the results are still useful for the examination of the distribution and the variation of elements at this scale in the soil.

The variation in P over the two soils is not consistent, at site A there is little difference between the variation at the two sampling intervals (0.001m & 0.0001m), virtually all the variation which is present over a 1cm square being present over a 1mm square. However, at site B there are greater differences between the two sampling intervals, and the variation which is present over a 1mm square is ~30% greater than that present over a 1cm square. It can be concluded that at these scales of sampling, it is difficult to generalise between soils, and pedogenic differences

will influence variation at this scale. The position of the sampling grid will also be important, and it is likely that if it were moved to another part of the thin section, the results could be considerably different. Only one sampling grid could be measured for each interval at each site, and to check the accuracy and precision of these results would require expensive replication, so the differences that are present over the thin section for each site could not be assessed.

Comparisons between the analysis area size revealed large differences between a 50μm square raster analysis area and a 5μm defocused beam. These differences are because the raster is able to average points of high and low P over the 50μm square whereas the diffuse point measured individually high and low areas of P. In other soils with textural differences there may not be as large a variation between these sizes of analysis, the heterogeneity of P at this level in the soil microfabric is dependent on the nature and size of individual mineral grains, concretions and the composition of the surrounding matrix.

Soil characteristics are known to display spatial dependence (Webster & Oliver, 1990), so their variation increases as the area examined increases up to a certain point where an increase in area does not add to the variation. This description is based on studies looking at the variation in soil from a 1m sampling interval to much larger sampling intervals. At this 'micro' scale of sampling, the soil does not display the same spatial dependence, and at site B a reduction in sampling area leads to an increase in the variation of P measured.

PHOSPHORUS MOBILITY AND REDISTRIBUTION

5.1 Introduction

The mobility of P in soils has been an area of agronomic study since the early work of Bouldin & Black (1954) on P diffusion in soils. There are a host of subsequent papers considering the theoretical (*e.g.* Cho, 1991) and practical (*e.g.* Eghball *et al.*, 1990) movement of P from fertiliser sources in the soil and the implications for fertiliser practice and crop growth. However, only a limited amount is known about the mobility of P in broader environmental terms, because much of the work appears to have been done on lowland soils. Many archaeological excavations take place on upland sites, in soils which are predominantly acidic, and phosphate surveys across these sites can be a useful source of information because under upland environmental conditions some artefacts, such as bone, can completely disappear. The movement of P from bone in these environments requires investigation to aid the interpretation of P survey results. An experimental column system was set up to examine the movement and redistribution of P from emplaced bone within an acidic upland soil leached with organic acids. These columns provide a controlled environment from which observations can be made, and which can be dismantled and analysed at the end of the experiment.

The second half of this chapter examines the redistribution of P in thin sections of cinerary urns prepared for a provenance and classification study (Williams & Jenkins, 1999). These urns have a potential concentrated P and Ca source in the form of cremated bone, and isotropic orange brown cutans, which could be evidence of P translocation were identified in an initial study of the thin sections. These cutans were of a similar appearance to those identified in recent work conducted on the sediments of Pontnewydd Cave, a Lower Palaeolithic hominid cave site in North Wales. The Pontnewydd study provided an opportunity to investigate P redistribution within the examination of the chemistry, mineralogy and micromorphology of a sediment column containing a bone-rich layer from within the cave (Jenkins, 1997). Cutans of a Ca-Fe-phosphate were identified, resulting from the translocation and redeposition of P from the bone-rich layers above, taking place over 200,000 years of neutral to alkaline conditions. The method

of translocation of P was not decided, but could have been in solution with precipitation at depth, or as colloidal material of appropriate composition.

5.2 Methods for the experimental column systems

5.2.1 Column design

Twenty glass and plastic columns (cross sectional area of 7.00cm^2) were filled with a brown earth soil (*Denbigh* series Rudeforth *et al.*, 1984) and a brown podzolic soil (*Manod* series *op.cit.*) to a total volume of 175cm^3, both soils being air dried and sieved <2mm. The glass tubes were covered to prevent algal growth. Pieces of weathered rabbit bone roughly 3.5cm in length, with the epiphyses removed and the core filled with soil, were placed in the centre (vertically and radially) of each experimental tube. Control tubes were also constructed of each soil type with no bone added.

5.2.2 Leaching regime

The columns were leached with (i) 0.05M acetic acid (*p*H 2.3) and (ii) carbon dioxide saturated water (from a soda syphon) (*p*H 4.4) for 30 weeks. Each week a total of 135mls of leachate was added to each column over a period of 7.5 hours, this amount of leachate corresponds to levels of precipitation for North Wales uplands (*i.e.* 1000cm^3 /cm^2/year). The leachate draining from the base of each column was collected.

5.2.3 Chemical analysis

The volume of leachate collected from each column was recorded. Phosphate was measured colorimetrically as described in section 3.5.2 (detection limit of 0.01 μg ml^{-1}), calcium was measured using a Jenway PFP7 flame photometer (detection limit of 0.5μg ml^{-1}), iron and aluminium were measured using air/acetylene flame and nitrous oxide/acetylene flame respectively on a Varian Spectre-AA (atomic absorption) Spectrophotometer, with detection limits of 0.1μg ml^{-1} for Fe and 0.5 μg ml^{-1} for Al. At the end of the leachate application the soil was carefully removed from all the plastic columns and sequentially sampled every 5mm down the column. Each 5mm section was milled in a Heiko ball mill and sub-sampled for P_{tot} analysis using the method described in 3.5.2. Sixty five of the 5mm sections

collected from the areas of 12 columns surrounding the emplaced bone were separated into the inner 1.5cm and the outer 1.5cm concentric samples before milling, to contrast the P_{tot} levels at the centre and the outside of the soil column.

5.2.4 Column layout and summary

Column No	Soil type	Tube type	Bone / no bone	Leachate
1	Bs	plastic	bone	CO_2 sat. water
2	Bs	plastic	bone	CO_2 sat. water
3	Bs	glass	bone	CO_2 sat. water
4	Bs	plastic	no bone	CO_2 sat. water
5	Bs	glass	no bone	CO_2 sat. water
6	Bw	plastic	bone	CO_2 sat. water
7	Bw	plastic	bone	CO_2 sat. water
8	Bw	glass	bone	CO_2 sat. water
9	Bw	plastic	no bone	CO_2 sat. water
10	Bw	glass	no bone	CO_2 sat. water
11	Bs	plastic	bone	0.05M acetic acid
12	Bs	plastic	bone	0.05M acetic acid
13	Bs	glass	bone	0.05M acetic acid
14	Bs	plastic	no bone	0.05M acetic acid
15	Bs	glass	no bone	0.05M acetic acid
16	Bw	plastic	bone	0.05M acetic acid
17	Bw	plastic	bone	0.05M acetic acid
18	Bw	glass	bone	0.05M acetic acid
19	Bw	plastic	no bone	0.05M acetic acid
20	Bw	glass	no bone	0.05M acetic acid

5.2.5 Impregnation and thin section production

At the termination of leachate application all the glass columns were air-dried and impregnated with an acetone-diluted monostyrene resin using the method described in section 4.2 (Fitzpatrick, 1984). When cured, a number of thin sections were made from each column, in transverse section (TS) through the soil and bone (figure 5.1) and in longitudinal section (LS) through the lower portion of the bone and into the soil matrix directly below it (figure 5.2). The thin sections were polished using 6μm, 3μm and 1μm diamond paste and examined under temporary oil-mounted cover slips using a petrographic light microscope.

5.2.6 Microprobe analysis

Three thin sections were selected for analysis by the Cameca, Camebax Microprobe with Link analytical AN10000 (10/85s) analysis system, using Link Spectra microprobe automation software, and link ZAF4 FLS data correction software at the

Electron Probe Unit, Manchester University. A suite of 11 elements (P, Si, Al, Fe, Mn, Mg, Na, K, Ca, S, and Cl) were measured in each thin section, in a series of 100μm raster analyses moving 50μm between each analysis, radially out from the bone in the TS slides and vertically down from the bone in the LS slide.

Figure 5.1: TS
soil column with bone

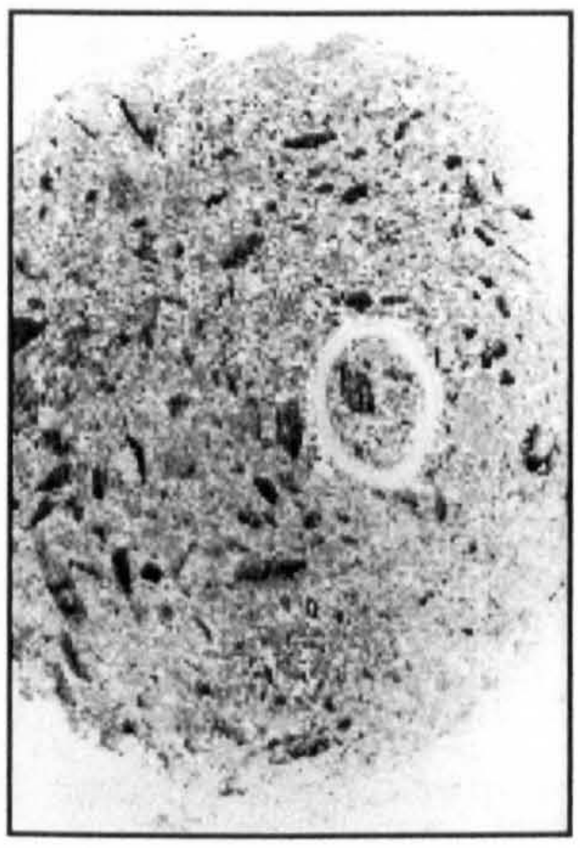
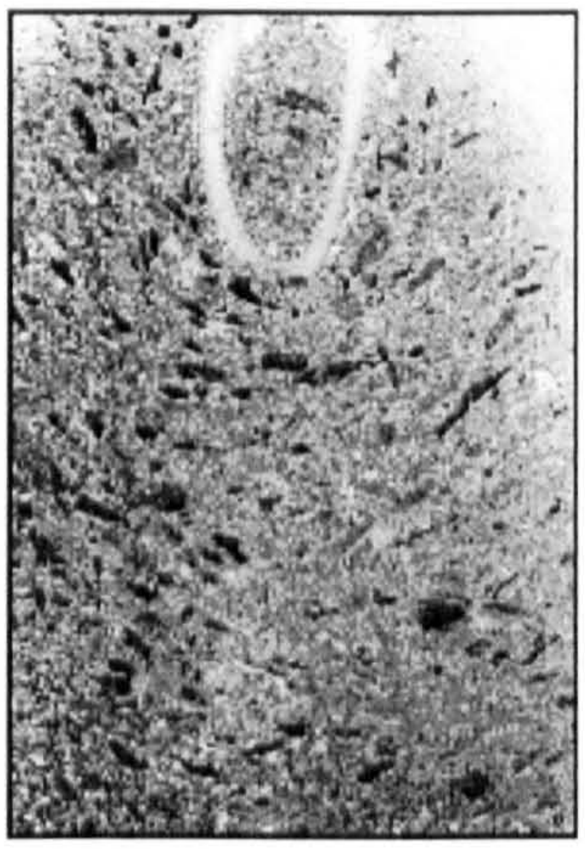


Figure 5.2: LS
soil column with bone



5.3 Results for the experimental column systems

5.3.1 Leachate analysis

The soil columns were leached for 30 weeks during which time roughly 80 leachate samples were collected (25mls each). The leachate samples were analysed for P, Ca, Fe and Al . The full set of results are presented in appendix I. The results for the initial leachate samples from each column are displayed in table 5.1 & 5.2.

Table 5.1 Initial Ca, Fe, Al & P concentrations (μg ml^{-1}) in the leachates collected from the columns leached with CO_2 saturated water

CO_2 sat. water leached columns

Bs soil – columns with bone

No	Ca	Fe	Al	P
1	**15**	**1**	**107**	<
5	**1**	<	**7**	<
10	**1**	<	**2**	<
15	<	<	**1**	<

Bs soil – columns without bone

No	Ca	Fe	Al	P
1	**17**	<	**163**	<
5	**2**	<	**4**	<
10	**3**	<	**4**	<
15	<	<	**1**	<

Bw soil – columns with bone

No	Ca	Fe	Al	P
1	**681**	<	**3**	<
5	**8**	<	**2**	<
10	**14**	<	**3**	<
15	**35**	<	**2**	<

Bw soil – columns without bone

No	Ca	Fe	Al	P
1	**594**	<	**3**	<
5	**15**	<	**3**	<
10	**10**	<	**3**	<
15	**32**	<	**2**	<

Table 5.2 Initial Ca, Fe, Al & P concentrations (μg ml^{-1}) in the leachates collected from the columns leached with 0.05M acetic acid

0.05M acetic acid leached columns

Bs soil – columns with bone

No	Ca	Fe	Al	P
1	19	<	81	<
5	<	<	12	<
10	<	<	5	<
15	<	<	4	<

Bs soil – columns without bone

No	Ca	Fe	Al	P
1	19	<	44	<
5	1	<	3	<
10	<	<	3	<
15	<	<	1	<

Bw soil – columns with bone

No	Ca	Fe	Al	P
1	150	<	3	<
5	22	<	4	<
10	13	<	1	<
15	8	<	1	<

Bw soil – columns without bone

No	Ca	Fe	Al	P
1	135	<	3	<
5	19	<	2	<
10	26	<	2	<
15	<	<	3	<

Only the initial results are shown in tables 5.1 & 5.2 because after the first few leachate samples the results for each element dropped below the detection limits and remained at this level until the end of the experiment (roughly leachate sample number 80). There was no significant removal of P, Ca, Fe or Al from the soil or the bone into the leachate over the course of the experiment, only an initial pulse of Ca and Al. Differences are apparent between the two soil types; some Al leached out initially from the Bs soil, and some Ca leached out initially from the Bw soil, however levels decline quickly. There are also initial differences between the two leaching agents; the 0.05M acetic acid leaches less Ca, and Al from the columns than the CO_2 saturated water.

5.3.2 Total P analysis of the soil columns

5.3.2.1 Sequential column samples

The phosphorus content of sequential soil samples taken from each plastic soil column were measured as described in section 5.2.4. The complete results are presented in appendix I. The mean results are plotted in figures 5.3-5.6

The four figures illustrate differences between the columns with bones and the columns without bones, but only in the area of the column surrounding the bone. No detectable differences in amounts of P were observed above and below the area of the bone. There is no overall significant increase in P down the column, however

Figure 5.3: Sequential Ptot contents of soil samples collected at 5mm intervals down column 1 (Bs soil, CO_2 saturated water leachate)

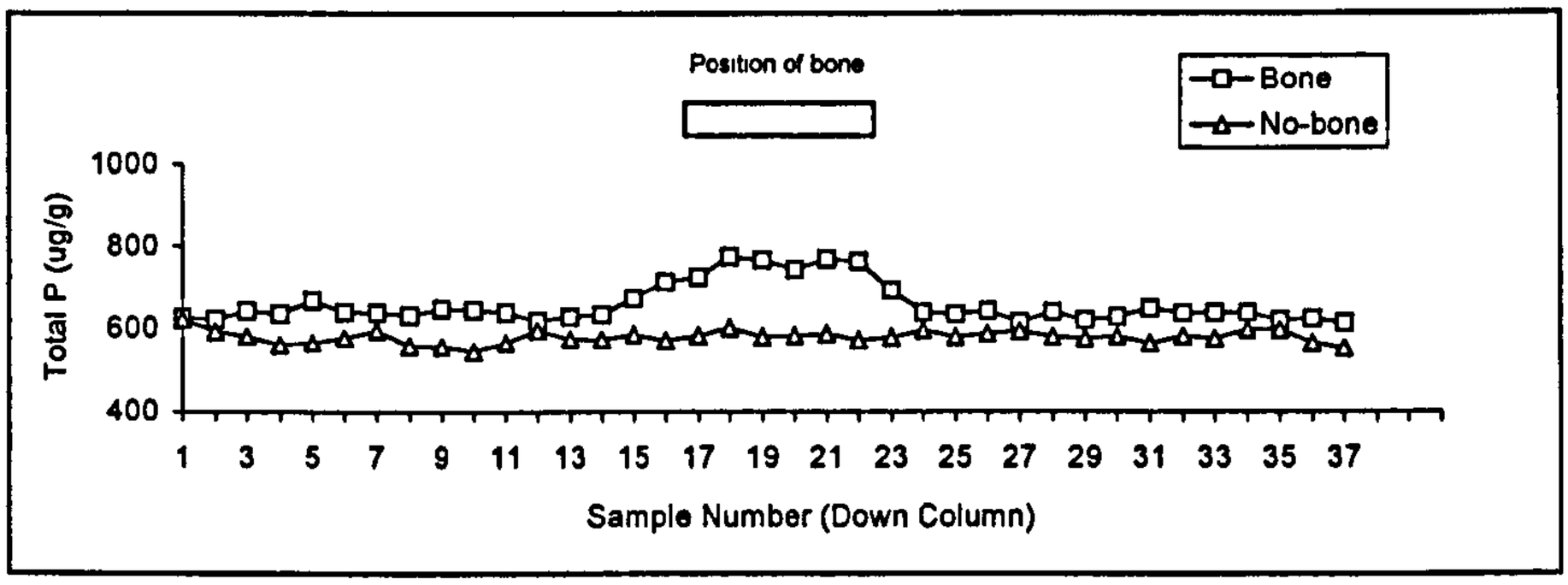


Figure 5.4: Sequential Ptot contents of soil samples collected at 5mm intervals down column 2 (Bw soil, CO_2 saturated water leachate)

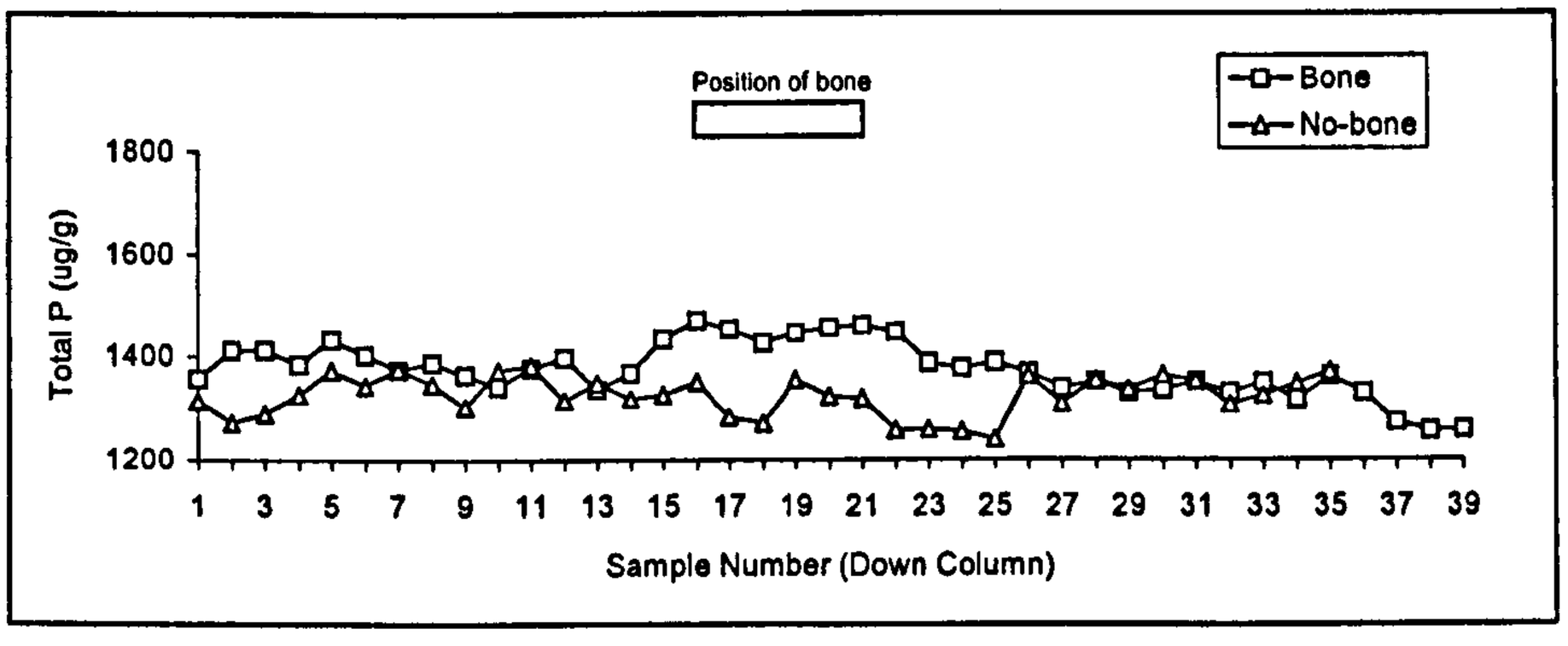


Figure 5.5: Sequential Ptot contents of soil samples collected at 5mm intervals down column 3 (Bs soil, 0.05M acetic acid leachate)

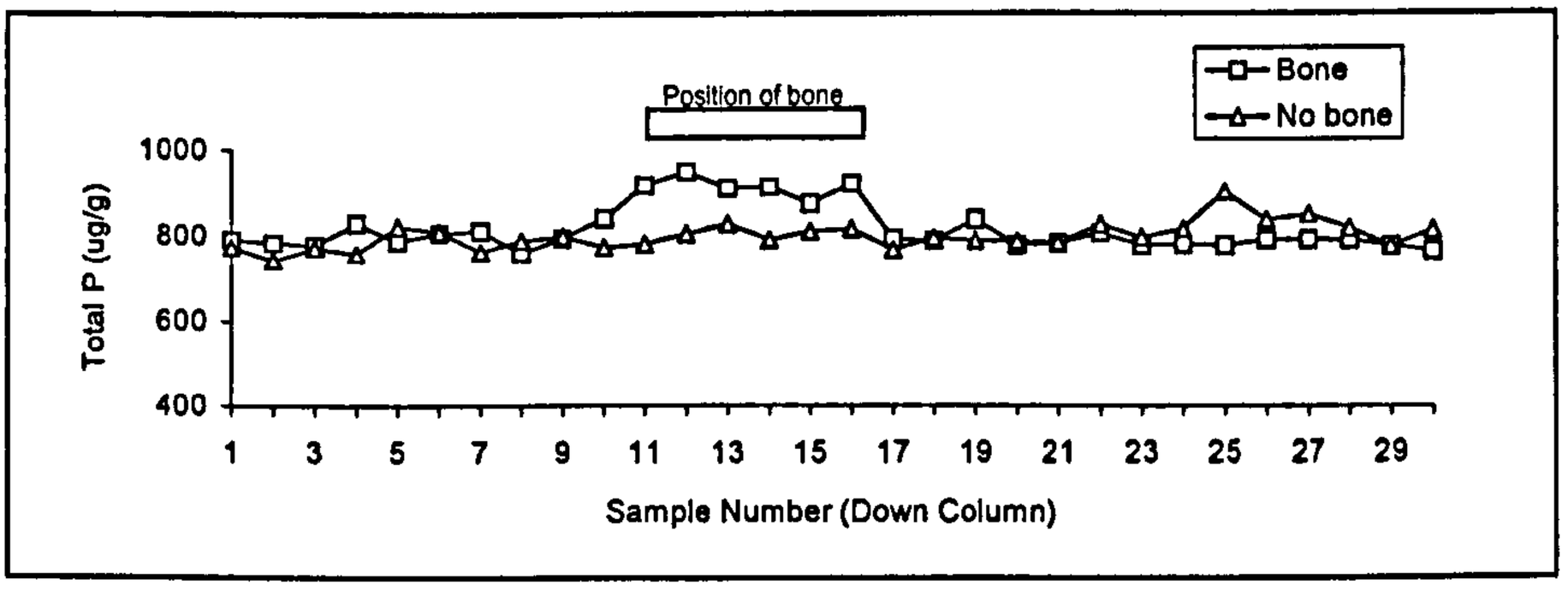
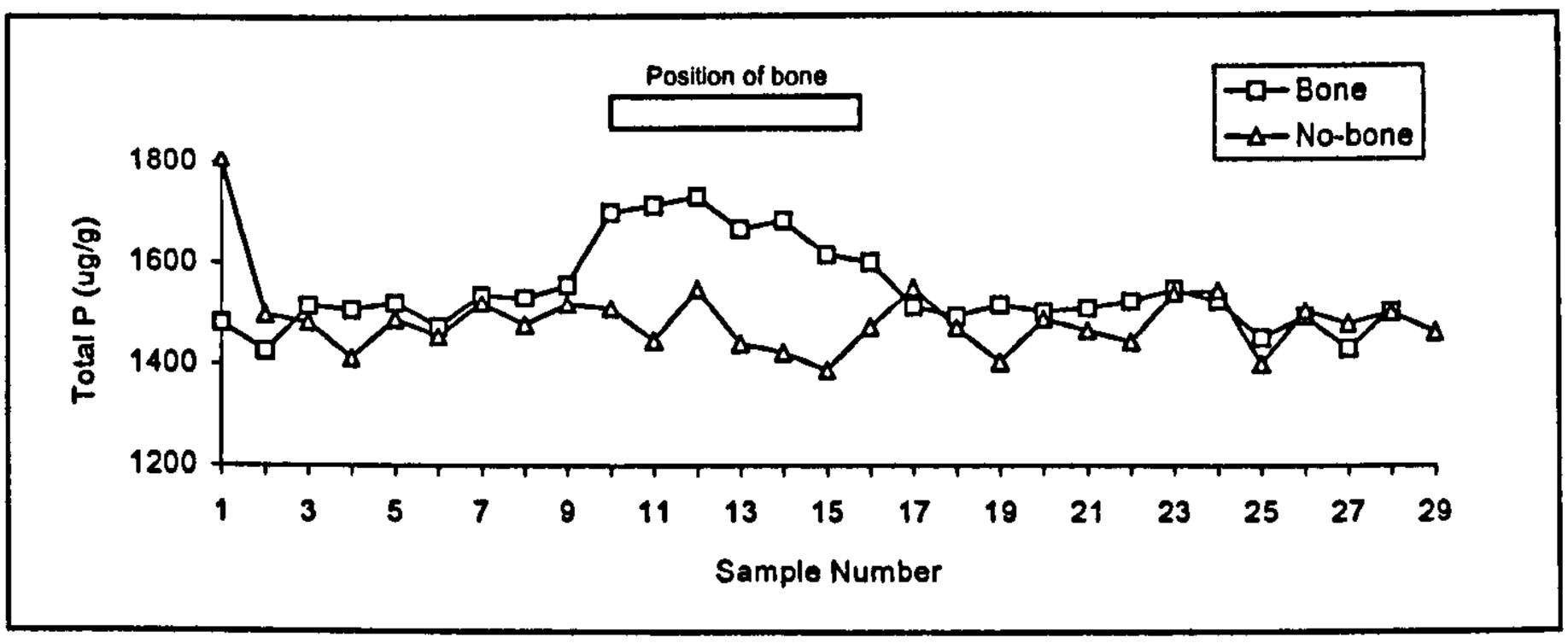


Figure 5.6: Sequential Ptot contents of soil samples collected at 5mm intervals down column 4 (Bw soil, 0.05m acetic acid extract)



P could be being diffused radially out from the bones and redistributed within the soil matrix.

5.3.2.2. Concentric P samples

Concentric samples were collected from each soil column. Two concentric samples, the inner 15mm Ø and the outer 15mm of soil surrounding the bone were collected from all the columns, to determine whether there was any difference in the P_{tot} concentration radially away from the emplaced bone. Samples were collected from a similar position in the columns without bone for comparison. The complete results are produced in appendix I. The mean results are produced in table 5.3

Table 5.3: Mean P_{tot} ($\mu g\ g^{-1}$) amounts measured in inner and outer samples taken surrounding the bone in the soil columns

	Number	P_{tot} inner	P_{tot} outer	
CO_2 saturated water leached columns				
Bs soil – with bone	10	880	660	*Significant @ P=0.01*
Bs soil without bone	4	584	583	*Not significant*
Bw soil – with bone	13	1980	1460	*Significant @ P=0.01*
Bw soil without bone	4	1328	1280	*Significant @ P=0.05*
0.05M Acetic acid leached columns				
Bs soil – with bone	11	1042	795	*Significant @ P=0.01*
Bs soil without bone	6	816	787	*Not significant*
Bw soil – with bone	12	1816	1564	*Significant @ P=0.01*
Bw soil without bone	5	1429	1479	*Not significant*

There are significant differences between the columns with bone and the columns without bone. Both the Bs and Bw soil types under each leachate application containing bone, displayed significant differences in P_{tot} contents between inner and outer samples. Whereas 3 of the 4 columns without bone had no significant differences in P_{tot} contents between inner and outer samples. It is possible that under both leachate regimes P is being mobilised from the bone and is diffusing laterally from the bone. However the columns could only be sampled crudely and a cross section of the column was only divided into two samples, an inner and an

outer one, splitting the radius of the column into two as evenly as possible. A more accurate sampling strategy could reveal more.

5.3.3 Analysis of the soil columns by microprobe

Thin sections of the impregnated glass tubed soil columns were made in TS and LS surrounding the bone as described in section 5.2.5. Four thin sections were examined by microprobe, identified in table 5.4

Table 5.4 Thin sections analysed by microprobe

Number	Soil type	Bone/no bone	Leachate	Column section
1	Bs	bone	CO_2 sat water	transverse
2	Bs	bone	0.05M acetic acid	transverse
3	Bs	bone	0.05M acetic acid	longitudinal
4	Bw	bone	0.05M acetic acid	transverse

A suite of 11 elements were measured in these thin sections as described in section 5.2.6. The full results are produced in appendix I. The results for P_{tot} can be seen in figures 5.7-5.11

Figure 5.7: % P measured along transverse section away from the bone:

Bs soil; CO_2 saturated water leachate

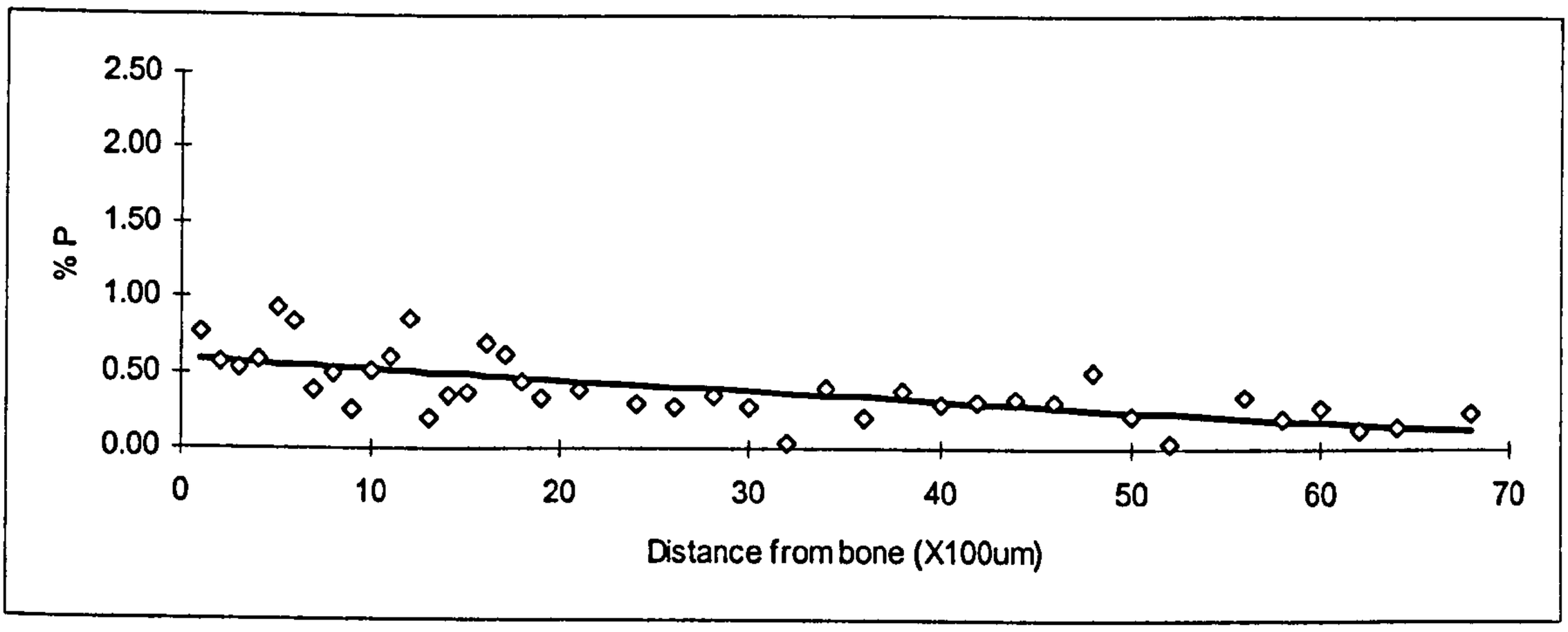


Figure 5.8: % P measured in transverse section, away from the bone.

Bs soil; 0.05M acetic acid leachate

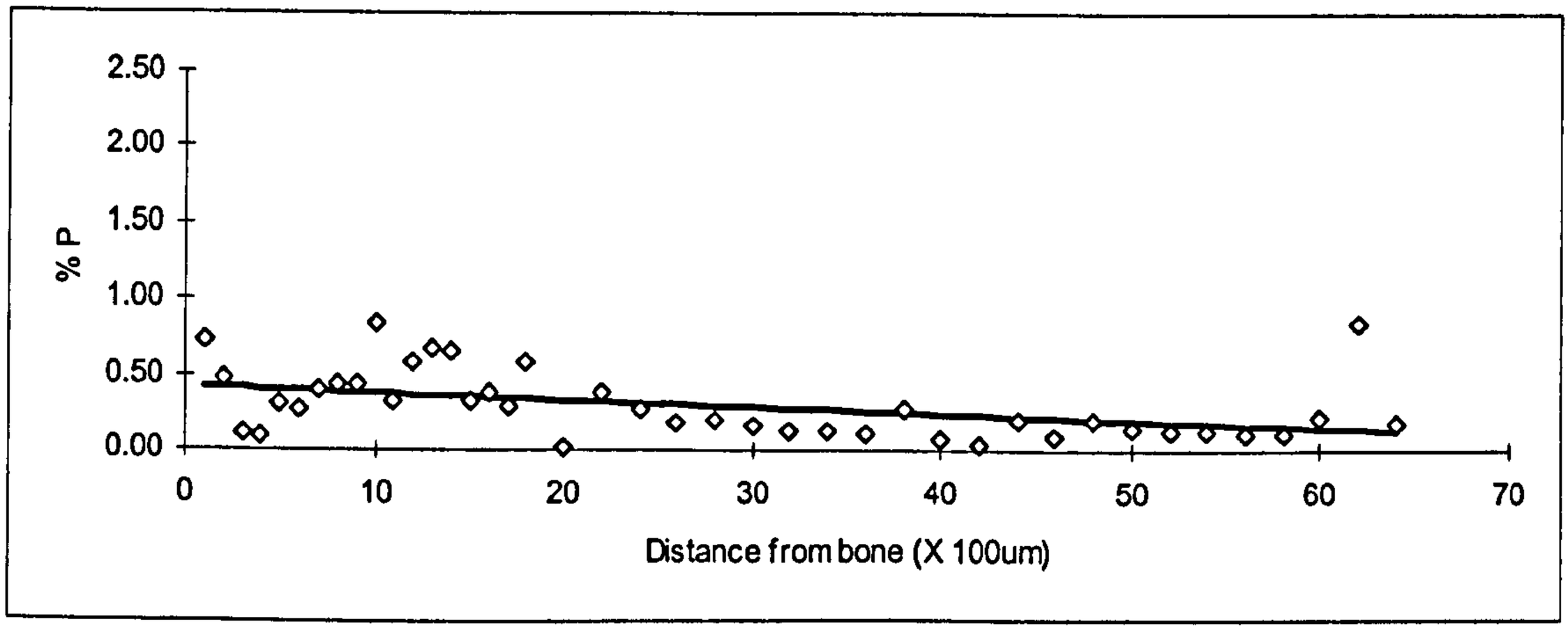


Figure 5.9: % P measured in longitudinal section, away from the bone.

Bs soil; 0.05M acetic acid leachate.

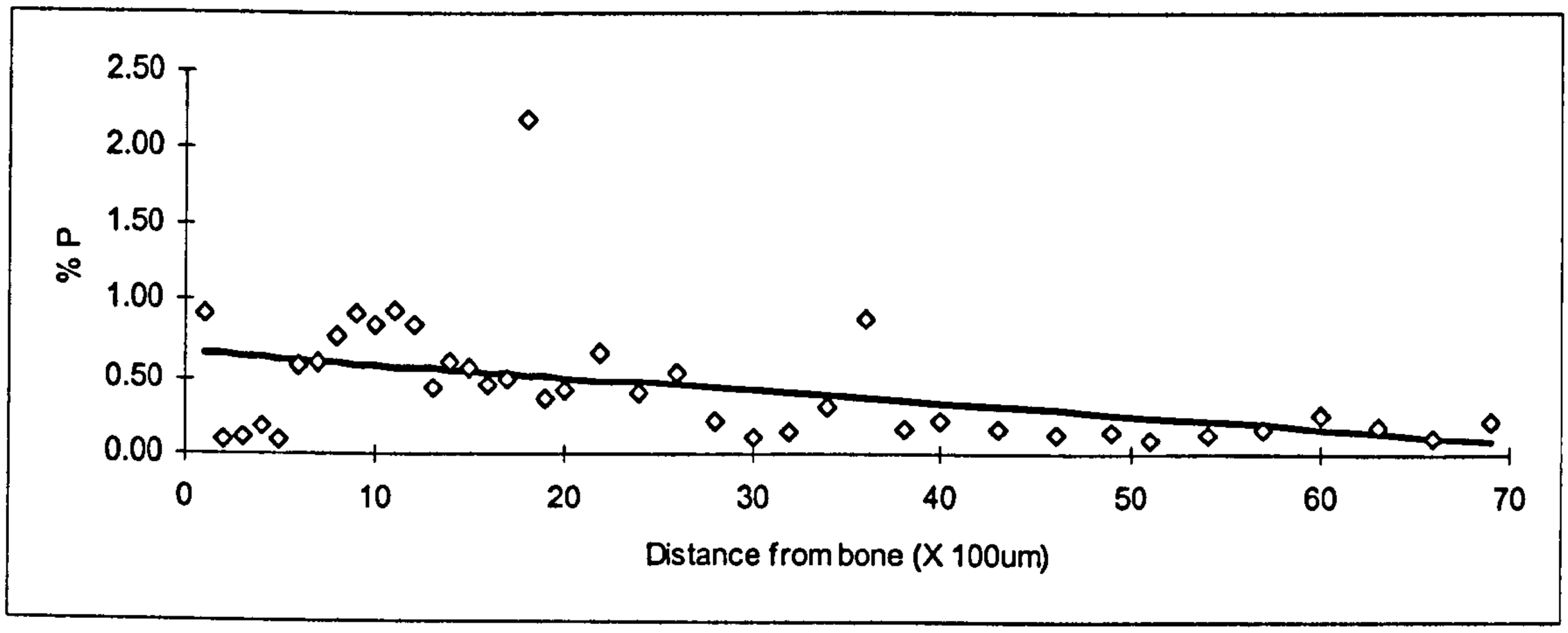
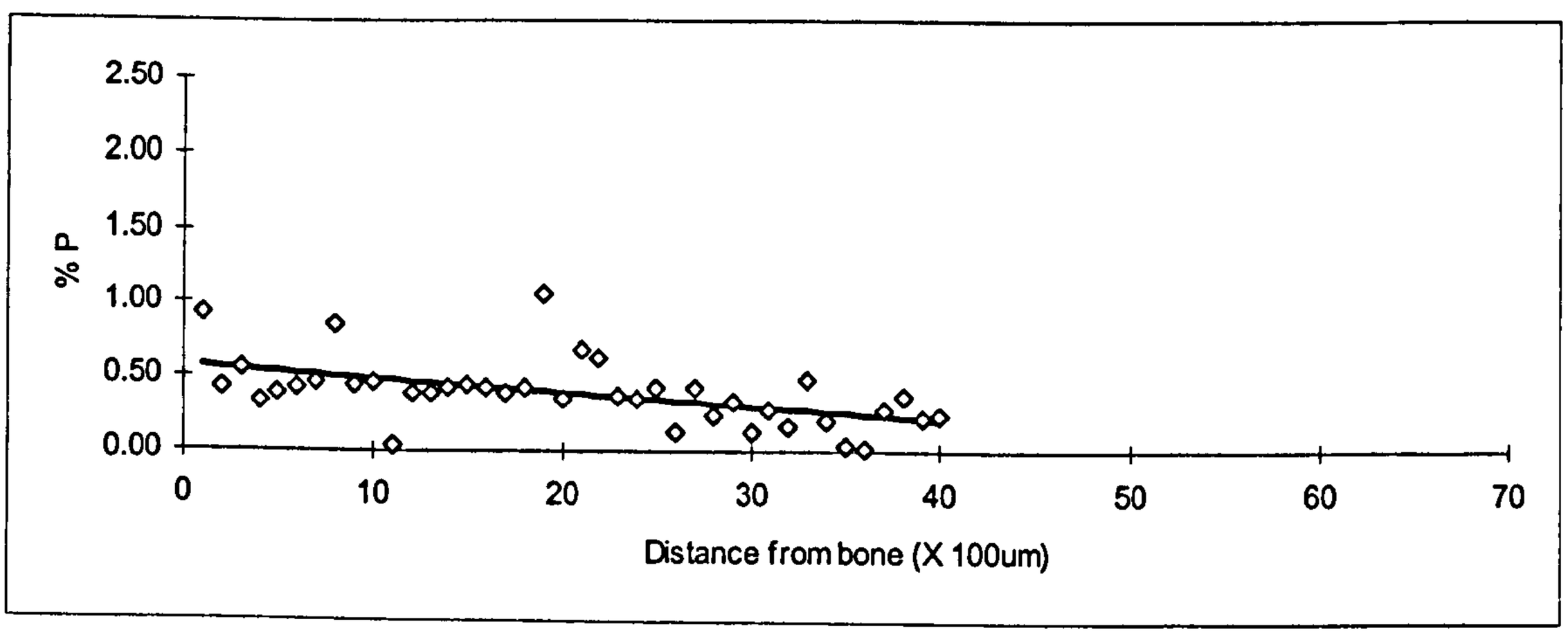


Figure 5.10: % P measured in transverse section, away from the bone.

Bw soil; 0.05M acetic acid leachate.



The P_{tot} content of the soil in these columns reduces laterally as the distance from the bone increases, as indicated in the lines of best fit on figures 5.7, 5.8, & 5.10. The P_{tot} content of the soil in the column also reduces as the distance below the bone increases (see figure 5.9). The effect is similar for both soil types and leaching agents. The distances over which the change in P_{tot} was measured were small, only 4mm for figure 5.10 and up to 7mm for figures 5.7-5.9. The values of P_{tot} appear large, over 2 % P in one case, but are commonly around 0.4 % P (4000 $\mu g\ g^{-1}$) for both soil types. These values are much greater than values of P_{tot} measured for the same soil using wet chemical methods (perchloric acid digestion followed by colorimetric measurement of orthophosphate in solution, see section 3.5.2) where the Bs soil is consistently ~ 800$\mu g\ g^{-1}$ and the Bw soil ~1900$\mu g\ g^{-1}$. This would suggest that either measurement by microprobe is overestimating the P_{tot} content or the wet chemical method is underestimating the P_{tot} content. This problem was reported in section 4.6.2 but no solution was obtained. It is difficult to conceive that the microprobe is overestimating the P_{tot} value, because in this section of work, fourteen measurements were made on areas of bone with no soil matrix. The mean percentage measured for Ca in the bone was 38.50, and the mean percentage measured for P was 18.75. These results agree very well with recognised percentages for Ca and P of bone dry weight; 38.7% & 19.6% (Dojlido & Best, 1993) or 37.3% & 16.4% (Eastoe, 1961).

The decrease in P_{tot} in the soil further from the bone could be because P is being mobilised from the bone as the columns are leached, then adsorbed onto the Fe and Al oxides and hydroxides within the soil matrix, a small distance from the bone. The increase in the P_{tot} amount only appears to be over the initial 1-2 mm from the bone. Other studies concentrating on the movement of P from point sources of fertiliser have observed a movement of ^{32}P of up to 7 cm after two weeks of soil leaching (Bouldin & Black, 1954). P movement, mainly by diffusion, was found to be dependent on the bulk density of the soil (Hira & Singh, 1977), and the moisture content, highlighting the importance of the soil texture (Mahtab, *et.al.*, 1971). These studies differ because the fertiliser P used will be more soluble than the P in bones so the movement of P in the soil will be enhanced.

The deposition of P within the soil matrix is likely to be associated with the Fe and Al components of the soil. Correlation matrices of all the % results from the microprobe are produced in figures 5.11 - 5.14.

Figure 5.11: Correlation matrix for all elements measured by microprobe. Bs soil; bone; CO_2 saturated water leachate; transverse section

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲									
Ca	▼▼	ns	ns								
K	▼▼	▲	ns	ns							
Mg	ns	ns	▲	ns	ns						
Mn	ns	ns	ns	ns	ns	ns					
Na	ns	ns	ns	▲	ns	ns	ns				
P	▼▼	ns	▲▲▲	▲▲▲	ns	ns	ns	ns			
S	▼▼▼	▲▲	ns	▲	ns	ns	ns	ns	ns		
Cl	▼▼	▲▲	ns	ns	ns	ns	ns	ns	ns	▲▲▲	
total ox.	▲▲▲	ns	▼▼	▼▼	ns	ns	ns	ns	ns	▼▼▼	▼▼▼

Figure 5.12: Correlation matrix for all elements measured by microprobe. Bs soil; bone; 0.05M acetic acid leachate; transverse section

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲									
Ca	ns	ns	ns								
K	▼▼	▲▲▲	ns	ns							
Mg	▼▼▼	▲▲▲	▲	ns	▲						
Mn	▼▼▼	ns	▲▲▲	ns	ns	ns					
Na	▼	▲▲	ns	ns	ns	ns	ns				
P	▼	ns	▲	▲▲	ns	ns	▲	ns			
S	ns	ns	ns	▲▲▲	ns	ns	ns	ns	▲		
Cl	ns	ns	ns	▲▲▲	ns	ns	ns	ns	ns	▲▲▲	
total ox.	▲	ns	ns	▼▼▼	ns	ns	ns	▼	▼	▼▼▼	▼▼▼

Figure 5.13: Correlation matrix for all elements measured by microprobe. Bs soil; bone; 0.05M acetic acid leachate; longitudinal section

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲▲▲									
Ca	▼▼▼	▲▲▲	▲								
K	▼▼▼	▲▲▲	ns	ns							
Mg	▼▼	▲	▲▲▲	ns	ns						
Mn	ns	ns	▲▲	ns	ns	ns					
Na	ns	ns	ns	▲▲▲	ns	▼	ns				
P	▼▼▼	▲▲▲	▲▲	▲▲▲	ns	ns	ns	▲▲▲			
S	▼▼▼	▲▲▲	▲	▲▲▲	ns	ns	ns	▲▲▲	▲▲▲		
Cl	▼▼	▲	ns	▲▲▲	ns	ns	ns	▲▲▲	▲▲▲	▲▲▲	
total ox.	▲▲	▼▼	ns	▼▼▼	▼▼	ns	ns	▼	▼▼▼	▼▼	▼▼▼

Figure 5.14: Correlation matrix for all elements measured by microprobe. Bw soil; bone; 0.05M acetic acid leachate; transverse section

	Si	Al	Fe	Ca	K	Mg	Mn	Na	P	S	Cl
Al	▼▼▼										
Fe	▼▼▼	▲									
Ca	ns	▼▼	ns								
K	▼▼	▲▲▲	ns	▼▼							
Mg	ns	▼▼	ns	▲▲▲	▼▼						
Mn	ns	ns	ns	ns	ns	ns					
Na	▼▼▼	▲▲	ns	ns	▲	ns	ns				
P	▼▼▼	▲▲	▲▲	ns	ns	ns	ns	▲▲			
S	▼	ns	ns	ns	ns	ns	ns	▲	ns		
Cl	ns	ns	ns	ns	ns	ns	ns	▲▲▲	▲	▲▲▲	
total ox.	▼▼▼	▼▼	ns	ns	▼	ns	▼	▼▼▼	▼▼	▼▼▼	▼▼▼

The r values used to calculate the significance of figures 5.11 – 5.14

▲	Positively correlated	P= 0.5	r = 0.304
▲▲	Highly positively correlated	P = 0.1	r = 0.393
▲▲▲	Very highly positively correlated	P = 0.01	r = 0.490
▼	Negatively correlated	P = 0.5	r = -0.304
▼▼	Highly negatively correlated	P = 0.1	r = -0.393
▼▼▼	Very highly negatively correlated	P = 0.01	r = -0.490
ns	Not significantly correlated		

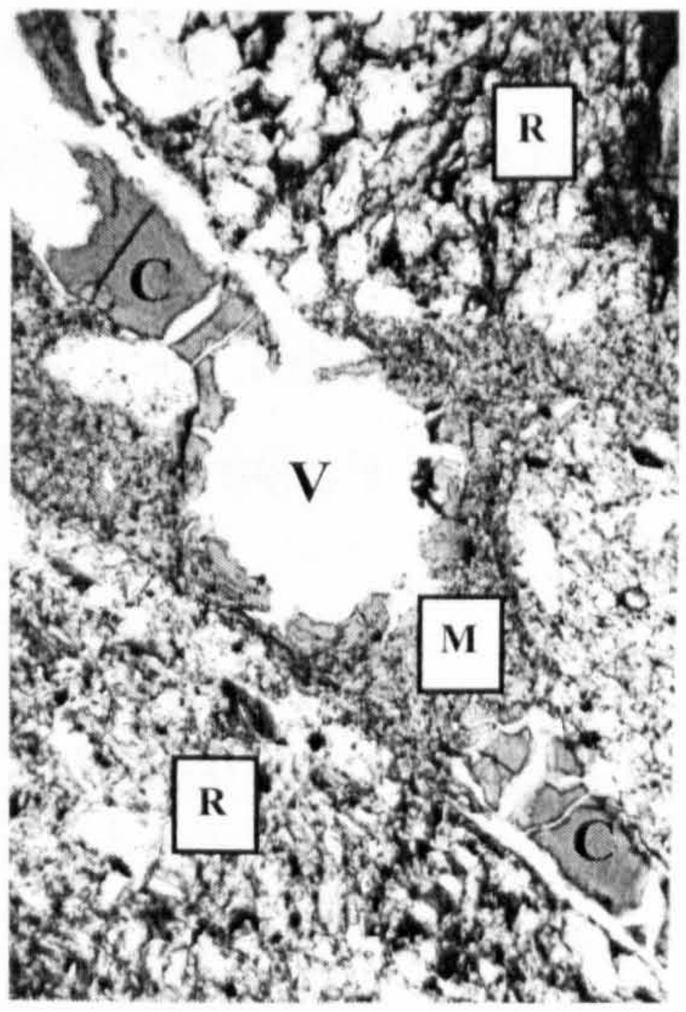
P only consistently and significantly correlates with Fe, although there are some differences between soil types. P correlates highly significantly with Fe and Al in the Bw soil, whereas in the Bs soil, P correlates with Fe and Ca in each case. P does not correlate consistently with any other element. In the Bw soil, Al and Fe appear to be important for the fixation of P, whereas in the Bs soil Fe and Ca seem to play a similar role. Si consistently significantly highly negatively correlates with most other elements, because samples which have high Si content will usually be predominantly quartz so few other elements will be present. S and Cl consistently very highly significantly positively correlate with each other, and both negatively correlate with % total oxides because they are both constituents of the impregnating resin.

5.4 Methods for the analysis of cinerary urns

5.4.1 Selection of cinerary urn sherds

A number of cinerary urn sherds were available for examination from a collection held for a pre-existing provenancing and classification study, however only a few had been found to display isotropic cutans similar to those described from the Pontnewydd sediments (figure 5.15). Five sherd thin sections, all displaying the isotropic cutans, were selected for further micro-analysis. The total phosphorus contents of a further 45 sherds available were also measured. If the sherds were to contain phosphatic cutans then their total P content would be expected to be higher when compared with cutan free sherds. A finely ground sample (0.2g) of each sherd was digested in perchloric acid at 200°C (Sommers & Nelson, 1972) and orthophosphate was measured in the digest as described in 3.5.2.

Figure 5.15
Soil micrograph showing isotropic P rich cutan



V = void
C = cutan
R = rock fragment
M = matrix between rock fragments

5.4.2 Production of thin sections

Each of the selected sherds had been impregnated using a polystyrene resin, and when cured, thin-sections prepared following the process described by Fitzpatrick, (1984) and Murphy, (1986), and polished using 6μm, 3μm and 1μm diamond pastes. Initial examination of the slides was under temporary oil-mounted cover slips on a petrographic microscope for routine fabric analysis.

5.4.3 Microscopic analysis

Selected portions of the slide were identified, photographed, mounted on a stub, coated with carbon and examined in a Hitachi S520 Microscope fitted with a Link QX2000-I/LZ4 detector system. Elemental X-ray spectra were obtained using point and raster analyses from which semi-quantitative results for P, Fe, Al, Ca, Mn & Si were calculated by reference to a sequence of standards prepared from analar/spectro-pure chemicals. Quantitative analysis of a single sherd and a selection of standards was obtained using a Cameca, Camebax Microprobe with Link analytical AN10000 (10/85s) analysis system, using Link Spectra microprobe automation software and link ZAF4 FLS data correction software at the Electron Probe Unit, Manchester University. This analysis was carried out to check the semi-quantitative results obtained from the Hitachi S520.

5.5 Results of the analysis of the cinerary urns

5.5.1 Total P content of cinerary urn sherds

The P_{tot} content of 45 available cinerary sherds were measured. The sherds are identified by a 2 letter site code followed by a number code (table 5.5)

Table 5.5: P_{tot} values for the cinerary sherds

ID Code	P content ($\mu g\ g^{-1}$)	ID Code	P content ($\mu g\ g^{-1}$)	ID Code	P content ($\mu g\ g^{-1}$)
CM1	2810	PP2	910	BB1	1560
CM2	2960	PP4	1990	BB2	1630
CM3	3000	LL4	2270	BB3	3930
CM4	5290	LL5	1550	BB4	3430
CM5	1340	LL6	2180	BB5	3470
CM8	2260	LL7	1520	BB6	4320
CM9	2210	LL8	2030	BB7	3560
CM10	2060	TR1	4280	BB8	3300
CM11	4640	TR2	2200	BB9	2310
CM12	2060	TR4	640	BB49	1430
CM13	2330	TR5	6140	BB1836	5910
CM14	1370	TR6	1500		
CM15	2060	TR12	1300		
CM15A	2930	MG2	1480		
CM17	2390	MG3	1030		
CM18	2450	MG4	1980		
CM19	2060	MG5	1360		

Three sherds had already been selected for analysis before the P_{tot} analyses had been conducted, on the basis of the presence of cutans identified by light microscopy. To these three, CM4 and CM11 were added on the basis of their high P_{tot} levels (5290 & 4640μg g^{-1} respectively). TR5 and BB1836 were noted as having high P_{tot} levels so possibly P cutans but were not included in the set for analysis because of logistical restrictions of time. The five sherds analysed were CM4, CM5, CM11, BF1 & PP1. P_{tot} analyses were not conducted on sherds BF1 and PP1 because no sherd material was available.

