

DISTRIBUTION AND BIOGEOCHEMICAL CYCLING OF TRACE METALS  
IN SOILS AT AN ABANDONED LEAD MINING AND SMELTING  
COMPLEX (PRIDDY, SOMERSET, ENGLAND).

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## ABSTRACT

The spatial distribution of lead, zinc, cadmium, copper, iron and manganese was investigated in the soils of an abandoned lead mining and smelting complex near Priddy, in the Mendip Hills, Somerset. Soils were collected at 0-200 mm and 200-400 mm depths over the period February 1995 to April 1997.

The study area was shown to be one of the most intensely Pb-enriched historic mining and smelting sites on a regional and national level. The concentration of Pb in the soils of the study area ranged from 1 394 to 138 800  $\mu\text{g g}^{-1}$  at 0-200 mm, and from 180 to 171 688  $\mu\text{g g}^{-1}$  at 200 to 400 mm. The concentration of Zn ranged from 28 to 10 349  $\mu\text{g g}^{-1}$  at 0-200 mm, and from 36 to 8 089  $\mu\text{g g}^{-1}$  at 200 to 400 mm. The concentration of Cd ranged from 1 to 12  $\mu\text{g g}^{-1}$  at 0-200 mm, and from 1 to 11  $\mu\text{g g}^{-1}$  at 200 to 400 mm. The concentration of Cu ranged from 7 to 182  $\mu\text{g g}^{-1}$  at 0-200 mm, and from 5 to 206  $\mu\text{g g}^{-1}$  at 200 to 400 mm. The concentration of Fe ranged from 5 060 to 59 754  $\mu\text{g g}^{-1}$  at 0-200 mm, and from 10 465 to 67 035  $\mu\text{g g}^{-1}$  at 200 to 400 mm. The concentration of Mn ranged from 2 500 to 3 769  $\mu\text{g g}^{-1}$  at 0-200 mm, and from 66 to 3690  $\mu\text{g g}^{-1}$  at 200 to 400 mm.

The greatest concentrations of Pb, Zn, Cd, Cu, Fe and Mn were present in the study area in the wastes associated with the beneficiation processes carried out during the final stage of the Mendip lead industry (1857-1908), when the wastes of Roman and Mediaeval operations were reworked. While most of the wastes from 1857-1908 were present as clearly identifiable tailings piles, previously unrecognised areas contaminated by beneficiation wastes were identified.

Based on the Greater London Council Contamination classification, 88.5% of the soil samples in the study area were contaminated to unusually heavily contaminated by Pb. Unusually heavy contamination by Pb was present in 44% of the soils ( $>10\,000\ \mu\text{g g}^{-1}$ ), and by Zn in 15% of the soils ( $>5\,000\ \mu\text{g g}^{-1}$ ). A ranking of the percentage of samples classified as contaminated showed that in terms of magnitude of contamination, the decreasing order for the study area was Pb>Zn>Cd>Mn>Cu.

The five soil types present in the study site were identified as the Maesbury, Thrupe, Ashen and Nordrach Series and Tailings, the wastes associated with beneficiation processes. Representative soils of the five types at 0-200 mm and 200-400 mm depths were collected and analysed each month between September 1998 and August 1999 to assess the temporal variation in Pb, Zn, Cd, Cu, Fe and Mn concentration. The general trend for Pb, Zn, Cu, Fe and Mn in the Maesbury and Thrupe soils and the Tailings was an overall decrease in concentration over the sampling period. The concentration of soil Pb, Zn and surface Cu also decreased in the Ashen soil, and Pb, Fe and surface Cu in the Nordrach soil.

A ranking of the soil series by % Coefficient of Variance (% CV) in trace metal concentrations at 0-400 mm showed that the degree of variation ranged from 31% CV in the Maesbury series to 11.32% CV in the Nordrach Series, in the following order of magnitude: Maesbury>Ashen>Thrupe>Tailings>Nordrach. Variation in soil trace metal concentrations by % CV for all soil series in the surface horizons showed that the degree of variation ranged from 8.41% CV for Mn to 11.97% CV for Fe in the following order: Mn>Zn>Cd>Pb>Cu>Fe. The variation in soil trace metal concentrations by % CV for all soil series at depth showed that the degree of variation ranged from 22.52% CV for Cu to 14.05% CV for Fe in the following order: Cu>Cd>Zn>Mn>Pb>Fe.

When expressed as a percentage of the Total trace metal concentration, the percentage of EDTA extractable metals were consistently higher in the surface horizons than at depth. The variation was thought to be related to the source of enrichment, the fraction of soil the trace metals were held in, soil pH and hydrology and the availability of trace metals in the surface horizons for plant uptake. The overall ranking of EDTA extractable trace metal concentration as a percentage of Total trace metal concentration for all soil series at both surface and depth was in the following order of magnitude: Pb>Cu>Cd>Mn>Zn.>Fe.

The EDTA extractable Pb as a percentage of the Total Pb was remarkably high in the Thrupe, Ashen and Maesbury soils. In the surface soils, this ranged from 84% to 102%, and at depth (200-400 mm) from 65% to 101%. Possible reasons for anomalous results where EDTA extractable Pb as a percentage of Total Pb

apparently exceeded 100% were discussed. In the Nordrach Series, EDTA extractable Pb ranged from 49% to 81% of Total Pb in the surface soil and from 52% to 69% of Total Pb at depth. The EDTA extractable Pb as a percentage of the Total Pb was lowest in Tailings at 20% to 41% at the surface to 14% to 38% at depth. The high EDTA extractability of Pb in the Thrupe, Ashen and Maesbury soils was thought to be related to the source of enrichment, the soil pH, soil redox reactions, mineral composition and texture and soil hydrology.

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# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 General introduction**

The Mendip Hills, a designated Area of Outstanding Natural Beauty since 1972, were worked for a variety of minerals in the past (Figure 1.1). Silver, zinc, iron, manganese, barytes and small amounts of copper were mined, although in terms of metallurgy, the area is perhaps most famous for its historical lead mines (Gough, 1967). The Mendip lead industry, which operated from before the second century BC until the first decade of the twentieth century, is acknowledged for its uniqueness in character and scale of operation when compared with the industries of other lead producing regions in Britain (Cranstone, 1992). This investigation is concerned with the environmental legacy of lead mining and processing at two of the four historical lead Mineries (ore processing centres) on Mendip, the Chewton and Priddy Mineries, and the adjoining Chewton Warren orefield.

The Chewton Minery, which is centred on ST 3548 1513, lies within an area known as the Priddy Mineries Reserve (Figure 1.2). The Priddy Minery adjoins the Priddy Mineries Reserve immediately to the south and is centred on ST 3545 1505. The Priddy Minery is also sometimes known as St. Cuthbert's. To emphasise its separateness from the Priddy Mineries Reserve, the Priddy Minery will be referred to as St. Cuthbert's from this point forward when discussing the site in a contemporary context.

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Figure 1.2. The study area showing the Priddy Mineries Reserve, St. Cuthbert's and part of the Stockhill Plantation.

The Chewton Warren orefield is now more commonly known as the Stockhill Plantation. The area of Stockhill Plantation of relevance to this study is a strip of approximately 350 m width, situated immediately to the east of the Priddy Mineries Reserve and St. Cuthbert's site (Figure 1.2). Although modern nomenclature will generally be used when discussing the sites in the main body of the study, the original names of Chewton Minery, Priddy Minery and Chewton Warren will be retained when referring to the sites in their historical context. In this study, the term 'historical' refers to the mining and smelting of metals from before the time of Roman conquest of 43 AD, to the first decade of the twentieth century.

Of the estimated 4 000 km<sup>2</sup> of land in England and Wales contaminated by one or more of the metals lead, zinc, cadmium, copper, mercury and arsenic, more than 1 000 km<sup>2</sup> lie within the Mendip region (Thornton, 1983; Davies and Ballinger, 1990). While the rocks and soils in some areas of Britain like Mendip are naturally highly mineralised (Fuge *et al.*, 1991), the main source of metal contamination to the soils of England and Wales is considered to be historical mining and smelting (Thornton, 1983). This occurred because metalliferous ore was subjected to a variety of treatments during historic mining and processing, which caused its metal content to become environmentally labile. In Britain, the historical mining and processing industry was for most of its existence largely unregulated and its technology grossly inefficient. This led to the release of massive emissions of metals at all stages of the process (Davies, 1983). In some mining areas such as Mendip however, there is evidence to suggest that early local legislation to prevent contamination did exist (Bucknell, 1924; Gough, 1967).

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Figure 1.1. Simplified geological map of the Mendip area showing some metal-mining locations (Martin and Fawcett, 1998)

When allowed to escape into the environment, trace metals and their compounds follow natural geochemical pathways until they eventually accumulate in sediments, soils or biomass (Davies, 1983). While the metals zinc, copper, iron and manganese are required by plants and animals as essential micronutrients, some such as lead and cadmium appear to have no known biological function. All, however, are potentially toxic to biota, including humans, in excessive quantities (Thornton, 1983). Because the extent to which metals are released into the environment depends on the efficiency of the industrial processes and technology employed, the pattern of environmental contamination by historic mining and processing was usually very different in character to that caused by modern operations. From the latter quarter of the nineteenth century, metal extraction and smelting operated under increasingly stringent pollution control legislation. More efficient and less polluting technologies were developed to reduce and monitor possible sources of metal contamination. While this has generally resulted in much smaller emissions, because modern operations are often large, there is the potential for their environmental effects to become widespread (Davies, 1983).

In modern mining industries, ore is often processed and smelted in a different region, country or even continent from its point of origin. For example, Britannia Zinc Limited, produces more than 100 000 tonnes of zinc, 50 000 tonnes of lead bullion and 400 tonnes of cadmium each year at its smelter at Avonmouth, Bristol, England. To achieve this, approximately 320 000 tonnes of mineral concentrates (metal-rich powdery material derived from the froth flotation process) are shipped in directly to Avonmouth, or nearby Newport, Gwent, Wales, from Australia, South America, Canada, Alaska, Iran, Scandinavia, and the Republic of Ireland

each year (Britannia Zinc Limited, 2001). On Mendip, historical mining and smelting operations were carried out on a much smaller scale. It has been estimated that during the entire two thousand year period of lead mining on the whole of Mendip, approximately 202 000 tonnes of lead ore concentrate was produced (Green, 1958). From this figure, it was further estimated that this would have yielded approximately 101 000 tonnes of metallic lead (Alabaster, 1982), just twice that produced by Britannia Zinc Limited in one year.

As well as producing on a small scale, the mining and processing of lead ore on Mendip was also carried out within a small area. At the Chewton and Priddy Mineries for example, it was possible for lead ore to be mined, processed and smelted within an area of less than 1 km<sup>2</sup>. The environmental consequences for such areas, including the Chewton and Priddy Mineries, were severe. The industry had a huge physical and geochemical impact on the immediate environment because a relatively small, discrete and already naturally highly mineralised area was subjected to intense perturbation (disturbance) and metal contamination from the full range of mining and metallurgical processes over a period of nearly two thousand years.

Towards the end of the Mendip lead industry, from the mid-nineteenth century onwards, wastes were still often dressed and resmelted at the Chewton and Priddy Mineries, but as the industry further declined, some concentrates (in this case dressed wastes) were sent to other smelters on Mendip, or even to Bristol (Page, 1911; Bucknell, 1924; Gough, 1967). At the end of their productive life in the late nineteenth and early twentieth centuries respectively, the Chewton and

Priddy Mineries, like many historic mining and smelting sites, were simply abandoned. As no legislation was in place at the time of closure to ensure land rehabilitation, the abandoned Chewton and Priddy Mineries exist at the start of the twenty-first century as highly disturbed post-industrial landscapes. Previous studies suggest that the sediments, soils and biota of such sites are often still highly contaminated by the metals they once produced, and have the potential to remain a continuing and important source of trace metal contamination to the surrounding area (Davies, 1983).

## **1.2 Background to the study**

Many investigations have been carried out into the environmental impact of historic lead mining and smelting in Britain, however, some mining and processing regions such as Wales, Derbyshire and the Pennines have received far more attention than Mendip. One of the earliest studies concerning the environmental impact of metalliferous mining in Wales was by Griffiths (1919), who investigated the influence of mines on land and livestock in Cardiganshire. Since the comprehensive study of the impact of the lead industry on the soils and vegetation of the Ystwyth Valley by Alloway (1969), Wales has continued to be well represented in the published literature including work by Alloway and Davies (1971), Davies and Roberts (1975, 1978), Harrison and Roberts (1978), Johnson *et al.* (1978), Davies and White (1981), Jones *et al.* (1983), Paveley (1988), Fuge *et al.* (1989) and Maskell *et al.* (1995). Of the historic lead mining and processing regions in England, studies of the soils and biota of sites in the North of England, especially Derbyshire and the Pennines, have featured largely in the body of published literature. This included work by Shimwell and Laurie

(1972), Bayliss *et al.* (1979), Clark and Clark (1981), Ineson (1981), Shaw (1984), Hadjar (1987), Merry (1988), Cotter-Howells, (1991), Buchanan (1992), Wild and Eastwood (1992) and Maskell *et al.* (1995). In comparison, little has been published concerning investigations into the soils and biota of historic lead mining and processing sites on Mendip.

An early unpublished study by Bucknell (1924) reviewed the history of the Mendip lead industry and described the chemical analysis of some metalliferous ores. The seminal work on the history of the mines of Mendip by Gough (1967) also included references to the chemical composition of ores and mining wastes. Anecdotal descriptions of the environmental impact of lead mining and smelting during the active period of the industry were recounted, and the historical legislative measures taken to minimise the impact on agricultural production by the Mineries Courts were described (Gough. 1967). Workers such as Stenner (1978) had begun to investigate the metal contamination of soils at the abandoned Chewton and Priddy Mineries in conjunction with his work on cave sediments, but the full scale of metal contamination in the Mendip region became apparent with the publication of the work of Webb *et al.* (1978). Webb *et al.* (1978) undertook a large-scale study of trace metals in active stream sediments in England and Wales. This resulted in the production of the *Wolfson Geochemical Atlas of England and Wales*, which was compiled from the analysis of approximately 50,000 samples for elements including lead, zinc, cadmium, copper, manganese, iron, arsenic and cobalt. Webb *et al.* (1978) found that concentrations of lead, zinc, cadmium and arsenic in sediments from the Mendip plateau were among the highest in England and Wales.



The work of Webb *et al.* (1978) stimulated an interest in certain aspects of the environmental geochemistry of the Mendip area (Simms and Morgan, 1988), particularly that of cadmium in the soils around the village of Shipham, a former site of intensive zinc mining and processing during the seventeenth and eighteenth centuries (Page, 1911; Bucknell, 1924; Gough, 1967). The historically important zinc ore of the area was calamine (smithsonite or zinc carbonate  $\text{ZnCO}_3$ ), which contained cadmium as an associated (guest) element. During the mining, processing and roasting of the ore, which took place around the village, cadmium was released to the local environment in high concentrations. The area around Shipham became the focus of several studies between 1979 and 1982 because of the abnormally and uniquely high levels of cadmium present in the soils of the area and the associated health concerns (Marples, 1979; Davies and Ginnever, 1979; Archer, 1980; Marples and Thornton, 1980; Thornton, 1980; Matthews and Thornton, 1980, 1982; Matthews, 1982). This body of work was reviewed by Simms and Morgan (1988) in the Shipham Report.

Cadmium concentrations in the soils in the Shipham area were found to range from  $29 \mu\text{g g}^{-1}$  to  $800 \mu\text{g g}^{-1}$  compared with concentrations of less than  $1 \mu\text{g g}^{-1}$  normally found in uncontaminated soils (Marples, 1979). This had serious health implications for the local population because cadmium in the soils of an area of Japan had been associated with an outbreak of 'itai itai', a disease characterised by severe bone decay (osteomalacia) and kidney damage (renal tubular dysfunction) (Simms and Morgan, 1988). Cadmium concentrations in the soils of Shipham were found to be much higher than those implicated in the Japanese outbreak, with some garden soils in the village containing in excess of  $300 \mu\text{g g}^{-1}$  (Archer, 1980).

Despite the cadmium anomaly, the overall conclusion from the investigations into Cd contamination and its implications for human health at Shipham was that no measurable health effects on the local population could be detected (Simms and Morgan, 1988). The soils and vegetation of the Shipham area continued to attract investigations by workers such as Li and Thornton (1992) and Li (1993), who studied multi-element associations in the soil-plant systems of the mining site, including lead, zinc cadmium and copper, and Lambkin (1999) who used soil from the site to investigate the availability of cadmium to vegetation. While the cadmium in the soils of the region continued to attract attention, there appeared to be relatively little interest in the environmental legacy of the Mendip lead mining and processing sites.

A large-scale general survey of the soils in the Mendip region, with special reference to the contamination from historic metalliferous mining, was carried out by Ginnever (1985) however, using a 2 x 2 km<sup>2</sup> sampling grid. The survey included a small-scale investigation into the soils of the Priddy Mineries Reserve and the St. Cuthbert's site, which consisted of the analysis of seven soil samples for trace metal content. A summary of the work was later published by Davies and Ballinger (née Ginnever) (1990). This and a later study by Fuge *et al.* (1991) confirmed the soils of the Priddy Mineries Reserve and St. Cuthbert's to be a lead anomaly or 'hotspot' (an area with soil unusually heavily enriched in lead).

Certain environmental aspects of some individual lead mining and processing sites on Mendip have also been investigated, but as in the work of Ginnever (1985), these have often only been a small part of the main objective of a study. Examples

of this include Cotter-Howells (1991) and Cotter-Howells and Caporn (1996). Cotter-Howells (1991) examined the solid speciation of lead in soil from Charterhouse in order to compare it with the soil of Winster, a village in the lead mining area of Derbyshire, the principle area of her study. Cotter-Howells (1991) found that pyromorphite, a stable lead phosphate soil mineral formed as the end-product of the weathering of the lead sulphide ore galena, was present as over 50% of the mineral phase of the soil lead at Winster. Pyromorphite was not present in the mine-waste spoil at Charterhouse, although cerussite, an intermediate in the galena-pyromorphite weathering sequence, was. Pyromorphite reduces the bioavailability of lead, and in experiments investigating the remediation of contaminated land, Cotter-Howells and Caporn (1996) added soluble inorganic phosphates to Charterhouse soil to enhance the formation of pyromorphite.

Very little work on the ecology of the flora associated with the Mendip Mineries appears to have been published. Baker (1974, 1978) investigated the populations of *Silene maritima* (With) (*Silene uniflora*), at the Priddy Mineries Reserve and at Charterhouse (the third of the four ancient Mineries) as part of a countrywide study. The individuals sampled from the *S. uniflora* population at the Priddy Mineries Reserve, along with those from Rhandirmwyn, showed the greatest capacity for the accumulation of zinc in their roots. Baker (1978) also found the greatest root:shoot ratio for zinc accumulation in the Priddy Mineries Reserve population. Other published work has included a short note on observations on the flora of the Mendip Mineries (Foster, 1970), and a review of the biological implications of trace metals in the Mendips by Martin and Fawcett (1998). The review by Martin and Fawcett (1998) provided a detailed, descriptive account of

the plant ecology of the Mendip Mineries, including previously unpublished data for the trace metal concentration of Minery lichen flora. Some trace metal data for smelter wastes were also described (Martin and Fawcett, 1998).

The literature search carried out as background to this project showed that data sets available from previous studies into the soil and biota of the Mendip lead Mineries were limited in quantity and fragmentary. It is clear therefore, that there are no major studies concerning the immediate local environmental impact of lead mining and processing at the Priddy Mineries Reserve, St. Cuthbert's site and Stockhill Plantation. This project addresses some of these issues.

### **1.3 Aims and objectives**

The aim of this project is the study of the distribution and biogeochemical cycling of some of the trace metals associated with the Mendip lead-zinc mineralisation in the soils of the Priddy Mineries Reserve, the St. Cuthbert's site, and Stockhill Plantation. This will be achieved by:

1. a baseline geochemical survey of the concentrations of lead, zinc, cadmium copper, iron and manganese in the soils of the study area
2. a temporal study of the concentrations of these trace metals in four representative soil types and a typical beneficiation (ore-processing) waste found at the sites by sampling from permanent quadrats on a monthly basis for the period of one year.

The value of this study will be to address the current lack of information on the environmental impact of mining and processing on the soils of these two historic

centres of the Mendip lead industry. The study will also provide soil metal data useful to those involved in the future management of the sites.

## **CHAPTER 2**

### **THE STUDY AREA**

#### **2.1 Introduction**

In terms of its geology, pedology, industrial history and current ownership, the study area falls neatly into three discrete sites; the Priddy Mineries Reserve, which incorporates the Chewton Minery, St. Cuthbert's, the site of the Priddy Minery, and the adjoining Stockhill Plantation, which overlies the Chewton Warren lead-zinc orefield (Figure 1.2). In order to interpret the results of this study, the data generated must be considered in the context of its geology, pedology and industrial history. The following sections describe these parameters and the post-industrial management of the sites.

#### **2.2 Geology**

The high, steep-sided plateau known as the Mendip Hills is an elongated massif of anticlinal structure, extending some 40 km West/East by 8 km North/South, with an average height of 244 m, rising to 325 m OD (Simms, 1998). The hills, which were formed as the result of complex interactions between their underlying geology, erosional processes, climate and time, are a discrete geological entity and as such are considered a distinct region in themselves (Farrant and Smart, 1995). The region is a predominantly limestone karst area with the inherent characteristic features and landscape of that formation (Green and Welch, 1965; Drew, 1975). It is covered by the Geological Survey of Great Britain Sheets 280 and 281.

The Mendip Hills represent about 425 million years of geological history which has been described in great detail by several authors including Green and Welch (1965), Donovan (1969), Ford (1969), and Simms (1998). Of particular interest is the geology of the North Hill pericline, the slopes of which contain the study area (Figure 2.1).



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Figure 2.1. Solid and drift geology of the study area, showing the extent of lead mineralisation in the Chewton Warren orefield. The study area is outlined in black, and present on the site are the Portishead Beds of the Old Red Sandstone (PoB), the Lower Limestone Shales (green), Black Rock Limestone (blue) and the Dolomitic Conglomerate (DCg). Peat (yellow-brown) and alluvium (pale yellow) are shown running North-South through the site.

The oldest exposed rocks on the Mendip massif are of the Wenlock Series, which were deposited 428-421 million years before present (BP) in the Silurian.

Although this succession is thought to underlie the geology of the North Hill pericline, no rocks of Silurian age are exposed in the immediate area (Green and Welch, 1965). In the study area, the earliest exposed rocks are the Portishead Beds, which are Old Red Sandstones of Upper Devonian age (Figure 2.1). Where the Old Red Sandstone of the Portishead Beds can be seen overlying the Silurian succession on Mendip, there is a major unconformity, or gap in the geological record of at least 57 million years (Green and Welch, 1965; Simms, 1998). The Portishead Beds were deposited around 367-362 million years BP, in what is now thought to be an alluvial, non-marine environment, by a meandering river system, perhaps in a delta setting (Simms, 1998; Haslett, 2000).

Exposed rocks from the Carboniferous epoch are also present in the study area. Between 362-330 million years BP, Carboniferous Limestone was deposited over the Old Red Sandstone succession when the area lay in a warm, shallow tropical sea, a few degrees south of the equator. The transition from the non-marine, continental Old Red Sandstone to marine limestones is thought to have been gradual. The low alluvial plains where the Old Red Sandstone had been deposited became inundated by the sea as sea levels in the Carboniferous steadily rose. During this time, it is thought that as there was no significant surrounding landmass, little sediment was washed into the sea, so the limestones were formed mostly by the biological and chemical precipitation of calcium carbonate directly from the seawater (Simms, 1998). The depth of the Carboniferous Limestone succession on Mendip ranges from approximately 800 m in the west to more than



1 100 m in the east, and was formed in four major units; the Lower Limestone Shales, and the Black Rock, Clifton Down and Hotwells Groups of limestones (Green and Welch, 1965). Of the Carboniferous Limestone succession, Lower Limestone Shales and Black Rock limestones are exposed in the study area (Figure 2.1).

While still in the Carboniferous, the limestone succession was succeeded by the Quartzic Sandstone Group (333-321 million years BP) and Coal Measures (321-305 million years BP), although all traces of these strata have been eroded from the main upland massif (Simms, 1998). Towards the end of the Carboniferous and the beginning of the Permian (305-250 million years BP), a series of major earth movements, which culminated in the Hercynian (Variscan) Orogeny, about 290 million years BP, forced the Mendip Region into four major asymmetric, anticlinal folds or en-echelon periclinal folds. These remain today as North Hill, Beacon Hill, Pen Hill and Blackdown, the highest point in the range. The exposed Old Red Sandstone core of Blackdown lies at 325 above OD, but it has been estimated that before the erosion of the Permian in this area, at least 3,000 m of strata deposited in the Carboniferous would have been overlying this (Green and Welch, 1965; Simms, 1998). Faulting and jointing associated with this period of earth movements was to have major structural control over the spatial distribution of the subsequent lead-zinc and manganese-iron mineralisation (Alabaster, 1982).

In contrast to the Permian, the Triassic (250-208 million years BP) was a period of deposition. The Triassic strata on Mendip lie unconformably over the uplifted

Palaeozoic rocks, because the conditions of severe erosion during the Permian stripped the massif to its Carboniferous Limestone and Old Red Sandstone core, allowing the sediments to be deposited directly above. The unconformity is thought represent a time gap of 60-125 million years (Simms, 1998). The Triassic succession on Mendip is broadly grouped into three main units: the Dolomitic Conglomerate and the Mercia Mudstone and Penarth Groups, although on the higher parts of the massif the succession is relatively thin or even absent. Of the three units, only Dolomitic Conglomerate is present in the immediate study area, where it forms the bedrock underlying the Stockhill Plantation (Figure 2.1).

Dolomitic Conglomerate was described by Simms (1998) as a Triassic regolith, a mantle of debris overlying solid rock. On Mendip, it is usually found surrounding what would have been outcrops of Carboniferous Limestone and Old Red Sandstone during the Triassic. It may or may not be dolomitised (enriched with magnesium), silicified, haematitised or mineralised with lead-zinc (Green and Welch, 1965). The Dolomitic Conglomerate is further divided into three major types where it occurs on Mendip: fossil scree deposits, clast-supported conglomerates, and matrix-supported breccias, depending on the geological environment under which it was formed. Fossil scree deposits contain highly angular blocks (breccia) of locally derived rock (clasts), some of which may be large, with a variable degree of matrix between clasts. The clast-supported conglomerate contains rounded clasts (conglomerates) embedded in a mud matrix and the matrix-supported breccias are dominated by a muddy to sandy matrix filled with small, angular fragments of limestone (Simms, 1998). The Dolomitic Conglomerate is the youngest exposed rock present in the study area. It occurs in

a highly mineralised form at a thickness of more than 60 m around North Hill. A roadside swallet (sinkhole), not named by Green and Welch (1965) but probably the Waldegrave Swallet on the site of the Priddy Mineries Reserve at ST 5473 5160 (Heathwaite *et al.*, 1999), showed over 9 m of red conglomerate with boulders of Black Rock Limestone (Green and Welch, 1965).

After the Triassic, the Mendip region underwent a further marine inundation during the Jurassic period (208-135 million years BP). At the time of the lower and middle Jurassic, the higher points of the Mendip Hills were a string of islands and shallow water reefs (Alabaster, 1982). During the Jurassic, fissures which opened in the faulting and jointing associated with the Hercynian earth movements were filled with Jurassic marine sedimentation, and the Harptree Beds were laid down (Alabaster, 1982). During the Tertiary (approximately 67-3 million years BP), the region was subjected to erosion, earth movements, exhumation and finally, further erosion, before emerging in its present form. Today it is thought that much of the topography was exhumed during the Tertiary, and subsequent erosion has occurred to such an extent that much of the modern landform reflects that of the original Triassic (Simms, 1998). For a more detailed description of the geological history of the Mendip area including that of the Triassic to the Pleistocene, see Green and Welch (1965) and Simms (1998).

## **2.3 Mineralisation**

At various times in its history, Mendip has been an important source of the ores of the metals silver, lead, zinc, iron and manganese (Figure 1.1). In common with many mineral deposits worldwide, a considerable proportion of the Mendip ore

deposits show evidence of both hypogene and supergene activity. The terms 'hypogene' and 'supergene' refer to the origin of mineralising solutions.

### **2.3.1 Hypogene deposition**

Hypogene deposits are formed from ascending mineralising solutions (brines) which originate deep within the earth. On Mendip it is thought that the hypogene ore deposits are a result of direct chemical precipitation from warm (<150 °C) brines, which ran along the faults, joints and bedding planes of rocks over a long period of time (Alabaster, 1982). These deposits included the economically important lead, zinc and copper sulphide mineralisation.

The bulk of the hypogene mineralisation is found in the west and central areas of the Mendip plateau, known as the central Mendip lead-zinc orefield (Green, 1958). The Mendip lead-zinc orefield was classified as a basic Mississippi-Type orefield, due to the nature of the mineralisation processes (Brown, 1967), but was considered sufficiently different from the basic Mississippi-Type to warrant the further classification under the category of Pennine-Type Deposits (Emblin, 1978). The lead-zinc mineralisation is patchy over the orefield, and each site of intense mineralisation is separated by poorly mineralised or barren ground. Recent work has shown that as well as the areas of intense mineralisation, when compared to the metal content of typical sedimentary rocks (Table 2.1), some country rocks of the Mendip plateau are also considerably enriched in lead, zinc and cadmium (Table 2.2).

Table 2.1. Typical trace metal concentrations ( $\mu\text{g g}^{-1}$ ) in sedimentary rocks (Levinson, 1974; Alloway 1990a).

<b>Rock Type</b>	<b>Lead</b>	<b>Zinc</b>	<b>Cadmium</b>
Sandstone	8.0 - 10.0	16.0 - 30.0	0.05
Shale	20.0 - 23.0	100.0 - 120.0	0.2
Limestone	5.7 - 7.0	20.0 - 25.0	0.028 - 0.1

Table 2.2. Trace metal concentrations ( $\mu\text{g g}^{-1}$ ) in some Mendip rocks Fuge *et al.* (1991).

<b>Rock Type</b>	<b>Lead</b>	<b>Zinc</b>	<b>Cadmium</b>
Portishead Beds (ORS)	13.0	735.0	9.4
Black Rock Limestone (CL)	1.5 - 45	6.0 - 167	0.8 - 10
Burrington Oolite (CL)	3.0 - 7.0	19.0 - 72.0	0.6 - 8.0
Hotwells Limestone (CL)	205.0	173.0	12.0
Dolomitic Conglomerate (TL)	7.6 - 98	67 - 137	1.4 - 12
Blue Lias (JL)	3.6	33.0	0.2

(TL) Triassic Limestone (JL) Jurassic Limestone  
(ORS) Old Red Sandstone (CL) Carboniferous Limestone

Lead ore from the Mendip orefield occurred principally as argentiferous galena (PbS), with silver as an economically significant impurity. Mendip galena was reported to contain  $4\ 200\ \mu\text{g g}^{-1}$  (0.04%) silver (Waldron, 1875; Elkington, 1976; Tylecote, 1986). Some hypogenically deposited zinc was also present in the orefield as the sulphide sphalerite, or 'blende' (ZnS). Although fairly widespread,

sphalerite was usually only found in trace quantities, and never in economically significant amounts (Green, 1958; Alabaster, 1982). The exact age of the hypogene mineralisation is uncertain (Alabaster, 1982), although Moorbath (1962) dated galena from the area by lead isotope analysis at  $230 \pm 30$  million years, which would suggest deposition during the Mid-Triassic.

Alabaster (1982) argued that in common with other areas of mineralisation, the hypogenic mineralisation of Mendip occurred in a number of discrete pulses, known as episodic or polyphase deposition, as local galena veins show field evidence of multiple filling. Alabaster (1982) concluded that the consensus of opinion was that this polyphase mineralisation occurred over a period of 100 million years, from the end of the Triassic, through the Jurassic (Kellaway 1967; Ford, 1976), before dying out during the Middle or Upper Cretaceous (Green and Welch, 1965). Later, a reappraisal of the work by Moore (1867), Curtis (1981), Stanton (1981) and Alabaster (1982) led Simms (1998) to believe that only one significant episode of lead-zinc mineralisation occurred on Mendip, at sometime during the Mid-Jurassic. After the Jurassic period, it is thought another mineralising episode occurred, where the brines were enriched with silica (Haslett, 1999). This led to the silification of a significant number of the Triassic and Jurassic rocks on the top of the Mendip plateau, including the Harptree Beds. Of the rocks on Mendip, the most important hosts of galena (PbS) were Dolomitic Conglomerate, followed by Lower Carboniferous Limestone and Old Red Sandstone.

In the study area, the heavily mineralised Dolomitic Conglomerate of the Chewton Warren orefield, now underlying the Stockhill Plantation, is one of the two main centres of mineralisation in the central Mendip lead-zinc orefield (Green, 1958). The dominant vein direction is east-south-east, and in the study area veins are adjacent to the Stockhill Fault (Figure 2.1). Before its subsequent erosion in the Permian, the Dolomitic Conglomerate of the Chewton Warren orefield was probably covered by fine-grained Mesozoic rocks (Green, 1958). While Dolomitic Conglomerate is the major host rock of lead ore in the Chewton Warren orefield, the site is one of only two places on Mendip where galena occurs in Old Red Sandstone (Alabaster, 1982). In the Dolomitic Conglomerate of the Chewton Warren orefield, the length of the lode outcrops (mineral veins) were measured at 46 000 yds (42 100 m), and were recorded as being worked to a depth of 16-20 fathoms (c.29-37 m) during the mid-seventeenth century, before problems with flooding occurred (Glanvil, 1667, 1668).

### **2.3.2 Supergene deposition**

Supergene deposition is a term used exclusively for processes involving water, either with or without dissolved material, percolating down from near surface sources. Typical supergene processes are solution, hydration, oxidation, deposition from solution and replacement which is the reaction of ions in solution with ions in existing minerals (Alabaster, 1982). The three major ores of economic importance deposited by supergene mineralisation on Mendip were manganese oxide, iron oxide (as ochre) and smithsonite, known locally as 'calamine' (zinc carbonate,  $\text{ZnCO}_3$ ). The processes involved in the manganese and

iron mineralisation are very different to that of the calamine.

The iron and manganese mineralisation on Mendip is thought to have been in place by the mid to late Triassic, predating the hypogene lead-zinc mineralisation (Alabaster, 1982; Simms, 1998). The iron and manganese mineralisation, which was deposited by similar processes, is primarily in the Dolomitic Conglomerate and is the result of intense weathering of Carboniferous rocks under semi-arid conditions. The action of water on iron-rich Carboniferous limestones and manganese-rich Upper Carboniferous Shales caused iron/manganese brines to be channelled by faults, joints and bedding planes through the rocks. Where conditions were suitable, the metals precipitated out forming veins, strings, pods and flats of iron, and pods of manganese (Alabaster, 1982). Iron and manganese were sporadically worked around North Hill, especially around the village of Priddy to the south of the St. Cuthbert's site (Figure 1.1), although never in the same quantities as lead (Gough, 1967). Iron ores on Mendip were frequently associated with manganese oxides ('wad'), and iron, in the form of its hydrated oxide, 'brown haematite', has been found in the mining wastes from the Chewton Warren workings (Green, 1958).

Of the zinc mineralisation on Mendip, calamine was the most economically important zinc ore. While the ore is considered of supergene origin, on Mendip, calamine deposits were formed by the combination of the hypogene and supergene processes (Alabaster, 1982). Many mineral veins of hypogenic origin on Mendip originally contained galena and sphalerite, usually with small amounts of pyrite



(FeS). When this occurred, in the porous Dolomitic Conglomerate especially, chemically active oxygenated groundwaters caused the alteration of sphalerite, particularly in the upper part of the veins. In the presence of pyrite, which forms sulphuric acid on oxidation, zinc went into solution where it reacted with carbonate ions present from the calcareous host rock, to precipitate calamine (Alabaster, 1982). Galena, although not so susceptible to chemical attack as sphalerite, would also undergo this process to form cerussite, or white lead ( $\text{PbCO}_3$ ). It is thought that cerussite formed a significant proportion of the lead ores worked on Mendip (Morgans, 1902; Tyelcote, 1986), and both calamine and cerussite were recorded as being present in the Chewton Warren lead-zinc mineralisation (Gough, 1967; Alabaster, 1982).

## **2.4 Pedology**

Overlying the solid geology of the region are the 38 soil series and 7 soil complexes identified by the Soil Survey of England and Wales Soil Map 1:25 000 Sheet 280. The four soil series represented in the study area are the Maesbury, Thrupe, Ashen and Nordrach Series (Figure 2.2). Their relationship to major soil groups and parent material is shown in Table 2.3.

### Maesbury Series

The Maesbury Series usually occurs on slopes above 213 m and, like the Ashen Series, is derived from Old Red Sandstone (Table 2.3). Soils of the Maesbury Series are usually stony and sandy, although some may have a loamy, silty texture. The presence of silt is thought to be from the addition of fine wind-borne material. These soils are well-drained due to their texture and occurrence on slopes, and

merging horizons, with typically little or no differentiation between texture, structure or colour throughout the profile is typical (Findlay, 1965). The Maesbury Series was present at the St. Cuthbert's site, and in a small area at the southern tip of the Priddy Mineries Reserve (Figure 2.2).

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*Reproduced from Soil Survey and Land Research Centre (Wells Sheet 280, 1968). © Cranfield University and for the Controller of HMSO (2001). No part of this publication may be reproduced without the express written permission of Cranfield University.*

**Figure 2.2.** Location of the Maesbury (Ms), Thrupe (Th), Ashen (Az) and Nordrach (Nb) soil series in the study area.

Table 2.3. Soils of the Priddy Mineries Reserve (PMR), St. Cuthbert's (SC) and Stockhill Plantation (SHP) and their relationship to major soil groups and parent materials. Constructed from Explanation of Mapping Units (Sheet 280 Wells) and data from Findlay (1965).

<i>Soil Series</i>	<i>Parent Material</i>	<i>Major Soil Group</i>	<i>Drainage Class</i>	<i>Site Present</i>
ASHEN	Old Red Sandstone and derived Head	Peaty Gleyed Podsol	Poor - Very Poor	PMR SC SHP
MAESBURY	Old Red Sandstone and derived Head	Brown Earth ( <i>sol brun acide</i> )	Free	SC PMR
THRUPE	Old Red Sandstone and derived Head	Surface Water Gley	Poor - Very Poor	PMR SC
NORDRACH	Silty Drift over Carboniferous Limestone	Brown Earth ( <i>sol lessive</i> )	Free	SHP

### Thrupe Series

Soils of the Thrupe Series commonly occur around the sites where springs rise at the junction of Old Red Sandstone with Limestone Shales, or where sandstone Head overlies shales (Table 2.3). The soils are very poorly drained and are seasonally waterlogged. The Thrupe Series is derived from a variety of parent materials including sand from Old Red Sandstone, clays of Liassic origin or from Lower Limestone Shales and loessial silts (Findlay, 1965). Thrupe soils covered

the dry valley floor on both the Reserve and at the St. Cuthbert's site (Figure 2.2).

### Ashen Series

Soils of the Ashen Series are peaty-gleyed podsols derived from Old Red Sandstone (Table 2.3). The surface horizons typically contain a thick, well-humified organic layer capable of retaining water for long periods. A grey, structureless, bleached horizon, leached of all free iron oxides is usually found beneath the surface horizons, and an iron pan may also be present in the lower horizons (Findlay, 1965). Soils of the Ashen Series were present on the Priddy Mineries Reserve and in the southern area of the Stockhill Plantation sampled during this study (Figure 2.2).

### Nordrach Series

Soil of the Nordrach Series appears to be largely stoneless and consists of weathered residues of the underlying rock with a cover of loessial silt. Nordrach soils are often found to incorporate the remains of soils formed in earlier stages of landscape evolution (Findlay, 1965). The soils are usually stoneless with occasional fragments of silicified limestone and often have a weak texture profile development. They may contain a significant amount of clay at depth, and are typically of a characteristic red colour throughout the profile. The Nordrach Series was present over most of the Stockhill Plantation sampled during this study (Figure 2.2).

The above soil classifications were described by Findlay (1965), and appear on the Soil Survey of England and Wales Sheet 280 (Wells) (Figure 2.2). However,

between April 1979 and March 1982, a new mapping programme was carried out resulting in the publication of new 1:250 000 soil maps in 1983, followed by the accompanying new texts in 1984. In the new work, the previous soil classification system was rationalised, resulting in the reclassification of some of the soil series present in the study area (Clayden and Hollis, 1984). It was decided that for the purpose of this study, the original soil classifications of Findlay (1965) would be retained. There were two major reasons for this decision. The first reason was that the new maps are small scale (1:250 000) when compared with the original Sheet 280 (Wells) (1:25 000), and as such do not have sufficient detail for a study of this nature. As the original Sheet 280 was used in the planning of the study, the original names were retained to avoid confusion. The second reason was that two of the four soil series present on the study area have been reclassified into two series (Table 2.4), and it was not immediately clear from the literature which one of the modern correlatives apply to these two soils in the study area.

Table 2.4. Original soil series and symbols and their modern correlatives  
Clayden and Hollis (1984). M7 refers to Monograph 7 (Findlay, 1965).

Soil Series	Series Symbol	First Publication	Modern Correlative
ASHEN	Az	M7 1965	BURCOMBE
MAESBURY	Ms	M7 1965	CREDITON or MILFORD
NORDRACH	Nb	M7 1965	NORDRACH
THRUPE	Th	M7 1965	WIGTON MOOR or FREN

## **2.5 Climate**

The annual rainfall in the Priddy area of Mendip is approximately 850 mm. This was calculated using data over the period 1916-1950 (Findlay, 1965). During 1995, the first full year of the sampling programme for this present baseline study, however, there was a drought of historic proportions (Heathwaite *et al.*, 1999). In the North Hill area, annual rainfall has been recorded in excess of 1 300 mm (Findlay, 1965). This was confirmed for the years 1998 and 1999, when data from the weather station at Priddy (Gauge Ref. 5212275SC) showed that the annual rainfall was 1 346 mm and 1 291 mm for those years respectively (Environment Agency, 2001).

Over the Mendip plateau, the monthly average temperatures were found to be approximately 1.5°C less than those at the North Somerset coast, shortening the growing season by about nine weeks (Findlay, 1965). It has been calculated that the temperature range on Mendip is approximately 14.0°C, from a minimum monthly average of 2.1°C in January to a maximum of 16.1°C in July (Ginnevar, 1985). The prevailing winds on the plateau are the south westerlies, which also tend to be of a higher velocity than winds from other directions. Although north winds are fairly uncommon, during the autumn and winter months, the wind direction is evenly distributed around the compass (Findlay, 1965).

## **2.6 Industrial history**

The presence of long barrows and henge monuments on the Mendip plateau suggest human activity in the area from at least the Neolithic, some 6 500-

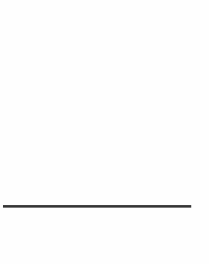
4 000 years ago (Stokes, 1999). To the north of the study area at ST 540 528 are the Priddy Circles, Mendip's most impressive henge monuments of approximately 158 m diameter (Taylor and Tratman, 1957). The Mendip plateau continued to be a place of significance to the people of the Bronze Age (4 000-2 650 years ago), which is reflected in the presence of over 300 round barrows, their burial mounds, dating from this period. This concentration is comparable with the large nucleations at Avebury, Stonehenge and the South Dorset Ridgeway (Stokes, 1999). The North Hill area contains two of the most famous Bronze Age cemeteries in Somerset, the Ashen Hill Barrows and Priddy Nine Barrows. In the study area, round barrows have also been preserved within the Mineries Reserve and in the heavily mined areas of Stockhill Plantation (Figure 1.2). It is not known exactly when lead mining began in the Mendip area, but a number of lead objects including lead weights thought to be sinkers for fishing nets were excavated in the Meare and Glastonbury lake villages (Gough, 1967). It is thought the lake villages were inhabited during the Iron Age (2 600-1 957 years ago), and one such artefact excavated from Meare weighed 20.8 g and was dated as between 1 950 and 2 250 years old (Bulleid and Gray, 1911; Friend and Thorneycroft, 1929; Gray and Bulleid, 1948, 1953; Tylecote, 1986).

In the absence of the archaeological evidence to suggest otherwise, the Romans appear to have been the first to exploit the metalliferous deposits of Mendip on a large scale. It is thought that the existence of extensive surface deposits of argentiferous lead in southwestern Britain was one of the main reasons for the Roman invasion of 43 AD (Webster, 1993). Rome depended heavily on the mines of Spain for silver to make coinage, but it had become increasingly difficult and

expensive to extract the metal from the mines. Four Roman legions were chosen for the invasion of Britain, the II Augusta, IX Hispania, XIV Gemina and the XX. Archaeological evidence suggests that the Mendip silver-lead mines were operational within six years of the invasion, under the command of the II Augusta, and that both mining and smelting were taking place on Mendip by this time (Elkington, 1976). While the largest Roman silver-lead mining centre on Mendip was at Charterhouse (ST 506 557), the existence of a Roman mining settlement on the slopes of North Hill has been known since the 1720s (Williams, 1998). The site, known as the St. Cuthbert's Roman Mining Settlement, covers an area of approximately 9 ha centred around ST 542 507 (Figure 2.3). The Roman St. Cuthbert's mining settlement probably only represents the western sector of an extensive mining complex, which was thought to have been the focal point for the Roman mining activities in the eastern district of the Mendip orefield (Williams, 1998). Archaeological evidence indicated that both silver and lead were being produced at this complex during the first to fourth centuries AD (Williams, 1998). A chemostratigraphical study by Haslett *et al.* (1998) further supported the evidence for metal production in the Priddy Mineries area during this period, and showed that wide-ranging metal enrichment of the surrounding areas through anthropogenic input was also occurring.

Elevated concentrations of lead and zinc at 0-350 mm depth were found in the upper blue/grey clay unit of a soil core taken from Rookery Farm (ST 460 502) in the Nyland Hill area of the Somerset Levels (Haslett *et al.*, 1998). Nyeland Hill is situated within the Axe Valley, and the River Axe catchment drains the Priddy Mineries area. Radiocarbon dating and the presence of pottery dated the lower





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Figure 2.3. Sketch map of the St. Cuthbert's Roman site and Stockhill Roman mining settlement in relation to the study area (Williams, 1998). The study area is outlined in grey.

lead and zinc deposits to the Roman occupation, leading Haslett *et al.* (1998) to suggest that the initial increase in lead and zinc concentrations represented the onset of Roman mining activity in the Priddy area of Mendip.

It has been suggested by Elkington (1976), that by the end of the fourth century, social conditions had deteriorated in Roman Britain to such a degree that many country villas and estates had been abandoned, while their owners sought refuge in towns. During this period, villas on the estates that had supplied the Mendip mining settlements with produce were also abandoned, to be occupied by baliffs and labourers. It is uncertain how long the Mendip mines continued to operate after this time (Elkington, 1976). While little is known about mining in the region after the breakdown of Roman rule in Britain, by the Middle Ages (approximately 1 000-1 400 AD) the lead industry on Mendip was run as four separate and distinct mining and processing regions known as 'Liberties', although it is not clear exactly when this began (Gough, 1967). Each Liberty was owned by one of 'Four Lords Royal of Mendip', and in the earliest recorded reference to these Lords Royal, the lordships were described as existing from ancient times (Gough, 1967). The Liberties were known as the West Liberty, the Harptree Liberty, the Chewton Liberty and the Wells Liberty (Figure 2.4).

The Mendip mining district had its own ancient customs and codes of laws which were thought to be collected and codified for the first time in the late fifteenth century by Sir Richard Chocke, Edward IV's Chief Justice of England. Lord Chocke's Laws, as they became known, were of general application over the whole of Mendip, but each of the four Liberties had its own separate mineral court,

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Figure 2.4. The boundaries of the Liberties of the Four Lords Royal (Gough, 1967).

with its own officers known as lead-reeves, and the power to make additional laws and orders binding to the miners of that Liberty (Gough, 1967). There was also a central site known as a 'Minery' in each Liberty, where ore was brought in by miners to be washed, smelted, weighed and stored (Table 2.5).

Table 2.5. Mediaeval Liberties and Mineries, and their current location.

Liberty	Minery	Location (2001)	Grid. Ref.
West	West	Charterhouse-on-Mendip	ST 505 555
Harptree	Harptree	East Harptree Woods	ST 553 547
Chewton	Chewton	Priddy Mineries Reserve	ST 548 513
Wells	Priddy	St. Cuthbert's	ST 545 505

Because of the need for water in ore processing, Mineries were situated in areas of running surface water. All four Mineries were also close to major concentrations of lead-bearing mineral veins. Although documentary evidence suggests that it was more usual for ore to be processed in the Liberty of origin, in accordance with the fourth of Lord Chocke’s Laws, a miner was free to take his ore to the minery of his choice for processing. However, 'lot-lead', a tithe of ten percent of the lead produced and paid in kind, was always due to the Lord Royal of the Liberty where the ore was mined as payment for the right to mine. Lot-lead from a Liberty was collected by a lead-reeve employed by the Lord Royal, a practise already documented as ancient by 1292 (Gough, 1967). While the law permitted miners to processes their ore at any minery, regardless of where it was mined, miners were often under extreme pressure from the Lord of the Liberty from where the ore was mined to process it at that Liberty’s minery (Page, 1911; Gough, 1967). It has been estimated that before 1615, only 47% of the total Chewton production was

treated at the Chewton Minery, while the bulk of the remaining 53% went to the Harptree and Priddy Mineries. After 1615, over 92% of the ore mined in the Chewton Liberty was treated at the Chewton (70%) and Priddy (22%) Mineries.

After reaching its productive prime between 1600-1670, lead mining on Mendip went into a decline, which continued throughout the eighteenth century. By the early decades of the nineteenth century, the mining and processing of fresh ore lingered on in what Gough (1967) described as a 'semi-moribund condition' until even this had ceased by 1850. During the final years of decline, the resmelting of old processing and smelter refuse was carried out on a limited scale at several Mineries by a few surviving mining labourers and local gentlemen landowners, who were keen to promote the traditional industry. At the Chewton and Priddy Mineries for example, the old industries had left lead waste in deposits that were 1.6 km long, 183-274 m wide and 3.7-6 m deep. Assays revealed the large slag (smelter waste) in the deposits to contain a minimum of 27% lead, medium slag 18% and small slag 21% (Gough, 1967). By the middle of the nineteenth century, the reworking had attracted the speculative attention of a number of Cornish mining engineers, who, with their modern mining technology and skill and experience of tin dressing, expected to rework the refuse of the old miners at a profit.

During this period, which lasted from 1857 to 1908, little mining for fresh ore took place but the tailings and slimes (metal-rich sand, silt and clays) and slags of the ancient industry were re-dressed and smelted to produce metallic lead. With investment in modern buildings and Cornish mining technology by the various

companies, in the early years of the venture at least, the four ancient Mineries seemed again to become viable centres of lead production. Some silver was also produced as the slag was still found to contain  $900 \mu\text{g g}^{-1}$  (0.009%) silver (Gough, 1967; Elkington, 1976). From 1853-1881, the recorded output of silver from the Mendip leadworks was 16 623 oz, or approximately 468 kg (Gough, 1967). By the last quarter of the nineteenth century however, the Mendip lead industry was faced with a series of problems that eventually brought about its demise. The fluctuation in the price of lead, which peaked at around  $\text{£}20 \text{ ton}^{-1}$  in the early 1870s had plunged to  $\text{£}11 \text{ ton}^{-1}$  by 1884 (Gough, 1967). Cheaper and higher quality lead was produced by competitors using technology that was more efficient, and a series of disputes and expensive court actions between interested parties on Mendip over water rights and pollution meant that one by one, each operation failed. The price of lead briefly recovered, rallying from  $\text{£}15 \text{ ton}^{-1}$  in 1899 to  $\text{£}19 \text{ ton}^{-1}$  in 1907, but it was too late for Mendip, and by 1908 the single remaining operation was wound up and its machinery sold two years later. The four ancient Mineries are clearly identifiable today as the Priddy Minery, Chewton Minery, East Harptree Minery and Charterhouse Minery, and the remaining watercourses, reservoirs, masonry and wastes remaining at these sites largely date from this final phase of reworking.

## **2.7 Site descriptions**

The study area contains three discrete sites, the Priddy Mineries Reserve, the St. Cuthbert's site and Stockhill Plantation. Although geographically close and with an interrelated industrial history, the three sites are very different in character in terms of their topography, geology, pedology, industrial archaeology and

present management. Throughout their history the three sites have also been known by various names, which can cause confusion when reviewing literature concerning the area. The following sections review the nomenclature of each site and provide a current site description.

### **2.7.1 Priddy Mineries Reserve**

#### Nomenclature

The Priddy Mineries Reserve incorporates the dressing floor of the former Waldegrave Leadworks, which was constructed over the site of the ancient Chuton (Chewton) Minery, and is owned by the Waldegrave family. The site is referred to variously as the Chewton Minery, Waldegrave Minery, Chewton Leadworks or Waldegrave Leadworks. In published literature, the site has also been described as the Chewton-Mendip Minery (Davies and Ballinger, 1990).

#### Site Description

The Priddy Mineries Reserve, which is centred around ST 548 513, lies in a shallow, blind dry valley on the east and south east side of North Hill at an altitude of between 250 and 285 m above OD (Figure 1.2). The remains of the dressing floor and smelter of the Waldegrave Leadworks, where the reworking of old refuse took place in the mid to late nineteenth century, covers approximately 21 ha of the 49 ha site. The underlying rocks of the Reserve are predominantly the Portishead Beds of the Lower Old Red Sandstone, although near the eastern boundary there is an extrusion of Dolomitic Conglomerate. The dry valley floor is filled with peat above the Waldegrave Pool (ST 5470 5150), and with alluvium below running south to the St. Cuthbert's site (Figure 2.1). The dominant soil type present on the

Priddy Mineries Reserve is the Ashen Series on the higher ground, with the Thrupe Series in the lower-lying areas (Figure 2.2). To the south of the site, a very small area of soil from the Maesbury Series is present (Figure 2.2).

Industrial features include one large and two much smaller minery reservoirs, leat (water channel) systems, tailings settlement ponds and associated dams, buddle depressions where lead ore was removed from waste by gravity separation through water, extensive tailings piles from the buddling process, masonry and condensing flues, and a small amount of smelter slag. In 2001, the Priddy Mineries Reserve is managed by the Somerset Wildlife Trust under an agreement with the Waldegrave Estate. The Reserve is part of the Priddy Pools and Priddy Caves SSSI, which was notified in 1971 under Section 23 of the National Parks and Access to the Countryside Act 1949, and in 1986 under the Wildlife and Countryside Act. This site, like the other two in the study area, has open public access and is heavily used as an amenity area for activities such as walking, dog-walking, picnicking, fishing, cycling and cave exploration.

### **2.7.2 St. Cuthbert's**

#### **Nomenclature**

The St. Cuthbert's site was often referred to as the Bishop's Minery in older literature, as it was once owned by the Bishopric of Bath and Wells (Gough, 1967). It was also called the Preddy, or Priddy Minery. During the last phase of industrial activity in the late nineteenth century, the site was home to the St Cuthbert's Leadworks, and it is sometimes referred to today as St Cuthbert's Minery, or St Cuthbert's. Although in 2001 it is a completely separate site under



different ownership and management, it is also sometimes referred to, together with the Priddy Mineries Reserve, as the Priddy Mineries. Local people appear to often refer to the site as the Priddy Minery.

### Site Description

The St. Cuthbert's site adjoins the Priddy Mineries Reserve immediately to the south, and is centred on ST 545 505 (Figure 1.2). The site covers an area of approximately 10 ha and is situated on the less eroded southern edges of the North Hill pericline. The underlying rocks are the younger Lower Limestone Shales and Blackrock Limestone, and the valley floor is filled with alluvium as it runs down to its lowest point at St. Cuthbert's Swallet, a sink hole in the St. Cuthbert's Depression (Figure 2.1). On the higher ground of the site, the soils are of the Maesbury Series, while the lower lying soils belong to the Thrupe Series (Figure 2.2).

The site is compact and dominated by the industrial remains of the St Cuthbert's Leadworks, latterly owned by the New Chaffers Extended Mining Company (1903) Ltd. (Gough, 1967). Here, the tailings, slags and slimes of previous operations were dressed and re-smelted in the late nineteenth and early twentieth centuries until the 23<sup>rd</sup> March 1908 (Irwin *et al.*, 1968). As well as the widespread masonry ruins and condensing flues of the smelter houses, the site contains the remains of an inclined tramway, a buddle system, extensive tailing piles and smelter waste heaps, a minery reservoir and settlement ponds. In 2001, the site is owned by the Inveresk Group of companies, and, like the Priddy Mineries Reserve, is often used by the public as an amenity area.

### **2.7.3 Stockhill Plantation**

#### Nomenclature

Stockhill is sometimes referred to on some Ordnance Survey maps erroneously as Stock Hill. Stockhill was the family name of the landowners during the sixteenth to eighteenth centuries (Williams, 1998).

#### Site Description

Stockhill Plantation adjacent to both the Mineries Reserve and St. Cuthbert's site to the east, and is centred on ST 555 515. Although it covers a total area of over 180 ha, for the purpose of this investigation soil samples were only taken from an area of approximately 48 ha, the western edge of the plantation immediately adjacent to the Mineries Reserve and St. Cuthbert's site (Figure 1.2). The northwestern area of Stockhill Plantation included in this study is part of the Dolomitic Conglomerate extrusion on the Priddy Mineries Reserve's eastern boundary, with Old Red Sandstone in the higher ground to the south (Figure 2.1). The Dolomitic Conglomerate is richly mineralised with lead/zinc veins running approximately East-South-East/West-North-West, and as part of the Chewton Warren orefield, was heavily mined (Figure 2.1). The remains of the mining grooves (long, narrow cuttings in the rock where the ore was mined), which probably date from before the eighteenth century (Gough, 1967), and quarries, which provided the stone for the construction of the Minery buildings, are clearly visible in the plantation in 2001.

At the north end of the plantation, the soils are of the Nordrach Series that overlay the Dolomitic Conglomerate, while soils from the Ashen Series appear to the south

over the Old Red Sandstone (Figure 2.2). The afforestation programme began at the northern end of Chewton Warren in 1938. The earliest plantings, which were on the Nordrach series, consisted of *Larix leptolepis*, and *Fagus sylvatica*. Later plantings were mainly *Picea abies* and *P. sitchensis*. Before afforestation, the wet sheltered sites in the Warren were dominated by *Molinia caerulea* (Findlay, 1965).

To the south of the heavily mined northern end of the plantation, is the site of a Roman Mining Settlement (Figure 2.3). There is also a record of a Celtic field system existing before the site was ploughed before afforestation in 1948 (Williams, 1998). In this area, which is on the Ashen Series, *Pinus sylvestris* was planted, as it was able to compete with *Calluna vulgaris* in the early stages of its growth. On the more freely drained areas, where *C. vulgaris* was not dominant, *P. nigra* var. *corsicana* (Loudon) was planted (Findlay, 1965). In 2001, the mixed conifer and deciduous plantation is owned and managed by Forest Enterprise, the successor to the Forestry Commission, and is greatly valued as an amenity site.

## **CHAPTER 3**

### **DEVELOPMENT OF ANALYTICAL METHODS**

#### **3.1 Introduction**

##### **3.1.1 Aims and objectives**

The aim of the work described in this chapter was to develop a methodology that would produce the most accurate and precise analytical data possible with the resources available. Methods for the determination of total and bioavailable soil trace metals were determined by experimentation and the analysis of the resultant data.

##### **3.1.2 Rationale for method development**

The determination of total metal content is recommended where a baseline knowledge of metal enrichment in the soils of an area is required. In environmental geochemistry, baseline surveys are used to monitor long-term changes in soil (Harrison and Laxen, 1978; Ure, 1990). Of particular interest to biologists are the metals in the soil phases which may be taken up by plants, and thence the food chain (Ure, 1990). When a metal is in such a form, it is described as being 'bioavailable', 'plant available' or 'available'. A number of soil extraction techniques have been developed for the determination both total and available trace metals. Of the extraction procedures designed to simulate the availability of trace metals to plants, EDTA ammonium ethylenediaminetetra-acetate (EDTA)  $[\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2]_2$  is often used because it can extract a wide range of metallic elements including lead (Pb), Zinc (Zn), cadmium (Cd), copper (Cu), and

nickel (Ni) from soil (Ure, 1990). EDTA has been shown to extract trace metals held in the soil system as soluble, exchangeable, adsorbed and organically bound fractions, and possibly a proportion of those occluded on oxides and secondary clay minerals (Ure, 1990).

EDTA extraction has become a standard method for the determination of available trace metals in soil (MAFF, 1985). However, the results of several unpublished studies, which were confirmed by preliminary work carried out in conjunction with this present study, suggested that EDTA produced anomalous results when used on some Mendip soils (Table 3.1) (Wilson, 1994; Lambkin, 1999).

Table 3.1. Summary of HNO<sub>3</sub> and EDTA extractable Pb and Cd from the floodplain soils of the Cheddar area of Mendip (Wilson, 1994).

Soil Depth	TOTAL HNO <sub>3</sub> EXTRACTABLE (µg g <sup>-1</sup> )		AVAILABLE EDTA EXTRACTABLE (µg g <sup>-1</sup> )	
	Mean	SD	Range	Mean SD
<b>INVESTIGATION A</b>				
Pb				
0-150 mm	6 268 ±2 477		2 000 - 11 400	3 306 ±1 136
150-300 mm	5 475 ±2 885		1 600 - 9 300	6 971 ±6 574
300-450 mm	5 250 ±3 938		1 400 - 10 450	3 690 ±1 219
Cd				
0-150 mm	2.85 ±0.92		1.50 - 4.50	3.67 ±1.06
150-300 mm	3.05 ±0.93		1.50 - 4.50	4.13 ±1.58
300-450 mm	1.90 ±0.65		1.00 - 2.50	2.60 ±0.82
<b>INVESTIGATION B</b>				
Pb				
0-150 mm	2 342 ±2 676		400 - 8 275	2 928 ±4 040
150-300 mm	2 652 ±3 112		250 - 10 100	3 666 ±4 630
Cd				
0-150 mm	0.96 ±0.47		0.50 - 2.00	1.77 ±1.01
150-300 mm	1.39 ±0.70		0.50 - 2.75	1.92 ±1.08

The results of the study by Wilson (1994), showed that the EDTA extractable Pb and Cd in some floodplain soils around the Cheddar area of Mendip, exceeded the total concentration of those trace metals in the same bulked soil samples (Table 3.1). In Wilson's (1994) study, the total trace metal content of soil was determined by 69% v/v nitric acid (HNO<sub>3</sub>) decomposition. These apparent anomalies were not restricted to Wilson's (1994) study, or to the Cheddar area of Mendip. The preliminary analysis of soils from the Charterhouse Minery and the Priddy Mineries Reserve occasionally produced a similar anomaly (pers. obs). It was concluded that there were several possible explanations:

1. an error occurred at some stage during the handling and labelling of the soil sample or subsequent analyte
2. an error in the recording of data
3. the enhancement of the EDTA data by metal contamination at some stage in the procedure
4. the total metal extracted by HNO<sub>3</sub> was not a true representation of the actual total present in the soil
5. During analysis by atomic absorption spectrophotometry (AAS), the signal produced by light absorbance was depressed in the HNO<sub>3</sub>, or enhanced in the EDTA analyte (Beatty and Kerber, 1993)
6. EDTA was a more efficient extractant than HNO<sub>3</sub> for some Mendip soils.

Duplicates of the samples from Charterhouse and the Priddy Mineries Reserve that were considered anomalous were reanalysed, and the apparent anomalies were confirmed. The possibility of systematic error in the labelling and handling of samples and analytes was discounted, as was the erroneous recording of data. It was decided, therefore, to examine the extraction and analytical techniques used for the determination of Total Pb and available Pb, Zn and Cd, to ascertain the most suitable methods for the analysis of the soils in this study.

## **3.2 Soil sampling and preparation**

The method of soil collection and preparation described in section 3.2.1 was used for the soils analysed in the methodology experiments and throughout the study. All equipment used during the course of this study was prepared as described in 3.2.2. Where used, the flame atomic absorption spectrophotometer (FAAS) was always operated under the conditions described in 3.2.3.

### **3.2.1 Sample collection and preparation**

#### Field sampling

Soil samples were collected using either a stainless steel screw auger of approximately 22 mm diameter, or a stainless steel trowel, and placed in new polyethylene bags to minimise sample contamination by trace metals. Plastics may contain Pb, Cd and tin (Sn), but in general, polyethylene is relatively free of these metals (Ure, 1990). Paper labels were attached to the outside of the sample bags to minimise further potential sources of metal contamination, including paper fillers, whiteners and marker pen ink (Ure, 1990). The sample bags were labelled with the site reference number, date and sampling depth. At each sampling site details on topography, plant species present and soil characteristics were recorded, where relevant. As much air as possible was expelled from the bag before sealing, although any compaction of the sample was avoided. Samples were transported to the laboratory within two hours of collection and stored in a refrigerator at 4°C in the original sampling bags.

### Laboratory preparation

All soil samples were prepared for drying within 48 hours of collection. The samples were spread on polyethylene-lined, labelled aluminium foil trays. At this stage, any visible macro-organic matter and stones were removed by hand. The samples were then air-dried at approximately 15-20°C. Oven drying is not a recommended preparatory procedure because it is thought to cause profound changes in soil chemistry (Hesse, 1971). When dry, samples were gently disaggregated using a porcelain pestle and mortar and passed through a nylon mesh of 2 mm to give the fine earth fraction, which is also known as the <2 mm air-dry sample. The <2 mm air-dry samples were placed in new, resealable polyethylene bags and labelled as before, with the addition of the soil series name. After the expulsion of excess air from the bags, the samples were sealed and stored under cool, dark and dry conditions until required for analysis.

Prior to analysis, each sample was homogenised, first by manually shaking the sample in the bag and then by quartering. The sample was spread uniformly over a clean sheet of polyethylene and divided into four equal portions (Figure 3.1).

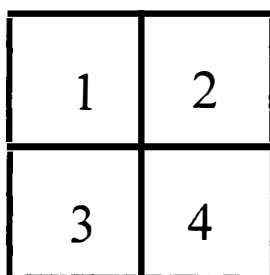


Figure 3.1. Reduction of a soil sample by quartering.



Portions 1 and 4 were disregarded and returned to the sample bag. Portions 2 and 3 were mixed together, spread out again as before and reduced to half by the same procedure. This was repeated until an aliquot of the required mass was obtained (Hesse, 1971). All sample aliquots were weighed to 0.01 g throughout the study.

### **3.2.2 Preparation of analytical equipment**

Depending on the nature of the contaminant, the use of contaminated equipment during any stage of an analytical procedure has the potential to compromise the quality of the data produced. To minimise the risk of contamination from equipment used during the analytical procedures, the following procedure was undertaken. All Pyrex™ glassware, porcelain, non-disposable polyethylene items and other washable equipment were initially left to soak overnight in a hot, 10% solution of Decon® 90, then washed in the same solution. After rinsing thoroughly with tap water, items were left to soak overnight in a 10% solution of HNO<sub>3</sub>. On removal from the acid solution, items were then rinsed three times in deionised water. After each analysis, glassware and polyethylene items were washed in hot water, soaked overnight in a 10% HNO<sub>3</sub>, rinsed three times in deionised water and dried. Glassware was dried in an air cabinet at 40°C, while polyethylene items were left to air-dry.

### **3.2.3 Atomic absorption spectrophotometry**

#### Principle

Flame atomic absorption spectrometry is based on the principle that electrons in the shell of an atom of a specific element will absorb light energy of a wavelength

specific to that element. As the number of atoms in a path of light increases, the amount of light absorbed will also increase. The absorbance follows a linear relationship with concentration as defined by Beer's Law, and by measuring the amount of light absorbed, a quantitative determination of the concentration of that element may be made (Beaty and Kerber, 1993).

In single-beam FAAS, a sample is nebulised and sprayed as an aerosol into the flame, most commonly an air-acetylene flame (2 300°C), so that a beam of light of specific wavelength to the element being analysed for may be passed through it. On heating, the sample molecules in the aerosol are dissociated into free atoms, and these absorb light from the beam (Beaty and Kerber, 1993). The beam of light is generated by a hollow cathode (HC) lamp, and is focused into a narrow beam that passes through the atomiser flame. After passing through the flame, the light is refocused onto the area around the entrance slit of the monochromator. The width of the entrance and exit slit of the monochromator is adjusted so that any light wavelengths other than that of the metal being analysed for is rejected. On reaching the photomultiplier, the light is converted into an electrical signal for measurement (Figure 3.2).

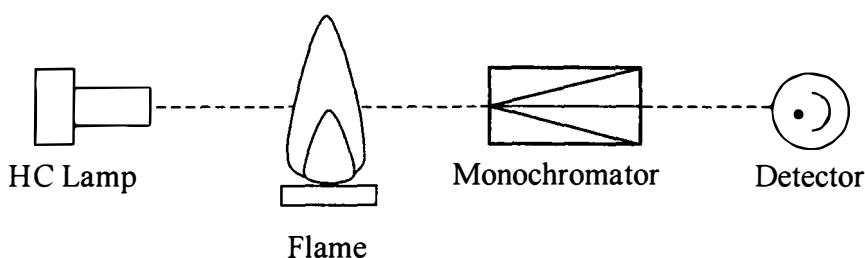


Figure 3.2. Schematic diagram of a single-beam FAAS system. Redrawn from Beaty and Kerber (1993).

The instrument available to this study was the Varian SpectrAA-40 Flame Atomic Absorption Spectrometer driven by SpectrAA Plus software. The AA-40 is a double beam system, which allows the light from the HC lamp to be divided mechanically by a chopper into a sample beam, which is focused through the flame, and a reference beam which is directed around the flame (Figure 3.3). This prevents any fluctuation in the source light intensity causing fluctuation in instrument readout, because the readout represents the ratio of the sample and reference beams (Beaty and Kerber, 1993).

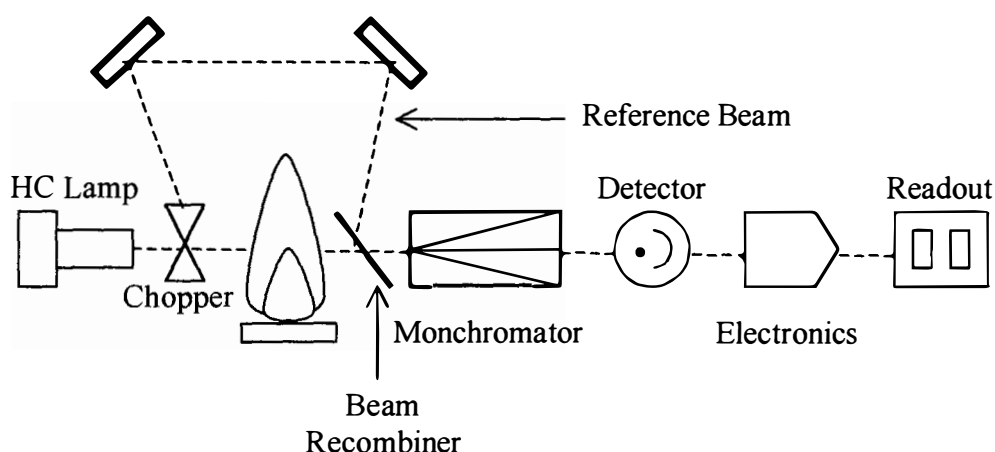


Figure 3.3. Schematic diagram of a double-beam FAAS system. Redrawn from Beaty and Kerber (1993).

### Operating conditions

To ensure operation conditions remained as consistent as possible throughout the study, the photomultiplier voltage was recorded for each element during every analytical run. The FAAS was always operated within  $\pm 5$  Volts of the photomultiplier voltage used during the first analytical run of the study (the baseline voltage). The baseline photomultiplier voltages are listed in Table 3.2.

Table 3.2. The standard operating conditions used with the Varian SpectrAA-40.

Element	Lamp Current (mA)	Slit Width (nm)	Wave Length (nm)	Precision (% RSD)	Default Time (sec)	Delay Time (sec)	Deuterium Background Correction
Pb	5	1.0	217.0	1.0	10	2	ON
Zn	5	1.0	213.9	1.0	10	2	ON
Cd	4	0.5	228.8	1.0	10	2	ON
Cu	4	0.5	324.8	1.0	10	2	ON
Fe	5	0.2	372.0	1.0	10	2	OFF
Mn	5	0.2	279.5	1.0	10	2	ON
Ca	10	0.5	422.7	1.0	10	2	OFF
Mg	5	0.5	285.2	1.0	10	2	ON

The Varian Spectra AA-40 has the capability to measure the concentration of an element in an analyte by one of two methods. The first method is by calculating the mean concentration in the analyte by the measurement of a pre-determined, fixed number of separate absorbance determinations. The second method is by measuring a pre-set number of determinations of the absorbance of an analyte until a pre-determined precision of analysis % RSD (% Relative Standard Deviation) is reached within a set default time. Throughout the study, the RSD was set at 1%, with a default time of 10 seconds, at a delay of 2 seconds (Table 3.2). This meant that every 2 seconds an absorbance reading was measured until the % RSD of the readings was 1% or less. When this point was reached, analysis ceased and the concentration of the element and its % RSD displayed. If the RSD of the absorbance readings had not reached 1% within 10 seconds of analysis, at 10 seconds, the concentration of the element was calculated from the mean of the total absorbance readings taken, and the actual % RSD was given.

## Calibration

In order to measure the concentration of a specific element in an analyte, a FAAS must first be calibrated by the measurement of the absorbance of known concentrations of that element. When calibrating a FAAS, the calibration relationship between absorbance of light and concentration follows a curved path. The relationship is directly proportional following Beer's Law over a certain range, known as the linear range, but as concentration and absorbance increase, a deviation from linearity occurs causing a curved effect. The accuracy of any readings made from the portion of the curve out of the linear range is reduced. Analysis for each element was carried out in the linear range of the calibration curve for that specific element (Table 3.3) (Perkin Elmer, 1982).

Table 3.3. Baseline photomultiplier voltage and top of the linear range values for the elements analysed with the Varian SpectraAA-40.

Element	Baseline Photomultiplier Voltage (V)	Linear Range (mg l <sup>-1</sup> )
Pb	373.5	20
Zn	345.2	1
Cd	310.8	2
Cu	376.5	5
Fe	332.7	25
Mn	385.8	2
Ca	257.7	5
Mg	310.8	0.5

If an analyte differs in viscosity, or has a considerably different surface tension to that of the calibrating standard, the nebulisation efficiency or analyte uptake rate might differ between analyte and standard creating matrix interference (Beatty and Kerber, 1993). To ensure standardisation of viscosity, during calibration, all calibration standards were made with SpectroSol® AAS standard solutions, and

made up to volume with the reagent used for sample decomposition, in the same percentage v/v as the analyte.

### Analytical protocol

During sample analysis, if a determination was found to be outside the linear range for the specific element under analysis, the analyte was diluted to bring it into range. Any analyte dilutions were also made with a reagent matched to the analyte in an attempt to reduce matrix interference. Analytes were numbered and analysed randomly. A prepared solution containing a known concentration of the element under analysis was also analysed throughout each analytical run to assess the accuracy of the FAAS. The solution was analysed after every fifth sample analysis, and if necessary, the FAAS was recalibrated. The concentration of an element in a soil sample ( $\mu\text{g g}^{-1}$ ) was calculated from the concentration of the element in the analyte (FAAS reading in  $\text{mg l}^{-1}$ ) as follows:

$$\begin{array}{ccccccc} \text{metal concentration} & & \text{FAAS} & & \text{analyte} & & \text{final volume of analyte (ml)} \\ \text{in soil sample} & = & \text{reading} & \times & \text{dilution} & \times & \text{-----} \\ (\mu\text{g g}^{-1}) & & (\text{mg l}^{-1}) & & \text{factor} & & \text{aliquot mass (g)} \end{array}$$

Results of all metal analyses were expressed on an oven-dry basis (DM). Where the concentration of an element was below the detection limit for the FAAS, a value of half the detection limit was recorded for data handling purposes. The detection limit is defined as the lowest concentration which can be clearly differentiated from zero (Beaty and Kerber, 1993).

### **3.3 Method development for total soil trace metal analysis**

Studies involving the determination of total trace metals in soil and sediment revealed a plethora of methods for the decomposition of soil samples. Most included the digestion of aliquots of soil or sediment in strong acid by boiling with a period of refluxing, separation of the supernatant from remaining solids and taking the analyte up to volume. Major variations in methods were noted for the type of reagent used, aliquot mass to reagent volume ratio and refluxing time. In the absence of an apparent standard method, a suitable technique needed to be determined experimentally and adopted throughout the study for the most efficient and reproducible digestion, within the context of health and safety and the equipment available. Of the reagents most commonly used for total extraction, hydrofluoric acid (HF) and perchloric acid (HClO<sub>4</sub>) were immediately rejected for reasons of safety. HF is capable of dissolving silica and silicates so cannot be used in glass vessels. HClO<sub>4</sub> is explosive when exposed to samples with high organic matter and its fumes may also accumulate in exhaust systems and cause explosion on contact with wood or plastic (Ure, 1990).

Several mineral acids such as sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), HNO<sub>3</sub> and their mixtures were extensively used. Although not able to dissolve silica or silicates, these acids are able to dissolve metals not bound to silicate. However, digestion by H<sub>2</sub>SO<sub>4</sub> is not suitable for analysis by FAAS because of its complex interference effects (Ure, 1990), which left HCl, HNO<sub>3</sub> and their mixtures for assessment. Digestions using these reagents are sometimes referred to as 'total', pseudo-total, or described according to the reagent used (e.g. HNO<sub>3</sub> extractable) in the literature. As well as a considerable variation in the reagent or

mixture of reagents used for decomposition, the actual method of decomposition was also found to vary considerably in the vessels used, aliquot mass to reagent volume ratio, refluxing period and final volume. The following series of three experiments were therefore undertaken to determine the most efficient, reproducible and safe method of sample decomposition by acid digestion for the analysis of total Pb concentrations in the soils of this study.

- Experiment 1. A comparison of extraction techniques and reagents
- Experiment 2. An assessment of refluxing times
- Experiment 3. A comparison of soil aliquot mass: reagent volume ratios.

### **3.3.1 Precision, accuracy and quality control**

The first stage of the experimental design involved the consideration of the general objective of an analysis, which is to produce results which are as precise and accurate as possible so that the data generated might be analysed with confidence. Precision is the reproducibility of data, and an analysis that is repeated with the same result each time has high precision. The accuracy of data produced by an analysis is its correctness relative to some absolute standard (Avery, 1982). The accuracy of a method is directly related to its efficiency. In this series of experiments, the efficiency of extracting total soil Pb was determined.

As with any analysis, errors may be introduced at any stage by contamination, but precautions were taken to minimise these and ensure quality control. During digestion, a control blank was prepared by carrying out the digestion procedure with the omission of the aliquot of soil. Control blanks were analysed with each batch to detect any contamination from vessels or reagents. AnalaR® grade



reagents and deionised water were used throughout, although it was noted that deionised water has been cited as a potential source of complexed trace metals such as Cu (Ure, 1990). Before selection for analysis, soil sample numbers were randomised using the random sample command in Minitab® for Windows 12.1. The use of a commercially prepared Certified Reference Material, analysed in an identical manner to the samples under investigation, is often used to validate the analysis in terms of accuracy, and, when used repeatedly as a routine quality control, precision. Although used later in this study in the main body of analyses, for this series of experiments a Certified Reference Material was not analysed.

Certified Reference Material is expensive, and the cost of using it in the quantities required for this series of experiments was prohibitive. It could also be argued that the use of a Certified Reference Material would have only determined the method best suited to the analysis of that particular Certified Reference Material. Each soil has unique physiochemical characteristics that may have the potential to influence the results of any analysis. As the major objective of the experiments was to determine a method of digestion suitable for soils typical of the site under investigation, it was considered more appropriate that a soil from the site be used. In terms of overall quality control throughout the set of experiments, the use of Certified Referenced Material would have been of questionable value because the experiments involved the manipulation of analytical factors both within and between experiments.

While accuracy was considered important, perhaps of greater relevance to the objective of the experiments was the precision of the results. Although analyses

may be carried out to the optimum standard possible, accuracy will always be limited by the techniques, reagents and instrumentation available to a study. Unless the exact method was duplicated by the same analyst, extreme caution must be employed when making comparisons between the data generated by different studies. What was considered crucial to this study was that results were precise so that data generated from the samples could be compared with confidence within the study.

The measure of precision may be given by the coefficient of variation (CV) between sample replicates. Coefficient of variation is expressed as a percentage ( $\% \text{ CV} = (\text{SD} / \text{mean}) \times 100$ ), and a precision target of  $\pm 10\%$  CV has been considered acceptable by many workers for this type of analysis (Thompson and Howarth, 1978; Sinex *et al.*, 1980; Davies, 1983a; Li and Thornton, 1992; Maskall *et al.*, 1995). To ensure the reproducibility of results, a precision target of  $\pm 10\%$  CV was adopted for the series of experiments. In the main body of the study, sample replication for all parameters was matched to the requirements of each investigation and is discussed in the appropriate section.

### **3.3.2 Experiment 1. Comparison of extraction techniques and reagents**

#### **Introduction**

Five series of decomposition procedures for the analysis of the Total Pb concentration of soil were carried out to evaluate the efficiency and precision of 69% (v/v)  $\text{HNO}_3$  and in combination with 69% (v/v)  $\text{HCl}$ . A pre-treatment of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), was also used in two procedures to oxidise organic matter before decomposition.

## Method and materials

A bulk sample of 20 sub-samples was collected from the Priddy Mineries Reserve at ST 3547 1511 at a depth of 100 mm using a stainless steel trowel. The bulk sample was removed from the site and prepared for analysis by the procedures described in 3.2.1. Five replicate soil aliquots of 5.0 g, 1.0 g or 0.5 g, depending on the decomposition procedure (Table 3.4), were weighed directly into the macro test tubes used with the Gerhardt Kjeldatherm macro digestion system. Where required, aliquots were treated with 20% (v/v) H<sub>2</sub>O<sub>2</sub> overnight, prior to the addition of the extractant to oxidise organic matter. The appropriate reagents (Table 3.4) were then added to the tubes by a tilt dispenser of appropriate volume. The tubes were placed into the digestion block, a thermostatically controlled heating block of aluminium designed to hold the digestion tubes.

Table 3.4. Soil mass, reagent type and volume, and pre-treatment.

<b>Mass/Volume/Reagents/Treatment</b>
5.0g/20 ml 3:1 HCl:HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>
1.0g/20 ml 3:1 HCl:HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>
0.5g/10 ml HNO <sub>3</sub>
0.5g/10 ml 9:1 HNO <sub>3</sub> :HCl
0.5g/10 ml 3:1 HNO <sub>3</sub> :HCl

A Gerhardt Turbosog TUR/6300 exhaust system was fitted to the digestion tubes and the thermostatic control of the digestion block was set at 150°C. After all reagents reached boiling point, the thermostat was reset at 140°C and the samples

were refluxed for 1 hour. All replicates of the two series that were pre-treated with  $\text{H}_2\text{O}_2$  were heated to near dryness by increasing the temperature to  $170^\circ\text{C}$ . After cooling, 20 ml deionised water were added to each analyte and the tube gently agitated to mix its contents. Analytes were filtered through a funnel lined with a Whatman® 451 paper into a 50 ml volumetric flask, and made up to volume with deionised water. Analytes were analysed by FAAS under the operating conditions described in 3.2.3. within 24 hours of preparation. If analysis was delayed by more than 1 hour after preparation, analytes were stored in a refrigerator at  $4^\circ\text{C}$  and on removal, left to reach equilibrium with room temperature before analysis. The mean, Standard Deviation about the mean (SD) and % CV were calculated for each data set. Data sets were also analysed to assess whether any differences between sets were significant using Analysis of Variance (ANOVA). All statistical analyses were carried out using either Microsoft Excel or Minitab® Version 12.1 for Windows Statistical software.

## Results

The most efficient extraction was with 0.5 g of soil in 10 ml 3:1  $\text{HNO}_3$ :HCl, while the least efficient was 5.0 g soil in 20 ml 3:1 HCl: $\text{HNO}_3$  with  $\text{H}_2\text{O}_2$  pre-treatment (Table 3.5). The greatest analytical precision was obtained with 1.0 g soil in 20 ml 3:1 HCl: $\text{HNO}_3$  with  $\text{H}_2\text{O}_2$  pre-treatment, while the poorest precision was obtained for 0.5 g soil in 10 ml 3:1  $\text{HNO}_3$ :HCl. There was a significant difference in extraction efficiency at the  $p=0.000$  level between all reagents, although there was no significant difference in extraction efficiency between 0.5g/10 ml  $\text{HNO}_3$ , 0.5g/10 ml 9:1  $\text{HNO}_3$ :HCl and 0.5g/10 ml 3:1  $\text{HNO}_3$ :HCl (Table 3.5).

Table 3.5. Extraction efficiency and analytical precision of some commonly used extraction procedures (n=sample number).

Mass/Volume/Reagents/Treatment	n=	Total Pb ( $\mu\text{g g}^{-1}$ )		
		Mean	SD	% CV
5.0g/20 ml 3:1 HCl:HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	5	6 440	467	$\pm 7.2$
1.0g/20 ml 3:1 HCl:HNO <sub>3</sub> + H <sub>2</sub> O <sub>2</sub>	5	32 000	1 204	$\pm 3.7$
0.5g/10 ml HNO <sub>3</sub>	5	95 400	5 128	$\pm 5.4$
0.5g/10 ml 9:1 HNO <sub>3</sub> :HCl	5	95 800	8 044	$\pm 8.4$
0.5g/10 ml 3:1 HNO <sub>3</sub> :HCl	5	97 600	11 696	$\pm 11.9$

## Discussion

Although 3:1 HNO<sub>3</sub>:HCl extracted 2 100  $\mu\text{g g}^{-1}$  more Pb than HNO<sub>3</sub> in this series of experiments, the % CV between the replicates was over twice that of HNO<sub>3</sub> (Table 3.5). This indicated that in terms of precision HNO<sub>3</sub> would be a more satisfactory reagent. The use of 3:1 HCl:HNO<sub>3</sub> with a pre-treatment of H<sub>2</sub>O<sub>2</sub> both 1:4 and 1:10 soil:reagent ratios reduced extraction efficiency.

### 3.3.3 Experiment 2. Assessment of refluxing periods

#### Introduction

A step in decomposition procedures involving HNO<sub>3</sub>, HCl and their mixtures that varies greatly between studies is the period of refluxing used. Extreme examples included refluxing for periods of up to 6 hours at 120°C (Johnson *et al.*, 1978), or overnight at 60°C (Agemian and Chau, 1976). A series of analyses to assess the efficiency and precision of the most efficient reagents from 3.3.1 for the extraction of Pb from soil was carried out using varying periods of refluxing.

## Method and materials

The soil samples were collected and prepared for decomposition in accordance with the methods described in 3.2.1. Five replicate 0.5 g aliquots of soil for each treatment were weighed into Kjeldatherm macro digestion tubes and 10 ml of either  $\text{HNO}_3$ , 9:1  $\text{HNO}_3\text{:HCl}$ , or 3:1  $\text{HNO}_3\text{:HCl}$  were added by tilt dispenser. All reagents were AnalaR® grade at 69% (v/v) strength. Decomposition was carried out using the procedure described in 3.3.2, but with refluxing periods for each of the three treatments varied in hourly increments from 1 hour up to a maximum of 4 hours. Analytes were analysed by FAAS under the operating conditions described in 3.2.3. within 24 hours of preparation. Data were statistically analysed using the tests described in 3.3.2.

## Results

The most efficient extraction was with  $\text{HNO}_3$  using a refluxing period of one hour, while the least efficient was with 3:1  $\text{HCl:HNO}_3$  using a refluxing period of three hours. The greatest analytical precision was obtained with  $\text{HNO}_3$  using a refluxing period of three hours, while the poorest precision was with 3:1  $\text{HCl:HNO}_3$  with a refluxing period of one hour (Table 3.6). There was a significant difference at the  $p=0.000$  level in extraction efficiency between the refluxing periods for all reagents. There was also a significant difference at the  $p=0.001$  level in extraction efficiency between the refluxing periods for the  $\text{HNO}_3$  treatment.

Table 3.6. Comparison of the extraction efficiency and analytical precision of three extractants and four refluxing periods (n=sample number).

Refluxing Time	n=	Mean Total Pb ( $\mu\text{g g}^{-1}$ )		
		HNO <sub>3</sub>	9:1 HNO <sub>3</sub> :HCl	3:1 HNO <sub>3</sub> :HCl
1 Hour	5	108 200	95 600	94 200
SD		$\pm 2\,490$	$\pm 4\,980$	$\pm 7\,694$
% CV		2.3%	5.2%	8.2 %
2 Hours	5	98 800	90 800	91 800
SD		$\pm 4\,648$	$\pm 5\,848$	$\pm 6\,140$
% CV		4.7%	6.4%	6.7%
3 Hours	5	98 800	91 800	86 600
SD		$\pm 2\,387$	$\pm 3\,564$	$\pm 3\,578$
% CV		2.4%	3.8%	4.1%
4 Hours	5	98 800	96 800	90 800
SD		$\pm 3\,493$	$\pm 3\,564$	$\pm 5\,850$
% CV		3.5%	3.7%	6.4%

## Discussion

For each period of refluxing, the HNO<sub>3</sub> extraction was more efficient and had greater reproducibility than either of the HNO<sub>3</sub>/HCl mixtures (Table 3.6). Within the HNO<sub>3</sub> treatments, there was a significant difference at the  $p=0.001$  level between refluxing periods, with the one hour refluxing period extracting 8.7% more Pb than at two, three or four hours (Table 3.6).

### 3.3.4 Experiment 3. Soil aliquot mass: reagent volume ratios

#### Introduction

A series of four analytical extractions for soil Pb were carried out to evaluate the efficiency and precision of various aliquot mass to reagent volume ratios.

### Method and materials

The soil samples were collected and prepared for decomposition in accordance with the methods described in 3.2.1. Five replicate aliquots of 0.5 g of soil were weighed into Kjeldatherm macro digestion tubes. This was repeated with aliquots of 1.0 g, 2.0 g and 5 g of soil. AnalaR® grade 69% (v/v) HNO<sub>3</sub> was added to the aliquots of soil in the volumes described in Table 3.7 by tilt dispenser, giving aliquot mass :reagent volume ratios of 1:20, 1:10, 1:10, and 1:5 respectively.

Decomposition was carried out using the procedure described in 3.3.2. Analytes were analysed by FAAS under the operating conditions described in 3.2.3. within 24 hours of preparation. Data were statistically analysed using the tests described in 3.3.2.

### Results

The most efficient soil aliquot mass:reagent ratio for the HNO<sub>3</sub> extraction of soil Pb with a refluxing period of one hour was 1:20, while the least efficient extraction was with a ratio of 1:5 (Table 3.7). The 1.0 g soil aliquot in 10 ml HNO<sub>3</sub> treatment had the highest reproducibility, but there was only 0.4% CV difference between that and the reproducibility of the 1:20 soil:HNO<sub>3</sub> ratio. The poorest reproducibility was for the 1:5 soil:HNO<sub>3</sub> ratio at  $\pm 79.4\%$ . Statistically, there was a significant difference at the  $p=0.000$  level in extraction efficiency between the different aliquot mass/HNO<sub>3</sub> volume treatments.



Table 3.7. Comparison of various soil aliquot mass:reagent volume ratios for extraction efficiency and analytical precision (n=sample number).

Aliquot Mass/HNO <sub>3</sub> Volume	Ratio	n=	Total Pb (µg g <sup>-1</sup> )		
			Mean	SD	% CV
0.5 g / 10 ml	1 : 20	5	104 500	2 592	± 2.5
1.0 g / 10 ml	1 : 10	5	100 500	2 044	± 2.1
2.0 g / 20 ml	1 : 10	5	100 287	12 592	± 12.6
5.0 g / 25 ml	1 : 5	5	25 175	19 995	± 79.4

### Discussion

Although there was no significant statistical difference between the 1:10 and 1:20 treatments, an aliquot mass to HNO<sub>3</sub> volume ratio of 1:20 where mass was 0.5 g to 10 ml volume appeared to be the most efficient extractant within an acceptable precision limit of >10% CV. The analyte produced with a ratio of 1:5 was found relatively inefficient in terms of extraction and precision. It was also noted that on cooling, white crystals formed in the analyte. It is proposed that this was an indication of reagent saturation that might have implications for extraction efficiency and precision in at least three ways:

1. the reduction of the total amount of Pb being brought into solution
2. the saturation of the solution by other elements may distort absorption measurements during analysis; an excess of particulate matter in the flame may cause light scattering for example. The presence of carbonate, acetate and iodine is also known to distort measurements (Beaty and Kerber, 1993)
3. a saturated solution may be very different in viscosity to the standard solutions used to calibrate the FAAS, causing further distortion.

### **3.3.5 Method selection**

For the extraction of Pb from soil, the results of this series of experiments confirmed the findings of Agemian and Chau (1976) and Harrison and Laxen (1977) that 69% (v/v) HNO<sub>3</sub> used alone was at least as efficient as when in combination with HCl. Agemian and Chau (1976) also reported that for the extraction of Zn, Cd and Cu from soil, HNO<sub>3</sub> was more efficient when used alone. It was concluded that the preferred analytical technique for soil sample decomposition throughout this study was an aliquot mass to reagent volume ratio of 1:20, where aliquot mass was 0.5 g and HNO<sub>3</sub> volume 10 ml, with a refluxing time of 1 hour, and final volume of 50 ml.

## **3.4 Method development for available soil trace metals analysis using EDTA**

### **3.4.1 Introduction**

EDTA is a chelating agent which complexes strongly with metal ions held on the surface of soil particles. After desorption from the soil, the metal ions are complexed into solution (Rowell, 1994). The standard method for the extraction of available trace metals by EDTA uses a soil aliquot mass:EDTA volume ratio of 1:5 (MAFF, 1985). The anomalous results produced by Wilson (1994) however, suggested that the method needed to be assessed for use on Mendip soils contaminated with Pb and Cd (Table 3.1). This view was supported by Lambkin (1999), who suggested that the concentration of Cd from the Mendip soil used in her study was underestimated by EDTA extraction, and that for highly contaminated soils, further investigation of the soil aliquot mass:EDTA volume ratio was needed. The following experiment was designed to manipulate the soil aliquot mass:EDTA volume to determine the most accurate and precise method for

the extraction of Pb, Zn and Cd from the Mendip soil collected especially for this trial.

### Method and materials

The soil used was a combination of the <2 mm fractions of a soil typical of the Thrupe series found on the Priddy Mineries Reserve collected from ST 3546 1511, and a soil from ST 3446 1581, the site of the former calamine ( $\text{ZnCO}_3$ ) workings at Shipham. A pilot study showed that the Cd concentration in the soil from the Priddy Mineries Reserve was at the detection limit of the FAAS used in this study. The addition of the Shipham soil provided measurable concentrations of Cd to the soil. The soils were collected and prepared by the methods described in 3.2.1. When dried and sieved, the two soils were combined and manually homogenised by placing in a large polyethylene container and shaking end over end for 30 minutes.

The 0.05 M ammonium EDTA was prepared by dissolving 14.6 g of AnalaR® EDTA in 950 ml deionised water, which contained 8 ml 35% (v/v) ammonia solution, in a 1 l beaker. The pH was adjusted to 7.0 by the addition of M  $\text{HNO}_3$  or 35% (v/v) ammonia solution. The solution was transferred to a 1 l volumetric flask, and made to volume with deionised water.

Aliquots of 0.5 g, 1.0 g, 2.5 g, 5.0 g, 7.5 g and 10.0 g of soil were weighed directly into polyethylene shaking bottles. A measuring cylinder was used to dispense 50 ml 0.05 M ammonium EDTA to each shaking bottle, giving the soil aliquot mass:EDTA ratios listed in Table 3.8. After sealing, the bottles were

shaken on a Gerhardt Laboshake LS/5 at a frequency of 120 cycles min<sup>-1</sup> for 1 hour at room temperature. Five replicate analyses were carried out for each ratio and a reagent blank of 50 ml EDTA was prepared. The extracts were filtered through funnels lined with a Whatman® 452 paper, and the filtrates retained for analysis by FAAS. All analytes were analysed within 2 hours of preparation. The FAAS was operated under the conditions described in 3.2.3, with the calibration standards and any necessary dilutions made with 0.05 M ammonium EDTA. The bioavailable metal concentration in soil was calculated as follows.

$$\begin{array}{ccccccc} \text{metal concentration} & & \text{FAAS} & & \text{analyte} & & \text{final volume of analyte (ml)} \\ \text{in soil sample} & = & \text{reading} & \times & \text{dilution} & \times & \text{-----} \\ (\mu\text{g g}^{-1}) & & (\text{mg l}^{-1}) & & \text{factor} & & \text{aliquot mass (g)} \end{array}$$

Results of all metal analyses were expressed on an oven-dry basis (DM). Data were statistically analysed using the tests described in 3.3.2.

## Results

For Pb, there was a significant difference at the p=0.000 level in extraction efficiency between soil:EDTA ratios (Table 3.8). The most efficient extraction was from the 1:100 soil:EDTA ratio, while the poorest was from the 1:5 soil EDTA ratio. However, at ±11.9 % CV, the precision was out of the limit of ±10% set for this study. There was a significant difference at the p=0.000 level in extraction efficiency between soil:EDTA ratios in the Zn treatments. The soil:EDTA ratio of 1:10 compared favourably for both the extraction efficiency and reproducibility with the other soil: EDTA ratios for Zn. The poorest extraction efficiency was at a 1:5 soil:EDTA ratio (Table 3.8). For Cd there was a significant

difference at the  $p=0.000$  level in the extraction efficiency between soil:EDTA ratios. A ratio of 1:100 soil:EDTA produced the most efficient extraction, while the 1:5 soil:EDTA ratio was the least efficient. The most reproducible results were from the 1:6.66 soil:EDTA extraction, and the least from the 1:100 soil:EDTA extraction (Table 3.8).

Table 3.8. Comparison of the extraction efficiency and analytical precision of various soil aliquot mass:EDTA volume ratios (n=sample number).

		Mean EDTA Extractable Trace Metals ( $\mu\text{g g}^{-1}$ )					
Aliquot Mass g Mass : EDTA	n=	0.5 g 1:100	1.0 g 1:50	2.5 g 1:20	5.0 g 1:10	7.5 g 1:6.6	10.0 g 1:5
<b>Pb</b> SD % CV	5	10 666 $\pm 1\ 204$ 11.3%	9 715 $\pm 221$ 2.3%	9 540 $\pm 143$ 1.5%	9 960 $\pm 412$ 4.1%	9 076 $\pm 169$ 1.9%	8 915 $\pm 179$ 2.0%
<b>Zn</b> SD % CV	5	4 236 $\pm 136$ 3.2%	4 218 $\pm 166$ 3.9%	4 400 $\pm 240$ 5.5%	4 579 $\pm 124$ 2.7%	3 926 $\pm 100$ 2.5%	3 619 $\pm 108$ 3.0%
<b>Cd</b> SD % CV	5	149 $\pm 12$ 8.0%	141 $\pm 6$ 4.5%	147 $\pm 7$ 4.8%	142 $\pm 4$ 2.7%	135 $\pm 2$ 1.3%	130 $\pm 3$ 2.0%

### Discussion

The soil aliquot mass:EDTA volume ratio of 1:10 appeared to be more efficient in terms of extraction for the trace metals Pb, Zn and Cd than 1:6.6 or the MAFF (1985) recommended 1:5. It is possible that the MAFF (1984) method may not have been efficient because it was intended for the analysis of agricultural soils, and not for soils from areas of anomalous mineralisation such as the Mendip Mineries. The improved efficiency of the 1:10 ratio over the 1:5 ratio of the

standard MAFF (1984) method was in agreement with the findings of Lambkin (1999) for Cd in Shiphams soils. This suggested three immediate possibilities:

1. the saturation of the EDTA by elements other than Pb, Zn and Cd might have occurred at 1:6.6 and 1:5, causing an actual decrease in the concentration of Pb, Zn and Cd being brought into solution,
2. the presence of elements other than Pb, Zn and Cd in high concentrations in the EDTA at 1:6.6 and 1:5 may have caused matrix interference, and light absorbance by Pb, Zn and Cd was depressed during analysis by FAAS,
3. if the EDTA was saturated at 1:6.6 and 1:5, there may have been a significant difference between the viscosity of the analyte and calibration standard solution.

For Zn, extraction was more efficient at a ratio of 1:10 than any other, while the 1:100 soil mass/EDTA ratio extracted a greater concentration of Pb and Cd (Table 3.8). However, the 1:100 method was rejected because as well as its lower precision, the concentration of Cd in the soils of the baseline study was expected to be much less than the Cd concentration in the soil used during these experiments (Ginnevar, 1985). The analytical results and expected low concentrations of soil Cd indicated that a soil aliquot mass:reagent volume ratio of 1:5, where aliquot mass was 5 g and reagent volume 50 ml, would be the most suitable method to determine the EDTA extractable trace metals in the soils of this study.

### **3.5 Statement of methods for routine analysis**

#### **3.5.1 Total soil trace metal analysis**

The routine analytical technique used for soil sample decomposition for total trace metal analysis throughout this study was an acid digestion using 69% (v/v)

AnalaR® HNO<sub>3</sub>. The >2 mm fraction of air-dried soil in an aliquot mass to reagent volume ratio of 1:20 was digested, where aliquot mass was 0.5 g and HNO<sub>3</sub> volume was 10 ml. A refluxing time of 1 hour and final volume of 50 ml were used throughout.

### **3.5.2 Available soil trace metal analysis**

The routine analytical technique used for soil sample decomposition for available trace metal analysis throughout this study was an EDTA extraction using AnalaR® grade EDTA. The >2 mm fraction of air-dried soil in an aliquot mass to reagent volume ratio of 1:5 was used, where aliquot mass was 5 g and reagent volume 50 ml. The reagent/soil suspensions were shaken on a Gerhardt Laboshake LS/5 at a frequency of 120 cycles min<sup>-1</sup> for 1 hour at room temperature

## **CHAPTER 4**

### **THE BASELINE SOIL STUDY**

#### **4.1 Introduction**

##### **4.1.1 Aim and objectives**

The primary aim of the baseline soil survey was to assess the local environmental impact of historical lead mining and processing on the soils of the Priddy Mineries Reserve, St. Cuthbert's site and an adjacent section of the Stockhill Plantation (Figure 1.2). This was achieved by the implementation of a geochemical survey of the area involving the sampling and analysing of soil samples and mapping the resulting data to produce distribution maps for soil pH, Loss-on-Ignition, Pb, Zn, Cd, Cu, Iron (Fe) and Manganese (Mn).

##### **4.1.2 Trace metals**

As well as contamination from the metal once produced at an historic mining and processing site, sediments and soils are often enriched with other elements that occur as a feature of that particular type of mineralisation. Although the mineralisation of the Mendip region is predominantly lead-zinc, other metals present include Cu, Cd, Fe, Mn, silver (Ag) and gold (Au) (Alabaster, 1982). These metals are often referred to as 'heavy metals' in literature concerned with environmental and pollution studies, although the terms 'trace metals' or 'Borderline elements' are used.



The term ‘heavy metal’ can be defined as a metal with an atomic number of greater than 20 (Tiller, 1989), or a metal with a specific gravity or relative density of greater than 5 g cm<sup>-3</sup> (Passow *et al.*, 1961), or 6 g cm<sup>-3</sup> (Alloway, 1990a). Because these metals are generally present in crustal rocks and soils at concentrations of less than 1%, and frequently below 0.01% (100 µg g<sup>-1</sup>) (Alloway, 1990a), or in soils at concentrations of less than 1 mol m<sup>-3</sup> (Mattigod *et al.*, 1981), they are also described as trace metals (Table 4.1).

Table 4.1. Physiochemical properties of selected trace metals (Constructed with data from Kaye and Laby (1973).

Element	Atomic Number	Atomic Weight	Relative Density g cm <sup>-3</sup>	Melting Point (°C)	Boiling Point (°C)	Crustal Abundance (µg g <sup>-1</sup> )
Lead (Pb)	82	207.200	11.343	372.502	1 760	10.00
Zinc (Zn)	30	65.380	7.135	419.580	913	82.00
Cadmium (Cd)	48	112.400	8.647	321.108	770	0.18
Copper (Cu)	29	63.540	8.933	1 084.500	2 580	58.00
Iron (Fe)	26	55.840	7.873	1 540.000	2 760	58 000.00
Manganese (Mn)	25	54.938	7.473	1 250.000	2 120	1 000.00

In a classification of elements that are commonly considered environmental pollutants, Nieboer and Richardson (1980) proposed a system that recognised three categories: Class A, Class B and Borderline elements. The system was based on equilibrium constants that describe the formation of metal ion/ligand complexes. Elements which showed preferences for ligands containing oxygen were classified as Class A, those with preferences for ligands containing nitrogen or sulphur, as Class B, and elements of intermediate character as Borderline (Martin and Coughtrey, 1982). The trace metals which are commonly environmental pollutants, including those under consideration in this study, all occur in the

Class B and Borderline groups, (Table 4.2). The classification was proposed to replace the non-descript term 'heavy metals' by a biologically and chemically significant classification of metal ions (Nieboer and Richardson, 1980).

Table 4.2. Class B and Borderline elements included in this study (Niebor and Richardson, 1980).

Class B	Borderline
Lead Pb (IV)	Lead $Pb^{2+}$
Copper $Cu^{+}$	Zinc $Zn^{2+}$
	Cadmium $Cd^{2+}$
	Iron $Fe^{2+}$ and $Fe^{3+}$
	Manganese $Mn^{2+}$

The confusion which has arisen with the uncritical use of the term 'heavy metal' in literature has been discussed by several authors, including Nieboer and Richardson (1980), Phipps (1981), Martin and Coughtrey (1982) and Ross (1994a). In this study, the metals of interest will be referred to collectively as 'trace metals' as a term of convenience. Where literature is cited however, the original terminology will be retained.

#### 4.1.3 Geochemistry of trace metals

The *in situ* chemical weathering of mineral rocks and anthropogenic activities provide the two main sources of trace metals into soils. Brady (1990) defined soil as the upper and biogeochemically weathered portion of the regolith or unconsolidated matter overlying rocks. Soil properties such as colour and texture are determined mainly by the physiochemical properties of the parent material

(Findlay, 1965). While the trace metal content of a soil may also be strongly related to the physiochemical properties of its parent material, as a consequence of industrialisation, agricultural practices and urbanisation, there are also many anthropogenic sources of trace metals to the soil. The input of trace metals to a soil from anthropogenic sources may enhance, or exceed those of natural geological sources (Thornton, 1981). As well as metalliferous mining and smelting, trace metals may also enter the soil through emissions from metal manufacturing industry, atmospheric emissions from power stations or factories powered by oil or coal, municipal incinerators or moving sources such as motor vehicles, the use of agriculture chemicals and waste disposal on land (Assami, 1988; Ross, 1994c). Martin and Coughtrey (1982) provided a comprehensive summary of literature concerning sources of trace metals into the environment.

Soil properties are continually modified by the actions of biological, hydrological and geological processes which influence the retention, transformation and mobility of trace metals held in the soil (Sposito, 1983). The main processes involved were described by Ross (1994c) to include:

1. *weathering of in situ* parent material
2. *dissolution and solubility* of minerals and complexes, accompanied by *precipitation* and *co-precipitation* of inorganic insoluble species, such as carbonates and sulphides
3. *uptake* by plant roots and *immobilisation* by soil organisms
4. *exchange* onto cation exchange sites of clays or organic matter
5. specific *chemisorption* and *adsorption/desorption* on oxides and hydroxides of aluminium (Al), Fe and Mn
6. *chelation* and *complexation* by different fractions of soil organic matter
7. *leaching* of mobile ions and soluble organo-metal chelates.

How these processes affect the behaviour of metals in soils depends entirely on the trace metal in question, its speciation (chemical form) within that soil and the

properties and conditions of that soil, including particle size distribution and particle surface area, bulk density, temperature, aeration and redox status, pH, ion exchange capacity, quantity and quality of organic matter, type and amount of Fe, Mn and Al oxides, and the type and amount of clay minerals (Sposito, 1983; Paveley, 1988; McBride, 1989; Fergusson, 1990; Ross, 1994c). Although the speciation of an individual metal might change with time, it has been estimated that metal atoms may have a residency time in a soil of hundreds or even thousands of years (e.g. first half lives: Pb 740-5 900 years; Cd 15-1 100 years and Cu 3 10-1 500 years) depending on soil type and its geochemistry (Alloway and Ayres, 1993).

The geochemical behaviour of a trace metal may also be described in terms of its soil phase distribution. Cotter-Howells (1991) described the following soil phases and associated chemical fractions in which a trace metal might be held:

1. *soil solution phase*: as soluble inorganic and organic complexes
2. *adsorbed phase*: on particle surfaces such as clays and organic matter, or Fe/Mn oxides and hydroxides
3. *organic phase*: as insoluble complexes with organic matter
4. *solid phase*: in primary and secondary minerals.

The adsorbed phase of a trace metal in a soil can be either as non-specific adsorption, which tends to be readily exchangeable, or specific adsorption, which is not readily exchangeable. Non-specific adsorption occurs on cation exchange sites, which are negatively charged permanent sites on soil particle surfaces such as silicate clays and pH-dependent sites on organic molecules. These sites retain cations by non-specific electrostatic attraction, and the bonds are not usually

strong so other trace metal cations, and other common soil ions such as including  $\text{Ca}^{2+}$ ,  $\text{K}^+$   $\text{Mg}^{2+}$  and  $\text{H}^+$  can compete for the sites (Ross, 1994c).

Specific adsorption, sorption or chemisorption are terms used to describe the non-exchangeable complexing of metal ions in mineral soils. Adsorption is more specific than exchangeable bonding, and specific trace metal-mineral surface bonding has been widely described (Ross, 1994c). There are a range of adsorbing mineral surfaces, including silicas (Si) and Al hydroxides, however, the consensus of opinion suggests that the most important adsorbing surfaces are the Fe and Mn oxides (Jenne 1977; Robert and Terce, 1989; McBride, 1989, Kinniburgh *et al.*, 1976, McKenzie, 1980). Specific adsorption has been shown to be controlled by pH; metal adsorption was reduced as soil became more acidic (Kinniburgh *et al.*, 1976, McKenzie, 1980). Generally, trace metal adsorption on Fe and Mn oxides is not wholly reversible, and although experimental evidence suggests that adsorbed metals may be exchanged by  $\text{H}^+$  or other metal ions with a specific affinity for the bonding oxide, sorbed trace metals are not generally labile (Brummer and Herms, 1984; McBride, 1989; Ross, 1994c). In general, Fe oxides have the strongest affinity for Pb or Cu, followed by Zn and then Cd (Kinniburgh *et al.*, 1976; McKenzie, 1980). The Fe minerals goethite and haematite also have an affinity for Mn, although this has been shown to be less than that for Pb, Cu and Zn (McKenzie, 1980).

Detailed discussion of the chemical behaviour of individual elements in soil may be found in Alloway (1990a) including separate chapters on Pb (Davies, 1990), Zn (Kiekens, 1990), Cd (Alloway, 1990b) and Cu (Baker, 1990).

#### 4.1.4 Geochemical surveys

Soil trace metal surveys were first carried out in the field of geochemical prospecting (Paveley, 1988). Modern methods using spectrographic techniques were developed in Scandinavia and the former USSR in the 1930s. By the late 1940s, the US Geological Survey was investigating experimental sampling surveys and improving methods of analysis (Hawkes, 1976). In the 1950s, the growth of active trace metal research spread to Britain and other western European countries (Paveley, 1988). Soil surveys may be carried out at national or regional level. In general, however, they are used at local level in sufficient detail to determine the exact location and dimension of an anomaly (Levinson, 1974).

Workers such as Swaine (1955), Vinogradov (1959), Aubert and Pinta (1977), Bowen (1978) and Ure and Berrow (1982) compiled total soil heavy metal concentration data on a world basis. More detailed studies have been carried out for a number of individual countries including Ireland (Brogan *et al.*, 1973), Japan (Imura, 1981), Belgium (De Temmerman *et al.*, 1982), the USA (Shacklette and Boerngen, 1984), Jamaica (Lalor, 1996; Johnson *et al.*, 1996) and Estonia (Bityukova, 2000). Several of these were based on the standard geochemical prospecting method of sampling stream sediments (Paveley, 1988). In Britain, a large scale study of active stream sediment from tributary drainage of England and Wales was presented in map form by The Applied Geochemistry Research Group, Imperial College, London. The *Wolfson Geochemical Atlas of England and Wales* was compiled from analysis of approximately 50,000 samples for elements including Pb, Zn, Cu, Cd, Mn, Fe and cobalt (Co) (Webb *et al.*, 1978).

Because trace metals occur naturally in soil parent material, there is a range of normal background concentrations of metals in soils. In order to recognise an anomaly or assess the possible contamination of a soil, trace metal concentrations must be compared with any previous analyses or with normal or typical background levels (Ure, 1990) (Table 4.3).

Table 4.3. Typical concentrations of some trace metals in soils. All concentrations expressed as  $\mu\text{g g}^{-1}$  ( <sup>a</sup> Swaine, 1955; <sup>b</sup> Kabata-Pendias and Pendias, 1984 and <sup>c</sup> Bowen, 1979).

Element	Normal Range in Soil (1955) <sup>a</sup>	Mean Value in Soil <sup>a</sup>	Normal Range in Soil (1979) <sup>c</sup>	Concentration in Soil Considered Toxic <sup>b</sup>
Pb	2-200	10	2-300	100-400
Zn	10-300	50	1-900	70-400
Cd	0.01-7.00	0.06	0.01-2.00	3.00-8.00
Cu	2-100	30	2-250	60-125
Mn	200-2 000	600	20-10 000	1 500-3 000

While workers such as Nriagu (1978) supported the assessment of values by Swaine (1955), others such as Archer (1980) and Davies (1983a) expressed certain reservations. Davies (1983a) disputed lead values in particular on the grounds of their being based on the subjective assessment of published data, rather than statistical analysis. After a graphical estimation of the normal lead content of some British soils, Davies (1983a) argued that uncontaminated soils were unlikely to contain more than  $110 \mu\text{g g}^{-1}$  Pb, almost half the value of the maximum suggested by Swaine (1955), while mean soil Pb should be revised up by a factor of four to  $40 \mu\text{g g}^{-1}$ .

#### 4.1.5 Sites contaminated by mining and smelting

Anthropogenic sources of metals in soils are classified as either primary or secondary sources. If metals are added to soil as a direct result of working that soil, with the application of fertiliser for example, the source is considered primary. When added as a result of nearby activities such as mining or smelting, the source is considered secondary (Fergusson, 1990). Davies (1983) developed the concept of sources, intermediates, pathways and sinks, in relation to the environmental pathways of trace metals into the biosphere through the mining, dressing and smelting process. Three general distribution processes, or pathways, were recognised as fluvial, atmospheric and gravitational dispersal (Figure 4.1). The sources and pathways of some trace metals to soil from mining and smelting were summarised by Ross (1994b) and shown in Table 4.4.

Table 4.4. Sources and pathways of trace metals from metalliferous mining and smelting to soil (Ross, 1994b).

- 
- |     |  |
|-----|--|
| (a) | Spoil heaps and tailings - contamination through weathering, wind erosion (As, Cd, mercury (Hg), Pb)   |
| (b) | Fluvially dispersed tailings - deposited on soil during flooding, river dredging, etc. (As, Cd, Hg, Pb)  |
| (c) | Transported ore separates - blown from conveyance onto soil (As, Cd, Hg, Pb)   |
| (d) | Smelting (at old sites mining, dressing and smelting often took place within one complex) - contamination due to wind-blown dust, aerosols from stack (As, Cd, Hg, Pb, antimony (Sb), selenium (Se)) |
-



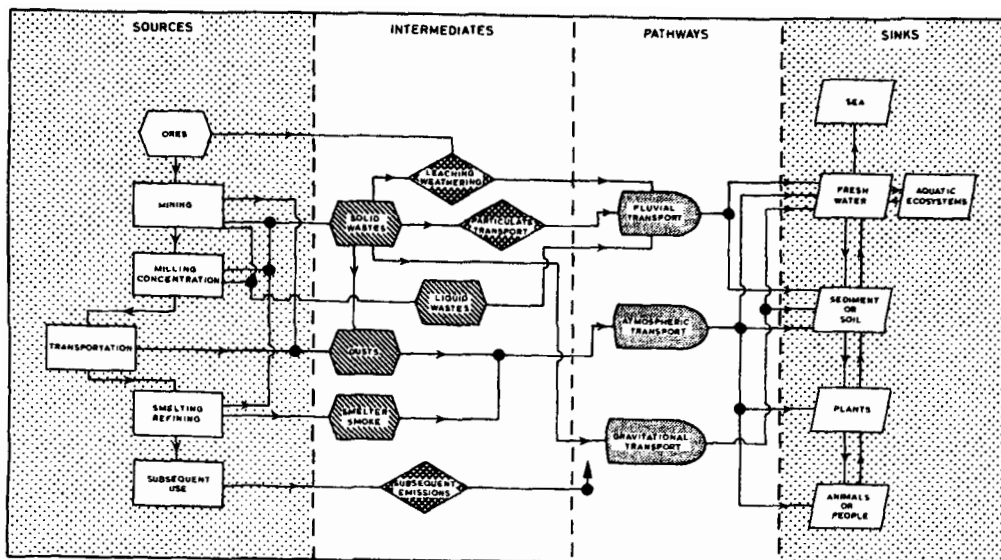


Figure 4.1. The dispersal of trace metals to the environment in mining and smelting areas (Davies, 1983).

Contamination from the wastes associated with metal extraction and processing has been categorised as primary, secondary and tertiary contamination by Moore and Luoma (1990). Wastes produced during ore extraction, dressing and smelting which had been deposited near their site of origin were classified as sources of primary contamination. If these contaminants were to be transported away from the site through fluvial, atmospheric or gravitational pathways, then secondary contamination would be generated in soils, groundwaters, rivers or air. Tertiary contamination would occur if after deposition through these pathways, the secondary contaminants were remobilised (Table 4.5). Primary, secondary and tertiary contamination may be considered analogous to the sources, intermediates and sinks described by Davies (1983) (Figure 4.1).

Table 4.5. Types of metal contamination resulting from metal extraction and processing (Moore and Luoma, 1990).

Primary	Secondary	Tertiary
Waste rock	Groundwater at open pits	River sediment from reworked floodplain
Tailings	Ground water beneath ponds	
Slag	Sediment in water channels	Groundwater from contaminated reservoir sediment
Flue dusts	Floodplain sediment/soil	
	Reservoir sediment	
	Soils from air pollution	

The nature and extent of contamination from mining, beneficiation and smelting technology is influenced by the historical period in which it originated and has changed over time with advances in technology. An example of this is the technology relating to the beneficiation of ore. The basic principle underlying the separation of ore from gangue, the liberation of the ore from its gangue by comminution then gravity separation of the ore from the crushed material by water, remained unchanged from the time of the ancient Greeks and Romans until the first decade of the 20<sup>th</sup> century (Day and Tylecote, 1991; Rieuwerts, 1998). Crushing techniques ranged from the early hammering, called variously spalling, balling, bucking or cobbing, depending on the size-grade of the material, where ore was crushed by hand using a tool such as a sledge hammer, spalling hammer or bucking iron, to mechanical hammering, stamping, grinding or milling powered by horse power, water-wheels or steam.

The earliest forms of gravity separation consisted of crushed ore and gangue being placed on a shovel and swilled in streams or a tub (Day and Tylecote, 1991; Rieuwerts, 1998). Later techniques involved jigs, which were washing boxes containing meshes, and buddles, where water was run down an inclined surface to wash the lighter gangue materials away from the relatively dense ore. Buddles took various forms, and reached their technological pinnacle in the form of the mechanised Cornish round buddle (Hunt, 1884). The Cornish round buddle was widely used in Britain during the 19<sup>th</sup> century, including at the Chewton and Priddy Mineries. However, by the end of the century, the technology was considered wasteful and obsolete (Morgans, 1902; Gough, 1967; Day and Tylecote, 1991). All the above techniques involved the release of water and wastes highly charged with trace metals into the environment, and it has been estimated that up to 25% of ore could be lost at the separation stage if practises were slovenly (Davies, 1983).

Modern ore separation however, is achieved by froth flotation, a technology patented in 1906. Froth flotation involves the dissolving of metals from gangue by organic solvents. Air is bubbled through the reagent/ore/gangue mix, and collector compounds in the reagent mix cause the ore particles to become hydrophobic and cling to air bubbles in the rising froth. Although froth flotation is an extremely efficient separation technique where the resulting tailings are less metal enriched than those from the older gravitational separation techniques, the solvents cause their own environmental problems such as damage to aquatic ecosystems and residual chemicals in tailings (Davies, 1983).

#### 4.1.6 Trace metals and the environment

The health implications of mining and smelting trace metals have been recognised for many centuries. However, some of the earliest legislation dealing with the environmental implications of Pb mining and smelting concerned the protection of livestock (Page, 1911; Bucknell, 1924; Gough, 1967). It is often quoted that for most of the British mining period, there were no regulations controlling the disposal of effluent from the separation processes (Davies, 1983). However, documentary evidence exists to suggest that on a local level, there were such regulations. From the earliest times on Mendip, agriculture and mining existed in close proximity, and interests sometimes came into conflict. Once granted licence by the Lord of the Liberty, miners were permitted by custom to prospect and break up ground in search of ore on any enclosed or wasteland within that Liberty. These rights took precedence even over commoner's rights to graze (Gough, 1967). It seems likely that miners also carried out at least a preliminary washing and buddling of their ore before taking it to the Minery. On the 14<sup>th</sup> March 1573, in what is perhaps one of the earliest documented example of such legislation, the Minery Court at Chewton dealt with the problem of cattle being minded (poisoned) by drinking water contaminated by the buddling and washing of ores. This was a common problem because the few streams on Mendip were scanty and a scarce resource for farmers and miners alike. The Court decreed that

*"....no man should buddle in a place called Widmore upon Mendip aforesaid, from the feast of the Annunciacō of our Lady untill the feast of St Michael the Archangell yearly (for that many cattel are hurt and killed)..."*.

Chewton Laws No 20 (Gough, 1967).

The modern feasts of the *Annunciacō of our Lady* (Annunciation) and *St Michael the Archangell* (St. Michael) on March 23<sup>rd</sup> and September 29<sup>th</sup>, which suggests that in the sixteenth century buddling was prohibited in that area for six months of each year.

There were also laws against releasing water from the Minery pond, and several other orders enforcing the prohibition of buddling during the months when cattle were turned out to graze (Gough, 1967). A further 'great complaint' was made to the jury of the Chewton Court in October 1617 by the inhabitants of Chewton *"...for that there are certain buddles newly layd at a place called Rush Meare and other places within Chewton aforesaid, and that the Tenants have, and are like to receive great losse thereby"*. The jury ruled that *"...if any persons shall buddle at the said Rush Meare, or at the Cleeves, or at any other new erected place within this Libertie"* he should be liable to certain penalties. To minimise pollution from effluent from established buddles, it was further ordered that *'all person or Persons that shall buddle in any Ancient place within this Libertie, shall keepe the water in his Course into the Swallowitt as it hath used heretofore to run, or else to lose twenty Shillings...'*

Further Order Chewton Law 63 (Gough, 1967).

Modern legislation concerned with elevated trace metal concentrations in the environment from all sources also consider the implications of metal toxicity for human health. Humans may be exposed to trace metals directly through the environment (metal enriched aerosols, dusts or drinking water) or indirectly by the accumulation of trace metals in contaminated soils and water through the food

chain. Nriagu (1988) argued that if measured by the quantity of water needed to dilute toxic wastes to the standards required for drinking water, the combined toxicity of all metals released annually into the environment far exceeds that of the combined total toxicity of radioactive and organic wastes. Metals such as Pb and Cd have no known function within the human body. Even at levels too low to produce morbidity or death, these and trace metals such as Zn, Cu, Fe and Mn have been implicated as initiators or promoters of carcinogenic activity in mammals (Nriagu, 1988). Lead has been associated with neurological damage, reproductive disorders in both genders and cardiovascular disease, including hypertension. Cadmium is known to cause renal damage and disrupt DNA and RNA function (Nriagu, 1988).

To address the problems associated with trace metals in the environment, contamination thresholds have been set for trace metals in soils. In designating soil contamination thresholds, factors such as the origin of the contamination, the mobility and bioavailability of the trace metals, and the possible future use of the site for which the thresholds are intended need to be considered. People, plants and animals are vulnerable to different routes of metal exposure and concentrations of trace metals (Ross and Kaye, 1994). These factors were recognised in a scheme produced by the Greater London Council (GLC), for land uses under their jurisdiction, that categorised soils according to the level of contaminated by trace metals (Table 4.6). The values are named after Kelly (1979) who developed the scheme (Ross and Kaye, 1994).

Table 4.6. Greater London Council Kelly values for total trace metal concentration in soil ( $\mu\text{g g}^{-1}$ ) (Kelly, 1979).

	Typical Uncontaminated	Slight Contamination Class 1	Contaminated Class 2	Heavily Contaminated Class 3	Unusually heavy Contamination Class B
Pb	0-500	500-1 000	1 000-2 000	2 000-10 000	>10 000
Zn	0-250	250-500	500-1 000	1 000-5 000	>5 000
Cd	0-1	1-3	3-10	10-50	>50
Cu	0-100	100-200	200-500	500-2500	>2 500
Mn	0-500	500-1000	1000-2000	2000-10 000	>10 000

National guidelines were later set out for recommended trigger values for total trace metal concentration in soil for land designated for development (Table 4.7), and the restoration and aftercare of metalliferous mining sites for pasture and grazing in the United Kingdom (Table 4.8) by the Inter-Departmental Committee on the Redevelopment of Contaminated Land (ICRCL, 1987 and 1990).

Table 4.7. ICRCL Threshold trigger values for total trace metal concentration in soil ( $\mu\text{g g}^{-1}$ ) of pH 6.5 for land development (ICRCL, 1987).

	Residential Use	Small Garden	Large Garden	Amenity Grass	Open Space	Hard Cover Use
Pb	500	550	550	1 500	1500	2 000
Zn	300	280	280	280-560	280-560	300
Cd	3	5	3	12	15	15
Cu	130	140	140	140-280	140-280	130

The ICRCL used the classifications 'threshold' and 'action' trigger concentrations. The threshold trigger concentration of an element was defined as the concentration below which the soil is considered safe for the specified use; i.e. the concentration present should not cause phytotoxic or zootoxic effects. The action trigger concentration was defined as that above which there would be a very high

probability of phytotoxic or zootoxic effects. In the case of grazing livestock, continual exposure to concentrations exceeding the action trigger concentration could result in death (ICRCL, 1990).

Table 4.8. ICRCL Trigger values for total trace metal concentration in minespoil-contaminated soil for agricultural use ( $\mu\text{g g}^{-1}$ ) (ICRCL, 1990).

	Threshold Trigger Concentrations	Maximum (Action Trigger) Concentrations Total concentration $\mu\text{g g}^{-1}$ Air-Dry Mass	
		For Grazing Livestock	For Crop Growth (risk of toxicity)
Pb	300	1 000	--
Zn	1 000	3 000	1 000
Cd	3	30	50
Cu	250	500	250

#### 4.1.7 Studies of mining and smelting sites in Britain

The metal enrichment of some soils in Britain through mining and metallurgical activity dates from pre-Roman history, although it is thought that the greatest contamination has occurred since the Industrial Revolution (Alloway, 1990a). Examples of studies carried out at historical Pb mining and smelting sites with typical soil trace metal concentrations are shown in Table 4.9.

One of the few published works to produce data specifically from the present study area was Stenner’s (1978) investigation into the concentration of Pb, Zn, Cd and Cu in cave and associated surface stream sediments (Table 4.10). While not concerned with soil *per se*, these data may be considered indicative of the potential range of metal concentrations in the site’s soils.



Table 4.9. Concentrations of trace metals in some British soils enriched by historical Pb mining and smelting activities

Site	Element	Depth (mm)	Concentration Range ( $\mu\text{g g}^{-1}$ )		Comments	Reference
			Min.	Max.		
Ystwyth Valley Mid-Wales	Pb	0 - 180	90	3 393	Alluvial soils below Gwnystwyth Pb mines. 90 years post river anti pollution legislation	Alloway (1990)
	Zn	0 - 180	95	1 750		
	Cd	0 - 180	1.2	4.0		
	Cu	0 - 180	15.7	42.3		
Tanant Valley North Powys Wales	Pb	0 - 150	28	4 800	Predominantly clay-rich podsols in area of Pb/Zn mining and smelting. Active from Iron Age, production peaked in 18/19 <sup>th</sup> centuries.	Fuge, Paveley and Holdham (1989)
		150 - 300	16	4 800		
	Zn	0 - 150	101	5 520		
		150 - 300	85	1 850		
	Cd	0 - 150	0.1	450		
Derbyshire England	Pb	0 - 150	635	>32 900	Sandy loam soil over Millstone Grit. Site of cupola Pb smelter active mid-18 <sup>th</sup> century onwards.	Maskell <i>et al.</i> (1995)
		150 - 600	>32 100	>35 000		
	Zn	0 - 150	39	8 930		
		150 - 600	1 970	2 980		
	Cd	0 - 150	0.3	47.3		
		150 - 600	31.8	45.4		
Clywd Wales	Pb	0 - 150	393	2 330	Soils developed on estuarine alluvium, range from sandy loam to clay loam. Site 150 m SE of Roman Pb smelter.	Maskell <i>et al.</i> (1995)
		150 - 600	1 490	3 500		
	Zn	0 - 150	272	703		
		150 - 600	259	302		
	Cd	0 - 150	<0.2	2.8		
		150 - 600	1.1	3.7		

Table 4.10. The concentration of trace metals in sediments from surface streams at Priddy Mineries Reserve and St. Cuthbert's ( $\mu\text{g g}^{-1}$ ) (Stenner, 1978).

Site	Grid Ref.	Pb	Zn	Cd	Cu
<u>Plantation stream</u>					
Minery Pool, near exit	ST 5451 5076	14 500	820	1.5	15
Stream near pool exit	St 5448 5076	47 000	4 000	7.5	35
Plantation Swallet	ST 5434 5059	34 000	1 700	2.0	35
<u>Fair Lady Well Stream</u>					
Spring	ST 5447 5078	7 300	1 500	2.5	16
50 m downstream of spring	ST 5440 5074	37 500	850	1.6	25
Near Plantation Swallet	ST 5433 5060	38 500	2 000	2.5	30
<u>St Cuthbert's Stream</u>					
St Cuthbert's Pool	ST 5432 5053	51 000	3 100	5.0	85
St. Cuthbert's Swallet	ST 5430 5050	55 000	3 400	4.5	72

Sediments from inside St. Cuthbert's Swallet, which drains the Priddy Mineries Reserve and the St. Cuthbert's catchment, were found to contain the following ranges of metal concentrations ( $\mu\text{g g}^{-1}$ ) by Stenner (1978):

Pb	Zn	Cd	Cu
270 – 330 000	74 – 4 200	0.6 - 16	8 - 107.

The largest body of data concerning the soils of the Priddy Mineries Reserve and St. Cuthbert's is that of Ginnever (1985). A total of seven soil samples were collected from the sites as a supplement to a large-scale geochemical survey of Mendip carried out over a 2 km x 2 km<sup>2</sup> grid. Ginnever (1985) found the soils to contain the following ranges of metal concentrations ( $\mu\text{g g}^{-1}$ );

Pb	Zn	Cd
27 854 - 68 251	438 - 10 051	0.6 - 10.2

The site map and elevated soil trace metal concentration data produced in Ginnever's (1985) study suggested that the samples were collected from tailings

piles on the Priddy Mineries Reserve and at St. Cuthbert's (Figure 1.2).

#### **4.1.8 Sources of trace metals to the soils of the study area**

As well as the natural input of trace metals from the weathering of enriched parent material, the soils of the study site have received inputs from metalliferous mining and smelting for over two millennia. Most of the industrial remains, watercourses and wastes present today at the Priddy Mineries Reserve and St. Cuthbert's, however, date from 1857 to 1908 (Figure 4.2). During this period, the industry was largely concerned with the reworking of metal-rich wastes left from previous workings (Curwen-Salmon, 1864; Hunt, 1884; Morgans, 1900; Spencer, 1923; Bucknell, 1924; Gough, 1967). While a few trial shafts were sunk in the area during this time, the grooves and rakes (larger mining grooves) visible today in the Stockhill Plantation are largely the legacy of earlier mining. The majority of the workings probably date from the sixteenth and seventeenth centuries, although some may be Mediaeval or Roman (Gough, 1967).

#### **4.1.9 Mining and smelting wastes**

The wastes present from mining and processing at the dressing floors of the Reserve and St. Cuthbert's may be considered under the two categories of pre- and post-smelter waste.

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Figure 4.2. Sketch map of the industrial remains at the Priddy Mineries Reserve and St Cuthbert's site (Gilson, 1970).

### Pre-smelter wastes

Pre-smelter wastes were generated from the sorting, washing and separation processes (beneficiation) used to separate material destined for the smelter from gangue. The wastes are present on the Priddy Minery Reserve and at St. Cuthbert's in piles of various dimensions, and although the texture of the waste material was found to vary between piles, each separate pile appeared to be homogenous in texture. For the majority of the time the ancient wastes were reworked at the Chewton and Priddy Mineries, the separation of Pb from the old wastes was largely by Cornish round buddle at both Mineries (Gough, 1967). The remains of three sets of Cornish round buddles are evident in the Priddy Mineries Reserve, and the pre-smelter waste piles are centred on these areas (Figures 1.2 and 4.2).

The Cornish round buddle was a shallow circular pit in the ground, of up to 10 m in diameter. The pit was lined with masonry, with its floor gently sloping away from the centre to the edge of the pit. A launder above the buddle held debris, slags and slimes, and water was passed over the wastes so that a slurry of fine waste flowed into the pit. Larger particles of waste were held back from entering the pit by a zinc mesh. In the pit, the slurry was gently agitated by four revolving paddles, which radiated from the centre of the pit. The dense Pb-rich particles in the slurry settled near the centre of the buddle, while the less dense particles travelled to the outer edge. When the buddle was full, the paddles were removed and the metal-rich centre portion of the buddle, known as the head, was taken to the smelter. The first and second middlings, the next outer third of the buddle, were rebuddled. The material nearest the edge of the buddle, the tail of the buddle,

was composed of soft clays, silts and fine sands. These 'tailings' were immediately discarded on to tailings piles (Gough, 1967). The coarse material retained by the mesh in the launder was periodically cleared out and dumped.

From 1900-1908, the relatively advanced technology of the revolving barrels, mechanical jiggers, Frue Vanner and Wilfley tables were employed at the St Cuthbert's Leadworks. All these techniques were, like the round buddle, based on gravitational separation (Curwen Salmon, 1864; Morgans, 1902, Gough, 1967). A photograph of the St. Cuthbert's Leadworks taken in the first decade of the 20<sup>th</sup> century, when it was still in operation, shows vast areas of pre-smelter wastes, or 'jigger-slag' (Stokes, 1999). These wastes are present today, and appear to be finer in texture than most of the pre-smelter wastes found at the Priddy Mineries Reserve.

The tailings in the study area inevitably contained small fragments of ore minerals, metals, old slags and the host rock, and sands, silts and clays (slimes) naturally enriched with trace metal-bearing minerals. Some of the minerals associated with the Mendip Pb/Zn mineralisation, and Pb smelter wastes (slag), have specific gravities closer to that of the gangue minerals such as calcite, barytes (barite) and quartz than that of the Pb minerals (Table 4.11). While the relatively dense Pb minerals were largely separated from the gangue during buddling or jigging and removed for smelting, the less dense minerals were retained with the gangue and concentrated in the areas of tailings (Rieuwerts, 1998).

Table 4.11 Relative Density ( $\text{g cm}^{-3}$ ) of trace metal and gangue minerals recorded as present in the Central Mendip lead-zinc orefield (Alabaster, 1982; Schumann, 1992). \* determined by present author at Bath Spa University College, 2001

Mineral	Relative Density ( $\text{g cm}^{-3}$ )
Calcite ( $\text{CaCO}_3$ )	2.60-2.80
Barite ( $\text{BaSO}_4$ )	4.48
Quartz (silica) ( $\text{SiO}_2$ ) (rare)	2.50-2.80
Celestine ( $\text{SrSO}_4$ ) (rare)	3.90-4.00
Fluorospars ( $\text{CaF}_2$ ) (rare)	3.18
Galena ( $\text{PbS}$ )	7.20-7.60
Cerussite ( $\text{PbCO}_3$ )	6.40-6.60
Pyromorphite ( $\text{Pb}[\text{Cl}(\text{PO}_4)_3]$ )	6.70-7.10
Black Vitrified Lead Slag*	3.08-3.42
Non-Vitrified Lead Slag*	1.65-2.28
Sphalerite ( $\text{ZnS}$ )	3.90-4.20
Calamine ( $\text{CaCO}_3$ )	4.30-4.50
Greenockite ( $\text{CdS}$ )	3.98-5.00
Bornite ( $\text{CuFeS}_4$ )	4.90-5.30
Chalcopyrite ( $\text{CuFeS}_2$ )	4.10-4.30
Malachite ( $\text{CuCO}_3$ )	3.75-3.95
Rhodochrosite ( $\text{MnCO}_3$ )	3.3-3.6
Haematite ( $\text{FeO}_2\text{O}_3$ )	5.2-5.3
Goethite (Ochre) ( $\text{FeOOH}$ )	3.8-4.3
Pyrite / Marcasite ( $\text{FeS}$ )	5.2-5.2

### Post-smelter waste

The post-smelter waste in the study area consisted of slag and debris from the roasting and smelting processes. The main area of smelter waste is on the St. Cuthbert's site around ST 3544 1505 (Figure 1.2). At St. Cuthbert's, the heaps are extensive, and both the black, glossy vitrified slags and non-vitrified wastes typical of Pb smelting are present. The waste in the heaps ranges from boulder size down to small fragments. Very little smelter waste is present on the Priddy Mineries Reserve. During the last phase of the reworking, smelter waste from the Priddy Mineries Reserve was taken to St. Cuthbert's by tram for reprocessing

(Gough, 1967). The remaining area of smelter waste on the Priddy Mineries Reserve is around ST 3547 1511 (Figure 1.2). The waste material is generally more homogenous and smaller in size (c.60 x 40 mm) than that found at St. Cuthbert's.

#### **4.1.10 Other soil parameters**

As well as total trace metal content, the soils of the study area were analysed for a number of other relevant parameters.

##### Soil reaction

Soil pH was an important parameter to determine because soil reaction has been identified as one of the most important factors controlling metal solubility in soil. Generally, solubility and availability of trace metals such as Pb, Zn, Cd and Cu increase with acidity and decrease with increasing alkalinity (Brummer and Hermes, 1983; Lobersli, Gjengedal and Steinnes, 1991; Martin and Bullock, 1994).

##### Soil moisture

Most soil analyses are carried out on air-dry samples, however, when air-dry, a soil sample contains some water depending on its properties and air humidity in the laboratory. In temperate climates, this can vary between 1 to 10 per cent for light to heavy textures (Rowell, 1994). For accuracy in the comparison of soil analyses, it is therefore preferable to express analytical results in terms of oven-dry soil (Hesse, 1971; Rowell, 1994). In order to convert air-dry to oven-dry results, the moisture content of the air-dry soil must be determined.



### Loss-on-Ignition

The complexation of metals in soils by organic matter is also considered an important factor governing solubility and bioavailability of metals in soil-plant systems. The composition of organic matter is dominated by humin and humic acid compounds which bind and immobilise metals and fulvic acids, which in terms of binding and transporting capacity are considered the most important organic fraction in soils (Ross, 1994c). The approximate organic matter content of an air-dry soil may be determined by measuring its Loss-on-Ignition, defined by Rowell (1994) as the mass of a soil lost between 105-500°C. Determination of organic matter content by this method is only ever approximate because on ignition at 500°C, a soil may lose structural water from clay sesquioxides such as goethite ( $\text{FeOOH}$ ) and haematite ( $\text{Fe}_2\text{O}_3$ ), which are dehydrated at between 280-400°C. For soils with a high clay content, Loss-on-Ignition may lead to the determination of values of up to twice the actual organic matter content, although for sandy soils the values may be considered a close approximation. Soil calcium carbonate may also start to lose  $\text{CO}_2$  during ignition, but this is usually thought to happen at approximately 770°C (Rowell, 1994).

#### **4.1.11 Precision, accuracy and quality control**

To maintain analytical quality control while minimising expense during the analysis of soils for trace metal concentrations, an in-house reference material was used throughout the study in conjunction with the Certified Reference Material. An in-house reference soil was specially prepared and stored for this purpose (4.2.2). During the preparation of a Certified Reference Material, the concentrations of a selection of elements are determined by a variety of analytical

methods in a number of laboratories. The value and a measure of uncertainty for the concentration of each of the elements of interest in the material are statistically determined from the results of the analyses.

With known elemental concentrations, Certified Reference Material is used to determine the accuracy and precision of a particular analytical method. An in-house reference material is only used as a measure of analytical precision within a series of analyses. In-house material does not undergo the rigorous analytical procedures associated with the production of a Certified Reference Material (Maier *et al.*, 1994), therefore unlike a Certified Reference Material its absolute elemental values are uncertain. Absolute values for any trace metal content in an in-house reference material, if established at all, would only be as good as the analytical procedure employed in-house. However, with the repeated inclusion of an in-house reference material in analytical batches, although the accuracy of a method cannot be established, some measure of the precision (% CV) of the method can be made.

## **4.2 Method and materials**

### **4.2.1 Soil sampling and preparation**

A soil sampling plan based on a regular orthogonal grid design was chosen for the baseline survey. A 100 m x 100 m grid was constructed using Ordnance Survey Sheet ST 55 SW 1:10,000 (Figure 1.2) and samples were collected from the Priddy Mineries Reserve, St. Cuthbert's and Stockhill Plantation sites at each grid intersection. Soils were collected from a total of 77 sampling points (Figure 4.3).

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Figure 4.3. Designated sampling points.

At each sampling point two bulk samples of soil were collected, one from the surface soil, and one at depth. Samples were collected during the period February 1995 to April 1997 (Table 4.22).

At each sampling point, a bulk sample consisting of nine sub-samples from 0-200 mm (surface) was collected using a 22 mm diameter stainless steel auger. The first of the nine sub-samples was removed from the centre of a metre quadrat; eight further samples were collected from around the quadrat in the pattern shown in Figure 4.4.

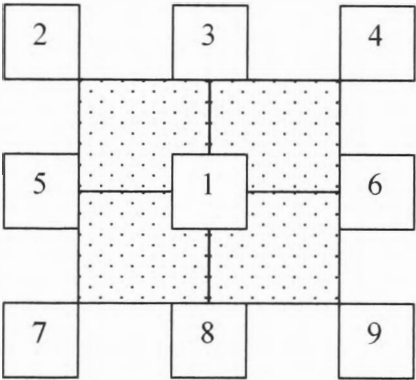


Figure 4.4. Collection points (numbered) of the nine sub-samples of soil around a 1 m<sup>2</sup> sampling quadrat.

After the removal of each surface core, the auger was reinserted into the boring and a core was taken from the subsoil at 200-400 mm (depth). This was repeated for the subsoil at each sampling point where the topsoil was collected. A total of two bulk samples consisting of nine sub-samples were collected at each sampling point. Bulk samples were collected in duplicate at 10% of the sampling points

chosen randomly to assess sampling error in the resulting data. The bulked samples were placed in new, labelled polythene bags for transport to the laboratory by the method described in 3.2.1. In the laboratory, the samples were dried and prepared for analysis by the method described in 3.2.1. All equipment used for the preparation and subsequent analysis of samples was prepared for use by the method described in 3.2.2. Samples that required the determination of soil reaction at field capacity were analysed within four hours of collection.

#### **4.2.2 Preparation of an in-house reference material**

An in-house reference material was prepared from soils of the Thrupe and Wrington Series. Soil of the Wrington Series (Findlay, 1965), from a site of former calamine workings at Shipham, Somerset (ST 3440 1580), was used to add measurable concentrations of Cd to the in-house reference material. A bulk sample of approximately 2 kg, comprising of 10 sub-samples of soil from the Thrupe Series was collected from the Reserve at ST 3548 1512. The soil was collected with a stainless steel trowel from a depth of 0-200 mm, and placed in two new, labelled polyethylene bags for transport to the laboratory. Approximately 2 kg of soil from the Wrington series were collected by the same method. The soils were dried and prepared for analysis by the method described in 3.2.1. The air-dry fine earth fractions (<2 mm) of both soils were combined at a ratio of 1:1 and manually homogenised by shaking for 15 minutes. The combined sample was manually shaken for 5 minutes each time prior to the preparation for analysis as described in 3.2.1.

#### **4.2.3 Analysis for total trace metals**

Aliquots of 0.5 g of <2 mm air-dry soil were prepared for digestion in the Gerhardt Kjeldatherm macro digestion system by the method described in 3.2.2. Sample decomposition was carried out using 10 ml 69% (v/v) HNO<sub>3</sub>, with a refluxing time of 1 hour and a final volume of 50 ml by the method described in 3.3.2. The samples were then analysed by FAAS according to the analytical protocol and operating conditions described in 3.2.3. Quality control procedures described in 3.3.1 were used, including the use of a control blank, Certified Reference Material, an in-house reference material and the randomisation of the analytical sequence of samples in each analytical batch.

The Certified Reference Material used was Community Bureau of Reference (BCR) CRM 143R Sewage Sludge Amended Soil certified for its total and aqua regia soluble contents (Commission of the European Communities (BCR), 1994). In each batch of samples analysed for trace metal content, one sample of either BCR CRM 143R Sewage Sludge Amended Soil or the in-house reference material was analysed. Throughout the study, BCR CRM 143R was used in one out of every three analytical batches, while the in-house reference material was used in the remaining two out of every three analytical batches.

Throughout the baseline soil survey, three replicate samples of each sample and the 10% sample replicates were analysed. For the assessment of the precision of the field sampling, samples were analysed in duplicate. Immediately after analysis, trace metal concentration data for three replicates were analysed for

% CV. As Pb was considered the primary metal of interest, analyses were repeated when there was more than a 10% CV between Pb replicates. However, if a % CV was considered anomalously high between the replicates of other metals, three replicate samples were re-analysed for all metals. The data were entered into Windows Excel and Minitab® for Windows Version 12.1 databases for statistical analysis. After statistical analysis of the means and standard deviations of the three replicates, the mean metal concentration values for each sample were entered into MapInfo Professional 5.1 for mapping.

#### **4.2.4 Soil reaction**

All samples and replicates in the study were analysed for air-dry soil reaction. For the determination of the pH of air-dry soil, a slurry of 1:2.5 soil to water ratio was used. An 10 g aliquot of <2 mm air-dry soil was weighed into a polyethylene sample pot and 25 ml of deionised water were added by tilt dispenser. After sealing with a lid, the pot was shaken on a Gerhardt Laboshake LS/5 at 120 cycles min<sup>-1</sup> for 15 minutes at room temperature. After removal from the shaker, pH was determined with a Jenaway 3150 pH meter that had been calibrated using buffers of pH 7.0 and pH 4.0. The pH meter was checked for calibration after every three readings and recalibrated where necessary. Three replicates of each sample and duplicate were analysed by this method. After statistical analysis of the means and standard deviations of the three replicates, the mean soil reaction values for each sample were entered into MapInfo Professional 5.1 for mapping.

#### 4.2.5 Soil moisture

An aliquot of 10 g <2 mm air-dry soil was weighed into a 50 ml beaker and dried in an oven at 105°C for 24 hours. The beaker was cooled in a desiccator for 24 hours and reweighed. The moisture content of air-dry soil was calculated as follows:

$$\begin{array}{l} \text{\%} \\ \text{air-dry soil} \\ \text{moisture} \end{array} = \frac{\text{mass of air-dry soil (g)} - \text{mass of oven-dry sample (g)}}{\text{mass of oven-dry soil (g)}} \times 100$$

Percentage moisture content of an air-dry soil was expressed as a percentage of oven-dry soil (Rowell, 1994).

Unless mentioned in the text, the results of all soil determinations in this study were adjusted for oven-dry mass (DM). The mean water content of three replicate determinations for each air-dry soil sample was used to adjust all analytical results, where appropriate, for oven-dry mass. The mean water content (g) of the air-dry soil replicates was subtracted from the air-dry mass of the corresponding soil aliquot used in the analysis to give the oven-dry mass of the aliquot. The oven-dry mass of the aliquot was then substituted in subsequent calculations.

#### 4.2.6 Loss-on-Ignition

An aliquot of 10 g air-dry <2 mm soil was weighed into a 50 ml beaker and placed in an oven at 105°C for 24 hours. The beaker was cooled in a desiccator and reweighed. The beaker was then placed in a Carbolite HRF 7/22 furnace and ignited at 500°C for eight hours. After leaving to cool for 2 hours, the beaker was



placed in a desiccator for 24 hours and reweighed to determine the mass of ignited soil. Loss-on-Ignition was calculated as follows:

$$\text{Loss-on-Ignition} \% = \frac{(\text{mass of oven-dry soil (g)} - \text{mass of ignited soil (g)})}{\text{mass of oven-dry soil (g)}} \times 100$$

The percentage loss on ignition refers to Loss-on-Ignition as a percentage of oven-dry rather than air-dry soil (Rowell, 1994). Three replicate analyses were carried out for each sample and duplicate were analysed, and the mean used in subsequent statistical analyses and mapping.

### 4.3 Data handling and the statistical analysis of data

The data were grouped in the following way for statistical analysis:

1. surface and depth data from the whole study area were analysed as one main data set, referred to as the 'All Soil Data' data set
2. four sub-sets of the main data set by site. Each sub-set consisted of surface and depth data grouped by geographical site. The four data sub-sets were i. the Priddy Mineries Reserve, ii. St. Cuthbert's, iii. Stockhill Plantation, iv. Agricultural Land

The sample number for each data sub-set by geographical site, and the sample number expressed as a percentage of the total number of sampling points within the study area are shown in Table 4.12.

Table 4.12. Sample number in each data sub-set by site and expressed as a percentage of the total number of sampling points within the study area (n=77).

<b>Priddy Mineries Reserve</b>	<b>St. Cuthbert's</b>	<b>Stockhill Plantation</b>	<b>Agricultural Land</b>
n=51	n=11	n=12	n=3
66.0%	14.0%	16.0%	4.0%

#### 4.3.1 Descriptive statistics

The arithmetic mean, standard deviation, minimum, 1<sup>st</sup> quartile, median, 3<sup>rd</sup> quartile and maximum values for soil parameter data were determined using Minitab® Release 12. Field observations, soil classification and raw data generated from soil laboratory analyses were tabulated.

#### 4.3.2 Cartographic representation of data

The spatial distribution of the raw data for each soil parameter at 0-200 mm and 200-400 mm was mapped using MapInfo Professional 5.1. Distribution maps were also produced for the relative topsoil enrichment ratio (RTE) for Pb, Zn, Cd, Cu, Fe and Mn at each sample point. The maps were constructed using coloured symbols based on the relative parameter values at each sample point. Parameter values were classified into groupings using a simple systematic approach where the arithmetic (raw) data were classified to produce nine groupings of data ranging from the minimum to maximum values. Because of the large ranges of metal concentrations involved, the colour key used to represent the concentration groupings for each trace metal during mapping was specific to each trace metal. Therefore, a colour representing a value range for a particular trace metal should not be used to interpret the maps of a different trace metal. However, the colour

key for an individual trace metal was used for mapping that trace metal at 0-200 mm and 200-400 mm, enabling a direct comparison of concentrations. It is possible to empirically allocate class limits from experience in this way, although the method was criticised as involving too high a degree of subjectivity (Davies, 1989).

While this criticism is acknowledged, the method was chosen for this study because of its simplicity. The numerical range of the raw data was immediately accessible and distribution trends readily discerned. The method was also favoured over isoline (contour) mapping, a method considered suitable for geochemical data (Davies, 1989), because isoline mapping assumes progressive change between sampling points. In this study, samples were collected from 1 m<sup>2</sup> quadrats at the intersects of 100 m x 100 m grid. Because of the distances involved between sample points, the parameter data should only be considered representative of that 1 m<sup>2</sup>. Progressive change between sampling points was not assumed.

The RTE is an arithmetic index that allows comparison of the contamination of the topsoil by trace metals. The analysis of soil data from a wide range of mining, smelting and uncontaminated sites in Britain suggested that RTE values of 1-2 indicate uncontaminated soils, while the RTE in contaminated soils ranged up to a value of 20 (Colbourn and Thornton, 1978; Martin and Coughtrey, 1982).

The RTE at each sampling point was calculated and mapped for each trace element. The RTE values in this study were calculated as:

$$\text{RTE} = \frac{\text{total metal in 0-200 mm zone of soil}}{\text{total metal in 200-400 mm zone of soil}}$$

#### 4.3.3 Statistical appraisal of normality of data

Trace metal data from geochemical surveys are essentially 'noisy', typically showing positively skewed distributions (Davies, 1989). However, a prerequisite for many statistical analyses is that the data be normally distributed (Ebdon, 1985; Shaw and Wheeler, 1985). Although Davies (1989) recommended that as a general rule, all soil trace metal data should be log-transformed before statistical analysis, the probability distributions of soil data for all parameters were assessed using the Anderson-Darling test for Normality. The Anderson-Darling test uses the following hypotheses:

- $H_0$  : data follows a normal distribution
- $H_1$ : data do not follow a normal distribution

If the p-value from the Anderson-Darling test is less than the selected  $\alpha$  level, then the  $H_0$  is rejected (Minitab, 1998). If an arithmetic data set was found to show a normal frequency distribution, it was left in its untransformed form during any subsequent statistical analyses.

Like standard deviation, kurtosis and skewness are measures of dispersion about the mean, but where standard deviation is useful in describing general characteristics of data and their distribution about the mean, these relate to the shape of the frequency distribution. Kurtosis and skewness also provide objective

measures of data which may be used when comparing different frequency distributions (Shaw and Wheeler, 1985).

### Kurtosis

Kurtosis is a measure of difference of distribution from a normal distribution, and the extent to which values are concentrated in one part of a frequency distribution (Ebdon, 1985). Negative values indicate a distribution with a heavier tail than normal, and positive values a lighter tail. If a frequency distribution has a high peak, it is described as peaky or '*leptokurtic*' (Figure 4.5). Distributions that are moderately peaked are termed '*mesokurtic*', and a relatively flat distribution '*platykurtic*' (Figure 4.5).

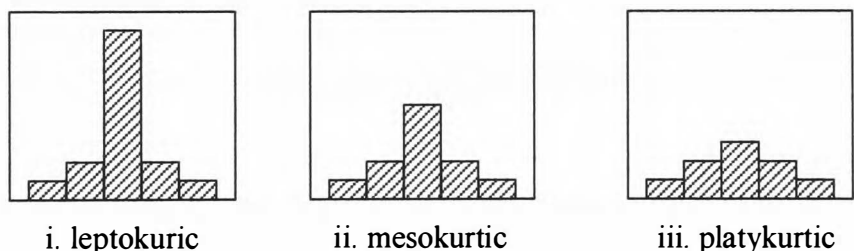


Figure 4.5. Types of frequency distributions by peakedness (Shaw and Wheeler, 1985).

The peakedness of a distribution may be defined statistically by calculating its coefficient of kurtosis. The Minitab® program calculated skewness as:

$$n(n+1) / (n-1)(n-2)(n-3) \sum (x - \bar{x})^4 / s^4 - 3(n-1)^2 / (n-2)(n-3)$$

A normal or symmetrical distribution has a coefficient of kurtosis of 3.0, leptokurtic greater than 3.0, and platykurtic less than 3.0 (Ebdon, 1985; Shaw and Wheeler, 1985).

### Skewness

Skewness is a measure of asymmetry in a distribution. A skewness value of zero indicates a perfectly symmetrical frequency distribution. If the bulk of the values in a distribution are greater than the mean, then the distribution is described as negatively skewed, and negative values indicate skewness to the left. If the bulk of the values are less than the mean, the distribution is positively skewed. Positive values indicate skewness to the right (Ebdon, 1985; Shaw and Wheeler, 1985; Minitab, 1998). Skewness can be statistically defined in a number of ways, but was calculated by the Minitab® program as

$$n / (n - 1)(n - 2) \sum (x - \bar{x})^3 / n^3$$

A normal distribution, therefore, would have a kurtosis of 3.0 and a skewness of 0.

#### **4.3.4 Two Sample Student T-Test**

The Student T-Test is a parametric test of the differences between two sample means (Ebdon, 1985). The T-test statistic (t) is calculated from the difference between the sample means divided by the standard error of that difference. The Two Sample Student T-Test hypotheses are  $H_0: \mu_1 = \mu_2$  versus  $H_1: \mu_1 \neq \mu_2$ . In the Minitab® program, the result of the test is displayed as a t-value and p-value. Where appropriate, soil data for each parameter at 0-200 mm and 200-400 mm were compared using the Minitab® Two Sample Student T-test.

#### 4.3.5 Two-Sample Mann-Whitney test

The Two-Sample Mann-Whitney test is a non-parametric test of the differences between two samples, where it is possible to determine whether there is a significant difference between two variables that are not normally distributed. In the Mann-Whitney test, variables are ranked and the equality of their medians compared. The Mann-Whitney test hypotheses are  $H_0: \eta_1 = \eta_2$  *versus*  $H_1: \eta_1 \neq \eta_2$ . In the Minitab® program, the result of the test is displayed as a statement of whether it is or is not possible to reject the  $H_0$  at the selected  $\alpha$ -level. (Minitab, 1998). Soil data for each parameter at surface and depth were compared using the Minitab® Two-Sample Mann-Whitney test.

#### 4.3.6 The Log transformation of data

It is possible to some extent to normalise data that show a positively skewed distribution by log transformation. Shaw and Wheeler (1985) argued that this was possible because in mathematical terms, the logs of positively skewed distributions have no lower cut-off value as smaller fractions become ever-larger negative logarithms, and the log of zero is minus infinity. When handling skewed geochemical data, a common transformation is to convert values to their common  $\text{Log}_{10}$  logarithm (Davies, 1989). Minitab® was used to  $\text{Log}_{10}$  transform data that required log transformation.

A normal curve was plotted onto a histogram of the arithmetic data distribution for each parameter at 0-200 mm and 200-400 mm. With the exception of pH data, the units of which are based on a logarithmic scale, this was repeated for the  $\text{Log}_{10}$  transformed data for each soil parameter at 0-200 mm and 200-400 mm to allow a

visual comparison of the difference in distributions between arethmetic and Log<sub>10</sub> transformed data for each parameter. If after Log<sub>10</sub> transformation the data set still did not follow a normal frequency distribution, Davies' (1989) recommendation was followed and Log<sub>10</sub> transformed data were used in subsequent parametric statistical analyses.

#### 4.3.7 Pearson correlation

The degree of linear relationship between two variables may be determined by Pearson correlations. The test hypotheses are  $H_0: \rho=0$  *versus*  $H_1: \rho \neq 0$ , where  $\rho$  is the correlation between a pair of variables (Minitab, 1998). Pearson correlations give an r-value, which is calculated thus:

$$r = \frac{\sum (x - \bar{x})(y - \bar{y})}{(n - 1)s_x s_y}$$

The correlation coefficient has an r-value between -1 and +1. A positive r-value indicates a relationship where both variables increase. A negative r-value indicates a relationship between the variables where one decreases and the other increases. Minitab® also displays a p-value for the correlation. If the p-value is smaller than the chosen  $\alpha$ -level, then  $H_0: \rho=0$  can be rejected, suggesting that there is a significant linear relationship between the two variables (Minitab, 1998).

Data for all parameters at surface and depth were analysed for Pearson correlations. The data for each soil parameter at 0-200 mm and 200-400 mm (n=77) were then stacked. This provided a data set for each soil parameter (0-400 mm) containing 154 samples (n=154). Pearson correlations were carried



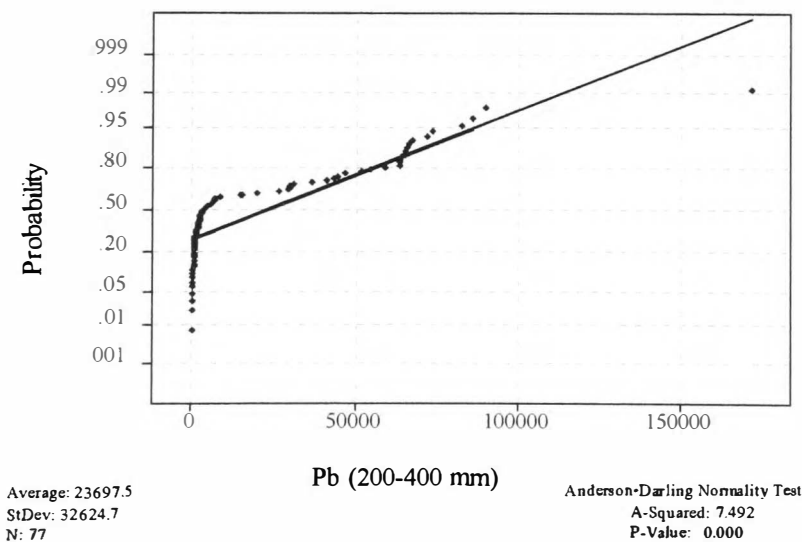
out between all soil parameters at 0-400 mm. Where appropriate, fitted line plots were constructed to show the degree of linear relationship between pairs of variables.

#### 4.4 Assessment of data frequency distributions prior to statistical analysis

##### 4.4.1 All Soil Data

The All Soil Data set was generated from the analysis of soils collected from the seventy-seven sampling points in the study area. An Anderson-Darling normal probability plot was carried out for each soil parameter. An example of an Anderson-Darling normal probability plot, for surface Pb is shown in Figure 4.6.

Figure 4.6. Anderson-Darling normal probability plot for Pb (200-400 mm) (n=77).



The null hypothesis for this test was  $H_0$  : data follow a normal distribution (Minitab, 1998). The p-value of  $p=0.000$  for surface Pb was less than the attained

significance level of  $\alpha=0.01$ .  $H_0$  was therefore rejected; indicating the data did not follow a normal distribution.

The results of the Anderson-Darling test for normality for all other soil parameters (Table 4.13) showed that for all parameters tested, the p-value at  $p = 0.000$  was smaller than the attained significance level of  $\alpha=0.01$ .  $H_0$  was therefore rejected; indicating the data did not follow a normal distribution.

Table 4.13. Probability distributions of All Soil Data (n=77) calculated by the Anderson-Darling Test for normality.

Soil Parameter	A <sup>2</sup>	Kurtosis	Skewness	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm)	3.006	-1.47	0.29	0.000	Rejected
pH (200-400 mm)	2.839	-1.48	0.22	0.000	Rejected
L-o-I % (0-200 mm)	6.289	8.92	2.74	0.000	Rejected
L-o-I % (200-400 mm)	3.084	16.59	3.14	0.000	Rejected
Pb (0-200 mm)	6.542	1.82	1.36	0.000	Rejected
Pb (200-400 mm)	7.492	4.15	1.75	0.000	Rejected
Zn (0-200 mm)	7.600	1.18	1.36	0.000	Rejected
Zn (200-400 mm)	8.326	-2.41	1.11	0.000	Rejected
Cd (0-200 mm)	11.456	1.69	1.58	0.000	Rejected
Cd (200-400 mm)	11.784	0.97	1.45	0.000	Rejected
Cu (0-200 mm)	4.576	2.86	1.64	0.000	Rejected
Cu (200-400 mm)	6.254	2.67	1.72	0.000	Rejected
Fe (0-200 mm)	3.537	-1.46	0.28	0.000	Rejected
Fe (200-400 mm)	2.259	-1.21	0.35	0.000	Rejected
Mn (0-200 mm)	4.143	0.31	1.06	0.000	Rejected
Mn (200-400 mm)	4.416	-2.22	0.91	0.000	Rejected

The largest coefficient of kurtosis was for Loss-on-Ignition at 0-200 mm, which indicated a leptokurtic distribution, with the lightest tail. The smallest coefficient of kurtosis was for Zn at 0-200 mm, which indicated a platykurtic distribution with the heaviest tail. The parameter closest to a symmetrical distribution with a normal tail was Cu at 0-200 mm.

All data showed a positive skewness, which indicated that all distributions were skewed to the right. The highest degree of skewness was shown by Loss-on-Ignition at 200-400 mm, which indicated this distribution was the most skewed towards the high end of the distribution. The least degree of skewness was shown by pH at 200-400 mm.

#### 4.4.2 Log<sub>10</sub> transformation of data

With the exception of pH data, the units of which are based on a logarithmic scale, the data for the remaining soil parameters were Log<sub>10</sub> transformed (Table 4.14).

Table 4.14. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=77) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
L-o-I % (0-200 mm)	0.018	Accepted
L-o-I % (200-400 mm)	0.475	Accepted
Pb (0-200 mm)	0.000	Rejected
Pb (200-400 mm)	0.000	Rejected
Zn (0-200 mm)	0.000	Rejected
Zn (200-400 mm)	0.000	Rejected
Cd (0-200 mm)	0.000	Rejected
Cd (200-400 mm)	0.000	Rejected
Cu (0-200 mm)	0.044	Accepted
Cu (200-400 mm)	0.176	Accepted
Fe (0-200 mm)	0.000	Rejected
Fe (200-400 mm)	0.000	Rejected
Mn (0-200 mm)	0.000	Rejected
Mn (200-400 mm)	0.000	Rejected

For Loss-on-Ignition at 0-200 mm and 200-400 mm and Cu at 0-200mm and 200-400 mm, the p-values were greater than the attained significance level of  $\alpha=0.01$ .

$H_0$  was therefore accepted; indicating the data did now follow a normal distribution. The results showed that for all other soil parameters, the p-value at  $p = 0.000$  was smaller than the attained significance level of  $\alpha=0.01$ .  $H_0$  was therefore rejected, indicating that these data did not follow a normal distribution.

#### 4.4.3 Data by Site: The Priddy Mineries Reserve Data set

From the total number of sampling points in the study area, fifty-one sampling points were located in the Priddy Mineries Reserve (Table 4.12). An Anderson-Darling normal probability plot was carried out for each soil parameter at 0-200 mm and 200-400 mm (Table 4.15).

Table 4.15. Probability distributions of soil data (n=51) for Priddy Mineries Reserve calculated by the Anderson-Darling Test for normality.

Soil Parameter	$A^2$	p-value	Kurtosis	Skewness	$H_0$ : data followed a Normal Probability Distribution
pH (0-200 mm)	3.128	0.000	-1.38	0.53	Rejected
pH (200-400 mm)	3.110	0.000	-1.39	0.50	Rejected
L-o-I % (0-200 mm)	4.730	0.000	6.18	2.42	Rejected
L-o-I % (200-400 mm)	3.058	0.000	17.16	3.41	Rejected
Pb (0-200 mm)	5.703	0.000	-8.20	0.88	Rejected
Pb (200-400 mm)	6.091	0.000	-5.30	0.99	Rejected
Zn (0-200 mm)	6.131	0.000	1.28	1.44	Rejected
Zn (200-400 mm)	6.084	0.000	-2.40	1.11	Rejected
Cd (0-200 mm)	7.616	0.000	3.33	1.91	Rejected
Cd (200-400 mm)	9.084	0.000	0.85	1.43	Rejected
Cu (0-200 mm)	4.187	0.000	2.10	1.57	Rejected
Cu (200-400 mm)	5.307	0.000	1.30	1.52	Rejected
Fe (0-200 mm)	3.659	0.000	-1.15	0.70	Rejected
Fe (200-400 mm)	2.999	0.000	-1.22	0.62	Rejected
Mn (0-200 mm)	5.258	0.000	1.68	1.47	Rejected
Mn (200-400 mm)	5.182	0.000	0.38	1.25	Rejected

For all parameters tested, the p-value at  $p = 0.000$  was smaller than the attained significance level of  $\alpha=0.01$  (Table 4.15).  $H_0$  was therefore rejected; indicating the

data did not follow a normal distribution. The largest coefficient of kurtosis was for Loss-on-Ignition at 200-400 mm, which indicated a leptokurtic distribution, with the lightest tail. The smallest coefficient of kurtosis was for Pb at 0-200 mm which indicated a platykurtic distribution with the heaviest tail. The parameter closest to a symmetrical distribution with a normal tail was Cd at 0-200 mm. All data showed a positive skewness, which indicated that all distributions were skewed to the right. The highest degree of skewness was shown by Loss-on-Ignition at 200-400 mm, which indicated this distribution was the most skewed towards the high end of the distribution. The least degree of skewness was shown by pH at 200-400 mm.

#### **4.4.4 $\text{Log}_{10}$ transformation of data**

With the exception of pH data, soil parameter data were  $\text{Log}_{10}$  transformed. The p-values of the soil parameters after  $\text{Log}_{10}$  transformation showed that for Loss-on-Ignition and Cu at 0-200mm and 200-400 mm and Mn 200-400 mm, the p-values were greater than the attained significance level of  $\alpha=0.01$  (Table 4.7).  $H_0$  was therefore accepted; indicating these data did now follow a normal distribution. tabulated (Table 4.16). The results showed that for all other soil parameters, the p-value was smaller than the attained significance level of  $\alpha=0.01$ .  $H_0$  was therefore rejected, indicating that these data still did not follow a normal distribution. Where appropriate,  $\text{Log}_{10}$  transformed data were used for these data in subsequent statistical analyses, as recommended by Davies (1989).

Table 4.16. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=51) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
L-o-I % (0-200 mm)	0.032	Accepted
L-o-I % (200-400 mm)	0.145	Accepted
Pb (0-200 mm)	0.000	Rejected
Pb (200-400 mm)	0.000	Rejected
Zn (0-200 mm)	0.000	Rejected
Zn (200-400 mm)	0.000	Rejected
Cd (0-200 mm)	0.000	Rejected
Cd (200-400 mm)	0.000	Rejected
Cu (0-200 mm)	0.037	Accepted
Cu (200-400 mm)	0.027	Accepted
Fe (0-200 mm)	0.003	Rejected
Fe (200-400 mm)	0.007	Rejected
Mn (0-200 mm)	0.000	Rejected
Mn (200-400 mm)	0.013	Accepted

#### 4.4.5 Data by Site: The St. Cuthbert's Data set

From the total number of sampling points in the study area, eleven points were located in the St. Cuthbert's site (Table 4.12). Anderson-Darling normal probability plots were carried out for soil parameters at 0-200 mm and 200-400 mm to determine the probability distributions of the data (Table 4.17). The results showed that for pH at 0-200 mm, at  $p = 0.003$  the p-value was smaller than the attained significance level of  $\alpha=0.01$ . H<sub>0</sub> was therefore rejected, indicating the data did not follow a normal distribution. For all other soil parameters at 0-200 mm and 200-400 mm, the p-values were all greater than the attained significance level of  $\alpha=0.01$ . H<sub>0</sub> was therefore accepted, indicating that those data did follow a normal distribution.

Table 4.17. Probability distributions of soil data (n=11) for St. Cuthbert's calculated by the Anderson-Darling Test for normality.

Soil Parameter	A <sup>2</sup>	p-value	Kurtosis	Skewness	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm)	1.159	0.003	1.08	-1.51	Rejected
pH (200-400 mm)	0.616	0.081	2.63	-1.53	Accepted
L-o-I % (0-200 mm)	0.658	0.062	3.66	1.63	Accepted
L-o-I % (200-400 mm)	0.439	0.238	0.12	0.76	Accepted
Pb (0-200 mm)	0.379	0.340	1.45	1.04	Accepted
Pb (200-400 mm)	0.709	0.045	3.53	1.54	Accepted
Zn (0-200 mm)	0.404	0.293	-8.00	-6.30	Accepted
Zn (200-400 mm)	0.430	0.250	-1.52	-2.30	Accepted
Cd (0-200 mm)	0.878	0.016	-1.62	-5.10	Accepted
Cd (200-400 mm)	0.435	0.243	-1.49	-9.80	Accepted
Cu (0-200 mm)	0.583	0.099	3.30	1.59	Accepted
Cu (200-400 mm)	0.596	0.091	3.44	1.67	Accepted
Fe (0-200 mm)	0.729	0.040	0.18	-5.00	Accepted
Fe (200-400 mm)	0.258	0.643	0.43	7.23	Accepted
Mn (0-200 mm)	0.347	0.410	-1.50	0.57	Accepted
Mn (200-400 mm)	0.258	0.645	-8.10	0.15	Accepted

The largest positive coefficient of kurtosis was for Loss-on-Ignition at 0-200 mm, which indicated a leptokurtic distribution, with the lightest tail. The smallest coefficient of kurtosis was for Mn at 200-400 mm, which indicated a platykurtic distribution with the heaviest tail. The parameter closest to a symmetrical distribution with a normal tail was Cu at 0-200 mm.

Data showed both positive and negative skewness. The highest degree of positive skewness was shown by Fe at 200-400 mm, which indicated that this distribution was the most skewed towards the high end of the distribution. The highest degree of negative skewness was shown by Cd at 200-400 mm, which indicated this distribution was the most skewed towards the low end of the distribution. The least degree of skewness was shown by Mn at 200-400 mm.

#### 4.4.6 Data by Site: The Stockhill Plantation Data set

From the total number of sampling points in the study area, twelve points were located in the Stockhill Plantation (Table 4.12). An Anderson-darling normal probability plot was carried out for each soil parameter at 0-200 mm and 200-400 mm to determine the probability distributions of the data (Table 4.18). The results showed that for Pb, Cd and Cu at 0-200 mm and 200-400 mm the p-values, all at  $p=0.000$ , were smaller than the attained significance level of  $\alpha=0.01$ .  $H_0$  was therefore rejected, indicating those data did not follow a normal distribution. For all other soil parameters at 0-200 mm and 200-400 mm, the p-values were greater than the attained significance level of  $\alpha=0.01$ .  $H_0$  was therefore accepted, indicating those data did follow a normal distribution.

Table 4.18. Probability distributions of soil data (n=12) for Stockhill Plantation calculated by the Anderson-Darling Test for normality.

Soil Parameter	A <sup>2</sup>	p-value	Kurtosis	Skewness	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm)	0.372	0.360	0.47	0.91	Accepted
pH (200-400 mm)	0.542	0.128	-8.90	0.33	Accepted
L-o-I % (0-200 mm)	0.179	0.895	-1.90	0.35	Accepted
L-o-I % (200-400 mm)	0.150	0.947	-7.30	0.15	Accepted
Pb (0-200 mm)	1.660	0.000	6.72	2.50	Rejected
Pb (200-400 mm)	2.130	0.000	9.28	2.97	Rejected
Zn (0-200 mm)	0.487	0.181	2.77	1.43	Accepted
Zn (200-400 mm)	0.637	0.073	1.66	1.66	Accepted
Cd (0-200 mm)	4.009	0.000	12.00	3.46	Rejected
Cd (200-400 mm)	2.512	0.000	1.13	1.64	Rejected
Cu (0-200 mm)	1.491	0.000	7.97	2.60	Rejected
Cu (200-400 mm)	2.025	0.000	10.02	3.05	Rejected
Fe (0-200 mm)	0.447	0.231	0.33	-8.20	Accepted
Fe (200-400 mm)	0.449	0.229	8.09	-8.10	Accepted
Mn (0-200 mm)	0.434	0.251	-2.70	0.74	Accepted
Mn (200-400 mm)	0.340	0.433	-3.20	0.58	Accepted

The largest positive coefficient of kurtosis was for Cd at 0-200 mm, which indicated a leptokurtic distribution, with the lightest tail. The smallest coefficient



of kurtosis was for Loss-on-Ignition at 0-200 mm, which indicated a platykurtic distribution with the heaviest tail. The parameter closest to a symmetrical distribution with a normal tail was Zn at 0-200 mm.

With the exception of Fe at 0-200 mm and 200-400 mm, which showed a negative skewness, all other parameters at 0-200 mm and 200-400 mm showed a positive skewness. The highest degree of positive skewness was shown by Cd 0-200 mm, which indicated this distribution was the most skewed towards the high end of the distribution. The highest degree of negative skewness was shown by Fe at 200-400 mm, which indicated this distribution was the most skewed towards the low end of the distribution. The least degree of skewness was shown by Loss-on-Ignition at 200-400 mm.

#### **4.4.7 Log<sub>10</sub> transformation of data**

With the exception of pH data, soil parameter data that did not fit a normal frequency distribution were Log<sub>10</sub> transformed. The results in Table 4.19 showed that for Pb at 0-200mm and 200-400 mm, Zn at 0-200 mm and 200-400 mm and Cu at 0-200 and 200-400 mm, the p-values were greater than the attained significance level of  $\alpha=0.01$ .  $H_0$  was therefore accepted; indicating these data did now follow a normal distribution. The results also showed that for Cd at 0-200 mm and 200-400 mm, the p-value was smaller than the attained significance level of  $\alpha=0.01$ .  $H_0$  was therefore rejected, indicating that these data still did not follow a normal distribution.

Table 4.19. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=12) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Pb (0-200 mm)	0.872	Accepted
Pb (200-400 mm)	0.940	Accepted
Cd (0-200 mm)	0.000	Rejected
Cd (200-400 mm)	0.000	Rejected
Cu (0-200 mm)	0.076	Accepted
Cu (200-400 mm)	0.114	Accepted

In order to statistically analyse data with normal distributions, a combination of raw data and Log<sub>10</sub> transformed data were used for the subsequent statistical analyses on the Stockhill Plantation soil parameters (Table 4.20).

Table 4.20. Type of data used for subsequent statistical analyses of soil parameter variables at Stockhill Plantation (n=12)

Soil Parameter	Raw or Log <sub>10</sub> data	H <sub>0</sub> : data followed a Normal Probability Distribution
L-o-I % (0-200 mm)	Raw	Accepted
L-o-I % (200-400 mm)	Raw	Accepted
Pb (0-200 mm)	Log <sub>10</sub>	Accepted
Pb (200-400 mm)	Log <sub>10</sub>	Accepted
Zn (0-200 mm)	Raw	Accepted
Zn (200-400 mm)	Raw	Accepted
Cd (0-200 mm)	Log <sub>10</sub>	Rejected
Cd (200-400 mm)	Log <sub>10</sub>	Rejected
Cu (0-200 mm)	Log <sub>10</sub>	Accepted
Cu (200-400 mm)	Log <sub>10</sub>	Accepted
Fe (0-200 mm)	Raw	Accepted
Fe (200-400 mm)	Raw	Accepted
Mn (0-200 mm)	Raw	Accepted
Mn (200-400 mm)	Raw	Accepted

Where appropriate, Log<sub>10</sub> transformed data for Cd at 0-200 mm and 200-400 mm were used for these data in subsequent statistical analyses, as recommended by Davies (1989).

#### **4.4.8 Data by Site: Agricultural Land Data set**

From the total number of samples sites in the study area, three sites were located in Agricultural land above the Priddy Mineries Reserve. As this was a small data set at  $n=3$ , no further statistical analyses were applied to these data.

### **4.5 Quality control - precision and accuracy**

#### **4.5.1 Sampling precision**

To assess the sampling precision between field duplicates, the % CV between the sample and its field duplicate was analysed for all soil parameters.

#### **4.5.2 Analytical accuracy and precision**

##### Certified Reference Material

To assess analytical accuracy, the percentage recoveries for Pb, Zn, Cd, Cu and Mn were calculated for the reference material BCR CRM 143R Sewage Sludge Amended Soil. The mean trace metal concentrations for Pb, Zn, Cd, Cu, Fe and Mn ( $\mu\text{g g}^{-1}$ ) and % CV were also calculated soil as a measure of analytical precision.

##### In-house reference material

The mean trace metal concentrations for Pb, Zn, Cd, Cu, Fe and Mn ( $\mu\text{g g}^{-1}$ ) and % CV were calculated for the in-house reference soil as a measure of analytical precision.

##### Soil data analytical replicates

The mean % CV of the % CV between the three replicate analyses for each sample was calculated for pH, Loss-on-Ignition, Pb, Zn, Cd, Cu, Fe and Mn.

## 4.6 Results

### 4.6.1 All Soil Data set: descriptive statistics

In the surface soils of the study area (0-200 mm), soil pH ranged from pH 3.0 to pH 7.3, with a median value of pH 4.5 (Table 4.21). At depth (200-400 mm), soil reaction ranged from pH 3.0 to pH 7.6, with a median value of pH 5.0. Surface Loss-on-Ignition ranged from 3.9% to 53.4%, and from 3.0% to 34.8% at depth. Median values for Loss-on-Ignition were 11.3% mm and 8.1% at surface and depth respectively (Table 4.21).

Soil Pb in the study area ranged from 262 to 138 800  $\mu\text{g g}^{-1}$  in the surface soils and from 180 to 171 668  $\mu\text{g g}^{-1}$  at depth (Table 4.21). The concentration of Zn in the surface soils ranged from 13 to 10 349  $\mu\text{g g}^{-1}$ , and from 14 to 8 089  $\mu\text{g g}^{-1}$  at depth. In the surface soils, Cd ranged from 1 to 12  $\mu\text{g g}^{-1}$ , and from 1 to 11  $\mu\text{g g}^{-1}$  at depth. The concentration of Cu in the soils of the study area were shown to range from 1 to 182  $\mu\text{g g}^{-1}$  in the surface soils, and from 1 to 206  $\mu\text{g g}^{-1}$  at depth. The Fe content of the surface soils ranged from 759 to 59 754  $\mu\text{g g}^{-1}$ , and from 751 to 67 035  $\mu\text{g g}^{-1}$  at depth. The range of soil Mn concentration in the study area was similar for surface and depth at 4 to 3 769  $\mu\text{g g}^{-1}$  and 3 to 3 690  $\mu\text{g g}^{-1}$  respectively (Table 4.21).

### 4.6.2 All Soil Data set: field observations

Field observations, soil classification and raw soil parameter data generated from the laboratory analyses are shown in Table 4.22. Field observations for the vegetation cover of each 1 m<sup>2</sup> sampling point are shown in Table 4.23.

Table 4.21. Summary of descriptive statistics at 0-200 mm and 200-400 mm for the All Soil Data set (n=77).

Parameter	Arithmetic Mean	St. Dev.	Minimum	1st Quartile	Median	3rd Quartile	Maximum
pH (0-200 mm)	4.88	1.43	3.00	3.50	4.50	6.40	7.30
pH (200-400 mm)	5.06	1.44	3.00	3.65	5.00	6.45	7.60
L-o-I % (0-200 mm)	13.13	8.52	3.90	8.15	11.3	14.5	53.4
L-o-I % (200-400 mm)	8.76	4.32	3.00	6.35	8.10	10.00	34.80
Pb $\mu\text{g g}^{-1}$ (0-200 mm)	23 316.80	29 115.80	262.00	1 394.00	4 502.00	41 142.00	138 800.00
Pb $\mu\text{g g}^{-1}$ (200-400 mm)	23 697.50	32 624.70	180.00	830.00	3 251.00	45 430.00	171 668.00
Zn $\mu\text{g g}^{-1}$ (0-200 mm)	1 819.12	2 446.86	13.00	28.00	455.00	3 979.50	10 349.00
Zn $\mu\text{g g}^{-1}$ (200-400 mm)	1 917.40	2 550.00	14.00	36.50	387.00	4 128.50	8 089.00
Cd $\mu\text{g g}^{-1}$ (0-200 mm)	2.65	2.72	1.00	1.00	1.00	4.00	12.00
Cd $\mu\text{g g}^{-1}$ (200-400 mm)	2.66	2.71	1.00	1.00	1.00	5.00	11.00
Cu $\mu\text{g g}^{-1}$ (0-200 mm)	35.47	38.84	1.00	7.00	18.00	58.50	182.00
Cu $\mu\text{g g}^{-1}$ (200-400 mm)	36.92	45.13	1.00	5.00	16.00	56.00	206.00
Fe $\mu\text{g g}^{-1}$ (0-200 mm)	22 654.70	17 718.00	759.00	5 060.00	20 961.00	42 011.00	59 754.00
Fe $\mu\text{g g}^{-1}$ (200-400 mm)	26 004.70	18 154.60	751.00	10 468.50	22 621.00	42 935.00	67 035.00
Mn $\mu\text{g g}^{-1}$ (0-200 mm)	901.32	1 004.68	4.00	25.00	565.00	1 629.00	3 769.00
Mn $\mu\text{g g}^{-1}$ (200-400 mm)	926.21	1 002.82	3.00	66.50	530.00	1 627.50	3 690.00

Table 4.22. Field observations, soil classification and summary of raw data from laboratory analysis for all soil data.

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
APR 97 1 3543 1504	<i>High above St Cuthbert's swallet in area of extensive tailings piles. Sample taken from slight depression in pile.</i>  <b>0-200</b> Brown, loamy with some grey clay and sand at 150-200 <b>200-400</b> Grey clay and sand with some sub-samples red at 300-400	TAILINGS OVER MAESBURY <b>0-200</b> <b>200-400</b>	6.4	16.7	69 983	4 255	6	92	44 958	2 992
			6.8	16.5	63 826	3 484	6	83	39 099	2 623
APR 97 2 3543 1505	<i>St Cuthbert's Swallet, with rock outcrop above. Abandoned tramway incline (1908) running from depression floor to transport old waste for reworking. Surrounded by tailings piles, subjected to episodic stream flooding causing alluvial deposition of silty clay.</i>  <b>0-200</b> Fine silty clay, bright red 0-100, fine black slag at 200 <b>200-400</b> Red clay 200-350, with gritty black slag at 350-400	DISTURBED OVER THRUPE  <b>0-200</b> <b>200-400</b>	7.1	13.3	138 800	3 617	3	182	59 753	3 416
			6.8	10.4	171 668	7 593	3	206	67 035	3 228
APR 97 3 3544 1505	<i>On site of abandoned inclined tramway, area disturbed during construction. Used as footpath and bridleway.</i>  <b>0-200</b> Brown and loamy, some sand and clay present <b>200-400</b> Similar to 0-200, soil apparently azonal	DISTURBED OVER THRUPE  <b>0-200</b> <b>200-400</b>	7.3	12.1	72 728	6 089	8	84	44 962	1 388
			7.4	11.2	73 747	7 294	11	111	49 020	1 599
MAR 97 4 3545 1505	<i>Site of minery buildings. Mostly foundations, paving and piles of fallen masonry. Close to condensing flue system.</i>  <b>0-200</b> Dark, dry, friable and stony <b>200-400</b> Similar to 0-200, soil apparently azonal	DISTURBED OVER MAESBURY  <b>0-200</b> <b>200-400</b>	6.9	11.4	78 618	4 548	8	84	44 609	2 097
			7.3	9.2	65 411	5 245	8	64	44 932	1 941
APR 97 5 3544 1506	<i>In carr, above disturbed land by leat carrying water to Priddy village.</i>  <b>0-200</b> Brown, crumbly, dark brown at 0-50, 150-200 grey, damp clay <b>200-400</b> very wet, pale grey clay. At 400 some samples pale pink, some contained streaks of dull orange sand. Clay stiff but plastic	DISTURBED OVER THRUPE  <b>0-200</b> <b>200-400</b>	6.5	11.8	16 233	1 629	1	18	16 665	501
			6.4	4.3	1 803	348	1	12	12 999	120
MAR 97 6 3545 1506	<i>Between tramway and top of smelter waste heaps. Heaps are collapsing, and contain black vitrified slag, cinder/cokey pitted and weathered slag and debris from smelters.</i>  <b>0-200</b> Black with some organic matter at 20-50. Coarse sandy gritty mix, black/dark brown at 50-200 <b>200-400</b> Azonal waste, gritty, small stones very coarse brown red	SMELTER WASTE OVER MAESBURY  <b>0-200</b> <b>200-400</b>	7.2	7.9	27 698	4 877	8	50	44 994	1 727
			7.5	6.2	29 751	5 509	10	55	46 379	1 599

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
MAR 97 7 3546 1506	On raised area at end of condensing flues. Very open ground  <b>0-200</b> Reddish brown, some clay. Some samples black in top 50 <b>200-400</b> Stony, gritty feel. Generally reddish brown, with red clay. Unusual white patches of clay not observed elsewhere on site.	DISTURBED OVER MAESBURY 0-200 200-400	7.1	12.0	21 716	3 044	6	32	37 933	1 345
			7.1	8.7	15 393	1 992	5	25	31 856	1 177
MAR 97 8 3547 1506	<i>Wooded area close to boundary wall. Mostly bare soil under deciduous tree canopy.</i> <b>0-200</b> Heavy clay, yellow brown, no apparent black/brown organic layer <b>200-400</b> Very heavy, stiff yellow brown clay	MAESBURY  <b>0-200</b> <b>200-400</b>	4.8	9.7	4 502	348	1	17	24 974	6 89
			5.0	8.4	4 750	345	1	15	25 449	7 73
DEC 95 9 3550 1506	<i>On very wet footpath, rough and overgrown with tree stumps, some still planted, others uprooted. Soil very wet, especially at depth.</i> <b>0-200</b> Some sub-samples dryer than others, brown crumbly texture under vegetation <b>200-400</b> Sub-samples often waterlogged and very dark brown	ASHEN  <b>0-200</b> <b>200-400</b>	5.2	11.3	29 600	712	1	24	21 363	772
			5.2	4.9	14 575	387	1	14	14 715	811
APR 97 10 544 1507	<i>Between footpath and a stream. Flat, open, with remains of planted row of large trees. Layer of undecomposed leaves (Fagus sylvatica) and twigs over soil.</i> <b>0-200</b> Dark brown, friable and loamy with some clay <b>200-400</b> Dark brown, more clay than 0-200. Some sub-samples were pale grey clay with orange patches at 350-400	DISTURBED OVER MAESBURY  <b>0-200</b> <b>200-400</b>	5.0	26.3	61 012	1 207	1	37	26 223	474
			6.1	17.5	65 401	1 232	1	29	22 621	242
MAR 97 11 3545 1507	<i>Very fine tailings, close to main tramway. Soil difficult to auger as very dry and fine. Tailings piles ran down to dried out pool. Small mammal runs evident in vegetation.</i> <b>0-200</b> Azonal, extremely fine sand/silt. No apparent darker organic layer, light sandy brown, homogenous in colour throughout profile <b>200-400</b> Similar to 0-200	TAILINGS OVER THRUPE  <b>0-200</b> <b>200-400</b>	7.1	6.0	29 553	5 109	6	45	44 547	1 763
			7.4	4.7	30 018	5 342	8	49	39 997	1 656
MAR 97 12 3546 1507	<i>Embankment apparently constructed from tailings. Sample taken close to area heavily used as an informal footpath.</i> <b>0-200</b> Dark brown, friable dry sand, apparently azonal with a little clay at 200 <b>200-400</b> Similar to 0-200, but with a higher percentage of clay	TAILINGS OVER THRUPE  <b>0-200</b> <b>200-400</b>	6.8	6.2	52 382	5 111	8	73	42 393	1 771
			6.8	9.4	63 745	5 917	8	83	44 759	1 808
FEB 97 13 3547 1507	<i>Low-lying in wet hollow, very open and exposed. Site of possible budding or tailings. After augering, water flooded holes to depths from approx. 100 to 400 mm.</i> <b>0-200</b> Wet, dark brown soil, slightly red/brown clay at 100-200 <b>200-400</b> Red clay, some fine sand at depth	TAILINGS OVER ASHEN  <b>0-200</b> <b>200-400</b>	6.6	11.4	64 392	7 393	7	81	46 596	2 141
			7.6	9.2	63 917	4 616	5	97	52 211	2 114

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
FEB 97 14 3547 1507	<i>Sample taken 30 m from road. Open area on edge of large stand of Calluna vulgaris.</i> <b>0-200</b> No dark organic layer, orange/brown in colour with some silt and clay, 0-150 very dry and crumbly <b>200-400</b> Darker orange/brown, with some sub-samples very bright orange. Stiff, dry clay with some sand, 350-400 very stiff clay throughout	TAILINGS OVER ASHEN								
		<b>0-200</b>	4.5	11.2	41 414	931	1	58	24 642	740
		<b>200-400</b>	5.1	11.6	89 647	3 211	2	87	37 364	1 957
NOV 95 15 3545 1508	<i>On side of minery pool, just off main tramway. Soil possibly originated from imported material used in tramway and pool construction.</i> <b>0-200</b> Sandy, red/brown in colour and well-drained <b>200-400</b> Sandy with some clay, still red/brown. Some sub-samples were a leached, grey coloured sand	DISTURBED OVER MAESBURY								
		<b>0-200</b>	6.7	8.1	38 781	5 478	6	66	42 456	1 877
		<b>200-400</b>	7.0	8.0	46 560	7 381	10	93	48 096	2 365
NOV 96 16 3546 1508	<i>Minery pool embankment, constructed from imported material, possibly tailings, some parts used as an informal footpath. Area generally open and grassy.</i> <b>0-200</b> Dark, slightly sandy with some sub-samples red at 150-200 <b>200-400</b> Dark with high percentage of clay. Some sub-samples were bright red, very plastic clay which held the auger shape	DISTURBED OVER THRUPE								
		<b>0-200</b>	6.0	12.8	40 709	3 345	4	90	43 251	927
		<b>200-400</b>	6.3	10.2	41 299	4 150	5	160	51 439	783
FEB 97 17 3547 1508	<i>Disturbed land, below a rectangular shaped depression. The whole area was generally stony, with masonry rubble. Large blocks of dressed masonry were under the surface of the soil and lying within the Calluna stand.</i> <b>0-200</b> Loose, sandy, pale brown. Some sub-samples contained black organic layer of <100, some contained no black layer <b>200-400</b> Wet, clay with some small stones. Generally at 250-400 a light yellow/brown colour, while some sub-samples were a very pale yellow colour from 200-400	ASHEN								
		<b>0-200</b>	4.4	9.9	4 006	575	1	18	26 195	565
		<b>200-400</b>	4.1	5.7	1 739	254	1	21	26 525	530
DEC 95 18 3549 1508	<i>Facing St. Cuthbert's works, on the edge of an old coniferous plantation, in an open glade. Young, apparently healthy Picea abies surrounded glade. Much loose, bare sandy soil present, with a large ant colony disturbing the soil. Ground was also noted to be hollow in some places at depth, possibly part of a rabbit warren.</i> <b>0-200</b> Dark, loose, very fine silty sand. Apparently azonal, some sub-samples were reddish in colour and slightly damp <b>200-400</b> Similar to 0-200 throughout	TAILINGS OVER ASHEN								
		<b>0-200</b>	5.1	12.2	76 887	1 997	1	76	42 641	2 679
		<b>200-400</b>	5.4	11.2	86 135	2 017	3	80	46 630	2 709



DATE SOIL No GRID REF.	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
FEB 97 19 3544 1509	<i>Tailings heap above main tramway. Appeared to be extensive rabbit warren over whole area. Very open vegetation on flat top.</i> <b>0-200</b> No organic black layer, although fine root and rhizomous material present. Fine, dry, sandy of pale brown colour, with some sub-samples slightly red. Apparently azonal <b>200-400</b> Similar to 0-200 without root and rhizomal material	TAILINGS OVER MAESBURY								
		<b>0-200</b> <b>200-400</b>	7.3 6.6	5.6 6.8	36 095 29 052	5 209 4 107	5 4	36 34	32 422 28 652	975 778
DEC 97 20 3544 1509	<i>Very high tailings pile above main tramway. Part of pile seemed to have been removed after deposition. Extensive ant colony, solitary Fraxinus excelsior on top of pile.</i> <b>0-200</b> Very gritty, sandy black/ dark grey, damp soil. Apparently azonal, some root and rhizomal material <b>200-400</b> Similar to 0-200, with no root or rhizomal material	TAILINGS OVER MAESBURY								
		<b>0-200</b> <b>200-400</b>	6.4 6.5	14.0 10.0	58 550 51 544	5 688 8 089	8 7	59 53	43 528 58 029	1 870 2 019
NOV 96 21 3545 1509	<i>Just off tramway on top of built-up tramway embankment. The embankment drops away to marshy area that was site of the old tailings pond in Thrupe series to east. Material used to construct tramway possibly imported from elsewhere on site.</i> <b>0-200</b> Azonal with no apparent dark organic layer. Sandy and red/brown in colour <b>200-400</b> Very red, plastic clay	DISTURBED OVER MAESBURY								
		<b>0-200</b> <b>200-400</b>	6.6 6.8	6.4 6.7	30 442 19 803	8 713 4 175	11 6	64 57	53 580 48 163	1 803 2 315
MAR 97 22 3546 1509	<i>Open, very disturbed land, with evidence of buildings.</i> <b>0-200</b> Peaty, dark with undecomposed litter at 0-100 and some sand, 100-200 sandy, pinkish in colour with some clay <b>200-400</b> Red clay and sand with stones	ASHEN/ THRUPE BOUNDARY								
		<b>0-200</b> <b>200-400</b>	3.4 3.8	12.6 6.1	4 127 2 690	60 94	1 1	9 14	20 085 29 465	289 826
DEC 95 23 3550 1509	<i>Summit of hill in Stockhill plantation. In area of older coniferous woodland, sheltered with damp microclimate. Ground quite open and light due to vast height of trees. Soil thickly covered with undecomposed needle litter, many undecomposed fallen tree trunks littered area.</i> <b>0-200</b> Stony soil, dark brown and loamy with a sandy feel throughout <b>200-400</b> Red and stony, some sub-samples contained dark brown/red mottling	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.3 3.5	12.6 9.0	1 258 946	22 42	1 1	4 10	7 308 16 887	32 90
MAR 97 24 3543 1510	<i>On hillside, by public footpath. Sample taken between footpath and boundary wall.</i> <b>0-200</b> Black, loose, dry and peaty. 170-200 orange in colour <b>200-400</b> Orange, sandy with some clay	MAESBURY								
		<b>0-200</b> <b>200-400</b>	3.5 3.6	15.5 8.5	1 090 660	29 74	1 1	8 6	4 723 10 638	58 87

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
FEB 97 25 3544 1510	<i>On hillside, close to rectangular remains. Masonry or large stones under soil in area.</i> <b>0-200</b> Dark brown/black at 0-180. Leached, light grey brown sand with some clay at 180-200 <b>200-400</b> Grey brown sandy soil with some clay at 200-300, with ochreous orange, stiff plastic clay with some sand at 300-400	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.4 4.3	7.6 6.1	3 026 2 379	64 1 627	1 1	8 5	7 488 9 689	51 74
FEB 97 26 3545 1510	<i>On open hillside above leat, south of condensing flues, below remains of rectangular junction/access shaft.</i> <b>0-200</b> Dark brown, rich peaty soil with undecomposed <i>Molinia</i> litter. Quite sandy, with some small stones <b>200-400</b> Stony and gritty. Bright yellow orange sand at 300-400	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.7 3.6	14.3 7.7	3 204 2 181	40 40	1 1	5 7	11 567 16 356	37 84
MAR 97 27 3546 1510	<i>Side of main tramway by condensing flues. Rock scattered under soil surface in the area appeared to be unweathered Dolomitic Conglomerate. Possibly imported from quarry area at Stockhill for construction purposes at time of minery operations.</i> <b>0-200</b> Light brown sandy clay, some roots at 50, but no darker organic layer present <b>200-400</b> Clay, same colour as 0-200, but appeared stony at depth, almost azonal. Either fairly young soil, alluvial inwash from hillside, modified Ashen soil or imported during construction work	TAILINGS ● OVER ASHEN								
		<b>0-200</b> <b>200-400</b>	5.8 6.2	18.9 14.6	39 409 67 752	4 289 4 655	3 1	87 128	45 809 53 150	1 106 1 008
DEC 95 28 3548 1510	<i>Felled coniferous woodland, with remains of stumps. Area very exposed on hillside. Ground very uneven and rocky in places, soil appeared to be generally shallow. Quite damp in hollows between rocks. Variety of microclimates in area.</i> <b>0-200</b> Black peaty soil, some sand <b>200-400</b> Stony, some sub-samples waterlogged. Black silty and sandy material	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.1 3.6	16.7 7.5	981 644	27 45	1 1	10 8	2 564 5 921	14 28
FEB 97 29 3543 1511	<i>On slopes of North Hill. Fairly flat and exposed with public footpath to west.</i> <b>0-200</b> Peaty and black throughout, with undecomposed <i>Molinia</i> litter at surface <b>200-400</b> Black and peaty to 350. 350-400 sandy, some sub-samples still black, although some were leached sand of a dark grey colour	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.4 3.6	24.6 13.5	1 222 630	32 18	1 1	6 5	2 206 4 059	14 31

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
FEB 97 30 3544 1511	<i>North Hill, south west of remains of small reservoir and smelter stack.</i> <b>0-200</b> All sub-samples were black and peaty, some had standing water at 200 above a clay layer <b>200-400</b> Black mire at 200 then apparently water impervious layer of very stiff, leached grey clay with ochreous orange patches	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.8 3.7	33.7 13.6	1 381 613	22 14	1 1	10 6	3 881 2 022	5 3
FEB 97 31 3545 1511	<i>South of remains of smelter stack. Very open, no footpath.</i> <b>0-200</b> Peaty, black at 0-100, with pale grey brown leached sandy soil at 100-200 <b>200-400</b> Pale grey brown leached and sandy to 300, at 300-400 some clay with occasional patches of ochreous orange sand	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.3 3.8	10.5 3.4	1 407 384	14 31	1 1	3 5	1 446 5 610	5 15
JAN 97 32 3546 1511	<i>Very disturbed land, in the 90° angle between south-west and west running condensing flues. Remains of smelter on outside of angle. The area appeared to collect water as the flues running south-west act as dam for water running down North Hill. Original soil appears to have been removed, turves possibly used to cover flues during smelting. Masonry present at depth under soil. Stony soil.</i> <b>0-200</b> Black at 0-100, then red/pink brown sandy soil to 200 <b>200-400</b> Very red at 250-400, sandy but with more clay than 0-200 Some sub-samples were leached to a pale grey pink colour	ASHEN								
		<b>0-200</b> <b>200-400</b>	3.8 3.6	7.0 4.8	2 065 1 152	115 67	1 1	9 9	8 838 10 343	86 87
SEPT 96 33 3547 1511	<i>Close to dam constructed of smelter waste in marshy area, site of the old tailings pond. Very disturbed, wastes and rubble just under surface of soil. Possible site of smelter waste heap before removal to St. Cuthbert's for re-smelting in late 19<sup>th</sup> / early 20<sup>th</sup> Century.</i> <b>0-200</b> Dry, black, gritty and friable <b>200-400</b> Stones and smelter waste, one sub-sample appeared to contain brick-like material	SMELTER WASTE OVER THRUPE								
		<b>0-200</b> <b>200-400</b>	6.8 7.1	16.9 13.4	46 022 44 300	5 468 5 884	6 5	76 72	40 566 46 874	1 282 1 177
SEPT 96 34 3548 1511	<i>On edge of marshy area, the site of the former tailings pond. Sample taken approx. 30 m into tailings pond from Milton road.</i> <b>0-200</b> Dry, friable, dark and peaty with high sand content <b>200-400</b> Red brown, sandy, bright red at 300-400	ASHEN								
		<b>0-200</b> <b>200-400</b>	4.5 4.7	6.9 4.0	5 073 4 348	755 681	1 1	13 17	14 639 14 386	304 235

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
FEB 97 35 3543 1512	<i>Junction of fence and dry stone wall, by stile and public footpath.</i> <b>0-200</b> Black, peaty. A few sub-samples were red brown with clay at 150-200 <b>200-400</b> Red brown with some sub-samples very orange with sand. Some stony sub-samples at 300-400	ASHEN  <b>0-200</b> <b>200-400</b>	 4.0 4.2	 13.0 9.0	 488 305	 32 44	 1 1	 3 5	 3 855 8 912	 35 41
FEB 97 36 3544 1512	<i>Very open moorland, close to informal footpath.</i> <b>0-200</b> Black, organic some clay at 0-150, pale red, pink grey with small patches of orange at 200 <b>200-400</b> Pale orange at 200-250, brighter orange 250-400. High percentage of clay throughout, with some sand	ASHEN  <b>0-200</b> <b>200-400</b>	 3.3 3.2	 14.7 6.4	 918 374	 19 27	 1 1	 4 5	 5 012 7 666	 40 36
FEB 97 37 3545 1512	<i>On south eastern face of slope of open moorland, Sample taken close to informal footpath.</i> <b>0-200</b> Black, peaty at 0-150, leached grey sand 150-200 <b>200-400</b> Leached grey sand at 200-250, orange red sand at 250-400	ASHEN  <b>0-200</b> <b>200-400</b>	 3.8 3.3	 9.0 6.6	 1 067 965	 24 38	 1 1	 3 3	 9 588 22 488	 21 31
FEB 97 38 3546 1512	<i>Open area above leat system running from reservoir.</i> <b>0-200</b> Black, sandy <b>200-400</b> Gritty and sandy, some sub-samples black at 200-250, grey leached sand with occasional patches of orange at 250-400	ASHEN  <b>0-200</b> <b>200-400</b>	 3.3 3.7	 9.2 7.1	 3 454 2 540	 23 21	 1 1	 6 3	 5 569 4 057	 7 14
SEPT 96 39 3547 1512	<i>By buddle area, to the side of the junction of two informal footpaths.</i> <b>0-200</b> Black, peaty, dry and friable <b>200-400</b> Peaty, contained some clay. Apparently azonal	ASHEN  <b>0-200</b> <b>200-400</b>	 6.2 6.1	 11.3 7.0	 12 796 6 548	 2 196 1 774	 3 1	 23 13	 15 741 10 633	 652 285
SEPT 96 40 3548 1512	<i>In marshy area, site of former tailings pond. Mixture of creeks and raised areas.</i> <b>0-200</b> Black, high percentage silt and clay, appeared azonal <b>200-400</b> Similar to 0-200 but very wet	TAILINGS OVER THRUPE  <b>0-200</b> <b>200-400</b>	 6.6 6.5	 11.7 11.8	 59 890 71 914	 5 496 6 233	 5 7	 128 143	 5 108 59 851	 1 361 865
DEC 97 41 3546 1512	<i>Top of tailings pile, above tramway. Large ant colony present and rabbit scrapings.</i> <b>0-200</b> Azonal, very fine, dark brown with sandy feel. <b>200-400</b> Similar to 0-200	TAILINGS OVER ASHEN  <b>0-200</b> <b>200-400</b>	 6.4 6.6	 6.7 5.0	 30 826 30 994	 4 140 4 005	 5 5	 46 49	 35 995 36 077	 2 144 2 353
AUG 97 42 3542 1513	<i>Arable grassland grazed by cattle and sheep.</i> <b>0-200</b> Dark brown, loamy, dry with some fine root material <b>200-400</b> Similar to 0-200 with some sub-samples red at 300-400. Occasional large stones	ASHEN  <b>0-200</b> <b>200-400</b>	 5.3 4.7	 15.4 9.3	 367 340	 26 24	 1 1	 50 37	 4 193 11 222	 282 250

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
JAN 97 43 3545 1513	<i>By corner of two boundary fences, pasture above site. Subjected to drainage from field above, channel had formed. Surface was heavily frozen when sample was collected.</i> <b>0-200</b> Black, peaty and sandy. Some sub-samples very wet, with some red at 200 <b>200-400</b> Very red at 300-400, still sandy but with much more clay	ASHEN								
		<b>0-200</b>	3.6	13.1	1 616	28	1	3	8 275	26
		<b>200-400</b>	3.3	8.5	1 244	27	1	3	15 053	42
JAN 97 44 3546 1513	<i>Hillside, very open moorland area, close to informal footpath.</i> <b>0-200</b> Black and peaty with some sand at 200. Rhizomous <b>200-400</b> Black, increasingly sandy down profile. At 400 clay present in sand, some sub-samples contained small patches of red sand and very occasionally patches of ochreous yellow sand	ASHEN								
		<b>0-200</b>	4.0	27.7	1 787	40	1	10	2 397	9
		<b>200-400</b>	3.9	10.0	612	39	1	8	4 246	22
JAN 97 45 3547 1513	<i>Very open, site prone to seasonal flooding. Sample taken within outline of filled-in buddle pit, at top of series of pits, nearest leat. Site either naturally filled in with alluvium, or purposely with tailings from nearby piles. Was wet at time of sampling.</i> <b>0-200</b> Black, peaty at 0-150, red brown, fine silts and clay from 150-200 <b>200-400</b> Red brown very fine silts and clay	DISTURBED OVER THRUPE								
		<b>0-200</b>	5.7	17.9	76 977	3 953	4	119	45 691	1 531
		<b>200-400</b>	6.0	12.6	82 422	6 623	6	115	45 593	1 458
FEB 95 46 3548 1513	<i>Flat top of tailings pile. This sandy pile is prone to drought conditions in dry weather, but long periods of flooding around base some winters and spring causes heap to stay very wet.</i> <b>0-200</b> Red, friable with high percentage of sand <b>200-400</b> Similar to 0-200, heap appears azonal	TAILINGS OVER THRUPE								
		<b>0-200</b>	6.6	6.4	59 923	10 349	12	165	51 978	2 617
		<b>200-400</b>	6.9	5.5	65 952	8 010	7	166	51 634	2 744
DEC 97 47 3549 1512	<i>Above large rocky depression in woodland. Area very disturbed and open. Depression prone to deep flooding in very wet weather.</i> <b>0-200</b> Very dark brown organic layer at 0-40 with network of fine roots and rhizomes. Red brown fine material, damp at 40-200 <b>200-400</b> Red brown, much drier than 0-200, crumbled easily	NORDRACH								
		<b>0-200</b>	3.9	9.6	5 629	401	1	19	28 005	624
		<b>200-400</b>	3.8	6.3	8 724	528	1	20	31 716	1 014
DEC 97 48 3547 1513	<i>South facing tailings pile. Bottom of pile borders on flowing water, top desiccated in dry weather. High degree of chlorosis in vegetation at bottom of pile.</i> <b>0-200</b> Red, very sandy and stony. Azonal <b>200-400</b> Similar to 0-200, azonal	TAILINGS OVER THRUPE								
		<b>0-200</b>	6.5	5.7	64 837	4 006	3	38	39 864	1 272
		<b>200-400</b>	6.4	8.4	63 740	6 013	6	61	54 353	1 801
JAN 97 49 3547 1513	<i>Freshly excavated buddle pit with flat, exposed buddle floor.</i> <b>0-200</b> Red sandy soil with clay, some sub-samples black fine sand <b>200-400</b> Similar to 0-200, azonal	DISTURBED OVER THRUPE								
		<b>0-200</b>	6.8	6.6	40 869	5 046	7	95	46 082	3 769
		<b>200-400</b>	6.8	7.5	54 642	5 715	7	102	50 732	3 372

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
AUG 97 50 3542 1514	<i>Arable grassland grazed by cattle and sheep.</i> <b>0-200</b> Dark brown, loamy, dry with some fine root material <b>200-400</b> Similar to 0-200 with some sub-samples red at 300-400. Occasional large stones at depth	ASHEN								
		<b>0-200</b>	5.5	13.9	317	28	1	64	5 306	203
		<b>200-400</b>	5.2	9.9	398	23	1	50	14 957	250
JAN 97 51 3545 1514	<i>Break in hillside slope. Sample taken just below fence line, arable pasture above.</i> <b>0-200</b> Black, peaty and organic, some sand <b>200-400</b> Very dark red brown, some clay and sand	ASHEN								
		<b>0-200</b>	3.3	18.2	1 119	30	1	3	4 965	23
		<b>200-400</b>	3.6	10.4	607	21	1	3	8 465	74
JAN 97 52 3546 1514	<i>Open Moorland, below break in hillside, above leat.</i> <b>0-200</b> Dark, black and peaty at 0-100. Very sandy at 150-200, some sub-samples contained bright yellow ochreous sand <b>200-400</b> Generally yellow/red and sandy	ASHEN								
		<b>0-200</b>	3.2	10.7	1 520	23	1	3	3 231	11
		<b>200-400</b>	3.2	8.3	1 030	20	1	1	7 777	19
FEB 95 53 3547 1514	<i>Below leat and site of waterwheel at Waldegrave Pool. Very wet, prone to flooding in wet weather.</i> <b>0-200</b> Very damp, black and humic <b>200-400</b> Extremely wet, apparently anaerobic. Sub-samples contained a high percentage of silts and clay, a few sub-samples were a liquid paste	DISTURBED OVER THRUPE								
		<b>0-200</b>	5.3	11.2	48 817	1 380	1	27	15 076	262
		<b>200-400</b>	5.3	8.4	36 451	1 316	1	16	12 783	273
FEB 95 54 3548 1514	<i>Base of buddle tailings area leading to swallet under the Milton road, near to stream. Seasonal flooding, depression was recently under 4-5 m water. Catchment for North Hill and Waldegrave Pool overflow. Soil compacted.</i> <b>0-200</b> Red, fine textured material <b>200-400</b> Generally fine textured, some small stones, very bright red at 300-400	TAILINGS OVER THRUPE								
		<b>0-200</b>	6.3	13.0	55 801	4 614	5	65	40 288	2 116
		<b>200-400</b>	6.4	8.0	58 824	4 342	5	64	50 072	2 345
DEC 95 55 3550 1514	<i>Top of mining groove, on fringe of felled coniferous woodland.</i> <b>0-200</b> Red brown, dry and friable at 0-100, brighter red, dry and crumbly at 100-200 <b>200-400</b> Wetter, but not water-logged, very firm plastic clay texture with light orange red clay at 300-400	NORDRACH								
		<b>0-200</b>	3.9	9.7	6 816	455	1	19	28 971	1 097
		<b>200-400</b>	5.5	6.7	7 116	485	1	18	29 707	1 431
DEC 96 56 3544 1515	<i>Arable field above moorland, grazed by sheep and cattle.</i> <b>0-200</b> Brown, dry and friable with fibrous roots. Some sub-samples were red brown at 150-200 <b>200-400</b> Red brown, 300-200 very red and sandy	ASHEN								
		<b>0-200</b>	5.1	14.9	1 046	28	1	2	6 422	1 090
		<b>200-400</b>	5.6	11.0	785	25	1	2	11 880	169
DEC 96 57 3545 1515	<i>Open moorland on hillside above Waldegrave Pool. Sample taken away from footpath.</i> <b>0-200</b> Peaty, dark brown at 0-100, red and sandy at 100-200 <b>200-400</b> Red sand and clay	ASHEN								
		<b>0-200</b>	3.4	14.0	1 426	19	1	2	5 602	21
		<b>200-400</b>	3.6	9.9	972	35	1	1	12 015	58

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
SEPT 96 58 3546 1515	<i>Sample location at western side of Waldegrave Pool., close to the edge of the pool.</i> <b>0-200</b> Black, damp with litter and root material <b>200-400</b> Black at 200-300, red layer at 300-400	ASHEN  <b>0-200</b> <b>200-400</b>	4.2 4.1	8.6 5.9	3 909 816	36 22	1 1	6 3	6 257 760	14 3
SEPT 96 59 3547 1515	<i>On open shore of Waldegrave Pool. Area heavily trampled, used for recreation. Sample taken near water's edge.</i> <b>0-200</b> Red sand and clay, few sub-samples had brown streaks. <b>200-400</b> Similar to 0-200, apparently azonal	DISTURBED OVER THRUPE  <b>0-200</b> <b>200-400</b>	5.5 6.1	3.9 3.0	1 987 2 367	185 195	1 1	9 7	4 398 4 600	29 33
MAY 95 60 3544 1516	<i>On break in slope, near footpath and boundary fence. Below arable land. Possibly relict of wooded or hedgerow area.</i> <b>0-200</b> Black, peaty and dry <b>200-400</b> Black, peaty and dry to 300, red, friable and sandy with some clay at 300-400	ASHEN  <b>0-200</b> <b>200-400</b>	3.1 3.0	10.2 7.9	397 289	19 26	1 1	3 3	3 576 12 872	21 118
OCT 96 61 3545 1516	<i>Slightly above very wet area.</i> <b>0-200</b> Black and peaty, at 150-200 some sub-samples contained leached grey sand <b>200-400</b> Some sub-samples still dark and peaty, but all were leached grey sand at 300-400	THRUPE  <b>0-200</b> <b>200-400</b>	3.7 3.9	44.9 15.7	782 273	22 15	1 1	10 8	2 472 1 266	16 10
OCT 96 62 3546 1516	<i>At top right angle of leat system to north of Waldegrave Pool. Sample site in break in slope, very wet and marshy..</i> <b>0-200</b> Black and peaty <b>200-400</b> Very wet, black peat	THRUPE  <b>0-200</b> <b>200-400</b>	3.5 3.6	53.4 15.3	2 319 843	13 21	1 1	10 2	1 660 751	9 3
NOV 95 63 3547 1516	<i>Moorland, very open and exposed. Mechanically cleared in 1997 as part of management plan, possibly to allow re-establishment of C. vulgaris.</i> <b>0-200</b> Dark, damp and plastic, with a gritty, sandy feel <b>200-400</b> As 0-200 to 300 mm, then red, with some sub-samples bright red at 350	ASHEN  <b>0-200</b> <b>200-400</b>	3.2 3.4	8.2 7.6	1 283 809	15 39	1 1	1 1	759 7 518	4 10
DEC 95 64 3549 1516	<i>Coniferous woodland with some F. sylvatica. Near footpath, soil appeared compacted. Light covering of Fagus litter.</i> <b>0-200</b> Dark brown and loamy at 0-50, red plastic clay at 50-200 <b>200-400</b> Red, very plastic clay	NORDRACH  <b>0-200</b> <b>200-400</b>	3.3 3.6	15.2 9.6	3 125 3 197	272 265	1 2	13 10	27 655 29 862	1 041 1 538
MAY 95 65 3544 1517	<i>By masonry wall on north boundary of reserve. Just above a wet area surrounding a small spring. Appeared to be textbook podsol.</i> <b>0-200</b> Black and peaty <b>200-400</b> Black and peaty to 300, bleached, very pale grey sand and clay soil at 300-400	ASHEN/ THRUPE BOUNDARY  <b>0-200</b> <b>200-400</b>	3.1 3.3	16.6 7.1	1 141 705	22 24	1 1	3 3	2 655 5 533	12 1 43

DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
NOV 95 66 3545 1517	<i>North west facing, exposed position on hillside, near bottom of slope. Sample area contained a high proportion of bare soil. Vegetation was low and stunted.</i> <b>0-200</b> Dark, dry and sandy with small stones <b>200-400</b> Red, damp, sandy, appeared to continue red at 500+	ASHEN								
		<b>0-200</b>	3.5	10.2	262	18	2	2	2 439	10
		<b>200-400</b>	3.7	7.1	180	33	1	2	11 222	76
NOV 95 67 3546 1517	<i>Sample site on west slope of hillside, below tumulus on break in slope. Open aspect, with some trampling of vegetation.</i> <b>0-200</b> Dark, peaty, gritty feel. One sub-sample contained red sand <b>200-400</b> Red, sandy and gritty	ASHEN								
		<b>0-200</b>	3.6	10.1	531	19	1	1	3 880	15
		<b>200-400</b>	3.4	8.1	367	34	1	1	10 594	160
MAY 95 68 3547 1517	<i>Approx. 1.5 m above Milton road in disturbed ground, behind dry stone boundary wall. Disturbed ground that had undergone a recent burn.</i> <b>0-200</b> Damp, black, very friable <b>200-400</b> Black to 300, red soil with clay at 300-400	ASHEN								
		<b>0-200</b>	3.4	10.1	2 202	53	1	8	5 846	25
		<b>200-400</b>	3.7	6.7	1 566	56	1	3	10 067	59
DEC 95 69 3549 1517	<i>Bottom of mining groove (4 m depth), with exposed rock on both sides. In Coniferous plantation. Soil in bottom of groove due to creep from surrounding areas. Deep standing crop of needle litter above soil.</i> <b>0-200</b> Red, silty clay and sand <b>200-400</b> Similar to 0-200, soil apparently azonal	DISTURBED OVER NORDRACH								
		<b>0-200</b>	6.7	9.0	25 731	1 140	4	31	33 591	3 594
		<b>200-400</b>	6.7	8.5	26 264	1 167	3	24	34 329	3 690
JAN 97 70 35455 15181	<i>Bare, flattened or excavated coarse tailings pile, slightly raised above alluvial, marshy area. Area surrounded by deep floodwater annually, very hot and desiccated in summer, extremely poor colonisation by vegetation.</i> <b>0-200</b> Red coarse sand, very wet, with standing water to 50 mm below surface when auger was removed <b>200-400</b> Similar to 0-200, but waterlogged	TAILINGS OVER THRUPE								
		<b>0-200</b>	4.7	5.6	67 488	1 135	1	42	42 856	2 146
		<b>200-400</b>	4.8	4.6	66 246	901	1	37	40 749	1 455
MAY 95 71 3545 1518	<i>Wet, marshy area, bottom of valley at base of North hill. Site was under deep water (up to 900 mm) for most of Feb/Mar 1995.</i> <b>0-200</b> Black, peaty and damp <b>200-400</b> Black, peaty and wet	THRUPE								
		<b>0-200</b>	3.0	39.7	3 579	90	1	15	10 987	25
		<b>200-400</b>	3.1	34.8	3 251	77	1	13	11 603	19
MAY 95 72 3546 1518	<i>Wet, marshy area. Site was under deep water (up to 900 mm) for most of Feb/Mar 1995, sample area slightly raised from surrounding area, appeared slightly drier. Deep undecomposed litter layer over soil. Probably old tailings.</i> <b>0-200</b> Red, sandy, wet <b>200-400</b> Very wet, paler red than 0-200	TAILINGS OVER THRUPE								
		<b>0-200</b>	5.2	7.5	73 540	1 002	1	44	24 046	239
		<b>200-400</b>	5.6	7.9	43 220	718	1	31	18 530	156



DATE SOIL No GRID REF	SITE AND SOIL (0-200 mm and 200-400 mm depth) FIELD OBSERVATIONS	SOIL SERIES / DEPTH (mm)	pH	% LOI	$\mu\text{g g}^{-1}$ Dry Mass					
					Pb	Zn	Cd	Cu	Fe	Mn
DEC 95 73 3548 1518	<i>Top of two very deep, steep mining grooves, possibly used as an informal footpath, some compaction of soil.</i>	NORDRACH								
	<b>0-200</b> Dark red brown at 0-50, red, dry but plastic at 50-200 <b>200-400</b> Red, wetter, still plastic with a high clay content	<b>0-200</b> <b>200-400</b>	5.4 .6	5.2 3.5	10 679 5 737	779 762	1 1	23 21	32 912 33 103	1 768 1 500
MAY 95 74 3546 1519	<i>Close to north boundary wall, close to P. sylvestris. On edge of marshy area.</i>	NORDRACH								
	<b>0-200</b> Red brown, stony, dry and friable with clay <b>200-400</b> Red, drier than 0-200, still crumbly	<b>0-200</b> <b>200-400</b>	3.2 3.8	11.0 6.5	1 351 1 195	233 223	1 1	25 16	20 961 27 914	258 1 022
DEC 95 75 3550 1519	<i>In mixed coniferous/F. sylvatica plantation. Close to series of deep depressions, probably a chain of mining pores or small pits.</i>	NORDRACH								
	<b>0-200</b> Compacted, light red, dry clay soil <b>200-400</b> Red, plastic, high proportion of clay	<b>0-200</b> <b>200-400</b>	3.6 3.9	10.0 8.1	2 007 1 724	395 324	1 1	18 15	41 629 41 111	1 000 973
DEC 95 76 3549 1520	<i>Clearing in P. abies plantation. Very open in circle of approx. 10 m diameter. Ground disturbed with mining grooves.</i>	NORDRACH								
	<b>0-200</b> Dark brown, organic, damp and crumbly with fibrous roots at 0-100, red and friable with a gritty feel at 100-200 <b>200-400</b> Red, stony and gritty	<b>0-200</b> <b>200-400</b>	4.3 4.6	7.8 5.2	7 800 6 918	933 765	1 1	18 15	46 740 40 539	2 835 2 817
DEC 95 77 3547 1521	<i>Highly disturbed mined gruffy ground in dense, mature coniferous plantation. Deep, undecomposed needle litter. Sample taken from soil above shallow mining grooves.</i>	NORDRACH								
	<b>0-200</b> Dark brown, damp soil at 0-20, red soil with clay at 20-200 <b>200-400</b> Red, dry soil with clay	<b>0-200</b> <b>200-400</b>	4.4 5.3	6.3 4.7	2 546 2 780	535 625	1 1	18 20	32 083 36 180	1 343 1 694

Table 4.23. Vegetation present in the 1 m<sup>2</sup> soil sample points.

Ref. No.	Grid Ref.	Soil Series	Vegetation notes
1	3543 1504	Tailings over Maesbury	Dominated by large <i>Deschampsia caespitosa</i> tussocks with litter and a mossy understorey. <i>Holcus lanatus</i> , <i>Galium saxatile</i> and <i>Lathyrus pratensis</i> also present.
2	3543 1505	Disturbed over Thrupe	Short grassland. Dominant species <i>Agrostis capillaris</i> with some <i>Juncus effusus</i> , <i>Carex flacca</i> , <i>Rumex acetosa</i> , <i>Potentilla erecta</i> , <i>Ranunculus acris</i> and <i>Achillea millefolium</i> . <i>Carex paniculata</i> , <i>D. caespitosa</i> , <i>Caltha palustris</i> and many seedlings of <i>Acer pseudoplatanus</i> growing by stream.
3	3544 1505	Disturbed over Thrupe	Low/tall grassland mix. <i>Festuca rubra</i> , <i>H. lanatus</i> , <i>Dactylis glomerata</i> , <i>Arrhenatherum elatius</i> , <i>Carex caryophylla</i> , <i>C. flacca</i> , <i>R. acetosa</i> , <i>G. saxatile</i> , <i>Heracleum sphondylium</i> and <i>L. pratensis</i> . <i>Holcus lanatus</i> highly chlorosed.
4	3545 1505	Disturbed over Maesbury	Very low, stunted vegetation including <i>Thymus polytrichus</i> , <i>Lotus corniculatus</i> , <i>Cerastium semidecandrum</i> , <i>Plantago lanceolata</i> , <i>R. acetosa</i> , <i>F. rubra</i> , <i>H. lanatus</i> , <i>G. saxatile</i> , and <i>D. glomerata</i> .
5	3544 1506	Disturbed over Thrupe	Medium vegetation with <i>Salix</i> spp. and <i>C. paniculata</i> along streamline. <i>F. rubra</i> , <i>D. glomerata</i> , <i>H. lanatus</i> , <i>Sanguisorba minor</i> , <i>G. saxatile</i> , <i>A. millefolium</i> , <i>Ranunculus bulbosa</i> , <i>Urtica dioica</i> and moss spp.
6	3545 1506	Smelter waste over Maesbury	Very low, stunted vegetation. Moss spp., <i>Cladonia</i> spp., <i>Thlaspi caerulescens</i> , <i>Arabis hirsuta</i> , <i>Agrostis stolonifera</i> , <i>Medicago lupulina</i> , <i>Trifolium repens</i> , <i>T. polytrichus</i> , <i>R. acetosa</i> , <i>S. minor</i> , <i>A. Millefolium</i> , <i>P. lanceolata</i> , <i>F. rubra</i> and <i>L. pratensis</i> .
7	3546 1506	Disturbed over Maesbury	Very low, stunted vegetation. <i>Silene uniflora</i> , <i>Veronica chamaedrys</i> , <i>T. repens</i> , <i>F. rubra</i> , <i>A. millefolium</i> , <i>C. flacca</i> , <i>Taraxacum</i> spp., <i>P. lanceolata</i> , <i>C. semidecandrum</i> , moss spp, and <i>Cladonia</i> spp.
8	3547 1506	Maesbury	<i>Crataegus monogyna</i> to 5 m. Understorey included <i>Dryopteris</i> spp., <i>Rubus fruticosus</i> , <i>Glechoma hederacea</i> , <i>Vicia sepium</i> , <i>D. glomerata</i> , <i>A. capillaris</i> and <i>U. dioica</i> .
9	3550 1506	Ashen	Dominated by tussocks of <i>Molinia caerulea</i> to 1.2 m. Also present were <i>Ulex europeus</i> , <i>J. effusus</i> , <i>C. caryophylla</i> , <i>H. lanatus</i> , <i>R. fruticosus</i> and <i>A. capillaris</i> .
10	544 1507	Disturbed over Maesbury	Under <i>Fraxinus excelsior</i> and <i>Fagus sylvatica</i> with <i>Pinus sylvestris</i> nearby to west. Medium Vegetation dominated by grasses including <i>Poa trivialis</i> , <i>D. caespitosa</i> , <i>F. rubra</i> , and <i>D. glomerata</i> with <i>C. paniculata</i> near stream. <i>Rubus fruticosus</i> and <i>Viola riviniana</i> also present.
11	3545 1507	Tailings over Thrupe	Short vegetation on top of piles, dominated by grasses <i>F. rubra</i> , <i>D. glomerata</i> , and <i>A. capillaris</i> , with individual stems of <i>Phragmites australis</i> and <i>C. paniculata</i> on sides, encroaching from pool below. Other spp included <i>Ranunculus repens</i> , <i>A. millefolium</i> , <i>R. acetosa</i> , <i>G. saxatile</i> , <i>A. hirsuta</i> , <i>L. pratensis</i> , and moss spp.
12	3546 1507	Tailings over Thrupe	Medium vegetation, grasses were tussocky including <i>F. rubra</i> , <i>H. lanatus</i> and <i>D. glomerata</i> . Other spp. included <i>H. sphondylium</i> , <i>U. dioica</i> , <i>G. saxatile</i> , <i>R. acris</i> , <i>R. acetosa</i> , and <i>L. pratensis</i> .
13	3547 1507	Tailings over Ashen	Site dominated by large tussocks of <i>C. paniculata</i> on wetter, lower areas, grading out to tussocks of <i>M. caerulea</i> with a mossy understorey in the drier, raised areas. Also present were many senesced <i>H. sphondylium</i> shoots and scattered <i>Equisetum palustre</i> individuals.
14	3547 1507	Tailings over Ashen	Medium vegetation dominated by <i>Deschampsia flexuosa</i> tussocks with mossy understorey. Lichen spp. were growing on older tussocks. <i>Calluna vulgaris</i> and <i>Ulex gallii</i> also present, with <i>C. vulgaris</i> more frequent.

15	3545 1508	Disturbed over Maesbury	Medium vegetation with a cover of <i>Salix</i> spp. and blown-in litter from <i>F. sylvatica</i> . <i>Festuca rubra</i> was dominant cover with <i>R. acris</i> , <i>A. millefolium</i> , <i>Galium mollugo</i> , <i>Taraxacum</i> spp. and <i>P. lanceolata</i> .
16	3546 1508	Disturbed over Thrupe	Short to medium tussocky vegetation. Grasses included <i>H. lanatus</i> , <i>A. elatius</i> , <i>A. capillaris</i> , <i>F. rubra</i> and <i>D. flexuosa</i> with <i>Equisetum arvense</i> , <i>G. saxatile</i> and <i>H. sphondylium</i> .
17	3547 1508	Ashen	Medium vegetation dominated by <i>C. vulgaris</i> , with a dense cover of <i>D. flexuosa</i> tussocks. The areas between tussocks were damp and contained moss spp. and some <i>M. caerulea</i> . <i>Ulex gallii</i> also present and noted to be dominant where masonry was very near the surface, in poor, shallow soil.
18	3549 1508	Tailings over Ashen	Medium and short vegetation dominated by small tussocks of <i>M. caerulea</i> with <i>F. rubra</i> and <i>Agrostis</i> spp. All grasses were rooted at shallow depth. <i>Ulex europeans</i> , <i>C. vulgaris</i> and <i>Dryopteris</i> spp. around fringes of glade.
19	3544 1509	Tailings over Maesbury	Low and short dune-like vegetation on top of pile, with medium/tall vegetation around sides. Dominant grass was <i>F. rubra</i> , with some <i>A. capillaris</i> and <i>Anthoxanthum odoratum</i> . Also <i>Cerastium fontanum</i> and <i>P. lanceolata</i> , with <i>S. uniflora</i> and <i>T. polytrichus</i> in bare soil around rabbit scrapings. <i>Arrhenatherum elatius</i> , <i>Trisetum flavescens</i> and <i>D. glomerata</i> around sides.
20	3544 1509	Tailings over Maesbury	Dominated by <i>A. elatius</i> . Other grasses included <i>F. rubra</i> , <i>H. lanatus</i> , <i>A. capillaris</i> , <i>D. glomerata</i> and <i>T. flavescens</i> . In summer, other species present were <i>Galium mollugo</i> , <i>R. bulbosus</i> , <i>R. acetosa</i> , <i>Heracleum sphondylium</i> , <i>Equisetum arvense</i> , <i>L. pratensis</i> , <i>Veronica chamaedrys</i> , and moss spp.
21	3545 1509	Disturbed over Maesbury	Low vegetation on top of embankment with <i>P. australis</i> on slope down to marshy area. Low grasses including <i>F. rubra</i> , <i>A. capillaris</i> , <i>H. lanatus</i> , <i>Koeleria cristata</i> and <i>P. trivialis</i> with <i>P. lanceolata</i> , <i>R. acris</i> and <i>Galium verum</i> . <i>Holcus lanatus</i> showed high degree of chlorosis.
22	3546 1509	Ashen/ Thrupe boundary	Medium tussocky vegetation with <i>D. flexuosa</i> dominant spp. Microclimate between tussocks was damp and sheltered with moss spp. <i>Molinia caerulea</i> , <i>Luzula campestris</i> , <i>G. saxatile</i> and <i>U. gallii</i> also present.
23	3550 1509	Ashen	Cover of very tall <i>Picea abies</i> . understorey of <i>R. fruticosus</i> with <i>M. caerulea</i> tussocks, <i>Dryopteris</i> and <i>Agrostis</i> spp. and <i>Brachypodium sylvaticum</i> present as ground cover. Grass spp. and moss spp. covered fallen <i>P. abies</i> trunks.
24	3543 1510	Maesbury	Medium grassland dominated by <i>M. caerulea</i> tussocks. <i>Ulex gallii</i> , <i>R. fruticosus</i> , <i>G. saxatile</i> and <i>D. flexuosa</i> also present, although <i>D. flexuosa</i> not tussocky.
25	3544 1510	Ashen	Medium to tall vegetation dominated by large tussocks of <i>M. caerulea</i> . Some smaller tussocks of <i>D. caespitosa</i> also present.
26	3545 1510	Ashen	Medium to tall vegetation with equal cover of <i>M. caerulea</i> and <i>D. flexuosa</i> tussocks. Deep covering of new and old <i>M. caerulea</i> litter.
27	3546 1510	Tailings over Ashen	Low vegetation. Very small <i>M. caerulea</i> and <i>D. flexuosa</i> tussocks, with <i>M. caerulea</i> as scattered individual tussocks rather than complete domination by large tussocks. <i>Taraxacum</i> spp. and <i>R. acris</i> also present. <i>Silene uniflora</i> had colonised recently disturbed areas of bare soil.
28	3548 1510	Ashen	Medium vegetation dominated by <i>M. caerulea</i> and <i>J. effusus</i> . Also present were <i>C. vulgaris</i> , <i>Dryopteris</i> spp., <i>R. fruticosus</i> , <i>Potentilla erecta</i> , <i>F. rubra</i> , <i>A. capillaris</i> , <i>G. saxatile</i> , <i>T. polytrichus</i> and Moss spp.
29	3543 1511	Ashen	Medium vegetation dominated by tussocky <i>M. caerulea</i> interspersed with <i>Vaccinium myrtillus</i> . <i>Calluna vulgaris</i> , <i>U. gallii</i> and <i>Pteridium aquilinum</i> also present. Large volumes of <i>M. caerulea</i> and woody <i>V. myrtillus</i> litter present.
30	3544 1511	Ashen	Medium vegetation dominated by <i>M. caerulea</i> tussocks. <i>Calluna vulgaris</i> , <i>D. flexuosa</i> , <i>Dryopteris</i> spp., <i>L. campestris</i> , moss spp. and occasional <i>V. myrtillus</i> also present.