5.5.2 Selected elemental composition of the sherds

The actual analytical results as percent oxides for all five sherds and 15 standards is presented in appendix I. The % elemental composition for each sherd is calculated from the results for the standards and displayed in table 5.6

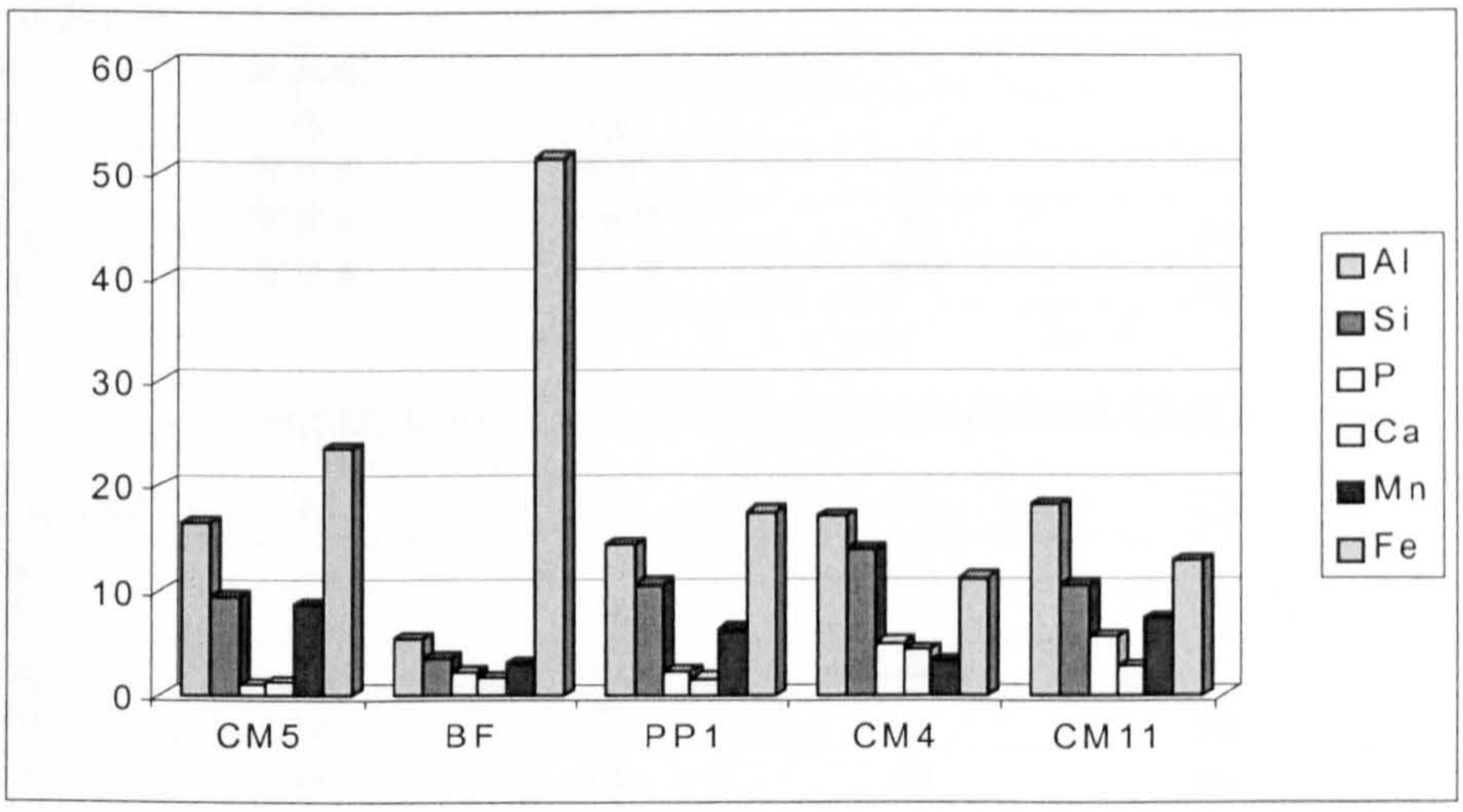
Table 5.6: Selected elemental composition (%) for the 5 sherds

	Al	Si	P	Ca	Mn	Fe
CM5 (N=13)						
Mean	16.54	9.52	0.91	1.12	8.68	23.54
Std. Dev.	*2.49*	*2.95*	*0.45*	*0.22*	*3.35*	*6.14*
Min-Max	*13.3-21.2*	*4.8-15.4*	*0.1-1.5*	*0.8-1.5*	*2.7-14.5*	*14.0-31.4*
BF (N=19)						
Mean	5.34	3.48	2.16	1.64	2.94	51.37
Std. Dev.	*2.88*	*0.69*	*0.78*	*2.42*	*1.54*	*12.88*
Min-Max	*2.7-13.6*	*2.8-6.0*	*0.8-3.5*	*0.5-9.5*	*0-4.6*	*14.0-60.3*
PP1 (N=26)						
Mean	14.4	10.7	2.2	1.6	6.3	17.4
Std. Dev.	*4.28*	*2.59*	*0.40*	*0.39*	*3.30*	*7.79*
Min-Max	*7.3-21.9*	*5.8-15.5*	*1.0-2.9*	*0.9-2.4*	*0.1-13.3*	*5.7-36.1*
CM11 (N=10)						
Mean	16.99	13.99	4.96	4.33	3.28	11.18
Std. Dev.	*3.67*	*4.40*	*2.13*	*2.31*	*4.12*	*6.66*
Min-Max	*11.9-22.7*	*9.4-21.0*	*2.6-10.4*	*2.5-9.7*	*0-10.5*	*1.3-20.3*

CM4 (N=20)						
Mean	18.14	10.55	5.52	2.84	7.34	12.87
Std. Dev.	*2.95*	*2.27*	*0.99*	*0.56*	*2.97*	*5.65*
Min-Max	*12.7-26.5*	*7.9-17.6*	*3.6-8.6*	*1.7-3.6*	*0-11.0*	*0-21.4*

The data in table 5.6 indicates that elemental concentrations vary quite widely from sherd to sherd, and for certain elements vary widely within each sherd, the standard deviation for some elements approached 50% of the mean (*e.g.* Fe for sherd CM11). The elemental composition of the cutans is not consistent for the 5 sherds, as displayed in figure 5.16

Figure 5.16: Mean elemental composition of the 5 sherds examined



The iron content of the BF sherd is strikingly higher than in any of the other sherds, reaching 50%, however the others do display some consistency in that Al and Fe are the dominant elemental constituents. The mean P content is 3.15%. The composition of the cutans examined in previous studies from Pontnewydd cave had a greater P component (Ca=14.5%, Fe= 20.5% & P= 14.5%), corresponding to a specific mineral (possibly calcioferrite) than those examined here.

5.5.3 Comparisons between sherd cutans

Comparisons can be made between the isotropic material from the five cinerary sherds examined to see if their composition is similar. Correlations between the six elements measured for the five individual sherds are presented in figures 5.17– 5.21.

Figure 5.17: Correlation matrix for sherd CM5

CM5 (n=13)	Al	Si	P	Ca	Mn
Si	ns				
P	ns	▼▼			
Ca	ns	ns	ns		
Mn	ns	ns	ns	ns	
Fe	ns	▼▼	▲	▼	▲▲▲

Figure 5.18: Correlation matrix for sherd BF

BF (n=19)	Al	Si	P	Ca	Mn
Si	ns				
P	ns	ns			
Ca	▲▲▲	ns	ns		
Mn	▼▼	ns	ns	▼▼▼	
Fe	▼▼▼	ns	ns	▼▼▼	▲▲

Figure 5.19: Correlation matrix for sherd PP1

PP1 (n=26)	Al	Si	P	Ca	Mn
Si	▲▲▲				
P	▲	ns			
Ca	▼▼▼	▼▼	ns		
Mn	▼▼▼	▼▼▼	▼	ns	
Fe	▼▼▼	▼▼▼	▼▼	ns	▲▲▲

Figure 5.20: Correlation matrix for sherd CM11

CM11 (n=10)	Al	Si	P	Ca	Mn
Si	ns				
P	ns	▼			
Ca	ns	ns	▲▲▲		
Mn	ns	▼	ns	ns	
Fe	ns	ns	ns	ns	ns

Figure 5.21: Correlation matrix for sherd CM4

CM4 (n=20)	Al	Si	P	Ca	Mn
Si	ns				
P	ns	ns			
Ca	▼▼	ns	ns		
Mn	ns	▼▼▼	ns	ns	
Fe	▼▼▼	▼▼	▼▼	ns	▲▲

Key for figures 5.17 – 5.21 (r values vary for each figure)

▲	Positively correlated	P= 0.5
▲▲	Highly positively correlated	P = 0.1
▲▲▲	Very highly positively correlated	P = 0.01
▼	Negatively correlated	P = 0.5
▼▼	Highly negatively correlated	P = 0.1
▼▼▼	Very highly negatively correlated	P = 0.01
ns	Not significantly correlated	

The selected elements do not consistently correlate between sherds, the only commonly correlating elements are Mn and Fe. The compositions of the colloidal cutans are different between the sherds, BF shows a very highly positive correlation between Ca and Al, whereas PP1 displays a very highly negative correlation between Ca and Al. P does not consistently correlate with any other element, and Si highly significantly correlates, negatively with Mn and Fe for two of the sherds. There is a very highly positive correlation between Ca and P for sherd CM11, and it is within this sherd that the highest concentrations of P (10.4%) and of Ca (9.7%) were recorded. The analytical results produced in appendix one show that these levels were recorded from a single cutan within this sherd and the other analyses for CM11 are lower.

5.5.4 Comparisons between semi-quantitative (EDXRA) and quantitative (microprobe) results for sherd CM4 and hand-mixed standards

All the analyses were conducted using a Hitachi SEM incorporating EDXRA for the elements Al, Si, Ca, P, Mn and Fe. The results are corrected by reference to an appropriate set of standards analysed by the same system. During the course of the analyses a visit to the Electron Probe Unit at Manchester University was made to run some analysis using WDXRA & EDXRA quantitatively, so checking the accuracy of the results. A set of six standards and sherd CM4 were checked at Manchester. The results can be seen in table 5.7

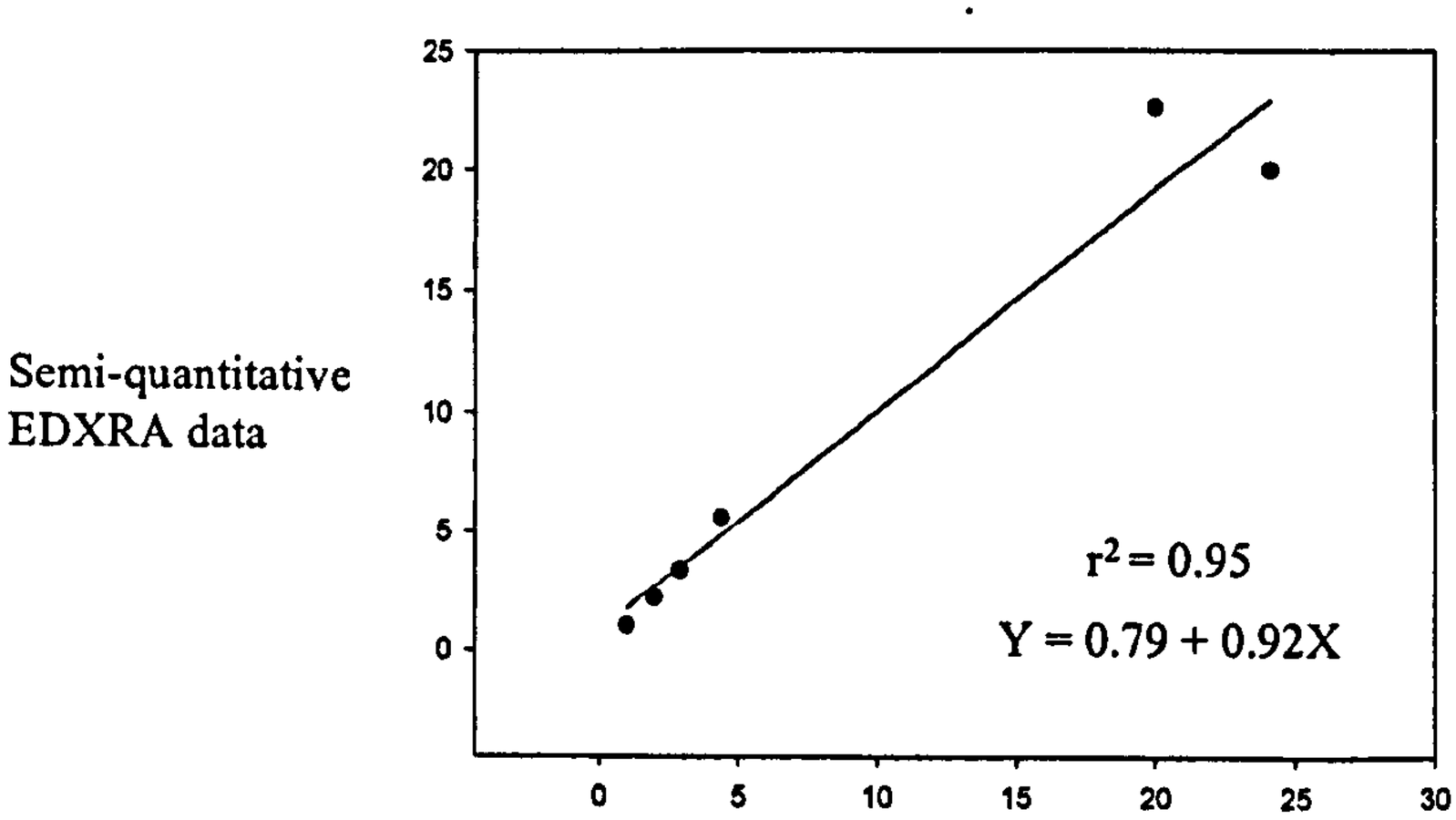
Table 5.7: A comparison between semi-quantitative and quantitative results for selected standards and sherd CM4

		Al	Si	P	Ca	Mn	Fe
Std A	Semi-quant	21.60	6.80	2.90	2.70	5.10	13.90
(N=5)	Quantitative	23.50	11.70	3.34	0.85	4.35	11.89
Std B	Semi-quant	36.80	1.60	2.00	1.90	3.40	9.30
(N=5)	Quantitative	34.70	6.32	2.18	0.76	3.20	7.75
Std C	Semi-quant	5.10	16.00	4.40	5.10	8.60	21.80
(N=5)	Quantitative	6.66	15.03	5.57	2.57	7.81	21.24

Std D	Semi-quant	4.90	2.50	1.00	4.50	21.30	31.00
(N=5)	Quantitative	7.95	4.45	1.01	5.62	19.91	30.33
Std E	Semi-quant	-	-	24.10	-	-	35.10
(N=5)	Quantitative	-	-	19.97	-	-	39.10
Std F	Semi-quant	-	-	20.00	39.20	-	-
(N=5)	Quantitative	-	-	22.60	34.09	-	-
Sherd CM4	Semi-quant	18.14	10.55	5.52	2.84	7.34	12.87
(N=12)	Quantitative	21.28	5.16	4.29	1.42	10.23	13.92

The differences between the results measured semi-quantitatively at Bangor and the results measured quantitatively at Manchester are about 30%, however they are not consistently lower or higher. The results for each element were examined using regression analysis, and the regression plot for P is produced in figure 5.22 showing a significant (P=0.05) r^2 value of 0.952. The r^2 values for the other elements are also significant (p=0.05) with the exception of Si, all the regression plots are produced in appendix I. The semi-quantitative method of analysis using EDXRA in Bangor followed by a calculation with reference to a set of standards is a satisfactory way of measuring the elemental composition of thin sections.

Figure 5.22: Regression plot for P



5.6 Discussion

The 'bone-in-soil' experimental columns leached with organic acids did not produce any visible phosphatic cutans. This is unsurprising considering the time-scale over which these cutans develop in the natural environment (10^3 years). However, a significant (P=0.05) lateral movement of P was detected within the columns over 1-2mm from the bone surface, following only 30 weeks of intermittent leaching. No increase in P was detected below the bone when sampling every 5mm sequentially down the soil column, however, analysis by microprobe in a section of soil taken from directly below the bone did detect higher P values closer to the bone. The bulking of every 5mm of soil down the column could have diluted any increase in P that might have occurred in the area directly below the bone. It is likely that if the columns had been leached for a longer time period a greater movement of P would have been detected, but it appears that even within the short time-scale of 30 weeks, diffusion of P from a concentrated source can be displayed. Within an archaeological time-scale, the diffusion from a concentrated, restricted source of P such as a bone could be potentially much larger, and would be dependent on the bulk density and moisture content of the soil. The redepostion of this P within the soil will be dependent on sorption to Fe and Al oxides and hydroxides in the acidic soils discussed in this thesis, and to calcium carbonate in higher *p*H soils, but it is likely that little (<1%) would be lost from the system. The capacity for most soils to fix P which could diffuse and leach from such a point source is large, Black (1957) reports over 3300 kg ha^{-1} being added to one plot over 11 years with only 0.5 kg ha^{-1} being lost through leaching.

The cinerary urn sherds contained cutans of a similar appearance to those described in Jenkins, (1997), from the sediment column in Pontnewydd cave, however, the elemental composition of the cutans was different. The Pontnewydd cutans were Ca-Fe-P rich, and a source of these elements - the cremated bone - within the urns could have accounted for a similar elemental composition. The sherds examined were Fe-Al dominated and Ca & P were minor constituents, in all but one analysis. The values of P measured did rise to 10.4% with a mean composition of 3.15%. This is at least 15× greater than the average P concentration for local soils, so there is a definite increase, which could be attributed to the redistribution of P from the ashed bones within the cinerary urn. The Fe-Al domination in these sherds is likely to be

a product of the burial environment, the sherds are all from soils in North Wales which are predominantly acidic. The correlation matrices calculated for the sherds do not show consistent correlations which is also likely to be a product of the varied burial conditions. The presence of phosphatic cutans within sherds from cinerary urns is not unlikely, there is a suitable source of concentrated P from the cremated bone, however these cutans may only be present within the sections of the urn directly below the bone. The chances of sampling the most useful piece of sherd from the correct part of the urn are low. The cutans examined here are essentially Fe/Al deposits and at a low soil *p*H, it might be expected that phosphates would be associated with these elements, however, P only correlates positively with Fe in one sherd and with Al in another. The presence of P in these cutans will be determined by its availability and movement through the sherd. Very little P would be derived from the local acidic soils, so if the sherd is from a position in the urn which has not come into contact with bone or bone ash, it is unsurprising that P is not a large component of the cutans identified.

The comparisons made between the analyses using the Hitachi SEM, a semi-quantitative method, and the Cameca, Camebax Microprobe incorporating ZAF software at the Electron Probe Unit, Manchester University, were useful. The semi-quantitative analyses, once corrected using standards, was within +/- 30% of the more accurate analyses.

SAMPLING FOR PHOSPHORUS OVER A GRAVE SITE: THEORETICAL AND PRACTICAL

6.1 Introduction

Phosphorus analysis is a particularly useful technique for the examination of cryptic archaeological features, *i.e.* suspected inhumations in acidic soils where there has been the complete dissolution of bone. Under these conditions it is difficult to visually establish whether there was an actual inhumation, and the measurement of soil phosphorus can help to clarify this. The preservation of bone within soil is dependent on the age of the bone at interment, (Gordon & Buikstra, 1981) and soil conditions, notably the soil *p*H. Hydroxy-apatite ($Ca_5(PO_4)_3OH$), the main inorganic component of bone, is relatively insoluble at *p*H values above 6.5-7.0, so in soils at this *p*H, bone is well preserved. However as the *p*H drops, protons replace the Ca in hydroxy-apatite which can then be leached from the soil, causing the bone to undergo dissolution. At lower *p*H values of <5.0, the rate of dissolution is accelerated by an increase in H^+ ions and the removal of P, which makes up 18.5% of hydroxy-apatite, by sorption onto Fe and Al oxides and hydrous oxides and precipitation into Fe & Al insoluble phosphates, so in acidic soils the complete dissolution of bone occurs and no physical trace of the bone is left. Under these conditions soil phosphate analysis can reveal the chemical trace of bone, because P released during the dissolution of the bone diffuses very slowly through the soil, so is fixed locally at concentrations greatly elevated above natural 'background' levels.

The first problem of archaeological investigation of a grave site is one of location. If a site is 'surveyed' by the phosphate analysis of soil samples collected on a point grid basis then large areas will remain unsampled. A feature such as a cist or a grave is small and compact and could be easily missed at the sampling intervals regularly employed (50m – 5m). Very few 'small' features will be located in this manner. Grave sites however, are often located in association with other archaeological features, and once discovered merit a separate sampling strategy to these other features. If the soil conditions are such that an inhumation cannot be visibly identified, then phosphate analysis is a useful technique to ascertain whether the feature is an inhumation, or whether the grave was never 'occupied' or perhaps

if a body was removed at some stage following burial. Commonly, graves will be stone-lined, with basal and top stones, and in these cases the process of collection of soil samples for phosphate analysis is simplified because the sample area is defined by the stones. If an inhumation is suspected through the presence of a change in soil colour or texture, but without any associated surrounding stones then sampling becomes a little more problematic, simply because a larger area must be sampled to ensure complete coverage of the burial area. The sampling strategy utilised, while being designed to suit the sampling area, can still remain problematic. The central problem being the choice of interval of sampling required to achieve a pattern of results that enable the distribution of P arising from an inhumation to be clearly displayed. Soil analyses are expensive, and excavation time often limited, so the smallest number to achieve the required results is usually preferred. An analytical experiment on an actual grave site to test various sampling grid intervals would not be easy because rarely would a grave site in ideal conditions become available for this sort of exercise.

A second problem facing this sort of P survey is the sampling depth. Any concentration of P in the soil is likely to accumulate in a particular layer, which could be only a few millimetres thick, so it is important to sample this layer completely. If a method collects only a small sample from a particular depth, it could easily miss the P enhanced layer, however coarse sampling could significantly dilute the P 'signal'. It has been calculated that an average human adult will contain 630g of P (Proudfoot, 1976), which if distributed evenly within a layer of soil 1cm thick over the whole of a grave with the dimensions 200cm×70cm, will enhance the P_{tot} content of every cm^3 by 45mg P. This is obviously significantly higher than an average background concentration of P (~1mg P g^{-1}) but assumes that all the body derived P remains fixed in the soil and undisturbed. If an auger sample collects $10cm^3$ of soil over a depth of 10cm surrounding this 'active' layer then the P concentration of the soil is diluted to 3.3mg P g^{-1}, which is still significantly higher than an average background concentration. Sampling by a standard soil auger is common, however this could be considered clumsy unless care is taken to just collect the soil from a particular depth, and often sampling just the 'active' layer in the soil with the tip of the auger or the end of a narrow trowel will be preferable.

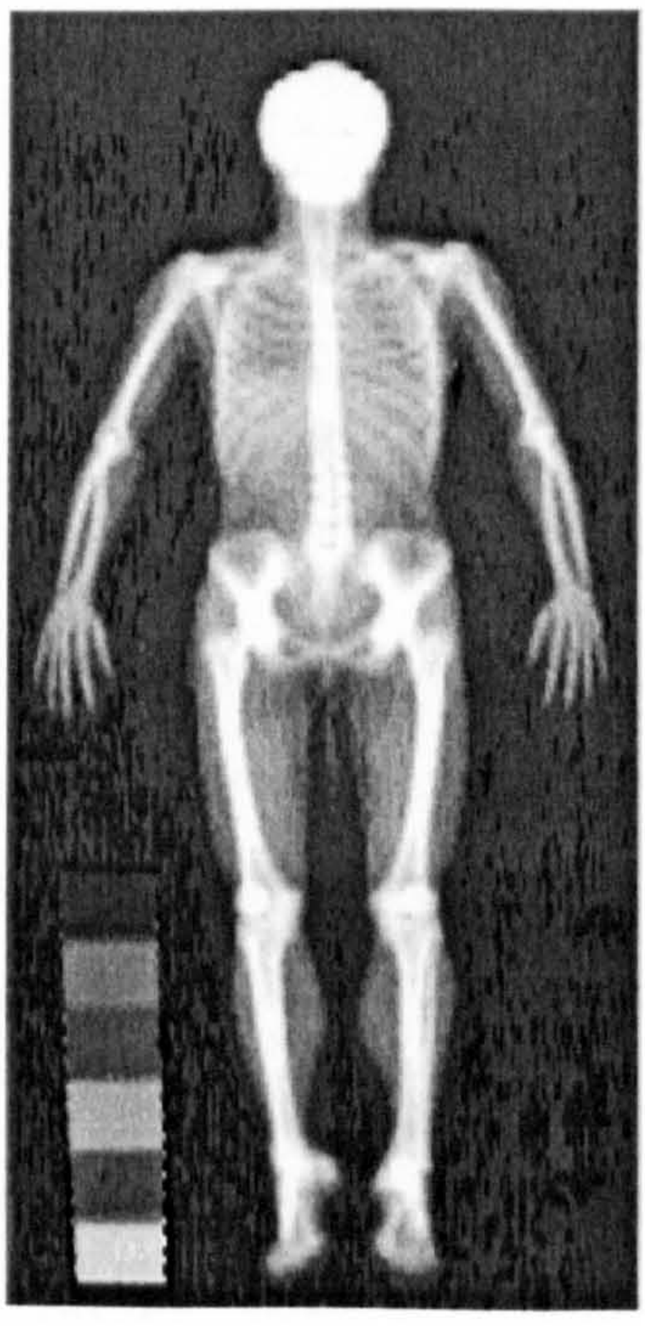
The first section of this chapter examines the theoretical example of sampling an inhumed body for phosphate analysis, with the novel approach of using a total body radiograph to represent a grave. The second part examines the sampling of phosphorus within an Early Christian grave site, a Bronze Age cist, and a suspected inhumation, all of which were being excavated by the Gwynedd Archaeological Trust (GAT) and discusses the techniques involved and compares the results with those from the theoretical example of phosphate analysis within a grave.

6.2 Grid sampling of a grave utilising a whole body radiograph

6.2.1 Methods

A whole body radiograph was obtained from Dr Michael Worsfold, The Charles Salt Research Centre, Robert Jones and Agnes Hunt Orthopaedic Hospital, Oswestry. This instrument is used in hospitals to obtain a whole body, bone density scan. The instrument scans the body using two X-ray wavelengths simultaneously at a spatial resolution of a few millimetres. From the transmission of the X-rays the dedicated software identifies areas of bone and calculates bone mineral content and its mean density after allowing for absorption by soft tissues. An image scan at pixel resolution is printed (figure 6.1), and a table of the mean results for 10 areas of the body produced (not reproduced here).

Figure 6.1 Whole body bone density scan.



This body scan is composed of 172 columns of pixels made up of 338 rows (58136 pixels in total), each pixel has a figure associated to it, to represent the level of shading in that pixel, and this level of shading is directly related to the bone density at that position. By stripping out all this data and arranging it in a text file alongside its location on the scan as 'x' and 'y' co-ordinates, a huge data set is realised, composed of 58136 'samples' collected from an area approximately 190cm × 95cm (each sample represents 0.55cm × 0.55cm). This is a unique sample set that could never be obtained as actual samples, and is used here to examine sampling strategies across this area, which is equivalent to an inhumation.

A program was written in Perl (Wall, 1997) by Paul Wood, Information Services Department, Bangor University, to pick out samples from this data set on a grid basis. The size of the sampling interval, the starting row, and the starting column, were all fed into the program, and the sampled cells were displayed with their accompanying co-ordinates. This data was then used to generate distribution maps which can be compared to the original body scan to see at what sampling interval the samples collected produce an image that is representative of the body scan. The distribution maps were plotted using Winsurf, surface mapping for windows package (Golden software, 1993) with a 'minimum curvature' data interpolation method (a discussion on a variety of interpolation methods is presented in appendix V).

6.2.2 Results and discussion

Data sets are generated for four different sampling intervals initially; every 20cm, 15cm, 10cm and 5cm, over the sample area of 190cm×95cm. The distribution patterns of these data sets are then plotted and is produced in figures 6.2 - 6.5.

The resolution of the generated image increases as a greater number of sample points are used to produce the image. At a 20cm sampling interval there are only 45 sampling points and the image shows a concentration in the upper central area of the map. This does tally with the position of the head of a skeleton, where the greatest concentration of P is likely to be found, but at this scale the area of concentrated P cannot be related to an inhumation. At the 15cm sampling interval there are 72 sampling points and an image is generated which is closer to a body

Figure 6.2: Single pixel sampling image from 20cm grid

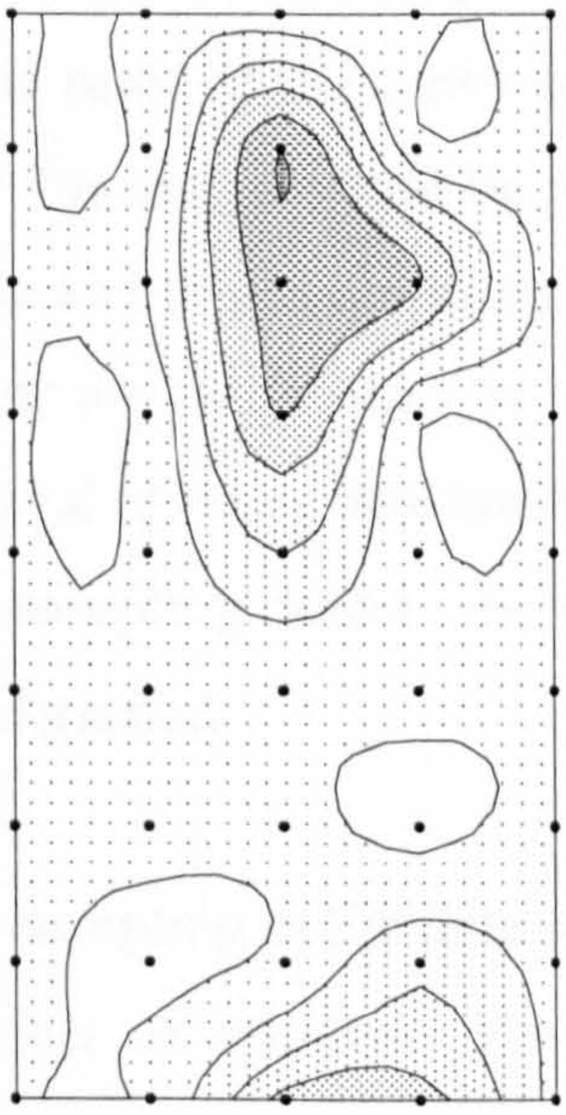


Figure 6.3: Single pixel sampling image from 15cm grid

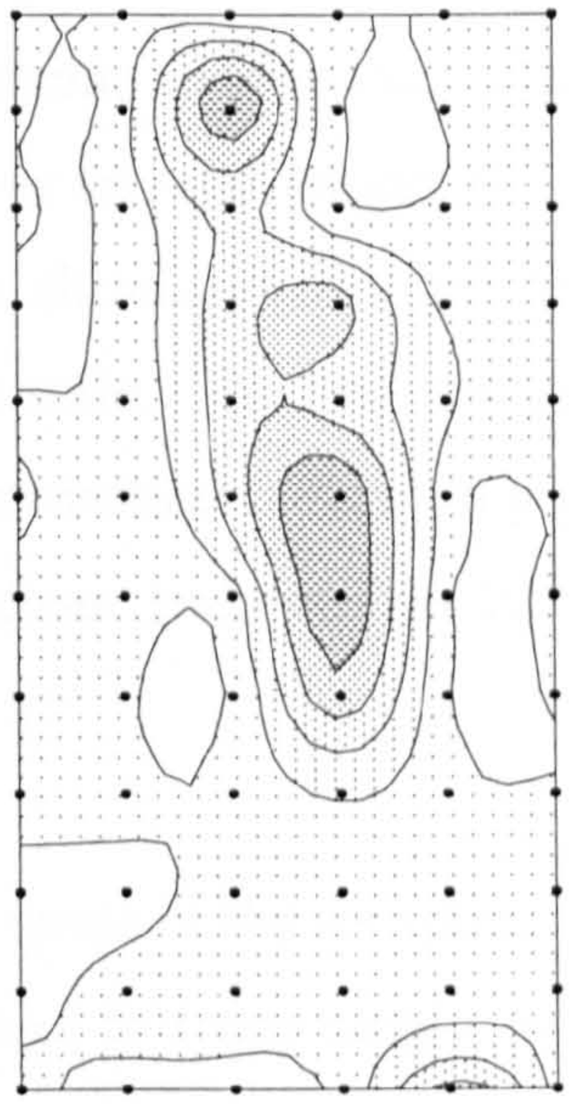


Figure 6.4: Single pixel sampling image from 10cm grid

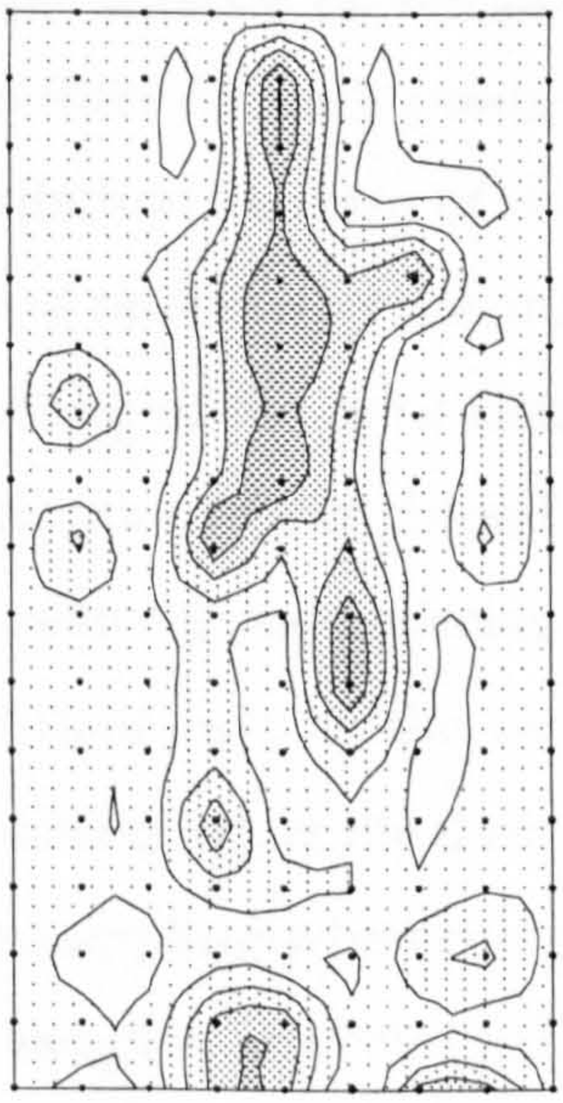
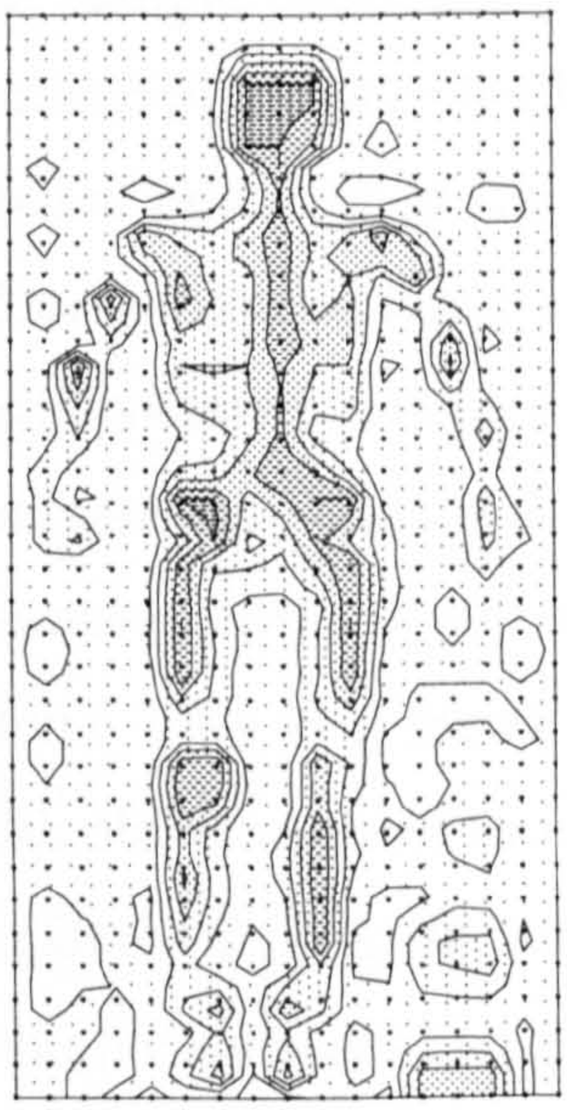


Figure 6.5: Single pixel sampling image from 5cm grid



shape, and a head and torso can be identified. However no limb areas have been identified, these have obviously all been missed at this size of sampling interval, the shape could not be positively identified as a body unless it was associated with a stone-lined grave or cist. At the 10cm sampling interval the image becomes clearer. At this sampling density there are 153 sample points which is a sufficient density to allow most of the limbs of the skeleton to become identifiable. There is no doubt that this image would be positively identified as an inhumation; the head shoulders, torso and thighs are identifiable, however, the shins and feet, and the forearms and hands are still missed by the sampling at this scale. The final image, at a sampling interval of every 5cm has a much greater concentration of sampling points - 578. At this sampling density the skeleton's image is clear, and even the hands and feet can be identified.

The sampling of the data-set is not realistic in terms of the sampling in the field for a number of reasons. Firstly, the data selected is from single pixels, each pixel relating to an area of 0.5cm×0.5cm on the skeleton. In the field, samples of this size could not be collected, and commonly a soil auger (roughly 2cmØ) would be used to collect samples, so each sample collected in the field is from an area which is 16 times greater than a single pixel in this image. The program was amended to sample a block of 4×4 pixels surrounding the sample point and produce a mean from these for each position which is more realistic in terms of field sampling. The distribution patterns of the amended data sets are produced in figures 6.6 - 6.9. A second reason why the analysis of this bone density data set is unrealistic is that the sampling of the bone density image is two dimensional, whereas in the field the distribution of P in the soil will be over three dimensions, and the depth from which the samples are collected and the size of sample collected will play an equally important role as the samples spatial location. This is a factor that cannot be accounted for by the theoretical sampling at this stage. A third inconsistency in the data sampling when compared with sampling in the field is the direction in which the samples are collected. At present, the sample data set can only be sampled across rows and down the columns, whereas in the field a grave might appear at any angle to the sample grid being used. Future work will examine the pattern of distribution of P from this artificial sample data set when it is sampled at an angle that is not in plane symmetry with the spine.

Figure 6.6: 4x4 pixel sampling image from 20cm grid

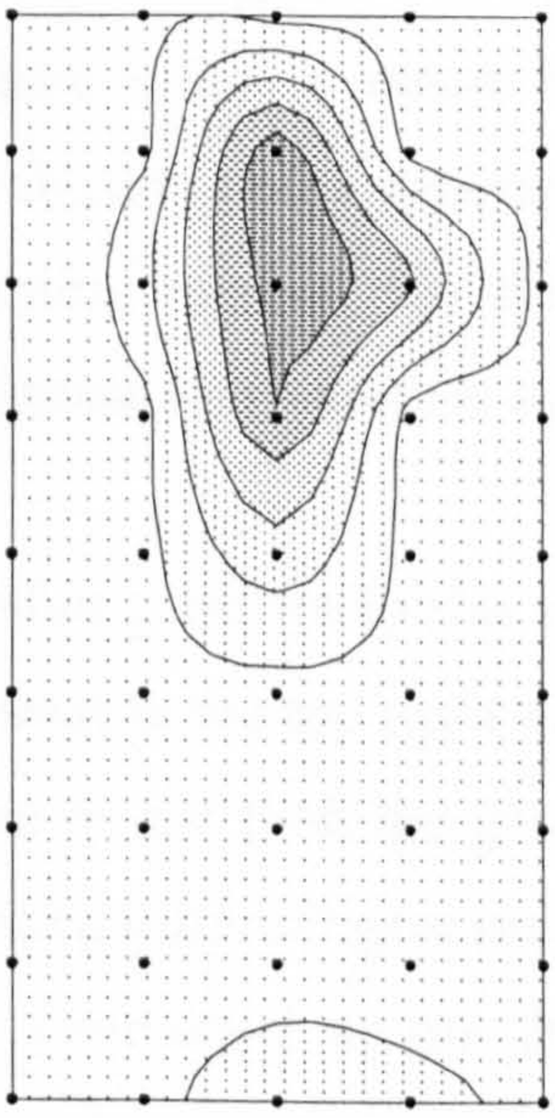


Figure 6.7: 4x4 pixel sampling image from 15cm grid

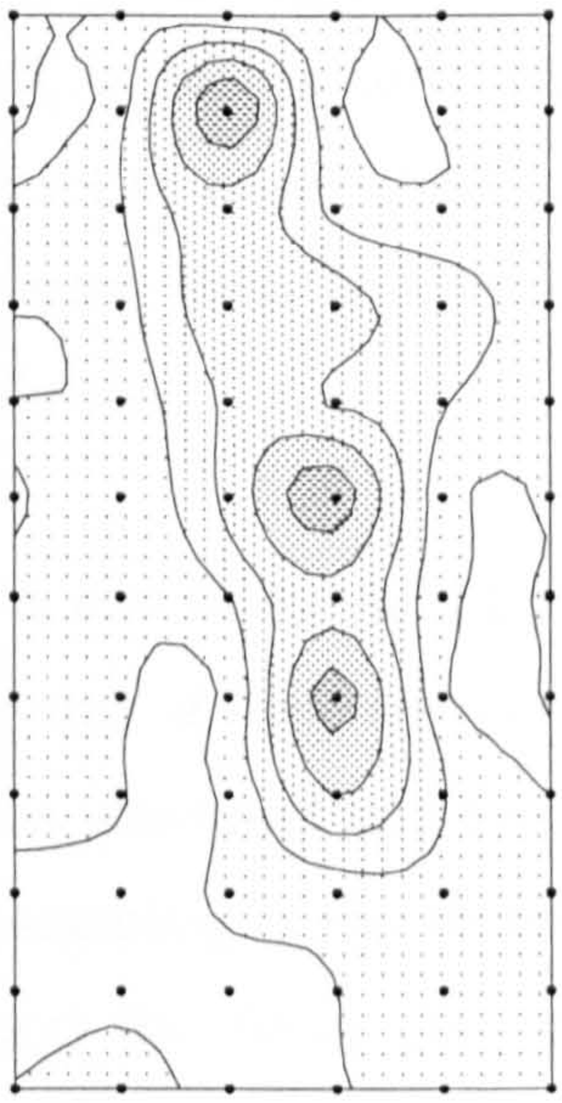


Figure 6.8: 4x4 pixel sampling image from 10cm grid

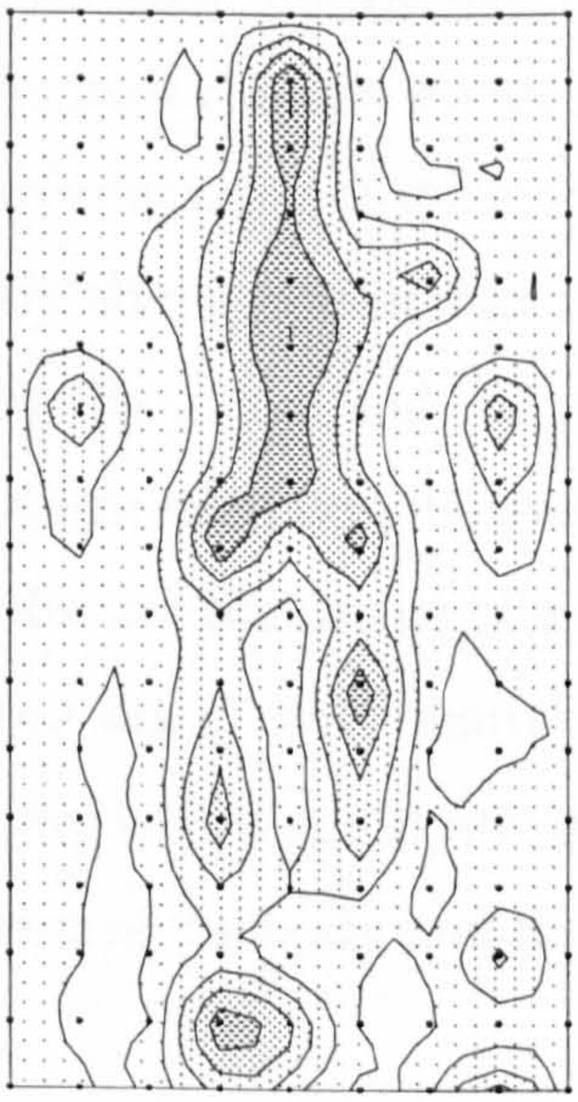
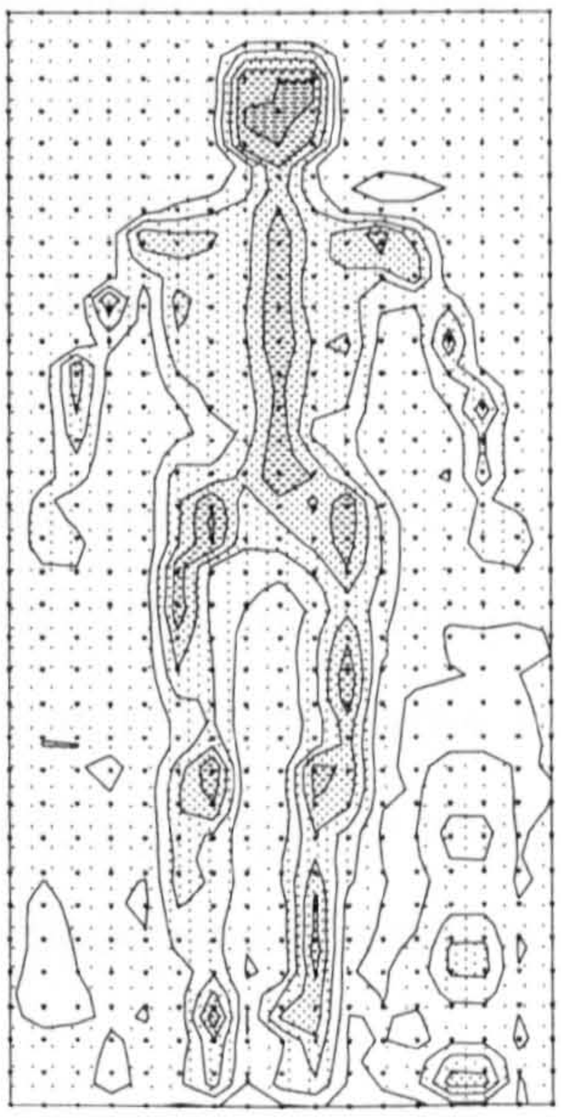


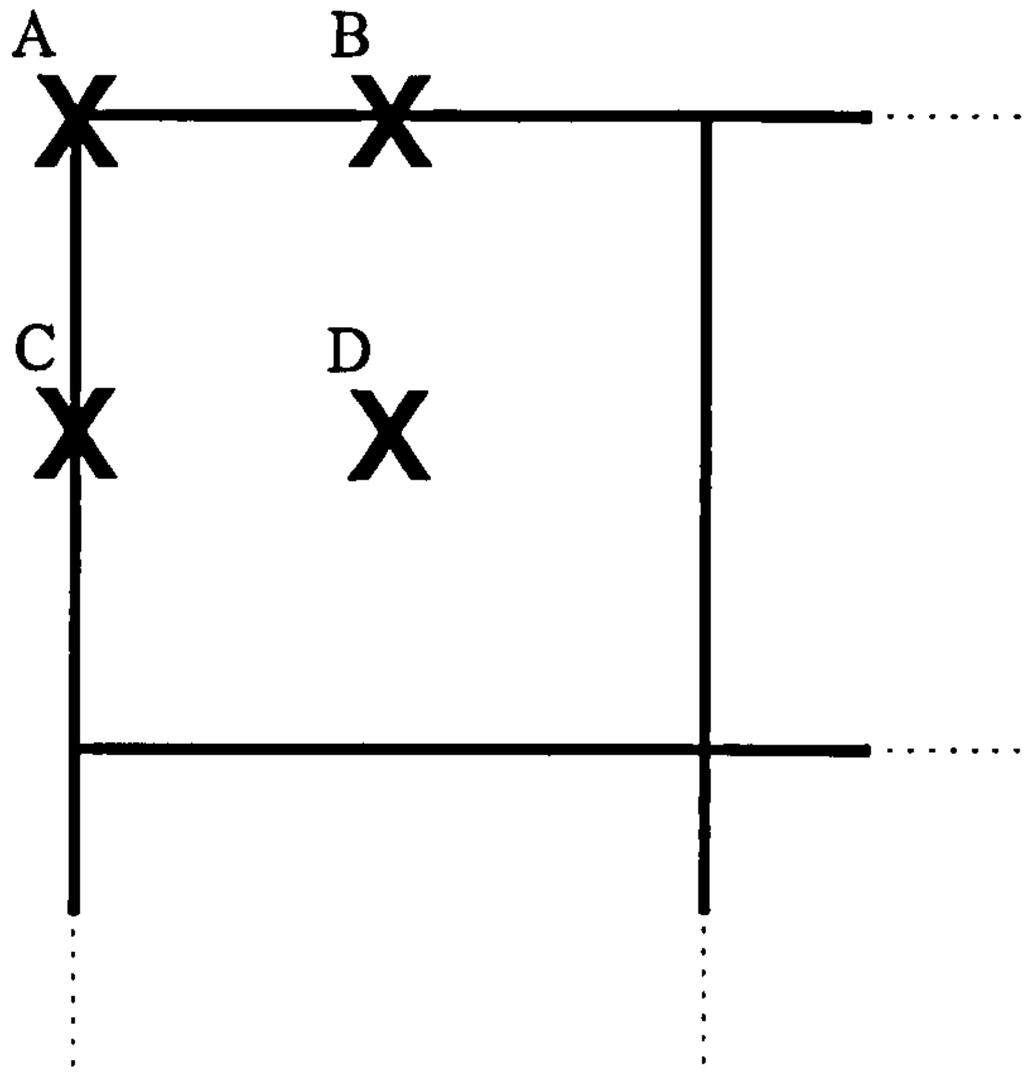
Figure 6.9: 4x4 pixel sampling image from 5cm grid



There are few differences to be observed between the distribution maps generated by the mean of 16 sample cells (figures 6.6 - 6.9) and the distribution maps from the data of single sample cells (figures 6.2 - 6.5). At the 20cm sampling interval the anomaly of high values at the centre of the image is much 'cleaner' and there are no associated high value areas surrounding it. Even though the sampling is more realistic when a mean of 16 cells is utilised, it makes little difference to the distribution maps generated; as with the first set of distribution maps, at a 10cm sampling interval the shape of a body; the head, torso and upper legs become recognisable, so there is no obvious loss of resolution.

Another problem to this theoretical sampling is that in the field the sampling may not start in the top right hand corner of a grave site. If there are no stones lining the grave or cist then the grave may not have been identified and so will be sampled within a different grid sampling strategy. The sampling of this theoretical grave site was conducted at the 20cm grid interval and the 10cm grid interval at four alternative starting positions (see figure 6.10), to examine the effect of small movements in the starting position of the sample grid. The distribution maps plotted from the four sets of data are reproduced in figures 6.11 and 6.12. At a 20cm sampling interval a change in the position of the sampling grid can have quite a marked effect on the distribution pattern uncovered. The position of the anomaly moves and changes shape with an adjustment of only 10cm in the sampling grid, however at none of the starting positions plotted could the anomaly be identified as a body shape, the change made in the starting position of the grid does nothing to clarify the image and the anomaly always consists of only 3 or 4 sampling points. At a 10cm sampling interval an adjustment to the position of the sampling grid does not obscure the image of a body when the distribution maps are plotted. However, it does affect how many samples are collected from the area of greatest bone density, which could affect the significance of the phosphate levels collected from the area of the body and the levels collected as 'background' samples.

Figure 6.10: Starting positions for grid sampling strategies



This method of theoretical sampling provides a useful illustration of the distribution patterns of P that may be expected when sampling grave sites, however it cannot be expected to accurately mirror the distribution patterns one might uncover in the field for a number of reasons. Firstly, the whole body bone density scan gives a value for bone density of the skeleton, set against a blank background surrounding the body. The range effectively goes from a zero value to one of high bone density in the skull area of the skeleton. In comparison, any grave site sampled in an archaeological phosphate survey would be set against background values of total phosphorus (P_{tot}) in the soil. P_{tot} values for soil can range from 200 to 5000+ $\mu g\ g^{-1}$ (Barber, 1984) which could be a considerable proportion of the value of P_{tot} measured in the skeletons position. The results for any P survey would not be as distinctive as the distribution this theoretical example suggests, as the values of P measured from the skeletal P will be adding to a background concentration inherent in the soil. This background concentration of P in the soil fabric can vary naturally by up to 50% (chapter 3) which will add to the background 'noise' of the P distribution making any discernible 'pattern' increasingly blurred.