31	3545 1511	Ashen	Medium vegetation dominated by <i>M. caerulea</i> and <i>D. flexuosa</i> tussocks. Some old <i>M. caerulea</i> tussocks had <i>D. flexuosa</i> growing on and through them. Large volume of standing <i>M. caerulea</i> litter.
32	3546 1511	Ashen	Medium vegetation dominated by <i>M. caerulea</i> tussocks with some small <i>D. flexuosa</i> tussocks and moss spp. growing underneath. Few small stands of <i>J. effusus</i> , and in drier areas some <i>C. vulgaris</i> individuals.
33	3547 1511	Smelter waste over Thrupe	Low, stunted vegetation. <i>Festuca rubra</i> , <i>M. caerulea</i> individuals, no tussocks, <i>T. caerulescens</i> , <i>A. hirsuta</i> , <i>G. saxatile</i> , <i>R. acetosa</i> , <i>C. caryophyllea</i> , <i>P. lanceolata</i> , <i>S. uniflora</i> , <i>C. fontanum</i> , and <i>Cladonia</i> spp.
34	3548 1511	Ashen	Short vegetation under solitary tall <i>P. sylvestris</i> . Tussocky <i>F. rubra</i> and <i>D. flexuosa</i> with <i>P. erecta</i> , <i>G. saxatile</i> , <i>Cladonia</i> spp. and moss spp. <i>Galium saxatile</i> chlorosed.
35	3543 1512	Ashen	Short and medium vegetation dominated by <i>M. caerulea</i> and <i>D. flexuosa</i> tussocks. Small stands of <i>Chamerion angustifolium</i> , <i>C. vulgaris</i> and <i>U. gallii</i> . Few individuals of <i>D. glomerata</i> and new growth of <i>M. caerulea</i> with <i>P. lanceolata</i> , <i>G. saxatile</i> , <i>A. millefolium</i> and <i>V. riviniana</i> .
36	3544 1512	Ashen	Medium vegetation with equal distribution of <i>M. caerulea</i> and <i>D. flexuosa</i> tussocks, with moss spp. below. Some <i>U. gallii</i> and large volume of standing <i>M. caerulea</i> litter.
37	3545 1512	Ashen	Medium vegetation with small <i>U. gallii</i> stand. A dense mat of <i>D. flexuosa</i> , containing moss spp. and <i>G. saxatile</i> dominated area, <i>M. caerulea</i> present around edges of mat
38	3546 1512	Ashen	Medium vegetation dominated by <i>M. caerulea</i> tussocks. Some <i>D. flexuosa</i> present. <i>Ulex gallii</i> and <i>C. vulgaris</i> lining and surrounding leat.
39	3547 1512	Ashen	Medium and tall vegetation. <i>Arrhenatherum elatius</i> dominant with some <i>D. glomerata</i> and <i>M. caerulea</i> . <i>Senecio jacobaea</i> , <i>R. bulbosa</i> , <i>A. millefolium</i> , <i>Hieracium</i> spp. and <i>Equisetum sylvaticum</i> also present.
40	3548 1512	Tailings over Thrupe	Tall and low vegetation. Dominated by <i>P. australis</i> and <i>Dryopteris</i> spp. in creeks. Some <i>D. flexuosus</i> and <i>R. acetosa</i> on raised ground above creeks
41	3546 1512	Tailings over Ashen	Medium and tall vegetation dominated by <i>A. elatius</i> . In summer species present included <i>R. acetosa</i> , <i>Heracleum sphondylium</i> , moss spp., <i>P. lanceolata</i> , <i>L. Pratensis</i> , <i>A. oderatum</i> , <i>C. fontanum</i> , <i>Carex hirta</i> , <i>F. rubra</i> , <i>V. chamaedrys</i> , <i>R. bulbosus</i> , <i>E. arvense</i> , <i>H. lanatus</i> , <i>Cardamine hirsuta</i> , <i>S. jacobaea</i> , <i>A. millefolium</i> , <i>D. glomerata</i> , and <i>M. caerulea</i> .
42	3542 1513	Ashen	Low vegetation, grazed pasture including <i>Lolium perenne</i> , <i>Cynosurus cristatus</i> , <i>A. capillaris</i> , <i>Poa annua</i> , <i>T. repens</i> , with some <i>Cirsium arvense</i> .
43	3545 1513	Ashen	Medium and short vegetation but flattened by wind. <i>Molinia caerulea</i> tussocks dominated with some areas of short <i>F. rubra</i> and <i>Agrostis</i> spp. Some stands of <i>P. aquilinum</i> and <i>U. gallii</i> with <i>J. effusus</i> in flushed area.
44	3546 1513	Ashen	Medium vegetation dominated by large <i>M. caerulea</i> tussocks. Some moss spp. present in undergrowth, large volumes of <i>M. caerulea</i> litter. Extensive stand of <i>C. vulgaris</i> on hillside above sampling site.
45	3547 1513	Disturbed over Thrupe	Short vegetation in a large, regular circular patch ringed with <i>M. caerulea</i> tussocks and a few individual tussocks of <i>D. caespitosa</i> . <i>Deschampsia flexuosa</i> dominated short vegetation, with isolated individuals of <i>H. lanatus</i> .
46	3548 1513	Tailings over Thrupe	Low stunted vegetation. When surveyed in summer included <i>Mimuartia verna</i> , <i>Linum catharticum</i> , <i>Botrychium lunaria</i> , <i>Lotus corniculatus</i> , <i>Euphrasia officianalis</i> , <i>S. uniflora</i> , <i>Festuca ovina</i> , <i>F. rubra</i> , <i>V. chamaedrys</i> , <i>C. semidecandrum</i> , <i>P. erecta</i> and <i>Cladonia</i> and moss spp.

47	3549 1512	Nordrach	Short vegetation in clearing surrounded by <i>P. abies</i> . Small hummocks of <i>F. rubra</i> and some <i>A. stolonifera</i> showing chlorosis. <i>Thymus polytrichus</i> and moss spp. Some very small, short <i>C. vulgaris</i> and <i>U. gallii</i> . <i>Rubus fruticosus</i> at margins.
48	3547 1513	Tailings over Thrupe	Low stunted vegetation including <i>Festuca rubra</i> , <i>F. ovina</i> , <i>Polygala vulgaris</i> , <i>A. oderatum</i> <i>P. erecta</i> , <i>C. caryophylla</i> , <i>R. acetosa</i> , <i>M. verna</i> , <i>S. vulgaris</i> , <i>R. acris</i> , <i>Trifolium pratense</i> , <i>M. caerulea</i> , <i>D. flexuosa</i> , <i>C. vulgaris</i> , <i>H. lanatus</i> and <i>Cladonia</i> spp.
49	3547 1513	Disturbed over Thrupe	No vegetation as buddle pit was freshly excavated by archaeologists.
50	3542 1514	Ashen	Low vegetation, grazed pasture including <i>L. perenne</i> , <i>C. cristatus</i> , <i>A. capillaris</i> , <i>P. annua</i> , <i>T. repens</i> , with some <i>C. arvense</i> .
51	3545 1514	Ashen	Medium vegetation. <i>Molinia caerulea</i> tussocks with <i>D. flexuosa</i> , <i>P. aquilinum</i> and <i>U. gallii</i> . Large volume of <i>Molinia</i> litter.
52	3546 1514	Ashen	Medium vegetation. Dominated by very large, deep tussocks of <i>M. caerulea</i> interspersed with <i>D. flexuosa</i> tussocks. Some <i>U. gallii</i> .
53	3547 1514	Disturbed over Thrupe	Medium vegetation dominated by <i>M. caerulea</i> tussocks with a mossy understorey. <i>Calluna vulgaris</i> was present on higher, drier ground, with some <i>D. flexuosa</i> . <i>Carex paniculata</i> in channels with constant running water.
54	3548 1514	Tailings over Thrupe	Low vegetation, damaged by floodwater. Dominated by <i>F. rubra</i> with <i>F. ovina</i> and moss spp. In previous growing season, species included <i>M. verna</i> , <i>P. vulgaris</i> , <i>S. uniflora</i> , <i>R. acris</i> , <i>T. polytrichus</i> and <i>L. corniculatus</i> .
55	3550 1514	Nordrach	Short vegetation. Woodland species included <i>P. abies</i> and <i>P. sylvestris</i> . <i>Festuca rubra</i> and <i>A. capillaris</i> dominated grasses, both species showed marked degree of chlorosis. <i>Rubus fruticosus</i> and <i>C. angustifolium</i> on wood margin.
56	3544 1515	Ashen	Low vegetation, grazed pasture including <i>L. perenne</i> , <i>C. cristatus</i> , <i>A. capillaris</i> , <i>P. annua</i> , <i>T. repens</i> , with some <i>C. arvense</i> .
57	3545 1515	Ashen	Medium vegetation. Tussocks of <i>M. caerulea</i> , <i>D. flexuosa</i> and <i>F. rubra</i> , with moss spp. below tussocks. Some <i>U. gallii</i> and <i>Dryopteris</i> spp.
58	3546 1515	Ashen	Medium vegetation below <i>Salix</i> spp. Dominated by <i>M. caerulea</i> with <i>Juncus articulatus</i> , <i>J. effusus</i> , <i>L. campestris</i> and <i>P. erecta</i> .
59	3547 1515	Disturbed over Thrupe	Bare soil, heavily trampled and washed by pool water. Sometimes inundated.
60	3544 1516	Ashen	Medium and short vegetation. <i>Calluna vulgaris</i> , <i>U. gallii</i> , <i>C. angustifolium</i> , <i>Digitalis purpurea</i> and <i>P. aquilinum</i> with some small to medium tussocks of <i>M. caerulea</i> . Short grasses included <i>F. rubra</i> , <i>D. flexuosa</i> and <i>Agrostis</i> spp. with <i>P. erecta</i> , <i>G. saxatile</i> , <i>P. lupulina</i> and a stand of <i>Hyacinthoides non-scripta</i> .
61	3545 1516	Thrupe	Medium vegetation dominated by tussocks of <i>D. flexuosa</i> with some <i>F. rubra</i> . Some <i>M. caerulea</i> tussocks with <i>P. erecta</i> , and <i>G. saxatile</i> . <i>Digitalis purpurea</i> and <i>Dryopteris</i> spp. also present.
62	3546 1516	Thrupe	Medium vegetation including some <i>M. caerulea</i> tussocks, <i>J. effusus</i> , <i>J. articulatus</i> , <i>L. campestris</i> , <i>Eriophorum angustifolium</i> , <i>E. palustre</i> , <i>Agrostis canina</i> and <i>Sphagnum</i> spp.
63	3547 1516	Ashen	Medium vegetation dominated by <i>M. caerulea</i> tussocks and litter in runnels between tussocks. Isolated stands of <i>C. vulgaris</i> with some <i>P. erecta</i> .
64	3549 1516	Nordrach	Medium and low vegetation under open coniferous plantation with some <i>F. sylvatica</i> . <i>Pteridium aquilinum</i> , <i>R. fruticosus</i> , <i>F. rubra</i> and <i>G. saxatile</i> also present.
65	3544 1517	Ashen/ Thrupe boundary	Shrubs with medium and low vegetation, possible woodland relict. Shrubs included <i>Salix</i> spp., <i>Crataegus monogyna</i> , <i>Ilex aquifolium</i> and <i>R. fruticosus</i> . Also present were <i>P. aquilinum</i> , <i>C. angustifolium</i> , <i>C. vulgaris</i> , <i>D. purpurea</i> , tussocks of <i>M. caerulea</i> , <i>H. non-scriptus</i> , <i>P. erecta</i> and <i>F. rubra</i> .

66	3545 1517	Ashen	Medium and low vegetation in cleared patch surrounded by <i>M. caerulea</i> tussocks, some bare soil. Very sparse <i>U. gallii</i> , small stands of <i>C. vulgaris</i> and <i>Erica cinerea</i> , <i>T. polytrichus</i> and <i>P. vulgaris</i> (still flowering), small patches of <i>Cladonia</i> and moss spp.
67	3546 1517	Ashen	Medium vegetation dominated by <i>M. caerulea</i> tussocks. Some <i>P. aquilinum</i> , with <i>F. rubra</i> , <i>U. gallii</i> and moss spp.
68	3547 1517	Ashen	Recent fire, new growth of low vegetation included <i>M. caerulea</i> , <i>Ulex</i> spp., <i>Festuca</i> spp., <i>T. polytrichus</i> and <i>P. aquilinum</i> . Before fire, area was mature <i>M. caerulea</i> , <i>P. aquilinum</i> and <i>U. gallii</i> community.
69	3549 1517	Disturbed over Nordrach	Some fungi on needle litter, no other vegetation present. Surrounding conifers were very black in colour and appeared stunted and unhealthy.
70	35455 15181	Tailings over Thrupe	Area mostly bare. Colonisation by very few lichen spp., one very small, stunted patch of <i>M. caerulea</i> , and several small, stunted <i>D. flexuosa</i> individuals colonising from the outside edge. There was a <i>D. flexuosa</i> stand on higher tailings area to west.
71	3545 1518	Thrupe	Medium vegetation dominated by large <i>M. caerulea</i> tussocks with some <i>D. caespitosa</i> . Some <i>M. caerulea</i> tussocks were old and rotting, with moss spp., <i>P. erecta</i> and <i>T. polytrichus</i> invading tops. <i>Eriophorum angustifolium</i> and <i>J. effusus</i> between tussocks.
72	3546 1518	Tailings over Thrupe	Low and medium vegetation on flat top of sampling site, with medium vegetation surrounding raised area. Some <i>M. caerulea</i> individuals, <i>R. acetosa</i> , <i>D. flexuosa</i> and <i>A. capillaris</i> on top, with <i>M. caerulea</i> tussocks, <i>J. effusus</i> and <i>E. angustifolium</i> around sides.
73	3548 1518	Nordrach	In <i>F. sylvatica</i> plantation. No apparent ground cover, but deep <i>F. sylvaticum</i> litter standing to 70 mm. Some moss spp. and lichen spp. on exposed rock.
74	3546 1519	Nordrach	Lush short vegetation, with <i>F. rubra</i> tussocks, <i>A. capillaris</i> , <i>H. lanatus</i> , <i>V. riviniana</i> , <i>G. saxatile</i> , <i>R. acetosa</i> , <i>L. pratensis</i> , very small <i>C. monogyna</i> individual and cone litter from <i>P. sylvestris</i> .
75	3550 1519	Nordrach	No apparent ground vegetation under a mixed coniferous/ <i>F. sylvatica</i> cover. Deep layer of twigs and <i>F. sylvatica</i> litter, some juvenile <i>P. abies</i> in understorey.
76	3549 1520	Nordrach	Short vegetation, very lush. <i>Festuca rubra</i> in small tussocks was dominant species, with some <i>A. capillaris</i> and areas of lush moss spp. Some <i>R. fruticosus</i> at edges of clearing.
77	3547 1521	Nordrach	Dense, mature coniferous woodland. Understorey consisted of one <i>I. aquilinum</i> individual (1 m), with occasional <i>Dryopteris</i> spp. Some moss spp. growing on bare ground and fallen trunks.

#### 4.6.3 All Soil Data set : cartographic representation of data

The soils with higher pH values were mainly clustered around the St. Cuthbert's site and in areas of tailings on the Reserve at both surface and depth. The soils with the lowest pH values at both depths were generally found in areas of the North Hill and Stockhill Plantation, where soils of the Ashen Series were present (Figures 4.7, 4.8 and 2.2 ).

Pages 143 - 164 have been removed from this digitized thesis for copyright reasons. The pages show figures of the data layered on to OS maps.

Surface soils with the greatest percentage Loss-on-Ignition were generally found where soils of the Ashen and Thrupe Series were present (Figures 4.9 and 2.2). Soils with the lowest percentage Loss-on-Ignition were usually found clustered around areas of tailings, and in the area of Stockhill Plantation where soil of the Nordrach Series was present. At depth, the distribution of percentage Loss-on-Ignition generally followed the same pattern in the soils as for Loss-on-Ignition at 0-200 mm (Figure 4.10). At both surface and depth, the greatest Pb concentrations were in the soils of the St. Cuthbert's site, and clustered around areas of tailings and land disturbed by beneficiation in the Reserve (Figures 4.11 and 4.12). The greatest RTE values for Pb were in the soils of the eastern slope of North Hill (Figure 4.16). The lowest RTE values were in the St. Cuthbert's site, around the areas of tailings in the Reserve, and in the soils of the Nordrach Series in Stockhill Plantation (Figures 4.13 and 2.2).

The distribution of soil Zn, Cd and Cu at surface and depth generally followed that for Pb, where the greatest concentrations were in the soils of the St. Cuthbert's site and clustered around tailings and land disturbed by beneficiation in the Reserve (Figures 4.11, 4.12, 4.14, 4.15, 4.17, 4.18, 4.20 and 4.21). The trend was particularly marked in the distribution of Cd (Figures 4.17 and 4.18). However, the distribution trends of RTE values for Zn and Cd were different to that for Pb (Figures 4.13, 4.16, 4.18). The greatest RTE values for Zn were shown to be in the soils of St. Cuthbert's, and just to the north of St. Cuthbert's, in the Reserve (Figure 4.16). The lower RTE values for Zn, like Pb, were clustered around areas of tailings at St. Cuthbert's and the Reserve. For Cd, there was a marked trend for



the greater RTE values to follow the course of the footpath that runs south through the Reserve to St. Cuthbert's. The lowest RTE values were widely distributed throughout the study area (Figure 4.18). The distribution of the RTE values for Cu generally followed that of Pb (Figures 4.13 and 4.22). The greatest RTE values for Cu were on North Hill, while the lowest RTE values were clustered around areas of tailings and soil disturbed by beneficiation.

One aspect of the distribution of soil Fe was similar for that of the other trace metals. At both depths, the greatest concentrations were in the soils of St. Cuthbert's and areas of tailings and soil disturbed by beneficiation in the Reserve (Figures 4.23 and 4.24). However, the distribution of Fe also had characteristics distinct from those of the other trace metals. The soils containing the greater concentrations of Fe were generally more widespread throughout the study area, including in the soils of the Nordrach Series in the Stockhill Plantation (Figures 4.23, 4.24 and 2.2). Another distinctive feature of the distribution was that in the majority of the soils of the study area there was no relative topsoil enrichment by Fe ( $RTE < 1.0$ ) (Figure 4.25). The two greatest RTE values for Fe were in the soil around the Minery pool on the Reserve.

The distribution pattern of Mn at both depths was similar to that of Fe, with the greatest concentration occurring in the soils of St. Cuthbert's, the areas of tailings and soil disturbed by beneficiation in the Reserve and in the soils of the Nordrach Series in the Stockhill Plantation (Figures 4.26, 4.27 and 2.2). With the exception of the soils in the agricultural land above the Reserve on North Hill, the lowest surface concentrations of Mn were in the soils of the Ashen Series. The general

distribution of RTE values of <1.0 throughout the study area, indicated that many of the soils were enriched with Mn at depth (Figure 4.28). The greatest RTE values for Mn occurred on the northeastern slope of North Hill in the Reserve.

#### 4.6.4 All Soil Data set: statistical analysis

The only significant difference between each soil parameter at surface and depth was for Loss-on-Ignition, where  $p=0.001$  (Table 4.24).

Table 4.24. Two-sample Mann-Whitney tests for soil parameters at 0-200 mm *versus* 200-400 mm ( $n=77$ ), where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter ( $n=77$ )	Mann-Whitney p-value	$H_0$ : $\eta_1 = \eta_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	0.3337	Accepted
L-o-I (0-200 mm) v L-o-I (2000-400 mm)	0.0000	Rejected
Pb (0-200 mm) v Pb (2000-400 mm)	0.3559	Accepted
Zn (0-200 mm) v Zn (200-400 mm)	0.6117	Accepted
Cd (0-200 mm) v Cd (200-400 mm)	0.9856	Accepted
Cu (0-200 mm) v Cu (200-400 mm)	0.6751	Accepted
Fe (0-200 mm) v Fe (200-400 mm)	0.1127	Accepted
Mn (0-200 mm) v Mn (200-400 mm)	0.5073	Accepted

Although there was only 0.9 % difference in the minimum values for Loss-on-Ignition at surface and depth, values at the 1<sup>st</sup> quartile, median, 3<sup>rd</sup> quartile and

maximum were increasingly greater for surface Loss-on-Ignition than for Loss-on-Ignition at depth (Table 4.21).

All trace metal and pH data at 0-200 mm and 200-400 mm were positively correlated with each other at the  $p=0.001$  level (Tables 4.25 and 4.26). There was a significant positive correlation at  $p=0.001$  for each parameter between its value at 0-200 mm and its value at 200-400 mm. Loss-on-Ignition at 0-200 mm was negatively correlated with all trace metal and pH data at 0-200 mm and 200-400 mm at the  $p\leq 0.05$  level. With the exception of Loss-on-Ignition at 0-200 mm, there were no significant correlations between Loss-on-Ignition at 200-400 mm and any other soil parameter at 0-200 mm or 200-400 mm.

All stacked pH and trace metal data (0-400 mm) were positively correlated with each other at the  $p=0.001$  level (Table 4.27). Loss-on-Ignition was negatively correlated with pH, Zn, Fe and Mn at the  $p\leq 0.05$  level, but not significantly correlated with Pb, Cd or Cu (Table 4.27).

Table 4.25. Levels of significance for all Log<sub>10</sub> transformed soil parameter data at 0-200 mm and 200-400 mm for the All Soil Data set (n=77).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
pH (200-400 mm)	***														
L-o-I (0-200 mm)	** -	** -													
L-o-I (200-400 mm)	N.S.	N.S.	***												
Pb (0-200 mm)	***	***	* -	N.S.											
Pb (200-400 mm)	***	***	* -	N.S.	***										
Zn (0-200 mm)	***	***	** -	N.S.	***	***									
Zn (200-400 mm)	***	***	** -	N.S.	***	***	***								
Cd (0-200 mm)	***	***	N.S.	N.S.	***	***	***	***							
Cd (200-400 mm)	***	***	N.S.	N.S.	***	***	***	***	***						
Cu (0-200 mm)	***	***	N.S.	N.S.	***	***	***	***	***	***					
Cu (200-400 mm)	***	***	N.S.	N.S.	***	***	***	***	***	***	***				
Fe (0-200 mm)	***	***	** -	N.S.	***	***	***	***	***	***	***	***			
Fe (200-400 mm)	***	***	*** -	N.S.	***	***	***	***	***	***	***	***	***		
Mn (0-200 mm)	***	***	** -	N.S.	***	***	***	***	***	***	***	***	***	***	
Mn (200-400 mm)	***	***	*** -	N.S.	***	***	***	***	***	***	***	***	***	***	***

\*\*\* p = 0.001    \*\* p = 0.01    \* p = 0.05    N.S. = Not Significant    - indicates a negative correlation

Table 4.26. Pearson values for significant correlations ( $p=0.001$ ,  $0.01$  and  $0.05$ ) between  $\text{Log}_{10}$  transformed soil parameter data at 0-200 mm and 200-400 mm for the All Soil Data set ( $n=77$ ).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
pH (200-400 mm)	0.968														
L-o-I (0-200 mm)	-0.324	-0.329													
L-o-I (200-400 mm)			0.765												
Pb (0-200 mm)	0.792	0.816	-0.248												
Pb (200-400 mm)	0.780		-0.281		0.977										
Zn (0-200 mm)	0.871	0.894	-0.364		0.918	0.921									
Zn (200-400 mm)	0.832	0.870	-0.385		0.908	0.931	0.969								
Cd (0-200 mm)	0.869	0.858			0.721	0.715	0.803	0.793							
Cd (200-400 mm)	0.827	0.821			0.757	0.777	0.809	0.823	0.910						
Cu (0-200 mm)	0.792	0.800			0.819	0.840	0.870	0.843	0.697	0.736					
Cu (200-400 mm)	0.788	0.797			0.804	0.840	0.873	0.859	0.705	0.753	0.962				
Fe (0-200 mm)	0.693	0.724	-0.375		0.804	0.832	0.881	0.852	0.608	0.649	0.783	0.803			
Fe (200-400 mm)	0.616	0.640	-0.433		0.666	0.748	0.781	0.803	0.595	0.643	0.661	0.749	0.835		
Mn (0-200 mm)	0.780	0.806	-0.370		0.778	0.812	0.892	0.864	0.631	0.677	0.821	0.837	0.913	0.845	
Mn (200-400 mm)	0.679	0.713	-0.429		0.697	0.764	0.831	0.832	0.606	0.666	0.738	0.791	0.874	0.919	0.938

- indicates a negative correlation

Table 4.27. Pearson correlation values (r-values) and degrees of significance at the  $p=0.001$  and  $0.05$  levels for  $\text{Log}_{10}$  transformed data for all soil parameters at 0-400 mm ( $n=154$ ).

	pH (0-400 mm)	L-o-I (0-400mm)	Pb (0-400 mm)	Zn (0-400 mm)	Cd (0-400 mm)	Cu (0-400 mm)	Fe (0-400 mm)
L-o-I (0-400 mm)	-0.192 *						
Pb (0-400 mm)	0.794 ***	-0.039 N.S.					
Zn (0-400 mm)	0.870 ***	-0.198 *	0.919 ***				
Cd (0-400 mm)	0.844 ***	-0.030 N.S.	0.474 ***	0.813 ***			
Cu (0-400 mm)	0.790 ***	-0.006 N.S.	0.830 ***	0.862 ***	0.725 ***		
Fe (0-400 mm)	0.669 ***	-0.257 **	0.755 ***	0.840 ***	0.620 ***	0.753 ***	
Mn (0-400 mm)	0.748 ***	-0.523 **	0.760 ***	0.863 ***	0.647 ***	0.800 ***	0.914 ***

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     N.S. = Not Significant  
 - Indicates a negative correlation

#### 4.6.5 The Priddy Mineries Reserve Data set: descriptive statistics

The descriptive statistics for this data set ( $n=51$ ) are shown in Table 4.28. Surface reaction ranged from pH 3.0 to pH 7.3 at 0-200 mm, and from pH 3.0 to pH 7.6 at depth. The median value of pH 4.0 at 0-200 mm and pH 4.1 at 200-400 mm were less than the median values of pH for the All Soil Data set at pH 4.5 for 0-200 mm and pH 5.0 at 200-400 mm (Table 4.21). Surface Loss-on-Ignition ranged from 3.9% to 53.4%, and from 3% to 34.8% at depth. Median values of 11.2% at 0-200 mm and 7.9% at 200-400 mm were comparable with the median values of Loss-on-Ignition for All Soil Data at 0-200 mm and 200-400 mm (Table 4.21).

Table 4.28 Descriptive statistics at 0-200 mm and 200-400 mm for the Priddy Mineries Reserve Data set (n=51).

<b>Parameter</b>	<b>Arithmetic Mean</b>	<b>St. Dev.</b>	<b>Minimum</b>	<b>1st Quartile</b>	<b>Median</b>	<b>3rd Quartile</b>	<b>Maximum</b>
pH (0-200 mm)	4.61	1.38	3.00	3.40	4.00	6.20	7.30
pH (200-400 mm)	4.76	1.42	3.00	3.60	4.10	6.30	7.60
L-o-I % (0-200 mm)	13.88	9.94	3.90	8.10	11.20	14.70	53.40
L-o-I % (200-400 mm)	8.87	4.76	3.00	6.50	7.90	10.00	34.80
Pb $\mu\text{g g}^{-1}$ (0-200 mm)	20 536.00	25 518.00	262.00	1 351.00	3 454.00	40 869.00	76 977.00
Pb $\mu\text{g g}^{-1}$ (200-400 mm)	21 038.00	28 057.00	180.00	705.00	2 367.00	44 300.00	89 647.00
Zn $\mu\text{g g}^{-1}$ (0-200 mm)	1 813.00	2 666.00	13.00	23.00	90.00	4 006.00	10 349.00
Zn $\mu\text{g g}^{-1}$ (200-400 mm)	1 880.00	2 605.00	14.00	31.00	94.00	4 150.00	8 089.00
Cd $\mu\text{g g}^{-1}$ (0-200 mm)	2.55	2.70	1.00	1.00	1.00	4.00	12.00
Cd $\mu\text{g g}^{-1}$ (200-400 mm)	2.41	2.40	1.00	1.00	1.00	5.00	10.00
Cu $\mu\text{g g}^{-1}$ (0-200 mm)	31.92	38.62	1.00	4.00	10.00	58.00	165.00
Cu $\mu\text{g g}^{-1}$ (200-400 mm)	34.65	45.90	1.00	3.00	9.00	57.00	166.00
Fe $\mu\text{g g}^{-1}$ (0-200 mm)	18 647.00	17 457.00	759.00	3 881.00	9 588.00	39 864.00	53 580.00
Fe $\mu\text{g g}^{-1}$ (200-400 mm)	23 127.00	19 185.00	751.00	7 777.00	12 872.00	45 593.00	59 851.00
Mn $\mu\text{g g}^{-1}$ (0-200 mm)	645.00	901.00	4.00	16.00	58.00	1 272.00	3 769.00
Mn $\mu\text{g g}^{-1}$ (200-400 mm)	698.00	923.00	3.00	33.00	143.00	1 177.00	3 372.00

The concentration of Pb in the surface soils of the Reserve was shown to range from 262 to 76 977  $\mu\text{g g}^{-1}$  at 0-200 mm, and from 180 to 89 674  $\mu\text{g g}^{-1}$  at depth. Zinc in surface soil ranged from 13 to 10 349  $\mu\text{g g}^{-1}$  and from 14 to 8 089  $\mu\text{g g}^{-1}$  at depth. Soil Cd ranged from 1 to 12  $\mu\text{g g}^{-1}$  at 0-200 mm and from 1 to 10  $\mu\text{g g}^{-1}$  at 200-400 mm. The concentration of Cu in the surface soils of the Reserve ranged from 1 to 165  $\mu\text{g g}^{-1}$ , and from 1 to 166  $\mu\text{g g}^{-1}$  at depth. Iron was present in concentrations ranging from 759 to 53 580  $\mu\text{g g}^{-1}$  and from 751 to 59 851  $\mu\text{g g}^{-1}$  at surface and depth respectively. Manganese in the surface soils ranged from 4 to 3 769  $\mu\text{g g}^{-1}$  and from 3 to 3 372  $\mu\text{g g}^{-1}$  depth (Table 2.8). As for the All Soil Data set, the arithmetic mean concentration value for each trace metal at surface and depth was greater than for its median value, which was indicative of the skewed nature of this data. With the exception of Cd, the median concentration value of each trace metal at surface and depth in the Reserve was lower than its corresponding median concentration value for the All Soil Data set (Table 4.21).

#### **4.6.6 The Priddy Mineries Reserve Data set: statistical analysis**

As with the All Soil Data set, the only significant difference between soil parameters at 0-200 mm and 200-400 mm was between percentage Loss-on-Ignition, which was at the  $p=0.01$  level (Table 4.29).



Table 4.29. Two-Sample Mann-Whitney tests for all soil parameters at 0-200 mm *versus* 200-400 mm (n=51), where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter (n=77)	Mann-Whitney p-value	$H_0$ : $\eta_1 = \eta_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	0.4297	Accepted
L-o-I (0-200 mm) v L-o-I (2000-400 mm)	0.0030	Rejected
Pb (0-200 mm) v Pb (2000-400 mm)	0.2753	Accepted
Zn (0-200 mm) v Zn (200-400 mm)	0.5536	Accepted
Cd (0-200 mm) v Cd (200-400 mm)	0.8278	Accepted
Cu (0-200 mm) v Cu (200-400 mm)	0.6855	Accepted
Fe (0-200 mm) v Fe (200-400 mm)	0.0795	Accepted
Mn (0-200 mm) v Mn (200-400 mm)	0.3090	Accepted

The pattern of positive and negative correlations for soil parameters at 0-200 mm and 200-400 mm in the Reserve Data set was similar to that for the All Soil Data (Tables 4.25, 4.26, 4.30 and 4.31). There were, however, differences between r-values for the same parameter relationships in each data set (Table 4.26 and 4.31). For the Reserve Data set, all trace metal and pH data at surface and depth were positively correlated with each other at the  $p=0.001$  level. There was a significant positive correlation at  $p=0.001$  for each parameter between its value at 0-200 mm and its value at 200-400 mm (Tables 4.30 and 4.31).

Table 4.30. Significant correlations ( $p=0.001$ ,  $0.01$  and  $0.05$ ) between  $\text{Log}_{10}$  transformed data for soil parameters at 0-200 mm and 200-400 mm for the Priddy Mineries Reserve Data set ( $n=51$ ).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
pH (200-400 mm)	***														
L-o-I (0-200 mm)	**_	**_													
L-o-I (200-400 mm)	N.S.	N.S.	***_												
Pb (0-200 mm)	***	***	*_	N.S.											
Pb (200-400 mm)	***	***	*_	N.S.	***										
Zn (0-200 mm)	***	***	**_	N.S.	***	***									
Zn (200-400 mm)	***	***	**_	N.S.	***	***	***								
Cd (0-200 mm)	***	***	N.S.	N.S.	***	***	***	***							
Cd (200-400 mm)	***	***	N.S.	N.S.	***	***	***	***	***						
Cu (0-200 mm)	***	***	N.S.	N.S.	***	***	***	***	***	***					
Cu (200-400 mm)	***	***	N.S.	N.S.	***	***	***	***	***	***	***				
Fe (0-200 mm)	***	***	**_	N.S.	***	***	***	***	***	***	***	***			
Fe (200-400 mm)	***	***	***_	N.S.	***	***	***	***	***	***	***	***	***		
Mn (0-200 mm)	***	***	**_	N.S.	***	***	***	***	***	***	***	***	***	***	
Mn (200-400 mm)	***	***	**_	N.S.	***	***	***	***	***	***	***	***	***	***	***

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     N.S. = Not Significant    - indicates a negative correlation

Table 4.31. Pearson values for significant correlations ( $p=0.001, 0.01$  and  $0.05$ ) between  $\text{Log}_{10}$  transformed data for soil parameters at 0-200 mm and 200-400 mm for the Priddy Mineries Reserve Data set ( $n=51$ ).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
PH (200-400 mm)	0.977														
L-o-I (0-200 mm)	-0.372	-0.370													
L-o-I (200-400 mm)			0.785												
Pb (0-200 mm)	0.858	0.867	-0.292												
Pb (200-400 mm)	0.851	0.867	-0.326		0.984										
Zn (0-200 mm)	0.937	0.939	-0.367		0.926	0.932									
Zn (200-400 mm)	0.899	0.922	-0.393		0.908	0.930	0.966								
Cd (0-200 mm)	0.898	0.990			0.740	0.736	0.844	0.820							
Cd (200-400 mm)	0.878	0.865			0.778	0.788	0.848	0.847	0.909						
Cu (0-200 mm)	0.831	0.850			0.899	0.894	0.920	0.844	0.763	0.798					
Cu (200-400 mm)	0.835	0.850			0.877	0.886	0.924	0.896	0.768	0.810	0.960				
Fe (0-200 mm)	0.758	0.757	-0.360		0.831	0.848	0.877	0.843	0.678	0.700	0.833	0.853			
Fe (200-400 mm)	0.652	0.655	-0.434		0.688	0.759	0.778	0.801	0.663	0.690	0.650	0.745	0.803		
Mn (0-200 mm)	0.856	0.857	-0.376		0.877	0.893	0.954	0.935	0.770	0.801	0.890	0.915	0.920	0.838	
Mn (200-400 mm)	0.741	0.758	-0.428		0.751	0.801	0.861	0.867	0.721	0.756	0.754	0.821	0.853	0.916	0.931

- indicates a negative correlation

There was a significant positive correlation at the  $p=0.001$  level between Loss-on-Ignition at 0-200 mm and Loss-on-Ignition at 200-400 mm, but Loss-on-Ignition at 0-200 mm was negatively correlated with all trace metal and pH data at 0-200 mm and 200-400 mm at the  $p\leq 0.05$  level. With the exception of Loss-on-Ignition at 0-200 mm, there were no significant correlations between Loss-on-Ignition at 200-400 mm and any other soil parameter at 0-200 mm or 200-400 mm.

Table 4.32. Pearson correlation values (r-values) and degrees of significance at the  $p=0.001$  and 0.05 levels for  $\text{Log}_{10}$  transformed data for all soil parameters at 0-400 mm ( $n=102$ ).

	pH (0-400 mm)	L-o-I (0-400mm)	Pb (0-400 mm)	Zn (0-400 mm)	Cd (0-400 mm)	Cu (0-400 mm)	Fe (0-400 mm)
L-o-I (0-400 mm)	-0.233 *						
Pb (0-400 mm)	0.852 ***	-0.080 N.S					
Zn (0-400 mm)	0.929 ***	-0.214 *	0.919 ***				
Cd (0-400 mm)	0.879 ***	-0.069 N.S.	0.761 ***	0.845 ***			
Cu (0-400 mm)	0.837 ***	-0.013 N.S.	0.891 ***	0.904 ***	0.786 ***		
Fe (0-400 mm)	0.707 ***	-0.262 **	0.768 ***	0.836 ***	0.676 ***	0.773 ***	
Mn (0-400 mm)	0.808 ***	-0.276 **	0.821 ***	0.911 ***	0.760 ***	0.846 ***	0.917 ***

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     N.S. = Not Significant  
 - indicates a negative correlation

The pattern of correlations between the stacked soil parameter data (0-400 mm) from the Reserve was similar to that shown for the stacked soil parameter data in the All Soil Data set (Tables 4.27 and 4.32). All stacked pH and trace metal data were positively correlated with each other at the  $p=0.001$  level (Table 4.23). Loss-on-Ignition was negatively correlated with pH, Zn, Fe and Mn at 0-400 mm at the  $p\leq 0.05$  level, but not significantly correlated with Pb, Cd or Cu at 0-400 mm.

#### **4.6.7 The St. Cuthbert's Data set: descriptive statistics**

A summary of the descriptive statistics for this data set ( $n=11$ ) in Table 4.33 showed that surface soil reaction ranged from pH 4.8 to pH 7.3, and from pH 5.0 to pH 7.5 at depth. The median values of pH 6.9 at 0-200 mm and pH 6.8 at 200-400 mm were greater than the median values of pH 4.5 and pH 5.0 at surface and depth respectively for the All Soil Data set (Table 4.21). In the St. Cuthbert's Data set, surface Loss-on-Ignition ranged from 6% to 26.3% and from 4.3% to 17.5% at depth. The median surface Loss-on-Ignition of 11.8% was comparable with the median value of 11.3% for the surface soil in the All Soil Data set (Table 4.21). At 9.2%, the median Loss-on-Ignition for the soils at depth at St. Cuthbert's was greater than that for the All Soil Data set at 8.1%.

The Pb concentration in the surface soil of the St. Cuthbert's was shown to range from 4 502 to 138 800  $\mu\text{g g}^{-1}$ , and from 1 803 to 171 688  $\mu\text{g g}^{-1}$  at depth Table 4.33). Soil Zn concentration ranged from 348 to 6 089  $\mu\text{g g}^{-1}$  in the surface soils, and from 345 to 7 593  $\mu\text{g g}^{-1}$  at depth.

Table 4.33. Descriptive statistics at 0-200 mm and 200-400 mm for the St. Cuthbert's Data set (n=11).

<b>Parameter</b>	<b>Arithmetic Mean</b>	<b>St. Dev.</b>	<b>Minimum</b>	<b>1st Quartile</b>	<b>Median</b>	<b>3rd Quartile</b>	<b>Maximum</b>
pH (0-200 mm)	6.56	0.87	4.80	6.40	6.90	7.10	7.30
pH (200-400 mm)	6.78	0.73	5.00	6.40	6.80	7.40	7.50
L-o-I % (0-200 mm)	12.13	5.66	6.00	7.90	11.80	13.30	26.30
L-o-I % (200-400 mm)	9.68	4.23	4.30	6.20	9.20	11.20	17.50
Pb $\mu\text{g g}^{-1}$ (0-200 mm)	52 111.00	38 241.00	4 502.00	21 716.00	52 382.00	72 728.00	138 800.00
Pb $\mu\text{g g}^{-1}$ (200-400 mm)	53 228.00	47 418.00	1 803.00	15 393.00	63 745.00	65 411.00	171 688.00
Zn $\mu\text{g g}^{-1}$ (0-200 mm)	3 621.00	1 849.00	348.00	1 629.00	4 255.00	5 109.00	6 089.00
Zn $\mu\text{g g}^{-1}$ (200-400 mm)	4 027.00	2 678.00	345.00	1 232.00	5 245.00	5 917.00	7 593.00
Cd $\mu\text{g g}^{-1}$ (0-200 mm)	5.09	3.02	1.00	1.00	6.00	8.00	8.00
Cd $\mu\text{g g}^{-1}$ (200-400 mm)	5.64	3.70	1.00	1.00	6.00	8.00	11.00
Cu $\mu\text{g g}^{-1}$ (0-200 mm)	64.90	47.10	17.00	32.00	50.00	84.00	182.00
Cu $\mu\text{g g}^{-1}$ (200-400 mm)	66.50	55.80	12.00	25.00	55.00	83.00	206.00
Fe $\mu\text{g g}^{-1}$ (0-200 mm)	39 274.00	12 127.00	16 665.00	26 223.00	44 547.00	44 962.00	59 753.00
Fe $\mu\text{g g}^{-1}$ (200-400 mm)	38 559.00	14 789.00	12 999.00	25 449.00	39 997.00	46 379.00	67 035.00
Mn $\mu\text{g g}^{-1}$ (0-200 mm)	1 651.00	946.00	474.00	689.00	1 727.00	2 097.00	3 416.00
Mn $\mu\text{g g}^{-1}$ (200-400 mm)	1 524.00	932.00	120.00	773.00	1 599.00	1 941.00	3 228.00

In surface soils, Cd was shown to range from 1 to 8  $\mu\text{g g}^{-1}$ , and from 1 to 11  $\mu\text{g g}^{-1}$  at depth. Soil Fe was present in the surface soils of St. Cuthbert's in concentrations ranging from 16 665 to 59 753  $\mu\text{g g}^{-1}$ , and from 12 999 to 67 035  $\mu\text{g g}^{-1}$  at depth. The Mn concentrations in the surface soils ranged from 474 to 3 416  $\mu\text{g g}^{-1}$ , and from 120 to 3 228  $\mu\text{g g}^{-1}$  at depth (Table 4.33). With the exception of Cu at both depths, the median concentration value of each trace metal was greater than its mean concentration value at 0-200 mm and 200-400 mm, which was reflected in its normal frequency distribution (Table 4.8). Each soil parameter at 0-200 mm and 200-400 mm in the St. Cuthbert's Data set had a greater median value than its corresponding median value in the All Soil Data set (Tables 4.21 and 4.33).

#### **4.6.8 The St. Cuthbert's Data set: statistical analysis**

There were no significant differences in any soil parameter between its value or concentration at 0-200 mm and 200-400 mm (Table 4.34).

Table 4.34. Two-Sample T-Tests for soil parameter at 0-200 mm *versus* soil parameter at 200-400 mm (n=11), where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter (n=77)	T-value	p-value	$H_0$ : $\mu_1 = \mu_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	-0.63	0.53	Accepted
L-o-I (0-200 mm) v L-o-I (200-400 mm)	1.15	0.27	Accepted
Pb (0-200 mm) v Pb (200-400 mm)	-0.06	0.95	Accepted
Zn (0-200 mm) v Zn (200-400 mm)	-0.41	0.68	Accepted
Cd (0-200 mm) v Cd (200-400 mm)	-0.38	0.71	Accepted
Cu (0-200 mm) v Cu (200-400 mm)	-0.07	0.94	Accepted
Fe (0-200 mm) v Fe (200-400 mm)	0.12	0.90	Accepted
Mn (0-200 mm) v Mn (200-400 mm)	0.32	0.75	Accepted

There was a significant positive correlation at the  $p=0.01$  level for each soil parameter between its value at 0-200 mm and its value at 200-400 mm (Tables 4.35 and 4.36). There were no significant correlations between Loss-on-Ignition in the soil at surface and depth, or between Loss-on-Ignition and any other soil parameter at 0-200 mm and 200-400 mm. At 0-200 mm and 200-400 mm, Pb, Cu, Fe and Mn were all positively correlated with each other at the  $p \leq 0.01$ . There were no significant negative correlations in this data set.



Table 4.35. Significant correlations ( $p=0.001$ ,  $0.01$  and  $0.05$ ) between soil parameter data at  $0-200$  mm and  $200-400$  mm for the St. Cuthbert's Data set ( $n=11$ ).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
pH (200-400 mm)	***														
L-o-I (0-200 mm)	N.S.	N.S.													
L-o-I (200-400 mm)	N.S.	N.S.	**												
Pb (0-200 mm)	N.S.	N.S.	N.S.	N.S.											
Pb (200-400 mm)	N.S.	N.S.	N.S.	N.S.	***										
Zn (0-200 mm)	**	***	N.S.	N.S.	N.S.	N.S.									
Zn (200-400 mm)	*	*	N.S.	N.S.	*	*	***								
Cd (0-200 mm)	**	**	N.S.	N.S.	N.S.	N.S.	***	N.S.							
Cd (200-400 mm)	*	**	N.S.	N.S.	N.S.	N.S.	***	**	***						
Cu (0-200 mm)	N.S.	N.S.	N.S.	N.S.	***	***	N.S.	**	N.S.	N.S.					
Cu (200-400 mm)	N.S.	N.S.	N.S.	N.S.	***	***	N.S.	**	N.S.	N.S.	***				
Fe (0-200 mm)	*	*	N.S.	N.S.	*	*	**	***	*	N.S.	**	**			
Fe (200-400 mm)	*	N.S.	N.S.	N.S.	**	**	*	***	N.S.	N.S.	***	***	***		
Mn (0-200 mm)	N.S.	N.S.	N.S.	N.S.	**	*	N.S.	*	N.S.	N.S.	**	**	***	**	
Mn (200-400 mm)	N.S.	N.S.	N.S.	N.S.	*	**	*	**	N.S.	N.S.	***	**	***	***	***

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     N.S. = Not Significant

Table 4.36. Pearson values for significant correlations ( $p=0.001$ ,  $0.01$  and  $0.05$ ) between soil parameter data at 0-200 mm and 200-400 mm for the St. Cuthbert's Data set ( $n=11$ ).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
pH (200-400 mm)	0.909														
L-o-I (0-200 mm)															
L-o-I (200-400 mm)			0.814												
Pb (0-200 mm)															
Pb (200-400 mm)					0.977										
Zn (0-200 mm)	0.829	0.874													
Zn (200-400 mm)	0.726	0.701			0.662	0.680	0.864								
Cd (0-200 mm)	0.734	0.806					0.909								
Cd (200-400 mm)	0.724	0.812					0.939	0.740	0.955						
Cu (0-200 mm)					0.947	0.954		0.752							
Cu (200-400 mm)					0.902	0.938		0.803			0.975				
Fe (0-200 mm)	0.660	0.635			0.716	0.729	0.742	0.897	0.624		0.831	0.827			
Fe (200-400 mm)	0.609				0.750	0.798	0.692	0.931			0.871	0.892	0.967		
Mn (0-200 mm)					0.733	0.721		0.688			0.868	0.802	0.886	0.825	
Mn (200-400 mm)					0.731	0.734	0.610	0.772			0.879	0.840	0.933	0.896	0.982

- indicates a negative correlation

Pearson correlations between the stacked soil parameter data (0-400 mm) from the St. Cuthbert's site showed that the stacked data followed a similar pattern to that of the stacked data in the All Soil Data set (Table 4.27). However, although the correlations between Loss-on-Ignition at 0-400 mm and other parameter data at 0-400 mm were negative, none were statistically significant (Table 4.37).

Table 4.37. Pearson correlation values (r-values) and degrees of significance for each soil parameter at 0-400 mm (n=22).

	pH (0-400 mm)	L-o-I (0-400mm)	Pb (0-400 mm)	Zn (0-400 mm)	Cd (0-400 mm)	Cu (0-400 mm)	Fe (0-400 mm)
<b>L-o-I (0-400 mm)</b>	-0.413 N.S.						
<b>Pb (0-400 mm)</b>	0.247 N.S.	0.336 N.S.					
<b>Zn (0-400 mm)</b>	0.735 ***	-0.237 N.S.	0.559 **				
<b>Cd (0-400 mm)</b>	0.762 ***	-0.328 N.S.	0.100 N.S.	0.800 ***			
<b>Cu (0-400 mm)</b>	0.370 N.S.	0.115 N.S.	0.941 ***	0.664 ***	0.240 N.S.		
<b>Fe (0-400 mm)</b>	0.579 **	-0.089 N.S.	0.757 ***	0.853 ***	0.581 **	0.866 ***	
<b>Mn (0-400 mm)</b>	0.470 *	0.004 N.S.	0.726 ***	0.655 ***	0.413 N.S.	0.846 ***	0.886 ***

\*\*\* p = 0.001    \*\* p = 0.01    \* p = 0.05    N.S. = Not Significant  
- indicates a negative correlation

Soil pH at 0-400 mm was positively correlated at the  $p \leq 0.05$  level with Zn, Cd, Fe and Mn. With the exception of Cd v Pb, Cd v Cu, and Cd v Mn, all trace metal parameters were positively correlated with each other at 0-400 mm at the  $p \leq 0.05$  level (Table 4.37).

#### **4.6.9 The Stockhill Plantation Data set: descriptive statistics**

The descriptive statistics for this data set (n=12) shown in Table 4.38 indicated that surface soil reaction ranged from pH 3.1 to pH 6.7, and from pH 3.5 to pH 6.7 at depth. The median values of pH 4.1 at 0-200 mm and pH 4.9 at 200-400 mm were less than the median values of pH 4.5 at 0-200 mm and pH 5.0 at 200-400 mm for the All Soil Data set (Figure 4.21). Loss-on-Ignition ranged from 5.2% to 16.7% in the surface soils, and from 3.5% to 11.2% at depth. Median values of 9.2% for surface soil and 7.1% for depth were lower than for the corresponding median values of Loss-on-Ignition in the All Soil Data set at 11.3% and 8.1% respectively.

The concentration of soil Pb in the surface soils of the Stockhill Plantation ranged from 981 to 76 887  $\mu\text{g g}^{-1}$ , and from 664 to 86 135  $\mu\text{g g}^{-1}$  at depth (Table 4.38). The concentration of Zn ranged from 22 to 1 997  $\mu\text{g g}^{-1}$  in the surface soils and from 42 to 2 017  $\mu\text{g g}^{-1}$  at depth. Soil Cd ranged from 1 to 4  $\mu\text{g g}^{-1}$  at the surface and from 1 to 3  $\mu\text{g g}^{-1}$  at depth. The concentration of surface Cu ranged from 4 to 76  $\mu\text{g g}^{-1}$ , and from 8 to 80  $\mu\text{g g}^{-1}$  at depth. Soil Fe was present in the surface soils of the Stockhill Plantation in concentrations ranging from 2 564 to 46 740  $\mu\text{g g}^{-1}$  and from 5 921 to 46 630  $\mu\text{g g}^{-1}$  at depth. The Mn concentrations ranged from 14 to 3 584  $\mu\text{g g}^{-1}$  in the surface soil, and from 28 to 3 690  $\mu\text{g g}^{-1}$  at depth. With the exception of surface pH and Fe at surface and depth, the mean value of each soil parameter was greater than its median value for both depths (Table 4.38).

Table 4.38. Descriptive statistics at 0-200 mm and 200-400 mm for Stockhill Plantation Data set (n=12).

<b>Parameter</b>	<b>Arithmetic Mean</b>	<b>St. Dev.</b>	<b>Minimum</b>	<b>1st Quartile</b>	<b>Median</b>	<b>3rd Quartile</b>	<b>Maximum</b>
pH (0-200 mm)	4.35	1.07	3.10	3.38	4.10	5.18	6.70
pH (200-400 mm)	4.73	1.04	3.50	3.65	4.90	5.48	6.70
L-o-I % (0-200 mm)	10.47	3.38	5.20	8.10	9.85	12.50	16.70
L-o-I % (200-400 mm)	7.10	2.29	3.50	4.98	7.10	8.88	11.20
Pb $\mu\text{g g}^{-1}$ (0-200 mm)	14 422.00	21 805.00	981.00	2 141.00	6 223.00	21 968.00	76 887.00
Pb $\mu\text{g g}^{-1}$ (200-400 mm)	13 730.00	23 911.00	644.00	1 988.00	6 328.00	13 112.00	86 135.00
Zn $\mu\text{g g}^{-1}$ (0-200 mm)	639.00	544.00	22.00	303.00	495.00	895.00	1 997.00
Zn $\mu\text{g g}^{-1}$ (200-400 mm)	618.00	544.00	42.00	280.00	506.00	764.00	2 017.00
Cd $\mu\text{g g}^{-1}$ (0-200 mm)	1.25	0.87	1.00	1.00	1.00	1.00	4.00
Cd $\mu\text{g g}^{-1}$ (200-400 mm)	1.42	0.79	1.00	1.00	1.00	1.00	3.00
Cu $\mu\text{g g}^{-1}$ (0-200 mm)	22.75	18.12	4.00	14.25	18.50	23.75	76.00
Cu $\mu\text{g g}^{-1}$ (200-400 mm)	21.25	19.15	8.00	11.00	16.50	20.75	80.00
Fe $\mu\text{g g}^{-1}$ (0-200 mm)	28 789.00	1 3267.00	2 564.00	22 936.00	30 527.00	39 619.00	46 740.00
Fe $\mu\text{g g}^{-1}$ (200-400 mm)	30 058.00	1 1932.00	5 921.00	20 092.00	32 410.00	39 449.00	46 630.00
Mn $\mu\text{g g}^{-1}$ (0-200 mm)	1 399.00	1 119.00	14.00	661.00	1 069.00	2 451.00	3 584.00
Mn $\mu\text{g g}^{-1}$ (200-400 mm)	1 525.00	1 094.00	28.00	851.00	1 466.00	2 455.00	3 690.00

The mean and median percentage Loss-on-Ignition at depth were identical. With the exception of Cd at surface and depth, which had identical median concentration values for Stockhill Plantation and the All Soil Data set, each trace metal parameter at surface and depth in the Stockhill Plantation had a greater median value than its corresponding median value in the All Soil Data (Table 4.21 and 4.38).

#### 4.6.10 The Stockhill Plantation Data set: statistical analysis

There was no significant difference between pH at 0-200 mm and 200-400 mm or for any trace metal between 0-200 mm and 200-400 mm (Tables 4.39 and 4.40).

Table 4.39. Two-Sample T-Tests for soil parameter at 0-200 mm *versus* soil parameter at 200-400 mm (n=21), where  $H_0: \mu_1 = \mu_2$  at  $\alpha=0.05$ .

Soil Parameter (n=77)	T-value	p-value	$H_0$ : $\mu_1 = \mu_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	-0.87	0.39	Accepted
L-o-I (0-200 mm) v L-o-I (2000-400 mm)	2.86	0.01	Rejected
Pb (0-200 mm) v Pb (2000-400 mm)	0.24	0.81	Accepted
Zn (0-200 mm) v Zn (200-400 mm)	0.10	0.92	Accepted
Cu (0-200 mm) v Cu (200-400 mm)	0.19	0.85	Accepted
Fe (0-200 mm) v Fe (200-400 mm)	-0.25	0.81	Accepted
Mn (0-200 mm) v Mn (200-400 mm)	-0.28	0.78	Accepted

Table 4.40. Two-Sample Mann-Whitney tests for Cd at 0-200 mm *versus* 200-400 mm (n=12), where  $H_0: \eta_1 = \eta_2$  at  $\alpha=0.05$ .

Soil Parameter (n=77)	Mann-Whitney p-value	$H_0$ : $\eta_1 = \eta_2$ at $\alpha=0.05$
Cd (0-200 mm) $\nu$ Cd (200-400 mm)	0.0885	Accepted

There was a significant difference at the  $p=0.01$  level however, between Loss-on-Ignition at 0-200 mm and 200-400 mm (Table 4.39). Surface Loss-on-Ignition values were consistently greater than the minimum, 1<sup>st</sup> quartile, median, 3<sup>rd</sup> quartile and maximum values of Loss-on-Ignition at depth by 2% to 5% (Table 38).

In common with the All Soil Data set, there was a significant positive correlation at the  $p \leq 0.05$  level for each parameter between its value at 0-200 mm and its value at 200-400 mm (Tables 4.25, 4.26, 4.41 and 4.42). There were significant positive correlations at the  $p=0.01$  and  $p=0.05$  levels between pH and all trace metal data at surface and depth, with the exception of Fe at surface and depth and Cd at 200-400 mm. With the exception of surface Pb  $\nu$  surface Fe and Pb at depth  $\nu$  Fe at depth, there were also significant positive correlations at the  $p \leq 0.05$  level between Pb, Zn, Cu, Fe and Mn at 0-200 mm and 200-400 mm (Tables 4.41 and 4.42). Loss-on-Ignition at surface and depth were not significantly correlated with any trace metal data except Cd at depth where  $p=0.05$ , and a significant negative correlation at the  $p=0.05$  level between Loss-on-Ignition at 0-200 mm and Fe at 0-200 mm.

Table 4.41. Significant correlations ( $p=0.001, 0.01$  and  $0.05$ ) between  $\log_{10}$  transformed soil parameter data at 0-200 mm and 200-400 mm for the Stockhill Plantation Data set ( $n=12$ ).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
pH (200-400 mm)	***														
L-o-I (0-200 mm)	N.S.	*													
L-o-I (200-400 mm)	N.S.	N.S.	*												
Pb (0-200 mm)	**	**	N.S.	N.S.											
Pb (200-400 mm)	**	*	N.S.	N.S.	***										
Zn (0-200 mm)	**	*	N.S.	N.S.	***	***									
Zn (200-400 mm)	*	*	N.S.	N.S.	***	***	***								
Cd (0-200 mm)	*	*	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.							
Cd (200-400 mm)	N.S.	N.S.	N.S.	*	N.S.	*	*	*	*						
Cu (0-200 mm)	*	*	N.S.	N.S.	***	***	***	***	N.S.	N.S.					
Cu (200-400 mm)	*	*	N.S.	N.S.	**	***	***	***	N.S.	N.S.	***				
Fe (0-200 mm)	N.S.	N.S.	*	N.S.	N.S.	*	*	*	N.S.	N.S.	*	*			
Fe (200-400 mm)	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	*	*	N.S.	N.S.	*	**	***		
Mn (0-200 mm)	**	**	N.S.	N.S.	*	**	***	**	*	*	*	*	**	*	
Mn (200-400 mm)	**	*	N.S.	N.S.	*	**	**	**	*	*	*	*	**	**	***

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     N.S. = Not Significant    - indicates a negative correlation



Table 4.42. Pearson values for significant correlations ( $p=0.001$ ,  $0.01$  and  $0.05$ ) between  $\text{Log}_{10}$  transformed soil parameter data at 0-200 mm and 200-400 mm for the Stockhill Plantation Data set ( $n=12$ ).

	pH (0-200 mm)	pH (200-400 mm)	L-o-I (0-200 mm)	L-o-I (200-400 mm)	Pb (0-200 mm)	Pb (200-400 mm)	Zn (0-200 mm)	Zn (200-400 mm)	Cd (0-200 mm)	Cd (200-400 mm)	Cu (0-200 mm)	Cu (200-400 mm)	Fe (0-200 mm)	Fe (200-400 mm)	Mn (0-200 mm)
PH (200-400 mm)	0.898														
L-o-I (0-200 mm)		-0.588													
L-o-I (200-400 mm)			0.660												
Pb (0-200 mm)	0.801	0.720													
Pb (200-400 mm)	0.749	0.684			0.971										
Zn (0-200 mm)	0.715	0.650			0.891	0.900									
Zn (200-400 mm)	0.676	0.634			0.825	0.871	0.975								
Cd (0-200 mm)	0.702	0.592													
Cd (200-400 mm)				0.691		0.606	0.621	0.661	0.600						
Cu (0-200 mm)	0.674	0.659			0.857	0.877	0.887	0.869							
Cu (200-400 mm)	0.591	0.598			0.775	0.837	0.907	0.953			0.863				
Fe (0-200 mm)			-0.594			0.593	0.666	0.644			0.687	0.637			
Fe (200-400 mm)							0.649	0.690			0.623	0.717	0.943		
Mn (0-200 mm)	0.777	0.731			0.693	0.722	0.810	0.797	0.615	0.624	0.688	0.645	0.744	0.694	
Mn (200-400 mm)	0.729	0.708			0.670	0.734	0.774	0.779	0.623	0.671	0.678	0.635	0.746	0.713	0.980

- indicates a negative correlation

The stacked soil parameter data (0-400 mm) from the Stockhill Plantation Data set followed a similar pattern to that of the All Soil Data set (Tables 4.27 and 4.43). With the exception of Fe, soil pH was positively correlated at the  $p \leq 0.01$  level or less with all trace metal data in the Stockhill set (Table 4.43). With the exception of Cd v Cu and Cd v Fe, all trace metal parameters were positively correlated with each other at the  $p \leq 0.05$  level or less. There was one significant negative correlation at the  $p = 0.05$  level between Loss-on-Ignition and pH.

Table 4.43. Pearson correlation values (r-values) and degrees of significance for all soil parameters at 0-400 mm (n=24).

	pH (0-400 mm)	L-o-I (0-400mm)	Pb (0-400 mm)	Zn (0-400 mm)	Cd (0-400 mm)	Cu (0-400 mm)	Fe (0-400 mm)
L-o-I (0-400 mm)	-0.430 *						
Pb (0-400 mm)	0.723 ***	-0.059 N.S.					
Zn (0-400 mm)	0.662 ***	-0.039 N.S.	0.880 ***				
Cd (0-400 mm)	0.535 **	0.102 N.S.	0.467 *	0.481 *			
Cu (0-400 mm)	0.623 ***	-0.071 N.S.	0.845 ***	0.915 ***	0.363 N.S.		
Fe (0-400 mm)	0.398 N.S.	-0.300 N.S.	0.528 **	0.674 ***	0.251 N.S.	0.697 ***	
Mn (0-400 mm)	0.741 ***	-0.224 N.S.	0.708 ***	0.729 ***	0.640 ***	0.658 ***	0.730 ***

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     N.S. = Not Significant  
 - indicates a negative correlation

#### 4.6.11 The Agricultural Data set: descriptive statistics

As this was such a small data set at  $n=3$ , the descriptive statistics summarised in Table 4.44 were included for reference only. No further statistical analyses were applied to these data.

Table 4.44. Descriptive statistics for soil parameters at 0-200 mm and 200-400 mm ( $n=3$ ) for Agricultural Land.

Parameter	Arithmetic Mean	St. Dev.	Minimum	Median	Maximum
pH (0-200 mm)	5.3	0.20	5.10	5.30	5.50
pH (200-400 mm)	5.17	0.45	4.70	5.20	5.60
L-o-I % (0-200 mm)	14.73	0.76	13.90	14.90	15.40
L-o-I % (200-400 mm)	10.07	0.86	9.30	9.90	11.00
Pb $\mu\text{g g}^{-1}$ (0-200 mm)	557.00	407.00	317.00	367.00	1 046.00
Pb $\mu\text{g g}^{-1}$ (200-400 mm)	508.00	242.00	340.00	398.00	785.00
Zn $\mu\text{g g}^{-1}$ (0-200 mm)	27.33	1.16	26.00	28.00	28.00
Zn $\mu\text{g g}^{-1}$ (200-400 mm)	24.00	1.00	23.00	24.00	25.00
Cd $\mu\text{g g}^{-1}$ (0-200 mm)	1.00	0.00	1.00	1.00	1.00
Cd $\mu\text{g g}^{-1}$ (200-400 mm)	1.00	0.00	1.00	1.00	1.00
Cu $\mu\text{g g}^{-1}$ (0-200 mm)	38.70	32.50	2.00	50.00	64.00
Cu $\mu\text{g g}^{-1}$ (200-400 mm)	29.70	24.80	2.00	37.00	50.00
Fe $\mu\text{g g}^{-1}$ (0-200 mm)	5 307.00	1 115.00	4 193.00	5 306.00	6 422.00
Fe $\mu\text{g g}^{-1}$ (200-400 mm)	12 686.00	1 994.00	112 22.00	11 880.00	14 957.00
Mn $\mu\text{g g}^{-1}$ (0-200 mm)	525.00	491.00	203.00	282.00	1 090.00
Mn $\mu\text{g g}^{-1}$ (200-400 mm)	233.00	46.80	169.00	250.00	250.00

#### 4.7 Quality control - precision and accuracy

##### Sampling Precision

The least variation in soil parameter values between soils and their field sample duplicates was for pH at 0.63% CV (Table 4.45). The greatest variation between sampling duplicates was for Cd at 20.70% CV.

Table 4.45. Mean % CV between the results of the analyses of soil samples and their field sample duplicates in the baseline and annual soil study (n=28).

Soil Parameter	Mean % CV	Standard Deviation
pH	0.63	0.24
L-o-I	3.22	0.32
Pb	5.56	0.74
Zn	7.32	0.48
Cd	20.70	1.69
Cu	2.56	0.75
Fe	13.26	0.90
Mn	18.56	0.62

#### Analytical Precision

The most efficient recovery from the reference material BCR CRM 143R Sewage Sludge Amended Soil was for Pb at 96.91% (Table 4.46). The least efficient recovery was for Mn at 78.25%. Cadmium recovery was the most precise at 5.34% CV, while the least precise was Fe at 11.40% CV. The results were calculated from the reference material used during the baseline and annual soil study (Chapter 5).

Table 4.46. Recovery of trace metals from BCR CRM 143R Sewage Sludge Amended Soil (n=15)

	Pb	Zn	Cd	Cu	Fe	Mn
BCR CRM 143R $\mu\text{g g}^{-1}$ (DM)	179.70 $\pm 2.10$	1 055.00 $\pm 14.00$	71.80 $\pm 1.20$	130.00 $\pm 1.40$	No Data Available	904.00 $\pm 13.00$
Mean Recovered $\mu\text{g g}^{-1}$ (DM) (n=16)	174.15 $\pm 11.10$	971.40 $\pm 63.99$	64.59 $\pm 3.45$	115.49 $\pm 3.90$	25078.22 $\pm 2859.18$	707.41 $\pm 65.70$
% CV	6.37	6.59	5.34	9.29	11.40	9.29
% Recovery	96.91	92.08	89.96	88.43	---	78.25

The most precise recovery of a trace metal from the in-house reference material was for Pb at 7.9% CV (Table 4.47). The least precise recovery was for Fe at 11.7% CV. The results were calculated from the in-house reference material used during the baseline and annual soil study (Chapter 5).

Table 4.47. Trace metal concentration of Pb, Zn, Cd, Cu, Fe and Mn ( $\mu\text{g g}^{-1}$ ) and % CV for in-house reference soil (n=31).

	Pb	Zn	Cd	Cu	Fe	Mn
Mean	14 484.5	2649.1	277.6	49.4	69 277.8	1 280.1
$\mu\text{g g}^{-1}$ (DM) (n=33)	$\pm 1\,149.6$	$\pm 2\,880.1$	$\pm 27.4$	$\pm 5.1$	$\pm 8088.4$	$\pm 124.0$
% CV	7.9	10.9	9.9	10.4	11.7	9.7

Of all the soil parameters in the baseline study, analyses for pH (n=3) showed the greatest reproducibility at 0.28% CV (Table 4.48). However, pH units are a logarithmic scale. Of the trace metals, analyses of Cd showed the greatest precision at 2.39% CV and Mn the least at 7.49% CV. Analyses for all soil parameters were within the target level of precision of 10% CV.

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Table 4.48. Mean % CV between the three replicate analyses for each sample in the baseline and annual soil studies (n=268).

Soil Parameter	Mean % CV	Standard Deviation
pH	0.28	0.2
L-o-I	2.33	2.17
Pb	3.00	1.97
Zn	5.53	4.46
Cd	2.39	6.05
Cu	6.30	7.20
Fe	4.96	3.78
Mn	7.49	6.56

#### 4.8 Discussion

In terms of soil trace metal content, the baseline soil survey identified the immediate local environmental impact of historical lead mining and processing on the Priddy Mineries Reserve, adjoining St. Cuthbert's and part of the adjacent Stockhill Plantation. The analytical results will be discussed in terms of trace metal distribution, the level of contamination and statistical relationships between soil parameters for the All Soil Data set, and the Priddy Mineries Reserve, St. Cuthbert's and Stockhill Plantation Data sets.

##### 4.8.1 The distribution of trace metals, pH and Loss-on-Ignition in the study area

The distribution of trace metals in the baseline study appeared to be related to the natural mineralisation of the area, historical mining, beneficiation and smelting activity and the subsequent retention and transformation and mobility of the metals in the soil system. The trace metals Pb, Zn, Cd and Cu were found in their greatest concentrations at surface and depth around the areas of wastes (tailings) associated

with beneficiation (Figures 4.11 to 4.22). Although the tailings present were the final product of many reworkings of more ancient wastes, the ultimate source of the tailings was the host rock Dolomitic Conglomerate and its Jurassic Pb-Zn mineralisation. The greatest concentrations of Pb, Zn, Cd and Cu were in the tailings piles on the Reserve centred around ST 35475 15135, the tailings pond running to the south of this area to the St. Cuthbert's site, and throughout St. Cuthbert's itself, which is centred on ST 35445 15055 and contains extensive areas of tailings piles (Figure 1.2). Soil Fe and Mn were similarly found in their greatest concentrations around areas of tailings, but were also present in high concentrations in the Nordrach soil. The difference in concentration between the wastes and Nordrach soil was markedly less for Fe and Mn than for Pb, Zn, Cd and Cu (Figures 4.11 to 4.28). This was strongly related to the pattern of mineralisation of the country rock of Mendip (2.3.2).

The high concentrations of Pb, Zn, Cd, and Cu, Fe and Mn found in the tailings largely originated from the Dolomitic Conglomerate host rock and its episodic hypogenic and subsequent supergenic mineralisation in the Jurassic (Alabaster, 1992; Simms, 1998). However, the high concentrations of Fe and Mn in the Nordrach soil partly originated from this mineralisation, but also probably from Fe and Mn mineralisation predating that of the Dolomitic Conglomerate. The mineral component of Nordrach soil consists of an accumulation of loessial silts incorporated with the weathered residues of the underlying rock. The two materials become ameliorated by frost action, tree fall and soil fauna (Findlay, 1965). In the Nordrach soil of the Stockhill Plantation, it is possible that the weathered residues of Dolomitic Conglomerate became mixed with accumulated

loessial silts from weathered Fe-rich Old Red Sandstone and Carboniferous Limestone and Mn-rich Lower Limestone Shales, forming the mineral fraction of the local Nordrach soil (Alabaster, 1982; Simms, 1998). Mn is commonly present as a substituent for  $\text{Fe}^{2+}$  in the mineral structure of ferro-magnesian silicate minerals (Gilkes and McKenzie, 1988). All these country rocks were exposed during the weathering of the North Hill pericline (Figure 2.1). The distribution of Pb, Zn, Cd, Cu, Fe and Mn enrichment of the Nordrach soil in the northern end of the Stockhill Plantation therefore reflected the pattern of natural mineralisation of the country rock and subsequent pedogenesis in the area (Figures 2.1, 2.2 and 4.11 to 4.28).

The high concentrations of Pb, Zn, Cd, Cu, Fe and Mn in the tailings were related to the methods of beneficiation that were carried out during the large-scale reworking of the Roman and mediaeval wastes in the area between 1857 and 1908. The subsequent retention of the trace metals was related to the geochemical composition of the tailings (Blowes *et al.*, 1991). The separation of Pb from its gangue material was by gravitational separation and wastes from this technology were inevitably metal-rich (Page, 1911; Bucknell, 1924; Gough, 1967). This was the case for Pb, and all other trace metals associated with the original Pb-Zn mineralisation of the ore-bearing rock. Metallic minerals and gangue minerals such as calcite, barytes (barite) and quartz were also present in the wastes, as well as fragments of black smelter slag (Table 4.11). The fragments of slag present in the tailings may also contribute to the high trace metal concentrations present. The occlusion of trace metals within the crystalline structures of slag particles was reported by Murphy (1992). Therefore, the slag particles present in the tailings



may also facilitate the retention of trace metals, as well as being a source of trace metals to the tailings.

The presence of  $\text{CaCO}_3$  in gangue minerals increases soil pH, limiting metal migration through the soil profile (Maskell *et al.*, 1995). The presence of carbonate species also enhances the precipitation of insoluble Pb, Zn, Cu and Cd compounds such as carbonates, oxides and hydroxides, and can facilitate the adsorption of trace metals onto hydrous oxides of Fe and Mn, thus retaining the trace metals in the tailings (Blowes *et al.*, 1991, Merrington, 1993; Ross, 1994c). The presence of Ca in pre-smelter wastes is also thought to be involved in the weathering of galena to pyromorphite (Cotter-Howells, 1991). Pyromorphite is an insoluble Pb phosphate, and one of the most stable Pb compounds in oxidising soil environments (Nriagu, 1978, 1984). There was evidence to suggest that geochemical conditions in the tailings on the study site might favour the weathering of galena to pyromorphite, which may also contribute to the retention of Pb in high concentrations.

In a study on Pb in soils contaminated by mining wastes in Winster, Derbyshire, Cotter-Howells (1991) identified pyromorphite as the dominant Pb mineral in the solid phase, accounting for up to 50% of the total soil Pb. X-ray diffraction showed that substantial amounts of Ca were present in most of the pyromorphite grains, although little was present in pyromorphite collected directly from the mineral vein. Cerussite was also present in the soil, but galena, the principle ore mined at Winster, was only present as a small proportion of the total soil Pb (<5%). Galena was shown to alter to cerussite in the Winster soil under oxidising

conditions, leading Cotter-Howells (1991) to propose that cerussite could represent an intermediate stage in the weathering sequence of galena to pyromorphite in soils. At the Charterhouse mining area, pyromorphite was present in small amounts in the solid phase of the mine-waste soils, although cerussite dominated the soil solid phase. There was evidence which suggest that much of the galena that was once present had weathered, but had been replaced by cerussite and not pyromorphite (Mattigod *et al.*, 1986; Cotter Howells, 1991; Cotter-Howells and Caporn, 1996).

The main geochemical conditions that were considered to influence the galena→ cerussite→ pyromorphite weathering sequence can be summarised from Cotter-Howells (1991) work as:

- length of time since Pb contamination
- total Pb concentration
- presence of Ca.

The greatest amounts of pyromorphite were found in mine-waste soils in Cotter-Howells (1991) study where Pb contamination was at least 200 years old, the soil contained Pb at in concentrations in excess of  $10\,000\ \mu\text{g g}^{-1}$ , and Ca was present. The tailings on the study site definitely fulfils the latter two criteria; calcite was a common gangue mineral, and the host rock Dolomitic Conglomerate, also discarded on the tailings piles as gangue, is a magnesium limestone. Although the construction of the tailings piles in their present form only ended a little over 100 years ago, they were the end product of a series of reworkings of much earlier wastes, perhaps even dating back to the first century AD in some cases. Cerussite

was found at the St Cuthbert's site in two clay-like sediment samples collected from the St Cuthbert's Swallet by Stenner (1978). The samples contained  $132\,000\ \mu\text{g g}^{-1}$  and  $330\,000\ \mu\text{g g}^{-1}$  Pb, with the latter containing 70% cerussite. Stenner (1978) concluded that from its agglutinated structure, the cerussite could not have been transported to the site, but was probably a localised product of the weathering of galena.

A process similar to podsolisation was described for tailings piles, which was also thought to be involved in the retention of trace metals (Blowes *et al.*, 1991). Tailings from the beneficiation of sulphide ores such as galena (PbS) are typically rich in ferrous sulphide minerals on deposition, and the action of percolating waters through tailings over time, is known to stimulate the formation of Fe cemented layers or hardpans in the presence of carbonates. Hardpans were found within the depth where active oxidation occurred, or up to 200-300 mm below the layer of active oxidation (Blowes *et al.*, 1991). A typical hardpan was characterised by the cementation of tailings by Fe (III) minerals such as goethite, ferrihydrite, lepidocrocite and jarosite into a layer, which restricted the movement of trace metals through the tailings. Hardpans were also found to act as zones of trace metal accumulation (Blowes *et al.*, 1991). If present, hardpans in the tailings of the study area could also contribute to the high concentrations of Fe at depth and the retention of trace metals in the tailings.

The greatest concentration of Pb in the study area at depth was found in sample 2 at  $171\,688\ \mu\text{g g}^{-1}$ , as were the greatest concentrations of Cu and Fe at surface and depth (Table 4.22, Figures 4.11, 4.20, 4.21, 4.23 and 4.24). The concentration of

Pb in one of Stenner's (1978) sediment samples from inside St Cuthbert's Swallet was  $132\,000\ \mu\text{g g}^{-1}$ , a concentration remarkable similar to the  $138\,300\ \mu\text{g g}^{-1}$  found at surface in sample 2 in this present study, which was collected from an area close to the entrance of St Cuthbert's Swallet (Table 4.22, Figures 4.11 and 4.12). The soil in sample 2 contained red alluvial clay at 0-100 mm, with very fine black slag at 100 - 200 mm and red clay at 200-350 mm with gritty black slag at 350-400 mm (Table 4.22). The sampling site was at the bottom of the blind valley that was recorded as containing an extensive tract of slags and wastes left by the ancients (Figure 1.2). It is possible that the black slag present in the sample is the residual waste left at the bottom of the valley from the original wastes of the ancients. The high concentrations of Pb, Cu and Fe are likely to be as a result of the relatively inefficient smelting techniques of the ancients, augmented by metal-enriched alluvial inwash from the surrounding tailings piles. The depression is prone to periodic flooding (Irwin *et al.*, 1968), and the silty clay present in the profile in discrete horizons was probably deposited as a result of repeated inwash of alluvial material from the surrounding tailings piles, many of which contain very fine, metal-enriched material, and its subsequent lessivage. Lessivage, or pervection, is the mechanical eluvation of clay particles from the A horizon without chemical alteration. The clay is progressively washed down the soil profile to form a horizon of clay accumulation (White, 1989). It is also possible that Zn, Cd and Mn may have been present in the samples at higher concentrations in the past, but repeated flooding and waterlogging may have caused some depletion through leaching.

Although some degree of enrichment was present, the lowest concentrations for Pb, Zn, Cd, Cu, Fe and Mn at surface and depth in the study area were shown to occur in the soils around North Hill. This can be related to the industrial history of the study area and its pedology. As shown by the distribution maps, the greatest concentrations of Pb, Zn, Cd, Cu, Fe and Mn in the study area were in soils affected by the wastes from mining and beneficiation (Figures 4.7 to 4.28). There was no evidence of mining or beneficiation, or wastes from those activities above 260 m on the east and southern slopes of North Hill. However, there was a smelter stack on North Hill at ST 35449 15112, known as the Waldegrave smelter stack (Figures 4.29 and 4.30).

During operation, emissions from the smelter would have enriched the surrounding soils with trace metals associated with the local Pb mineralisation. Smelter stacks are known point sources of trace metals in soils. Plumes of elevated concentrations of trace metals in soils have been shown to occur away from smelters in the direction of the prevailing wind, with the trace metal concentration in the soils decreasing exponentially away from the smelter point source (Davies, 1983; Ross, 1994b). With the exception of Cd, which showed no measurable elevation in concentration at surface and depth throughout the North Hill area, there was a distribution pattern of elevated concentrations of trace metals associated with the smelter stack and prevailing southwesterly winds in varying degrees. However, the magnitude of enrichment was small compared with that of the enrichment associated with the pre-smelter wastes in the study area.

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**Figure 4.29. Map of the study area (1887) showing significant features associated with beneficiation and smelting (Original Scale 1:10 560).**

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Figure 4.30. Map of the study area (1903) showing significant features associated with beneficiation and smelting (Original Scale 1:10 560).

Despite historical deposition by smelter emissions, it is likely that trace metals were at their lowest concentrations in the soils on North Hill because of the chemical form in which they were deposited (Ledward, 1960; Foster and Lott, 1980; Gibb and Cartwright, 1982; Martin and Coughtrey, 1982; Li, 1993; Cotter-Howells, 1991; Maskell *et al.*, 1996), and their subsequent patterns of retention and mobilisation in the highly acid soil (Campbell *et al.*, 1983; Bergkvist *et al.*, 1989).

In a study of the behaviour of trace metals in acidic soils, Campbell *et al.* (1983) suggested that the following order of mobility occurred with increasing soil acidity:

$$\text{Al, Mn, Zn (high)} > \text{Cd, Co, Cu, Ni} > \text{Pb, V (low)}.$$

Bergkvist *et al.* (1989) proposed that more specifically, the mobility and leaching of Zn, Cd, and Mn was associated with increasing soil acidity, while Pb, Fe and Cu was more associated with the solubility of organic matter. In accordance with the sequence suggested by Campbell *et al.* (1983) and the findings of Bergkvist *et al.* (1989), Pb and Cu deposited on acid soil by smelter emissions might be expected to be retained to some extent in the upper zones of a soil relative to Zn, Cd and Mn, which was what the general pattern of distribution on North Hill could be argued to suggest. The lowest concentrations of Mn were found on the lower slopes of North Hill, at the northern end of the Reserve. The soils here, especially to the Northwest of the Minery Reservoir were acidic, and often water-logged for much of the year. The lowest Mn concentrations were found in these areas, which would be expected under these edaphic conditions. In waterlogged acidic soils,



high levels of exchangeable Mn occur, which may lead to increased plant uptake of Mn, or its leaching down through the soil profile (White, 1989).

In other historical mining and smelting sites, soil acidity has also been linked with the migration of trace metals through soil profiles (Maskell *et al.*, 1995). Despite its relative immobility in soil, Pb has also been shown to leach vertically through profiles on sites affected by mining and smelting with time (Ledward, 1960; Gibb and Cartwright, 1982; Martin and Coughtrey, 1982; Maskell *et al.*, 1995). This mobility was possibly linked with the compounds deposited by smelter emissions. Sulphates are the principle forms of Pb in smelter emissions (Foster and Lott, 1980), and Cotter-Howells (1991) showed that anglesite ( $\text{PbSO}_4$ ), which is relatively soluble, was the predominant lead mineral in the solid phase of the soils around a smelter site in Derbyshire.

Ledward (1960) reported that in ferralitic soil and sandstone beneath smelters used in Burma, Pb could migrate through the soil profile to depths of 0.6 to 2.4 m over a 500 year period. Gibb and Cartwright (1982) found that in areas of former smelters in the USA, Pb, Zn and Cd had migrated vertically down various soil profiles to depths of up to several metres in 70-90 years. In Britain, Maskell *et al.* (1995) found that in historical mining and smelting sites in Derbyshire, trace metal mobility increased at lower soil pH, with a greater vertical migration rate through soils underlain by sandstone. In smelter waste deposited from 1300 to 1500 AD, Pb and Zn were found to have moved distances of 4.3 m and 2.6 m respectively through the soil and underlying sandstone (Maskell *et al.*, 1995).

Comparisons between the solubility and mobility of trace metals in the soils of smelting and mining sites at Shipham also showed that Pb, Zn and Cd deposited by smelter emissions had a greater mobility and availability in soils than when deposited by mining or beneficiation (Li, 1993). The solubility and mobility of Cd was found to be much higher than that of Zn in the smelting sites. This was in agreement the work of Tills and Alloway (1983), who found that the soluble  $\text{Cd}^{2+}$  was the dominant Cd species in smelter soils, and would explain the distinctive distribution pattern of low concentrations of Cd in the soils of North Hill.

The median pH values for soils over the study site were pH 4.50 at surface and pH 5.0 at depth (Table 4.21). However, pH mapping data for these parameters showed very distinctive patterns within this distribution. The soils of the Reserve showed two distinct pH groupings, the Ashen soils of the east slopes of North Hill and at Stockhill Plantation, and the Thrupe soils of valley floor (Figures 4.7 and 4.8). These groupings were loosely based on the distribution of the solid geology and soil series, but the industrial heritage and vegetation cover were also shown to exert a considerable influence on the soil pH distribution (Figures 2.1, 2.2, 4.7 and 4.8). The acidic grouping of the distribution (pH 3.0 to pH 6.0) included the podsolised soils of the Ashen Series, the soils of the Nordrach Series, and the area mapped as Thrupe Series in the north section of the Reserve (Figure 2.2).

The pH of soils mapped as the Ashen Series ranged from pH 3.1 to pH 6.2, at surface and from pH 3.0 to pH 6.0, at depth (Figures 4.7 and 4.8). This range was comparable with the range of reaction for Old Red Sandstone, which underlies the Ashen soils, at pH 4.2 to pH 6.6 (Fuge *et al.*, 1991). The median soil reaction for

the study area was slightly lower than those shown by Findlay (1965), who recorded the soil reaction of a typical soil of the Ashen Series as pH 4.3 at 0-300 mm and pH 4.7 at 300-400 mm. Soil acidity is associated with leached soils, and the development of an acid soil, like podsolisation, depends on its parent material, rainfall and rate of leaching, the soil microbial biomass and the inputs of acidity from vegetation (Rowell, 1994). The acidic, base-unsaturated Fe-rich sandstone and conglomerate parent material, the relatively high rainfall and their former cover of true heath species (Findlay, 1965) has contributed to the podsolisation and acidification of the soils of the Ashen Series. The least acidic samples from the Ashen Series were collected from the agricultural land under production above the Reserve (Figure 4.7 and 4.8), and sample 39, which was mapped as the Ashen Series, but was close to the tramway and may have been affected by the material used in its construction (Figure 4.30). The agricultural soils may have undergone some amendment in the past, but the presence of cultivated pasture species rather than species typical of upland grasslands may have also influenced the soil reaction (Table 4.23).

The distribution of pH values in the soils mapped as the Thrupe Series was directly related to the industrial history of the site. In the valley running through the Reserve and St. Cuthbert's where the soils were of the Thrupe Series, much of the area was overlain by former tailings ponds and tailings piles. In these areas, soil reaction ranged from pH 4.5 to pH 7.3 at surface, and from pH 4.8 to pH 7.6 at depth (Figures 4.7 and 4.8). The tailings piles in the Reserve and St. Cuthbert's contain Dolomitic Conglomerate host rock (pH 6.2 - pH 7.5 [Fuge *et al.*, 1991]), and calcite gangue which would have elevated the pH of the material. However,

some tailings, such as those at sampling points 70 and 72 were overlying areas of the Thrupe Series where there is often standing water for long periods in the year (Figure 4.3). The lower soil pH here may have been as a result of the constant waterlogging, which could have caused the leaching of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from the gangue and host rock over a long period.

The reaction of the soils from the Nordrach Series ranged from pH 3.2 to pH 5.4 at surface, and from pH 3.6 to pH 5.6 at depth (Figures 4.7 and 4.8). Sample 69 showed an anomalously high pH for the Nordrach soils of pH 6.7 (Figures 4.7 and 4.8; Table 4.22), and after consideration of all its parameters and description, was considered to be disturbed by beneficiation waste, and not true Nordrach soil. The Nordrach soils in this study area were considerably more acidic in reaction than the underlying Dolomitic Conglomerate at pH 6.2 - pH 7.5 (Fuge *et al.*, 1991). They were also more acidic than the Nordrach soils described by Findlay (1965), who found soil reactions ranging from pH 5.7 to pH 6.4 at approximately surface and pH 6.2 to pH 6.8 at approximately depth. The acidic nature of the Nordrach soils in this study can be explained in terms of land use and vegetation cover.

The sampling points are in the Stockhill Plantation, and were found to have a mixed coniferous/deciduous cover. At each sampling point where the soil reaction was below pH 4.5 at surface, the dominant cover was coniferous (Table 4.23). Coniferous canopies and freshly fallen litter are the source of strongly reducing polyphenols, which are organic acids and highly active compelling agents (White, 1989). The acidifying Fe hydrolysis - oxidation reaction described previously in conjunction with the podsolisation of the Ashen Series, may also be

taking place in the Fe-rich soils of the Nordrach series further contributing to their acidification.

Trace metal concentrations and analysis of the physical characteristics showed that with the exception of two sampling points, the sampling points in the Maesbury soils in the Reserve and St. Cuthbert's were overlain with tailings, or were physically disturbed by beneficiation or smelter wastes (Figures 2.2, 4.11 to 4.28; Table 4.22). Soil reaction was generally higher in the soils of St. Cuthbert's for the Reserve or Stockhill Plantation, many soils were approaching neutral in reaction (Figures 4.7 and 4.8). This was due to the geochemical composition of the extensive piles tailings and pre-smelter wastes present at the site.

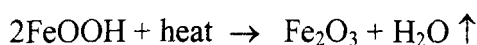
The distribution of percentage Loss-on-Ignition data over the study showed that in general, the greatest percentages were in the Ashen soils of North Hill and in the southern area of Stockhill Plantation, and in the wetter areas of the soils mapped as the Thrupe Series in the valley running from north to south through the Reserve and St. Cuthbert's. This was related to the plant communities in these areas. The acidic upland grassland and heath dominated by *Molinia caerulea* on the soils of the Ashen Series and the plant communities of the mires on the Thrupe Series (Table 4.23) typically produce large volumes of acid-forming litter. Soil pH, moisture, temperature, presence of O<sub>2</sub> and high concentrations of trace metals in soils have been shown to retard the decomposition rate of litter leading to accumulation (White, 1989; Rowell, 1994; Coughtrey *et al.*, 1979; Martin and Bullock, 1994). When soils are base-unsaturated and highly acidic, such as those of the Ashen Series, litter decomposition is retarded because earthworms

(Annelida), one of the major litter decomposers, are rarely present in soils of pH<4.5 (White, 1989; Rowell, 1994).

The accumulation of litter in the surface horizons of ecosystems enriched with trace metals through aerial deposition is well documented (Coughtrey *et al.*, 1979; Martin and Bullock, 1994). In a study of three woodlands at varying distance of 2.9 km to 23 km from a primary Zn smelter at Avonmouth, UK, Coughtrey *et al.* (1979) found that when compared with a relatively uncontaminated control woodland at 23 km from the smelter, the standing crop of litter in Hallen Wood at 2.9 km was nine times greater. The accumulation was strongly related to the Zn and Cd concentrations in the litter. To determine the explanation for this phenomenon, Coughtrey *et al.* (1979) studied the micro and macro fauna in the soil and litter of the woodlands. Laboratory experiments showed that when microbial populations of the soil and leaf litter collected from the woodlands were grown in agar culture plates enriched with Pb, Zn and Cd, the populations, which included fungi, showed tolerance to the trace metals, but significant changes in abundance or diversity were not apparent (Gingell *et al.*, 1976; Martin *et al.*, 1980). There were marked differences however, between the taxa of invertebrate fauna present in soil and litter from uncontaminated and contaminated woodlands (Hopkin *et al.*, 1985). Woodlice (Isopoda), millipedes (Diplopoda) and earthworms, the most important invertebrates in terms of litter comminution and decomposition, were greatly reduced in numbers per unit area in woodlands contaminated by the smelter (Martin and Bullock, 1994).

A notable feature of this present study at the Mineries was the absence of invertebrates in the soil samples collected. With the exception of ants, whose colonies were often a feature of the fine tailings piles in the study area, just two earthworms and one millipede were present in the total number of soil samples collected in the course of the study. The apparent absence of soil and litter invertebrates across the study area in general may partly explain the relatively high percentage of organic matter in the soils throughout the area (Figures 4.9 and 4.10). The normal range of organic matter in temperate soils was described by Alloway (1990) as being between 1% and 8%. Using Loss-on-Ignition as a rough estimate of the organic matter content of the soil (Rowell, 1994), 77.9% of the soils in the study area at surface were above 8% Loss-on-Ignition, and 85.7% were above 8% at depth. However, the relatively high Loss-on-Ignition values may not be a true reflection of organic matter. Although Loss-on-Ignition is often used in geochemical studies of this nature as an indication of the organic matter content of a soil, the gravimetric method used in its determination has some serious limitations that must be considered.

Loss-on-Ignition is usually determined by heating to 500 °C for approximately eight hours (Rowell, 1994). If a soil contains considerable amounts of clay and sesquioxides, it may lose water inherent in the structure of these soil components at temperatures of between 105 °C and 500 °C. At 280°C to 400 °C for example, goethite is dehydrated to haematite, releasing structural water thus:



Further losses in sample mass may also occur as  $\text{CaCO}_3$  loses  $\text{CO}_2$  to form calcium oxide, although this reaction tends to take place at temperatures from around

707°C. Rowell (1994) argued that because of these factors, Loss-on-Ignition may be an approximate measure of the organic matter content of a sandy soil, but in soils with a high clay content, the percentage Loss-on-Ignition may be up twice that of the true organic matter content. Findlay's (1965) study showed that samples of Maesbury, Nordrach, Thrupe and Ashen topsoils contained 22%, 20%, 17% and 13% clay respectively. In all cases, silt at 42%, 56%, 60% and 43% were the greatest single soil component.

The loss of soil structural water and CO<sub>2</sub> may go some way to explain the % Loss-on-Ignition content in some of the wastes on the site that had little or no vegetation cover. Sampling point 70 for example was devoid of vegetation, yet showed Loss-on-Ignition values of 5.6% at surface and 4.6% at depth (Table 4.22). However, although no vascular plants had colonised the sampling point where the nine subsamples were taken, an input of organic matter may have occurred through the deposition of litter and seeds from the surrounding plant communities, or from residues of previous growths of mosses or lichen, the presence of soil algae, fungi and other soil microbes, or organic residues from animals. As the area contained no apparent microhabitats for soil invertebrates and elevated concentrations of trace metals, what organic input there was may have remained in an undecomposed state and had accumulated over time.

An apparent anomaly in the distribution of Loss-on-Ignition throughout the study area was that in 35% of the sampling points, percentage Loss-on-Ignition was greater at depth than at surface (Figures 4.9 and 4.10). It is likely that this distribution may have been a reflection of the geological composition of the samples rather than a true reflection of organic matter distribution. The majority



of these sampling points were in areas of tailings and in the mineralised soil of the Nordrach Series. Among the common trends in variables shared by the samples were the elevated concentrations of trace metals, including Fe at depth, and the Dolomitic Conglomerate host rock and gangue mineral content of the tailings, which included calcite (Table 4.11). The Fe in the soil would have contained goethite, and the tailings  $\text{CaCO}_3$  in appreciable quantities. Although the clay content of the samples were not determined as part of this study, there may have been a significant presence of clay at depth in tailings through lessivage from the surface zone (White, 1987; Rowell, 1994). The possibility of the formation of Fe hardpans described by Blowes *et al.* (1991) also cannot be discounted. If lessivage and Fe hardpan formation occurred, the presence of greater concentrations of clays,  $\text{CaCO}_3$  and Fe at depth may have caused a greater reduction in sample mass during analysis for Loss-on-Ignition by water and  $\text{CO}_2$  loss, than in the corresponding samples at surface.

#### **4.8.2 Relative Topsoil Enrichment of trace metals in the study area**

Of all the trace metals, Pb showed the widest distribution of RTE at the greatest RTE ratios (Figure 4.13). The greatest RTE ratios for Pb in the study area were clustered around the Waldegrave smelter stack, a point source which was situated at the top of the condensing flue at ST 35449 15112 on the Reserve (Figures 4.13, 4.29 and 4.30). Elevated RTE ratios continued in sampling points to the north and north east of the point source, through to the north end of the Reserve. There were relatively high RTE ratio in samples on the south and southwest faces of the hill at ST 35455 15165, which directly faced the stack, and into the Stockhill Plantation (Figures 1.2 and 4.13). With the prevailing southwesterly winds, this hillside

would have presented an elevated, exposed surface liable to contamination by aerial deposition from the stack. The pattern of RTE for Cu was similar to that of Pb, although the RTE ratios were lower (Figure 4.22). The elevated RTE ratios for Pb on the hillside immediately adjacent to St. Cuthbert's at the southern end of the Stockhill Plantation (ST 3549 1510) could also have been as a result of the aerial deposition of metal-enriched smelter emissions (flight) from the smelter stacks that once operated at the St. Cuthbert's site between 1857-1908 (Figures 4.29 and 4.30).

The pattern of elevated RTE of Pb on North Hill in relation to the relatively lower RTE of Zn, Cd, Cu, Fe and Mn can be explained in terms of the relative concentrations of trace metals in the smelter emissions, and the retention and mobility of trace metals in the acidic soils of the Ashen Series. As Pb was the metal in production, smelter emissions would have been relatively enriched with this element compared with that of Zn, Cd, Cu, Fe and Mn, so there were relatively higher concentrations of Pb in the soil at surface to begin with. Although all the metals may have leached vertically through the soil profile under the extreme acidic soil conditions, in accordance with the mobility sequence proposed by Campbell *et al.* (1983), it is possible that Pb, and to a lesser extent Cu, has leached out of the surface soils at a slower rate, leaving a relatively high concentration at the surface over the one hundred years since smelting ceased. Lead and Cu has a strong affinity for the fulvic and humic acid components of organic matter in the following series:

Fulvic acid (pH 5) Cu > Pb > Zn (Schnitzer and Skinner, 1967)

Humic acid (pH 4-6) Cu > Pb > Cd > Zn (Stevenson, 1977).

Although no other trace metal showed such a pronounced pattern of RTE as Pb around the Waldegrave stack, a clustering of slightly elevated RTE for Cu, Fe and Mn were shown in the area of the St. Cuthbert's smelter stacks (ST 3545 1515). With the exception of Cd, which showed no RTE, where RTE was present, all trace metals showed a general pattern of elevated RTE ratios that followed the prevailing southwesterly wind direction. The reason for the elevated RTE for Fe and Mn to the north and north east of the Waldegrave smelter stack point source may be related to the possible smelting of Fe ore, and the use of Fe in the smelting process. Iron (and consequently its substitutive Mn) may have been smelted on the Reserve for a short period in the late 19<sup>th</sup> century, and this may have been one source of the pattern of elevated RTE for Fe (Gough, 1967).

The Waldegrave Leadworks was bought in 1873 by the Mendip Haematite and Lead Mining Company. The company's prospectus stressed the importance of investment in additional dressing machinery and other technology for the working of both Pb and Fe. The company went into liquidation in 1877, and there appears to be no surviving records of the company's output of Fe, if any. However, Curwen-Salmon (1864) recorded that limestone and Fe in the form of ironstone was added to the Pb smelting process at St Cuthbert's as a flux to aid smelting. When used as a flux, FeO<sub>2</sub> combines with any silica present in the smelter to form a free-running fayalitic slag (Willies, 1990). While there is no specific documentary evidence to support the intentional use of an Fe flux at the Waldegrave Leadworks, Curwen-Salmon's (1864) report is contemporary with the Waldegrave operation, and it is possible that Fe was also used as an aid to smelting on that site, leading to the pattern of RTE to the north and north east of the

Waldegrave stack, and the cluster of RTE around the area of the St Cuthbert's stacks. The lower RTE and enrichment at depth for Fe in the soils of the Ashen Series immediately around the Waldegrave stack, can be explained in terms of the cheluvation processes which occur in podsoles of this type (White, 1989). The chelation and leaching of the ferrous-organic complexes is called cheluvation, and podsolisation is the cheluvation of Fe and Al from insoluble oxides in the surface layers of a soil, and their subsequent deposition, along with organic matter, in a deeper layer of the profile (White, 1989). During podsolisation, precipitated Fe at depth gives the soil an orange-red colour, which was recorded in a number of samples from the study area (Table 4.22) (White, 1981).

There is the possibility that localised RTE for all trace metals present in tailings may have took place since the closure of leadworking in the study area. Before the study area was colonised by vegetation in the post-industrial phase, photographic evidence showed that considerable areas of tailings and disturbed ground were virtually devoid of vegetation and vulnerable to being blown by wind (Stokes, 1999). Several workers have shown that windblown dust from tailings produce wide halos of metal enhancement around the source (Johnson *et al.*, 1978; Davies and White, 1981). Wind-borne enriched dusts may have been redeposited around the study area, but the redistribution, like the deposition of flight, would have followed the pattern of the prevailing winds. The gravitational creep of tailings from piles may also transport metal-enriched wastes around a site, and over relatively uncontaminated areas causing RTE. Davies (1983) described the fan of contaminated land that can originate from tailings piles and waste heaps. The extent of the deliberate movement of tailings and other refuse around the site after

closure is not recorded, although the large complex of tailings piles, terraces and settlement ponds at the St Cuthbert's Works, (ST 35455 15065) shown in Stokes (1999), no longer exist.

Most noticeably in the case of Cd, but for all trace metals, there was a pattern of elevated RTE ratios following the pathway running south from the Reserve to St. Cuthbert's. From 1893 to 1908, the lease for the Waldegrave Minery on the Reserve and adjoining Chewton Warren ore-field was owned by the leaseholder of the St. Cuthbert's, and for the first time in the recorded history of the Mineries, the two sites were worked as one, by the same concern. During period, the pathway was actually a tramway used to transport wastes from the Waldegrave Leadworks and Chewton Warren, south to the dressing floor and smelters at the St Cuthbert's Leadworks (Figure 4.30). The notable lack of smelter wastes on the Reserve today is most likely a result of this operation. Dusts and other fine particulate matter were probably blown from the material carried in the trams and deposited along the tramway representing a line source of contamination. The deposition and subsequent retention of Cd and other trace metals at surface in this pattern on the eastern edge of the tramway may be due to the prevailing southwesterly winds, and the soil reaction along the tramway. Along the eastern edge of the tramway in the Reserve, soil reaction at surface ranged from pH 5.6 - pH 7.0 (Figure 4.7), which suggests that the geochemistry of these soils may favour the retention of trace metals blown in on the wastes, enhancing RTE.

It is also possible that the tramway itself is continuing to exert an influence on the trace metal concentrations and soil reaction along its path. The tramway bed and

embankments appear to have been constructed, at least in parts, by Dolomitic Conglomerate, probably quarried from the Stockhill Plantation, overlain by mine-waste material. The bed was constructed in a break in the slope at the base of North Hill, and now effectively forms a distinct, physical barrier between the soils of the Ashen Series around North Hill, and the Thrupe Series which lie along the valley bottom (Figure 2.2). The reddish brown colour and sandy texture of the material used in construction appear similar to the coarser wastes on the site, and there are fragments of glassy black and grey slags embedded in the surface.

However, it is equally possible that the surface layers of the tramway bed had this material deposited on it during its subsequent use. Whatever the origin, it is possible that continuing gravitational creep, the windblown movement of material, and the leaching of soil solutes is occurring to the east of the tramway along its length, as the ground falls steeply away to the east. This would indicate the possibility that as well as being an historical source of RTE of trace metals to the surrounding soils, the tramway itself may be a continuing, present-day line source of trace metal contamination to the surface horizons of the surrounding soils, increasing their RTE. Similarly, this argument may be applied to the pH distribution of soils surrounding the tramway. The material used to construct the tramway may be the source of Ca and Mg cations, either continually leaching into the surrounding soils from the tramway itself, or from the movement of material into the area, causing a localised elevation of soil pH values.

In general, there was little or no RTE for all trace metals in the areas of tailings in the Reserve centred around ST 35475 15135, the area to the south of the

St. Cuthbert's pool around ST 3546 1507 and a number of sampling points in the Stockhill Plantation. Several explanations are proposed for the absence of RTE in these areas. The topography of the Stockhill Plantation is typical of gruffy ground; the long, sometimes deep mining grooves remain. Samples were taken from the bottom of grooves, the sides of which may have physically sheltered the soil from the smelter emissions. Soils in the Stockhill Plantation must also have undergone considerable disturbance and possible remediation from 1938, when the area was put under forestry. The geochemistry of the tailings at the Reserve and St. Cuthbert's, and the soils of Stockhill may be such that there was aerial deposition of trace metals from smelter emissions, but the trace metals have leached out of the surface zone to depth or lower in the profile. This may have been the case in the Nordrach soils, where pH values were mostly acidic (Figures 4.7 and 4.8).

The soil pH in the areas of little or no RTE in the tailings on the Reserve and at the St. Cuthbert's were generally not acidic (Figure 4.7 and 4.8), and in soils where pH is elevated there is usually a reduction in trace metal mobility (Campbell *et al.*, 1984; Alloway, 1990). However, while the presence of  $\text{CaCO}_3$  and generally elevated pH in tailings were found to inhibit the mobilisation of trace metals down through soil profiles at historical smelting sites in Derbyshire, migration did occur under these conditions, but to a lesser degree than under conditions of lower soil pH (Maskell *et al.*, 1995). Therefore, it is possible that where there was little or no RTE, trace metal migration in the tailings of the study area did take place to an extent where concentrations were lowered at surface and enriched at depth. The possible presence of a Fe hardpan in areas of tailings where trace metals are

leached down through the profile until their accumulation in the hardpan at depth described by Blowes *et al.* (1991) could also account for this particular distribution of sites where there was little or no RTE.

The absence of RTE in the tailings of the Reserve and St. Cuthbert's may also have been influenced by the upward movement of trace metals through the soil profile. Although most workers investigate the downward movement of trace metals through soil profiles, due to the potential threat of contamination of the water table, a small scale study by Smith and Bell (1985) showed that it is possible for Pb, Zn and Cd to migrate upwards through a soil column. In a field soil, groundwater (water which permanently saturates soil pore space below the soil surface) is drawn up through the profile in continuous pores until the suction gradient acting upwards is balanced by the gravitational potential gradient (White, 1989). Depending on the pore size distribution in the soil, this capillary rise can occur up to 1 m in sandy soils and up to 2 m in some silt-loams. In some soils, prolonged evaporation losses, which happen when the water table is within the range of the capillary rise zone of a soil, can cause salts to accumulate at the surface (White, 1989). After periods of prolonged rainfall, standing water was frequently observed in the valley running through the study area. If samples were collected from the study area in dry periods after the rainfall, it is possible that dissolved trace metal salts, or metal-enhanced colloidal particles from zones of enrichment lower down the profile may have migrated upwards in groundwater by capillary rise and accumulated in surface layers.



Uncontaminated soils from remote agricultural areas were found to have RTE ratios of 1.2-2.0 for Pb, while at metal mining sites RTE ratios for Pb were typically 4-20 (Colbourne and Thornton, 1978). Forty-five percent of the sampling points were shown to have a RTE for Pb of below 2.0 (Figure 4.13) and does not fit the pattern suggested by Colbourne and Thornton (1978) or Martin and Coughtrey (1982). However, the soils of the study area are clearly not uncontaminated by Pb, and it is suggested that on sites such as this, if RTE is considered along with other evidence such as trace metal concentration data, pH, Loss-on-Ignition, soil texture and vegetation cover, the source of trace metal contamination might be determined. This can be useful tool in the reconstruction of the movement of contaminated material around a site. For example, the absence of RTE combined with high Pb concentrations in the order of tens of thousands of  $\mu\text{g g}^{-1}$  at surface and depth, elevated concentrations of other trace metals and a loose, sandy or clay texture different to that expected for the soil Series, indicated the presence of tailings. The tailings may be in the form of discrete piles, the remains of former piles, transported to the area of the sample point as infill, or used in the construction of dams or embankments. Data was examined for these factors and results were mapped to show the pattern of deposition of tailings and beneficiation wastes in the study area (Figure 4.31) A number of sites within the study area were identified by this method as former area of tailings that had not been previously mapped.

This map has been removed from the digitized thesis for copyright reasons.

Figure 4.31. Distribution of tailings and smelter wastes in the study area.

### 4.8.3 Contamination of the study area by trace metals

As shown in Table 4.49, nearly 39% of the samples collected from the whole study area was considered to be physically disturbed in some way by mining, beneficiation or smelting processes. Of the sites within the study area, the St. Cuthbert's was the most affected with 91% of samples considered disturbed by beneficiation and smelting. The soil samples collected from the agricultural area above the Reserve had apparently not been disturbed by the industry at all.

Table 4.49. Percentage of soil samples considered to be disturbed by mining, beneficiation and/or smelting at each site in the study area.

Site	Number of soil samples collected from site	Number of soil samples considered disturbed	Percentage of total soil samples considered disturbed
Study Area	77	30	39
Priddy Mineries Reserve	51	18	35
St. Cuthbert's	11	10	91
Stockhill Plantation	12	2	17
Agricultural Land	3	0	0

Trace metal concentration data for surface in the study area were compared with the Kelly values used in the Greater London Council classification system for contaminated land (Table 4.6).

An assessment of the soil of the study area showed that using this classification, 93.5% of the samples collected were classified as slightly to unusually heavily contaminated by Pb (Table 4.50).

Table 4.50. Percentage of soils (surface) in the All Soil Data set falling (n=77) within the Greater London Council Contamination Classes for total trace metal concentrations ( $\mu\text{g g}^{-1}$ ).

	Typical Uncontaminated	Slight Contamination Class 1	Contaminated Class 2	Heavily Contaminated Class 3	Unusually heavy Contamination Class B
Pb	6.5	5.0	21.0	23.5	44.0
Zn	44.0	12.0	6.5	22.0	15.5
Cd	15.5	57.0	25.0	2.5	0.0
Cu	96.0	4.0	0.0	0.0	0.0
Mn	48.0	13.0	22.0	17.0	0.0

Of the 44% of samples that were considered unusually heavily contaminated by Pb, 44% contained over 50 000  $\mu\text{g g}^{-1}$  Pb (Table 4.50). For Zn, 66% of the samples collected were classified as slightly to unusually heavily contaminated, while over 50% of the samples collected were classified as slightly to heavily contaminated for Cd and Mn. Only 4% of the samples collected were classified as slightly contaminated by Cu. The order of contamination magnitude as a ranking of the percentages of samples classified as contaminated for the All Soil Data set was Pb>Zn>Cd>Mn>Cu, which was the same as described for the soils of Mendip (Ginnevar, 1985), and for Halkyn mining district by Davies and Roberts (1978).

Compared with Ginnevar's (1985) case study of the Priddy Mineries area, where soil samples were collected from 0-150 mm depth, the median values of all soil parameters at surface in the All Soil Data set were smaller (Table 4.51). The range of values for soil parameters in Ginnevar's (1985) data conformed more closely to the parameters values of tailings in the All Soil Data set. Ginnevar's (1985) samples were collected from the St. Cuthbert's Leadworks (St. Cuthbert's) and Waldegrave Works (Priddy Mineries Reserve). The grid references of the sampling points and comparison of the parameter values with the values found in

this study indicated that Ginnevar (1985) sampled exclusively from areas of tailings or disturbed ground.

Table 4.51. Comparison of parameter range and median values between the All Soil Data set, tailings and Ginnevar's (1985) Priddy Case Study.

	<b>Ginnevar (1985) Priddy Case Study (N=6) Trace Metals in <math>\mu\text{g g}^{-1}</math></b>		<b>Present Study All Soil Data Set (n=77) Trace Metals in <math>\mu\text{g g}^{-1}</math></b>		<b>Present Study tailings (n=16) Trace Metals in <math>\mu\text{g g}^{-1}</math></b>	
	<b>Range</b>	<b>Median</b>	<b>Range</b>	<b>Median</b>	<b>Range</b>	<b>Median</b>
Pb	27 854-68 251	54 139	262-138 800	4 502	29 553-76 887	59 220
Zn	438-10 051	5 229	13-10 349	455	931-10 349	4 451
Cd	0.6-10.2	8.3	1-12	1	1-12	5
pH	5.4-7.2	6.9	3.0-7.3	4.5	4.5-7.3	6.4
L-o-I	9.9%-27.1%	14.4%	3.9 %-53.4%	11.3%	5.6%-18.9%	6.4%

In terms of sample spread and number, it could be argued that the results of this study are more representative of the environmental legacy of mining, beneficiation and smelting in this area.

It was possible to match three of the seven sampling points used by Ginnevar (1985) to sampling points used in this study. The difference between Ginnevar's (1985) trace metal data and the matched data from this study was calculated as % CV (Table 4.52). The least variability between samples from this study and from Ginnevar's (1985) study was for soil Pb and the greatest was for Cu.

Table 4.52. Variability between the data from this study and Ginnevar's (1986) data from the Priddy Mineries Reserve and St. Cuthbert's.

Sample Reference Number		% CV			
Ginnevar (1985)	This Study	Pb	Zn	Cd	Cu
2388	46	5.07	1.47	10.35	43.91
2385	45	18.72	35.73	43.66	67.25
2363	33	1.98	13.64	17.64	29.47

When variables such as possibly not collecting from the exact sampling point, the 10 years between sample collection, possible differences in the month of collection, climactic conditions immediately preceding collection, difference in sample depth (surface for this study, and 0-150 mm for Ginnevar (1985)) and equipment and analytical methods used are considered, the variability of soil Pb concentrations between the studies was remarkably small. It could equally be argued that the same variables could also account for the greater variation between some samples, such as that between samples 2385 and 45 for example.

As the land surrounding the study area is under agriculture, the data for the study area at surface were also compared with the ICRCL Trigger values for total trace metal concentration in minespoil-contaminated soil (Tables 4.7 and 4.8). For Pb, only one soil sample was below the ICRCL threshold trigger concentration of 300  $\mu\text{g g}^{-1}$ , and only 19% of the samples were below the action trigger concentrations, making the land generally unsuitable for agricultural use (Table 4.53).

Table 4.53. Percentage of soils (surface) in the study area (n=77) falling within the ICRCL Threshold and Action Trigger concentrations for total trace metal concentrations ( $\mu\text{g g}^{-1}$ ).

	Percentage of soil samples less than Threshold Trigger Concentration	Percentage of soil samples less than the maximum 'Action Trigger' concentrations	
		Grazing Livestock	Crop Growth
Pb	1	19	--
Zn	60	70	60
Cd	66	100	100
Cu	100	100	100

Of the three soil samples at surface taken from the agricultural land above the Reserve, two were only slightly above the threshold trigger concentration of  $300 \mu\text{g g}^{-1}$  at  $317 \mu\text{g g}^{-1}$  and  $367 \mu\text{g g}^{-1}$ , while the third was slightly above the action trigger concentration of  $1\,000 \mu\text{g g}^{-1}$  at  $1046 \mu\text{g g}^{-1}$ . Zinc, Cd and Cu at surface were below the ICRCL threshold trigger concentrations (Tables 4.6 and 4.22).

Trace metal concentration data for surface in the Priddy Mineries Reserve Data set were compared with the Kelly values used in the Greater London Council classification system for contaminated land (Table 4.6). For soil Pb, 94% of the samples classified as slightly to unusually heavily contaminated, with 39% classified as unusually highly contaminated (Table 4.54). For soil Zn, 43% of the samples were classified as contaminated to unusually heavily contaminated. A total of 33.5% of the soil samples showed slight to heavy Cd contamination, while only 4% of samples were found to be slightly contaminated by Cu. For soil Mn, 46% of the samples were in the slight to heavy contamination classification (Table 4.54).

Table 4.54. Percentage of soils (surface) in the Priddy Mineries Reserve Data set falling within the Greater London Council Contamination Classes for total trace metal concentrations ( $\mu\text{g g}^{-1}$ ).

	Typical Uncontaminated	Slight Contamination Class 1	Contaminated Class 2	Heavily Contaminated Class 3	Unusually heavy Contamination Class B
Pb	6.0	6.0	27.5	21.5	39.0
Zn	57.0	0.0	6.0	19.5	17.5
Cd	66.5	8.0	21.5	4.0	0.0
Cu	96.0	4.0	0.0	0.0	0.0
Mn	63.0	10.0	18.0	9.0	0.0

The order of contamination magnitude as a ranking of the percentages of samples classified as contaminated for the Priddy Mineries Reserve Data set was slightly different to that of the All Soil Data set at  $\text{Pb} > \text{Mn} > \text{Zn} > \text{Cd} > \text{Cu}$ .

The data for the Priddy Mineries Reserve at surface were compared with the ICRCL trigger values for total trace metal concentration in minespoil-contaminated soil. With the exception of Zn, where the percentage of samples below the action trigger concentration for grazing livestock was lower at 12% than that of 19% for the study area, the pattern of contamination was similar to that for the whole study area (Table 4.55). For Pb, only one soil sample was below the ICRCL threshold trigger concentration of  $300 \mu\text{g g}^{-1}$ , and only 10% of the samples were below the action trigger concentrations, making the land generally unsuitable for agricultural use (Table 4.55). The unsuitability of the Reserve in terms of metal contamination for the grazing of livestock has been acknowledged. The Somerset Wildlife Trust's interpretation boards at the Priddy Mineries Reserve states that because of the trace metal contamination, the grazing of livestock is not permitted.



Table 4.55. Percentage of soils (surface) in the Priddy Mineries Reserve Data set (n=51) falling within the ICRCL Threshold and Action Trigger concentrations for total trace metal concentrations ( $\mu\text{g g}^{-1}$ ).

	Percentage of soil samples less than Threshold Trigger Concentration	Percentage of soil samples less than the maximum 'Action Trigger' concentrations	
		Grazing Livestock	Crop Growth
Pb	2	12	--
Zn	61	70	61
Cd	69	100	100
Cu	100	100	100

The percentage of soil samples in the St. Cuthbert's Data set (n=11) falling within the Greater London Council heavily to unusually heavily contamination classes was 100% for Pb, with 91% classified as unusually heavily contaminated (Table 4.56). For Zn, 100% of the soil samples were in the slight to unusually heavily contaminated classes, with 27% in the unusually heavily contaminated classification. Soils were slightly contaminated to contaminated by Cd in 73% of the samples and 91% of samples showed slight to heavy contamination by Mn.

Table 4.56. Percentage of soils (surface) in the St. Cuthbert's Data set falling within the Greater London Council Contamination Classes for total trace metal concentrations ( $\mu\text{g g}^{-1}$ ).

	Typical Uncontaminated	Slight Contamination Class 1	Contaminated Class 2	Heavily Contaminated Class 3	Unusually heavy Contamination Class B
Pb	0.0	0.0	0.0	9.0	91.0
Zn	0.0	9.0	0.0	64.0	27.0
Cd	27.0	9.0	64.0	0.0	0.0
Cu	91.0	9.0	0.0	0.0	0.0
Mn	9.0	18.0	45.5	27.5	0.0

Of the sites in the study area, St. Cuthbert's was the most highly contaminated both in terms of number of samples and range of metal concentrations for Pb, Zn and

Cu. The order of contamination magnitude as a ranking of the percentages of samples classified as contaminated for the St. Cuthbert's Data set at  $Pb=Zn>Mn>Cd>Cu$  was slightly different to that of the All Soil Data and Priddy Mineries Reserve data sets. Without major remediation, the extensive chemical and physical disturbance of the soils of St. Cuthbert's, and its remaining industrial archaeology precludes the site from being returned to agriculture.

The concentration of soil Pb at some sampling points in the St. Cuthbert's site were found to be among the greatest recorded in geochemical studies carried out on historical mining and smelting sites in the British Isles (Table 4.9). However, there is evidence to suggest that Pb could be present in the soils at St. Cuthbert's at even greater concentrations. Stenner (1978) recorded one sediment sample from St Cuthbert's Swallet, a sinkhole in the St. Cuthbert's where the water from the three steams draining the Mineries enter the local cave system, as containing over  $300\,000\ \mu\text{g g}^{-1}$  Pb. The sample was prepared for analysis by  $\text{HNO}_3$  decomposition, the same method used in this study, and the result was confirmed by X-ray fluorescence.

A comparison between the concentration of Pb, Zn, Cd and Cu in the soils from St. Cuthbert's found in this study and Stenner's (1978) study showed that although Stenner's (1978) samples were taken from around hydrological features on the site, at some distance from the tailings piles, in terms of order of magnitude of concentration, the results were similar (Table 4.57). The results of the St. Cuthbert's Data set in the present study confirmed Stenner's (1978) results, which indicated the widespread contamination of soils by Pb, Zn and Cd at the

St. Cuthbert's site.