The level of background P present in the soil would not be a problem if all the P that was present in the bone at the time of burial was 'fixed' in the soil, remaining in this fixed form until the archaeologist measured it many years later. The P content

Figure 6.11: Images from 20cm grid at four starting positions

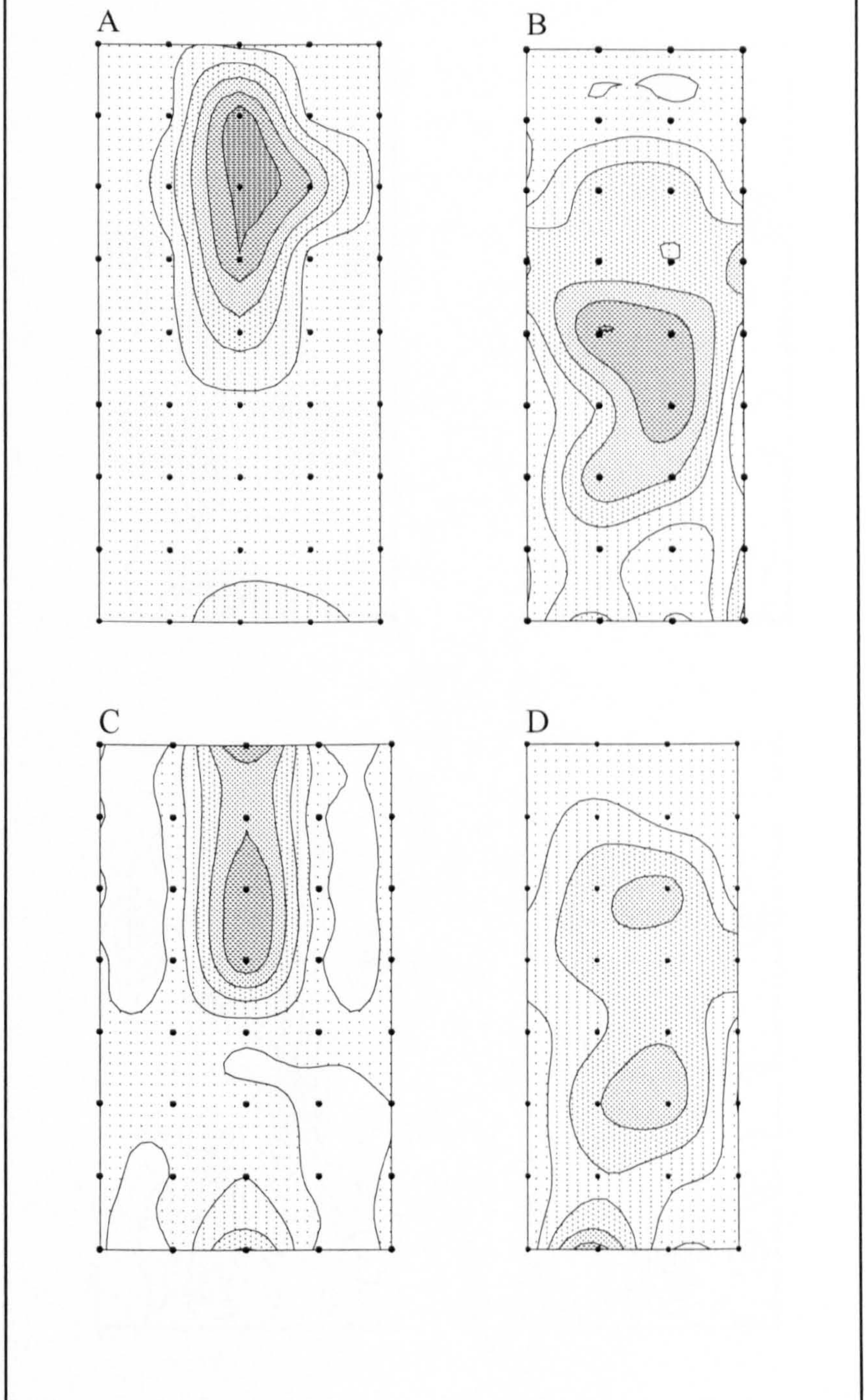
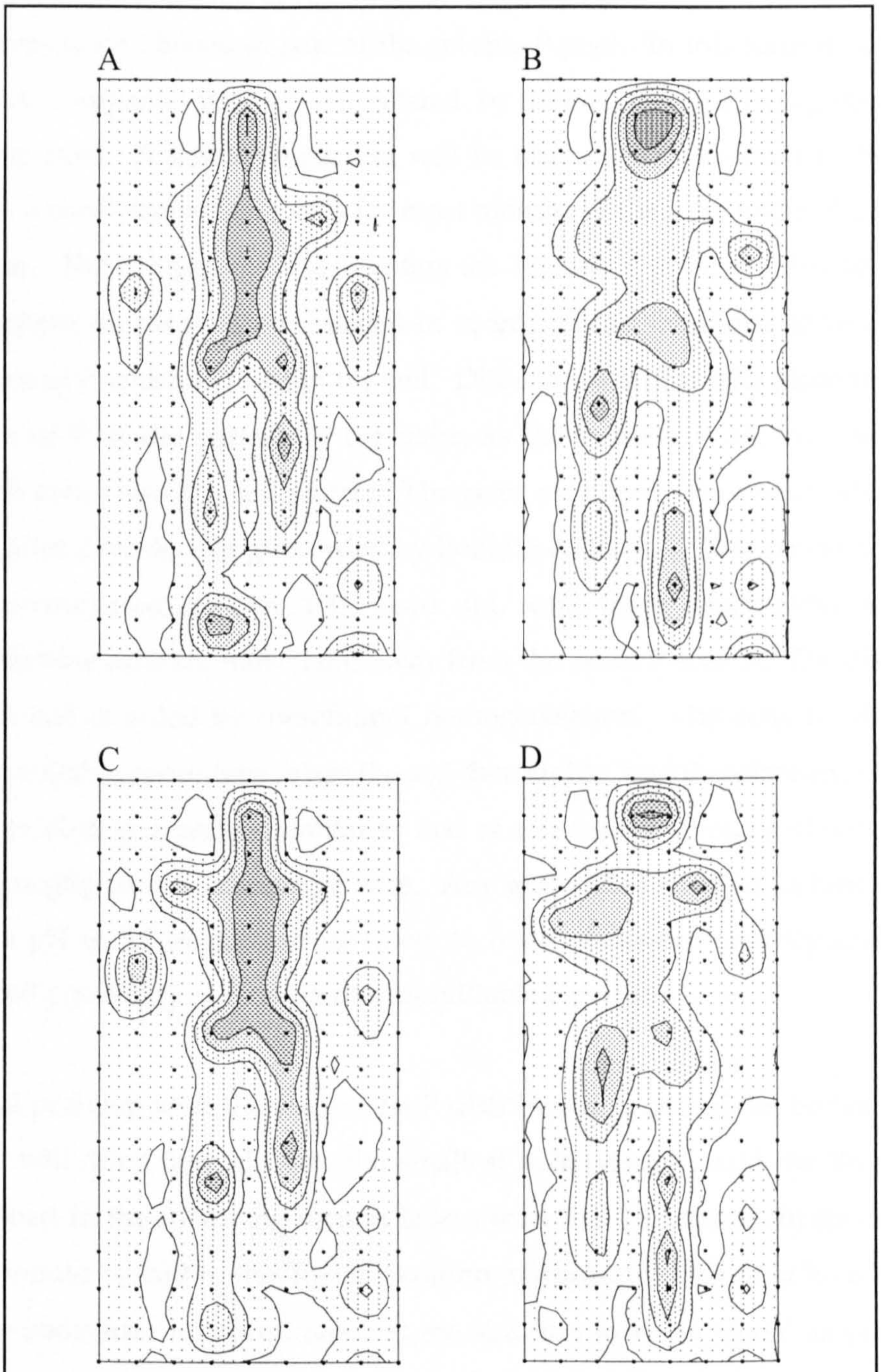


Figure 6.12: Images from 10cm grid at four starting positions



of bone has been measured at between 16% (Eastoe, 1961) and 20% (Dojlido & Best, 1993), whereas the P_{tot} content of soils could be roughly 0.2%, a 100 times difference. However, many processes take place to reduce the amount of P from the bone which is actually fixed in the soil. Primarily, as is discussed in chapters 1 and 2, the P from bone is gradually released as it is broken down by the soil microbial population, and becomes part of the soluble P pool. In this form it can be fixed in the soil inorganic pool or assimilated by plants and micro-organisms into the organic pool. A small proportion will be leached from the soil if there is excess water, a condition which exists for most months of the year under the North Wales climate. The component which enters the organic P pool can also be leaked from the system, as plants are harvested or eaten. These situations serve to reduce the amount of P which is fixed in the soil. Diffusion will also take place from the point source of P at the surface of the bone, as the mineral P becomes soluble it will diffuse away into the soil matrix. The rates of diffusion are relatively slow, up to 7cms after 2 weeks being recorded by Bouldin & Black, (1954); however many grave sites investigated are over 1000 years old, some being much older, which allows considerable time for movement away from the point P source. The dispersion of P within soil is aided by mesofaunal homogenisation. The activity of earthworms under suitable conditions mixes the soil thoroughly, and therefore the chances of a P trace exhibiting a pattern similar to that of a skeletons layout will depend on there being negligible mesofaunal activity. Any grave sites situated in brown earth soils with a *p*H of 5.5 or greater are likely to have earthworm activity and therefore a reduced possibility of retaining an identifiable P pattern.

A final problem with the theoretical P distribution is one of the bodies position. A burial will often take place in the smallest hole possible, and the Bronze Age cist examined in the following section is less than 1m×1m square, in this situation the body would be laid in the 'foetal' position minimising the size of hole needed. The whole body scan however, requires the skeleton to be as 'open' as possible so the prone position with the person lying on their back is used. It is unlikely that many grave sites contain bodies which would be laid out in this position, so the theoretical images generated are of limited applicability. It would perhaps be possible to obtain further total body scans of people in a variety of positions, but that remains as work for a future study.

6.3 Investigation of an early Christian burial site, and a Bronze age burial cist and suspected inhumation

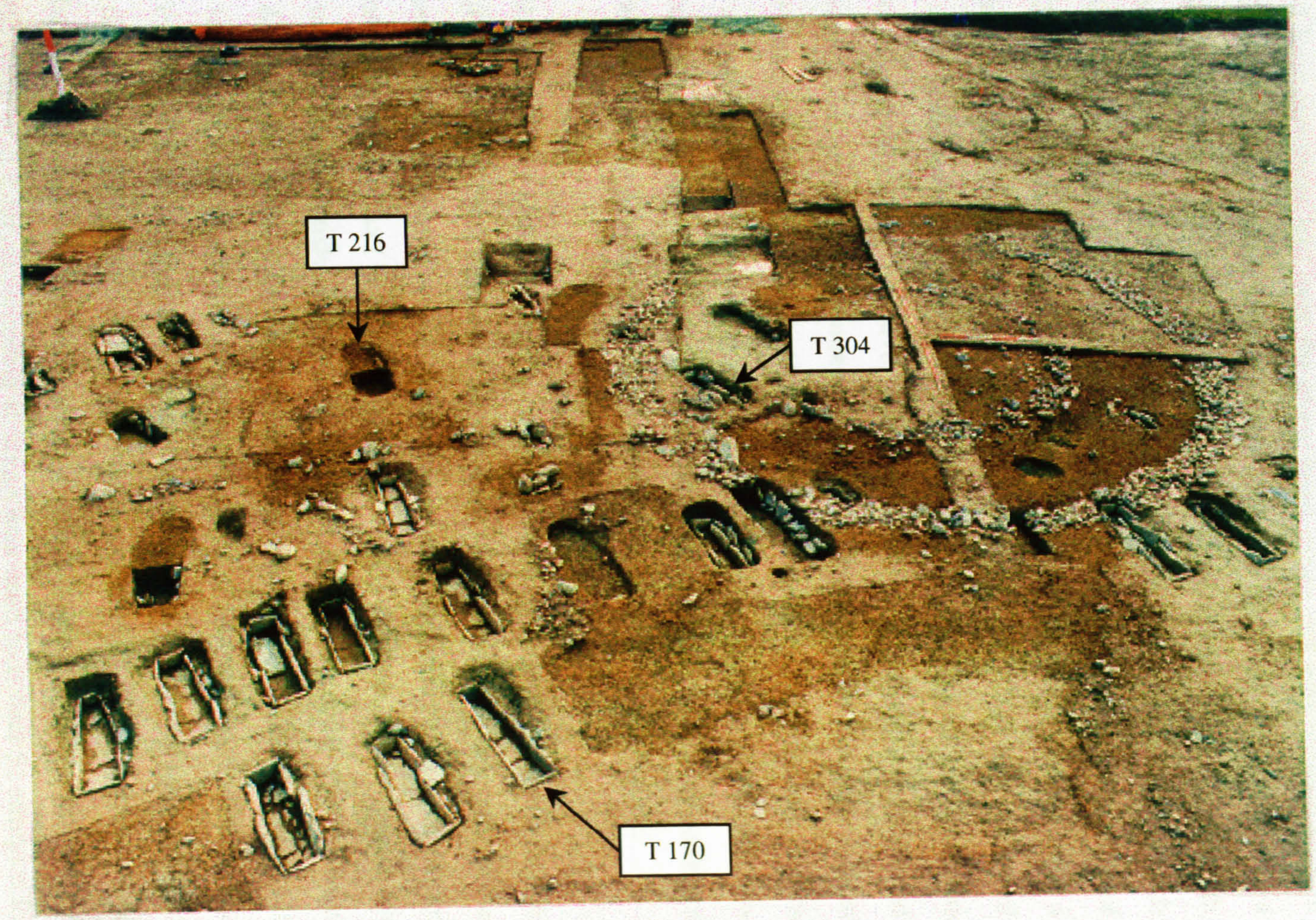
6.3.1 Site locations

The field work for this study took place at two burial sites on Anglesey (map 1.1), both being surveyed and partially excavated by the Gwynedd Archaeological Trust before the construction of the A55 dual carriageway across the island. The first burial site was located at Ty Mawr farm, GR 252814 located on map 6.1 (GAT project number: G1572, figure 6.13) and consisted of a number of stone-lined and capped graves similar in style to other excavated burial sites dated to the early Christian period 400-800AD (Ian Grant *pers. comm.*). Samples were collected from this site on two occasions, initially one grave was examined, however it became possible to sample two further graves when the site was completely excavated at a later date. The recent history of the field is not recorded, however until the time of excavation it was utilised as cattle and sheep grazings with annual fertiliser applications. The land had been improved at some stage but luckily the capstones of the grave were located at a depth of roughly 50cm below the surface, and well below maximum plough depth, so the graves remained intact. A cist before excavation can be seen in figure 6.14. The soil at this site is mapped as *East Keswick 1* series (Rudeforth, *et.al.*, 1984) and is a brown earth developed on drift material with siliceous shales.

The second site was located at Cleiriog Ucha, Anglesey (GR 285795 see map 6.1). An isolated stone lined cist, possibly dating to the Bronze age, was located and excavated. During examination of the surrounding area other features were uncovered, including an area where the soil texture and colour changed abruptly, and which had similar dimensions to a grave so was suspected as a possible inhumation. These features were located in an improved pasture field, but again the recent land use history was unknown. The soil at this site is mapped as the *Brickfield* 2 association (Rudeforth *et al.*, 1984) and is a typical clay loam brown earth, with sporadic seasonal waterlogging. Samples were collected from both features for phosphorus analysis.

Map 6.1: **Location of two burial sites**

Figure 6.13: Overview of Early Christian Burial Site



6.3.2 Sampling strategy: Ty Mawr (TM) Early Christian burial cists

The whole site was roughly 50×30m and consisted of approximately 20 graves, from which the topsoil had been cleared using a JCB excavator, awaiting further excavation. Initially a single cist was examined for this study (GAT: G1572, T170) which had four capstones laid over the stone lined grave and was roughly 80cm × 220cm. Due to time constraints samples were collected from two horizontal layers only within the grave. The first set of samples were collected from 15cm depth within the grave, on a 10cm grid (figure 6.15), using a 1cm Ø soil auger. Each sample was bulked from a 5cm depth of soil on the auger, thus comprising of roughly 2-3g soil, which was air-dried and hand-ground in the laboratory with a sub-sample taken for P analysis as described in section 3.5. The second set of samples were collected using the same procedure and grid layout but from the bottom 5cm of soil fill within the grave. A background set of samples were collected from alongside the grave at 10cm intervals along a 150cm line, at a depth of 15cm using the same soil auger, and a single set of samples were collected at 5cm depths down to a total depth of 50cm alongside the grave. The sampling at this site was completed once the basal stones had been uncovered and six samples were collected from between the three basal stone slabs at positions where this was possible.

Two further cists were sampled during the complete excavation of the whole site, the first (GAT: G1572, T216) displayed a clear dark stain thought to be a relic of the decomposed body, containing several areas of paler material thought to be imparted by the bone. This grave had been completely excavated to the subsoil (figure 6.18) because unlike the previously sampled cist T170, it was constructed with no basal stones. A systematic 10cm grid interval sampling strategy was used to collect 112 samples for P_{tot} analysis from the subsoil over an area of 180cm× 50cm. The second cist (GAT: G1572, T304) was partially excavated to reveal a dark soil stain at roughly half the depth of the cist (figure 6.20) covering approximately 5% of the excavated cist surface. At this level the remains of a single tooth was also visible. A systematic 10cm grid interval sampling strategy was used to collect 91 samples for P_{tot} analysis from the excavated surface over an area of 190cm × 40cm. Both cists were sampled using a metal scoop designed to take about 1g soil from each grid node.

6.3.3 Sampling strategy: Cleiriog Ucha (CU) Bronze Age burial cist

The cist, roughly 1m×1m in size, had been excavated to the upper level of the side walls roughly 30cm below the soil surface and the capstones removed by the Gwynedd Archaeological Trust (GAT). The cist was sampled at two levels, the first at roughly 20cm depth, and the second at just above the basal stones. Soil samples were collected on a 10cm grid interval within the cist (figure 6.22) using a 1cm∅ soil auger. Only the lowest 1cm of soil material was collected from the auger for the basal set since it is likely that the P from the body would be concentrated into a single layer just above the basal stones and a larger volume sample would dilute the P 'signal' measured. Each sample was air dried and finely ground in the laboratory and a sub-sample was taken for P_{tot} analysis using the method described in section 3.5. Background samples were collected from 21 positions surrounding the cist using a trowel.

6.3.4 Sampling strategy: Cleiriog ucha (CU) suspected inhumation

One set of grid samples were collected at a 10cm sampling interval over an area of 50cm×50cm, there were no surrounding or underlying stones as in the previous cist examined, and this site was only delineated by a difference in colour and texture of the soil. All samples were collected using a 1cm∅ soil auger to a total depth of 10cm. Two sets of samples were also collected down through the soil at 2cm intervals to the base of the 'altered' soil material.

6.3.5 Results

The P_{tot} results measured for the 350 samples collected from the TM site are listed in appendix 1. The means and selected descriptive statistics for cist T170 are produced in table 6.1 and for cists T216 & T304 in table 6.2. The mean P_{tot} results for the three sets of samples collected from the T170 cist were low (490-680 $\mu g\ g^{-1}$) compared to the mean value for agricultural surface soils that might be expected (1500-2000$\mu g\ g^{-1}$), however the values are reasonable because the samples were collected from below the plough layer and P_{tot} values usually decrease with depth of sampling (see section 3.6.1). P_{tot} results collected from the basal layer of the cist are significantly greater (P=0.01) than those collected from the upper layer, but the mean is only 100$\mu g\ g^{-1}$ greater, though both are greater than the mean for the background samples. A much greater mean P_{tot} result would be expected if there was a large

portion of skeletal P still present fixed in the soil, values of >1% (10,000μg g^{-1}) having been reported (Keeley, *et. al.*, 1977). The significant (P=0.01) differences present between the two layers does suggest that the P_{tot} levels in the basal layer have been enhanced, perhaps by skeletal P from the graves 'occupant'.

Table 6.1: Descriptive statistics of P_{tot} results for Early Christian cist T170

	Upper layer	Basal layer	Background samples
Mean	597	679	487
Standard error	14.0	17.8	19.7
Median	605	655	470
Standard deviation	109	138	101
Range	450	720	370
Minimum-Maximum	420-870	450-1170	300-670
Count (n)	60	60	26
Coefficient of variation (%)	18	20	21

The distribution of P_{tot} levels in the grave at each layer have been plotted using the Winsurf mapping package (Golden software, 1993) and are displayed in figure 6.16 and 6.17. No pattern is discernible in either distribution, and certainly no 'skeletal' image can be ascertained, but they both reach their maximum P_{tot} concentration at a position roughly one third of the total length of the grave, at the narrow end. This does not correspond to any skeletal P_{tot} maximum, which would be at the head end of a body, assuming the body would be laid in the grave conventionally with the feet at the narrow end. The slight increase in P_{tot} values to the base of the grave indicates that it is likely that a body had occupied the grave, but the high values of P which would be associated with a skeleton, if all its P content were fixed in the soil, have not been detected. The mean P_{tot} concentration for the six samples collected from between the basal slabs was 550μg g^{-1} and these six results were not significantly different to the results for the background samples. The lack of high P readings could be attributed to a number of factors; sample collection, P leaching, method of burial and subsequent in-fill of the grave and the homogenisation of the soil under post burial conditions. These factors are relevant to the following examples and so will be discussed in full at the end of this chapter in section 6.3.6.

Figure 6.14: Cist T170 before excavation

Figure 6.15: Cist T170 showing 10cm sampling grid

P distribution over cist T170

Figure 6.16: Upper layer

Figure 6.17: Basal layer

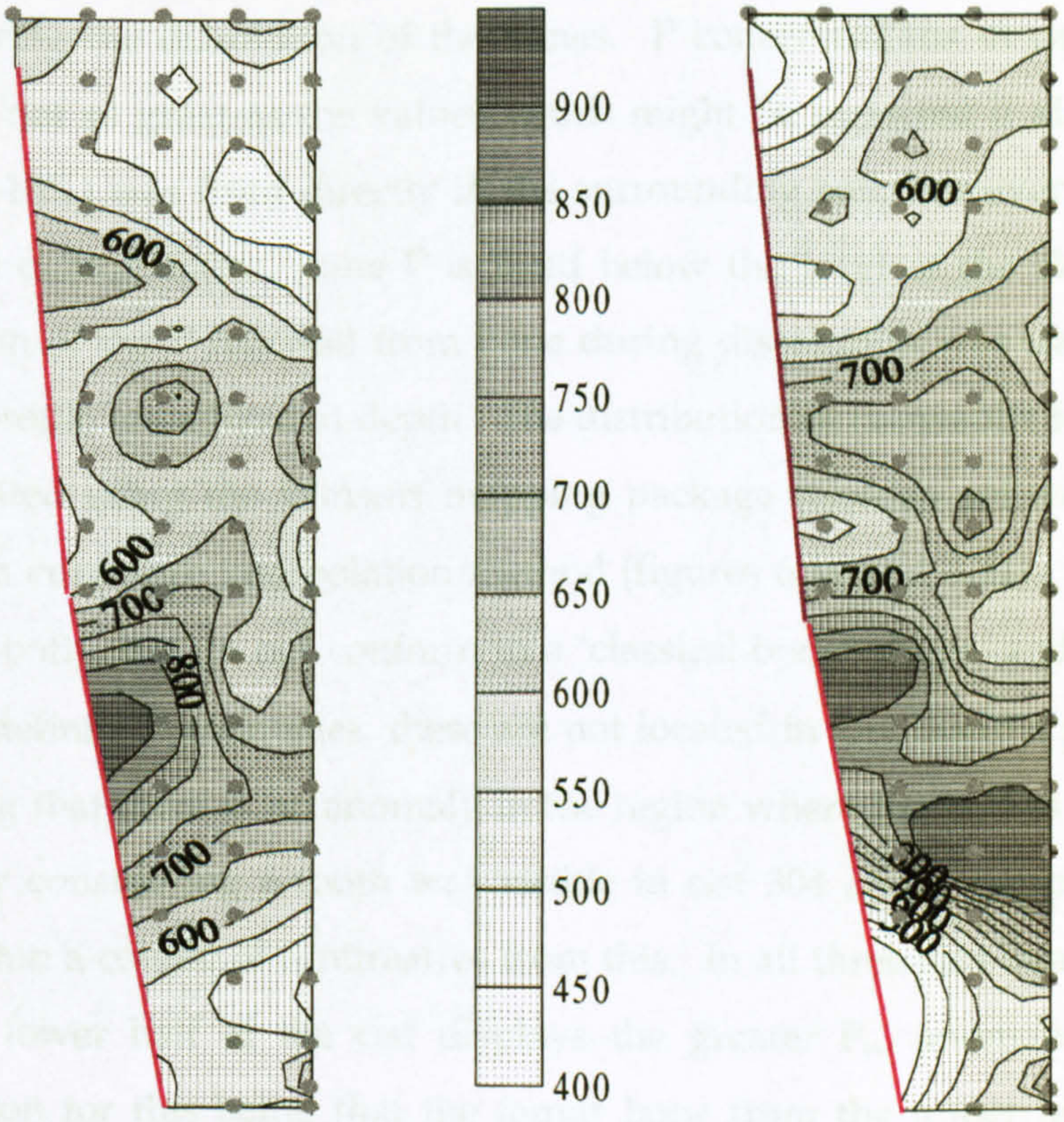


Table 6.2: Descriptive statistics of P_{tot} results for Early Christian cists 216 & 304

	Cist 216	Cist 304
Mean	902	3522
Standard error	38	610
Median	800	1470
Standard deviation	399	5819
Range	1840	30314
Minimum-Maximum	300 – 2140	496 – 30810
Count (n)	112	91
Coefficient of variation (%)	44.2	165

The P_{tot} results from cists 216 & 304 are greater than those for cist 170, with cist 304 being considerably greater than cist 216. The P_{tot} content of soil samples collected from both these cists have been enhanced relative to background soil levels (table 6.1). The high levels from cist 216 indicate that some P from the dissolution of the skeleton has been fixed in the soil at the base of the grave, most likely carried there by percolating water, as it was released from the dissolution of the bone under the acidic soil conditions. The high concentrations measured in a number of samples collected from cist 304 indicate that the soil P_{tot} has been enhanced by skeletal P fixed during the dissolution of the bones. P concentrations in cist 304 reach 3%, which is not as great as the values which might be expected if all the P from the bone (16-18%) was fixed directly in the surrounding soil, however, as the example from 216 demonstrates, some P is fixed below the level of the skeleton and so a proportion of the P released from bone during dissolution was translocated down the soil profile to be fixed at depth. The distribution of P_{tot} results for each cist have been plotted using the Winsurf mapping package (Golden software, 1993) and a minimum curvature interpolation method (figures 6.19 and 6.21). The distribution of P_{tot} in both cists do not conform to a 'classical body' shape, and while there are areas of definite P anomalies, these are not located in any distinct pattern, and it is surprising that there is no anomaly in the region where the bodies head should be, especially considering a tooth was visible in cist 304 and a sample was collected from within a couple of centimetres from this. In all three cists examined from this site, the lower half of the cist displays the greater P_{tot} anomalies, one possible explanation for this being that the femur bone from the upper leg is particularly

Figure 6.18: Cist T216 excavated

Figure 6.19: P distribution over cist T216

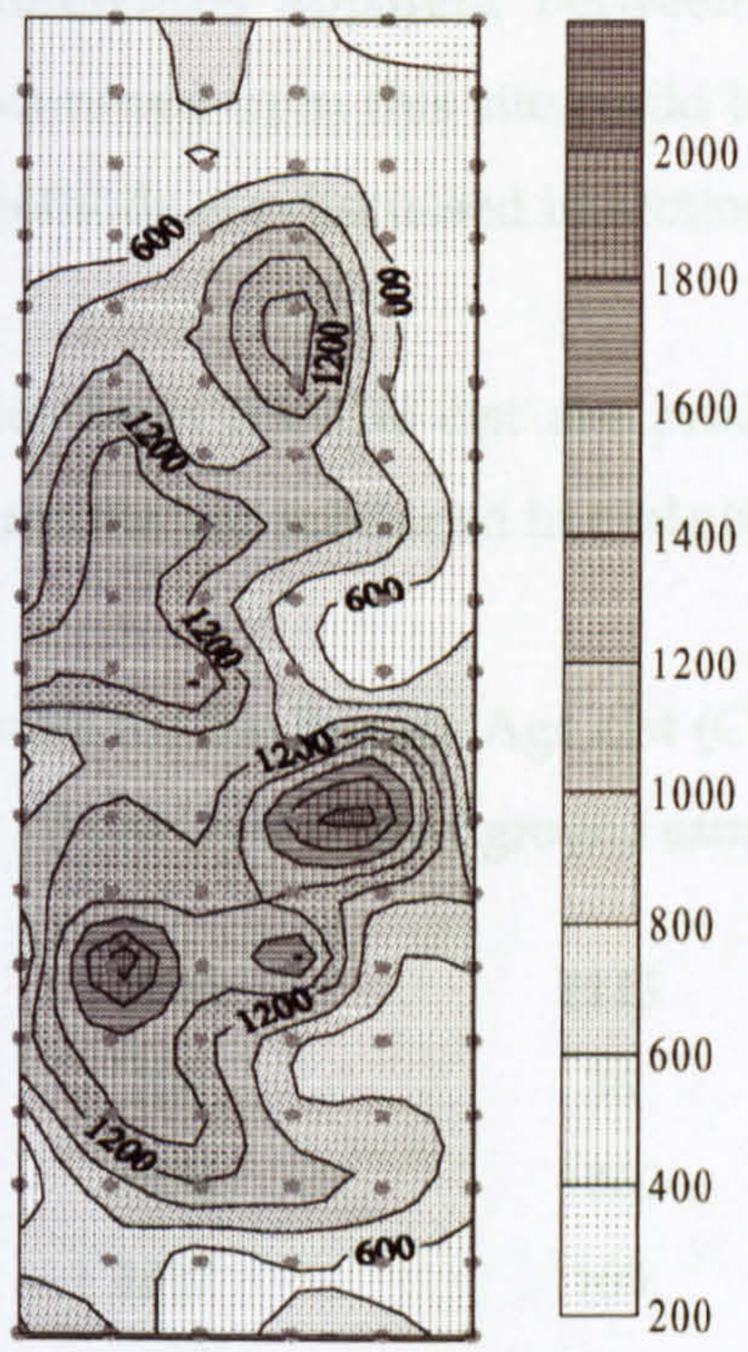
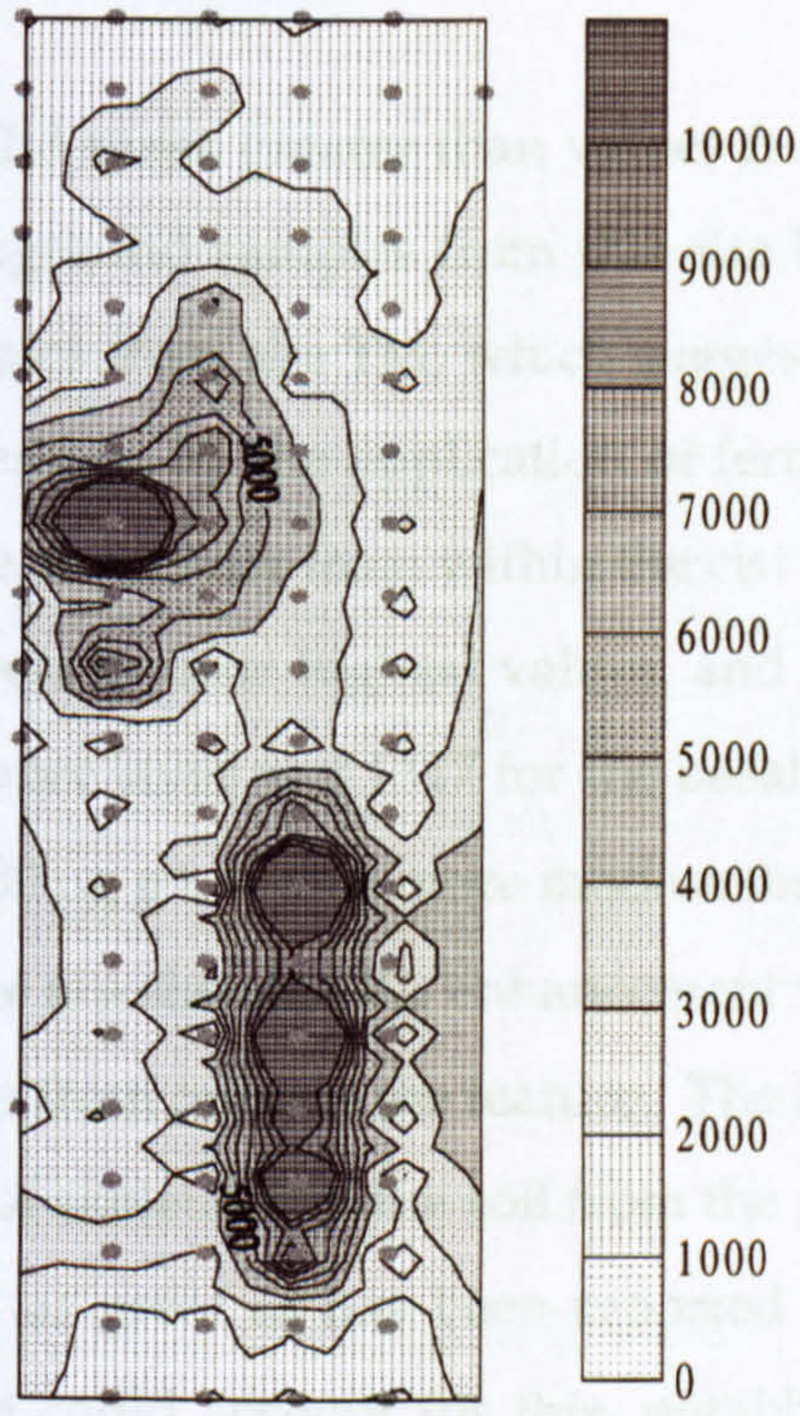


Figure 6.20: Cist T304 partially excavated

Figure 6.21: P distribution over cist T304



dense and weathers more slowly than many of the other less dense bones. The slower weathering could allow a greater proportion of the phosphorus from these bones to be fixed within the soil. The differences apparent between the P_{tot} distributions displayed from the three cists examined from this site could be due to the altered method of burial used, and such methods are discussed in section 6.3.6.

The P_{tot} results measured for the 147 samples from the CU cist are produced in appendix one. Descriptive statistics for these results are produced in table 6.3

Table 6.3 descriptive statistics of P_{tot} results for the Bronze Age cist (CU)

	Upper layer	Basal layer	Background samples
Mean	1379	2190	1113
Standard error	166	109	36
Median	1680	1370	1060
Standard deviation	862	1317	163
Range	5110	5940	590
Minimum-Maximum	220-5330	700-6640	890-1480
Count (n)	63	63	21
Coefficient of variation (%)	62	60	15

The mean P_{tot} values for the CU cist site are 2-3 times greater than values from the T170 cist, but not as great as T304. The background samples from this site have a greater P_{tot} content than the background samples from site TM, which suggests that P in the soil at this site has been enriched, perhaps by the application of fertilisers. There is a wide range of values measured here, especially from within the cist where P_{tot} values increase 10–20 fold from their lowest to their highest values, and so the data has standard deviations of 862 for the upper layer and 1317 for the basal layer. Outside the cist the values range from 890–1480 $\mu g\ g^{-1}$, with a more modest standard deviation of 163. These results show that there is a sizeable P_{tot} enhancement within the cist when compared to the control samples from outside the feature. The logical explanation of this enhancement is the fixing of skeletal P in the soil from the graves 'occupant'. The level of enhancement is not as great as has been reported in the literature, but there are several factors which could account for this, notably post burial soil homogenisation which will be discussed below. There is a significant

difference (P=0.01) between the values measured in the basal layer and the values measured in the upper layer, so there is a definite P_{tot} enhancement towards the base of the cist, which is probably due to the presence of skeletal P. The distribution of P_{tot} within the cist at the two levels has been plotted using the Winsurf mapping program with minimum curvature interpolation (Golden software,1993: figures 6.23 and 6.24). Both layers display the highest P_{tot} values in the top right corner of the cist, a feature which could correspond to the head of a body buried in a 'foetal' position in the grave. Unfortunately, there are no other clues from the P_{tot} distribution as to the position of a body in the grave.

The P_{tot} results measured for the 33 samples from the CU suspected inhumation are produced in appendix one. Descriptive statistics for these results are produced in table 6.4

Table 6.4: Descriptive statistics for the suspected inhumation -CU

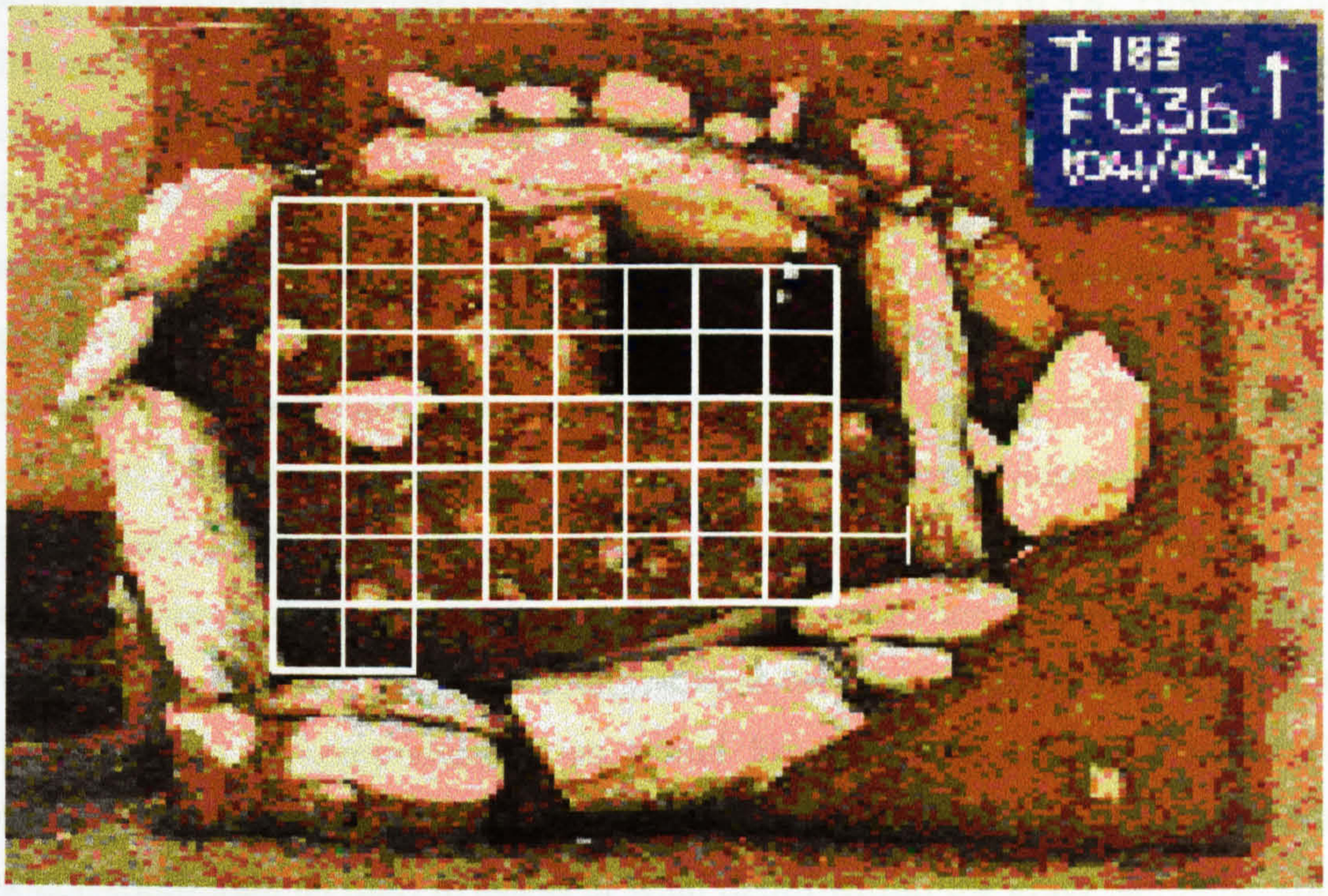
Mean	780
Standard error	56
Median	640
Standard deviation	320
Range	970
Minimum-Maximum	310-1280
Count	33
Coefficient of variation	41

The P_{tot} results measured for this suspected feature are not high. The feature was located only 20m from the cist yet the P_{tot} values are lower than the background samples collected from around the cist. This feature does not exhibit the elevated P_{tot} levels than would be expected from an inhumation. It was therefore concluded that an alternative explanation was needed for the abrupt change in soil colour and texture that was noted in the field.

6.3.6 Discussion

In both cases where the P_{tot} distribution was examined at two depths within a cist in this chapter (T170 & CU183) the values of P_{tot} measured in the basal soil samples are

Figure 6.22: Bronze Age cist at Cleirog Ucha shoeing 10cm sampling grid



P Distribution over the CU burial cist

Figure 6.23: Upper layer

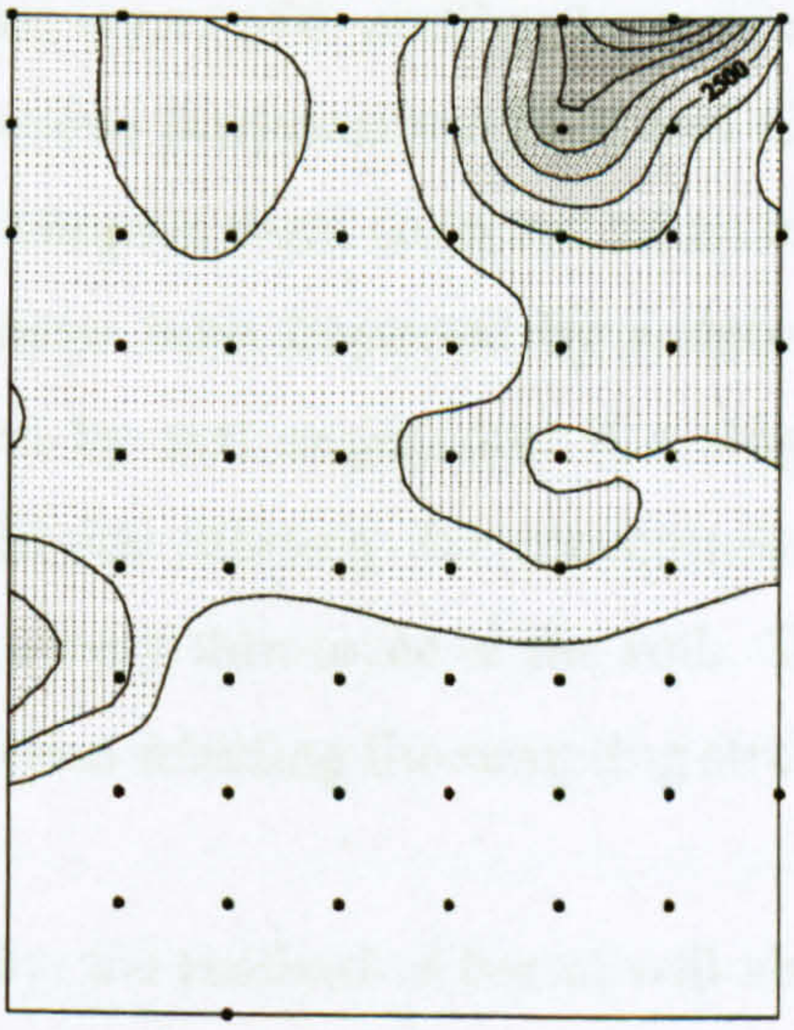
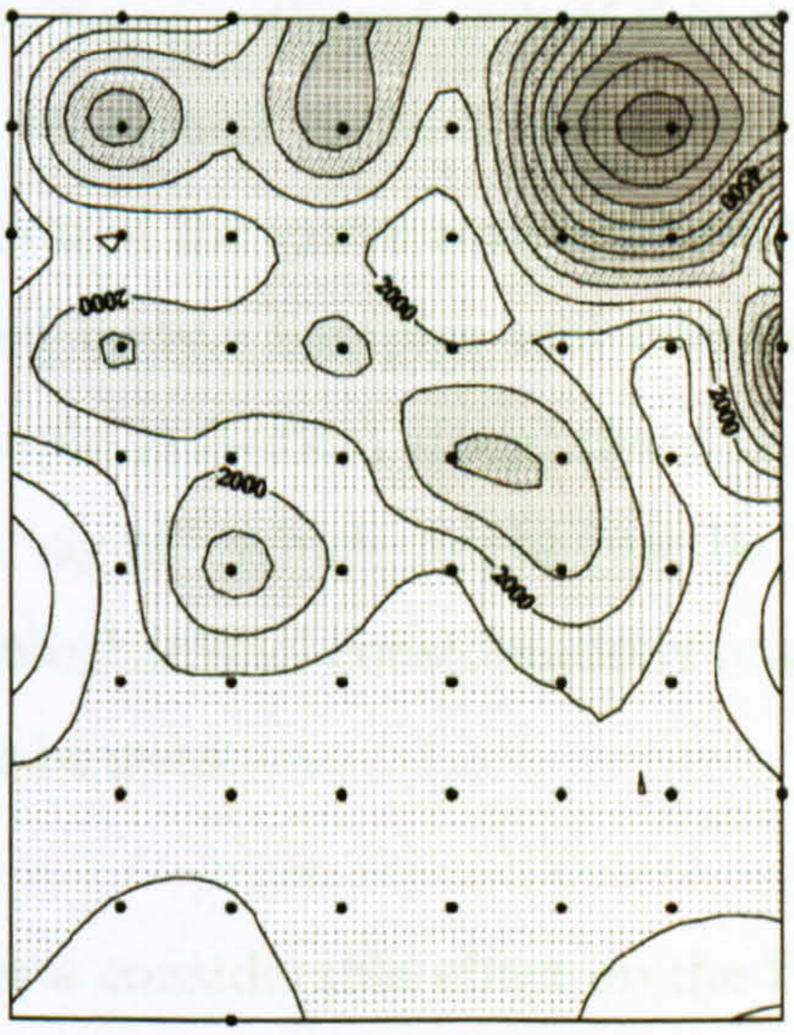
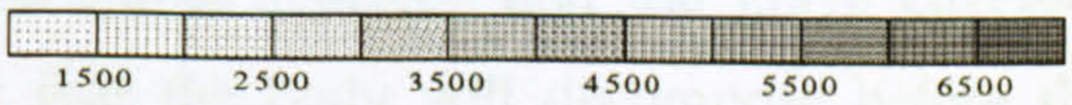


Figure 6.24: Basal layer



Ptot (ug / g)



significantly greater (P=0.01) than values measured in the upper soil samples. The concentration of P_{tot} measured in the subsoil of an excavated cist (T216) appeared to be enhanced relative to background levels, and the concentrations of P_{tot} measured in the soil from another cist (T304) were greatly enhanced, up to 3%. However, the P concentrations are not as great as those reported in the literature, or those which might be expected if the majority of skeletal P was fixed in the soil, and there are three main reasons why this could be the case. Firstly, the constraints of the sampling strategy chosen to fit with the archaeological excavation can cause problems. The primary constraints are money and time. Any P_{tot} analysis is expensive, with estimated costs being at least £5.00 per sample, and rarely can an archaeological excavation afford a large number of these analyses. The time constraint is particularly relevant in the excavations at Ty Mawr and Cleiriog Ucha, the sites sampled in this study, as all the cist samplings had to fit in with a scheduled excavation. Such constraints meant that the sampling strategy at both sites was not as comprehensive as would be desired to achieve the best P_{tot} coverage. Ideally samples would be collected and analysed prior to the excavation, which could then be used to assess at what depth within the grave sampling grids could be established, with a view to sampling the depth showing the greatest level of P_{tot} enhancement. Without this initial prospecting, samples were collected from the depths within the grave where P_{tot} levels would be expected to be highest, *i.e.* at the basal layer, with another layer of samples being collected at half this depth for comparative purposes for T170 and CU183. A second method was used for T304 where samples were collected when excavation of the grave revealed features that could have been imparted by a decomposed body. Samples will commonly be collected by soil auger, and if a single sample is 5-10cm deep, there is a large potential for diluting the concentrated P_{tot} 'signal' which might just be present within a very thin layer of the soil. These 'mechanistic' considerations have to be made when selecting the sampling strategy to be used.

Secondly, the method of burial will also have a considerable effect on the P_{tot} trace uncovered, for which there are two main scenarios. The body could be placed in the empty grave, the top stones replaced and the grave covered with soil. In this situation it is likely that the body will decompose before the percolating water transports enough soil material into the grave through the gaps between the

capstones to cover it, the P will accumulate on the surface of the basal stones and, under conditions of high rain infiltration/percolation, could be easily removed from the grave. Fixation of P will take place to the soil material which is carried into the grave, but this will only occur in a thin layer of soil at the basal surface, and it is therefore vital that this layer is sampled if the P_{tot} trace is to be detected. The majority of soil which will eventually fill the grave will do so after the P has been fixed and so will not have an unusually high P content. A second scenario is envisaged where the body is placed in a grave which is back-filled with soil, in this situation the body decomposes and as P is slowly released from the bones it will be fixed within the soil material; only a small amount would be leached from the system. When sampling this sort of burial, the P will be relatively more diffuse but should still be concentrated at a specific layer within the soil which, if sampled, should yield an informative P_{tot} body trace. The large differences in P_{tot} content between cists T170 and T304 could be due to these two different burial methods. The lower levels in T170 could be due to the body decomposing before the in-fill of the grave, with soil carried in by percolating water contrasted to, perhaps, the body being buried in soil in cist T304, thus leaving more soil fixed P.

The third reason why the values measured were not as high as might have been expected is due to the effect of the soil conditions in the subsequent years following burial, which are important primarily for the affect they have on the soil fauna. The organisation of a P_{tot} skeletal trace will be destroyed if the soil within the grave is homogenised by mesofauna. If at some stage after burial the soil *p*H rises above *p*H 5.5, perhaps with the application of agricultural lime, conditions become suitable for the mesofauna, especially earthworms (*Lumbricus terrestris*), which homogenise the soil disturbing the trace of the skeleton. Only if conditions have remained acidic since burial is there likely to be an undisturbed skeletal P trace. The soil *p*H at site TM was 6.8 compared with 5.6 at CU, and this is sufficiently different to make soil conditions since burial much more favourable for mesofauna at TM than they have been at site CU, thus homogenising distribution of P_{tot} in all the cists examined.

DISCUSSION

7.1 General introduction

The analysis of total phosphorus (P_{tot}) in soils can be a useful method of gaining further information about an archaeological site and can help to guide any further excavation. An anomalous soil P_{tot} content can be an indicator of past biological activity and human influence on a site. However, it is difficult to make any conclusions as to a distribution of anomalous concentrations without some understanding of how P_{tot} levels vary in the soil naturally. Chapter three and four of this thesis quantify the variation of P_{tot} in acidic soils at two sites from North Wales, at a comprehensive range of scales, from a 100m grid interval to a 10μm grid interval. The variation of P_{tot} is examined in detail and comparisons are drawn between the two background sites sampled and a third archaeological site (a medieval long-hut) on a similar soil.

The second focus of the research in this thesis has been the mobility and redistribution of P in acid upland soils. The mode and extent of P dispersion from a concentrated source such as bone will determine the level of P redistribution in archaeological soils. The mobility of P in acidic soils was examined using experimental soil columns leached with dilute organic acids and carbonated water in the laboratory. The redistribution of P was investigated in thin sections made from sherds of bronze Age cinerary urns within which amorphous cutanic deposits had been observed. Similar features had already been identified as Ca/Fe phosphates in Paleolithic cave deposits from Pontnewydd (Jenkins, 1994) and, with a source of Ca and P from the cremated bone, it was thought that the cutans present in the cinerary sherds could be of similar composition.

A final area of research reported in the thesis examines the specific example of sampling an archaeological grave for phosphate. Under acidic conditions, such as are found locally in North Wales, the body and bones of any grave occupant would soon decompose and undergo dissolution, yet a chemical signal of elevated P should remain, fixed in the soil. The problem investigated was to select a method of sampling at a suitable interval from which a body trace of elevated P levels could be reproduced. Chapter six examines the strategies and methods required to achieve satisfactory sampling of a grave.

This chapter will discuss these areas of interest in turn, examining the decisions which will need to be made by anyone conducting phosphate analysis, and discuss the options of sampling strategy, sample collection, preparation and measurement, data generation, analysis and presentation. The results will be discussed in the light of information gained as to the background variation of P_{tot} in relevant soils, its redistribution and mobility. The specific example of P_{tot} analysis over a grave site will be examined in detail, and discussed in relation to the data generated by the novel theoretical sampling of a data-set derived from a whole body radiograph, and the subsequent sampling and analysis of 4 cists from two archaeological excavations on Anglesey. Finally, conclusions from the thesis are drawn and five areas of possible further work are considered.

7.2 Sampling strategy

The choice of sampling strategy is the first decision to be made when sampling an area of soil for P_{tot}, and to make this decision the objectives of the survey must be considered. The sampling strategies which can be used are described in a number of statistical textbooks (*e*.g. Beckett & Webster, 1990), and if the purpose of the survey is to describe the characteristics of a variable population, then a form of random sampling is often recommended. This avoids the bias that will be inherent in any selection of sampling points and ensures that every member of the population has an equal chance of being sampled. The objectives of a soil survey of P and an archaeological survey of P are slightly different. The archaeologist is interested in locating anomalous values of P superimposed in a background population and so requires the complete coverage of an area. A random sampling strategy will therefore not be suitable because it leaves regions unsampled. Samples collected on the rigid grid basis of a systematic strategy ensure the complete coverage of an area, so this form of sampling is usually more suitable for an archaeological soil survey. Systematic sampling has potentially greater efficiency which is essential for the often time constrained archaeological excavation, and provides a set of samples which are more easily located, indexed and simpler to map. Problems will arise when there is periodicity in the data so changes in the variable examined correspond to the sampling interval; however, background

samples collected away from the grid can identify this. The statistical analysis of data collected systematically can be problematical, especially with estimates of standard error, since the sampling points are not located at random. However, within the field of geostatistics some allowance can be made because, although the sample points are not located at random, a soil characteristic such as P_{tot} could be assumed to be randomly variable across an area and so the data is still randomly generated (Richard Webster, *pers. com.*).

The selective collection of soil samples for analysis, for example the collection of samples from a soil stain located in the centre of a chambered cairn by Johnson, 1956, ensures that the relevant samples are analysed and can be a useful sampling strategy. However, the introduction of such sampling bias means that only very limited statistical analysis can be conducted, and it is difficult to comment on the significance of such results. Selective sampling is useful on some occasions but should be avoided for prospective archaeological P survey.

The spacing of the sampling grid interval is another important decision facing the organiser of any archaeological P survey, and this is governed by a number of constraints which include the total number of samples which can be collected, the size of the area surveyed and, perhaps most importantly, the size of the features which need to be identified. Phosphate surveys are commonly conducted at a range of scales (50m – 1m grid intervals) and the chances of locating a feature of a limited size vary considerably depending on the grid interval used. For example, there is only a 4% chance of locating a 1m×1m feature if sampling is conducted on a 5m×5m systematic grid interval. Clearly it is impossible to say categorically what sampling interval should be used in any or all circumstances as each case should be considered on its merits, but the smallest grid interval which can be used under the constraints of the survey will yield the most useful information.

The study of P_{tot} in soil at the three sites examined in chapter three took place using a systematic sampling strategy over a range of sampling intervals in the field; 100m, 10m, 1m, & 0.1m at two sites and 10m, 1m, 0.5m & 0.1m at the third site. This strategy ensured that there was complete coverage of the sample sites and that the variation in P_{tot} could be assessed at a range of intervals at each site. For this study

the systematic sampling strategy was ideal because it allowed the large numbers of samples collected at each site to be located and indexed quickly, and the complete coverage meant that the interpolated maps used to display the data and its variation were more representative of the actual soil P_{tot} distribution. The distribution maps plotted for the data collected at the medieval long-hut clearly illustrate that a coarse sampling strategy misses potential features which show up when the area is sampled at a finer grid spacing.

The examination of the soil P_{tot} distribution in samples collected in the field was complemented by the study of P_{tot} in the laboratory at a scale which is impossible to sample in the field. Soil thin sections were made from soils collected from sites A and B and the distribution of P_{tot} examined over 1cm×1cm, and 1mm×1mm. At these scales measurements were made by electron microprobe analysis (EMPA) utilising WDXRA for P and EDXRA for other elements measured. The only simple way to collect such data for 121 sample points over a 1cm or a 1mm square was on a systematic grid, where the instrument stage was pre-programmed to move between analyses. Analysis on any random basis would have been too time consuming.

7.3 Sample collection and processing

Several methods have been devised for the analysis of P in the field (*e*.g. Eidt, 1977) however these methods only tend to measure a portion of the P_{tot} present. If this portion measured is not related directly to the 'archaeological P' then important information could be missed, or the results could appear misleading. A number of methods can be employed for sample collection and subsequent laboratory analysis. It is important that all samples are collected from the same depth because the P_{tot} content of a soil can vary considerably with depth, site A had a P_{tot} content of 2260μg g^{-1} in the top 5cm but decreased to 1290μg g^{-1} at 45-50cm. Similarly, site B saw a reduction from 940μg g^{-1} to 260μg g^{-1}, and site C from 1630μg g^{-1} to 1090μg g^{-1} (section 3.6.1). The reduction in P_{tot} with depth is a common feature in soils which is described in many standard texts (*e*.g. Wild, 1987 ch.21) and is attributed to the reduction in organic matter content of the soil. P in the organic fraction can account for up to 60% of P_{tot} in the surface horizons of soils. This relationship was shown in detail by the examination of the distribution of P_{tot}, total organic C and extractable

Fe and Al in a 5cm square portion of the soil taken from 2cm below the soil surface (section 3.6.4). The distribution of P_{tot} correlated closely ($p=0.01$) with the distribution of total organic C. In cultivated soils, the reduction of P_{tot} with depth can be exacerbated by the addition of fertilisers, which are generally fixed within the plough layer.

Before soil samples are collected it is useful to dig a soil profile pit to describe and sample the soil horizons present and to provide a soil classification. It is common for unimproved upland soils to have a well developed A_h horizon which varies in depth, as described for site B. This A_h soil has a greater P_{tot} concentration than the soil in the B horizon below (section 3.6.3), so to avoid increasing the variation in P_{tot}, each sample should be collected from the same horizon. A more general sampling method could introduce an anomalous P pattern which could complicate the interpretation of the results. The soil sampled at site B was a stagno-gleyic brown soil which had a very distinct organic A_h horizon. It was decided not to sample this horizon but to take samples from directly below it, from the B_g horizon, to avoid collecting a variable amount of organic matter which would increase the variability of P_{tot} measured. Other problems can arise on sloped sites where soil erosion has removed the topsoil from a section of the sampled area. In these situations the organic matter content can be estimated (*e*.g. by loss on ignition) and some allowance made.

The common method of sample collection is by soil auger which is usually 2.5cm in diameter. It provides a simple way to collect similar samples from each grid node and the depth of each sample can be easily regulated by marking the thread of the auger. It is important that samples which are to be statistically compared are collected in a similar manner, the size, the shape and the orientation of each sample; a factor known as the 'sample support' should be the same and sampling by soil auger achieves this. However, problems can arise when sampling by auger, for example under the very stony conditions encountered over the floor of the long-hut at site C or when a soil is very hard or dry. In these conditions samples can only realistically be collected using a spade, a narrow bladed trowel or spatula, so altering the sample support. When statistical comparisons are made between samples collected with differing sample support this should be clearly stated. The

second problem with augering for samples occurs when the grid interval size is reduced. Samples can be comfortably collected with a 2.5cm Ø auger at a 0.1m grid interval but at certain sites, for example an archaeological grave, samples may be collected in the field at a finer resolution than this. In these cases samples can be collected more precisely with a trowel, knife or spatula.

Prior to the measurement of P_{tot} in the laboratory, soil samples should be air-dried, sieved and ground before being sub-sampled, because many methods require only one gram or less of soil and commonly 10 grams or more are collected. In order to sub-sample a representative portion of the whole sample it should be finely ground, a process which reduced the range and standard deviation of selected samples analysed in this thesis by 70% (section 3.8.2). This grinding allows a more accurate assessment of the variation between samples.

The total amount of P in soil can be split into a number of fractions which have been highlighted in figure 2.2 and there is a variety of techniques available to measure each of these fractions. However, because of the large number of samples measured from each site and the absence of detailed information regarding the use of P fractionation for archaeological analysis, only total P (P_{tot}) was measured throughout this study, although a number of easily extractable P analyses were conducted for comparison. A modified version of the perchloric acid digestion described by Sommers & Nelson, (1972) was chosen because of its good precision and simplicity (appendix II). In situations where a water-scrubbed fume chamber and dri-blocks are not available, then the ashing and extraction method is recommended. Phosphorus in solution was measured using a flow injection analyser for speed of analysis (200+ samples/day), accuracy (±1%) and precision (±0.5%). A number of extractable P analyses were conducted as well as the total P analyses, and the P_{tot} and P_{ext} results from the two sites correlated significantly, (site A, $p=0.01$ and site B, $p=0.05$). If P_{tot} analyses can not be conducted, the simpler P_{ext} analyses can still provide useful information as to the pattern of distribution of the total P fraction.

7.4 The background variation of P_{tot} in two specific soils

To examine the natural variation of P_{tot} in soil, two sites were sampled; site A was an improved pasture which had been ploughed, fertilised and re-seeded in the 1950-60s, but had been subsequently left as rough grazings, and site B was unimproved rough grazings. Both sites appeared to have no related archaeological features and so were considered suitable for the measurement of inherent soil P. Over 500 soil samples were collected from a range of grid intervals at each site and their P_{tot} content measured. The mean values for each grid interval at site A (1614-1974 μg g^{-1}) were more than double those at site B (615-732μg g^{-1}), which can probably be accounted for by the persistence of phosphate fertilisers (basic slag) applied to site A in the 1950-60s, and this interpretation is visually confirmed by the interpolated distribution maps (section 3.6.5.1) and the increased amounts of organic matter in the soils from site A (15-20%) when compared to site B (<10%).

The variation in P_{tot} at these two sites can be assessed simply by plotting the calculated coefficients of variation (figure 7.1), which expresses the dispersion or variation of the data in relative terms, even though the mean at site A is twice as high as the mean at site B.

Figure 7.1: Coefficients of variation for decreasing grid interval

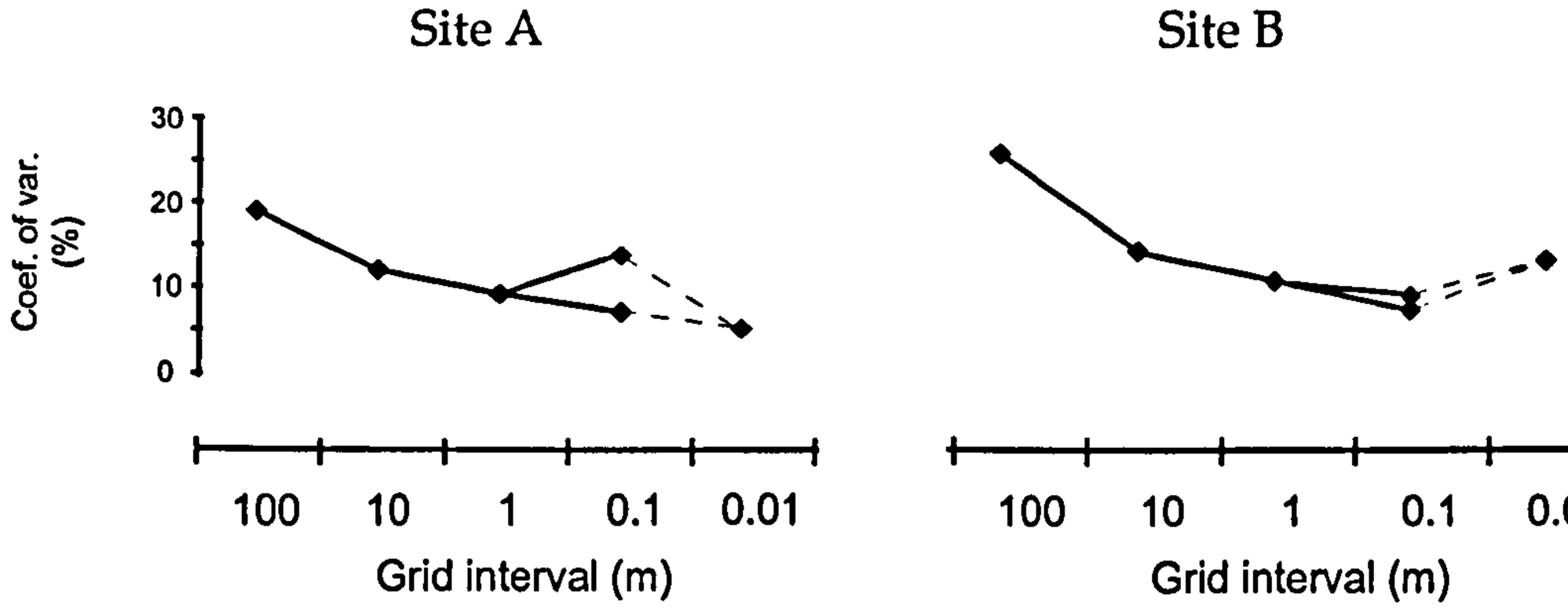


Figure 7.1 shows similar amounts of variation in P_{tot} at both sites, with the greatest variation in P_{tot} at the largest grid interval. Gradually a reduction in variation in P_{tot} occurs at both sites as the sample area decreases, however a definite increase is observed at site B when the interval reduces from 0.1m to 0.01m. Beckett & Webster

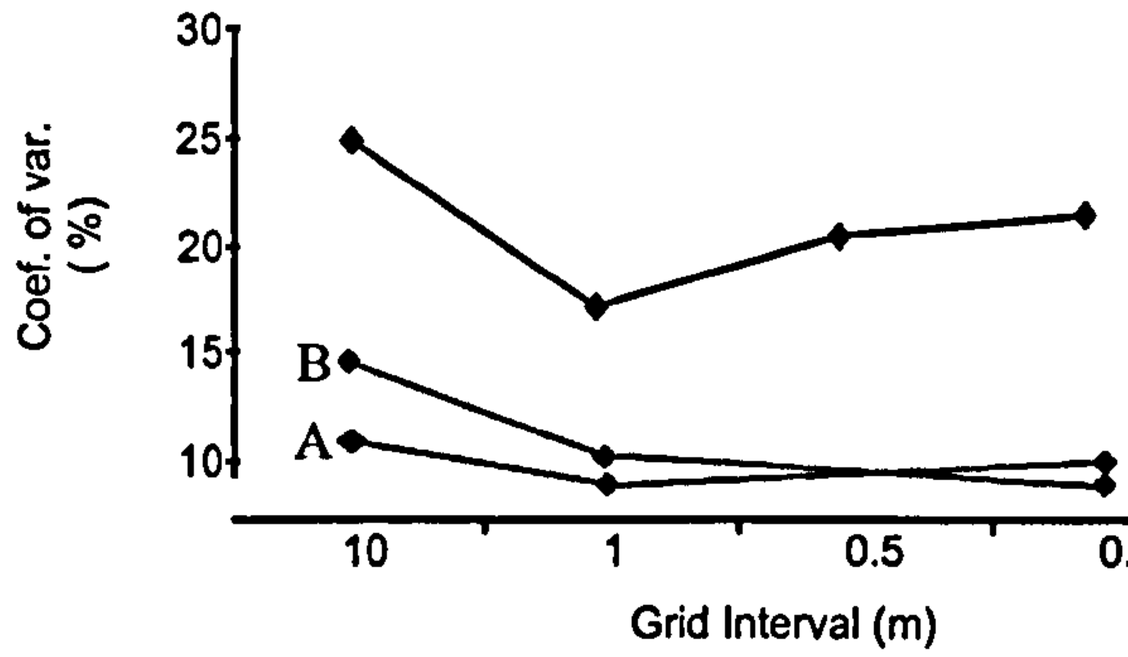
(1971) report that the variation in certain soil parameters increases as the size of the area sampled increases (spatial dependence) and this study confirms this for P_{tot}, a soil parameter Beckett & Webster did not examine. Site A displays spatial dependence in P_{tot} from 100m down to 0.01m grid spacing. As a sample area is increased, a greater variety of soil conditions are encountered which can increase the variation measured, these sources of variation are considered in section 7.9.

A thorough investigation of variation can be achieved through the use of semi-variograms, which model the variation present in the data according to lag distance (the distance between sample points). Semi-variograms were plotted for the two sites to summarise the variation within each sample square (section 3.6.6). Overall, the variograms displayed large "nugget" variances and fairly flat lines (maximum rise of <10%), which suggests that there was as much variation in P_{tot} measured between the closest grid points within each sample square as there was between the most distant sample points within each square. The variograms were plotted for four directions from a central point and for all of site B and most of site A there was no difference between the variances plotted in any direction. The only exception was that of 0.1m sampling interval at site A, which showed some difference in directional variance, an artefact of the banded pattern of P_{tot} distribution arising from the basic slag applications. In general the features of the variograms plotted suggest that the P_{tot} data displays stationarity; that P_{tot} is a semi-random variable and is not spatially dependent, so samples located closer together do not necessarily have similar P_{tot} values.

7.5 A comparison between the P_{tot} values from background sites and those measured at an archaeological site.

The results of the P surveys over the two background sites were compared with a routine archaeological P survey carried out over a medieval long-hut: site C. The area surrounding the long-hut was initially surveyed and then sampling focused on a central cleared area within the long-hut itself (section 3.4.2.2). The measured P_{tot} values increase as the sampling interval decreases, and the variation in P_{tot} encountered is greater than that measured at sites A and B with the coefficients of variation for the four grid intervals measured dropping below 20% only once (figure 7.2)

Figure 7.2: Coefficients of variation for decreasing grid intervals from site C (showing site A and B)



The variation measured at site C increases with the smallest two grid intervals sampled because these samples were collected from within the long-hut where areas of enhanced P of up to double the mean value were measured. Whether values such as this can be categorised as archaeologically enhanced will be considered in section 7.6. The semi-variograms calculated for site C displayed a variance which was roughly 10 times greater than that at sites A and B but which similarly showed little directional difference. The variograms for the 0.1m grid interval had a large nugget variance and reached a sill at roughly a 0.5m lag. This variogram shape suggests that samples collected at the closest sampling interval over the grid square had considerably different P_{tot} values, and variation across the sample square reaches a maximum at a 0.5m separation. Samples collected at a greater than 0.5m separation across the sample area do not increase the variation encountered.

7.6 A guideline for data assessment within P survey for archaeology.

The data generated from an archaeological P survey can be examined in a variety of ways, and precise conclusions can only be made if the methods of data analysis are suitable. Initially, the methods of sampling strategy, sample collection and processing should be clearly explained, and any modifications made to these methods within comparative sets of data outlined.

P survey is conducted over archaeological sites to try and locate areas with anomalous P_{tot} values which could be due to human influence on the site. Any

elevated values can be compared to a mean value of P_{tot} for the site to assess whether they could be classed as significantly high. A simple test of significance in this case would be to assume that any value 3× the standard deviation higher than the mean is significant (Hammond, 1983). Using these parameters, several of the P_{tot} results from the 0.5m and 0.1m grid intervals at site C can be classed as significantly enhanced; however the 0.1m-i grid at site A has one result and at site B has two results which could also be considered as significantly enhanced using the same parameters. Site A and site B, examined as background sites, show that the "natural" variation in P_{tot} was sufficiently high to be classed as a significant anomaly. The "3× the standard deviation" check for significant results should therefore only be used as a guide to anomalous results.

The human influence on a site can increase P_{tot} values in the soil over a large area so the mean value is elevated and anomalous values do not appear so high. It is important therefore to obtain background values of P_{tot} in the soil for comparative purposes and to consider the variation of P_{tot} over the whole site rather than consider whether the values in a few areas are anomalous. Background values have been considered as the lowest repeatedly recorded concentration of P encountered within the sample area (Sieveking, 1973), or have been calculated from samples taken a few feet away from the site (McCawley & McKerrell, 1971). It is recommended that control samples are collected from some distance away from the site under similar conditions of management, or in a continuous series of samples stretching away from the area of interest.

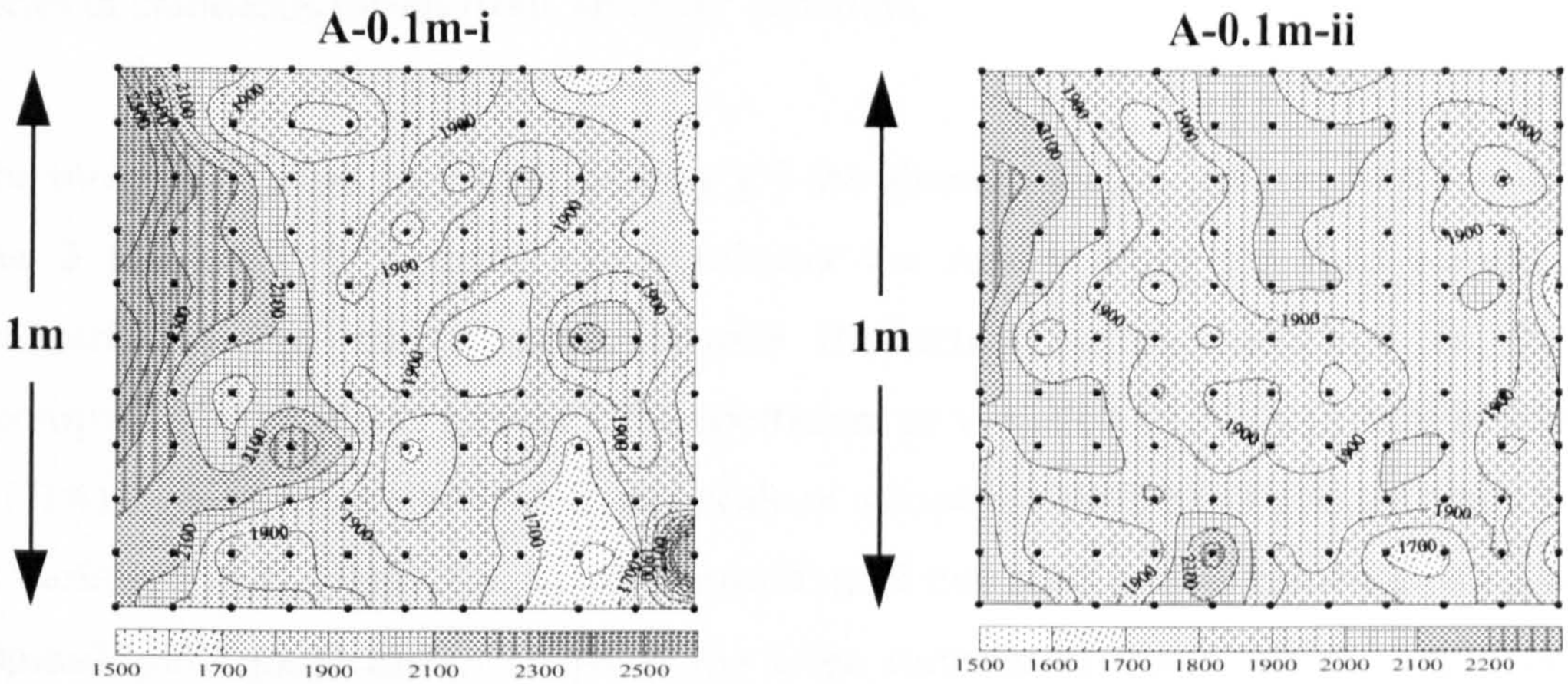
Human influence can be identified as increasing the variation of P_{tot} over a site, so the assessment of the variation of P_{tot} is useful. The variation of P_{tot} in the data collected can be examined in several ways; initially, simple statistics should be calculated from the data-set, and a visual representation of the data distribution produced using a histogram. Many soil parameters have a normal continuous distribution, however, the data can display distinct separate populations, so be regarded as discontinuous, or display a positive or negative skew. These non-normal population distributions can be indicative of anomalous values of P_{tot} and so perhaps of man's influence on the site. The dispersion of the data can also be considered using the range, the standard deviation and the variance, and the

coefficient of variation used to examine the variation of sets of data with different means. If all the field data collected at each site is grouped, and the descriptive statistics compared, there are obvious differences. Site A and site C had similar means and yet the standard deviation ($\mu g\ g^{-1}$) at the archaeological site was 2.5 times greater (A= 196, C= 471) and the variance ($\mu g\ g^{-1}$) six times greater (A= 38266, C= 221749) than that at site A, the coefficient of variation (%) was also twice as high (A= 10, C= 25). The descriptive statistics provide a reasonable indication of variation of data measured, but where mean P_{tot} values differ *i.e.* between site A and B, only the coefficient of variation becomes a useful parameter.

Variograms are useful to identify spatial trends in the data, and summarise the variation of a property within a region, however they should only be used with a minimum of 100 and ideally 250 sample points (Beckett & Webster, 1992). The large numbers of sample points required might often preclude the study of variograms within the analysis of data from archaeological P surveys, but if numbers are sufficient, variograms can help to identify and classify the variation present.

A final qualitative method for examining the variation present is through the plotting of interpolated distribution maps which will also display any pattern present in the data and regions of high values. For example, the distribution maps plotted for the two 1m sampling intervals at site A (figure 7.3) reveal the difference in variation between two 1m×1m squares less than 3m apart. The maps were plotted using the *Winsurf* mapping package (Golden Software, 1993) using a 'minimum curvature' interpolation method. The A-1m-i square had nearly double the standard deviation of A-1m-ii yet both have quite similar mean P_{tot} values.

Figure 7.3: Two distribution maps plotted for 1m×1m sample squares.



The use of distribution maps is common within archaeology and there are a number of computer packages which are designed to produce maps simply: however they should be used with caution. Attention should be given to the method of interpolation of the data because a different interpolation method can produce strikingly different interpolated maps. Several interpolation methods have been examined in appendix V, and for archaeological distributions a method which honours the original data points, such as a minimum curvature interpolation, is recommended. It is important to indicate the sample points on the distribution maps because the mapping packages used can interpolate into areas of no sample points and produce tenuous features in the distribution. When utilised correctly, plotted distribution maps can provide a useful illustration of the P_{tot} distribution highlighting areas of anomalous values and spatial trends.

7.7 Variation of P_{tot} at a scale of less than 1cm in two soils

Phosphorus was measured over a 1cm square, a 1mm square and a 100μm square in thin sections prepared from soils collected from sites A and B, to extend the range of sampling previously discussed down to the ultimate scale of individual soil components. P_{tot} was measured using a microprobe system which produced results of % P_2O_5 within the total oxides measured at each point. The P_{tot} concentrations for soils from site A and B were greater than those measured in the laboratory by a variety of wet chemical techniques, and so the microprobe was thought to be over-estimating the result. The reason for this over-estimation has still not been resolved,

particularly since the microprobe produced expected results for both bone and a series of standards mixed from '*specpure*' powders.

The mean P_{tot} values for site A (5036µg g^{-1}) are almost twice as great than those for site B (2724µg g^{-1}), a trend which mirrors the results from the field samples measured at the 'macro' scale, despite the actual values measured on the microprobe being much greater. The coefficient of variation of P_{tot} is greater at site B (51%) than at site A (36%) so at this scale of sampling site B has a greater amount of variation in P_{tot} than site A. The sampling at this scale was conducted using a 50µm×50µm square raster, to avoid the large number of voids which would be sampled if a point analysis was conducted. At this sampling scale the important factors which govern the heterogeneity of P_{tot} in soil will be its texture and the organisation and composition of the constituent particles. A raster size of 50µm × 50µm could sample a single mineral grain, which if it were quartz would only measure Si, but a detrital apatite grain would yield 18% P. Textural analysis of both soils revealed differences mainly between the proportions of silt and sand, with both soils containing roughly 30% clay. Site B had a much greater proportion of sand (41%) than site A (16%) which could account for the greater heterogeneity of P because more analyses would be located on individual mineral grains which could have high or low P concentrations.

Samples were collected initially at two grid intervals for each site. At site A the variation measured at the 1mm grid interval was greater than that measured at the 100µm grid interval, whereas at site B this trend was reversed. At the field scale, if the variation of a soil parameter increases with increasing sampling interval the soil parameter is described as 'spatially dependent', so generally as a larger area is sampled, a greater variety of soil conditions are encountered which affect the soil parameter. At the 'macro' greater than 10cm sampling interval scale, P_{tot} was found to be spatially dependent at both sites. However, at this much smaller scale of sampling the same can be considered for site A, but not for site B. The changes in soil conditions which are encountered during field sampling are less likely to have an effect at this sampling scale, and the organisation and composition of the soil matrix and the soil texture will be more important.

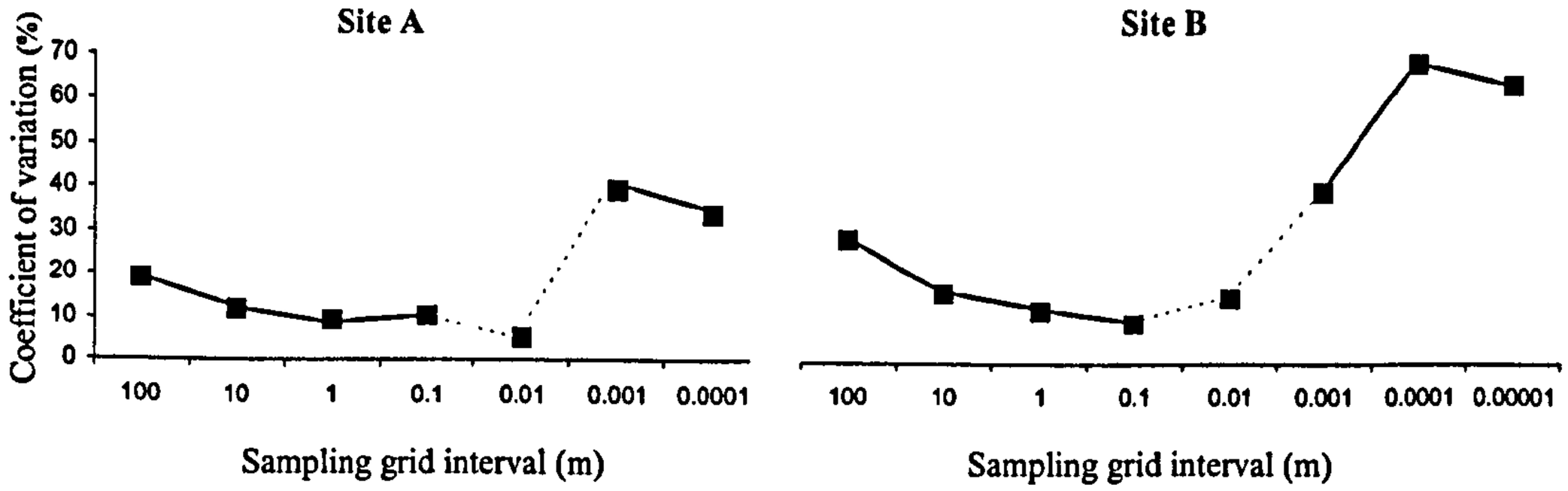
A single set of samples were collected from site B over a 100μm sampling grid interval, using a defocused beam (roughly 5μm diameter), which predictably reveals a greater amount of variation than the 50μm×50μm raster sampling over the same area. The coefficient of variation rises from 62% to 82% and the sample variance from 3.2×10^6 to 5.3×10^6. This difference in variation is due to the defocused beam measuring whole areas or individual mineral grains within the sample area, which could have high or low P values, the 50μm×50μm raster will average out areas of high and low P within each sample

A large proportion of P in the soil will be fixed onto iron and aluminium oxides on the surfaces of sand, silts and clay particles within the soil. This is illustrated clearly through extracting each mineral fraction with dithionite which cleans off all the Fe and Al from the particle surfaces. After extraction with dithionite the P_{tot} content of the fraction was reduced to roughly 15% of what it was originally.

7.8 The variation of P_{tot} in soil

The variation in P_{tot} measured at the whole range of scales examined in this thesis is displayed in figure 7.4, and shows very similar trends for both sites. These figures must be considered cautiously because the sample support was not the same for all samples collected, and the method of P_{tot} measurement was not continuous throughout. However, the variation reduces to a minimum at the 0.01m/0.1m sampling intervals, after which it increases distinctly.

Figure 7.4: The coefficients of variation for all sampling intervals



A reason for this dramatic change in variation could be the change in the sample support and method of P_{tot} measurement from 0.01m to the 0.001m samples. However, there are different sources of variation in P_{tot} depending on the scale of sampling, which are considered in section 7.9, and these could produce a considerable proportion of the differences in variation encountered.

7.9 Sources of P_{tot} soil variability

It has been identified that the variation in P_{tot} encountered over two sampling sites varies as the grid interval at which the samples were collected changes. The actual amount of P_{tot} in the soil at any single position will be dependent on a number of factors, but the primary source is the soils parent material (PM), from which P is gradually redistributed by the action of plants and animals. The influence of man can also produce patterns of P enhancement surrounding settlements and through cultivation.

The variation of PM across a landscape can produce changes in the P_{tot} content of a soil, and these changes can occur over only a few metres where the parent material has been sorted in soliflucted materials, or by the action of water in streams and rivers. These changes can be further complicated by soil creep or erosion and the variation encountered vertically through a profile will be further enhanced where the land surface has been covered several times by these natural events. The background sites considered in this thesis were selected for uniform PM (shale), and the largest area examined was 300m×300m, so there was no change in PM and no subsequent change in soils series or soil type.

It is unlikely that the soil from the three sites was disturbed by erosion, soil creep or solifluction so added variation would not be encountered through these causes. The topography of the areas sampled could have an effect on the variation of P_{tot}. Small scale changes in slope over only a few metres will affect the drainage of an area, and at each site there were topographical changes within the largest grid sample area. If there is a receiving site for water draining from surrounding areas, even on the 10m scale, this will have an effect on the soil P_{tot} content. Continually wet soils become anaerobic and gleyed, under these conditions P can be removed from the soil by

leaching and water movement, thus depleting the P_{tot} content. A 'mor' humus can also develop thus concentrating P in the surface horizon and increasing the variation encountered down a soil profile.

In general, most causes of variation in P_{tot} at the scale 10m-0.1m over the areas sampled in this thesis will be through the cycling of vegetation and the actions of animals and humans, all factors which are affected by the PM, climate and topography over time.

The large difference between sites is produced by changes in management practice, if a site has been ploughed the humus layer will be mixed into the surface horizon, increasing P_{tot} levels throughout this horizon. The fertilising of a field can uniformly increase levels of soil nutrients if applied evenly, however the non-uniform application of fertiliser can produce long-lasting patterns. At site A the application of basic slag in the 1950-60s from a tractor-pulled rear-spreading trailer left a pattern of strips of elevated soil P_{tot}, roughly 2m apart, running up and down the field. This sort of management practice can drastically affect the patterns and variation of P_{tot} uncovered over a site, and it is important that the previous land use history of an area is considered where possible.

The presence of grazing animals can add significantly to the variation of P_{tot} encountered. Random dunging will considerably enhance the P_{tot} content of surface soils. It could be considered that over a long period of time, every part of a field will be subject to a similar amount of P enhancement through the activity of animals but Briggs & Courtney (1985) showed that the edges of fields received preferential dunging, presumably as animals use walls and hedges for shelter, so gradients of P_{tot} could be encountered if samples were collected moving infield from a wall or hedge. Site A and B were selected as being away from obvious areas which animals might use as shelter so as to reduce the chances of preferential dunging. However the long-hut examined within site C was located next to a dry stone wall, which was probably partly built from stone robbed from the long-hut structure, but because of the long-huts position next to the wall it was used as a dumping site for field stones which led to its preservation. The fact which led to its preservation could therefore have increased its chances of having an elevated soil P_{tot} content due to the

preferential dunging of livestock. Measured P_{tot} levels within the remains of the long-hut were significantly enhanced, presumably by human activity, but some subsequent enhancement of the P_{tot} values by sheltering animals should not be ruled out.

The activity of mesofauna such as earthworms is important for homogenising the surface organic matter from dead plant material and animal waste into the soil. Mesofaunal activity therefore could reduce the localised enhanced P_{tot} concentrations in the soil directly below animal dung and in the surface organic soil horizon. Soil conditions are not always suitable for mesofaunal activity and where the soil is too acidic, wet or cold the organic matter is not broken down as effectively and a surface organic A_h horizon is formed, which adds to the surface P_{tot} variation.

When conducting a P survey it is important to consider the past land use of a site and to look for the presence of grazing animals, especially areas which may have been used for shelter or tracks which pass through the sample area, as these are likely to have enhanced P levels. The topography, parent material and climate will play a decisive role in determining the P content of soil both directly and indirectly through the influence on vegetation and human activity, the parameters which provide the greatest source of P variation.

7.10 The mobility and redistribution of P

There is a host of published work examining the practical and theoretical mobility of P in the soil from fertiliser sources and the implications of this for agronomic practice. However, much of this work appears to have been conducted on lowland agricultural soils, and there is only a limited amount of work on the mobility of P in broader environmental terms. The movement of P in acidic environments requires investigation to aid archaeological surveys under conditions where some artefacts, such as bone, can completely disappear.

Sections of weathered rabbit bone within soil-filled columns were leached over 30 weeks with organic acids and carbonated water. Examination of the soil columns indicated a significant ($p=0.05$) lateral and downward movement of P into the soil

over 1-2mm, and P_{tot} concentrations in the soil were increased by roughly 15%. It is likely that the distance P was leached would increase with time. The leaching of P from fertilisers has been shown to be as far as 7.5cm from the source in 2 weeks, but was more often 1-4cm from the source (Bouldin & Black, 1954); however, the P from fertilisers will be more soluble than apatite from bone. Diffusion from concentrated sources is dependent on the bulk density, moisture content and texture of the soil, but even in the wide variety of soils examined in the literature, the movement of P was restricted to only a few cm by precipitation and adsorption. P is less soluble in acidic soils such as those examined in this thesis (*p*H values of 4.0 – 5.0) than under neutral conditions, and adsorption is generally greater at *p*H values of 3-5, but this is dependent on time, the soil:solution ratio and the nature and concentration of the salts present.

In 30 weeks of leaching for this experiment, the soil immediately surrounding the bone was enhanced by roughly 500μg of P. At this rate of movement, assuming the leaching conditions of this experiment remained unaltered, the complete dissolution of the bone would occur after 370 weeks. The bones used in these experiments were weathered and hollow, and the rate of dissolution of whole bones could be faster due to associated organic material which would be broken down by specialist decomposing micro-organisms which excrete organic acids, speeding up the rate of dissolution. If all the P from a fragment of bone, similar to that used in this study, was fixed in just 1cm of soil surrounding the bone then it would enhance P_{tot} levels by roughly 5000μg g^{-1}, which would be easily detected over background soil P concentrations. However, if movement of P took place up to 10cm from the bone before it was fixed, then P levels would be enhanced by only 80μg g^{-1}, which is unlikely to be detected over the background noise of P in soil.

The redistribution of P was examined in detail by microprobe analysis within thin sections made from sherds of bronze age cinerary urns. It was thought that cutans observed in these sherds could be of a similar composition to those examined in limestone cave sediments from Pontnewydd (Jenkins, 1997), and certainly the cinerary urns had a potential rich P source in the cremated bones they contained when buried. The cutans did not have a similar composition to those examined

from Pontnewydd, (Ca=14%, Fe=20%, P=14.5%) and were predictably mainly Fe/Al dominated with a mean P content of 3.15%. This amount of P still represents a significant enhancement on what is present in the environment, but is not as high as those examined from Pontnewydd. The presence of phosphatic cutans within some sherds from cinerary urns could still be possible but sampling a cutan-rich sherd is problematic. Only a few sherds are available for thin section production from any urn, and it may only contain phosphatic cutans if the sherd was from a section of the urn directly below the cremated bone and so received the in-wash of P from many years of leaching. Only a single sherd is normally available for impregnation and a thin section is just a small proportion of the sherd, so the thin section may not be representitive of the remainder of the sherd, or the urn. It is likely that a number of thin sections would have to be made from a variety of sherds from the same urn, if P rich cutans are to be discovered, a procedure impractical in such studies.

7.11 The distribution of P in archaeological graves

P analysis is a particularly useful technique for the examination of cryptic archaeological features *i.e.* suspected inhumations in acidic soils where there has been the complete dissolution of bone. Under these conditions P analysis can help to clarify whether there has been an inhumation because, if the grave is undisturbed, there should be large P anomalies present. However, the choice of sampling strategy to be employed over a grave is problematical; the grid interval has to be fine enough to give some resolution to the anomalous values that might be located and yet the constraints of time, cost and damage will limit the number of samples which can be collected for analysis. An ideal situation to resolve this problem might involve the analysis of many hundreds of samples from an undisturbed grave, to identify a suitable sampling strategy, but a model grave for this sampling scheme is rarely available.

This thesis uses the data generated from a whole body bone density scan to represent an inhumation, so providing a data-set of 58000 values over an area of 190cm×95cm, to examine suitable sampling strategies. A computer program was used to 'sample' this data-set at a number of increasing grid intervals and the data selected was plotted using the Winsurf software with minimum curvature

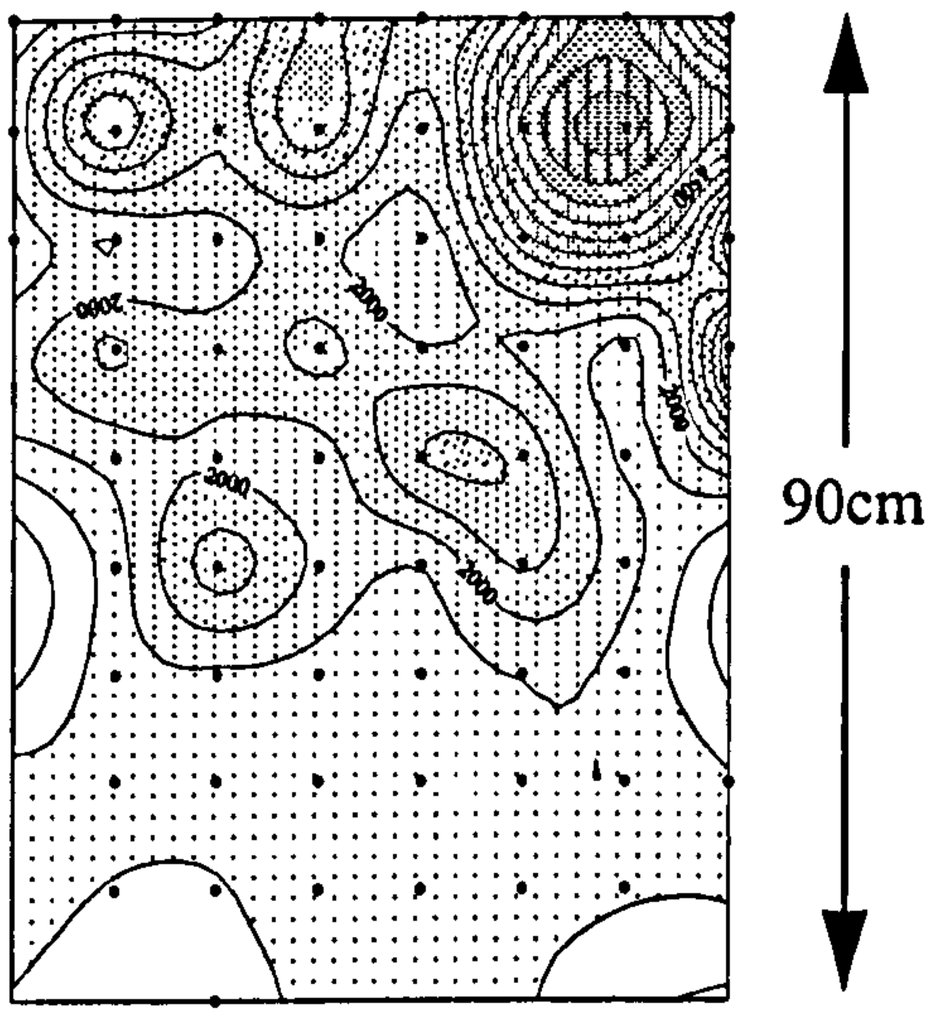
interpolation. The resulting images (figures 6.2-6.5) show that at a 20cm and a 15cm grid interval the generated image is not recognisable as an inhumation, however at a 10cm interval a body is recognisable as a torso, head and thighs. At a 5cm grid interval almost a complete body image is recognisable with even the hands and feet becoming apparent. It is concluded that for the identification of a body image across a grave a sampling grid interval of 10cm or less is needed.

It is recognised that the use of data generated from a whole body bone density scan to represent the P distribution across a grave has a number of drawbacks. Firstly, the values of bone density from a scan are given against a blank background, whereas soil could have from 200-5000 μg-P g^{-1} which could be a considerable portion of the bone P in the soil, thus obscuring the bodies image. Secondly, not all the bone-derived P will be fixed within the soil and remain there until measured. Some P might be lost through leaching or by plant uptake, but disturbance by the soil mesofauna, especially earthworms, will be a greater problem. At *p*H values of greater than 5.0, soil homogenisation by earthworms will diffuse any distinct P distribution. Typically, only grave sites in acidic soils which are, and have been, devoid of earthworms will avoid this fate. Finally, it is unlikely that any body would be buried in the position of the total body bone density scan, and it is more likely for the arms to be folded over the body with the legs together, or even for the body to be buried in the 'foetal' position. In reality the sampling of the soil of a grave would not produce a distinct 'body-like' trace of high P concentrations. However, despite this, the theoretical sampling of a grave provides a useful insight into the different sampling intervals which could be used when examining the P distribution over a grave site.

The distribution of P across a grave was examined in detail during the excavation and investigation of a single Bronze Age burial cist and three burial cists at an early Christian grave site. The sampling strategies utilised and the results are described in chapter 6. The Bronze age cist was sampled twice on a corresponding grid at an upper and lower level, and a significant ($p=0.01$) increase in P_{tot} was measured in the lower, basal layer. This increase was however, on average only 800μg g^{-1}, but the most likely explanation for such an enhancement would be the fixing in the soil at the base of the cist of body/skeletal derived P. The distribution of P across the

cist does not display any pattern (figure 7.5), with the highest measured values located in one corner. The soil excavated from the cist had a current *p*H value of 5.6, which is suitable for some mesofauna, which could have diluted and homogenised any anomalous P pattern. The cist was only 90cm×70cm in size and so it is assumed that a body would be interred in a 'foetal' position, so obscuring any obvious pattern to the P distribution, and it is likely that the conditions and style of burial discussed below play an important part in the P distribution which remains.

Figure 7.5: P_{tot} distribution measured across a Bronze Age cist.



The three cists examined from the early Christian burial site were selected for different reasons. Cist T170 was a closed cist with cap, side and basal stones, and was sampled at an upper layer and a basal layer. Cist T216 had only side stones and was sampled once at a position below the cist base, and cist T304 was without capstones but had side and basal stones, and was sampled once at roughly 10cm above the base where the excavation had revealed a dark soil stain which could have been imparted by the decomposed body. The results from cist T170 revealed significantly ($p=0.01$) enhanced P_{tot} concentrations in the basal set of samples when compared to the upper set. However, the mean difference was only 100μg g^{-1}, and the highest values measured only 1100μg g^{-1} which is considerably lower than the values which might be expected if skeletal derived P remained fixed in the soil. The sampling of soil from the base of cist T216 revealed mean values of 900μg g^{-1}, and a

data set which was significantly (p=0.01) greater than that of the samples collected from cist T170. These two cists were only a few metres apart and presumably of a similar age and yet the inhumation has left a slightly different level of P enhancement within the soil. It is assumed that these differences are due to the style of grave as discussed below. Cist T304 revealed much greater P enhancement than the previous two, with mean values of 3500μg g^{-1} rising to 30800μg g^{-1} in one sample. The enhancement of P up to 30× its background value will be due to the fixing of skeletal P within the soil. It was possible to collect samples from cist T304 at the exact layer at which the P had been fixed in the soil from the body because the position was marked by a dark soil stain. This identifier had not been found in cist T170 so the depth of sampling could not be gauged exactly.

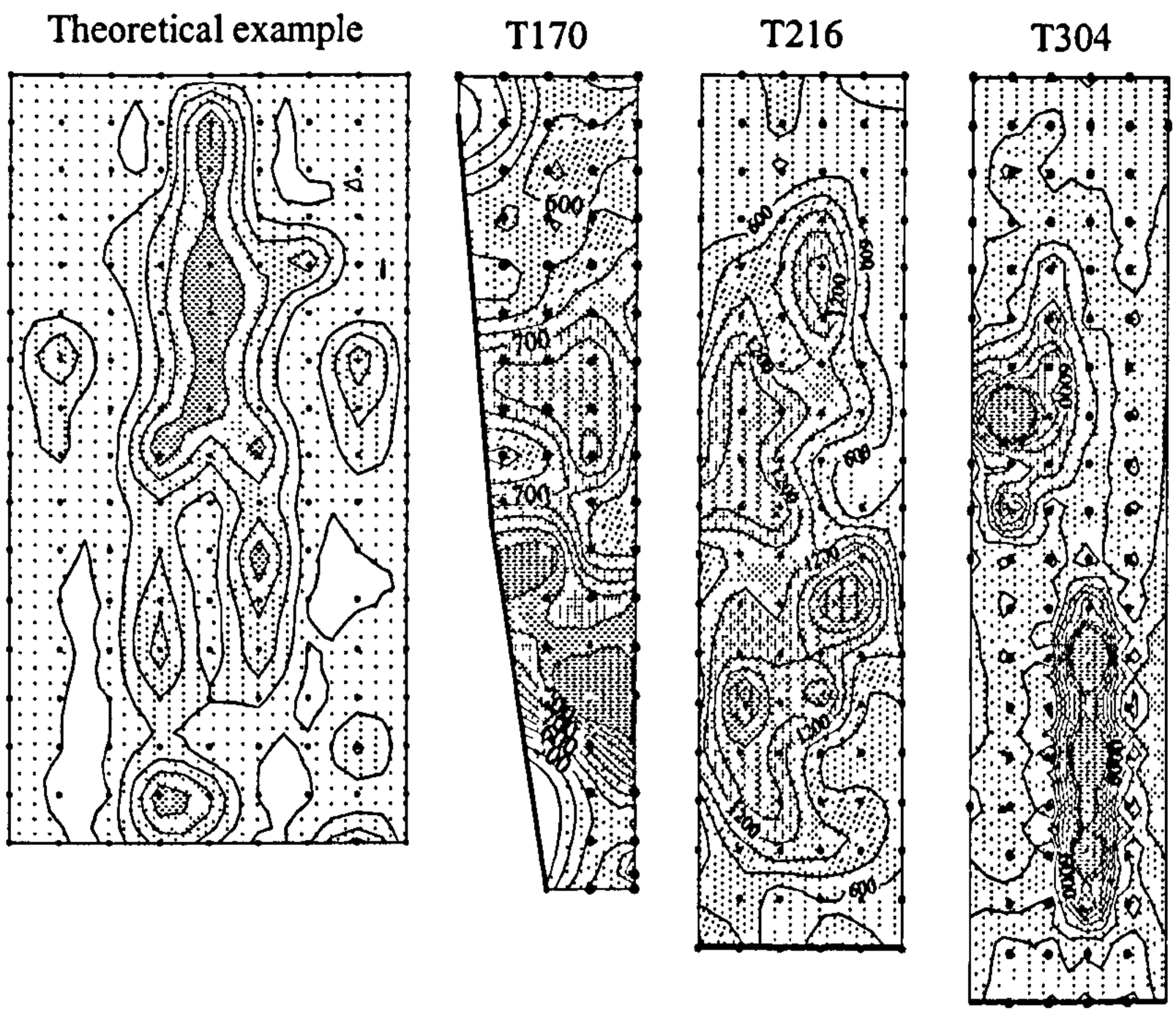
It is vitally important to collect soil samples from the exact depth within the grave to ensure the measurement of enhanced P levels. The concentrated P might just be present in a thin layer within the grave which could even undulate between certain depths over the grave and could be easily missed. It is possible that the seven samples from T304 which contained greater than 1% P were not just isolated 'hotspots', but part of a larger number which were missed because the correct depth was not sampled. It is impossible to ensure that all samples are collected from the correct depth without the collection of excessive numbers, however in an ideal situation the careful excavation of a cist will uncover a level where there is an indicative soil stain, which is the level which should be sampled. In cists where no soil stain is revealed then a suitable sampling depth can be identified by the pre-excavation measurement of a series of samples down through the grave, employing field techniques for P analysis if there is no time for a laboratory based analysis. If samples are collected by soil auger over a 5cm or 10cm depth through the grave there is the potential for the dilution of high P values. If these values are in the order of 1% then even a dilution at this level would leave a detectable high trace. However, if the values have already been depleted then dilution fivefold or tenfold can mean they are no longer recognisable above the natural background variation of P in the soil.

The method of burial will have a considerable effect on the P_{tot} trace uncovered and there are two main scenarios which could explain the differences encountered

between the P_{tot} distributions of T304 and T170. Cist T170 had basal and cap-stones and it is though that a body was placed in this type of cist without being back-filled with soil (Ian Grant *pers. comm.*). In this situation the body will decompose and the P will accumulate on the surface of the basal stones and, under conditions of high rain infiltration/percolation could easily be physically transported and removed. The grave will be gradually filled with soil material transported by percolating rain, but it is likely that any trace of skeletal derived P will only be fixed on the thinnest layer of soil over the basal stones. To be effective, sampling would have to be of this layer of soil which, if using an auger, is difficult. The results from cist T170 are consistent with this as there was no great P enhancement, and P_{tot} values could have been diluted because the bottom 5cm of the soil in the cist was collected at each sample point. Cist T304 had no capstones but did have basal stones, and in this situation the cist would be back-filled, so the P released from the decomposing body and the bones could be fixed immediately within the soil. The body can also increase the organic matter content of the soil, leaving a dark soil stain which helps indicate the position of P enhancement.

The 10cm grid interval sampling size which was used to collect all the samples from the four cists examined, did not reveal any recognisable P distribution, although the examination of data from the whole body bone density scan revealed this to be a suitable grid interval. Examination of the distribution maps presented in figures 7.5 and 7.6 indicates that a finer resolution might not have revealed any more defined 'skeleton shape' to the distribution. None of the high-spots were located around the head/shoulders region where the greatest concentration of P_{tot} might be expected.

Figure 7.6: P Distribution measured across three Early Christian cists, compared to the theoretical example of a 10cm sampling grid across a grave



A major consideration of the analysis of the cists at the early Christian burial site is the role played by mesofauna. The soil had a *p*H of 6.8, so would be considered close to ideal for earthworm activity, and analysis in the laboratory of a section of soil removed from the site reveals earthworm faecal pellets. The activity of the mesofauna could have homogenised the soil and blurred the organisation of the P_{tot} distribution within the three cists.

CONCLUSIONS AND FURTHER WORK

8.1 Conclusions

As stated in the introduction of this thesis, in order to understand the distribution of P_{tot} in soils of an archaeological site it is important to consider how it varies naturally in the soil. The P_{tot} values measured over an archaeological site display greater variation that those measured over a 'background' site despite having similar mean P_{tot} concentrations. The statistical examination of soil P_{tot} measurements from an archaeological site reveals a greater dispersion of data points over the histogram, a larger standard deviation, variance and coefficient of variation, than a similar number of samples collected from a background site.

In many archaeological surveys it is not practical to collect a large number of background samples for statistical comparisons, and in these cases some indicator of the significance of anomalous high values of P_{tot} is required. A guideline has been quoted in the literature whereby any result which is "3× the standard deviation larger than the mean" is classified as significant. However, work in this thesis shows that even background sites, which are not associated with any known archaeology, can contain soil samples which would be classed as significantly greater than the mean using this method. It is therefore important to note that results which qualify as being significantly greater than the mean are not necessarily the result of any archaeological enhancement of P.

A systematic sampling strategy is recommended for archaeological P survey to provide complete area coverage and ease of sample location and reporting. Soil samples can be efficiently collected with an auger, to a constant depth, but it is advisable to examine the soil profile before sampling.

Interpolated distribution maps are useful to assess trends and 'hotspots' in the data. Caution is advised when interpreting these maps because artefacts can be generated within the distribution: a product of the interpolation method, which can occur in areas with a low sample density. The validity of the distribution is improved by incorporating the sample points on the distribution map so the reader can assess the

importance of the pattern. There are a number of interpolation methods which can be utilised, and for archaeological purposes, those which honour the original data are most useful and based on this study the 'minimum curvature' interpolation method is particularly recommended.

The data collected in this thesis indicates that the variation in P_{tot} reduces as the size of the sample area and grid interval reduces. Therefore, P_{tot} in soil displays some spatial dependence, from 0.01m×0.01m up to 100m×100m. However, when the sampling was extended down to the level of the soil constituents (0.001m-0.0001m-0.00001m grid spacing) the variation in P_{tot} increased as the grid interval decreased. Spatial dependence for soil P_{tot} does not exist below a 1cm grid interval. The measurements made at the smaller grid intervals have a different 'sample support' to the samples collected in the field and comparisons between sets of data with different sample supports can only be conducted with caution. Any differences described could be due to the different data collecting techniques.

Amorphous cutans within cinerary urn sherds with an average P concentration of 3.15% (range 0.1-10%) were described and examined. The P values, roughly 15× that of soil, are interpreted as the result of in-wash from the cremated human bones within the urns. The P-rich cutans, also high in Fe and Al, as expected in the acidic local soils have rarely been described previously and the movement of P and its redeposition in these systems merit further study. The distribution of P-rich cutans within the cinerary urn will be variable and this study highlights the problems of making a thin section from an optimum position within the urn.

The movement of phosphate from rabbit bone within leached soil columns was at least 50× less than that published for fertiliser pellets. A consistent leaching rate would mean the complete dissolution of bone in 370 weeks which, if fixed in the surrounding 1cm of soil, would be easily detected, enhancing P levels by 5 mg g^{-1}. However, if the bone derived P was fixed in the surrounding 10cm of soil, P levels would only be enhanced by 0.08mg g^{-1} and may not be detected above the background variation of P in soil.

Theoretical sampling models from a total body bone density scan have shown that a

10cm sampling interval is adequate to produce a distribution map which displays an identifiable body shape. At a sampling interval larger than 10cm the image produced is not identifiable as a body.

Several cists were sampled where complete dissolution of the bone had occurred due to the local acidic conditions. All the cists had significantly enhanced soil P_{tot} levels from the body-derived P fixed within the soil. However, sampling at a 10cm interval did not reveal the expected complete body image of raised P levels. This highlights the importance of the selection of correct sampling depth and the effect that homogenisation by mesofauna and the type of burial can have on the distribution of soil P over a grave.

8.2 Further studies

It is inevitable that a research project of this size produces a number of questions which have yet to be answered, either being related to the original theme of research but not forming one of the original aims of the study, or being a natural progression of the work discussed in this chapter but which could not be conducted due to logistical constraints.

The first area of further research is a direct progression of the examination of the variation of P in an acidic soil over an archaeological site. It would be useful to measure P over a larger, more complex site than the medieval long-hut examined in this thesis. If such a site were located, a programme of P analysis could be undertaken at a range of grid intervals 100m - 10m - 1m - 0.1m, and if time was not a constraint, the measurements could be made for each level of sampling interval before the next set of sampling, to focus in on the areas of most interest. Often excavations are subject to time constraints which mean that the most useful samples for P analysis cannot be collected. The data collected from such a programme of sampling would allow the comprehensive statistical examination of the variation of P over a large archaeological site and provide a data-set from which interpolation methods for mapping archaeological anomalies can be examined. Such an examination could be undertaken for a site which has already been excavated and P analysis conducted. However it is unlikely that the soil samples would have been collected at a variety of sampling intervals and it is this data-set which could prove invaluable for future excavations.

A second study based on a set of soil samples collected from an archaeological feature would be to carry out P fractionation, and examine the proportions of P which are present in the different fractions within the soil. Archaeological P could be fixed within a particular fraction in the soil which would make the routine location of archaeological anomalies a simpler operation. The fractionation of P has been conducted for a variety of soils in relation to pedogenesis (Walker & Syers, 1976; Smeck, 1985; Sharpley *et al.*, 1987), to natural drainage (Runge & Riecken, 1966) to soil texture (Williams & Saunders, 1956) and to a variety of fertiliser applications (*eg.* Khasawneh *et al.*, 1974) but does not appear to have been examined for archaeological soils.

The basis for the success of archaeological P analysis is that because of its unique chemistry, P is relatively immobile in soil and is fixed to either the Fe/Al oxides and hydroxides or $CaCO_3$ surfaces, depending on the soil *p*H. However, dispersion of P can occur from the mineral or organic source of P before it becomes fixed within the soil. According to the chemical regime of the soil this dispersion will increase the level of P heterogeneity in the soil and perhaps confuse any P survey analysis. This thesis examines the movement of P from bones emplaced in soil columns and leached with 0.05M acetic acid and with carbonated water. It would be useful to examine similar systems but under a variety of conditions, for example the movement of P from bone in neutral or calcareous soils being leached with organic acids or rainwater. Systems could also be examined for gleyed soils or seasonally waterlogged soils so a more complete picture of how P disperses from point sources such as bone can be obtained.

Further examination of the distribution of P within a mottled gley soil would be interesting. The size of mottles within soil (<5mm) means that any examination of the distribution of properties (P_{tot}, Fe_{ext}, Al_{ext} & TOC) is limited by the sampling size. The examination of the distribution of such properties utilising thin sectioning and sampling under the microprobe would yield useful results.

Evidence for the movement of P in the environment was sought by the examination of cutanic features within thin sections prepared from cinerary urn sherds. It was thought that these cutans could be a secondary deposit of P derived from the cremated bone within the cinerary urn after being buried in the acidic north Wales environment for many years. Only a limited number of sherds could be examined and none of the cutanic features observed contained sufficiently elevated levels of P to be re-precipitated phosphates. Any further thin sections of cinerary sherds should be examined for the presence of these cutans and the elemental composition measured by EDXRA. It is possible that sherds from appropriate portions of the cinerary urn could contain phosphatic cutans.

Chapter six examines the theoretical distribution of P over a grave using a data set derived from a total body radiograph. Initially this data set was examined at a

variety of sampling intervals for two different sample sizes in plane symmetry with the spine of the body. It is planned to examine the pattern of P distribution when this artificial data set is skewed to other angles up to 45° to the direction of the spine of the body. A more realistic set of results will be obtained if the data-set is blurred, perhaps by averaging the pixels surrounding each sample point. This is all work for the future and will hopefully improve the sampling strategies which could be used when sampling archaeological grave sites. A second exercise is planned using the data set from the whole body radiograph, whereby the values from the radiograph are superimposed over a distribution map showing the background variation of P_{tot} in soil. This will give an indication of how clear the elevated levels of P would be set against the natural variation of P_{tot} in soil. Several cists were also sampled, one showing a good example of a soil stain, and on analysis, elevated P levels of up to 3%. However, a recognisable body image interpolated from the soil P data was not achieved, possibly due to the problems of sampling at the ideal depth within the grave (discussed in section 7.11), the speed at which sampling had to be done to fit in with the site excavation and possible past faunal homogenisation. Further sample collection is needed on an undisturbed grave site over a number of days to enable P analyses to be conducted before the complete grave is sampled.