Table 4.57. Comparison of mean trace metal concentrations between soils at surface from the St. Cuthbert's site in the present study and of mixed profile in Stenner's (1978) study.

	Present Study St. Cuthbert's Data Set Trace Metals in $\mu\text{g g}^{-1}$ (n=11)		Stenner (1978) St. Cuthbert's Trace Metals in $\mu\text{g g}^{-1}$ (n=8)		means of both studies % CV
	mean	median	mean	median	
Pb	52 111 $\pm$ 38 241	52 382	35 662 $\pm$ 1 6969	38 000	18.7
Zn	3 621 $\pm$ 1 849	4 255	2 231 $\pm$ 1 127	1 850	23.8
Cd	5.09 $\pm$ 3.02	6.0	3.38 $\pm$ 2.1	2.5	20.2
Cu	64.90 $\pm$ 47.1	50.0	39.5 $\pm$ 26.25	32.5	24.3

The trace metal concentration data for surface in the Stockhill Plantation Data set (n=12) were compared with the Greater London Council Soil Contamination Classes, and it was found that 100% of soils were classified as slight to unusually heavy contaminated by Pb (Table 4.58). Of the Pb contaminated samples, 33% were in the unusually heavy contamination class. For soil Zn, 83.5% of the samples were slightly contaminated to contaminated, while 8% of the samples were classified as showing slight contamination by Cd. No samples in the Stockhill Plantation were contaminated by Cu, but 83% of samples were classified as showing slight to heavy contamination by Mn.

Table 4.58. Percentage of soils (surface) in the Stockhill Plantation Data set (n=12) falling within the Greater London Council Contamination Classes for total trace metal concentrations ( $\mu\text{g g}^{-1}$ ).

	Typical Uncontaminated	Slight Contamination Class 1	Contaminated Class 2	Heavily Contaminated Class 3	Unusually heavy Contamination Class B
Pb	0.0	8.5	8.5	50.0	33.0
Zn	16.5	67.0	16.5	0.0	0.0
Cd	92.0	8.0	0.0	0.0	0.0
Cu	100.0	0.0	0.0	0.0	0.0
Mn	17.0	25.0	33.0	25.0	0.0

The order of contamination magnitude as a ranking of the percentages of samples

classified as contaminated for the Stockhill Plantation was Pb>Zn>Mn>Cd>Cu, which was slightly different to that of the all soil data, Priddy Mineries Reserve and St. Cuthbert's Data sets.

The percentage of soil samples below the ICRCL threshold and action trigger concentrations for minespoil-contaminated soil showed a slightly different pattern than that of the All Study and Reserve Data sets (Table 4.59). For Zn and Cd, the percentage of samples less than the threshold trigger concentrations were higher, as was the action trigger concentrations for grazing livestock and crop growth for Zn. Although in this data set only 17% of the samples were classified as above the threshold and action trigger concentrations for crop growth, during the early years of stocking the plantation some of the forest species were reported to have suffered from the toxic effects of Pb and Zn in the soils (Findlay, 1965). *Larix leptolepis* failed to thrive beyond a height of 2.5 -3 m, and the subsequent re-stocking with *Pinus sylvestris* fared little better. Findlay (1965) reported that in the lowest part of the Warren, trees made practically no growth.

Table 4.59. Percentage of soils (surface) in the Stockhill Plantation Data set (n=12) falling within the ICRCL Threshold and Action Trigger concentrations for total trace metal concentrations ( $\mu\text{g g}^{-1}$ ).

	Percentage of soil samples less than Threshold Trigger Concentration	Percentage of soil samples less than the maximum 'Action Trigger' concentrations	
		Grazing Livestock	Crop Growth
Pb	0	8	--
Zn	83	100	83
Cd	92	100	100
Cu	100	100	100

#### **4.8.4 Statistical relationships between soil parameters**

##### All Soil Data set

The significant correlations between the trace metals at the  $p=0.001$  level were typical of soils enriched by mining and smelting in the Mendip area and reflects the local mineralisation (Tables 4.25, 4.26 and 4.27) (Ginnevar, 1985; Li, 1993). Lead mineralisation is strongly associated with Zn, Cd, Fe and Mn in the Dolomitic Conglomerate, and because a large number of the soil samples were enriched by tailings and beneficiation wastes, the metals would be concentrated together in the soils. Trace metals such as Pb, Zn, Cd and Cu are also strongly associated with Fe and Mn oxides in the soil. Lead, Zn, Cd and Cu may be strongly held by specific adsorption sites on Fe and Mn oxides, or be occluded in their structure (Kinniburgh *et al.*, 1976; Jenne 1977; McKenzie, 1980; Robert and Terce, 1989; McBride, 1989).

Soil pH was also significantly correlated at the  $p=0.01$  level with all metals (Tables 4.25, 4.26 and 4.27). The relationship between trace metal retention and increasing soil pH is well documented (Brummer and Hermes, 1983; Campbell, *et al.*, 1983; Bergkvist 1986; LaZerte, 1986; Xian and Shokohifard, 1989). In the soils of the study area, the relationship was related to the industrial wastes and the geochemistry of the surrounding soils. The greatest trace metal concentrations were found in the tailings and wastes, which because of their mineral composition were less acidic than the surrounding soils. The lowest concentrations of trace metals were found in soils less contaminated by the wastes, which happened to be in areas where the soils were more acidic (Figures 4.7 and 4.8). Where these soils were contaminated by smelter emissions, the acidity of the

soil would have depressed adsorption and enhanced leaching down the profile (Brummer and Hermes, 1983; Campbell *et al.*, 1983; Bergkvist 1986).

There were significant negative correlations at the  $p=0.001$  level between Loss-on-Ignition and Fe and Mn at depth (Tables 4.25 and 4.26) and between Loss-on-Ignition, Pb, Zn, Fe and Mn in the stacked All Soil Data set (Table 4.27). This could be argued to reflect the source of trace metal concentrations in the majority of the soils of the study area. The relationship between trace metals in soils and organic matter is well documented, organic matter can hold metals on cation exchange sites and in Organo-metal complexes (Ross, 1994c). Positive correlations between organic matter and trace metal concentrations might be expected, especially if the source of the trace metal enrichment was through aerial deposition. However, if trace metals were inherent in the parent material of the soil, as is the case in the study site, then their concentrations would be distributed throughout the mineral fraction of the soil and not necessarily associated with the surface horizons, where most organic matter occurs. The presence of an Fe pan in many of the soils also meant that concentrations of Fe and associated Mn was greater at depth, so therefore again not associated with high concentrations of organic matter. In soils where enrichment occurred through aerial deposition, trace metal concentrations might be expected to be more strongly associated with organic matter. However, in the study site, the soils of North Hill, where the greatest contamination by aerial emissions occurred, was highly acidic, preventing adsorption and enhancing leaching down through the soil profile (Brummer and Hermes, 1983; Campbell, *et al.*, 1983; Bergkvist 1986).

Another possible interpretation of the significant negative relationship between these trace metals and Loss-on-Ignition is that greater trace metal concentrations inhibit the production of organic matter, which might be reflected in lower loss-on-Ignition values. The highest concentrations of trace metals were found in the tailings piles, and the physiochemical factors found on tailings piles, such as desiccation, extreme variation in substrate temperature, substrate instability and low nutrient status inhibit colonisation (Marrs and Bradshaw, 1993). The concentrations of trace metals are also often high enough to cause severe phytotoxic effects (Turner, 1994). This acts as a powerful selection force on plant population, and metal tolerant genotypes have evolved (Bradshaw, 1984). On many of the tailings piles in the study area the plant communities were low-growing, dune-like communities, and compared with the *Molinia caerulea* and mire communities on the Ashen and Thrupe soils, produced relatively little biomass or plant litter (Table 4.23). The negative correlations between trace metal concentrations and Loss-on-Ignition, therefore, may be a function of the influence of the substrate and metal concentrations of the tailings on the production of litter.

#### Priddy Mineries Reserve Data set

The pattern of Pearson correlations between soil parameters in this data set followed that of the All Soil Data set exactly (Tables 4.30, 4.31 and 4.32). This was because the data from the Priddy Mineries Reserve Data set made up the majority of the data in the All Soil Data set (51/77). The ranges of soil parameter values for both data sets were very similar as the acid soil with low trace metal concentrations and the less acidic tailings with greater metal concentrations were present in both data sets.

### St. Cuthbert's Data set

Although there were still the general significant positive correlations between trace metals, the Pearson correlations between the soil parameters of the St. Cuthbert's data set also differed slightly from those of the All Soil Data and Priddy Mineries Reserve Data sets (Tables 4.35, 4.36 and 4.37). There were fewer significant positive correlations at the  $p=0.001$  level, and generally at the  $p\leq 0.05$  level between pH and trace metal parameters, and no significant negative correlations between Loss-on-Ignition and any other parameter. There were significant positive correlations at the  $p\leq 0.05$  level between surface Pb, Cu, Fe and Mn and between Zn and Cd. There were also significant positive correlations at the  $p\leq 0.05$  level between these metals at depth.

The St. Cuthbert's Data set was a much smaller data set than the All Soil Data or Priddy Mineries Reserve Data sets. The range of values for each soil parameter was also generally smaller, and the soils showed a greater degree of homogeneity because the origin of the trace metals in most samples was beneficiation waste. (Tables 4.21, 4.33 and 4.28). Although the higher pH and related greater trace metal concentrations observed in the wastes in the Priddy Mineries Reserve were present, the low soil pH values and corresponding lower trace metal concentrations found in the Ashen and Nordrach soils were absent. These factors were reflected in the fewer significant statistical trends between soil parameters.

### Stockhill Plantation Data set

The number and pattern of significant positive correlations at the  $p\leq 0.05$  level generally followed that of the St. Cuthbert's Data set, except that all trace metals



were positively correlated with Mn at the  $p \leq 0.05$  level (Tables 4.41, 4.42 and 4.43). As with all data sets, there were significant positive correlations at the  $p \leq 0.05$  level between most trace metals at the same depth and pH, but again like the St. Cuthbert's Data set, the sample number was smaller, the Ashen soil series was absent, and the range of soil parameter values smaller than those in the All Soil Data and Priddy Mineries Reserve Data set.

#### **4.8.5 Sampling and analytical precision**

The precision of the field sampling varied between 0.63% CV for pH and 20.70% CV for Cd (Table 4.45). Soil is a heterogeneous material, significant variation in trace metal concentrations may occur within short distances. In soils such as those in the study area, variation in concentrations between duplicates may be caused by the presence mineral or slag fragments or weathering products like cerussite (Stenner, 1978). The precision of analytical replicates however, should be greater and this was the case in this study for BCR CRM 143R Sewage Sludge Amended Soil, the in-house reference soil and the sample replicate analyses (Tables 4.46, 4.47 and 4.48). With the exception of Fe in the reference soils, the % CV for all sample replicates were within the target of 10% CV. In Mendip soil, Fe is usually associated with the mineral fraction (Li, 1993), and it is possible that  $\text{HNO}_3$  was not always able to fully decompose the Fe from the mineral structure of these soils (Ure, 1990). The accuracy of the soil analysis as measured by the % recovery of trace metals from BCR CRM 143R Sewage Sludge Amended soil, showed that the combined analytical error from the decomposition procedure and analysis by FAAS was below 15% for Pb, Zn, Cd and Cu (Table 4.46). This suggested the possibility that as a guide, the results of the baseline study were

accurate within  $\pm 15\%$ . However, the only accurate way to confirm the accuracy of the analyses would have been for the concentration of the trace metals in the soils to be determined by a technique such as X-ray fluorescence (Stenner, 1978; Ure, 1990).

#### **4.8.6 Summary**

In summary, the most distinctive feature of the distribution of Pb, Zn, Cd, Cu, Fe and Mn in the soils of the study area was that their greatest concentrations were strongly associated with the wastes generated by mining and beneficiation. The high concentrations of the trace metals in the wastes were probably maintained by the geochemical composition of the wastes. This was in agreement with the conclusions of Blowes *et al.* (1991) Murphy (1992) and Merrington (1993), who reported that the retention of trace metals was related to the geochemical composition of the tailings, and the slag particles they often contain.

The lowest trace metal concentrations were associated with the areas of podsolised acidic soil in the study area, where the inputs of Pb, Zn, Cd and Cu were mainly from historic smelter emissions. After aerial deposition, it is possible that the speciation of the trace metals in the smelter emissions and the geochemistry of the soil inhibited the adsorption of the trace metals onto specific adsorption sites, and the acidity of the soil continued to enhance leaching from the surface horizons. In the study area, this was particularly marked for Zn and Cd. This confirmed the work of Li (1993) at Shiphams, where Pb, Zn and Cd deposited by smelter emissions had greater mobility and availability in soils than that deposited with mining and beneficiation wastes.

Although it was beyond the scope of this study to examine metal speciation in the soils, Foster and Lott (1980) and Cotter-Howells (1993) reported that anglesite ( $\text{PbSO}_4$ ), which is relatively soluble species of soil Pb, was the predominant lead mineral in the solid phase of the soils around a Pb smelter site in Derbyshire. It is possible that anglesite may have also been present in the soils of this study area around the smelter site on North Hill.

It is likely that there was some aerial deposition of Fe and Mn into the soils of the study site around the smelters, but Fe and Mn were also inherent in the mineral fraction of the soil. There was further evidence of trace metal enrichment in some soils through natural mineralisation. The Nordrach soils in the Stockhill Plantation, which were overlying the Dolomitic Conglomerate of the Chewton Warren orefield, were enriched with Pb, Zn and Mn above normal background levels as a result of the pattern of mineralisation in the area. Of the three discrete sites in the study area, the most heavily contaminated by trace metals according to the Greater London Council soil contamination scheme was St. Cuthbert's, where most of the soils were enriched by beneficiation wastes and smelter emissions from 1857-1908. The high concentration of Pb at sampling sites 2 and 10 (Figure 4.3), the soil texture and colour and written records suggested that some of the enrichment at St. Cuthbert's probably dated from the Roman and Mediaeval periods (Gough, 1967).

The soils of the study area were shown to contain higher concentrations of Pb and Zn than earlier similar studies on other Pb mining and smelting areas in Britain, which is indicative of the uniqueness of the site. In the study area, the maximum

concentration of soil Pb was  $171\,668\ \mu\text{g g}^{-1}$ , and the maximum concentration of soil Zn  $10\,349\ \mu\text{g g}^{-1}$  (Table 4.21). In comparison, the Ystwyth Valley and Tanant Valley soils of Pb mining areas in Wales contained maxima of  $3\,393\ \mu\text{g g}^{-1}$  and  $4\,800\ \mu\text{g g}^{-1}$  soil Pb respectively, and  $1\,750\ \mu\text{g g}^{-1}$  and  $5\,520\ \mu\text{g g}^{-1}$  soil Zn (Table 4.9) (Fuge, Paveley and Holdham, 1989; Alloway, 1990). More recent studies by Maskell *et al.* (1995) at Derbyshire and Clwyd, Wales, determined soil Pb at maximum concentrations of  $>35\,000\ \mu\text{g g}^{-1}$  and  $3\,500\ \mu\text{g g}^{-1}$  respectively, and soil Zn at  $8\,930\ \mu\text{g g}^{-1}$  and  $703\ \mu\text{g g}^{-1}$ . However, the maximum soil Pb concentration of  $171\,668\ \mu\text{g g}^{-1}$  in this present study was lower than Stenner's (1978) earlier work on the soils of the St. Cuthbert's site, where a maximum value of  $330\,000\ \mu\text{g g}^{-1}$  for soil Pb was determined. The maximum concentration of soil Zn at  $4\,200\ \mu\text{g g}^{-1}$  determined by Stenner (1978) was less than that of the present study at  $10\,349\ \mu\text{g g}^{-1}$  (Table 4.21 and Section 4.1.7).

The data generated by this present baseline study went some way to address Ginnevar's (1985) recommendation for a more detailed investigation into the trace metal enrichment of the Mendip uplands. Ginnevar (1985) concluded from her study that compared with other mining areas, the mean concentrations of Pb, Zn, Cd and Cu were lower for the Somerset area, and that the contamination from mining and smelting wastes were less widespread than that for the Halkyn Pb mining area in Wales. However, Ginnevar (1985), divided the Somerset region into the Mendip uplands, Lowland moors and Liassic lowlands, and collected 62% of the total samples from the moors and lowlands, areas where mining did not take place. Furthermore, she suspected that the 2 km x 2 km sampling grid

employed in her sampling regime was not of sufficient resolution to identify the local geochemical variation on Mendip. This study confirmed Ginnevar's (1985) suspicions about the Mendip uplands and demonstrated that the area around the Priddy Mineries is not only one of the most intensely metal-enriched historic mining and smelting sites on Mendip, but may also be considered to be intensely metal-enriched in a national context.

## **CHAPTER 5**

### **ASSESSMENT OF TEMPORAL VARIATION IN SOIL TRACE METAL CONTENT**

#### **5.1 Introduction**

##### **5.1.1 Aim and objectives**

The geochemical data from which the baseline study was constructed were derived from samples collected during the period February 1995 to April 1997. The aim of this phase of the study was to evaluate the reliability of the baseline data in terms of seasonal variation in geochemical parameters. This was achieved by monthly sampling and analysis of soils from representative profiles of the four soil series and one beneficiation waste (Tailings) present on the site, during the period September 1998 - August 1999.

##### **5.1.2 Rationale for a temporal study**

A baseline soil survey is essentially a record of the distribution of geochemical data; in this case, that of selected trace metals, in a particular area at the specific time the samples were collected. How representative of the true distribution of the geochemical parameters under investigation is dependent on the minimisation of error arising from sampling and subsequent chemical and statistical analysis and presentation of data. If errors are minimised and confidence limits of the data recognised, the data may then be assessed in a number of ways. The data generated from the sampling points within the area of such a survey may be compared with each other to assess the relative distribution of geochemical

parameters at that site, as a data set to compare with data generated from similar surveys of other sites, with 'typical' or 'normal' values described in 4.1.3 (Swaine, 1955; Kabata-Pendias and Pendias, 1984), or some recommended contamination threshold such as described in 4.1.11 (Kelly, 1979). Although the data generated from the baseline study was used in each of these contexts in 4.21, the primary aim of the study was to assess the local environmental impact of historical lead mining and processing on the soils of the study area, so was therefore essentially an assessment of the geochemical data generated from each sampling point in relation to each other.

Errors may arise from each phase of a geochemical study, from field sampling to statistical analysis. The results from the baseline study indicated the analytical protocol described in 4.2.3 was successful in ensuring that analytical error was minimised to below the 10% CV target for all parameters (Table 4.48). The analysis of field duplicates also showed that the field sampling error ranged from 2.56% CV for Cu, and 20.70% CV for Cd (Table 4.45). The fact remained, however, that the samples were collected at various times on different days, and in different months over a two-year period from February 1995 to April 1997. This raised the following questions: 1. Did temporal variation in geochemical parameters occur at the site? 2. If so, for which parameters in which soils, and by how much? If these questions could be answered, then a more realistic assessment of the reliability of the data in the baseline study could be made.

### **5.1.3 Potential causes of temporal change in trace metal concentration**

Ultimately, change in the concentration of total trace metal content in a soil system over time can only be caused by input to the system, or output from the system.

Trace metal input to a soil system may be through naturally occurring biogeochemical processes within that system, such as the weathering of ore bodies or the recycling of metals in fallen plant litter and faunal residues. Input may also come from outside the system as alluvial inwash of metal-enriched material, or wind blown dusts (Davies and White, 1981). Input may also be of direct anthropogenic origin, such as during the application of agricultural amendments such as sewage sludge or the deposition of mine or smelter wastes (Ross, 1994b; Martin and Coughtrey, 1982). Similarly, losses from the soil system may occur through natural biogeochemical processes such as plant uptake or geochemical leaching, or be of anthropogenic origin. For example, metal-enriched soil may be removed from the system or remediated, or the profile disturbed in some way.

Losses from a soil system may be permanent. Metals leaching down through soil profiles may eventually reach the ground and be transported away (Blowes *et al.*, 1991). In a study of trace metal migration through soils at historical metals sites, Maskell *et al.* (1995) found that the extent and rate of metal migration were influenced by the nature of the soil parent material. Migration distances were greater in soils underlain by sandstone than by clay. Natural losses of trace metals from a soil system may also be temporary, such as in the case of biogeochemical cycling through a closed system, where plant uptake of metals occurs during the growing season, and is returned to the soil through litter fall. As well as true losses, during a monitoring programme, metal 'losses' may occur as an artefact of



sampling error or geochemical processes and analytical procedure. Soil is naturally heterogeneous (Davies *et al.*, 1999), and if during sampling a large fragment of galena was collected as part of a monthly tailings for example, then that sample might show a relatively high Pb concentration compared with that of the following month. However, no true loss (or gain) has actually occurred in the system through temporal variation.

In the case of geochemical processes and analytical procedure, it is well recorded that the chemical speciation of a metal in a soil is not fixed, but dynamic (Ross, 1994c). If the balance of speciation were to change in favour of the residual fraction, where metals become incorporated in the structure of secondary minerals, then extractants such as HNO<sub>3</sub> may not be able to fully decompose the sample so efficiently as it did before. Again, no true temporal loss or gain from the system would have occurred in terms of total metal concentration, although in this case the loss from the available pool would be important if the bioavailable variation of a trace metal were being examined.

#### **5.1.4 Review of previous temporal soil studies**

Much of the temporal soil data available comes from studies carried out on the seasonal variability of trace metals in plants. While many of these contained basic baseline soil data (Flemming and Murphy, 1968; Matthews and Thornton, 1982), some such as those by Shaw (1984), Hajar (1987) and Andrews *et al.* (1989a, 1989b) included temporal soil data. Shaw (1984) studied the uptake of Pb, Zn and Cd in a range of plants in Tideslow Rake, Derbyshire. In common with other studies of this nature, Shaw (1984) analysed soils for bioavailable trace metals,

using 1M ammonium acetate as the extractant. Concentrations of Pb, Zn and Cd were generally found lowest between October and January, and at their greatest in July, August, and March.

Hajar (1987) studied the accumulation of trace metals by *Minuartia verna* and *Thlaspi caeruleans*, both metal hyperaccumulators, in Derbyshire. By using 1M ammonium acetate, Hajar (1987) assessed the seasonal variation of bioavailable metals in soils. Hajar (1987) concluded that there were seasonal changes, the greatest occurring in Pb (Table 5.1). The variation in metal concentration expressed as % CV in Table 5.1 was calculated from Hajar's (1987) raw data in order to allow comparison with data from other studies. The variability represented by the % CV in this context would be the combination of any sampling error, analytical error, seasonal effects and revisit error (Davies *et al.*, 1999)

Table 5.1. Seasonal variation (n=4) of bioavailable trace metals in Dovegang Pb mine-waste soil as expressed by % CV (After Hajar, 1987).

	Pb	Zn	Cd
% CV	53.41	16.79	27.85

Hajar (1987) proposed that the changes might have been related to climate. The lowest concentration of Pb occurred in months of high rainfall, which could have had a leaching effect in the free draining mine spoil.

Andrews *et al.* (1989a) analysed soil samples taken during three months from a revegetated tailings dam at Cavendish Mill, Derbyshire for Total Pb. There was no significant difference in Pb concentrations at the  $p < 0.05$  level between months (Andrews *et al.*, 1989a). The variation expressed as % CV varied from 10.43% to 16.21% CV (Table 5.2).

Table 5.2. Seasonal variation (n=3) of total trace metals in Cavendish Mill tailings dam as expressed by % CV (after Andrews *et al.*, 1989).

Depth (mm)	% CV in Pb concentration
10	10.43
20	16.21
40	15.56
80	14.60

One study solely concerned with the total trace metal concentration of soil, and included a larger scale analysis of seasonal variation was that of Davies *et al.* (1999). The study was carried out on surface soils (0-150 mm) in Venezuela and samples were decomposed with Aqua regia. Seventy samples from each transect were collected along two transects running west-east and south-north in the dry season. Sampling was repeated at the same sampling points in the rainy season. Davies *et al.* (1999) calculated the % CV for each (Table 5.3). Statistical analysis carried out on the data by Davies *et al.* (1999) showed there was no significant difference at the  $p < 0.05$  level between metal trace concentrations in soils in the wet and dry seasons.

Table 5.3. Seasonal variation (n=2) of total trace metals along two transects in Venezuela as expressed by % CV (after Davies *et al.*, 1999).

<b>Transect</b>	<b>% CV in Pb concentration</b>	<b>% CV in Zn concentration</b>	<b>% CV in Cu concentration</b>	<b>% CV in Mn concentration</b>
west-east	17.4	15.3	15.8	25.5
south-north	29.7	30.7	34.2	34.2

### 5.1.5 The temporal soil study

Unfortunately, the issue of temporal change was considered with hindsight, and the time limitations of the study meant that the chance was lost to monitor any seasonal variation of trace metals during the same two-year period of sampling as the baseline study. Another consideration was the environmental impact of a large-scale long-term temporal monitoring regime on the soil system and its surrounding environment. The monthly sampling required for temporal monitoring is destructive to the soil system under study, especially as repeated sampling is carried out within a relatively small area. The process of repeated sampling may also subsequently influence the physical and geochemical characteristics of the soil under study. The effects on the soil would be accumulative over the sampling period, and the resulting data may be influenced and compromised, especially towards the latter stages of such a programme.

An example of how sampling can influence the geochemistry of the system under study is the repeated removal of vegetation and soil organic matter from a small sampling area. Large flushes of acidity are known to be released as a result of the leaching of nitrogen when an area is deforested, or a grassland ploughed

(Rowell, 1994). Scaled down into a 2 m<sup>2</sup> permanent quadrat, for example, it is theoretically possible that the accumulated effects of the monthly removal of 5 samples of vegetation and associated organic matter in the surface horizon could result in changes in soil pH that would have otherwise not have happened. The effects the increase in acidity would have on the soil would be dependent on factors such as its buffering capacity (Rowell, 1994). However, any change in soil geochemistry, especially an overall increase in soil acidity might also subsequently influence other aspects of the soil geochemistry, such as the mobility of trace metals (Ross, 1994c). The immediate environment around a sampling area, including its plant communities, may also suffer other forms of degradation such as trampling and the ensuing compaction of surrounding soil. These considerations are especially important if, like this study area, the land is designated as an SSSI.

Ideally, the baseline survey sampling regime with the addition of duplicate field sampling would have been implemented over a two-year period for the temporal study. However, for the reasons discussed, this would have been unsuitable and the following sampling regime was designed to obtain good quality data with the minimum environmental impact. Rather than sample soils on the site at random, it was decided to sample just five soils, but each of those five soils were chosen as representative of one of the four soil series present and tailings in the study area. Each soil was not only representative of a typical profile for that series, but also supported a plant community typical and abundant on that series. The soils were also chosen for their accessibility. In order to minimise trampling over surrounding plant communities, none were far from an informal footpath, although

the samples were taken away from the footpath itself to avoid the soil compaction associated with trampling. A tailings pile with complete vegetation cover, but with the least abundance of the regionally rare *Minuartia verna* and *Botrychium lunaria* and no *Thlaspi caerulescens*, was chosen to prevent the erosion which may have occurred on a more open tailings pile with repeated visits.

The soil sampling protocol used in the in the baseline study was used as basis when planning the soil sampling programme for the temporal study, however, the following modifications were employed to minimise the environmental impact of the sampling. The collection of samples was restricted to a 2 m<sup>2</sup> area on each soil series. The volume of soil removed in each bulked sample was minimised by reducing the number of sub-samples to five rather than the nine collected in the baseline study. The area covered by the pattern of sampling (4.2.1) was reduced accordingly to a 0.5 m<sup>2</sup> quadrat. Duplicate field samples were collected for 10% of the total samples and sampling was carried out on a monthly basis for one year.

#### **5.1.6 Representative soil profiles**

##### Maesbury Series (ST 35445 15075)

The sampling site was situated in the top Northwest corner of the St. Cuthbert's site, between the mediaeval liberty boundary of Fair Lady Well, and the boundary wall of St. Cuthbert's (Figure 5.1). Samples were collected away from the footpath and leat running west-east down from North Hill, and the stream channel and footpath running north-south along St. Cuthbert's western boundary. The sampling area was flat with a grassland cover of  $\leq 100$  mm height.

This map has been removed from the digitized thesis for copyright reasons.

Figure 5.1. Location of representative soil profiles in the study area.

#### Thrupe Series (ST 35465 15116)

The sampling site was situated approximately 10 m to the west of the tramway, down-slope from a leat draining a small minery reservoir, in open, tussocky vegetation of up to 500 mm height (Figure 5.1). The grassland appeared to be a boundary between a marshy site to the north, and dry, open *Deschampsia flexuosa* grassland to the south. There was a dip in the topography of approximately 3° East, and the site was subjected to sub-surface water running through from the hillside above during the wetter months.

#### Ashen Series (ST 35460 15125)

The sampling site was situated on the eastern slope of North Hill, approximately 5 m from an informal footpath (Figure 5.1). The site was covered by tussocky *Molinia caerulea* grassland, where vegetation was up to 1 000 mm height. Samples were collected from an area where *D. flexuosa* had colonised decaying *M. caerulea* tussocks. The remains of the *M. caerulea* was covered in a dense mat of *D. flexuosa* and its litter, which lifted easily to expose the mineral soil for sampling. The area was on a slope of approximately 12 ° dip to the East, and was subjected to surface water run-off from the higher ground above.

#### Tailings (ST 35475 15132)

The sampling area was situated on the flat top of top of a tailings pile, approximately 20 m to the north of the tramway (Figure 5.1). The pile was immediately above an informal pathway running through the area of tailings, north from the tramway to the Waldegrave pool. The tailings were gritty and sandy in



texture, and were among the coarsest grade pre-smelter waste on the Priddy Mineries Reserve. The vegetation cover was very low at <30 mm.

#### Nordrach Series (ST 35489 15159)

The sampling area was situated approximately 5 m north of the public footpath, in an open area on the edge of an area of a recently felled coniferous woodland (Figure 5.1). Although slightly raised from the footpath and plantation to the north, the sampling site was flat, and the grassland vegetation cover was up to 400 mm in height.

#### **5.1.7 Other soil parameters**

As well as the main aim of assessing the reliability of pH, Loss-on-Ignition and Total trace metal data generated by the baseline soil study, the temporal soil study presented an opportunity to study other soil parameters often associated with trace metals in soils. Determinations of EDTA available trace metals, CEC, Total P, Exchangeable Ca, Mg, K, and particle size analysis were also made.

#### EDTA available trace metals

The use and limitations of EDTA as an indication of bioavailable trace metals was described in 3.1. The % EDTA extractable trace metal of the total trace metal content was of interest to the temporal study because it is an indication of the form the metal is held in the soil. The pattern of variability of EDTA extractable trace metals over the years could also be indicative of loss from the soil system through plant uptake, or by leaching from the system.

### Cation Exchange Capacity

The clay minerals, sesquioxides and particles of humus in a soil have negative electrical charges associated with their surfaces that hold positively charged cations by electrostatic forces. These cation exchange sites commonly hold calcium (Ca), magnesium (Mg), potassium (K), ammonium (NH<sub>4</sub>), sodium (Na), hydrogen (H) and aluminium (Al) cations (Rowell, 1994). Cations that replace, or are replaced by, other cations are termed 'exchangeable', although soil cations hardly ever exist solely in their exchangeable form. The exchangeable form of a cation in a soil is important because it is the most readily available to a plant. Exchangeable cations are also referred to in the literature as 'available' (Hess, 1971). Cation exchange sites are also strongly associated with the retention and mobility of trace metals in soils (Ross, 1994c). The total amount of exchangeable cations a soil has the potential to hold is its Cation Exchange Capacity (CEC) and is expressed as centimole charge per kilogram (cmol<sub>c</sub> kg<sup>-1</sup>) oven-dry soil. In older texts, CEC is often expressed in the traditional unit of charge milliequivalents per 100 g (meq 100 g<sup>-1</sup>). In the context of CEC, a value expressed in either term is equivalent (Rowell, 1994).

There are several methods for the determination of CEC, an adaptation of the standard method developed for temperate soils was chosen for the soils of this study (MAFF, 1985). During this method, soil is leached with a solution of ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) which replaces cations held on the soil exchange sites with ammonium. The ammonium cations are then replaced by K from a leaching solution of potassium chloride (KCl 10% m/V) and the leached ammonium cations estimated by distillation and titration.

### Exchangeable calcium, magnesium and potassium

Determinations of these major elements were carried out because of their relevance to the soil in terms of their geochemistry and as an indication of the nutrient status of the soils. Calcium, Mg and K along with Fe and Na, are important controls of the primary distribution and secondary dispersion of trace metals (Plant and Raiswell, 1983). Exchangeable, rather than total, was chosen as a determined parameter because the standard extractant used is 1M ammonium acetate, which was the first stage of the CEC method, and there were detailed data sets available in Findlay (1965) for available calcium, magnesium and potassium in Mendip soils (Table 5.4).

Table 5.4. Particle size distribution and selected soil parameters for typical soils present on the study site (Findlay, 1965). S and D refers to profile depth where S = 0-200 mm and D = 200-400 mm. Depths for data approximate as converted from original inches in Findlay (1965).

Parameter/Depth	Maesbury Series		Thrupe Series		Ashen Series		Nordrach Series	
	S	D	S	D	S	D	S	D
<b>pH</b>	3.9	4.4	5.8	6.1	4.3	4.3	5.7	6.2
<b>CEC cmol<sub>c</sub> kg<sup>-1</sup></b>	18.3	10.9	15.9	11.2	40.0	25.0	18.4	7.7
<b>Exch. Ca cmol<sub>c</sub> kg<sup>-1</sup></b>	1.1	3.1	11.4	8.4	1.7	0.7	6.8	2.1
<b>Exch. Mg cmol<sub>c</sub> kg<sup>-1</sup></b>	0.2	0.5	1.1	0.4	0.3	0.1	0.3	0.1
<b>Exch. K cmol<sub>c</sub> kg<sup>-1</sup></b>	0.1	0.1	0.2	0.1	0.3	0.1	0.1	0.0
<b>clay %</b>	22.0	15.0	17.0	17.0	13.0	16.0	20.0	12.0
<b>silt %</b>	42.0	40.0	60.0	49.0	43.0	49.0	56.0	63.0
<b>fine sand %</b>	18.0	25.0	8.0	16.0	10.0	19.0	9.0	11.0
<b>coarse sand %</b>	8.0	7.0	8.0	17.0	10.0	10.0	7.0	12.0

### Total phosphorous

The determination of Total phosphorus was carried out because of its relevance to the soil in terms of geochemistry. As discussed in 4.21, phosphate compounds of trace metals, especially of Pb as pyromorphite, have low solubilities and a reduced

bioavailability and are implicated in the retention of Pb in mining wastes (Lindsay, 1979; Nriagu, 1984; Cotter-Howells, 1991; Ruby, Davis and Nicholson, 1994; Cotter-Howells and Caporn, 1996). Phosphates of Cd and Zn may also form in soils (Lindsay, 1979 in Ross 1994c).

Particle size analysis

Certain physiochemical properties of a soil are profoundly affected by the sizes of its mineral particles. Properties of particular relevance to this study include drainage and the retention of water and trace metal cations. Andersson (1977), for example, found that the HNO<sub>3</sub> soluble fractions of Pb, Zn, Cd and Cu were positively correlated with the % clay content of a soil. Mineral particles are classified by size and not by the type of minerals present in each class, although certain minerals are often predominant in a size class (Table 5.5). Sand-sized particles are often quartz, while clay-sized particles are commonly, but not necessarily, clay minerals (Rowell, 1994).

Table 5.5. Particle size classes by European particle size classification.  
Source: Rowell (1995).

Particle Size (mm)		
Stones		
> 2		
Fine earth:	coarse sand	2 – 0.2 (2 000-200 µm)
	fine sand	0.2 – 0.06 (200 – 60 µm)
	silt	0.06 – 0.002 (60 – 2 µm)
	clay	< 0.002 (< 2 µm)

Particle size analysis was carried out by a hydrometer method adapted from that described by Gilchrist Shirlaw (1967). The principle underlying the hydrometer method is that the specific gravity of a soil suspension is proportional to the mass of soil in the suspension and that depending on the size of a soil particle, its density and the properties of the liquid in which it is in suspension, it will settle out of suspension at a velocity proportional to its size. The settling velocity is derived from Stoke's Law for streamlined flow (Rowell, 1994).

#### **5.1.8 Plant community analysis**

An assemblage of species populations existing in the same area is known as a community (Krebs, 1985). The plant community present in the 2 m<sup>2</sup> sampling area on each soil series was surveyed using the National Vegetation Classification Scheme (NVC) (Rodwell, 1991). This was carried out to compare similarities and differences between communities on different soil series and to identify the species present. Vegetation influences the fate and distribution of metals in plant-soil systems in at least four ways: 1. the physical form of a plant can affect the way incoming metal-enriched aerosols and dusts are trapped and incorporated into the system, 2. plant roots can alter soil in the rhizosphere through exudation, slight changes in soil pH and organic matter status, 3. by the differential trace metal uptake of different species, genera and families 4. accumulated metals in plant litter are returned to the soil system (Martin and Coughtrey, 1981).

Trace metals have a variety of roles in biological systems. Metals such as Fe, Zn and Cu are micronutrients essential for plant growth, nickel (Ni) is essential for animal growth yet apparently not required by plants (Brady, 1990), while Pb and

Cd appears to have no known biological function. A common feature is that in high concentrations all trace metals are toxic to most plants (Turner, 1994). The mechanisms of metal toxicity to plants has been well documented and was summarised into five groups by Ochaia (1987):

- (1) The displacement of essential metal ions from biomolecules and other biologically functional units.
- (2) Blocking essential groups of biomolecules, especially enzymes and polynucleotides.
- (3) Modifying the active conformation of biomolecules, especially enzymes and polynucleotides.
- (4) Disrupting the integrity of biomolecules.
- (5) Modifying other biologically active agents.

However, on the study area there is a wide range of plant communities apparently thriving in the sometimes phenomenally high concentrations of soil trace metals (Tables 4.22 and 4.23).

Plant survival in metal-contaminated soils can be either due to true tolerance mechanisms involving survival from the effects of internal metal stress, or by avoidance or exclusion mechanisms where a plant is protected in some way from metal stress (Baker, 1987). The two strategies are not mutually exclusive and Baker and Walker (1990) considered it likely that survival is dependent on an orchestrated or integrated response involving a number of mechanisms.

### True tolerance

When a plant tolerates internally accumulated metals in its parts beyond the plasmalemma (plasma membrane or ectoplast of a plant cell), it may be described as possessing true tolerance. Mechanisms of true tolerance include the production of metal-binding polypeptides which reduce the concentration of free metals by

chelation in the cytoplasm and alterations in membrane structure, metal compartmentation patterns and cellular metabolism (Turner, 1994). Detailed reviews of the extensive literature pertaining to the mechanisms of tolerance and patterns of uptake were also included in the work of Antonovics *et al.* (1971), Macnair (1981), Jackson *et al.* (1990), Baker and Walker (1990), and Cumming and Tomsett (1992).

Most evidence suggests that physiological mechanisms of true tolerance may be genetically inherited (Turner, 1994) and there have been many investigations which support this theory. A classic study was by Prat (1934), who when working with *Silene dioica* seedlings derived from Cu mine waste reported that while seedlings from non-contaminated sources could not survive on soil treated with  $\text{CuCO}_3$ , the mine seedlings could.

#### Avoidance tolerance

A plant may effectively avoid excessive metal uptake by several mechanisms. Martin and Coughtrey (1982) described the relationship between rooting depth and location of soil metal enrichment, and how roots may proliferate in uncontaminated soil horizons within the profile avoiding metal uptake. Verkleij and Schat (1990) described several further avoidance mechanisms including mycorrhiza formation, alteration of plant membrane permeability, changes in metal-binding capacity of the cell wall and increased exudation of metal-chelating substances.

Baker (1981) reviewed the different mechanisms of tolerance and their influence on the pattern of metal uptake within a plant. He considered there were three basic strategies: The excluder strategy; the indicator or index strategy, where internal metal concentrations reflect external concentrations; and the accumulator strategy. While much is known about the mechanisms of tolerance and patterns of metal uptake, there is relatively little known about the exact concentrations at which a metal is toxic and the point at which no further adaptation can be made (Jackson *et al.*, 1990; Dickinson *et al.*, 1991).

Many early community studies on the vegetation of mining and smelting sites concentrated on mine-spoil communities, that is highly specialised communities that were adapted to the high metal concentrations present in mine-waste. Workers such as Koch (1932), Schubert (1953), Ernst (1965) and Baumeister (1967) investigated communities of contaminated soils on mine sites in Germany. Ernst (1968) described the mine-vegetation of the British and noted that, in general, communities were species poor. Further work by Shimwell (1968) classified the flora of the Pennines, Mendip and North Wales mining areas in more detail. Although many biogeochemical studies have examined the soils and vegetation specific to mine-waste communities (Thompson and Proctor, 1983; Baker, 1984; Shaw, 1984; Hajar, 1987), other workers have studied the wider communities found on abandoned mining and smelting sites (Buchaver, 1973; Baker, 1981; Li, 1993; Andrews *et al.*, 1989a, 1989b). There is now a considerable volume of trace metal data available for mine-waste specific and the more common gramineae and plant species in Britain for comparison.



## 5.2 Methods and materials

### 5.2.1 Sampling sites and soil description

Permanent 2 m<sup>2</sup> quadrats were set up at each of the five sampling sites (Figure 5.1). At each sampling site, the vegetation covering the 2 m<sup>2</sup> permanent quadrat was surveyed. The abundance of each species in the 2 m<sup>2</sup> quadrat was recorded using the Domin Scale (Dahl and Hadač, 1941) (Table 5.6).

Table 5.6. The Domin Scale (Dahl and Hadač, 1941).

% Cover	Domin Value
91 - 100	10
76 - 90	9
51 - 75	8
34 - 50	7
26 - 33	6
11 - 25	5
4 - 10	4
- with many individuals	3
<4 - with several individuals	2
- with few individuals	1

The species data were analysed by Match, part of the VESPAN suite of programs, which were designed to handle individual data records from homogenous plant communities (Rodwell, 1991). At each sampling site, one soil core of 500 mm depth was removed with a soil gouge and the following observations were recorded: soil colour, texture, plant roots and horizon depth. Soil colour was recorded using Munsell® Soil Colour Charts (Munsell®, 1992). A profile description in diagrammatic form was constructed for each soil series.

**5.2.2 Soil sampling and preparation**

Soil samples were collected on a monthly basis for one year from September 1998 to August 1999 from the 2 m<sup>2</sup> permanent quadrat at each site. Samples from each site were collected on the Friday nearest to the 15<sup>th</sup> day of each month between the hours of 14.00 - 16.30 (Table 5.7). On each date, soil samples were collected in the following sequence: Maesbury Series, Thrupe Series, Ashen Series, Tailings and Nordrach Series.

Table 5.7. Sample collection schedule.

16 Sept 1998	14 Oct 1998	18 Nov 1998	16 Dec 1998
13 Jan 1999	17 Feb 1999	16 Mar 1999	13 Apr 1999
18 May 1999	15 June 1999	13 July 1999	17 Aug 1999

Soil samples were collected by the method described in 4.2.1, with the following modification. At each sampling site, the bulk sample consisted of five sub-samples at 0-200 mm and 200-400 mm collected around a 0.5 m<sup>2</sup> quadrat within the 2 m<sup>2</sup> permanent quadrat (Figure 5.2). Sub-sample 1 was collected from the centre of the 0.5 m<sup>2</sup> quadrat, four further sub-samples were collected around the quadrat in from the numbered points to make a bulk sample of five sub-samples. At each of the 5 sampling sites, soil was collected in this manner from 0-200mm and 200-400 mm. On each sampling date at each site, the 0.5 m<sup>2</sup> quadrat was positioned randomly within the 2 m<sup>2</sup> permanent quadrat. Increasingly as the monthly sampling regime progressed, the position of the 0.5 m<sup>2</sup> quadrat was adjusted to avoid auger borings from previous sample collections.

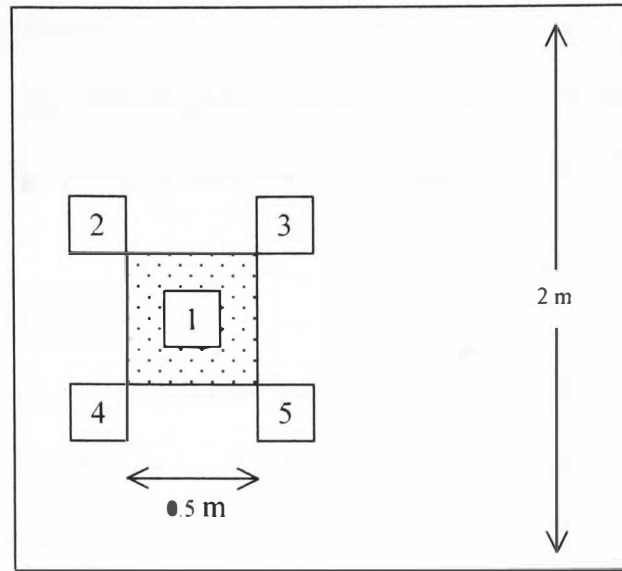


Figure 5.2. Collection points (numbered) of the five sub-samples of soil around a 0.5 m<sup>2</sup> sampling quadrat, within a 2 m<sup>2</sup> permanent quadrat.

In the laboratory, the samples were dried and prepared for analysis by the method described in 3.2.1. Samples that required the determination of soil reaction at field capacity were analysed within four hours after collection. Where the determination of the > 2 mm stone fraction of a soil was required, the method described in 5.7.2 was used after the soil had dried, but before it was disaggregated. All equipment used in the preparation and subsequent analysis of samples was prepared for use by the method described in 3.2.2.

### 5.2.3 Soil moisture

The soil moisture content of <2 mm air-dry soil was determined for all soil samples by the method described in 4.2.5, using a modified aliquot mass of 5g.

Three replicate aliquots of each soil sample were determined.

#### **5.2.4 Loss-on-Ignition**

Loss-on-Ignition was determined for three replicate aliquots of all <2 mm air-dry soil samples by the method described in 4.2.6, using a modified soil mass of 5 g.

#### **5.2.5 Soil reaction**

The reaction of soils at field capacity was determined by the method described in 4.2.4. Air-dry soil reaction was determined by the method described in 4.2.4, using a modified aliquot mass of 5g. of <2 mm air-dry soil in 12.5 ml of deionised water. Soil reaction of <2 mm air-dry soil was determined for three replicate aliquots of all soil samples and duplicates.

#### **5.2.6 Analysis for Total trace metals**

Three replicate aliquots of 0.5 g of <2 mm air-dry soil for each sample were prepared for digestion and analysis by the method described for the baseline soil survey in 4.2.3. All samples collected were analysed for Total Pb, Zn, Cd, Cu, Fe and Mn concentration. After statistical analysis of the means and standard deviations of the three replicates, the mean soil reaction values for each sample were entered into Microsoft Excel and Minitab® Release 12 for further statistical analysis.

#### **5.2.7 EDTA extractable trace metals**

The EDTA extractable Pb, Zn, Cd, Cu, Fe and Mn concentrations were determined for selected soil samples by the method described in 3.4. Three replicate aliquots were analysed for each soil sample, and the mean used in the subsequent statistical analyses. EDTA extractable trace metal concentrations were determined for

samples from all soil series at 0-200 mm and 200-400 mm collected in September 1998, December 1998, March 1999 and June 1999.

#### **5.2.8 Cation Exchange Capacity (CEC)**

An aliquot of 5 g <2 mm air-dry soil was weighed into a 100 ml beaker and 20 ml of M ammonium acetate were added. Ethanoic acid ( $\text{CH}_3\text{COOH}$ ) and ammonia ( $\text{NH}_3$ ) had been used to adjust the M ammonium acetate to pH 7. The M ammonium acetate and all other solutions used in this procedure were made using AnalaR® grade chemicals and deionised water. The solution was stirred and left to stand at room temperature overnight. The contents of the beaker was transferred to a polyethylene filter funnel fitted with a Whatman® 452 filter paper and the filtrate collected in a 250 ml volumetric flask. The soil in the funnel was leached with successive 25 ml volumes of M ammonium acetate, allowing the funnel to drain between each addition, until 250 ml were collected. The leachate (extract I), was retained for the determination of Ca, Mg, and K.

The filter funnel containing the leached soil was then placed over a 250 ml conical flask. Five successive 25 ml volumes of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) were used to wash the interior of the funnel, the filter paper and soil. The soil and paper were allowed to drain between washings. The 125 ml of ethanol removed any ammonium acetate remaining in the soil not held on exchange sites, and was discarded after use. After transferring the filter funnel and its contents over a 100 ml volumetric flask, the soil was leached with eight successive 25 ml volumes of KCl, again allowing the soil to drain between each addition. The KCl had previously been acidified to

pH 2.5 with M HCl. The resulting 100 ml of leachate (extract II) were retained for the determination of ammonium ion content.

The leachate was transferred to a macro test tube that was placed to receive pressurised steam in a Tecator Kjeltec System 1002 Distilling unit. An aliquot of 25 ml of 4% boric acid ( $\text{H}_3\text{BO}_3$ ) containing bromocresol green/methyl red indicator was measured into a 250 ml conical flask by tilt dispenser and placed to receive the distilled ammonia from the leachate. An automatic aliquot of 15 ml 40% sodium hydroxide (NaOH) was dispensed into the extract to liberate ammonia from the solution as a gas, while pressurised steam was fed into the tube to remove the ammonia by distillation. The ammonia was collected in the conical flask and absorbed into the boric acid solution until a 125 ml volume was obtained. The ammonia and boric acid solution was titrated with 0.1M  $\text{H}_2\text{SO}_4$  until end-point was reached when the solution changed colour to grey. The volume of titre required to reach end-point was recorded and used to determine the CEC of the soil as follows:

$$\begin{array}{l} \text{CEC} \\ \text{cmol}_c \text{ kg}^{-1} \\ \text{air-dry soil} \end{array} = \text{titre (ml)} \times \frac{3.6}{\text{soil mass (g)}} \times \frac{\text{extract I volume (ml)}}{18}$$

Where 1 ml 0.1M  $\text{H}_2\text{SO}_4$  = 3.6 mg ammonium ions, and 18 the equivalent mass of ammonium.

Results were adjusted for oven-dry weight from the results of the oven drying of air-dry soil described in 5.7.3. The mass of water (g) present in air-dry soil was calculated for water content per 1 kg air-dry soil. Analytical results were then corrected to oven dry-weight by the following calculation:

$$\frac{\text{CEC}}{\text{cmol}_c \text{ kg}^{-1} \text{ oven-dry soil}} = \frac{\text{CEC}}{\text{cmol}_c \text{ kg}^{-1} \text{ air-dry soil}} \times \frac{1\,000 \text{ (g)}}{\text{mass of oven-dry soil (g)}}$$

Paveley (1988) suggested that precision should be controlled by the random selection of 20% of the samples from each batch for duplication. To insure quality control, 20% of samples were analysed in duplicate for CEC. The CEC of samples from all soil series at 0-200 mm and 200-400 mm collected in September 1998, December 1998, March 1999 and June 1999 were determined.

#### **5.2.9 Exchangeable calcium, magnesium and potassium**

During the determination of CEC, extract I was retained for the analysis of exchangeable calcium and magnesium by FAAS, and potassium by a Jenway PFP7 flame photometer. The FAAS was operated under the standard conditions described in section 5.4.5, with two modifications. Calibration of the FAAS was carried out using M ammonium acetate to make up standard solutions and for any dilutions to eliminate matrix interference. A releasing agent of 10% lanthanum chloride ( $\text{LaCl}_3$ ) was added at a concentration of 1ml 10% lanthanum chloride to each 10 ml of standard or extract before introduction to the FAAS.

Molar ammonium acetate was also used during the preparation of calibration standards for the flame photometer, and for all analyte dilutions. A standard curve using potassium standard solutions of 10, 7.5, 5, 2.5, 1.25 and 0  $\text{mg l}^{-1}$  was generated by the AVP Computing Powergraph COM 130 program run by a BBC Master Microcomputer System. The value determined for potassium concentration

in an analyte by flame photometry was plotted on the standard. The value read from the curve was used in the subsequent calculation to determine exchangeable potassium in the soil. An explanation of the full working of the calculation used to determine exchangeable calcium, magnesium and potassium were described by Rowell (1994). The following equations were Rowell's (1994) recommended simplifications:

$$\begin{array}{l} \text{exchangeable calcium} \\ \text{cmol}_c \text{ kg}^{-1} \\ \text{air-dry soil} \end{array} = 0.249y \times \frac{5}{\text{aliquot mass (g)}}$$

$$\begin{array}{l} \text{exchangeable magnesium} \\ \text{cmol}_c \text{ kg}^{-1} \\ \text{air-dry soil} \end{array} = 0.4.12y \times \frac{5}{\text{aliquot mass (g)}}$$

$$\begin{array}{l} \text{exchangeable potassium} \\ \text{cmol}_c \text{ kg}^{-1} \\ \text{air-dry soil} \end{array} = 0.1283y \times \frac{5}{\text{aliquot mass (g)}}$$

Where  $y$  was the concentration of the element in the extract ( $\mu\text{g ml}^{-1}$ ). For potassium, this was the value read from the standard curve.

As quality control, 20% of the samples were analysed in duplicate for calcium, magnesium and potassium (Paveley, 1988). Where a sample was analysed in duplicate, the mean value of the duplicates was used as the result of the analysis

#### 5.2.10 Total phosphorus

An aliquot of 5 g <2 mm air-dry soil was decomposed by 69% (v/v)  $\text{NH}_4\text{OH}$  following the method described in 5.4.5 and 5.4.9. This was an adaptation of the method described by Cotter-Howells and Caporn (1996). An extract was prepared



for colorimetry by the addition of 0.3 g activated charcoal decolourising powder (DARCO G 60) to the mixture, which was then gently shaken. The mixture was filtered through a Whatman® 452 paper. If colour remained, the decolourising procedure was repeated.

Total phosphorus concentrations were determined from the  $\text{HNO}_3$  extracts by colorimetry using a Pharmacia Biotech Ultraspec 200 UV Visible Spectrophotometer set to 400 nm. Phosphorus standards were prepared matching the matrix to the appropriate extractant. Colour was developed in the extracts using a phosphovanadomolybdate method adapted from a method described in CCAM (1967). The vanadomolybdate reagent used in this method was made in the following way. A solution of 20 g ammonium molybdate tetrahydrate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$  dissolved in 250 ml deionised water was added to a solution of 1 g ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) dissolved in 40 ml M nitric acid and 200 ml deionised water and mixed. The combined solutions were transferred to a 1 l volumetric flask and 100 ml M nitric acid were added. The solution was then made to volume with deionised water.

The spectrophotometer was calibrated with phosphate standards made to volume with 20% nitric acid. An aliquot of 2 ml standard solution and 2 ml vanadomolybdate were pipetted into a cuvette, and left for 3 minutes to allow the colour to develop. This procedure was repeated for all standards, and a blank of 2 ml vanadomolybdate reagent and 2 ml 20% nitric acid was also made. A standard curve was generated from the absorbance results of the standard solutions using the AVP Computing Powergraph COM 130 program run by a BBC Master

Microcomputer System. An extract was prepared for colorimetry by pipetting 2 ml of the extract and 2 ml of vanadomolybdate reagent into a cuvette. The solution was left for 3 minutes to allow the colour to develop before introduction to the spectrophotometer. The result was plotted on the standard curve and the value read from the curve was used in the following calculation to determine total phosphorus in the soil.

$$\text{total soil phosphorus} = \text{phosphorus in extract} \times \frac{\text{extract final volume (ml)}}{\text{aliquot mass (g)}}$$

$(\mu\text{g g}^{-1} <2 \text{ mm air-dry soil})$ 
 $(\mu\text{g ml}^{-1})$

Where phosphorus in the extract was the value read from the standard curve.

Results were corrected for oven-dry weight by the calculation described in 5.7.6, and as a quality control, 20% of the samples were analysed in duplicate (Paveley, 1988). Where samples were analysed in duplicate, the mean value of the duplicates was used as the result of the analysis.

#### **5.2.11 Particle size analysis of <2 mm air-dry soil**

An aliquot of 50 g <2 mm soil was weighed into a polyethylene shaking bottle. A 5% sodium hexametaphosphate solution buffered to pH 8 was made by dissolving 50 g of sodium hexametaphosphate and 5.724 g sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in 1 l deionised water. An aliquot of 25 ml of the solution and 200 ml deionised water were added to the soil. The bottle was sealed and placed on the Gerhardt LS/5 Laboshake for 20 minutes at  $120 \text{ cycles min}^{-1}$  at room temperature. The soil suspension was decanted from the bottle into a 1 l glass measuring cylinder. The bottle was carefully washed with deionised water to remove any remaining soil and the washings transferred directly to the measuring cylinder. The suspension was made up to 1 l with deionised water and the top of the cylinder was sealed

with Parafilm®. The cylinder was manually shaken end over end until its contents were mixed. The time the shaking ceased was recorded and after being left to stand for exactly 4 minutes 30 seconds, the hydrometer was placed in the suspension. The hydrometer reading was taken at exactly 5 minutes and recorded. On removal of the hydrometer, the temperature of the suspension was measured and recorded. Where excessive froth was present on the surface of the suspension after shaking, it was immediately dispersed by the addition of a drop of iso-amyl alcohol ( $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_2\text{OH}$ ) to prevent froth obscuring the hydrometer graduations. At the time of the hydrometer reading, the sand had settled below the region where it could affect the hydrometer reading, however, the silt and clay was still in suspension so the hydrometer reading was the weight of silt and clay per litre. The hydrometer was factory-calibrated at 20°C, so the reading had to be corrected for the temperature of the suspension. For every 1°C above 20°C, 0.3 of a unit was added to the hydrometer reading, while 0.3 of a unit was subtracted for every 1°C below 20°C.

The suspension was left to stand undisturbed for 5 hours. About 30 seconds before the 5 hours had elapsed, the hydrometer was placed in the suspension and the reading was taken at exactly 5 hours and recorded. The temperature was also taken on removal of the hydrometer and recorded. The hydrometer reading was adjusted for temperature as before. At this stage, the silt had settled enough to discount it from the hydrometer reading, and the reading could be considered as the weight of clay per litre. Most of the supernatant was carefully poured off so that the whole sand fraction, which consisted of the coarse and fine sand fractions, was retained in the bottom of the cylinder. The sand was washed with deionised

water into a 400 ml glass beaker that had been marked at the 100 mm level. Deionised water was added to the 100 mm mark and the contents of the beaker were stirred with a glass rod. The temperature of the resulting suspension was measured, and then allowed to stand until the whole sand fraction had settled. The supernatant was carefully poured off and the whole sand fraction retained. The time allowed for this sedimentation process varies with suspension temperature, at 20°C the time allowed was 4 minutes 48 seconds. Adjustments were made to sedimentation time according to the values in Table 5.8.

Table 5.8. The time of sedimentation of fine sand at different temperatures (Gilchrist Shirlaw, 1967).

Temperature (°C)	Sedimentation time through 100 mm		Temperature (°C)	Sedimentation time through 100 mm	
	Min	Sec		Min	Sec
14	5	40	20	4	48
15	5	30	21	4	40
16	5	20	22	4	30
17	5	10	23	4	30
18	5	0	24	4	20
19	5	0	25	4	15

The process of washing, sedimentation and decanting was repeated until at the end of the sedimentation time the supernatant was clear. To separate the remaining coarse and fine sands, the sediment was washed with deionised water onto a 200 µm soil sieve placed over a filter funnel lined with a Whatman® No.1 filter paper. The oven-dry mass of the filter paper had been determined previously after drying in an oven at 105°C for 24 hours. Washing continued until no more fine

sand passed through the sieve with the water. The coarse sand retained on the sieve was washed on to a second filter paper of known oven-dry mass. Both filter papers of sand were dried in an oven at 105°C for 48 hours and reweighed. The oven-dry mass of each sand fraction was calculated by subtracting the mass of its oven-dry filter paper from the mass of the oven-dry filter paper of sand. The results, which at this stage were the weights of silt plus clay, clay, fine sand and coarse sand in the original 50 g aliquot, were converted to percentage values as follows:

The % silt and clay fractions = the first corrected hydrometer reading  $\times 2$

The % clay fraction = the second corrected hydrometer reading  $\times 2$

The % silt fraction = % silt and clay - % clay fraction

The % fine sand fraction = oven-dry mass  $\times 2$

The % coarse sand fraction = oven-dry mass  $\times 2$ .

The difference between the sum of the clay, silt, fine sand and coarse sand determined percentage fractions and 100% is the loss by solution. The percentage determined fractions were corrected to 100% by the following calculation:

$$\text{corrected \%} = \text{determined \%} \times \frac{100}{(100 - \text{loss by solution})}$$

The corrected % soil fractions were used to allocate a textural class to the soil under analysis and to plot cumulative curves for soil-particle size distribution.

The textural class of a soil was determined by plotting the corrected percentage soil fractions on the UK soil texture classification system (Figure 5.3).

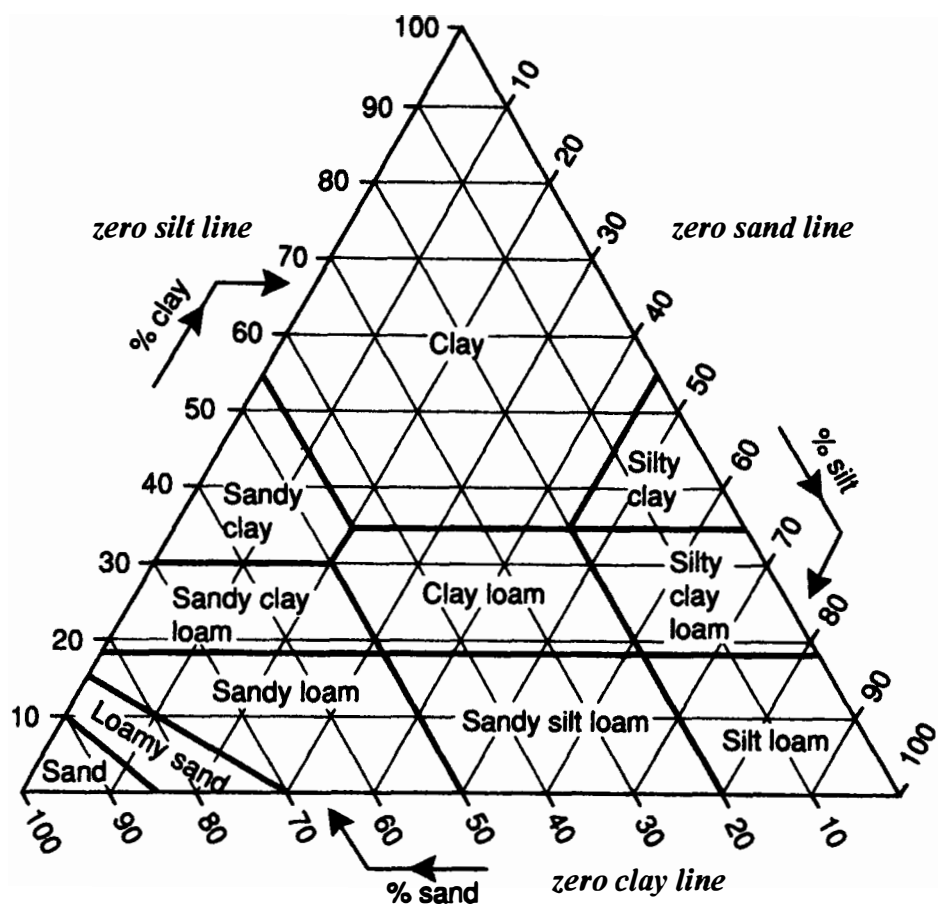


Figure 5.3. The UK system of soil textural classes and their particle size distribution (Rowell, 1994).

The percentage sand was found on the base of the triangle and a line was drawn parallel to the zero sand line. The percentage clay was then found on the percentage clay side, and a line was drawn parallel to the zero clay line. The point where the two lines crossed represented the textural class of the soil. A line drawn from the percentage silt line, parallel to the zero silt line crossed the transect at the

same point, confirming the textural class. Particle size analysis was determined on samples at 0-200 mm and 200-400 mm for June. For quality control, determinations were duplicated on 20% of the samples, and the mean of the two replicate determinations was used in subsequent calculations. Results were accepted when the % CV between duplicates was <10%.

### 5.2.12 Summary of analyses

The analyses that were determined on each of the five soil series collected each month at 0-200 mm and 200-400 mm were summarised in Table 5.9.

Table 5.9. Summary of the analytical regime for soils.

	>2 mm stone content	Soil Moisture	L-O-I %	Soil reaction	Total trace metals	EDTA trace metals	CEC	Exchangeable Ca, Mg, K	Total P	Particle size analysis
Sept 98	X	X	X	X	X	X	X	X	X	X
Oct 98		X	X	X	X					
Nov 98		X	X	X	X					
Dec 98	X	X	X	X	X	X	X	X	X	
Jan 99		X	X	X	X					
Feb 99		X	X	X	X					
Mar 99	X	X	X	X	X	X	X	X	X	
Apr 99		X	X	X	X					
May 99		X	X	X	X					
Jun 99	X	X	X	X	X	X	X	X	X	
Jul 99		X	X	X	X					
Aug 99		X	X	X	X					

### 5.3 Data handling and the statistical analysis of data

The data were handled as

1. individual data sets for each soil series
2. a combined data set of all soil series data.

### **5.3.1 Descriptive Statistics**

The arithmetic mean, standard deviation, minimum, 1<sup>st</sup> quartile, median, 3<sup>rd</sup> quartile and maximum values for annual and quarterly soil parameter data were determined using Minitab® Release 12.

### **5.3.2 Presentation of data**

#### Intra-soil series data

For each soil series, the particle size distribution for 0-200 mm and 200-400 mm were plotted as cumulative curves. The mean monthly values for soil pH and Loss-on-Ignition, and concentrations of Total Pb, Zn, Cd, Cu, Fe and Mn at 0-200 mm and 200-400 mm were plotted on line graphs. The mean monthly concentrations for Total and EDTA extractable Pb, Zn, Cd, Cu, Fe and Mn were plotted as bar charts. The annual variation for each soil parameter was calculated as % CV (3.3.1). The data underwent Two-Sample analyses (4.2.4 and 2.3.5) where appropriate. Pearson Correlations (4.3.7) were calculated for the stacked data (0-400 mm) for each soil series.

#### Inter-soil series data

##### a. Baseline soil study parameters

The annual variation of each soil parameter (% CV) was tabulated for each soil series. The soil series were ranked by annual variation % CV. The mean annual % CV for each soil parameter from all soil series at 0-200 mm and 400-mm was calculated and an overall ranking of annual variation by soil parameter was constructed. The soil parameters for all soil series at 0-200 mm and 200-400 mm



were ranked by % CV. Pearson Correlations were calculated for the stacked data for all soil parameters (0-400 mm).

#### b. All soil parameters

Annual variation in pH, Loss-on-Ignition, Total and EDTA extractable Pb, Zn, Cd, Cu, Fe and Mn, CEC, available Ca, Mg, K and Total P (% CV) were tabulated for each soil series. The soil series were ranked by annual variation % CV. The mean annual % CV for each soil parameter from all soil series at 0-200 mm and 200-400mm was calculated and an overall ranking of annual variation by soil parameter was constructed. The soil parameters for all soil series at 0-200 mm and 200-400 mm were ranked by % CV. For each trace metal, the median EDTA extractable trace metal as a percentage of the total trace metal for each month from all soil series were calculated for 0-200 mm and 200-400 mm and 0-400 mm depths. The results were displayed as bar charts. Pearson Correlations were calculated for all stacked soil parameter data (0-400 mm). Pearson Correlations were also calculated for all stacked soil parameter data (0-400 mm), including particle size analysis data, from all soil series for June 1999.

### **5.3.3 Statistical appraisal of normality and the normalisation of data**

To assess the normality of the data distribution over the year, frequency distributions were calculated for all soil parameter data (0-200 mm and 200-400 mm) in each soil series using an Anderson-Darling normal probability plot (4.3.3 and Figure 4.5). The frequency distributions were also calculated for the stacked data (0-400 mm) for the parameters in the baseline study. The attained significance level was  $\alpha=0.01$  for all data (4.3.3). Where appropriate,  $\text{Log}_{10}$

transformed data were used for statistical analysis as recommended by Davies (1989).

### 5.3.4 Maesbury Series

Table 5.10. Probability distributions of Maesbury Series data (0-200 mm and 200-400 mm) for September 1998 - August 1999 (n=12) and quarterly (n=4) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm) (n=12)	0.007	Rejected
pH (200-400 mm) (n=12)	0.017	Accepted
L-o-I % (0-200 mm) (n=12)	0.512	Accepted
L-o-I % (200-400 mm) (n=12)	0.759	Accepted
Total Pb (0-200 mm) (n=12)	0.673	Accepted
Total Pb (200-400 mm) (n=12)	0.674	Accepted
Total Zn (0-200 mm) (n=12)	0.054	Accepted
Total Zn (200-400 mm) (n=12)	0.759	Accepted
Total Cd (0-200 mm) (n=12)	0.000	Rejected
Total Cd (200-400 mm) (n=12)	0.000	Rejected
Total Cu (0-200 mm) (n=12)	0.921	Accepted
Total Cu (200-400 mm) (n=12)	0.484	Accepted
Total Fe (0-200 mm) (n=12)	0.536	Accepted
Total Fe (200-400 mm) (n=12)	0.041	Accepted
Total Mn (0-200 mm) (n=12)	0.127	Accepted
Total Mn (200-400 mm) (n=12)	0.023	Accepted
EDTA Pb (0-200 mm) (n=4)	0.589	Accepted
EDTA Pb (200-400 mm) (n=4)	0.648	Accepted
EDTA Zn (0-200 mm) (n=4)	0.253	Accepted
EDTA Zn (200-400 mm) (n=4)	0.855	Accepted
EDTA Cd (0-200 mm) (n=4)	0.412	Accepted
EDTA Cd (200-400 mm) (n=4)	0.188	Accepted
EDTA Cu (0-200 mm) (n=4)	0.510	Accepted
EDTA Cu (200-400 mm) (n=4)	0.013	Accepted
EDTA Fe (0-200 mm) (n=4)	0.304	Accepted
EDTA Fe (200-400 mm) (n=4)	0.771	Accepted
EDTA Mn (0-200 mm) (n=4)	0.582	Accepted
EDTA Mn (200-400 mm) (n=4)	0.028	Accepted
CEC (0-200 mm) (n=4)	0.763	Accepted
CEC (200-400 mm) (n=4)	0.340	Accepted
Exch. Ca (0-200 mm) (n=4)	0.365	Accepted
Exch. Ca (200-400 mm) (n=4)	0.520	Accepted
Exch. Mg (0-200 mm) (n=4)	0.388	Accepted
Exch. Mg (200-400 mm) (n=4)	0.155	Accepted
Exch. K (0-200 mm) (n=4)	0.079	Accepted
Exch. K (200-400 mm) (n=4)	0.186	Accepted
Total P (0-200 mm) (n=4)	0.028	Accepted
Total P (200-400 mm) (n=4)	0.147	Accepted

With the exception of pH at 0-200 mm and Total Cd at 0-200 mm and 200-400 mm, all monthly and quarterly soil parameter data in the Maesbury Series followed a normal probability distribution (Table 5.10).

Table 5.11. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=12) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Cd (0-200 mm)	0.015	Accepted
Total Cd (200-400 mm)	0.000	Rejected

After Log<sub>10</sub> transformation, Total Cd at 200-400 mm did not follow a normal probability distribution (Table 5.11). In subsequent statistical analyses, the Log<sub>10</sub> transformed values for Total Cd were used.

Table 5.12. Probability distributions of stacked Maesbury Series data (0-400 mm) for September 1998 - August 1999 (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-400 mm)	0.010	Accepted
L-o-I % (0-400 mm)	0.006	Rejected
Total Pb (0-400 mm)	0.849	Accepted
Total Zn (0-400 mm)	0.441	Accepted
Total Cd (0-400 mm)	0.000	Rejected
Total Cu (0-400 mm)	0.404	Accepted
Total Fe (0-400 mm)	0.316	Accepted
Total Mn (0-400 mm)	0.381	Accepted

With the exception of Loss-on-Ignition and Total Cd, all stacked soil parameter data followed a normal probability distribution (Table 5.12).

Table 5.13. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
L-o-I % (0-400 mm)	0.015	Accepted
Total Cd (0-400 mm)	0.000	Rejected

After Log<sub>10</sub> transformation, Total Cd did not follow a normal probability distribution (Table 5.13). In subsequent statistical analyses, the Log<sub>10</sub> transformed values for Total Cd were used.

### 5.3.5 Thrupe Series

With the exception of Total Cd 0-200 mm and 200-400 mm and Exchangeable Mg at 200-400 mm, all soil data followed a normal probability distribution (Table 5.14). After Log<sub>10</sub> transformation, Total Cd at 0-200 mm and 200-400 mm and Exchangeable Mg at 200-400 mm did not follow a normal probability distribution (Table 5.15).

- 5.14. Probability distributions of Thrupe Series data (0-200 mm and 200-400 mm) for September 1998 - August 1999 (n=12) and quarterly (n=4) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm) (n=12)	0.479	Accepted
pH (200-400 mm) (n=12)	0.454	Accepted
L-o-I % (0-200 mm) (n=12)	0.078	Accepted
L-o-I % (200-400 mm) (n=12)	0.002	Accepted
Total Pb (0-200 mm) (n=12)	0.018	Accepted
Total Pb (200-400 mm) (n=12)	0.023	Accepted
Total Zn (0-200 mm) (n=12)	0.064	Accepted
Total Zn (200-400 mm) (n=12)	0.810	Accepted
Total Cd (0-200 mm) (n=12)	0.000	Rejected
Total Cd (200-400 mm) (n=12)	0.000	Rejected
Total Cu (0-200 mm) (n=12)	0.449	Accepted
Total Cu (200-400 mm) (n=12)	0.074	Accepted
Total Fe (0-200 mm) (n=12)	0.112	Accepted
Total Fe (200-400 mm) (n=12)	0.724	Accepted
Total Mn (0-200 mm) (n=12)	0.433	Accepted
Total Mn (200-400 mm) (n=12)	0.511	Accepted
EDTA Pb (0-200 mm) (n=4)	0.786	Accepted
EDTA Pb (200-400 mm) (n=4)	0.118	Accepted
EDTA Zn (0-200 mm) (n=4)	0.377	Accepted
EDTA Zn (200-400 mm) (n=4)	0.565	Accepted
EDTA Cd (0-200 mm) (n=4)	0.332	Accepted
EDTA Cd (200-400 mm) (n=4)	0.122	Accepted
EDTA Cu (0-200 mm) (n=4)	0.069	Accepted
EDTA Cu (200-400 mm) (n=4)	0.015	Accepted
EDTA Fe (0-200 mm) (n=4)	0.538	Accepted
EDTA Fe (200-400 mm) (n=4)	0.071	Accepted
EDTA Mn (0-200 mm) (n=4)	0.129	Accepted
EDTA Mn (200-400 mm) (n=4)	0.750	Accepted
CEC (0-200 mm) (n=4)	0.239	Accepted
CEC (200-400 mm) (n=4)	0.451	Accepted
Exch. Ca (0-200 mm) (n=4)	0.141	Accepted
Exch. Ca (200-400 mm) (n=4)	0.331	Accepted
Exch. Mg (0-200 mm) (n=4)	0.267	Accepted
Exch. Mg (200-400 mm) (n=4)	0.007	Rejected
Exch. K (0-200 mm) (n=4)	0.506	Accepted
Exch. K (200-400 mm) (n=4)	0.165	Accepted
Total P (0-200 mm) (n=4)	0.540	Accepted
Total P (200-400 mm) (n=4)	0.357	Accepted

Table 5.15. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=12) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Cd (0-200 mm)	0.000	Rejected
Total Cd (200-400 mm)	0.000	Rejected
Exch. Mg (200-400 mm)	0.007	Rejected

Table 5.16. Probability distributions of Thrupe Series data (0-400 mm) for September 1998 - August 1999 (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-400 mm)	0.073	Accepted
L-o-I % (0-400 mm)	0.059	Accepted
Total Pb (0-400 mm)	0.205	Accepted
Total Zn (0-400 mm)	0.154	Accepted
Total Cd (0-400 mm)	0.000	Rejected
Total Cu (0-400 mm)	0.142	Accepted
Total Fe (0-400 mm)	0.138	Accepted
Total Mn (0-400 mm)	0.102	Accepted

With the exception of Total Cd, all soil parameter data followed a normal probability distribution (Table 5.16).

Table 5.17. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=24) calculated by the Anderson-Darling Test for normality

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Cd (0-400 mm)	0.000	Rejected

After Log 10 transformation, Total Cd did not show a normal probability distribution (Table 5.17).

### 5.3.6 Ashen Series

Table 5.18. Probability distributions of Ashen Series data (0-200 mm and 200-400 mm) for September 1998 - August 1999 (n=12) and quarterly (n=4) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm) (n=12)	0.000	Rejected
pH (200-400 mm) (n=12)	0.000	Rejected
L-o-I % (0-200 mm) (n=12)	0.645	Accepted
L-o-I % (200-400 mm) (n=12)	0.142	Accepted
Total Pb (0-200 mm) (n=12)	0.421	Accepted
Total Pb (200-400 mm) (n=12)	0.672	Accepted
Total Zn (0-200 mm) (n=12)	0.008	Rejected
Total Zn (200-400 mm) (n=12)	0.984	Accepted
Total Cd (0-200 mm) (n=12)	0.000	Rejected
Total Cd (200-400 mm) (n=12)	0.000	Rejected
Total Cu (0-200 mm) (n=12)	0.142	Accepted
Total Cu (200-400 mm) (n=12)	0.337	Accepted
Total Fe (0-200 mm) (n=12)	0.939	Accepted
Total Fe (200-400 mm) (n=12)	0.155	Accepted
Total Mn (0-200 mm) (n=12)	0.006	Rejected
Total Mn (200-400 mm) (n=12)	0.174	Accepted
EDTA Pb (0-200 mm) (n=4)	0.178	Accepted
EDTA Pb (200-400 mm) (n=4)	0.149	Accepted
EDTA Zn (0-200 mm) (n=4)	0.107	Accepted
EDTA Zn (200-400 mm) (n=4)	0.718	Accepted
EDTA Cd (0-200 mm) (n=4)	--	N.A.
EDTA Cd (200-400 mm) (n=4)	--	N.A.
EDTA Cu (0-200 mm) (n=4)	0.031	Accepted
EDTA Cu (200-400 mm) (n=4)	0.384	Accepted
EDTA Fe (0-200 mm) (n=4)	0.162	Accepted
EDTA Fe (200-400 mm) (n=4)	0.321	Accepted
EDTA Mn (0-200 mm) (n=4)	0.199	Accepted
EDTA Mn (200-400 mm) (n=4)	0.438	Accepted
CEC (0-200 mm) (n=4)	0.036	Accepted
CEC (200-400 mm) (n=4)	0.299	Accepted
Exch. Ca (0-200 mm) (n=4)	0.579	Accepted
Exch. Ca (200-400 mm) (n=4)	0.610	Accepted
Exch. Mg (0-200 mm) (n=4)	0.255	Accepted
Exch. Mg (200-400 mm) (n=4)	0.255	Accepted
Exch. K (0-200 mm) (n=4)	0.130	Accepted
Exch. K (200-400 mm) (n=4)	0.752	Accepted
Total P (0-200 mm) (n=4)	0.249	Accepted
Total P (200-400 mm) (n=4)	0.775	Accepted

Soil pH and Total Cd at 0-200 mm and 200-400 mm, and Total Zn and Mn 0-200 mm did not follow a normal probability distribution. The data in the columns EDTA Cd at 0-200 and EDTA Cd at 200-400 mm were identical, therefore this test was not applicable. All other soil parameter data followed a normal probability distribution (Table 5.18).

Table 5.19. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=12) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Zn (0-200 mm)	0.093	Accepted
Total Cd (0-200 mm)	0.000	Rejected
Total Cd (200-400 mm)	0.000	Rejected
Total Mn (0-200 mm)	0.231	Accepted

After Log<sub>10</sub> transformation, Total Zn and Mn at 0-200 mm followed a normal probability distribution. Total Cd at 0-200 mm and 200-400 mm did not follow a normal frequency distribution (Table 5.19).

Table 5.20. Probability distributions of Ashen Series data (0-400 mm) for September 1998 - August 1999 (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-400 mm)	0.001	Rejected
L-o-I % (0-400 mm)	0.317	Accepted
Total Pb (0-400 mm)	0.943	Accepted
Total Zn (0-400 mm)	0.008	Rejected
Total Cd (0-400 mm)	0.000	Rejected
Total Cu (0-400 mm)	0.181	Accepted
Total Fe (0-400 mm)	0.660	Accepted
Total Mn (0-400 mm)	0.052	Accepted

Total Zn and Cd did not follow a normal probability distribution (Table 5.20).



Table 5.21. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Zn (0-400 mm)	0.242	Accepted
Total Cd (0-400 mm)	0.000	Rejected

After Log<sub>10</sub> transformation, Total Zn followed a normal probability distribution, but Total Cd did not follow a normal frequency distribution (Table 5.21).

### 5.3.7 Tailings

All parameter data for Tailings at 0-200 mm and 200-400 followed a normal probability distribution (Table 5.22).

All stacked parameter data for Tailings (0-400 mm) followed a normal probability distribution (Table 5.23).

- 5.22. Probability distributions of Tailings data (0-200 mm and 200-400 mm) for September 1998 - August 1999 (n=12) and quarterly (n=4) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm) (n=12)	0.510	Accepted
pH (200-400 mm) (n=12)	0.070	Accepted
L-o-I % (0-200 mm) (n=12)	0.642	Accepted
L-o-I % (200-400 mm) (n=12)	0.264	Accepted
Total Pb (0-200 mm) (n=12)	0.260	Accepted
Total Pb (200-400 mm) (n=12)	0.299	Accepted
Total Zn (0-200 mm) (n=12)	0.868	Accepted
Total Zn (200-400 mm) (n=12)	0.094	Accepted
Total Cd (0-200 mm) (n=12)	0.640	Accepted
Total Cd (200-400 mm) (n=12)	0.509	Accepted
Total Cu (0-200 mm) (n=12)	0.520	Accepted
Total Cu (200-400 mm) (n=12)	0.084	Accepted
Total Fe (0-200 mm) (n=12)	0.990	Accepted
Total Fe (200-400 mm) (n=12)	0.114	Accepted
Total Mn (0-200 mm) (n=12)	0.186	Accepted
Total Mn (200-400 mm) (n=12)	0.272	Accepted
EDTA Pb (0-200 mm) (n=4)	0.647	Accepted
EDTA Pb (200-400 mm) (n=4)	0.388	Accepted
EDTA Zn (0-200 mm) (n=4)	0.052	Accepted
EDTA Zn (200-400 mm) (n=4)	0.033	Accepted
EDTA Cd (0-200 mm) (n=4)	0.145	Accepted
EDTA Cd (200-400 mm) (n=4)	0.262	Accepted
EDTA Cu (0-200 mm) (n=4)	0.716	Accepted
EDTA Cu (200-400 mm) (n=4)	0.320	Accepted
EDTA Fe (0-200 mm) (n=4)	0.134	Accepted
EDTA Fe (200-400 mm) (n=4)	0.679	Accepted
EDTA Mn (0-200 mm) (n=4)	0.336	Accepted
EDTA Mn (200-400 mm) (n=4)	0.320	Accepted
CEC (0-200 mm) (n=4)	0.555	Accepted
CEC (200-400 mm) (n=4)	0.185	Accepted
Exch. Ca (0-200 mm) (n=4)	0.706	Accepted
Exch. Ca (200-400 mm) (n=4)	0.508	Accepted
Exch. Mg (0-200 mm) (n=4)	0.850	Accepted
Exch. Mg (200-400 mm) (n=4)	0.691	Accepted
Exch. K (0-200 mm) (n=4)	0.227	Accepted
Exch. K (200-400 mm) (n=4)	0.610	Accepted
Total P (0-200 mm) (n=4)	0.176	Accepted
Total P (200-400 mm) (n=4)	0.661	Accepted

Table 5.23. Probability distributions of Tailings data (0-400 mm) for September 1998 - August 1999 (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-400 mm)	0.190	Accepted
L-o-l % (0-400 mm)	0.483	Accepted
Total Pb (0-400 mm)	0.113	Accepted
Total Zn (0-400 mm)	0.272	Accepted
Total Cd (0-400 mm)	0.671	Accepted
Total Cu (0-400 mm)	0.350	Accepted
Total Fe (0-400 mm)	0.137	Accepted
Total Mn (0-400 mm)	0.102	Accepted

### 5.3.8 Nordrach Series

Total Fe at 200-400 mm did not follow a normal probability distribution (Table 5.24). The data in the columns Total Cd at 0-200 mm, Total Cd at 200-400 mm and EDTA Cd at 200-400 mm were identical, therefore this test was not applicable. All other soil parameter data followed a normal probability distribution (Table 5.24).

After Log<sub>10</sub> transformation, the Fe at 200-400 mm data followed a normal probability distribution (Table 5.25).

Table 5.24. Probability distributions of Nordrach Series data (0-200 mm and 200-400 mm) for September 1998 - August 1999 (n=12) and quarterly (n=4) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-200 mm) (n=12)	0.277	Accepted
pH (200-400 mm) (n=12)	0.231	Accepted
L-o-I % (0-200 mm) (n=12)	0.798	Accepted
L-o-I % (200-400 mm) (n=12)	0.757	Accepted
Total Pb (0-200 mm) (n=12)	0.039	Accepted
Total Pb (200-400 mm) (n=12)	0.426	Accepted
Total Zn (0-200 mm) (n=12)	0.659	Accepted
Total Zn (200-400 mm) (n=12)	0.791	Accepted
Total Cd (0-200 mm) (n=12)	--	N.A.
Total Cd (200-400 mm) (n=12)	--	N.A.
Total Cu (0-200 mm) (n=12)	0.436	Accepted
Total Cu (200-400 mm) (n=12)	0.248	Accepted
Total Fe (0-200 mm) (n=12)	0.389	Accepted
Total Fe (200-400 mm) (n=12)	0.002	Rejected
Total Mn (0-200 mm) (n=12)	0.460	Accepted
Total Mn (200-400 mm) (n=12)	0.688	Accepted
EDTA Pb (0-200 mm) (n=4)	0.370	Accepted
EDTA Pb (200-400 mm) (n=4)	0.522	Accepted
EDTA Zn (0-200 mm) (n=4)	0.526	Accepted
EDTA Zn (200-400 mm) (n=4)	0.294	Accepted
EDTA Cd (0-200 mm) (n=4)	0.404	Accepted
EDTA Cd (200-400 mm) (n=4)	--	N.A.
EDTA Cu (0-200 mm) (n=4)	0.243	Accepted
EDTA Cu (200-400 mm) (n=4)	0.674	Accepted
EDTA Fe (0-200 mm) (n=4)	0.010	Accepted
EDTA Fe (200-400 mm) (n=4)	0.233	Accepted
EDTA Mn (0-200 mm) (n=4)	0.611	Accepted
EDTA Mn (200-400 mm) (n=4)	0.220	Accepted
CEC (0-200 mm) (n=4)	0.609	Accepted
CEC (200-400 mm) (n=4)	0.117	Accepted
Exch. Ca (0-200 mm) (n=4)	0.198	Accepted
Exch. Ca (200-400 mm) (n=4)	0.024	Accepted
Exch. Mg (0-200 mm) (n=4)	0.047	Accepted
Exch. Mg (200-400 mm) (n=4)	0.017	Accepted
Exch. K (0-200 mm) (n=4)	0.413	Accepted
Exch. K (200-400 mm) (n=4)	0.240	Accepted
Total P (0-200 mm) (n=4)	0.757	Accepted
Total P (200-400 mm) (n=4)	0.026	Accepted

Table 5.25. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=12) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Fe (200-400 mm)	0.966	Accepted

Table 5.26. Probability distributions of Nordrach Series data (0-400 mm) for September 1998 - August 1999 (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	A <sup>2</sup>	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-400 mm)	0.509	0.179	Accepted
L-o-I % (0-400 mm)	0.297	0.561	Accepted
Total Pb (0-400 mm)	0.737	0.047	Accepted
Total Zn (0-400 mm)	0.185	0.896	Accepted
Total Cd (0-400 mm)	--	--	N.A.
Total Cu (0-400 mm)	0.330	0.493	Accepted
Total Fe (0-400 mm)	1.088	0.006	Rejected
Total Mn (0-400 mm)	0.178	0.909	Accepted

With the exception of Fe, all stacked soil parameter data followed a normal probability distribution (Table 5.26).

Table 5.27. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=24) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Fe (0-400 mm)	0.001	Rejected

After Log<sub>10</sub> transformation, Fe at 0-400 mm did not follow a normal probability distribution (Table 5.27).

### 5.3.9 Annual soil parameter data from all soil series

Table 5.28. Probability distributions of all stacked soil data (0-400 mm) from all soil series for September 1998-August 1999 (n=120) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-400 mm)	0.000	Rejected
L-o-I % (0-400 mm)	0.000	Rejected
Total Pb (0-400 mm)	0.000	Rejected
Total Zn (0-400 mm)	0.000	Rejected
Total Cd (0-400 mm)	0.000	Rejected
Total Cu (0-400 mm)	0.000	Rejected
Total Fe (0-400 mm)	0.000	Rejected
Total Mn (0-400 mm)	0.000	Rejected

None of the stacked soil parameter data followed a normal probability distribution (Table 5.28).

Table 5.29. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=120) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
L-o-I % (0-400 mm)	0.071	Accepted
Pb (0-400 mm)	0.000	Rejected
Zn (0-400 mm)	0.000	Rejected
Cd (0-400 mm)	0.000	Rejected
Cu (0-400 mm)	0.000	Rejected
Fe (0-400 mm)	0.000	Rejected
Mn (0-400 mm)	0.000	Rejected

With the exception of Loss-on-Ignition, which followed a normal probability distribution, after Log<sub>10</sub> transformation none of the soil parameter data followed a normal probability distribution (Table 2.9).

### 5.3.10 Quarterly soil parameter data from all soil series

Table 5.30. Probability distributions of stacked quarterly soil data (0-400 mm) from all soil series for September 1998, December 1998, March 1999 and June 1999 (n=40) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
pH (0-400 mm)	0.008	Rejected
L-o-I % (0-400 mm)	0.140	Accepted
Total Pb (0-400 mm)	0.000	Rejected
Total Zn (0-400 mm)	0.000	Rejected
Total Cd (0-400 mm)	0.000	Rejected
Total Cu (0-400 mm)	0.000	Rejected
Total Fe (0-400 mm)	0.000	Rejected
Total Mn (0-400 mm)	0.000	Rejected
EDTA Pb (0-400 mm)	0.000	Rejected
EDTA Zn (0-400 mm)	0.000	Rejected
EDTA Cd (0-400 mm)	0.000	Rejected
EDTA Cu (0-400 mm)	0.011	Accepted
EDTA Fe (0-400 mm)	0.004	Rejected
EDTA Mn (0-400 mm)	0.000	Rejected
CEC (0-400 mm)	0.088	Accepted
Exch. Ca (0-400 mm)	0.000	Rejected
Exch. Mg (0-400 mm)	0.007	Rejected
Exch. K (0-400 mm)	0.108	Accepted
Total P (0-400 mm)	0.000	Rejected

With the exception of Loss-on-Ignition, EDTA Cu, CEC and Exchangeable K, no stacked soil parameters followed a normal probability distribution (Table 5.30).

After Log<sub>10</sub> transformation, Total Cd, Fe and Mn, EDTA Zn, Cd and Mn and Exchangeable Ca did not follow a normal probability distribution (Table 5.31).

Table 5.31. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=40) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Pb (0-400 mm)	0.018	Accepted
Total Zn (0-400 mm)	0.013	Accepted
Total Cd (0-400 mm)	0.000	Rejected
Total Cu (0-400 mm)	0.046	Accepted
Total Fe (0-400 mm)	0.007	Rejected
Total Mn (0-400 mm)	0.002	Rejected
EDTA Pb (0-400 mm)	0.014	Accepted
EDTA Zn (0-400 mm)	0.000	Rejected
EDTA Cd (0-400 mm)	0.001	Rejected
EDTA Fe (0-400 mm)	0.014	Accepted
EDTA Mn (0-400 mm)	0.000	Rejected
Exch. Ca (0-400 mm)	0.009	Rejected
Exch. Mg (0-400 mm)	0.076	Accepted
Total P (0-400 mm)	0.021	Accepted

**5.4 Quality control - precision and accuracy**

Field sample duplicates, analytical duplicates, BCR CRM 143R Sewage Sludge

Amended Soil and the in-house reference material were analysed to assess

precision and accuracy as described in 4.5. The quality control data for the annual

soil study were combined with the quality control data from the baseline study in

4.7.



Table 5.31. Summary of the probability distributions of Log<sub>10</sub> transformed soil data (n=40) calculated by the Anderson-Darling Test for normality.

Soil Parameter	p-value	H <sub>0</sub> : data followed a Normal Probability Distribution
Total Pb (0-400 mm)	0.018	Accepted
Total Zn (0-400 mm)	0.013	Accepted
Total Cd (0-400 mm)	0.000	Rejected
Total Cu (0-400 mm)	0.046	Accepted
Total Fe (0-400 mm)	0.007	Rejected
Total Mn (0-400 mm)	0.002	Rejected
EDTA Pb (0-400 mm)	0.014	Accepted
EDTA Zn (0-400 mm)	0.000	Rejected
EDTA Cd (0-400 mm)	0.001	Rejected
EDTA Fe (0-400 mm)	0.014	Accepted
EDTA Mn (0-400 mm)	0.000	Rejected
Exch. Ca (0-400 mm)	0.009	Rejected
Exch. Mg (0-400 mm)	0.076	Accepted
Total P (0-400 mm)	0.021	Accepted

## 5.4 Quality control - precision and accuracy

Field sample duplicates, analytical duplicates, BCR CRM 143R Sewage Sludge Amended Soil and the in-house reference material were analysed to assess precision and accuracy as described in 4.5. The quality control data for the annual soil study were combined with the quality control data from the baseline study in 4.7.

## 5.5 Results

### 5.5.1 Soil series characteristics

#### Plant communities

Analysis of the distribution and abundance of plant species showed that while several species were common to more than one soil series (Table 5.32), each soil series supported a distinctive community.

Table 5.32. Species List and Domin values for permanent 2 m<sup>2</sup> quadrats for each soil series (Nomenclature follows Stace, 1997).

Species	Maesbury Series	Thrupe Series	Ashen Series	Tailings	Nordrach Series
<i>Deschampsia flexuosa</i>	8		9		
<i>Agrostis capillaris</i>	7	5		2	8
<i>Festuca ovina</i> agg./ <i>rubra</i>	6	7		9	4
<i>Potentilla erecta</i>	5	4	2		5
Moss spp.	4	5	5	3	4
<i>Rumex acetosa</i>	2			3	4
<i>Molinia caerulea</i>	1	7	7		
<i>Deschampsia cespitosa</i>	1				
<i>Arrhenatherum elatius</i>	1				
<i>Holcus lanatus</i>	1	2		4	9
<i>Galium saxatile</i>		4			
<i>Juncus effusus</i>		4			
<i>Ranunculus acris</i>		3		2	2
<i>Equisetum arvense</i>		2			
<i>Dryopteris carthusiana</i>		2			
<i>Agrostis canina</i>		3			
<i>Ophioglossum vulgatum</i>		1			
<i>Thymus polytrichus</i>				8	
<i>Cladonia</i> spp.				6	
<i>Carex caryophylla</i>				5	
<i>Leontodon saxatilis</i>				5	
<i>Lotus corniculatus</i>				4	
<i>Plantago lanceolata</i>				4	3
<i>Silene uniflora</i>				3	
<i>Achillea millefolium</i>				3	1
<i>Mimuartia verna</i>				3	
<i>Peltigera</i> spp				3	
<i>Cerastium semidecandrum</i>				3	
<i>Euphrasia officianalis</i> agg.				3	
<i>Trifolium repens</i>				3	
<i>Linum catharticum</i>				3	
<i>Anthoxanthum odoratum</i>				2	2
<i>Botrychium lunaria</i>				1	
<i>Prunella vulgaris</i>				1	
<i>Rubus fruticosus</i>					5
<i>Veronica chamaedrys</i>					4
<i>Stellaria graminea</i>					4
<i>Cerastium fontanum</i>					3
<i>Chamerion angustifolium</i>					2
<i>Cirsium arvense</i>					2

The communities present in the 2 m<sup>2</sup> quadrat on each soil series were identified as:

#### Maesbury Series

NVC U 2a *Deschampsia flexuosa* grassland  
*Festuca ovina-Agrostis capillaris* sub-community

#### Thrupe Series

NVC M 25 *Molinia caerulea-Potentilla erecta* mire

#### Ashen Series

NVC U 2 *Deschampsia flexuosa* grassland

#### Tailings

NVC OV 37b *Festuca ovina-Minuartia verna* community  
*Achillea millefolium-Euphrasia officinalis* sub-community

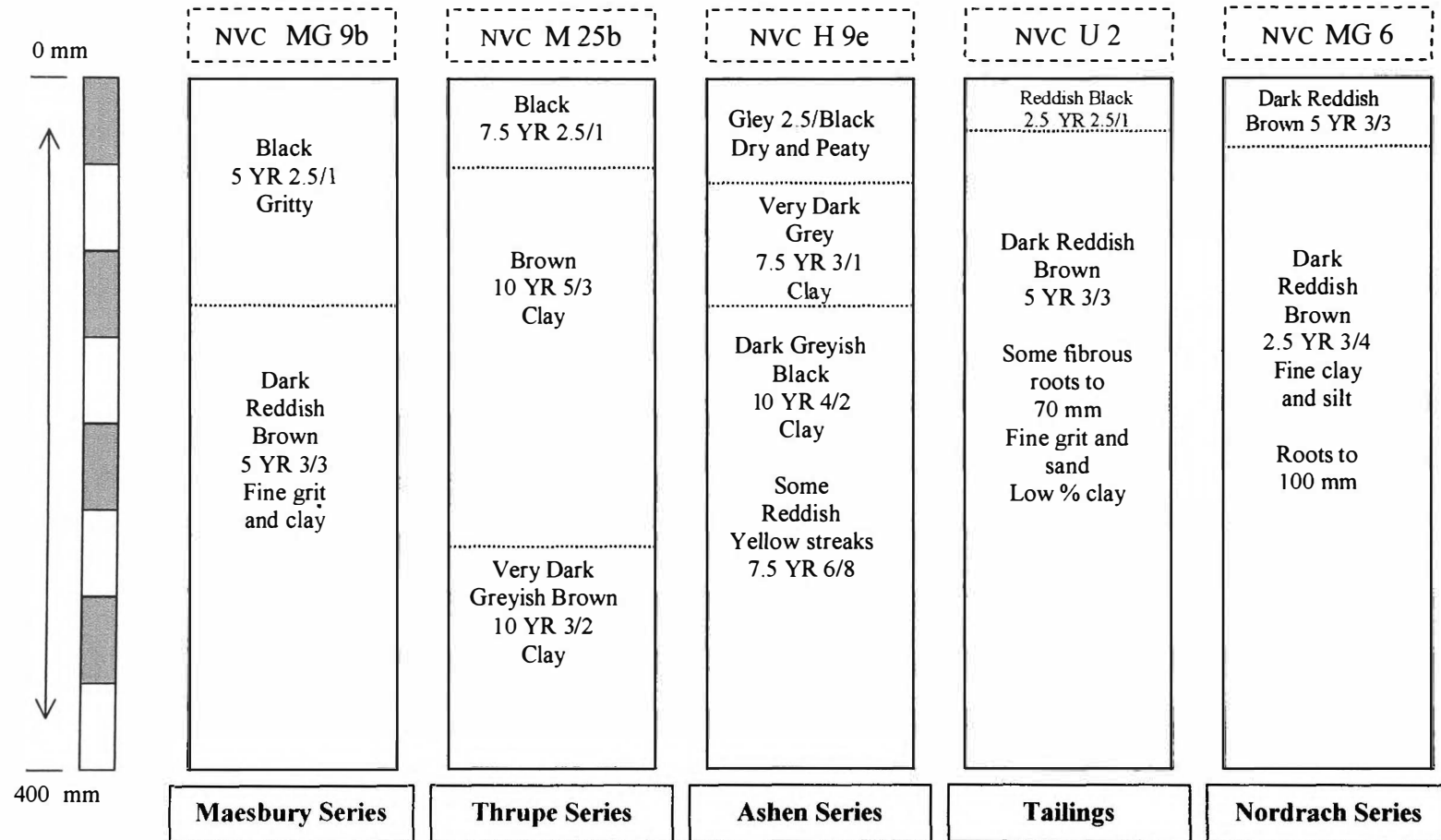
#### Nordrach Series

NVC U 4b *Festuca ovina-Agrostis capillaris-Galium saxatile* grassland  
*Holcus lanatus-Trifolium repens* sub-community

#### Soil profiles

The profiles of each soil series at 0-400 mm were markedly different in horizon depth and colour (Figures 5.33). The Thrupe and Ashen profiles showed the most distinct zonation in soil horizons, with the Thrupe profile exhibiting the characteristics typical of an iron podsol (White, 1987).

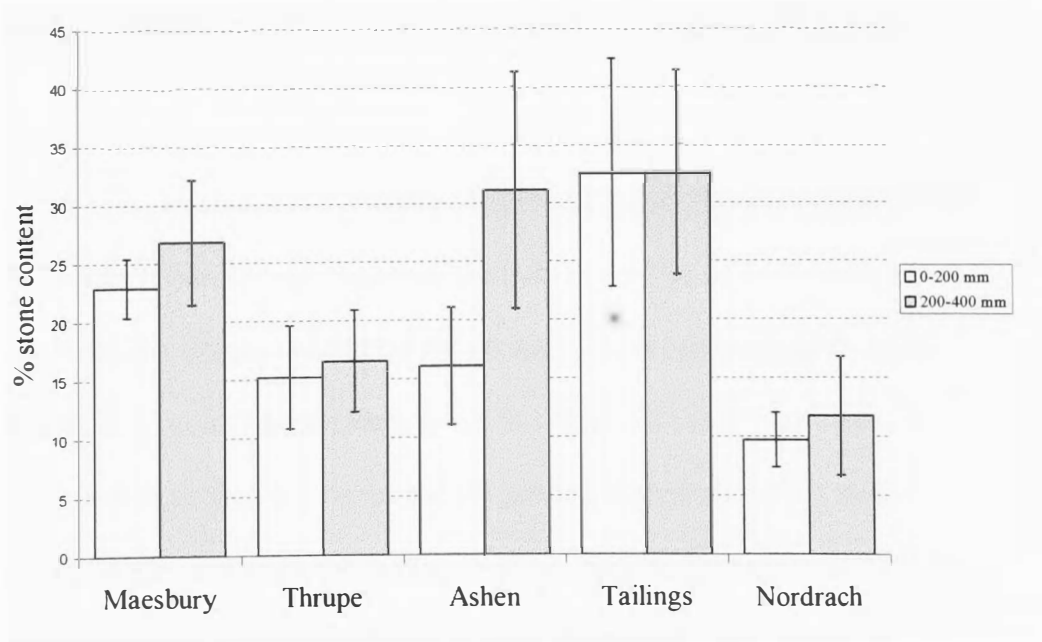
Figure 5.4. N.V.C. and soil profile descriptions. Soil colour was classified using Munsell® soil colour charts (Munsell, 1992).



Although texturally very different, the Tailings and Nordrach profiles were similar in that both had a shallow organic humic horizon at 25 mm and 40 mm respectively, with an apparently azonal profile to 400 mm (Figures 5.4, 5.6 and 5.7 and Table 5.33). The Maesbury profile was most similar in texture to that of the Tailings in the upper horizon, although there was a distinct horizon boundary at 130 mm (Figure 5.4 and 5.6 and Table 5.33). At this depth the colour of the Maesbury profile changed from Black YR 2.5/1 to Dark Reddish Brown 5 YR 3/3 and texture changed from sand to loamy sand (Figures 5.4 and 5.6 and Table 5.33).

Particle Size Analysis

Figure 5.5. Percentage stone content (> 2 mm fraction) of soil cores collected from each soil series at 0-200 mm and 200-400 mm (n=4).



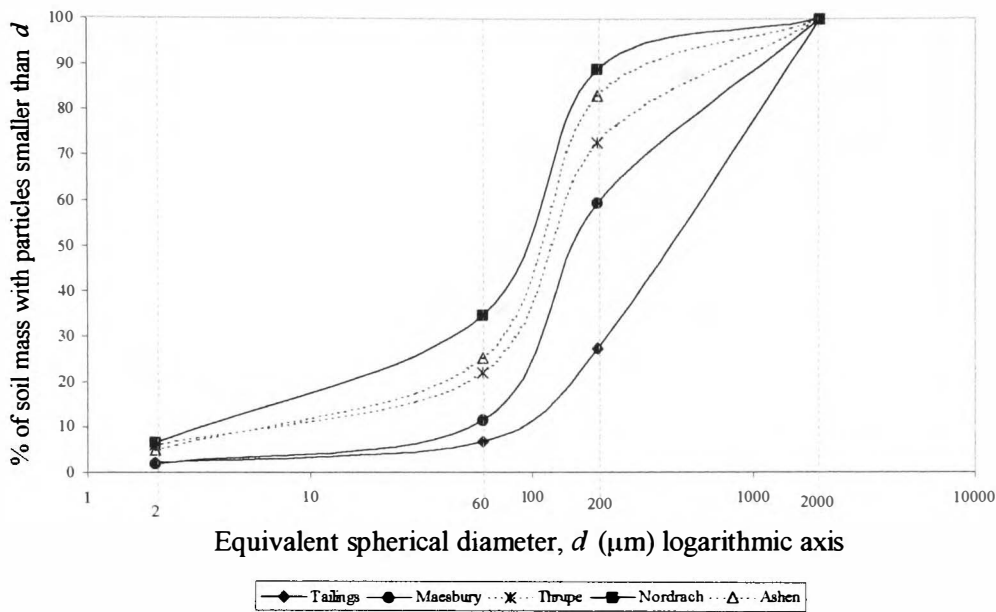
For all series, the stone content of the soil was greater at depth although the difference was most marked in the Ashen Series (Figure 5.5). The greatest percentage stone content occurred in Tailings at depth at 32.59%, although there was only 0.3% difference between depth and surface tailings at 32.56%. The surface Nordrach soil contained the lowest stone content at 9.77%.

Table 5.33. Particle size distribution in the < 2 mm fraction and textural class of all soil series.

<b>Soil Series</b>	<b>Depth (mm)</b>	<b>% clay</b>	<b>% silt</b>	<b>% fine sand</b>	<b>% coarse sand</b>	<b>Textural Class</b>
<b>Maesbury</b>	0 - 200	1.82	9.62	48.13	40.43	Sand
<b>Maesbury</b>	200-400	5.00	10.03	51.13	33.85	Loamy Sand
<b>Thrupe</b>	0 - 200	6.08	15.83	50.82	27.27	Loamy Sand
<b>Thrupe</b>	200-400	9.12	17.35	47.06	26.48	Silty Loam
<b>Ashen</b>	0 - 200	5.03	20.26	57.95	16.76	Loamy Sand
<b>Ashen</b>	200-400	9.04	19.30	49.48	22.18	Loamy Sand
<b>Tailings</b>	0 - 200	2.22	4.52	20.75	72.51	Sand
<b>Tailings</b>	200-400	3.49	8.02	19.41	69.08	Sand
<b>Nordrach</b>	0 - 200	6.52	28.08	54.40	11.00	Silty Loam
<b>Nordrach</b>	200-400	10.85	14.15	61.98	13.02	Silty Loam

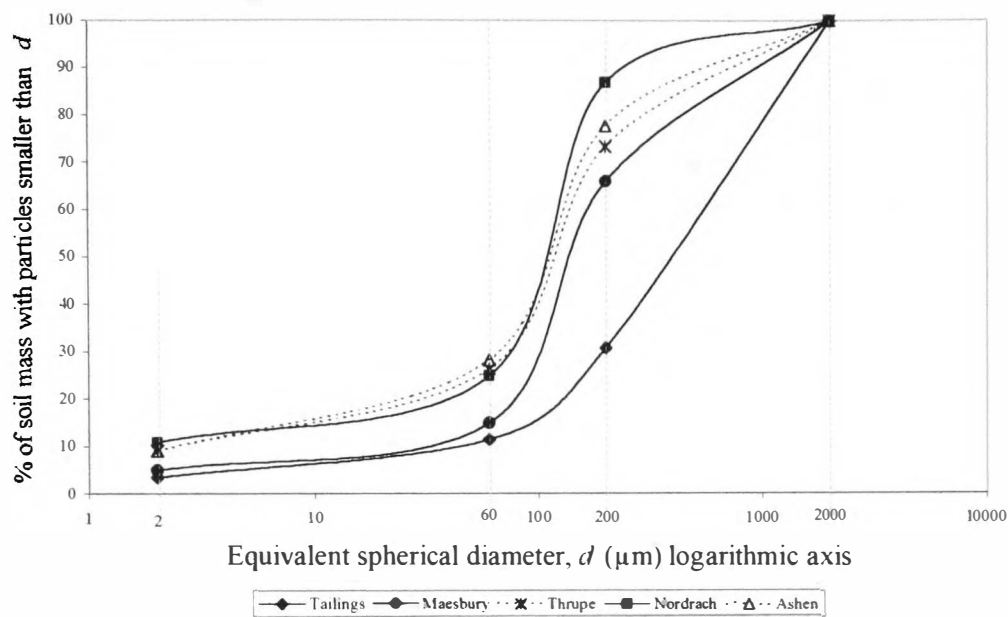
Of all the soils, Nordrach soil at depth contained the greatest clay content 10.85%, while Maesbury surface soil contained the least at 1.82% (Table 5.33, Figure 5.67). Nordrach soil also contained the greatest silt content at 28.08%, while surface Tailings contained the least at 4.52% (Table 5.33 and Figure 5.6). At 57.95 %, Ashen surface soil contained the greatest fine sand content, while Tailings at depth contained the least at 19.41%. Surface Tailings contained the greatest percentage of coarse sand at 72.51% and surface Nordrach soil the least at 11.00%.

Figure 5.6. Cumulative curve displaying particle size distribution of all soils at 0-200 mm.



With the exception of Tailings, which was dominated by coarse sand in both horizons, the < 2 mm fraction of all soil series at the surface and at depth was dominated by fine sand (Table 5.33 and Figures 5.6 and 5.7). All soils comprised of at least 60% sand (fine + coarse sand), with Nordrach soil at depth containing the least at 65.40%, and Tailings at depth the greatest at 93.26% (Figures 5.6 and 5.7). In the surface soils, the Thrupe and Ashen Series showed the most similar particle size distribution, while Nordrach and Tailings showed the most different distribution.

Figure 5.7. Cumulative curve displaying particle size distribution of all soils at 200-400 mm.



In the surface soils, the Thrupe and Ashen Series showed the most similar particle size distribution, while Nordrach and Tailings showed the most different distribution at depth (Figure 5.7).

### 5.5.2 Maesbury Series

#### Particle Size Analysis

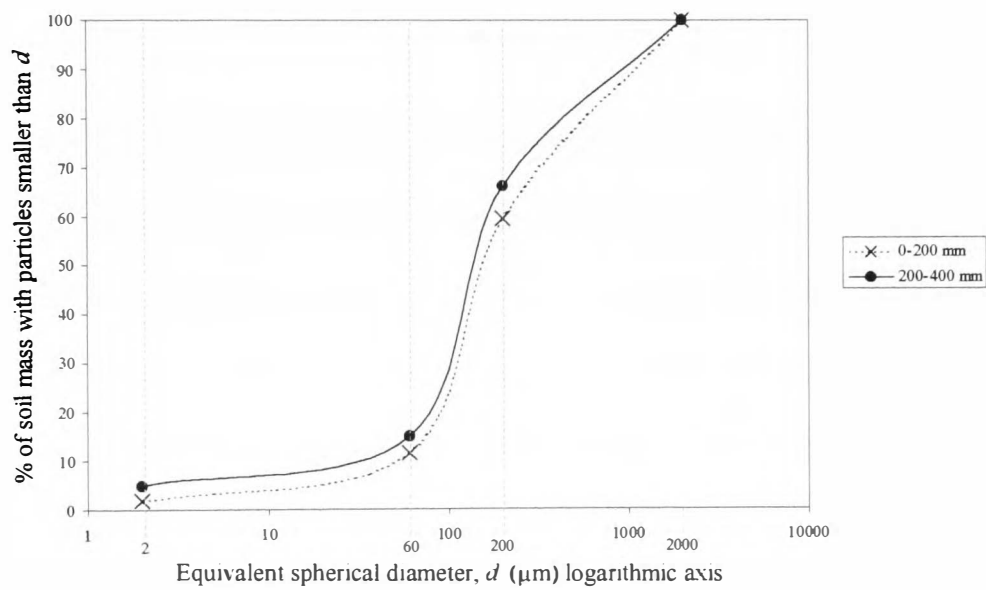
Table 5.34. Particle size distribution and soil textural class for Maesbury Series.

Depth (mm)	% clay	% silt	% fine sand	% coarse sand	Textural Class
0 - 200	1.82	9.62	48.13	40.43	Sand
200-400	5.00	10.03	51.13	33.85	Loamy Sand



The surface soil was classified as sand, with fine sand as the most abundant particle size (Table 5.34). At depth, although still dominated by fine sand, the soil contained a higher % of clay and silt and was classified as loamy sand.

Figure 5.8. Cumulative curve displaying particle size distribution of Maesbury soil at 0-200 mm and 200-400 mm.



The cumulative curve plot showed that at approximately 85% and 90% of the particles at surface and depth respectively, sand (fine + coarse sand) dominated the < 2 mm soil fraction at both surface and depth (Figure 5.8).

### Descriptive statistics

The Maesbury Series data set consisted of monthly data for pH, Loss-on-Ignition and Total Pb, Zn, Cd, Cu, Fe and Mn at 0-200 mm and 200-400 mm (n=12), and quarterly data for EDTA Pb, Zn, Cd, Cu, Fe and Mn, CEC, Exchangeable Ca, Mg and K and Total P at 0-200 mm and 200-400 mm (n=4). Surface soil reaction ranged from pH 3.88 to pH 6.46 and from pH 4.72 to pH 6.92 at depth. Loss-on-Ignition ranged from 19.78 % to 26.14% in surface soil and from 9.21% to 12.47% at depth (Table 5.35).

The concentration of surface Total Pb ranged from 4 137.00  $\mu\text{g g}^{-1}$  to 13 863.00  $\mu\text{g g}^{-1}$  and from 7 730.00  $\mu\text{g g}^{-1}$  to 20 760.00  $\mu\text{g g}^{-1}$  at depth. Total Zn in surface soil ranged from 256.67  $\mu\text{g g}^{-1}$  to 2 500.00  $\mu\text{g g}^{-1}$  and from 576.67  $\mu\text{g g}^{-1}$  to 1 833.33  $\mu\text{g g}^{-1}$  at depth. Total Cd was present in surface soil at 1.00  $\mu\text{g g}^{-1}$  to 2.00  $\mu\text{g g}^{-1}$  and from 0.05  $\mu\text{g g}^{-1}$  to 2.00  $\mu\text{g g}^{-1}$  at depth. Total Cu ranged from 19.67  $\mu\text{g g}^{-1}$  to 32.67  $\mu\text{g g}^{-1}$  in surface soil and from 15.67  $\mu\text{g g}^{-1}$  to 28.00  $\mu\text{g g}^{-1}$  at depth. Total Fe was present at 12 683.30  $\mu\text{g g}^{-1}$  to 19 666.67  $\mu\text{g g}^{-1}$  in surface soil and from 17 020.00  $\mu\text{g g}^{-1}$  to 23 386.00  $\mu\text{g g}^{-1}$  at depth. Total Mn ranged from 78.33  $\mu\text{g g}^{-1}$  to 531.33  $\mu\text{g g}^{-1}$  in surface soil and from 576.67  $\mu\text{g g}^{-1}$  to 1 833.33  $\mu\text{g g}^{-1}$  at depth (Table 5.35).

Table 5.35. Soil parameter data for Maesbury Series at 0-200 mm and 200-400 mm (n=12) for September 1998 - August 1999 and (n=4) for quarterly sampling.