APPENDIX I: RAW DATA

Site A: Selected soil parameters with depth

Depth (cm)	pH	I-o-i (%)	Ptot (ug/g)	Pav (ug/g)	Fep (mg/g)	Alp (mg/g)	Fed (mg/g)	Ald (mg/g)
5	4 2	25 81	2260	5.74	12.0	4 2	21.6	2.7
10	4 4	17.18	1800	6.47	13.5	4.7	25.6	3.7
15	4.4	11.66	1636	2.20	12.9	5.3	21.2	4.4
20	4 5	11.73	1550	1.78	11.8	4.7	24.4	4.4
25	4.5	10.44	1590	1.76	13.2	6.6	22.0	4.3
30	4.5	9 65	1490	1.12	13.6	6.6	23.2	4.2
35	4 5	8 46	1490	1.24	13.9	7.4	22.0	3.1
40	4 6	8.04	1440	1.20	13.2	5.9	23.2	3.0
45	4.7	8.46	1490	1.90	13.8	5.7	22.0	2.9
50	4 7	7.64	1290	1.67	13.3	5.9	20.8	2.7
55	4 8	7.94	1340	1.74	12.9	6.2	26.4	3.4
60	4 7	8.74	1480	1.91	13.0	5.3	24.0	4.0
65	4 8	7.99	1500	1.93	15.1	8.0	24.8	4.0
70	4 9	7.72	1960	6.63	9.0	3.9	28.0	4.9
75	4.8	7.94	2400	5.62	5.4	2.1	19.2	3.6
80	4.9	7.87	2340	11.83	4.5	1.7	14.8	4.1
85	4.8	7.45	1970	6.50	4 2	1.7	22.8	4.6
90	4.9	7.19	2000	6.95	4.3	1.4	18.4	4.2
95	4 9	7.46	1890	6.12	4 6	1.5	14.8	2.7
100	4 8	7.30	1980	4.83	5.8	1.7	25.6	3.0

Site B: Selected soil parameters with depth

Depth (cm)	pH	I-o-i (%)	Ptot (ug/g)	Pav (ug/g)	Fep (mg/g)	Alp (mg/g)	Fed (mg/g)	Ald (mg/g)
5	3.7	23.9	940	2.62	7.4	1.8	14 8	24.4
10	4.0	12.0	260	1.15	9.9	1.9	23.6	28.4
15	4.1	9.3	520	0.73	17.0	3.3	28.8	38.4
20	4.1	7.9	530	0.68	17.0	3.4	30.0	42.8
25	4.2	6.5	430	0.66	13.0	2 9	23.2	34.8
30	4.2	7.6	460	0.51	15.0	3.5	26.0	38.0
35	4.2	6.7	440	0.49	14.0	3.8	24.8	42.4
40	4.3	6.6	430	0.47	10.2	4.1	22.0	45.6
45	4.3	5.5	400	0.64	6.4	3.9	16.8	39.6
50	4.4	4 6	490	0.62	5 6	3.8	18.0	36.8
55	4.4	4 0	410	0.51	5.6	4.5	13.2	42.4
60	4.5	4.0	380	1.31	3.2	4.7	9.6	41.2
65	4.5	4 8	470	0.94	2.6	5.6	8.4	54.4
70	4.6	4.1	400	1.43	1.7	5.2	6.8	49.6
75	4.5	4.1	410	1.18	1.8	5.4	7.6	54 8
80	4 6	5 7	520	2.07	3.4	6.4	12.4	79.2
85	4 6	4.9	530	1.55	2.4	6.3	8.8	63.6
90	4.5	5.6	710	1.55	3.1	6.9	10.8	80.4
95	4.5	5.2	560	2.64	2.6	7.0	10.0	81.6

Site C: Selected soil parameters with depth

Depth (cm)	pH	I-o-i (%)	Ptot (ug/g)	Pav (ug/g)
5	5.2	19 9	1630	3.5
10	5.2	13.9	1410	2.2
15	5.1	10.9	1200	1.6
20	5.1	10.4	1150	1.6
25	5.1	10.8	1150	1.7
30	5.0	14.9	2030	13.8
35	5.1	11.5	1090	5.5

APPENDIX ONE: SITE A DATA

Number	A-100			A-10			A-1; A-01a; A-01b					A-001			A-0001, A 00001			
	X	Y	Z (ug P /g)	X	Y	Z (ug P /g)	X	Y	Z1 (ug P /g)	Z2 (ug P /g)	Z3 (ug P /g)	X	Y	Z (ug P /g)	X	Y	Z (% P)	Z (%P)
1	0	2	1820	0	4	2020	0	10	1780	2310	1860	0	9	2030	0	10	5122	4944
2	0	1	1460	0	3	1940	0	9	1930	2610	2120	0	8	1910	0	9	6345	4644
3	0	0	1770	0	2	2150	0	8	1820	2770	2250	0	7	1970	0	8	4429	705
4	1	2	2010	0	1	1900	0	7	1770	2680	2240	0	6	2020	0	7	0	5863
5	1	1	1550	0	0	1770	0	6	1540	2450	2290	0	5	1880	0	6	95	5009
6	1	0	950	1	4	2090	0	5	1530	2680	2220	0	4	1960	0	5	3304	5558
7	2	2	1630	1	3	1980	0	4	1620	2510	2190	0	3	1790	0	4	5535	2312
8	2	1	1810	1	2	1610	0	3	1700	2340	1830	0	2	1850	0	3	3421	5455
9	2	0	1540	1	1	2480	0	2	1810	2240	2040	0	1	1890	0	2	4786	5565
10				1	0	1780	0	1	1840	2110	2080	0	0	1960	0	1	0	6169
11				2	4	2020	0	0	1970	2210	1810	1	9	2050	0	0	5890	6272
12				2	3	2180	1	10	1810	2090	1940	1	8	2050	1	10	0	10875
13				2	2	1810	1	9	1790	2170	2120	1	7	1930	1	9	5590	5400
14				2	1	1760	1	8	1720	2400	2190	1	6	1950	1	8	3503	4126
15				2	0	2020	1	7	1720	2250	2080	1	5	1990	1	7	0	3821
16				3	4	1620	1	6	1780	2330	2050	1	4	1990	1	6	6206	5156
17				3	3	1670	1	5	1670	2280	1800	1	3	2020	1	5	966	5342
18				3	2	1970	1	4	1800	2150	2030	1	2	1930	1	4	3160	5014
19				3	1	1780	1	3	1670	2220	2080	1	1	1900	1	3	4537	3190
20				3	0	1750	1	2	1700	2120	1890	1	0	1950	1	2	6377	5957
21				4	4	1840	1	1	1540	2190	1840	2	9	1980	1	1	4851	5547
22				4	3	1690	1	0	1840	1990	2100	2	8	1970	1	0	3707	4979
23				4	2	1710	2	10	2040	2080	1810	2	7	1910	2	10	0	7012
24				4	1	1550	2	9	1700	1860	1860	2	6	1890	2	9	7031	5986
25				4	0	1490	2	8	1850	2230	2010	2	5	1980	2	8	5420	6614
26							2	7	1810	2170	2030	2	4	2130	2	7	6902	3999
27							2	6	1860	2290	1870	2	3	1940	2	6	0	3639
28							2	5	1930	2130	2000	2	2	1920	2	5	5446	7343
29							2	4	1720	1930	2030	2	1	1910	2	4	0	4613
30							2	3	1760	1980	2050	2	0	1980	2	3	5292	6275
31							2	2	1610	2170	1950	3	9	1990	2	2	0	2684
32							2	1	1690	1770	1840	3	8	2010	2	1	3985	6508
33							2	0	1690	2000	1840	3	7	1970	2	0	5524	5678
34							3	10	1750	1860	1920	3	6	1900	3	10	7304	6948
35							3	9	1890	1790	1720	3	5	1850	3	9	6627	7071
36							3	8	2130	1950	1810	3	4	2020	3	8	0	4905
37							3	7	2000	1970	1880	3	3	1750	3	7	0	6806
38							3	6	1770	2060	1750	3	2	1790	3	6	0	5525
39							3	5	2010	2080	1900	3	1	1780	3	5	4756	4694
40							3	4	2240	2050	1770	3	0	1710	3	4	0	4662
41							3	3	1840	2350	1950	4	9	2050	3	3	0	6311

APPENDIX ONE: SITE A DATA

Number	A-100 X	A-100 Y	A-100 Z (ug P /g)	A-10 X	A-10 Y	A-10 Z (ug P /g)	A-1, A-01a, A-01b X	Y	Z1 (ug P /g)	Z2 (ug P /g)	Z3 (ug P /g)	A-001 X	Y	Z (ug P /g)	A-0001, A-00001 X	Y	Z (% P)	Z (%P)
42							3	2	1970	2000	2020	4	8	2040	3	2	5148	4555
43							3	1	2020	1820	1810	4	7	1980	3	1	2502	5716
44							3	0	1760	1950	2060	4	6	1690	3	0	4376	2626
45							4	10	2030	1940	2040	4	5	2030	4	10	7332	8513
46							4	9	1840	1750	2090	4	4	1980	4	9	7392	5795
47							4	8	2170	2010	1840	4	3	1710	4	8	806	6401
48							4	7	1980	1950	1930	4	2	1670	4	7	8703	5188
49							4	6	1860	1860	1880	4	1	1700	4	6	6349	5175
50							4	5	1810	1900	1770	4	0	1820	4	5	4522	4886
51							4	4	1690	1870	1930	5	9	1880	4	4	4274	11690
52							4	3	1710	2110	1870	5	8	1930	4	3	261	5787
53							4	2	1630	1870	1920	5	7	2000	4	2	4899	5618
54							4	1	1780	2010	2300	5	6	1890	4	1	6609	4682
55							4	0	1730	1840	2090	5	5	1880	4	0	0	6366
56							5	10	1920	1980	2000	5	4	1830	5	10	3970	2052
57							5	9	1850	1950	2050	5	3	1940	5	9	0	8099
58							5	8	1950	1910	2030	5	2	1660	5	8	8796	5051
59							5	7	1660	1720	2030	5	1	1720	5	7	5904	5663
60							5	6	1780	2000	2030	5	0	1810	5	6	5605	5593
61							5	5	1850	1970	1850	6	9	1990	5	5	6543	3511
62							5	4	1750	1910	1930	6	8	2000	5	4	5042	5357
63							5	3	1990	1650	1900	6	7	1920	5	3	4907	3380
64							5	2	1780	1750	1930	6	6	1800	5	2	4086	5452
65							5	1	1900	1850	1880	6	5	1710	5	1	5170	6767
66							5	0	1810	1990	1900	6	4	1830	5	0	0	0
67							6	10	1620	2030	1800	6	3	1810	6	10	0	6640
68							6	9	1920	1900	2010	6	2	1780	6	9	7177	2965
69							6	8	1870	1730	2050	6	1	1860	6	8	5304	5924
70							6	7	2120	1980	1940	6	0	1930	6	7	5440	6015
71							6	6	1920	1930	2020	7	9	2040	6	6	5081	2575
72							6	5	2190	1630	1810	7	8	1990	6	5	5769	3804
73							6	4	2270	1800	1780	7	7	1960	6	4	5167	6285
74							6	3	1990	1820	1820	7	6	1850	6	3	3481	5106
75							6	2	2030	1860	1950	7	5	1880	6	2	0	5170
76							6	1	2030	1850	1940	7	4	1900	6	1	5190	5717
77							6	0	1820	1830	1880	7	3	2020	6	0	294	5589
78							7	10	2060	1840	1890	7	2	1850	7	10	6115	2044
79							7	9	1990	1840	2030	7	1	1900	7	9	0	5111
80							7	8	2040	2060	1930	7	0	1810	7	8	0	5729
81							7	7	2280	1980	2000	8	9	2030	7	7	0	5956
82							7	6	1980	1770	1960	8	8	1990	7	6	0	5359

APPENDIX ONE: SITE A DATA

Number	A-100 X	A-100 Y	A-100 Z (ug P /g)	A-10 X	A-10 Y	A-10 Z (ug P /g)	A-1, A-01a, A-01b X	Y	Z1 (ug P /g)	Z2 (ug P /g)	Z3 (ug P /g)	A-001 X	Y	Z (ug P /g)	A-0001, A-00001 X	Y	Z (% P)	Z (%P)
83							7	5	1970	1730	1920	8	7	1950	7	5	4900	5505
84							7	4	2120	1810	1820	8	6	1900	7	4	3602	5568
85							7	3	2310	2010	2010	8	5	2080	7	3	0	4303
86							7	2	2210	1710	2000	8	4	1920	7	2	4558	8163
87							7	1	1930	1780	1670	8	3	1920	7	1	3574	1756
88							7	0	1840	1710	1850	8	2	1970	7	0	0	2749
89							8	10	1810	1570	2000	8	1	1820	8	10	4267	6854
90							8	9	1980	1840	1810	8	0	1980	8	9	4445	6729
91							8	8	1820	1900	1910	9	9	1990	8	8	4436	9166
92							8	7	1930	1850	1870	9	8	1940	8	7	2471	7016
93							8	6	2120	1880	1990	9	7	1850	8	6	3793	6218
94							8	5	1960	2200	1950	9	6	1980	8	5	4030	4950
95							8	4	1890	1850	1990	9	5	1870	8	4	5768	338
96							8	3	1710	1620	2010	9	4	1930	8	3	7059	0
97							8	2	1800	1630	1950	9	3	1870	8	2	1067	6022
98							8	1	1620	1600	1660	9	2	1950	8	1	0	5521
99							8	0	1760	1600	1740	9	1	1940	8	0	6995	0
100							9	10	1780	1740	1940	9	0	2050	9	10	0	5684
101							9	9	1880	1750	1880				9	9	0	4111
102							9	8	1740	1910	1650				9	8	3406	7864
103							9	7	1860	1750	1940				9	7	0	6468
104							9	6	1390	1960	2030				9	6	4557	6372
105							9	5	1940	2020	1960				9	5	5320	1633
106							9	4	1840	1920	1930				9	4	4860	4298
107							9	3	1770	2030	1770				9	3	5992	4960
108							9	2	1930	1830	1920				9	2	3451	6246
109							9	1	1520	1630	1940				9	1	4921	1663
110							9	0	1790	1780	1840				9	0	0	0
111							10	10	1760	1710	1780				10	10	4262	7693
112							10	9	1970	1660	2000				10	9	1762	4810
113							10	8	1830	1620	1820				10	8	5543	6324
114							10	7	2050	1710	1830				10	7	0	5708
115							10	6	1920	1680	1540				10	6	0	5344
116							10	5	1710	1860	1760				10	5	4717	2421
117							10	4	2050	1720	1800				10	4	4426	6294
118							10	3	1930	1760	1800				10	3	5218	3548
119							10	2	1750	1810	1860				10	2	5270	6423
120							10	1	1730	3110	1590				10	1	0	3219
121							10	0	1780	1800	1850				10	0	0	6200

APPENDIX ONE: SITE B DATA

Number	B-100			B-10			B-1, B-01a, B-01b					B-001			B-0001				B-00001		B-00001P		B-000001P	
	X	Y	Z (ug P /g)	X	Y	Z (ug P /g)	X	Y	Z1 (ug P /g)	Z2 (ug P /g)	Z3 (ug P /g)	X	Y	Z (ug P /g)	X	Y	Z1 (% P)		Z2 (% P)		Z3 (% P)		Z4 (% P)	
1	0	2	840	0	4	620	0	10	680	700	620	0	9	550	0	10	3430		2581		0		878	
2	0	1	780	0	3	620	0	9	570	630	660	0	8	600	0	9	1693		2469		0		1590	
3	0	0	600	0	2	550	0	8	650	640	710	0	7	620	0	8	1725		0		0		1376	
4	1	2	790	0	1	510	0	7	800	640	710	0	6	680	0	7	1124		1263		2210		1468	
5	1	1	860	0	0	510	0	6	660	680	800	0	5	680	0	6	3598		0		4367		0	
6	1	0	270	1	4	790	0	5	650	720	660	0	4	800	0	5	2521		2929		6069		904	
7	2	2	890	1	3	510	0	4	650	700	680	0	3	830	0	4	1919		2994		6474		0	
8	2	1	810	1	2	680	0	3	650	680	610	0	2	780	0	3	2383		0		378		1482	
9	2	0	750	1	1	600	0	2	680	690	660	0	1	710	0	2	4229		0		722		0	
10				1	0	590	0	1	630	710	630	0	0	750	0	1	3008		0		2141		0	
11				2	4	630	0	0	600	650	610	1	9	560	0	0	330		0		1985		0	
12				2	3	750	1	10	700	610	660	1	8	660	1	10	1744		15222		0		1962	
13				2	2	590	1	9	660	670	620	1	7	600	1	9	2146		1297		2591		1387	
14				2	1	710	1	8	630	620	680	1	6	660	1	8	2980		762		4869		1979	
15				2	0	530	1	7	710	700	680	1	5	690	1	7	2648		2833		4036		575	
16				3	4	710	1	6	600	670	820	1	4	720	1	6	2224		0		89		1952	
17				3	3	790	1	5	660	750	710	1	3	690	1	5	3521		0		1426		1147	
18				3	2	670	1	4	730	650	690	1	2	830	1	4	3025		2632		460		1289	
19				3	1	620	1	3	640	690	680	1	1	780	1	3	697		0		230		2625	
20				3	0	620	1	2	630	710	770	1	0	660	1	2	2587		276		477		2792	
21				4	4	500	1	1	550	720	750	2	9	600	1	1	3136		0		93		853	
22				4	3	500	1	0	540	660	660	2	8	640	1	0	2395		0		1664		1668	
23				4	2	550	2	10	610	730	560	2	7	670	2	10	3427		548		2773		1561	
24				4	1	520	2	9	680	650	650	2	6	640	2	9	3811		1597		230		2424	
25				4	0	700	2	8	640	700	670	2	5	870	2	8	3675		3135		179		2121	
26							2	7	570	730	730	2	4	690	2	7	2354		3617		2428		4026	
27							2	6	620	690	740	2	3	670	2	6	3478		295		0		2431	
28							2	5	650	740	780	2	2	690	2	5	3089		2618		7326		3405	
29							2	4	630	650	600	2	1	700	2	4	3471		0		2063		1308	
30							2	3	600	670	710	2	0	640	2	3	2977		0		3452		2977	
31							2	2	580	650	660	3	9	660	2	2	3366		93		580		0	
32							2	1	570	680	680	3	8	720	2	1	1548		0		3419		1937	
33							2	0	490	560	660	3	7	660	2	0	2518		0		2558		2821	
34							3	10	720	660	630	3	6	670	3	10	2573		4114		4308		1475	
35							3	9	740	620	580	3	5	670	3	9	2945		2019		1392		1075	
36							3	8	670	690	700	3	4	670	3	8	5830		1926		0		2091	
37							3	7	800	760	740	3	3	660	3	7	2459		3332		2612		3479	
38							3	6	590	720	800	3	2	680	3	6	1536		2801		2367		561	
39							3	5	700	710	760	3	1	650	3	5	2672		2726		0		1969	
40							3	4	650	810	720	3	0	640	3	4	177		0		0		588	

APPENDIX ONE: SITE B DATA

Number	B-100 X	B-100 Y	B-100 Z (ug P /g)	B-10 X	B-10 Y	B-10 Z (ug P /g)	B-1, B-01a, B-01b X	B-1, B-01a, B-01b Y	B-1, Z1 (ug P /g)	B-01a, Z2 (ug P /g)	B-01b Z3 (ug P /g)	B-001 X	B-001 Y	B-001 Z (ug P /g)	B-0001 X	B-0001 Y	B-0001 Z1 (% P)	B-00001 Z2 (% P)	B-00001P Z3 (% P)	B-000001P Z4 (% P)
41							3	3	690	670	710	4	9	630	3	3	2096	3390	1821	327
42							3	2	570	730	720	4	8	640	3	2	2764	4806	0	807
43							3	1	570	700	650	4	7	630	3	1	2624	3961	0	867
44							3	0	560	670	650	4	6	700	3	0	3088	0	2210	4025
45							4	10	650	600	660	4	5	680	4	10	2634	2785	0	1564
46							4	9	660	450	710	4	4	710	4	9	3157	3681	1769	1321
47							4	8	600	650	650	4	3	680	4	8	3137	2222	0	1931
48							4	7	630	650	600	4	2	670	4	7	2974	2987	3528	2152
49							4	6	670	760	750	4	1	670	4	6	2935	2428	3693	2456
50							4	5	700	720	730	4	0	560	4	5	2170	2825	2935	1141
51							4	4	650	690	680	5	9	670	4	4	3390	3274	0	2343
52							4	3	630	680	640	5	8	690	4	3	900	3218	3377	1052
53							4	2	630	690	670	5	7	870	4	2	2889	1230	3572	100
54							4	1	510	690	610	5	6	660	4	1	3545	3493	3651	1615
55							4	0	570	660	680	5	5	630	4	0	2955	2700	1833	2006
56							5	10	550	610	570	5	4	680	5	10	2261	2848	5299	1644
57							5	9	690	650	710	5	3	710	5	9	2663	0	17026	631
58							5	8	810	690	730	5	2	660	5	8	288	5033	3345	980
59							5	7	710	630	760	5	1	670	5	7	2409	2885	0	2328
60							5	6	670	720	620	5	0	660	5	6	981	3843	3487	2305
61							5	5	580	680	680	6	9	670	5	5	2213	2305	1499	1357
62							5	4	590	710	720	6	8	780	5	4	3506	2790	0	3974
63							5	3	610	700	610	6	7	410	5	3	0	2827	3441	439
64							5	2	630	610	680	6	6	920	5	2	3144	0	4923	556
65							5	1	540	650	550	6	5	720	5	1	1591	1946	1866	825
66							5	0	540	750	580	6	4	730	5	0	3572	4227	4032	1904
67							6	10	610	510	630	6	3	710	6	10	2905	3144	1133	2823
68							6	9	830	660	670	6	2	620	6	9	2698	0	0	1075
69							6	8	540	670	650	6	1	650	6	8	3015	4794	4006	2158
70							6	7	670	760	560	6	0	660	6	7	2017	3392	2041	3245
71							6	6	730	770	720	7	9	830	6	6	2782	1950	0	3016
72							6	5	700	650	700	7	8	400	6	5	3426	3472	1081	1671
73							6	4	670	680	660	7	7	240	6	4	2595	4041	0	1287
74							6	3	620	620	670	7	6	960	6	3	3017	4350	3492	835
75							6	2	620	600	640	7	5	660	6	2	1944	1196	3233	935
76							6	1	540	650	590	7	4	660	6	1	2829	4002	3730	2669
77							6	0	600	860	550	7	3	660	6	0	2075	3088	3059	4009
78							7	10	650	620	660	7	2	700	7	10	2608	1276	7314	3528
79							7	9	650	630	730	7	1	770	7	9	3562	6893	3004	1640
80							7	8	620	630	570	7	0	760	7	8	3562	3229	0	2989
81							7	7	610	640	610	8	9	660	7	7	2208	3470	5450	1419

APPENDIX ONE: SITE B DATA

Number	B-100 X	B-100 Y	B-100 Z (ug P /g)	B-10 X	B-10 Y	B-10 Z (ug P /g)	B-1, B-01a, B-01b X	B-1, B-01a, B-01b Y	B-1 Z1 (ug P /g)	B-01a Z2 (ug P /g)	B-01b Z3 (ug P /g)	B-001 X	B-001 Y	B-001 Z (ug P /g)	B-0001 X	B-0001 Y	B-0001 Z1 (% P)	B-00001 Z2 (% P)	B-00001P Z3 (% P)	B-000001P Z4 (% P)
82							7	6	670	660	690	8	8	620	7	6	3082	423	2859	1734
83							7	5	710	700	700	8	7	720	7	5	976	3281	5516	2054
84							7	4	840	650	600	8	6	670	7	4	1930	1749	2402	1957
85							7	3	640	650	690	8	5	670	7	3	2619	3099	1931	0
86							7	2	570	670	700	8	4	720	7	2	0	3568	1401	3409
87							7	1	530	710	670	8	3	620	7	1	476	2838	2763	2233
88							7	0	630	650	650	8	2	650	7	0	3157	5712	0	2380
89							8	10	690	570	720	8	1	720	8	10	2995	732	0	0
90							8	9	610	660	860	8	0	770	8	9	2686	3266	2950	160
91							8	8	640	680	710	9	9	840	8	8	2394	2929	3121	382
92							8	7	610	670	710	9	8	710	8	7	3651	2399	1823	2110
93							8	6	670	710	750	9	7	730	8	6	3513	3553	88	1367
94							8	5	620	670	620	9	6	700	8	5	2579	3415	2243	986
95							8	4	740	620	680	9	5	890	8	4	3794	3318	5162	1614
96							8	3	730	670	630	9	4	720	8	3	3559	3528	3279	2192
97							8	2	600	720	710	9	3	690	8	2	3167	4787	91	3116
98							8	1	500	640	630	9	2	700	8	1	0	845	3752	3683
99							8	0	520	650	580	9	1	640	8	0	3120	0	2488	80
100							9	10	710	650	580	9	0	670	9	10	3297	3489	4501	1238
101							9	9	610	710	680				9	9	1202	201	0	557
102							9	8	680	670	610				9	8	0	2775	323	1512
103							9	7	830	660	760				9	7	408	2190	3426	1718
104							9	6	730	620	720				9	6	2496	3782	0	3056
105							9	5	610	700	580				9	5	2812	3996	2300	2578
106							9	4	580	650	700				9	4	2085	3385	3047	2629
107							9	3	620	590	740				9	3	2703	758	1196	1634
108							9	2	550	690	640				9	2	1183	2977	3102	0
109							9	1	730	620	600				9	1	782	3808	2518	975
110							9	0	610	720	600				9	0	3293	3956	4796	205
111							10	10	590	580	640				10	10	2822	1149	11261	551
112							10	9	560	600	650				10	9	2949	495	3000	382
113							10	8	620	680	620				10	8	2596	3894	3689	285
114							10	7	750	640	850				10	7	3186	0	2933	2343
115							10	6	720	680	840				10	6	687	2536	3752	4002
116							10	5	690	710	670				10	5	3218	844	807	753
117							10	4	570	670	630				10	4	2777	3623	1869	3349
118							10	3	550	640	630				10	3	2509	3785	3065	2565
119							10	2	560	590	650				10	2	2198	2883	3315	3194
120							10	1	520	580	630				10	1	0	0	0	5178
121							10	0	710	590	610				10	0	2810	3140	2415	2931

APPENDIX ONE: SITE C DATA

Number	C-10m X	C-10m Y	C-10m Z (ug P /g)	C-1m X	C-1m Y	C-1m Z (ug P /g)	C-0 5m X	C-0 5m Y	C-0 5m Z1 (ug P /g)	C-0 1m X	C-0 1m Y	C-0 1m Z (ug P /g)
1	90	130	1220	115	100	2300	101 5	97	2070	102	96	2540
2	90	120	970	115	99	2030	101 5	96 5	1610	102	95 9	1880
3	90	110	1440	115	98	2010	101 5	96	2170	102	95 8	2200
4	90	100	1540	115	97	1790	101 5	95 5	1680	102	95 7	1740
5	90	90	840	115	96	1520	101 5	95	1920	102	95 6	2060
6	100	130	1370	115	95	1370	101 5	94 5	2020	102	95 5	2330
7	100	120	1350	115	94	1370	102	97 5	1540	102	95 4	2770
8	100	110	1460	116	100	1960	102	97	1480	102	95 3	2770
9	100	100	2020	116	99	1790	102	96 5	1680	102	95 2	2760
10	100	90	1020	116	98	1830	102	96	2540	102	95 1	2480
11	110	130	1520	116	97	1680	102	95 5	2330	102	95	2790
12	110	120	1910	116	96	1990	102	95	2790	102	94 9	2420
13	110	110	1740	116	95	1920	102	94 5	1640	102	94 8	1380
14	110	100	2380	116	94	2120	102 5	97 5	1660	102	94 7	1840
15	110	90	1030	117	100	1730	102 5	97	2050	102	94 6	1390
16	120	130	1200	117	99	2130	102 5	96 5	2140	102	94 5	1640
17	120	120	1520	117	98	1880	102 5	96	2050	102 1	96	1700
18	120	110	1460	117	97	2320	102 5	95 5	2570	102 1	95 9	2050
19	120	100	1840	117	96	1980	102 5	95	2130	102 1	95 8	1780
20	130	130	1130	117	95	1890	102 5	94 5	1690	102 1	95 7	2220
21	130	120	1360	117	94	1890	103	97 5	2200	102 1	95 6	1730
22	130	110	1290	118	100	1590	103	97	2010	102 1	95 5	4220
23	130	100	1310	118	99	1650	103	96 5	2750	102 1	95 4	1550
24	130	90	1370	118	98	1510	103	96	2180	102 1	95 3	1730
25				118	97	2130	103	95.5	2110	102 1	95 2	3660
26				118	96	1420	103	95	2000	102 1	95 1	2430
27				118	95	1550	103	94 5	1600	102.1	95	2410
28				118	94	1430	103 5	97 5	2620	102 1	94 9	1880
29				118	93	1710	103 5	97	1760	102 1	94 8	2120
30				119	100	1720	103 5	96 5	2140	102 1	94 7	1880
31				119	99	2080	103 5	96	3330	102 1	94 6	1540
32				119	98	2050	103 5	95 5	3360	102 1	94 5	1680
33				119	97	2190	103 5	95	2060	102 2	96	1920
34				119	96	1660	103 5	94 5	1960	102 2	95 9	1760
35				119	95	1530	104	97 5	2050	102 2	95 8	1780
36				119	94	1860	104	97	1760	102 2	95 7	1850
37				119	93	1600	104	96 5	2140	102 2	95 6	2320
38				120	100	1840	104	96	2330	102 2	95 3	2890
39				120	99	1990	104	95 5	1940	102 2	95 2	2850
40				120	98	1970	104	95	1960	102 2	95 1	2350
41				120	97	2150	104	94 5	1800	102 2	95	3100

APPENDIX ONE: SITE C DATA

Number	C-10m X	C-10m Y	C-10m Z (ug P /g)	C-1m X	C-1m Y	C-1m Z (ug P /g)	C-0 5m X	C-0 5m Y	C-0 5m Z1 (ug P /g)	C-0 1m X	C-0 1m Y	C-0 1m Z (ug P /g)
42				120	96	1830	104 5	97 5	1460	102 2	94 8	2110
43				120	95	1950	104 5	97	1680	102 2	94 7	1570
44				120	94	2040	104 5	95 5	2060	102 2	94 6	1740
45				120	93	2020	104 5	95	2270	102 2	94 5	1680
46				120	92	1610	104 5	94 5	1790	102 3	96	1690
47				121	100	1760				102 3	95 9	2020
48				121	99	1870				102 3	95 8	2000
49				121	98	1900				102 3	95 7	1820
50				121	97	1860				102 3	95 6	2350
51				121	96	2180				102 3	95 4	2220
52				121	95	1860				102 3	95 3	2930
53				121	94	1720				102 3	95 2	1920
54				121	93	1970				102 3	95 1	1940
55				121	92	1610				102 3	95	1940
56				121	91	1540				102 3	94 9	2680
57				122	100	1560				102 3	94 8	2270
58				122	99	1560				102 3	94 7	2130
59				122	98	1750				102 3	94 6	1850
60				122	96	2630				102 3	94 5	2030
61				122	95	1850				102 4	96	1820
62				122	94	1780				102 4	95 9	2210
63				122	93	1900				102 4	95 8	1980
64				122	92	1710				102 4	95 7	2220
65				122	91	1500				102 4	95 6	2360
66				122	90	1900				102 4	95 5	2270
67				123	100	1650				102 4	95 4	2280
68				123	99	1520				102 4	95 3	1660
69				123	98	1670				102 4	95 2	2320
70				123	97	1630				102 4	95 1	2780
71				123	96	1790				102 4	95	2730
72				123	95	1800				102 4	94 9	2350
73				123	94	1780				102 4	94 8	1870
74				123	93	1840				102 4	94 7	1990
75				123	92	1630				102 4	94 6	2300
76				123	91	1550				102 4	94 5	1940
77				123	90	2140				102 5	96	2050
78				123	89	2450				102 5	95 9	1670
79				124	100	1480				102 5	95 8	1710
80				124	99	1610				102 5	95 7	1640
81				124	98	1660				102 5	95 5	2570
82				124	97	1770				102 5	95 4	2460

APPENDIX ONE: SITE C DATA

Number	C-10m X	C-10m Y	C-10m Z (ug P /g)	C-1m X	C-1m Y	C-1m Z (ug P /g)	C-0 5m X	C-0 5m Y	C-0 5m Z1 (ug P /g)	C-0 1m X	C-0 1m Y	C-0 1m Z (ug P /g)
83				124	96	1720				102 5	95 3	2610
84				124	95	1680				102 5	95 2	1800
85				124	94	1830				102 5	95 1	2300
86				124	93	1690				102 5	95	2130
87				124	92	1570				102 5	94 8	2200
88				124	91	1450				102 5	94 7	1760
89				124	90	1590				102 5	94 6	1690
90				124	89	1720				102 5	94 5	1690
91				124	88	1660				102 6	96	1880
92				125	100	1520				102 6	95 9	2080
93				125	99	1370				102 6	95 7	2130
94				125	98	1420				102 6	95 6	1750
95				125	97	1490				102 6	95 5	3950
96				125	96	1580				102 6	95 4	2760
97				125	95	1550				102 6	95 3	2730
98				125	94	1450				102 6	95 2	2560
99				125	93	1510				102 6	95 1	2550
100				125	92	1350				102 6	95	2200
101				125	91	1370				102 6	94 9	1980
102				125	90	1570				102 6	94 8	1810
103				125	89	1970				102 6	94 7	1870
104				125	88	1900				102 6	94 6	1730
105				126	100	1400				102 6	94 5	1970
106				126	99	1400				102 7	96	2120
107				126	98	1250				102 7	95 9	2470
108				126	97	1810				102 7	95 8	2120
109				126	96	1910				102 7	95 7	2110
110				126	95	1620				102 7	95 6	1700
111				126	94	1460				102 7	95 5	2400
112				126	93	1330				102 7	95 4	2150
113				126	92	1430				102 7	95 3	3250
114				126	91	1420				102 7	95 2	1650
115				126	90	1370				102 7	95 1	2190
116				126	89	1730				102 7	94 8	1720
117				126	88	2030				102 7	94 7	2290
118				127	100	1300				102 7	94 6	1730
119				127	99	1400				102 7	94 5	1620
120				127	98	1340				102 8	96	2070
121				127	97	1420				102 8	95 9	2370
122				127	96	1330				102 8	95 8	2470
123				127	95	1460				102 8	95 7	1800
124				127	94	1460				102 8	95 6	2000

APPENDIX ONE: SITE C DATA

Number	C-10m X	C-10m Y	C-10m Z (m P.D.)	C 1m X	C 1m Y	C 1m Z (m P.D.)	C 0.5m X	C 0.5m Y	C 0.5m Z1 (m P.D.)	C 0.1m X	C 0.1m Y	C 0.1m Z (m P.D.)
125				127	93	1360				1028	955	1940
126				127	92	1350				1028	954	3700
127				127	91	1280				1028	952	2140
128				127	90	1390				1028	951	2010
129				127	89	1440				1028	95	2340
130				127	88	2080				1028	949	2160
131				126	100	1410				1028	947	1960
132				126	99	1410				1028	946	1860
133				126	98	1420				1028	945	1810
134				126	97	1230				1029	959	1930
135				126	96	1340				1029	958	1900
136				126	95	1350				1029	957	2350
137				126	94	1410				1029	956	2630
138				126	93	1310				1029	955	2180
139				126	92	1330				1029	954	2110
140				126	91	1630				1029	953	2460
141				125	93	1450				1029	952	2180
142				125	89	1300				1029	951	2140
143				125	88	1920				1029	95	2270
144				125	100	1400				1029	949	2040
145				125	99	1140				1029	948	2110
146				125	98	1410				1029	947	2030
147				125	97	1320				1029	946	2070
148				125	96	1440				1029	945	2020
149				125	95	1530				103	95	2180
150				125	94	1380				103	959	2040
151				125	93	1450				103	958	2930
152				125	92	1310				103	957	2290
153				125	91	1400				103	956	3010
154				125	90	1360				103	955	2110
155				125	89	1230				103	954	2240
156				125	88	1600				103	953	2970
157				130	100	1310				103	952	2220
158				130	99	1430				103	951	3040
159				130	98	1230				103	95	2000
160				130	97	1360				103	949	2450
161				130	96	1410				103	948	2220
162				130	95	1360				103	947	2220
163				130	94	1130				103	946	1860
164				130	93	1480				103	945	1600
165				130	92	1350						
166				130	91	1400						
167				130	90	1370						
168				130	89	1220						
169				130	88	1480						

APPENDIX ONE: Site A - College farm: 0.001m Data, 50um raster (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0.714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total Oxides
1	33.78	9.20	2 85	0 59	2 51	0 00	0 00	1 44	0.00	0 36	0 00	0 00	10 92
2	15.38	12.10	10 68	1.57	4.78	1 65	0 85	0 00	2 72	0 88	0 98	7.78	10 93
3	19 20	10 21	8 48	1.14	4.39	1.01	0 91	0 99	3.11	0.73	0 84	7 19	11 92
4	23 70	10 02	6 84	0 72	3 82	0 81	0 00	0 53	2 51	0 74	0 59	5 71	14 78
5	31.38	9.15	5 18	1.00	2 37	1 20	0 00	0 00	1 48	0.55	0 00	0 00	15 03
6	21.13	12 47	9 42	0.64	2 38	1 15	0 99	1 00	0 95	0 53	0 55	4 94	15 69
7	19 16	12 45	10 33	0 78	4 61	0 72	0 00	0 95	2 24	0 87	0 68	4 89	16 57
8	21.71	11 76	7 86	0.79	4 32	0 91	0 00	1.99	2 25	0 68	0 61	3 85	19 79
9	26 40	12 17	7 39	1.50	2 99	0 60	0 00	0 79	1 48	0.70	0 00	0 00	19 99
10	22 45	10 97	9 27	0.85	3 81	0 79	2 05	0 70	1 64	0 56	0 56	3 00	22 67
11	32 73	8.06	6 44	0 68	2 20	0 00	0 34	0 34	0 00	0 44	0 20	0 15	22 97
12	25 97	11 65	8 13	1.04	2 85	0 67	0 58	0 88	1 66	0 72	0 32	0 00	26.79
13	28.82	10 82	6 65	0.77	2 90	0.89	0 58	0 59	0.83	0.36	0 00	0 00	26 9
14	31.70	1.37	0 00	4.21	0.98	2.43	0 00	0 00	9.58	0.08	0.42	3 01	27.11
15	22.48	12.15	8 94	0.74	4.17	0 65	0 28	0.85	2.13	0 69	0 45	2 31	27 86
16	28 82	10.25	5 58	1.59	2.65	0 65	0 28	0.85	1.06	0 61	0 22	0 20	27 87
17	21.35	13 31	8 55	0.56	4.71	0 85	0 55	0 84	2.37	0.54	0.35	2.50	28.22
18	27 93	10 90	6 57	1.06	2 86	0.61	0.79	0 53	1 25	0 52	0 20	0 00	29 6
19	26 49	11 90	6 09	1.35	3 33	0.39	0 76	1 80	1.21	0.46	0 22	0.00	30 68
20	21.13	13 99	8 67	0 77	4.79	0 96	0 49	1 00	2.13	0.65	0.42	1 57	31 39
21	21.51	12 35	10 55	0 86	4.08	1.32	0.24	0.75	1.87	0.70	0 36	1 86	31.7
22	23 70	11.46	7.46	0.84	4.16	0 93	0.48	1.22	2.53	0 66	0.37	1 68	32.31
23	22 57	13.18	7 24	1.31	4 61	0.54	0 93	0.71	2 23	0.59	0.36	1.19	33.31
24	28 00	11.58	5 83	0.64	3.31	0.54	0 23	0 94	0 67	0.34	0 24	1.07	33 36
25	24 82	13 66	6 24	0.51	4.71	0.53	0 69	0.47	1 54	0.35	0.22	0 81	33 68
26	23 52	13 24	6 87	1.30	4.13	0.71	0 91	1.39	1 97	0.55	0 29	0.59	33 95
27	26 47	11 84	6.11	0.83	4.20	0 52	0.45	0 69	1 51	0 51	0.29	0.36	34 4
28	28 28	10 87	7.03	1.06	2 87	0.49	0 00	1 08	1.02	0 51	0.16	0 00	36 5
29	22.49	13 66	9 21	0 67	3 95	0 81	0.42	0 64	2.00	0 63	0.38	0 81	37 17
30	24 96	13 10	7.71	1.08	3.18	0.78	0 61	1 03	0 97	0 66	0 21	0 00	38 35
31	19 48	10 76	9 94	0 99	2.75	0.47	12.12	0 41	1 35	0.46	0.23	0.16	38 36
32	22.28	14.11	8 38	0 86	4 47	0 92	0.40	0 81	1 71	0.56	0 22	0 74	38 98
33	29 93	10 43	6 14	0.88	2 64	0 44	0.38	0 58	0 55	0.52	0 13	0 00	40 57
34	22 87	14 77	8 38	1.05	3 74	0 73	0.76	0.77	1 27	0 60	0 16	0 00	40 84
35	26 36	12 63	6 38	1 05	3 72	0 58	0 56	0.76	0 89	0 53	0 23	0 00	41 46
36	23.46	14 62	6 55	0 76	4 59	0.58	0 56	0 95	1.25	0 50	0 22	0 73	41 6
37	22.56	13 54	7 82	0.77	4 57	0 86	0.37	1.13	1 95	0 51	0 22	1.26	41 81
38	23.10	13 77	8 29	1.17	4.13	0.57	0.73	0.93	1.40	0 62	0 32	0.32	42.25
39	27.99	10 81	6 79	0.95	2 67	0 83	0.53	1 09	1.19	0 47	0 17	0 00	43.54
40	26 41	11.58	7 98	0.94	3.12	0.55	0.53	0 90	1.18	0 64	0 24	0 00	43 86
41	25.82	12.35	7.23	0.79	3 61	0 68	0.53	0.71	1.18	0 54	0.23	0.37	44.13
42	27 82	10 82	6 82	0.59	3.47	0.54	0 35	1.06	1.17	0 53	0.28	0.22	44.49
43	25.46	12 46	7 68	1.01	3.26	0.67	0.35	1.06	1.33	0 71	0.22	0.00	44.57
44	27.10	11 62	6 45	0.74	3.09	0.67	0 35	2.12	1.00	0 52	0.16	0 00	44 63
45	25.28	12 66	7 66	0 96	3 55	0.81	0 52	0.88	1.16	0 58	0.25	0 00	44.7

APPENDIX ONE: Site A - College farm: 0.001m Data, 50um raster (corrected to %)

Number	Si	Al	Fe	Ca	K	Mg	Mn	Ti	Na	P	S	Cl	Total Oxides
	0 467	0 529	0 778	0 714	0 83	0 6	0 775	0 788	0 742	0 437	0 667	0 686	
46	26 70	11 86	6 67	0 86	3 07	0.79	0.34	1 39	1.47	0.49	0.22	0 09	45 48
47	26 40	12 08	7.10	0 82	2 81	0 65	0 17	0 86	1.94	0.53	0.13	0 00	46
48	26 46	12 52	7.09	0 90	3.24	0 65	0 50	0 86	0 81	0.52	0 19	0 00	46 06
49	26.12	11.99	6.72	0.97	3 03	1.30	0.33	1 02	1.76	0.49	0 23	0.00	46 31
50	26 24	12 84	7.12	0 85	3.11	0 64	0.33	1 17	0 95	0.47	0.18	0 00	46 98
51	24 55	12.34	9 57	0 97	2.82	1 40	0 66	0 67	0 94	0.43	0.11	0 26	47.17
52	28 05	11.64	6.09	0.97	3 23	0.25	0 49	0 67	1.26	0 49	0.17	0.00	47 28
53	25 67	13.09	7 07	0 92	3 68	0 63	0 33	1 17	0 78	0 55	0 20	0 00	47.3
54	23.17	11.95	10 02	1 00	3.51	0.89	2.13	0 83	1.72	0.44	0.23	0.32	47 36
55	25.57	12 26	7.54	0 87	3 50	0 88	0 49	1 00	1.25	0 48	0 22	0.25	47.48
56	25.74	12.19	8.15	0 75	3.48	0 63	0.32	0 83	1 40	0.58	0 18	0 10	47.72
57	27 50	11.67	6.48	0 68	3.06	0 50	0.32	0 82	1 85	0 43	0 17	0 00	48 06
58	25 80	13.30	6.79	0 64	3.79	0 62	0.32	0 98	0.92	0 43	0 17	0.10	48.14
59	24.82	12.19	8.24	0 99	3.62	0 62	0.48	2 29	1 08	0.45	0 24	0.13	48.16
60	27.92	11.09	7.11	0 65	2 96	0 87	0.32	0 65	0 92	0 44	0 17	0 13	48 17
61	25 97	12.18	8 07	0.77	3.44	0.50	0.32	0 82	1.39	0 54	0 26	0.00	48 2
62	25.32	11 62	10 22	0 65	3 41	0 62	0.64	0 65	1 07	0 48	0.19	0.13	48 7
63	30.12	10.18	6.05	0 57	2 62	0 49	0 48	0 65	0.76	0 49	0 12	0 00	48 84
64	28.01	11 47	5.83	0.71	2.27	0 49	0.47	0 64	2 86	0.40	0.18	0 00	49 35
65	27.62	12.11	5 67	0.67	3.70	0.49	0.31	0 96	1.05	0 44	0 20	0 00	49.37
66	23.92	13 60	8 28	0.62	3 50	1.33	0.47	1 27	1.34	0.32	0.13	0 21	49 78
67	27.69	11.47	6.04	0 60	3 47	0.60	0.31	0 94	1.48	0.45	0 17	0.15	50.25
68	32.00	8.36	5 53	0 63	2.41	0.59	0.46	0 47	0 88	0.40	0.14	0.14	50 64
69	26.38	12 57	6 06	0 70	3 88	0 82	0.30	1 23	1.30	0.41	0.23	0 00	51.34
70	31.04	9 35	5 98	0 66	2.77	0.46	0.30	0 76	0 71	0 40	0.14	0.00	52.05
71	28.36	10.74	6 89	0 58	2 91	0.55	0.57	1 02	1.10	0.44	0.15	0.00	54.18
72	28.15	12.55	4 51	0 57	4 21	0.54	0.28	0 71	0.94	0.35	0.10	0.00	55.24
73	30 65	9.85	5 49	0 52	2.85	0.54	0.28	0 57	0 81	0.38	0.17	0.11	55 3
74	30.08	9 85	5.69	0 53	2.89	0.63	0.13	1.23	1.03	0.38	0.20	0.00	57.44
75	30.95	9 66	5 68	0 50	2.74	0 63	0.00	0 82	0.77	0.34	0.20	0.00	57 48
76	22.29	11.58	16.11	0.72	2.46	0.62	0.66	0 81	1.14	0.49	0.08	0 00	58 45
77	31.37	8.97	5 54	0 63	2 32	0.41	0.53	0 94	0 88	0.37	0.18	0.00	58 95
78	29 41	10.96	5.11	0 43	1.76	0.40	0.39	0 53	3.25	0.25	0 00	0 10	59.39
79	34.09	6 07	5 56	0.30	1.96	0.40	0.00	2 62	0 62	0.25	0 10	0.16	60.13
80	15.39	8.08	29 64	0.80	1.53	0.39	4 24	1 39	0.95	0 57	0.09	0.00	62.21
81	32.29	6 95	6.74	0.35	1.74	2.15	0.23	0 71	0.66	0.18	0.12	0.11	66 96
82	42.41	2.45	1.90	0.00	0 60	0.15	0.00	0 20	0 29	0.11	0 09	0 00	77 85
83	27.69	10.07	10.98	0.13	3 06	0.29	0 00	0 77	1 46	0.10	0 07	0.00	81 45
84	26.54	11.14	10.15	0.09	4.17	0.43	0.37	0 47	0.98	0.35	0 00	0.00	83.57
85	25 54	17.00	1.95	0.09	5.55	0.36	0.19	1 04	1.15	0.03	0 00	0.00	83 73
86	32 67	10 42	2.44	0 00	3.25	0.67	0.00	0 71	0 91	0.03	0 00	0 00	89.33
87	46.21	0.35	0.25	0.00	0.00	0.00	0.00	0 00	0.00	0.01	0 00	0 00	91 86
88	34.32	0 56	0.00	4 62	0.88	2.61	0.00	0 00	9 99	0.00	0.11	0 00	94 29
89	34.30	0.45	0.00	4 54	0.79	2.73	0.00	0 00	10.07	0.00	0.10	0 00	94 35

APPENDIX ONE: Site A- 0.0001m Data, 50 um raster (corrected to %)

Number	Si	Al	Fe	Ca	K	Mg	Mn	Ti	Na	P	S	Cl	Total oxides
	0 47	0 53	0 78	0.71	0 83	0 6	0.78	0 79	0 74	0 437	0 67	0 69	
1	39 94	5 00	2 68	0 00	1 35	0 00	0 00	0 00	0 00	0 26	0 00	0 00	11 65
2	29.28	11.30	5 11	0 47	3 61	0 00	0 64	0 78	1 21	0 43	0 00	0 34	12 20
3	23 82	11.97	7.19	2.29	3 86	0 83	0 36	0.73	2 05	1 09	0 99	0 00	21.70
4	26.56	11.60	6.75	0.74	2 69	1 09	0.36	1 08	2 36	0 50	0.18	0 00	21 94
5	27.08	11.16	5.89	2.06	3.36	0 48	0.93	0 63	1.47	0 57	0 21	0 00	25 17
6	26.46	12.10	7.68	1.03	3.10	0.71	0.61	0.93	0 87	0 64	0.21	0.00	25 40
7	25.55	12 61	7.48	1.34	3 30	0.85	0.55	0 84	1.31	0 56	0.21	0 00	28.15
8	22.41	13.57	8 03	2 93	3 25	1.24	0 46	1.39	1.31	0.58	0 57	0.00	33 98
9	23.29	13 06	7.98	1 60	3.53	0 79	1.02	0 83	1.75	0 92	0 42	0 14	38.14
10	25.36	12 47	7.98	1.23	3.63	0.46	0 60	1 41	0.76	0.59	0.22	0 18	39 10
11	24 60	12 74	8.20	1.28	3.08	0.75	0 59	0 99	1.48	0 81	0.25	0 00	39 93
12	28 65	10.19	6.43	0.55	2.61	0.90	0.39	1.18	1.11	0.47	0.20	0 86	40 03
13	25 44	11 98	9 10	1.02	2 99	0.89	0.97	0.78	0 74	0.63	0.18	0.12	40.27
14	24 01	13.79	7.78	0.83	3.90	0.73	0 38	1.15	1.26	0.70	0.24	0 00	41.11
15	29 60	8.25	6.07	0.76	2 22	0.58	0.38	3 27	0.90	0.79	0.28	0.72	41.12
16	26.91	11 44	6 81	1.29	2.82	0.58	1.14	0.77	1.08	0 82	0.24	0.00	41.22
17	24 98	12.95	7.59	1.08	4.14	0.43	0.74	0 94	1.05	0.69	0.25	0.18	42.14
18	25.56	12.76	7.76	0.92	3.13	0.69	0 54	1.10	1.37	0.62	0 17	0.00	43.21
19	24.59	13 50	8 59	0 75	3.18	0.96	0.72	0.73	0 85	0 57	0.17	0 00	43.58
20	25.77	12.68	7.76	0.83	3 49	0 66	0.52	0 87	0 82	0.73	0.18	0 00	45.23
21	28 09	11.36	6.76	1 00	2.98	0.39	0.51	0.68	1.12	0.57	0.16	0 00	46.18
22	23.70	13 65	8 61	1.12	3.43	0.65	0.51	1.54	0.80	0 85	0 23	0 00	46 20
23	23 98	13 87	7.59	1.03	3.95	0.52	0.51	1.20	1.28	0 66	0.23	0 00	46 25
24	25.73	11.88	8.91	0 89	3.11	0.52	0.67	1.02	1.12	0 63	0.16	0.12	46.39
25	27.19	11.24	7.86	1.11	3.06	0.51	0.84	0.85	0.79	0.56	0.14	0 00	46 67
26	27.58	11.24	7.52	0.73	3.07	0.77	0 50	0.85	0.95	0 57	0.20	0 00	46.70
27	24.37	13 00	9.15	0.88	3.54	0 64	0 67	0.84	1.11	0 68	0.17	0 00	46 87
28	28 09	11.05	5.81	0.72	2.93	0.77	0 50	1.68	1.26	0 46	0.19	0 09	47.01
29	25.74	12.15	7.45	1.21	3.35	0.64	0.50	1.68	1.10	0 64	0.21	0 00	47.11
30	25.10	12 81	8.27	1.02	3 52	0.89	0.50	0 67	0.94	0 69	0 23	0 00	47.18
31	25.79	12.08	8.72	0 91	2 98	0.89	0.82	0.83	0 78	0 57	0.16	0 00	47.39
32	29 88	9 87	5.22	1.49	2 80	0.50	0.65	0.99	0.93	0 47	0.20	0 00	47 81
33	28.32	10.94	6.67	0 80	2 98	0.63	0.65	0.66	0.93	0 65	0.21	0 00	47.97
34	27.13	11.16	7.15	1.02	3.03	0.75	0.65	1.32	1.54	0.50	0.17	0 00	47.98
35	24.79	12.61	9 68	0 93	3.09	0.50	0 65	0.82	1.07	0.65	0.22	0 00	48.35
36	25.65	12.49	7.26	0 91	3 26	0.74	0.65	1.80	1.07	0.63	0.25	0 00	48 37
37	25.76	13.11	6 43	1.08	3.93	0.49	0 48	0 65	1.68	0 47	0.15	0 00	48.53
38	24.42	13 61	7.53	0.90	3.75	0.86	0 64	1.14	1.22	0.56	0.26	0 00	48 69
39	25.69	13.13	6.55	1.09	3 57	0.74	0.64	0.81	1.06	0.77	0.26	0 00	48 85
40	24.98	12.79	8.77	0.80	3.22	0.86	0 64	0 81	1.21	0.60	0.23	0 14	48 91
41	25.29	13.29	7.79	0.91	2.59	1.47	0 48	0.64	1.06	0.48	0.25	0 00	49 06

APPENDIX ONE: Site A- 0.0001m Data, 50 um raster (corrected to %)