	Unit	n	Arithmetic Mean	St. Dev.	Minimum	Median	Maximum
pH (0-200 mm)	pH	12	5.27	1.13	3.88	5.23	6.46
pH (200-400 mm)	pH	12	6.01	0.91	4.72	6.35	6.92
L-o-I (0-200 mm)	%	12	19.78	3.66	14.27	18.71	26.14
L-o-I (200-400 mm)	%	12	10.61	0.89	9.21	10.62	12.47
Total Pb (0-200 mm)	$\mu\text{g g}^{-1}$	12	8 929.83	3 295.47	4 137.00	8 630.00	13 863.00
Total Pb (200-400 mm)	$\mu\text{g g}^{-1}$	12	12 802.40	3 692.00	7 730.00	12 498.00	20 760.00
Total Zn (0-200 mm)	$\mu\text{g g}^{-1}$	12	887.22	569.99	256.67	685.00	2 500.00
Total Zn (200-400 mm)	$\mu\text{g g}^{-1}$	12	1 555.00	613.78	576.67	1 565.00	1 833.33
Total Cd (0-200 mm)	$\mu\text{g g}^{-1}$	12	1.50	0.522	1.00	1.50	2.00
Total Cd (200-400 mm)	$\mu\text{g g}^{-1}$	12	1.07	0.34	0.05	1.00	2.00
Total Cu (0-200 mm)	$\mu\text{g g}^{-1}$	12	26.17	4.15	19.67	25.84	32.67
Total Cu (200-400 mm)	$\mu\text{g g}^{-1}$	12	20.53	3.23	15.67	20.50	28.00
Total Fe (0-200 mm)	$\mu\text{g g}^{-1}$	12	15 678.80	1 965.10	12 683.30	14 990.00	19 666.67
Total Fe (200-400 mm)	$\mu\text{g g}^{-1}$	12	20 038.60	2 369.90	17 020.00	18 970.00	23 386.70
Total Mn (0-200 mm)	$\mu\text{g g}^{-1}$	12	240.22	147.78	78.33	281.50	531.33
Total Mn (200-400 mm)	$\mu\text{g g}^{-1}$	12	332.52	122.79	2 13.33	287.00	602.00
EDTA Pb (0-200 mm)	$\mu\text{g g}^{-1}$	4	7 922.50	2 949.08	4 786.67	7 521.67	11 860.00
EDTA Pb (200-400 mm)	$\mu\text{g g}^{-1}$	4	8 961.67	1 217.87	7 696.67	8 781.67	10 586.67
EDTA Zn (0-200 mm)	$\mu\text{g g}^{-1}$	4	396.13	102.47	287.87	401.67	493.33
EDTA Zn (200-400 mm)	$\mu\text{g g}^{-1}$	4	290.58	99.05	179.00	286.67	410.00
EDTA Cd (0-200 mm)	$\mu\text{g g}^{-1}$	4	1.16	0.76	0.10	1.35	1.83
EDTA Cd (200-400 mm)	$\mu\text{g g}^{-1}$	4	0.93	0.44	0.30	1.05	1.33
EDTA Cu (0-200 mm)	$\mu\text{g g}^{-1}$	4	16.44	5.66	11.20	15.20	24.17
EDTA Cu (200-400 mm)	$\mu\text{g g}^{-1}$	4	12.09	6.28	8.70	9.08	21.50
EDTA Fe (0-200 mm)	$\mu\text{g g}^{-1}$	4	2 103.50	1 230.01	1 113.00	1 780.50	3 740.00
EDTA Fe (200-400 mm)	$\mu\text{g g}^{-1}$	4	1 290.08	432.14	803.00	1 288.67	1 780.00
EDTA Mn (0-200 mm)	$\mu\text{g g}^{-1}$	4	125.69	95.13	27.43	120.00	235.33
EDTA Mn (200-400 mm)	$\mu\text{g g}^{-1}$	4	106.50	39.03	83.67	88.83	164.67
CEC (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	25.15	3.21	20.99	25.54	28.51
CEC (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	17.62	2.16	15.84	17.03	20.59
Exch. Ca (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	12.44	9.44	1.47	13.57	21.16
Exch. Ca (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	8.47	5.42	2.27	8.84	13.94
Exch. Mg (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.63	0.12	0.49	0.62	0.78
Exch. Mg (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.41	0.06	0.33	0.43	0.45
Exch. K (0-200 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.25	0.06	0.21	0.23	0.34
Exch. K (200-400 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.17	0.06	0.12	0.16	0.26
Total P (0-200 mm)	$\mu\text{g g}^{-1}$	4	702.60	88.79	570.10	740.70	758.90
Total P (200-400 mm)	$\mu\text{g g}^{-1}$	4	900.05	237.26	555.10	982.05	1 081.00

EDTA Pb was present in surface soil at 4 786.67  $\mu\text{g g}^{-1}$  to 11 860.00  $\mu\text{g g}^{-1}$  and from 7 696.67  $\mu\text{g g}^{-1}$  to 10 586.67  $\mu\text{g g}^{-1}$  at depth. EDTA Zn was present in surface soil at 287.87  $\mu\text{g g}^{-1}$  to 493.33  $\mu\text{g g}^{-1}$  and from 179.00  $\mu\text{g g}^{-1}$  to 410.00  $\mu\text{g g}^{-1}$  at depth. Surface EDTA Cd ranged from 0.10  $\mu\text{g g}^{-1}$  to 1.83  $\mu\text{g g}^{-1}$  and from 0.30  $\mu\text{g g}^{-1}$  to 1.33  $\mu\text{g g}^{-1}$  at depth. The concentration of surface EDTA Cu ranged from 11.20  $\mu\text{g g}^{-1}$  to 24.17  $\mu\text{g g}^{-1}$  and from 8.70  $\mu\text{g g}^{-1}$  to 21.50  $\mu\text{g g}^{-1}$  at depth.

Surface EDTA Fe ranged from 1 113.00  $\mu\text{g g}^{-1}$  to 3 740.00  $\mu\text{g g}^{-1}$  and from 803.00  $\mu\text{g g}^{-1}$  to 1 780.00  $\mu\text{g g}^{-1}$  at depth. EDTA Mn was present in surface soil at 27.43  $\mu\text{g g}^{-1}$  to 235.33  $\mu\text{g g}^{-1}$  and from 83.67  $\mu\text{g g}^{-1}$  to 164.67  $\mu\text{g g}^{-1}$  at depth (Table 5.35).

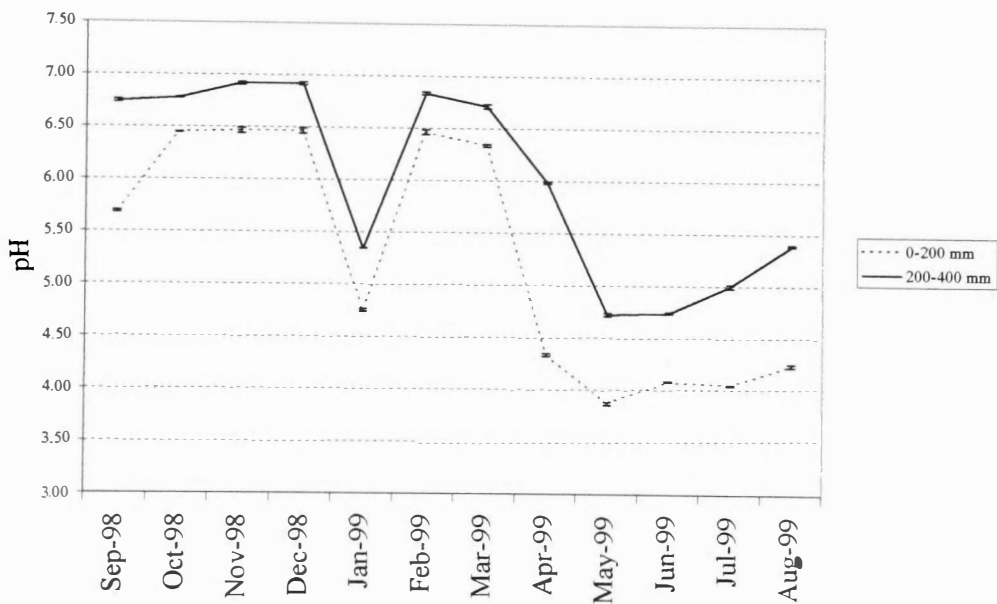
Surface CEC ranged from 20.99  $\text{cmol}_\text{c kg}^{-1}$  to 28.51  $\text{cmol}_\text{c kg}^{-1}$  and from 15.84  $\text{cmol}_\text{c kg}^{-1}$  to 20.59  $\text{cmol}_\text{c kg}^{-1}$  at depth. The concentration of surface Exchangeable Ca ranged from 1.47  $\text{cmol}_\text{c kg}^{-1}$  to 21.16  $\text{cmol}_\text{c kg}^{-1}$  and from 2.27  $\text{cmol}_\text{c kg}^{-1}$  to 13.94  $\text{cmol}_\text{c kg}^{-1}$  at depth. Exchangeable Mg was present in surface soil at 0.49  $\text{cmol}_\text{c kg}^{-1}$  to 0.78  $\text{cmol}_\text{c kg}^{-1}$  and from 0.33  $\text{cmol}_\text{c kg}^{-1}$  to 0.45  $\text{cmol}_\text{c kg}^{-1}$  at depth. Surface Exchangeable K ranged from 0.21  $\text{cmol}_\text{c kg}^{-1}$  to 0.34  $\text{cmol}_\text{c kg}^{-1}$  and from 0.12  $\text{cmol}_\text{c kg}^{-1}$  to 0.26  $\text{cmol}_\text{c kg}^{-1}$  at depth. The concentration of surface Total P ranged from 570.10  $\mu\text{g g}^{-1}$  to 758.90  $\mu\text{g g}^{-1}$  and from 555.10  $\mu\text{g g}^{-1}$  to 1 081.00  $\mu\text{g g}^{-1}$  at depth (Table 5.35).

Generally, the mean and median values of each individual soil parameter were similar, with the exception of surface Total Zn, surface Exchangeable Fe and

Exchangeable Mn at depth (Table 5.35). For Total Zn in surface soil, the mean and median values were 887.22  $\mu\text{g g}^{-1}$  and 685.00  $\mu\text{g g}^{-1}$  respectively. The mean and median values for Exchangeable Fe were 2 103.50  $\mu\text{g g}^{-1}$  and 1 780.50  $\mu\text{g g}^{-1}$ , and for Exchangeable Mn at depth 106.50  $\mu\text{g g}^{-1}$  and 88.83  $\mu\text{g g}^{-1}$  (Table 5.35).

Monthly variation in pH, Loss-on-Ignition and Total metals

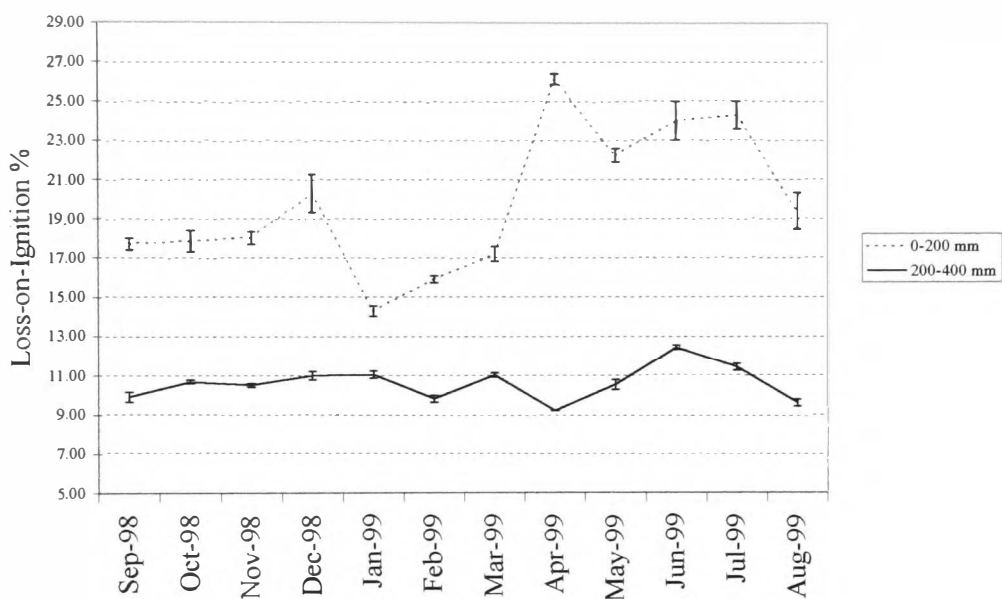
Figure 5.9. Mean monthly pH at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



Soil reaction at surface and depth generally followed a similar pattern of variation throughout the year, with pH at depth consistently greater than surface pH in each month (Figure 5.9). The lowest pH values in the surface soil occurred in May 1999 at pH 4.04  $\pm$ 0.00, while the highest at pH 6.46  $\pm$ 0.02 occurred in November and December 1998 and February 1999 (Figure 5.9). For soil at depth, the lowest

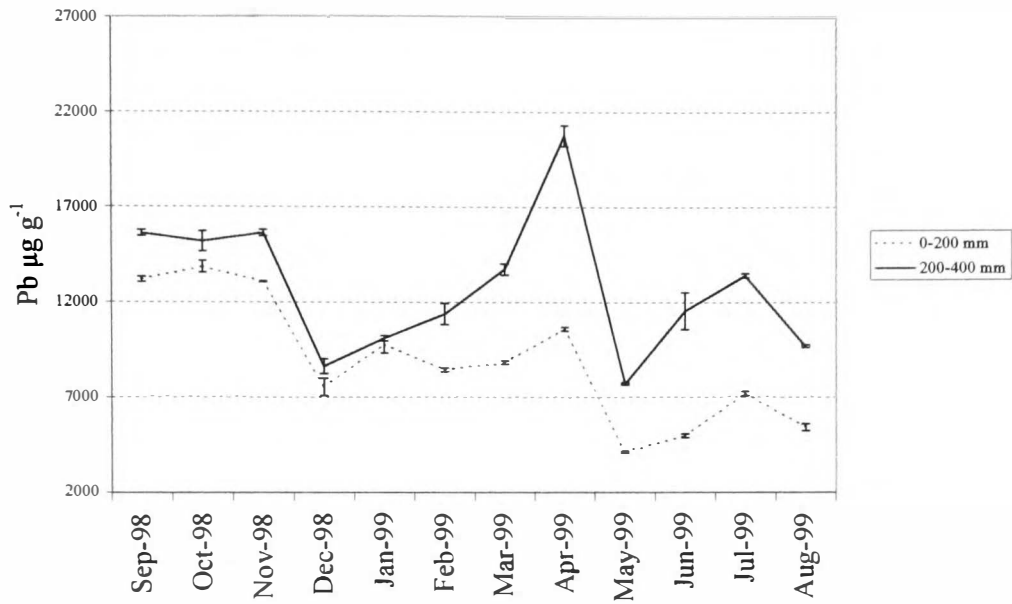
pH occurred in May 1999 at  $\text{pH } 4.72 \pm 0.02$ , while the highest pH of  $6.92 \pm 0.01$  occurred in November and December 1998.

Figure 5.10. Mean monthly % Loss-on-Ignition at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



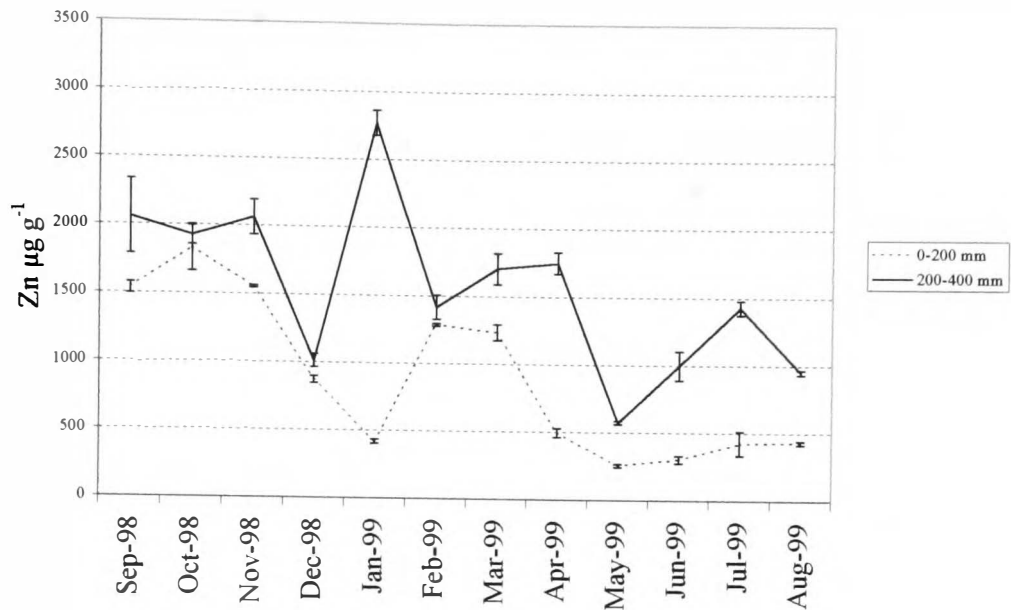
For each month, Loss-on-Ignition was consistently greater for surface soil than that at depth (Figure 5.10). The lowest % Loss-on-Ignition in the surface soil occurred in January 1999 at  $14.27 \pm 0.26\%$ , while the greatest % Loss-on-Ignition of  $26.14 \pm 0.26\%$  occurred in April 1999 (Figure 5.10). The lowest % Loss-on-Ignition at depth occurred in April 1999 at  $9.21 \pm 0.01\%$ , while the greatest % Loss-on-Ignition of  $12.47 \pm 0.01\%$  occurred in June 1999 (Figure 5.10).

Figure 5.11. Mean monthly Total Pb at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



Total Pb in surface soil and at depth generally followed a similar pattern of variation throughout the year. For each month, the concentration of Total Pb was consistently greater for soil at depth than that at the surface (Figure 5.11). The lowest concentration of Total Pb in the surface soil occurred in May 1999 at  $4\,137 \pm 0.26 \mu\text{g g}^{-1}$ , while the greatest at  $13\,863 \pm 310 \mu\text{g g}^{-1}$  occurred in October 1998 (Figure 5. 11). The lowest concentration of Total Pb at depth occurred in May 1999 at  $9.21 \pm 0.01 \mu\text{g g}^{-1}$ , while the greatest occurred in April 1999 at  $20\,760 \pm 543 \mu\text{g g}^{-1}$  (Figure 5.11).

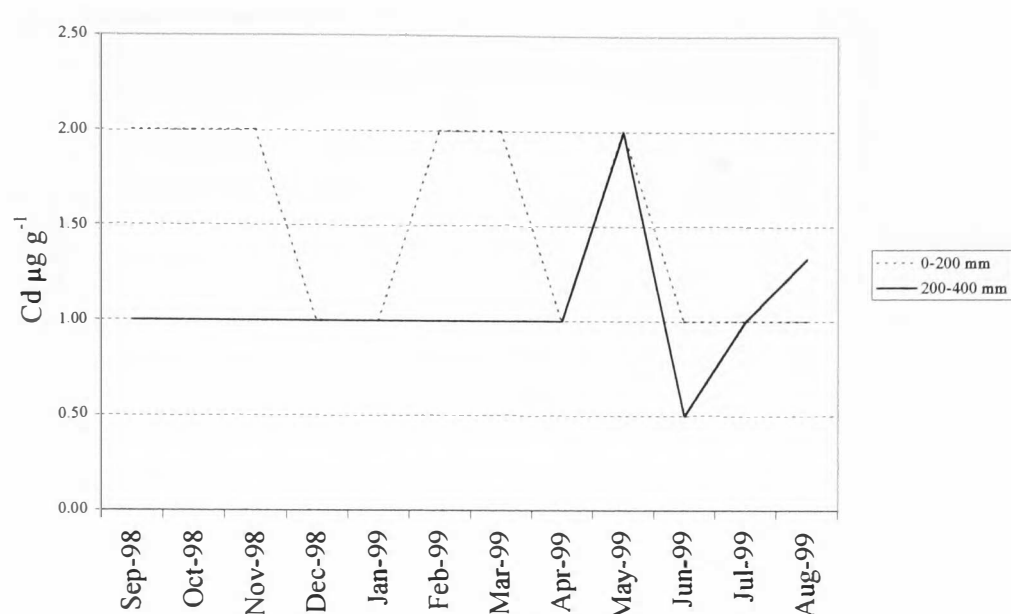
Figure 5.12. Mean monthly Total Zn at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



For each month, the concentration of Total Zn was consistently greater for soil at depth than that at the surface (Figure 5.12). The lowest concentration of Total Zn in the surface soil occurred in May 1999 at  $256.67 \pm 12.47 \mu\text{g g}^{-1}$ , while the greatest at  $1833 \pm 169.97 \mu\text{g g}^{-1}$  occurred in October 1998 (Figure 5.12). At  $576.67 \pm 12.47 \mu\text{g g}^{-1}$ , the lowest concentration of Total Zn at depth occurred in May 1999, while the greatest occurred in January 1999 at  $20760 \pm 543 \mu\text{g g}^{-1}$  (Figure 5.12).

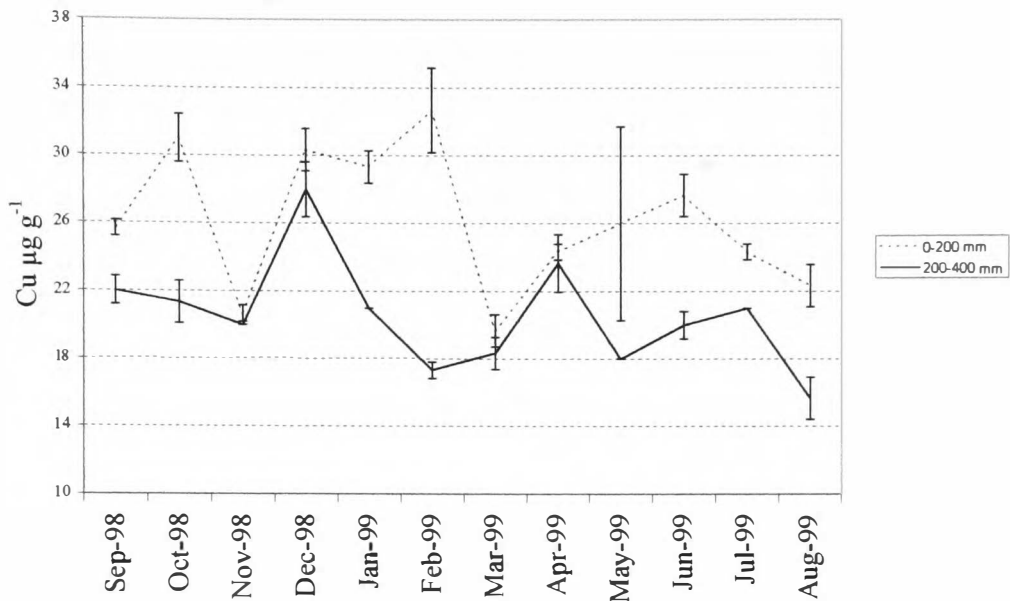


Figure 5.13. Mean monthly Total Cd at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



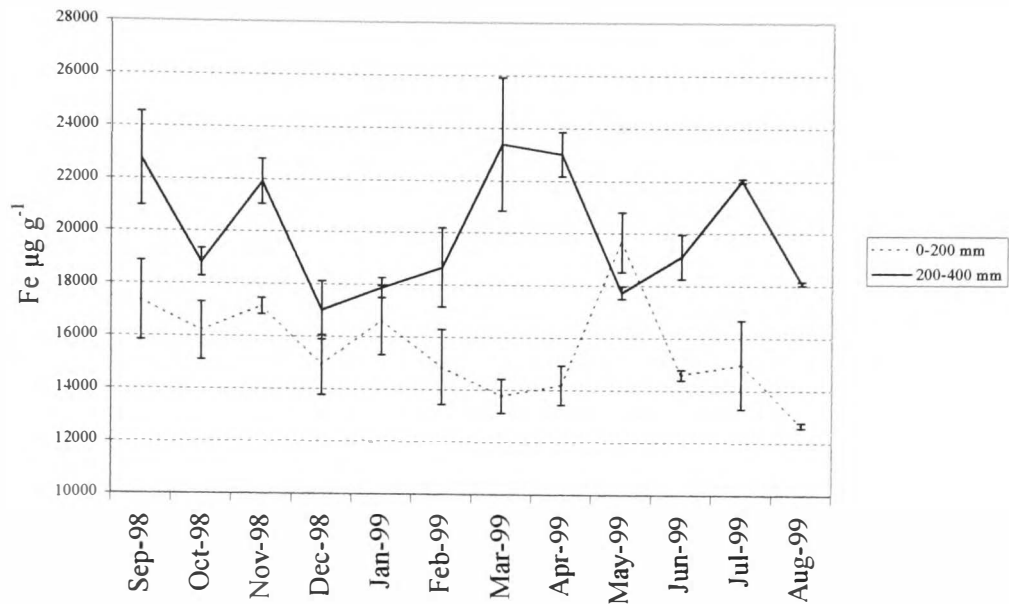
For each month, the concentration of Total Cd was mostly greater for surface soil than that at depth (Figure 5.13). The lowest concentration of Total Cd in the surface soil occurred in December 1998 and January, April, June and July 1999 at  $1.00 \pm 0 \mu\text{g g}^{-1}$ . The greatest concentration of Total Cd in the surface soil at  $2.00 \pm 0 \mu\text{g g}^{-1}$  occurred in February, March and May 1999 (Figure 5.13). At depth, the lowest concentration of Total Cd at  $0.50 \pm 0 \mu\text{g g}^{-1}$  occurred in June 1999, while the greatest occurred in May 1999 at  $2.00 \pm 0 \mu\text{g g}^{-1}$  (Figure 5.13).

Figure 5.14. Mean monthly Total Cu at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



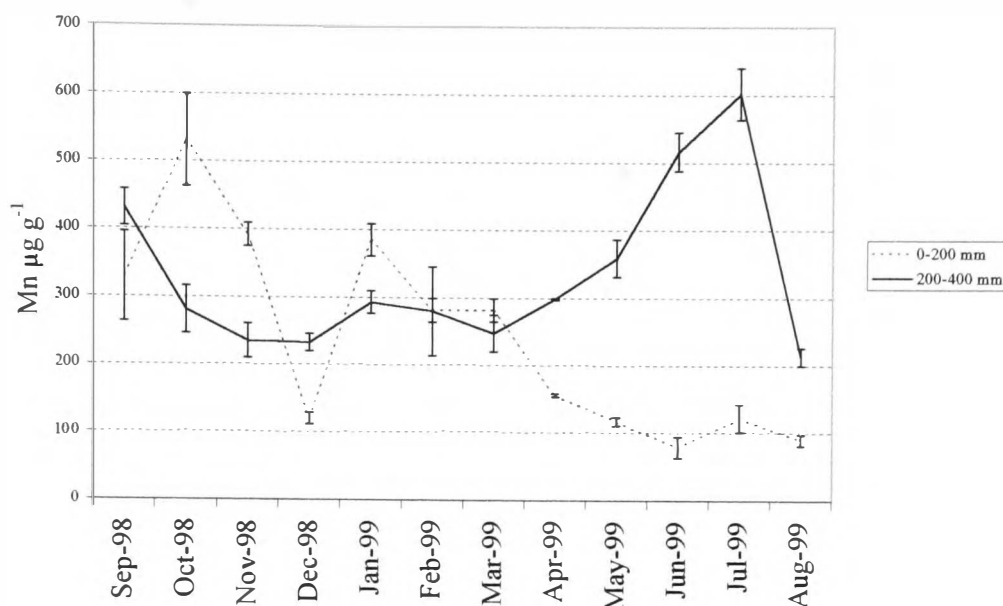
For each month, the concentration of Total Cu was consistently greater for surface soil than that at depth (Figure 5.14). The lowest concentration of Total Cu in the surface soil occurred in March 1999 at  $19.67 \pm 0.94 \mu\text{g g}^{-1}$ , while the greatest occurred in February 1998 at  $32.67 \pm 2.49 \mu\text{g g}^{-1}$  (Figure 5.14). At depth, the lowest concentration of Total Cu at  $15.67 \pm 1.25 \mu\text{g g}^{-1}$  occurred in August 1999, while the greatest occurred in December 1998 at  $28.00 \pm 1.63 \mu\text{g g}^{-1}$  (Figure 5.14).

Figure 5.15. Mean monthly Total Fe at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



For each month, the concentration of Total Fe was consistently greater for soil at depth than that at surface (Figure 5.15). The lowest concentration of Total Fe in the surface soil occurred in August 1999 at  $12\,683 \pm 97 \mu\text{g g}^{-1}$ , while the greatest at  $19\,667 \pm 1\,146 \mu\text{g g}^{-1}$  occurred in March 1999 (Figure 5.15). At depth, the lowest concentration of Total Fe of  $17\,020 \pm 1\,104 \mu\text{g g}^{-1}$  occurred in December 1998, while the greatest occurred in March 1999 at  $23\,386 \pm 2\,538 \mu\text{g g}^{-1}$  (Figure 5.15).

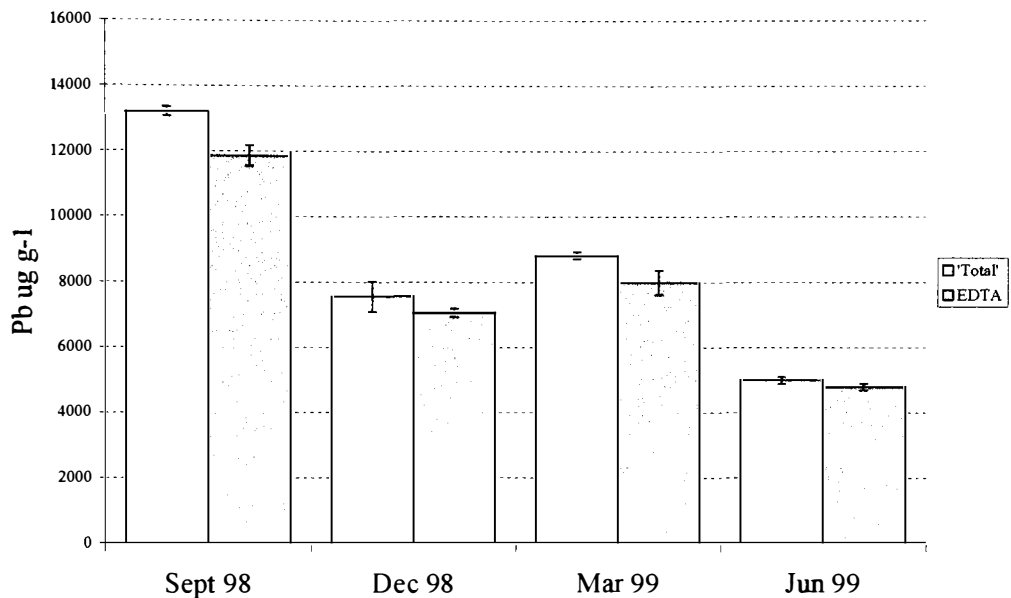
Figure 5.16. Mean monthly Total Mn at 0-200 mm and 200-400 mm for Maesbury Series (n=3).



With the exception of December 1998, for each month from September 1998 to March 1999, the concentration of Total Mn was consistently greater for surface soil than that at depth. For each month from April 1999 to August 1999, the concentration of Total Mn was consistently greater for soil at depth than that at surface. In January 1999, there was only  $1.33 \mu\text{g g}^{-1}$  difference between the mean concentration of Total Mn at surface and depth at  $281.33 \pm 17.33 \mu\text{g g}^{-1}$  and  $280.00 \pm 65.58 \mu\text{g g}^{-1}$  respectively (Figure 5.16). The lowest concentration of Total Mn in the surface soil occurred in June 1999 at  $78.33 \pm 13.37 \mu\text{g g}^{-1}$ , while the greatest at  $531.33 \pm 68.51 \mu\text{g g}^{-1}$  occurred in October 1998 (Figure 5.16). At depth, the lowest concentration of Total Mn occurred in August 1999 at  $213.33 \pm 12.97 \mu\text{g g}^{-1}$ , while the greatest at  $602.00 \pm 38.44 \mu\text{g g}^{-1}$  occurred in July 1999 (Figure 5.16).

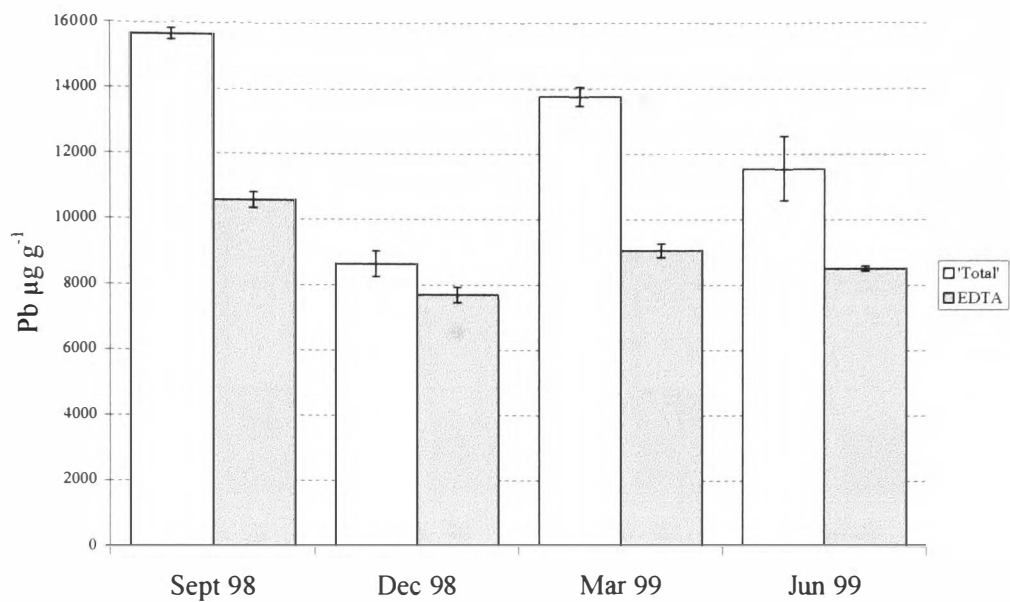
Monthly variation in Total and EDTA metals

Figure 5.17. Mean monthly concentration of Total Pb and EDTA Pb at 0-200 mm for Maesbury Series (n=3).



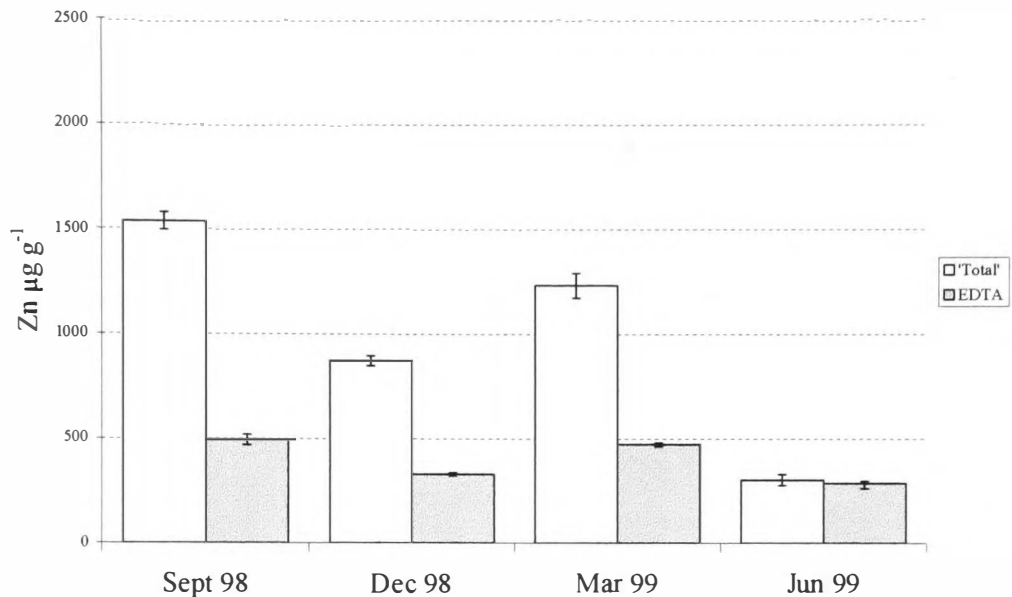
For each month, the Total Pb concentration was higher than that of the EDTA Pb concentration, although EDTA Pb as a percentage of Total Pb varied from 89.80% in September 1998 to 95.99% in June 1999 (Figure 5.16). EDTA Pb followed the same monthly pattern in variation in concentration as that of Total Pb. The lowest EDTA Pb concentration occurred in June 1999 at  $4\,986.67 \pm 91.77 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $11\,860 \pm 313.79 \mu\text{g g}^{-1}$  (Figure 5.17).

Figure 5.18. Mean monthly concentration of Total Pb and EDTA Pb at 200-400 mm for Maesbury Series (n=3).



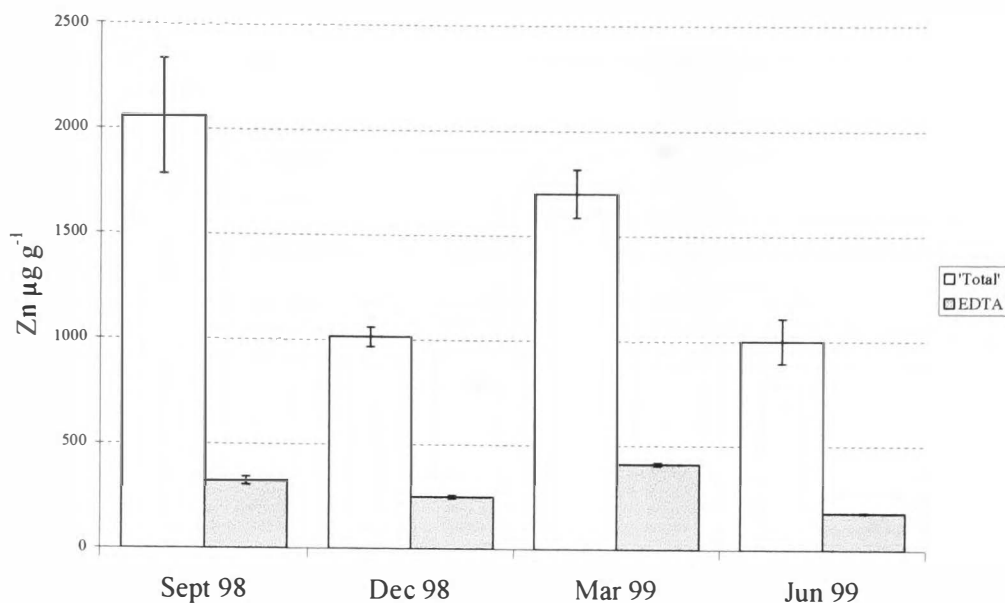
For each month, the Total Pb concentration was higher than that of the EDTA Pb concentration, although EDTA Pb as a percentage of Total Pb varied from 65.79% in March 1999 to 89.05% in December 1998 (Figure 5.18). EDTA Pb followed the same monthly pattern of variation in concentration as that of Total Pb. The lowest EDTA Pb concentration of  $7\,696.67 \pm 226.91 \mu\text{g g}^{-1}$  occurred in December 1998 and the greatest in September 1998 at  $10\,586.67 \pm 237.53 \mu\text{g g}^{-1}$  (Figure 5.18).

Figure 5.19. Mean monthly concentration of Total Zn and EDTA Zn at 0-200 mm for Maesbury Series (n=3).



For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 32.10% in September 1998 to 94.90% in June 1999 (Figure 5.19). EDTA Zn followed the same monthly pattern of variation in concentration as that of Total Zn. The lowest EDTA Zn concentration occurred in June 1999 at  $287.87 \pm 24.85 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $493.33 \pm 24.94 \mu\text{g g}^{-1}$  (Figure 5.19).

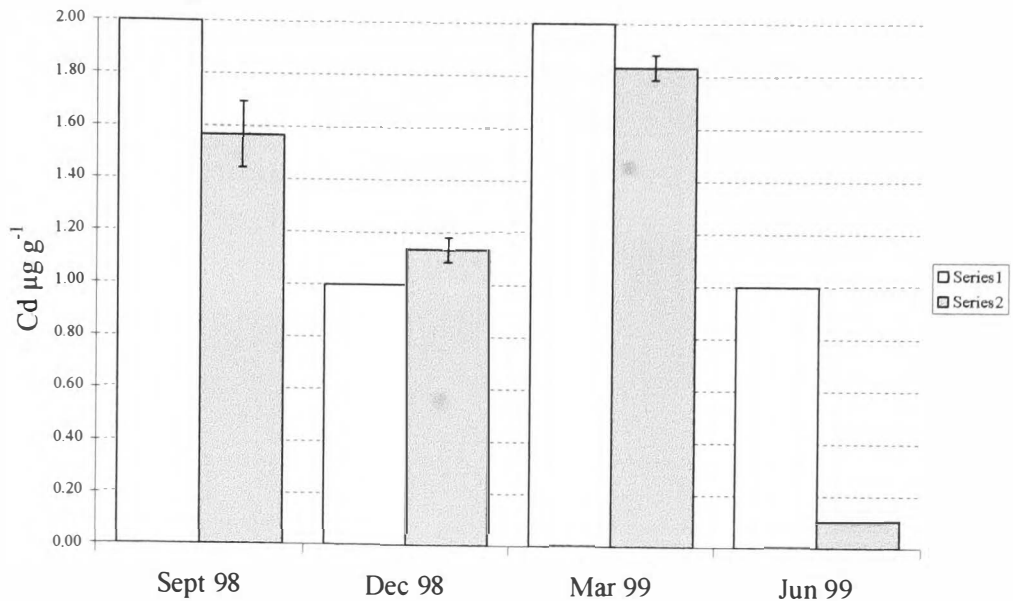
Figure 5.20. Mean monthly concentration of Total Zn and EDTA Zn at 200-400 mm for Maesbury Series (n=3).



For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 15.70% in September 1998 to 24.67% in December 1998 (Figure 5.20). The EDTA Zn concentration did not follow the same monthly trend in concentration as that of the Total Zn. The lowest EDTA Zn concentration occurred in June 1999 at  $179.00 \pm 3.56 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $410.00 \pm 8.16 \mu\text{g g}^{-1}$  (Figure 5.20).

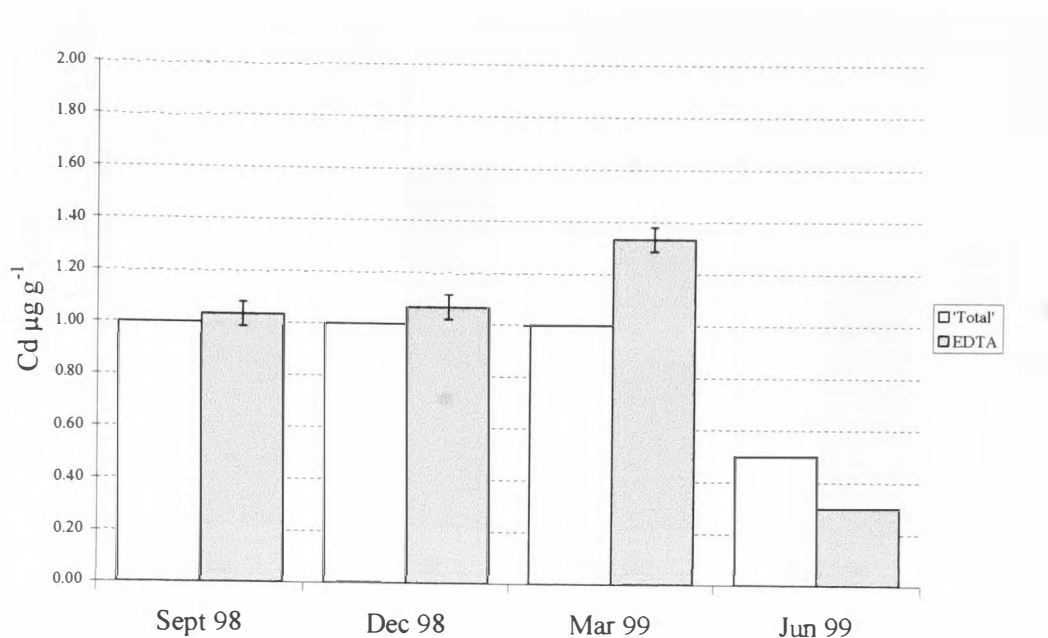


Figure 5.21. Mean monthly mean concentration of Total Cd and EDTA Cd at 0-200 mm for Maesbury Series (n=3).



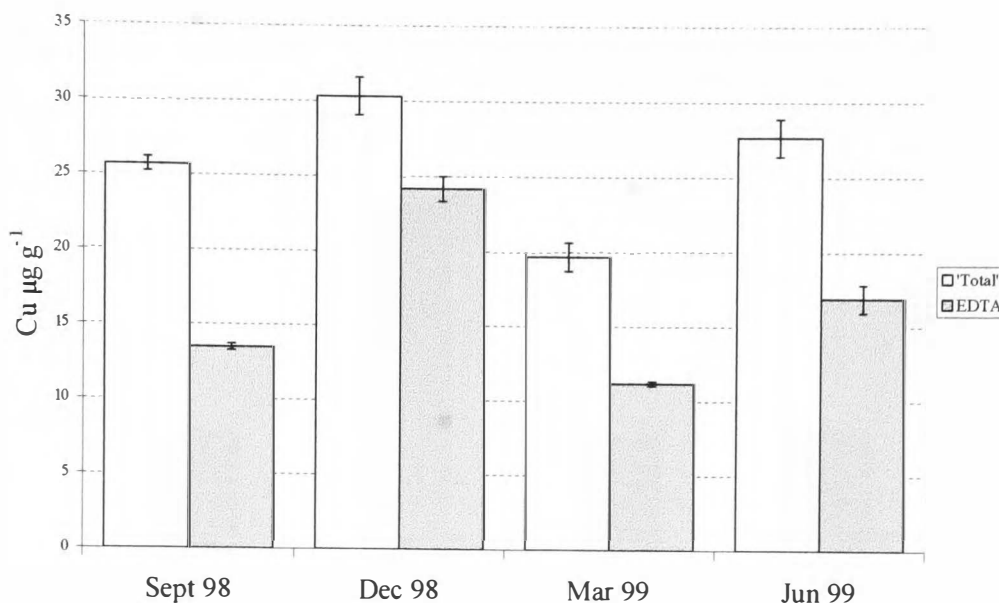
With the exception of December 1998, where the concentration of EDTA Cd was greater than that of Total Cd, for the remainder of the months, Total Cd concentration was greater than EDTA Cd concentration (Figure 5.21). EDTA Cd as a percentage of Total Cd varied from 10.00% in June 1999 to 113.33% in December 1998. The EDTA Cd concentration did not follow the same monthly trend in concentration as that of Total Cd. The lowest EDTA Cd concentration occurred in June 1999 at  $0.10 \pm 0.01 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $1.83 \pm 0.05 \mu\text{g g}^{-1}$  (Figure 5.21).

Figure 5.22. Mean monthly concentration of Total Cd and EDTA Cd at 200-400 mm for Maesbury Series (n=3).



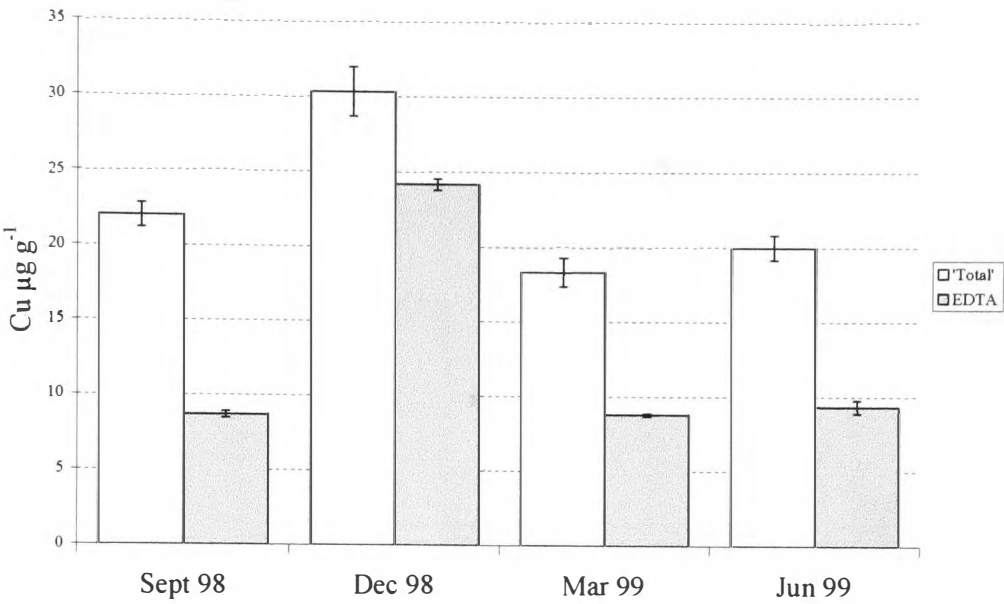
With the exception of June 1999, where the concentration of Total Cd was greater than that of the EDTA Cd, the concentration of EDTA Cd was greater than that of Total Cd for the remainder of the months (Figure 5.22). EDTA as a percentage of Total Cd varied from 60.00% in June 1999 to 133.33% in March 1999. The EDTA Cd concentration did not follow the same monthly trend in concentration as that of Total Cd, although the lowest concentrations for both occurred in June 1999. The lowest EDTA Cd concentration occurred in June 1999 at  $0.30 \pm 0.05 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $1.33 \pm 0.05 \mu\text{g g}^{-1}$  (Figure 5.22).

Figure 5.23. Mean monthly concentration of Total Cu and EDTA Cu at 0-200 mm for Maesbury Series (n=3).



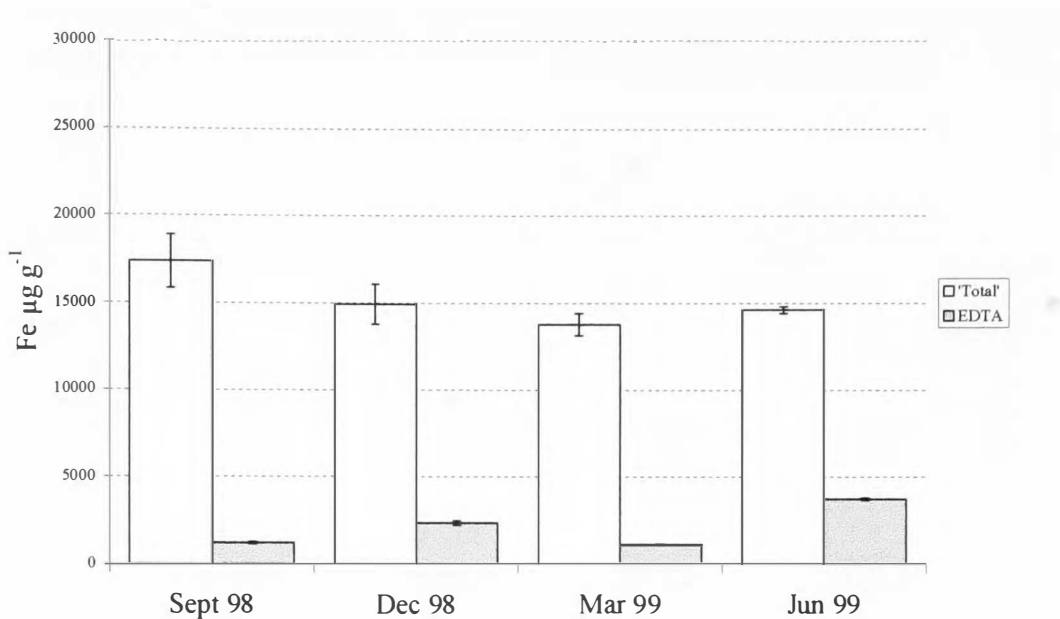
For each month, the Total Cu concentration was higher than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 52.60% in September 1998 to 79.67% in December 1998 (Figure 5.23). EDTA Cu followed the same monthly pattern of variation in concentration as that of Total Cu. The lowest EDTA Cu concentration occurred in March 1999 at  $11.20 \pm 0.14 \mu\text{g g}^{-1}$  and the greatest in December 1998 at  $13.50 \pm 0.22 \mu\text{g g}^{-1}$  (Figure 5.23).

Figure 5.24. Mean monthly concentration of Total Cu and EDTA Cu at 200-400 mm for Maesbury Series (n=3).



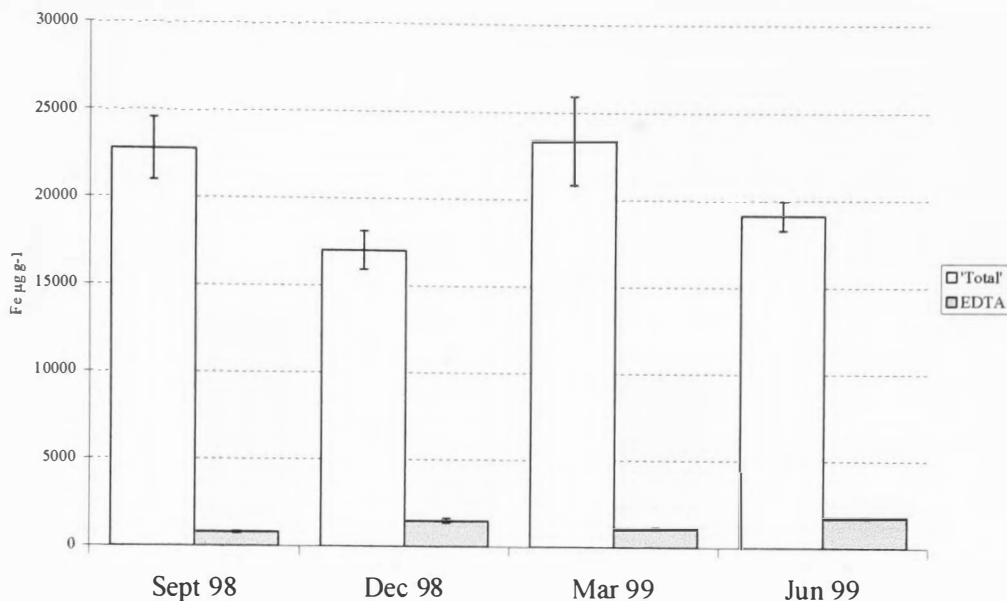
For each month, the Total Cu concentration was higher than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 39.55% in September 1998 to 76.79% in December 1998 (Figure 5.24). The EDTA Cu concentration did not follow the same monthly trend in concentration as that of Total Cu. The lowest EDTA Cu concentration of  $8.70 \pm 0.22 \mu\text{g g}^{-1}$  occurred in September 1998 and the greatest in December 1998 at  $24.17 \pm 0.36 \mu\text{g g}^{-1}$  (Figure 5.24).

Figure 5.25. Mean monthly concentration of Total Fe and EDTA Fe at 0-200 mm for Maesbury Series (n=3).



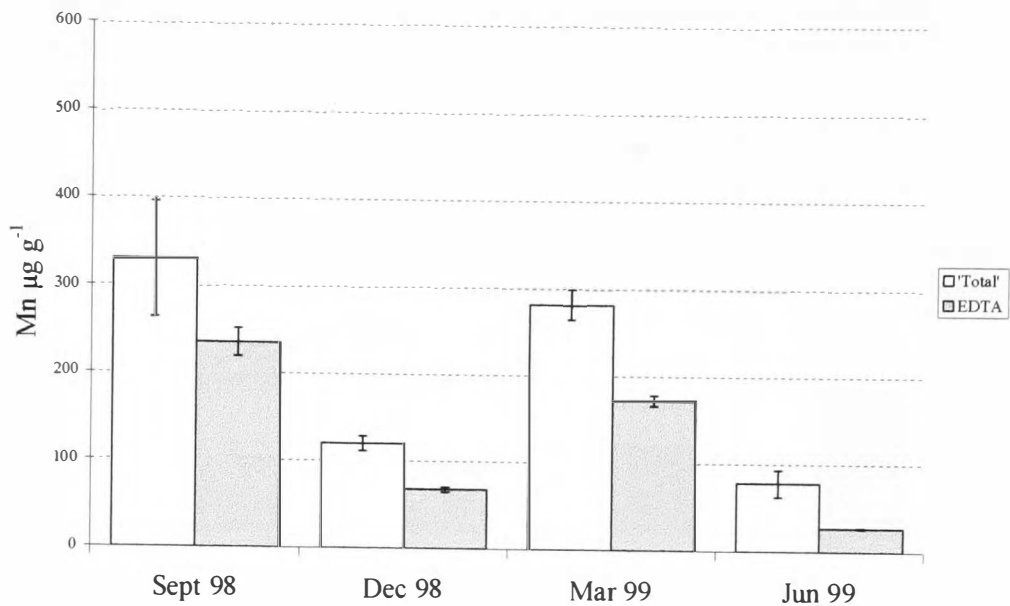
For each month the Total Fe concentration was higher than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 6.92% in September 1998 to 25.59% in June 1999 (Figure 5.25). The EDTA Fe concentration did not follow the same monthly trend in concentration as that of Total Fe. The lowest EDTA Fe concentration occurred in March 1999 at  $1\,113.00 \pm 30.01 \mu\text{g g}^{-1}$  and the greatest in June 1999 at  $3\,740 \pm 72.57 \mu\text{g g}^{-1}$  (Figure 5.25).

Figure 5.26. Mean monthly concentration of Total Fe and EDTA Fe at 200-400 mm for Maesbury Series (n=3).



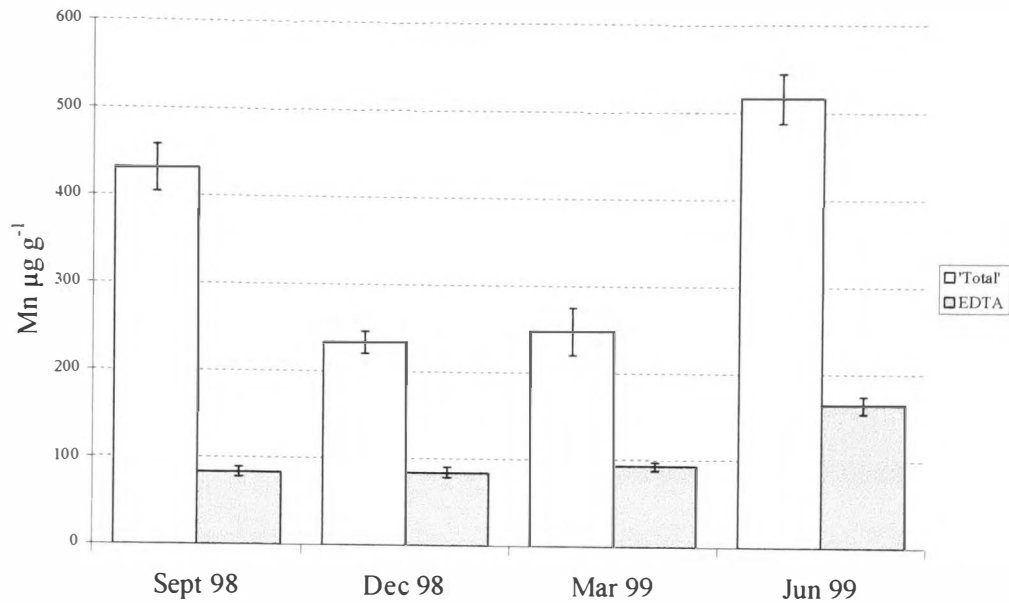
For each month, the Total Fe concentration was higher than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 3.53% in September 1998 to 9.31% in June 1999 (Figure 5.26). The EDTA Fe concentration did not follow the same monthly trend in concentration of that of Total Fe. The lowest EDTA Fe concentration occurred in September 1998 at  $803.00 \pm 46.67 \mu\text{g g}^{-1}$  and the greatest in June 1999 at  $1\,780 \pm 40.82 \mu\text{g g}^{-1}$  (Figure 5.26).

Figure 5.27. Mean monthly concentration of Total Mn and EDTA Mn at 0-200 mm for Maesbury Series (n=3).



For each month, the Total Mn concentration was higher than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 35.02% in June 1999 to 71.39% in September 1998 (Figure 5.27). The EDTA Mn concentration followed the same monthly pattern of variation in concentration as that of Total Mn. The lowest EDTA Mn concentration of  $27.43 \pm 0.62 \mu\text{g g}^{-1}$  occurred in June 1999, and the greatest in September 1998 at  $235.33 \pm 16.05 \mu\text{g g}^{-1}$  (Figure 5.27).

Figure 5.28. Mean monthly concentration of Total Mn and EDTA Mn at 200-400 mm for Maesbury Series (n=3).



For each month, the Total Mn concentration was higher than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 19.40% in September 1998 to 37.69% in March 1999 (Figure 5.28). The EDTA Mn concentration did not follow the same monthly trend in concentration as that of Total Mn. The lowest EDTA Mn concentration of  $83.67 \pm 5.56 \mu\text{g g}^{-1}$  occurred in September 1998, and the greatest in June 1999 at  $164.67 \pm 9.98 \mu\text{g g}^{-1}$  (Figure 5.28).



Table 5.36. Median percentage of monthly EDTA trace metals as a percentage of Total trace metals for Maesbury Series at 0-200 mm and 200-400 mm

Depth	Pb %	Zn %	Cd %	Cu %	Fe %	Mn %
0-200 mm	92.03	38.08	85.00	59.02	11.94	58.79
200-400 mm	70.66	20.99	105.00	47.42	6.70	34.04

In the surface soil, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 11.90%, while the greatest was Pb at 92.03% (Table 5.36). At depth, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 6.70%, while the greatest was Cd at 105.00%.

#### Monthly variation of other soil parameters

Table 5.37. Monthly values for CEC, Exchangeable Ca, Mg and K and Total P at 0-200 mm and 200-400 mm for Maesbury Series.

Parameter	Unit	Sept 1998	Dec 1998	Mar 1999	Jun 1999
CEC (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	20.99	26.53	24.55	28.51
CEC (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	15.84	17.82	20.59	16.24
Exch. Ca (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	21.16	7.72	19.42	1.47
Exch. Ca (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	11.95	5.73	13.94	2.27
Exch. Mg (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.62	0.78	0.49	0.62
Exch. Mg (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.33	0.45	0.41	0.45
Exch. K (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.21	0.24	0.34	0.21
Exch. K (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.12	0.16	0.26	0.15
Total P (0-200 mm)	µg g <sup>-1</sup>	759.90	570.10	737.50	743.90
Total P (200-400 mm)	µg g <sup>-1</sup>	1025.00	555.10	939.10	1081.00

For all months, the monthly CEC, Exchangeable Mg and Exchangeable K in the surface soil were consistently greater than that at depth (Table 5.37). For September and December 1998 and March 1999, the monthly Exchangeable Ca was greater at surface than at depth, while in June 1999, the Exchangeable Ca was greater at depth than at the surface. In September 1998 and March and June 1999, the concentration of Total P in soil at depth was greater than the concentration in surface soil. In December 1998, the concentration of Total P was similar for surface and depth at 570.10  $\mu\text{g g}^{-1}$  and 555.10  $\mu\text{g g}^{-1}$  respectively (Table 5.37)

### Two-Sample analysis

Mann-Whitney analysis or a Two-sample T-test between surface and depth for each stacked soil parameter ( $n=12$  or  $n=4$ ) showed a significant difference at the  $p \leq 0.05$  level for 12 /19 of the Maesbury Series soil parameters (Tables 5.38 and 5.39).

Table 5.38. Two-sample Mann-Whitney tests for Maesbury soil parameters at 0-200 mm *versus* 200-400 mm, where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter	n=	Mann-Whitney p-value	$H_0$ : $\eta_1 = \eta_2$ at $\alpha=0.05$
L-o-I (0-200 mm) $\nu$ L-o-I (2000-400 mm)	12	0.0000	Rejected
Total Cd (0-200 mm) $\nu$ Total Cd (200-400 mm)	12	0.0465	Rejected

Table 5.39. Two-sample Mann-Whitney tests for Maesbury soil parameters at 0-200 mm *versus* 200-400 mm, where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$

Soil Parameter	n=	T-value	p-value	$H_0: \mu_1 = \mu_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	12	-6.38	0.000	Rejected
Total Pb (0-200 mm) v Total Pb (200-400 mm)	12	-4.83	0.001	Rejected
Total Zn (0-200 mm) v Total Zn (200-400 mm)	12	-3.65	0.004	Rejected
Total Cu (0-200 mm) v Total Cu (200-400 mm)	12	-4.40	0.001	Rejected
Total Fe (0-200 mm) v Total Fe (200-400 mm)	12	-4.77	0.001	Rejected
Total Mn (0-200 mm) v Total Mn (200-400 mm)	12	-1.45	0.175	Accepted
EDTA Pb (0-200 mm) v EDTA Pb (200-400 mm)	4	-1.01	0.387	Accepted
EDTA Zn (0-200 mm) v EDTA Zn (200-400 mm)	4	4.50	0.020	Rejected
EDTA Cd (0-200 mm) v EDTA Cd (200-400 mm)	4	1.26	0.297	Accepted
EDTA Cu (0-200 mm) v EDTA Cu (200-400 mm)	4	3.66	0.035	Rejected
EDTA Fe (0-200 mm) v EDTA Fe (200-400 mm)	4	1.94	0.148	Accepted
EDTA Mn (0-200 mm) v EDTA Mn (200-400 mm)	4	0.31	0.779	Accepted
CEC (0-200 mm) v CEC (200-400 mm)	4	4.01	0.028	Rejected
Exch. Ca (0-200 mm) v Exch. Ca (200-400 mm)	4	1.83	0.164	Accepted
Exch. Mg (0-200 mm) v Exch. Mg (200-400 mm)	4	3.81	0.032	Rejected
Exch. K (0-200 mm) v Exch. K (200-400 mm)	4	12.32	0.001	Rejected
Total P (0-200 mm) v Total P (200-400 mm)	4	-2.60	0.081	Accepted

Of the 12 soil parameters that showed a significant difference at the  $p \leq 0.05$  level between values at surface and at depth, pH, Loss-on-Ignition, Total Pb, Total Cu Total Fe and Exchangeable K were significant at the  $p \leq 0.001$  level (Tables 5.38 and 5.39).

Pearson correlations

Table 5.40. Pearson correlation values (r-values) and degrees of significance at the  $p=0.001$ , 0.01 and 0.05 levels for stacked Maesbury soil parameters at 0-400 mm (n=24) September 1998 - August 1999.

	pH (0-400 mm)	L-o-I (0-400mm)	Total Pb (0-400 mm)	Total Zn (0-400 mm)	Total Cd (0-400 mm)	Total Cu (0-400 mm)	Total Fe (0-400 mm)
L-o-I (0-400 mm)	-0.519 **						
Total Pb (0-400 mm)	0.527 **	-0.583 **					
Total Zn (0-400 mm)	0.693 ***	-0.584 **	0.724 ***				
Total Cd (0-400 mm)	0.103	0.252	-0.165	-0.020			
Total Cu (0-400 mm)	-0.050	0.525 **	-0.239	-0.237	0.185		
Total Fe (0-400 mm)	0.333	-0.707 ***	0.687 ***	0.526 **	-0.242	-0.410 *	
Total Mn (0-400 mm)	0.261	-0.443 *	0.545 **	0.451 *	0.016	-0.115	0.419 *

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     - Indicates a negative correlation

Loss-on-Ignition was negatively correlated at the  $p \leq 0.05$  level with pH and Total Pb, Zn, Fe and Mn, and positively correlated with Total Cu at the  $p=0.01$  level (Table 5.40). Total Pb, Zn, Fe and Mn were all positively correlated with each

other at the  $p \leq 0.05$  level. Soil pH was positively correlated with Total Pb and Zn at the  $p \leq 0.01$  level (Table 5.40).

**5.5.3 Thrupe Series**

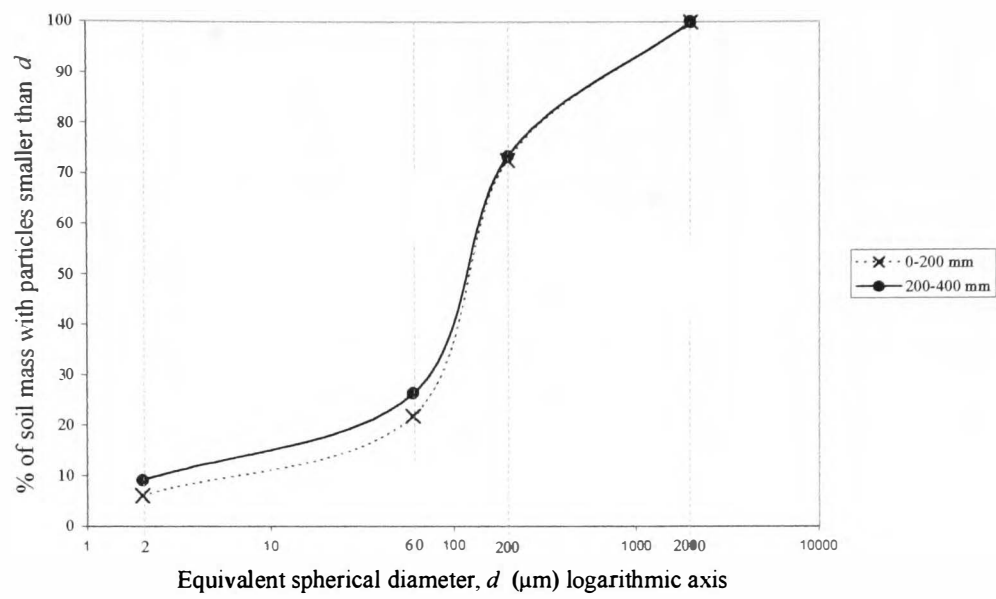
Particle Size Analysis

Table 5.41. Particle size distribution and soil textural class for Thrupe Series.

Depth (mm)	% clay	% silt	% fine sand	% coarse sand	% Stones	Textural Class
0 - 200	6.08	15.83	50.82	27.27	15.20	Loamy Sand
200-400	9.12	17.35	47.06	26.48	16.56	Silty Loam

The surface soil was classified as loamy sand, with fine sand as the most abundant particle size (Table 5.41). At depth, although still dominated by fine sand, the soil contained a slightly higher % of clay and silt than the surface soil and was classified as silty loam. The cumulative curve plot showed that at approximately 80% and 74% of the particles at surface and depth respectively, sand (fine + coarse sand) dominated the < 2 mm soil fraction at both surface and depth (Figure 5.29).

Figure 5.29. Cumulative curve displaying particle size distribution of Thrupe soil at 0-200 mm and 200-400 mm.



### Descriptive statistics

The Thrupe Series data set consisted of monthly ( $n=12$ ) and quarterly ( $n=4$ ) data for the same soil parameters as the Maesbury Series described in 5.5.2. The descriptive statistics for this data set are shown in Table 5.42. Soil reaction ranged from pH 5.21 to pH 6.04 in the surface soil and from pH 5.82 to pH 6.22 at depth. Loss-on-Ignition in the surface soil ranged from 7.33% to 14.65% and from 6.01% to 11.13% at depth (Table 5.42).

Table 5.42. Soil parameter data for Thrupe Series at 0-200 mm and 200-400 mm (n=12) for September 1998 - August 1999 and (n=4) for quarterly sampling.

	Unit	n	Arithmetic Mean	St. Dev.	Minimum	Median	Maximum
pH (0-200 mm)	pH	12	5.67	0.28	5.21	5.64	6.04
pH (200-400 mm)	pH	12	5.99	0.13	5.82	5.98	6.22
L-o-I (0-200 mm)	%	12	10.11	1.78	7.33	10.05	14.65
L-o-I (200-400 mm)	%	12	7.22	1.36	6.01	6.75	11.13
Total Pb (0-200 mm)	$\mu\text{g g}^{-1}$	12	13 220.10	2 735.30	8 093.00	13 091.50	20 140.00
Total Pb (200-400 mm)	$\mu\text{g g}^{-1}$	12	11 063.50	2 923.50	7 763.00	10 073.00	18 227.00
Total Zn (0-200 mm)	$\mu\text{g g}^{-1}$	12	1 219.44	227.12	800.00	1 181.66	1 763.30
Total Zn (200-400 mm)	$\mu\text{g g}^{-1}$	12	1 252.22	244.66	803.30	1 200.00	1 650.00
Total Cd (0-200 mm)	$\mu\text{g g}^{-1}$	12	0.92	0.19	0.50	1.00	1.00
Total Cd (200-400 mm)	$\mu\text{g g}^{-1}$	12	0.79	0.58	0.50	1.00	1.00
Total Cu (0-200 mm)	$\mu\text{g g}^{-1}$	12	18.22	4.48	11.33	17.33	27.33
Total Cu (200-400 mm)	$\mu\text{g g}^{-1}$	12	14.17	3.55	8.67	15.33	19.00
Total Fe (0-200 mm)	$\mu\text{g g}^{-1}$	12	17 630.80	2 156.60	15 350.00	17 366.70	22 123.30
Total Fe (200-400 mm)	$\mu\text{g g}^{-1}$	12	17 297.50	2 077.90	14 530.00	17 121.70	21 443.30
Total Mn (0-200 mm)	$\mu\text{g g}^{-1}$	12	421.72	97.95	218.67	436.50	542.33
Total Mn (200-400 mm)	$\mu\text{g g}^{-1}$	12	258.44	56.17	187.67	253.00	374.33
EDTA Pb (0-200 mm)	$\mu\text{g g}^{-1}$	4	12 957.50	4 983.90	6 823.33	13 066.67	18 873.33
EDTA Pb (200-400 mm)	$\mu\text{g g}^{-1}$	4	11 137.50	4 285.55	7 846.67	9 648.33	17 406.67
EDTA Zn (0-200 mm)	$\mu\text{g g}^{-1}$	4	98.50	30.00	64.00	101.67	126.67
EDTA Zn (200-400 mm)	$\mu\text{g g}^{-1}$	4	87.42	18.85	69.00	83.83	113.00
EDTA Cd (0-200 mm)	$\mu\text{g g}^{-1}$	4	0.63	0.24	0.40	0.57	0.97
EDTA Cd (200-400 mm)	$\mu\text{g g}^{-1}$	4	0.54	0.16	0.43	0.48	0.77
EDTA Cu (0-200 mm)	$\mu\text{g g}^{-1}$	4	8.94	2.88	4.70	10.12	10.83
EDTA Cu (200-400 mm)	$\mu\text{g g}^{-1}$	4	6.51	1.16	4.77	7.05	7.17
EDTA Fe (0-200 mm)	$\mu\text{g g}^{-1}$	4	1 047.25	219.46	839.67	1 002.00	1 345.33
EDTA Fe (200-400 mm)	$\mu\text{g g}^{-1}$	4	862.25	333.47	561.33	863.67	1 160.33
EDTA Mn (0-200 mm)	$\mu\text{g g}^{-1}$	4	261.83	118.79	90.33	305.67	345.67
EDTA Mn (200-400 mm)	$\mu\text{g g}^{-1}$	4	113.50	31.17	75.67	116.00	146.33
CEC (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	16.83	3.21	12.28	17.62	19.80
CEC (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	12.77	1.22	11.09	13.07	13.86
Exch. Ca (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	4.38	2.68	2.49	3.41	8.22
Exch. Ca (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	3.34	1.06	2.44	3.04	4.83
Exch. Mg (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.76	0.16	0.62	0.72	0.99
Exch. Mg (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.74	0.08	0.70	0.70	0.86
Exch. K (0-200 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.25	0.06	0.19	0.25	0.32
Exch. K (200-400 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.21	0.05	0.17	0.20	0.28
Total P (0-200 mm)	$\mu\text{g g}^{-1}$	4	581.95	144.13	430.70	560.50	776.10
Total P (200-400 mm)	$\mu\text{g g}^{-1}$	4	519.23	67.54	462.90	502.60	608.80

The concentration of Total Pb in the surface soil ranged from 8 093.00  $\mu\text{g g}^{-1}$  to 20 140.00  $\mu\text{g g}^{-1}$  and from 7 763.00  $\mu\text{g g}^{-1}$  to 18 227.00  $\mu\text{g g}^{-1}$  at depth (Table 5.42). Total Zn ranged from 800.00  $\mu\text{g g}^{-1}$  to 1 763.30  $\mu\text{g g}^{-1}$  in the surface horizon and from 803.30  $\mu\text{g g}^{-1}$  to 1 650.00  $\mu\text{g g}^{-1}$  at depth. Total Cd was present in surface soil at 0.50  $\mu\text{g g}^{-1}$  to 1.00  $\mu\text{g g}^{-1}$  and from 0.50  $\mu\text{g g}^{-1}$  to 1.00  $\mu\text{g g}^{-1}$  at depth. The concentration of Total Cu ranged from 11.33  $\mu\text{g g}^{-1}$  to 27.33  $\mu\text{g g}^{-1}$  in the surface soil and at depth from 8.67  $\mu\text{g g}^{-1}$  to 19.00  $\mu\text{g g}^{-1}$ . Total Fe was present in surface soil at 15 350.00  $\mu\text{g g}^{-1}$  to 22.123.30  $\mu\text{g g}^{-1}$  and from 14 530.00  $\mu\text{g g}^{-1}$  to 21 443.30  $\mu\text{g g}^{-1}$  at depth. Total Mn in surface soil ranged from 218.67  $\mu\text{g g}^{-1}$  to 542.33  $\mu\text{g g}^{-1}$  and from 187.67  $\mu\text{g g}^{-1}$  to 374.33  $\mu\text{g g}^{-1}$  at depth (Table 5.42).

EDTA Pb was present in surface soil at 6 823.33  $\mu\text{g g}^{-1}$  to 18 873  $\mu\text{g g}^{-1}$  and from 7 864.67  $\mu\text{g g}^{-1}$  to 17 406.67  $\mu\text{g g}^{-1}$  at depth. Surface EDTA Zn was present at 64.00  $\mu\text{g g}^{-1}$  to 126.67  $\mu\text{g g}^{-1}$  and from 69.00  $\mu\text{g g}^{-1}$  to 113.00  $\mu\text{g g}^{-1}$  at depth. Surface EDTA Cd ranged from 0.40  $\mu\text{g g}^{-1}$  to 0.97  $\mu\text{g g}^{-1}$  and from 0.43  $\mu\text{g g}^{-1}$  to 0.77  $\mu\text{g g}^{-1}$  at depth (Table 5.42). The concentration of surface EDTA Cu ranged from 4.70  $\mu\text{g g}^{-1}$  to 10.38  $\mu\text{g g}^{-1}$  and from 4.77  $\mu\text{g g}^{-1}$  to 7.17  $\mu\text{g g}^{-1}$  at depth. EDTA Fe ranged from 839.67  $\mu\text{g g}^{-1}$  to 1 345.33  $\mu\text{g g}^{-1}$  in surface soil and from 561.33  $\mu\text{g g}^{-1}$  to 1 160.33  $\mu\text{g g}^{-1}$  at depth. EDTA Mn was present in surface soil at 90.33  $\mu\text{g g}^{-1}$  to 345.67  $\mu\text{g g}^{-1}$  and from 75.67  $\mu\text{g g}^{-1}$  to 146.33  $\mu\text{g g}^{-1}$  at depth.

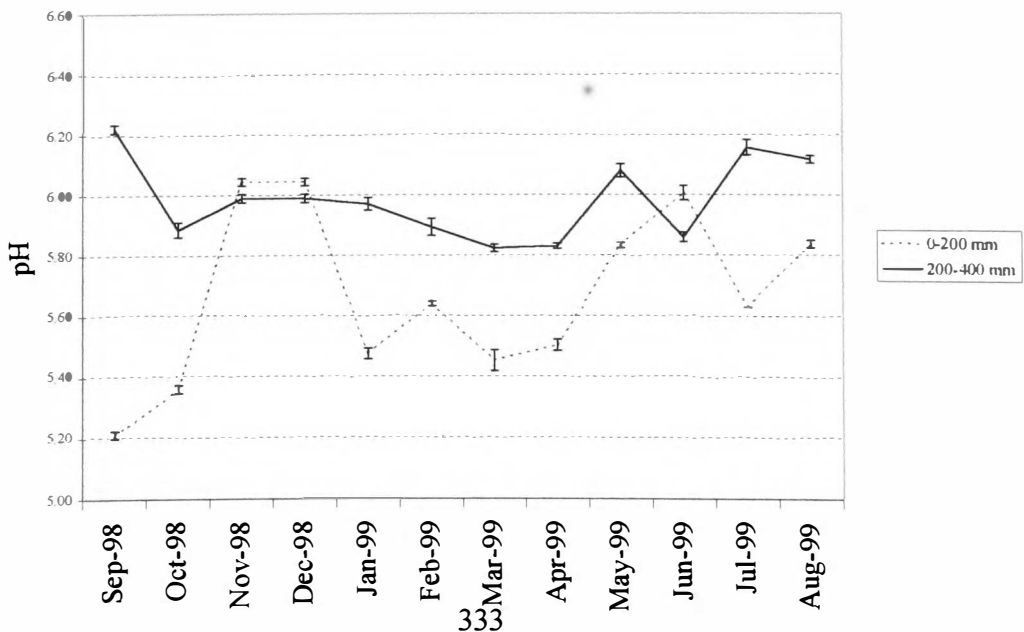
Surface CEC ranged from 12.28  $\text{cmol}_c \text{kg}^{-1}$  to 19.80  $\text{cmol}_c \text{kg}^{-1}$  and from 11.09  $\text{cmol}_c \text{kg}^{-1}$  to 13.86  $\text{cmol}_c \text{kg}^{-1}$  at depth. The concentration of surface Exchangeable Ca ranged from 2.49  $\text{cmol}_c \text{kg}^{-1}$  to 8.22  $\text{cmol}_c \text{kg}^{-1}$  and from



2.44 cmol<sub>c</sub> kg<sup>-1</sup> to 4.83 cmol<sub>c</sub> kg<sup>-1</sup> at depth. Exchangeable Mg was present in surface soil at 0.62 cmol<sub>c</sub> kg<sup>-1</sup> to 0.99 cmol<sub>c</sub> kg<sup>-1</sup> and from 0.70 cmol<sub>c</sub> kg<sup>-1</sup> to 0.86 cmol<sub>c</sub> kg<sup>-1</sup> at depth. Surface Exchangeable K ranged from 0.19 cmol<sub>c</sub> kg<sup>-1</sup> to 0.32 cmol<sub>c</sub> kg<sup>-1</sup> and from 0.17 cmol<sub>c</sub> kg<sup>-1</sup> to 0.28 cmol<sub>c</sub> kg<sup>-1</sup> at depth. The concentration of surface Total P ranged from 430.70 µg g<sup>-1</sup> to 776.10 µg g<sup>-1</sup> and from 462.90 µg g<sup>-1</sup> to 608.80 µg g<sup>-1</sup> at depth (Table 5.4). Generally, the mean and median values of each individual soil parameter were similar, with the exception of Total Pb at depth, surface EDTA Pb at depth and surface EDTA Mn (Table 5.42). The mean and median values for surface Total Pb were 11 063.50 µg g<sup>-1</sup> and 10 073.00 µg g<sup>-1</sup> respectively, for EDTA Pb at depth 11 137.50 µg g<sup>-1</sup> and 9 648.33 µg g<sup>-1</sup>, and surface EDTA Mn 261.83 µg g<sup>-1</sup> and 305.67µg g<sup>-1</sup> (Table 5.42).

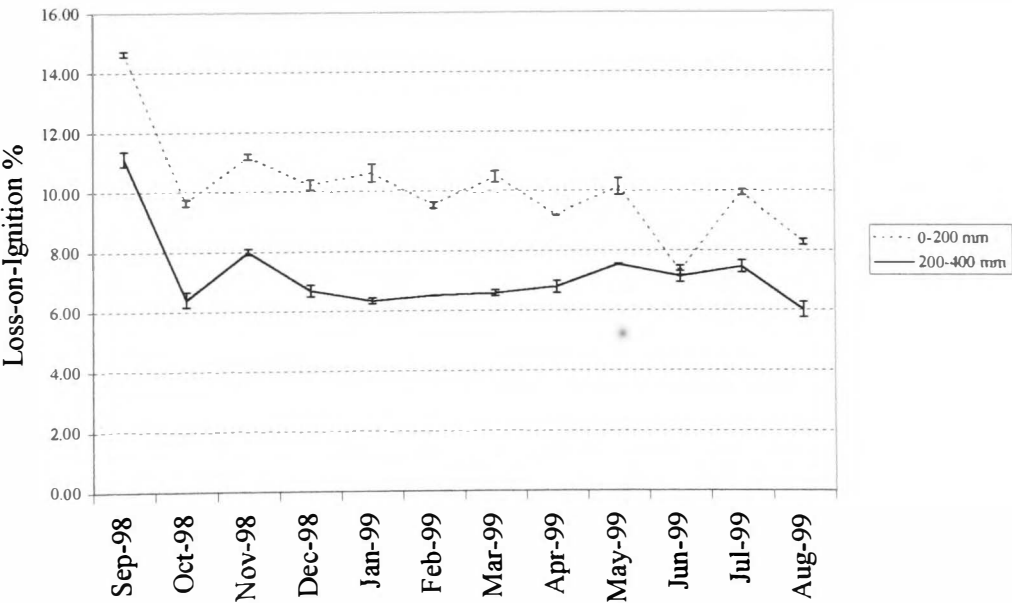
Monthly variation in pH, Loss-on-Ignition and Total metals

Figure 5.30. Mean monthly pH at 0-200 mm and 200-400 mm for Thrupe Series (n=3).



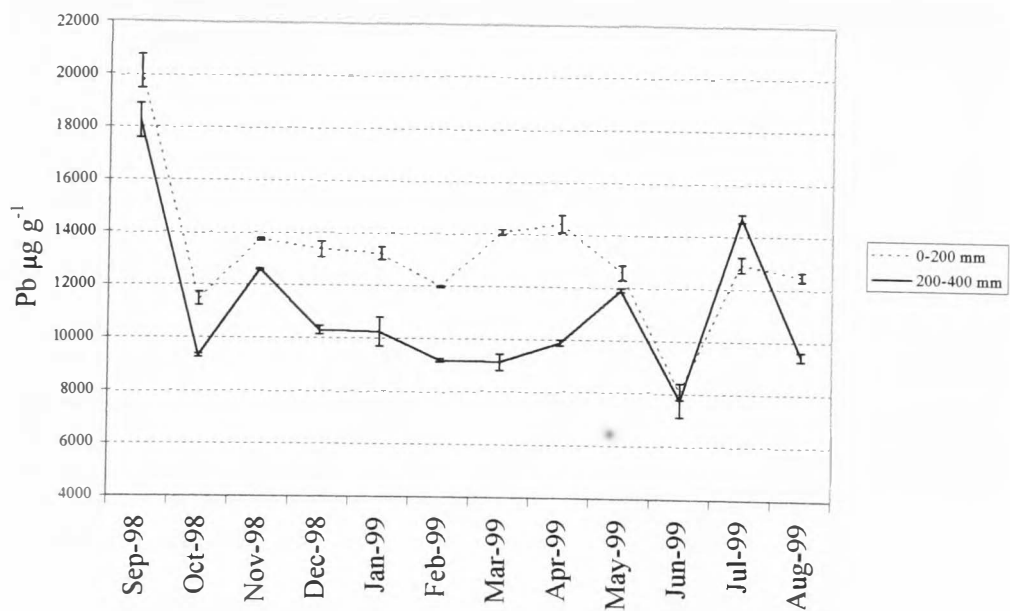
Soil reaction at surface and depth did not show a similar trend throughout the year. With the exception of November 1998, December 1998 and June 1999, when surface pH was higher than pH at depth, soil pH at depth was consistently higher than surface pH in each month (Figure 5.30). The lowest pH values in the surface soil occurred in September 1998 at  $\text{pH } 5.21 \pm 0.01$ , while the highest value of  $\text{pH } 6.04 \pm 0.01$  occurred in November and December 1998. For soil at depth, the lowest pH occurred in March 1999 at  $\text{pH } 5.82 \pm 0.01$ , while the highest at  $\text{pH } 6.22 \pm 0.01$  occurred in September 1998 (Figure 5.30).

Figure 5.31. Mean monthly % Loss-on-Ignition at 0-200 mm and 200-400 mm for Thrupe Series (n=3).



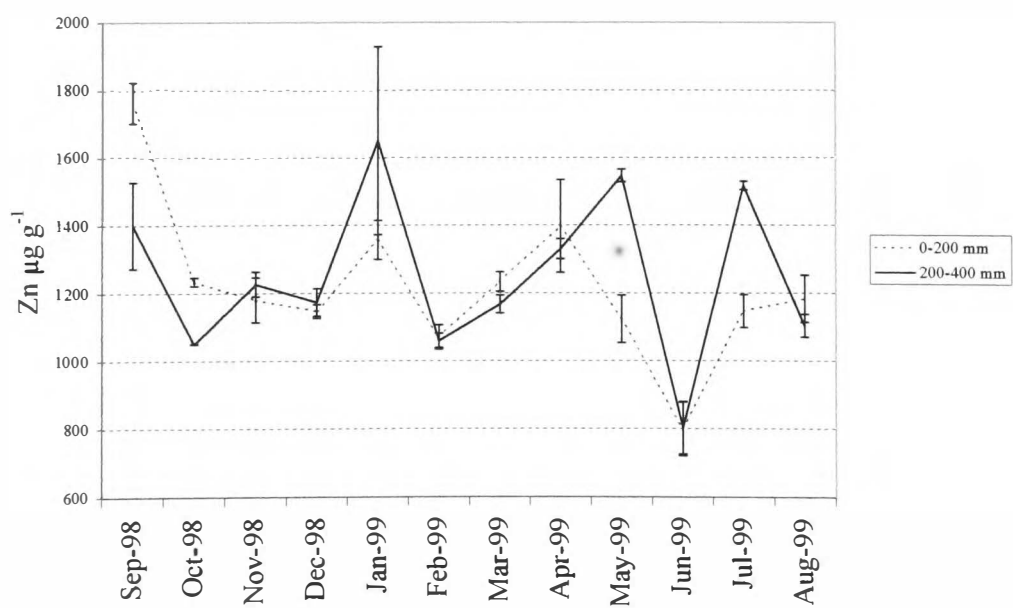
For each month, Loss-on-Ignition was consistently greater for surface soil than that at depth (Figure 5.31). In general, Loss-on-Ignition in surface soil and at depth showed a similar overall pattern of variation throughout the year. The lowest % Loss-on-Ignition of  $7.33 \pm 0.09\%$  in the surface soil occurred in June 1999, while the greatest % Loss-on-Ignition of  $14.65 \pm 0.09\%$  occurred in September 1998 (Figure 5.31). The lowest % Loss-on-Ignition at depth occurred in August 1999 at  $6.01 \pm 0.26\%$ , while the greatest % Loss-on-Ignition of  $11.13 \pm 0.25\%$  occurred in September 1998 (Figure 5.31).

Figure 5.32. Mean monthly Total Pb at 0-200 mm and 200-400 mm for Thrupe Series (n=3).



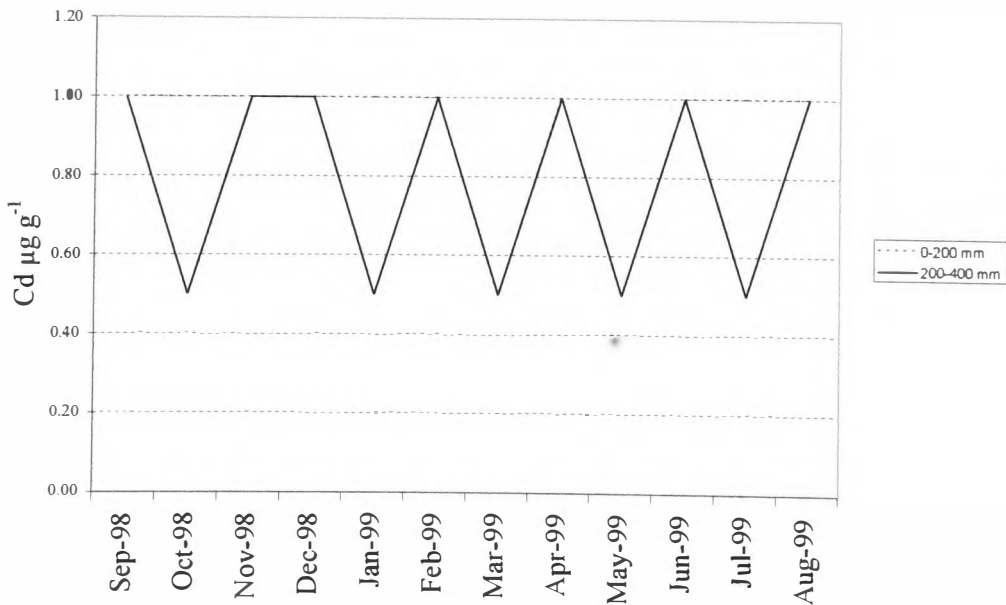
In general, Total Pb in surface soil and at depth showed a similar overall pattern of variation throughout the year. With the exception of July 1999, when the concentration of Total Pb at depth was greater than that in the surface soil, for each month, the concentration of Total Pb was consistently greater for surface soil than at depth (Figure 5.32). The lowest concentration of Total Pb in the surface soil occurred in June 1999 at  $8\,093 \pm 316 \mu\text{g g}^{-1}$ , while the greatest concentration of  $20\,140 \pm 631 \mu\text{g g}^{-1}$  occurred in September 1998 (Figure 5.32). The lowest concentration of Total Pb at depth occurred in June 1999 at  $7\,763 \pm 649 \mu\text{g g}^{-1}$ , while the greatest occurred in September 1998 at  $20\,760 \pm 543 \mu\text{g g}^{-1}$  (Figure 5.32).

Figure 5.33. Mean monthly Total Zn at 0-200 mm and 200-400 mm for Thrupe Series (n=3).



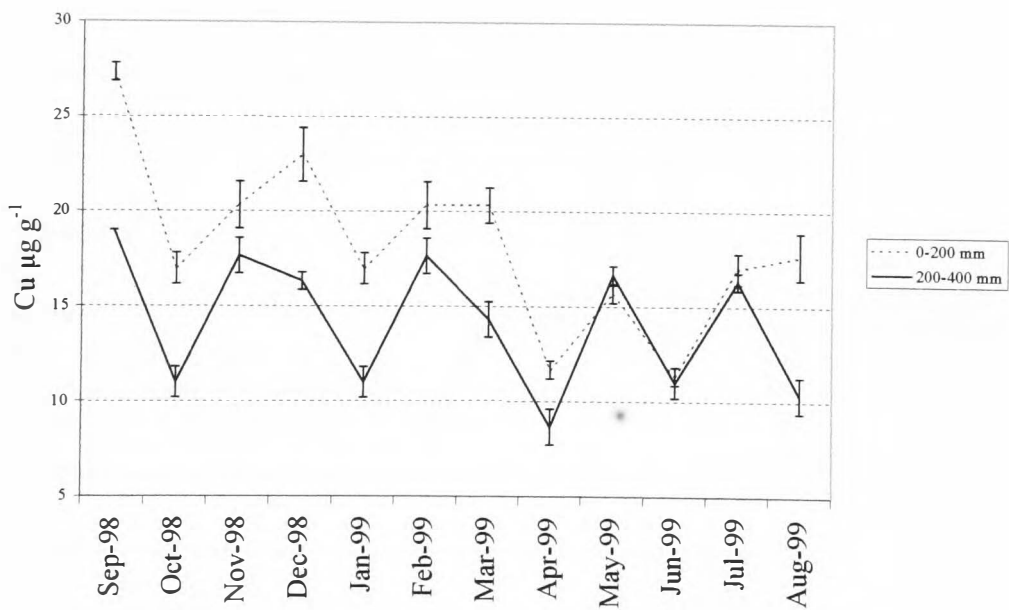
For six non-consecutive months, the mean Total Zn concentration was greater for soil at depth than that at the surface. For the remaining six non-consecutive months, the situation was reversed. (Figure 5.33). In general, throughout the year the Total Zn in surface soils and at depth showed a similar pattern of variation in concentration. The lowest concentration of Total Zn in the surface soil occurred in June 1999 at  $800.00 \pm 78.74 \mu\text{g g}^{-1}$ , while the greatest at  $1\,763.33 \pm 61.28 \mu\text{g g}^{-1}$  occurred in September 1998 (Figure 5.33). At  $803.33 \pm 77.17 \mu\text{g g}^{-1}$ , the lowest concentration of Total Zn at depth occurred in June 1999, while the greatest occurred in January 1999 at  $1\,650.00 \pm 278.21 \mu\text{g g}^{-1}$  (Figure 5.33).

Figure 5.34 Mean monthly Total Cd at 0-200 mm and 200-400 mm for Thrupe Series (n=3).



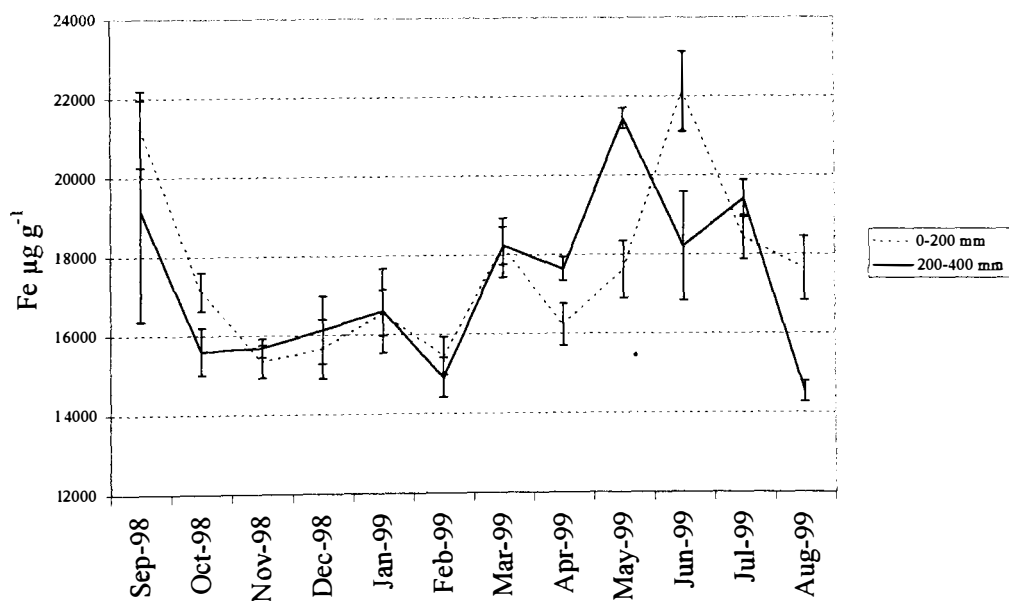
With the exception of October 1998, January 1999 and July 1999, when the Total Cd concentration was greater in the surface soil than at depth, for each remaining month, the concentration of Total Cd was identical in the surface soil and at depth (Figure 5.34). The lowest concentration of Total Cd in the surface soil occurred in March 1999 and May 1999 at  $0.50 \pm 0 \mu\text{g g}^{-1}$ , while the greatest at  $1.00 \pm 0 \mu\text{g g}^{-1}$  occurred in the remaining 10 months. At depth, the lowest concentration of Total Cd at  $0.50 \pm 0 \mu\text{g g}^{-1}$  occurred in October 1998 and January, March, May and July 1999. The greatest concentration of  $1.00 \pm 0 \mu\text{g g}^{-1}$  occurred in the remaining 7 months of the year (Figure 5.34).

Figure 5.35. Mean monthly Total Cu at 0-200 mm and 200-400 mm for Thrupe Series (n=3).



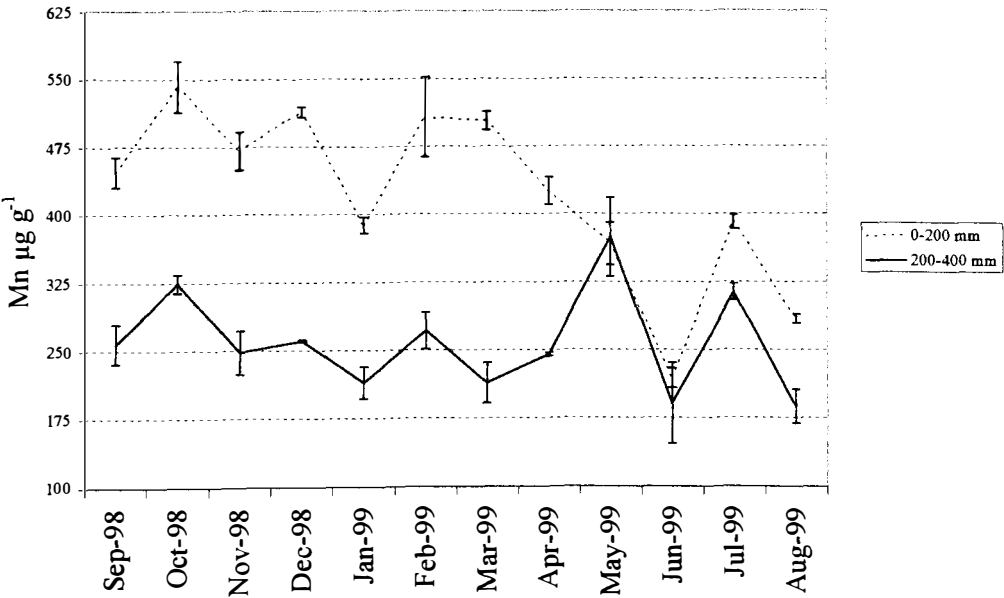
With the exception of May 1999, when the concentration of Total Cu at depth was greater than in surface soil, for each month, the concentration of Total Cu was consistently greater for surface soil than at depth (Figure 5.35). Throughout the year, the Total Cu in surface soils and at depth showed a similar pattern of variation in concentration. The lowest concentration of Total Cu in the surface soil occurred in June 1999 at  $11.33 \pm 0.47 \mu\text{g g}^{-1}$ , while the greatest occurred in September 1998 at  $27.33 \pm 0.47 \mu\text{g g}^{-1}$  (Figure 5.35). At depth, the lowest concentration of Total Cu at  $8.67 \pm 0.94 \mu\text{g g}^{-1}$  occurred in April 1999, while the greatest occurred in September 1998 at  $28.00 \pm 1.63 \mu\text{g g}^{-1}$  (Figure 5.35).

Figure 5.36. Mean monthly Total Fe at 0-200 mm and 200-400 mm for Thrupe Series (n=3).



For seven non-consecutive months, the mean Total Fe concentration was greater for soil at depth than that at the surface. For the remaining five non-consecutive months, the situation was reversed. (Figure 5.36). In January 1999 and March 1999, the mean Total Fe concentrations in the surface soil and at depth were similar. The surface and depth Total Fe concentrations for January 1999 were  $16\,553 \pm 578 \mu\text{g g}^{-1}$  and  $16\,610 \pm 1057 \mu\text{g g}^{-1}$  respectively, and  $18\,183 \pm 746 \mu\text{g g}^{-1}$  and  $18\,227 \pm 472 \mu\text{g g}^{-1}$  respectively for March 1999. The lowest concentration of Total Fe in the surface soil occurred in November 1998 at  $15\,350 \pm 416 \mu\text{g g}^{-1}$ , while the greatest at  $22\,123 \pm 1017 \mu\text{g g}^{-1}$  occurred in June 1999 (Figure 5.36). At depth, the lowest concentration of Total Fe at  $14\,530 \pm 255 \mu\text{g g}^{-1}$  occurred in August 1999, while the greatest at  $21\,443 \pm 1\,375 \mu\text{g g}^{-1}$  occurred in May 1999 (Figure 5.36).

Figure 5.37. Mean monthly Total Mn at 0-200 mm and 200-400 mm for Thrupe Series (n=3).

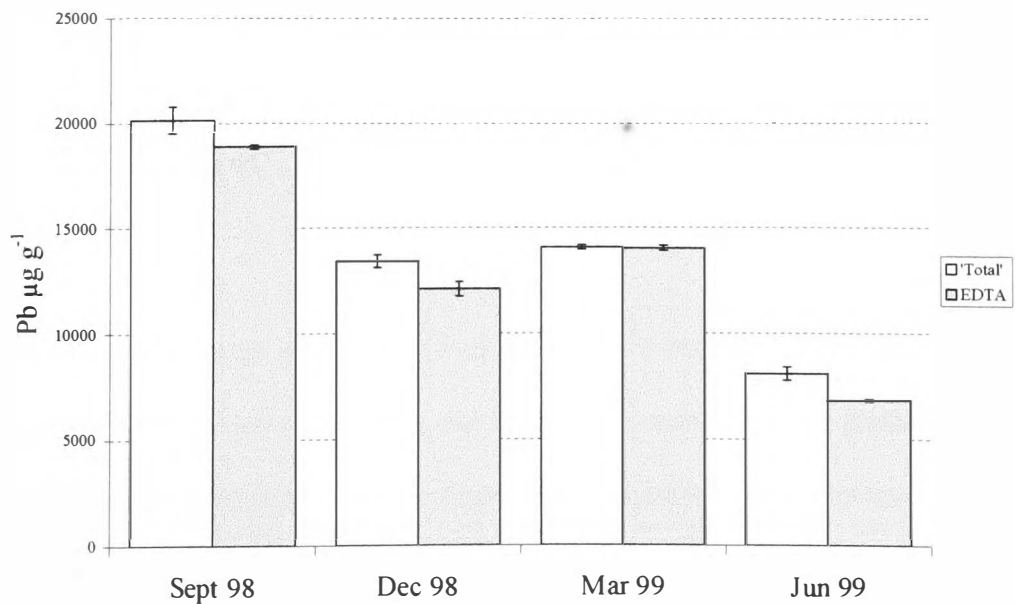




With the exception of May 1999, when the concentration of Total Mn was greater at depth than in surface soil, for each remaining month the concentration of Total Mn was consistently greater for surface soil than that at depth. In May 1999, there was little difference between the mean concentration of Total Mn at surface and depth at  $367 \pm 23.37 \mu\text{g g}^{-1}$  and  $374.33 \pm 43.19 \mu\text{g g}^{-1}$  respectively (Figure 5.37). The lowest concentration of Total Mn in the surface soil occurred in June 1999 at  $218.67 \pm 10.87 \mu\text{g g}^{-1}$ , while the greatest at  $542.33 \pm 28.29 \mu\text{g g}^{-1}$  occurred in October 1998 (Figure 5.37). At depth, the lowest concentration of Total Mn occurred in June 1999 at  $191.00 \pm 44.64 \mu\text{g g}^{-1}$ , while the greatest occurred in May 1999 at  $374.33 \pm 43.49 \mu\text{g g}^{-1}$  (Figure 5.37).

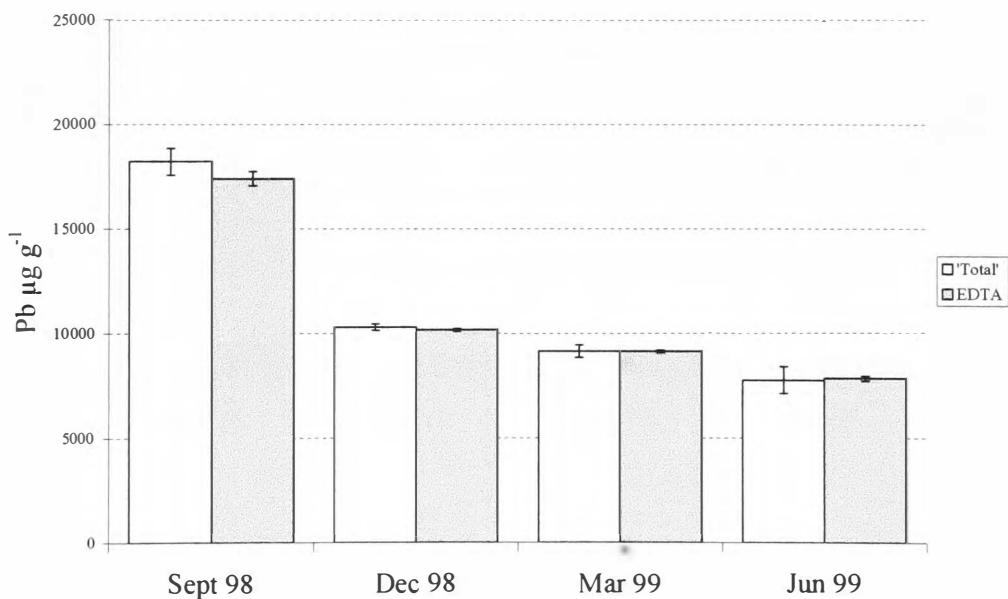
Monthly variation in Total and EDTA metals

Figure 5.38. Mean monthly concentration of Total Pb and EDTA Pb at 0-200 mm for Thrupe Series (n=3).



For each month, the Total Pb concentration was higher than that of the EDTA Pb concentration, although EDTA Pb as a percentage of Total Pb varied from 84.31% in June 1999 to 99.76% in March 1999. The EDTA Pb concentration followed the monthly variation in concentration of that of the Total Pb concentration. The lowest EDTA Pb concentration occurred in June 1999 at  $6\,823.33 \pm 47.84 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $18\,873.33 \pm 89.94 \mu\text{g g}^{-1}$  (Figure 5.38).

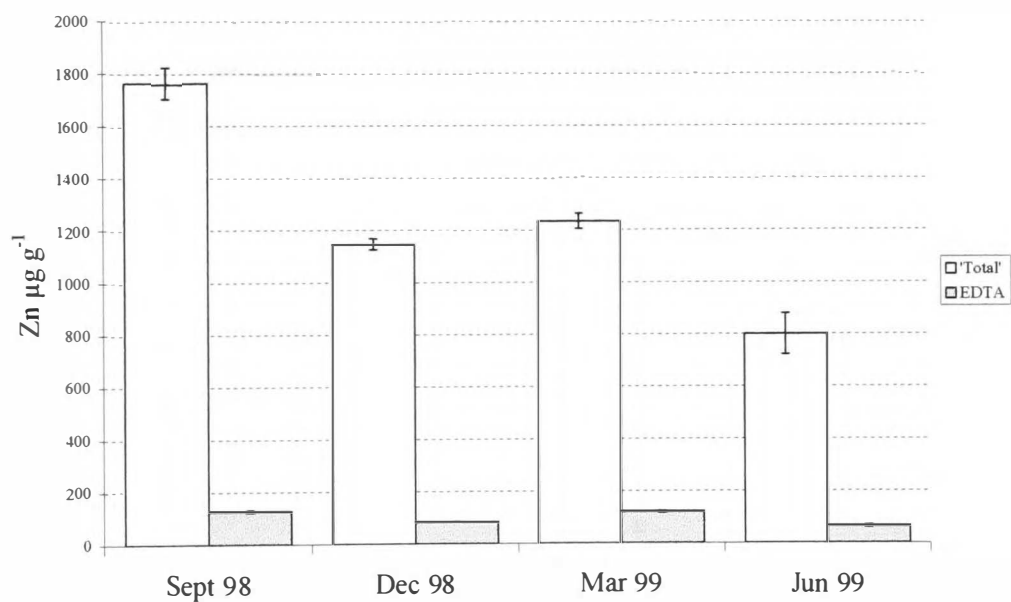
Figure 5.39. Mean monthly concentration of Total Pb and EDTA Pb at 200-400 mm for Thrupe Series (n=3).



For each month except June 1999, when the Total Pb concentration was lower than that of the EDTA Pb concentration, the Total Pb concentration was greater than that of the EDTA Pb concentration (Figure 5.39). EDTA Pb as a percentage of Total Pb varied from 95.50% in September 1998 to 101.07 % in June 1999. The

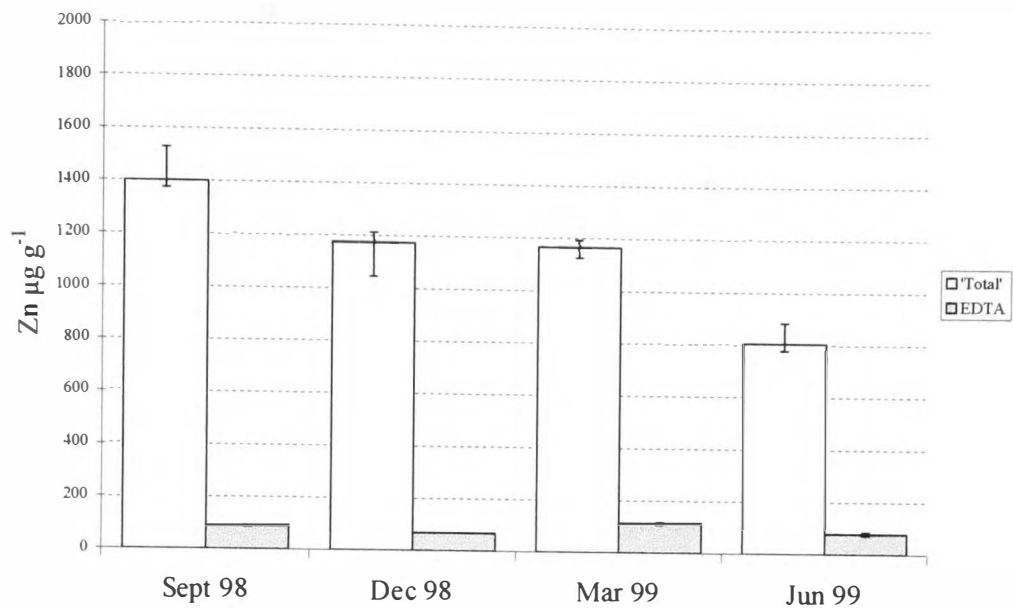
EDTA Pb followed the same monthly pattern of variation in concentration as that of Total Pb. The lowest EDTA Pb concentration occurred in June 1999 at  $7\,846.67 \pm 111.16 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $17\,406.67 \pm 324.96 \mu\text{g g}^{-1}$  (Figure 5.39).

Figure 5.40. Mean monthly concentration of Total Zn and EDTA Zn at 0-200 mm for Thrupe Series (n=3).



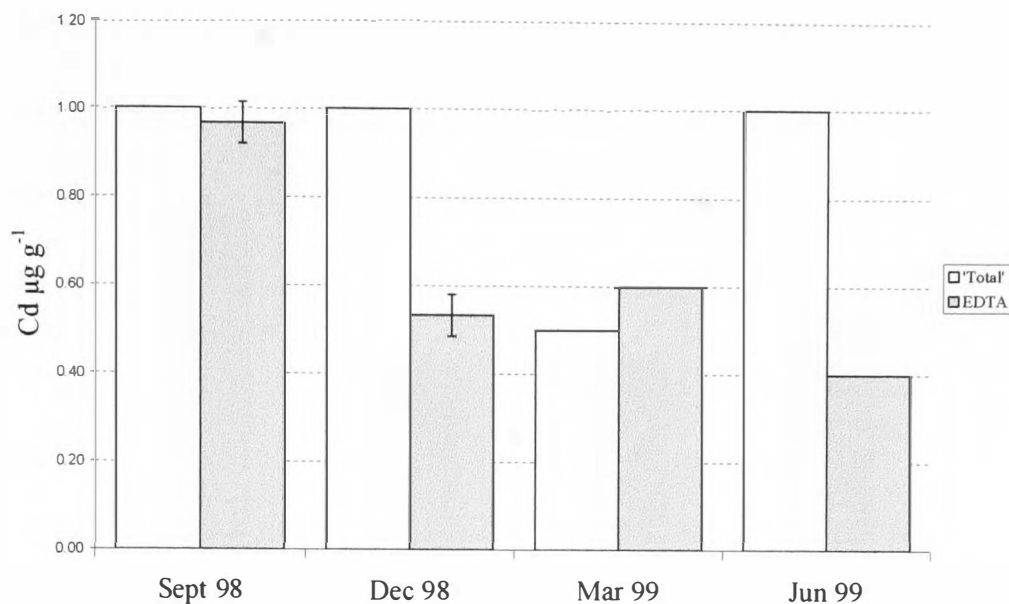
For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 7.18% in September 1998 to 9.76% in March 1999 (Figure 5.40). EDTA Zn followed the same monthly pattern of variation in concentration as that of Total Zn. The lowest EDTA Zn concentration of  $64.00 \pm 4.55 \mu\text{g g}^{-1}$  occurred in June 1999 and the greatest in September 1998 at  $126.67 \pm 3.86 \mu\text{g g}^{-1}$  (Figure 5.40).

Figure 5.41. Mean monthly concentration of Total Zn and EDTA Zn at 200-400 mm for Thrupe Series (n=3).



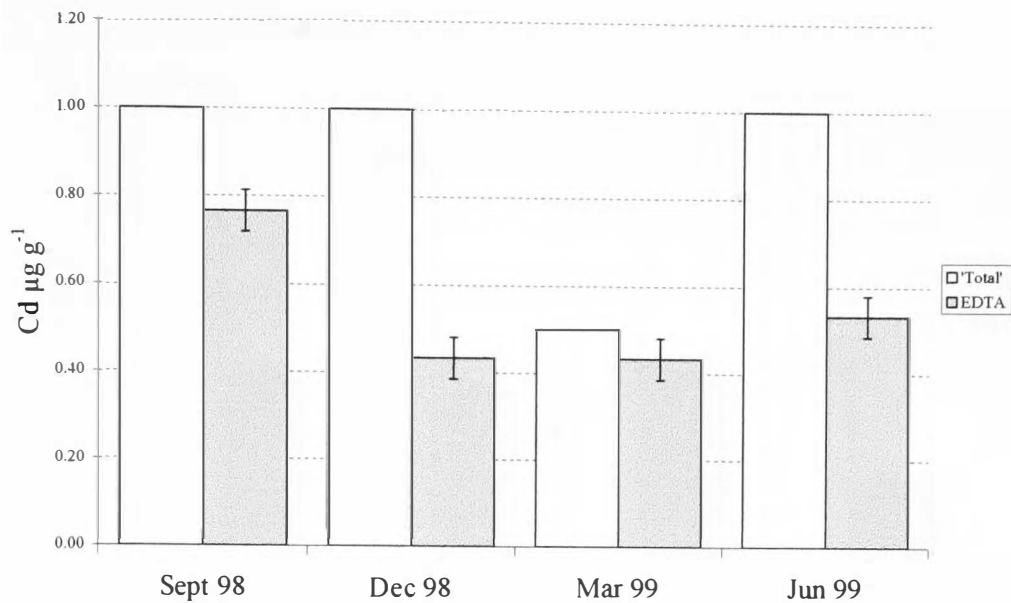
For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 5.88% in December 1998 to 9.83% in June 1999 (Figure 5.41). EDTA Zn did not follow the same monthly variation in pattern of concentration as that of Total Zn. The lowest EDTA Zn concentration at  $69.00 \pm 0 \mu\text{g g}^{-1}$  occurred in December 1998 and the greatest in March 1999 at  $113.00 \pm 4.90 \mu\text{g g}^{-1}$  (Figure 5.41).

Figure 5.42. Mean monthly mean concentration of Total Cd and EDTA Cd at 0-200 mm for Thrupe Series (n=3).



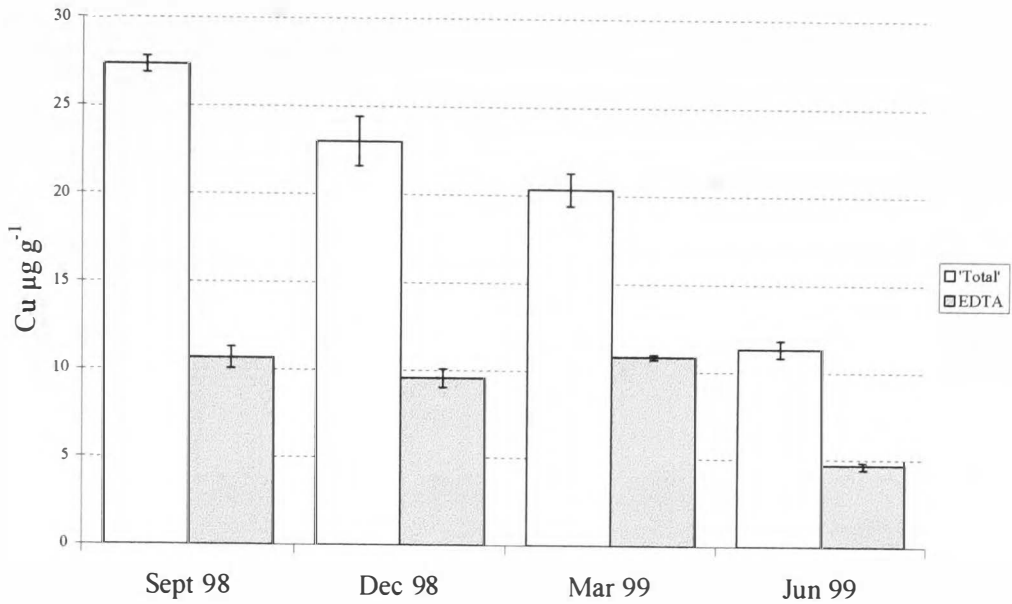
With the exception of March 1999, when the concentration of EDTA Cd was greater than that of Total Cd, for the remainder of the months, the Total Cd concentration was greater than that of EDTA Cd (Figure 5.42). EDTA Cd as a percentage of Total Cd varied from 40.00% in June 1999 to 120.00% in March 1999. The EDTA Cd concentration did not follow the same monthly trend in concentration as that of Total Cd. The lowest EDTA Cd concentration occurred in June 1999 at  $0.40 \pm 0 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $0.97 \pm 0.05 \mu\text{g g}^{-1}$  (Figure 5.42).