Number	Si 0 47	Al 0 53	Fe 0 78	Ca 0 71	K 0 83	Mg 0 6	Mn 0 78	Ti 0 79	Na 0 74	P 0 437	S 0 67	Cl 0 69	Total oxides
42	24 67	13.16	8.66	0.75	3 02	1 09	0 47	1.44	0.75	0.56	0.18	0 00	49 53
43	24.70	12.59	8.79	0 91	3.34	0 85	1.26	0 95	1.19	0 64	0.19	0 00	49 67
44	25.73	12 33	7 67	0 80	3 66	0.48	0.47	1 11	1 63	0 70	0 24	0 00	49 86
45	26 52	12.09	6.56	1 28	2 99	0.72	0 78	0 63	1.93	0 57	0 21	0 00	49 97
46	27.52	11.61	6 06	0 89	2 99	0.72	0 47	1.26	1 62	0 46	0.19	0 00	50 21
47	28 62	10.30	7.89	0 68	2.65	0.83	0.62	0.63	0.73	0 55	0.15	0 00	50 42
48	27.94	10.92	7.57	0 83	2.80	0.48	0 46	0 94	1.03	0 55	0 19	0 00	50 47
49	25.04	11 82	6 62	0 85	3.28	0.71	0.77	4 21	1.17	0 66	0.20	0 00	50.68
50	25.65	12 84	7.22	0.74	3 60	0.71	0 92	0 93	1 02	0 63	0.24	0 00	50 76
51	28.97	10 65	6.76	0 82	2.75	0.59	0 61	0 62	0.73	0.49	0.18	0 00	50.78
52	24.59	13.76	7.98	0 77	3 43	0.59	0.61	1 09	1.02	0 63	0.24	0 00	50.84
53	22.75	13 09	10.85	0 90	3 09	1.29	0 92	0 93	1.16	0 68	0.20	0 00	51 02
54	29 59	9 92	6 84	0 60	2.75	0.47	0.76	0 77	0 87	0 55	0.10	0 00	51.30
55	24.49	13.50	8 04	0.97	3 39	0.82	0 61	0.61	1.29	0 59	0.23	0 00	51.43
56	32.70	8.45	5.00	0.44	2 60	0.47	0.45	0 61	0.58	0.38	0.14	0 46	51.46
57	27.78	11.40	7.10	0.74	3 22	0.23	0 91	1.22	0.72	0.55	0.18	0 00	51 60
58	27.64	11 82	6 45	0.70	3.51	0.69	0.30	0 76	1 00	0 58	0.15	0 00	52 03
59	27.64	12.00	6 83	0 81	3.16	0.46	0.45	0 45	0.99	0.52	0.14	0 00	52.55
60	26.19	12.70	7.27	0.72	3.31	0.57	0.74	0.75	1.13	0 56	0.19	0 00	52 58
61	24.84	12 60	8.75	0.88	3.16	0 80	0.89	0.90	1.13	0 67	0 24	0 00	52 60
62	25 54	12.44	8.12	0.70	3.14	0 80	0 74	1.20	1.12	0.64	0.19	0 00	52 81
63	30 23	9 50	5 89	0.71	2.76	1.02	0.59	0.75	0.84	0.51	0.15	0 00	53 01
64	26 67	11.89	7.50	0 88	2.97	0.79	0 59	1.04	0 98	0.60	0 15	0 00	53 04
65	30.20	10.09	5 59	0.80	2 50	0 68	0.44	0 89	0 84	0 52	0.19	0 00	53 07
66	18 84	11.27	18 49	1.06	2.45	0.56	4.40	0.45	0.84	0.71	0.10	0.32	53 15
67	25 97	13.15	7.18	0 64	3 28	0.90	0 44	0.89	0 97	0 52	0.11	0 00	53.20
68	25 95	11.35	7.32	1 07	2.71	1.24	0.88	1 19	2 36	0 52	0.18	0 00	53 25
69	26 22	11.61	8 91	0.78	2.80	1 01	0 58	0.74	0 97	0 62	0 13	0 00	53.41
70	26 20	12.51	7.83	0 55	3.24	0.45	0.72	1.17	0 96	0 55	0.17	0.00	53 82
71	25 65	12.99	7.24	0 80	3.54	0.56	0.72	0.73	1.24	0 62	0.17	0 00	53 87
72	27.98	10 62	6 94	0 99	2 92	0.56	0 87	1.47	0 82	0 49	0.20	0 00	53.92
73	28.18	13 83	3 61	0.51	3.69	0.33	0 00	0.58	1.37	0 27	0.16	0 00	54 04
74	24.36	14.17	6.76	0.76	4.44	0.89	0.58	0.73	1.23	0 54	0.17	0 00	54 22
75	30.55	9 61	5 85	0.61	2 74	0.55	0 86	0.72	0 68	0.50	0.15	0 00	54.62
76	25.38	11.93	8.99	0.73	3 04	0.77	0.71	1.73	0 95	0 54	0.16	0 00	54 64
77	27.93	11.14	7.70	0 65	2.73	0.66	0.57	0.58	1.08	0 56	0.13	0.00	54 69
78	27.54	11.61	7.40	0.58	3 03	0.55	0.57	0.87	0.95	0 57	0.17	0.00	54.79
79	27.22	11.78	6.82	0.89	3 02	0 66	0.57	1.01	1.35	0 50	0.18	0.00	54.91
80	25.40	13 21	6.81	0.75	3 47	0.76	0.43	0.72	1.08	1.17	0.15	0 00	54.95
81	27.59	11 56	6 80	0.76	3.17	0.55	0.71	0 86	1.21	0 60	0.11	0 00	55.03
82	31.91	8 95	4 96	0 67	2.44	0.44	0.42	1.00	0 81	0 41	0.17	0.00	55 08

APPENDIX ONE: Site A- 0.0001m Data, 50 um raster (corrected to %)

Number	Si	Al	Fe	Ca	K	Mg	Mn	Ti	Na	P	S	Cl	Total oxides
	0.47	0.53	0.78	0.71	0.83	0.6	0.78	0.79	0.74	0.437	0.67	0 69	
83	28.73	10.96	4.81	0.57	2.17	0.65	0.42	0.57	3.49	0.38	0.16	0.20	55.14
84	26.50	11.92	7.78	0.62	3.01	0.87	0.99	1.00	0.81	0.60	0.17	0.00	55.15
85	30.13	9.19	7.18	0.60	2.46	0.65	0.56	0.57	1.07	0.51	0.18	0.00	55.37
86	28.22	11.37	6.19	0.77	2.84	0.43	0.56	1.14	1.07	0.54	0.21	0.00	55.47
87	28.58	11.06	6.17	0.47	2.64	0.76	0.42	0.71	1.86	0.34	0.11	0.15	55.59
88	25.77	12.67	7.99	0.63	3.13	0.86	0.56	0.85	1.20	0.53	0.12	0.00	55.63
89	26.61	12.10	6.45	0.60	3.28	0.65	0.70	2.13	0.93	0.51	0.13	0.00	55.63
90	29.34	10.74	6.44	0.66	2.83	0 65	0.42	0.57	0.66	0.60	0.18	0.00	55.75
91	22.68	12.17	10.00	0.76	5.32	0.53	3.06	0.98	0.66	0.55	0.13	0.00	56.16
92	27.74	11.18	7.60	0.69	2.94	0.43	1.11	0.70	0.92	0.53	0.17	0.00	56.42
93	29.70	9.42	8.10	0.57	2.63	0.42	0.69	0.56	0.91	0.40	0.13	0.00	56.82
94	27.68	11.73	6.79	0.62	3.18	0.63	0.41	0.96	1.16	0.46	0.13	0.00	57.40
95	33.33	7.76	5.16	0.64	2.11	0.52	0.41	0.55	0.90	0.41	0.16	0.00	57.40
96	30.05	10.10	2.97	0.49	7.91	0.31	0.14	0.41	0.51	0.26	0.14	0.00	57.71
97	28.66	11.35	4.99	0.49	3.01	0.62	0.81	1.64	1.28	0.43	0.13	0.00	57.89
98	28.54	11.03	6.31	0.62	2.86	0.72	0.40	1.63	0.76	0.49	0.13	0.00	58.13
99	28.15	11.28	6.69	0.69	2.71	0.41	0.67	1.08	1.27	0.49	0.13	0.00	58.27
100	39.27	4.53	3.40	0.18	1.21	0.30	0.39	0.26	0.00	0.18	0.13	0.00	59.72
101	33.74	7.68	5.46	0.54	2.07	0.30	0.39	0.39	0.49	0.36	0.18	0.00	60.04
102	36.14	6.32	4.27	0.41	1.75	0.00	0.39	0.52	0.61	0.35	0.10	0.00	60.35
103	25.99	10.62	4.63	0.33	3.59	0.29	0.25	8.99	0.59	0.23	0.08	0.25	62.38
104	33.19	8.16	4.95	0.32	2.24	0.48	0.50	1.13	0.70	0.32	0.10	0.00	63.02
105	33.92	7.93	4.42	0.69	2.01	0.57	0.37	0.62	0.58	0.35	0.07	0.00	63.47
106	27.86	12.62	3.35	0.46	4.08	0.46	0.12	3.15	1.02	0.27	0.11	0.00	65.12
107	8.90	6.64	27.75	0.76	1.42	0.46	20.60	0.36	0.68	0.63	0.09	0.00	65.49
108	30.35	10.40	2.47	0.96	1.25	0.36	0.24	0.36	5.58	0.20	0.15	0.07	66.27
109	37.42	5.59	3.65	0.30	1.53	0.36	0.24	0.48	0.45	0.30	0.07	0.00	66.32
110	39.31	4.67	2.17	0.26	2.07	0.26	0.00	0.23	0.43	0.21	0.10	0.00	68.15
111	34.24	7.84	2.80	0.14	2.74	0.34	0.34	2.27	0.64	0.16	0.08	0.00	69.59
112	31.28	8.45	8.04	0.19	2.89	0.24	0.42	0.53	0.69	0.32	0.07	0.06	74.67
113	38.25	5.36	2.97	0.00	1.85	0.24	0.20	0.31	0.58	0.17	0.10	0.00	76.19
114	39.32	6.01	0.60	0.00	1.71	0.00	0.00	0.00	1.53	0.03	0.00	0.00	77.57
115	44.57	1.45	1.26	0.00	0.31	0.00	0.19	0.00	0.00	0.07	0.07	0.00	80.46
116	27.43	11.23	8.55	0.17	3.78	0.37	1.06	0.78	0.91	0.24	0.00	0.00	81.21
117	27.01	6.81	16.91	0.24	2.19	0.28	0.63	0.63	1.10	0.62	0.00	0.00	87.19

APPENDIX ONE: Site B - 0.001m Data, 50 um raster (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0.775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total Oxides
1	23.39	7.68	14.74	0.31	2 41	0.48	0 00	6.49	1.93	0 27	0.42	0 16	11 96
2	30.99	8.35	5.25	1.49	2.25	0 51	0.00	1.44	1 07	0 30	0.75	0.25	14 22
3	25.52	8.79	16.06	1.15	2 20	0.54	0.08	0.18	0 90	0.42	0 27	0.03	15 81
4	25 83	8 66	13 64	0 09	2.44	0 65	0.32	2 67	1 10	0 34	0.27	0 11	15 81
5	25 66	9 00	11 67	0.77	2 65	0.52	0.13	3 39	1 47	0.35	0.28	0.16	16 24
6	22.71	6.90	23 14	0.57	2.56	0 56	0 05	0.63	1.14	0.25	0.29	0 25	16 35
7	35.25	4.77	6 91	0 32	2.54	0.16	0 00	0 45	0 74	0 26	0.33	0.14	16 51
8	31.43	8.11	5 46	0 52	2.55	0.50	0.27	1.23	1 46	0 31	0.53	0 23	16 95
9	29.91	9.28	6.38	0 89	2 81	1.05	0 00	0.70	1 45	0.33	0.15	0 00	17.90
10	31 86	8 57	5.88	0 21	2.56	0.51	0.00	1.03	1 20	0.26	0 18	0 00	18.10
11	33.20	7.01	5.71	0.53	2.07	0.55	0 39	1.03	0 87	0 34	0 20	0.07	19 72
12	28.48	10.13	7.67	0.22	3.16	0.91	0.10	0 88	1 83	0 24	0.07	0 02	20 25
13	33.63	7.00	4.70	1.13	1.64	0.73	0 00	0.45	1.29	0.35	0 31	0.25	20.40
14	13.02	9.78	32 86	0 31	3.05	0.69	0.07	0.59	2 48	0 29	0 41	0.44	24 48
15	24.59	11.05	12 46	0.18	2.74	0.37	0 67	1.60	1 69	0.32	0 24	0 00	26.58
16	28.26	11.69	7.01	0.25	3.04	0.64	0.14	0.31	1.14	0.38	0.13	0 07	27 88
17	31.61	8.10	6.16	0.27	2.58	0.68	0 00	0 64	1.28	0.28	0 05	0.17	27 96
18	30.45	9.85	6.04	0.21	2.59	0 52	0.04	0 90	1.00	0.36	0 23	0 29	28 85
19	38 02	5.11	3 37	0.00	1.52	0.26	0 02	0.44	0.77	0.19	0 05	0.14	28 99
20	27 02	11.13	8 95	0.32	2.82	0.70	0.14	1.10	1.40	0.36	0.19	0.01	29 45
21	27.52	10.92	8 78	0.49	3.12	0 61	0.11	0.85	0 95	0 34	0 18	0.11	29 60
22	28.55	11.09	6 45	0.14	2.65	0.78	0 25	1.05	1.53	0 29	0.23	0.12	29 65
23	29.20	9.57	8 06	0.48	3.00	0.59	0.14	0.90	0 84	0 36	0 24	0.07	30 24
24	28 82	9 42	7.02	0.32	2.25	0.66	0 07	3 41	1.19	0.32	0.25	0.05	31.27
25	31.26	8 40	5 92	1.02	2 41	0.53	0.29	0 82	0.91	0 28	0 49	0 22	31.42
26	28 57	10.98	6 84	0.27	2.89	0.93	0.19	0.52	1.26	0.31	0 23	0.13	31.76
27	27.24	11.66	8 07	0.26	0.39	0.60	0.10	0.70	1.68	0.32	0.20	0.02	32.39
28	30.20	9.28	6 62	0.41	2.52	0.59	0.16	1.19	1.19	0.35	0 23	0.15	32.54
29	29.78	9.88	6 48	0.45	2.61	0.56	0.13	1.41	0.86	0.35	0.33	0 06	32.79
30	28.71	9 84	5.89	0.03	6.25	0.40	0.12	0.34	2.13	0.19	0 09	0 06	32 80
31	27.07	11.60	7.52	0.10	2.87	0.59	0 00	2.44	1.28	0.30	0 20	0 03	34 43
32	24.21	10.39	13 40	0.34	2 29	0.97	1.30	0.55	2 25	0.24	0.23	0.10	34 65
33	28.23	10.90	7.47	0 49	3.11	0.52	0.37	1 01	0 82	0.33	0 19	0.10	35 03
34	30.21	9.85	6.55	0.36	2 60	0.66	0 20	0 90	0 73	0.36	0.14	0.08	35 21
35	31.59	9 15	5.49	0.11	2.50	0 64	0.24	0 87	0 98	0.28	0 24	0.03	35 28
36	33 65	7.45	4 62	0.35	3.76	0.20	0.10	0 45	0 71	0.19	0.17	0.16	35.33
37	17.64	10.11	10 79	0 58	2.08	0.77	15 43	1.20	1.42	0.22	0 31	0 23	35 59
38	21.56	10.30	19.34	0.38	2 35	0.87	0.41	1.10	1.14	0.31	0 28	0 07	36.21
39	32.06	8.54	5 54	0.28	2 67	0.63	0.00	0 89	0.64	0.38	0 25	0.13	36.24
40	22.09	8 69	9 60	1.75	0.35	3.63	0.67	5.50	4.55	0.20	0 12	0.26	37.06
41	29.19	10.85	6.19	0.98	2.88	0.60	0.00	0.59	0 89	0.35	0.16	1.27	37.24

APPENDIX ONE: Site B - 0.001m Data, 50 um raster (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total Oxides
42	29.16	9 83	8 35	0 08	2.73	0 46	0 14	0 93	1 28	0 30	0 15	0 06	37 62
43	42.17	2 01	1.49	0 61	0.50	0.06	0.06	0.38	0 51	0 05	0.52	0 21	37 63
44	29.72	10.11	6 92	0.10	2.80	0 61	0 00	1.05	1.13	0.30	0 13	0 06	37.73
45	24 41	9 60	16.67	0 38	2.54	0.54	0 24	0 57	1 31	0.37	0 20	0.14	37.82
46	29 85	9.59	7.77	0 08	2.34	0 76	0.11	0 57	1 52	0.25	0 11	0 07	37.97
47	28 01	10.01	7 34	1 84	2.71	0 59	0 31	0.78	0 92	0.31	0 91	0 07	38 23
48	27.16	10.30	10 65	0 26	3 39	0.49	0.34	0 63	0 91	0 29	0 12	0.07	38 42
49	29.67	8.53	10 45	0.12	2.30	0 51	0.25	0.56	0 88	0.30	0.13	0 00	38 43
50	33 62	6 60	6.29	0.43	1.91	0 33	0 35	0.58	1.02	0 27	0 35	0 20	38 56
51	27.69	11.12	7.81	0 31	2.71	0 64	0.73	1.02	1 09	0.32	0 23	0.09	38.78
52	27.98	11.15	6 63	0 59	3 12	0 50	0.42	0 74	1.16	0 58	0.35	0 11	39 28
53	34.10	6.71	5.99	0.47	1 99	0 26	0.00	0 47	1 08	0.27	0.22	0 08	39.42
54	31.98	8.95	5 87	0 07	2.49	0.51	0.11	0.80	0.68	0.28	0 21	0 03	39.49
55	27.58	9.56	10 22	0.34	2.46	0.95	0.35	0.74	1.57	0 36	0.19	0.08	39 64
56	28.73	10 89	6.86	0.57	2.60	0.66	0.10	0 84	1 06	0.34	0.36	0 06	39 93
57	33 68	7.83	4 62	0.44	2.17	0.41	0.11	0.56	1.09	0.23	0.17	0.08	40 02
58	31.67	8 06	7 66	0 26	2.17	0.48	0 00	0 65	1 01	0 28	0.20	0.14	40 47
59	28.35	10 64	7.64	0.96	2.41	0.48	0 05	0.97	1.41	0.30	0.19	0.09	41 74
60	37.76	4.59	4 47	0.16	1.21	0.18	0 25	0.26	1.12	0 15	0 13	0 02	42 06
61	31.53	8.77	5.35	0.74	2.29	0 64	0.17	0 90	1.31	0.26	0.19	0.11	42.09
62	31.01	9.73	5.51	0 29	2.54	0 51	0.18	0.70	1.11	0.29	0 31	0.05	42 12
63	30 54	9.22	6 50	0 34	2 71	0.81	0.05	0 61	1 32	0.31	0 17	0.10	42 64
64	31.47	9.34	5.43	0 43	2.73	0.58	0.17	0.65	0 66	0 25	0.28	0.12	42.99
65	33.13	7.91	5 87	0.37	2.18	0.24	0 00	0.50	1 05	0.26	0.16	0 09	43.14
66	30.60	8.91	6 89	0.61	2.59	0.59	0.16	0.82	1.06	0 29	0 20	0.12	43.28
67	26.10	10 61	11.79	0.25	2.67	0.59	0.48	1.00	1.01	0.30	0.19	0.08	43.30
68	31.82	8.36	7.02	0.15	2.47	0.40	0.11	0.59	0 84	0.30	0.21	0 11	44 80
69	32.37	9.07	4.25	0 28	2.57	0 80	0.05	0 68	1.14	0 24	0 07	0 08	44 93
70	28 00	8.98	11.21	0 31	2 49	0.50	0.00	1.18	1.20	0.24	0.33	0.18	44.93
71	30.34	9 64	6.29	0.31	2 20	0.73	0.08	0.71	1.77	0 30	0.20	0.02	45 04
72	26.69	10.71	9.95	0.10	2.32	0.61	0.62	1.32	1 68	0.31	0.15	0 13	45 15
73	35.98	6 00	4.31	0.66	1.70	0.26	0 00	0.44	1.02	0.22	0.11	0.04	45.42
74	22 62	9 05	20.56	0.36	1 89	0.60	0.44	0.76	1.28	0.25	0 20	0.07	45.53
75	22.46	7.76	21.53	0.90	0.22	1.08	0.12	0.83	1.14	0.26	0.23	0 25	45 63
76	29.91	9 82	6.10	0.90	2.39	0.58	0.18	0.61	1.51	0 28	0.41	0 09	45 80
77	29.75	10.00	6 62	0.16	2.63	0.52	0.42	1.31	0.95	0.32	0.19	0.08	46.03
78	30.51	9.89	4 91	0.14	2 86	0.60	0.28	0.58	2.23	0.24	0.13	0.10	46.37
79	29.15	10.79	6.25	0.12	2.76	0.78	0.27	0.76	1.54	0.27	0.18	0 05	46.48
80	21.35	9.02	22.80	0 32	1.95	0.66	0.69	0.80	0.96	0.25	0.15	0 02	46.68
81	28.97	9 82	7.92	0.55	2.22	0.48	0.17	0.71	2.15	0.26	0.24	0 00	46.80
82	23.71	9 93	17.08	0 31	2.33	0.71	0.00	1.05	1.19	0.35	0.16	0 11	46.87

APPENDIX ONE: Site B - 0.001m Data, 50 um raster (corrected to %)

Number	Si 0.467	Al 0.529	Fe 0.778	Ca 0.714	K 0.83	Mg 0.6	Mn 0.775	Ti 0.788	Na 0.742	P 0.437	S 0.667	Cl 0.686	Total Oxides
83	29.48	10.49	7.47	0.07	2.70	0.62	0.29	0.84	0.63	0.26	0.07	0.05	47.05
84	28.94	10.86	6.50	0.22	3.23	0.50	0.26	0.76	1.27	0.34	0.15	0.06	47.26
85	12.54	6.78	42.65	0.11	1.42	0.43	0.12	0.47	0.91	0.22	0.21	0.09	47.56
86	29.54	10.27	7.16	0.13	2.52	0.62	0.32	0.96	1.03	0.27	0.11	0.06	47.58
87	33.61	7.59	5.36	0.11	2.11	0.45	0.05	0.49	1.31	0.22	0.16	0.10	48.09
88	37.60	5.02	3.47	0.37	1.50	0.34	0.10	0.38	0.94	0.17	0.14	0.12	48.26
89	44.07	1.37	0.52	0.77	0.27	0.14	0.04	0.06	0.23	0.04	0.06	0.09	49.30
90	20.39	9.46	24.12	0.18	2.04	0.41	0.81	0.53	0.95	0.31	0.10	0.15	49.35
91	26.90	11.14	3.97	2.52	3.92	0.85	0.00	2.01	1.74	0.37	0.32	0.26	49.43
92	40.04	3.41	3.16	0.39	0.93	0.17	0.04	0.25	0.47	0.15	0.18	0.13	50.07
93	35.24	6.13	6.11	0.04	1.66	0.40	0.11	0.37	0.69	0.22	0.07	0.02	50.15
94	32.97	8.24	5.40	0.18	2.54	0.49	0.02	0.60	0.78	0.26	0.17	0.04	50.50
95	31.23	8.70	7.10	0.44	2.30	0.52	0.22	0.79	0.68	0.28	0.20	0.11	50.67
96	33.18	6.89	4.01	2.11	2.53	0.51	0.38	0.54	0.77	0.21	0.68	0.13	51.34
97	31.48	9.51	4.99	0.34	2.22	0.55	0.03	0.61	1.80	0.26	0.10	0.09	52.31
98	33.17	8.37	4.67	0.33	2.22	0.66	0.01	0.51	1.03	0.26	0.14	0.03	52.87
99	29.48	7.92	10.49	1.39	1.77	0.43	0.03	0.61	1.59	0.21	0.08	0.05	53.16
100	26.92	10.15	10.97	0.16	2.16	0.54	0.30	0.92	2.26	0.21	0.10	0.08	53.70
101	41.06	3.11	2.88	0.10	0.69	0.14	0.00	0.28	0.27	0.10	0.19	0.05	54.60
102	35.24	6.24	5.92	0.17	1.29	1.02	0.16	0.19	0.52	0.12	0.09	0.04	55.64
103	21.52	6.69	27.29	0.18	1.18	0.29	0.87	0.37	1.16	0.17	0.20	0.15	56.73
104	38.28	4.40	3.94	0.36	1.12	0.33	0.11	0.56	0.59	0.16	0.16	0.00	57.13
105	44.03	0.89	0.59	0.85	0.27	0.12	0.00	0.16	0.25	0.07	0.40	0.18	66.11
106	42.39	2.49	1.22	0.07	1.68	0.09	0.00	0.02	0.20	0.07	0.14	0.01	68.36
107	38.51	5.60	1.58	0.05	2.03	0.35	0.00	0.17	0.92	0.10	0.04	0.06	73.54
108	32.24	9.31	2.13	0.13	0.49	0.23	0.01	0.08	6.66	0.09	0.09	0.00	73.83
109	37.80	5.05	2.23	0.13	1.56	0.42	0.09	0.25	2.22	0.11	0.09	0.06	74.23
110	26.85	11.51	9.59	0.01	2.59	0.97	0.27	1.05	0.77	0.17	0.03	0.04	76.93
111	26.03	11.52	10.79	0.53	2.83	0.74	0.29	0.81	0.72	0.21	0.24	0.01	79.43
112	24.32	6.76	9.16	0.58	5.84	1.47	0.11	9.15	0.52	0.12	0.19	0.04	81.25
113	32.69	7.09	4.30	0.11	6.87	1.13	0.02	0.00	0.28	0.08	0.08	0.03	83.79
114	45.35	0.40	1.17	0.00	0.00	0.04	0.08	0.00	0.17	0.03	0.04	0.08	86.63
115	44.78	0.79	1.33	0.00	0.02	0.23	0.14	0.01	0.14	0.02	0.02	0.03	91.56
116	30.92	9.80	0.40	0.05	6.67	0.18	0.05	0.04	4.47	0.03	0.04	0.05	95.40

APPENDIX ONE: Site B - 0.0001m Data, 50um raster (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total Oxides
1	32 63	8.33	3 83	0 00	2 37	2.36	0.00	0 00	1.46	0 26	0 00	0 41	10.16
2	21 51	11.68	12 69	0.75	2 87	1.15	0 00	0.76	2 14	0 50	0.51	2 37	10 42
3	22 29	10.45	8 96	0.00	2 73	0.99	0 64	9 73	1 83	0 40	0 27	0 00	12.15
4	29 10	8.92	8 56	0 42	2.37	0.00	0 00	2 31	0 00	0.48	0 49	0 65	13 64
5	21.13	16.86	6 45	1.00	2 80	0.76	0.00	0 00	2.36	0 28	1.91	0 87	15 69
6	25.53	11 63	7 86	0.34	2 61	1.07	0.00	1.40	1.76	0.57	0 63	0 69	16 83
7	30 77	2.68	2.19	17.69	0 79	0 00	0.00	0 00	0 00	0.12	0 00	0.00	17 76
8	28.45	11.49	6 18	0 00	2 95	0.64	0 00	1.25	1.57	0.35	0 21	0 00	18 88
9	26 09	12.47	8.77	0 48	2 81	0.62	0 00	0.40	1.90	0.38	0 00	0 00	19 51
10	27.83	11.59	6 74	0.55	3 47	0.92	0 00	0.40	1 13	0.38	0 54	0 00	19 63
11	28.43	10.91	7.64	0.00	2 65	0 88	0.00	0.77	1 09	0 32	0.26	0.00	20.37
12	27 88	10.45	8.05	1.24	2 34	0.85	0.73	0.74	1.05	0.35	0.44	0.23	21 27
13	23.78	12.87	8.41	0.48	3.74	0.81	0.70	0 71	2 01	0.69	0.27	0 87	22 19
14	19.12	8.23	9 55	13.15	2.31	1.72	0 63	1.29	1.21	0.41	0.74	0.45	24 43
15	27.18	11.33	8 81	0.00	2 68	0.49	0.63	2.23	0 90	0 00	0.24	0.00	24.74
16	27.99	11.13	8 03	0 23	2.93	0 95	0.00	0.94	0 88	0.35	0.21	0 00	25.19
17	32.06	5.25	4.01	4.02	1.94	0.95	0 00	1.56	0 59	0 28	1.27	0.74	25.20
18	42 90	2.07	1.52	0 00	0.78	0.00	0.00	0.00	0.00	0.12	0.37	0 27	25 58
19	35.14	6.26	5 94	0.00	1.78	0 69	0 00	0.00	1.13	0 28	0.18	0.00	26.18
20	34.92	6.71	4.00	0 32	2 56	0.41	0 00	0.54	0.76	0.28	0.43	0 14	29.15
21	20.37	7.33	8.16	8.21	4.13	1.01	0 00	0.80	2.76	1.52	3 61	0.16	29 57
22	31.90	7.86	5 91	0.49	1.97	0.59	0.00	0.52	0.73	0.39	1.14	0 52	30 30
23	32.07	9 00	5.09	0.00	2.55	0.59	0.00	0.77	0.73	0.31	0.33	0 40	30 58
24	25.92	11.95	7.78	1.13	3.05	0.77	0.00	0.76	1.44	0.48	0.39	0.58	30 99
25	30.48	9.19	6.76	0 00	2.39	0.72	0.00	1.42	1.11	0.31	0.28	0 00	33 40
26	14.01	14.14	12.71	0.00	1.70	0.53	17.03	0 47	0.66	0.27	0.18	0 00	33 67
27	38.14	4 66	3 66	0 78	1.19	0 00	0 00	0 69	0.00	0.19	0.35	0.12	34 04
28	26.42	11 94	8 44	0 00	2 80	1 06	0 68	0.92	0 87	0.42	0.37	0 00	34.12
29	35.76	5.01	4.77	0 95	1 50	0.50	0 00	0 44	0.83	0 22	0 48	0 71	35 91
30	24.11	13.37	10.65	0 00	3.39	0.95	0.00	0 83	0.98	0.36	0.21	0.13	37.97
31	29.40	10.14	6.05	0.31	2.32	0.78	0.20	0 82	1.15	0.36	0.97	0 30	38 60
32	28.37	10.53	8.74	0 00	2.86	0.61	0.40	0 80	0.76	0.37	0.26	0.16	39.18
33	30.69	9.26	5.33	0.34	2.63	0.61	0.00	1.00	1.32	0.30	0.39	0.54	39.41
34	24.16	13.21	8.44	0.14	3.33	0.61	2.54	0.99	1.31	0.31	0.15	0 00	39 63
35	27.80	10.14	5 89	0.00	2.55	0.61	0.39	5.37	0.94	0.30	0.13	0.10	39.64
36	30.27	9.23	6.01	0.73	2.57	0.60	1.16	0.79	0.74	0.28	0.32	0.12	40.11
37	30.80	8.69	5.23	0.00	2.11	0.60	0.00	1.37	1.29	0.44	1.31	0.55	40.18

APPENDIX ONE: Site B - 0.0001m Data, 50um raster (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0.778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total Oxides
38	28.39	9.68	7.50	0 64	2.17	0 59	1.92	0.78	0 55	0 40	0.81	0.34	40.46
39	28.32	10.22	1.32	1.73	11.43	0 43	0 00	0.00	0.54	0 08	0.18	0 12	41.39
40	29.29	10.51	5.77	0.00	3.10	0.57	1.30	1 13	0 89	0 28	0.14	0 00	41.77
41	30.59	10.06	5.11	0.18	3.55	0.56	0.36	0.56	1 05	0 35	0 14	0 00	42 59
42	30.05	8 94	8 28	0 28	2.44	0.69	0 00	0 91	0 86	0 31	0.26	0.17	43.21
43	26.45	12 60	8.09	0 00	2.78	0.97	0 00	1.09	1.03	0 40	0 23	0.14	43 26
44	28.51	10.85	7.35	0.00	2.52	0.97	0 00	1 09	0 68	0 26	0.32	0.52	43 40
45	29.93	9 32	6.41	0.28	2.11	0.55	0 53	1 26	1 36	0 28	0.37	0 53	43 69
46	27.44	11.63	7 68	0.00	2 87	0.67	0 87	0 53	1.00	0 35	0 24	0 17	44 59
47	27.01	11.37	7.07	1.58	2.70	0 80	0 00	0.87	1 64	0 34	0.46	0 00	45.12
48	24.81	10.89	11.19	0.19	2.68	0 66	0.51	3.31	0.99	0 34	0 24	0.12	45 18
49	25.07	11.36	12.27	0.14	2.75	0.79	0 34	0.69	0 65	0 48	0.23	0 15	45 64
50	26.22	13.06	7.22	0.17	3 68	0.89	0.00	0 83	1.10	0 38	0 23	0.12	47.38
51	30.12	9 97	7.01	0.25	2.49	0.63	0.00	0.99	0.78	0 29	0.17	0.00	47 75
52	28.87	10.90	7.22	0.00	2.74	0.62	0.16	0.81	1 07	0.33	0.27	0 00	48 52
53	29.49	9 68	6 56	0 98	2.32	0.62	0.48	0.81	1.07	0.34	0.66	0.11	48.62
54	29.10	11.67	6 04	0.00	2.54	0.61	0.00	0.97	1.06	0 34	0.20	0.00	48 95
55	28.64	10.53	6.64	0.22	2.29	0.61	0.47	1.76	1.51	0 29	0.20	0.10	49 24
56	26.40	11.00	10.05	0.17	2.58	0.73	0.16	1.11	1.05	0.36	0.63	0.12	49.53
57	32.01	8 83	5.79	0.22	2.20	0 60	0.00	0 63	0.75	0.30	0.16	0.40	49 75
58	32.41	7.97	7.10	0 00	2.19	0.36	0.00	0 63	0.59	0 36	0.36	0.00	50 43
59	26.24	13.25	6.14	0.14	3.44	0.59	0.31	0 78	1.90	0 33	0.34	0.20	50.72
60	34.40	7.44	3.34	0.32	1.46	0.35	0.00	1.23	2.03	0 23	0.20	0.12	51.18
61	28.06	11.93	6.05	0 00	2.79	0.70	0 00	1.38	1.30	0.32	0.17	0.21	51.42
62	30 90	9 75	6.94	0.00	2.27	0.58	0.30	0 61	0.58	0 29	0.17	0.08	51.54
63	37.31	5 09	3.74	0 85	1.33	0.35	0.00	0 46	0.57	0 20	0 21	0.12	51.95
64	32.21	7.10	5.66	1.78	2.12	0.46	0.00	1 51	0.57	0.24	0.40	0.50	52.19
65	39.44	4.13	2 67	0.15	1.00	0.23	0.00	0 30	0.57	0.17	0.37	0.31	52 46
66	32.54	8 91	5.30	0.00	2.39	0.34	0.00	0 90	0.98	0 24	0.18	0.09	52 82
67	27.63	11.69	5.83	1 20	2.80	0.67	1.02	0.74	0.97	0 25	0.46	0.22	53 41
68	28.79	11.17	6.98	0.00	2.79	0.67	0.00	0 88	1.11	0 33	0.19	0 09	53 52
69	29.38	11.19	3 61	0.17	1.29	0.56	0.00	0 44	5.51	0 19	0.11	0.09	53 89
70	28 63	10.38	7.78	0.12	2.63	0.89	0.43	1.17	0 82	0.33	0.15	0.11	54.00
71	30.98	9.78	6.33	0.00	2.44	0.67	0.14	0.58	0 69	0.28	0.23	0.14	54.11
72	28.70	11.10	6.81	0.00	2.72	0.77	0.28	1.29	0.95	0 28	0.13	0.10	54 83
73	28 01	10 80	9.22	0.46	2.56	0.66	0.00	0 57	1 08	0 25	0.19	0.00	54 86

APPENDIX ONE: Site B - 0.0001m Data, 50um raster (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total Oxides
74	35.76	6.51	4 44	0.11	1 60	0.54	0.00	0.42	1 06	0.19	0.15	0 00	56 03
75	31.01	9 32	6 03	0.33	2 24	0.32	0.14	0.97	1.18	0.40	0 28	0 08	56.78
76	38.90	3.88	2.72	1.37	0.99	0.21	0.00	0.14	0.52	0.13	0.75	0 10	57.27
77	28 05	11 36	7.33	0.16	2.75	0.73	0.27	0.83	1.04	0.33	0.19	0.12	57.28
78	38.59	4 88	3.11	0 29	1.13	0.31	0 00	0.41	0 39	0 16	0.19	0.10	57.48
79	29.97	9.79	7.40	0.12	2.37	0.62	0 27	0.82	1.16	0 31	0.20	0 00	57.81
80	31.17	9 67	6.04	0.00	2.10	0.62	0.00	0.54	1 41	0 38	0.18	0 00	57.99
81	29.73	10.38	6.56	0.00	2.34	0.72	0 00	0 54	1.92	0 26	0.13	0.12	58.11
82	30.52	10.46	2.35	0.00	0.50	0.60	0.00	0 26	7.21	0 07	0 00	0.00	59 68
83	29 06	12.14	5.14	0.00	2.88	0.99	0.00	0.78	0.98	0.29	0.18	0 08	60.59
84	41.22	3 39	1.79	0.00	0 67	0.00	0.25	0.26	0.61	0.11	0.09	0.14	60.84
85	23.24	10.92	9.74	0.00	2.56	0.59	1.76	6.92	0.72	0 27	0.17	0.00	61.50
86	44.84	1.20	0.63	0.00	0.20	0.29	0 00	0.00	0.00	0 05	0.16	0.00	61.86
87	31.16	10.23	1.73	0.19	0.64	0.29	0.00	0.25	7.17	0 08	0.00	0 00	63.10
88	28.28	11.41	4.91	0.28	1.91	0.46	0 00	0.97	4.57	0 22	0.15	0.00	64.90
89	29.42	11 54	2.15	0.38	2.68	0.37	0.00	0.36	5.36	0 13	0.12	0 00	65.09
90	8.23	4 28	48.78	0.52	0.85	0.35	0.45	5.35	0.75	0.13	0.26	0.11	69.22
91	44.49	1.40	0.98	0 00	0 37	0.00	0.00	0 00	0.00	0.05	0.08	0 00	71.80
92	45.20	0 95	0.54	0.00	0.22	0.00	0 00	0 00	0 00	0 04	0.08	0 08	72.33
93	42.25	1.75	1.29	1.48	0.43	0.17	0.00	0.22	0 00	0 08	0 64	0.14	72.51
94	44.67	1.28	0.52	0.00	0.36	0.00	0.00	0.00	0.00	0 03	0.35	0.10	74 13
95	31.90	8 82	1.14	0.19	9.30	0 00	0.00	0.53	0.79	0 08	0.08	0.08	74 95
96	44.16	1.94	0.39	0.00	0.88	0.00	0.00	0.00	0.00	0.03	0.05	0.00	79 21
97	45.55	0.49	0.27	0.41	0.00	0.00	0.00	0.00	0.00	0.02	0.36	0.00	86.94
98	46.35	0.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 01	0.06	0.00	94.40

APPENDIX ONE: Site B - 0.0001m Data, 5 um diffuse point (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0.775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total oxides
1	10.59	12.52	29.92	0 00	2 86	1.18	0 76	1.40	2 93	0.73	0 33	0 00	10.14
2	18 84	14.39	16.79	0.00	3.74	2.25	0 00	0 00	0.00	0.37	0.38	0.00	10 66
3	30.46	7.52	3.25	0.00	1.18	0.00	0 65	6.59	3.10	0.26	0 00	0.34	11 96
4	39.07	4.18	4.10	0 00	1.15	0.00	0.00	0 00	0 98	0.26	0.26	0 00	15.18
5	18.50	13 05	10 61	0.51	5.12	1.17	1 01	1.02	3 85	1.70	0.69	0 36	15.40
6	31.29	6.75	4.47	1.82	2 44	0.00	0.00	0.70	1.42	0.53	1.11	2.15	15 67
7	20.55	13.63	11.25	0.90	4.54	0.75	0.00	0.00	2 33	1.13	0 50	0 26	15 91
8	21.47	17.08	1.28	1.09	6.95	0 99	0 00	1.73	0 81	0.12	1.57	1.76	18 27
9	42.74	2.81	1 03	0 00	0 84	0.00	0.00	0.70	0 00	0.06	0.00	0.00	22 62
10	31.53	7.53	7.59	0.81	1.45	1.22	0 63	0.32	0 60	0.25	0.16	0 00	24.59
11	26 64	16.37	1.56	0.00	5.67	0.48	0.00	0 00	1.19	0.19	0 00	0 00	24 89
12	29.02	12.65	4.34	0.00	3.70	0.72	0.00	0.63	0.89	0.26	0.19	0 00	25.10
13	29 67	10.17	6.95	0.00	2.71	0 82	0 53	0.27	1.02	0.35	0.32	0 00	29.12
14	23.16	15.71	4.20	0.39	5.77	0.61	0.00	3 99	1.00	0.18	0.00	0.16	29.64
15	35.11	1.03	0.76	8.10	1 96	1.56	0.00	0 00	3.13	0.11	0.56	0.33	30 86
16	21.88	14.81	8 44	0 00	4.05	0.86	0.00	4.05	1.48	0.31	0.29	0 00	35 01
17	24.03	9.51	12.44	1.69	3.30	1.35	0.58	0 59	1.48	0.44	0.53	0 60	40.03
18	20.38	14.04	12.54	0.28	4.20	0.89	0.58	0 98	1.47	0.61	0.40	0.49	40.32
19	25.98	14 07	6.77	0.22	4.07	0.44	0.19	0.57	0.90	0.31	0.21	0 00	41.35
20	34.08	8.28	4 87	0.00	2.44	0.00	0.00	0 38	0.54	0.22	0.11	0.00	41.52
21	35.21	6.48	5.42	0 00	1.32	1.15	0.00	0.00	0.89	0 25	0.11	0.00	41.65
22	22.76	13.89	10.86	0.71	3.28	1.42	0.18	0 56	1.05	0.40	0.21	0 00	42.27
23	28 82	11.17	6.32	0 25	2.95	0.70	0.36	0 55	1.03	0.38	0.14	0.11	43.10
24	35 81	6 62	4.87	0 00	1.94	0.28	0 00	0.37	0 69	0.18	0 00	0 00	43 16
25	23.20	13.26	11.77	0.00	3.17	0.27	2.10	0.71	0.67	0.37	0.17	0.14	44 29
26	32.19	8.46	4.21	0.13	2.52	0.41	0.35	2.13	0.84	0.40	0.18	0 19	44.39
27	16.40	13.76	23.35	0.00	3.32	0.40	0.86	0.53	1.15	0.24	0.13	0 00	44 99
28	28.24	10.12	2.88	0.33	10.83	0.65	0.00	0.17	0.97	0.14	0.16	0 00	45 98
29	0 61	10.64	13.63	0.26	0.36	0.00	45.26	0.17	0.48	0.20	0.17	0.00	46.23
30	29.19	9.93	7.70	0.00	2.89	0.50	1.12	0.49	0.77	0.34	0.30	0.11	48.47
31	11.41	12 81	32.67	0.16	1.74	0.36	0.63	2.70	0.75	0.35	0.12	0 24	49 54
32	18.51	12.03	20.66	0.00	2.66	0.60	2.34	1.11	1.05	0.37	0.16	0 00	49.70
33	17.97	9.43	9.20	0.00	1.10	0.36	20.81	0.47	1.19	0.17	0.11	0.00	49.91
34	29.65	9.76	6.64	0.00	3.06	0.83	0.46	0.78	1.18	0.18	0.12	0.15	50 40
35	29.88	11.32	5.19	0.00	3.19	0.47	0.00	0.77	0.87	0.33	0.16	0 08	50.95
36	25.91	13.60	6.47	0.59	4.01	0.46	0.00	1.22	0.72	0.43	0.24	0.12	51.73
37	26.93	7.18	5.42	0 52	1.16	0.00	13.58	0.59	0.42	0.21	0.09	0.14	53.07

APPENDIX ONE: Site B - 0.0001m Data, 5 um diffuse point (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total oxides
38	21.46	10.74	10.05	11.99	1.29	0.33	0.14	0 00	0 27	0 08	0 42	0 28	54 18
39	15.40	10.76	15.11	0 00	0.79	0.33	18.03	0 72	0.54	0 24	0.18	0.00	54 59
40	20.93	16.06	10.26	0 00	4.35	0 87	0.42	0 85	0 80	0 54	0 28	0.19	55 33
41	22.24	11.03	9.23	0.12	3.58	0.86	0 42	8 36	0 80	0 40	0.23	0.17	55 64
42	42.91	1 22	1.25	0.74	0.52	0.11	0 00	0 00	0 40	0 14	0 55	0 57	56 16
43	31.36	9 02	7.46	0.11	2.05	0.53	0.28	0 42	0 66	0 30	0 09	0 00	56 29
44	20.73	16.72	9.12	0 30	4.57	0 85	1.10	0 70	1 05	0 45	0 17	0 00	56 31
45	26 92	12.76	8.00	0 00	3 24	0.74	0 14	0 70	0 66	0 35	0 09	0 00	56 39
46	24.12	12.82	10 46	0.37	3.38	0 64	0.41	1 25	0 92	0 49	0 21	0 24	56 54
47	31.69	8.76	5.07	0.00	4.24	0.42	0.27	0.83	0.52	0 30	0.15	0 08	56 74
48	24.54	13.99	8.15	0.00	4.28	0.93	0.27	0.81	1.02	0 38	0.17	0.00	58 23
49	23.38	13.97	10.67	0.16	3.42	0.72	0.27	0.95	0 89	0 48	0.21	0.00	58.32
50	22.07	14.22	12.25	0.22	3 55	0 82	0 00	1.08	1.14	0.52	0.22	0.00	58.41
51	23.41	14.34	10.22	0.18	3.40	0.82	0.66	0.67	1.01	0.33	0.13	0.00	58 64
52	26.29	11.79	9.92	0.00	2.64	0.82	1.05	0.94	0 50	0 34	0.15	0.00	58 80
53	36.99	6.36	3.29	0.00	1.84	0.20	0.00	0.40	0.38	0 24	0.11	0.09	59 09
54	21.38	13.35	14 01	0.14	2 93	0.81	0.26	1.06	1 75	0 55	0.19	0.12	59 42
55	24.71	13.46	6 38	0.13	3.20	0.70	0.26	1.45	3 73	0 30	0.10	0.00	59.72
56	21.06	14.35	12.69	0.21	4.01	0 60	0.39	0.66	1.24	0 65	0.30	0.24	60.08
57	22.56	15.00	9.75	0 00	3 70	0.69	0.64	0.65	1.71	0 33	0.14	0.00	60 64
58	34.29	7.58	5 32	0 00	2 05	0.39	0.00	0.51	0 48	0.21	0.10	0 08	61.43
59	32.25	8.75	5.55	0.15	2.14	0.58	0.25	1.15	0 60	0.28	0.19	0.18	61 69
60	27.86	11.14	8.07	0.00	2 56	0.48	0.00	0.38	2 84	0 23	0.10	0.00	62 69
61	22.51	15.55	8.73	0.12	3.15	0.85	0.12	2.37	0.82	0.37	0.16	0.11	63 27
62	31.48	8 69	7.71	0.13	2.29	0.56	0.00	0.73	0 57	0.30	0.11	0 00	64 54
63	30.65	10.21	6.25	0.15	2 50	0 56	0.12	0.37	0 57	0.34	0.15	0 08	64 76
64	32.75	8 64	4.56	0.12	1 93	0.46	0.24	1.58	0 80	0.32	0.13	0.00	64 88
65	27.35	13.31	5.58	0.00	4 43	0.55	0.24	0.60	0 68	0.29	0.16	0 00	65 56
66	31.33	8 45	8.05	0.00	1.87	1.00	0.35	0.72	0 45	0.29	0.14	0 00	65.73
67	40.72	3.85	2.36	0 00	1 02	0.18	0.00	0.36	0 00	0.14	0.09	0.00	65.94
68	27.46	12.59	6.72	0.12	3 65	0 64	0.12	0.72	0 79	0.34	0.11	0.00	65.99
69	22.50	15.66	9.05	0.15	4 51	0.72	0.00	1.07	1 01	0.31	0.13	0.00	66.21
70	28.73	10.69	8.56	0.13	2.10	0.72	0.35	0.48	0 78	0.35	0.18	0.00	66.33
71	22.17	13.35	12.39	0.25	3 24	1.71	0.70	0.71	0.78	0 49	0.20	0.00	66.57
72	26.02	13.99	7.20	0.00	4 22	0.63	0.23	0.35	0.78	0 24	0.11	0.00	66.95
73	26.31	14.90	4.36	0.00	4 90	0.62	0.23	0.81	0.77	0.19	0.15	0.00	67.81

APPENDIX ONE: Site B - 0.0001m Data, 5 um diffuse point (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total oxides
74	33.28	8.49	5.50	0.00	1.92	0 62	0.23	0 58	0.44	0.19	0.11	0.00	67.91
75	25.57	13 67	7.84	0.00	3.64	0.44	0.23	0 58	1 84	0.29	0.09	0 00	68 50
76	22.56	10.73	18.28	0 00	3.15	0.44	0.45	0 58	0.76	0.36	0.13	0 07	68.51
77	28 34	10.32	9.67	0 00	1 94	0.43	1.57	0.57	0.54	0.22	0.13	0.10	69.22
78	23.21	15.26	8 56	0.10	3.79	0.77	0 44	1.35	0 85	0 31	0.11	0 00	70.01
79	37.82	5.28	3.55	0.00	1.74	0.34	0.00	0.45	0 42	0 22	0.07	0 08	70.14
80	23.12	9.85	18 87	0 00	1.90	0.59	0 22	1.56	0.73	0.28	0.11	0.10	70 91
81	37.40	5.31	3 53	0.00	2.05	0.49	0.32	0.32	0 41	0.20	0.09	0.12	72.79
82	42.17	2.83	2 03	0 00	0.81	0.00	0 00	0.22	0 00	0.15	0.08	0 00	72.86
83	34.62	6.58	6.53	0 00	1 46	0 49	0.42	0 43	0 40	0.18	0 09	0.06	73 92
84	46.42	0.28	0 00	0.00	0.00	0.00	0 00	0 00	0.00	0.00	0 09	0.00	75 86
85	41 64	2.62	3.44	0 00	0.42	0.23	0.00	0 00	0.00	0.11	0.12	0 00	76.82
86	45.81	0.59	0.29	0 00	0.00	0.00	0.00	0 00	0.18	0.03	0.06	0.00	81.24
87	41.73	0.93	1.03	0.00	0.13	0.00	1.88	3 21	0.33	0.07	0.06	0 00	90.75
88	41.29	3.75	0.42	0 00	1.54	0.00	0.00	0.86	0.57	0.05	0 07	0 05	91.61
89	43.52	2.52	0.25	0 00	1.17	0.00	0.00	0.00	0.00	0.04	0.06	0 07	92.39
90	44.66	1.80	0.00	0.00	0 66	0.00	0.00	0 08	0 00	0.01	0 00	0.00	94 01
91	46 54	0.17	0 00	0.00	0.00	0.00	0 00	0.00	0.00	0 00	0.00	0 00	94.73
92	46.34	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 02	0.05	0 00	94 84
93	46.40	0.33	0 00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0 00	0 00	94.90
94	43.57	2.39	0.25	0.00	0.96	0.13	0.00	0 00	0.23	0.05	0 00	0 00	95 07
95	46.51	0.22	0 00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 00	96.10
96	46.50	0.16	0.00	0.00	0.00	0.00	0.00	0 00	0 00	0.01	0.08	0.00	96 52
97	46.50	0.16	0.00	0.00	0.00	0 00	0.00	0.00	0.00	0 02	0.04	0.00	97.51
98	46 52	0.16	0.00	0.00	0.00	0.00	0.00	0 00	0.00	0.00	0 00	0.05	97.67
99	46.56	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 00	97.80
100	46.50	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0 01	0.00	0 00	97.82
101	45 23	0.16	0.00	0 00	0.00	0.18	0.00	0 00	0.97	0.01	0.11	0.76	99.74

APPENDIX ONE: Site B - 0.00001m Data, 5 um diffuse point (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total oxides
1	31.44	11.35	6.07	0.00	2.59	0.00	0.00	0 00	0 00	0 09	0.00	0 00	10 25
2	23.35	13 82	9.87	0 00	3.65	0.90	0.58	0.00	1 66	0 20	0.50	0 00	13 40
3	37.20	3.13	4.10	1.08	0.87	0.79	0 00	0 00	0.98	0 52	0.75	0.95	15 19
4	45.15	0.65	0.96	0 00	0 41	0.00	0 00	0.00	0.00	0 08	0.00	0 00	16 24
5	33.65	8.68	6.03	0.00	2.20	0.00	0 00	0.36	0 00	0 22	0.00	0.00	21 93
6	25.53	14.23	8.23	0.00	3 73	1.06	0 00	0.00	0 98	0 17	0.00	0 00	22 68
7	23.79	16.01	7.45	0.00	4.51	0 92	0 00	0 60	0 85	0 23	0.00	0 00	26 11
8	38.54	4 78	2 93	0.00	2.41	0.23	0.00	0.00	0 00	0 15	0.23	0 28	26 54
9	42.47	3.49	1.43	0 00	0.79	0 00	0.00	0.00	0 00	0 02	0 00	0 00	27 27
10	37.55	5.13	3 78	0.00	1.27	0.62	0 00	0.55	0 51	0 20	0.28	0.19	28 85
11	33.18	9 31	4.83	0.00	2 49	0 62	0 00	0.54	0 00	0 21	0.14	0 00	28 99
12	44.80	1.01	1.24	0 00	0.00	0 00	0.00	0 00	0.47	0 10	0.00	0.00	31 38
13	27.36	11.14	8.76	1.24	1.89	0 52	0.45	0 45	1.28	0.34	0.25	0.14	34 65
14	30.93	7.69	7.39	0.30	2.74	0.34	0.65	0 66	1.45	0 29	0.41	0.25	35 78
15	29.72	13.01	2.91	0.00	2.02	0 64	0.00	0.42	2.58	0 09	0.16	0 00	37 40
16	35.37	6.43	6.03	0.00	1.46	0 47	0 00	0.61	0.58	0 15	0.14	0.00	38 69
17	45 45	0.92	0.58	0 00	0.21	0.00	0.00	0.00	0.00	0 03	0.00	0.00	40 07
18	26.89	11.37	5.77	0.21	3.90	0 44	0.00	5.06	0 55	0 15	0.15	0.14	40 47
19	17.64	9.02	29.38	0.38	2.31	0 58	0 00	0.38	0 90	0 32	0.26	0.12	41 04
20	23.63	12.75	14 11	0.00	2.12	2.15	0 00	0.38	0.00	0 11	0.22	0.00	41 90
21	20.52	15.58	13.16	0.00	4 01	0.66	1 02	0 69	0 49	0 30	0 22	0 00	45 51
22	19.32	13.79	17 27	0 00	4.47	0 52	1.17	0 85	0.64	0 08	0.17	0 00	46 41
23	19 64	15.09	14.90	0.24	3 63	0.87	0 48	0.82	0.77	0 40	0.21	0.11	48 04
24	13 74	16.00	18.37	0 00	2 41	0.62	7.38	0 49	1.08	0 33	0.19	0.10	48 28
25	40.85	3.60	2.89	0 00	1.04	0 00	0.00	0.00	0.46	0 06	0.08	0 00	48 47
26	22.12	13.48	7.96	0.17	3.00	0.84	0.00	7.43	0.74	0 37	0.17	0.00	49 83
27	30.42	9.77	7.88	0.00	2.47	0.48	0.31	0.31	0.74	0 15	0.11	0.00	50.36
28	26.71	11.85	9.33	0.00	3 59	0.71	0.46	0.46	0.88	0 17	0.16	0 00	50 87
29	29.51	11.14	7.17	0.15	2.03	0.90	0.00	0.59	0.70	0 21	0.13	0.00	53 18
30	20.81	15.71	12.43	0.00	3 90	0.79	0 44	0.74	0 98	0 26	0.16	0.00	53 19
31	24.57	12.52	8.07	0.39	4.53	0.87	0.00	3.16	0.68	0 26	0.29	0.19	54 93
32	26.65	12.11	9.47	0 00	2.56	0.98	0.28	1.00	0 81	0 17	0.17	0.00	55 02
33	23 63	15.26	7.85	0.25	4.11	0.96	0.00	1.39	0.53	0 35	0.21	0.13	56 52
34	43 51	2.03	1.36	0 00	0.41	0.00	0.00	0 00	0.39	0 04	0.00	0.00	57 21
35	29.22	4.09	21.13	0 00	0.87	0.21	0.00	0.00	0.38	0 11	0.15	0.08	58 18
36	39 08	4.24	3.98	0.00	0.72	0.31	0.00	0.40	0.51	0 19	0.09	0.00	58 67
37	30.63	10.29	6.39	0.00	2.09	0.70	0.26	0.40	1.12	0 20	0.16	0.00	59 62
38	27.37	10.28	12.30	0.00	2.32	0.59	0.00	0 65	0.61	0.22	0.14	0.00	60 74
39	31.12	9.83	5.76	0.12	2.32	0.69	0.26	0.65	0.37	0 40	0.32	0.16	60 78
40	20.95	16.41	11.02	0.00	4.09	0 86	0.25	1.00	0.83	0.30	0.16	0.00	62 86

APPENDIX ONE: Site B - 0.00001m Data, 5 um diffuse point (corrected to %)