Figure 5.43. Mean monthly concentration of Total Cd and EDTA Cd at 200-400 mm for Thrupe Series (n=3).



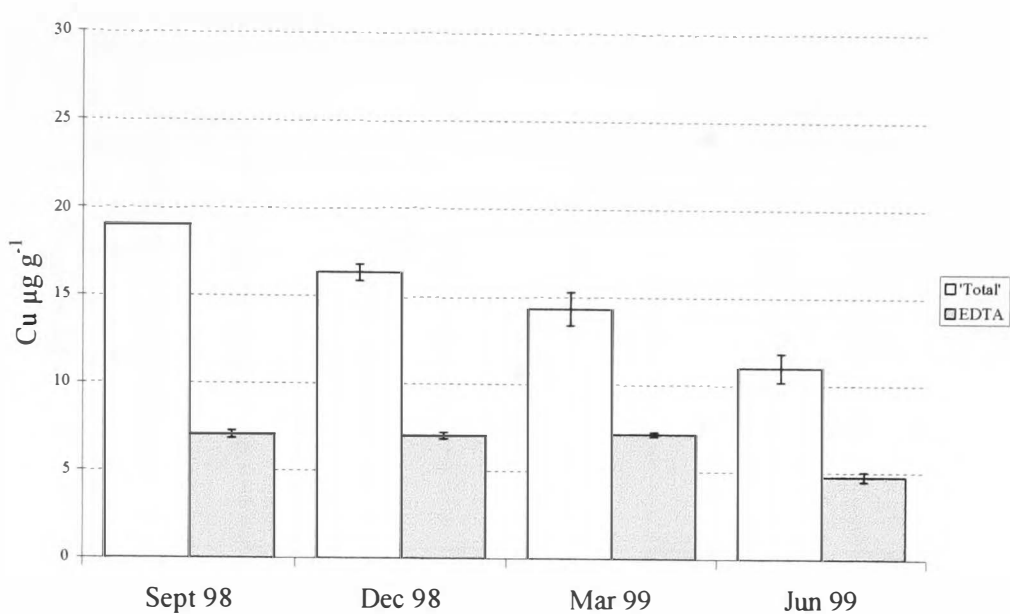
For each month, the concentration of Total Cd was greater than that of EDTA Cd, although EDTA as a percentage of Total Cd varied from 43.33% in December 1998 to 86.67% in March 1999 (Figure 5.43). The EDTA Cd concentration did not follow the same monthly trend in concentration as that of Total Cd, although the lowest concentrations for both occurred in March 1999. The lowest EDTA Cd concentration occurred in March 1999 at  $0.43 \pm 0.05 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $0.77 \pm 0.05 \mu\text{g g}^{-1}$  (Figure 5.43).

Figure 5.44. Mean monthly concentration of Total Cu and EDTA Cu at 0-200 mm for Thrupe Series (n=3).



For each month, the Total Cu concentration was greater than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 39.02% in September 1998 to 53.28% in March 1999 (Figure 5.44). Total Cu showed a pattern of decline in concentration from September 1998 to June 1999, but EDTA Cu did not follow this trend. The lowest EDTA Cu concentration of  $4.70 \pm 0.16 \mu\text{g g}^{-1}$  occurred in January 1999, and the greatest concentration in March 1999 at  $10.83 \pm 0.12 \mu\text{g g}^{-1}$  (Figure 5.44).

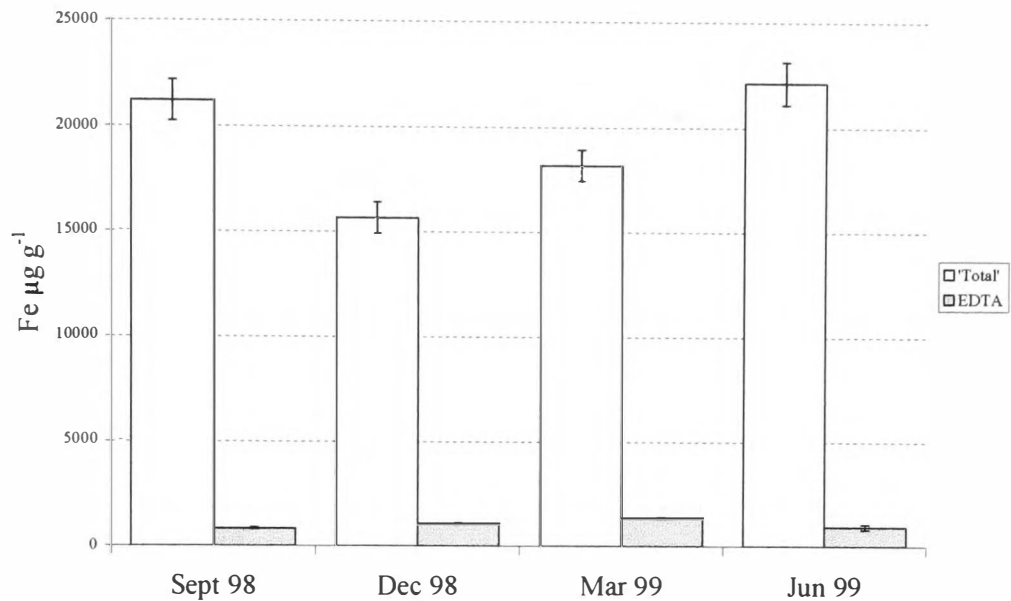
Figure 5.45. Mean monthly concentration of Total Cu and EDTA Cu at 200-400 mm for Thrupe Series (n=3).



For each month, the Total Cu concentration was greater than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 37.19% in September 1998 to 50.00% in March 1999 (Figure 5.45). As with surface Cu concentration, Total Cu showed a pattern of decline in concentration from September 1998 to June 1999, but EDTA Cu did not follow the trend. The lowest EDTA Cu concentration of  $4.77 \pm 0.26 \mu\text{g g}^{-1}$  occurred in June 1999 and the greatest in March 1999 at  $7.17 \pm 0.12 \mu\text{g g}^{-1}$  (Figure 5.45).

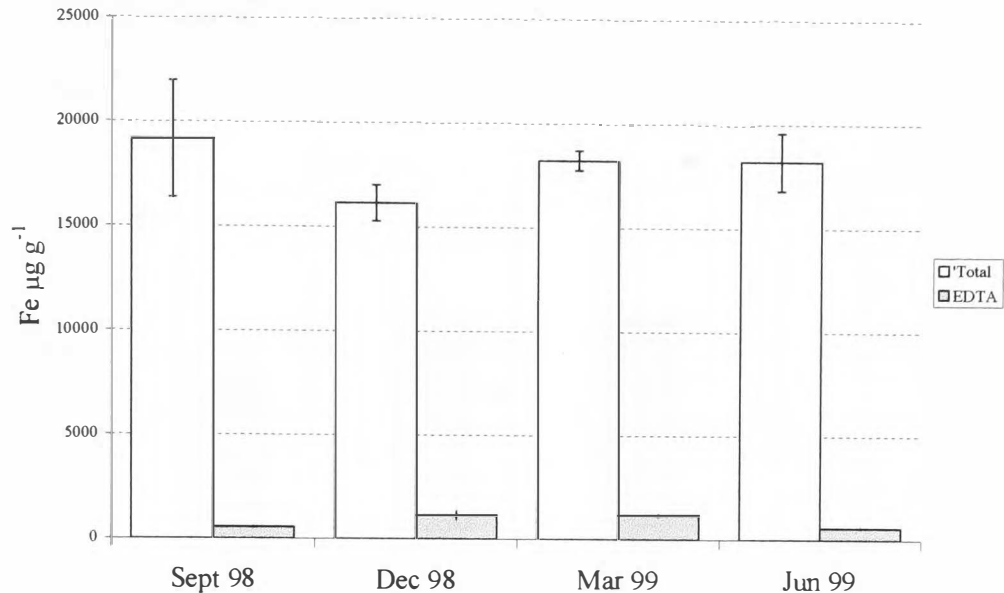


Figure 5.46. Mean monthly concentration of Total Fe and EDTA Fe at 0-200 mm for Thrupe Series (n=3).



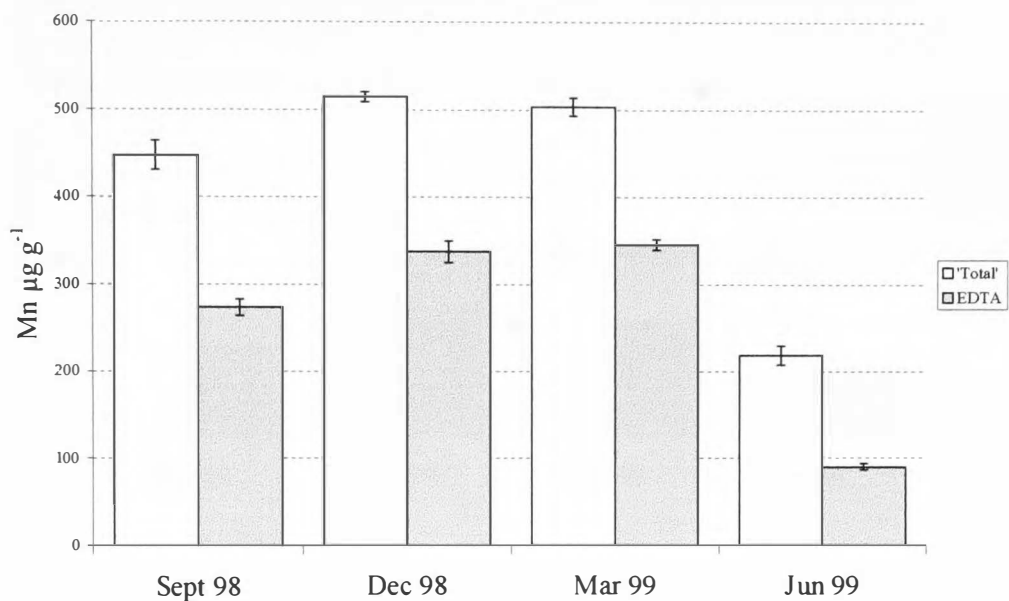
For each month, the Total Fe concentration was greater than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 3.96% in September 1998 to 7.40% in March 1999 (Figure 5.46). The EDTA Fe concentration did not follow the same monthly trend in concentration as that of Total Fe. The lowest EDTA Fe concentration occurred in September 1998 at  $839.67 \pm 31.90 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $1\,345.33 \pm 48.73 \mu\text{g g}^{-1}$  (Figure 5.46).

Figure 5.47. Mean monthly concentration of Total Fe and EDTA Fe at 200-400 mm for Thrupe Series (n=3).



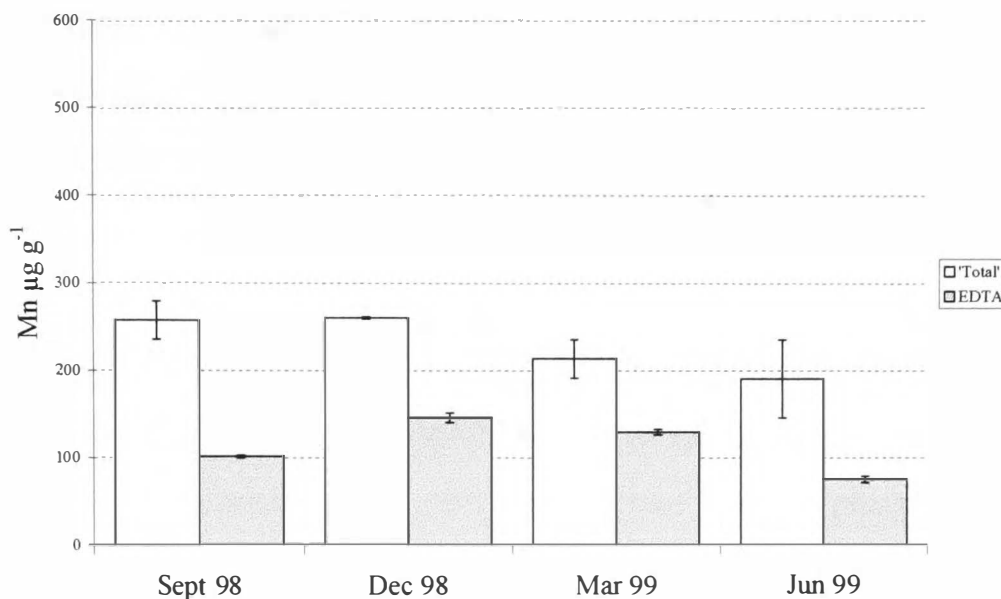
For each month, the Total Fe concentration was greater than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 2.90% in September 1998 to 7.07% in December 1998 (Figure 5.47). The EDTA Fe concentration did not follow the same monthly trend in concentration of that of Total Fe. The lowest EDTA Fe concentration occurred in September 1998 at  $561.33 \pm 20.04 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $1\,160.33 \pm 47.77 \mu\text{g g}^{-1}$  (Figure 5.47).

Figure 5.48. Mean monthly concentration of Total Mn and EDTA Mn at 0-200 mm for Thrupe Series (n=3).



For each month, the Total Mn concentration was greater than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 41.31% in June 1999 to 68.68% in March 1999. The EDTA Mn concentration generally followed the monthly trend in concentration of that of the Total Mn concentration. The lowest EDTA Mn concentration of  $90.33 \pm 3.68$  occurred in June 1999, and the greatest in March 1999 at  $345.67 \pm 6.13 \mu\text{g g}^{-1}$  (Figure 5.48).

Figure 5.49. Mean monthly concentration of Total Mn and EDTA Mn at 200-400 mm for Thrupe Series (n=3).



For each month, the Total Mn concentration was greater than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 39.59% in September 1998 to 60.84% in March 1999 (Figure 5.49). The EDTA Mn concentration did not follow the same monthly trend in concentration as that of Total Mn. The lowest EDTA Mn concentration of  $146.33 \pm 5.23 \mu\text{g g}^{-1}$  occurred in December 1998, and the greatest in June 1999 at  $75.67 \pm 3.68 \mu\text{g g}^{-1}$  (Figure 5.49).

Table 5.43. Median percentage of monthly EDTA trace metals as a percentage of Total trace metals for Thrupe Series at 0-200 mm and 200-400 mm.

Depth	Pb %	Zn %	Cd %	Cu %	Fe %	Mn %
0-200 mm	91.95	7.62	75.00	41.53	5.52	63.39
200-400 mm	99.30	8.01	65.00	43.20	4.79	47.88

In the surface soil, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 5.52%, while the greatest was Pb at 91.95% (Table 5.43). At depth, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 4.79%, while the greatest was Pb at 99.30% (Table 5.43).

#### Monthly variation of other soil parameters

Table 5.44. Monthly values for CEC, Exchangeable Ca, Mg and K and Total P at 0-200 mm and 200-400 mm for Thrupe Series.

Parameter	Unit	Sept 1998	Dec 1998	Mar 1999	Jun 1999
CEC (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	19.8	17.82	17.42	12.28
CEC (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	13.86	12.67	13.46	11.09
Exch. Ca (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	4.23	2.49	2.59	8.22
Exch. Ca (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	4.83	2.74	2.44	3.34
Exch. Mg (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.74	0.62	0.70	0.99
Exch. Mg (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.70	0.70	0.70	0.86
Exch. K (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.19	0.28	0.32	0.21
Exch. K (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.19	0.20	0.28	0.17
Total P (0-200 mm)	µg g <sup>-1</sup>	776.10	580.90	540.10	430.70
Total P (200-400 mm)	µg g <sup>-1</sup>	608.80	533.70	462.90	471.50

For all months, the monthly CEC, and Exchangeable K in the surface soil were consistently greater than that at depth (Table 5.44). In September and December 1998, Exchangeable Ca was greater at depth than in surface soil, while in March and June 1999, the monthly Exchangeable Ca was greater in the surface soil than at depth. In September 1998 and June 1999, the concentration of Exchangeable Mg was greater in surface soil than at depth. The concentration of Exchangeable Mg in surface soil and at depth were identical at  $0.07 \text{ cmol}_e \text{ kg}^{-1}$  in March 1999, and greater at depth than in surface soil in December 1998. The concentration of Total P in surface soil was greater than the concentration at depth for September and December 1998 and March 1999. In June 1999, Total P concentration was greater at depth than in surface soil (Table 5.44).

#### Two-Sample analysis

Mann-Whitney analysis or the Two-sample T-test between surface and depth for each stacked soil parameter ( $n=12$  or  $n=4$ ) showed a significant difference at the  $p \leq 0.05$  level for 7/19 of the Thrupe Series soil parameters (Tables 5.45 and 5.46)

Table 5.45. Two-sample Mann-Whitney tests for Thrupe soil parameters at 0-200 mm *versus* 200-400 mm, where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter	n=	Mann-Whitney p-value	$H_0$ : $\eta_1 = \eta_2$ at $\alpha=0.05$
L-o-I (0-200 mm) v L-o-I (200-400 mm)	12	0.0007	Rejected
Total Cd (0-200 mm) v Total Cd (200-400 mm)	12	0.1998	Accepted
Exch. Mg (0-200 mm) v Exch. Mg (200-400 mm)	4	1.0000	Accepted

Table 5.46. Two-Sample T-Tests for Thrupe soil parameters at 0-200 mm *versus* 200-400 mm where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter	n=	T-value	p-value	$H_0$ : $\mu_1 = \mu_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	12	-3.46	0.005	Rejected
Total Pb (0-200 mm) v Total Pb (200-400 mm)	12	9.51	0.000	Rejected
Total Zn (0-200 mm) v Total Zn (200-400 mm)	12	4.02	0.002	Rejected
Total Cu (0-200 mm) v Total Cu (200-400 mm)	12	-0.50	0.629	Accepted
Total Fe (0-200 mm) v Total Fe (200-400 mm)	12	4.59	0.593	Accepted
Total Mn (0-200 mm) v Total Mn (200-400 mm)	12	0.55	0.000	Rejected
EDTA Pb (0-200 mm) v EDTA Pb (200-400 mm)	4	1.50	0.231	Accepted
EDTA Zn (0-200 mm) v EDTA Zn (200-400 mm)	4	1.02	0.384	Accepted
EDTA Cd (0-200 mm) v EDTA Cd (200-400 mm)	4	1.14	0.338	Accepted
EDTA Cu (0-200 mm) v EDTA Cu (200-400 mm)	4	2.79	0.069	Accepted
EDTA Fe (0-200 mm) v EDTA Fe (200-400 mm)	4	1.99	0.140	Accepted
EDTA Mn (0-200 mm) v EDTA Mn (200-400 mm)	4	3.26	0.047	Rejected
CEC (0-200 mm) v CEC (200-400 mm)	4	3.91	0.030	Rejected
Exch. Ca (0-200 mm) v Exch. Ca (200-400 mm)	4	0.81	0.476	Accepted
Exch. K (0-200 mm) v Exch. K (200-400 mm)	4	2.45	0.092	Accepted
Total P (0-200 mm) v Total P (200-400 mm)	4	1.46	0.240	Accepted

While the majority of the Thrupe soil parameters (12/19) showed no significant difference between values at surface and at depth, pH, Loss-on-Ignition, Total Pb, Total Zn , Total Mn, EDTA Mn and CEC showed a significant difference at the  $p \leq 0.05$  level (Tables 5.45 and 5.46).

### Pearson correlations

Table 5.47. Pearson correlation values (r-values) and degrees of significance at the  $p=0.001$ ,  $0.01$  and  $0.05$  levels for stacked Thrupe soil parameters at 0-400 mm ( $n=24$ ) September 1998 - August 1999.

	pH (0-400 mm)	L-o-I (0-400mm)	Total Pb (0-400 mm)	Total Zn (0-400 mm)	Total Cd (0-400 mm)	Total Cu (0-400 mm)	Total Fe (0-400 mm)
L-o-I (0-400 mm)	-0.535 **						
Total Pb (0-400 mm)	-0.288	0.847 ***					
Total Zn (0-400 mm)	-0.190	0.355	0.658 ***				
Total Cd (0-400 mm)	-0.143	0.244	0.094	-0.257			
Total Cu (0-400 mm)	-0.305	0.785 ***	0.724 ***	0.310	0.168		
Total Fe (0-400 mm)	-0.071	0.234	0.258	0.250	-0.219	0.110	
Total Mn (0-400 mm)	-0.564 **	0.690 ***	0.497 *	0.190	0.058	0.642 **	-0.074

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     - Indicates a negative correlation

In the soil of the Thrupe Series, pH was negatively correlated at the  $p \leq 0.05$  level with Loss-on-Ignition and Total Mn. Loss-on-Ignition was positively correlated at the  $p=0.001$  level with Total Pb, Total Cu and Total Mn. Total Pb was positively correlated with Total Zn, Total Cu and Total Mn at the  $p \leq 0.05$  level (Table 5.47).



5.5.4 Ashen Series

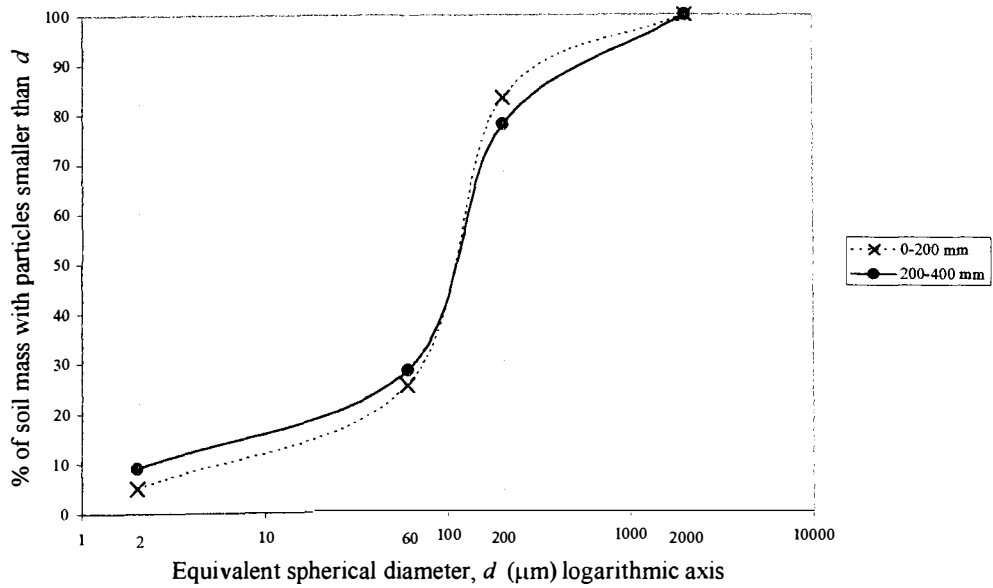
Particle Size Analysis

Table 5.48. Particle size distribution and soil textural class for Ashen Series.

Depth (mm)	% clay	% silt	% fine sand	% coarse sand	Textural Class
0 - 200	5.03	20.26	57.95	16.76	Loamy Sand
200-400	9.04	19.30	49.48	22.18	Loamy Sand

The surface soil was classified as loamy sand, with fine sand as the most abundant particle size (Table 5.48). At depth, although still dominated by fine sand and classified as loamy sand, the soil contained a slightly higher % of clay, silt, and coarse sand than the surface soil.

Figure 5.49. Cumulative curve displaying particle size distribution of Ashen soil at 0-200 mm and 200-400 mm



The cumulative curve plot showed that at approximately 75% and 70% of the particles at surface and depth respectively, sand (fine + coarse sand) dominated the < 2 mm soil fraction at both surface and depth (Figure 5.49).

### Descriptive statistics

The Ashen Series data set consisted of monthly (n=12) and quarterly (n=4) data for the same soil parameters as the Maesbury Series described in 5.5.2. Soil reaction ranged from pH 3.32 to pH 4.02 in the surface soil and from pH 3.36 to pH 4.28 at depth (Table 5.49). Loss-on-Ignition in the surface soil ranged from 9.87% to 13.40% and from 6.57% to 9.56% at depth (Table 5.49).

The concentration of Total Pb in the surface soil ranged from 1 656.00  $\mu\text{g g}^{-1}$  to 2 125.00  $\mu\text{g g}^{-1}$  and from 1 228.00  $\mu\text{g g}^{-1}$  to 1 466.50  $\mu\text{g g}^{-1}$  at depth. Total Zn ranged from 26.67  $\mu\text{g g}^{-1}$  to 63.33  $\mu\text{g g}^{-1}$  in the surface horizon and from 18.67  $\mu\text{g g}^{-1}$  to 36.67  $\mu\text{g g}^{-1}$  at depth. Total Cd was present in surface soil at 0.50  $\mu\text{g g}^{-1}$  to 1.00  $\mu\text{g g}^{-1}$  and from 0.50  $\mu\text{g g}^{-1}$  to 1.00  $\mu\text{g g}^{-1}$  at depth (Table 5.49). The concentration of Total Cu ranged from 4.00  $\mu\text{g g}^{-1}$  to 7.33  $\mu\text{g g}^{-1}$  in the surface soil and at depth from 2.33  $\mu\text{g g}^{-1}$  to 7.33  $\mu\text{g g}^{-1}$ . Total Fe was present in surface soil at 4 636.67  $\mu\text{g g}^{-1}$  to 9 043.33  $\mu\text{g g}^{-1}$  and from 7 683.30  $\mu\text{g g}^{-1}$  to 16 350.00  $\mu\text{g g}^{-1}$  at depth. Total Mn in surface soil ranged from 23.00  $\mu\text{g g}^{-1}$  to 153.00  $\mu\text{g g}^{-1}$  and from 92.33  $\mu\text{g g}^{-1}$  to 189.33  $\mu\text{g g}^{-1}$  at depth (Table 5.49).

Table 5.49. Soil parameter data for Ashen Series at 0-200 mm and 200-400 mm (n=12) for September 1998 - August 1999 and (n=4) for quarterly sampling.

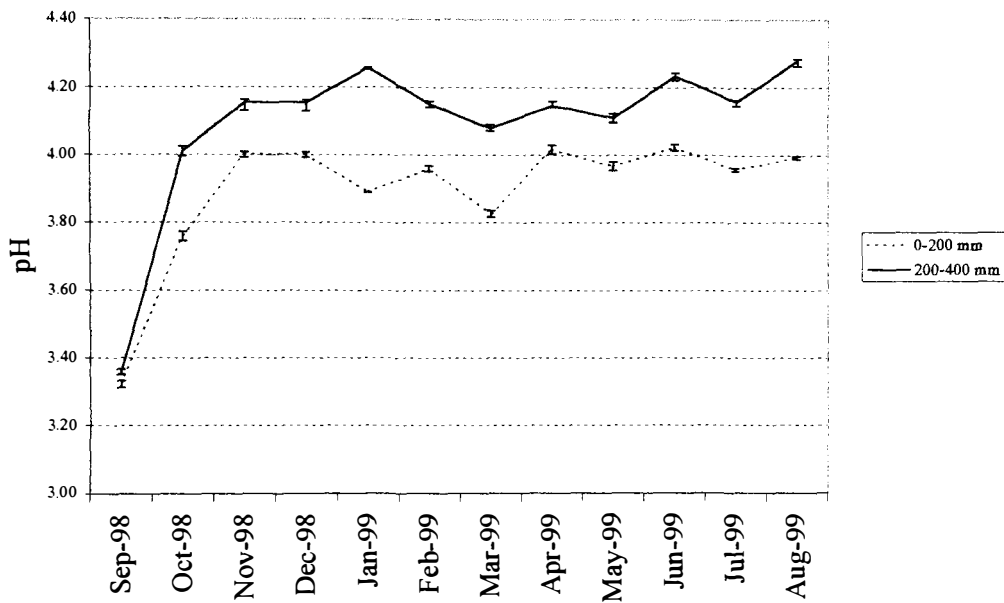
	Unit	n	Arithmetic Mean	St. Dev.	Minimum	Median	Maximum
pH (0-200 mm)	pH	12	3.89	0.20	3.32	3.97	4.02
pH (200-400 mm)	pH	12	4.09	0.24	3.36	4.15	4.28
L-o-I (0-200 mm)	%	12	11.66	1.20	9.87	11.48	13.40
L-o-I (200-400 mm)	%	12	8.12	0.91	6.59	8.37	9.56
Total Pb (0-200 mm)	$\mu\text{g g}^{-1}$	12	1 825.50	140.60	1 656.00	1 783.00	2 125.00
Total Pb (200-400 mm)	$\mu\text{g g}^{-1}$	12	1 490.67	130.67	1 228.00	1 466.50	1 736.00
Total Zn (0-200 mm)	$\mu\text{g g}^{-1}$	12	36.36	9.85	26.67	33.67	63.33
Total Zn (200-400 mm)	$\mu\text{g g}^{-1}$	12	28.08	5.08	18.67	28.00	36.67
Total Cd (0-200 mm)	$\mu\text{g g}^{-1}$	12	0.54	0.14	0.50	0.50	1.00
Total Cd (200-400 mm)	$\mu\text{g g}^{-1}$	12	0.54	0.14	0.50	0.50	1.00
Total Cu (0-200 mm)	$\mu\text{g g}^{-1}$	12	5.28	1.10	4.00	5.00	7.33
Total Cu (200-400 mm)	$\mu\text{g g}^{-1}$	12	4.53	1.64	2.33	4.33	7.33
Total Fe (0-200 mm)	$\mu\text{g g}^{-1}$	12	6 807.50	1 380.89	4 636.67	6 835.00	9 043.33
Total Fe (200-400 mm)	$\mu\text{g g}^{-1}$	12	11 525.00	2 950.90	7 683.30	10 286.70	16 350.00
Total Mn (0-200 mm)	$\mu\text{g g}^{-1}$	12	56.75	38.01	23.00	41.67	153.00
Total Mn (200-400 mm)	$\mu\text{g g}^{-1}$	12	136.44	29.27	92.33	129.165	189.33
EDTA Pb (0-200 mm)	$\mu\text{g g}^{-1}$	4	1 744.25	93.34	1 661.67	1 735.83	1 843.67
EDTA Pb (200-400 mm)	$\mu\text{g g}^{-1}$	4	1 429.00	97.30	1 288.67	1 457.00	1 513.33
EDTA Zn (0-200 mm)	$\mu\text{g g}^{-1}$	4	4.86	0.42	4.50	4.73	5.47
EDTA Zn (200-400 mm)	$\mu\text{g g}^{-1}$	4	3.83	0.13	3.67	3.83	3.97
EDTA Cd (0-200 mm)	$\mu\text{g g}^{-1}$	4	0.05	0.00	0.05	0.05	0.05
EDTA Cd (200-400 mm)	$\mu\text{g g}^{-1}$	4	0.05	0.00	0.05	0.05	0.05
EDTA Cu (0-200 mm)	$\mu\text{g g}^{-1}$	4	2.25	0.61	1.87	1.98	3.17
EDTA Cu (200-400 mm)	$\mu\text{g g}^{-1}$	4	1.41	0.22	1.10	1.45	1.63
EDTA Fe (0-200 mm)	$\mu\text{g g}^{-1}$	4	1 213.42	219.19	999.33	1 216.17	1 422.00
EDTA Fe (200-400 mm)	$\mu\text{g g}^{-1}$	4	1 099.33	198.99	904.00	1 091.00	1 311.33
EDTA Mn (0-200 mm)	$\mu\text{g g}^{-1}$	4	3.40	0.50 *	2.70	3.57	3.77
EDTA Mn (200-400 mm)	$\mu\text{g g}^{-1}$	4	5.68	1.76	3.23	6.07	7.33
CEC (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	17.03	1.33	15.05	17.62	17.82
CEC (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	15.64	1.31	13.86	15.84	17.03
Exch. Ca (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.50	0.08	0.42	0.49	0.60
Exch. Ca (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.31	0.07	0.22	0.33	0.38
Exch. Mg (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.24	0.02	0.21	0.24	0.25
Exch. Mg (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.11	0.04	0.08	0.10	0.16
Exch. K (0-200 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.21	0.05	0.17	0.20	0.29
Exch. K (200-400 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.16	0.03	0.12	0.16	0.19
Total P (0-200 mm)	$\mu\text{g g}^{-1}$	4	338.48	114.87	226.90	313.80	499.40
Total P (200-400 mm)	$\mu\text{g g}^{-1}$	4	300.90	19.09	280.50	298.75	325.60

EDTA Pb was present in surface soil at 1 661.67  $\mu\text{g g}^{-1}$  to 1 843.67  $\mu\text{g g}^{-1}$  and from 1 288.67  $\mu\text{g g}^{-1}$  to 1 513.33  $\mu\text{g g}^{-1}$  at depth. Surface EDTA Zn was present at 4.50  $\mu\text{g g}^{-1}$  to 5.47  $\mu\text{g g}^{-1}$  and from 3.69  $\mu\text{g g}^{-1}$  to 3.97  $\mu\text{g g}^{-1}$  at depth. In both the surface soil and at depth, EDTA Cd was consistent at 0.05  $\mu\text{g g}^{-1}$  (Table 5.49). The concentration of surface EDTA Cu ranged from 1.87  $\mu\text{g g}^{-1}$  to 3.17  $\mu\text{g g}^{-1}$  and from 1.10  $\mu\text{g g}^{-1}$  to 1.63  $\mu\text{g g}^{-1}$  at depth. EDTA Fe ranged from 999.33  $\mu\text{g g}^{-1}$  to 1 422.00  $\mu\text{g g}^{-1}$  in surface soil and from 904.00  $\mu\text{g g}^{-1}$  to 1 311.33  $\mu\text{g g}^{-1}$  at depth. EDTA Mn was present in surface soil at 2.70  $\mu\text{g g}^{-1}$  to 3.77  $\mu\text{g g}^{-1}$  and from 3.23  $\mu\text{g g}^{-1}$  to 7.33  $\mu\text{g g}^{-1}$  at depth (Table 5.49).

Surface CEC ranged from 15.05  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 17.82  $\text{cmol}_\text{c} \text{kg}^{-1}$  and from 13.86  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 17.03  $\text{cmol}_\text{c} \text{kg}^{-1}$  at depth. The concentration of surface Exchangeable Ca ranged from 0.42  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 0.60  $\text{cmol}_\text{c} \text{kg}^{-1}$  and from 0.22  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 0.38  $\text{cmol}_\text{c} \text{kg}^{-1}$  at depth. Exchangeable Mg was present in surface soil at 0.21  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 0.25  $\text{cmol}_\text{c} \text{kg}^{-1}$  and from 0.08  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 0.16  $\text{cmol}_\text{c} \text{kg}^{-1}$  at depth. Surface Exchangeable K ranged from 0.17  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 0.29  $\text{cmol}_\text{c} \text{kg}^{-1}$  and from 0.12  $\text{cmol}_\text{c} \text{kg}^{-1}$  to 0.19  $\text{cmol}_\text{c} \text{kg}^{-1}$  at depth (Table 5.49). The concentration of surface Total P ranged from 226.90  $\mu\text{g g}^{-1}$  to 499.40  $\mu\text{g g}^{-1}$  and from 280.50  $\mu\text{g g}^{-1}$  to 325.60  $\mu\text{g g}^{-1}$  at depth. Generally, the mean and median values of each individual soil parameter were very similar, with the exception of Total Fe at depth (Table 5.49). The mean and median values for Total Fe at depth were 11.525.00  $\mu\text{g g}^{-1}$  and 10 286.70  $\mu\text{g g}^{-1}$  respectively (Table 5.49).

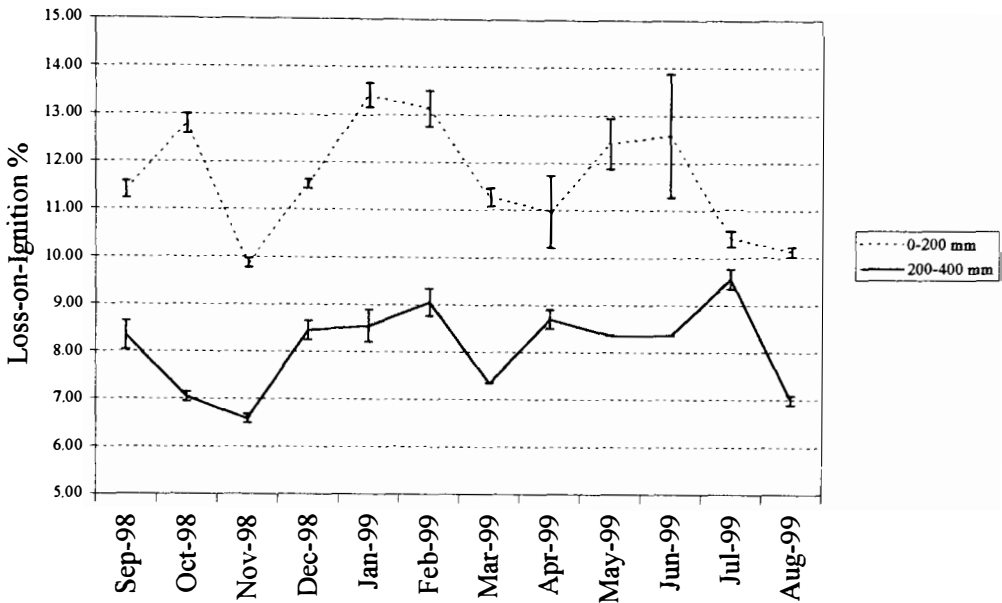
Monthly variation in pH, Loss-on-Ignition and Total metals

Figure 5.50. Mean monthly pH at 0-200 mm and 200-400 mm for Ashen Series (n=3).



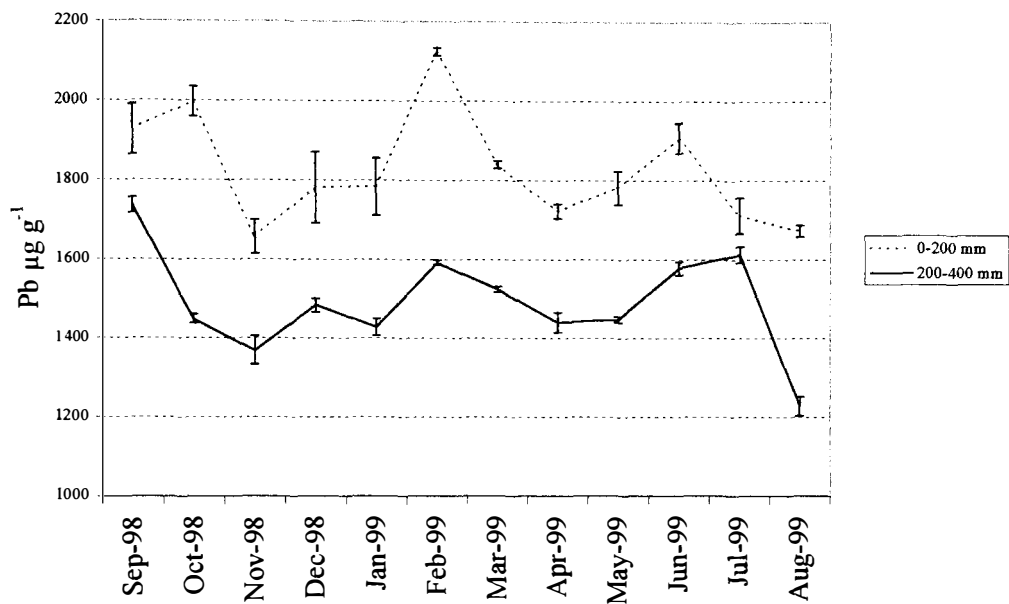
Soil reaction at surface and depth both showed a general overall trend of increasing values throughout the year (Figure 5.50). Soil pH at depth was consistently higher than surface pH in each month (Figure 5.50). The lowest pH values in the surface soil occurred in September 1998 at pH  $3.32 \pm 0.01$ , while the highest value of pH  $4.02 \pm 0.01$  occurred in June and April 1999. For soil at depth, the lowest pH occurred in September 1998 at pH  $3.36 \pm 0.01$ , while the highest at pH  $4.28 \pm 0.02$  occurred in August 1999 (Figure 5.50).

Figure 5.51. Mean monthly % Loss-on-Ignition at 0-200 mm and 200-400 mm for Ashen Series (n=3).



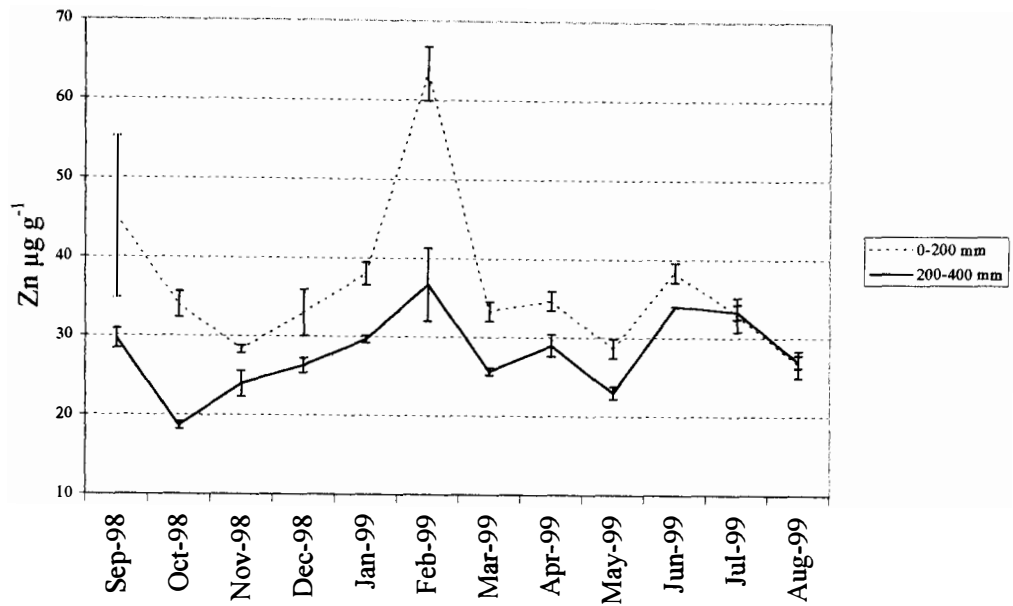
For each month, Loss-on-Ignition was consistently greater for surface soil than that at depth (Figure 5.51). The lowest % Loss-on-Ignition of  $9.87 \pm 0.09\%$  in the surface soil occurred in November 1998, while the greatest % Loss-on-Ignition of  $13.12 \pm 0.38\%$  occurred in January 1999 (Figure 5.51). The lowest % Loss-on-Ignition at depth occurred in November 1999 at  $6.59 \pm 0.09\%$ , while the greatest % Loss-on-Ignition of  $9.56 \pm 0.21\%$  occurred in July 1999 (Figure 5.51).

Figure 5.52. Mean monthly Total Pb at 0-200 mm and 200-400 mm for Ashen Series (n=3).



In general, Total Pb in surface soil and at depth showed a similar pattern of variation throughout the year. The concentration of Total Pb in surface soil was consistently greater than that at depth for each month. The lowest concentration of Total Pb in the surface soil occurred in November 1998 at  $1\,656 \pm 43 \mu\text{g g}^{-1}$ , while the greatest concentration of  $2\,125 \pm 10 \mu\text{g g}^{-1}$  occurred in February 1999 (Figure 5.52). The lowest concentration of Total Pb at depth occurred in August 1999 at  $1\,228 \pm 25 \mu\text{g g}^{-1}$ , while the greatest occurred in September 1998 at  $1\,736 \pm 19 \mu\text{g g}^{-1}$  (Figure 5.52).

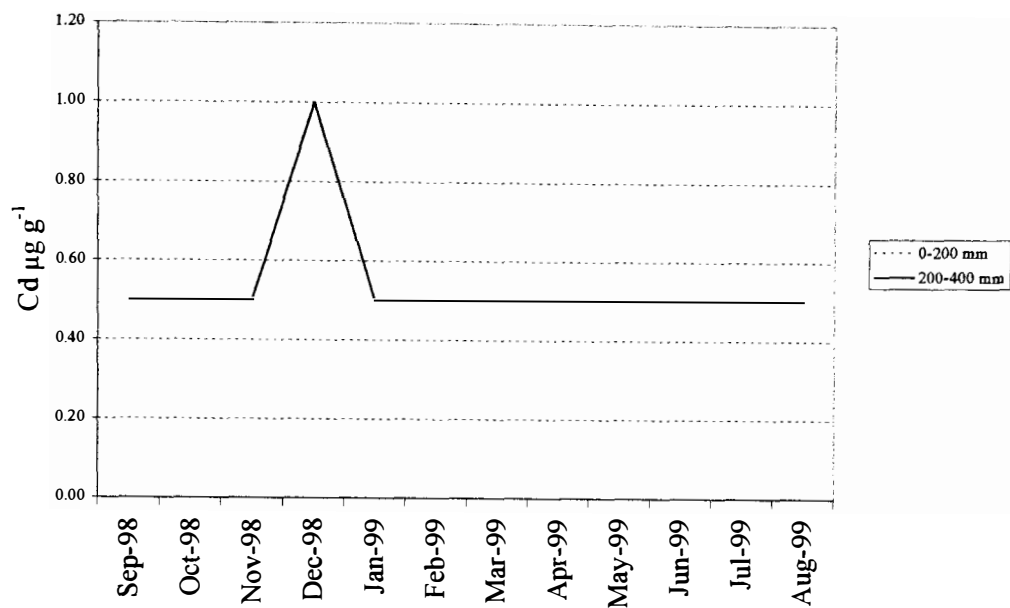
Figure 5.53. Mean monthly Total Zn at 0-200 mm and 200-400 mm for Ashen Series (n=3).



The concentration of Total Zn was consistently greater in surface soil than at depth for each month (Figure 5.53). In general, Total Zn in surface soils and at depth showed a similar pattern of variation in concentration throughout the year. The lowest concentration of Total Zn in the surface soil occurred in August 1999 at  $26.67 \pm 1.70 \mu\text{g g}^{-1}$ , while the greatest at  $63.33 \pm 3.40 \mu\text{g g}^{-1}$  occurred in February 1998 (Figure 5.53). At  $18.67 \pm 0.47 \mu\text{g g}^{-1}$ , the lowest concentration of Total Zn at depth occurred in October 1998, while the greatest occurred in February 1999 at  $36.67 \pm 4.46 \mu\text{g g}^{-1}$  (Figure 5.53).

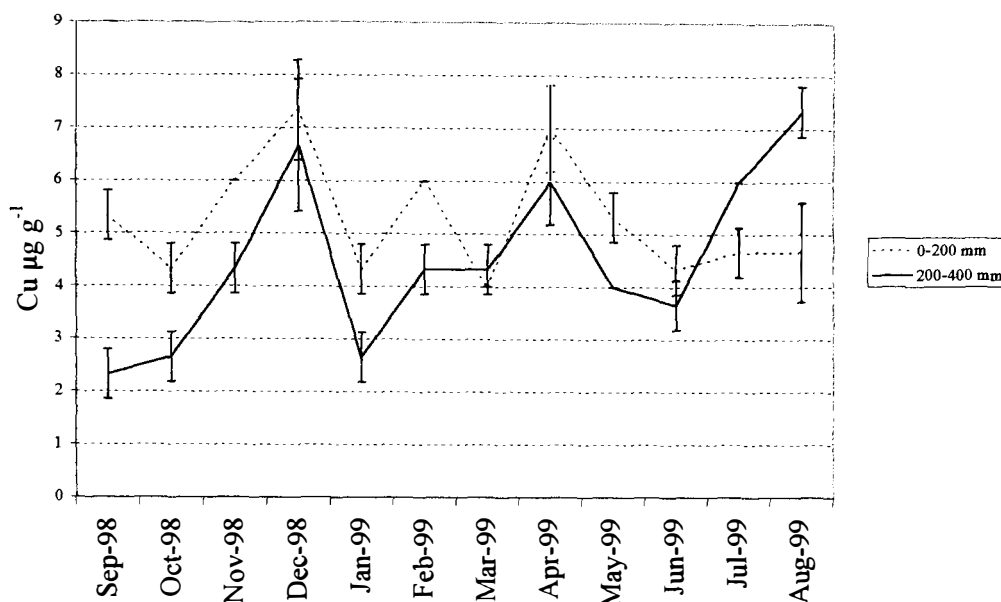


Figure 5.54. Mean monthly Total Cd at 0-200 mm and 200-400 mm for Ashen Series (n=3).



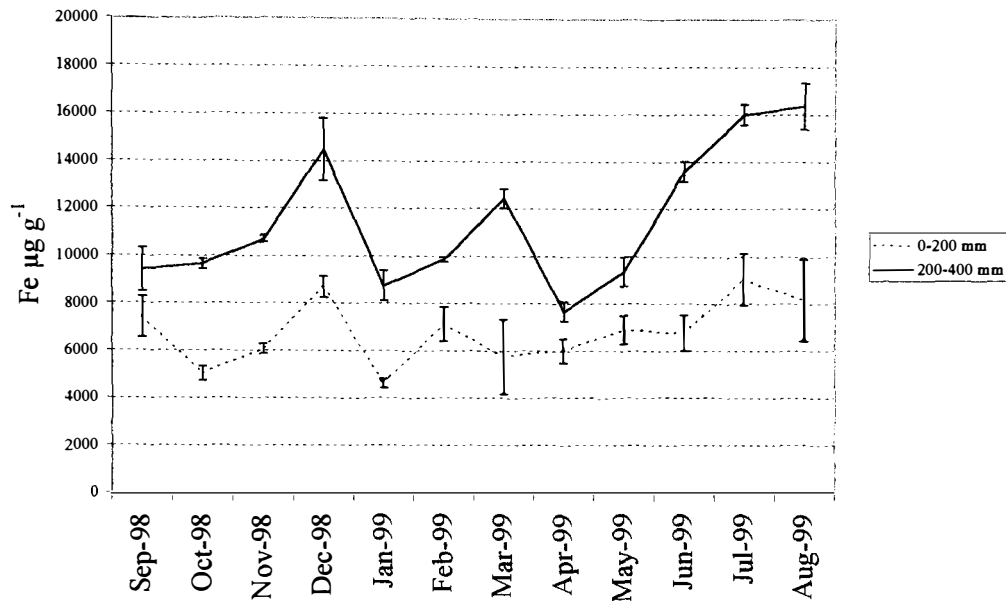
With the exception of December 1998, when the Total Cd concentration was  $1.00 \pm 0$  for both surface and depth, for the remaining months, the concentration of Total Cd was identical in the surface soil and at depth at  $0.05 \pm 0 \mu\text{g g}^{-1}$  (Figure 5.54).

Figure 5.55. Mean monthly Total Cu at 0-200 mm and 200-400 mm for Ashen Series (n=3).



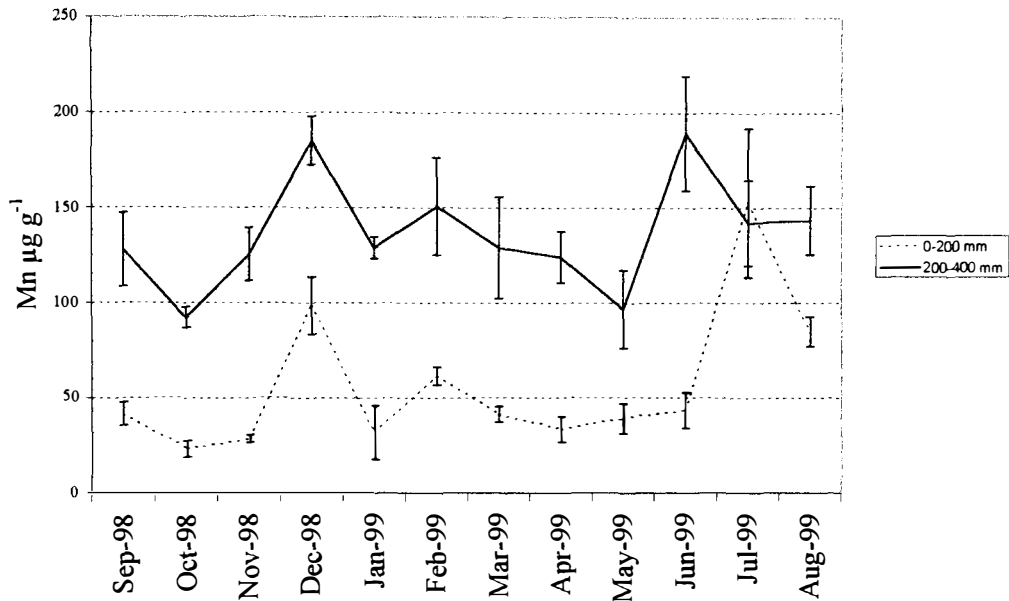
With the exception of July and August 1999, when the concentration of Total Cu at depth was greater than in surface soil, for each month, the concentration of Total Cu was consistently greater for surface soil than at depth (Figure 5.55). Until July and August 1999, when Total Cu in surface soil showed a significant increase in concentration, the Total Cu in surface soils and at depth showed a similar pattern of variation in concentration. The lowest concentration of Total Cu in the surface soil occurred in March 1999 at  $4.00 \pm 0.47 \mu\text{g g}^{-1}$ , while the greatest occurred in December 1998 at  $7.33 \pm 0.94 \mu\text{g g}^{-1}$  (Figure 5.55). At depth, the lowest concentration of Total Cu at  $2.33 \pm 0.47 \mu\text{g g}^{-1}$  occurred in September 1998, while the greatest occurred in August 1999 at  $7.33 \pm 0.47 \mu\text{g g}^{-1}$  (Figure 5.55).

Figure 5.56. Mean monthly Total Fe at 0-200 mm and 200-400 mm for Ashen Series (n=3).



The Total Fe concentration was consistently greater at depth than in surface soil and both horizons showed a similar pattern in variation in concentration throughout the year (Table 5.56). The lowest concentration of Total Fe in the surface soil occurred in January 1999 at  $4\,636 \pm 632 \mu\text{g g}^{-1}$ , while the greatest at  $9\,043 \pm 438 \mu\text{g g}^{-1}$  occurred in July 1999 (Figure 5.56). At depth, the lowest concentration of Total Fe at  $7\,683 \pm 507 \mu\text{g g}^{-1}$  occurred in April 1999, while the greatest at  $16\,350 \pm 1\,724 \mu\text{g g}^{-1}$  occurred in August 1999 (Figure 5.56).

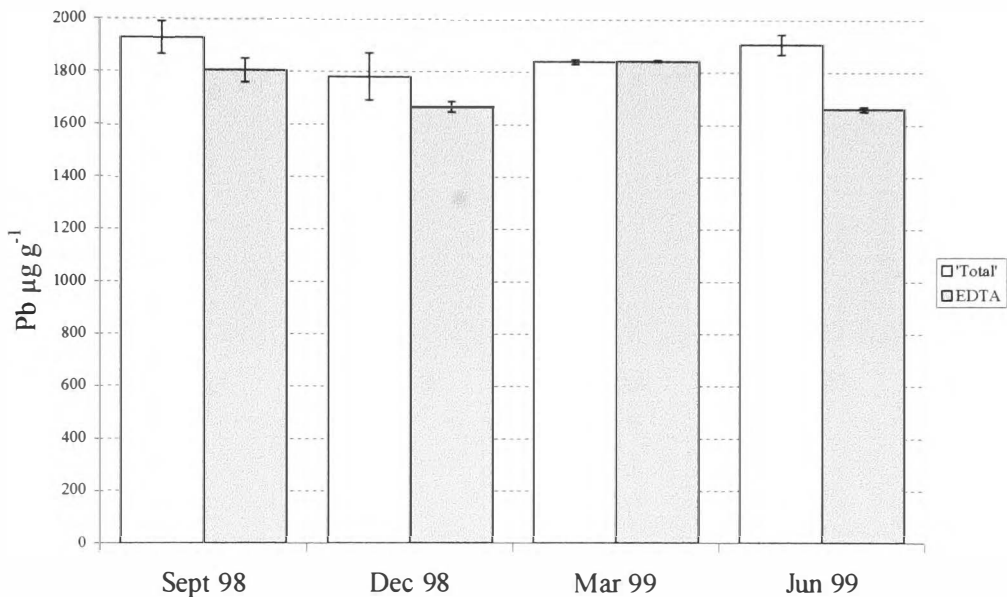
Figure 5.57. Mean monthly Total Mn at 0-200 mm and 200-400 mm for Ashen Series (n=3).



With the exception of July 1999, when the concentration of Total Mn was greater in the surface soil than at depth, for each remaining month the concentration of Total Mn was consistently greater at depth than in surface soil (Figure 5.57). In general, the concentration of Total Mn in both horizons showed a similar pattern in variation throughout the year. The lowest concentration of Total Mn in the surface soil occurred in October 1998 at  $23.00 \pm 4.32 \mu\text{g g}^{-1}$ , while the greatest at  $153.00 \pm 39.15 \mu\text{g g}^{-1}$  occurred in July 1999 (Figure 5.57). At depth, the lowest concentration of Total Mn occurred in October 1998 at  $92.33 \pm 5.44 \mu\text{g g}^{-1}$ , while the greatest occurred in June 1999 at  $189.33 \pm 30.13 \mu\text{g g}^{-1}$  (Figure 5.57).

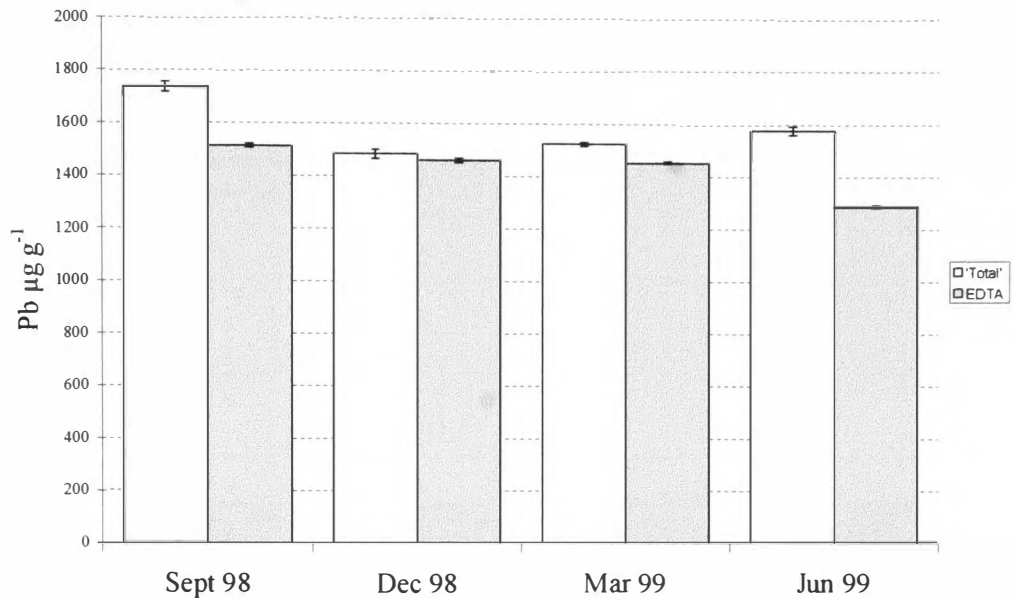
Monthly variation in Total and EDTA metals

Figure 5.58. Mean monthly concentration of Total Pb and EDTA Pb at 0-200 mm for Ashen Series (n=3).



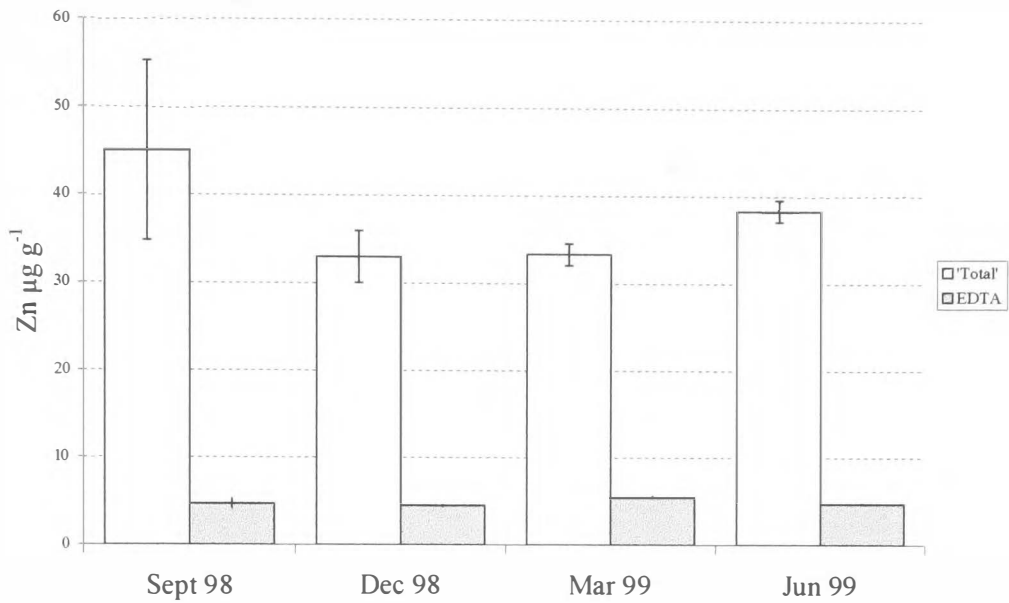
With the exception of March 1999, where the EDTA Pb concentration was greater than the Total Pb by 0.2%, for the remaining months, Total Pb concentration was greater than that of EDTA Pb (Figure 5.58). EDTA Pb as a percentage of Total Pb varied from 87.14% in June 1999 to 102.20% in March 1999. The EDTA Pb concentration followed the monthly variation in concentration of that of the Total Pb concentration. The lowest EDTA Pb concentration occurred in June 1999 at  $1\,661.67 \pm 8.99 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $1\,843.33 \pm 3.09 \mu\text{g g}^{-1}$  (Figure 5.58).

Figure 5.59. Mean monthly concentration of Total Pb and EDTA Pb at 200-400 mm for Ashen Series (n=3).



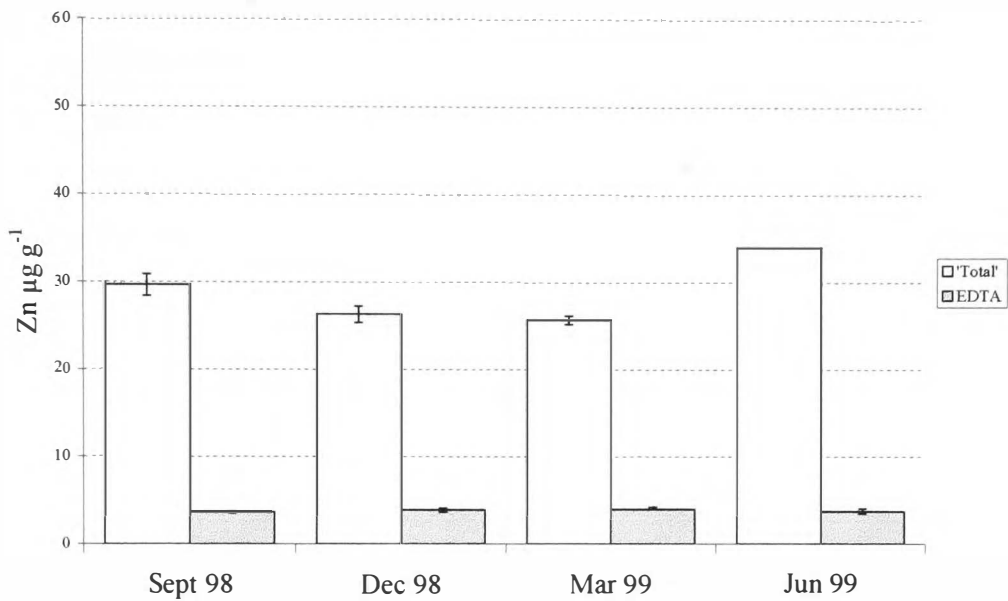
For each month, the Total Pb concentration was greater than that of the EDTA Pb concentration (Figure 5.59). EDTA Pb as a percentage of Total Pb varied from 81.68% in June 1999 to 98.45% in September 1998. The lowest EDTA Pb concentration occurred in June 1999 at  $1\,288.67 \pm 4.11 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $1\,513.33 \pm 7.59 \mu\text{g g}^{-1}$  (Figure 5.59).

Figure 5.60. Mean monthly concentration of Total Zn and EDTA Zn at 0-200 mm for Ashen Series (n=3).



For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 10.52% in September 1998 to 16.40% in March 1999 (Figure 5.60). EDTA Zn followed the same monthly variation in concentration as that of Total Zn. The lowest EDTA Zn concentration of  $4.50 \pm 0.08 \mu\text{g g}^{-1}$  occurred in December 1998 and the greatest in March 1999 at  $5.47 \pm 0.12 \mu\text{g g}^{-1}$  (Figure 5.60).

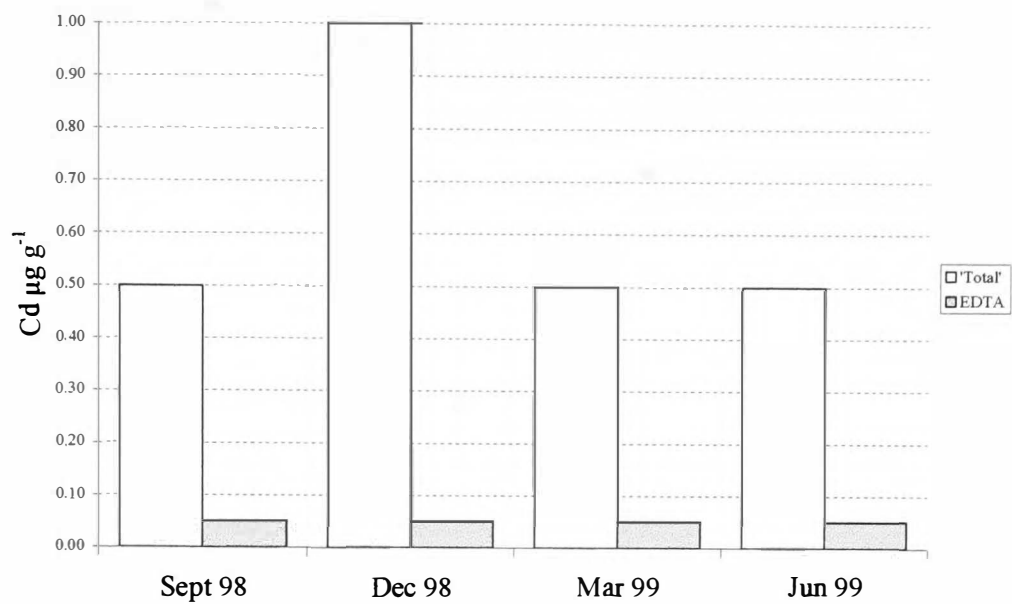
Figure 5.61. Mean monthly concentration of Total Zn and EDTA Zn at 200-400 mm for Ashen Series (n=3).



For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 11.08% in June 1999 to 15.45% in March 1999 (Figure 5.61). EDTA Zn did not follow the same monthly pattern of variation in concentration as that of Total Zn. The lowest EDTA Zn concentration at  $3.67 \pm 0.09 \mu\text{g g}^{-1}$  occurred in September 1998 and the greatest in March 1999 at  $3.97 \pm 0.25 \mu\text{g g}^{-1}$  (Figure 5.61).

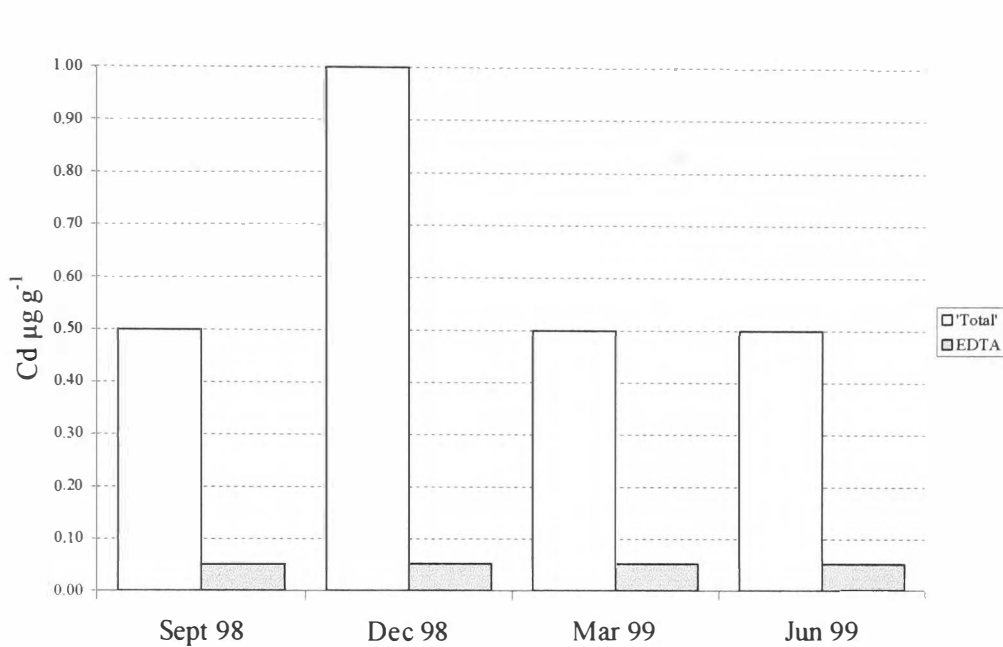


Figure 5.62. Mean monthly mean concentration of Total Cd and EDTA Cd at 0-200 mm for Ashen Series (n=3).



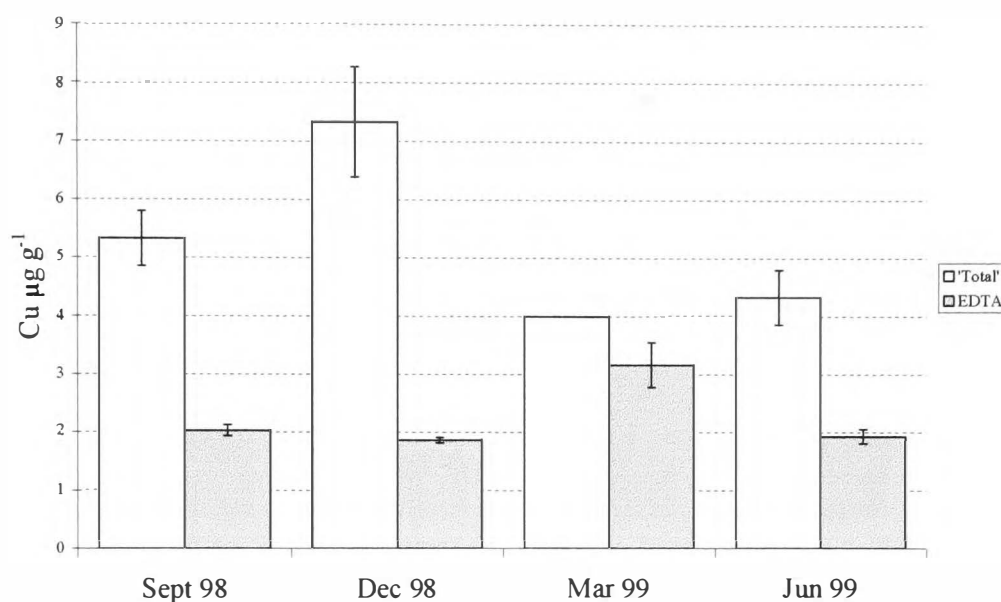
The Total Cd concentration was greater than that of EDTA Cd for each month (Figure 5.62). EDTA Cd as a percentage of Total Cd varied from 5.00% in December 1998 to 10.00% for the remainder of the months. There was no variation in EDTA Cd throughout the year; the concentration for each month was identical at  $0.005 \pm 0 \mu\text{g g}^{-1}$  (Figure 5.62).

Figure 5.63. Mean monthly concentration of Total Cd and EDTA Cd at 200-400 mm for Ashen Series (n=3).



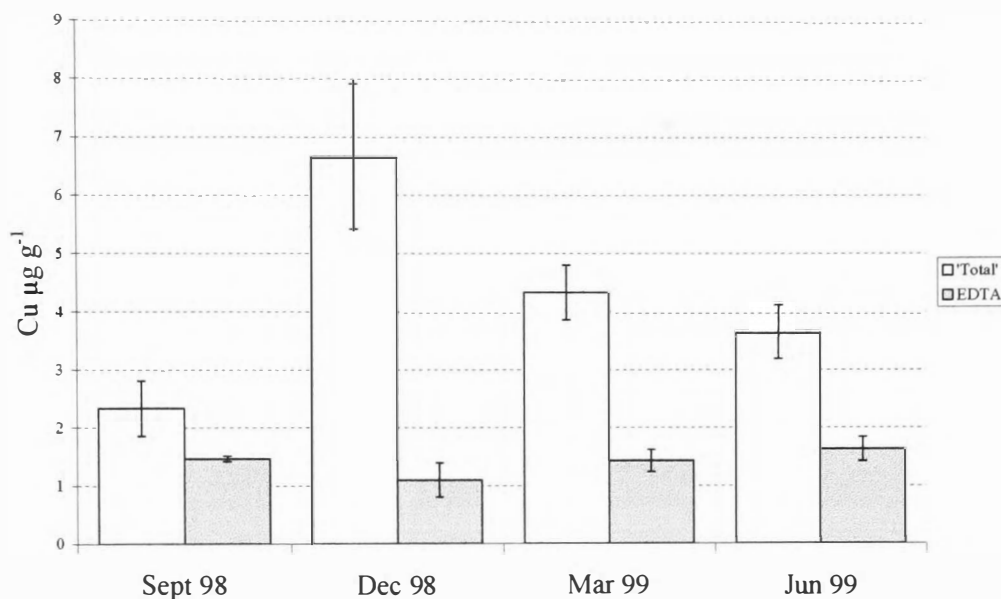
The patterns of concentration for Total Cd and EDTA Cd were identical for the Ashen Series at 0-200 mm and 200-400 mm (Figures 5.62 and 5.63). The Total Cd concentration at depth was greater than that of EDTA Cd for each month (Figure 5.63). EDTA Cd as a percentage of Total Cd varied from 5.00% in December 1998 to 10.00% for the remainder of the months. There was no variation in EDTA Cd throughout the year; the concentration for each month was identical at  $0.005 \pm 0 \mu\text{g g}^{-1}$  (Figure 5.63).

Figure 5.64. Mean monthly concentration of Total Cu and EDTA Cu at 0-200 mm for Ashen Series (n=3).



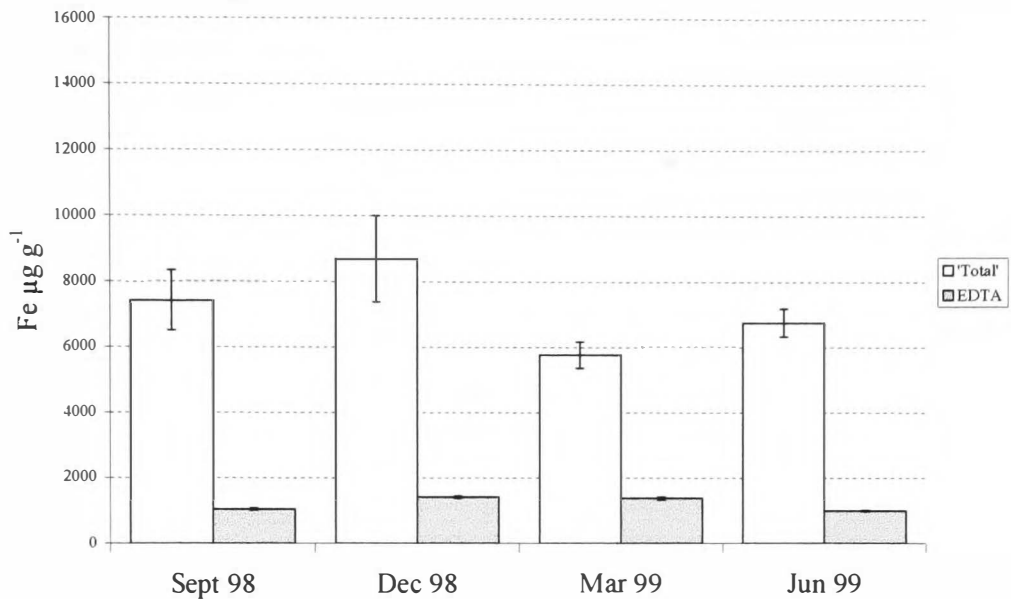
For each month, the Total Cu concentration was higher than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 25.45% in December 1998 to 79.17% in March 1999 (Figure 5.64). The percentage of Total Cu varied from 16.50% in December 1998 to 62.86% in September 1998. The EDTA Cu concentration did not follow the same monthly pattern of variation as that of Total Cu. The lowest EDTA Cu concentration of  $1.87 \pm 0.05 \mu\text{g g}^{-1}$  occurred in December 1999, and the greatest concentration in March 1999 at  $3.17 \pm 0.39 \mu\text{g g}^{-1}$  (Figure 5.64).

Figure 5.65. Mean monthly concentration of Total Cu and EDTA Cu at 200-400 mm for Ashen Series (n=3).



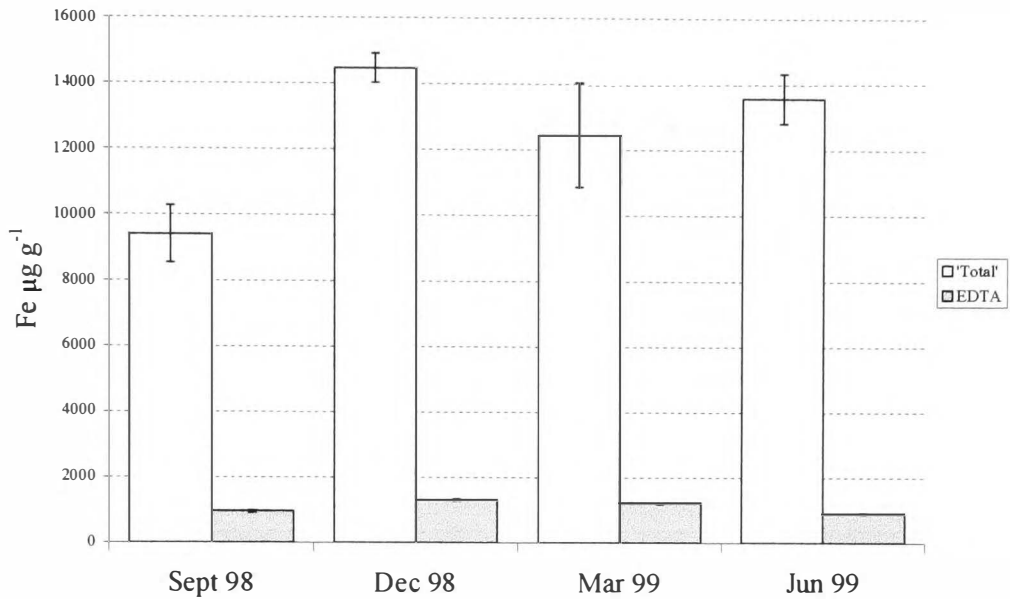
For each month, the Total Cu concentration was higher than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 16.50% in December 1998 to 62.86% in September 1998 (Figure 5.65). The EDTA Cu concentration did not follow the same monthly pattern in variation as that of Total Cu. The lowest EDTA Cu concentration of  $1.10 \pm 0.29 \mu\text{g g}^{-1}$  occurred in December 1998 and the greatest in June 1999 at  $1.63 \pm 0.21 \mu\text{g g}^{-1}$  (Figure 5.65).

Figure 5.66. Mean monthly concentration of Total Fe and EDTA Fe at 0-200 mm for Ashen Series (n=3).



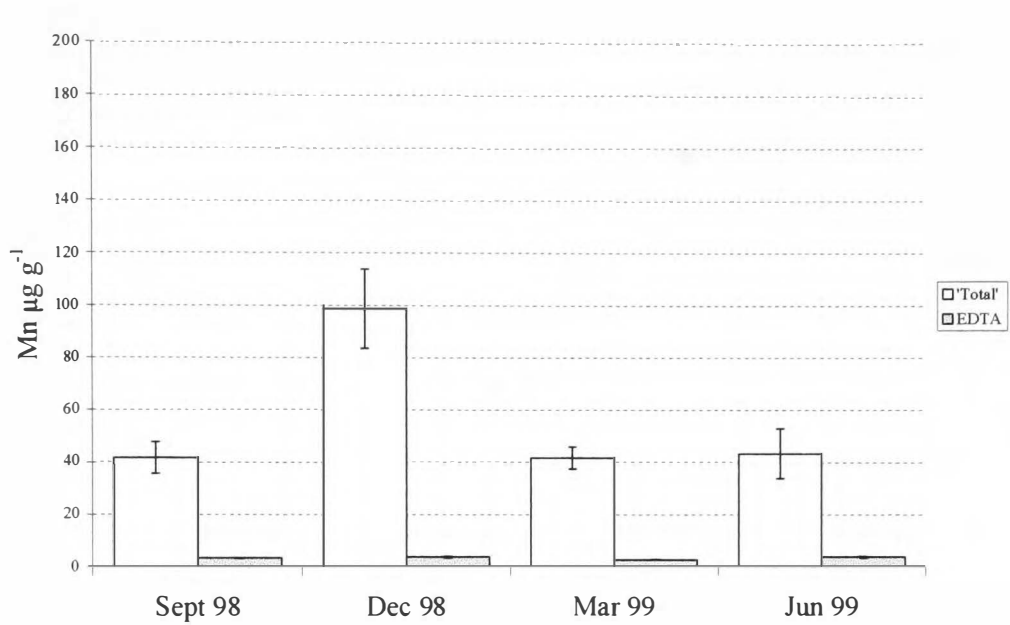
For each month, the Total Fe concentration was higher than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 14.17% in September 1998 to 23.95% in March 1999 (Figure 5.66). The EDTA Fe concentration did not follow the same monthly pattern of variation as Total Fe. The lowest EDTA Fe concentration occurred in September 1998 at  $1\,050.67 \pm 33.92 \mu\text{g g}^{-1}$  and the greatest in December 1998 at  $1\,422.00 \pm 31.21 \mu\text{g g}^{-1}$  (Figure 5.66).

Figure 5.67. Mean monthly concentration of Total Fe and EDTA Fe at 200-400 mm for Ashen Series (n=3).



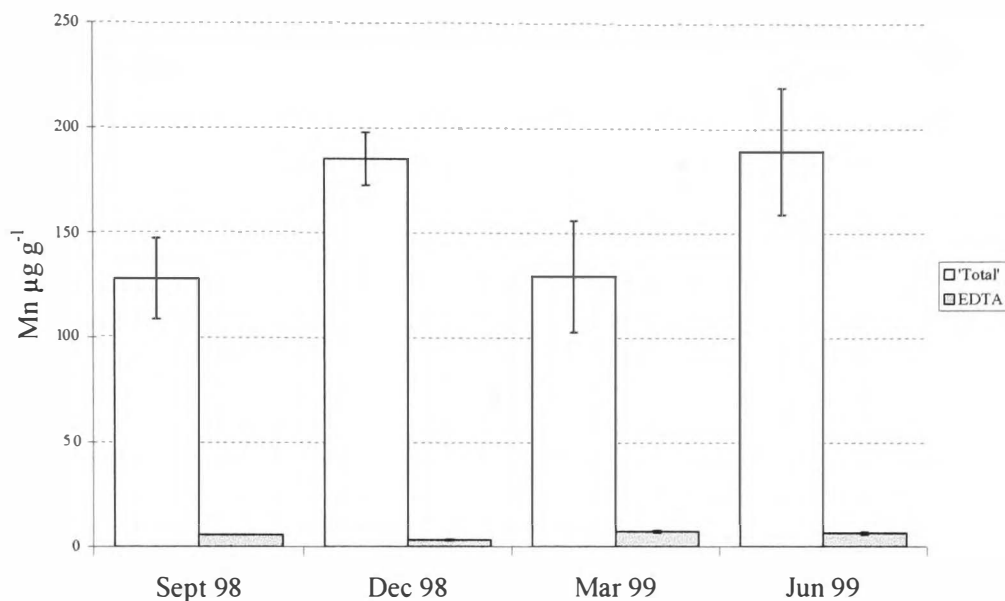
For each month, the Total Fe concentration was greater than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 6.65% in June 1999 to 10.18% in September 1998 (Figure 5.67). The EDTA Fe concentration did not follow the same monthly pattern of variation as Total Fe. The lowest EDTA Fe concentration occurred in June 1999 at  $904.00 \pm 11.05 \mu\text{g g}^{-1}$  and the greatest in December 1998 at  $1311.33 \pm 21.75 \mu\text{g g}^{-1}$  (Figure 5.67).

Figure 5.68. Mean monthly concentration of Total Mn and EDTA Mn at 0-200 mm for Ashen Series (n=3).



For each month, the Total Mn concentration was higher than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 3.82% in December 1998 to 8.62% in June 1999 (Figure 5.68). The EDTA Mn concentration followed the same monthly pattern of variation as that of Total Mn. The lowest EDTA Mn concentration of  $2.70 \pm 0.14 \mu\text{g g}^{-1}$  occurred in March 1999, and the greatest in December 1998 at  $3.77 \pm 0.33 \mu\text{g g}^{-1}$  (Figure 5.68).

Figure 5.69. Mean monthly concentration of Total Mn and EDTA Mn at 200-400 mm for Ashen Series (n=3).



For each month, the Total Mn concentration was higher than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 1.74% in December 1998 to 5.67% in March 1999 (Figure 5.69). The EDTA Mn concentration did not follow the same monthly pattern in variation as Total Mn. The lowest EDTA Mn concentration of  $3.23 \pm 0.21 \mu\text{g g}^{-1}$  occurred in December 1998, and the greatest in March 1999 at  $7.33 \pm 0.50 \mu\text{g g}^{-1}$  (Figure 5.69).



Table 5.50. Median percentage of monthly EDTA trace metals as a percentage of Total trace metals for Ashen Series at 0-200 mm and 200-400 mm.

Depth	Pb %	Zn %	Cd %	Cu %	Fe %	Mn %
0-200 mm	93.62	12.99	10.00	41.37	15.57	7.32
200-400 mm	91.26	13.58	10.00	38.81	9.44	3.93

In the surface soil, the least EDTA available trace metal as a percentage of the Total metal concentration was Mn at 7.32%, while the greatest was Pb at 93.62% (Table 5.50). At depth, the least EDTA available trace metal as a percentage of the Total metal concentration was Mn at 3.93%, while the greatest was Pb at 91.26% (Table 5.50).

#### Monthly variation of other soil parameters

Table 5.51. Monthly values for CEC, Exchangeable Ca, Mg and K and Total P at 0-200 mm and 200-400 mm for Ashen Series.

Parameter	Unit	Sept 1998	Dec 1998	Mar 1999	Jun 1999
CEC (0-200 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	17.42	17.82	17.82	15.05
CEC (200-400 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	15.84	17.03	15.84	13.86
Exch. Ca (0-200 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	0.50	0.42	0.47	0.60
Exch. Ca (200-400 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	0.35	0.22	0.30	0.38
Exch. Mg (0-200 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	0.25	0.21	0.23	0.25
Exch. Mg (200-400 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	0.12	0.08	0.08	0.16
Exch. K (0-200 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	0.20	0.19	0.29	0.17
Exch. K (200-400 mm)	cmol <sub>e</sub> kg <sup>-1</sup>	0.14	0.17	0.19	0.12
Total P (0-200 mm)	µg g <sup>-1</sup>	317.00	310.60	226.90	499.40
Total P (200-400 mm)	µg g <sup>-1</sup>	293.40	325.60	304.10	280.50

For all months, the monthly CEC, Exchangeable Ca, Exchangeable Mg and Exchangeable K in the surface soil were consistently greater than that at depth (Table 5.5). In September 1998 and June 1999, the Total P concentration was greater in surface soil than at depth. In December 1998 and March 1999, the monthly Total P concentration at depth was greater than in the surface soil (Table 5.51).

Two-Sample analysis

Mann-Whitney analysis or a Two-Sample T-test between surface and depth for each stacked soil parameter (n=12 or n=4) showed a significant difference at the  $p \leq 0.05$  level for 14/19 of the Ashen Series soil parameters (Tables 5.52 and 5.53). Because the values for EDTA Cd were identical, neither the Two-sample T-test or Mann-Whitney analysis were applicable.

Table 5.52. Two-sample Mann-Whitney tests for Ashen soil parameters at 0-200 mm *versus* 200-400 mm, where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter	n=	Mann-Whitney p-value	$H_0$ : $\eta_1 = \eta_2$ at $\alpha=0.05$
Total Pb (0-200 mm) v Total Pb (200-400 mm)	12	0.0001	Rejected
Total Zn (0-200 mm) v Total Zn (200-400 mm)	12	0.0165	Rejected
Total Cd (0-200 mm) v Total Cd (200-400 mm)	12	1.0000	Accepted

Table 5.53. Two-Sample T-Tests for Ashen soil parameters at 0-200 mm *versus* 200-400 mm, where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter	n=	T-value	p-value	$H_0: \mu_1 = \mu_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	12	9.07	0.000	Rejected
L-o-I (0-200 mm) v L-o-I (200-400 mm)	12	9.78	0.000	Rejected
Total Cu (0-200 mm) v Total Cu (200-400 mm)	12	1.69	0.119	Accepted
Total Fe (0-200 mm) v Total Fe (200-400 mm)	12	-7.45	0.000	Rejected
Total Mn (0-200 mm) v Total Mn (200-400 mm)	12	-7.58	0.000	Rejected
EDTA Pb (0-200 mm) v EDTA Pb (200-400 mm)	4	7.48	0.005	Rejected
EDTA Zn (0-200 mm) v EDTA Zn (200-400 mm)	4	5.56	0.011	Rejected
EDTA Cd (0-200 mm) v EDTA Cd (200-400 mm)	4	--	--	N.A.
EDTA Cu (0-200 mm) v EDTA Cu (200-400 mm)	4	2.68	0.075	Accepted
EDTA Fe (0-200 mm) v EDTA Fe (200-400 mm)	4	7.68	0.005	Rejected
EDTA Mn (0-200 mm) v EDTA Mn (200-400 mm)	4	-2.13	0.123	Accepted
CEC (0-200 mm) v CEC (200-400 mm)	4	5.42	0.012	Rejected
Exch. Ca (0-200 mm) v Exch. Ca (200-400 mm)	4	11.90	0.001	Rejected
Exch. Mg (0-200 mm) v Exch. Mg (200-400 mm)	4	9.93	0.002	Rejected
Exch. K (0-200 mm) v Exch. K (200-400 mm)	4	3.48	0.040	Rejected
Total P (0-200 mm) v Total P (200-400 mm)	4	5.89	0.010	Rejected

While the majority of the Thrupe soil parameters (14/19) showed a significant difference at the  $p \leq 0.05$  level between values at surface and at depth, pH, Loss-

on-Ignition, Total Pb, Total Fe, Total Mn, and Exchangeable Ca showed a significant difference at the  $p \leq 0.001$  level (Tables 5.52 and 5.53).

### Pearson correlations

In the soil of the Ashen Series, Loss-on-Ignition was negatively correlated at the  $p \leq 0.05$  level with pH, Total Fe and Total Mn, and positively correlated at the  $p = 0.001$  level with Total Pb and Total Zn (Table 5.54). Total Pb was negatively correlated the  $p \leq 0.05$  level with Total Fe and Total Mn, and positively correlated at the  $p = 0.001$  level with Total Zn. Total Fe and Total Mn were positively correlated at the  $p = 0.001$  level (Table 5.54).

Table 5.54. Pearson correlation values (r-values) and degrees of significance at the  $p = 0.001$ , 0.01 and 0.05 levels for stacked Ashen soil parameters at 0-400 mm (n=24) September 1998 - August 1999.

	pH (0-400 mm)	L-o-I (0-400mm)	Total Pb (0-400 mm)	Total Zn (0-400 mm)	Total Cd (0-400 mm)	Total Cu (0-400 mm)	Total Fe (0-400 mm)
L-o-I (0-400 mm)	-0.393						
Total Pb (0-400 mm)	-0.616 **	0.888 ***					
Total Zn (0-400 mm)	-0.316	0.715 ***	0.762 ***				
Total Cd (0-400 mm)	0.107	0.017	-0.036	-0.075			
Total Cu (0-400 mm)	0.228	0.206	0.032	0.241	0.455 *		
Total Fe (0-400 mm)	0.463 *	-0.691 ***	-0.638 **	-0.326	0.226	0.165	
Total Mn (0-400 mm)	0.462 *	-0.713 ***	-0.639 **	-0.301	0.266	-0.066	0.0827 ***

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     - Indicates a negative correlation

5.5.5 Tailings

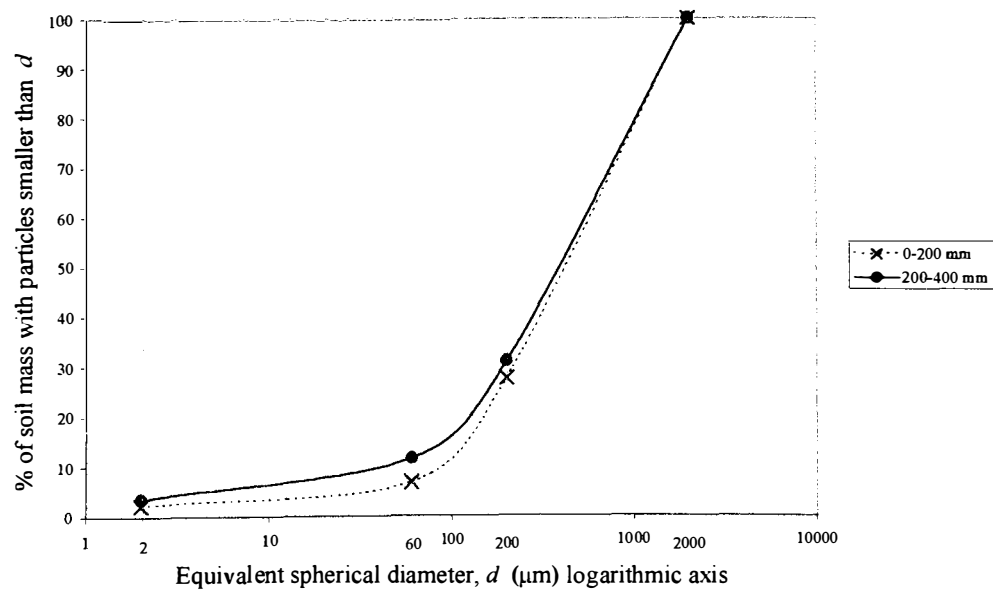
Particle Size Analysis

Table 5.55. Particle size distribution and soil textural class for Tailings.

Depth (mm)	% clay	% silt	% fine sand	% coarse sand	Textural Class
0 - 200	2.22	4.52	20.75	72.51	Sand
200-400	3.49	8.02	19.41	69.08	Sand

The surface Tailings were classified as sand, with coarse sand as the most abundant particle size (Table 5.55). At depth, although still dominated by sand and classified as sand, the soil contained a slightly higher % of clay and silt than the surface Tailings (Table 5.55 and Figure 5.70)

Figure 5.70. Cumulative curve displaying particle size distribution of Tailings at 0-200 mm and 200-400 mm.



The cumulative curve plot showed that at approximately 93% and 88% of the particles at surface and depth respectively, sand (fine + coarse sand) dominated the < 2 mm soil fraction at both surface and depth (Figure 5.70).

### Descriptive statistics

The Tailings data set consisted of monthly (n=12) and quarterly (n=4) data for the same parameters as the Maesbury Series described in 5.5.2. Tailings reaction ranged from pH 7.01 to pH 7.49 in surface Tailings and from pH 7.31 to pH 7.79 at depth. Loss-on-Ignition in surface Tailings ranged from 12.84% to 18.81% and from 8.19% to 14.86% at depth (Table 5.56).

The concentration of Total Pb in the surface Tailings ranged from 49 067.00  $\mu\text{g g}^{-1}$  to 99 500.00  $\mu\text{g g}^{-1}$  and from 54 933.00  $\mu\text{g g}^{-1}$  to 112 767.00  $\mu\text{g g}^{-1}$  at depth. Total Zn ranged from 7 666.77  $\mu\text{g g}^{-1}$  to 14 400.00  $\mu\text{g g}^{-1}$  in the surface horizon and from 8 566.70  $\mu\text{g g}^{-1}$  to 16 866.70  $\mu\text{g g}^{-1}$  at depth. Total Cd was present in surface Tailings at 10.00  $\mu\text{g g}^{-1}$  to 18.67  $\mu\text{g g}^{-1}$  and from 9.67  $\mu\text{g g}^{-1}$  to 22.33  $\mu\text{g g}^{-1}$  at depth (Table 5.56). The concentration of Total Cu ranged from 64.67  $\mu\text{g g}^{-1}$  to 105.67  $\mu\text{g g}^{-1}$  in surface Tailings and at depth from 76.33  $\mu\text{g g}^{-1}$  to 119.00  $\mu\text{g g}^{-1}$ . Total Fe was present in surface Tailings at 52 200.00  $\mu\text{g g}^{-1}$  to 82 866.00  $\mu\text{g g}^{-1}$  and from 57 033.00  $\mu\text{g g}^{-1}$  to 100 267.00  $\mu\text{g g}^{-1}$  at depth. Total Mn in surface Tailings ranged from 2 050.00  $\mu\text{g g}^{-1}$  to 4 500.00  $\mu\text{g g}^{-1}$  and from 2 240.00  $\mu\text{g g}^{-1}$  to 3 833.33  $\mu\text{g g}^{-1}$  at depth (Table 5.56).

Table 5.56. Parameter data for Tailings at 0-200 mm and 200-400 mm (n=12) for September 1998 - August 1999 and (n=4) for quarterly sampling.

	Unit	n	Arithmetic Mean	St. Dev.	Minimum	Median	Maximum
pH (0-200 mm)	pH	12	7.25	0.15	7.01	7.29	7.49
pH (200-400 mm)	pH	12	7.62	0.17	7.31	7.70	7.79
L-o-I (0-200 mm)	%	12	15.40	1.94	12.84	15.52	18.81
L-o-I (200-400 mm)	%	12	10.39	1.97	8.19	9.97	14.86
Total Pb (0-200 mm)	$\mu\text{g g}^{-1}$	12	72 511.20	19 039.00	49 067.00	71 800.00	99 500.00
Total Pb (200-400 mm)	$\mu\text{g g}^{-1}$	12	77 891.60	19 965.30	54 933.00	75 183.00	112 767.00
Total Zn (0-200 mm)	$\mu\text{g g}^{-1}$	12	10 777.80	2 035.10	7 666.77	10 783.30	14 400.00
Total Zn (200-400 mm)	$\mu\text{g g}^{-1}$	12	11 952.80	2 647.00	8 566.70	10 616.70	16 866.70
Total Cd (0-200 mm)	$\mu\text{g g}^{-1}$	12	14.45	2.91	10.00	13.84	18.67
Total Cd (200-400 mm)	$\mu\text{g g}^{-1}$	12	16.70	3.89	9.67	16.00	22.33
Total Cu (0-200 mm)	$\mu\text{g g}^{-1}$	12	89.08	13.17	64.67	91.34	105.67
Total Cu (200-400 mm)	$\mu\text{g g}^{-1}$	12	96.89	16.04	76.33	96.84	119.00
Total Fe (0-200 mm)	$\mu\text{g g}^{-1}$	12	68 125.80	8 673.70	52 200.00	67 800.00	82 866.70
Total Fe (200-400 mm)	$\mu\text{g g}^{-1}$	12	76 447.20	14 316.90	57 033.00	71 583.00	100 267.00
Total Mn (0-200 mm)	$\mu\text{g g}^{-1}$	12	2 871.95	644.08	2 050.00	3 201.67	4 500.00
Total Mn (200-400 mm)	$\mu\text{g g}^{-1}$	12	2 946.39	487.16	2 240.00	2 898.34	3 883.33
EDTA Pb (0-200 mm)	$\mu\text{g g}^{-1}$	4	23 928.33	3 182.87	19 850.00	24 141.67	27 580.00
EDTA Pb (200-400 mm)	$\mu\text{g g}^{-1}$	4	21 120.00	4 317.77	16 730.00	21 015.00	25 720.00
EDTA Zn (0-200 mm)	$\mu\text{g g}^{-1}$	4	1 700.83	335.25	1 456.67	1 575.00	2 196.67
EDTA Zn (200-400 mm)	$\mu\text{g g}^{-1}$	4	1 413.33	208.08	1 286.67	1 321.67	1 723.33
EDTA Cd (0-200 mm)	$\mu\text{g g}^{-1}$	4	3.33	0.34	3.07	3.22	3.83
EDTA Cd (200-400 mm)	$\mu\text{g g}^{-1}$	4	2.82	0.32	2.53	2.78	3.17
EDTA Cu (0-200 mm)	$\mu\text{g g}^{-1}$	4	12.66	1.53	10.80	12.65	14.53
EDTA Cu (200-400 mm)	$\mu\text{g g}^{-1}$	4	11.05	2.47	8.70	10.87	13.77
EDTA Fe (0-200 mm)	$\mu\text{g g}^{-1}$	4	269.26	109.31	190.33	229.52	427.67
EDTA Fe (200-400 mm)	$\mu\text{g g}^{-1}$	4	215.51	84.66	123.67	213.35	311.67
EDTA Mn (0-200 mm)	$\mu\text{g g}^{-1}$	4	102.50	13.86	90.67	98.67	122.00
EDTA Mn (200-400 mm)	$\mu\text{g g}^{-1}$	4	92.92	14.09	75.00	96.00	104.67
CEC (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	17.33	2.59	14.26	17.23	20.59
CEC (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	12.28	1.41	11.09	12.08	13.86
Exch. Ca (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	24.40	4.72	18.18	25.02	29.38
Exch. Ca (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	26.95	5.80	19.92	26.89	34.11
Exch. Mg (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.44	0.12	0.29	0.45	0.58
Exch. Mg (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.30	0.09	0.21	0.29	0.41
Exch. K (0-200 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.32	0.07	0.24	0.34	0.38
Exch. K (200-400 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.21	0.07	0.12	0.23	0.28
Total P (0-200 mm)	$\mu\text{g g}^{-1}$	4	1 813.25	402.65	1 520.00	1 675.00	2 383.00
Total P (200-400 mm)	$\mu\text{g g}^{-1}$	4	1 874.75	609.77	1 066.00	1 974.50	2 484.00

EDTA Pb was present in surface Tailings at 19 850.00  $\mu\text{g g}^{-1}$  to 27 580.00  $\mu\text{g g}^{-1}$  and from 16 730.00  $\mu\text{g g}^{-1}$  to 25 720.00  $\mu\text{g g}^{-1}$  at depth (Table 5.56). Surface EDTA Zn was present at 1 456.67  $\mu\text{g g}^{-1}$  to 2 196.67  $\mu\text{g g}^{-1}$  and from 1 286.67  $\mu\text{g g}^{-1}$  to 1 723.33  $\mu\text{g g}^{-1}$  at depth. Surface EDTA Cd ranged from 3.07  $\mu\text{g g}^{-1}$  to 3.38  $\mu\text{g g}^{-1}$  and from 2.53  $\mu\text{g g}^{-1}$  to 3.17  $\mu\text{g g}^{-1}$  at depth. The concentration of surface EDTA Cu ranged from 10.80  $\mu\text{g g}^{-1}$  to 14.53  $\mu\text{g g}^{-1}$  and from 8.70  $\mu\text{g g}^{-1}$  to 13.77  $\mu\text{g g}^{-1}$  at depth. EDTA Fe ranged from 190.33  $\mu\text{g g}^{-1}$  to 427.67  $\mu\text{g g}^{-1}$  in surface Tailings and from 123.67  $\mu\text{g g}^{-1}$  to 311.67  $\mu\text{g g}^{-1}$  at depth. EDTA Mn was present in surface Tailings at 90.67  $\mu\text{g g}^{-1}$  to 112.00  $\mu\text{g g}^{-1}$  and from 75.00  $\mu\text{g g}^{-1}$  to 104.67  $\mu\text{g g}^{-1}$  at depth (Table 5.56).

Surface CEC ranged from 14.26  $\text{cmol}_c \text{kg}^{-1}$  to 20.59  $\text{cmol}_c \text{kg}^{-1}$  and from 11.09  $\text{cmol}_c \text{kg}^{-1}$  to 13.86  $\text{cmol}_c \text{kg}^{-1}$  at depth. The concentration of surface Exchangeable Ca ranged from 18.18  $\text{cmol}_c \text{kg}^{-1}$  to 29.38  $\text{cmol}_c \text{kg}^{-1}$  and from 19.92  $\text{cmol}_c \text{kg}^{-1}$  to 34.11  $\text{cmol}_c \text{kg}^{-1}$  at depth (Table 5.56). Exchangeable Mg was present in surface Tailings at 0.29  $\text{cmol}_c \text{kg}^{-1}$  to 0.58  $\text{cmol}_c \text{kg}^{-1}$  and from 0.21  $\text{cmol}_c \text{kg}^{-1}$  to 0.41  $\text{cmol}_c \text{kg}^{-1}$  at depth. Surface Exchangeable K ranged from 0.24  $\text{cmol}_c \text{kg}^{-1}$  to 0.38  $\text{cmol}_c \text{kg}^{-1}$  and from 0.12  $\text{cmol}_c \text{kg}^{-1}$  to 0.28  $\text{cmol}_c \text{kg}^{-1}$  at depth. The concentration of surface Total P ranged from 1 520.00  $\mu\text{g g}^{-1}$  to 2 232.00  $\mu\text{g g}^{-1}$  and from 1 066.00  $\mu\text{g g}^{-1}$  to 2 484.00  $\mu\text{g g}^{-1}$  at depth (Table 5.56).

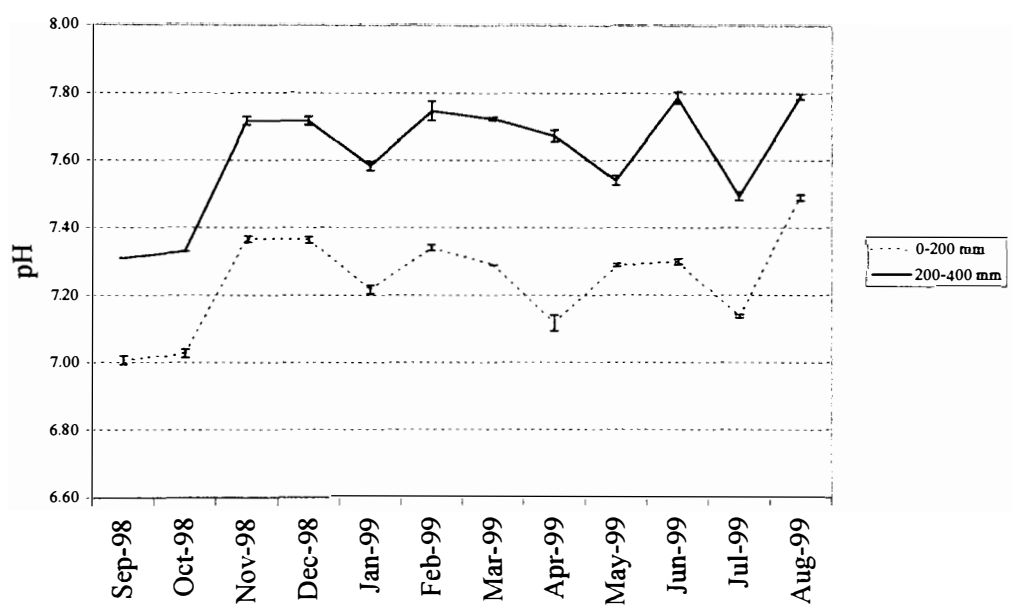
Generally, the mean and median values of each individual Tailings parameter were similar, with the exception of Total Pb at depth, Total Zn at depth and surface EDTA Fe and surface Total P (Table 5.56). The mean and median values for Total



Pb at depth were 77 891.60  $\mu\text{g g}^{-1}$  and 75 183.00  $\mu\text{g g}^{-1}$  respectively, for surface Total Zn 11 952.80  $\mu\text{g g}^{-1}$  and 10 616.70  $\mu\text{g g}^{-1}$ , surface EDTA Fe 269.26  $\mu\text{g g}^{-1}$  and 229.52  $\mu\text{g g}^{-1}$ , and surface Total P 1 813.25  $\mu\text{g g}^{-1}$  and 1 675.00  $\mu\text{g g}^{-1}$ .

Monthly variation in pH, Loss-on-Ignition and Total metals

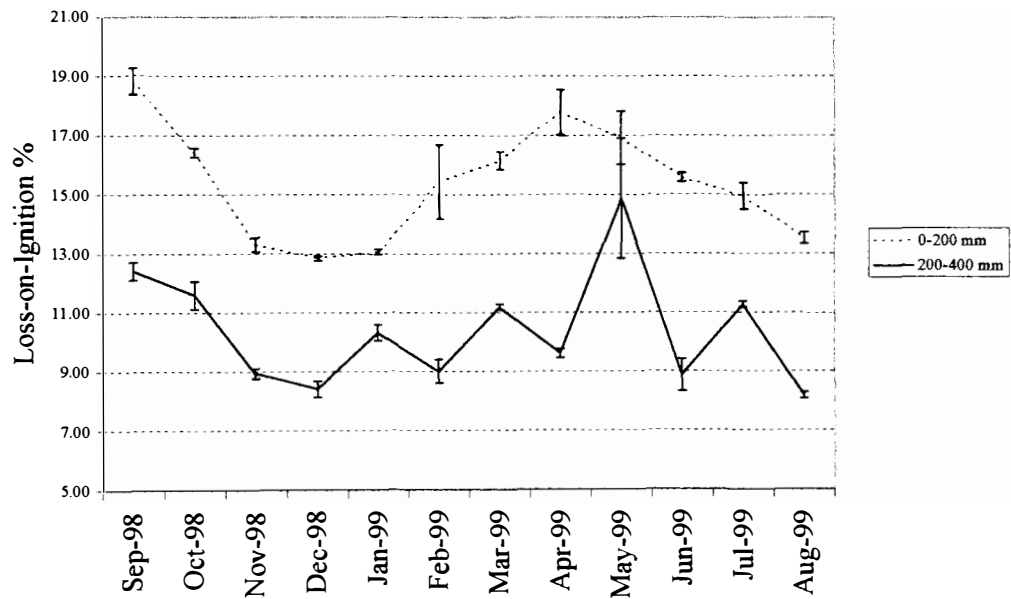
Figure 5.71. Mean monthly pH at 0-200 mm and 200-400 mm for Tailings (n=3).



Tailings reaction at surface and depth generally showed a similar pattern in variation throughout the year (Figure 5.71). For each month, pH at depth was consistently higher than that for surface Tailings. The lowest pH values in surface Tailings occurred in September 1998 at pH 7.01  $\pm$ 0.01, while the highest value of

pH  $7.49 \pm 0.01$  occurred in August 1999. For Tailings at depth, the lowest pH occurred in September 1998 at pH  $7.31 \pm 0$ , while the highest at pH  $7.79 \pm 0.01$  and pH  $7.79 \pm 0.02$  occurred in August and June 1999 respectively (Figure 5.71).

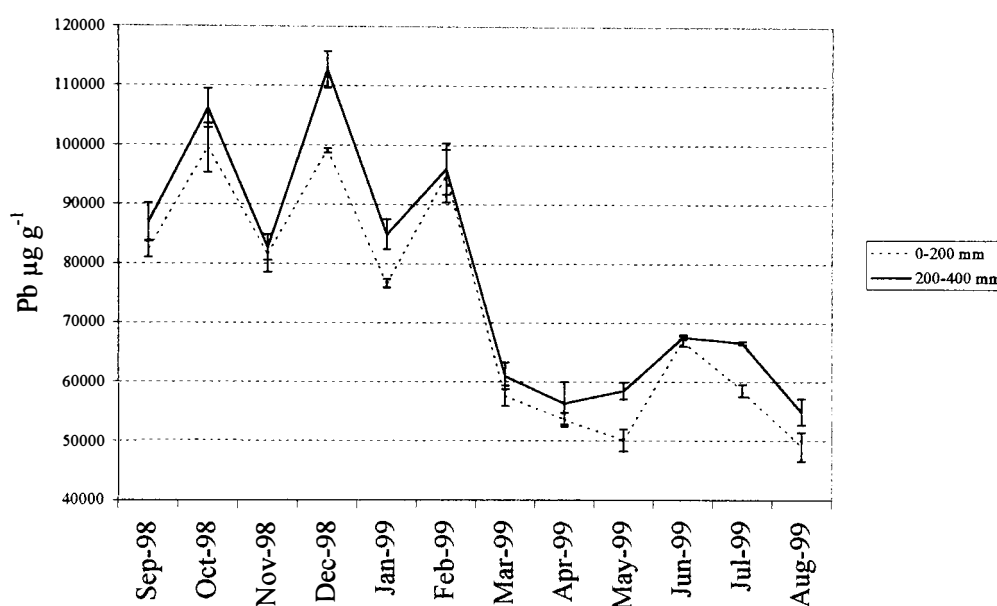
Figure 5.72. Mean monthly % Loss-on-Ignition at 0-200 mm and 200-400 mm for Tailings (n=3).



For each month, Loss-on-Ignition was consistently greater for surface Tailings than that at depth (Figure 5.72). In general, Loss-on-Ignition in surface Tailings and at depth showed a similar overall pattern of variation throughout the year. The lowest % Loss-on-Ignition of  $12.84 \pm 0.0\%$  in the surface Tailings occurred in December 1998, while the greatest % Loss-on-Ignition of  $18.81 \pm 0.45\%$  occurred in September 1998 (Figure 5. 72). The lowest % Loss-on-Ignition at depth

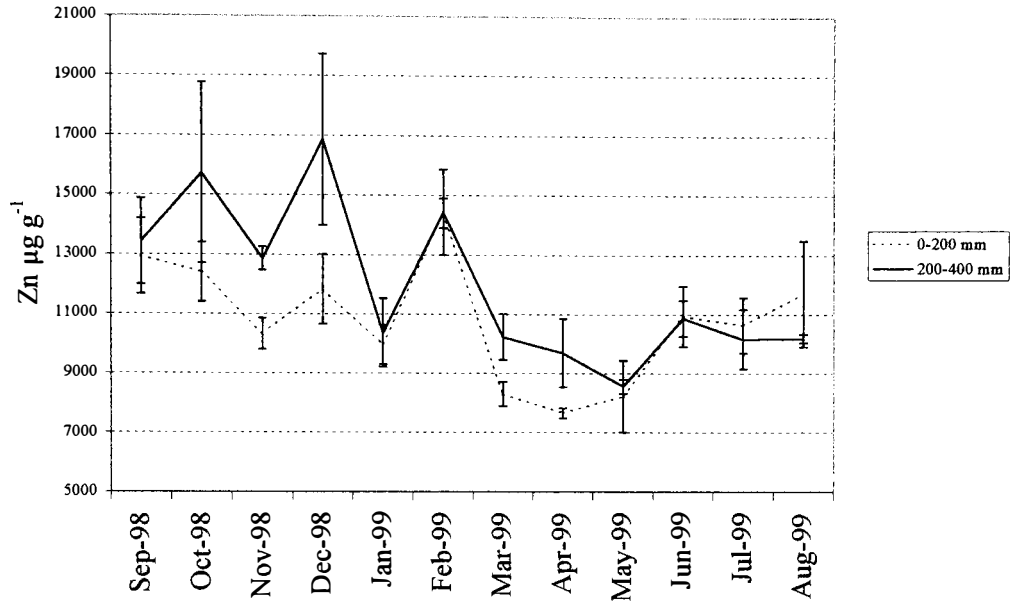
occurred in August 1999 at  $8.19 \pm 1.00\%$ , while the greatest % Loss-on-Ignition of  $14.86 \pm 2.03\%$  occurred in May 1999 (Figure 5.72).

Figure 5.73. Mean monthly Total Pb at 0-200 mm and 200-400 mm for Tailings (n=3).



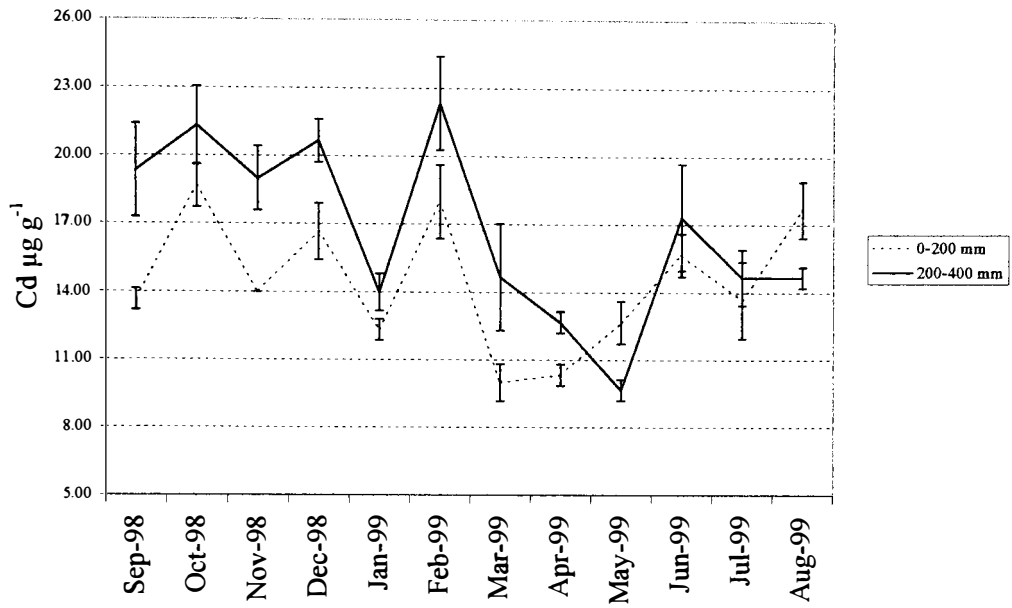
Total Pb in surface Tailings and at depth showed a similar overall pattern of variation throughout the year. The concentration of Total Pb was consistently greater for Tailings at depth than surface Tailings (Figure 5.73). The lowest concentration of Total Pb in the surface Tailings occurred in August 1999 at  $49\,067 \pm 2\,446 \mu\text{g g}^{-1}$ , while the greatest concentration of  $99\,500 \pm 4\,174 \mu\text{g g}^{-1}$  occurred in October 1998 (Figure 5.73). The lowest concentration of Total Pb at depth occurred in August 1999 at  $54\,933 \pm 2\,248 \mu\text{g g}^{-1}$ , while the greatest occurred in December 1998 at  $112\,767 \pm 3\,091 \mu\text{g g}^{-1}$  (Figure 5.73).