Number	Si 0 467	Al 0 529	Fe 0 778	Ca 0 714	K 0 83	Mg 0 6	Mn 0 775	Ti 0 788	Na 0 742	P 0 437	S 0 667	Cl 0 686	Total oxides
41	19.06	15.59	15.32	0.11	3.53	0.57	0.85	0 99	0 94	0 28	0.18	0 00	63.47
42	23 06	12 61	14.39	0 15	2.73	0.56	0 00	0 86	1 05	0 40	0 15	0.10	63 78
43	19.32	16 41	13 66	0 00	3 64	1.22	0.49	0.74	1 16	0 16	0.18	0 00	63 81
44	25.45	12 97	9 84	0 22	2 85	0.75	0.24	0 74	0 70	0 40	0.11	0 00	64 05
45	42.86	2.46	1 69	0.00	0.54	0.00	0 00	0.00	0 00	0.13	0 16	0 17	64 39
46	34.94	7.00	5.51	0.00	1.79	0.37	0 00	0 49	0 69	0.16	0 12	0 00	64.95
47	30.61	9.77	7.18	0 00	2 30	0.65	0 00	0.97	0 69	0 22	0.17	0.00	64 99
48	32.23	10 25	3.35	0.00	2 81	0.46	0 00	1.09	1.03	0.11	0 09	0 00	65.06
49	19.32	16 68	13 80	0 00	3.65	0.64	0.59	0.72	0.79	0 32	0.23	0.12	65 98
50	30.92	9.28	6.47	0 43	2.13	0.73	0.35	1.67	0.45	0.14	0.10	0 00	66.16
51	13.07	35.72	1.28	0.25	0.47	0.27	0.00	0.00	0 56	0.13	0 09	0.11	66 80
52	21.84	15 84	10.31	0 21	3 83	1.16	0.00	0.82	0 77	0 27	0.12	0 09	67.14
53	25.33	12 26	11.56	0.16	2 47	1.16	0.23	0.23	0 88	0 28	0 22	0 00	67.30
54	27.90	10 40	10.59	0.00	2 45	0.71	0 34	0.47	0 66	0 25	0.12	0 00	67.62
55	23.03	13.36	13.13	0 00	2 92	0.26	0.46	1.27	0 87	0 35	0 21	0 00	68.13
56	21.81	16.37	10.22	0 21	3 88	0.88	0 00	0.58	0 87	0.24	0.14	0 00	68.51
57	41.36	3.00	3.28	0.00	0.43	0.35	0.00	0.00	0 00	0 08	0.10	0 00	68 87
58	24.07	14.74	7.53	0 00	3.12	0.78	0.00	2.84	1.18	0.16	0.15	0 00	69.27
59	33.85	8.54	4.71	0.00	2 03	0.35	0.00	0.79	0.43	0.20	0.12	0 00	69 39
60	19.14	14.68	14.77	0.00	3 58	0.78	0.56	2.72	1 07	0.30	0.18	0.09	69.54
61	32.35	9.79	4.58	0.00	2.74	0.77	0.00	0.34	0 64	0 20	0 09	0 00	69.72
62	31.12	10.46	5.46	0 00	2.26	0.86	0 00	0 45	0.64	0.24	0.18	0.10	69.77
63	22.93	16.28	8.02	0.10	5.47	0 69	0.00	0.45	0.53	0.16	0.11	0 00	69.85
64	22.69	17.68	6 28	0.10	5.05	0.59	0.00	0.56	0.95	0.12	0.13	0.00	70 61
65	22.71	15.83	9.62	0.20	3.38	1.10	0.00	1.00	0.73	0.19	0.10	0 00	71.16
66	19.33	15.29	10.92	0.30	3.26	0 67	0.22	6.30	0 83	0 20	0.16	0 07	71.27
67	32.60	9.57	3.38	0.00	2.21	1.85	0.22	0.33	0.73	0 10	0 00	0 00	71.34
68	23.44	14.57	11.10	0 10	3.48	0.59	0 00	0 66	0.73	0.31	0.18	0 00	71.52
69	26.50	10 42	13.48	0.10	2.55	0 42	0 00	0.44	0 62	0.26	0.13	0 09	71.56
70	23.01	14.69	8.64	0.10	3.57	0.50	1 08	2.52	0.72	0.23	0.14	0 09	72.04
71	26.19	12 29	9.30	0.20	3.76	0 82	0 00	0.43	0.82	0.23	0.15	0 08	72.75
72	25.03	15.49	4 28	0.10	3.76	0 58	0.00	0.32	3 88	0.11	0.07	0 00	72 76
73	30.19	12 65	2.87	0 00	4.08	0.49	0.21	0.22	0.71	0.11	0.15	0 00	73.16
74	43.03	2.24	1.17	0.00	0.52	0.16	0 21	0.43	0.00	0 08	0.14	0.10	73.25
75	44.84	1.07	1.26	0.00	0.12	0.00	0.00	0.00	0 00	0.06	0.07	0.00	74.37
76	33.68	7.63	5.40	0.19	1.88	0.24	0.00	1.68	0.50	0.16	0.17	0.00	74.88
77	19.87	14.07	12.93	0.19	2.76	0.88	0.31	5.03	0 89	0.40	0.18	0 00	75.22
78	24.89	14.13	8.58	0.00	3.31	0.64	0 21	0.84	1.38	0 21	0.14	0 00	75.23
79	44.03	2.09	0.51	0.00	0 68	0.00	0.00	0.00	0.00	0.06	0.10	0.00	75.94
80	25.84	12.97	9 59	0.00	3.48	0.31	0.20	0.93	0 68	0.26	0.09	0.00	76.28

APPENDIX ONE: Site B - 0.00001m Data, 5 um diffuse point (corrected to %)

Number	Si	Al	Fe	Ca	K	Mg	Mn	Ti	Na	P	S	Cl	Total oxides
	0.467	0.529	0.778	0.714	0.83	0.6	0.775	0.788	0.742	0.437	0.667	0.686	
81	27.00	13.13	6.16	0.00	3.56	0.62	1.81	0.41	0.58	0.16	0.08	0.00	76.98
82	26.76	12.93	8.55	0.00	2.79	0.78	0.00	0.61	0.67	0.24	0.09	0.00	77.30
83	38.87	3.86	4.78	0.00	0.83	0.23	0.20	0.61	0.29	0.13	0.11	0.00	78.09
84	24.31	11.64	14.43	0.00	2.55	0.61	0.20	0.40	1.14	0.34	0.15	0.00	78.20
85	28.86	11.48	7.15	0.00	3.29	0.46	0.00	0.60	0.66	0.21	0.21	0.11	78.31
86	19.69	18.47	1.39	0.09	6.56	0.31	0.00	8.53	0.95	0.06	0.08	0.07	78.49
87	40.25	2.90	4.85	0.00	0.32	0.76	0.00	0.30	0.00	0.06	0.06	0.00	78.55
88	20.66	15.54	12.76	0.09	3.17	1.60	0.49	0.60	0.75	0.31	0.12	0.00	78.66
89	15.54	13.66	26.19	0.09	2.52	0.53	0.49	0.80	0.56	0.28	0.12	0.00	79.01
90	21.17	16.30	9.73	0.00	3.67	0.61	2.74	0.60	0.84	0.19	0.13	0.00	79.19
91	43.07	2.46	0.98	0.00	0.63	0.23	0.00	0.00	0.28	0.04	0.08	0.08	79.58
92	21.47	16.94	9.02	0.09	4.76	0.52	0.00	0.49	1.76	0.22	0.10	0.08	80.25
93	21.81	18.27	7.15	0.09	4.85	0.75	0.19	0.69	0.74	0.14	0.00	0.00	80.51
94	27.79	12.64	7.48	0.09	3.07	0.74	0.00	0.49	0.73	0.16	0.14	0.00	81.17
95	19.76	16.50	12.61	0.00	3.51	2.25	0.47	0.38	0.63	0.13	0.12	0.07	82.70
96	33.20	9.10	4.59	0.34	2.00	0.72	0.00	0.19	0.54	0.14	0.14	0.07	83.12
97	23.04	18.33	4.74	0.00	4.96	0.65	0.00	0.47	1.33	0.17	0.12	0.00	83.71
98	31.49	10.21	5.38	0.09	2.27	0.57	0.18	0.47	0.71	0.16	0.10	0.07	83.93
99	21.90	16.28	9.03	0.00	5.11	0.92	0.28	0.65	0.79	0.23	0.09	0.00	84.46
100	42.03	2.59	1.63	0.00	0.48	0.00	0.00	1.75	0.00	0.06	0.07	0.00	85 67
101	35.03	7.90	3.63	0.00	2.03	0.49	0.27	0.46	0.61	0.14	0.06	0.00	85.72
102	35.15	8.71	3.70	0.00	0.96	0.35	0.00	0.55	0.43	0.14	0.05	0.00	86.23
103	22.71	17.41	5.35	0.08	6.19	1.24	0.18	0.54	0.43	0.06	0.06	0.07	87.20
104	44.08	2.11	0.27	0.00	0.66	0.21	0.00	0.00	0.00	0.01	0.07	0.07	87.72
105	40.80	3.76	2.55	0.00	0.75	0.27	0.00	0.27	0.25	0.10	0.08	0.00	88.60
106	34.34	10.39	2.95	0.00	0.83	0.27	0.26	0.70	0.00	0.09	0.05	0.00	89.63
107	40.60	3.79	2.31	0.00	0.73	0.20	0.00	0.69	0.33	0.09	0.10	0.06	90.76
108	42.01	2.71	1.19	0.00	0.90	0.20	0.00	1.20	0.00	0.09	0.11	0.06	91.82
109	22.71	20.72	0.68	0.00	7.95	0.39	0.00	0.26	0.65	0.03	0.00	0.00	91.93
110	22.15	17.12	2.19	0.00	7.34	1.22	0.00	4.52	0.43	0.04	0.07	0.00	102.90
111	44.98	1.59	0.15	0.00	0.47	0.00	0.00	0.00	0.00	0.02	0.00	0.00	106.62
112	46.51	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	107.64
113	45.20	1.46	0.14	0.00	0.23	0.00	0.00	0.00	0.00	0.01	0.00	0.00	108.80

TOTAL PHOSPHORUS LEVELS (ug/g) IN SEQUENTIAL SAMPLES DOWN THE SOIL COLUMNS

	CO2 Saturated Water Leached Columns						0 5m Acetic Acid Leached Columns					
soil type i d. bone/no bone	Bs G bone	Bs H bone	Bs I no bone	Bw J bone	Bw K bone	Bw L no bone	Bs M bone	Bs N bone	Bs O no bone	Bw P bone	Bw Q bone	Bw R no bone
1	613	641	621	1387	1324	1314	759	821	772	1481	1479	1805
2	602	642	593	1462	1360	1272	783	783	741	1379	1472	1496
3	616	666	581	1432	1392	1289	766	788	771	1529	1498	1481
4	631	639	560	1407	1362	1325	862	797	757	1523	1488	1411
5	639	696	565	1498	1367	1372	788	788	822	1519	1517	1488
6	639	640	577	1417	1389	1344	814	800	811	1504	1441	1454
7	645	630	595	1378	1371	1376	825	799	763	1517	1552	1519
8	621	641	557	1396	1379	1347	755	766	789	1535	1523	1475
9	626	667	555	1417	1311	1302	807	783	800	1595	1516	1516
10	637	651	544	1376	1306	1372	Position of bone 923	758	775	Position of bone 1678	Position of bone 1720	1508
11	614	663	565	1404	1350	1382	1019	816	782	1816	1611	1445
12	607	630	595	1429	1364	1315	978	Position of bone 922	806	1822	1640	1548
13	611	644	574	1417	1255	1348	939	883	829	1774	1560	1440
14	591	673	573	1367	1367	1318	965	861	791	1721	1648	1422
15	615	730	584	Position of Bone 1478	1390	1325	893	856	811	1701	1532	1388
16	663	Position of bone 761	570	1545	1394	1350	929	917	816	1624	1579	1472
17	627	820	582	1441	Position of bone 1466	1281	768	818	769	1496	1527	1550
18	Position of Bone 763	787	600	1442	1410	1270	824	755	794	1454	1531	1471
19	771	762	580	1460	1430	1354	857	814	789	1474	1558	1403
20	718	769	582	1476	1436	1322	784	774	787	1473	1529	1488
21	707	831	586	1474	1447	1318	763	803	784	1444	1574	1465
22	758	770	572	1483	1412	1256	791	821	824	1555	1490	1443
23	703	683	578	1404	1368	1257	762	793	795	1499	1596	1540
24	601	674	595	1397	1356	1253	777	784	815	1418	1628	1544
25	598	667	579	1475	1301	1237	768	786	902	1416	1484	1400
26	594	688	587	1395	1342	1362	776	805	825	1468	1517	1540
27	581	644	592	1371	1304	1308	784	797	848	1417	1444	1478
28	587	691	580	1379	1324	1353	794	785	816	1503		1499
29	586	651	575	1375	1285	1336	771	781	775			1461
30	583	672	581	1364	1306	1363	766	761	810			1450
31	577	719	564	1377	1325	1353						
32	579	694	581	1346	1315	1307						
33	577	699	575	1326	1373	1324						
34	580	694	596	1327	1305	1348						
35	599	639	596	1355	1370	1370						
36	558	688	565	1330								
37	559	664	552	1272								
38	563	732		1255								
39		723		1257								
40		764										
41												

TOTAL PHOSPHORUS LEVELS (UG G) IN INNER/OUTER SAMPLES SURROUNDING BONE IN SOIL COLUMNS

Column G With bone	
inner	outer
884	633
811	603
844	592
910	633
899	627

Column H With bone	
inner	outer
925	738
861	677
838	686
887	686
943	697

Column J With bone	
inner	outer
2109	1467
2070	1477
2165	1490
2047	1502
2140	1452
2093	1506
2227	1869

Column K With bone	
inner	outer
1921	1358
1965	1416
1073	1383
1895	1358
1951	1369
2273	1425

Column M With bone	
inner	outer
1885	1516
1931	1511
1982	1566
2042	1603
2000	1633
1826	1529

Column N With bone	
inner	outer
1547	1517
1651	1645
1627	1522
1663	1682
1736	1509
1902	1538

Column P With bone	
inner	outer
999	787
1125	805
1091	787
1164	792
1274	765
1052	794

Column Q With bone	
inner	outer
1021	812
896	816
916	806
956	811
1043	801

Column I Without bone	
inner	outer
608	591
584	580
560	579
585	584

Column L Without bone	
inner	outer
1343	1300
1361	1346
1293	1246
1315	1247

Column O Without bone	
inner	outer
805	784
746	792
850	783
818	807
825	756
856	801

Column R Without bone	
inner	outer
1490	1610
1435	1510
1369	1407
1377	1467
1476	1403

SELECTED CONCENTRATIONS (ug/ml) IN LEACHATES FROM 'CO_2 SATURATED WATER' LEACHED COLUMNS

Bs Soil: Columns With - Bone

Sample Number	Ca	Fe	Al	P
1	15	1	107	0
5	1	0	7	0
10	1	0	2	0
15	0	0	1	0
20	0	0	0	0
25	0	0	0	0
30	0	0	0	0
35	0	0	0	0
40	0	0	1	0
45	1	0	0	0
50	0	0	0	0
55	0	0	0	0
60	0	0	1	0
65	0	1	0	0
70	0	0	0	0
75	0	0	0	0

Bw Soil: Columns With - Bone

Sample Number	Ca	Fe	Al	P
1	681	N/R	3	0
5	8	0	2	0
10	14	0	3	0
15	35	0	2	0
20	23	0	2	0
25	4	0	2	0
30	4	0	2	0
35	3	0	2	0
40	2	0	1	0
45	1	0	1	0
50	0	0	0	0
55	0	0	1	0
60	1	0	0	0
65	0	0	0	0
70	0	0	0	0
75	0	0	0	0

Bs Soil: Columns Without - Bone

Sample Number	Ca	Fe	Al	P
1	17		163	0
5	2	0	4	0
10	3	0	4	0
15	0	0	1	0
20	0	0	2	0
25	0	0	1	0
30	0	0	1	0
35	0	0	1	0
40	0	0	0	0
45	0	0	1	0
50	0	0	1	0
55	0	0	0	0
60	0	0	0	0
65	0	0	0	0
70	0	0	0	0
75	0	0	0	0

Bw Soil: Columns Without - Bone

Sample Number	Ca	Fe	Al	P
1	594		3	0
5	15	0	3	0
10	10	0	3	0
15	32	0	2	0
20	35	0	2	0
25	6	0	2	0
30	2	0	2	0
35	2	0	2	0
40	2	0	2	0
45	1	0	2	0
50	0	0	1	0
55	0	0	1	0
60	1	0	0	0
65	1	0	1	0
70	0	0	0	0
75	0	0	0	0

SELECTED CONCENTRATIONS (ug/ml) IN LEACHATES FROM '0.05M ACETIC ACID' LEACHED COLUMNS

Bs Soil: Columns With - Bone

Sample Number	Ca	P
1	19	0
5	0	0
10	0	0
15	0	0
20	0	0
25	1	0
30	0	0
35	0	0
40	0	0
45	0	0
50	1	0
55	0	0
60	0	0
65	0	0
70	0	0
75	0	0

Bw Soil: Columns With - Bone

Sample Number	Ca	P
1	150	0
5	22	0
10	13	0
15	8	0
20	7	0
25	5	0
30	6	0
35	10	0
40	5	0
45	4	0
50	10	0
55	7	0
60	7	0
65	12	0
70	6	0
75	7	0
80	3	0
85	1	0
90	2	0
95	0	0
100	3	0

Bs Soil: Columns Without - Bone

Sample Number	Ca	P
1	19	0
5	1	0
10	0	0
15	0	0
20	0	0
25	0	0
30	0	0
35	0	0
40	0	0
45	0	0
50	0	0
55	0	0
60	0	0
65	1	0
70	0	0
75	0	0
80	0	0
85	0	0
90	0	0

Bw Soil: Columns Without - Bone

Sample Number	Ca	P
1	135	0
5	19	0
10	26	0
15	0	0
20	41	0
25	8	0
30	13	0
35	19	0
40	20	0
45	17	0
50	15	0
55	8	0
60	6	0
65	4	0
70	4	0
75	5	0
80	2	0
85	5	0

Cinerary Sherd CM5: Microprobe data (corrected to %)						
	Al	Si	P	Ca	Mn	Fe
1	18.45	9.79	0.06	1.16	8.35	18.38
2	16.57	10.55	0.84	1.49	6.34	15.99
3	17.68	12.31	0.39	1.22	5.41	13.96
4	18.83	15.44	0.39	1.29	2.69	15.17
5	13.48	5.79	1.49	1.10	6.55	30.53
6	14.72	11.07	0.74	1.14	7.47	24.10
7	15.18	10.86	0.78	1.02	9.10	24.03
8	21.21	9.59	0.84	1.01	12.63	30.36
9	18.21	8.70	1.38	0.92	13.52	29.68
10	18.60	8.35	0.93	1.04	14.48	31.44
11	13.71	5.59	1.22	1.50	9.54	23.85
12	15.13	4.75	1.50	0.76	9.48	26.45
13	13.27	11.03	1.30	0.88	7.22	22.11
mean	*16.54*	*9.52*	*0.91*	*1.12*	*8.68*	*23.54*

Cinerary Sherd BF: Microprobe data (corrected to %)						
	Al	Si	P	Ca	Mn	Fe
1	4.93	3.17	1.74	0.73	4.08	55.46
2	3.05	3.13	1.54	0.76	3.76	60.30
3	4.67	3.54	2.11	0.45	3.44	56.49
4	3.68	2.82	2.60	0.73	4.53	55.52
5	5.15	3.38	3.49	0.59	4.08	50.68
6	3.86	3.38	2.92	0.69	4.48	54.04
7	4.64	3.29	2.62	0.80	2.57	55.70
8	4.18	3.43	2.06	0.68	2.99	57.45
9	4.92	3.23	2.60	0.56	2.82	55.24
10	4.34	3.32	2.14	0.73	2.83	56.90
11	2.70	3.15	3.47	1.16	0.32	57.60
12	3.58	3.79	0.82	1.14	3.74	58.42
13	4.16	3.31	1.31	0.75	3.47	58.16
14	5.79	3.51	1.79	0.45	4.59	53.24
15	4.88	3.65	2.03	0.98	3.71	53.52
16	7.12	6.01	3.09	2.71	0.42	47.07
17	3.88	2.81	1.56	0.68	3.75	58.45
18	12.40	3.03	0.85	9.47	0.19	17.73
19	13.59	4.11	2.32	7.04	0.03	14.02
mean	*5.34*	*3.48*	*2.16*	*1.64*	*2.94*	*51.37*

Cinerary Sherd CM11: Microprobe data (corrected to %)						
	Al	Si	P	Ca	Mn	Fe
1	13.41	9.38	4.70	4.41	10.48	18.61
2	20.60	19.35	3.65	2.47	0.64	8.55
3	19.44	11.59	5.47	3.20	7.16	9.47
4	19.87	13.42	4.75	5.64	0.68	2.99
5	22.73	13.36	5.12	3.27	1.22	6.11
6	15.37	10.04	4.94	3.30	9.62	17.38
7	18.29	19.85	2.93	2.54	0.68	11.46
8	15.09	21.00	2.63	2.78	0.54	15.67
9	11.93	10.90	10.36	9.96	0.01	1.26
10	13.14	11.03	5.06	5.76	1.73	20.33
mean	*16.99*	*13.99*	*4.96*	*4.33*	*3.28*	*11.18*

Cinerary Sherd PP1: Microprobe data (corrected to %)						
	Al	Si	P	Ca	Mn	Fe
1	12.00	8.44	2.12	1.68	10.02	27.71
2	13.89	8.06	2.05	2.28	9.45	24.84
3	7.59	5.79	1.88	1.72	13.31	32.55
4	7.32	6.65	1.02	1.19	12.30	36.09
5	12.55	9.54	2.27	1.40	7.91	26.56
6	13.19	9.81	2.05	1.73	9.57	22.41
7	21.19	12.66	2.76	1.26	5.49	13.27
8	15.65	14.24	1.95	1.34	0.77	10.14
9	14.92	15.48	2.27	1.85	0.09	5.68
10	16.57	13.81	2.34	1.11	1.61	8.23
11	18.09	12.22	2.87	1.48	2.50	9.87
12	18.04	12.40	2.68	1.36	2.41	9.81
13	21.00	11.87	2.48	0.91	5.12	14.72
14	21.89	12.63	2.17	0.95	4.93	14.02
15	20.78	12.68	2.21	1.21	4.21	15.08
16	20.53	12.82	2.20	0.99	4.82	13.83
17	12.66	10.17	2.44	1.64	6.65	13.98
18	13.20	13.32	1.64	1.33	6.58	16.24
19	13.46	13.39	1.99	1.72	4.46	11.06
20	13.21	10.41	2.05	1.74	6.39	13.80
21	10.73	8.15	2.21	1.82	8.79	20.86
22	14.44	9.76	2.65	1.87	5.32	11.76
23	13.00	8.54	2.57	2.03	7.21	14.33
24	10.22	7.33	2.72	2.38	7.37	19.41
25	10.26	8.54	2.59	1.94	8.22	18.60
26	8.36	9.05	1.97	1.76	7.94	27.51
mean	*14.41*	*10.68*	*2.24*	*1.57*	*6.29*	*17.40*

Cinerary Sherd CM4: Microprobe data (corrected to %)						
	Al	Si	P	Ca	Mn	Fe
1	17.29	8.59	5.19	3.13	6.82	18.51
2	16.92	7.94	5.25	2.91	8.19	19.59
3	13.91	8.54	4.41	3.62	8.90	21.39
4	17.48	9.48	5.14	3.51	6.79	17.93
5	15.72	9.87	5.43	3.59	5.75	15.72
6	14.22	9.04	5.21	3.54	8.18	19.90
7	18.06	17.62	3.57	2.82	2.95	10.63
8	26.48	13.25	5.89	3.08	0.00	0.00
9	19.80	9.30	6.53	2.38	8.68	9.22
10	18.12	10.89	5.08	2.49	11.03	10.83
11	18.92	13.97	8.62	3.34	1.13	0.57
12	20.59	9.25	6.28	2.71	8.64	8.85
13	16.99	10.40	4.85	2.53	10.58	14.76
14	18.56	9.92	5.46	2.61	10.56	12.34
15	12.74	12.24	6.07	3.59	7.13	12.98
16	18.45	8.88	5.57	1.67	10.27	12.40
17	21.34	10.85	4.75	2.28	8.22	10.61
18	19.18	10.08	6.06	2.30	7.50	13.57
19	19.53	11.04	5.48	2.51	7.04	11.91
20	18.44	9.82	5.65	2.27	8.49	15.74
mean	*18.14*	*10.55*	*5.52*	*2.84*	*7.34*	*12.87*

EDXRA standards: Bangor, point analyses for 60 seconds
(values are for elemental oxides)

Standard	Al	Si	P	Ca	Mn	Fe
A	40.55	14.38	6.90	3.58	6.38	17.66
A	41.09	14.00	6.77	3.73	6.50	17.93
A	41.36	14.91	6.74	3.56	6.37	17.92
A	41.66	13.73	6.78	3.71	6.66	17.96
A	39.85	15.29	6.54	4.12	6.78	17.69
MEAN	*40.90*	*14.46*	*6.74*	*3.74*	*6.54*	*17.83*
AMMENDED**	**21.64**	**6.75**	**2.95**	**2.67**	**5.07**	**13.87**
B	70.49	3.29	4.41	2.73	4.05	12.07
B	69.96	3.36	4.81	2.42	4.37	11.80
B	69.58	3.62	4.56	2.52	4.64	12.49
B	68.73	3.34	4.81	2.73	4.34	12.16
B	69.42	3.54	4.60	3.10	4.36	11.38
MEAN	*69.64*	*3.43*	*4.64*	*2.70*	*4.35*	*11.98*
AMMENDED**	**36.84**	**1.60**	**2.03**	**1.93**	**3.37**	**9.32**
C	9.72	33.77	10.42	6.97	11.11	28.33
C	9.46	36.51	9.61	7.08	10.60	27.21
C	9.99	32.24	10.49	7.57	11.51	28.28
C	9.32	34.36	9.69	7.55	11.13	28.28
C	9.63	34.89	10.11	6.84	11.36	27.91
MEAN	*9.62*	*34.35*	*10.06*	*7.20*	*11.14*	*28.00*
AMMENDED**	**5.09**	**16.04**	**4.40**	**5.14**	**8.63**	**21.79**
D	9.10	5.06	2.37	15.60	28.28	40.66
D	8.97	5.16	2.18	15.55	28.79	40.49
D	8.79	5.42	2.36	16.35	26.74	40.27
D	9.83	5.65	2.68	16.52	27.04	38.96
D	9.76	5.88	2.28	16.30	26.56	39.10
MEAN	*9.29*	*5.44*	*2.37*	*16.07*	*27.48*	*39.90*
AMMENDED**	**4.92**	**2.54**	**1.04**	**11.47**	**21.30**	**31.04**
E			54.24			45.10
E			54.69			45.10
E			54.90			44.60
E			55.77			45.80
E			55.99			45.02
MEAN			*55.12*			*45.12*
AMMENDED**			**24.09**			**35.11**
F			45.45	54.66		
F			45.61	54.55		
F			45.32	54.07		
F			46.30	55.70		
F			46.17	55.76		
MEAN			*45.77*	*54.95*		
AMMENDED**			**20.00**	**39.23**		

Ammended** values are element concentrations calculated from the elemental oxides (Al_2O_3, SiO_2, FeO, CaO, MnO, P_2O_5)

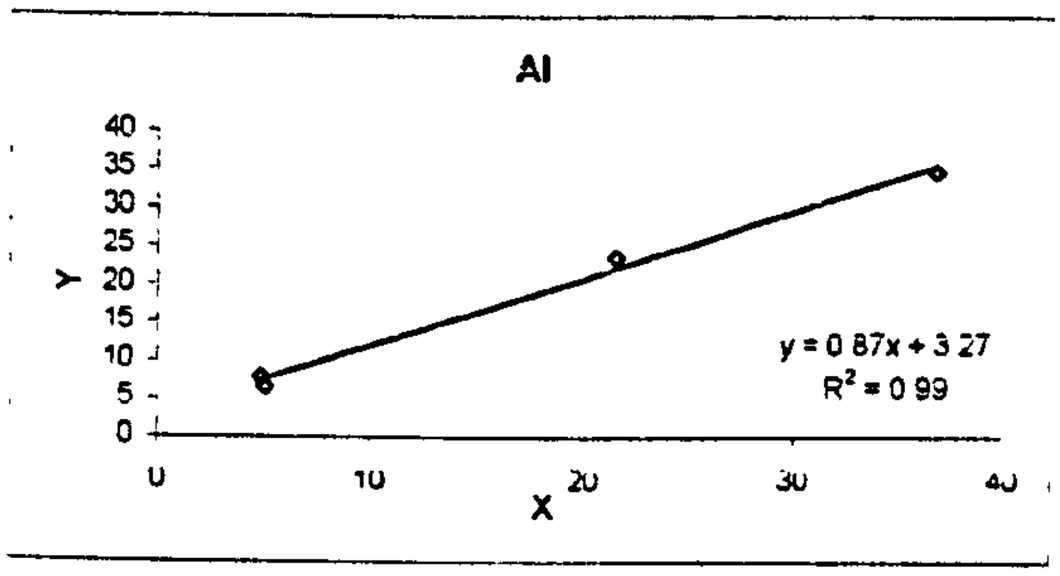
Microprobe standards: Manchester 07.01.98
50um raster size for 200 seconds

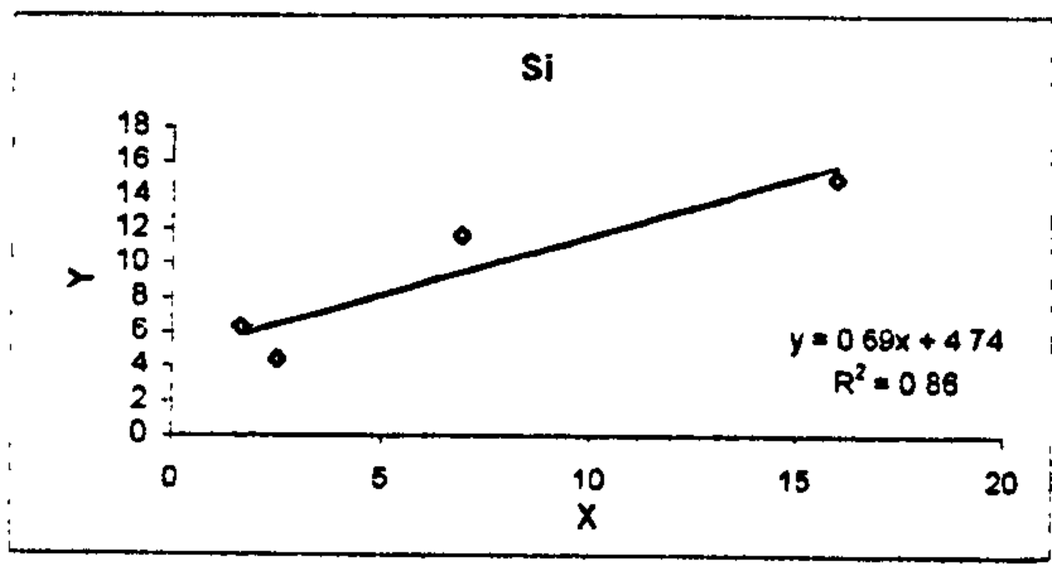
Standard	Al	Si	P	Ca	Mn	Fe
A	20.90	15.13	2.94	0.93	2.97	11.87
A	22.52	11.96	3.28	0.68	4.81	12.77
A	24.51	9.91	3.26	1.05	6.09	11.67
A	27.56	8.38	3.70	0.57	3.66	11.79
A	22.04	13.11	3.53	1.03	4.23	11.35
MEAN	***23.50***	***11.70***	***3.34***	***0.85***	***4.35***	***11.89***
B	32.65	7.93	2.04	0.40	4.78	7.23
B	34.19	7.09	2.33	1.17	2.51	7.22
B	34.58	6.34	2.40	0.63	2.58	8.42
B	36.10	4.42	2.17	0.64	3.46	8.65
B	35.96	5.82	1.98	0.94	2.66	7.21
MEAN	***34.70***	***6.32***	***2.18***	***0.76***	***3.20***	***7.75***
C	7.45	10.44	6.56	3.07	7.39	25.65
C	6.20	16.75	5.49	2.30	7.71	19.44
C	6.74	15.86	4.97	3.11	7.75	19.99
C	6.38	15.94	5.56	2.15	7.80	20.90
C	6.54	16.14	5.24	2.23	8.41	20.19
MEAN	***6.66***	***15.03***	***5.57***	***2.57***	***7.81***	***21.24***
D	8.19	3.76	1.03	5.44	20.07	31.35
D	7.84	5.14	1.04	5.37	20.01	29.46
D	7.44	4.75	0.98	5.78	19.73	30.45
D	8.38	4.04	1.08	5.88	19.35	30.57
D	7.91	4.58	0.91	5.63	20.39	29.81
MEAN	***7.95***	***4.45***	***1.01***	***5.62***	***19.91***	***30.33***
E	0.00	0.00	20.12	0.00	0.00	38.42
E	0.00	0.00	20.00	0.00	0.00	38.77
E	0.00	0.00	20.03	0.00	0.00	39.58
E	0.00	0.00	19.82	0.00	0.00	38.90
E	0.00	0.00	19.90	0.00	0.00	39.85
MEAN	***0.00***	***0.00***	***19.97***	***0.00***	***0.00***	***39.10***
F	0.00	0.00	22.66	33.91	0.00	0.00
F	0.00	0.00	22.58	33.99	0.00	0.00
F	0.00	0.00	22.58	33.98	0.00	0.00
F	0.00	0.00	22.68	34.28	0.00	0.00
F	0.00	0.00	22.52	34.28	0.00	0.00
MEAN	***0.00***	***0.00***	***22.60***	***34.09***	***0.00***	***0.00***

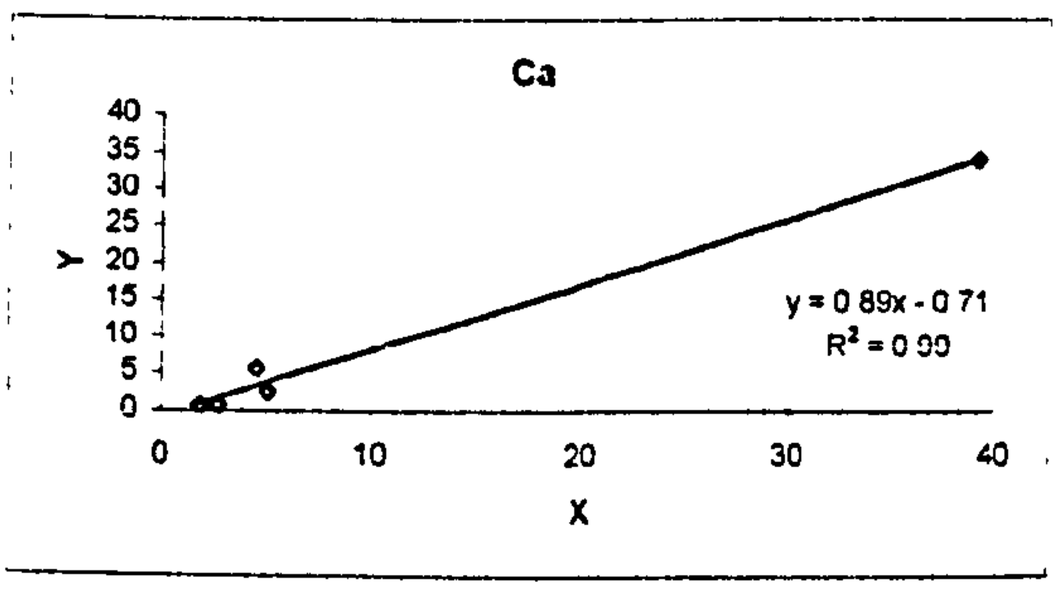
Regression plots displaying regression equations and r2 values

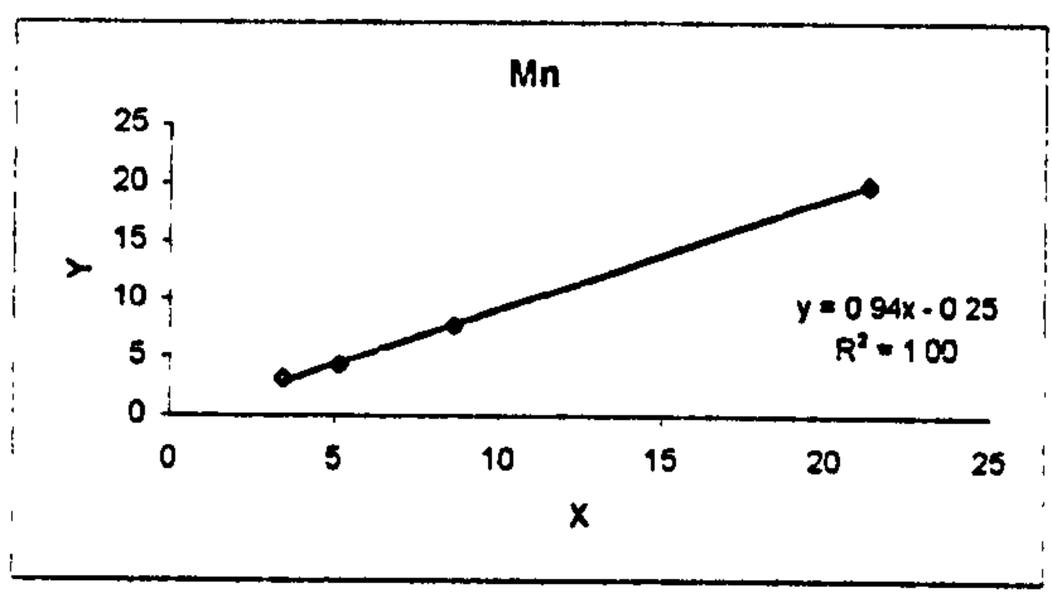
Y axis = Semi-quantitative EDXRA data

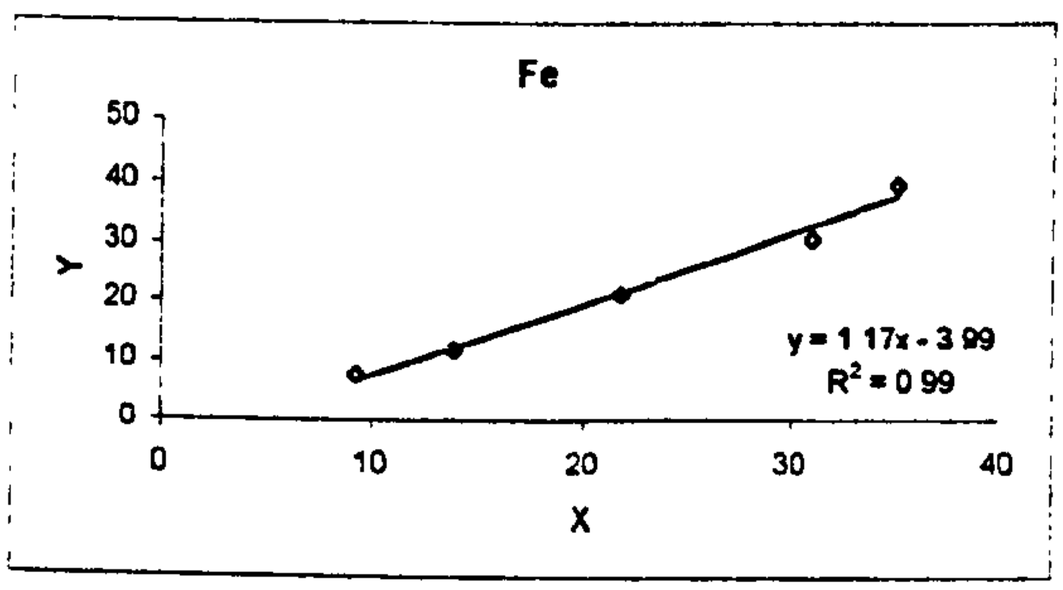
X axis = Quantitative microprobe data

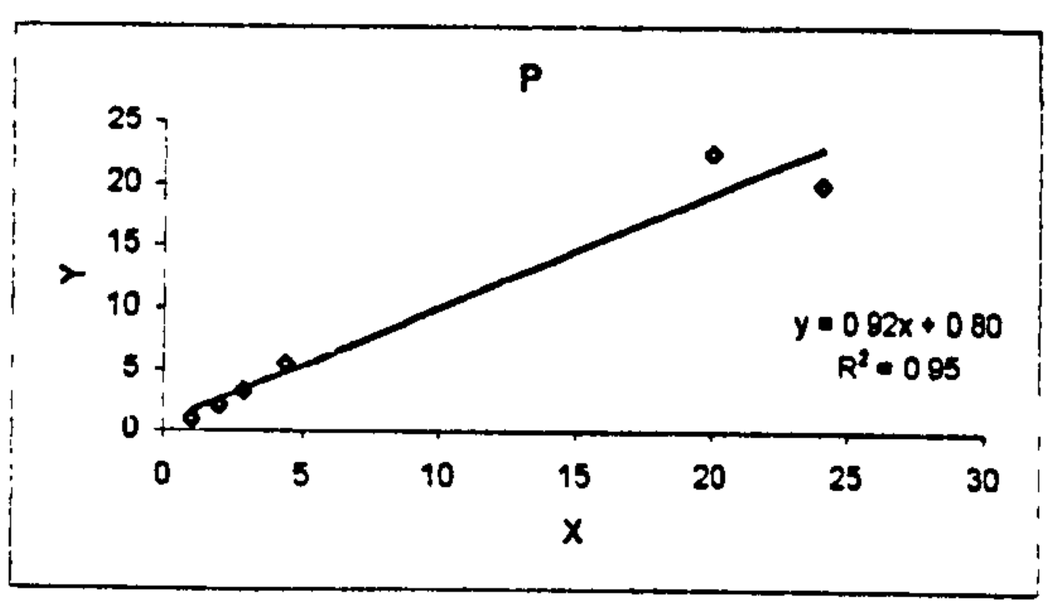












P_{tot} results for early Christian cists at Ty Mawr

Sample No	Cist T 170 Location		Cist T 170 Ptot (ug g)		Cist T 170 Location		Cist T 170 Ptot (ug g)	Cist T216 Location		Cist T216 Ptot (ug g)	Cist T304 Location		Cist T304 Ptot (ug g)
	x	y	upper	basal	x	y	background	x	y		x	y	
1	60	20	620	410	0	0	460	0	1	780	1	1	977
2	60	30	540	480	10	0	420	0	2	800	2	1	694
3	60	40	470	590	20	0	530	0	3	430	3	1	535
4	60	50	560	540	30	0	420	0	4	800	4	1	496
5	60	60	530	510	40	0	300	0	5	740	1	2	1197
6	70	30	520	450	50	0	480	0	6	530	2	2	1075
7	70	40	440	610	60	0	670	1	1	740	3	2	1568
8	70	50	480	600	70	0	380	1	2	790	4	2	662
9	70	60	460	660	80	0	470	1	3	510	1	3	3221
10	80	30	500	550	90	0	370	1	4	640	2	3	2324
11	80	40	500	660	100	0	550	1	5	560	3	3	10880
12	80	50	440	610	110	0	500	2	1	450	4	3	680
13	80	60	510	560	120	0	430	2	2	870	1	4	1761
14	90	30	570	610	130	0	420	2	3	1090	2	4	1547
15	90	40	500	540	140	0	390	2	4	1040	3	4	20390
16	90	50	420	600	150	0	430	2	5	940	4	4	950
17	90	60	450	600	160	0	440	2	6	650	0	5	1062
18	100	30	690	530	170	0	470	3	1	690	1	5	1392
19	100	40	640	610	180	0	350	3	2	1440	2	5	1305
20	100	50	530	630	190	0	660	3	3	1470	3	5	14360
21	100	60	470	690	200	0	590	3	4	850	4	5	1230
22	110	30	600	560	210	0	660	3	5	880	1	6	1510
23	110	40	550	630	220	0	580	3	6	730	2	6	1473
24	110	50	620	690	230	0	620	4	1	1130	3	6	27200
25	110	60	520	610	240	0	530	4	2	1600	4	6	1320
26	120	30	620	740	250	0	540	4	3	1280	1	7	1600
27	120	40	760	740				4	4	820	2	7	1533
28	120	50	610	790				4	5	720	3	7	11120
29	120	60	690	670				4	6	740	4	7	950
30	130	30	620	740				5	1	790	1	8	1331
31	130	40	660	780				5	2	2140	2	8	982
32	130	50	610	770				5	3	1420	3	8	30640
33	130	60	730	720				5	4	1830	4	8	1490
34	140	30	570	580				5	5	910	1	9	1010
35	140	40	610	660				5	6	850	2	9	1287
36	140	50	660	840				6	1	1040	3	9	8340
37	140	60	510	610				6	2	1390	4	9	1070
38	150	30	620	740				6	3	1360	0	10	1147
39	150	40	720	720				6	4	1310	1	10	1143
40	150	50	690	660				6	5	1020	2	10	1289

P_{tot} results for early Christian cists at Ty Mawr

Sample No	Cist T 170 Location x	Location y	Ptot (ug g) upper	Ptot (ug g) basal	Location x	Location y	Ptot (ug g) background	Cist T216 Location x	Location y	Ptot (ug g)	Cist T304 Location x	Location y	Ptot (ug g)
41	150	60	560	630				6	6	1000	3	10	2260
42	160	40	840	920				7	1	970	4	10	1170
43	160	50	600	660				7	2	1340	0	11	1173
44	160	60	730	630				7	3	1100	1	11	10250
45	170	40	870	840				7	4	1950	2	11	1540
46	170	50	690	840				7	5	2050	3	11	3420
47	170	60	690	860				7	6	740	4	11	1340
48	180	40	780	880				8	1	850	0	12	1361
49	180	50	770	890				8	2	1010	1	12	2764
50	180	60	720	880				8	3	1180	2	12	5850
51	190	40	740	900				8	4	960	3	12	3510
52	190	50	660	1170				8	5	1400	4	12	1170
53	190	60	660	970				8	6	610	1	13	30810
54	200	40	650	560				9	1	580	2	13	7740
55	200	50	630	710				9	2	1510	3	13	4250
56	200	60	650	730				9	3	1450	4	13	1450
57	210	50	490	510				9	4	1610	1	14	4460
58	210	60	440	650				9	5	840	2	14	9400
59	220	50	510	500				9	6	510	3	14	3860
60	220	60	510	510				10	1	760	4	14	1470
61	230	50	510	550				10	2	1100	0	15	1032
62	230	60	450	540				10	3	1530	1	15	2394
63								10	4	1120	2	15	7060
64								10	5	650	3	15	2290
65								10	6	550	4	15	1570
66								11	1	540	0	16	1004
67								11	2	1100	1	16	1823
68								11	3	1480	2	16	5640
69								11	4	1470	3	16	2500
70								11	5	1140	4	16	1010
71								11	6	970	0	17	989
72								12	1	490	1	17	1506
73								12	2	790	2	17	2131
74								12	3	1480	3	17	2374
75								12	4	800	4	17	1197
76								12	5	1030	0	18	780
77								12	6	770	1	18	3731
78								13	1	460	2	18	1413
79								13	2	630	3	18	1743
80								13	3	1100	4	18	1579
81								13	4	860	0	19	1015

P_{tot} results for early Christian cists at Ty Mawr

Sample No	Cist T 170 Location x	y	Ptot (ug g) upper	basal	Location x	y	Ptot (ug g) background	Cist T216 Location x	y	Ptot (ug g)	Cist T304 Location x	y	Ptot (ug g)
82								13	5	1410	1	19	1902
83								13	6	660	2	19	2461
84								14	1	470	3	19	1177
85								14	2	630	4	19	1173
86								14	3	950	5	19	932
87								14	4	980	0	20	854
88								14	5	1520	1	20	844
89								14	6	730	2	20	823
90								15	1	410	3	20	665
91								15	2	510	4	20	935
92								15	3	450			
93								15	4	760			
94								15	5	1080			
95								15	6	590			
96								16	1	470			
97								16	2	550			
98								16	3	570			
99								16	4	360			
100								16	5	500			
101								16	6	560			
102								17	1	600			
103								17	2	410			
104								17	3	420			
105								17	4	680			
106								17	5	420			
107								17	6	470			
108								18	1	480			
109								18	2	510			
110								18	3	560			
111								18	4	650			
112								18	5	470			

P_{tot} results for Bronze Age cist site at Cleiriog Ucha

Sample No	Location		Ptot (ug g)		Location		Ptot (ug g)
	x	y	Upper	Basal	x	y	Inhumation
1	10	10	1020	1150	60	50	630
2	10	20	1680	1560	60	60	460
3	10	30	1950	1400	60	70	310
4	10	40	3580	1420	60	80	440
5	10	50	2680	1840	60	90	490
6	10	60	3950	4020	60	100	620
7	10	70	5470	5330	70	50	500
8	10	80	2480	2370	70	60	520
9	20	10	1630	1320	70	70	430
10	20	20	3910	1530	70	80	570
11	20	30	2510	1980	70	90	640
12	20	40	3990	1350	70	100	450
13	20	50	2160	2030	80	50	580
14	20	60	5510	3970	80	60	420
15	20	70	6640	2310	80	70	470
16	20	80	5090	1440	80	80	430
17	30	10	1180	1310	80	90	350
18	30	20	1480	1390	80	100	1160
19	30	30	1780	1530	90	50	930
20	30	40	2120	1250	90	80	1280
21	30	50	1700	1570	90	90	1200
22	30	60	3770	1940	90	100	1060
23	30	70	4410	1910	100	60	1040
24	30	80	1640	1650	100	70	1150
25	40	20	2590	1380	100	80	890
26	40	30	2140	1420	100	90	1140
27	40	40	2680	1370	100	100	1010
28	40	50	1920	1260	110	50	960
29	40	60	1910	1570	110	60	1100
30	40	70	1400	1530	110	70	1100
31	40	80	4930	1560	110	80	1160
32	50	20	1630	1150	110	90	1200
33	50	30	1930	1370	110	100	1040
34	50	40	1730	1400			
35	50	50	3030	1580			
36	50	60	2930	1470			
37	50	70	1360	1490			
38	60	20	1150	1410			
39	60	30	2770	1250			
40	60	40	1940	1260			

P_{tot} results for Bronze Age cist site at Cleirlog Ucha

Sample No	Location		Ptot (ug g)		Location		Ptot (ug g)
	x	y	Upper	Basal	x	y	Inhumation
41	60	50	1540	1360			
42	60	60	2620	1520			
43	60	70	1580	1310			
44	70	20	1210	1720			
45	70	30	1340	220			
46	70	40	1290	540			
47	70	50	1250	720			
48	70	60	1520	700			
49	70	70	1240	480			
50	80	20	1140	510			
51	80	30	1110	720			
52	80	40	1120	790			
53	80	50	1280	690			
54	80	60	1420	470			
55	80	70	1450	520			
56	80	80	1040	470			
57	90	20	1010	450			
58	90	30	980	650			
59	90	40	1220	700			
60	90	50	1280	500			
61	90	60	1200	750			
62	90	70	1030	610			
63	100	30	700	460			

APPENDIX II: THE MEASUREMENT OF TOTAL PHOSPHORUS (P_{TOT})

2.1 Introduction

Levels of P_{tot} in soil can be measured in the laboratory using a variety of techniques. The simplest method would be analysis by X-ray fluorescence (XRF), a technique which requires little sample preparation (drying and grinding improves precision and accuracy). XRF analysis has the advantage of producing results for a number of elements simultaneously in a few minutes, and for phosphorus, a range of 0.01–1% ± 0.005 is usual. The equipment is expensive however (£100K +), and costly to run ~£1 per sample, which is too expensive for many environmental/archaeological departments. Other methods of measuring P_{tot} require the conversion of P in all forms, into orthophosphate (PO_4^{3-}) in solution prior to the analysis. There are a variety of techniques available to achieve this, Jackson (1958) suggests four; a precipitation technique, HF digestion, sodium carbonate fusion and perchloric acid digestion. Other methods include ashing and extraction (Anderson, 1976), and alkaline oxidation (Dick & Tabatabai, 1977). This appendix considers these methods and tests the most suitable for use in this study.

2.2 Requirements

An archaeological P survey processes large numbers of samples so requiring a method which is quick and simple. The method needs to be accurate (*i.e.* recover most of the phosphorus present) and precise (*i.e.* be reproducible). These considerations preclude the use of the precipitation method, which has a low recovery, the sodium carbonate fusion method which is the most accurate but is time consuming, and the HF digestion method which requires specialised laboratory equipment. The ashing and HCl extraction method (Anderson, 1976), the alkaline oxidation method (Dick & Tabatabai, 1977) and a rapid perchloric acid digestion method (Sommers & Nelson, 1972) will be examined in more detail.

2.3 Methods

Total phosphorus levels were measured in 20 replicate samples of both a brown earth and a brown podzolic soil (air-dried, sieved < 2mm and further ground <0.2mm) using the three methods outlined below. Orthophosphate methods were

measured in all extracts using the Perstorp "Flow Solution 3000" flow injection analyser (FIA), employing the colorimetric method (ascorbic acid reducing antimony-phospho-molybdate complex) of Murphy & Riley (1962), by which orthophosphate can be measured in solution over the range of 5-0.05 μg P ml^{-1} and costs only 0.5p/sample to run (appendix III "Flow injection analysis"). Orthophosphate in solution could also be measured using colorimetric bench-top techniques, of which several are described by Jackson (1958), but these are slower and less accurate than F.I.A.. P can also be measured using inductively coupled plasma spectrometry (ICP -AES/MS) but this is slower than FIA analysis, more expensive per sample and the equipment is costly, with no improvement in accuracy or precision. Two samples of each soil type were measured using sodium carbonate fusion to provide a value for P_{tot} from which the accuracy of each method can be ascertained.

2.3.1 Ashing and extraction. *Measure 0.5g finely ground soil into a crucible, ignite in a muffle furnace at 500 ℃ overnight. All ashed material is washed into a 100ml conical flask with 25ml 1N HCl and boiled for 15 minutes, transferred into a 100ml graduated flask, made up to the mark and mixed. An aliquot is removed for orthophosphate measurement. Time for 1000 samples = 20 days. Equipment needed = Muffle furnace, hotplate, crucibles, conical flasks and graduated flasks.*

2.3.2 Rapid perchloric acid digestion. *Measure 0.2g finely ground soil into a digestion tube marked at 15ml. 2ml of perchloric acid is added and digested in a driblock at 200 ℃ for 4 hours. When cooled it is made up to 15ml and mixed. An aliquot is taken for orthophosphate measurement. Time for 1000 samples = 14 days. Equipment needed: driblock, 20ml digestion tubes and water-scrubbed fume chamber.*

2.3.3 Alkaline oxidation. *Measure 0.2g finely ground soil in a 50ml boiling tube and add 3ml of NaOBr (prepared on the day). Heat until dryness (10-15 minutes) in a driblock at 260-280 ℃, continue to heat for 30 minutes, then remove and allow to cool. Add 4ml of distilled water and 1ml of formic acid and mix. Add 25ml of 1N H_2SO_4 and mix, allow to settle for 1 hour. Take an aliquot for orthophosphate measurement. Time for 1000 samples = 24 days. Equipment needed: driblock, 50ml boiling tubes and fume chamber.*

2.4 Results & Discussion (all units $\mu g\ g^{-1}$)

	Ashing & acid extraction (AAE)	Perchloric acid digestion (PAD)	Alkali oxidation (AO)
Podzolised soil			
Mean	790	716	765
Standard error	21.2	19.8	21.1
Median	785	715	755
Std. Deviation	95	89	94
Range	630-1000	610-840	620-990
Count	20	20	20

Total P by sodium carbonate fusion (SCF) = 1324

	AAE	PAD	AO
Brown Earth			
Mean	2014	1742	2078
Standard error	44.7	24.1	43.1
Median	2035	1730	1985
Std. Deviation	200	108	193
Range	1710-2340	1560-1950	1810-2500
Count	20	20	20

Total P by sodium carbonate fusion (SCF) = 2220

The results for the sodium carbonate fusion analyses are considered the total phosphorus present in each soil, because the SCF procedure is regarded as an accurate method (Jackson, 1958).

Levels of P_{tot} in the brown earth soil are double those in the podzolised soil, the reasons for which are discussed elsewhere in the thesis. The perchloric acid digestion (PAD) method accounted for the lowest recovery of phosphorus for both soils, only 55% and 80% of the SCF totals. The ashing and acid extraction (AAE) method and the alkali oxidation (AO) method had recoveries of 60% and 91% and 60% and 93% respectively. The results for these two soils are similar to results for soils previously measured. Sherrell & Saunders (1966) found that PAD underestimated the P_{tot} by up to 15%, an effect which varied with soil type.

Anderson (1977) showed that the AAE method became less accurate as the organic matter levels in the soil increased. However these results have differences to other studies, Dick & Tabatabai (1976) had similar results for the PAD and AO methods, and Hammond (1983) showed the AAE method gave 10% lower P levels than the PAD method, whereas for the soils in this study they are 10% higher. The lower recovery of P from the soil by the three methods examined in comparison with recoveries from sodium carbonate fusion has been attributed to the presence of phosphatic mineral *e.g.* apatites within particles of resistant minerals *e.g.* quartz (Dick & Tabatabai, 1976). Lower recoveries of P_{tot} using the PAD method could be due to the limiting volume in the method: PAD uses 0.2g and 2ml, AAE uses 0.5g and 25ml and AO uses 0.2g and 3ml.