Figure 5.74. Mean monthly Total Zn at 0-200 mm and 200-400 mm for Tailings (n=3).



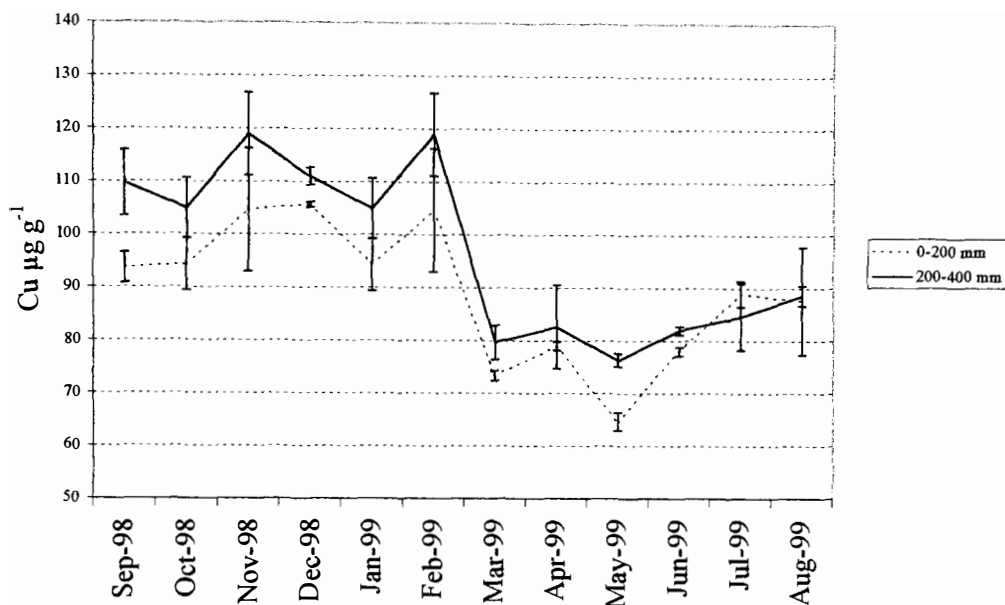
With the exception of June 1999, the mean Total Zn concentration was greater for Tailings at depth than in the surface Tailings (Figure 5.74). In June 1999, there was a greater concentration of Total Zn in surface Tailings than at depth. The lowest concentration of Total Zn in the surface Tailings occurred in April 1999 at  $7\,666.67 \pm 169.97 \mu\text{g g}^{-1}$ , while the greatest at  $14\,400 \pm 496.66 \mu\text{g g}^{-1}$  occurred in February 1999 (Figure 5.74). At  $8\,566.67 \pm 249.44 \mu\text{g g}^{-1}$ , the lowest concentration of Total Zn at depth occurred in May 1999, while the greatest occurred in December 1998 at  $16\,868.67 \pm 2\,875.57 \mu\text{g g}^{-1}$  (Figure 5.74).

Figure 5.75. Mean monthly Total Cd at 0-200 mm and 200-400 mm for Tailings (n=3).



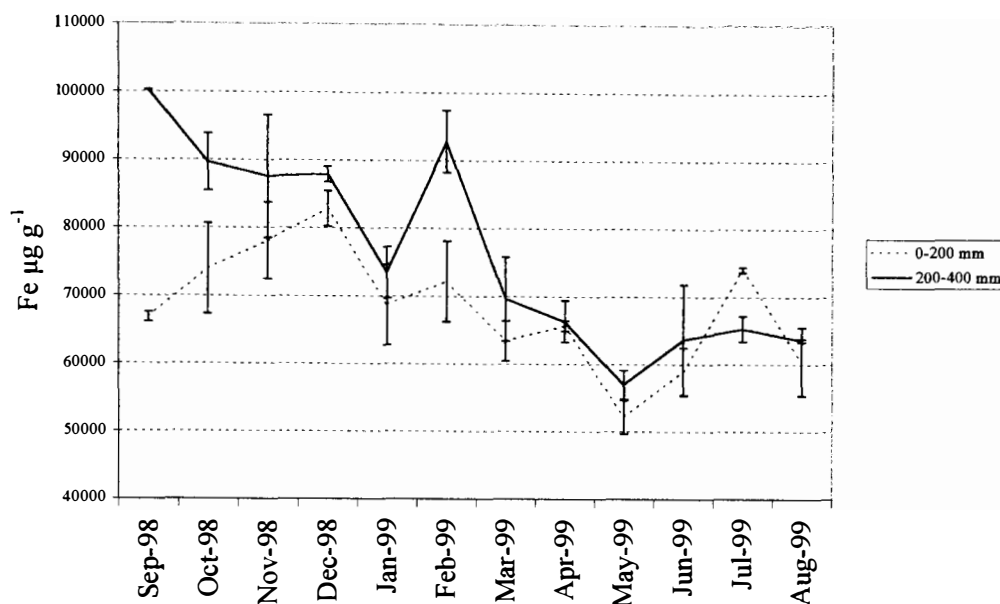
With the exception of May and August 1999, when the Total Cd concentration was greater in the surface Tailings than at depth, for each remaining month, the concentration of Total Cd was greater at depth than in surface Tailings (Figure 5.75). Total Cd in surface Tailings and at depth generally showed a similar pattern in variation throughout the year. The lowest concentration of Total Cd in the surface Tailings occurred in March 1999 at  $10.00 \pm 0.82 \mu\text{g g}^{-1}$ , while the greatest at  $18.67 \pm 0.94 \mu\text{g g}^{-1}$  occurred in October 1998. At depth, the lowest concentration of Total Cd occurred in May 1999 at  $9.67 \pm 0.47 \mu\text{g g}^{-1}$ . The greatest concentration of  $22.33 \pm 2.05 \mu\text{g g}^{-1}$  occurred in February 1999 (Figure 5.75).

Figure 5.76. Mean monthly Total Cu at 0-200 mm and 200-400 mm for Tailings (n=3).



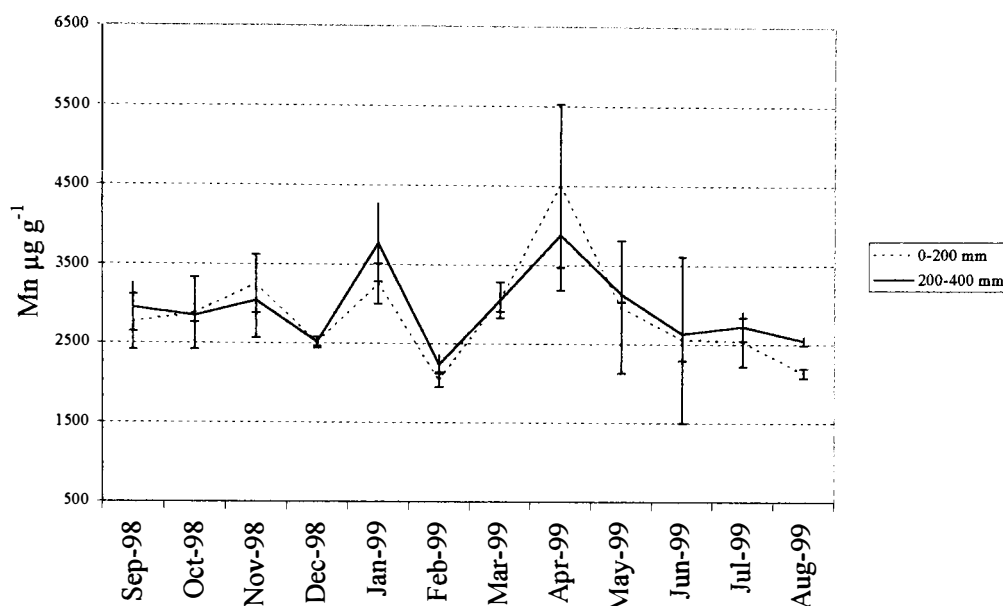
With the exception of July 1999, when the Total Cu concentration was greater in the surface Tailings than at depth, for each remaining month, the concentration of Total Cu was greater at depth than in surface Tailings (Figure 5.76). Total Cu in surface Tailings and at depth showed a similar pattern in variation throughout the year. The lowest concentration of Total Cu in the surface Tailings occurred in May 1999 at  $64.67 \pm 1.70 \mu\text{g g}^{-1}$ , while the greatest at  $105.67 \pm 0.47 \mu\text{g g}^{-1}$  occurred in December 1998. At depth, the lowest concentration of Total Cu occurred in May 1999 at  $76.33 \pm 1.25 \mu\text{g g}^{-1}$ . The greatest concentration of  $119.00 \pm 7.79 \mu\text{g g}^{-1}$  occurred in November 1998 and February 1999 (Figure 5.76).

Figure 5.77. Mean monthly Total Fe at 0-200 mm and 200-400 mm for Tailings (n=3).



For July 1999, the Total Fe concentration was greater for surface Tailings than at depth . For the remaining months, the situation was reversed and Total Fe concentration was greater at depth than in surface Tailings (Figure 5.77). In January 1999 and March 1999, the mean Total Fe concentrations in the surface Tailings and at depth were similar. The lowest concentration of Total Fe in the surface Tailings occurred in May 1999 at  $52\,200 \pm 2\,483 \mu\text{g g}^{-1}$ , while the greatest at  $82\,867 \pm 2\,608 \mu\text{g g}^{-1}$  occurred in December 1998 (Figure 5.77). At depth, the lowest concentration of Total Fe at  $57\,033 \pm 2\,131 \mu\text{g g}^{-1}$  occurred in May 1999, while the greatest at  $100\,267 \pm 47 \mu\text{g g}^{-1}$  occurred in September 1998 (Figure 5.77).

Figure 5.78. Mean monthly Total Mn at 0-200 mm and 200-400 mm for Tailings (n=3).

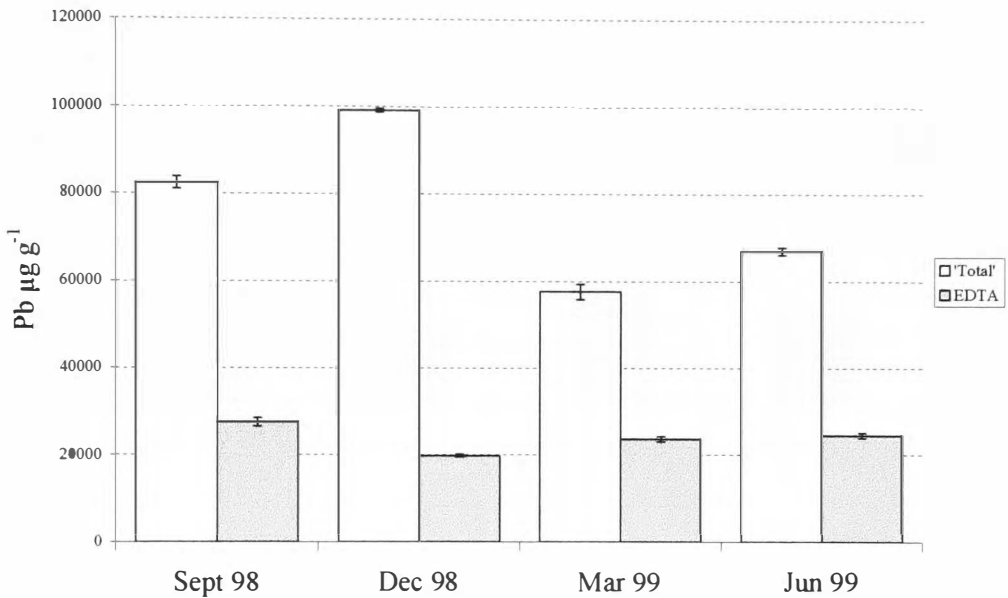


With the exception of November 1998 and March and April 1999, when the concentration of Total Mn was greater in surface Tailings than at depth, for each remaining month the concentration of Total Mn was consistently greater at depth than in surface Tailings (Table 5.78). In March 1999, there was little difference between the mean concentration of Total Mn at surface and depth at  $3\,056.67 \pm 229.83 \mu\text{g g}^{-1}$  and  $3\,053 \pm 143.84 \mu\text{g g}^{-1}$  respectively (Figure 5.78). The lowest concentration of Total Mn in the surface Tailings occurred in February 1999 at  $2\,050 \pm 192.74 \mu\text{g g}^{-1}$ , while the greatest at  $4\,500.00 \pm 1\,027.67 \mu\text{g g}^{-1}$  occurred in April 1999. At depth, the lowest concentration of Total Mn occurred in February 1999 at  $2\,240.00 \pm 115.18 \mu\text{g g}^{-1}$ , while the greatest occurred in April 1999 at  $3\,883.33 \pm 698.11 \mu\text{g g}^{-1}$  (Figure 5.78).



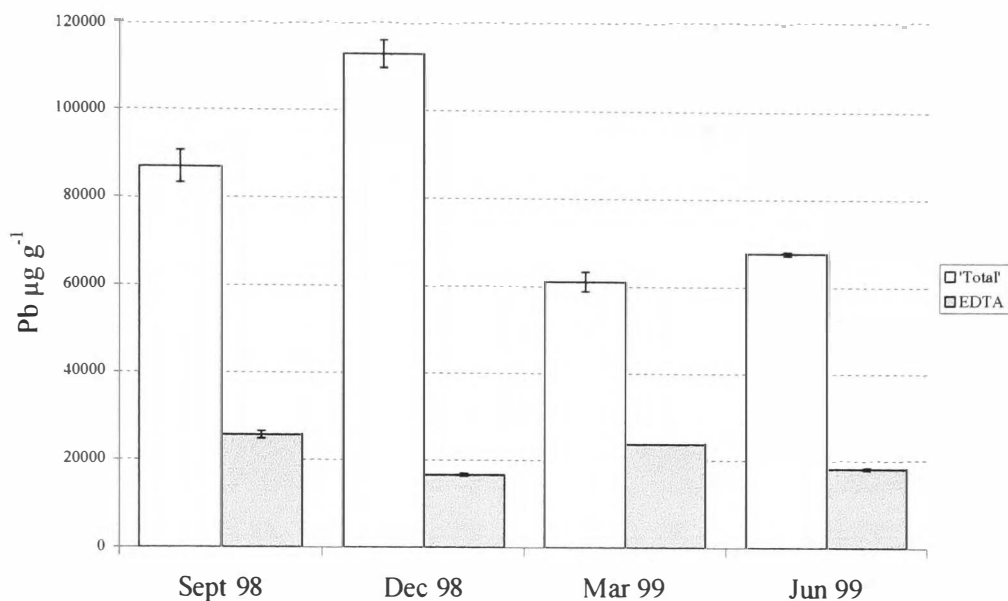
Monthly variation in Total and EDTA metals

Figure 5.79. Mean monthly concentration of Total Pb and EDTA Pb at 0-200 mm for Tailings (n=3).



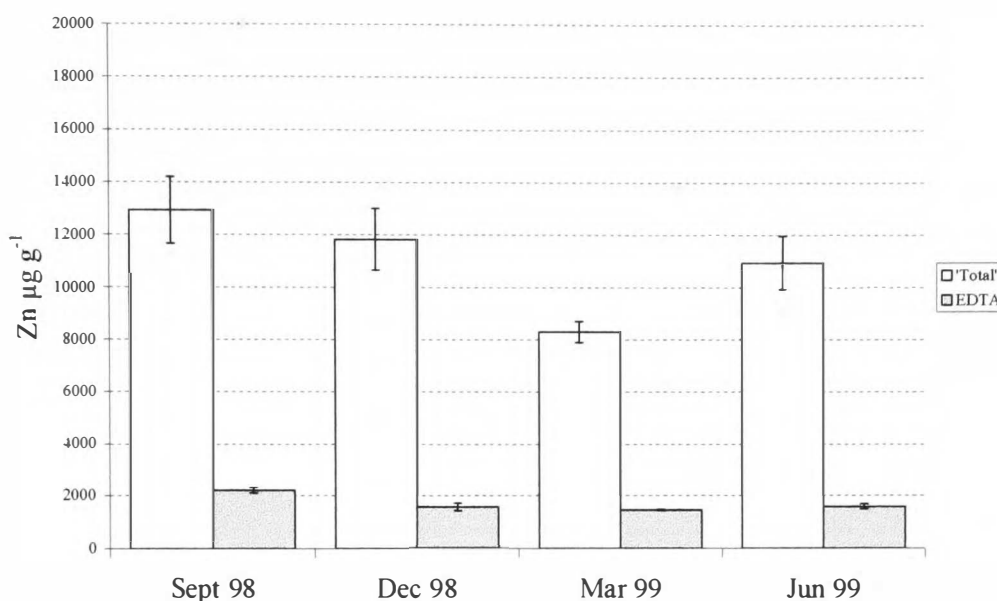
For each month, the Total Pb concentration was higher than that of the EDTA Pb concentration, although EDTA Pb as a percentage of Total Pb varied from 20.03% in December 1998 to 41.18% in March 1999 (Figure 5.79). EDTA Pb did not follow the same monthly variation in concentration as that of Total Pb. The lowest EDTA Pb concentration occurred in December 1998 at  $19\,850.00 \pm 319.48 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $27\,580.00 \pm 924.37 \mu\text{g g}^{-1}$  (Figure 5.79).

Figure 5.80. Mean monthly concentration of Total Pb and EDTA Pb at 200-400 mm for Tailings (n=3).



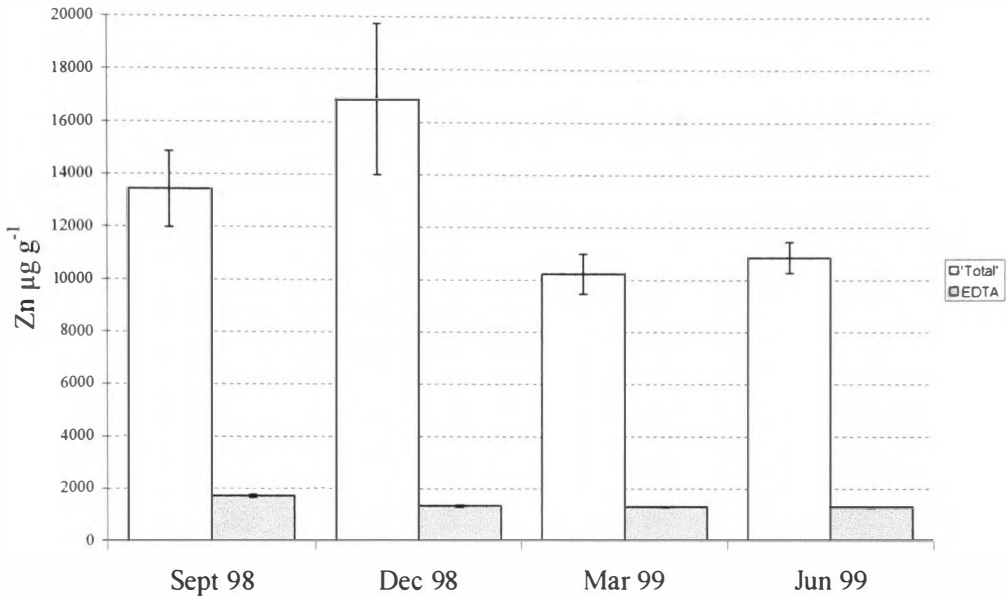
For each month, the Total Pb concentration was greater than that of the EDTA Pb concentration (Figure 5.80). EDTA Pb as a percentage of Total Pb varied from 14.84% in December 1998 to 38.99% in March 1999. The EDTA Pb did not follow the same monthly pattern of variation in concentration as that of Total Pb. The lowest EDTA Pb concentration of  $16\,730.00 \pm 332.57 \mu\text{g g}^{-1}$  occurred in December 1998 and the greatest in September 1998 at  $25\,720.00 \pm 817.84 \mu\text{g g}^{-1}$  (Figure 5.80).

Figure 5.81. Mean monthly concentration of Total Zn and EDTA Zn at 0-200 mm for Tailings (n=3).



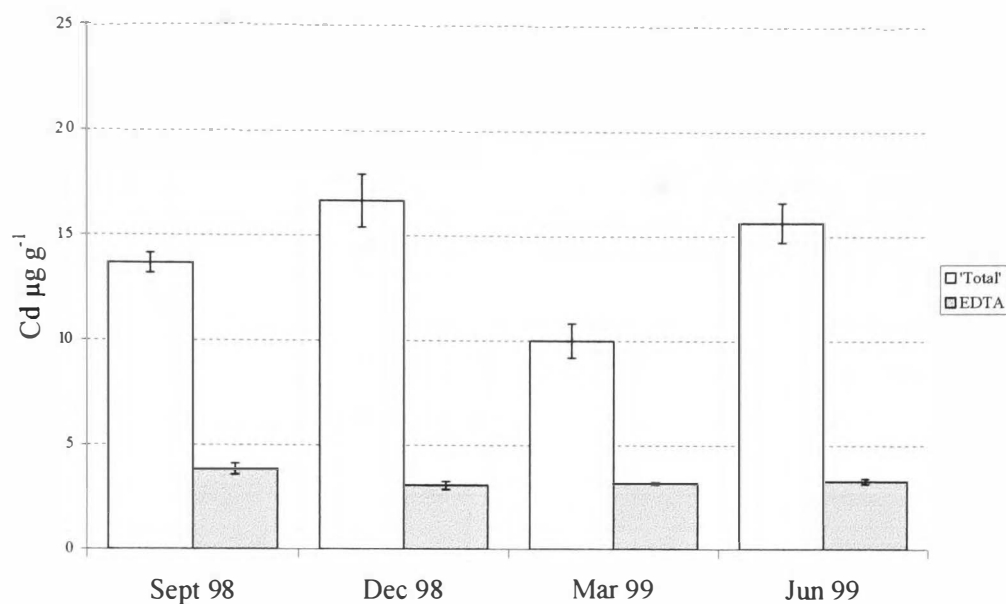
For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 13.27% in December 1998 to 17.55% in March 1999 (Figure 5.81). EDTA Zn followed a similar monthly pattern of variation in concentration as that of Total Zn. The lowest EDTA Zn concentration of  $1\,456.67 \pm 17.00 \mu\text{g g}^{-1}$  occurred in March 1999 and the greatest in September 1998 at  $2\,196.67 \pm 113.24 \mu\text{g g}^{-1}$  (Figure 5.81).

Figure 5.82. Mean monthly concentration of Total Zn and EDTA Zn at 200-400 mm for Tailings (n=3).



For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 7.96% in December 1998 to 12.83% in September 1999 (Figure 5.82). EDTA Zn did not follow the same monthly variation in pattern of concentration as that of Total Zn. The lowest EDTA Zn concentration at  $1\,286.67 \pm 12.47 \mu\text{g g}^{-1}$  occurred in June 1999 and the greatest in September 1998 at  $1\,723.33 \pm 41.90 \mu\text{g g}^{-1}$  (Figure 5.82).

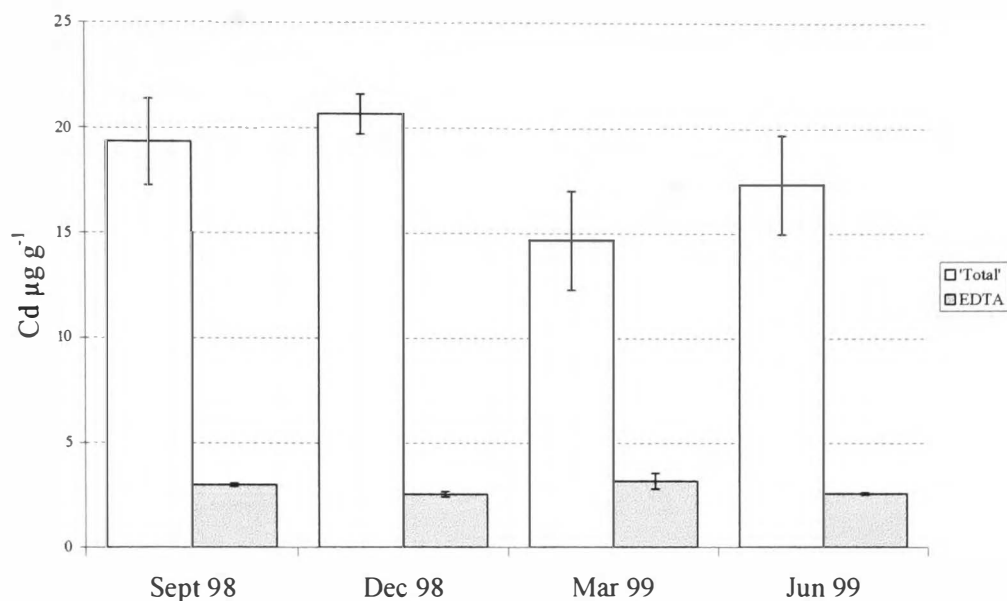
Figure 5.83. Mean monthly mean concentration of Total Cd and EDTA Cd at 0-200 mm for Tailings (n=3).



The Total Cd concentration was greater than that of EDTA Cd (Figure 5.83).

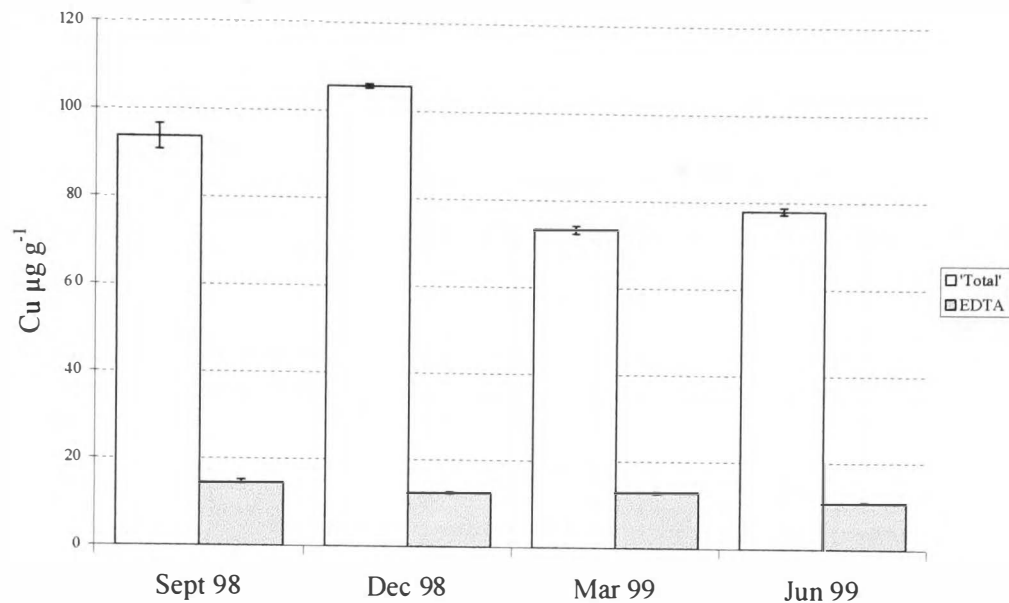
EDTA Cd as a percentage of Total Cd varied from 18.40% in December 1998 to 31.67% in March 1999. The EDTA Cd concentration did not follow the same monthly trend in concentration as that of Total Cd. The lowest EDTA Cd concentration occurred in December 1998 at  $3.07 \pm 0.19 \mu\text{g g}^{-1}$  and the greatest in September 1999 at  $3.83 \pm 0.26 \mu\text{g g}^{-1}$  (Figure 5.83).

Figure 5.84. Mean monthly concentration of Total Cd and EDTA Cd at 200-400 mm for Tailings (n=3).



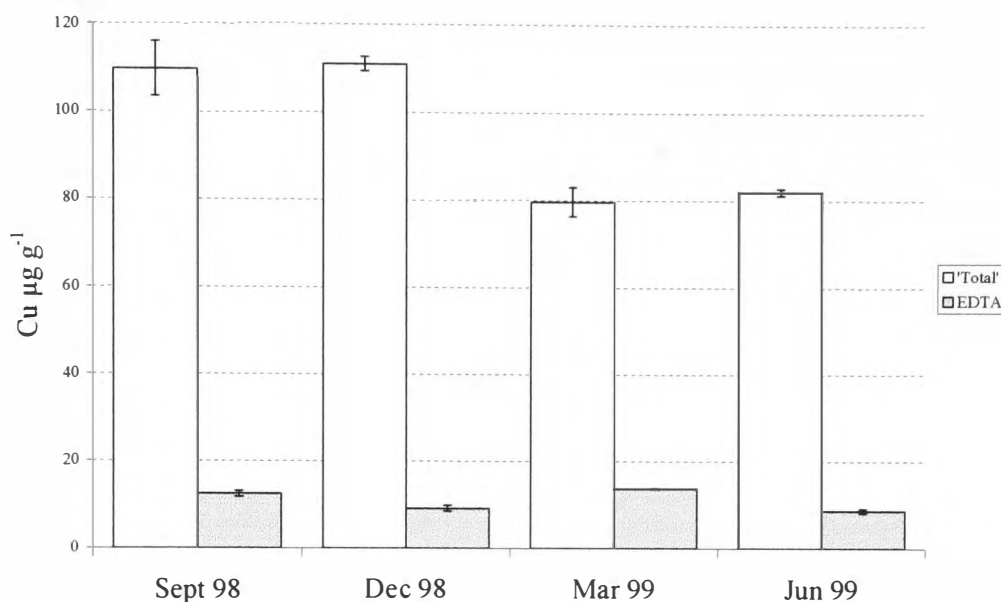
For each month, the concentration of Total Cd was greater than that of EDTA Cd, although EDTA as a percentage of Total Cd varied from 12.26% in December 1998 to 21.59% in March 1999 (Figure 5.8). The EDTA Cd concentration did not follow the same monthly trend in concentration as that of Total Cd. The lowest EDTA Cd concentration occurred in December 1998 at  $2.53 \pm 0.12 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $3.17 \pm 0.39 \mu\text{g g}^{-1}$  (Figure 5.84).

Figure 5.85. Mean monthly concentration of Total Cu and EDTA Cu at 0-200 mm for Tailings (n=3).



For each month, the Total Cu concentration was greater than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 11.77% in December 1998 to 17.55% in March 1999 (Figure 5.85). The lowest EDTA Cu concentration of  $10.80 \pm 0.22 \mu\text{g g}^{-1}$  occurred in June 1999, and the greatest concentration in September 1998 at  $14.53 \pm 0.69 \mu\text{g g}^{-1}$  (Figure 5.85).

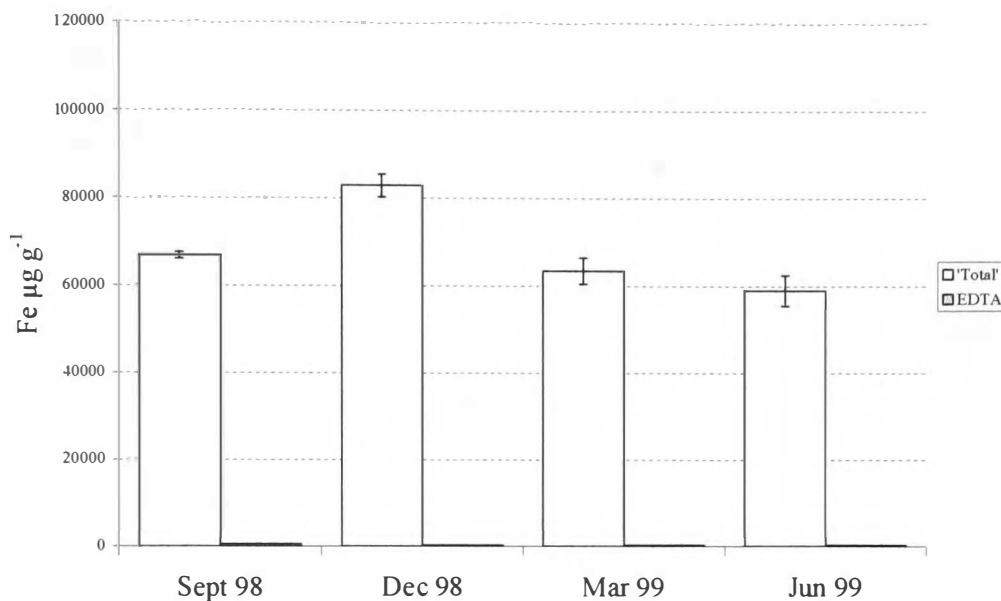
Figure 5.86. Mean monthly concentration of Total Cu and EDTA Cu at 200-400 mm for Tailings (n=3).



For each month, the Total Cu concentration was greater than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 8.32% in December 1998 to 17.28% in March 1999 (Figure 5.86). The lowest EDTA Cu concentration of  $8.70 \pm 0.43 \mu\text{g g}^{-1}$  occurred in June 1999 and the greatest in March 1999 at  $13.77 \pm 0.12 \mu\text{g g}^{-1}$  (Figure 5.86).

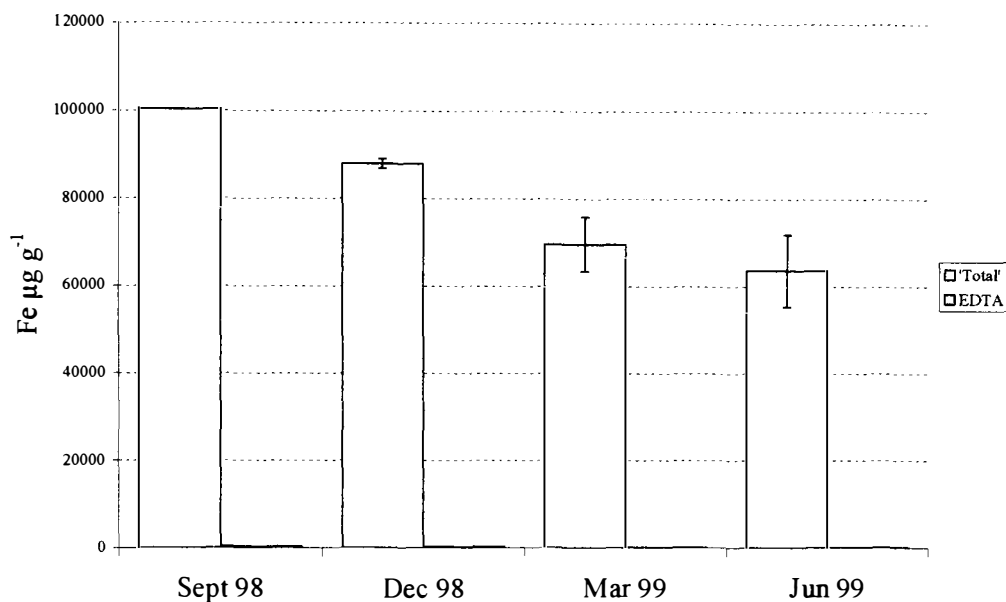


Figure 5.87. Mean monthly concentration of Total Fe and EDTA Fe at 0-200 mm for Tailings (n=3).



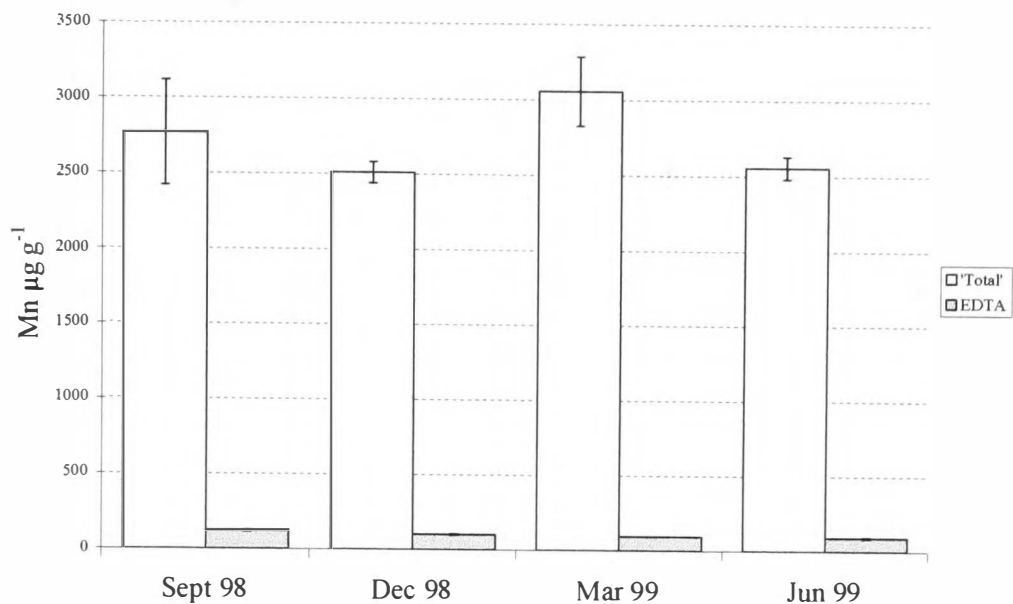
For each month, the Total Fe concentration was significantly greater than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 0.23% in December 1998 to 0.64% in September 1998 (Figure 5.87). EDTA Fe did not follow the same monthly pattern in variation of concentration as Total Fe. The lowest EDTA Fe concentration occurred in December 1998 at  $190.33 \pm 34.84 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $427.67 \pm 15.547 \mu\text{g g}^{-1}$  (Figure 5.87).

Figure 5.88. Mean monthly concentration of Total Fe and EDTA Fe at 200-400 mm for Tailings (n=3).



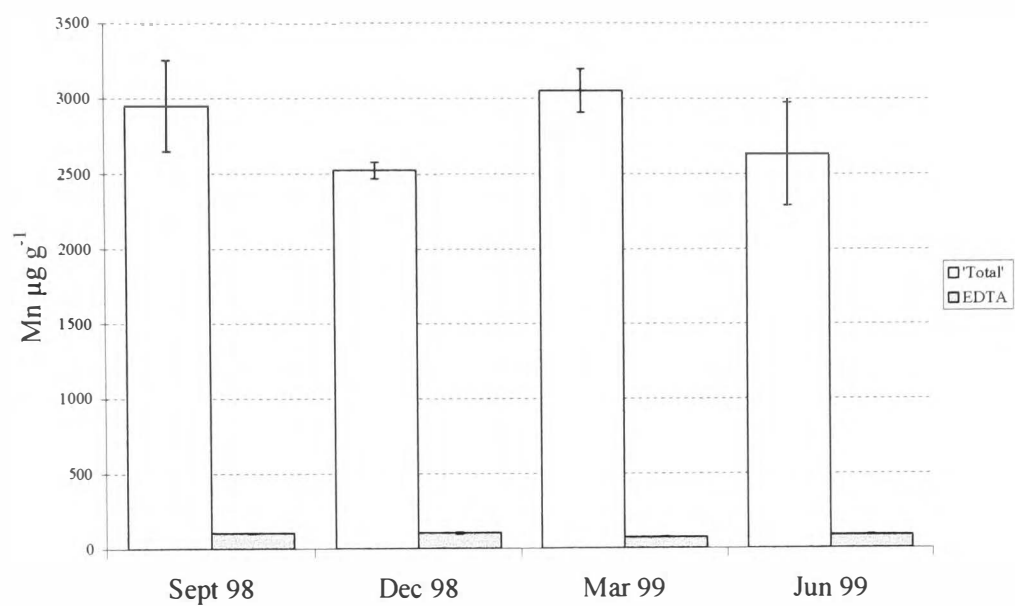
For each month, the Total Fe concentration was greater than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 0.19% in June 1999 to 0.31% in September 1998 (Figure 5.88). Both Total Fe and EDTA Fe followed the same monthly trend in decreasing concentration throughout the year. The lowest EDTA Fe concentration occurred in June 1999 at  $123.67 \pm 2.46 \mu\text{g g}^{-1}$  and the greatest in September 1998 at  $311.67 \pm 21.17 \mu\text{g g}^{-1}$  (Figure 5.88).

Figure 5.89. Mean monthly concentration of Total Mn and EDTA Mn at 0-200 mm for Tailings (n=3).



For each month, the Total Mn concentration was greater than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 3.11% in March 1999 to 4.41% in September 1998 (Figure 5.89). EDTA Mn did not follow the monthly trend in concentration of Total Mn concentration. The lowest EDTA Mn concentration of  $90.67 \pm 3.86 \mu\text{g g}^{-1}$  occurred in June 1999, and the greatest in September 1998 at  $122.00 \pm 6.68 \mu\text{g g}^{-1}$  (Figure 5.89).

Figure 5.90. Mean monthly concentration of Total Mn and EDTA Mn at 200-400 mm for Tailings (n=3).



For each month, the Total Mn concentration was greater than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 2.46% in March 1999 to 4.11% in December 1998 (Figure 5.90). The EDTA Mn concentration did not follow the same monthly trend in concentration as that of Total Mn. The lowest EDTA Mn concentration of  $75.00 \pm 1.41 \mu\text{g g}^{-1}$  occurred in March 1999, and the greatest in December 1998 at  $104.67 \pm 1.258 \mu\text{g g}^{-1}$  (Figure 5.90).

Table 5.57. Median percentage of monthly EDTA trace metals as a percentage of Total trace metals for Tailings at 0-200 mm and 200-400 mm.

Depth	Pb %	Zn %	Cd %	Cu %	Fe %	Mn %
0-200 mm	35.06	15.72	24.45	14.68	0.37	3.81
200-400 mm	28.27	11.89	15.16	11.00	0.27	3.45

In the surface Tailings, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 0.37%, while the greatest was Pb at 35.06% (Table 5.57). At depth, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 0.27%, while the greatest was Pb at 28.27% (Table 5.57).

Monthly variation of other soil parameters

Table 5.58. Monthly values for CEC, Exchangeable Ca, Mg and K and Total P at 0-200 mm and 200-400 mm for Tailings.

Parameter	Unit	Sept 1998	Dec 1998	Mar 1999	Jun 1999
CEC (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	20.59	14.26	17.42	17.03
CEC (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	13.07	11.09	11.09	13.86
Exch. Ca (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	26.14	18.18	23.90	29.38
Exch. Ca (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	19.92	26.64	27.14	34.11
Exch. Mg (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.49	0.29	0.41	0.58
Exch. Mg (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.25	0.21	0.33	0.41
Exch. K (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.29	0.24	0.38	0.38
Exch. K (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.20	0.12	0.25	0.28
Total P (0-200 mm)	µg g <sup>-1</sup>	1812.00	2383.00	1520.00	1538.00
Total P (200-400 mm)	µg g <sup>-1</sup>	1787.00	2484.00	1066.00	2162.00

For all months, the monthly CEC, Exchangeable Mg and Exchangeable K in the surface Tailings were consistently greater than that at depth (Table 5.58). In September 1998, Exchangeable Ca was greater in surface Tailings than at depth while in December 1998 and March and June 1999, the monthly Exchangeable Ca was greater at depth than in the surface Tailings. The concentration of Total P in surface Tailings was greater than the concentration at depth for September 1998. In December 1998, and March and June 1999, Total P concentration was greater at depth than in surface Tailings (Table 5.58).

Table 5.60 Pearson correlation values (r-values) and degrees of significance at the  $p=0.001$ , 0.01 and 0.05 levels for stacked Tailings parameters at 0-400 mm ( $n=24$ ) September 1998 - August 1999.

Tailings Parameter	n=	T-value	p-value	$H_0$ : $\mu_1 = \mu_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	12	-14.81	0.000	Rejected
L-o-I (0-200 mm) v L-o-I (200-400 mm)	12	9.95	0.000	Rejected
Total Pb (0-200 mm) v Total Pb (200-400 mm)	12	-4.83	0.001	Rejected
Total Zn (0-200 mm) v Total Zn (200-400 mm)	12	-2.21	0.049	Rejected
Total Cd (0-200 mm) v Total Cd (200-400 mm)	12	-2.72	0.020	Rejected
Total Cu (0-200 mm) v Total Cu (200-400 mm)	12	-4.39	0.001	Rejected
Total Fe (0-200 mm) v Total Fe (200-400 mm)	12	-2.68	0.021	Rejected
Total Mn (0-200 mm) v Total Mn (200-400 mm)	12	-0.88	0.396	Accepted
EDTA Pb (0-200 mm) v EDTA Pb (200-400 mm)	4	2.10	0.127	Accepted
EDTA Zn (0-200 mm) v EDTA Zn (200-400 mm)	4	4.23	0.024	Rejected
EDTA Cd (0-200 mm) v EDTA Cd (200-400 mm)	4	2.84	0.066	Accepted
EDTA Cu (0-200 mm) v EDTA Cu (200-400 mm)	4	1.83	0.164	Accepted
EDTA Fe (0-200 mm) v EDTA Fe (200-400 mm)	4	1.31	0.280	Accepted
EDTA Mn (0-200 mm) v EDTA Mn (200-400 mm)	4	1.80	0.170	Accepted
CEC (0-200 mm) v CEC (200-400 mm)	4	4.54	0.020	Rejected
Exch. Ca (0-200 mm) v Exch. Ca (200-400 mm)	4	-0.82	0.474	Accepted
Exch. Mg (0-200 mm) v Exch. Mg (200-400 mm)	4	3.67	0.035	Rejected
Exch. K (0-200 mm) v Exch. K (200-400 mm)	4	12.05	0.001	Rejected
Total P (0-200 mm) v Total P (200-400 mm)	4	-0.28	0.800	Accepted

## Two-Sample analysis

The Two-sample T-test between surface and depth for each stacked Tailings parameter (n=12 or n=4) showed a significant difference at the  $p \leq 0.05$  level for 11/19 of the Tailings Series Tailings parameters (Tables 5.59). While the majority of the Tailings parameters (11/19) showed a significant difference at the  $p \leq 0.05$  level between values at surface and at depth, pH, Loss-on-Ignition, Total Pb, Total Cu and Exchangeable K showed a significant difference at the  $p \leq 0.001$  level (Table 5.59).

## Pearson correlations

Table 5.60. Pearson correlation values (r-values) and degrees of significance at the  $p=0.001$ , 0.01 and 0.05 levels for stacked Tailings parameters at 0-400 mm (n=24) September 1998 - August 1999.

	pH (0-400 mm)	L-o-I (0-400mm)	Total Pb (0-400 mm)	Total Zn (0-400 mm)	Total Cd (0-400 mm)	Total Cu (0-400 mm)	Total Fe (0-400 mm)
L-o-I (0-400 mm)	-0.833 ***						
Total Pb (0-400 mm)	-0.037	-0.222					
Total Zn (0-400 mm)	0.131	-0.334	0.833 ***				
Total Cd (0-400 mm)	0.278	-0.472 *	0.714 ***	0.892 ***			
Total Cu (0-400 mm)	0.188	-0.450 *	0.808 ***	0.771 ***	0.727 ***		
Total Fe (0-400 mm)	0.117	-0.414 *	0.767 ***	0.731 ***	0.720 ***	0.883 ***	
Total Mn (0-400 mm)	-0.137	0.125	-0.275	-0.551 **	-0.573 **	-0.246	-0.139

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     - Indicates a negative correlation

In the Tailings, Loss-on-Ignition was negatively correlated at the  $p \leq 0.05$  level with pH, and Total Cd, Cu and Fe (Table 5.60). Total Pb, Zn, Cd, Cu and Fe were all positively correlated with each other at the  $p = 0.001$  level, while Total Mn was negatively correlated with Total Zn and Total Cd at the  $p = 0.01$  level.

### 5.5.6 Nordrach Series

#### Particle Size Analysis

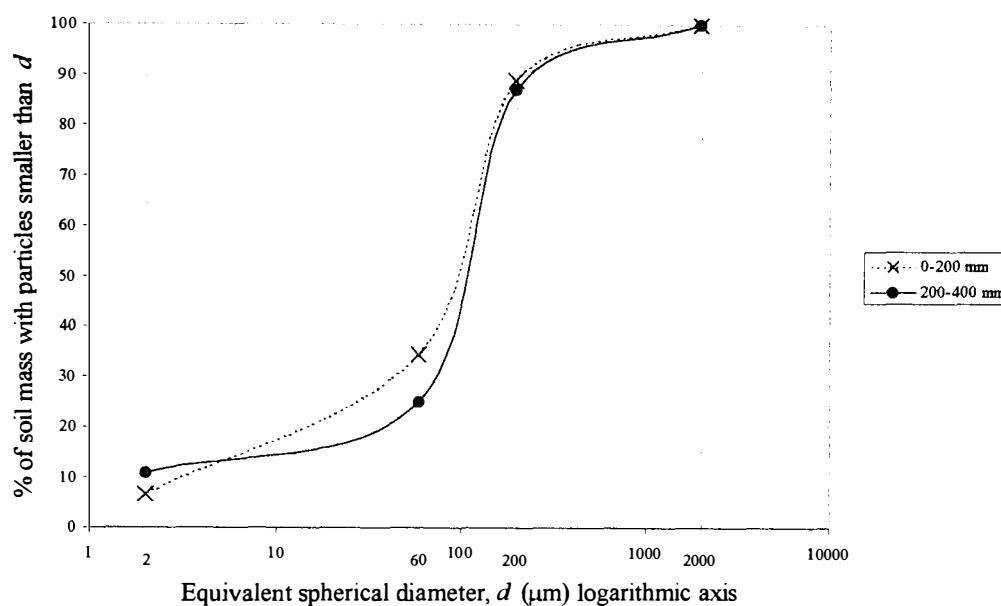
Table 5.61. Particle size distribution and soil textural class for Nordrach Series.

Depth (mm)	% clay	% silt	% fine sand	% coarse sand	Textural Class
0 - 200	6.52	28.08	54.40	11.00	Silty Loam
200-400	10.85	14.15	61.98	13.02	Silty Loam

The surface soil was classified as silty loam with fine sand as the most abundant particle size (Table 5.61). At depth, although still dominated by fine sand and classified as silty loam, the soil contained a greater % of fine and coarse sand, and lower % of clay and silt than the surface soil (Table 5.61 and Figure 5.91). The cumulative curve plot showed that at approximately 65% and 75% of the particles at surface and depth respectively, sand (fine + coarse sand) dominated the < 2 mm soil fraction at both surface and depth (Figure 5.91).



Figure 5.91. Cumulative curve displaying particle size distribution of Nordrach soil at 0-200 mm and 200-400 mm.



### Descriptive statistics

The Nordrach Series data set consisted of monthly ( $n=12$ ) and quarterly ( $n=4$ ) data for the same soil parameters as the Maesbury Series described in 5.5.2. Soil reaction ranged from pH 4.47 to pH 5.16 in the surface soil and from pH 3.88 to pH 5.22 at depth. Loss-on-Ignition in the surface soil ranged from 11.35% to 13.69% and from 9.45% to 11.67% at depth (Table 5.62).

The concentration of Total Pb in the surface soil ranged from 4 123.00  $\mu\text{g g}^{-1}$  to 4 883.00  $\mu\text{g g}^{-1}$  and from 3 347.00  $\mu\text{g g}^{-1}$  to 8 347.00  $\mu\text{g g}^{-1}$  at depth. Total Zn ranged from 213.00  $\mu\text{g g}^{-1}$  to 836.67  $\mu\text{g g}^{-1}$  in the surface horizon and from 240.00  $\mu\text{g g}^{-1}$  to 393.33  $\mu\text{g g}^{-1}$  at depth. The Total Cd concentration in surface soil and at depth was identical for all samples at 0.05  $\mu\text{g g}^{-1}$  (Table 5.62).

Table 5.62. Soil parameter data for Nordrach Series at 0-200 mm and 200-400 mm (n=12) for September 1998 - August 1999 and (n=4) for quarterly sampling.

	Unit	n =	Arithmetic Mean	St. Dev.	Minimum	Median	Maximum
pH (0-200 mm)	pH	12	4.77	0.25	4.47	4.72	5.16
pH (200-400 mm)	pH	12	4.79	0.38	3.88	4.76	5.22
L-o-I (0-200 mm)	%	12	12.48	0.74	11.35	12.45	13.69
L-o-I (200-400 mm)	%	12	10.42	0.72	9.45	10.35	11.67
Total Pb (0-200 mm)	$\mu\text{g g}^{-1}$	12	4 659.08	205.25	4 123.00	4 727.00	4 883.00
Total Pb (200-400 mm)	$\mu\text{g g}^{-1}$	12	4 377.75	487.56	3 347.00	4 358.00	5 347.00
Total Zn (0-200 mm)	$\mu\text{g g}^{-1}$	12	294.69	55.56	213.00	288.33	836.67
Total Zn (200-400 mm)	$\mu\text{g g}^{-1}$	12	309.78	42.76	240.00	313.36	393.33
Total Cd (0-200 mm)	$\mu\text{g g}^{-1}$	12	0.50	0.00	0.50	0.50	0.50
Total Cd (200-400 mm)	$\mu\text{g g}^{-1}$	12	0.50	0.00	0.50	0.50	0.50
Total Cu (0-200 mm)	$\mu\text{g g}^{-1}$	12	12.00	2.30	7.67	11.50	15.67
Total Cu (200-400 mm)	$\mu\text{g g}^{-1}$	12	12.36	2.97	9.00	12.67	19.00
Total Fe (0-200 mm)	$\mu\text{g g}^{-1}$	12	25 153.30	1 284.10	23 026.30	25 043.30	27 763.30
Total Fe (200-400 mm)	$\mu\text{g g}^{-1}$	12	26 005.00	1 077.80	24 326.70	26 095.00	28 123.30
Total Mn (0-200 mm)	$\mu\text{g g}^{-1}$	12	1 621.95	428.73	1 096.67	1 571.67	2 580.00
Total Mn (200-400 mm)	$\mu\text{g g}^{-1}$	12	1 995.83	297.56	1 513.33	1 978.34	2 436.67
EDTA Pb (0-200 mm)	$\mu\text{g g}^{-1}$	4	3 206.67	713.96	2 313.33	3 343.33	3 826.67
EDTA Pb (200-400 mm)	$\mu\text{g g}^{-1}$	4	2 596.00	340.80	2 283.33	2 526.67	3 047.33
EDTA Zn (0-200 mm)	$\mu\text{g g}^{-1}$	4	8.72	1.41	7.27	8.48	10.63
EDTA Zn (200-400 mm)	$\mu\text{g g}^{-1}$	4	6.58	2.16	4.73	6.18	9.20
EDTA Cd (0-200 mm)	$\mu\text{g g}^{-1}$	4	0.10	0.08	0.01	0.10	0.20
EDTA Cd (200-400 mm)	$\mu\text{g g}^{-1}$	4	0.10	0.00	0.10	0.10	0.10
EDTA Cu (0-200 mm)	$\mu\text{g g}^{-1}$	4	3.76	0.58	2.97	3.93	4.20
EDTA Cu (200-400 mm)	$\mu\text{g g}^{-1}$	4	2.68	0.68	1.83	2.68	3.50
EDTA Fe (0-200 mm)	$\mu\text{g g}^{-1}$	4	821.58	334.61	642.67	660.17	1 323.33
EDTA Fe (200-400 mm)	$\mu\text{g g}^{-1}$	4	435.92	176.98	301.67	382.50	677.00
EDTA Mn (0-200 mm)	$\mu\text{g g}^{-1}$	4	382.33	100.01	248.33	400.33	480.33
EDTA Mn (200-400 mm)	$\mu\text{g g}^{-1}$	4	300.33	113.47	180.00	308.17	405.00
CEC (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	20.00	2.11	17.42	20.00	22.57
CEC (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	16.63	2.17	15.05	15.84	19.80
Exch. Ca (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.86	0.26	0.50	0.95	1.05
Exch. Ca (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	1.01	1.04	0.35	0.56	2.56
Exch. Mg (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.19	0.03	0.16	0.19	0.21
Exch. Mg (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.11	0.02	0.08	0.12	0.12
Exch. K (0-200 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.24	0.06	0.19	0.23	0.32
Exch. K (200-400 mm)	$\text{cmol}_c \text{ Kg}^{-1}$	4	0.23	0.11	0.12	0.23	0.33
Total P (0-200 mm)	$\mu\text{g g}^{-1}$	4	526.18	69.42	454.30	517.60	615.20
Total P (200-400 mm)	$\mu\text{g g}^{-1}$	4	542.28	112.21	469.30	495.10	709.60

The concentration of Total Cu ranged from  $7.67 \mu\text{g g}^{-1}$  to  $15.67 \mu\text{g g}^{-1}$  in the surface soil and at depth from  $9.00 \mu\text{g g}^{-1}$  to  $19.00 \mu\text{g g}^{-1}$  (Table 5.62). Total Fe was present in surface soil at  $23\,026.30 \mu\text{g g}^{-1}$  to  $27\,763.30 \mu\text{g g}^{-1}$  and from  $24\,326.70 \mu\text{g g}^{-1}$  to  $28\,123.30 \mu\text{g g}^{-1}$  at depth. Total Mn in surface soil ranged from  $1\,096.67 \mu\text{g g}^{-1}$  to  $2\,580.00 \mu\text{g g}^{-1}$  and from  $1\,513.33 \mu\text{g g}^{-1}$  to  $2\,436.67 \mu\text{g g}^{-1}$  at depth.

EDTA Pb was present in surface soil at  $2\,313.33 \mu\text{g g}^{-1}$  to  $3\,826.67 \mu\text{g g}^{-1}$  and from  $2\,283.33 \mu\text{g g}^{-1}$  to  $3\,047.33 \mu\text{g g}^{-1}$  at depth (Table 5.62). Surface EDTA Zn was present at  $7.27 \mu\text{g g}^{-1}$  to  $10.63 \mu\text{g g}^{-1}$  and from  $4.73 \mu\text{g g}^{-1}$  to  $9.20 \mu\text{g g}^{-1}$  at depth. Surface EDTA Cd ranged from  $0.01 \mu\text{g g}^{-1}$  to  $0.02 \mu\text{g g}^{-1}$ . At depth, the concentration of EDTA Cd was identical for all samples at  $0.10 \mu\text{g g}^{-1}$ . The concentration of surface EDTA Cu ranged from  $2.97 \mu\text{g g}^{-1}$  to  $4.20 \mu\text{g g}^{-1}$  and at depth from  $1.83 \mu\text{g g}^{-1}$  to  $3.50 \mu\text{g g}^{-1}$ . EDTA Fe ranged from  $642.67 \mu\text{g g}^{-1}$  to  $1\,323.33 \mu\text{g g}^{-1}$  in surface soil and from  $301.67 \mu\text{g g}^{-1}$  to  $677.00 \mu\text{g g}^{-1}$  at depth. EDTA Mn was present in surface soil at  $248.33 \mu\text{g g}^{-1}$  to  $480.33 \mu\text{g g}^{-1}$  and from  $180.00 \mu\text{g g}^{-1}$  to  $405.00 \mu\text{g g}^{-1}$  at depth (Table 5.62).

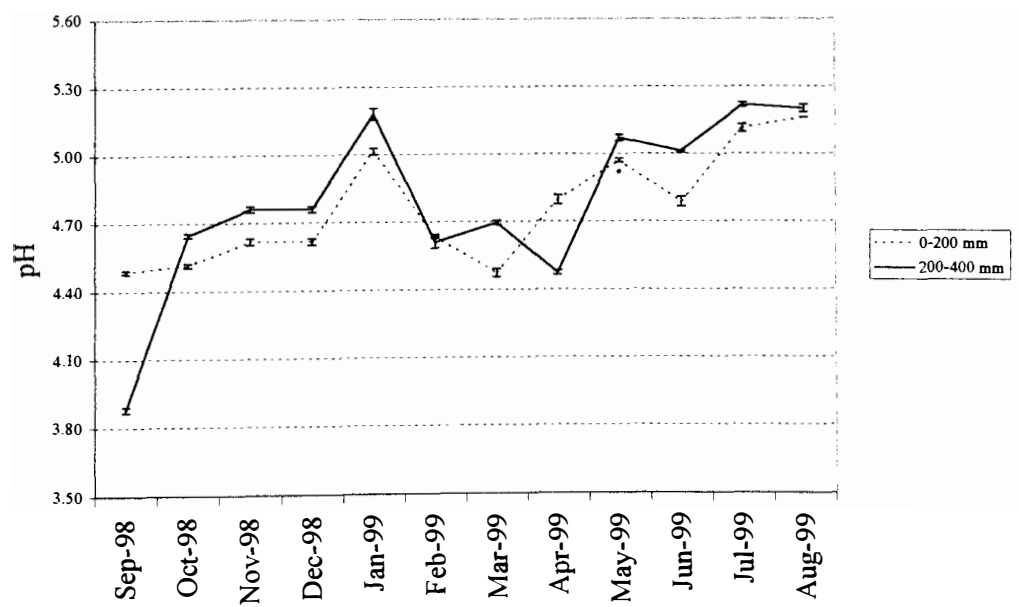
Surface CEC ranged from  $17.42 \text{ cmol}_c \text{ kg}^{-1}$  to  $22.57 \text{ cmol}_c \text{ kg}^{-1}$  and from  $15.05 \text{ cmol}_c \text{ kg}^{-1}$  to  $19.80 \text{ cmol}_c \text{ kg}^{-1}$  at depth. The concentration of surface Exchangeable Ca ranged from  $0.50 \text{ cmol}_c \text{ kg}^{-1}$  to  $1.05 \text{ cmol}_c \text{ kg}^{-1}$  and from  $0.35 \text{ cmol}_c \text{ kg}^{-1}$  to  $2.56 \text{ cmol}_c \text{ kg}^{-1}$  at depth (Table 5.62). Exchangeable Mg was present in surface soil at  $0.16 \text{ cmol}_c \text{ kg}^{-1}$  to  $0.21 \text{ cmol}_c \text{ kg}^{-1}$  and from

0.08 cmol<sub>c</sub> kg<sup>-1</sup> to 0.12 cmol<sub>c</sub> kg<sup>-1</sup> at depth. Surface Exchangeable K ranged from 0.19 cmol<sub>c</sub> kg<sup>-1</sup> to 0.32 cmol<sub>c</sub> kg<sup>-1</sup> and from 0.12 cmol<sub>c</sub> kg<sup>-1</sup> to 0.33 cmol<sub>c</sub> kg<sup>-1</sup> at depth. The concentration of surface Total P ranged from 454.30 µg g<sup>-1</sup> to 615.20 µg g<sup>-1</sup> and from 469.30 µg g<sup>-1</sup> to 709.60 µg g<sup>-1</sup> at depth (Table 5.62).

Generally, the mean and median values of each individual soil parameter were similar, with the exception of surface EDTA Fe and surface Exchangeable Ca (Table 5.62). The mean and median values for surface EDTA Fe were 821.58 µg g<sup>-1</sup> and 660.17 µg g<sup>-1</sup> respectively, and for surface Exchangeable Ca 1.01 cmol<sub>c</sub> kg<sup>-1</sup> and 0.56 cmol<sub>c</sub> kg<sup>-1</sup> (Table 5.62).

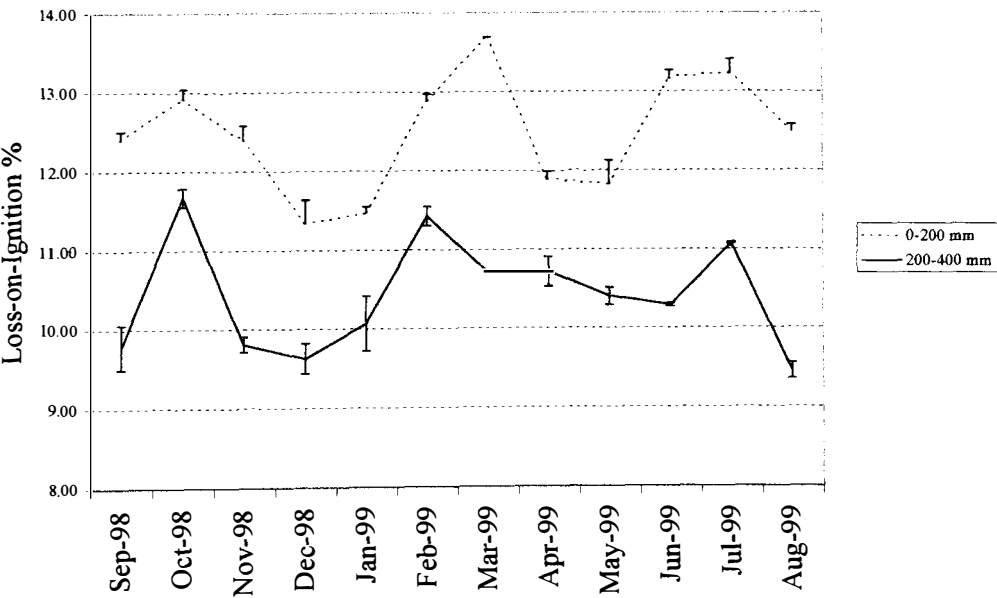
Monthly variation in pH, Loss-on-Ignition and Total metals

Figure 5.92. Mean monthly pH at 0-200 mm and 200-400 mm for Nordrach Series (n=3).



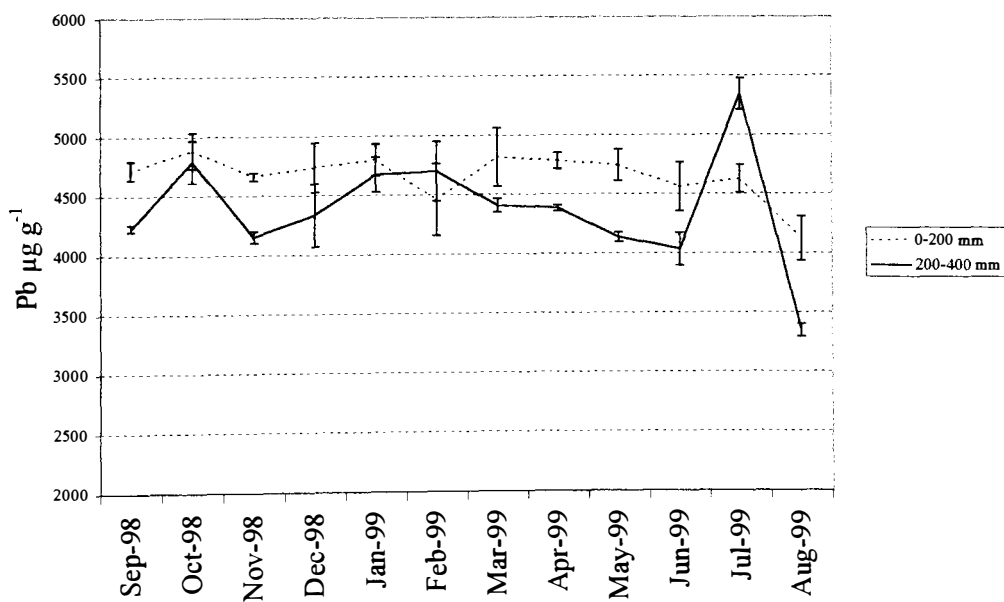
The pattern of variation for soil reaction at both surface and at depth was generally similar. Each showed an overall increase in pH throughout the year (Figure 5.92). With the exception of September 1998, February and April 1999, when surface pH was higher than pH at depth, soil pH at depth was higher than surface pH in each month (Figure 5.92). The lowest pH values in the surface soil occurred in March 1998 at  $\text{pH } 4.47 \pm 0.01$ , while the highest value of  $\text{pH } 5.16 \pm 0.02\%$  occurred in August 1999. For soil at depth, the lowest pH occurred in September 1999 at  $\text{pH } 3.88 \pm 0.01$ , while the highest at  $\text{pH } 5.22 \pm 0.02$  occurred in July 1998 (Figure 5.92).

Figure 5.93. Mean monthly % Loss-on-Ignition at 0-200 mm and 200-400 mm for Nordrach Series (n=3).



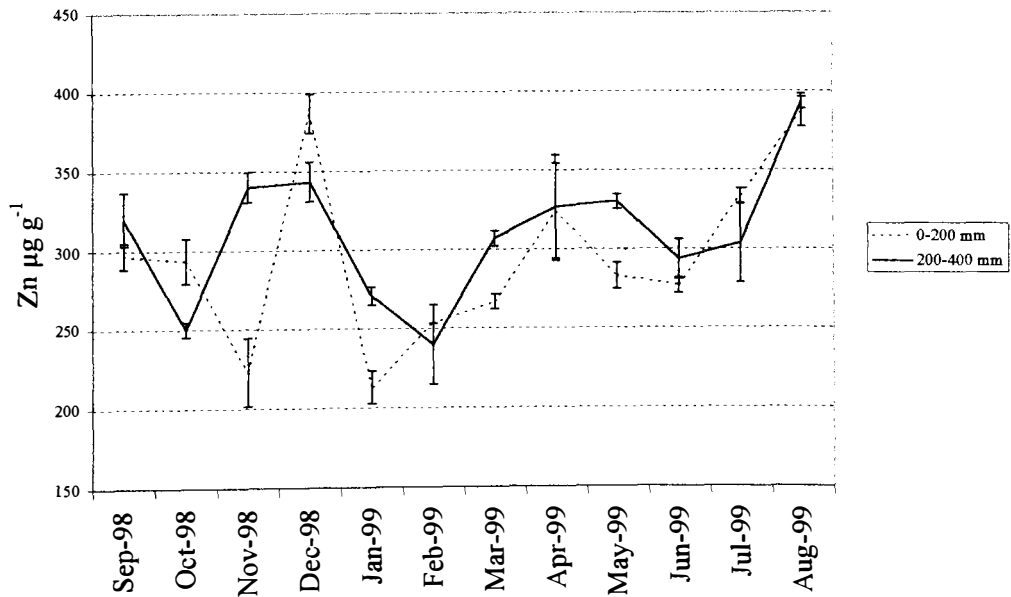
For each month, Loss-on-Ignition was consistently greater for surface soil than that at depth (Figure 5.93). In general, Loss-on-Ignition in surface soil and at depth showed a similar overall pattern of variation throughout the year. The lowest % Loss-on-Ignition of  $11.35 \pm 0.70.09\%$  in the surface soil occurred in December 1998, while the greatest % Loss-on-Ignition of  $13.69 \pm 0$  occurred in March 1999 (Figure 5.93). The lowest % Loss-on-Ignition at depth occurred in August 1999 at  $9.45 \pm 0.10\%$ , while the greatest % Loss-on-Ignition occurred in October 1998 at  $11.67 \pm 0.12\%$  (Figure 5. 93).

Figure 5.94. Mean monthly Total Pb at 0-200 mm and 200-400 mm for Nordrach Series (n=3).



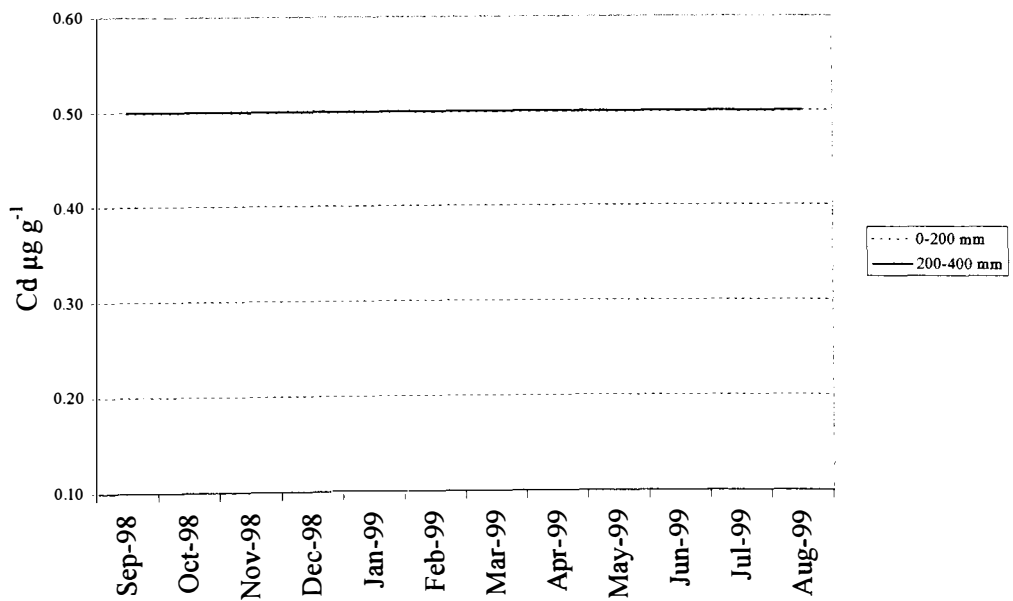
In general, Total Pb in surface soil and at depth showed a similar overall pattern of variation throughout the year. With the exception of February and July 1999, when the concentration of Total Pb at depth was greater than that in the surface soil, for each month, the concentration of Total Pb was greater for surface soil than at depth (Figure 5.94). The lowest concentration of Total Pb in the surface soil occurred in October 1998 at  $4\,883 \pm 151 \mu\text{g g}^{-1}$ , while the greatest concentration of  $4\,123 \pm 187 \mu\text{g g}^{-1}$  occurred in August 1999 (Figure 5.94). The lowest concentration of Total Pb at depth occurred in August 1999 at  $3\,347 \pm 54 \mu\text{g g}^{-1}$ , while the greatest occurred in July 1999 at  $5\,347 \pm 133 \mu\text{g g}^{-1}$  (Figure 5.94).

Figure 5.95. Mean monthly Total Zn at 0-200 mm and 200-400 mm for Nordrach Series (n=3).



In general, Total Zn at surface and depth showed a similar pattern of variation in concentration throughout the year. With the exception of October and December 1998 and July 1999, when the concentration was greater at depth, for the majority of the months, Total Zn occurred in greater concentrations at depth (Figure 5.95). The lowest concentration of Total Zn in the surface soil occurred in January 1999 at  $213 \pm 5.66 \mu\text{g g}^{-1}$ , while the greatest at  $386.67 \pm 12.47 \mu\text{g g}^{-1}$  and  $386.67 \pm 4.71 \mu\text{g g}^{-1}$  occurred in December 1998 and August 1999 respectively (Figure 5.95). At  $240 \pm 0 \mu\text{g g}^{-1}$ , the lowest concentration of Total Zn at depth occurred in February 1999, while the greatest occurred in August 1999 at  $393.33 \pm 9.43 \mu\text{g g}^{-1}$  (Figure 5.95).

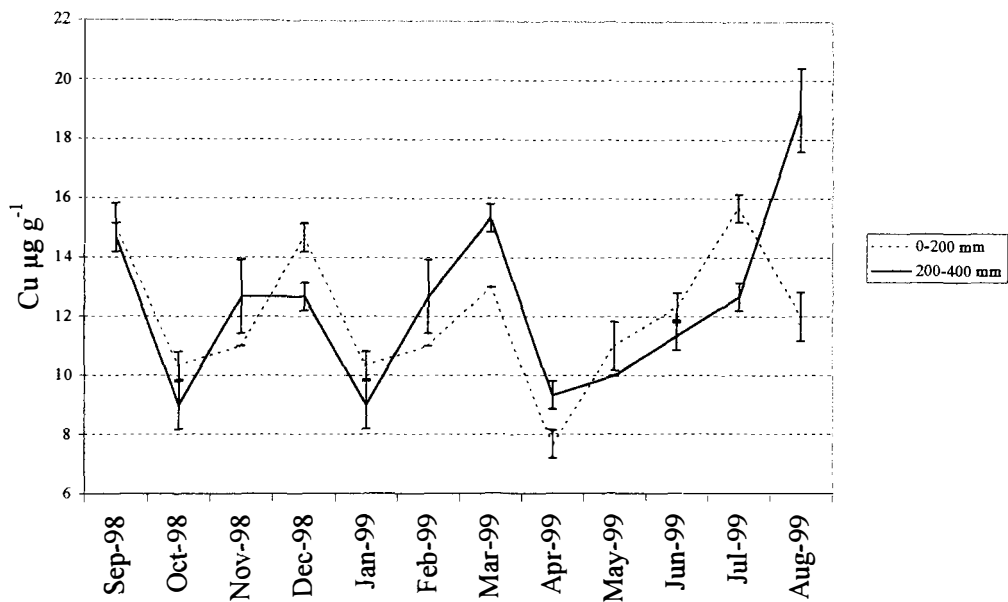
Figure 5.96. Mean monthly Total Cd at 0-200 mm and 200-400 mm for Nordrach Series (n=3).





The concentration of Total Cd was identical in the surface soil and at depth at  $0.05 \pm 0$  for all months (Figure 5 96).

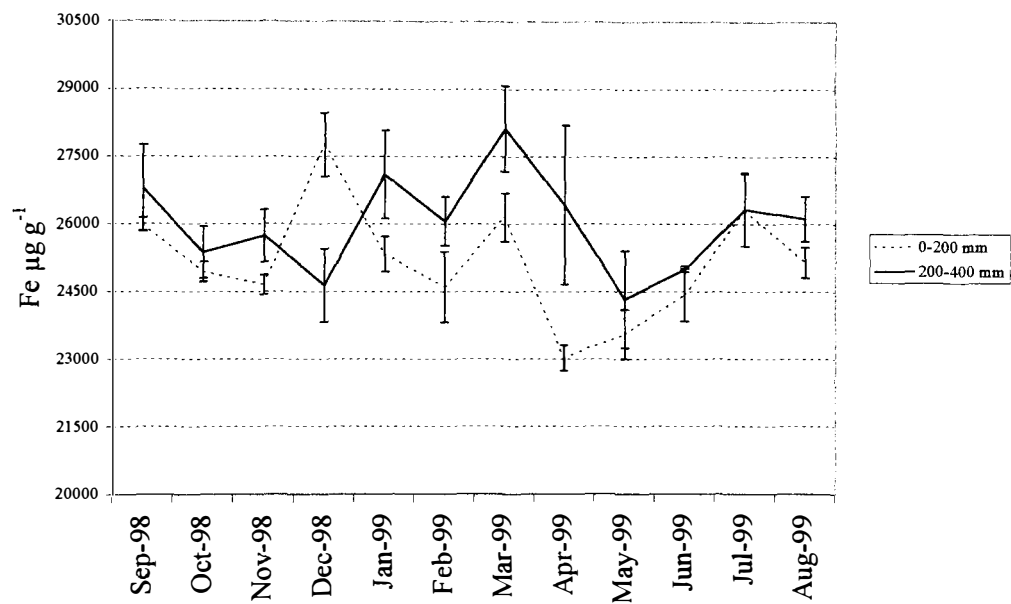
Figure 5.97. Mean monthly Total Cu at 0-200 mm and 200-400 mm for Nordrach Series (n=3).



For six non-consecutive months in the year, the concentration of Total Cu in surface soil was greater than at depth. In the remaining six non-consecutive months, the situation was reversed (Figure 5.97). Throughout the year, the Total Cu in surface soils and at depth generally showed a similar pattern of variation in concentration. The lowest concentration of Total Cu in the surface soil occurred in April 1999 at  $7.67 \pm 0.47 \mu\text{g g}^{-1}$ , while the greatest occurred in July 1998 at

15.67 ±0.47 µg g<sup>-1</sup> (Figure 5.97). At depth, the lowest concentration of Total Cu at 9.00 ±0.82 µg g<sup>-1</sup> occurred in October 1998, while the greatest occurred in August 1999 at 19.00 ±1.41 µg g<sup>-1</sup> (Figure 5.97).

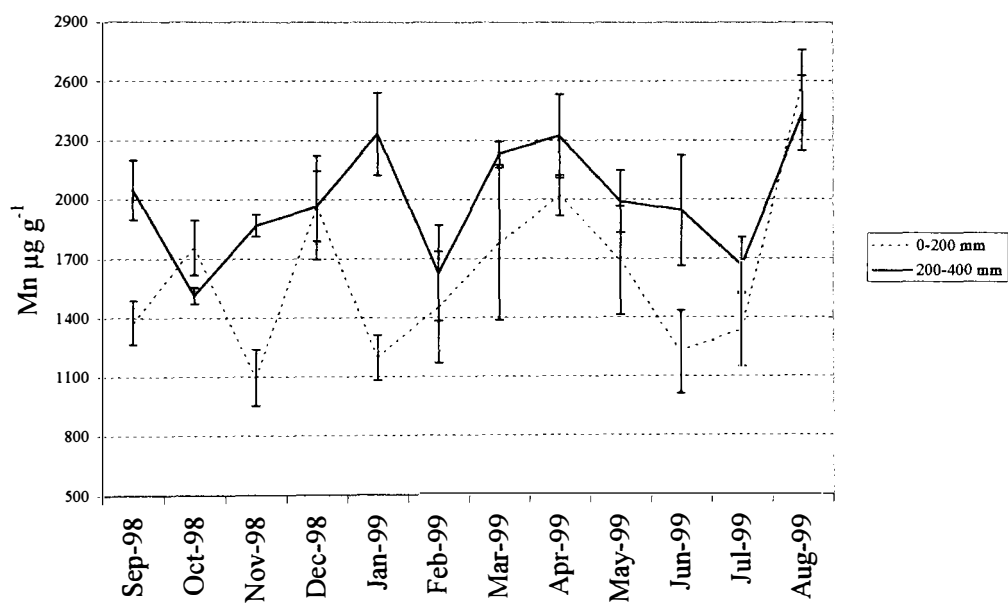
Figure 5.98. Mean monthly Total Fe at 0-200 mm and 200-400 mm for Nordrach Series (n=3).



With the exception of December 1998 when Total Fe was greater in surface soil, for the remaining months the Total Fe concentration was greater for soil at depth than that at the surface (Figure 5.98). In July 1999, the mean Total Fe concentrations in the surface soil and at depth were similar at 26 323 ±804 µg g<sup>-1</sup> and 26 333 ±816 µg g<sup>-1</sup> respectively. The lowest concentration of Total Fe in the surface soil occurred in April 1999 at 23 026 ±287 µg g<sup>-1</sup>, while the greatest at

27 763 ±704 µg g<sup>-1</sup> occurred in December 1998 (Figure 5.98). At depth, the lowest concentration of Total Fe at 24 327 ± 1 082 µg g<sup>-1</sup> occurred in May 1999, while the greatest at 28 123 ±955 µg g<sup>-1</sup> occurred in August 1999 (Figure 5.98).

Figure 5.99. Mean monthly Total Mn at 0-200 mm and 200-400 mm for Nordrach Series (n=3).

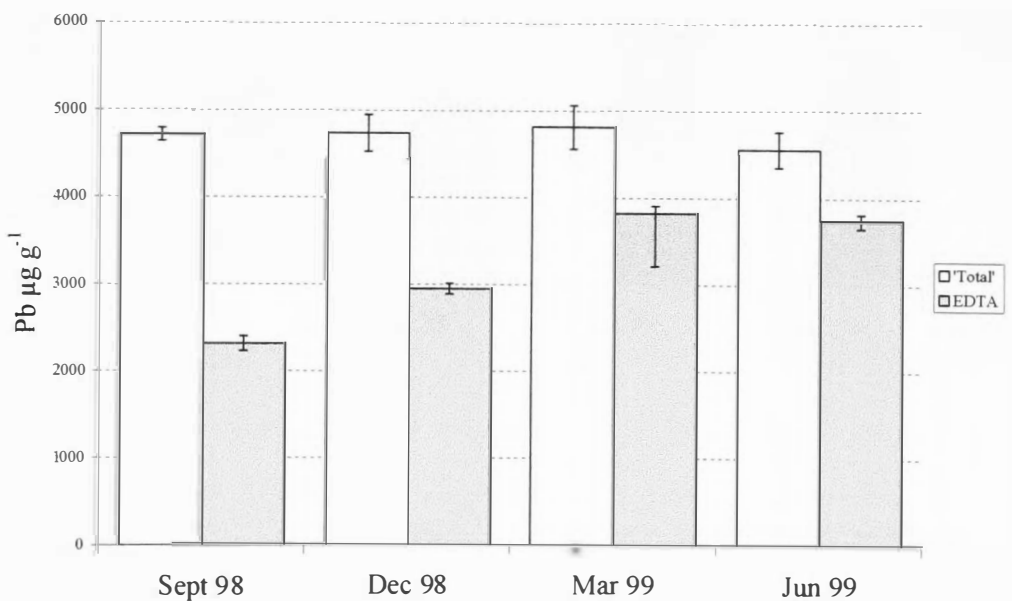


With the exception of October 1998 and August 1999, when the concentration of Total Mn was greater in surface soil than at depth, for each remaining month the concentration of Total Mn was consistently greater at depth than for surface soil. In December 1998, there was little difference between the mean concentration of Total Mn at surface and depth at 1 960.00 ±263.19 µg g<sup>-1</sup> and 1 966 ±177.83 µg g<sup>-1</sup> respectively (Figure 5.99). The lowest concentration of Total Mn in the surface

soil occurred in November 1998 at  $11\,096.67 \pm 143.84 \mu\text{g g}^{-1}$ , while the greatest at  $2\,580.33 \pm 179.07 \mu\text{g g}^{-1}$  occurred in August 1999 (Figure 5.99). At depth, the lowest concentration of Total Mn at  $1\,513.33 \pm 41.10 \mu\text{g g}^{-1}$  occurred in October 1998, while the greatest occurred in August 1999 at  $2\,436.67 \pm 192.24 \mu\text{g g}^{-1}$  (Figure 5.99).

Monthly variation in Total and EDTA metals

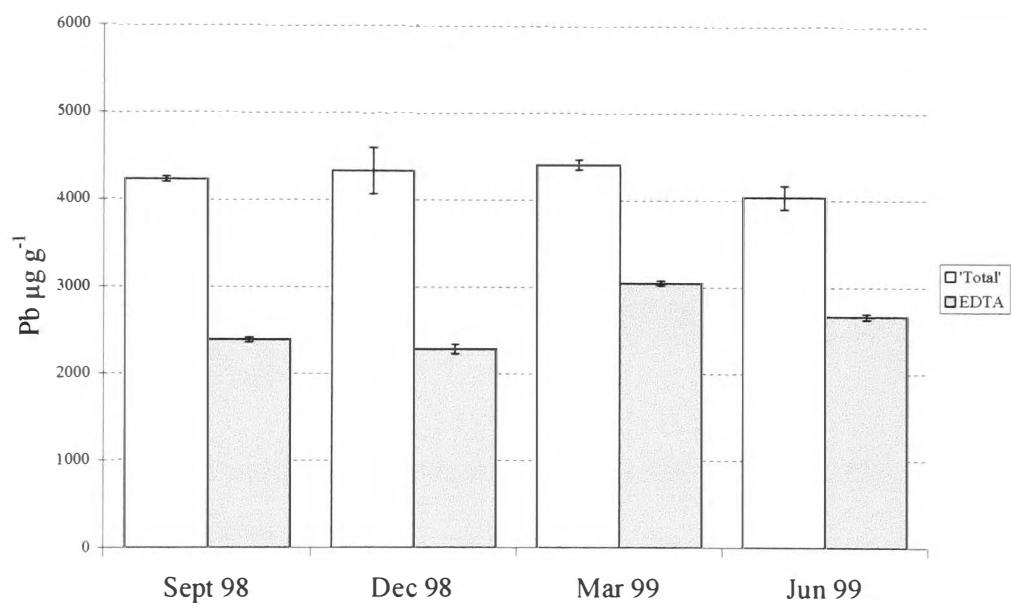
Figure 5.100. Mean monthly concentration of Total Pb and EDTA Pb at 0-200 mm for Nordrach Series (n=3).



For each month, the Total Pb concentration was higher than that of the EDTA Pb concentration, although EDTA Pb as a percentage of Total Pb varied from 49.05% in September 1999 to 81.96% in June 1999 (Figure 5.100). EDTA Pb followed a monthly variation in concentration similar to that of Total Pb. The lowest EDTA

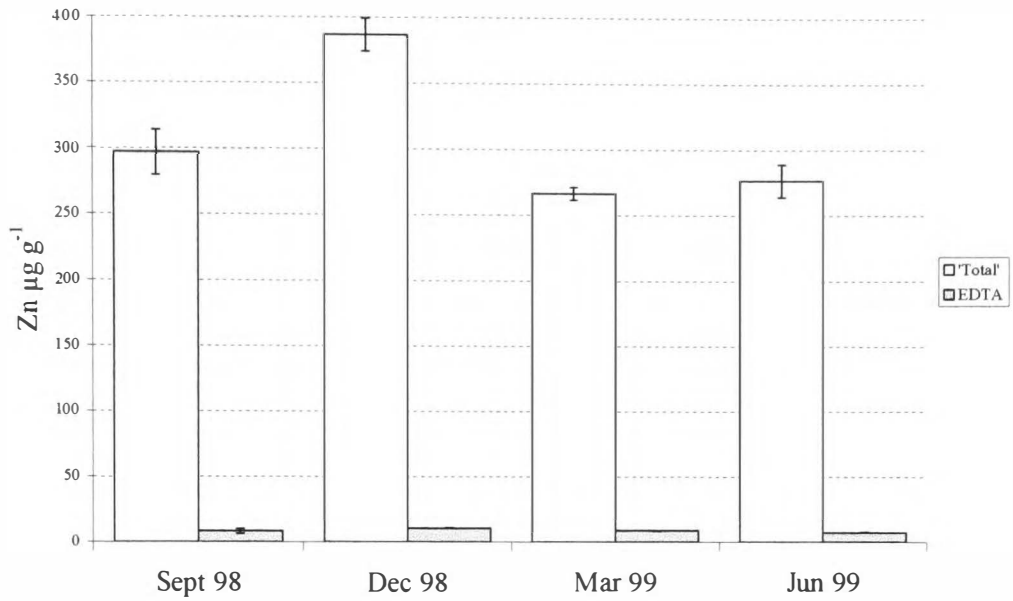
Pb concentration occurred in September 1998 at  $2\,313.33 \pm 83.40 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $3\,826.67 \pm 80.55 \mu\text{g g}^{-1}$  (Figure 5.100).

Figure 5.101. Mean monthly concentration of Total Pb and EDTA Pb at 200-400 mm for Nordrach Series (n=3).



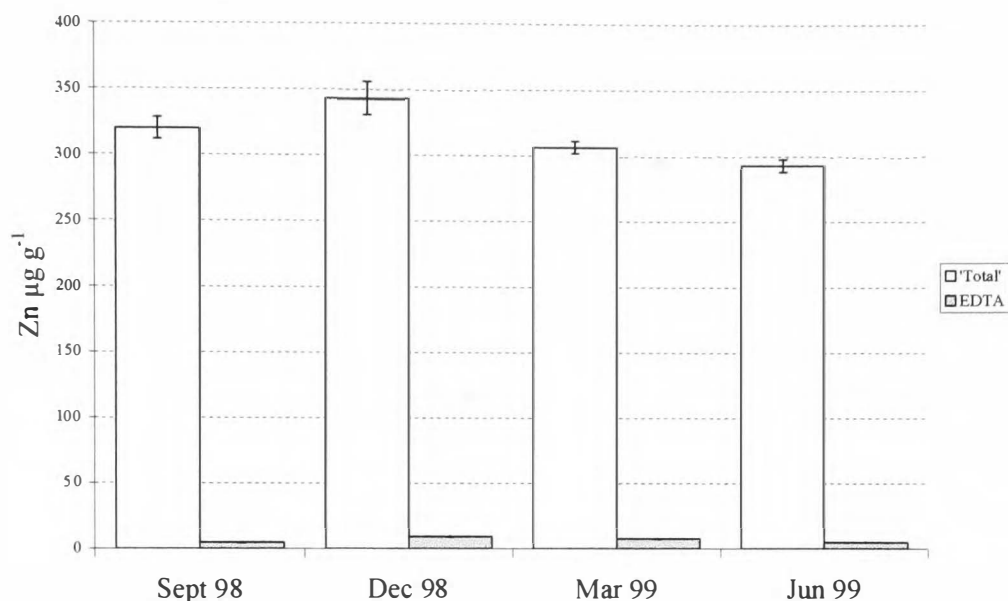
For each month, the Total Pb concentration was greater than that of the EDTA Pb concentration (Figure 5.101). EDTA Pb as a percentage of Total Pb varied from 52.67% in December 1998 to 69.15 % in March 1999. The EDTA Pb did not follow the same monthly pattern of variation in concentration as that of Total Pb. The lowest EDTA Pb concentration of  $2\,283.33 \pm 53.12 \mu\text{g g}^{-1}$  occurred in December 1998 and the greatest in March 1999 at  $3\,047.33 \pm 25.98 \mu\text{g g}^{-1}$  (Figure 5.101).

Figure 5.102. Mean monthly concentration of Total Zn and EDTA Zn at 0-200 mm for Nordrach Series (n=3).



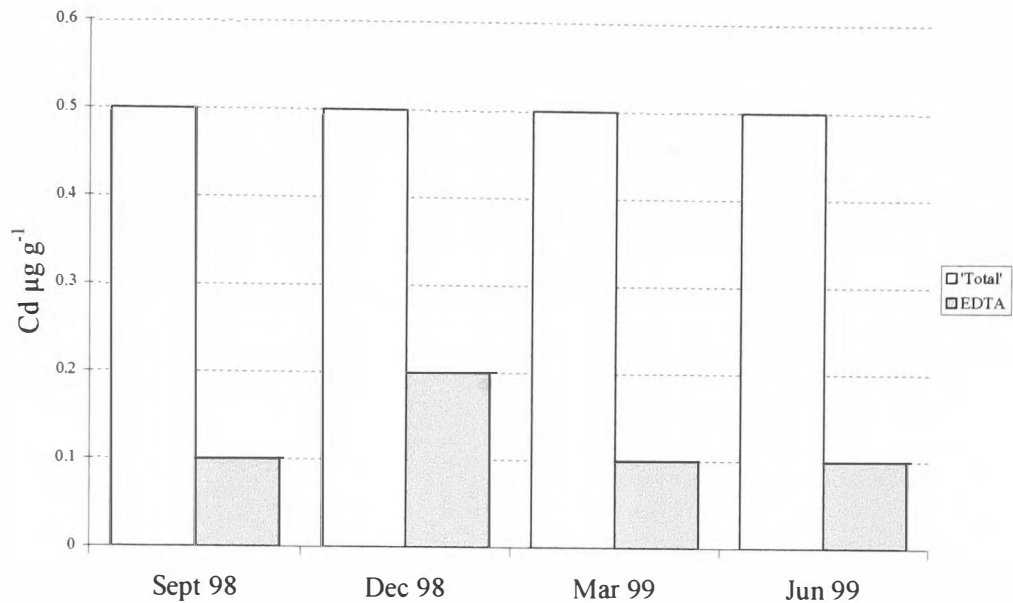
For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 2.63% in June 1999 to 3.26% in March 1999 (Figure 5.102). EDTA Zn did not follow the same monthly pattern of variation in concentration as Total Zn. The lowest EDTA Zn concentration of  $7.27 \pm 0.19 \mu\text{g g}^{-1}$  occurred in June 1999 and the greatest in December 1998 at  $10.63 \pm 0.29 \mu\text{g g}^{-1}$  (Figure 5.102).

Figure 5.103. Mean monthly concentration of Total Zn and EDTA Zn at 200-400 mm for Nordrach Series (n=3).



For each month, the Total Zn concentration was higher than that of the EDTA Zn concentration, although EDTA Zn as a percentage of Total Zn varied from 1.48% in September 1998 to 2.68% in December 1998 (Figure 5.103). EDTA Zn did not follow the same monthly variation in pattern of concentration as that of Total Zn. The lowest EDTA Zn concentration at  $4.73 \pm 0.26 \mu\text{g g}^{-1}$  occurred in September 1998 and the greatest in December 1998 at  $9.20 \pm 0.29 \mu\text{g g}^{-1}$  (Figure 5.103).

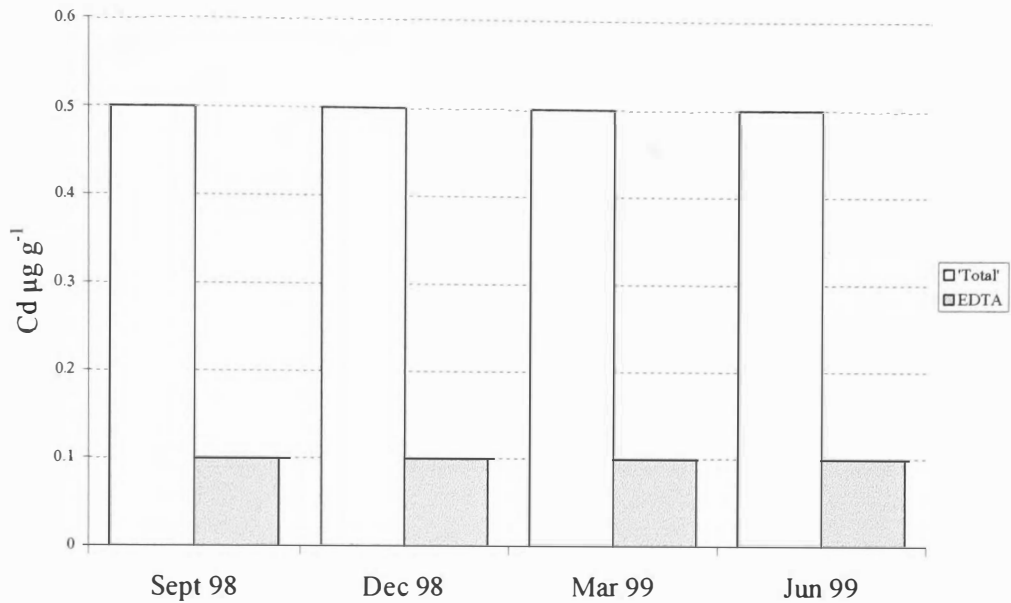
Figure 5.104. Mean monthly mean concentration of Total Cd and EDTA Cd at 0-200 mm for Nordrach Series (n=3).



The Total Cd concentration was greater than that of EDTA Cd (Figure 5.104) for all months. EDTA Cd as a percentage of Total Cd varied from 20.00% in September 1998. March and June 1999 to 40.00% in December 1998 (Figure 5.104). The lowest EDTA Cd concentration occurred in Sept 1998, March, and June 1999 at  $0.0 \pm 0 \mu\text{g g}^{-1}$  and the greatest in December 1998 at  $0.20 \pm 0 \mu\text{g g}^{-1}$  (Figure 5.104).

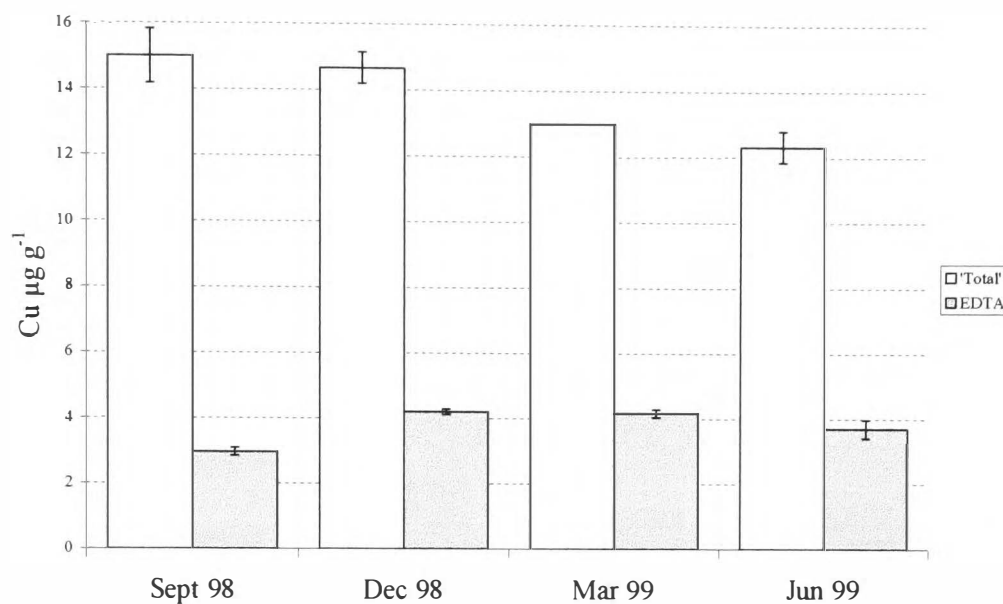


Figure 5.105. Mean monthly concentration of Total Cd and EDTA Cd at 200-400 mm for Nordrach Series (n=3).



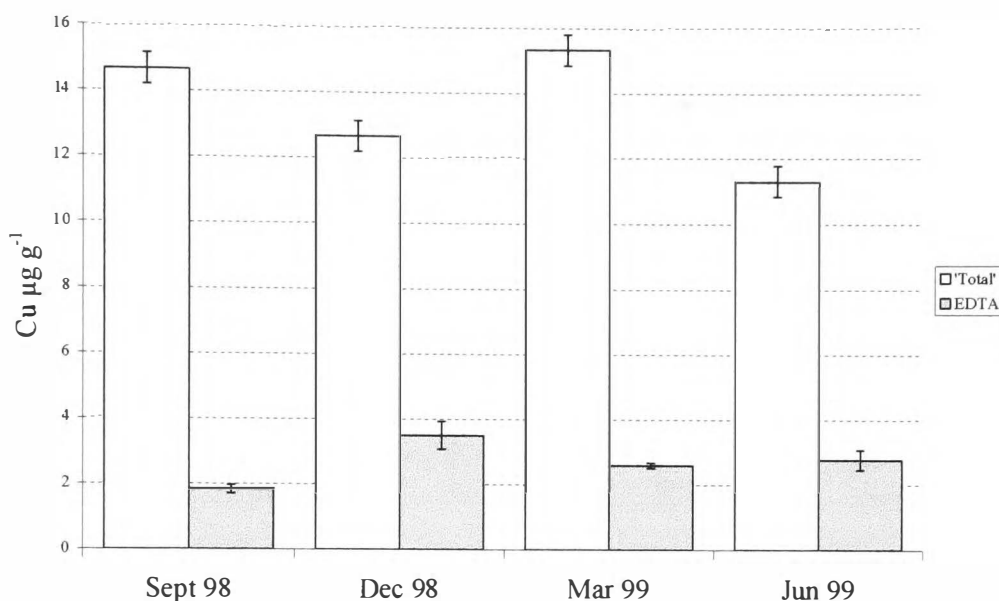
For each month, the concentration of Total Cd was greater than that of EDTA Cd. EDTA as a percentage of Total Cd was identical for each month at 20.00%. There was no monthly variation in concentration for either Total Cd at  $0.50 \pm 0 \mu\text{g g}^{-1}$  or EDTA Cd at  $0.10 \pm 0 \mu\text{g g}^{-1}$  (Figure 5.105).

Figure 5.106. Mean monthly concentration of Total Cu and EDTA Cu at 0-200 mm for Nordrach Series (n=3).



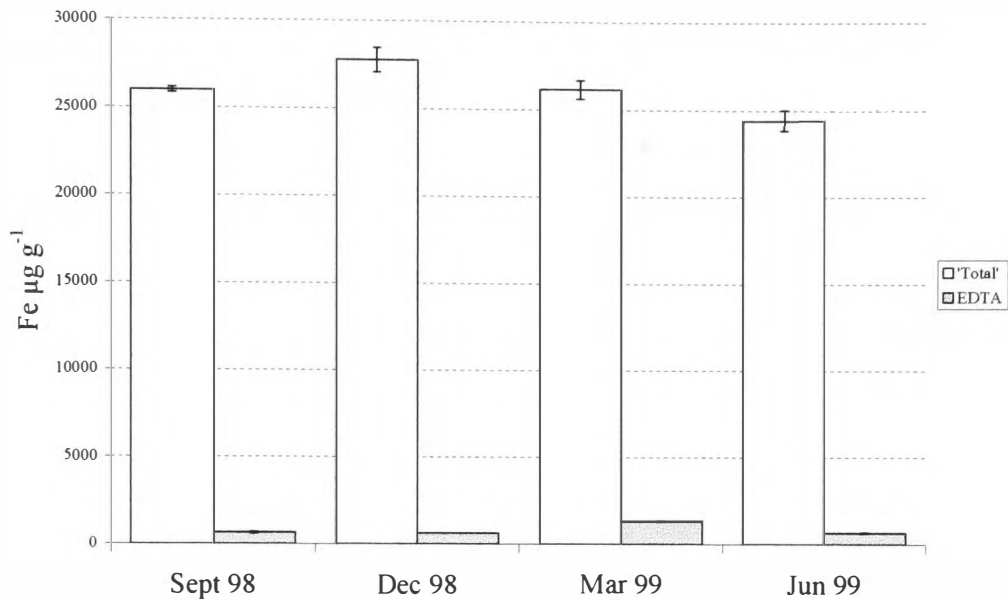
For each month, the Total Cu concentration was greater than that of the EDTA Cu concentration, although EDTA Cu as a percentage of Total Cu varied from 19.78% in September 1998 to 32.05% in March 1999 (Figure 5.106). Total Cu showed a pattern of decline in concentration from September 1998 to June 1999, but EDTA Cu did not follow this trend. The lowest EDTA Cu occurred in September 1998 at  $2.97 \pm 0.12 \mu\text{g g}^{-1}$ , and the greatest concentration of  $4.20 \pm 0.08 \mu\text{g g}^{-1}$  in December 1998 (Figure 5.106).

Figure 5.107. Mean monthly concentration of Total Cu and EDTA Cu at 200-400 mm for Nordrach Series (n=3).



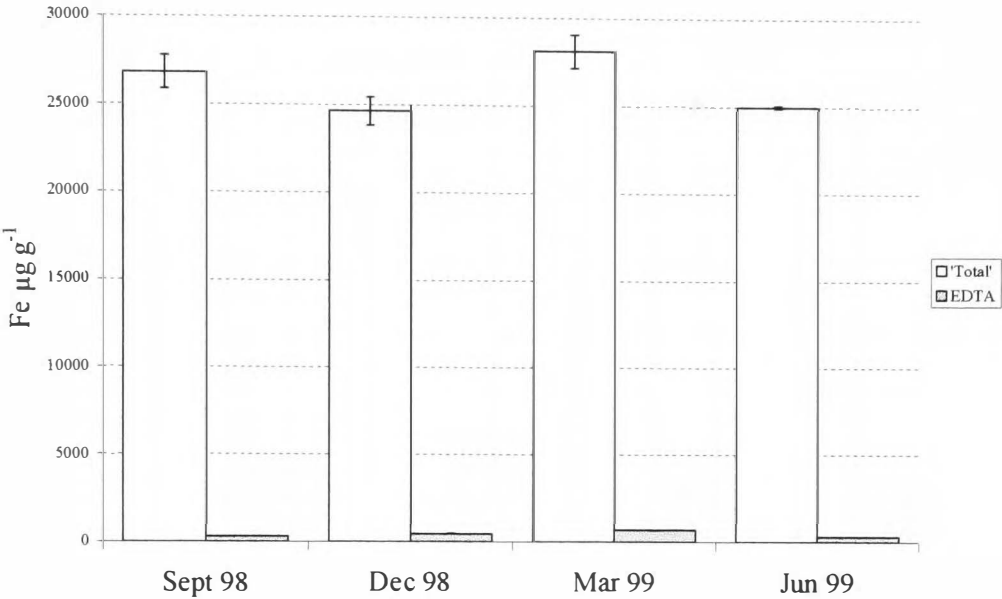
For each month, the Total Cu concentration was greater than that of the EDTA Cu, although EDTA Cu as a percentage of Total Cu varied from 12.50% in September 1998 to 27.63% in December 1998 (Figure 5.107). The lowest EDTA Cu concentration of  $1.83 \pm 0.12 \mu\text{g g}^{-1}$  occurred in September 1998 and the greatest in December 1998 at  $3.50 \pm 0.42 \mu\text{g g}^{-1}$  (Figure 5.107).

Figure 5.108. Mean monthly concentration of Total Fe and EDTA Fe at 0-200 mm for Nordrach Series (n=3).



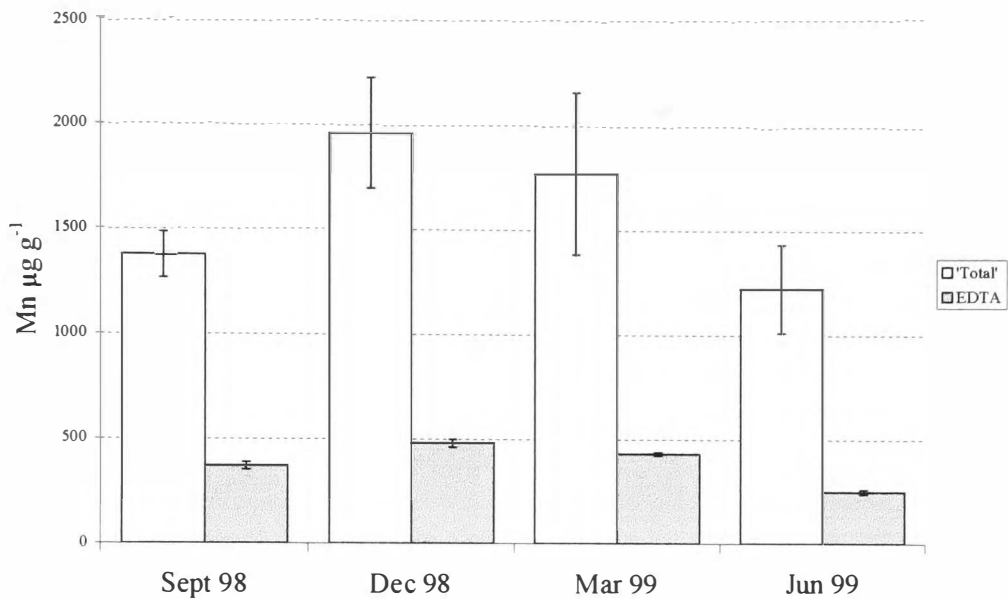
For each month, the Total Fe concentration was significantly greater than that of the EDTA Fe concentration, although EDTA Fe as a percentage of Total Fe varied from 2.31% in December 1998 to 5.06% in March 1999 (Figure 5.108). The EDTA Fe concentration did not follow the same monthly trend in concentration as that of Total Fe. The lowest EDTA Fe concentration occurred in December 1998 at  $642.67 \pm 7.85 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $1\,323.33 \pm 22.90 \mu\text{g g}^{-1}$  (Figure 5.108).

Figure 5.109. Mean monthly concentration of Total Fe and EDTA Fe at 200-400 mm for Nordrach Series (n=3).



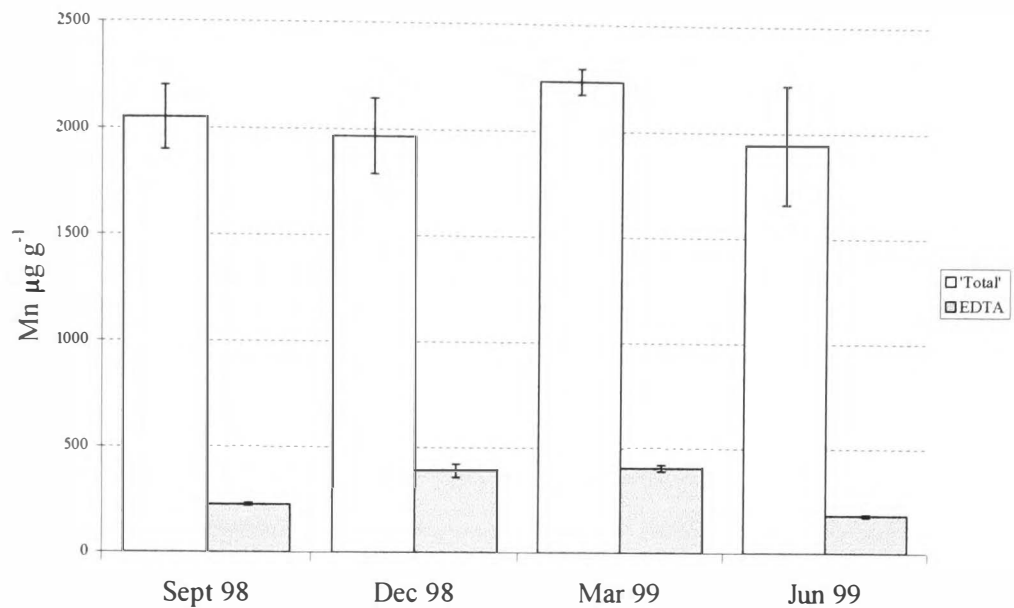
For each month, the Total Fe concentration was significantly greater than that of EDTA Fe, although EDTA Fe as a percentage of Total Fe varied from 1.14% in September 1998 to 2.41% in March 1999 (Figure 5.109). The EDTA Fe concentration did not follow the same monthly trend in concentration of that of Total Fe. The lowest EDTA Fe concentration occurred in June 1999 at  $301.67 \pm 12.12 \mu\text{g g}^{-1}$  and the greatest in March 1999 at  $677.00 \pm 16.51 \mu\text{g g}^{-1}$  (Figure 5.109).

Figure 5.110. Mean monthly concentration of Total Mn and EDTA Mn at 0-200 mm for Nordrach Series (n=3).



For each month, the Total Mn concentration was greater than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 20.30% in June 1999 to 26.90% in September 1998 (Figure 5.110). EDTA Mn followed the same pattern of monthly variation in concentration as that of Total Mn (Figure 5.110). The lowest EDTA Mn concentration of  $248.33 \pm 10.21 \mu\text{g g}^{-1}$  occurred in June 1999, and the greatest in December 1998 at  $480.33 \pm 18.37 \mu\text{g g}^{-1}$  (Figure 5.110).

Figure 5.111. Mean monthly concentration of Total Mn and EDTA Mn at 200-400 mm for Nordrach Series (n=3).



For each month, the Total Mn concentration was greater than that of the EDTA Mn concentration, although EDTA Mn as a percentage of Total Mn varied from 9.26% in June 1999 to 19.78% in December 1998 (Figure 5.111). The EDTA Mn concentration did not follow the same monthly trend in concentration as that of Total Mn. The lowest EDTA Mn concentration of  $180.00 \pm 5.35 \mu\text{g g}^{-1}$  occurred in June 1999, and the greatest in March 1999 at  $405.00 \pm 15.64 \mu\text{g g}^{-1}$  (Figure 5.111).

Table 5.63. Median percentage of monthly EDTA trace metals as a percentage of Total trace metals for Nordrach Series at 0-200 mm and 200-400 mm.

Depth	Pb %	Zn %	Cd %	Cu %	Fe %	Mn %
0-200 mm	70.89	2.77	20.00	29.32	2.62	24.39
200-400 mm	61.27	2.05	20.00	20.68	1.54	14.61

In the surface Tailings, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 2.62%, while the greatest was Pb at 78.09% (Table 5.63). At depth, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 1.54%, while the greatest was Pb at 61.27% (Table 5.63).

#### Monthly variation of other soil parameters

For all months, the monthly CEC, and Exchangeable Mg in the surface soil were consistently greater than at depth (Table 5.64). In September 1998 and March and June 1999, Exchangeable Ca was greater in surface soil than at depth. December 1998, the monthly Exchangeable Ca concentration was greater at depth than in the surface soil. In September 1998 and March and June 1999, the concentration of Exchangeable K was greater in surface soil than at depth. The concentration of Exchangeable Mg was greater at depth than in surface soil in December 1998 (Table 5.64). The concentration of Total P in surface soil was only greater than the concentration at depth in September 1998 and March 1999. In March 1999, Total P concentration was similar for both horizons at  $492.90 \text{ cmol}_c \text{ kg}^{-1}$  and  $495.10 \text{ cmol}_c \text{ kg}^{-1}$  respectively. In September and December 1998, the concentration of Total P was greater at depth than in surface soil (Table 5.64).



Table 5.64. Monthly values for CEC, Exchangeable Ca, Mg and K and Total P at 0-200 mm and 200-400 mm for Nordrach Series.

Parameter	Unit	Sept 1998	Dec 1998	Mar 1999	Jun 1999
CEC (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	20.20	17.42	22.57	19.80
CEC (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	15.05	16.24	19.80	15.44
Exch. Ca (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.50	1.05	0.85	1.04
Exch. Ca (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.35	2.56	0.55	0.57
Exch. Mg (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.16	0.21	0.16	0.21
Exch. Mg (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.08	0.12	0.12	0.12
Exch. K (0-200 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.19	0.26	0.32	0.20
Exch. K (200-400 mm)	cmol <sub>c</sub> kg <sup>-1</sup>	0.15	0.33	0.30	0.12
Total P (0-200 mm)	µg g <sup>-1</sup>	454.30	615.20	492.90	542.30
Total P (200-400 mm)	µg g <sup>-1</sup>	469.30	709.60	495.10	495.10

### Two-Sample analysis

Mann-Whitney analysis or a Two-sample T-test between surface and depth for each stacked soil parameter (n=12 or n=4) showed a significant difference at the  $p \leq 0.05$  level for 8/19 of the Nordrach Series soil parameters (Tables 5.65 and 5.66).

Table 5.65. Monthly values for CEC, Exchangeable Ca, Mg and K and Total P at 0-200 mm and 200-400 mm for Nordrach Series.

Soil Parameter	n=	Mann-Whitney p-value	H <sub>0</sub> : η <sub>1</sub> = η <sub>2</sub> at α=0.05
Total Fe (0-200 mm) v Total Fe (200-400 mm)	12	0.3708	Accepted
Exch. Mg (0-200 mm) v Exch. Mg (200-400 mm)	4	0.0247	Rejected

Table 5.66. Two-Sample T-Tests for Nordrach soil parameters at 0-200 mm *versus* 200-400 mm, where  $H_0: \eta_1 = \eta_2$  was accepted at  $\alpha=0.05$ .

Soil Parameter	n=	T-value	p-value	$H_0: \mu_1 = \mu_2$ at $\alpha=0.05$
pH (0-200 mm) v pH (200-400 mm)	12	-0.37	0.718	Accepted
L-o-I (0-200 mm) v L-o-I (200-400 mm)	12	9.79	0.000	Rejected
Total Pb (0-200 mm) v Total Pb (200-400 mm)	12	-2.36	0.038	Rejected
Total Zn (0-200 mm) v Total Zn (200-400 mm)	12	-1.13	0.284	Accepted
Total Cd (0-200 mm) v Total Cd (200-400 mm)	12	--	--	N.A.
Total Cu (0-200 mm) v Total Cu (200-400 mm)	12	-0.47	0.651	Accepted
Total Mn (0-200 mm) v Total Mn (200-400 mm)	12	-3.21	0.008	Rejected
EDTA Pb (0-200 mm) v EDTA Pb (200-400 mm)	4	2.50	0.088	Accepted
EDTA Zn (0-200 mm) v EDTA Zn (200-400 mm)	4	4.02	0.028	Rejected
EDTA Cd (0-200 mm) v EDTA Cd (200-400 mm)	4	0.06	0.935	Accepted
EDTA Cu (0-200 mm) v EDTA Cu (200-400 mm)	4	5.87	0.010	Rejected
EDTA Fe (0-200 mm) v EDTA Fe (200-400 mm)	4	4.01	0.028	Rejected
EDTA Mn (0-200 mm) v EDTA Mn (200-400 mm)	4	3.35	0.044	Rejected
CEC (0-200 mm) v CEC (200-400 mm)	4	3.82	0.032	Rejected
Exch. Ca (0-200 mm) v Exch. Ca (200-400 mm)	4	-0.32	0.769	Accepted
Exch. K (0-200 mm) v Exch. K (200-400 mm)	4	0.55	0.620	Accepted
Total P (0-200 mm) v Total P (200-400 mm)	4	-0.55	0.621	Accepted

While the majority of the Nordrach soil parameters (11/19) showed no significant difference between values at surface and at depth, only Loss-on-ignition showed a significant difference at the  $p \leq 0.001$  level (Table 5.66). As all values were equal, it was not possible to carry out a Two-sample T-test analysis between Total Cd at surface and depth.

### Pearson correlations

Table 5.67. Pearson correlation values (r-values) and degrees of significance at the  $p=0.001$ , 0.01 and 0.05 levels for stacked Nordrach soil parameters at 0-400 mm (n=24) September 1998 - August 1999.

	pH (0-400 mm)	L-o-I (0-400mm)	Total Pb (0-400 mm)	Total Zn (0-400 mm)	Total Cd (0-400 mm)	Total Cu (0-400 mm)	Total Fe (0-400 mm)
L-o-I (0-400 mm)	-0.099						
Total Pb (0-400 mm)	-0.116	0.515 **					
Total Zn (0-400 mm)	0.178	-0.353	-0.524 **				
Total Cd (0-400 mm)	--	--	--	--			
Total Cu (0-400 mm)	-0.031	-0.136	-0.404 *	0.458 *	-- --		
Total Fe (0-400 mm)	-0.057	-0.028	0.081	0.136	-- --	0.007	
Total Mn (0-400 mm)	0.138	-0.553 **	-0.528 **	0.685 ***	-- --	0.098	-0.025

\*\*\*  $p = 0.001$     \*\*  $p = 0.01$     \*  $p = 0.05$     - Indicates a negative correlation  
 -- all values same in column

Loss-on-Ignition was positively correlated at the  $p=0.01$  level with Total Pb, and negatively correlated with Mn at the  $p=0.01$  level (Table 5.67). Total Pb was

negatively correlated at the  $p \leq 0.05$  level with Total Zn, Cu and Mn. Total Zn was positively correlated at the  $p \leq 0.05$  level with Total Cu and Total Mn.

### 5.5.7 Inter-soil series comparison of monthly variation in soil parameter values

#### Monthly variation of baseline soil study parameters

Of the soil parameters studied in the baseline soil study, the greatest variation in value over the year as represented by its % CV was for surface Total Mn in the Ashen Series at 64.12 % (Table 5.68). Total Cd at both surface and depth in the Nordrach series showed the least variation over the year at 0 %.

Table 5.68. Annual change in soil parameter values as measured by % CV of values for each soil in the baseline soil survey at 0-200 mm and 200-400 mm September 1998 - August 1999 (n=12).

Parameter	Maesbury Series	Thrupe Series	Ashen Series	Tailings	Nordrach Series
pH (0-200 mm) n=12	20.54	4.76	4.84	1.95	4.96
pH (200-400 mm) n=12	14.46	2.13	5.68	2.11	7.67
L-o-I (0-200 mm) n=12	0.18	0.17	0.10	0.12	0.06
L-o-I (200-400 mm) n=12	0.08	0.18	0.11	0.18	0.07
Total Pb (0-200 mm) n=12	35.33	19.80	7.37	25.14	4.22
Total Pb (200-400 mm) n=12	27.61	25.30	8.39	24.54	10.66
Total Zn (0-200 mm) n=12	61.51	17.83	25.93	18.08	18.05
Total Zn (200-400 mm) n=12	37.79	18.71	17.30	21.58	13.22
Total Cd (0-200 mm) n=12	33.33	20.33	25.51	19.27	0.00
Total Cd (200-400 mm) n=12	30.85	31.14	25.51	22.35	0.00
Total Cu (0-200 mm) n=12	15.18	23.55	19.94	14.15	18.3
Total Cu (200-400 mm) n=12	15.05	23.99	34.72	15.86	23.00
Total Fe (0-200 mm) n=12	11.66	11.71	19.42	12.19	4.89
Total Fe (200-400 mm) n=12	11.32	11.50	25.51	17.93	3.97
Total Mn (0-200 mm) n=12	58.90	22.24	64.12	21.47	25.31
Total Mn (200-400 mm) n=12	35.34	20.81	20.54	15.83	14.27

In the Maesbury Series, surface Total Mn showed the greatest variation over the year at 58.90%, and Loss-on-Ignition at depth showed the least at 0.08%. Total Cd at 31.14% was the most variable and surface Loss-on-Ignition at 0.17% the least variable parameter over the year in the Thrupe Series (Table 5.68). In the Ashen Series, surface Total Mn was the most variable parameter at 64.12%, and surface Loss-on-Ignition at 0.10% was the least variable. For Tailings, surface Total Pb was the most variable parameter over the year at 25.14%, while surface Loss-on-Ignition at 0.12% was the least. Surface Total Mn was the most variable parameter at 25.31% in the Nordrach Series, and Total Cd at both surface and depth were the least variable at 0%.

Table 5.69. Soil series ranked by order of magnitude of variability over the year as expressed by % CV for each soil parameter.

<b>Soil Parameter</b>	<b>Soil Series in order of magnitude of variance (%CV) over the year</b>
pH (0-200 mm) n=12	Maesbury>Nordrach>Ashen>Thrupe>Tailings
pH (200-400 mm) n=12	Maesbury>Nordrach>Ashen>Thrupe>Tailings
L-o-I (0-200 mm) n=12	Maesbury>Thrupe>Tailings>Ashen>Nordrach
L-o-I (200-400 mm) n=12	Thrupe>Tailings>Ashen>Maesbury>Nordrach
Total Pb (0-200 mm) n=12	Maesbury>Tailings>Thrupe>Ashen>Nordrach
Total Pb (200-400 mm) n=12	Maesbury>Thrupe>Tailings>Nordrach>Ashen
Total Zn (0-200 mm) n=12	Maesbury>Ashen>Tailings>Nordrach>Thrupe
Total Zn (200-400 mm) n=12	Maesbury>Tailings>Thrupe>Ashen>Nordrach
Total Cd (0-200 mm) n=12	Maesbury>Ashen>Thrupe>Tailings>Nordrach
Total Cd (200-400 mm) n=12	Thrupe>Maesbury>Ashen>Tailings>Nordrach
Total Cu (0-200 mm) n=12	Thrupe>Ashen>Nordrach>Maesbury>Tailings
Total Cu (200-400 mm) n=12	Ashen>Thrupe>Nordrach>Tailings>Maesbury
Total Fe (0-200 mm) n=12	Ashen>Tailings>Thrupe>Maesbury>Nordrach
Total Fe (200-400 mm) n=12	Ashen>Tailings>Thrupe>Maesbury>Nordrach
Total Mn (0-200 mm) n=12	Ashen>Maesbury>Nordrach>Thrupe>Tailings
Total Mn (200-400 mm) n=12	Maesbury>Thrupe>Ashen>Tailings>Nordrach

The order of magnitude of variation over the year for each parameter at surface and depth ranked by soil series in the baseline soil study showed that for the majority of the parameters (8/12 or 66.66% ), the greatest variation occurred in the

Maesbury Series (Table 5.69). Table 5.70 confirmed that in terms of the mean % CV of all soil parameter % CV for the five soil series, the Maesbury Series showed the greatest variability throughout the year at 25.57%. The Nordrach Series showed the least annual variation for the majority of the soil parameters in the baseline study (8/12 or 66.66%) (Table 5.69). Table 5.70 confirmed that in terms of the mean % CV of all soil parameter % CV for the five soil series, the Nordrach Series showed the least variability throughout the year at 9.29%.

Table 5.70. Ranked mean annual change of all parameter values at 0-200 mm and 200-400 mm measured in baseline study by soil series expressed as % CV.

Soil Series	Mean % CV	S.D.
Maesbury (n=16)	25.57	17.49
Ashen (n=16)	19.06	15.42
Thrupe (n=16)	15.88	9.36
Tailings (n=16)	14.55	8.49
Nordrach (n=16)	9.29	8.22

In terms of the trace metal parameters measured in the baseline soil survey, the Maesbury Series showed the greatest variation at 31.16% CV (Table 5.71), while the Nordrach Series showed the least variation between all soil parameters over the year at 8.37% CV.

Table 5.71. Ranked mean annual change of trace metal values at 0-200 mm and 200-400 mm measured in baseline study by soil series expressed as % CV.

Soil Series	Mean % CV	S.D.
Maesbury (n=12)	31.16	16.01
Ashen (n=12)	24.52	13.98
Thrupe (n=12)	20.58	5.24
Tailings (n=12)	19.03	3.92
Nordrach (n=12)	11.32	8.37

Of those parameters analysed in the baseline soil survey, Total Mn in the surface soil was the most variable parameter at 38.41% CV, while Loss-on-Ignition at depth was the least variable over the year at 0.12% CV (Table 5.72).

Table 5.72. Ranked mean % CV of parameter values at 0-200 mm and 200-400 mm in the baseline study soil for all soil series.

<b>Soil Parameter</b>	<b>Mean % CV</b>	<b>S.D.</b>
Total Mn (0-200 mm) n=12	38.41	18.98
Total Zn (0-200 mm) n=12	28.28	16.90
Total Cu (200-400 mm) n=12	22.52	7.09
Total Cd (200-400 mm) n=12	21.97	11.47
Total Zn (200-400 mm) n=12	21.72	8.47
Total Mn (200-400 mm) n=12	21.36	7.45
Total Cd (0-200 mm) n=12	19.69	11.03
Total Pb (200-400 mm) n=12	19.30	8.08
Total Pb (0-200 mm) n=12	18.37	11.46
Total Cu (0-200 mm) n=12	18.22	3.38
Total Fe (200-400 mm) n=12	14.05	7.24
Total Fe (0-200 mm) n=12	11.97	4.60
pH (0-200 mm) n=12	7.41	6.66
pH (200-400 mm) n=12	6.41	4.55
L-o-I (0-200 mm) n=12	0.13	0.04
L-o-I (200-400 mm) n=12	0.12	0.05

The general trend for all trace metals in the Maesbury and Thrupe soils and the Tailings was an overall decrease in concentration over the sampling period. Soil Pb, Zn and Cu at 0-200 mm also decreased in the Ashen soil and Pb, Fe and Cu at 0-200 mm in the Nordrach soil (Table 5.73).

Table 5.73. Summary of overall percentage loss (%), no change (N/C) or Net Gain (N.G) of trace metals from four soil series and Tailings between September 1998-August 1999.

			Overall Percentage Loss between Sept 1998-Aug 1999 (%)				
Parameter	Unit	n =	Maesbury Series	Thrupe Series	Ashen Series	Tailings	Nordrach Series
Total Pb (0-200 mm)	$\mu\text{g g}^{-1}$	12	58.8	38.0	13.2	40.5	14.0
Total Pb (200-400 mm)	$\mu\text{g g}^{-1}$	12	37.8	48.1	29.3	36.8	20.9
Total Zn (0-200 mm)	$\mu\text{g g}^{-1}$	12	72.0	32.9	42.2	9.5	N.G
Total Zn (200-400 mm)	$\mu\text{g g}^{-1}$	12	53.7	21.2	6.9	24.1	N.G
Total Cu (0-200 mm)	$\mu\text{g g}^{-1}$	12	12.9	34.8	13.2	6.5	20.0
Total Cu (200-400 mm)	$\mu\text{g g}^{-1}$	12	29.1	47.3	N.G	19.3	N.G
Total Cd (0-200 mm)	$\mu\text{g g}^{-1}$	12	50	N/C	N/C	N.G	N/C
Total Cd (200-400 mm)	$\mu\text{g g}^{-1}$	12	N.G	N/C	N/C	27	N/C
Total Fe (0-200 mm)	$\mu\text{g g}^{-1}$	12	26.9	16.9	N.G	9.5	3.2
Total Fe (200-400 mm)	$\mu\text{g g}^{-1}$	12	24.1	24.2	N.G	36.6	2.5
Total Mn (0-200 mm)	$\mu\text{g g}^{-1}$	12	72.9	36.5	N.G	22.9	N.G
Total Mn (200-400 mm)	$\mu\text{g g}^{-1}$	12	50.6	27.2	N.G	13.7	N.G

#### Pearson correlations

When all monthly soil parameter data were stacked, pH and all Total metals were positively correlated with each other at the  $p=0.001$  level (Table 5.74). Loss-on-Ignition was positively correlated with Total Pb, Cd and Cu at the  $p\leq 0.05$  level.



Table 5.74. Pearson correlation values (r-values) and degrees of significance at the p=0.001, 0.01 and 0.05 levels for all stacked soil parameters (0-400 mm) for September 1998 - August 1999 (n=120).

	pH (0-400 mm)	L-o-I (0-400mm)	Total Pb (0-400 mm)	Total Zn (0-400 mm)	Total Cd (0-400 mm)	Total Cu (0-400 mm)	Total Fe (0-400 mm)
L-o-I (0-400 mm)	0.033						
Total Pb (0-400 mm)	0.918 ***	0.210 *					
Total Zn (0-400 mm)	0.912 ***	0.179	0.975 ***				
Total Cd (0-400 mm)	0.815 ***	0.267 **	0.879 ***	0.801 ***			
Total Cu (0-400 mm)	0.857 ***	0.360 ***	0.945 ***	0.923 ***	0.888 ***		
Total Fe (0-400 mm)	0.784 ***	0.161	0.854 ***	0.842 ***	0.809 ***	0.870 ***	
Total Mn (0-400 mm)	0.606 ***	0.131	0.656 ***	0.678 ***	0.559 ***	0.675 ***	0.896 ***

\*\*\* p = 0.001    \*\* p = 0.01    \* p = 0.05    - Indicates a negative correlation

#### Monthly and quarterly variation of baseline soil study parameters

Of all pararameters for all soil series as represented by % CV, Exchangeable Ca at depth in the Nordrach Series showed the greatest variation in value over the year at 89.38 % CV, with a range of 0.35 - 2.56 cmol<sub>c</sub> kg<sup>-1</sup> (Tables 5.75 and 5.77).

Total Cd at both surface and depth in the Nordrach series showed the least variation over the year at 0 %, with a soil concentration of 0.5 µg g<sup>-1</sup> (Tables 5.75 and 5.76).

Table 5.75. Annual change in soil parameter values as measured by % CV of values for each soil at 0-200 mm and 200-400 mm September 1998 - August 1999 (n=12) and quarterly (n=4).

Parameter	Maesbury Series	Thrupe Series	Ashen Series	Tailings Series	Nordrach Series
pH (0-200 mm) n=12	20.54	4.76	4.84	1.95	4.96
pH (200-400 mm) n=12	14.46	2.13	5.68	2.11	7.67
L-o-I (0-200 mm) n=12	0.18	0.17	0.10	0.12	0.06
L-o-I (200-400 mm) n=12	0.08	0.18	0.11	0.18	0.07
Total Pb (0-200 mm) n=12	35.33	19.80	7.37	25.14	4.22
Total Pb (200-400 mm) n=12	27.61	25.30	8.39	24.54	10.66
Total Zn (0-200 mm) n=12	61.51	17.83	25.93	18.08	18.05
Total Zn (200-400 mm) n=12	37.79	18.71	17.30	21.58	13.22
Total Cd (0-200 mm) n=12	33.33	20.33	25.51	19.27	0.00
Total Cd (200-400 mm) n=12	30.85	31.14	25.51	22.35	0.00
Total Cu (0-200 mm) n=12	15.18	23.55	19.94	14.15	18.3
Total Cu (200-400 mm) n=12	15.05	23.99	34.72	15.86	23.00
Total Fe (0-200 mm) n=12	11.66	11.71	19.42	12.19	4.89
Total Fe (200-400 mm) n=12	11.32	11.50	25.51	17.93	3.97
Total Mn (0-200 mm) n=12	58.90	22.24	64.12	21.47	25.31
Total Mn (200-400 mm) n=12	35.34	20.81	20.54	15.83	14.27
EDTA Pb (0-200 mm) n=4	32.24	33.31	4.63	11.52	19.28
EDTA Pb (200-400 mm) n=4	11.77	33.32	5.90	17.71	11.37
EDTA Zn (0-200 mm) n=4	22.40	26.38	7.49	17.07	14.03
EDTA Zn (200-400 mm) n=4	29.52	18.68	3.04	12.75	28.51
EDTA Cd (0-200 mm) n=4	29.80	27.92	23.67	10.50	13.25
EDTA Cd (200-400 mm) n=4	44.97	15.47	13.74	19.36	22.14
EDTA Cu (0-200 mm) n=4	50.64	18.15	15.64	34.27	35.27
EDTA Cu (200-400 mm) n=4	29.01	33.16	15.68	34.02	35.16
EDTA Fe (0-200 mm) n=4	29.80	27.92	23.67	10.50	13.25
EDTA Fe (200-400 mm) n=4	44.97	15.47	13.74	19.36	22.14
EDTA Mn (0-200 mm) n=4	65.54	39.29	12.61	11.71	22.65
EDTA Mn (200-400 mm) n=4	31.74	23.78	26.78	13.13	32.72
CEC (0-200 mm) n=4	12.32	20.29	18.89	20.84	20.88
CEC (200-400 mm) n=4	16.41	21.95	13.75	23.88	22.78
Exch. Ca (0-200 mm) n=4	65.71	52.96	13.21	16.74	25.88
Exch. Ca (200-400 mm) n=4	55.35	27.58	19.38	18.64	89.38
Exch. Mg (0-200 mm) n=4	16.38	18.13	7.06	24.10	13.51
Exch. Mg (200-400 mm) n=4	11.95	9.36	30.15	25.60	15.75
Exch. K (0-200 mm) n=4	21.35	20.98	21.66	18.65	21.50
Exch. K (200-400 mm) n=4	30.50	19.92	17.37	28.50	40.55
Total P (0-200 mm) n=4	10.94	21.45	29.39	19.23	11.43
Total P (200-400 mm) n=4	22.83	11.26	5.49	28.17	17.90

In the Maesbury Series, surface EDTA Mn showed the greatest variation over the year at 65.54% CV with a range of 27 - 235  $\mu\text{g g}^{-1}$ , and Loss-on-Ignition at depth showed the least at 0.08% CV with a range of 9.21 - 12.47 %. In the Thrupe Series, surface Exchangeable Ca at 52.96% CV with a range of 2.49 - 8.22  $\text{cmol}_\text{c} \text{ kg}^{-1}$  was the most variable and surface Loss-on-Ignition at 0.17% CV with a range of 7.33 - 14.65% the least variable parameter over the year (Tables 5.75 - 5.77).

In the Ashen Series, surface Total Mn was the most variable parameter at 64.12% CV with a range of 23 - 153  $\mu\text{g g}^{-1}$ , and surface Loss-on-Ignition at 0.10% CV was the least variable with a range of 9.87 - 13.40% (Tables 5.75 and 5.77). For Tailings, surface EDTA Cu was the most variable parameter over the year at 34.27% CV with a range of 10.80 - 14.53  $\mu\text{g g}^{-1}$ , while surface Loss-on-Ignition at 0.12% CV was the least variable with a range of 12.84 - 18.81% (Tables 5.75 - 5.77). In the Nordrach Series, Exchangeable Ca at depth was the most variable parameter at 89.38% CV, with a range of 0.35 - 2.56  $\text{cmol}_\text{c} \text{ kg}^{-1}$ , and Total Cd at both surface and depth were the least variable at 0% CV with a soil concentration of 0.5  $\mu\text{g g}^{-1}$  (Tables 5.75 - 5.77).

Table 5.76. Summary of ranges of parameter data (min-max) for all soil series at 0-200 mm and 200-400 mm (n=12) September 1998 - August 1999.

Parameter	Unit	n	Maesbury Series	Thrupe Series	Ashen Series	Tailings	Nordrach Series
<b>pH (0-200 mm)</b>	pH	12	3.88 - 6.46	5.21 - 6.04	3.32 - 4.02	7.01 - 7.49	4.47 - 5.16
<b>pH (200-400 mm)</b>	pH	12	4.72 - 6.92	5.82 - 6.22	3.36 - 4.28	7.31 - 7.79	3.88 - 5.22
<b>L-o-I (0-200 mm)</b>	%	12	14.27 - 26.14	7.33 - 14.65	9.87 - 13.40	12.84 - 18.81	11.35 - 13.69
<b>L-o-I (200-400 mm)</b>	%	12	9.21 - 12.47	6.01 - 11.13	6.59 - 9.56	8.19 - 14.86	9.45 - 11.67
<b>Total Pb (0-200 mm)</b>	µg g <sup>-1</sup>	12	4 137 - 13 863	8 093 - 20 140	1 656 - 2 125	49 067 - 99 500	4 123 - 4 883
<b>Total Pb (200-400 mm)</b>	µg g <sup>-1</sup>	12	7 730 - 760	7 763 - 18 227	1 228 - 1 736	54 933 - 112 767	3 347 - 5 347
<b>Total Zn (0-200 mm)</b>	µg g <sup>-1</sup>	12	257 - 2 500	800 - 1 763	26.67 - 63.33	7 667 - 14 400	213 - 837
<b>Total Zn (200-400 mm)</b>	µg g <sup>-1</sup>	12	572 - 1 833	803 - 1 650	18.67 - 36.67	8 567 - 16 867	240 - 393
<b>Total Cd (0-200 mm)</b>	µg g <sup>-1</sup>	12	1.00 - 2.00	0.50 - 1.00	0.50 - 1.00	10.00 - 18.67	0.5 - 0.5
<b>Total Cd (200-400 mm)</b>	µg g <sup>-1</sup>	12	0.05 - 2.00	0.50 - 1.00	0.50 - 1.00	9.67 - 22.33	0.5 - 0.5
<b>Total Cu (0-200 mm)</b>	µg g <sup>-1</sup>	12	20.00 - 33.00	11.33 - 27.33	4.00 - 7.33	65 - 106	7.67 - 15.67
<b>Total Cu (200-400 mm)</b>	µg g <sup>-1</sup>	12	16.00 - 28.00	8.67 - 19.00	2.33 - 7.33	76 - 119	9.00 - 19.00
<b>Total Fe (0-200 mm)</b>	µg g <sup>-1</sup>	12	12 683 - 19 667	15 350 - 22 123	4 637 - 9.043	52 200 - 82 867	23 026 - 27 763
<b>Total Fe (200-400 mm)</b>	µg g <sup>-1</sup>	12	17 020 - 23 386	14 530 - 21 443	7 683 - 16 350	57 033 - 100 267	24 327 - 28 123
<b>Total Mn (0-200 mm)</b>	µg g <sup>-1</sup>	12	78 - 531	219 - 542	23 - 153	2 050 - 4 500	1 097 - 2 580
<b>Total Mn (200-400 mm)</b>	µg g <sup>-1</sup>	12	213 - 602	188 - 374	92 - 189	2 240 - 3 883	1 513 - 2 437

Table 5.77. Summary of ranges of parameter data (min-max) for all soil series at 0-200 mm and 200-400 mm quarterly sampling (n=4) September 1998 - August 1999.

Parameter	Unit	n =	Maesbury Series	Thrupe Series	Ashen Series	Tailings	Nordrach Series
EDTA Pb (0-200 mm)	$\mu\text{g g}^{-1}$	4	4 787 - 11 860	6 823 - 18 873	1 662 - 1 844	19 850 - 27 580	2 313 - 3 827
EDTA Pb (200-400 mm)	$\mu\text{g g}^{-1}$	4	7 697 - 10 587	7 847 - 17 407	1 289 - 1 513	16 730 - 25 750	2 283 - 3 047
EDTA Zn (0-200 mm)	$\mu\text{g g}^{-1}$	4	288 - 493	64 - 127	4.50 - 5.47	1 457 - 2 197	7.27 - 10.63
EDTA Zn (200-400 mm)	$\mu\text{g g}^{-1}$	4	179 - 410	69 - 113	3.67 - 3.97	1 287 - 1 723	4.73 - 9.20
EDTA Cd (0-200 mm)	$\mu\text{g g}^{-1}$	4	0.10 - 1.83	0.40 - 0.97	0.05 - 0.05	3.07 - 3.83	0.01 - 0.20
EDTA Cd (200-400 mm)	$\mu\text{g g}^{-1}$	4	0.30 - 1.33	0.43 - 0.77	0.05 - 0.05	2.53 - 3.17	0.10 - 0.10
EDTA Cu (0-200 mm)	$\mu\text{g g}^{-1}$	4	11.2 - 24.17	4.70 - 10.83	1.87 - 3.17	10.80 - 14.53	2.97 - 4.20
EDTA Cu (200-400 mm)	$\mu\text{g g}^{-1}$	4	8.70 - 21.50	4.77 - 7.17	1.10 - 1.63	8.70 - 13.77	1.83 - 3.50
EDTA Fe (0-200 mm)	$\mu\text{g g}^{-1}$	4	1 113 - 3 740	840 - 1 345	999 - 1 422	190 - 428	643 - 1 323
EDTA Fe (200-400 mm)	$\mu\text{g g}^{-1}$	4	803 - 1 780	561 - 1 160	904 - 1 311	124 - 312	302 - 677
EDTA Mn (0-200 mm)	$\mu\text{g g}^{-1}$	4	27 - 235	90 - 346	2.70 - 3.77	91 - 122	248 - 480
EDTA Mn (200-400 mm)	$\mu\text{g g}^{-1}$	4	84 - 165	76 - 146	3.23 - 7.33	75 - 105	180 - 405
CEC (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	20.99 - 28.51	12.28 - 19.80	15.05 - 17.82	14.26 - 20.59	17.42 - 22.57
CEC (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	15.84 - 20.59	11.09 - 13.86	13.86 - 17.03	11.09 - 13.86	15.05 - 19.80
Exch. Ca (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	1.47 - 21.16	2.49 - 8.22	0.42 - 0.60	18.18 - 29.38	0.50 - 1.05
Exch. Ca (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	2.27 - 13.94	2.44 - 4.83	0.22 - 0.38	19.92 - 24.11	0.35 - 2.56
Exch. Mg (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.49 - 0.78	0.62 - 0.99	0.21 - 0.25	0.29 - 0.58	0.16 - 0.21
Exch. Mg (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.33 - 0.45	0.70 - 0.86	0.08 - 0.16	0.21 - 0.41	0.08 - 0.12
Exch. K (0-200 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.21 - 0.34	0.19 - 0.32	0.17 - 0.29	0.24 - 0.38	0.19 - 0.32
Exch. K (200-400 mm)	$\text{cmol}_c \text{ kg}^{-1}$	4	0.12 - 0.26	0.17 - 0.28	0.12 - 0.19	0.12 - 0.28	0.12 - 0.33
Total P (0-200 mm)	$\mu\text{g g}^{-1}$	4	570 - 759	431 - 776	227 - 499	1520 - 2 383	454 - 615
Total P (200-400 mm)	$\mu\text{g g}^{-1}$	4	555 - 1 081	463 - 609	281 - 326	1 066 - 2 484	469 - 710

The order of magnitude of variation over the year for each parameter at surface and depth ranked by soil series showed that for the majority of the parameters, the greatest variation occurred in the Maesbury Series (Table 5.78).

Table 5.78. Soil series ranked by order of magnitude of variability over the year as expressed by % CV for each soil parameter.

<b>Soil Parameter</b>	<b>Ranked order of variance (% CV)</b>
pH (0-200 mm) n=12	Maesbury>Nordrach>Ashen>Thrupe>Tailings
pH (200-400 mm) n=12	Maesbury>Nordrach>Aahen>Thrupe>Tailings
L-o-I (0-200 mm) n=12	Maesbury>Thrupe>Tailings>Ashen>Nordrach
L-o-I (200-400 mm) n=12	Thrupe>Tailings>Ashen>Maesbury>Nordrach
Total Pb (0-200 mm) n=12	Maesbury>Tailings>Thrupe>Ashen>Nordrach
Total Pb (200-400 mm) n=12	Maesbury>Thrupe>Tailings>Nordrach>Ashen
Total Zn (0-200 mm) n=12	Maesbury>Ashen>Tailings>Nordrach>Thrupe
Total Zn (200-400 mm) n=12	Maesbury>Tailings>Thrupe>Ashen>Nordrach
Total Cd (0-200 mm) n=12	Maesbury>Ashen>Thrupe>Tailings>Nordrach
Total Cd (200-400 mm) n=12	Thrupe>Maesbury>Ashen>Tailings>Nordrach
Total Cu (0-200 mm) n=12	Thrupe>Ashen>Nordrach>Maesbury>Tailings
Total Cu (200-400 mm) n=12	Ashen>Thrupe>Nordrach>Tailings>Maesbury
Total Fe (0-200 mm) n=12	Ashen>Tailings>Thrupe>Maesbury>Nordrach
Total Fe (200-400 mm) n=12	Ashen>Tailings>Thrupe>Maesbury>Nordrach
Total Mn (0-200 mm) n=12	Ashen>Maesbury>Nordrach>Thrupe>Tailings
Total Mn (200-400 mm) n=12	Maesbury>Thrupe>Ashen>Tailings>Nordrach
EDTA Pb (0-200 mm) n=4	Thrupe>Maesbury>Nordrach>Tailings>Ashen
EDTA Pb (200-400 mm) n=4	Thrupe>Tailings>Maesbury>Nordrach>Ashen
EDTA Zn (0-200 mm) n=4	Thrupe>Maesbury>Tailings>Nordrach>Ashen
EDTA Zn (200-400 mm) n=4	Maesbury>Nordrach>Thrupe>Tailings>Ashen
EDTA Cd (0-200 mm) n=4	Maesbury>Thrupe>Ashen>Nordrach>Tailings
EDTA Cd (200-400 mm) n=4	Maesbury>Nordrach>Tailings>Thrupe>Ashen
EDTA Cu (0-200 mm) n=4	Maesbury>Thrupe>Ashen>Nordrach>Tailings
EDTA Cu (200-400 mm) n=4	Maesbury>Nordrach>Tailings>Thrupe>Ashen
EDTA Fe (0-200 mm) n=4	Maesbury>Nordrach>Tailings>Thrupe>Ashen
EDTA Fe (200-400 mm) n=4	Nordrach>Tailings>Thrupe>Maesbury>Ashen
EDTA Mn (0-200 mm) n=4	Maesbury>Thrupe>Nordrach>Ashen>Tailings
EDTA Mn (200-400 mm) n=4	Nordrach>Maesbury>Ashen>Thrupe>Tailings
CEC (0-200 mm) n=4	Ashen>Nordrach>Thrupe>Tailings>Maesbury
CEC (200-400 mm) n=4	Tailings>Nordrach>Thrupe>Maesbury>Ashen
Exch. Ca (0-200 mm) n=4	Maesbury>Thrupe>Nordrach>Tailings>Ashen
Exch. Ca (200-400 mm) n=4	Nordrach>Maesbury>Thrupe>Ashen>Tailings
Exch. Mg (0-200 mm) n=4	Tailings>Thrupe>Maesbury>Nordrach>Ashen
Exch. Mg (200-400 mm) n=4	Ashen>Tailings>Nordrach>Maesbury>Thrupe
Exch. K (0-200 mm) n=4	Ashen>Nordrach>Maesbury>Thrupe>Tailings
Exch. K (200-400 mm) n=4	Nordrach>Maesbury>Tailings>Thrupe>Ashen
Total P (0-200 mm) n=4	Ashen>Thrupe>Tailings>Nordrach>Maesbury
Total P (200-400 mm) n=4	Tailings>Maesbury>Nordrach>Thrupe>Ashen

Table 5.79 confirmed that in terms of the mean % CV of all soil parameter % CV for the five soil series, the Maesbury Series showed the greatest variability throughout the year at 28.82% CV. The Ashen Series and Tailings showed the least variability at 17.05% CV and 17.61% CV respectively.

Table 5.79. Ranked Mean annual change of all soil parameter values at 0-200 mm and 200-400 mm by soil series expressed as % CV.

Soil Series	Mean % CV	S.D.
Maesbury (n=38)	28.82	17.10
Thrupe (n=38)	20.81	10.41
Nordrach (n=38)	18.37	15.52
Tailings (n=38)	17.61	8.05
Ashen (n=38)	17.05	11.78

In a ranking of the soil parameters for all soil series, Exchangeable Ca at depth showed the greatest variability throughout the year at 42.07% CV (Table 5.80). Loss-on-Ignition at depth was the least variable parameter throughout the year at 0.12 % CV, although Loss-on-Ignition in surface soil was only 0.01% greater at 0.13% CV (Table 5.80).

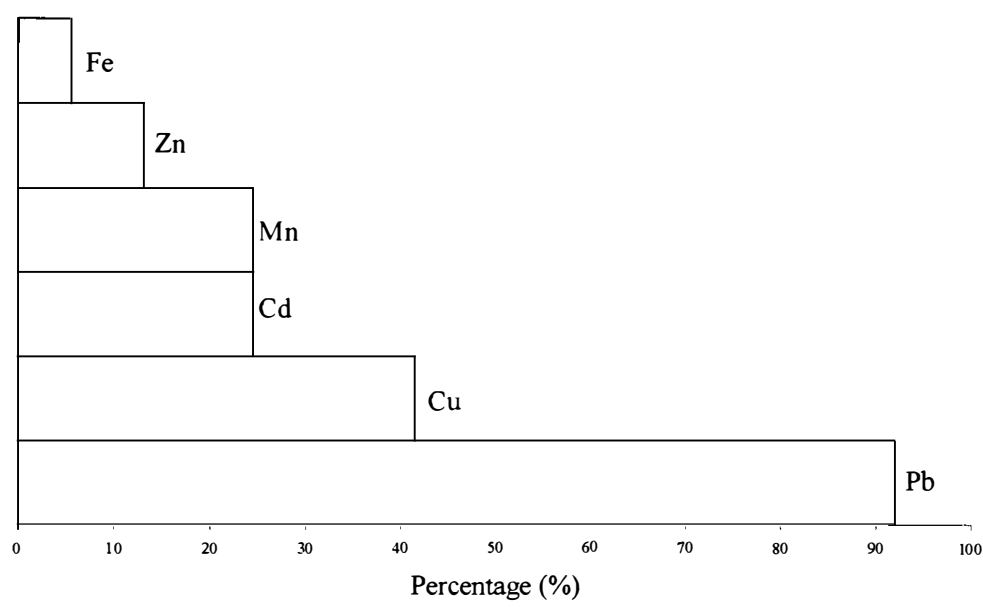
Table 5.80. Ranked mean % CV of soil parameter values at 0-200 mm and 200-400 mm in all soil series.

<b>Soil Parameter</b>	<b>Mean % CV</b>	<b>S.D.</b>
Exch. Ca (200-400 mm) n=4	42.07	27.16
Total Mn (0-200 mm) n=12	38.41	18.98
Exch. Ca (0-200 mm) n=4	34.90	20.77
EDTA Cu (0-200 mm) n=4	30.79	12.77
EDTA Mn (0-200 mm) n=4	30.36	20.20
EDTA Cu (200-400 mm) n=4	29.41	7.17
Total Zn (0-200 mm) n=12	28.28	16.90
Exch. K (200-400 mm) n=4	27.37	8.25
EDTA Mn (200-400 mm) n=4	25.63	7.05
EDTA Cd (200-400 mm) n=4	23.14	11.31
EDTA Fe (200-400 mm) n=4	23.14	11.31
Total Cu (200-400 mm) n=12	22.52	7.09
Total Cd (200-400 mm) n=12	21.97	11.47
Total Zn (200-400 mm) n=12	21.72	8.47
Total Mn (200-400 mm) n=12	21.36	7.45
EDTA Cd (0-200 mm) n=4	21.03	7.78
EDTA Fe (0-200 mm) n=4	21.03	7.78
Exch. K (0-200 mm) n=4	20.83	1.11
EDTA Pb (0-200 mm) n=4	20.20	11.27
CEC (200-400 mm) n=4	19.75	3.96
Total Cd (0-200 mm) n=12	19.69	11.03
Total Pb (200-400 mm) n=12	19.30	8.08
CEC (0-200 mm) n=4	18.64	3.24
Exch. Mg (200-400 mm) n=4	18.56	8.00
EDTA Zn (200-400 mm) n=4	18.50	9.94
Total P (0-200 mm) n=4	18.49	6.86
Total Pb (0-200 mm) n=12	18.37	11.46
Total Cu (0-200 mm) n=12	18.22	3.38
EDTA Zn (0-200 mm) n=4	17.47	6.56
Total P (200-400 mm) n=4	17.13	8.06
EDTA Pb (200-400 mm) n=4	16.01	9.43
Exch. Mg (0-200 mm) n=4	15.84	5.59
Total Fe (200-400 mm) n=12	14.05	7.24
Total Fe (0-200 mm) n=12	11.97	4.60
pH (0-200 mm) n=12	7.41	6.66
pH (200-400 mm) n=12	6.41	4.55
L-o-I (0-200 mm) n=12	0.13	0.04
L-o-I (200-400 mm) n=12	0.12	0.05



For surface soil in all soil series, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 5.52% (Figure 5.112). The greatest EDTA available trace metal as a percentage of the Total trace metal concentration was Pb at 91.95%.

Figure 5.112. Median percentage of EDTA trace metals as a percentage of Total trace metals for all soil Series at 0-200 mm.



For all soil series at depth, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 4.79% (Figure 5.113). The greatest EDTA available trace metal as a percentage of the Total trace metal concentration was Pb at 70.66%.

Figure 5.113. Median percentage of EDTA trace metals as a percentage of Total trace metals for all soil Series at 200-400 mm.

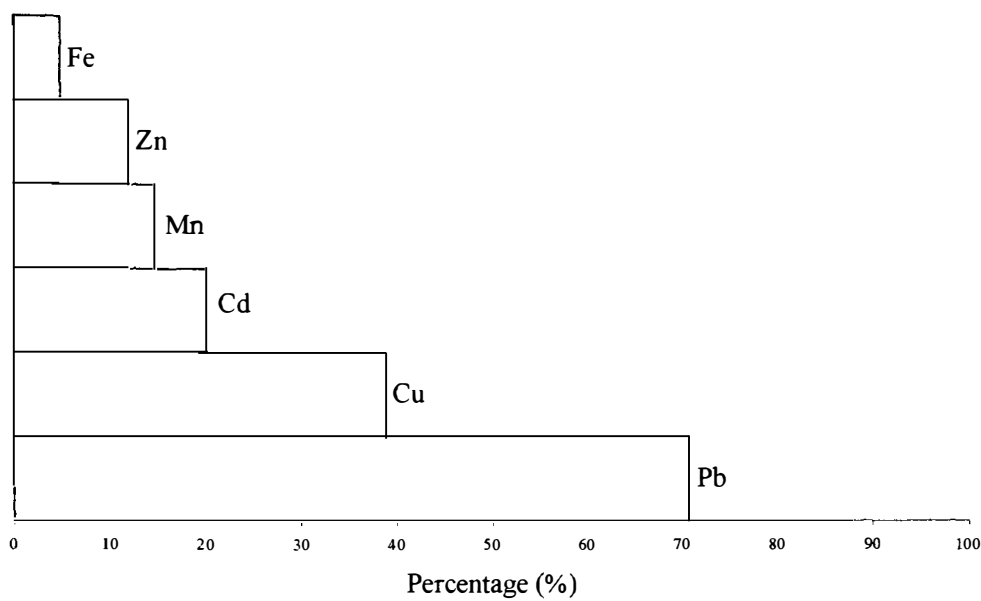
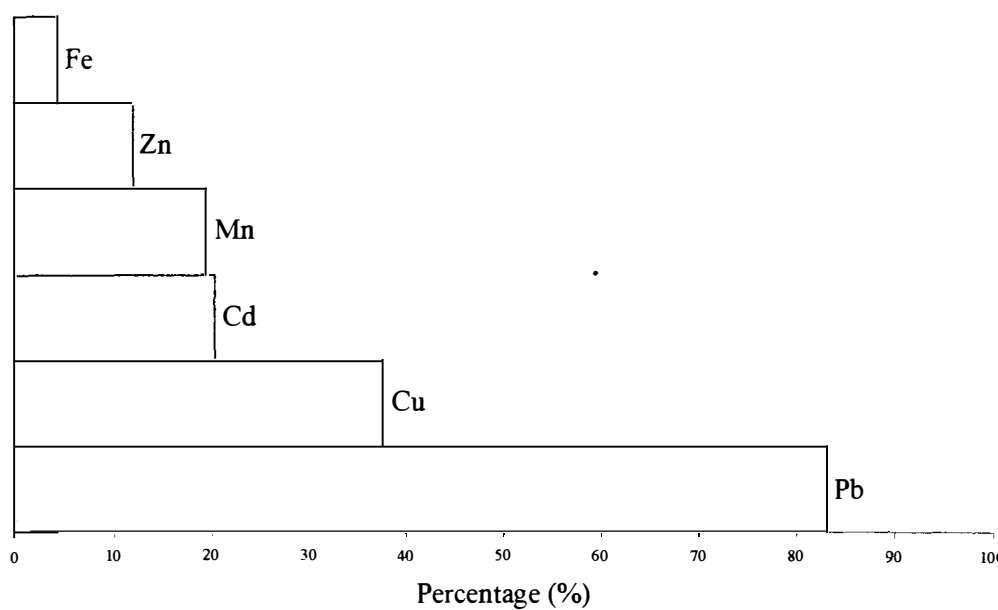


Figure 5.114. Median percentage of EDTA trace metals as a percentage of Total trace metals for all soil Series at 0-400 mm.



For all soil series, the least EDTA available trace metal as a percentage of the Total metal concentration was Fe at 4.43% (Figure 5.114). The greatest EDTA available trace metal as a percentage of the Total trace metal concentration was Pb at 83.13%.

The greatest EDTA available Pb and Fe as a percentage of the Total Pb and Fe concentration for both surface and depth occurred in the Ashen soil (Table 5.81).

The greatest EDTA available Zn, Cd and Cu as a percentage of the Total Zn, Cd and Cu concentration for both surface and depth occurred in the Maesbury soil (Table 5.81). The greatest EDTA available Mn as a percentage of the Total Mn concentration for both surface and depth was found in the Ashen soil (Table 5.81).

Table 5.81. Summary of median percentage of monthly EDTA trace metals as a percentage of Total trace metals for all soil series at 0-200 mm and 200-400 mm.

<b>Parameter</b>	<b>Maesbury Series</b>	<b>Thrupe Series</b>	<b>Ashen Series</b>	<b>Tailings</b>	<b>Nordrach Series</b>
Pb % 0-200 mm	92.03	91.95	93.62	35.06	70.89
Pb % 200-400 mm	70.66	99.30	91.62	28.27	61.27
Zn % 0-200 mm	38.08	7.62	12.99	15.72	2.77
Zn % 200-400 mm	20.99	8.01	13.58	11.89	2.05
Cd % 0-200 mm	85.00	75.00	10.00	24.45	20.00
Cd % 200-400 mm	105.00	65.00	10.00	15.16	20.00
Cu % 0-200 mm	59.02	41.53	41.37	14.68	29.32
Cu % 200-400 mm	47.42	43.20	38.81	11.00	20.68
Fe % 0-200 mm	11.94	5.52	15.57	0.37	2.62
Fe % 200-400 mm	6.70	4.79	9.44	0.27	1.54
Mn % 0-200 mm	58.79	63.39	7.32	3.81	24.39
Mn % 200-400 mm	34.04	47.88	3.93	3.45	14.61

With the exception of Zn and Cd, the majority of the least EDTA available trace metals as a percentage of the Total concentration for both surface and depth occurred in the Tailings (Table 5.81). The least EDTA available Zn as a percentage of the Total Zn concentration for both surface and depth occurred in the Nordrach soil. The least EDTA available Cd as a percentage of the Total Cd concentration for both surface and depth occurred in the Ashen soil (Table 5.81).

#### Pearson correlations

When all quarterly soil parameter data were stacked, all Total metals, pH and EDTA Zn and Cd were positively correlated with each other at the  $p \leq 0.05$  level (Table 5.82). There were also significant positive correlations at the  $p \geq 0.05$  level between all Total metals and EDTA metals, with the exception of EDTA Fe, which was negatively correlated with all Total metals at the  $p \leq 0.05$  level, and EDTA Cu and Mn, which showed no significant correlation. Exchangeable Ca and Total P were positively correlated with all Total and EDTA metals at the  $p \leq 0.05$  level, except EDTA Fe, which showed significant negative correlations at the  $p \leq 0.01$  level. Exchangeable Mg was positively correlated at the  $p = 0.001$  level with EDTA Pb, Zn, Cd and Cu (Table 5.82).

Table 5.82. Pearson correlation r-values and degrees of significance for all stacked quarterly soil parameters at 0-400 mm (n=40).

	pH	L-o-I	Total Pb	Total Zn	Total Cd	Total Cu	Total Fe	Total Mn
L-o-I	0.039							
Total Pb	-0.921 ***	0.215						
Total Zn	0.924 ***	0.227	0.979 ***					
Total Cd	0.830 ***	0.231	0.869 ***	0.794 ***				
Total Cu	0.845 ***	0.373 *	0.949 ***	0.949 ***	0.849 ***			
Total Fe	0.806 ***	0.096	0.858 ***	0.842 ***	0.802 ***	0.870 ***		
Total Mn	0.592 ***	0.033	0.644 ***	0.660 ***	0.542 ***	0.686 ***	0.889 ***	
EDTA Pb	0.877 ***	0.260	0.945 ***	0.949 ***	0.740 ***	0.879 ***	0.696 ***	0.477 **
EDTA Zn	0.867 ***	0.389 *	0.915 ***	0.919 ***	0.809 ***	0.894 ***	0.673 ***	0.387 ***
EDTA Cd	0.916 ***	0.270	0.934 ***	0.948 ***	0.799 ***	0.885 ***	0.714 ***	0.484 **
EDTA Cu	0.490 ***	0.614 ***	0.604 ***	0.645 ***	0.488 ***	0.695 ***	0.353 *	0.131
EDTA Fe	-0.645 ***	0.196	-0.625 ***	-0.579 ***	-0.681 ***	-0.560 ***	-0.780 ***	-0.763 ***
EDTA Mn	0.430 **	0.128	0.482 **	0.605 ***	0.110	0.528 ***	0.533 ***	0.693 ***
CEC	-0.188	0.642 ***	-0.143	-0.098	-0.162	-0.004	-0.179	-0.094
Exch. Ca	0.916 ***	0.301	0.899 ***	0.917 ***	0.797 ***	0.848 ***	0.675 ***	0.429 *
Exch. Mg	0.477 **	0.298	0.470 ***	0.525 **	0.238	0.399 *	0.059	-0.164
Exch. K	0.321 *	0.322 *	0.302 ***	0.324 *	0.261	0.327 *	0.244	0.304
Total P	0.846 ***	0.308	0.927 ***	0.904 ***	0.844 ***	0.922 ***	0.854 ***	0.666 ***
	EDTA Pb	EDTA Zn	EDTA Cd	EDTA Cu	EDTA Fe	EDTA Mn	CEC	Exch. Ca
EDTA Zn	0.930 ***							
EDTA Cd	0.948 ***	0.956 ***						
EDTA Cu	0.691 ***	0.799 ***	0.732 ***					
EDTA Fe	-0.424 **	-0.353 *	-0.472 **	0.046				
EDTA Mn	0.508 **	0.362 *	0.460 **	0.298	-0.264 *			
CEC	-0.049	0.038	-0.037	0.303	0.427 **	0.108		
Exch. Ca	0.902 ***	0.951 ***	0.964 ***	0.704 ***	-0.448 **	0.407 **	-0.028	
Exch. Mg	0.683 ***	0.640 ***	0.605 ***	0.624 ***	0.161	0.268	0.051	0.615 ***
Exch. K	0.333 *	0.313 *	0.328 *	0.228	-0.153	0.319 *	0.552 ***	0.351 *
Total P	0.811 ***	0.859 *	0.834 ***	0.550 ***	-0.611 ***	0.441 **	-0.120	0.841 ***
	Exch. Mg	Exch. K						
Exch. K	0.248							
Total P	0.300	0.248						

\*\*\* p = 0.001    \*\* p = 0.01    \* p = 0.05    - Indicates a negative correlation

CEC was positively correlated with Loss-on-Ignition, EDTA Fe and Exchangeable K at the  $p \leq 0.01$  level. Soil pH was positively correlated at the  $p \leq 0.01$  level with all Total and EDTA metals except Total Pb and EDTA Fe, where the correlations were negative at the  $p = 0.001$  level. Loss-on-Ignition was positively correlated with Total Cu, EDTA Zn and EDTA Cu at the  $p \leq 0.05$  level (Table 5.83).

Although not all significant at the  $p \leq 0.05$  level, all correlations between clay, silt and fine sand and pH, Loss-on-Ignition, Total and EDTA metals were negative, with the exception of silt and fine sand and EDTA Fe, EDTA Mn and CEC, which were positive (Table 5.82). Clay was negatively correlated at the  $p \leq 0.05$  level with Loss-on-Ignition, Total Pb, Total Cd and Total P, EDTA Zn, Cd and Cu and Exchangeable Ca. Silt was negatively correlated at the  $p \leq 0.05$  level with pH, Total Zn, Cd, Cu, Fe and P, EDTA Zn, Cd and Cu and Exchangeable Ca. Fine sand was negatively correlated at the  $p \leq 0.05$  level with pH and all Total and EDTA metals with the exception of EDTA Fe and Total and EDTA Mn. Coarse sand was positively correlated at the  $p \leq 0.05$  level with pH, Total P and Exchangeable Ca and all Total and EDTA metals, with the exception of Total Mn and EDTA Fe. There was a significant positive correlation at the  $p \leq 0.05$  level between fine sand and silt, while coarse sand was negatively correlated with clay, silt and fine sand at the  $p \leq 0.05$  level (Table 5.83).

Table 5.83. Pearson correlation r-values and degrees of significance for all stacked soil series particle size and soil parameters at 0-200 mm and 200-400 mm for September 98 (n=10).

	Clay	Silt	Fine Sand	Coarse Sand
<b>Silt</b>	0.540			
<b>Fine Sand</b>	0.590	0.657 *		
<b>Coarse Sand</b>	-0.704 *	-0.831 **	-0.957 ***	
<b>pH</b>	-0.560	-0.713 *	-0.755 *	0.808 **
<b>L-o-I</b>	-0.769 **	-0.449	-0.484	0.572
<b>Total Pb</b>	-0.635 *	-0.565	-0.709 *	0.740 *
<b>EDTA Pb</b>	-0.539	-0.715 *	-0.710 *	0.776 **
<b>Total Zn</b>	-0.556	-0.741 *	-0.752 *	0.814 **
<b>EDTA Zn</b>	-0.738 *	-0.815 **	-0.800 **	0.895 ***
<b>Total Cd</b>	-0.673 *	-0.771 **	-0.964 ***	0.981 ***
<b>EDTA Cd</b>	-0.649 *	-0.797 **	-0.749 *	0.845 **
<b>Total Cu</b>	-0.581	-0.685 *	-0.748 *	0.797 **
<b>EDTA Cu</b>	-0.717 *	-0.700 *	-0.658 *	0.761 *
<b>Total Fe</b>	-0.370	-0.583	-0.789 **	0.762 **
<b>EDTA Fe</b>	-0.205	0.329	0.447	-0.374
<b>Total Mn</b>	-0.208	-0.271	-0.428	0.400
<b>EDTA Mn</b>	-0.225	0.055	0.056	-0.024
<b>CEC</b>	-0.473	0.081	0.102	-0.28
<b>Exch. Ca</b>	-0.745 *	-0.806 **	-0.715 *	0.837 **
<b>Exch. Mg</b>	-0.531	-0.363	-0.319	0.402
<b>Exch. K</b>	-0.575	-0.260	-0.576	0.546
<b>Total P</b>	-0.638 *	-0.807 **	-0.827 **	0.897 ***

\*\*\* p = 0.001    \*\* p = 0.01    \* p = 0.05    - Indicates a negative correlation

Although not all significant at the  $p \leq 0.05$  level, all correlations between clay, silt and fine sand and pH, Loss-on-Ignition, Total and EDTA metals were negative, with the exception of silt and fine sand and EDTA Fe, EDTA Mn and CEC, which were positive. (Table 5.83). Clay was negatively correlated at the  $p \leq 0.05$  level with Loss-on-Ignition, Total Pb, Total Cd and Total P, EDTA Zn, Cd and Cu and Exchangeable Ca. Silt was negatively correlated at the  $p \leq 0.05$  level with pH, Total Zn, Cd, Cu, Fe and P, EDTA Zn, Cd and Cu and Exchangeable Ca. Fine sand was negatively correlated at the  $p \leq 0.05$  level with pH and all Total and EDTA metals with the exception of EDTA Fe and Total and EDTA Mn. Coarse sand was positively correlated at the  $p \leq 0.05$  level with pH, Total P and Exchangeable Ca and all Total and EDTA metals, with the exception of Total Mn and EDTA Fe. There was a significant positive correlation at the  $p \leq 0.05$  level between fine sand and silt, while coarse sand was negatively correlated with clay, silt and fine sand at the  $p \leq 0.05$  level (Table 5.83).

## **5.6 Discussion**

The aim of evaluating the data collected in the baseline study in terms of seasonal variation in the geochemical parameters was achieved. The results showed that the variation in soil parameters surveyed in the baseline study ranged from a maximum of 64.12% CV for surface Total Mn in the Ashen Series to a minimum of 0% CV for Total Cd at surface and depth in the Nordrach Series (Table 5.68). The results also indicated variation in soil parameters by soil series (Table 5.69). A ranking of the mean % CV of soil parameter % CV in the baseline study



(Table 5.70) indicated that of the soils, the Maesbury Series showed the greatest overall variability over the year, and the Nordrach Series the least. The order of decreasing overall variability in the soil series was:

Maesbury>Ashen>Thrupe>Tailings>Nordrach.

The order was identical when EDTA trace metals, CEC, Exchangeable Ca, Mg, K and Total P were included in the calculation (Tables 5.70 and 5.71).

The general trend for Pb, Zn, Cu, Fe and Mn in the Maesbury and Thrupe soils and the Tailings was an overall decrease in concentration over the sampling period.

Soil Pb, Zn and surface Cu also decreased in the Ashen soil and Pb, Fe and surface Cu in the Nordrach soil (Table 5.73). With the exception of Maesbury at 0-200 mm and Tailings at 200-400 mm, the trend for soil Cd was to either remain at the same concentration or show a net gain in concentration over the sampling period (Table 5.73). However, the concentrations of Cd were near to, or on the detection limit for all soils except Tailings, so this data must be interpreted with caution.

As the data were only collected over the period of one year, it is not known whether the overall decrease in concentrations represented a short term cycle of depletion and enrichment of trace metals within the soil systems, or whether the decrease was part of a long-term trend of trace metal migration down through the soil profiles. There have been previous reports of long-term losses of trace metals by migration down through the soil profile from a number of international and national historic mining and smelting sites (Ledward, 1960; Gibbs and Cartwright, 1982; Maskell *et al.*, 1995). The presence of sandstone, or soils with sandstone

parent material at a site has been shown to enhance trace metal losses through a soil profile. At historic smelting sites in Derbyshire, Maskell *et al.* (1995) noted that there were greater vertical migration rates for trace metals through sandstone profiles, which were linked with the increased acidity of the sandstone. The Ashen, Maesbury and Thrupe Series all originated from Old Red Sandstone and derived Head, and showed greater losses from the 0-400 mm horizon over the sampling period than the Nordrach soil, which had parent material of Silty Drift over Carboniferous Limestone (Table 2.3).

**5.6.1 Maesbury Series**

Of the trace metal data in the baseline study, the greatest variation over the year in Total Pb and Zn at surface and depth, and Total Cd and Total Mn at depth occurred in the Maesbury Series (Tables 5.68 and 5.75). Of all the soil series, pH in the Maesbury soil at surface and depth also showed the greatest variation over the year, ranging from pH 3.88 - pH 6.46 in the surface soil, and from pH 4.72 - 6.92 at depth over the year (Table 5.35, 5.68 and 5.75). Within the Maesbury Series, the decreasing order of variability in soil trace metal concentration over the year was:

Surface soil	Zn>Mn>Pb>Cd>Cu>Fe
Soil at depth	Zn>Mn>Cd>Pb>Cu>Fe.

The most significant trends in soil trace metal concentrations were:

1. concentrations were generally greater in the soil at depth, except for Total Cu, which was always in a greater concentration in the surface soil. With the

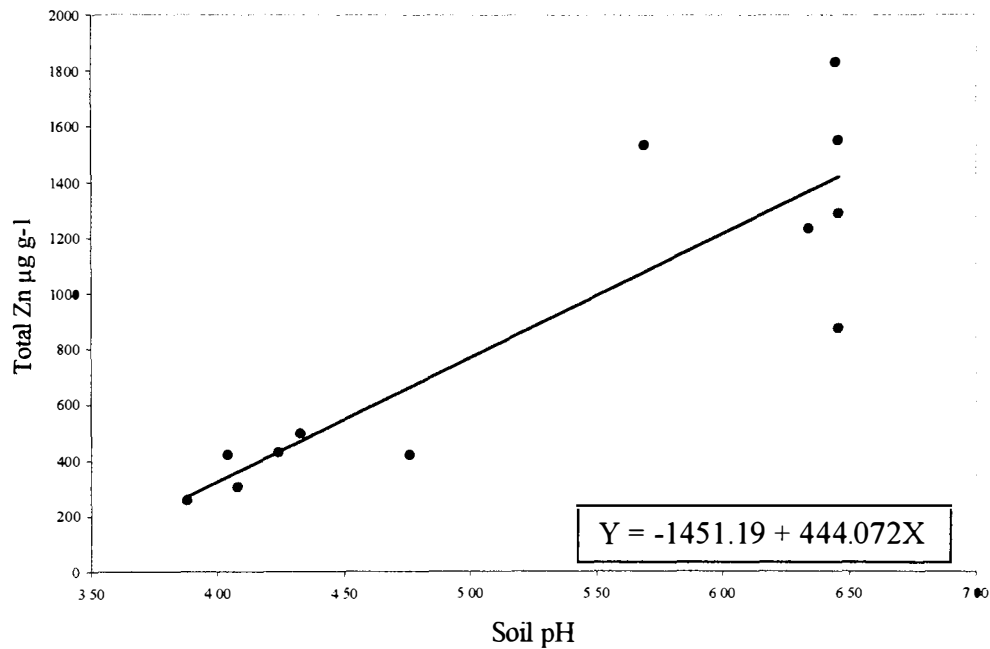
exception of Total Mn, these differences were significant at the  $p \leq 0.05$  level (Tables 5.38 and 5.39)

2. with the exception of Total Cd, there was an overall decrease in concentration at surface and depth in all trace metals from September 1998 to August 1999, with soil concentrations at their greatest in September 1998 (Figures 5.11-5.16 and Table 5.73). Within this overall trend, there were also patterns of variation in concentration over the year. These patterns showed similarities for Total Pb, Zn, Mn, and to a lesser extent, Total Fe, while the pattern was different for Total Cu (Figures 5.11-5.16). In general, after February 1999, the overall trend for Total Pb, Zn, Fe and Mn in the surface soil was a decrease in concentration. This trend corresponded with a decrease in soil pH from February 1999 (Figure 5.9), and a general increase in surface Loss-on-Ignition (Figure 5.10).

In the surface soil, there were significant positive correlations at the  $p \leq 0.05$  level between pH and Total Pb, Zn and Mn, which suggested that the decrease in concentration of these trace metals was associated with the decrease in soil pH (Table 5.40). The relationship was highly significant at the  $p = 0.001$  level for Zn and pH in the surface soil (Table 5.40 and Figure 5.115). Similar significant correlations at the  $p \leq 0.05$  level were found in the baseline study (Tables 4.25 and 4.26). In the Maesbury soil at surface and depth, Zn, Mn and Cd were found to show the most variability in concentration over the year (Table 5.75). The solubility and mobility of these trace metals were show to be strongly associated with soil pH (Lindsay, 1979; Alloway, 1990; Kiekens, 1990). The relationship between soil pH and the mobility of trace metals was also described by a number

of other workers including Brummer and Hermes (1983), Campbell, *et al.* (1983), Bergkvist (1986), LaZerte (1986) and Xian and Shokohifard (1989).

Figure 5.115. Fitted line plot for Total Zn ( $\mu\text{g g}^{-1}$ ) against soil pH in the Maesbury Series at 0-200 mm.

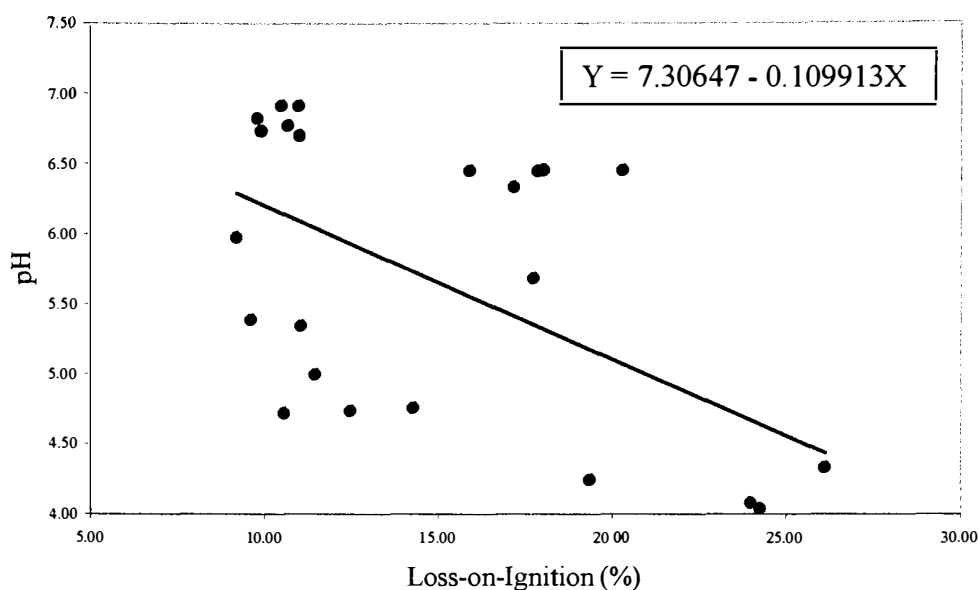


In the mining and smelting soils of Shipham, Somerset, Li (1993) described how the solubility of Pb, Zn and Cd was very sensitive to small changes in soil reaction over the range pH 6.90 - pH 7.70. The range of soil pH in the Maesbury Series over the year was greater and generally more acidic than that quoted by Li (1993), however, it is possible that the mobility of Total Pb, Zn and Mn under conditions of increasing acidity may have also been a significant factor in their variability in concentration in the Maesbury soil over the year.

Increasing trace metal mobility with increasing soil acidity is a well recorded phenomenon (Brummer and Hermes, 1983; Campbell, *et al.*, 1983; Bergkvist, 1986; LaZerte, 1986; Xian and Shokohifard, 1989 and Li, 1993). The development of soil acidity requires the input of  $H^+$ , and the removal through leaching of any cations the  $H^+$  may have replaced on exchange sites (Rowell, 1994). The input of acidity into a soil system may be external, as in the case of acid rain, or as a result of internal soil processes (White, 1987; Rowell, 1994). The Mendip area was recorded as receiving minimal  $H^+$  deposition as acid rain at  $<0.20 \text{ kg } H^+ \text{ ha}^{-1}$  from 1986-1988 (DOE, 1990). It was also calculated, by subtracting the  $Ca^{2+}$  and  $Mg^{2+}$  input from the total nitrogen and sulphur entering the soil by wet and dry deposition, that minimal acidity was entering the soil at  $<1 \text{ kg } H^+ \text{ ha}^{-1}$  (DOE 1990). Unless there was a significant increase in acidity entering the soils of the Mendip area from atmospheric sources during the 1990s, the most significant source of acidity was probably from within the soil system itself.

In soil systems, internal acidification processes may be geochemical, such as the weathering of acid-releasing soil minerals, or of biological origin. The decomposition of organic matter releases  $H^+$  during mineralisation, nitrification and leaching (Rowell, 1994). Root and soil microbial respiration produces  $CO_2$ , which dissolves in the soil solution to carbonic acid, and plant roots release organic acids and  $H^+$  (White, 1987; Xian and Shokohifard, 1989; Rowell, 1994). Loss-on-Ignition, a crude measurement of the organic matter content of a soil (Rowell, 1997), showed a significant negative correlation at the  $p=0.05$  level with surface pH, and at  $p=0.01$  in the stacked Maesbury data (Table 5.40 and Figure 5.116).

Figure 5.116. Fitted line plot for pH against % Loss-on-Ignition in the Maesbury Series at 200-400 mm.



One interpretation of this correlation is that the increase in soil organic matter caused a decrease in soil pH (Figure 5.116). If this were the case, this would indicate that the accumulation of organic matter was a significant source for  $H^+$  input into the Maesbury soil. The variation in surface Loss-on-Ignition in the Maesbury soil was greater than in any of the other soil series (Tables 5.68 and 5.76). If Loss-on-Ignition were to be taken as an indication of soil organic matter, then soil organic matter was at its highest concentration in the Maesbury soil between March to August 1999 (Figure 5.10). This corresponded with a general decrease in soil pH, which was especially marked in the surface soil (Figure 5.9). During the spring and summer months, an increase in soil temperature may encourage microbial activity and the decomposition of plant residues. Many plant species are also in their most active period of growth during the spring and summer, and the increase in mineral uptake, root activity and respiration might be

expected to increase the release of  $H^+$  (Rowell, 1994). As well as there being a significant negative correlation at the  $p=0.01$  level between Loss-on-Ignition and pH, Loss-on-Ignition also showed significant negative correlations at the  $p\leq 0.05$  level with Total Pb, Zn, Fe and Mn in the stacked Maesbury data, and at the  $p=0.05$  level with Mn in the surface soil (Tables 5.40).

It is suggested that these negative correlations can be explained in terms of the relationship between the nature of the organic acids in the organic matter and metal mobility. Organic matter contains organic acids, principally humic, humin and fulvic acids (Ross, 1994c), but also the chelating oxalic, malic, citric, protocatechuic and salicylic acids (McColl and Pohlman, 1986). The humic, humin and fulvic acids have important metal binding capacities in a soil, but their transporting capacities differ, depending on the size and shape of the acid molecule and the viscosity of the soil solution (Ross, 1994c). Humin and humic acids have a large relative molecular weight (2 000-10 000), and their size and configuration inhibits their movement through soil pore space, so are less vulnerable to leaching. Trace metals complexed with humin and humic acids therefore tend to be retained in a soil (Schnitzer and Khan, 1972; Piccolo, 1989; Ross, 1994c). Fulvic acids have a lower relative molecular weight (500-2 000), and are associated with the transportation of the trace metals complexed onto their structures through the soil profile (Ross, 1994c). Many organo-metallic complexes, including very small molecular weight citrate-metallic complexes, are resistant to biodegradation, so trace metals held in this form may be persistent in the soil (Francis *et al.*, 1992).

If fulvic and the lower molecular weight organic acids were present in considerable concentrations in the organic matter of the Maesbury soil, as surface water percolated through the soil, movement of trace metals associated with these acids might have occurred through the profile. Percolating surface water might also have mobilised  $H^+$  released from decomposing organic matter and root exudation in the surface soil. If the  $H^+$  travelled down through the profile, then trace metals may have been released into the soil solution, either by desorption by  $H^+$ , or if  $H^+$  had replaced metal cations on exchange sites. The desorbed and/or exchanged trace metal cations might have then been leached down the profile with the percolating water until re-adsorption or cation exchange occurred, while  $H^+$  would have initially remained on the adsorption and exchange sites, further acidifying the soil (Alloway, 1990).

The predominately sandy texture of the Maesbury soil would facilitate the free drainage of percolating surface waters, enhancing the leaching processes (Table 5.34 and Figure 5.8). Depletion of trace metal concentrations in the surface soil and enrichment at depth, accompanied by an increase in soil acidity occurred several times over the year. This was most notable for Total Zn in January 1999 and April 1999, Total Mn between March and June 1999, and Total Fe between February and April 1999 (Figures 5.11, 5.15 and 5.16). Soil particle size analysis showed that the percentages of clay and silt were greater at depth than in the surface soil (Table 5.34 and Figure 5.8). This suggested lessivage, the movement of clays and silts down through the profile, which indicated the profile had been subjected to the action of percolating waters over a considerable period.



For acidity to have leaching effects on trace metals, the trace metals must be held in soil in fractions susceptible to the actions of  $H^+$  concentration. EDTA extractable trace metal concentration was assessed as an indication of the trace metals held in the soil system as soluble, exchangeable, adsorbed and organically bound fractions, and possibly a proportion of those occluded on oxides and secondary clay minerals (Ure, 1990). EDTA extractable trace metals as a percentage of the Total trace metal content of a sample followed this sequence in decreasing order of magnitude in the Maesbury soil (Table 5.36):

Surface	Pb>Cd>Cu>Mn>Zn>Fe
Depth	Cd>Pb>Cu>Mn>Zn>Fe.

This order of magnitude generally corresponded with the findings of Li (1993) in the mining and smelting soils of Shiphams. The EDTA extractability of Fe in the Maesbury soil ranged from 6.29% to 25.59% of the Total Fe concentration in the surface soil, and from 3.53% to 9.31% at depth (Figures 5.25 and 5.26). This corresponded closely with Li's (1993) estimate that at 87% - 94% of the Total Fe in the Shiphams soils was held in the residual fraction of the extraction sequence, either associated with primary minerals or occluded by stable secondary minerals. Earlier work by Mattigod *et al.* (1986) showed that Fe was mostly associated with crystalline goethite and haematite in the Shiphams soils. The high EDTA extractability of Pb also corresponded with the results found by Li (1993) in the Shiphams soils. The percentage of soil Pb retained in the residual fraction ranged from 7.68% to 19.86% at Shiphams (Li, 1993). The remaining 80% to 92% would have been a pool of Pb potentially extractable by EDTA. This corresponds closely with the 89.80% to 95.99% of the Total Pb found to be EDTA extractable in the Maesbury soil at a similar depth (Figures 5.17 and 5.18).

EDTA extractable Zn as a percentage of Total Zn in the surface Maesbury soil ranged from 32.10% in June 1999 to 94.94% in September 1998. Surface EDTA extractable Pb, Cu and Fe as a percentage of the Total concentration also showed the same temporal pattern in the Maesbury soil (Figures 5.17, 5.19, and 5.23). This corresponded with the highest soil pH values in September 1998 and the lowest pH values in June 1999 (Figure 5.9). This conformed to the correlation between increased soil pH and decreased trace metal availability observed by many other workers (Lindsay, 1979; Brummer and Hermes, 1983; Campbell, *et al.*, 1983; Bergkvist, 1986; LaZerte, 1986; Xian and Shokohifard, 1989; Li, 1993). However, this temporal pattern of percentage EDTA extractable of Total Pb, Zn, Cu and Fe might also have been associated with the vegetation cover.

September is near the end of the growing season for many species, and the trace metals may have accumulated in plant tissues throughout the spring and summer of 1998, lowering concentrations in the soil. Merrington (1993) showed that the uptake of Pb, Cu, Cd and Mn by mixed grasses at mining sites in West Chiverton and Wemyss peaked in September. Many other workers have shown that plants accumulate metals throughout the growing season (Ross, 1994d), including those species present on the Maesbury soil (Table 5.32). *Agrostis capillaris* was shown to have accumulated between 100-500  $\mu\text{g g}^{-1}$  Pb, *Festuca rubra* 120-420  $\mu\text{g g}^{-1}$  Pb and *Rumex acetosa* up to 800  $\mu\text{g g}^{-1}$  Pb on Scottish Pb mine wastes (Thompson and Proctor, 1983).

The significant correlation at the  $p \leq 0.05$  level between Total Pb, Zn, Fe and Mn in the stacked data for the Maesbury soil could be interpreted as evidence that Pb and Zn were associated in the Maesbury soil with Fe and Mn (Table 5.40).

Li (1993) found that the Fe and Mn oxides were important in holding Pb in mining and smelting soils in Shipham, and this could also be the case in the Maesbury soil. Unlike the other trace metals in the baseline study, the concentration of Total Cu in the Maesbury soil was consistently greater in the surface soil than at depth. The difference between the concentration at surface and depth was significant at the  $p=0.05$  level (Table 5.38).

Total Cu also showed a significant positive correlation at the  $p=0.01$  level with Loss-on-Ignition, and a significant negative correlation at the  $p=0.05$  level with Total Fe (Table 5.40). This indicated that the Cu held in this soil might have been associated with organic matter rather than with Fe oxides. Copper has been shown to be strongly bound by the humic and fulvic acids in soil organic matter (Stevenson, 1977; Harrison *et al.*, 1981; Dudka and Chlopecka, 1990; Li, 1993).

Li (1993) found that in the soils contaminated by mining and smelting at Shipham, the close relationship between Cu and organic matter was associated with the organic sulphide phase of the soil. Copper is also specifically adsorbed in soils, and has been described as one of the trace metals which is most strongly retained in soils (Baker, 1990). In the Maesbury soil, Total Cu showed less variation in concentration over the year compared with Total Pb, Zn, Cd and Mn. The lower variability in concentration could be argued to indicate that Cu was not so influenced by variation in soil pH in the Maesbury soil as the other trace metals.

Change in soil pH has been shown to have less effect on Cu adsorption at lower concentrations than on other metals (Ross, 1994c).

**5.6.2 Ashen Series**

Of the trace metal data in the baseline study, the Ashen Series showed the greatest variation over the year in Total Cu and Mn at surface, and Total Fe at surface and depth and occurred in the Ashen Series (Tables 5.68 and 5.76). Within the Ashen Series, the decreasing order of variability in soil trace metal concentration over the year was:

Surface soil	Mn>Zn>Cd>Cu>Fe>Pb
Soil at depth	Cu>Cd=Fe>Mn>Zn>Pb.

The most significant trends in soil trace metal concentrations were:

1. concentrations of Total Pb, Zn and Cu were generally greater in the surface soil, while Total Fe and Mn concentrations were greater at depth (Figures 5.52-5.57). With the exception of Total Cu, the differences were significant at the  $p \leq 0.05$  level (Tables 5.52 and 5.53)
2. there was an overall decrease in concentration of Total Pb and Zn over the (Figures 5.52-5.57 and Table 5.73) from September 1998 to August 1999, with soil concentrations at their greatest in February 1999 (Figures 5.52-5.57).

Unlike the Maesbury soil, there was no immediate apparent trend of variation over the year in trace metal concentrations in the Ashen soil, although Total Pb and Zn, and Fe and Mn followed similar patterns of variation (Figures 5.52-5.57). This was reflected in the significant positive correlation between Pb and Zn, and Fe and Mn at the  $p=0.001$  level (Table 5.54). There were also significant positive

correlations at the  $p=0.001$  level between Pb and Zn and Loss-on-Ignition, and significant negative correlations at the  $p=0.001$  level between Total Pb and Zn and Fe and Mn (Table 5.54). This indicated that unlike the Maesbury soil, Total Pb and Zn were more strongly associated in the Ashen soil with the organic fraction of the soil, rather than the Fe and Mn oxides. This would be consistent with trace metal enrichment from aerial smelter emissions, rather than if the trace metals were present as an inherent part of the mineral fraction of the soil, or as beneficiation wastes (Cotter-Howells, 1991; Li, 1993).

Total Pb was the least variable of the trace metals in the Ashen soil at surface and at depth, which might indicate that it was associated with the humic acid fraction of the organic matter. Humic and humin acids tends to fix trace metals in the organic layer, and have been described as the metal immobilising fraction of organic matter (Schnitzer and Khan, 1972; Piccolo, 1989; Ross, 1994c). Total Zn was also correlated with Loss-on-Ignition at the  $p=0.001$  level, but showed a greater variation over the year than Pb in the Ashen soil (Tables 5.54 and 5.68). This suggested that Total Zn may have been bound in the organic matter by fulvic acids, which are associated with trace metal mobility within the soil (Ross, 1994c).

EDTA extractable trace metals as a percentage of the Total trace metal content of a sample followed this sequence in decreasing order of magnitude in the Ashen soil:

Surface	Pb>Cu>Fe>Zn>Cd>Mn
Depth	Pb>Cu>Zn>Cd>Fe>Mn.

As with the Maesbury soil, the percentage of all EDTA extractable metals as a percentage of Total trace metal concentration in the Ashen soil were greater in the

surface soil than at depth (Tables 5.36 and 5.50). Although Pb was the most EDTA available of the trace metals in the Ashen Series at 93.62% and 91.26% of the Total Pb content at surface and depth respectively, in terms of overall annual variation, Total Pb was the least variable trace metal (Table 5.68, Figures 5.58 and 5.59). This could be argued to further associate the trace metal with the humic and humic acid components of the organic matter, because if it were less strongly complexed, then the variability of Total Pb would be expected to be greater. The EDTA extractable as a percentage of the Total trace metal concentration were low for Fe and Mn at depth, and for Mn at surface, which suggested that in the Ashen soil, Fe and Mn were strongly associated with mineral fraction of the soil. This was generally similar for Mn and Fe concentrations in the mining and smelting soils of Shipham (Li, 1993).

The surface concentration of Total Pb, Zn and Mn generally decreased during April 1999 to June 1999 (Figures 5.52-5.57 and Table 5.73). EDTA extractable Pb as a percentage of Total Pb was also at its lowest in the surface soils for June (Figure 5.58). The decrease in Total Pb, Zn and Mn may have been caused by plant uptake. The dominant species in the 2 m<sup>2</sup> quadrat on the Ashen Series was *Deschampsia flexuosa*, which was one of the early summer flowering *gramineae* species in the study area (Table 5.32). It is possible that April 1999 to June 1999 was an active period of nutrient acquisition for the species, therefore an associated increase in the uptake of these trace metals may have occurred.

**5.6.3 Thrupe Series**

Of the trace metal data in the baseline study, the greatest variation over the year in Total Cu at surface and Total Cd depth occurred in the Thrupe Series. Loss-on-Ignition at depth also showed the greatest variability of all the soil series (Tables 5.68 and 5.76). Within the Thrupe Series, the decreasing order of variability in soil trace metal concentration over the year was:

Surface soil	Cu>Mn.Cd>Pb>Zn>Fe
Soil at depth	Cd>Pb>Cu>Mn>Zn>Fe.

Within this ranking, there was little difference in %CV between all trace metal parameters (Table 5.68).

The most significant trends in soil trace metal concentrations were:

1. concentrations were generally greater in the surface soil for Total Pb, Cu and Mn, while Total Zn, Cd and Fe were similar at surface and depth (Figures 5.32-5.37). For Total Pb, Zn and Mn, these differences were significant at the  $p \leq 0.05$  level (Tables 5.45 and 5.46)
2. as in the Maesbury soil, with the exception of Total Cd, there was an overall decrease in concentration at surface and depth in all trace metals in the Thrupe soil from September 1998 to August 1999, with soil concentrations of trace metals at their greatest in September 1998 (Figures 5.11-5.16 and 5.32-5.37 and Table 5.73).

Although the overall % CV in trace metal concentrations was not the greatest of all the soil series (Table 5.71), a notable feature within the temporal variation was the monthly pattern of variation in the data (Figures 5.32-5.37). Within the overall downward trend in concentration from September 1998 to August 1999, trace

metals appeared to cyclically rise and fall through the soil profile throughout the year. It is proposed that the change in trace metal concentrations within the profile was related to the movement of water in the soil. The sampling sites was at the base of North Hill, beneath the leat running from the small reservoir at ST 3546 1511, and above the tramway (Figure 5.1). After periods of heavy rain, water could be heard running out of the leat below the surface of the soil. The water appeared to flow down the hillside below the surface of the soil. On several occasions when the auger was removed during sampling, flowing water broke through the side of the auger boring. Water was also observed rising from the bottom of the auger boring. The fluctuating hydrological conditions might have caused periodic geochemical or physical change in the soil.

Over the year, the soil pH ranged between pH 5.21 and pH 6.04 in the surface, and from pH 5.82 to pH 6.22 at depth (Table 5.42). Li (1993) showed that small changes in soil pH mobilised trace metals in mining and smelting soils at Shipham. However, all correlations between pH and trace metals were negative in the Thrupe soils, and with the exception of Fe were not significant (Table 5.47). It is possible that changes in the redox status of the soil due to periodic waterlogging were occurring. When soils are waterlogged, the reduction of trace metals such as Fe or Mn can occur, and trace metals associated with the Fe and Mn, such as Pb, Zn, Cd and Cu, may be released into solution during these reactions (Ross, 1994c). Co-precipitation of trace metals may also occur with changes in the redox status of a soil (Ross, 1994c). The cyclic change in trace metal concentrations may also have been related to physical changes in the soil associated with the fluctuating water content. Trace metals occluded on particulates, colloids or the very small



molecular weight citrate-metal complexes in organic matter may have been transported though the profile with the water (Merrington, 1993; Ross, 1994c).

As with the Ashen soil, Total Pb, Cu and Mn were positively correlated with Loss-on-Ignition at the  $p=0.001$  level, indicating that the trace metals were probably associated with the organic matter fraction in the Thrupe soil (Table 5.47). The significant correlations between Total Pb, Cu and Mn at the  $p\leq 0.05$  level suggested that Pb and Cu might have also been associated with Mn oxides in this soil (Murray, 1975; McKenzie, 1980). Many workers have suggested a positive correlation between trace metals and pH (Brummer and Hermes, 1983; Campbell, *et al.*, 1983; Bergkvist, 1986; LaZerte, 1986; Xian and Shokohifard, 1989; Li, 1993). The significant negative correlation at the  $p=0.01$  level between Total Mn and pH in the stacked data from the Thrupe soil probably occurred because Mn was strongly associated with organic matter in the surface horizon, which was generally more acidic than in the soil at depth (Figure 5.30).

The decreasing order of EDTA extractable as a % of the Total trace metal concentrations were:

Surface	Pb>Cd>Mn>Cu>Zn>Fe
Depth	Pb>Cd>Mn>Cu>Zn>Fe.

The sequence was identical at surface and depth and similar to that of the Maesbury soil. With the greatest EDTA extractability for Pb between 84.31% to 99.76% and the least for Fe at 3.96% to 7.4% in the surface soil, these results were in agreement with sequential extractions for Pb and Fe carried out on soil from Shipham (Li, 1993). For Pb, Cu, Fe at surface and depth, and Mn at depth, the lowest EDTA concentration as the percentage of the Total was September 1998.

Again, it is possible that by September 1998, the available trace metal content of the soil was depleted by continual plant uptake throughout the summer months (Merrington, 1993). The low % EDTA of the Total Zn concentration indicated that the greatest proportion of the Zn in the Thrupe soil was held in the mineral fraction. If the water content of the Thrupe soil was continually fluctuating, then it is possible that much of the Zn held in the readily exchangeable forms in the soil may have leached away, leaving the more strongly bound Zn associated with the mineral fraction of the soil.

**5.6.4 Tailings**

Within the Tailings, the decreasing order of variability in soil trace metal concentration over the year was:

Surface soil	Pb>Mn>Cd>Zn>Cu>Fe
Soil at depth	Pb>Cd>Zn>Fe>Cu>Mn.

Within this ranking, there was little difference in %CV between Pb, Mn and Cd at surface and Pb, Cd, Zn, and Fe at depth (Table 5.68).

The most significant trends in the Tailings were:

1. all Total trace metal concentrations were greater at depth than in the surface horizon (Figures 5.73-5.78). With the exception of Total Mn, all these differences were significant at the  $p \leq 0.05$  level (Table 5.60)
2. with the exception of Total Cd in the surface horizon, there was an overall

decrease in concentration at surface and depth in all trace metals from September 1998 to August 1999, with concentrations at their greatest in September 1998 (Figures 5.73-5.78 and Table 5.73).

3. there was little variation in pH (pH 7.01 to pH 7.49 at surface, pH 7.31 to pH 7.79 at depth, Table 5.56), which was probably associated with the buffering capacity of the minerals in the tailings (Table 4.11 and Figure 5.71)
4. the EDTA concentration as a percentage of the Total concentration for the majority of trace metals (Pb, Cu, Fe and Mn) was the lowest for all soil series (Table 5.81).

After February 1999, the general pattern in concentration was a decrease in all Total trace metals except for Cd at surface and depth (Figures 5.73-5.78). The decrease was not apparently correlated with pH (Table 5.60). The low % EDTA concentration as a percentage of the Total trace metal concentration, and the significant positive correlations at the  $p=0.001$  level between Pb, Zn, Cu and Cd and Fe indicated that in the Tailings, trace metals were strongly associated with Fe oxides (Kinniburgh *et al.*, 1976; McKenzie, 1980). This suggested the possibility of the presence of a cemented Fe hardpan in the Tailings, probably somewhere below the 400 mm maximum sampling depth used in this study.

Cemented Fe hardpans in Pb tailings piles were described by Blowes *et al.* (1991) and Merrington (1993). The hardpans were present in the tailings at depths below 400 mm, and were shown to retain trace metals associated with the Fe in a zone of enrichment, often just above the cementation layer. Cementation layers were also

observed to be impermeable to water percolation, which enhanced the retention of trace metals in the tailings (Blowes *et al.*, 1991; Merrington, 1993).

EDTA extractable trace metals as a percentage of the Total trace metal content of a sample followed this sequence in decreasing order of magnitude in the Tailings (Table 5.57):

Surface	Pb>Cd>Zn>Cu>Mn>Fe
Depth	Pb>Cd>Zn>Cu>Mn>Fe.

The EDTA extractable trace metals as a percentage of the Total trace metals were greater in the surface soil, and the pattern of EDTA availability corresponded with the sequences in the Maesbury surface soil and Thrupe soils at surface and depth (Tables 5.36 and 5.43).

A striking feature of the EDTA trace metal concentration as a percentage of the Total trace metal concentrations was that with the exception of Total Fe at depth, the lowest percentage for all trace metals was in December 1998 (Figures 5.79-5.90). This was associated with the lowest % Loss-on-Ignition at surface and depth for the whole year (Figure 5.72). It is possible that the EDTA extractable trace metals in Tailings were those associated with organic matter, in which case, if there was less organic matter present, then there would have been less exchange sites for the trace metals to be held on. Another possibility is the presence of the chemolithoautotrophic bacterium *Thiobacillus ferrooxidans*, an organism found in sulphide tailings (Merrington, 1993).

The bacterium species is involved in the catalysis of sulphide oxidation, enhancing reaction times; the oxidation rate of Fe (II) to Fe (II) is approximately one million times faster than the abiotic oxidation of Fe. The leaching of trace metals is the end result of these processes (Lundgren and Silver, 1980). It is possible that if *T. ferrooxidans* was present in the Tailings in the study area, then during the winter months the decrease in temperature might have inhibited microbial activity, suppressing the production of the more available chemical forms of the trace metals. The widespread depletion of the available forms of the trace metals in the Tailings in December might also have been the result of heavy rainfall immediately prior to sample collection, and the associated increased leaching of the available form of the trace metals through the Tailings profile.

### 5.6.5 Nordrach series

Within the Nordrach Series, the decreasing order of variability in soil trace metal concentration over the year was:

Surface soil	Mn>Cu>Zn>Fe>Pb>Cd
Soil at depth	Cu>Mn>Zn>Pb>Fe>Cd.

The order of ranking was different to that of the other soil series.

The most significant trends in the Nordrach Series were:

1. greater concentrations of Total Pb were in the surface soil than at depth. The concentration of Total Zn, Fe and Mn was greater at depth than in the surface soil. The concentration of Total Cd and Cu was generally similar at surface and depth (Figures 5.94-5.99). The differences between both Pb and Mn at surface and depth were significant at the  $p \leq 0.05$  level (Table 5.66)

2. unlike the other soil series, only Pb and Fe at surface and depth and Cu at the surface showed an overall decrease over the year. The concentrations of the other trace metals had either stayed similar or increased. However, overall, all the magnitude of change was small (Figures 5.94-5.99 and table 5.73).
3. soil pH increased over the year from pH 4.7 to pH 5.16 in the surface soil, and from pH 3.88 to pH 5.22 at depth (Table 5.6).

The annual variation in Total trace metal concentrations over the year was less in the Nordrach soil than for the majority of the Total trace metals despite similar variations in pH (Table 5.69). However, the Nordrach soil differed from the other series in its texture, and hydrology. The Nordrach soil had a greater percentage of silt and clay, and lower percentage coarse sand than the other series (Table 5.33, Figures 5.5 and 5.6). It is not known whether the profile was natural or had been disturbed by forestry, apart from the surface horizon, the soil was azonal (Figure 5.4). The soil also seemed more compacted than the other soils, and over the year, water did not appear to penetrate it beyond the top 50 mm. In a soil with these physical characteristics, the clay content and its associated cation exchange sites may enhance the retention of trace metals, although exchange sites associated with organic matter is considered more important overall to the retention of trace metals in soils (Ross, 1994c). With the exception of Tailings, the CEC at both surface and depth was greater in the Nordrach soil than in the other soil series (Tables 5.37, 5.44, 5.51 and 5.61). The clay may also act as a physical barrier to water migration through the soil, again enhancing trace metal retention through inhibition of leaching and reducing seasonal variability (White, 1981).

The EDTA trace metals as a percentage of Total trace metals for the Nordrach soil was:

Surface	Pb>Cu>Mn>Cd>Zn>Fe
Depth	Pb>Cu>Cd>Mn>Zn>Fe.

Like the other soil series, the ranking showed Pb to be the most EDTA available trace metal (Figures 5.108 and 5.109). The high EDTA extractability for Pb was related to its origin and the form in which it was held in the soil. In the Nordrach soil, Total Pb was positively correlated with Loss-on-Ignition at the  $p=0.01$ , and negatively correlated with Zn, Cu and Mn at the  $p\leq 0.05$  level (Table 5.67). This indicated that in this soil, Total Pb was probably associated with organic matter in the surface horizons, possibly after aerial deposition. Total Zn was positively correlated with Cu and Mn at the  $p\leq 0.05$  level, indicating that Zn was likely to be associated with Mn oxides in the mineral fraction of the soil. The low EDTA availability of Zn as a percentage of the Total Zn confirmed that over 95% of the Zn was adsorbed on Fe, Mn or Al oxides, or was within the mineralised fraction of the soil (Figures 5.102 and 5.103).

#### 5.6.6 Inter-soil correlations of soil parameters

There was an identical pattern of significant correlations between the stacked soil parameter data from all soil series and that of the stacked parameter data for the All Soil Data and Priddy Mineries Reserves Data sets (Tables 4.27, 4.32 and 5.74). All Total trace metals were positively correlated with each other and pH at the  $p=0.001$  level (Table 5.75). For further discussion of the relationship between pH and trace metal concentrations in soil, see section 4.8.1.

There were a number of significant positive correlations between all soil parameters from all soil series (Table 5.82). As well as the significant positive correlations between all Total trace metals, there were significant positive correlations between the EDTA concentration and total concentration of a particular trace metal. EDTA Pb, Zn, Cd, Cu and Mn were positively correlated at the  $p \leq 0.05$  level with Total Pb, Zn, Cd, Cu and Mn respectively (Table 5.82). Similar correlations were noted by Ginnevar (1995) and Li (1993) for Mendip soils. Rowell (1994) suggested that the relationships between the EDTA and Total metal concentration in a soil was so consistent for Zn and Cu, that the EDTA concentration could be used to calculate approximate total concentrations.

There was a significant positive correlation between CEC and Loss-on-Ignition at the  $p = 0.001$  level. This reflects the chemical structure and importance of the organic matter in a soil, as the organic fraction is where the majority of the non-specific adsorption sites occur (Ross, 1994c). Exchangeable Ca and Total P were positively correlated with pH, all soil Total trace metals and the majority of the EDTA extractable metals at the  $p \leq 0.05$  level (Table 5.82). These relationships reflected the high concentrations of trace metals associated with beneficiation wastes, which may have been present to a certain degree in the Maesbury and Thrupe soils as well as the Tailings. In beneficiation wastes, the retention of trace metals is often associated with metallo-phosphates and calcite (Mattigod *et al.*, 1981; Davies, 1990; Cotter-Howells, 1991; Li, 1993).

The significant positive correlations between coarse sand, soil pH, Total and EDTA Pb, Zn, Cd, Cu, Exchangeable Ca and Total P again reflected the presence



of beneficiation wastes in the soils. Coarse sand is a size class and not a mineral description (Rowell, 1994). In these soils, coarse sand would include particles of calcite, fragments of metallic minerals and slag, all of which would contribute to the concentration of trace metals in the soils. While the coarse sands were associated with the metal-enriched beneficiation wastes, the soils such as Ashen and Nordrach, which contained higher proportions of silts and clay in their texture, were associated with lesser enrichment from aerial deposition. Although the relationship between clay and trace metal concentrations has been identified by a number of studies (Ross, 1994c), the results of this study suggested that clay might be of more significance in a soil in retaining trace metals where the source enrichment is from outside the system, such as through aerial deposition, rather than inherent in the mineral components of the soil as with beneficiation wastes.

#### **5.6.7 Summary**

In the absence of sufficient monthly data replicates for statistical comparison by Analysis of Variance, a comparison between the % CV of monthly values for the baseline study over the year were compared with the results of Hajar (1987), Andrews *et al.* (1989) and Davies *et al.* (1999). The annual variation expressed as % CV in Total Pb, Zn, Cu and Cd for all soils in the surface soils of the study were within the same range as these previous studies (Table 5.84). The annual variation in surface Total Mn was slightly greater in this study than for Davies *et al.* (1999). To assess the true extent of seasonal variation, sampling and analytical error would have to be calculated and subtracted from each sample before calculating the final % CV, which would revise the figure downwards.

Table 5.84. Comparison of annual variation in soil trace metal concentration.

	Hadjar (1987) % CV	Davies <i>et al.</i> (1999) % CV	This Study, mean %CV of all soil series
Pb	53.41	17-29	18.37
Zn	16.79	13-30	28.28
Cu	No Data	15-34	18.22
Cd	27.85	No Data	19.69
Mn	No Data	25-34	38.40

As a validation of the data collected in the baseline study, the temporal study provided a framework in which to assess the baseline data, in terms of potential annual variation in trace metal concentrations in the baseline soils. The temporal study showed that while annual variation occurred for all trace metals in all soils, the trace metal concentration in a soil usually remained within the same magnitude.

The general trend for Pb, Zn, Cu, Fe and Mn in the Maesbury and Thrupe soils and the Tailings was an overall decrease in concentration over the sampling period. Soil Pb, Zn and Cu at 0-200 mm also decreased in the Ashen soil and Pb, Fe and Cu at 0-200 mm in the Nordrach soil (Table 5.73). It was beyond the scope of this study to conclude whether this represented a long-term trend of trace metal losses from the soils, or whether it was part of a shorter cycle of depletion and enrichment within the soil system. However, this trend confirmed previous reports of long-term losses of trace metals down the soil profile from a number of international and national historic mining and smelting sites (Ledward, 1960; Gibbs and Cartwright, 1982; Maskell *et al.*, 1995).

The degree of annual variation in trace metal concentrations appeared to be linked with the particular trace metal, its origin within the soil system, the chemical forms the trace metals were held in the soil, soil pH and the soil hydrology. This concurred with the conclusions of a number of studies on similar sites, including Foster and Lott (1980), Tills and Alloway (1983), Blowes *et al.* (1991), Cotter-Howells (1993) Li (1993) and Merrington (1993). From the data analysed in this study, it was predicted that the greatest annual variation of trace metals would occur in a soil where the source of enrichment was from aerial deposition, where the soil pH was relatively low and the soil water content fluctuated. Of all the metals, Mn would be the most likely to show the greatest monthly variation under these conditions.

The data generated in the baseline soil survey (n=77) and the temporal study (n=120) also contributed to the wider debate on the association of trace metal concentrations in soil with pH, Loss-on-Ignition and Fe and Mn oxides. In both studies there were significant positive correlations at the  $p=0.001$  level between all Total trace metals and pH (Tables 4.26 and 5.81). This was in agreement with a number of soil studies and laboratory-based experimentation which have suggested that the retention of trace metals in soils is associated with increasing in pH, while decreasing pH is associated with the solubility, mobility and transport of trace metals through a soil profile (Lindsay, 1979; Brummer and Hermes, 1983; Campbell *et al.*, 1983; Berkavist *et al.*, 1989; Xian and Shokohifard 1989; Alloway, 1990; Kiekens, 1990; Loberli, Gjengedal and Steinnes, 1991; Li, 1993; Martin and Bullock, 1994; Maskell *et al.*, 1995).

In the baseline survey and temporal study, all Total trace metals also showed significant positive correlations at the  $p=0.001$  level with Fe and Mn (Tables 4.25 and 5.81). In the soil, the adsorbing surfaces of Fe and Mn oxides are the most important sites for specific adsorption, and these correlations reflected this well documented association (Kinniburgh *et al.*, 1976; Jenne, 1977; McKenzie, 1980; Robert and Terce, 1989; McBride, 1989). With the exception of Total Fe, there were no significant correlations between CEC and Total or EDTA trace metals, which suggested that in the soils of the study area, the Fe and Mn oxides were of greater significance than CEC in the overall retention of trace metals (Table 5.81). However, there were also significant positive correlations between all Total trace metals and Total P (Table 5.81), which supported the observations of Mattigod *et al.* (1981), Cotter-Howells (1991), Cotter-Howells and Caporn (1996) and Li (1993) that the retention of trace metals in the soils and wastes of former mining and processing sites are often associated with metallo-phosphates.

## **CHAPTER 6**

### **CONCLUSION AND RECOMMENDATIONS**

#### **6.1 Conclusions**

The aim of this project was to determine the distribution and study the biogeochemical cycling of some of the trace metals associated with the Mendip lead-zinc mineralisation in the soils of the Priddy Mineries Reserve, the St. Cuthbert's site, and Stockhill Plantation. This was achieved by:

1. the execution of a baseline geochemical survey of the concentrations of lead, zinc, cadmium copper, iron and manganese in the soils of the study area, and the presentation of soil metal data in a cartographic form useful to those involved in the future management of the sites.
2. an assessment of the biogeochemical cycling of these trace metals in four representative soil types and a typical beneficiation waste found in the study area. The data were generated by sampling from permanent quadrats on a monthly basis for the period of one year from September 1998 to August 1999.

The baseline study of the trace metals in the soils of the Priddy Mineries Reserve, St. Cuthbert's and Stockhill Plantation showed that there was considerable enrichment of Pb, Zn, Cd, Mn and Fe above background levels in some of the soils, and that where this occurred, it was closely linked with the industrial history of the area. The greatest concentrations of Pb, Zn, Cd, Cu, Fe and Mn were present in the study area in the wastes associated with the beneficiation processes carried out during the final stage of the Mendip lead industry (1857-1908), when the wastes of Roman and Mediaeval operations were reworked. While most of the wastes from 1857-1908 were present as clearly identifiable tailings piles, previously unrecognised areas contaminated by beneficiation wastes were

identified by field-walking, the analysis of soil trace metal concentrations, RTE, soil texture and colour, and consideration of photographic and cartographic evidence and documentation.

Based on the Greater London Council Contamination classification system (Kelly, 1979), 88.5% of the samples in the study area were contaminated to unusually heavily contaminated by Pb. Unusually heavy contamination by Pb was present in 44% of the soils ( $>10\,000\ \mu\text{g g}^{-1}$ ), and by Zn in 15% of the soils ( $>5\,000\ \mu\text{g g}^{-1}$ ). Only 4% of the soils were classified as slightly contaminated by Cu ( $100\text{--}200\ \mu\text{g g}^{-1}$ ), with the remaining 96% were uncontaminated ( $0\text{--}100\ \mu\text{g g}^{-1}$ ). A ranking of the percentage of samples classified as contaminated showed that in terms of magnitude of contamination, the decreasing order for the study area was  $\text{Pb} > \text{Zn} > \text{Cd} > \text{Mn} > \text{Cu}$ .

The highest concentrations of Pb, Zn, Cd, Cu, Fe and Mn in the soils of the Priddy Mineries Reserve were shown to be in the areas of tailings piles. Elevated concentrations were also found in the area of a former tailings settlement pond. The source of the high concentrations of trace metals in areas of tailings was the mineral composition of the tailings. As well as primary ore minerals, tailings were observed to contain fragments of smelter wastes in the sand and fine sand fractions. The retention of the high concentrations of trace metals in the tailings piles appeared to be related to the following factors:

1. chemical weathering in the presence of phosphorus and calcite in the tailings enhanced the formation of environmentally stable metal phosphates
2. the occlusion of metals onto particles of smelter waste and calcite

3. the retention of trace metals on cation exchange and specific adsorption sites, especially in piles with tailings of higher pH values
4. the possible presence of an impermeable Fe hardpan at depth in some piles.

Analysis of the patterns of RTE in the soils of the Priddy Mineries Reserve identified the Waldegrave smelter stack on North Hill as a historical point source for Pb enrichment in the surrounding soils. Little RTE was shown for Zn, Cd, Cu, Mn and Fe around the stack however, and the strongly acidic nature of the podsolised North Hill soils of the Ashen Series was thought to be the most likely cause of the depletion of these trace metals from the surface soil horizon. The abandoned tramway running North-South through the site was identified as a possible line source of Cd and Mn. The percentage of soils classified as contaminated were very similar to those of the whole study area, although the ranking of magnitude of contamination was slightly different at Pb>Zn>Mn>Cd>Cu.

Of the three sites in the study area, the soils of the St Cuthbert's site was found to be the most heavily enriched by Pb, Zn, Cd, Cu and Mn. The soils also contained the greatest concentrations of Fe found in the study area. The enrichment over the whole site was linked to historical beneficiation and smelting. Archaeological evidence suggested that the site was very close to, or was even perhaps once part of a Roman mining and smelting settlement (Williams, 1998). Written records also indicated that the valley running through the site was extensively filled with the wastes associated with the ancients, probably dating from the 16-17<sup>th</sup> centuries or earlier, before the extensive reworking of 1857 -1908 (Curwen Salmon, 1864).

The St Cuthbert's site was the smallest of the sites in the study area, and its industrialisation during the last phase of the Mendip lead industry was later and more intensive than that of the Chewton Minery on the Priddy Minery Reserve. The site has continued to be physically disturbed by industrial remains and extensive areas of beneficiation and smelter wastes since closure in 1908.

All the soil samples collected from the St. Cuthbert's site were either heavily or unusually heavily contaminated by Pb, with 91% of the soil samples classified as showing unusually heavy Pb contamination. For Zn, 91% of the soil samples were classified as heavy to unusually heavy contamination. Only 9% of the soil samples were slightly contaminated by Cu, the remaining 91% were classified as uncontaminated. The ranking of magnitude of contamination was slightly different to that of either the whole study area or the Priddy Mineries Reserve at  $Pb=Zn>Mn>Cd>Cu$ .

Soil contamination by Pb, Zn and Mn was generally more widespread in the samples collected from the Stockhill Plantation than in those from the Priddy Mineries Reserve, but less widespread than in those from the St. Cuthbert's site. The soil samples from the Stockhill Plantation were the least contaminated by Cd and Cu of all the sites. Like the St. Cuthbert's site, all soil samples were contaminated to some degree by Pb, with 91.5% of the soils classified as contaminated to unusually heavily contaminated, and 33% unusually heavily contaminated (Kelly, 1979). The ranking of magnitude of contamination was again slightly different to that of the whole study area, and the Priddy Mineries Reserve and St. Cuthbert's site at  $Pb>Zn>Mn>Cd>Cu$ .



The Stockhill Plantation is situated in the Chewton Warren orefield. The area was worked for ore from at least the Roman era, however, little mining for fresh ore was carried out after the 16<sup>th</sup> and 17<sup>th</sup> centuries (Gough, 1967; Williams, 1998). Between 1857-1908, beneficiation and smelting activities were centred on the Chewton Minery and St. Cuthbert's site, although some trial shafts were sunk in the orefield. The widespread distribution and pattern of trace metal enrichment indicated that source of enrichment in the majority of soil samples from the Stockhill Plantation appeared to be because of the weathering metal-enriched parent material. However, the texture and metal concentrations of several samples indicated that the soil originated from beneficiation wastes. These may have been the wastes of the ancients, which had been processed in situ, or imported from the Mineries as infill, perhaps to prepare the land for afforestation. The soil samples from Stockhill Plantation generally showed relatively little RTE of trace metals, although the surface horizons were slightly enriched with Pb and Cu in the direction of the prevailing winds from the Mineries. The smelter stacks on the Priddy Mineries Reserve and at St. Cuthbert's appeared to have been historical point sources for the surface enrichment. In the past, the RTE of trace metals may have been more widespread in the Stockhill Plantation. The median soil reaction for the soils of Stockhill Plantation was pH 4.4, and metals may have been lost from surface horizons over time through leaching. The afforestation of Stockhill may have also physically disturbed the soil profiles.

Of the four soil series present in the study area, the Thrupe and Maesbury Series were found to be the most physically disturbed by beneficiation and smelting between 1857-1908, while the Nordrach Series was the most disturbed by mining

some centuries earlier. The soils of the Ashen Series covered the higher ground of the study area, and apart from the construction of a small reservoir, a leat system, and the condensing flue and smelter stack on North Hill, were largely unaffected by physical disturbance during 1857-1908.

At the Priddy Minery Reserve and St. Cuthbert's site, the Thrupe Series was present in the valley running through both sites. The extensive wastes of the ancients were recorded as having been piled along the valley floor, before reworking between 1857-1908 (Curwen Salmon, 1864). Because of the presence of water, the main Chewton Minery reservoir was constructed in the valley on the Priddy Mineries Reserve. In the valley to the south of the reservoir, there was an extensive settlement pond. The relatively low altitude of the valley on the site, led to the construction of several sets of buddles where the gravitational flow of the water running down the valley and from North Hill was harnessed to power the machinery (Gough, 1967). At St. Cuthbert's, the valley was also the site of the main Minery reservoir and buddling area. Beneficiation and smelter wastes were also deposited in the valley, disturbing the Thrupe soil. The Maesbury series was present in a small area to the south of the Priddy Mineries Reserve and over the whole of the St. Cuthbert's site, and was subjected to extensive physical disturbance by beneficiation and smelting.

The data generated in the baseline study showed an acceptable degree of precision and accuracy within the limitations of the analytical techniques and instrumentation used. The accuracy of the technique used to analyse the trace metal content of the soils was assessed by examining the recovery of trace metals

from BCR CRM 143R Sewage Sludge Amended Soil. Recovery ranged from 78.25% for Mn to 96.91% for Pb. As a measure of the analytical precision of the technique used in the analysis of soil in the baseline study and annual cycling study, three sub-samples of each soil sample were analysed for Total and EDTA available trace metal content, pH and Loss-on-Ignition. The mean % CV of the results of the sub-sample analyses were below the target of 10% CV for all these parameters.

The data generated the baseline study addressed Ginnevar's (1985) recommendation for a more detailed investigation into the trace metal enrichment of the Mendip uplands. Ginnevar (1985) suspected that her sampling regime was not of sufficient resolution to identify the local geochemical variation on Mendip. This study confirmed Ginnevar's (1985) suspicions and demonstrated that the area around the Priddy Mineries is not only one of the most intensely metal-enriched historic mining and smelting sites on Mendip, but may also be considered to be intensely metal-enriched in a national context.

The survey of the vegetation cover at each 1 m<sup>2</sup> sampling point indicated the extent of the diversity of the flora present on the Priddy Mineries Reserve and St. Cuthbert's site. Mining and processing initially causes direct habitat destruction. It directly affects the environment directly through physical and chemical modification. Excavation and the erection of technology, construction of buildings, leats, reservoirs and the production of wastes alters landform, drainage and soil conditions. Beneficiation, smelter emissions and wastes may also chemically modify the soil (Ratcliffe, 1974). However, on the Priddy Mineries

Reserve and St. Cuthbert's site, the long term gains in terms of the biodiversity generated by the historic disruption can be argued to outweighed the initial loss of habitat.

At the beginning of the 21<sup>st</sup> century, the Mendip uplands are predominantly under agriculture, but the abandonment and lack of subsequent reclamation and development of the Mineries sites appears to have ultimately created a wide range of habitats in a relatively small area, which now contain species which might have otherwise been lost from the region. The presence of Pb wastes have maintained populations of local plant species such as *Minuartia verna*, *Thlaspi caerulescens* and *Botrychium lunaria*, while others on the study area, such as *Typha angustifolia* and *Ophioglossum vulgatum* are of regional importance. The study area supports populations six species of butterfly that are of regional importance, including a small and very vulnerable colony of *Eurodryas aurinia* (Marsh Fritillaries), which may already be extinct locally. Three species of dragonfly (Odonata) found in the area are also of regional importance. The nationally important *Triturus cristatus* (great crested newt) is also present in the study area, and the minery pools are local breeding sites for *Bufo bufo* (common toad). Sites such as the Priddy Mineries Reserve and St. Cuthbert's site are very special areas. Although they bear hardly any resemblance to natural habitats, and at one time were thought to be of little interest to ecologists, they are now recognised as sites of great scientific and conservational value (Kelcey, 1976; Bradshaw, 1977).

The data presented in the baseline study were validated by the results of the duplicate field sampling as being representative of the trace metal concentration in

the soil from the sampling point on that day. The number of soil samples collected for the baseline study, and the protected SSSI status of the study area precluded the large-scale duplication of field samples. Field samples were duplicated at 10% of the total number of samples, and three sub-samples of each soil sample were analysed for Total and EDTA available trace metal content, pH and Loss-on-Ignition. In all cases, the mean % CV of the results of the field samples and their duplicates were below 10% CV for all those parameters.

While the data collected during the baseline study were shown to be representative of the trace metal concentrations in the soils of the study area on the day they were collected, an assessment of the temporal variation in the trace metals was carried out. Five representative soil profiles of the four soil series present in the study area, and one tailings profile was sampled at surface and depth on a monthly basis for one year. The concentrations of Pb, Zn, Cd, Cu, Fe and Mn, and pH and Loss-on-Ignition were found to vary over the year. The general trend for Pb, Zn, Cu, Fe and Mn in the Maesbury and Thrupe soils and the Tailings was an overall decrease in concentration over the sampling period. Soil Pb, Zn and surface Cu also decreased in the Ashen soil and Pb, Fe and surface Cu in the Nordrach soil.

The degree of variation in the soil parameters depended on the parameter and the soil series in which it occurred. A ranking of the soil series by % CV in all trace metal concentrations at 0-400 mm over the year showed that the degree of variation range from 31.16% CV in the Maesbury Series to 11.32% CV in the Nordrach Series, in the following order:

Maesbury>Ashen>Thrupe>Tailings>Nordrach.

A ranking of variation in soil trace metal concentrations by % CV for all soil series in the surface horizons showed that the degree of variation ranged from 8.41% CV for Mn to 11.97% CV for Fe in the following order:

$$\text{Mn} > \text{Zn} > \text{Cd} > \text{Pb} > \text{Cu} > \text{Fe}.$$

A ranking of variation in soil trace metal concentrations by % CV for all soil series at depth showed that the degree of variation ranged from 22.52% CV for Cu to 14.05% CV for Fe in the following order:

$$\text{Cu} > \text{Cd} > \text{Zn} > \text{Mn} > \text{Pb} > \text{Fe}.$$

There was a greater range of variation in trace metal concentration in the surface horizons than at depth. This was also reflected in the EDTA extractability of soil trace metals. When EDTA extractable trace metal concentration was expressed as a percentage of the HNO<sub>3</sub> extractable concentration, the percentage of EDTA extractable trace metals were consistently higher in the surface horizons than at depth. The variation was thought to be related to the source of enrichment, the fraction of soil the trace metals were held in, soil pH and hydrology and the availability of trace metals in the surface horizons for plant uptake.

While temporal variation in trace metal concentrations in the soils of the study area was shown, the relevance to the data collected in baseline study is open to debate. The aim of the baseline study was to determine the environmental legacy of mining, processing and smelting by mapping the distribution of trace metals in the soils of the study area. In the field, soil is heterogeneous, and trace metal

concentrations can vary within short distances of each other. The method of sample collection, and the fact that only 1.5 g of the total field sample of 500 g or more were actually analysed, meant that whatever measures were taken to minimise sampling and analytical error, the results were only ever very good estimate of the absolute concentration found in the soil. What is perhaps more relevant in a baseline study or an environmental impact assessment is that the magnitude of trace metal concentration determined in the sample be as close as possible to reflecting the magnitude of concentration in the field soil. It could be argued that these factors are taken into consideration when designing soil contamination classification schemes such as the GLC scheme produced by Kelly (1979).

The GLC scheme has increasing interval bands for each contamination category as soil contamination increases (Kelly, 1979). For example, the band for the soil typically uncontaminated by Pb was  $500 \mu\text{g g}^{-1}$ , while the heavily contaminated classification was  $8\,000 \mu\text{g g}^{-1}$  (Kelly, 1979). Absolute concentrations have their importance in ecological studies, but baseline soil studies and contamination assessments are more broadly based.

The overall ranking of EDTA extractable trace metal concentration as a percentage of Total trace metal concentration for all soil series at both surface and depth was in the following order of magnitude:

$$\text{Pb} > \text{Cu} > \text{Cd} > \text{Mn} > \text{Zn} > \text{Fe}.$$

The EDTA extractable Pb as a percentage of the Total Pb ( $\text{HNO}_3$  extractable) was remarkably high in the Thrupe, Ashen and Maesbury soils. In the surface soils,

this ranged from 84% to 102%, and at depth (200-400 mm) from 65% to 101%. In the Nordrach Series, EDTA extractable Pb ranged from 49% to 81% of Total Pb in the surface soil and from 52% to 69% of Total Pb at depth. The EDTA extractable Pb as a percentage of the Total Pb was lowest in Tailings at 20% to 41% at the surface to 14% to 38% at depth. The high EDTA extractability of Pb in the Thrupe, Ashen and Maesbury soils was thought to be related to the source of enrichment, the soil pH, soil redox reactions, mineral composition and texture and soil hydrology. The source of Pb enrichment in these soils largely originated from the aerial deposition of smelter flight. Li (1993) also observed that trace metals were much more mobile and available in soils contaminated by smelter emissions than by mining processes at Shiphams, Somerset. The Maesbury, Thrupe and Ashen soils were often saturated with water during the sampling period of 1998-1999. Periodic waterlogging has been associated with the reduction of Fe and Mn and the release of metals such as Pb into more soluble phases (Ross, 1994c).

The lower EDTA extractability of Pb in the Nordrach Series where the source of enrichment was predominantly natural mineralisation with some aerial deposition, and the lowest in tailings, where the source of enrichment was beneficiation, confirmed the observations of Li (1993). The Tailings had the highest median soil reaction of all the soil series at pH 7.29 in the surface horizon and pH 7.7 at depth. The Tailings also showed the least variation in pH over the year. The origin and mineral composition of the tailings was such that Pb and other trace metals were present as small fragments of metallic ores, occluded onto fragments of slag, had weathered into stable secondary metallo-phosphate minerals such as pyromorphite,



or were generally held in the mineral fraction. Trace metals held in these forms are not easily extractable by EDTA (Ure, 1990).

In some instances, EDTA extractable Pb was apparently greater than 100% of the Total Pb. Where this anomaly occurred, the result could have been due to heterogeneity within the soil sample. The concentration value for both EDTA and HNO<sub>3</sub> extractable Pb used in the final calculation was the arithmetic mean of three replicate analyses of soil taken from the bulk sample. The anomalous results could have also occurred if soil Pb was held in fractions completely extractable by EDTA in some, or all of the replicates, but in some, or all of the replicates, HNO<sub>3</sub> extraction was incomplete or inhibited for some reason. When dealing with such small percentage differences in concentration, instrument variation or analytical error could also be the source of apparently anomalous results such as this.

Assessments of 69% (v/v) HNO<sub>3</sub> and EDTA were carried out to determine the most efficient and precise procedure for the decomposition of the soil samples collected from the study area during trace metal analysis. It was found that for the heavily mineralised soils of the study area, a soil to HNO<sub>3</sub> ratio of 1:20, where soil mass was 0.5 g and HNO<sub>3</sub> volume was 10 ml was the most efficient method for decomposition. A soil to HNO<sub>3</sub> ratio of 1:5, where soil mass was 5 g and HNO<sub>3</sub> volume was 25 ml was found to effectively reduce Pb concentration in the analyte by over 75% (Table 3.8). A similar problem was encountered with the standard EDTA extraction method for trace metal analysis (MAFF, 1985). The recommended soil:EDTA ratio was 1:5, where soil mass was 10 g and EDTA volume was 50 ml (MAFF, 1985). Experiments with soil from the study area and

the soil to EDTA ratio showed that above a ratio of 1:10, where soil mass was 5 g and EDTA volume 50 ml, the concentrations of Pb, Zn and Cd in the analyte were reduced. It was hypothesised that in both the HNO<sub>3</sub> and EDTA extractions, the heavily mineralised nature of the soil caused saturation of the analyte at the higher soil:extractant ratios. The extractant might have become saturated with elements other than those being analysed for, and if this occurred, then trace metals would have been left in the residual undecomposed soil. In the HNO<sub>3</sub> decomposition using a soil to HNO<sub>3</sub> ratio of 1:5, white needle-like crystalline structures precipitated out of the cooling analyte, which suggested that saturation point had been reached.

## **6.2 Further recommendations**

It was beyond the scope of the study to determine whether the variation in trace metal concentrations were part of a long-term trend of depletion in the soils of the study area. A long term monitoring programme would be of value. It would also be of interest to determine to what extent the migration of trace metals has occurred down through the soil profile, and possible differences in migration rates between soil types.

The sequential extraction of trace metals from the soils would be of interest in a study such as this to further determine which the chemical speciation of the trace metals and their associated soil phase distribution. As shown with the Total and EDTA extraction techniques, existing sequential extraction techniques might require modification to successfully analyse the highly mineralised Mendip mining and smelting soils.

The role of plants in the annual variation of soil trace metal concentrations were touched on briefly in this study, and it would be of interest to expand this area of research. Some soils in the study area were highly contaminated, but very few areas were devoid of vegetation. Cycling studies of the full soil-plant system are needed to understand how vegetation survives, and apparently thrives, in this environment.

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