Archaeological P survey makes comparisons between P_{tot} results to discover anomalies in concentrations which could be attributed to human activity. It is important that results are precise as the level of variation of P_{tot} between samples contributes to a calculation of the significance of the results. For this reason a more precise method is to be favoured. The precision of the methods examined here in terms of the standard errors (SE) varies. The SE of all methods for the podzolised soil is very similar 19.8, 21.1 & 21.2. However, for the brown earth soil the SE for the PAD method is 24.1, roughly half that calculated for the AAE and AO methods, 44.7 & 43.1 respectively.

2.5 Conclusions

The PAD method is not as accurate as the AAE and AO methods but is more precise, and in an archaeological survey of P, precision of the results is more important than accuracy once an acceptable level of accuracy has been achieved. The PAD method is only a two-stage operation so is simpler and quicker than the other methods. For these reasons this method has been chosen to be used in this study. In situations where a water scrubbed fume chamber is not available then the AAE method is recommended.

APPENDIX III: FLOW INJECTION ANALYSIS

3.1 Introduction

A Perstorp "Flow Solution 3000" flow injection analyser was purchased to measure orthophosphate in solution for this research project. This appendix provides an introduction to the technique known as flow injection analysis, outlining how the "Flow Solution 3000" works. The report continues with tests of accuracy and precision of the instrument.

3.2 Background

Flow injection analysis (F.I.A.) is a technique which evolved from Continuous Flow Analysis systems (C.F.A.) developed in the 1960s. A known volume of sample is injected into a continuous flow of a carrier stream containing colorimetric reagents. Mixing of the sample and reagents occurs in-stream and a colour reaction occurs. The carrier stream flows through a detector and each sample is measured separately but in a continuous sequential system. F.I.A. gives a high sampling/measurement rate, at a low unit cost, using only small volumes of sample. For these reasons the FIA is an ideal system for use where large numbers of samples are to be processed.

3.3 System Design

The Perstorp 'Flow Solution 3000' Flow Injection Analyser system consists of:

3.3.1 Propelling system

A peristaltic pumping system which can accommodate eight manifold tubes is used. The pumping rate is altered by changing the colour coded pump tubes which have different internal diameters.

3.3.2 Injection system

This consists of an injection valve, mechanically activated by an electric motor. The sampler flushes the valve with sample to reduce carryover, before injecting a known volume of sample into the carrier stream. Injection volumes can be altered by swapping screw-in-loops, three sizes are available 50µl, 100µl and 200µl, which are changed when different concentration ranges are measured.

3.3.3 The reaction zone

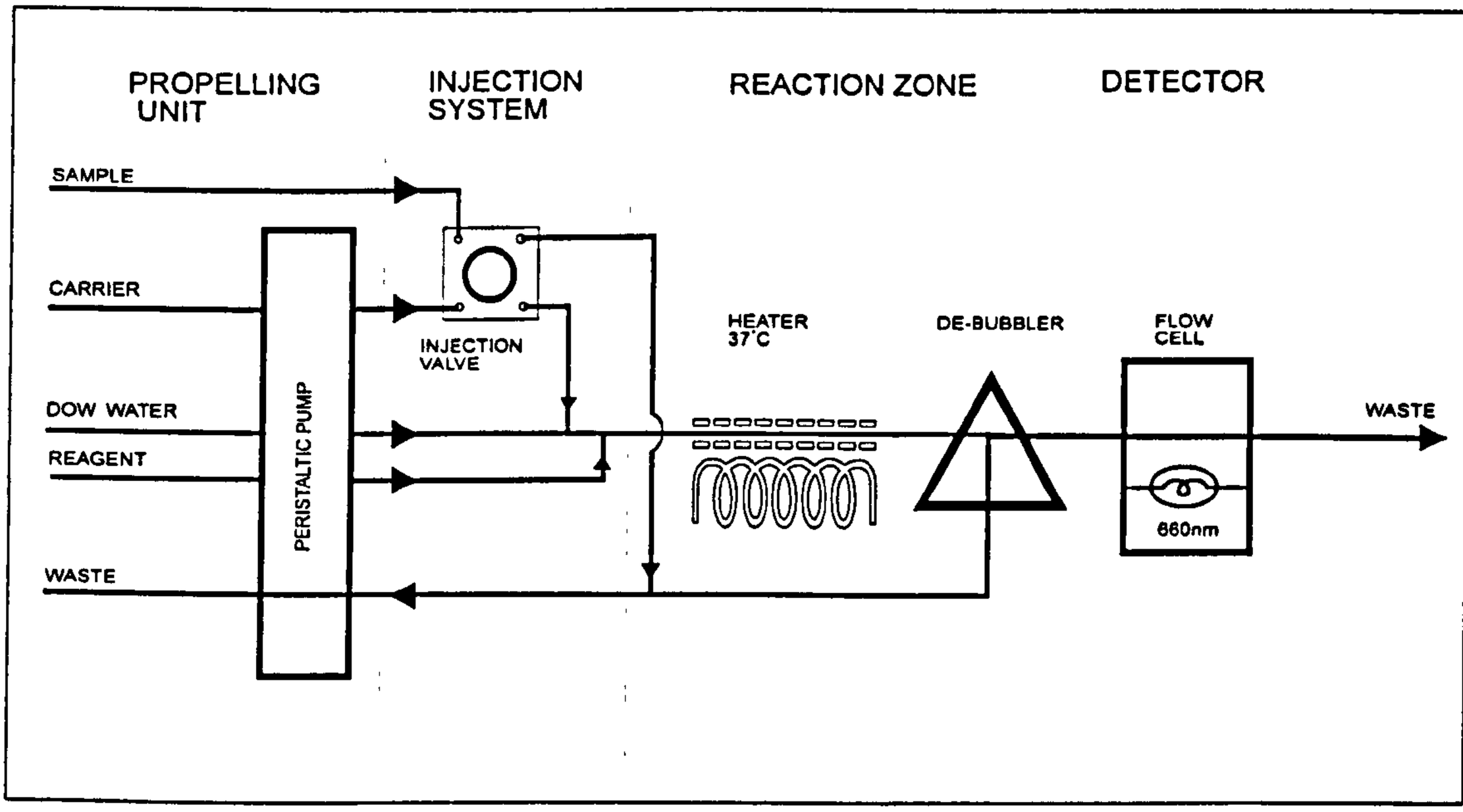
The mixing of reagents and sample occurs in standard PTFE tubing, the measurement of orthophosphate requires heating at 37°C to ensure complete colour development, so the carrier stream passes through a heating coil.

3.3.4 Detector

The absorbance of the solution is measured at 660nm. A digital detector is employed enabling a wide detection limit of 0.01-1mg L^{-1}-P with a claimed detection limit of 0.001mg L^{-1}- P (*Perstorp, 1995*).

These four components are coupled with a random access sampler capable of holding 120 sample tubes, and a microprocessor data acquisition system.

3.5 Schematic Diagram of the Perstorp 'Flow Solution 3000'



3.4 Orthophosphate measurement

Orthophosphate reacts with molybdenum VI in the presence of antimony III in an acid medium to form phosphomolybdic acid. This complex is subsequently reduced with ascorbic acid forming a blue colour. The absorbance is measured at 660nm. This is a modified version of Murphy and Rileys *"A modified single solution method for the determination of phosphorus in natural waters"* method, (1962).

3.5 Data Acquisition

The response of the detector to the changing concentration of sample is monitored and fed as a continuum of data points into a computer system programmed to provide individual sample points. A series of standards are analysed first and responses from subsequent samples are compared to this calibration. A peak height system of measurement is used. A base line or zero signal is established, and then values are obtained from an identification of the maximum signal relative to the baseline, produced from each sample.

3.6 Precision and reproducibility

Perstorp's sales literature (1995) for the "Flow Solution 3000" F.I.A. suggests it has a detection range of 0.01 - 1mg L^{-1}-P with a detection limit of 0.001mg L^{-1}.

3.7 Testing the accuracy and reproducibility of the Perstorp " Flow Solution 3000"

3.7.1 Method

A range of samples with the following P concentrations (µg ml^{-1}) were made up;

5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.25, 0.05

Eight sample tubes were filled for each sample concentration and these tubes were located randomly on the sampler. A single run was completed with each of the screw-in-loops.

3.7.2 Results

The results are displayed in table III.1. Some simple descriptive statistics (mean, standard error, standard deviation and coefficient of variation) have been calculated for each data set and are produced in table III.2.

3.7.3 Precision

Precision in this context is taken to mean the inclusiveness or breadth of the measurements. The mean result is the first indication of the precision of the measurements. In all cases in this data the mean result is close to the actual

TABLE ONE: PHOSPHATE MEASUREMENT FOR THREE LOOP VOLUMES
(EIGHT REPLICATE MEASUREMENTS OF TWELVE STANDARDS)

Sample Concentration (ug/ml)	Orthophosphate Measured (ug/ml) 50ul Loop	100ul Loop	200ul Loop
0.05 ug/ml - P	0.052	0.052	0.062
	0.052	0.051	0.063
	0.048	0.056	0.063
	0.064	0.065	0.098
	0.049	0.053	0.069
	0.045	0.050	0.067
	0.056	0.049	0.064
	0.045	0.050	0.063
0.25 ug/ml - P	0.241	0.243	0.248
	0.242	0.244	0.251
	0.248	0.245	0.252
	0.243	0.246	0.250
	0.252	0.247	0.253
	0.243	0.242	0.244
	0.254	0.247	0.253
	0.249	0.248	0.250
0.50 ug/ml - P	0.500	0.496	0.495
	0.497	0.497	0.499
	0.493	0.497	0.497
	0.501	0.498	0.493
	0.499	0.503	0.500
	0.505	0.501	0.494
	0.499	0.503	0.497
	0.501	0.501	0.498
1.00 ug/ml - P	0.983	0.987	0.975
	1.012	0.988	0.986
	1.011	1.003	0.985
	0.988	0.992	0.978
	0.996	1.001	0.987
	1.000	1.000	0.981
	1.002	1.001	0.988
	0.992	1.002	1.001
1.50 ug/ml - P	1.519	1.512	1.488
	1.517	1.512	1.498
	1.517	1.516	1.497
	1.517	1.514	1.485
	1.521	1.521	1.495
	1.518	1.515	1.485
	1.526	1.520	1.502
	1.510	1.502	1.499
2.00 ug/ml - P	2.018	2.011	1.991
	1.988	2.012	2.006
	2.007	2.015	2.004
	2.017	2.000	1.954
	2.017	2.017	2.005
	2.010	2.007	1.989
	2.014	2.019	2.002
	2.010	2.080	1.993

TABLE ONE: Continued

Sample Concentration (ug/ml)	Orthophosphate Measured (ug/ml)		
	50ul Loop	100ul Loop	200ul Loop
2.50 ug/ml - P	2.492	2.496	2.492
	2.480	2.504	2.494
	2.489	2.501	2.493
	2.505	2.517	2.473
	2.516	2.525	2.496
	2.511	2.506	2.465
	2.515	2.528	2.495
	2.501	2.508	2.490
3.00 ug/ml - P	2.985	2.973	2.956
	2.988	2.985	2.997
	2.980	3.005	3.002
	2.990	3.010	2.954
	2.992	3.005	2.981
	2.984	3.007	2.946
	2.996	3.014	2.971
	2.988	3.004	2.982
3.50 ug/ml - P	3.496	3.492	3.508
	3.512	3.521	3.523
	3.490	3.514	3.533
	3.495	3.534	3.508
	3.508	3.521	3.508
	3.516	3.535	3.492
	3.510	3.543	3.511
	3.505	3.503	3.512
4.00 ug/ml - P	3.986	3.968	4.012
	4.027	3.967	4.020
	4.014	3.986	4.011
	3.999	4.028	4.004
	4.000	4.035	4.013
	4.009	4.040	3.984
	4.006	4.040	4.002
	4.012	4.012	3.996
4.50 ug/ml - P	4.607	4.496	4.549
	4.507	4.527	4.553
	4.503	4.525	4.517
	4.512	4.548	4.473
	4.510	4.544	4.476
	4.499	4.530	4.431
	4.503	4.536	4.514
	4.496	4.503	4.548
5.00 ug/ml - P	4.990	5.003	4.960
	5.001	5.000	4.965
	4.993	5.000	4.938
	4.998	5.043	4.957
	5.000	5.047	4.947
	5.009	5.037	4.904
	5.009	5.048	4.903
	4.995	5.012	4.982

Table Two: Summary statistics of orthophosphate measurements using three loop volumes

		50ul Loop	100ul Loop	200ul Loop
0.05 ug/ml - P	Mean	0.05	0.05	0.07
	Standard error	0 002	0.002	0 004
	Standard deviation	0 007	0.005	0.012
	Coefficient of variation (%)	12.72	10.16	17.81
0.25 ug/ml - P	Mean	0.25	0.25	0.25
	Standard error	0.002	0.001	0.001
	Standard deviation	0.005	0.002	0.003
	Coefficient of variation (%)	1.97	0.79	1.15
0 50 ug/ml - P	Mean	0.50	0.50	0.50
	Standard error	0.001	0.001	0.001
	Standard deviation	0.003	0.003	0.002
	Coefficient of variation (%)	0.70	0.56	0.50
1.00 ug/ml - P	Mean	1.00	1.00	0.99
	Standard error	0.004	0.002	0.003
	Standard deviation	0.010	0.007	0.008
	Coefficient of variation (%)	1.05	0.67	0.80
1 50 ug/ml - P	Mean	1.52	1.51	1.49
	Standard error	0.002	0.002	0.002
	Standard deviation	0.005	0.006	0.007
	Coefficient of variation (%)	0.30	0.39	0.44
2.00 ug/m - P	Mean	2.01	2.02	1.99
	Standard error	0.004	0.009	0.006
	Standard deviation	0.010	0.025	0.017
	Coefficient of variation (%)	0.49	1.24	0.85
2.50 ug/ml - P	Mean	2.50	2.51	2.49
	Standard error	0.005	0.004	0.004
	Standard deviation	0.013	0.011	0.011
	Coefficient of variation (%)	0.52	0.46	0.46
3.00 ug/ml - P	Mean	2.99	3.00	2.97
	Standard error	0.002	0.005	0.007
	Standard deviation	0.005	0.014	0.021
	Coefficient of variation (%)	0.16	0.47	0.69
3.50 ug/ml - P	Mean	3.50	3.52	3.51
	Standard error	0.003	0.006	0.004
	Standard deviation	0.01	0.02	0.01
	Coefficient of variation (%)	0.27	0.49	0.34
4.00 ug/ml - P	Mean	4.01	4 01	4.01
	Standard error	0.004	0.011	0.004
	Standard deviation	0.01	0.03	0.01
	Coefficient of variation (%)	0.30	0.79	0.29
4.50 ug/ml - P	Mean	4.52	4.53	4.51
	Standard error	0.013	0.007	0.016
	Standard deviation	0.04	0.02	0.04
	Coefficient of variation (%)	0.81	0.41	0.98
5.00 ug/ml - P	Mean	5.00	5.02	4.94
	Standard error	0.002	0.008	0.010
	Standard deviation	0.01	0.02	0.03
	Coefficient of variation (%)	0.14	0.44	0.58

concentration in the sample solution. Only for the measurement of 0.05µg ml^{-1} concentration with the 200µl loop can the mean be considered to be unacceptable. This is close to the detection limit stated by the manufacturers (0.01mg L^{-1}), however it is of concern that the largest volume loop, supposedly the most sensitive, had the greatest discrepancy. Standard deviation values behave similarly, the dispersion of results being largest for the lowest concentrations. It can be considered that if a standard deviation value is more than a third of the mean then the dispersion is so great as to cast doubts on the validity of the measurements. On no occasion is the standard deviation greater than a twentieth of the mean, so these results can be considered to be accurate. The coefficient of variation is a useful method to compare variation within groups of data with widely differing means. For these results the coefficients calculated are low throughout, though become slightly larger as the detection limits are reached. The measurements for 0.05µg ml^{-1} aside, there are no discernible differences between the three loops.

The reproducibility of the machine can be discerned from standard errors of the groups of data. The standard errors measured in this test range from 0.001 to 0.017µg/ml.

3.8 Cost

If the initial purchase of the machine is not considered (£18,000), cost per sample is low. Running costs are at less than 0.5 pence per sample.

3.9 Conclusions

Under these test conditions the "Perstorp Flow Solution 3000" measures orthophosphate in solution to an accuracy of roughly 1%, with mean standard errors of 0.2% of the mean, and coefficients of variation of less than 0.5% of the mean. There are little differences apparent between the three loop volumes, all providing acceptable results over the ranges tested (5.0 - 0.05µg ml^{-1}). This range is similar to that suggested by the manufacturer but is not quite so sensitive.

Since results can only be as accurate as the standards that are initially used, care must be taken in their preparation.

3.10 Notes on the use of FIA

It is important to note the following:

All reagents and samples used must be free from particulate matter, the tubes and detector cell are narrow bored, minute particles (dust from the atmosphere, fibres from filter papers) can cause anomalous results.

Interferences from ferric iron over 50mg L^{-1}, copper over 10mg L^{-1} and silica over 10mg L^{-1} occur with this method. These interferences preclude the analysis of samples derived from sodium carbonate fusion analyses.

The manifold tubes have a limited life and are expensive ≅ £40.00 for 12. They become mis-shapen with use (estimated 200 hours lifespan) so reducing the accuracy of analysis.

Set up time is roughly an hour, before which the baseline is unsettled.

The associated software, while being Windows compatible, (results files saved as text files) has limitations. There is no file overwriting facility, and application errors often throw the user out of the system once a run has been completed, (all results are saved though). Print facility is not always available or active.

Alkaline extractions (sodium bicarbonate) need to be acidified before analysis.

APPENDIX IV: A COMPARISON OF FIELD METHODS FOR P MEASUREMENT

4.1. Introduction

The measurement of phosphorus in the soil as a technique to aid the location, delineation and internal investigation of archaeological sites has been developing since the first work by Arrhenius in the 1930s (Bethel and Mate, 1989). The measurement of total P (P_{tot}) using a variety of methods in the laboratory has been established as a standard procedure. However a great deal of time is saved if a method of P analysis can be used in the field to locate areas of interest and guide the sampling before an area is selected in which to concentrate the sample collection. One such field method is the phosphate spot test developed by Eidt (1973, 1977) as described below. This method of prospection has now been widely used (Bakkevig, 1980, 1982; Hammond, 1983; and Bethel & Mate, 1989) but does have some drawbacks.

4.2 Problems with the Eidt spot test

4.2.1 The level of P in the sample is related to the appearance, extent and intensity of a blue colour on a test filter paper. The results can be recorded on a scale of 5 or 6 points. However, this description of the colour is subjective, and tests by Woods, (1975 in Hammond, 1983) show that 17% of samples from a test set were estimated to be in different P classes by different workers.

4.2.2 The reproducibility of results can be poor, Schwarz, (1967) has shown that a small increase in quantity of sample or reagents used can increase a samples P rating.

4.2.3 The P extraction in the spot test only releases a small proportion of the P_{tot} present, and this might not correlate closely to any anthropogenic inputs, although in general the higher the P_{tot} the higher the P recorded in the Eidt spot test.

4.2.4 The method might not be suitable for all soil types, and different proportions of P will be extracted from different soil series. Soils with strong P fixative properties do not release much P for the spot test.

These problems with the spot test can be resolved by analysing a proportion of samples in the laboratory and calibrating the field results.

A simple method for phosphate analysis in the field using 'phosphate indicator sticks' has recently been developed. These were initially produced for the measurement of orthophosphates in solution, but with the addition of a simple extraction step, they can be used for soils. The strips are sold with a "barcode" of calibration colours for comparison, and potentially could improve the problems of precision and comparison of colour development, extent and intensity, which are associated with the Eidt spot test. The results from the 'Quantofix' phosphate test kit produced by Macherey-Nagel and the Eidt spot test, have been compared for a small number of soil samples, and also the results contrasted with those for laboratory measured available phosphorus (P_{ext}) and P_{tot}.

4.3 Methods

Levels of phosphorus were measured in 9 homogenised soil samples from three sites, using the Eidt spot test and Quantofix test strips, as described below. P_{tot} and P_{ext} were measured using the perchloric acid digestion (Sommers & Nelson, 1973) and an acetic acid extraction methods respectively. In both cases orthophosphate was measured using a Perstorp "Flow Solution 3000" flow injection analyser.

4.3.1 Eidt spot test method.

Reagent A: 5g ammonium molybdate is dissolved in 100ml of distilled water to which 30ml of 5N HCl is added.

Reagent B: 0.5g ascorbic acid dissolved in 100ml of distilled water, prepared freshly each day.

50mg of soil is placed on the centre of phosphate free filter paper, 2 drops of reagent A are added followed, 30 seconds later by 2 drops of reagent B. A blue ring forms, and its size and colour traits are related to the amount of P in the sample. The time the colours appears, its intensity, and the size of the ring after 2 minutes should be recorded. To make a permanent record the filter papers can be washed in saturated sodium citrate solution after 2 minutes which halts the

reaction.

4.3.2 *Quantofix P strip test*

The Quantofix test kit consists of reagent A (1N nitric acid), reagent B, 100 test strips and a test tube. Shake 1ml of soil with 5mls of reagent A for 2 minutes, place 6 drops of reagent B into the supplied test tube. Place the test strip into the sample tube for 15 seconds, remove and shake off any excess liquid, place test strip into the test tube with reagent B for 15 seconds, remove and shake off any excess liquid. After 60 seconds compare the colour of the test strip with the indicator colour scale on the side of the carton.

4.4 Results

Table 1: Results of P tests for 9 soils; P_{tot}, P_{ext}, & P_{quan} in $\mu g\ g^{-1}$; Eidt test rated 1-5.

	Sample Number								
	1	2	3	4	5	6	7	8	9
P_{tot}	400	560	940	2060	1750	1170	2850	3850	3760
P_{ext}	1.43	2.64	2.62	6.12	11.83	1.2	300	180	170
P_{quan}	200	320	40	200	200	40	400+	400+	400+
P_{eidt}	3	3	1	3/4	3/4	2	5	5	5

Table 2: Correlation matrix of results

	P_{tot}	P_{ext}	Quantofix
P_{ext}	0.828**		
Quantofix	0.742*	0.804**	
Eidt	0.829**	0.755*	0.863**

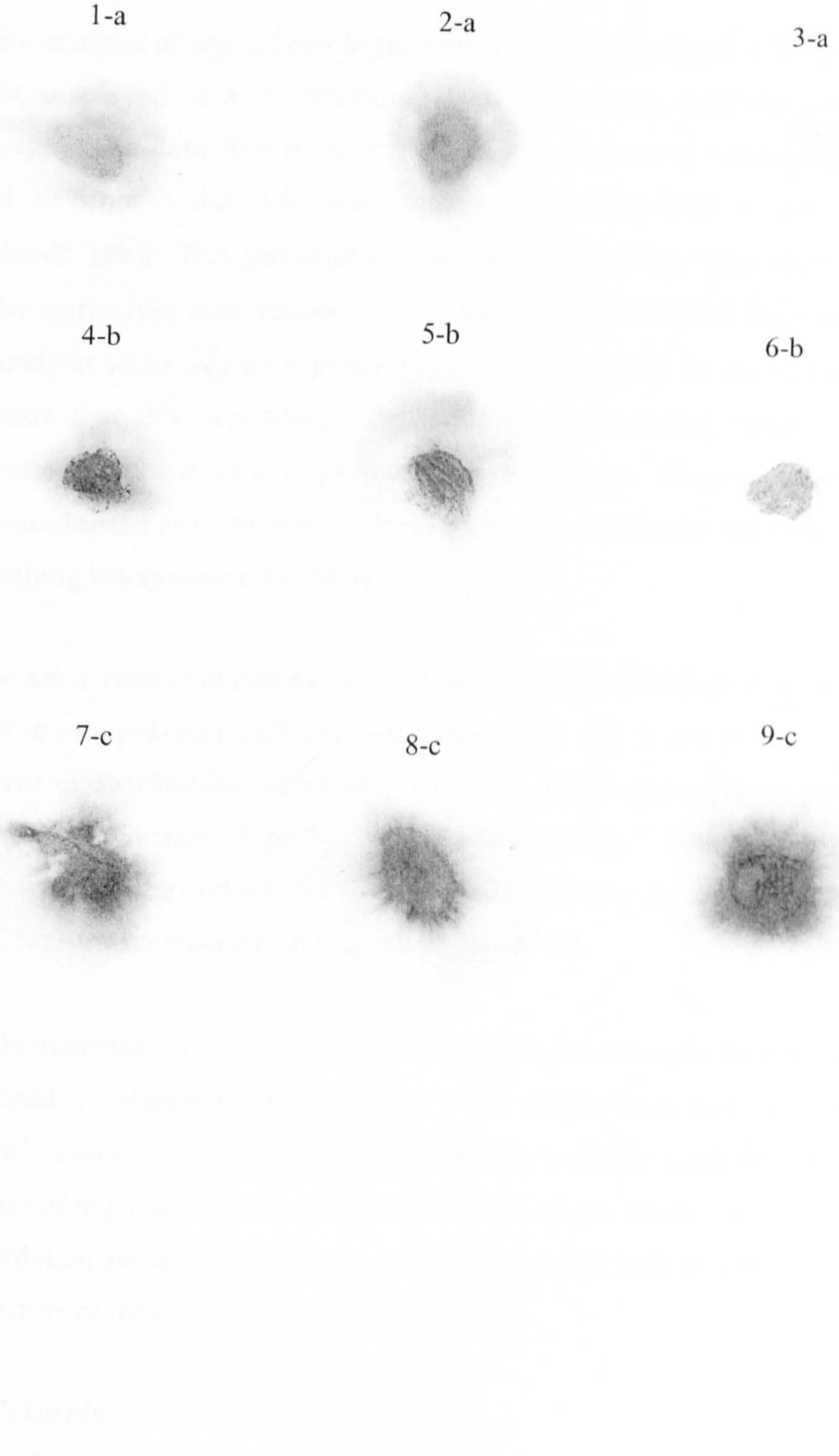
4.5 Discussion and conclusions

The results show significant correlations between all the methods of P analysis, with the best correlation between the Eidt spot test and the Quantofix phosphate strips. It is likely that they are measuring the same portion of P_{tot}, that which is easily extracted in acid. Both methods have advantages, the filter papers from the Eidt method can be saved to form a permanent record, so

further comparisons can be made. The Quantofix method is more convenient for field use, the test strips are less affected by poor weather conditions than the filter papers used for the Eidt test. However, once the colour of the Quantofix strip has been recorded the colour change continues so no permanent record can be made. The method of reading the colour off the Quantofix box is less subjective than the Eidt spot test and it only considers colour, not time of colour appearance and extent of colour, so provides a much simpler and more reproducible method. Both methods still create interpretation problems however, and no phosphorus test can reliably indicate high P values due to anthropomorphic deposits.

Phosphate test strips are a useful alternative to the Eidt spot test, reducing the subjectivity and improving the reproducibility of any field soil P survey. Both methods are dependent on the soil conditions, as field samples tend to be measured by volume rather than weight, and it is recommended that a selection of samples from each set of analyses are also analysed in a laboratory.

Figure 1: Eidt spot test filter papers



APPENDIX V: MAPPING

5.1 Introduction

In the analysis of any archaeological phosphorus (P) survey it is usual for the data to be displayed as a P distribution map generated from the array of samples collected. The data first need interpolating, which is a "mathematical technique used to smooth out data sets without distorting their meaning or validity" (Uniras©, 1990). This generates a continuous surface from the original discrete data set by estimating data values at the nodes of a dense grid. Each estimated value depends in some way on the surrounding original data values and the assumption is made that this dependency decreases with increasing distance. The grid of estimated values is used to produce a contour map. Original data values can be honoured using exact interpolation methods or modified to even out the data using smoothing interpolation methods.

There are a variety of computer mapping packages which provide the user with a range of interpolation methods and options, and which can produce quite different patterns in distribution, which may affect the interpretation of the results. For this example the "Surface Mapping for Windows Package" Winsurf (Golden Software, 1993) was utilised, which provides six interpolation methods, plus a large scale trend analysis method which will not be described.

The six interpolation methods will be examined for a sample data set and the results discussed in relation to their patterns. The distribution map must represent the original dataset closely, and should produce simple contours that enable the location of high and low areas, and define the trends in the data set. On this basis interpolation methods within the Winsurf package will be recommended for the production of distribution maps.

5.2 Methods

Twenty five samples were collected on a coarse 10m interval grid using a standard 2.5cm Ø soil auger to a depth of 10cm. Total phosphorus (P_{tot}) was measured in a sub-sample of the air-dried, sieved to <2mm material which was ground to <0.1mm, before digestion using a modified version of the rapid perchloric acid

digestion method of Sommers and Nelson (1972). Orthophosphate was measured in the digested samples using a Perstorp "Flow Solution 3000" flow injection analyser employing the colorimetric method of Murphy and Riley, (1962). The P_{tot} values and their location on the grid are displayed in figure 1. P_{tot} for this data set has a mean of 1860 $\mu g\ g^{-1}$, with a range of 1490-2480 $\mu g\ g^{-1}$, and a standard deviation of 224 $\mu g\ g^{-1}$.

This data set is used to demonstrate the results from a number of interpolation methods calculated using the Winsurf mapping package and shown in figure 2. A small data set was chosen for clarity and brevity.

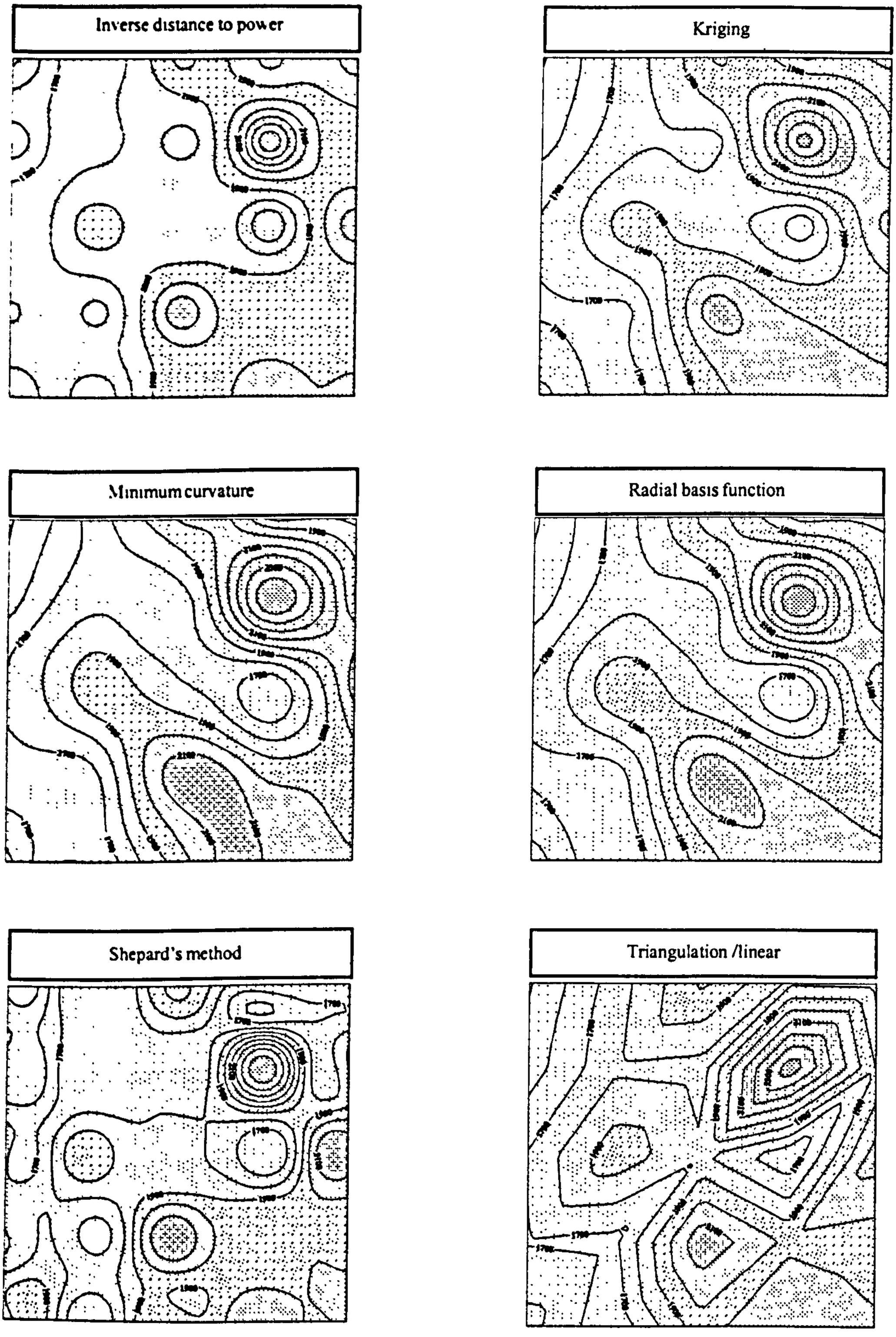
Figure 1. Position of P_{tot} ($\mu g\ g^{-1}$) values on grid

1490	1750	2020	1780	1770
1550	1780	1760	2480	1900
1710	1970	1810	1610	2150
1690	1670	2180	1980	1940
1840	1620	1960	2090	2020

5.3 Interpolation methods.

5.3.1 Inverse distance to a power. This can be an exact or a smoothed interpolator. Grid nodes are assigned a weight, proportional to the inverse of the distance to the specified power of the data point, from the original grid point. The user has the control over a power parameter to adjust how a weighting factor drops off as the distance from an original data point increases. This interpolation method can produce "bulls eyes" surrounding the observations where the grid nodes align with the data points. A smoothing parameter reduces this "bulls eye" effect by smoothing the interpolated grid.

Figure 2: Total P distribution maps produced using six interpolation methods



5.3.2 **Minimum curvature.** This is a widely used interpolation method where the smoothest possible surface is generated while the original data is honoured as closely as possible. Minimum curvature is described as a linearly elastic plate passing through each of the original data points with a minimum of bending.

5.3.3 **Shepard's method.** This method uses an inverse distance weighted least squares method in a similar manner to the inverse distance to a power method. The use of least squares can reduce the "bulls eye" effect.

5.3.4 **Triangulation with linear interpolation.** This method draws lines between data points creating a patchwork of triangles over the grid surface. The original data points are honoured closely and define the tilt and elevation of the triangles. If data sets are sparse distinctly triangular facets emerge.

5.3.5 **Radial basis functions.** This applies chosen functions to the data set and attempts to honour the original data exactly. The functions used define optimal sets of weights to apply to data points for each grid node.

5.3.6 **Kriging.** This attempts to address trends which are suggested in the data, perhaps connecting high points rather than isolating them. It is commonly used in geostatistics for estimating the values at unsampled places of properties that vary in one, two or three dimensions, from sparse sample data. To do this a sample variogram is computed from the data and a model fitted to the values of this variogram. The model then enables the estimation of values at unsampled places. Where kriging is used for interpolation, the type of kriging, its configurations and the type of variogram must be stated. A map of kriging errors should also accompany each map of concentration.

5.4 Discussion and Conclusions

The maps can be divided into three groups by the patterns they produce from the original data set. Inverse distance to a power and Shepard's method both produce circular "bulls eye" patterns, inverse distance to a power being less circular than Shepard's method. Trends are not highlighted and high and low P_{tot} levels are

isolated. Triangulation with linear interpolation produces a distinctly triangular pattern for this data set which isolates areas of similar value which other interpolation methods link up. It is likely that this method suffers from an inadequate number of sample points.

The final three interpolation methods, minimum curvature, kriging and radial basis function produce smoother interpolated maps showing similar features. The kriged interpolation is the simplest, however, kriging has a number of drawbacks. To use a kriging interpolation method correctly for any data set, a graphical representation of the spatial variation of the data set, known as a semi-variogram, needs to be plotted. Once plotted, a model is used to define the structure and shape of the semi-variogram, and this model is chosen as one of the kriging functions. The process of constructing a variogram from a data set and fitting models is complex and a good introduction to the topic can be found in Webster and Oliver's textbook *"Statistical methods in land use survey"*, (1990). A variogram needs roughly 150 randomly selected sample points to accurately represent the spatial variation present (Webster & Oliver, 1992). This precludes its use for the data set given here and for many archaeological survey studies. It is important to note that some mapping packages use kriging as a default interpolation method which is incorrect. The use of kriging without first producing variograms means that assumptions are being made which might not be accurate.

The P_{tot} distribution maps produced with minimum curvature interpolation and radial basis functions are quite similar to the kriged map, and these methods make fewer assumptions of the data. Both these methods produce realistic maps and the minimum curvature interpolation method is recommended for the production of simple distribution maps as it is a simpler model than the radial basis functions interpolation. In the discussion of soil characteristic distribution, the location, spread and value of the actual data points must be considered, so that a reasoned judgement can be made as to the validity of the interpolated map.

REFERENCES

Anderson, C.A. 1973. *Microprobe Analysis*. Wiley - Interscience, New York.

Anderson, G. 1980. Assessing organic phosphorus in soils. In: *The Role of Phosphorus in Agriculture*. (eds. F.E. Khasawneh, E.C. Sample & E.J. Kamprath), pp. 411-431, American Society of Agronomy, Madison, Wisconsin, USA.

Anderson, J.M. 1976. An ignition method for determination of total phosphorus in lake sediments. *Water Research,* **10**, 329-331.

Avery, B.W. 1990. *Soils of the British Isles*. CAB International, Wallingford, UK.

Bailey, T.C. & Gatrell, A.C. 1995. *Interactive spatial data analysis*. Longman Scientific & Technical. England.

Bakkevig, S. 1980. Phosphate analysis in archaeology: problems and recent progress. *Norwegian Archaeological Review*, **13**, 73-100.

Bakkevig, S. 1982. Three dimensional field mapping of phosphate content. PACT (Rixensart, Belg.), **7**, Part 2, 279-284.

Balaam, N.D. & Porter, H.M. 1982. The phosphate surveys in the Shaugh Moor project: a fourth report. Environment, Context and Conclusion. *Proceedings of the Prehistoric Society*, **48**, 215-219.

Ball, D.F. 1964. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *Journal of Soil Science*, **15**, 84-92.

Barber, S.A. 1984. *Soil Nutrient Bioavailability - A mechanistic approach*. Wiley - Interscience, New York.

Bascomb, C.L. 1974. Physical and chemical analyses of <2mm soil samples. In: *Soil Survey Laboratory Methods*, Technical monograph No 6. (eds. B.W. Avery & C.L. Bascomb) pp. 14-41, Harpendon press.

Beckett, P.H.T. & Webster, R. 1971. Soil variability: a review, *Soils and Fertilisers*, **34**, 1-15.

Bethel, P. & Mate, I. 1989. The use of phosphate analysis in archaeology: a critique. In: *Scientific Analysis in Archaeology* (ed. J. Henderson), pp. 1-29, OUC for Archaeology, Oxbow, Oxford, England.

Binkley, D. 1986. *Forest Nutrition Management*. Wiley-Interscience, New York.

Birks, L.S. 1963. *Electron Probe Microanalysis*. 2nd Edn. Wiley - Interscience, New York.

Black, C.A. 1957. *Soil-Plant Relationships*. Wiley. New York

Bouldin, D.R. & Black, C.A. 1954. Phosphorus diffusion in soils. *Soil Science Society of America Journal*, **18**, 255-259

Briggs, D. & Courtney, F. 1985. *Agriculture and the Environment: the physical geography of temperate agriculture systems*. Longman scientific and technical, UK.

Cathcarte, J.B. 1980. World phosphate reserves and resources. In: *The Role of Phosphorus in Agriculture* (eds. F.E. Khasawneh, E.C. Sample & E.J. Kamprath), pp. 1-18, American Society of Agronomy, Madison, Wisc, USA.

Cavanagh, W.G., Buck, C.E. & Litton, C.D. 1988. The interpretation of noisy data from archaeological field survey: phosphate analysis. *Environmental Geochemistry and Health*, **10**, (3/4), 92-95.

Cescas, M.P., Tyner, E.H. & Syers, J.K. 1970. The distribution of apatite and other mineral inclusions in rhyolitic ash and beach sands from New Zealand. An electron microprobe study. *Journal of Soil Science*, **21**, (1). 78-84.

Cescas, M.P., Tyner, E.H. & Gray, L.J. 1968. The electron microprobe X-ray analyser and its use in soil investigations. *Advances in Agronomy*, **20**, 153-198.

Chang, S.C. & Jackson, M.L. 1957. Fractionation of soil phosphorus. *Soil Science*, **84**, 133-144.

Cho, C.M. 1991. Phosphate transport in calcium-saturated systems: I. Theory. *Soil Science Society of America Journal*, **55**, 1275-1281.

Coffin, D.E. 1963. A method for the determination of free iron in soils and clays. *Canadian Journal of Soil Science*, **43**, 7-17.

Conway, J. S. 1983. An investigation of soil phosphorus distribution within occupation deposits from a Romano-British hut group. *Journal of Archaeological Science*, **10**, 117-128.

Craddock, P.T., Gurney, D., Pryor, F. & Hughes, M. 1985. The application of phosphate analysis to the location and interpretation of archaeological sites. *The Archaeological Journal*, **142**, 361-376.

Dalal, R.C. 1977. Soil organic phosphorus. *Advances in Agronomy*, **29**, 83-113.

Dauncey, K.D.M. 1952. Phosphate content of soils on archaeological sites. *The Advancement of Science*, **9**, 33-36.

Davidson, D.A. 1982. Soils and man in the past. In: *The Principles and Applications of Soil Geography*. (eds. E.M. Bridges, & D.A. Davidson), pp. 1-27, Longmans.

Dick, W.A. & Tabatabai, M.A. 1977. An alkaline oxidation method for determination of total phosphorus in soils. *Soil Science Society Of America Journal*, **41**, 511-514.

Dojlido, J.R. & Best, G.A. 1993. *Chemistry of Water and Water Pollution*. Ellis Horwood Limited, Hemel Hemstead

Eastoe, J.E. 1961. The chemical composition of bone. In: *The Biochemists Handbook.* (ed. C. Long), pp. 715-720, E & F.N. Spon Ltd, London.

Edwards, K.J., Hammond, F.W. & Sims, A. 1983. The medieval settlement of Newcastle Lyons, County Durham. An interdisciplinary approach. *Proceedings of the Royal Irish Acadamy,* **83**, 351-376.

Eghball, B., Sander, D.H. & Skopp, J. 1990. Diffusion, adsorption, and predicted longevity of banded phosphorus fertiliser in three soils. *Soil Science Society of America Journal,* **54**. 1161-1165.

Eidt, R.C. 1977. Detection and examination of anthrosols by phosphate analysis. *Science,* **197**, 1327-1333.

Fitzpatrick, E.A. 1984. *Micromorphology of soils.* Chapman & Hall Ltd., London.

Fogg, D.N. & Wilkinson, N.T. 1958. The colorimetric determination of phosphorus. *Analyst,* **83**, 406-414.

Foy, R.H. & Bailey-Watts, A.E. 1998. Observations on the spatial and temperal variation in the phosphorus status of lakes in the British Isles. *Soil Use and Management,* **14**, 131-139.

Freese, D., Van-De-Zee, S.E.A.T.M. & Van Riemsdijk, W.H. 1992. Comparison of different models for phosphate sorption as a function of the iron and aluminium oxides of soils. *Journal of Soil Science,* **43**, 729-738.

Golden Software inc., 1993. *Winsurf: surface mapping for windows.* Release 3.1.

Gordon, C.C. & Buikstra, J.E. 1981. Soil pH, bone preservation and sampling bias at mortuary sites. *American Antiquity,* **46**, 566-571.

Gressel, N. & McColl, J.G. 1997. Phosphorus mineralisation and organic matter decomposition: a critical review. In: *Driven by Nature: plant litter quality and decomposition.* (eds. G. Cadisch. & K.E. Giller), pp.297-309, CAB International, Wallingford.

Hammond, F.W. 1983. Phosphate analysis of archaeological sediments. In: *Landscape Archaeology in Ireland.* (eds. T. Reeves-Smythe & F.W. Hammond), pp.47-80, British Archaeological Report, **116**, 47-80.

Harrison, A.F. 1987. *Soil Organic Phosphorus, A Review of World Literature.* Cab International, Wallingford, Oxon. UK.

Haygarth, P.M. & Jarvis, C.S. 1999. Transfer of phosphorus from agricultural soils. *Advances in Agronomy,* **66**, 196-236.

Haygarth, P.M., Chapman, S.C., Jarvis, S.C. & Smith, R.V. 1998. Phosphorus budgets for two contrasting grassland farming systems in the UK. *Soil Use and Management,* **14**, 160-168.

Hill, D.E. & Sawhney, B.L. 1971. Electron microprobe analysis of soils. *Soil Science,* **112,** 32-38.

Hira, G.S. & Singh, N.T. 1977. Observed and predicted rates of phosphorus diffusion in soils of varying bulk density and water content. *Soil Science Society of America Journal,* **41,** 537-540.

H.M.S.O. 1990. *Flow Injection Analysis. An essay review and analytical methods.* H.M.S.O. London.

Hodgson, J.M. (Ed.) 1976. *Soil Survey Field Handbook.* Soil Survey of England and Wales. Technical monograph No 5, Harpenden.

Hooper, L.J. 1970. The basis of current fertiliser recommendations in England and Wales: soil phosphorus. *Proceedings of the Fertiliser Society,* **118,** 10-12.

Howard, P.F. 1979. Phosphate. *Economic Geology,* **74,** 192-194.

Jackson, M.L. 1958. *Soil chemical analysis,* Prentice - Hall, New Jersey, USA.

Jahnke, R.A. 1992. The phosphorus cycle. In: *Global Biogeochemical Cycles,* (eds. S.S. Butcher, R.J. Charlson, G.H. Orians & G.V. Wolfe), pp. 300-314, Academic Press, London.

Jenkins, D.A. 1994a. Trace element geochemistry in archaeological sites. *Environmental Geochemistry and Health,* **11,** 57-62.

Jenkins, D.A. 1994b. Interpretation of interglacial cave sediments from Pontnewyedd, North Wales: international working meeting on soil micromorphology, Townsville, Queensland.

Jenkins, D.A. 1997. Phosphorus redistribution in cave sediments from the lower Palaeolithic site of Pontnewydd. In: *Archaeological Sciences 1995, Proceedings of a conference on the application of scientific techniques to the study of archaeology,* (eds. A. Sinclair, E. Slater & J. Gowlett), pp 282-286, Oxbow Monograph 64.

Johnes, P.J. & Hodgkinson, R.A. 1998. Phosphorus loss from agricultural catchments: pathways and implications for management. *Soil Use and Management,* **14,** 175-186.

Johnson, A.H. 1956. Examination of soil from Corrimony chambered cairn, Glenurquhart. *Proceeding of the Society of Antiquaries of Scotland,* 88, 200-207.

Johnston, A.E. & Poulton, P.R. 1977. Yields on the exhaustion land and changes in the N, P & K content of the soils due to cropping and manuring, 1852-1975. *Rothamstead experimental station report for 1976,* **2,** 53.

Kalambasa, S.J. & Jenkinson, D.S. 1973. A comparative study of titrimetric and gravimetric methods for the determination of organic carbon in soil. *Journal of the Science of Food and Agriculture,* 24, 1085-1090.

Keeley, H.C.M., Hudson, G.E. & Evans, J. 1977. Trace element contents of human bones in various states of preservation. *Journal of Archaeological Science,* 4, 19-24.

Khasawneh, F.E., Sample, E.C. & Hashimoto, I. 1974. Reactions of ammonium, ortho- and polyphosphate fertilisers in soil: I. Mobility of phosphorus. *Soil Science Society of America Proceedings,* 38, 446-450.

Khasawneh, F.E., Sample, E.C. & Kamprath, E.J. 1980. *The Role of Phosphorus in Agriculture.* American Society of Agronomy. Madison, Wisconsin, USA.

Larson, S. 1967. Soil phosphorus. *Advances in Agronomy,* 19, 151-210.

Lewis, E.T. & Racz, G.J. 1969. Phosphorus movement in some calcareous and non-calcareous Manitoba soils. *Canadian Journal of Soil Science,* 49, 305-312.

Lindsay, W.L. & Vlek, P.L.G. & Chien, S.H. 1989. Phosphate Minerals. In: *Minerals in Soil Environments.* (eds. J.B. Dixon & S.B. Weed), pp. 639-672, 2nd edn., Soil Science Society of America, Madison.

Macherey-Nagel. 1994. *Quantofix® Phosphate.* GmbH & Co. Duren, Germany.

Mahtab, S.K., Godfrey, A.R.S. & Thomas, G.W. 1971. Phosphorus diffusion in soils: I. The effect of applied P, clay content, and water content. *Soil Science Society of America Proceedings,* 35, 393-397.

Marschner, H. 1995. *Mineral Nutrition of Higher Plants.* Academic Press, Cambridge.

McCawley, J.C. & McKerrell, H. 1972. Soil phosphorus levels at archaeological sites. *Proceedings of the Society of Antiquities of Scotland,* 104, 301-306.

Ministry of Agriculture, Fisheries & Food, 1986. Reference book RB427; *The Analysis of Agricultural Materials* (3rd edition), London, HMSO.

Morgan, M.F. & Jacobson, H.G.M. 1942. In: Black, C.A. 1957. *Soil plant relationships.* pp. 251, John Wiley and Sons, New York.

Muir, J.W. 1952. The determination of total phosphorus in soil. *Analyst,* 77, 313-317.

Munsell colour, 1975. *Munsell Soil Colour Charts.* Macbeth division of Kollmorgan corp., Baltimore, USA.

Murphy, C.P. 1986. *Thin Section Preparation of Soils and Sediments.* A. B. Academic, Berkhamsted.

Murphy, J. & Riley, J.P. 1962. A modified single solution method for the determination of phosphorus in natural waters. *Analytical Chimica Acta,* 27, 21-26.

Perstorp Analytical. 1995. *Perstorp Analytical F.I.A. Flow Solution 3000 and Tecator Aquatec.* Perstorp Ltd. Berkshire.

Powlson, D.S. 1998. Phosphorus, Agriculture and Water Quality. *Soil Use and Management*, **14**, 123.

Price, T.D. 1989. Bones, chemistry and the human past. In: *The Chemistry of Prehistoric Human Bone*. (ed. T.D. Price), pp. 1-9, Cambridge University Press.

Proudfoot, B. 1976. The analysis and interpretation of soil phosphorus. In: *Geoarchaeology*, (eds. D.A. Davidson. & M.L. Shackley), pp. 93-113, Duckworth and Co, London.

Qureshi, R.H. & Jenkins, D.A. 1978. Electron probe micoanalysis of calcite grains containing phosphorus in soil. *Soil Science Society of America Journal*, **42**, 703-705.

Qureshi, R.H., Jenkins, D.A. & Davies, R.I. 1978. Electron probe micro-analytical studies of phosphorus distribution within soil fabric. *Soil Science Society of America Journal*, **42**, 698-703.

Qureshi, R.H. & Jenkins, D.A. 1987. Concentration of phosphorus and sulphur at soil ped surfaces. *Journal of Soil Science*, **38**, 255-265.

Qureshi, R.H., Jenkins, D.A., Davies, R.I. & Rees, J.A. 1969. Application of microprobe analysis to the study of phosphorus in soils. *Nature*, **221**, 1142-1143.

Reed, S.J.M. 1996. *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*. Cambridge University Press, GB.

Richey, J.E. 1983. The phosphorus cycle. In: *The Major Biogeochemical Cycles and Their Interactions*. (eds. B, Bolin & R.B. Cook), pp. 51-56, Scientific Committee on Problems of the Environment. John Wiley & Sons, New York.

Rottlander, R.C.A. 1976. Variation in the chemical composition of bone as an indicator of climatic change. *Journal of Archaeological Science*, **3**, 83-88.

Rudeforth, C.C., Hartnup, R., Lea, J.W., Thompson, T.R.E. & Wright, P.S. 1984. *Soils and Their Use in Wales*. Soil Survey of England and Wales Bulletin 11, Harpendon Press.

Runge, E.C.A. & Riecken, F.F. 1966. Influence of natural drainage on the distribution and forms of phosphorus in some Iowa prairie soils. *Soil Science Society of America Proceedings*, **30**, 624-630.

Russell, E.J. 1971. *The World of Soil*. Collins, London.

Schwarz, G.T. 1967. A simplified chemical test for archaeological fieldwork. Archaeometry, 10, 57-63.

Sharma, P.K., Sinha, A.K. & Chaudhary, T.N. 1985. Movement of surface and deep-placed phosphorus in a sandy loam soil in relation to initial soil wetness, amount of water applied, and evaporation potentials. *Soil Science*, **140/4**, 256-263.

Sharpley, A.N., Tiessen, H. & Cole, C.V. 1987. Soil test phosphorus and forms extracted as a function of soil pedogenesis. *Soil Science Society of America Journal,* **51,** 362-365.

Sherrell, C.G. & Saunders, W.H.M. 1966. An evaluation of methods for the determination of total phosphorus in soils. *New Zealand Journal of Agricultural Research,* **9,** 972-979.

Sieveking, G.G., Longworth, I.H., Hughes, M.J. & Clark, A.J. 1973. A new survey of Grime's Graves. *Proceedings of the Prehistoric Society,* **39,** 182-218.

Sillen, A. 1989. Diagenesis of the inorganic phase of cortical bone. In: *The Chemistry of Prehistoric Human Bone.* (ed. T.D. Price), pp. 211-227, Cambridge University Press.

Smeck, N.E. 1985. Phosphorus dynamics in soils and landscapes. *Geoderma,* **36,** 185-199.

Smeck, N.E. & Runge, E.C.A. 1971. Phosphorus availability and redistribution in relation to profile development in an Illinois landscape segment. *Soil Science Society of America Proceedings,* **35,** 952-959.

Sommers, L.E. & Nelson, D.W. 1972. Determination of total phosphorus in soils: a rapid perchloric acid digestion procedure. *Soil Science Society of America Proceedings,* **36,** 902-906.

Stevenson, F.J. 1986. *Cycles of Soil: carbon, nitrogen, phosphorus, sulphur, micronutrients.* John Wiley and Sons, New York.

Tate, K.R. 1985. Soil phosphorus, pp 329-365. In: *Soil Organic Matter and Biological Activity.* (eds. D. Vaughan. & R.E. Malcolm), pp. 329-365, Developments in plant and soil sciences **16.** John Wiley & Sons, New York.

Tousimis, A.J. and Marton, L. 1969. *Electron Probe Microanalysis.* Academic press, London.

Uniras. 1990, *Unimap Users Manual.* Version 6.0, Soborg, Denmark: Uniras A/S

Walker, T.W. & Adams, A.F.R. 1958. Studies on soil organic matter. Influence of phosphorus content of parent material on accumulations of C, N, S and P-organic in grassland soils. *Soil Science,* **85,** 307-318.

Walker, T.W. & Syers, J.K. 1976. The fate of phosphorus during pedogenesis. *Geoderma,* **15,** 1-19.

Wall, L. 1997. *PERL: Practical Extraction and Report Language.* O'Reilly & Associates Inc. USA.

Webster, R. & Oliver, M.A. 1990. *Statistical Methods in Soil and Land Resource Survey.* Oxford University Press.

Webster, R. & Oliver, M.A. 1992. Sample adequately to estimate variograms of soil properties. *Journal of Soil Science*, **43**, 177-192.

Westheimer, F.H. 1987. Why nature chose phosphates. *Science*, **235**, 1173-1178.

White, R.E. 1997. *The Principles and Practice of Soil Science.* 3rd edition. Blackwell Science, Oxford.

White, E.M. & Hannous, L.A. 1983. Chemical weathering of bone in archaeological sites. *American Antiquity*, **48**, 316-322.

Wild, A. 1988. *Russell's soil conditions and plant growth.* Longman scientific and technical, U.K.

Williams, E.G. & Saunders, W.M.H. 1956. Distribution of phosphorus in profiles and particle size fractions of some Scottish soils. *Journal of Soil Science*, **7**, 90-108.

Williams, J. & Jenkins, D.A. 1999. Investigation of a corpus of bronze age cinerary urns from the Isle of Anglesey. *Proceedings of the Prehistoric Society*, forthcoming.

Wright, C.H. 1939. *Soil Analysis, a handbook of physical and chemical methods.* 2nd edition. Thomas Murby & Co., London.